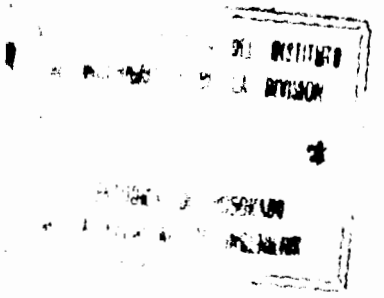
COLLECTION, TREATMENT AND DISPOSAL OF LIQUID WASTES

FOR

PRESENTATION AT MEXICO CITY, MEXICO

December 2, 3 & 4, 1991



Dr. Davis L. Ford
Dr. Earnest F. Gloyna
Dr. Joseph F. Malina, Jr.



HEALTH EFFECTS

- NEUROTOXICITY
- REPRODUCTIVE TOXICITY
- RESPIRATORY SYSTEM EFFECTS
- CARCINOGENICITY
- BIOLOGICAL MARKERS OF DISEASE
- METHODS OF EXTRAPOLATING ANIMAL EFFECTS TO HUMANS
- EPIDEMIOLOGY

RISK REDUCTION

- PREVENTING POLLUTANT GENERATION
- COMBUSTION AND THERMAL DESTRUCTION
- SEPARATION TECHNOLOGIES
- BIOLOGICAL APPROACHES FOR DETOXIFICATION AND DEGRADATION
- CHEMICAL TREATMENT OF CONCENTRATED WASTES AND RESIDUES
- ULTIMATE CONTAINMENT METHODS AND APPROACHES
- EXPOSURE AVOIDANCE
- RISK COMMUNICATION
- INCENTIVES FOR RISK REDUCTION
- EDUCATION AND TECHNOLOGY TRANSFER
- ENVIRONMENTAL MANAGEMENT AND CONTROL SYSTEMS

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GENERAL OUTLINE OF TOPICS

MONDAY – DEC. 2, 1991

8:30-9:00	General Regulatory Criteria in USA	Gloyna
9:00-9:30	Overview of Waste Management	Gloyna
9:30-10:00	Toxicity Reduction Evaluation	Gloyna
9:30-10:50	Monitoring and Wastewater Characterization	Ford
10:50-11:00	BREAK	
11:00-1:30	Primary Separators, Equalization and Dissolved Air Flotation	Ford
1:30-2:30	LUNCH	
2:30-3:50	Low-Cost Waste Treatment (Ponds) and Innovative Technology (Supercritical Water Oxidation)	Gloyna
3:50-4:00	BREAK	
4:00-5:30	Process Engineering -- Secondary and Effluent Polishing	Ford

TUESDAY –DEC. 3, 1991

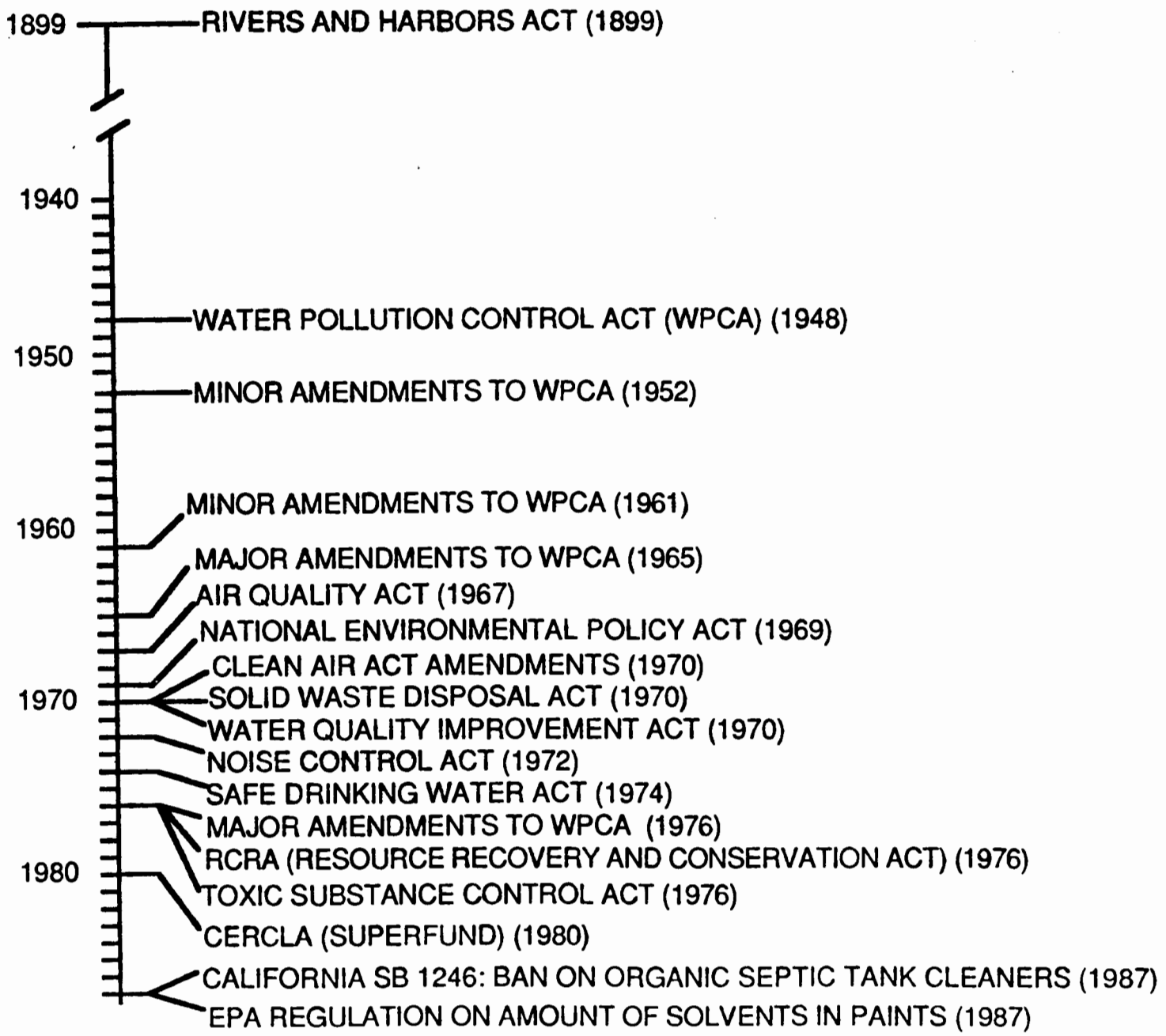
9:00-10:50	Aerated Lagoons, Polishing Ponds, Wetlands, Reuse through Land Application	Gloyna
10:50-11:00	BREAK	
11:00-1:30	Case Histories	Ford
1:30-2:30	LUNCH	
2:30-3:50	In situ Biodegradation	
3:50-4:00	BREAK	
4:00-5:30	Biological Waste Treatment	

15417

WEDNESDAY -- DEC. 3, 1991

9:00-10:50	Biological Treatment
10:50-11:00	BREAK
11:00-1:30	Anaerobic Waste
1:30-2:30	LUNCH
2:30-3:50	Treatment Processes and Residuals Solid Waste Disposal
3:50-4:00	BREAK
4:00-5:30	Problem Session

MAJOR ENVIRONMENTAL LEGISLATION



IMPLEMENTATION OF THE CLEAN AIR ACT AMENDMENTS OF 1990 FOR YEARS 1991 THROUGH 1995

YEAR	NONATTAINMENT	PERMITS	AIR TOXICS
1991	U.S. EPA PROMULGATES MINIMUM SIP CRITERIA (AUG., 1991)	U.S. EPA PROMULGATES MINIMUM ELEMENTS OF PERMIT PROGRAM (NOV., 1991)	U.S. EPA CREATES LIST OF SOURCE CATEGORIES (NOV., 1991)
			U.S. EPA PUBLISHES ACCIDENTAL RELEASE GUIDANCE (NOV., 1991)
1992			U.S. EPA PUBLISHES SCHEDULE FOR EMISSION STANDARDS FOR CATEGORIES (NOV., 1992) REGULATIONS FOR 40 SOURCE CATEGORIES (NOV., 1992)
	STATES SUBMIT SIP REVISIONS FOR PERMITS (NOV., 1992)	STATES SUBMIT SMALL BUSINESS PROGRAM (NOV., 1992)	LIST OF 100 SUBSTANCES (NOV., 1992) U.S. EPA PUBLISHES GUIDANCE ON CONSTRUCTION & MODIFICATION (MAY, 1992)
1993	VOC EMISSION REDUCTION FOR OZONE (NOV., 1993)	STATES TO PERMIT PROGRAMS (NOV., 1993)	
	EMISSION INVENTORY DUE (NOV., 1993)		U.S. EPA PROMULGATES ACCIDENTAL RELEASE REGS. (NOV., 1993)
1994			
			REGULATIONS FOR 25 PERCENT OF SOURCE CATEGORIES (NOV., 1994)
1995			LIST OF 90 PERCENT AREA SOURCES TOP 30 HAZARDOUS CHEMICALS (NOV., 1995)
			POTW REGS PROMULGATED (NOV., 1995)

NEW STORMWATER RULE PROPOSED BY EPA

A PROPOSED RULE AIMED AT CLARIFYING A NUMBER OF ISSUES SURROUNDING THE ISSUANCE OF NPDES PERMITS FOR STORMWATER DISCHARGES ASSOCIATED WITH INDUSTRIAL ACTIVITIES WAS PROMULGATED AUGUST 16 (56 *FED REG.* 40948) BY THE ENVIRONMENTAL PROTECTION AGENCY.

THIS STORMWATER NOTICE ADDRESSES AND SEEKS COMMENT:

- LONG-TERM STORMWATER PERMIT ISSUANCE STRATEGY
- PROPOSED GENERAL PERMITS
- MINIMUM MONITORING REQUIREMENTS
- NOTICE OF INTENT (NOI) REQUIREMENTS
- SPECIAL REQUIREMENTS FOR SARA TITLE III, SECTION 313 FACILITIES
- REQUIREMENTS FOR CONSTRUCTION ACTIVITIES

EPA HAS DEVISED A FOUR-TIERED STRATEGY FOR MANAGING THE LARGE NUMBER OF INDUSTRIAL DISCHARGES WHICH ARE SUBJECT TO STORMWATER REQUIREMENTS:

- BASELINE PERMITTING (TIER 1)--GENERAL PERMITS WILL BE DEVELOPED TO COVER MOST STORMWATER DISCHARGES.
- WATERSHED PERMITTING (TIER 2)--INDIVIDUAL OR WATERSHED-SPECIFIC GENERAL PERMITS WILL BE TARGETED TOWARD FACILITIES WHOSE STORMWATER DISCHARGES ADVERSELY AFFECT WATERSHEDS.
- INDUSTRY-SPECIFIC PERMITTING (TIER 3)--SPECIFIC CATEGORIES OF INDUSTRIES WILL BE TARGETED FOR INDIVIDUAL OR INDUSTRY-SPECIFIC GENERAL PERMITS.
- FACILITY-SPECIFIC PERMITTING (TIER 4)--INDIVIDUAL PERMITS FOR SPECIFIC FACILITIES.

THE DRAFT GENERAL PERMIT PUT FORTH BY EPA INCLUDES MONITORING REQUIREMENTS, NUMERIC EFFLUENT LIMITATIONS FOR TWO CLASSES OF DISCHARGES, STORMWATER POLLUTION PREVENTION PLAN DEVELOPMENT, AND PROHIBITIONS, IN ADDITION TO NOTICE OF INTENT REQUIREMENTS.

BASELINE MONITORING

- ANNUAL MONITORING; RECORD-KEEPING
- NO GENERAL REQUIREMENT TO REPORT DATA TO EPA
- SEMI-ANNUAL MONITORING AND REPORTING FOR:
  1. SECTION 313 FACILITIES
  2. PRIMARY METAL FACILITIES
  3. LAND DISPOSAL UNITS
  4. WOOD PRESERVERS USING CHOROPHENOLIC/CREOSOTE FORMULATIONS

NEW STORMWATER RULE
PROPOSED BY EPA (CONTINUED)

5. WOOD PRESERVERS USING ARSENIC/CHROMIUM PRESERVATIVES
6. COAL PILE RUNOFF

- SPECIAL REQUIREMENTS FOR OIL AND GAS/MACHINE OPERATIONS.

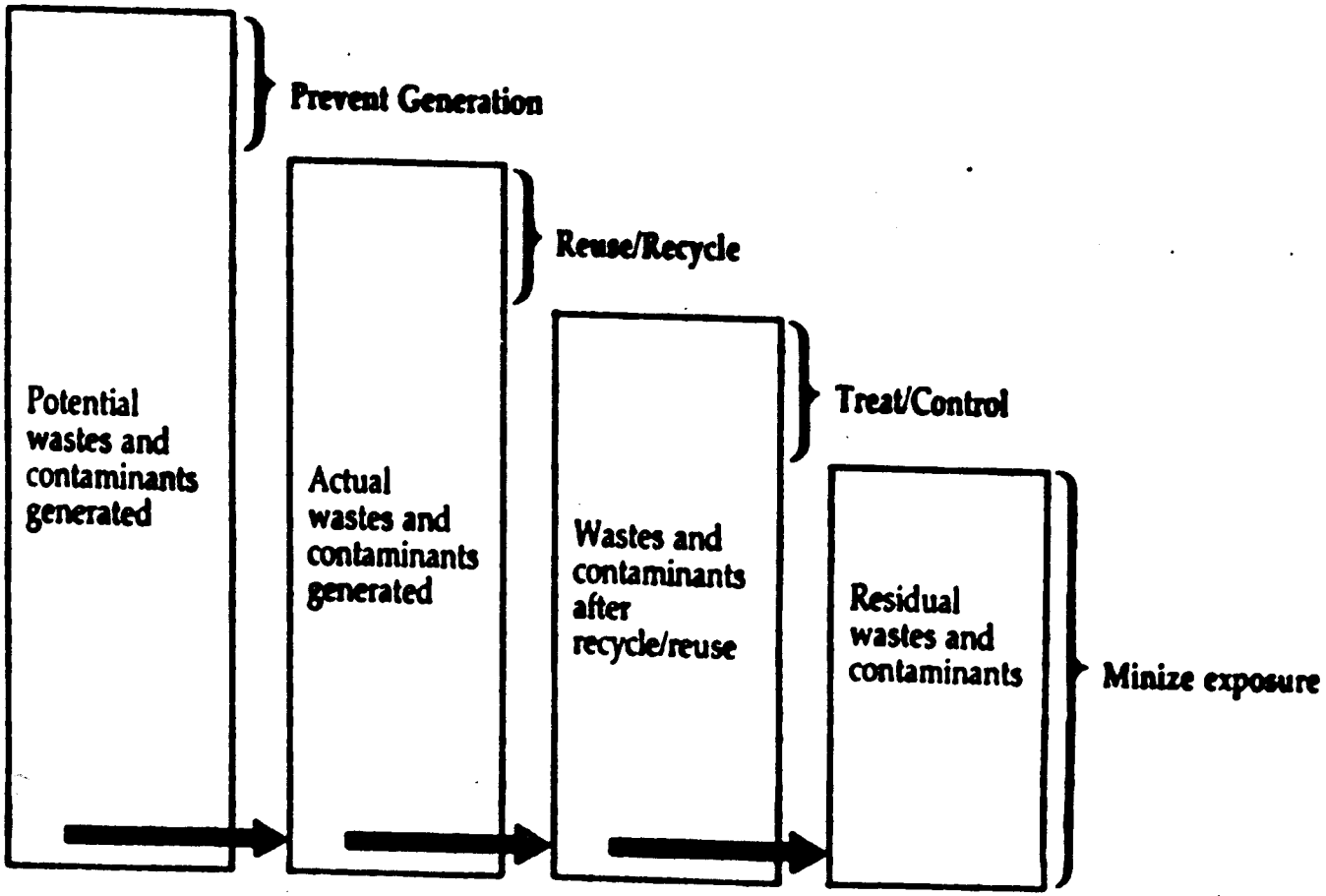
EPA PROPOSES THE FOLLOWING SIX OPTIONS FOR MINIMUM DISCHARGE MONITORING REQUIREMENTS:

1. CONDUCT, MONITOR, AND REPORT AT LEAST TWICE PER PERMIT TERM.
2. CONDUCT ANNUAL SAMPLING. PERMITTEE RETAINS INFORMATION UNLESS IT IS REQUESTED IN A PERMIT OR BY PERMITOR.
3. SAME AS OPTION 2, EXCEPT FOR OIL AND GAS OPERATIONS AND INACTIVE MINING OPERATIONS WHERE AN OPERATOR CANNOT BE FOUND. FOR THESE SPECIAL CASES, EPA RECOMMENDS EITHER ANNUAL SAMPLING WITHOUT REPORTING, OR A PROFESSIONAL ENGINEER'S CERTIFICATION THAT GOOD ENGINEERING PRACTICES ARE BEING EMPLOYED ON-SITE TO MEET PERMIT CONDITIONS. OPTION 3 IS FAVORED BY EPA.
4. ANNUAL SAMPLING AND REPORTING FOR TARGETED CLASSES OF DISCHARGES OCCURRING IN A WATERSHED WHICH IS SENSITIVE TO SUCH DISCHARGES.
5. NO MINIMUM REQUIREMENT FOR ANNUAL SAMPLING.
6. REPORT MONITORING RESULTS ANNUALLY FOR FIRST FIVE YEARS, WITH NO MINIMUM REQUIREMENT AFTER THAT.

FACILITIES WHICH DESIRE TO BE COVERED BY A GENERAL PERMIT MAY APPLY BY FILING A NOTICE OF INTENT:

- NAME, ADDRESS, AND LOCATION OF FACILITY
- UP TO FOUR DIGIT SIC CODES
- OPERATOR'S NAME, ADDRESS, TELEPHONE NUMBER, OWNERSHIP STATUS AND STATUS AS A FEDERAL, STATE, PRIVATE, PUBLIC OR OTHER ENTITY
- LATITUDE AND LONGITUDE OR NEAREST QUARTER SECTION OF THE FACILITY
- NAME OF THE RECEIVING WATER, OR NAME OF THE MUNICIPAL OPERATOR OF THE STORM SEWER AND ULTIMATE RECEIVING WATER
- EXISTING QUANTITATIVE DATA
- ADDITIONAL INFORMATION FOR CONSTRUCTION OPERATIONS

Hierarchy for Risk Reduction Research



C.E. 385-N E.F.G.

"Toxicity Reduction Evaluation"

TRE

OBJECTIVE OF TRE:

REDUCE EFFLUENT TOXICITY TO ACCEPTABLE LEVELS

APPROACH:

1. IDENTIFY CAUSES OF EFFLUENT TOXICITY
2. IDENTIFY SOURCES
3. EVALUATE TREATMENT OPTIONS

Policy Language

- To control pollutants beyond Clean Water Act technology-based requirements, the EPA will use an integrated strategy consisting of both biological and chemical methods to address toxic and non-conventional pollutants from industrial and municipal sources

- Where ambient toxicity is identified as a problem, TREs may be required to identify sources of the toxicity and to determine how the toxicity can be reduced to acceptable levels

TOXICS REDUCTION PROGRAM
DRIVING FACTORS

- RECEIVING WATER QUALITY UNABLE TO MEET NUMERICAL STANDARDS
- TOXICITY TESTING INDICATES EFFLUENT IS TOXIC

leating the Municipal Effluent From
5 – 10° C) up to 25° C Increases
the Percent Unionized Ammonia
Substantially, as Does an
Increase in pH From 7.0 to 8.0

ne Result Is a More Toxic Effluent

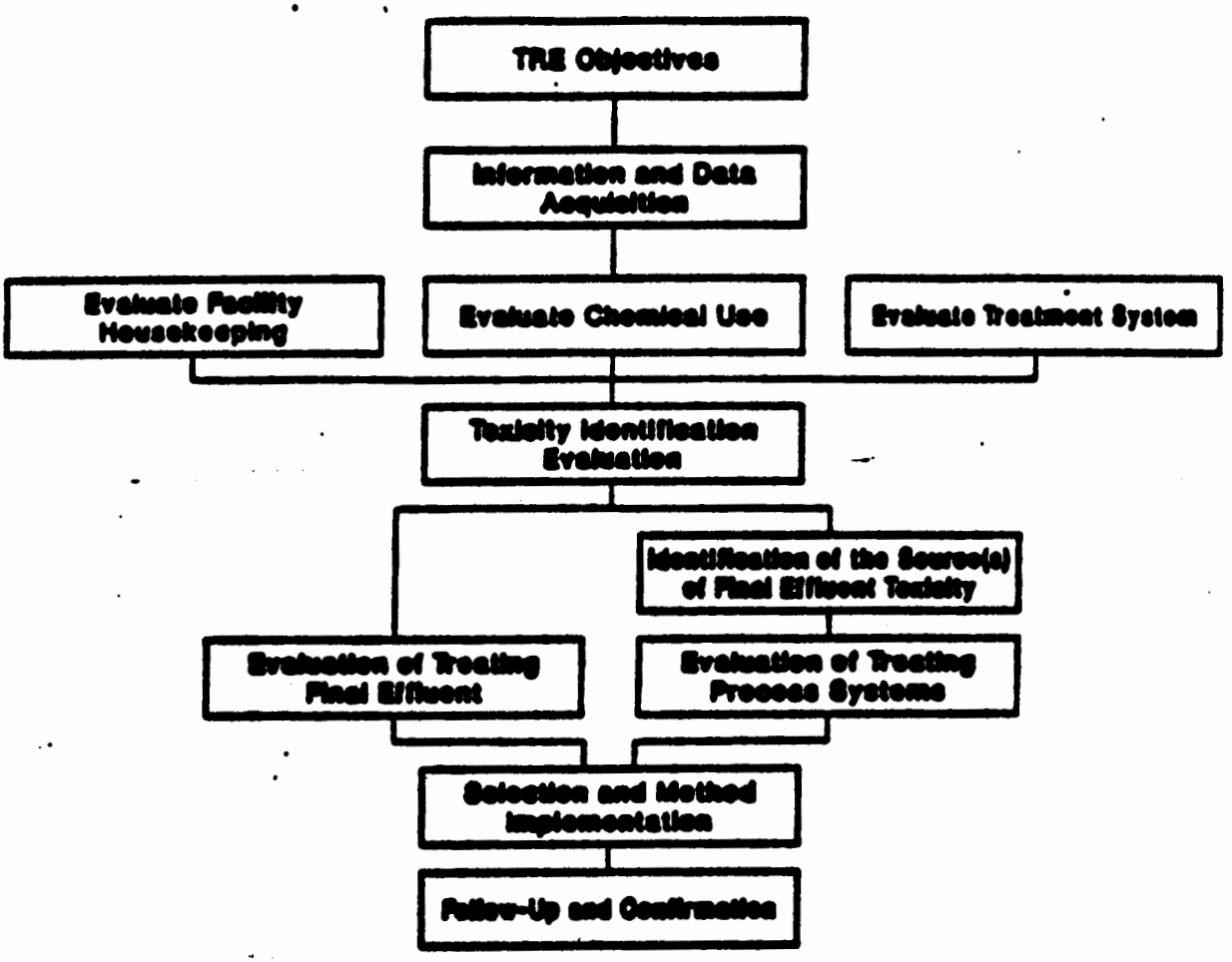
TRE DEFINITIONS

- TOXICS REDUCTION EVALUATION
- TOXICITY REDUCTION EVALUATION

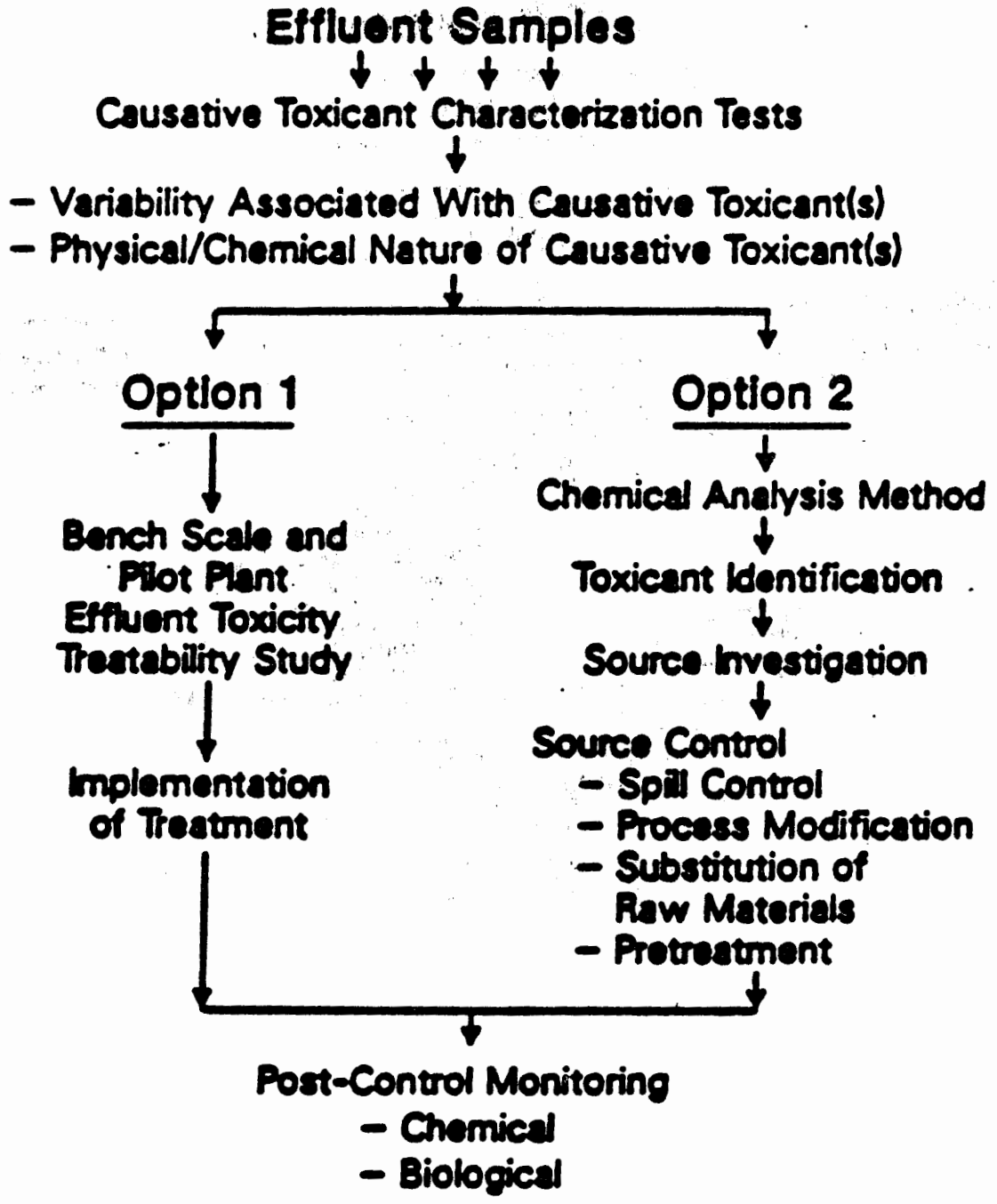
TRE STEPS
INDUSTRIAL FACILITY

- IDENTIFY PROBLEM
- PROCESS ENGINEERING EVALUATION
- CONTROL ALTERNATIVES EVALUATION
- SUBMITTAL AND APPROVAL

TRE Flowchart



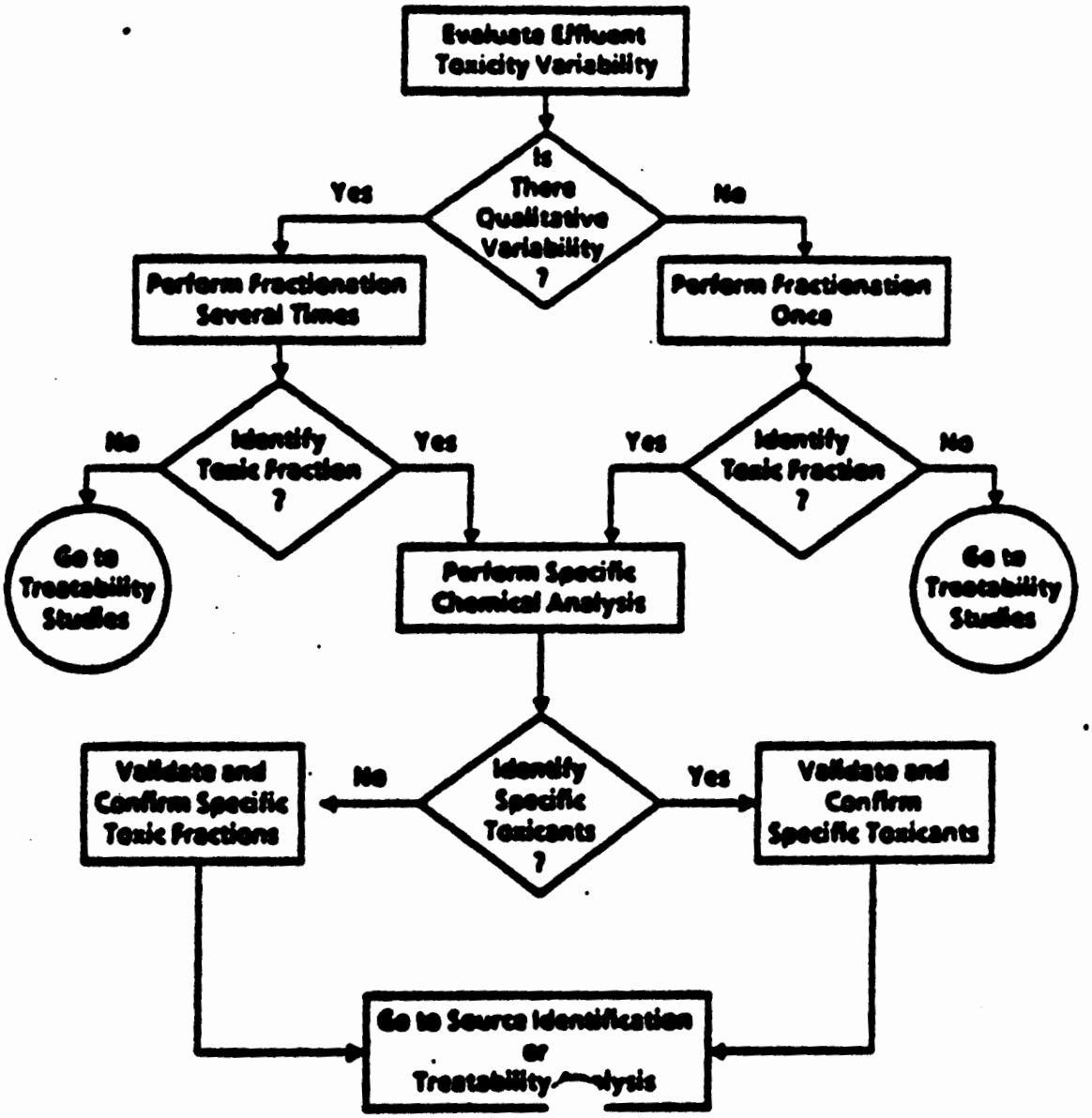
Flow Chart of Suggested Effluent Toxicity Reduction Evaluation



TOXICITY IDENTIFICATION EVALUATION

"TIE"

TIE Strategy Flow Chart



PROCESS ENGINEERING EVALUATION

- FLOW BALANCE
- MASS BALANCE
- RAW MATERIAL INVENTORY
- EXISTING DISCHARGE QUALITY

CONTROL ALTERNATIVE EVALUATION

- PROCESS MODIFICATION
- RECYCLE/REUSE
- WASTE SEGREGATION
- WASTE MINIMIZATION
- AT-SOURCE TREATMENT
- END-OF-PIPE-TREATMENT

SUBMITTAL AND APPROVAL

- PREPARE REPORT
- SUBMIT TO REGULATORY AGENCY
- REVIEW MEETING WITH AGENCY
- REVISE AND SUBMIT REPORT

Toxicity Test Uses

- Is the material acutely toxic?
- Are there sublethal effects?
- How do organisms differ in their sensitivity?
- What is the relative toxicity of different effluents or test materials?
- Does toxicity change over time?
- Doe the material accumulate in the test organisms?

EPA'S EFFLUENT TOXICITY CONTROL STRATEGY

- **Use biological techniques as a complement to chemical-specific analyses to assess effluent discharges and to express permit limitations for industrial and municipal sources.**

Frequently Used Freshwater Toxicity Tests

- 48-hour static (or flow-through) acute test with *Daphnia* or *Ceriodaphnia*
- 21-day static-renewal (or flow-through) chronic test with *Daphnia*
- 7-day static-renewal "rapid" chronic test with *Ceriodaphnia*
- 96-hour static (or flow-through) acute test with fish (e.g., fathead minnows, rainbow trout)

  Flow-through chronic tests with fathead minnows (~30 days) and rainbow trout (~60 days)
- 7-day static-renewal "rapid" chronic test with fathead minnows
- 96-hour static acute test with *Selenastrum capricornutum*

ADVANTAGES OF BIOLOGICAL TECHNIQUES

- Toxic effects of complex effluent discharges can be measured directly.
- Bioavailability of pollutants in effluents can be assessed directly.
- Interactions of constituents can be measured.
- Complex and costly analytical methods are not required.

Factors to Consider When Selecting a Test Procedure

- Species sensitivity
- Dilution water
- Effluent variability
- Type of test (flow-through, static, static-renewal)
- Sampling method (grab, composite, one-time, daily)
- Test location (offsite, onsite)

The Selection of Dilution Water for Effluent Toxicity Tests Is Extremely Important

- Laboratory water
- Receiving water
- Reconstituted water

PROBLEMS WITH THE REGULATION OF TOXIC POLLUTANTS IN EFFLUENTS

- **Complex Chemical Analyses**
- **Chemical/Physical/Biological Reactions with other Constituents**
- **Interpretation of Chemical-Specific Data**
- **Inability to Predict Toxic Effects**

FLOW-THROUGH TEST

ADVANTAGES

More Representative

Toxicant Concentration Remains Stable

Metabolites Do Not Accumulate

)xygen Not Depleted

Can Complete Full Life-Cycle Test With Fish

Exposure Method

- Static
- Static renewal
- Flow-through (intermittent and continuous)
- Instream

STATIC TESTS

ADVANTAGES

- Simple
- Relatively Inexpensive
- Minimal Test Volumes Required
- Complex Facilities/Equipment Not Essential
- Minimal Waste Disposal Volumes

STATIC TESTS

DISADVANTAGES

- Changes in Toxicity of Test Material
- Accumulation of Metabolites
- Reduction in Dissolved Oxygen Concentration
- Volatility
- Adsorption
- Biological/Chemical Degradation
- Photolytic Decay of Compounds

FLOW-THROUGH TEST

DISADVANTAGES

Complex Facilities and Equipment Required

Expensive

Large Volumes of Waste and Dilution Water Required

- **Disposal of waste can be a real problem.**

Toxic Upstream Receiving Water

- Sample further upstream
- Sample from a similar surface water in the same watershed
- Sample from a similar surface water in a separate watershed

Effluent Collection Shipping and Storage

- Grab Sample vs. Composite
- Shipped on Ice in the Dark
- Overnight Courier
- Stored Until Use at About 4°C

Variations in Permit Requirements

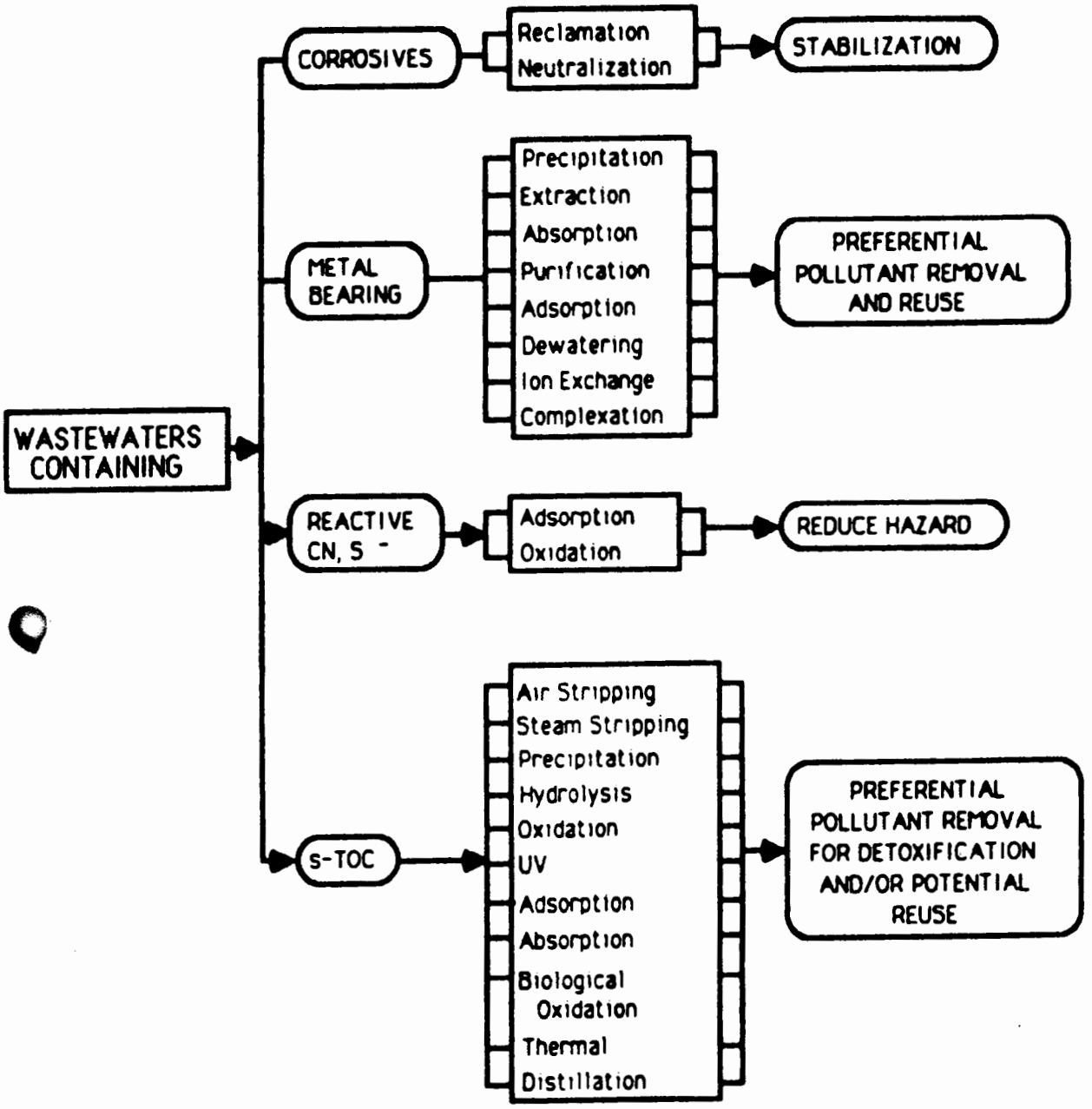
- Test Organisms (Species and Number of Species)
- Test Methods
- Test Frequency
- Duration of Monitoring Program

TOXICITY TESTING COSTS

	Test	Cost
48-Hour	Daphnia acute (static)	$500-600
96-Hour	Fathead minnow or rainbow trout acute (static)	$500-900
24-Hour	Screening test (100% effluent)	$200-300
96-Hour	Onsite flow-through	$5,000-7,000
'-Day	Ceriodaphnia or fathead minnow chronic	$1,200-2,000
21-Day	Daphnia chronic (static-renewal)	$5,000-7000

- These are ballpark costs.

OVERVIEW



Waste management strategies having application to wastewater.

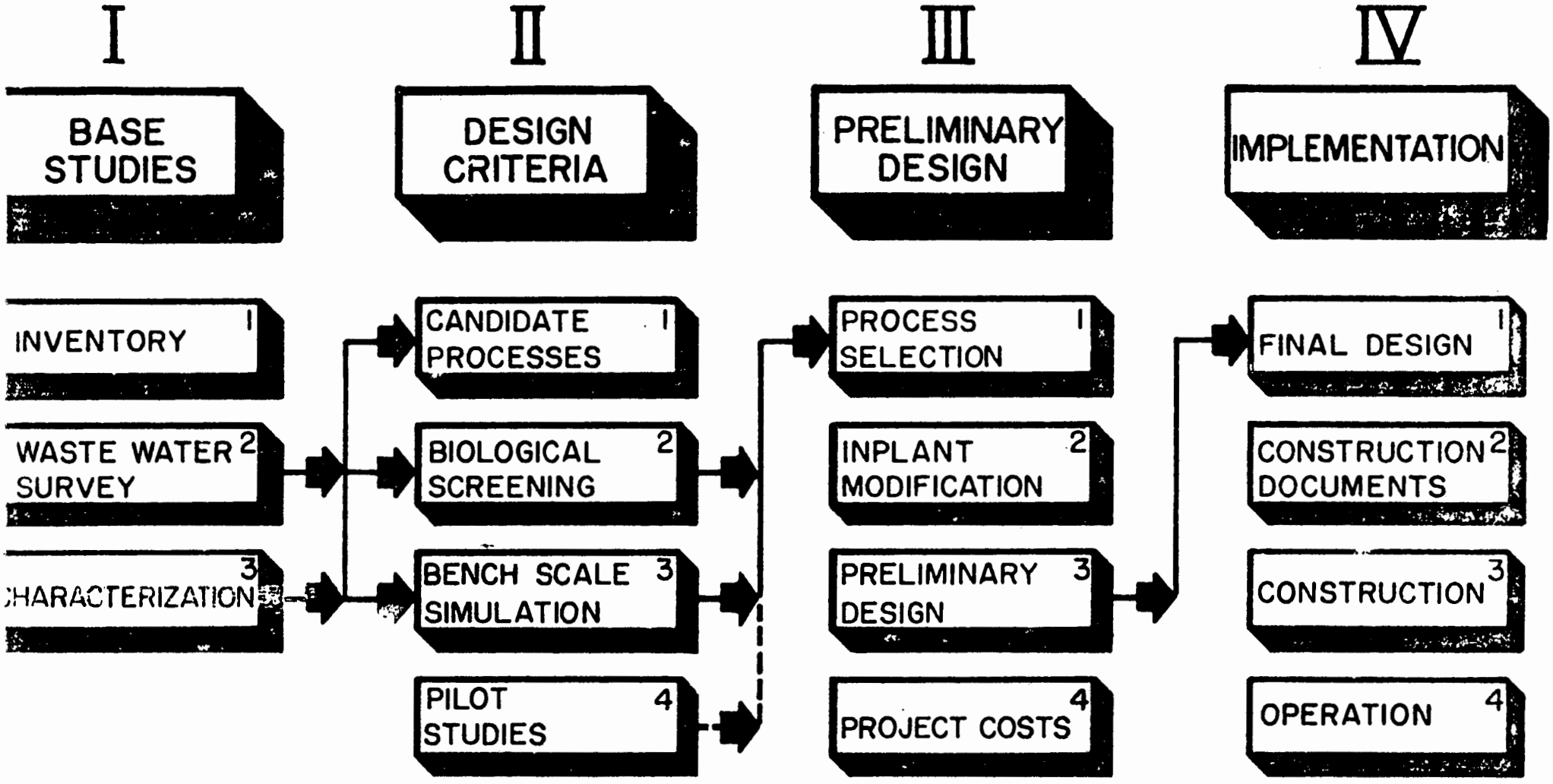
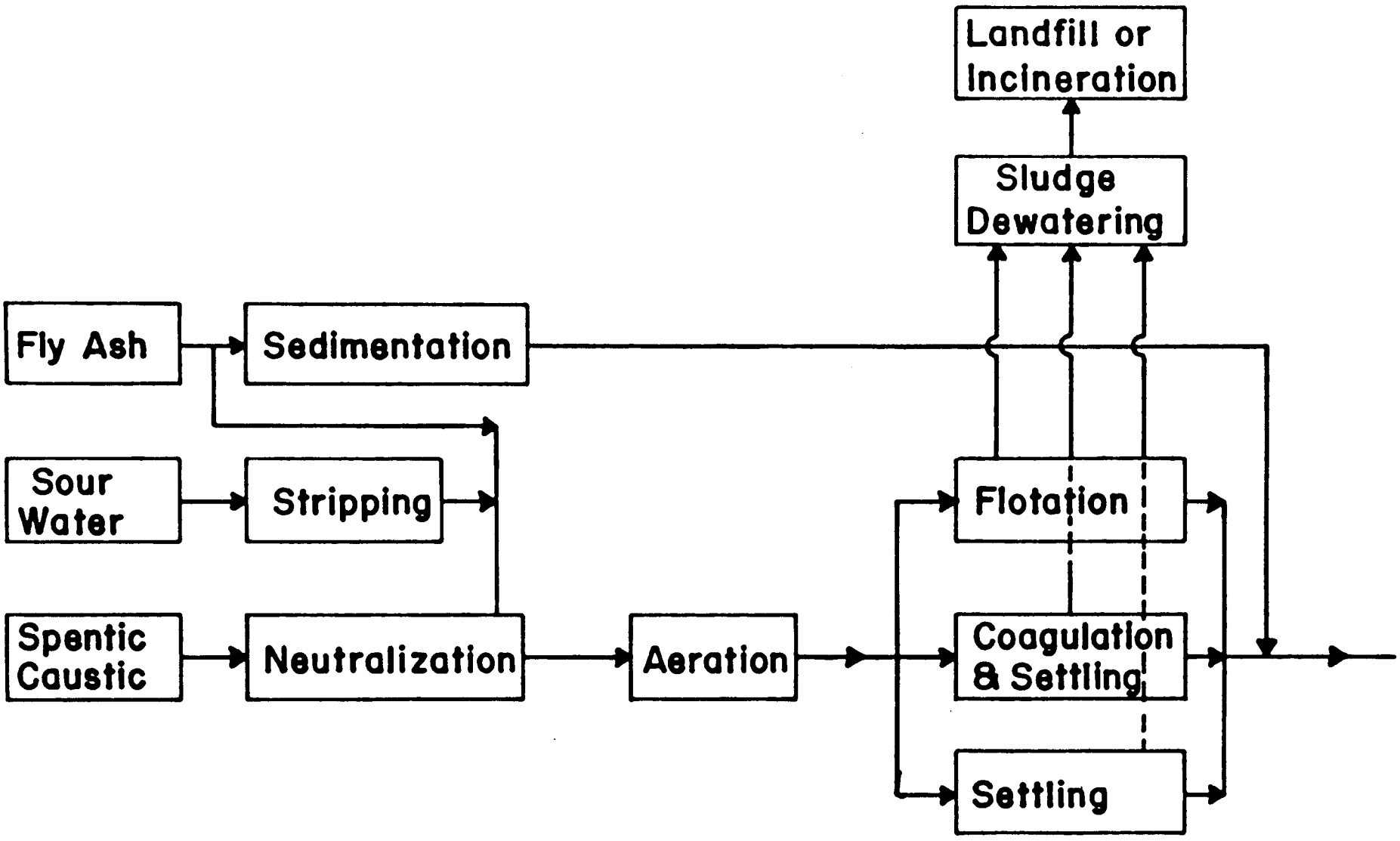
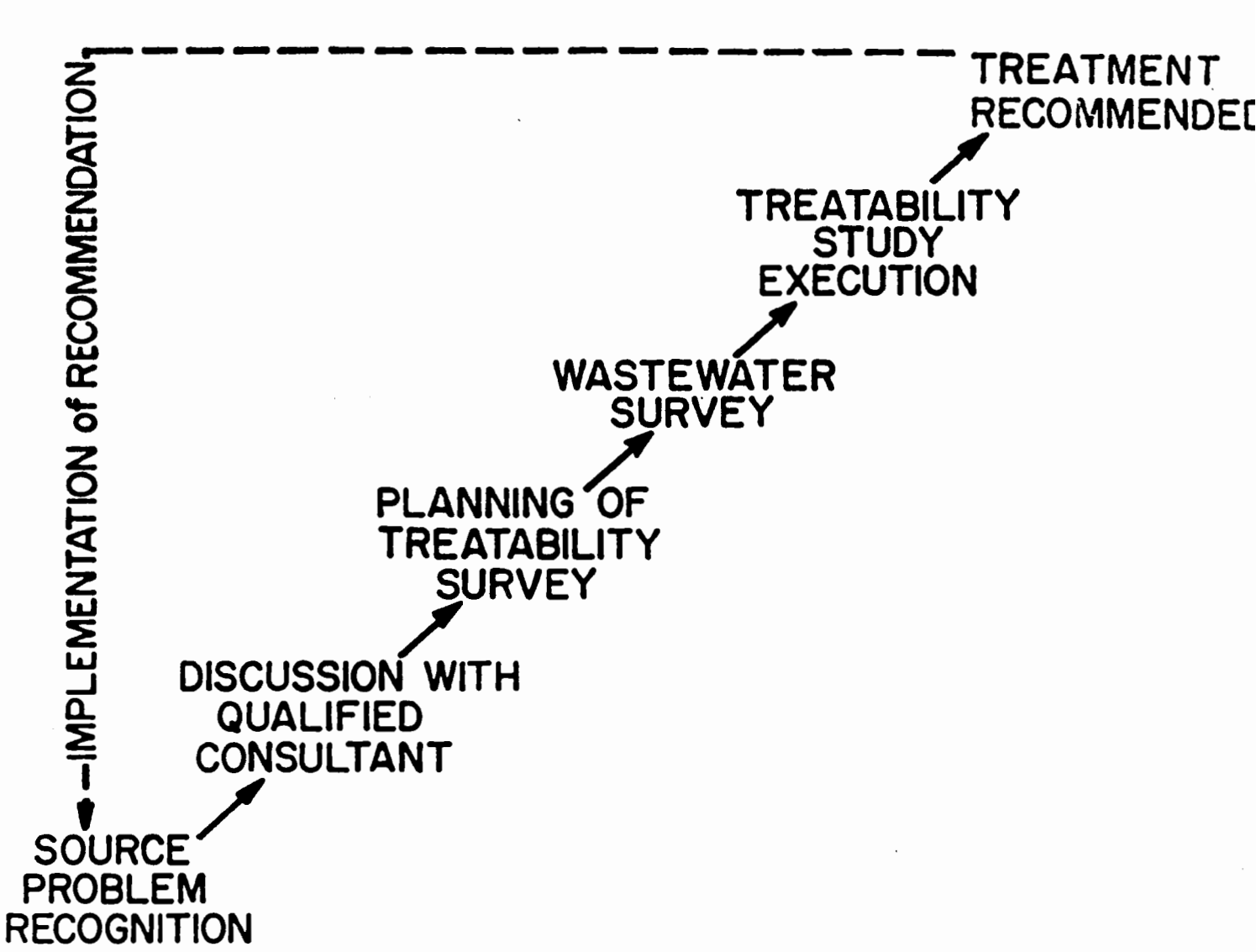


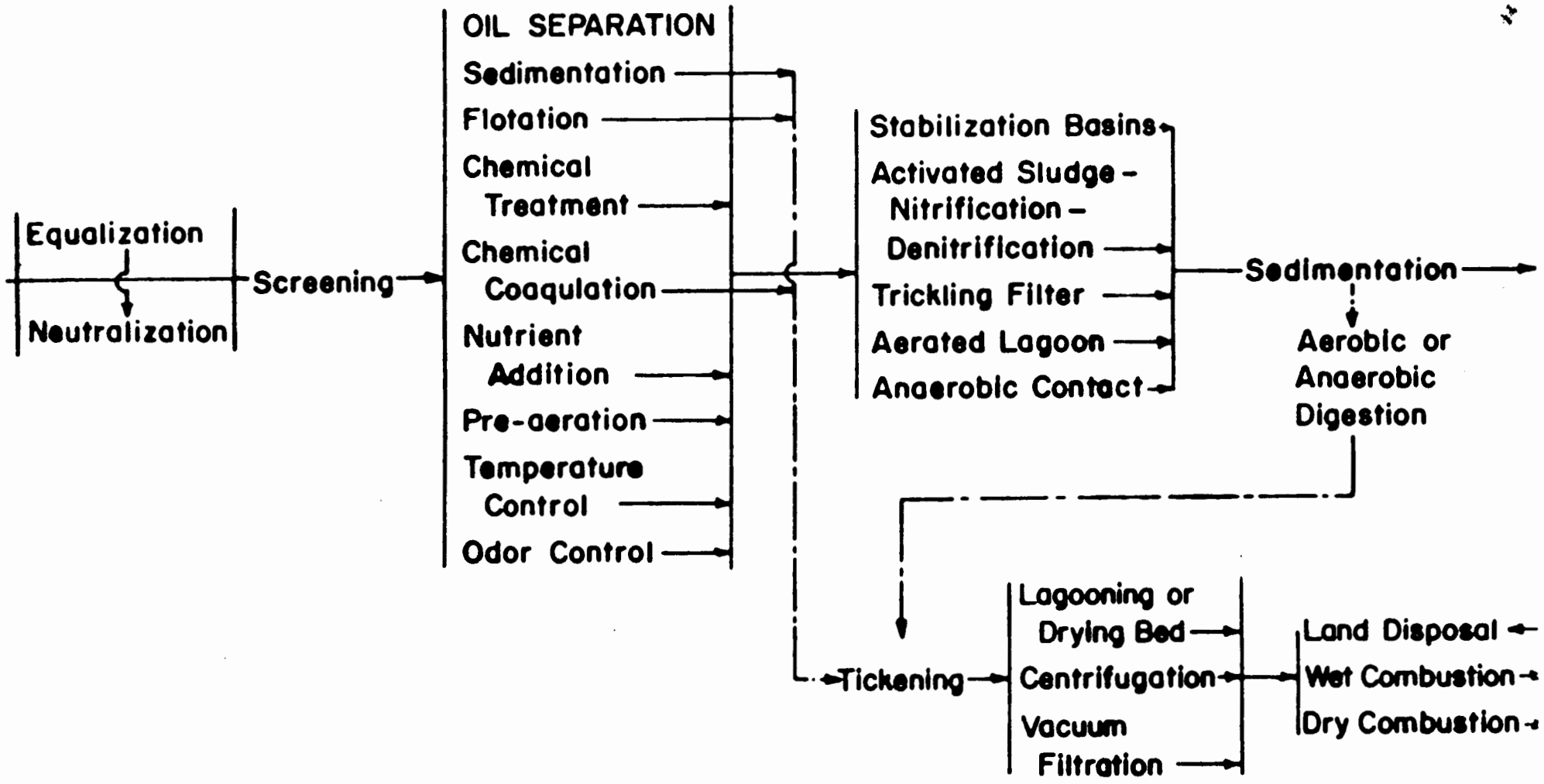
FIG.1 STEPS LEADING TO WATER POLLUTION CONTROL.



TREATMENT SCHEMES OF INORGANIC WASTES.



SEQUENCE OF EVENTS IN A TREATABILITY STUDY.



WASTEWATER TREATMENT UNIT OPERATIONS.

CANDIDATE PROBLEM AREAS

SOURCES, TRANSPORT, AND FATE

- CHARACTERIZING SOURCES AND DISCHARGES
- TRANSPORT, CONVERSION, AND INTERACTION IN THE ENVIRONMENT
- MODELS FOR PREDICTING FORM & CONCENTRATION OF POLLUTANTS
- METHODS FOR ANTICIPATING FUTURE ENVIRONMENTAL PROBLEMS

EXPOSURE ASSESSMENT

- TOTAL EXPOSURE ASSESSMENT METHODOLOGY
- PERSONAL MONITORING
- MODELS FOR PREDICTING EXPOSURE
- BIOLOGICAL MARKERS OF EXPOSURE

ECOLOGICAL EFFECTS

- ASSESSING RISKS TO ECOLOGICAL SYSTEMS
- DEFINING THE STATUS OF ECOLOGICAL SYSTEMS
- DETECTING TRENDS AND CHANGES IN ECOLOGICAL SYSTEMS
- PREDICTING CHANGES IN ECOLOGICAL SYSTEMS

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   - Implementation of Clean Air Act Amendments
   - New Stormwater Rules, Clean Water Act
   - Sludge Regulation and Residuals Disposal
   - Hierarchy for Risk Reduction

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   - Waste Management Strategies Having Application to Wastewater
   - Steps Leading to Water Pollution Control
   - Sequence of Events in a Treatability Study
   - Treatment Schemes of Inorganic Wastes
   - Wastewater Treatment Unit Operation
   - Relationship Between Oxygen and Carbon Parameters
   - Problem Areas
   - Summary Characterization of Waste
   - Discharge Characterization

3. MONITORING AND WASTEWATER CHARACTERIZATION
   - Industrial Waste Characterization
   - Waste Characterization, Monitoring and Evaluation of Permitting Process
   - Analytical Techniques and Treatment of Oil and Grease in Industrial Wastewater

4. PRIMARY SEPARATORS, EQUALIZATION AND DISSOLVED AIR FLOTATION
   ALSO
   PROCESS ENGINEERING -- SECONDARY AND EFFLUENT POLISHING

5. LOW COST WASTE TREATMENT (PONDS)
   AND INNOVATIVE TECHNOLOGY (SCWO)
   AND WATER REUSE THROUGH LAND APPLICATION

6. CASE HISTORIES

7. IN SITU BIODEGRADATION

8. BIOLOGICAL WASTE TREATMENT

9. ANAEROBIC WASTE TREATMENT

10. TREATMENT PROCESSES AND RESIDUALS

11. PROBLEMS AND REVIEW

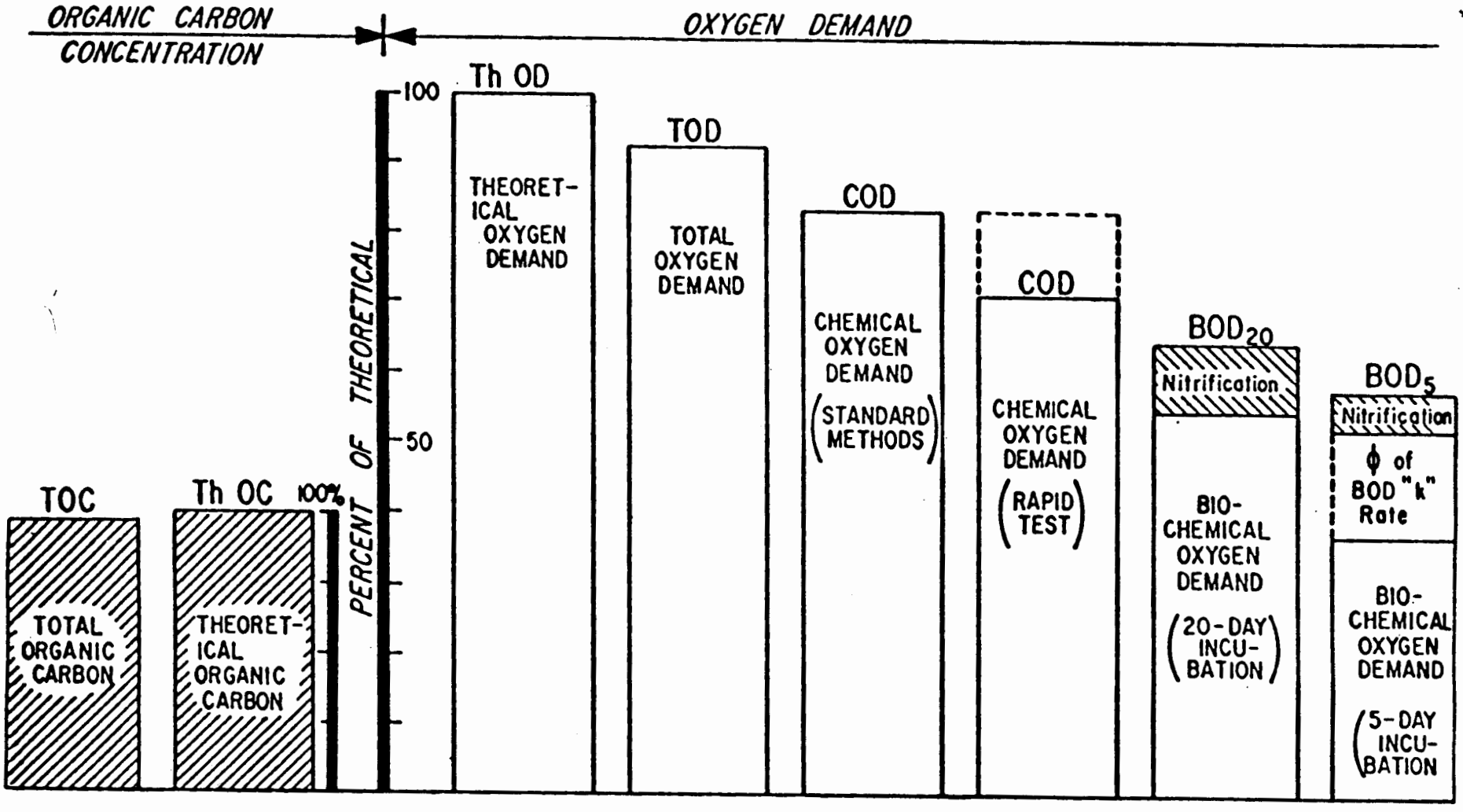


FIG. 1 RELATIONSHIP BETWEEN OXYGEN AND CARBON PARAMETERS

MONITORING AND WASTEWATER CHARACTERIZATION

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INDUSTRIAL WASTE CHARACTERIZATION

1. Large volume of organic load per day with extreme fluctuations in volume and organic load at various times of the day,
2. Seasonal operations resulting in large volumes at certain periods of the year,
3. High temperature,
4. High dissolved or suspended solids content,
5. Acid or alkaline,
6. Grease, oils, or floatables
7. Toxic substances: (a) salts of lead, chromium, copper; and other heavy metals, (b) cyanide, sulfides, and (c) organic bactericidal compounds,
8. Odor forming substances
9. Deficiency or unbalance in essential biological nutrients; and
10. Corrosive materials.

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WASTE CHARACTERIZATION, MONITORING AND EVALUATION OF PERMITTING PROCESS

Group I

- Classification of Industrial Waste
- Industrial Waste Characterization
- Steps to Water Pollution Control
- Accuracy vs. Objective

Group II

- Steps Involved in Establishing an Effluent Monitoring Program
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- Suggested Sampling
- Sample Preservation
- Volume of Sample
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CE 385N

WASTE CHARACTERIZATION, MONITORING AND EVALUATION OF PERMITTING PROCESS

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- Treatment Schemes of Inorganic Wastes
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- Predicted Dispersion Pattern

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- Capitol Cost vs. Effluent Quality
- Reuse Application and Costs
- Comparison with Municipal Costs
- Land Costs for Ponds.

TABLE 1

METHODS FOR DETERMINATION OF OIL IN WATER AND WASTEWATER

Society or Institute	Method Name and Designation	Solvent Used	Solvent Boiling Point °C	Method Description	Interference Material
American Public Health Ass'n., American Water Works Ass'n., and Water Pollution Control Fed.	Oil and Grease	Petroleum ether	35-60	Direct extraction	
	Grease	n-hexane	69	Soxhlet extraction method	Elemental sulfur and organic dyes
American Society for Testing and Materials	Oily Matter in Industrial Wastewater	Benzene, carbon tetrachloride, or chloroform	60-80	Distillation of volatile oils followed by direct extraction	Phenolic type material and colloidal sulfur
American Petroleum Institute	Volatile and nonvolatile oil oily material ---------- Method 731-53	Benzene	80	Distillation of volatile oils followed by direct extraction	Alcohols, cresols, and organic acids
	Nonvolatile oily material ---------- Method 732-53	ethyl ether	35	Ferric hydroxide floccu-lation followed by direct extraction of oil from floc by solvent	Elemental sulfur and chlorophyll
	"A Safe Sol-vent for Oil and Grease Analysis	Freon (CCl_2F-$CClF_2$)	48	Direct or soxhlet extrac-tion	

ANALYTICAL TECHNIQUES AND TREATMENT OF OIL AND GREASE IN INDUSTRIAL WASTEWATERS

INTRODUCTION

The definition of oil and grease (O & G) ranges from Webster, "any of numerous, unctious, combustible substances which are liquid, or at least easily liquifiable on warming, and are soluble in ether but not in water; and leave a greasy stain on paper or cloth," to a more appropriate classification of materials which are extracted in defined solvents. These substances may be mineral, vegetable, or animal in origin and the solvent action exerted on these different chemical structures will vary to a marked degree. The test method used for oil and grease will therefore produce a variety of results, depending on the solvent used (Ref. 1). One solvent may favor extraction of mineral oil while another would favor extraction of vegetable oils. The magnitude of measured oil and grease therefore depends on the solvent used, the source of the oil and grease, the sample to solvent ratio, the pH of the sample, and other factors. Commonly used solvents include hexane, petroleum ether, benzene, chloroform, and carbon tetrachloride. Freon has been more recently proposed as the solvent as (1) it is nonflammable, (2) it leaves essentially no residue upon evaporation, and (3) the oil and grease recovery values for Freon are comparable to or higher than for n-hexane (Ref. 2). For this reason, the Environmental Protection Agency (EPA) has adopted the Freon extraction-gravimetric detection method as the standard procedure for oil and grease evaluation for discharge monitoring required by NPDES permits (Ref. 3). The Freon extraction-infrared detection method, which generally has a higher oil and grease yield, is not used by EPA in determining oil and grease compliance or noncompliance with respect to NPDES operating permits.

A summary of some of the more common methods which have been used for determining oil and grease concentrations in water is presented in Table 1 (Ref. 4).

ANALYTICAL ACCURACY AND PRECISION

The accuracy and precision of the approved analytical techniques for measuring oil and grease should be considered in both the formulation and enforcement of effluent quality standards. An "oil and grease precision round-robin" study of these methods was conducted by the

TABLE 2

RESULTS OF ROUND-ROBIN ANALYSES

Laboratory Number	Sample #1		Sample #2		Sample #3		Sample #4		Sample #5		Sample #6	
	Gravimetric (mg/l)	Infrared (mg/l)	Gravimetric (mg/l)	Infrared (mg/l)	Gravimetric (mg/l)	Infrared (mg/l)	Gravimetric (mg/l)	Infrared (mg/l)	Gravimetric (mg/l)	Infrared (mg/l)	Gravimetric (mg/l)	Infrared (mg/l)
1	171	23	155	198	84.9	126	65.4	35.3	34.2	24.3	14.8	10.5
2	201	273	215	279	85	131	71	122	31	52	13	24
3	220	284	224	286	100	134	76.5	104	32.5	46.9	16.3	22.5
4	-	254	-	259	-	130	-	104	-	46	-	26
5	176	273	237	307	62	130	62	107	29	54	22	24
6	164	239	292.3	255	88.5	126	271.4	111	5.5	49	60.3	22
7	258.6	227	212.	224	110.3	86.3	252.7	115.6	27.3	44.1	25.7	21.5
8	220.8	383	217.8	342	99.8	177	-	-	37.4	71	19.3	23
9	188.4	-	185	-	80.8	-	68.3	-	22.8	-	12.1	-
11	222.7	268.7	234.4	28H5	89.2	132.3	75.7	103.5	31.7	52.2	17.7	19.8
12	232	662	327	693	210	338	319	227	334	140	520	59.1
13	221	278	207	266	104.5	141	94	121	53.5	52	20.0	26.8
14	183	255	208	265	101	134	87	114	38	50	23	24
15	192	236.3	211.6	278.5	101.9	131.1	81.5	110.2	35.4	48.5	11.4	21.9
16	222	-	231	-	148	-	77	-	36	-	16	-
17	215	261	8221	272	70.8	130	82.5	118	26.3	47.8	24.2	26.8
18	90	-	88	-	40	-	21	-	9	-	1	-
19	223	-	173	-	106	-	114	-	40	-	37	-
20	228.5	240	215.9	242.9	154.1	133.4	92.1	112.4	66.1	45.7	29.0	17.7
21	176	234	172	236	72	122	63	92	22	42	13	22
22	180	214	179	203	90	127	32	111	32	60	5	11
25	208	-	194	-	90	-	53	-	24	-	13.2	-
26	220	-	230	-	150	-	78	-	36	-	16	-

American Society of Testing Materials (ASTM) (Ref. 5). American Petroleum Institute member companies, the U.S. Environmental Protection Agency, and private commercial laboratories participated in this study. Replicate samples containing oil and grease at six concentration levels were sent to 31 laboratories for analysis. Results for Freon extraction-gravimetric detection were reported by 22 of these laboratories and 17 laboratories reported results for the Freon extraction-infrared detection method. These results are shown in Table 2.

The nature of the oil and grease analytical methods and the method used for collecting the round-robin samples precludes the use of an exact and known oil and grease content for each sample set. The oil and grease content of each sample is strictly a function of the analytical method used in determining the sample concentrations. In lieu of a known oil and grease content, a "true value" or most probable value may be established for each sample set.

Visual analysis of the gravimetric detection data in Table 2 indicates that the results from two laboratories are conspicuously outside the apparent "normal" ranges of sample values for all sample sets. These are the laboratories designated as Nos. 12 and 18. In developing the "true value" for each sample set, these values were removed from consideration. Additionally, the samples within each sample set are treated as a distribution of values. This arithmetic distribution is transformed to a logrithmic distribution and a student's t test at the 90 percent confidence level is used to compare each individual sample to the sample set mean. Those individual values which are not members of the distribution based on this criterion are also removed from the analysis for the "true values." These values are underscored on Table 2. Utilizing the remaining values, the arithmetic means for each population are calculated directly and used as the "true values."

The determination of analytical error may be measured conventionally utilizing typical population parameters such as the standard deviation within a sample set, the 95 percent confidence level of a sample set, or other methods. However, preliminary attempts to utilize these approaches indicated a heavy weighting of errors toward the high side of the "true value." This weighting effect is believed to be due to the fact that the lower limit of error is bounded (at 0 mg/l) while the upper limit is effectively unbounded. Thus, to provide equal weighting of both positive

and negative deviations from the "true value," an absolute error term is defined as:

$$E_a = \left| \log_{10} \left(\frac{\text{sample value}}{\text{true value}} \right) \right|$$

Using this method, both the negative and positive errors may extend from zero to infinity. This approach is believed to be especially justified as the "true value" approaches zero. This absolute error term was calculated for each sample analyzed by the gravimetric detection method at each laboratory. The absolute error as a function of the true oil and grease concentration is plotted in Figure 1 (Ref. 6).

This figure may be utilized to estimate the expected analytical error from an average laboratory at any concentration level. Table 3 provides values for the expected error range at typical oil and grease concentrations. These values should be interpreted as follows: If 100 laboratories each analyze one sample with a "true" oil and grease concentration of 50 mg/l, 50 samples may be expected to be measured in the range from 41 mg/l to 62 mg/l and 95 samples may be expected to be in the range from 27 mg/l to 93 mg/l. Thus, as can be seen from this analysis, extremely large analytical errors may be expected at low oil and grease concentrations.

Similar tests were conducted for the Freon extraction-infrared detection method. The results for these analyses are very similar to those for the Freon extraction-gravimetric detection method and are presented in Figure 2 and Table 4. It should be noted that the variability of this detection method is less than that associated with the gravimetric procedure, particularly at low concentrations. This is probably due to the fact that the infrared procedure involves a spectrographic analysis which should be subject to less error than a gravimetric determination. However, the yield of the infrared detection method may be considerably different than that of the gravimetric method since it is highly dependent on the standard used to define oil and grease for the infrared technique.

The "precision round-robin" demonstrated that the two detection methods for oil and grease do not give equivalent results. The infrared method shows a uniformly higher oil and grease concentration on the same sample as compared to gravimetric detection. A comparison of the round-robin results using these two proposed detection methods is shown in

FIGURE 1

ABSOLUTE ERROR AS A FUNCTION OF CONCENTRATION FOR FREON EXTRACTION-GRAVIMETRIC DETECTION METHOD

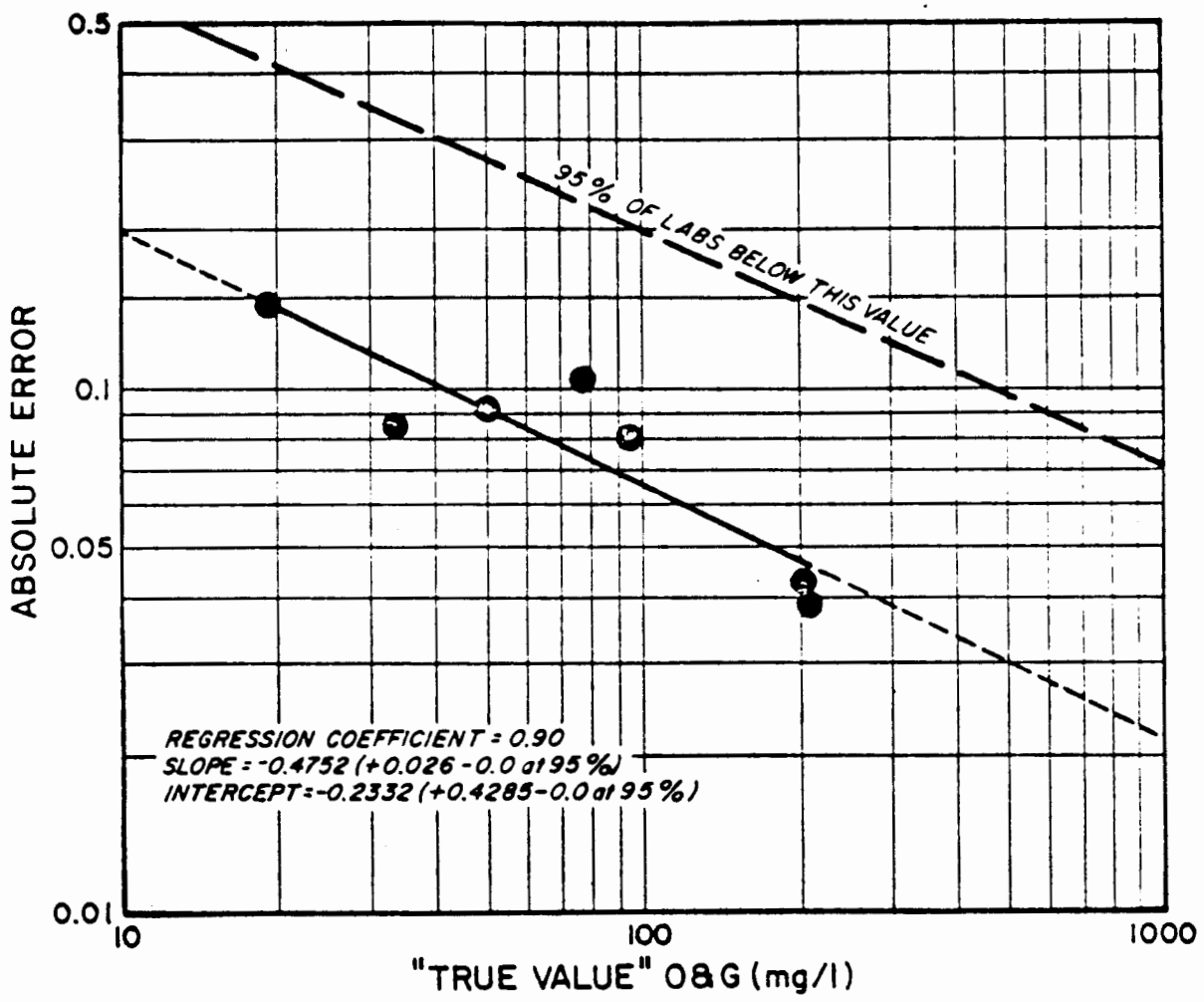


FIGURE 2

ABSOLUTE ERROR AS A FUNCTION OF CONCENTRATION FOR FREON EXTRACTION - INFRARED DETECTION

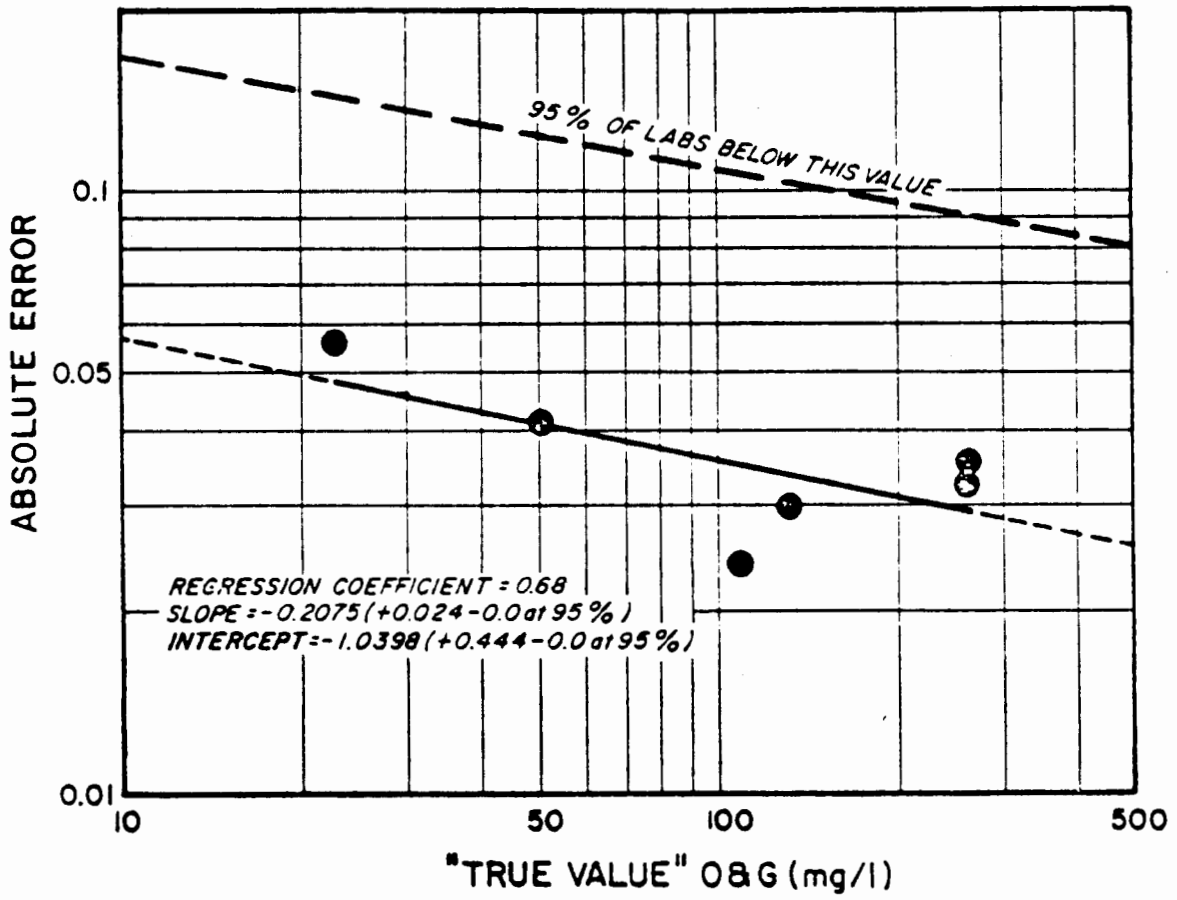


TABLE 3

ERROR RANGES FOR SELECTED "TRUE" OIL AND GREASE CONCENTRATIONS: FREON EXTRACTION-GRAVIMETRIC DETECTION PROCEDURE

"True" Concentration (mg/l)	Absolute Error		50% Analytical Range		95% Analytical Range	
	50%	95%	Low (mg/l)	High (mg/l)	Low (mg/l)	High (mg/l)
100	0.0655	0.1977	86	116	63	158
50	0.0910	0.2701	41	62	27	93
25	0.1266	0.3688	19	33	11	58
15	0.1614	0.4641	10	22	5.1	44
10	0.1957	0.5569	6.4	16	2.8	36
5	0.2720	0.7605	2.7	9.4	0.9	29
1	0.5845	1.5681	0.26	3.8	0.03	37

Table 5. This phenomenon is termed "yield" and is extremely important in defining what the oil and grease analysis measures and what type of concentration limits should be established. As Table 5 indicates, the infrared method yields at least 20 percent more oil than the gravimetric methods. In the lower concentration ranges (Group 5), the yield can be as much as 50 percent greater for the infrared method. This is the reason EPA is not using the infrared technique to evaluate effluent oil and grease levels based on guidelines developed from gravimetric detection methods.

Another result of the "precision round-robin" was to show the high potential for extreme errors in the estimates of oil and grease concentration in single samples and by certain laboratories. The statistical analyses shown were performed using only data passing a 90 percent confidence level t test. Data from two participating laboratories were not used in this analysis: One had uniformly very high concentrations for all samples, and the other was inordinately low. The characteristics were obvious with only a visual review of the data base. In addition, other samples were discarded if they did not meet the "throw-out" criteria. The initial data base contained 131 gravimetric determinations of oil and grease. After applying the stated rejection criterion, 107 data points were used to estimate the "true values." The relatively large amount of data discarded reveals the high potential for error in this analysis.

The sampling and analytical constraints on the determination of oil and grease in wastewater samples are significant in the development of quality control standards, particularly at lower concentration levels. Since oil and grease effluent standards will be used to determine compliance or noncompliance for industrial discharges, allowances must be made for these sampling and analytical variations.

OIL REMOVAL PROCESSES

A discussion of the principal oil removal processes is presented in this section. Performance data, when available, is also included.

Gravity Separation

Gravity oil separation equipment, which includes API separators, simple tanks with skimming, and various skimming clarifier designs, is efficient in removing large amounts of free oil from wastewaters. While

TABLE 4

ERROR RANGES FOR SELECTED "TRUE" OIL AND GREASE CONCENTRATIONS: FREON EXTRACTION-INFRARED DETECTION PROCEDURE

"True" Concentration (mg/l)	Absolute Error		50% Analytical Range		95% Analytical Range	
	50%	95%	Low (mg/l)	High (mg/l)	Low (mg/l)	High (mg/l)
100	0.035	0.109	92.3	108	77.8	128
50	0.041	0.124	45.5	55.0	37.6	66.5
25	0.047	0.141	22.4	27.8	18.1	34.6
15	0.052	0.154	13.3	16.9	10.5	21.4
10	0.057	0.166	8.77	11.4	6.82	14.7
5	0.065	0.189	4.30	5.81	3.24	7.73
1	0.091	0.254	0.81	1.23	0.56	1.79

it is effective in removing free and some emulsified oils, soluble oil fractions and most emulsions are not removed by this type of separation equipment.

There are three common types of gravity separators: the API-type separators, the corrugated plate interceptor (CPI), and the parallel plate interceptor (PPI). The CPI and PPI separators are similar in design although the PPI is not used extensively. The API separator consists of a rectangular or circular trough or basin in which the wastewater flows horizontally while the free oil particles rise due to buoyancy forces. Theoretically, the oil droplets rise linearly as predicted by Stoke's Law, although in practice considerable turbulence and short circuiting usually prevails (Ref. 7). A typical API separator is shown in Figure 3. The performance of API separators from five typical refineries is presented in Figure 4. This figure indicates median effluent oil and grease concentrations ranging from 40 to 100 mg/l for API separators (Ref. 8 and 9). It should be noted, however, that effluent oil and grease variations are rather pronounced; this being attributed to hydraulic variations, inherent short circuiting, and varying influent concentrations of free, emulsified, and soluble oils.

The CPI consists of corrugated plate packs which consist of 12 to 48 corrugated plates (.05 inches thick) mounted parallel to each other at separation distances of .75 to 1.5 inches as shown in Figure 5 (Ref. 10). As the wastewater flows between the plates, the lighter oil globules float upwards into the tops of the corrugation, coalesce into larger drops which move up the plates, and are collected in the process tank. The plates establish laminar flow conditions through the plate pack, drastically reducing the distance that the oil drops must rise to be collected. The following CPI efficiencies in refineries have been reported (Ref. 11):

Influent Oil and Grease	Effluent Oil and Grease
150 - 500 mg/l	50 - 86 mg/l
500 - 700 mg/l	178 - 330 mg/l

and typical performance for PPI's treating oil and gas production wastewaters is shown in Figure 6. Plate-containing separators such as CPI or PPI generally require only 15 to 20 percent of the installation area of plateless separators which reduces construction and maintenance

TABLE 5

OIL AND GREASE ANALYTICAL METHOD COMPARISON

RELATIVE ANALYTICAL YIELD

Group	Average Round-Robin Results		Yield
	Gravimetric	Infrared	Infrared/ Gravimetric
1	201.7	261.3	1.30
2	209.3	265.4	1.27
3	95.5	131.0	1.37
4	77.6	110.4	1.42
5	33.7	50.7	1.50
6	19.1	23.0	1.20

* All data within ±2 standard deviations of "true value".

FIGURE 4

PERFORMANCE OF API SEPARATORS

5 REFINERIES

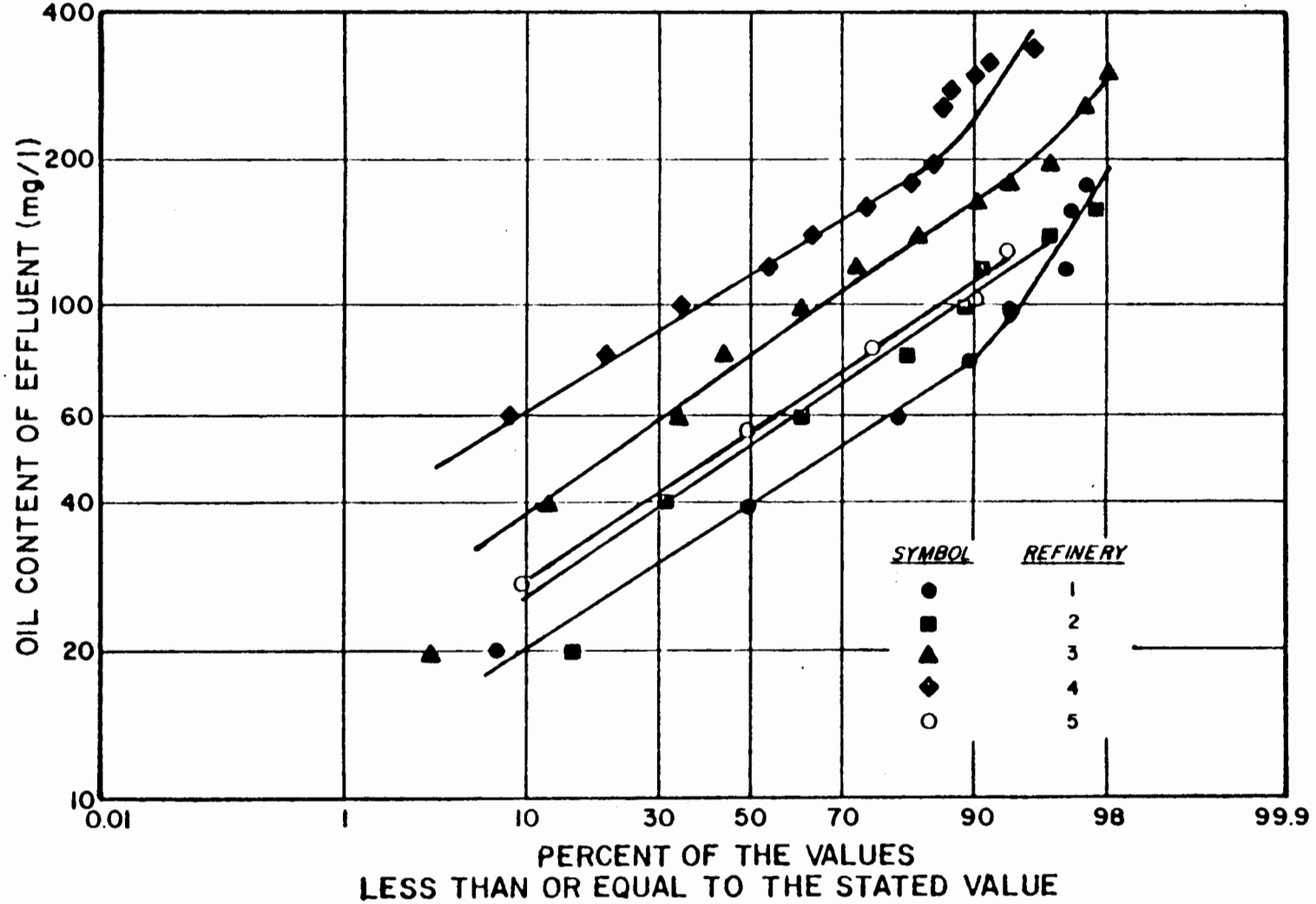


FIGURE 3

API OIL-WATER SEPARATOR

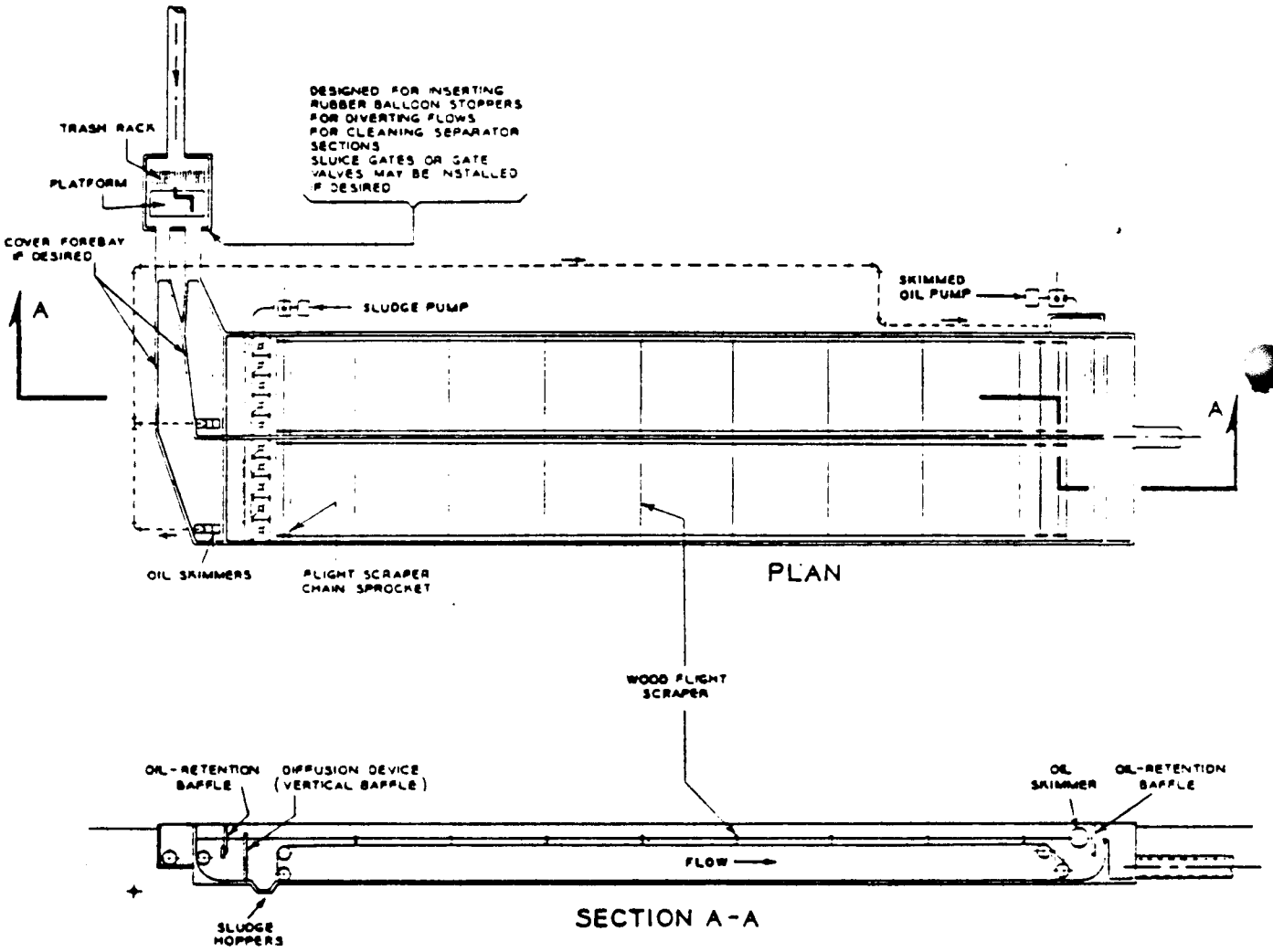


FIGURE 6

PARALLEL PLATE COALESCER PERFORMANCE ON OIL AND GAS PRODUCTION WASTEWATERS

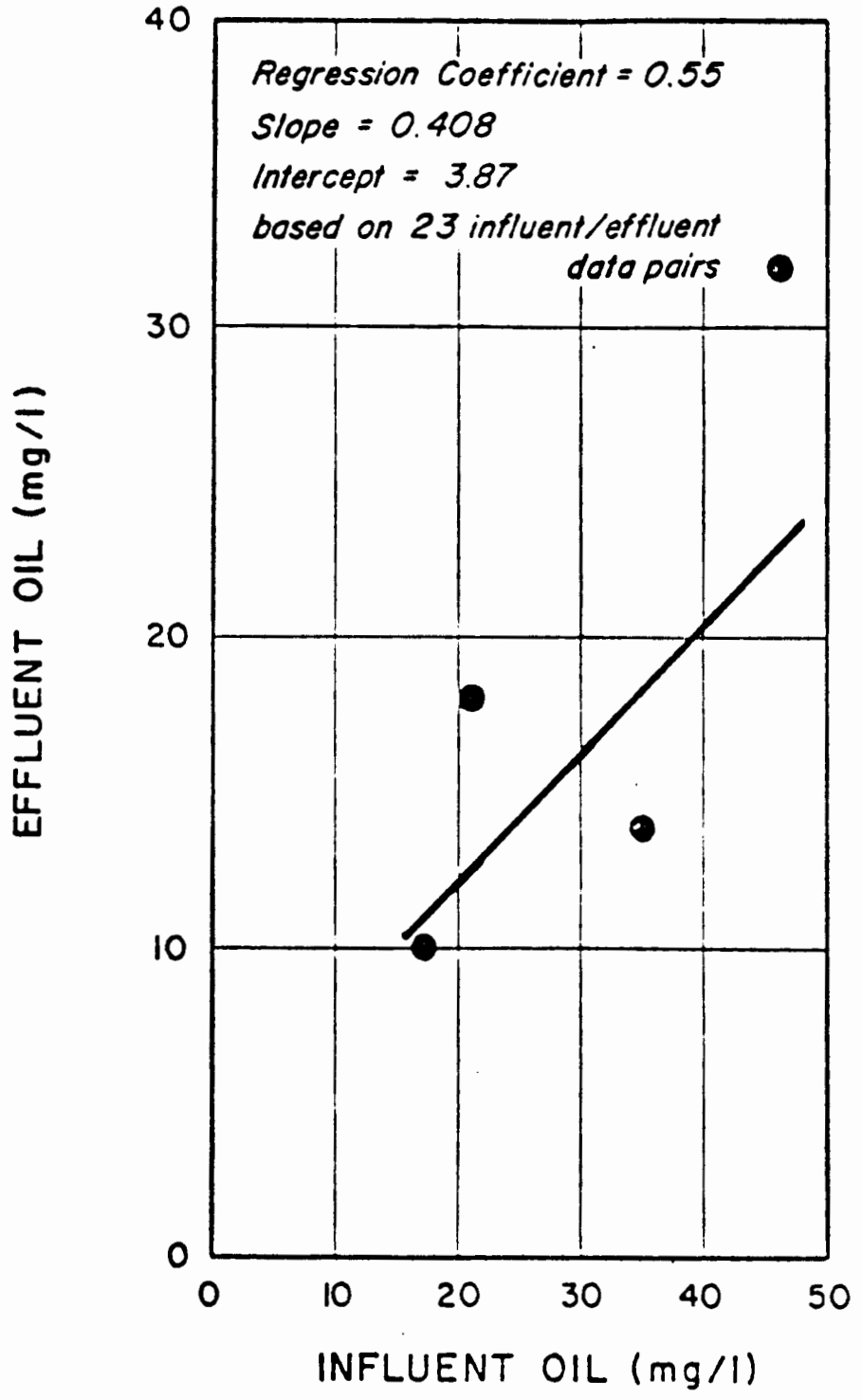
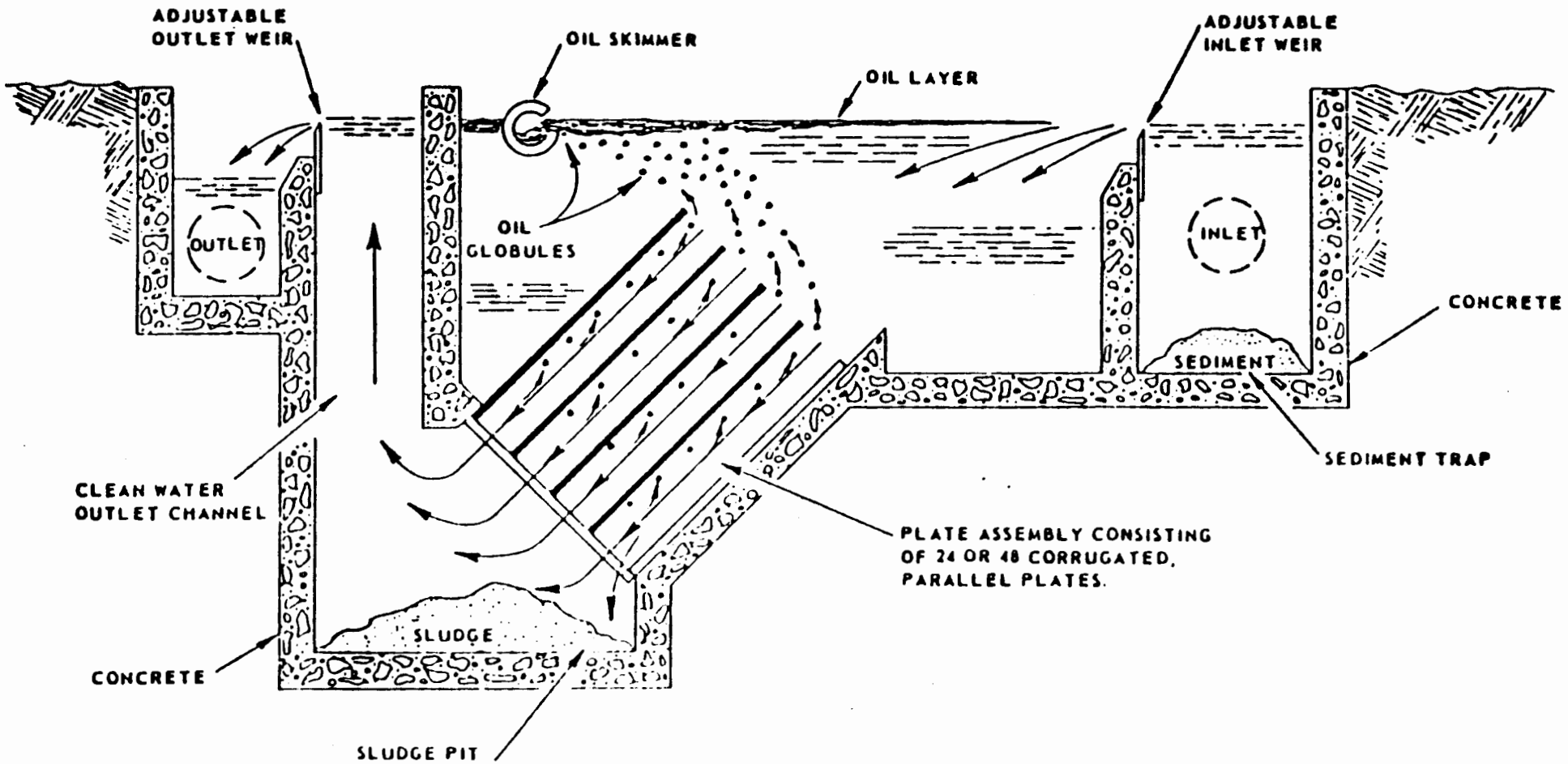


FIGURE 5

CORRUGATED PLATE INTERCEPTOR OR CPI OIL SEPARATOR



costs. As in any phase separator, care must be taken not to emulsify any of the free oil in the influent wastewater.

Dissolved Air Flotation

Dissolved air flotation (DAF) is another process used in removing oil and grease constituents. In this process, the entire wastewater or some fraction thereof is saturated under pressure with a gas - usually air. Upon release of this pressure, the air in excess of the atmospheric saturation concentration is released from solution, forming bubbles approximately 30-120u in diameter. The bubbles form on the surfaces of the suspended or oily materials or are attached to the particles by surface energies. Thus, an aggregate is formed whose average density is less than that of water and which will rise to the surface. A schematic of the DAF Unit is shown in Figure 7 (Ref. 10). In order to insure maximum effectiveness, it is necessary to incorporate chemical coagulation and flocculation. The chemical treatment aspects of DAF operation are extremely important, particularly when colloidal or emulsified oil components are present. Coagulants such as lime, alum ferric salts, or polyelectrolytes are used to improve floc formation and provide good separation. They can be injected at several points depending on the flotation process and the chemical used.

The design variables for pressurized DAF include pressure, recycle ration, overflow rates, retention period, and chemical addition. The pressurized tank is usually maintained at 40 to 60 psig (approximately 3 to 5 atmospheres), a 30 to 40 percent recycle ratio is normally applied, the overflow rates varying from one to four gpm/ft^2 (including recycle), and the retention period generally falls between 20 and 40 minutes. The choice of gas depends on the nature of the wastewater and any regulations concerning disposal of the unit off-gas. Usually air is preferred because it is cheap and it oxidizes most of the sulfides thus releasing any adsorbed oil. On occasion an inert gas (methane or nitrogen) is used to minimize corrosion by keeping reduced iron in solution.

The performance of DAF units using various configurations is tabulated in Table 6 (Ref. 9). The performance, based on maximum control of the aforementioned variables, is sensitive to influent oil concentration. This is underscored by taking a range of influent oil and grease concentrations, and plotting the response effluent concentrations as

FIGURE 7

DISSOLVED AIR FLOTATION UNIT

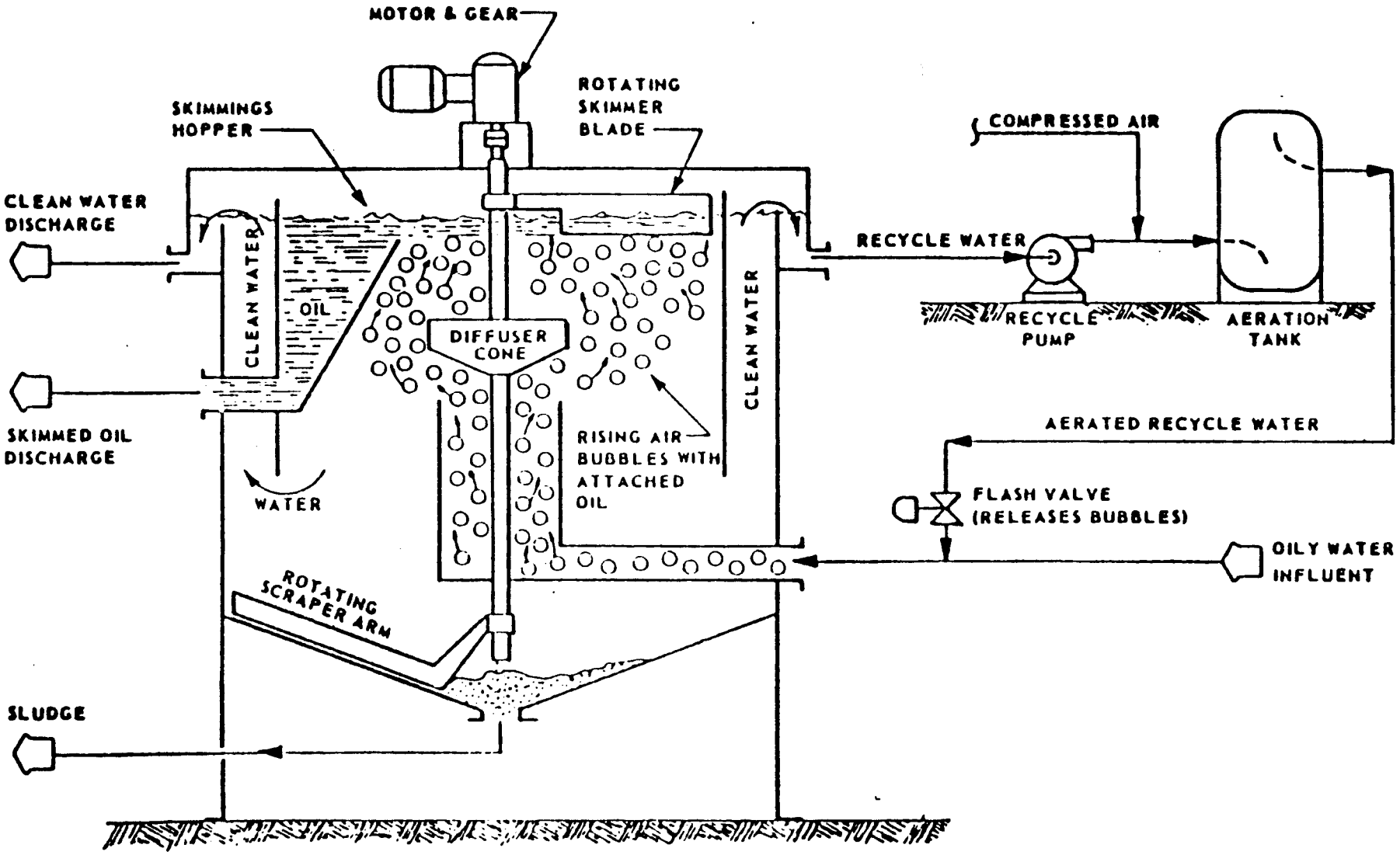


TABLE 6

DAF OIL REMOVAL PERFORMANCE

Influent oil mg/l	Effluent oil mg/l	% Removal	Chemicals*	Configuration
1930 (90%)	128 (90%)	93	Yes	Circular
* 580 (50%)	68 (50%)	88	Yes	Circular
* 105 (90%)	26 (90%)	78	Yes	Rectangular
68 (50%)	15 (50%)	75	Yes	Rectangular
170	52	70	No	Circular
125	30	71	Yes	Circular
100	10	90	Yes	Circular
133	15	89	Yes	Circular
94	13	86	Yes	Circular
638	60	91	Yes	Rectangular
153	25	83	Yes	Rectangular
75	13	82	Yes	Rectangular
61	15	75	Yes	Rectangular
360	45	87	Yes	Rectangular

*Alum most common, 100-130 mg/l
Polyelectrolyte, 1-5 mg/l occasionally added

shown in Figure 8 for refineries and Figure 9 for production wastewaters. Using DAF units in series following gravity separators, a median API separator effluent concentration (DAF influent) of 100 mg/l would infer a DAF effluent level of 10 to 25 mg/l under optimum conditions.

The induced air flotation unit (IAF) as shown in Figure 10 operates using the same principles as the pressurized DAF units. The gas, however, is self-induced by a rotor disperser mechanism. The rotor forces the liquid through the disperser openings, thereby creating a negative pressure that pulls the gas downward into the liquid, causing an intimate gas-liquid contact. The oily water moves through a series of four cells before leaving the tank, and the float skimmings pass over the effluent weirs on each side of the unit. Assuming positive hydraulic control can be maintained, IAF oil removal efficiencies are usually comparable to DAF systems.

Chemical Coagulation-Flocculation and Sedimentation

This process includes the addition of chemical coagulants to produce microflocs by coagulation and the flocculation of these small particles which are then removed by sedimentation.

Upflow clarifiers have been used in lieu of the conventional flocculation-sedimentation system with chemical addition. In an upflow clarifier, the floc formed is removed in the sludge blanket as the water flows upward. Chemicals such as lime, alum, and polyelectrolytes are added before the wastewater enters the clarifier.

The combination of flocculation and filtration is also practiced. In an attempt to remove solid-stabilized oil emulsion in a six-foot filter column containing sand and anthrafilt, the addition of polyelectrolyte prior to filtration was found to improve the performance significantly (Ref. 12).

Filtration

Filtration systems have recently been applied to the separation of free and emulsified oil from wastewater streams. A broad spectrum of materials ranging from glass, porous ceramic, metals, plastics, sand, and anthracite to graphite, have been tested as filter media. The oil removal mechanism is by direct filtration and induced coalescence. As the wastewater flows down through the filter, depositing its solids in the top few inches of the filter bed, the oil droplets, without their combined solids, will more readily coalesce. The remaining bed, several

FIGURE 3

DAF PERFORMANCE ON OIL AND GREASE PRODUCTION WASTEWATERS

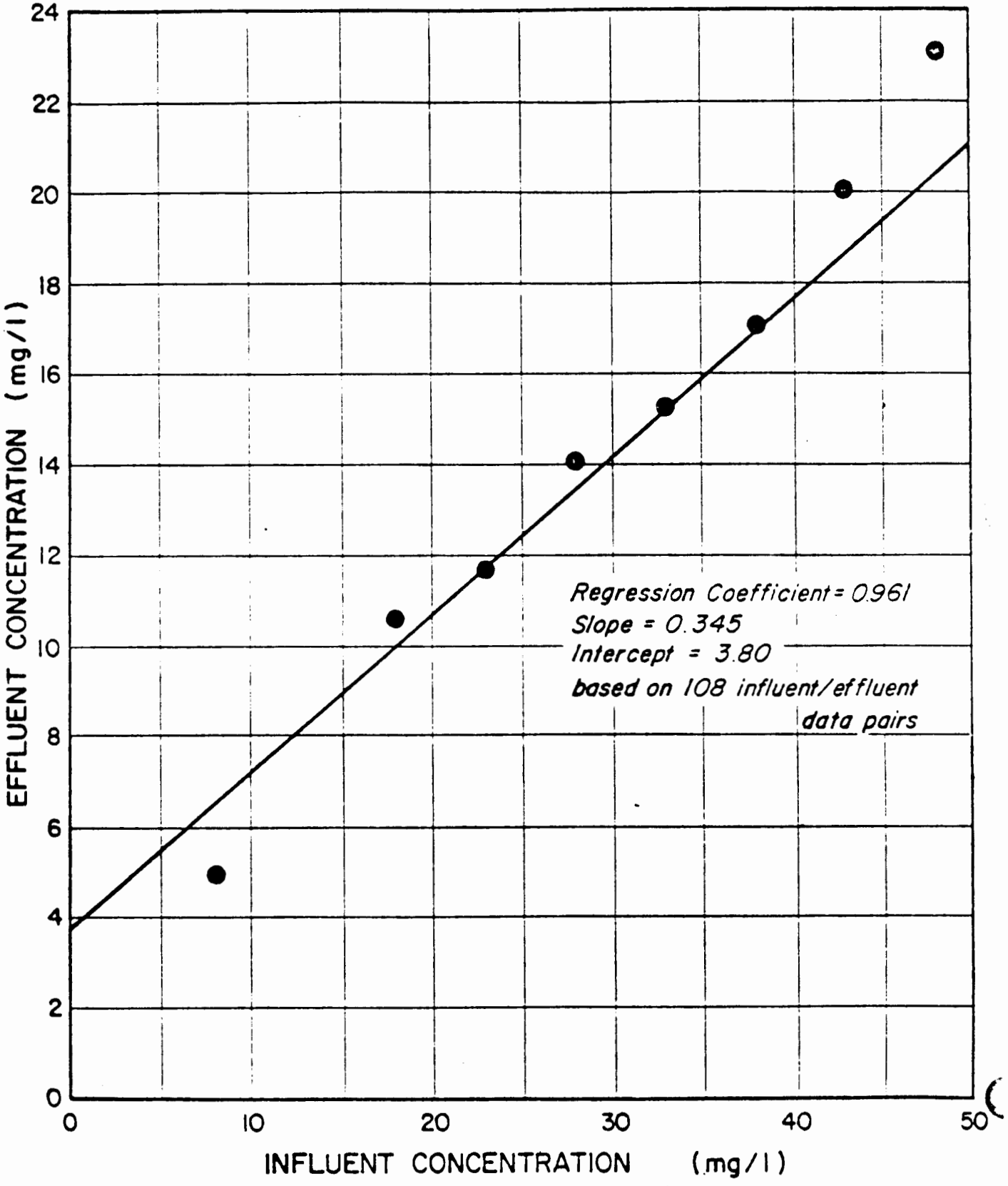
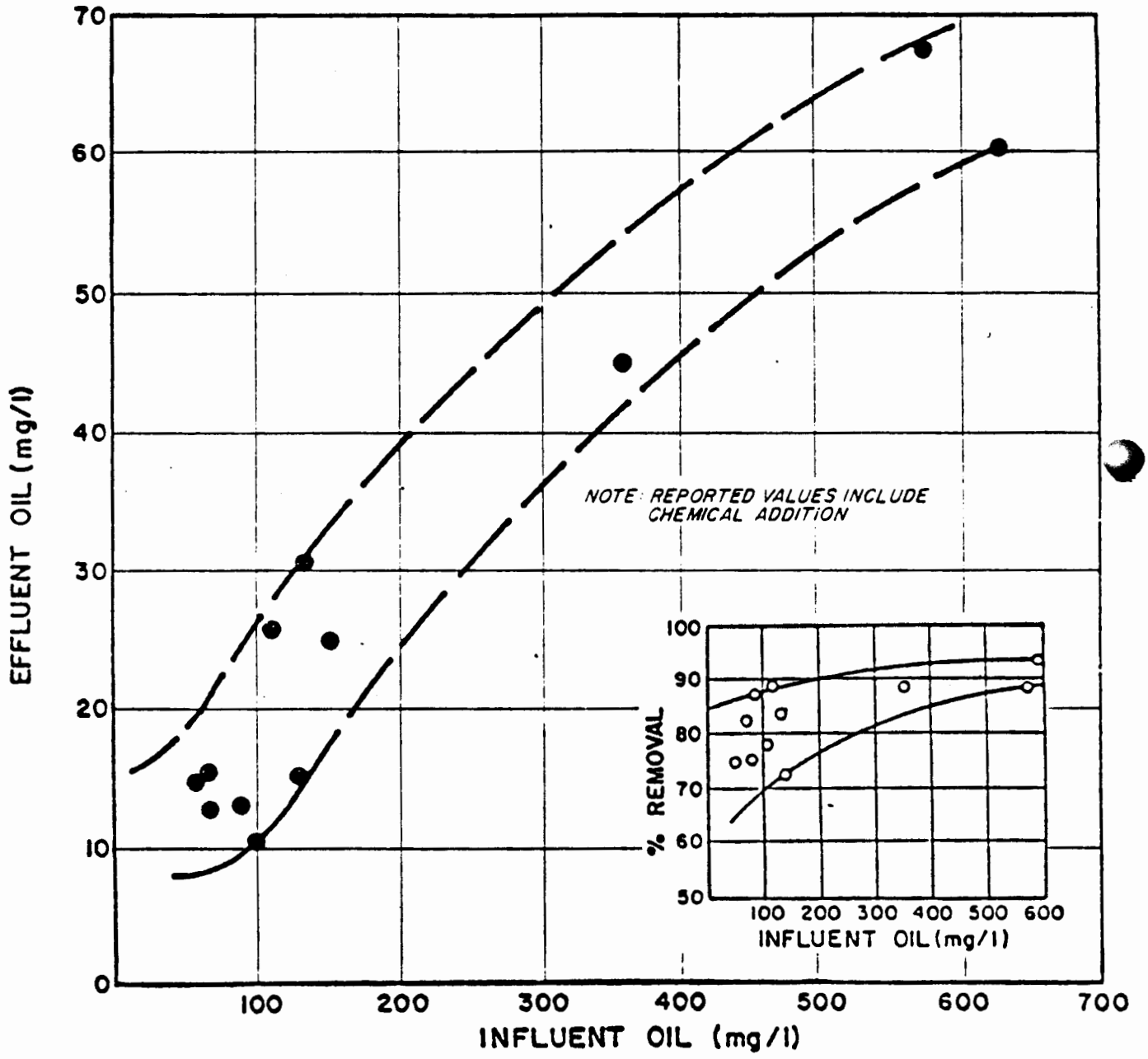


FIGURE 8

DAF OIL REMOVAL PERFORMANCE AS A FUNCTION OF INFLUENT CONCENTRATION FOR REFINERIES



feet deep, coalesces the oil droplets as they collide with each other and with oil-wet sand surfaces (Ref. 13). Coalesced oil tends to collect in the upper part of the filter and may not accumulate in sufficient quantities to flow out with the filtered water by the time backwashing is needed due to headloss considerations. The effectiveness of the filtration process in resolving emulsions is probably due to the rupturing of the oil globules on passing through the filter medium, allowing these particles to coalesce into separate phases.

A pilot filter column containing 5.5 feet of sand, 2.5 feet anthrafilt, and 16 inches of gravel was used to treat API separator effluent. The oil concentration in the influent ranged from 35 to 178 mg/l, and the effluent contained from 7 to 17 mg/l with an average of 11 mg/l oil. Addition of coagulant (1 to 5 mg/l) did not improve performance.

Higher oil-bearing capacities were found when crushed graphite ore was used instead of sand media. Better oil removals are believed to be due to the irregular shape and preferential sorption on the oil-wet graphite surface.

Coalescers

Finely dispersed or emulsified droplets may be coalesced and agglomerated by passing the dispersion or emulsion through a coalescer. These processes can be classified as plate, fibrous media, or loose media. Plate coalescers use gravity separation and parallel plates, fibrous media coalescers have a fixed element of fiberglass or other suitable material, while loose media coalescers use multi-grade sand or other loose media. Plate coalescers are sensitive to changes in flow rates and the plates must be cleaned regularly as sand and other small particles build up. Fibrous coalescers generally are quite efficient for coalescing oil droplets and removing fine solids. However, the accumulation of these solids within the filter has a deleterious effect on performance. Filter replacement is therefore a major problem (Ref. 14). Oil and suspended solids also accumulate in loose media coalescers, thus requiring replacement and/or frequent backwashing of the filtration media.

The operation and separation efficiency of coalescers is highly dependent on the characteristics of the wastewater being treated. This is documented for oil and gas production wastewaters by the data presented in Tables 7 and 8 (Ref. 15 and 14, respectively). Additionally, there are large variations in oil removal efficiencies as shown

FIGURE 10

INDUCED AIR FLOTATION SYSTEM (AFTER WEMCO)

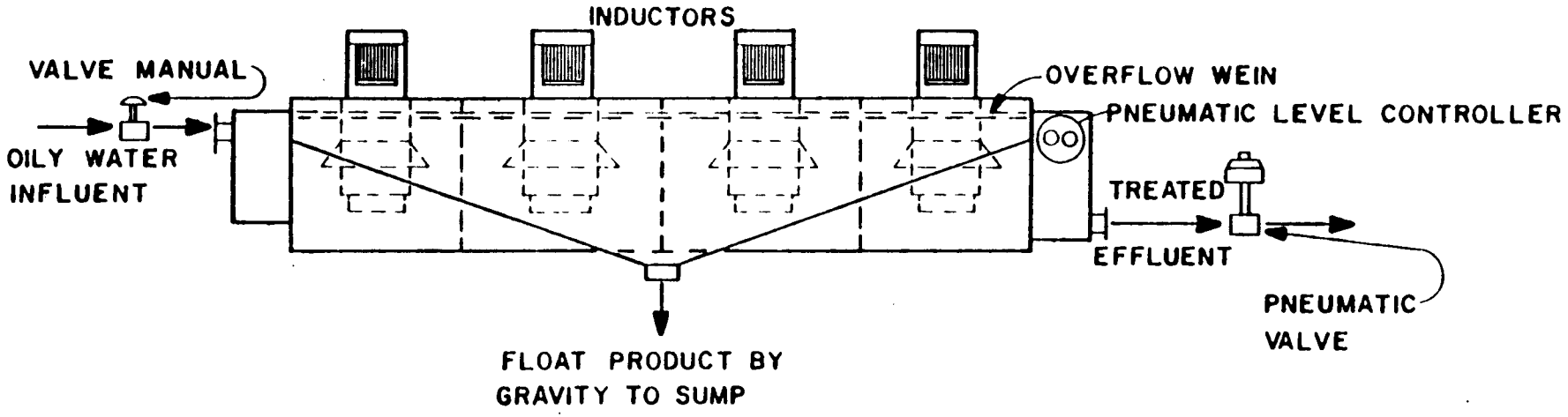


TABLE 8

SUMMARY OF OIL SEPARATION PROCESSES

Process Type	Units Analyzed	Mean Effluent Oil Concentration: Average ppm	Achieved by 75% of Units ppm	Achieved 98% of Time ppm	Remarks
Plate Coalescers	21	56.8	78	200	Requires periodic solids cleanout.
Fibrous Media Coalescers	6	42.0	55	180	Frequent filter replacement is usually required. Filter disposal presents an operational problem. Units require frequent backwashing to maintain hydraulic conductivity.
Loose Media Coalescers	13	21.8	24	60	Frequent backwashing or flushing and subsequent disposal of suspended solids represents an operational problem. Installations require tanks for handling backwash or flush water and influent flow equalization. Sophisticated instrumentation requires frequent attention creating a problem at remote locations.

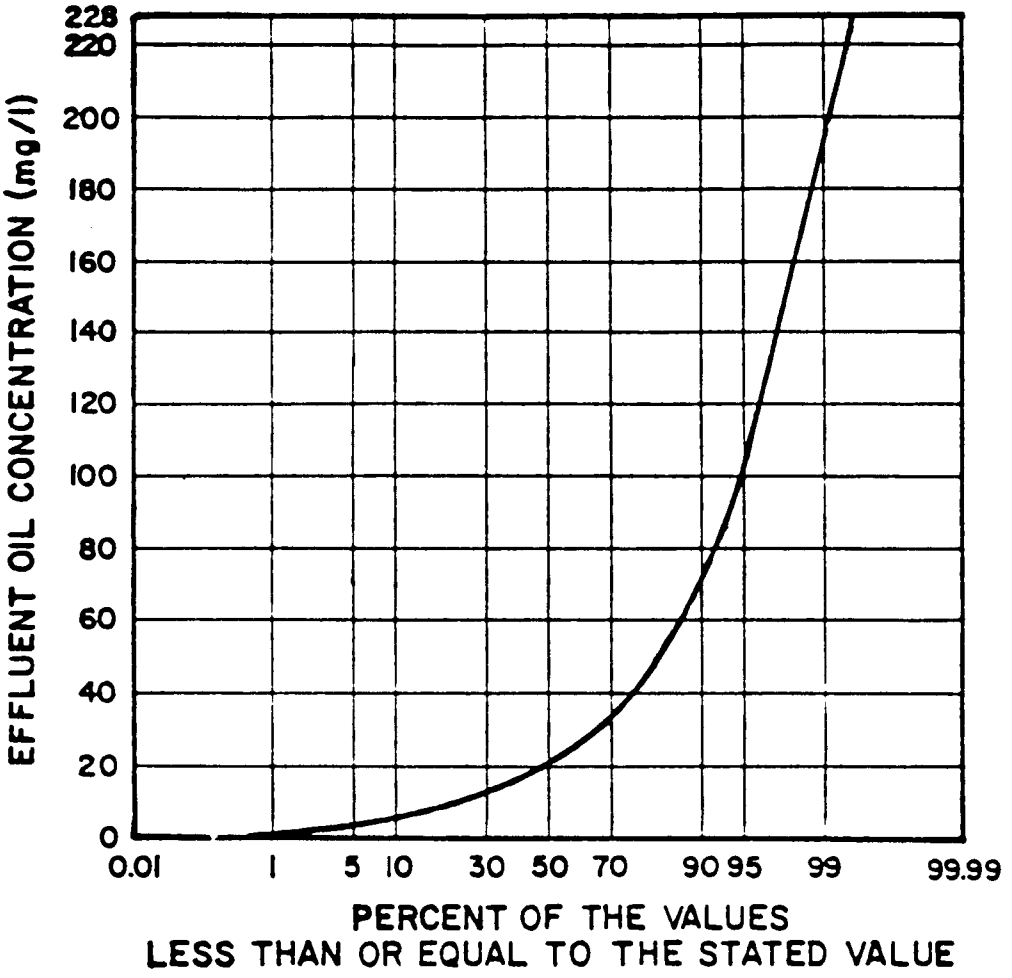
TABLE 7

MEDIA COALESCERS: A RANDOM SAMPLING-OPERATING EFFICIENCY

Rated Capacity, bbl	Throughput, B/D	Oil and Grease Concentrations, mg/l Influent	Effluent
8,000	1,050	347	135
6,000	3,500	284	22
3,000	1,930	172	86
4,000	4,677	206	42
5,000	8,000	186	86
10,000	8,000	105	96
4,500	1,500	88	21
4,000	7,500	116	14
4,000	7,500	116	4
6,000	1,800	15	4

FIGURE 11

PROBABILITY DISTRIBUTION OF EFFLUENT OIL DATA FOR FIBROUS MEDIA COALESCERS



for the fibrous media coalescer in Figure 11 and the loose media coalescer in Figure 12. This variability has been attributed to two major factors, namely:

(1) variation in crude oil characteristics, degree of emulsion, droplet sizes, and suspended solids; and

(2) fluctuations in flow rates, influent oil concentrations, and equipment upsets.

The effect of influent oil concentration on effluent quality for loose media coalescers is illustrated in Figure 13.

Membrane Processes

Membrane processes such as ultrafiltration or reverse osmosis have been proposed as oil removal processes. Laboratory tests have indicated good oil removal but relatively low flux rates, membrane fouling, and membrane-life problems prevent the practical application of membrane processes for oil and grease removal from most wastewaters.

Biological Processes

Biological treatment processes have limitations in their applicability to oil removal. Biological organisms are efficient in oxidizing soluble organic compounds including some dispersed or emulsified oil. Large amounts of free oil, in excess of approximately 0.10 lb per lb MLVSS, must be avoided as it coats the biological floc, prohibits efficient oxygen transfer within the biomass, and reduces sludge settleability. Therefore, while biological treatment processes may be required to meet discharge standards, care should be taken to design pretreatment facilities capable of removing oil to concentration levels that biological treatment processes may effectively treat.

While the biological treatment process is tolerant of feed quality changes, it is subject to toxic effects and can be upset by high loadings of organic constituents. Continued operation at high removal efficiency is difficult if not impossible to assure at all times.

The best documentation of process effectiveness for removing any parameter is a review of full-scale plant operations. Therefore, effluent quality data from selected treatment plants handling refinery wastewater were analyzed.

FIGURE 15

LOOSE MEDIA COALESCERS PERFORMANCE ON OIL AND GAS PRODUCTION WASTEWATERS

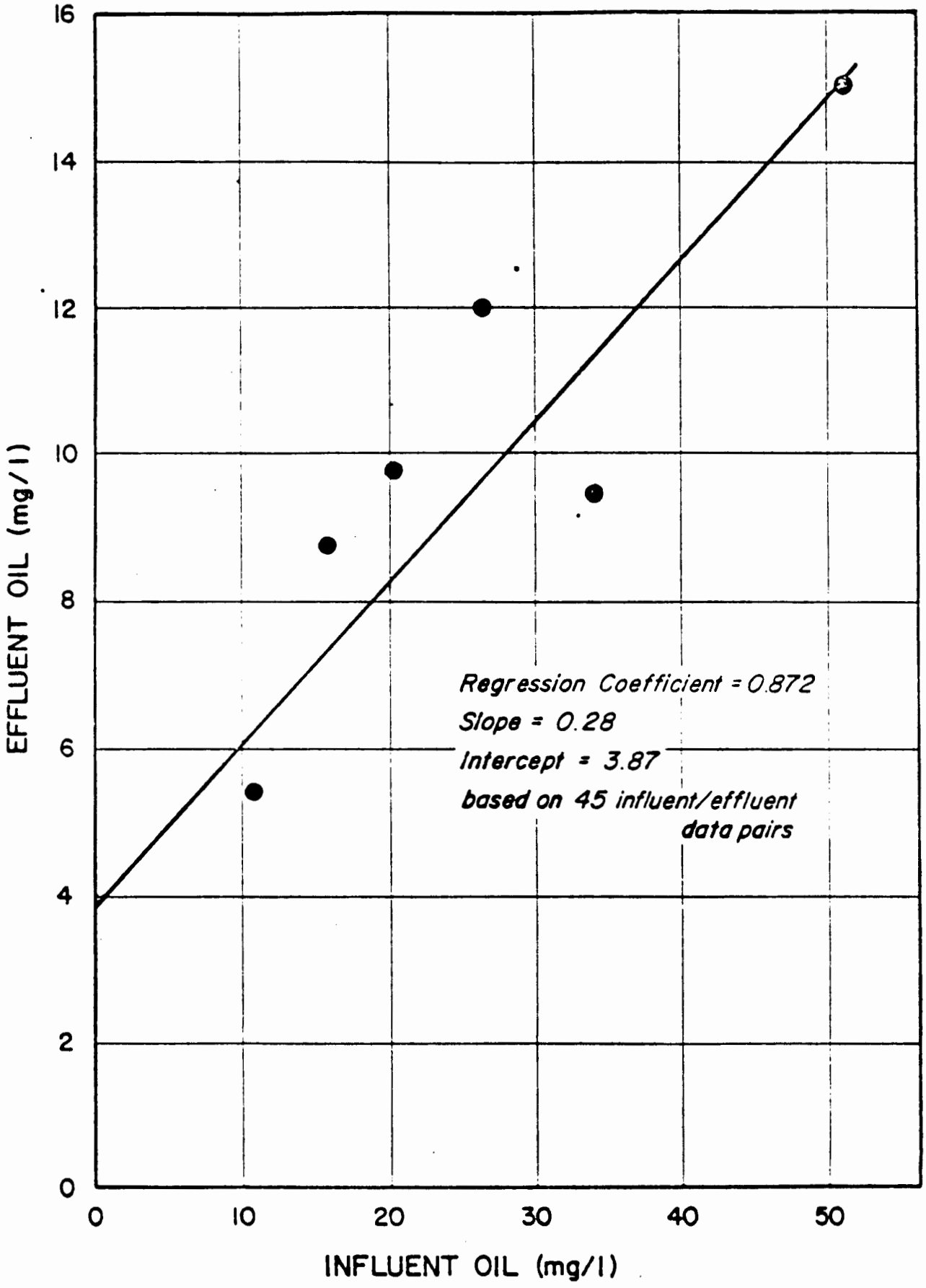
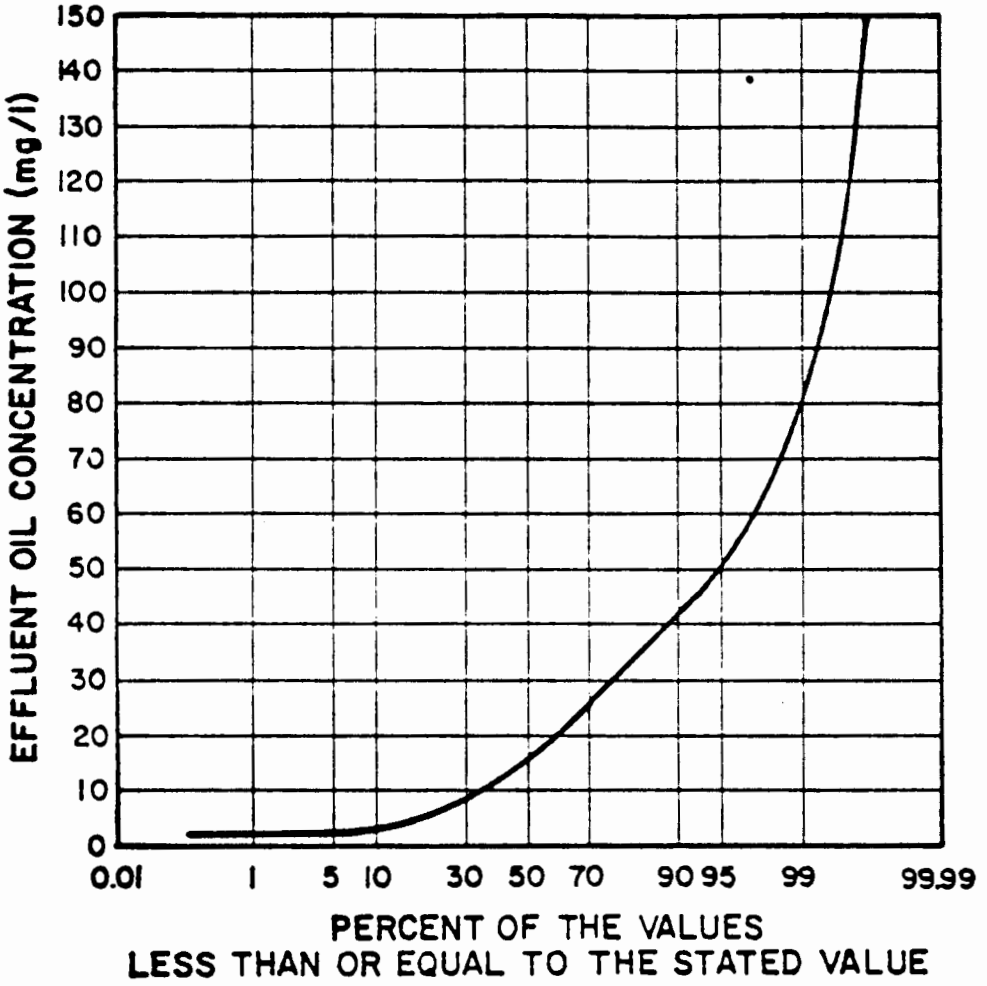
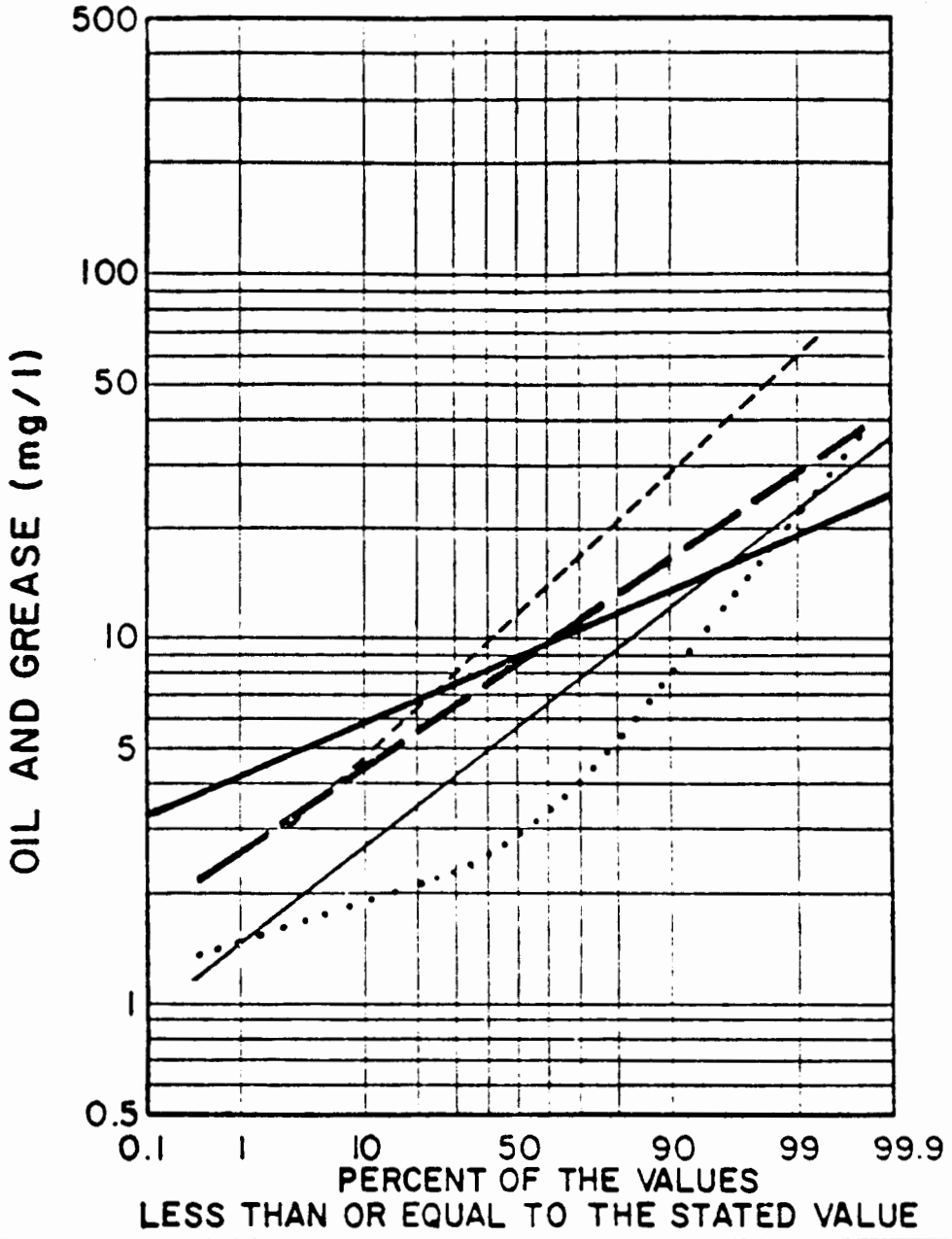


FIGURE 12

PROBABILITY DISTRIBUTION OF EFFLUENT OIL DATA FOR LOOSE MEDIA COALESCERS



OIL AND GREASE PROBABILITY BIOLOGICAL TREATMENT



CASE A

Median = 9.0 | Geom. Std. Dev. = 1.5 | Arithmetic Avg. = 9.7 | N= 396

CASE B

Median = 8.7
Arithmetic Avg = 9.6
Geom. Std Dev = 1.7
N= 161

CASE C

Median = 2.9
Arithmetic Avg = Not applicable
Geom. Std. Dev = Not applicable
N= 89

CASE D

WITH POLYMER

Median = 5.4
Arithmetic Avg = 6.4
Geom. Std Dev = 2.0
N= 41

WITHOUT POLYMER

Median = 10.3
Arithmetic Avg. = 11.5
Geom. Std. Dev. = 2.4
N= 75

Four biological treatment plants treating refinery wastewaters, each preceded by primary and secondary oil removal facilities, were selected for analysis as each is well designed and properly operated. A probability distribution of effluent oil and grease for each facility is shown in Figure 14. Case Histories A, B, and D are activated sludge plants, while Case History C represents an aerated lagoon system. Although these refineries represent various production subcategories as defined by EPA, refined crudes of varying characteristics, and have other process idiosyncrasies, a range of obtainable oil and grease levels can be defined. The median values, for example, range from 3 to 12 mg/l oil and grease, while two percent of the observed values (98 percent probability equal to or less than) exhibited a range of 20 to 60 mg/l. It should be underscored that this effluent quality cannot be obtained if an oil and grease overload is imposed on the system. An overload condition is normally assumed to exceed either an influent oil and grease concentration of greater than approximately 50 mg/l or 0.10 lb oil and grease per lb MLVSS in the aeration basin (Ref. 9).

The addition of post filtration to a biological system lowers the effluent oil and grease concentration, depending on the level of solids removal. A relatively good correlation has been obtained between effluent TSS from an activated sludge plant treating refinery wastewaters and oil and grease as shown in Figure 15. Typical oil and grease levels from activated sludge-post filtration systems treating petroleum refinery wastewaters have been reported to range from 3 to 15 mg/l, much of this obviously associated with the effluent TSS (Ref. 9).

It should also be recognized that oil and grease has an associated BOD and COD, although the correlation is generally poor. One correlation for composite samples collected in a petroleum refinery wastewater treatment system is presented in Figure 16 (Ref. 16).

Carbon Adsorption

Activated carbon adsorption has very limited use in the removal of oil. Adsorption primarily removes soluble oil. In addition, wastewater applied to activated carbon adsorption units must be pretreated to a high degree to prevent clogging and coating of the activated carbon. If the activated carbon adsorption units are not adequately protected, the units will have to be frequently backwashed and the activated carbon possibly replaced.

FIGURE 10

RELATIONSHIP BETWEEN BOD_5, COD, AND O&G IN INFLUENT REFINERY WASTEWATER AND TREATED EFFLUENT

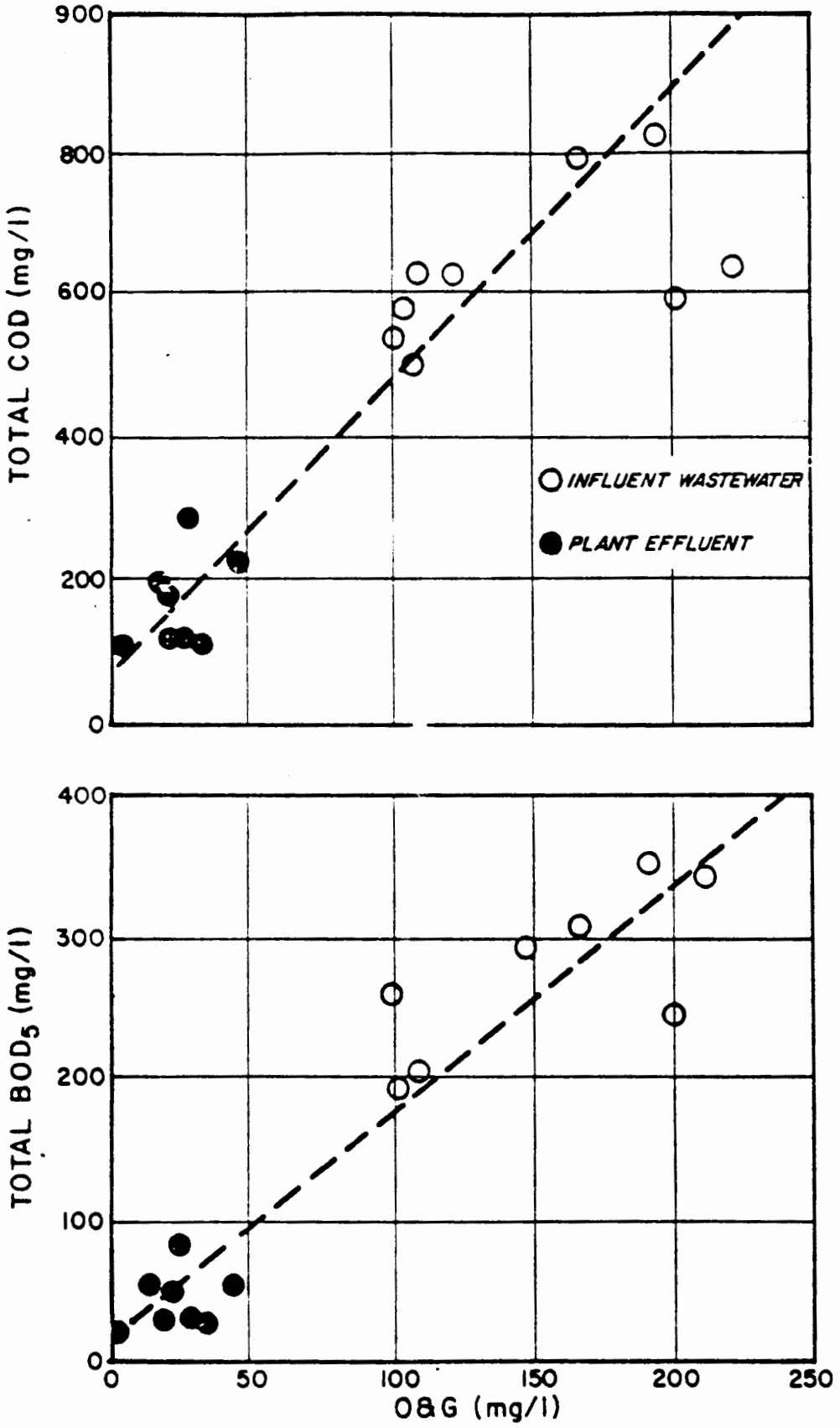
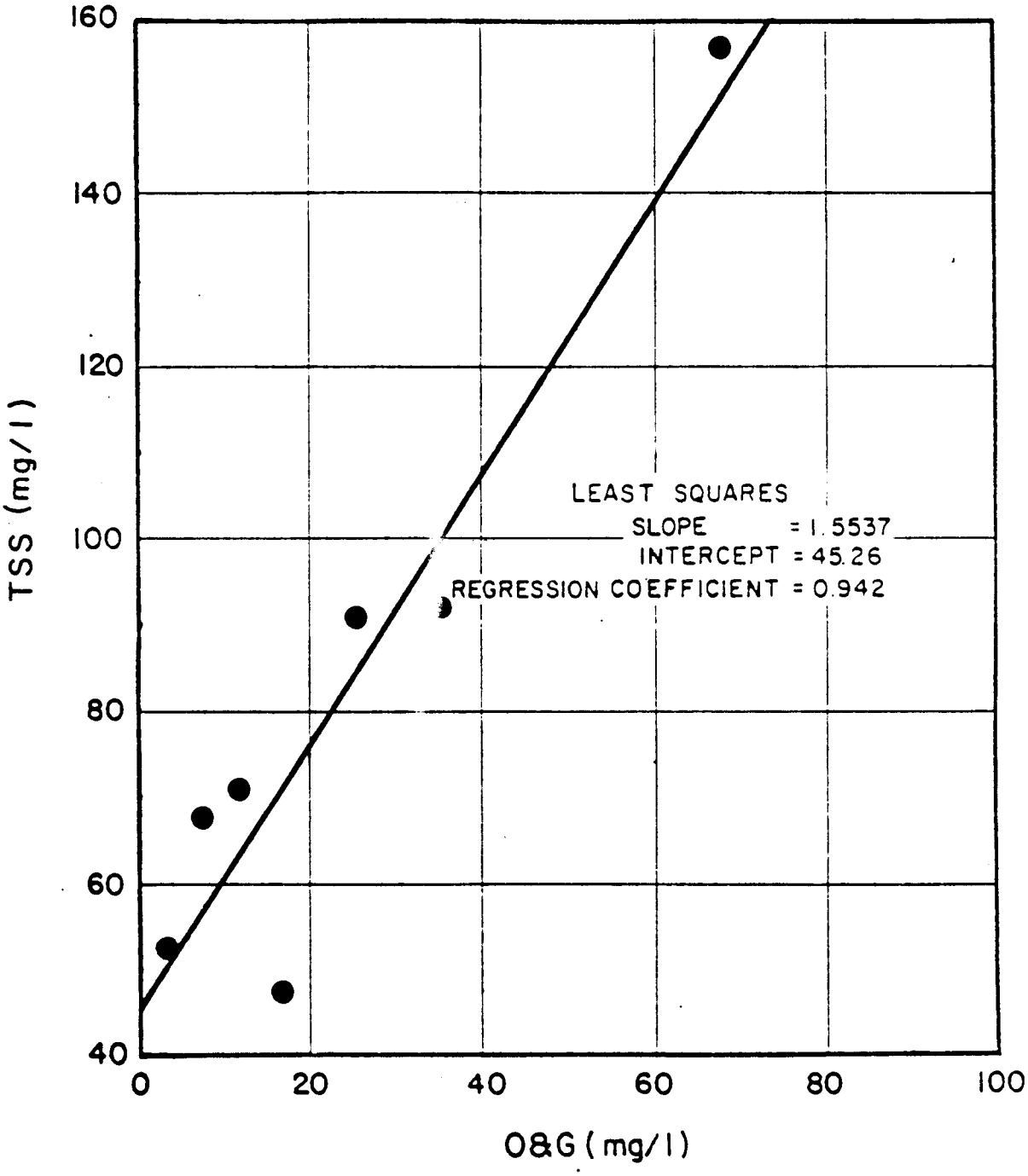
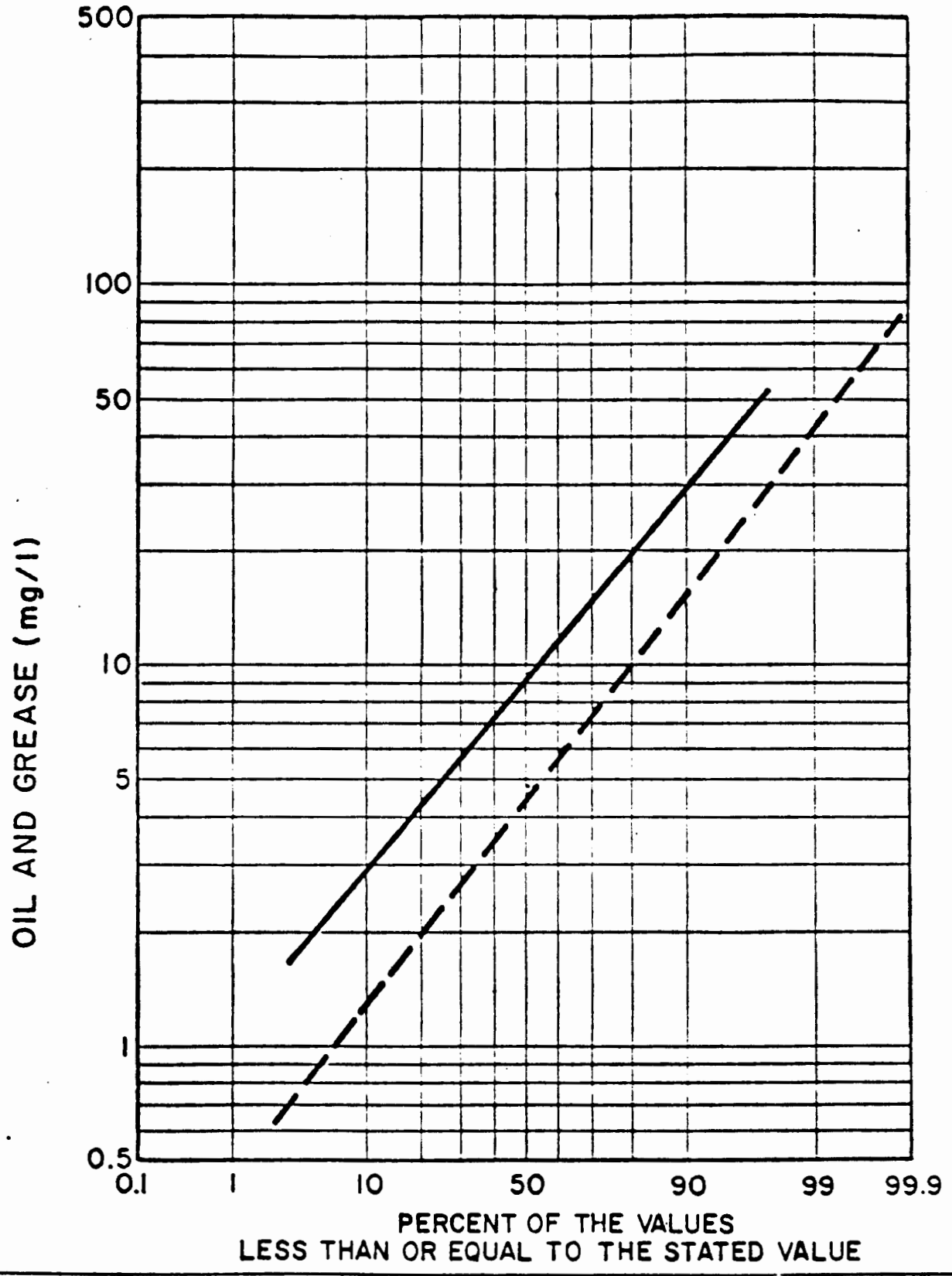


FIGURE 15

EFFECT OF EFFLUENT OIL AND GREASE ON EFFLUENT TOTAL SUSPENDED SOLIDS



OIL AND GREASE PROBABILITY CARBON ADSORPTION



CASE A	CASE B
Median = 9.3 Arithmetic Avg = 10.6 Geom. Std. Dev = 2.7 N= 13	Median = 4.4 Arithmetic Avg = 5.9 Geom. Std. Dev = 3.1 N= 55

The documented effectiveness of carbon adsorption reactors in removing oil and grease from refinery wastewaters on a full scale is limited to two case histories in the refining industry. These data are shown in Figure 17 and fall in the same general quality range as those from activated sludge plants (Ref. 17 and 18). Levels of 1.7 to 10 mg/l of oil and grease have been reported from activated carbon pilot studies, particularly when carbon is used as a polishing system for activated sludge effluent, although there are presently no full-scale systems using this series mode currently operating in the refining industry.

SUMMARY

The analytical techniques utilized for the measurement of oil and grease, with special attention paid to the precision and accuracy of the most common methods, have been presented. Based on the difficulty in obtaining samples from multiphase systems as well as the analytical variability, a large degree of bias may be expected to limit the reliability of oil and grease results, especially at low concentration levels. Due to these limiting and inherent biases, substantial latitude in the interpretation of oil and grease analyses for the purpose of establishing effluent discharge permit compliance must be allowed.

A review of the treatment technology typically utilized for oil and grease removal along with examples of treatment efficiency and typical effluent quality has been presented. Additionally, brief discussions were included for several processes which, although not in general use, have been suggested as potentially applicable for oil and grease removal. The advantages and disadvantages of the various processes are summarized in Table 9.

As the results presented in earlier portions of this treatise illustrate, the efficiency of any single or combination of unit processes in the removal of oil and grease from industrial wastewaters is highly dependent on process variables, influent concentration, and other often uncontrollable parameters such as temperature and production upsets. It is thus important, when considering the various oil and grease removal processes available, to recognize both the pertinent operational variables for each unit and the demonstrated performance capabilities based on full-scale operations. Only when all those factors have been weighed can a reasonable process selection be made for any specific application.

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TABLE 9

OIL REMOVAL PROCESS SUMMARY

Process	Advantages	Disadvantages
Gravity Separation (API Separators, CPI Separators, PPI Separators)	1. Economical 2. Simple operation	1. Limited efficiency 2. Susceptible to weather conditions 3. Removes little or no soluble oil 4. Limited removal of emulsified oil
Air Flotation (DAF & IAF)	1. Handles high solids 2. Reliable process (handles shock load)	1. Chemical sludge disposal when coagulants are used (DAF only) 2. Requires chemicals
Chemical Coagulation-Flocculation and Sedimentation	1. Handles high solids	1. Excessive chemical sludge produced 2. Not cost-effective
Filtration	1. Handles high solids	1. Requires backwashing 2, Backwash stream is a subsequent problem
Coalescers (Plate, Fibrous and Loose Media)	1. High potential efficiency	1. Cannot handle high solids due to fouling 2. Potential biological fouling 3. Demonstration as a practical process for oil and grease removal is limited
Membrane Processes	1. Soluble oil removal indicated in laboratory tests	1. Low flux rates 2. Membrane fouling and questionable membrane life 3. Not demonstrated as a practical process for oil and grease removal
Biological	1. Removes soluble oil 2. Relatively high tolerance for oil and grease	1. Solids carryover 2. Prone to upset 3. Pretreatment prerequisite
Carbon Adsorption	1. Removes soluble oil 2. High potential efficiency	1. Expensive 2. Regeneration required 3. Requires extensive pretreatment 4. Full-scale operation not proven in refinery 5. Energy intensive

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PRIMARY SEPARATORS -- EQUALIZATION AND DISSOLVED AIR FLOTATION

AND

PROCESS ENGINEERING -- SECONDARY AND EFFLUENT POLISHING

THE USE OF BIOLOGICAL SYSTEMS TO REMOVE TOXIC CONSTITUENTS

by

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to the

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THE USE OF BIOLOGICAL SYSTEMS TO REMOVE TOXIC CONSTITUENTS*

Introduction

With the increasing scrutiny of hazardous and toxic materials present in liquid effluents, their fate through the various treatment methodologies, and their ultimate impact on the environment, it is appropriate to reconsider the applicability of biological systems in treating such constituents.

There are many incentives to engineer biological systems that are capable of removing or reducing constituents with toxic or hazardous implications to acceptable concentration levels. As biological treatment processes are universally applied in many industries, the incentives to modify or retrofit as compared to constructing new facilities are obvious. The capital and annual costs associated with biological systems are normally lower than process alternatives, and as the biochemical reactions proceed toward completion, the toxicity potential of the by-products or end-products is generally far less than that of the reactants. It is, therefore, the purpose of this treatise to discuss some of the major elements of system analysis, biochemical concepts, and performance in terms of toxic constituent removal.

The literature is rather consistent in endorsing the activated sludge process (and its appropriate modifications) as capable of removing the priority pollutants to concentration levels at or below the analytical detection limits (1)(2)(3)(4)(5). By definition, there are approximately 85 toxic organic pollutants on EPA's list of priority pollutants and sub-categorized as volatile, base/-neutral, or acid. Other compounds found in industrial effluents may also have deleterious impacts on the environment as they are discharged to the receiving waters.

It is recognized that there are three major pathways by which these constituents can be removed in a high-rate biological system. These include biochemical oxidation

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(biotic), sorption (abiotic) or volatilization (abiotic). It may then become important to identify the importance and relevance of these pathways so that the proper engineering decisions can be made. The preponderance of evidence points to biodegradation being the dominant removal mechanism when an active biomass is present (6)(7)(8)(9). Each situation is unique, however. The physical constants of the liquid phase such as the vapor pressures, the partition coefficients, and the relative solubilities of the dissolved constituents are important as well as the biodegradability of these organic compounds. Moreover, the mixing intensity of the biological reactor, the air flow, the physical geometry, and the inventory of active bio-mass all play an important role. The complexity of such a system, the process and environmental variables which prevail, and the level of operational control all interrelate and force the engineer to judge and configure each system on its technical merits.

Screening Analyses

The first step in developing the necessary information relative to evaluating the applicability of biological treatment systems in removing specified constituents from the liquid fraction is to review the literature for biodegradability and physical characterization data for specific compounds. The most comprehensive sources for listing compound biodegradation information are cited as references (4) and (10). The next logical step is performing the necessary screening tests. There are three basic approaches presented herein, namely, the Warburg analysis, the EBOD analysis, and the bench-scale batch reactor analysis. Each are briefly discussed:

The Warburg Analysis. The Warburg apparatus consists of a monometer and a reaction flask and is frequently used to screen xenobiotic compounds which may be present in the wastewater. The reaction flasks are connected to a monometer and as biochemical oxidation proceeds, the carbon dioxide produced by the respiring microorgnisms is absorbed in a potassium hydroxide solution which occupies the center well of the reaction flask. The acclimated biological seed, which has been added to the flask along with the desired proportion of the wastewater, biochemically oxidizes this substrate to the extent that conditions allow. As the microorganisms utilize the organic constituents of the wastewater sample, the gas phase oxygen is reduced within the closed system, and a corresponding pressure differential is recorded. The cumulative oxygen utilization values can be plotted

versus time and the toxic or inhibitory thresholds are indicated by significant drops in the relative oxygen uptake rates. The Warburg assembly allows the evaluation of several flasks at one time, and different substrates and/or dilutions can be evaluated concurrently. A detailed procedural analysis in utilizing the Warburg approach is described in reference (11).

The Electrolytic BOD Analysis (EBOD). A screening approach using the same principles of the Warburg analysis but applying a different methodology is the application of the Electrolytic BOD Respirometer System (12). This system consists of a reaction vessel, an electrolysis cell, a proportionately controlled incubator, an electronically operated measuring unit, and a printer. The reaction chamber consists of a one liter stirred vessel, the manometric switch, and an electrolytic oxygen generator mounted on the top. The acclimated biological seed and substrate are added to the reaction chamber using the same approach as the one used with the reaction flasks in the Warburg apparatus. As the dissolved oxygen in the liquid phase is biologically utilized, carbon dioxide is released and absorbed in a potassium hydroxide-filled container. This results in a slight vacuum in the air space being produced, and a manometric switch is triggered and oxygen is produced electrolytically to replace the oxygen consumed. The oxygen generated by electrolysis is related to the current applied and to the length of time the generator is on. Therefore, accumulative oxygen demand may be recorded at any time during the test period and is proportional to the degree of biochemical oxidation that takes place. The relative biological activity can then be recorded.

The Batch Reactor Analysis. The Batch Reactor Analysis can be conducted on the bench-scale using several containers affixed with air sparjers. As in the two methods previously described, aliquots of acclimated seed and the substrate in question are added to each reactor and the aeration commences. The volatile suspended solids (VSS) concentration and soluble organic fractions are recorded and monitored as a function of aeration time. The reduction of the soluble organic fraction in each of the reactors is monitored, and this profile is indicative of the relative biodegradability of the substrate. Although the procedure is tedious and requires considerable time to correctly implement, it can be used successfully to delineate approximate threshold concentrations for constituent toxicity and to develop a bio-

logical seed which can effectively reduce recalcitrant compounds. A detailed approach in utilizing the Batch Reactor Analysis are cited in reference (11).

The Empirical Development of Process Kinetics

The formulation of design criteria for the biochemical oxidation of liquid streams containing toxic or hazardous constituents can be developed through the application of bench and full-scale treatability studies using continuous flow reactors (11). Such studies are normally conducted after the screening tests have been performed and the literature thoroughly researched. There are obviously many variables involved with such studies and one must be careful not to oversimplify the process simulation. However, if the environmental conditions, such as temperature, pH, and dissolved solid concentrations are held relatively constant, then one is able to generally predict the achievable levels of biochemical oxidation at predetermined hydraulic retention time and sludge ages. Representative samples of wastewater should be used and the degree of variability in the raw wasteload would determine how much pretreatment and equalization is required prior to introducing the liquid stream into the biological reactor. This analysis, of course, is complicated when the relative concentrations of the toxic or hazardous constituents in the wastewater vary significantly with time.

If one monitors the biodegradation rates for a single substrate in a controlled reactor using acclimated seed, the biodegradation rate normally approximates zero order (a linear reduction of substrate concentration as a function of aeration time.) The "K" rate of the zero order reaction is a function of the intrinsic properties of the organic compounds as determined by the molecular structure and configuration. When many compounds are present, which is normally the case in an industrial waste stream, then concurrent zero order reactions of varying "K" rates are occurring with the total reaction rate of the soluble organic fraction approximating first order. Most of these biodegradation rates have been interpreted using the Monod equation (13). This is basically an approximation of the Michaelis-Menten equation using enzyme kinetics as basically presented in the following equation:

$$\frac{S_o - S_e}{X_a t} = \frac{\left[\frac{S_o - S_e}{X_a t}\right]_{max}\left[S\right]}{\left[S\right] + \left[K_s\right]} \qquad \text{(Eq.1)}$$

Where:

S_o = initial substrate cocentration
S_e = final substrate concentration
X_a = active biomass
t = substrate contact time
K_s = half velocity coefficient

The more recognized form of this equation is:

$$\frac{dS}{dt} = \frac{KS_e}{K_s + S_e} \qquad \text{(Eq. 1-a)}$$

Where: K = the maximum substrate utilizaton rate

and

$$K = kX_a$$

The K and Ks values can be determined graphically by plotting 1/Se as a function of

$$1 \Big/ \frac{S_o - S_e}{X_a \cdot t}$$

with the intercept equal to 1/K and the slope being K_s/K.

For a continuous stirred-reactor (CSTR) at steady state, then the change of concentration with respect to time is zero and the simplified model as presented in Equation 1 can be solved algebraically. In addition to the steady state assumption, one must further assume that the enzyme amount remains constant throughout the experiment, the substrate concentration does not change appreciably during the measurement, substrate feed is sterile, and monitoring of the substrate concentration represents the soluble fraction only. The development of the kinetic equations for batch are plug-flow reactors involved differential equations and are much more difficult to solve.

It is important to recognize that the development of process kinetics using bench or pilot-scale treatability studies have inherent limitations, but properly conducted, can approximate what will occur in the full-scale application. The key elements of predicting effluent concentrations using these simulation techniques center around the utilization of representative wastewater samples, sequestering the variability of the raw wasteload

through pretreatment and equalization, insuring complete mixing in the biological reactor, and properly defining the effects of process and environmental variables. Of particular importance is the effect of the liquid temperature on the biodegradation of toxic or hazardous constituents. One must recognize that the temperature effects could be much more pronounced for recalcitrant molecules as compared to those which are easily biodegradable. The energies of activation of potentially toxic or hazardous molecules are normally higher than that of other organic compounds. The effect of this energy of activation on the "K" rate of a particular molecule is developed as follows:

$$\frac{d \ln k}{dt} = \frac{E}{RT^2} \qquad \text{(Eq.2)}$$

and

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E(T_2 - T_1)}{RT_1T_2}$$

and

$$\frac{k_1}{k_2} = \theta^{T_2-T_1}$$

Where:

E = energy of activation
R = gas constant
T_1, T_2 = liquid temperatures
k_1, k_2 = organic removal velocities
θ = temperature coefficient

It is noted from this equation that the temperature coefficient, θ, is a direct function of the molecular energy of activation, which generally indicates that the more complex and recalcitrant the molecule, the more significant is the effect of liquid temperature. The implications of this are obvious when trying to biologically treat xenobiotic compounds in cold climates. There are engineering approaches to overcome this problem, such as providing a longer sludge age, a higher inventory of active biomass, or minimizing heat losses, but the system should be engineered in recognition of these effects.

Biotic and Abiotic Pathways In The Biological System

As previously mentioned, there are three major pathways by which a toxic or hazardous constituent can be removed in a biological reactor. These include the

straight biochemical oxidation of water soluble organic substrates, the sorption of these constituents on the biological mass, and the volatilization of these compounds into the atmosphere. Mathematically this can be expressed on a mass balance basis by:

$$dS/dt \cdot V =$$

$$QS_o - \left[QS_e + dS/dt_{bio} \cdot V + dS/dt_{str} \cdot V + dS/dt_{sorb} \cdot V\right] \quad \text{(Eq.3)}$$

The development of the various constants for each component removal is discussed elsewhere (2)(18). The precise delineation of these pathways may or may not be important depending on the particular situation. A brief discussion on each of these pathways is presented as follows:

Biochemical Oxidation. The biochemical degradation of both the readily biodegradable and recalcitrant compounds is generally the dominant removal mechanism as documented in the literature. There are several approaches one can take in order to establish the veracity of this removal mode. The most convenient approach is to establish an oxygen material balance. This can be accomplished by determining the oxygen uptake rate in the biological reactor, dividing this value by the volatile suspended solids concentration to put it on a specific basis, and comparing it to uptake rates of similar systems. Furthermore, the system oxygen demand can be compared to the corresponding removal of organic constituents in the system as measured by BOD_5, TOC, or COD, by assuming the fraction of a theoretical oxygen demand that the BOD, TOC, or COD represents, then calculating the balance. If a relatively good balance is obtained, then removal of the organic constituents via the biochemical oxidation pathway can be presumed. This can further be verified by measuring the gas phase concentration of the organic constituents in a closed system in order to verify the closure. If the results are consistent, namely, a good oxygen material balance is obtained by measuring the liquid phase uptake rate and comparing with the organic removal, combined with the detection of nominal constituent concentration in the gas phase, then the biochemical oxidation pathway is confirmed. If this is not the case, then one needs to further analyze the other removal mechanisms.

Sorption. Sorption is basically a mechanism where the constituent colloidal, suspended, and sometimes sol-

uble fractions are physically sorbed on the biological floc. It is precisely this mechanism that led to the development of the contact stabilization process for the treatment of municipal wastewaters, where a significant fraction of the organic constituents is in the colloidal or suspended form. It also may be responsible for removal of toxic or hazardous constituents in the biological treatment of industrial wastewaters. This can basically be determined by monitoring the soluble and nonsoluble fraction of the organic constituents in question throughout the biological process. If an oxygen balance on the liquid side is not achieved, and the selected constituents are measured in the sludge fraction of the system, then the sorption pathway takes on added significance. If sorption does play a dominant role in the removal process, then the system kinetics based on the soluble fraction would obviously be altered. More attention to handling the sludge fraction, however, may be an issue based on the ultimate disposal methodologies in handling the sludge. For example, one could make the case that a significant biocumulation or sorption of toxic or hazardous constituents onto the biological sludge might affect its classification as a hazardous or nonhazardous sludge. This would have obvious implications in the handling and disposal of this sludge under the Resource Conservation and Recovery Act (RCRA).

Volatilzation. The potential for air stripping high vapor pressure compounds into the atmosphere from biological wastewater treatment facilities has been the subject of many investigations because of air pollution implications. As the theoretical prediction of the air stripping phenomenon in a biological treatment system is difficult because of the many physical and biological variables, the quantification of the stripped component can be estimated by bench or full-scale testing. It is first presumed that the equilibrium between the gas and aqueous phases of the constituent is governed by Henry's law for the organic solids in the dilute concentration range.

$$C_g = H_c C_l \qquad \text{(Eq.4)}$$

Where:

C_g = mass concentration in the gas phase
C_l = mass concentration in the liquid phase
H_c = the Henry coefficient expressed as a dimensionless mass concentration partition ratio

and

$$H' = H_c RT \qquad \text{(Eq.5)}$$

Where:

H' = the Henry coefficient of a molecule ($atm/mol/m_3$)
R = the universal gas constant
T = the absolute temperature, °K

The Henry partition ratio can be used to approximate the gas and liquid concentrations of a solute, although this is a simplified approach and must be verified by field testing which incorporates the applicable process variables. Although the kinetics of air stripping are complex, proposed models are (14)(22):

$$\frac{S_e}{S_o} = \frac{1}{1 + (Q_a/Q_l) H_c} \qquad \text{(Eq.6)}$$

Where: Q_a/Q_l = airflow to liquid flow ratio

and

$$K_a{}^a \cdot V/Q = bH_c{}^m \qquad \text{(Eq.7)}$$

Where:

$K_a{}^a$ = stripping rate constant
V = volume of the liquid in the reactor
Q = air flow rate
b,m = power function constants

It is important to note that the stripping rate constant is a direct function of liquid temperature (Equation 5) and air flow rate (Equation 6, 7). Therefore, while the Henry coefficient of the compounds in the liquid phase is important relative to the stripping potential, the air flow rate and liquid temperature also play a major role as to what potential

fraction of the organic constituent can be stripped from solution. The temperature effects are exemplified by biodegradability and volatility studies with selected halogenated aliphatics showing 27 to 34 percent volatilization at 25° C, with no volatilization at 5° C (15). Perhaps the most significant factor relative to air stripping, however, is the presence or absence of active biomass in the liquid phase. Most investigators agree that the presence of an active microbial culture shifts the removal pathway from air stripping to biodegradation, even when conditions favor the stripping mechanism. Consequently, one should carefully analyze the total regime in terms of the physical characteristics of the solute, the liquid temperature range, the sorbability potential, and the level of biological activity in the biological reactor prior to predicting the air stripped fraction. Once this is done, then appropriately measuring the organics in the gas phase can be accomlished in order to verify the liquid phase measurements (such as oxygen uptake and organic reduction) and complete the material balance. The relative importance of the stripped fraction with respect to ambient air quality will dictate the extent to which such tests should be performed.

Summary

In summary, the evidence infers that the preponderance of "priority pollutants" in a waste stream being treated biologically are removed through the biodegradation pathway. A recent study was conducted by EPA to determine the biodegradability of 114 organic priority pollutants cited in the EPA consent Decree list (16). This study was based on static flask screening techniques using enrichment cultures and two concentrations of the test compound. The results of these tests, along with those data observed from a cooperative field study between EPA and the Chemical Manufacturing Association (CMA) are presented in Table 1. (1)(6) Even with the stripping modification of these static tests, the volatilization losses were generally less than 30 percent. More comprehensive testing in terms of delineating the biotic and abiotic pathways for removing benzene, toulene, ethylbenzene and o-xylene were recently conducted. (17)(18)(19) The results of these tests, conducted using bench-scale activated sludge reactors are presented in Table 2.

These results were derived from operating bench-scale activated sludge reactors at a sludge age of 2 to 6 days, an operating temperature of approximately 20° C, and at air

TABLE 1

Comparison of Biodegradability of Toxic Organic Pollutants as Predicted by EPA Study to the Five-Plant Study Results

Volatile Compound	EPA Percent Degradation*	Five-Plant Study Percent Removal**
Acrylonitrile	100	99
Benzene	100	100
Bromomethane	48	100
Bromodichloromethane	67	89
Carbon tetrachloride	100	100
Chlorobenzene	100	56***
Chloroethane	NA	91
Chloroform	100	99
Dibromochloromethane	55	100
1,1-dichloroethane	100	79***
1,2-dichloroethane	100	99
1,1-dichloroethene	100	100
t-1,2-dichloroethene	100	98
1,2-dichloropropane	92	97
1,3-dichloropropane	100	98
Ethylbenzene	100	99
Methylene chloride	100	75
1,1,2,2-tetrachloroethane	36	93
Tetrachloroethene	100	27***
1,1,1-trichloroethane	100	38***
1,1,2-trichloroethane	59	72***
Trichloroethene	100	40***
Toluene	100	100
Vinyl chloride	NA	100

Base/Neutral Compound	EPA Percent Degradation*	Five-Point Study Percent Removal**
Acenaphthene	100	95
Acenaphthylene	98	93
Anthracene	92	97
Benzo(a)anthracene	35	56***
Benzo(b)fluoranthene	100	--***
Benzo(a)pyrene	NA	--***
Bis(2-ethylhexyl)phthalate	95	64
Butylbenzylphthalate	100	87***

Dibenzo(a,h)anthracene	NA	--***
Di-n-butylphthalate	100	99
1,3-dichlorobenzene	35	100***
1,2-dichlorobenzene	29	94
Diethylphthalate	100	99
Dimethylphtnalate	100	99
Dioctylphthalate	94	90
Fluoranthene	100	83***
Fluorene	77	93
Isophorone	100	100
Naphthalene	100	100
Nitrobenzene	100	98
Pyrene	100	84***
1,2,4-trichlorobenzene	24	82

Acid Compound	EPA Percent Degradation*	Five-Plant Study Percent Removal**
2-chlorophenol	100	41
2,4-dichlorophenol	100	91
2,4-dimethylphenol	100	100
2,4-dinitrophenol	100	84
2-nitrophenol	100	77
Pentachlorophenol	100	36
Phenol	100	98
2,4,6-trichlorophenol	100	45

* Includes volatilization losses at 25 C and initial concentration of 5 mg/l

**Based on arithmetic means

***Influent concentration less than 40 ppb

NA = not available

Table 2

Fate of Benzene, Ethylbenzene, Toulene, and Xylene
in Activated Sludge Reactors

Reference		Benzene	Toulene	Ethylbenzene	O-xylene
	% Biodegraded	97.8	94.90	94.6	--
(17)	% Air Stripped	2.0	5.10	5.2	--
	% Sorbed	--	.02	.2	--
	% Biodegraded	83.6	83.8	80.0	78
(18)	% Air Stripped	15.9	15.6	19.5	21
	% Sorbed	0	0	0	0
	% Biodegraded	--	88.4	--	--
(19)	% Air Stripped	--	11.6	--	--
	% Sorbed	--	--	--	--

flow rates in the range of 185 to 400 ml air/liter of reactor volume/min. (2.47 to 5.35 cfm/1000 gal) These data support the removal totals tabulated in Table 1 and confirm dominance of the biological pathway preference even with moderate liquid temperatures and high air flow rates, both of which favor air stripping.

Addition of Powdered Activated Carbon to Biological Systems

The addition of powdered activated carbon (PAC) to the biological treatment systems is receiving considerable attention in the United States today, particularly with respect to the removal of the recalcitrant organic constituents, many of which constitute the "priority pollutants". With emphasis of the State and Federal regulatory authorities on upgrading effluent quality in terms of both the traditional organic pollutants as expressed by BOD, COD, TOC, or TOD, as well as the priority pollutants, both the industrial and municipal sectors of the economy are evaluating this approach based on its potential economic and process advantages over alternative systems.

The applicability of activated carbon in removing specific substrates depends on the molecular weight, solubility, polarity, location of functional groups, and overall molecular configuration. However, many of the organic constituents included in the list of 129 "priority pollutants", as cited by the United States Environmental Protection Agency, are amenable to carbon adsorption as shown in Table 3. (20). This increases the attractiveness of this process, particularly when the removal of priority pollutants becomes the critical requirement for effluent quality control.

Investigations of PAC systems have centered around several process enhancement approaches. These include the enhancement of a system to receive shock loadings or temperature changes, improving non-biodegradable or persistant organics removal, improving removal of priority pollutants, improving color removal, enhancing the resistance to biologically toxic or static substances, improving the organic capacity of existing facilities, improving nitrification, suppressing foam in aeration system, improving sludge handling, and reducing sludge bulking. The emphasis in recent years has been primarily directed toward removal of toxic or hazardous pollutants, and removal of other residual organic compounds.

The applicability of activated carbon in upgrading

TABLE 3

Priority Pollutant Removals Across PACT System*

Compound	Concentration in ug/liter (ppb) Feed	PACT Effluent	Removal (%)
Volatile Organics			
Benzene	105	0.9	98
Carbon Tetrachloride	94	1.4	95
Chlorobenzene	1720	30	98
Chloroethane	280	12	94
Chloroform	201	21	81
Ethylbenzene	41	1.7	94
Methyl Chloride	1770	Nil	99
Tetrachloroethylene	24	1.7	93
Toluene	519	1.7	99
1,1,1-Trichloroethane	13	0.6	89
Trichloroethylene	41	1.9	94
Trichlorofluoromethane	155	3.0	95
Base-Neutral Extractables			
1,2-Dichlorobenzene	259	120	44
2,4-Dinitrotoluene	1900	243	65
2,6-Dinitrotoluene	1640	575	64
Nitrobenzene	454	2	99
1,2,4-Trichlorobenzene	523	169	66
Acid Extractables			
2-Chlorophenol	11	1.6	95
2,4-Dinitrophenol	161	5.0	98
4-Nitrophenol	1020	10	97
Phenol	489	38	94

*Values are averages of data which show significant day-to-day variations in removals. Results were obtained by GC/MS analyses of plant samples and are subject to analytical error.

treatment systems by removing organic and selected inorganic constituents should first be tested using batch reactors in an isotherm approach (21). This involves adding washed, powdered activated carbon to predetermined volumes of wastewater at various concentrations, then measuring the residual constituent concentration at equilibrium. The isotherms can be analyzed in terms of COD, TOC, TOD, or specific compound concentrations. The general equation for such a test can be expressed as follows:

$$\log (C_o - C_f) - \log M = \log K + 1/n \log C_f$$

Where: (Eq.8)

C_o = initial concentration, mg/l
C_f = final concentration, mg/l
K = Freundlich constant, mg/gm
$1/n$ = Freundlich constant
M = carbon dosage, mg/l

A PAC dosage can be estimated from such data, although these requirements should be considered as approximations only.

Following screening tests, bench-scale continuous reactors can be used to develop basic design criteria. These reactors can be used in parallel, using one as a control unit with no PAC addition and adding PAC to the other units controlling operating variables, such as temperature, pH, MLSS, and organic loading. PAC relationships can then be developed for selecting the desired carbon dosage and PAC mixed liquor to achieve the stipulated effluent quality in terms of both conventional parameters and specific toxic constituents. The two are interrelated and are a function of sludge age. By definition, biological sludge age in an activated sludge plant is:

$$\theta = \frac{X_{a_{bio}} V}{Q_w X_u + (Q - Q_w) X_e} \qquad \text{(Eq.9)}$$

Where:

θ = biological sludge age
$X_{a_{bio}}$ = average MLSS concentration (biological)
Q_w = sludge wastage flow
X_u = sludge underflow concentration
Q = total flow
X_e = effluent TSS concentration

The PAC dosage-equilibrium PAC MLSS concentration can then be defined, based on a mass balance, as follows:

$$X_{e_{PAC}} = \frac{X_i \theta}{HRT} \qquad \text{(Eq.10)}$$

Where:

$X_{e_{PAC}}$ = equilibrium PAC MLSS concentration
X_i = PAC dosage
θ = sludge age
HRT = hydraulic retention time

It should be noted that the total MLSS in a PAC aeration basin will normally be half biological and half carbon, the exact ratio depending on the nature of the substrate (or adsorbate), the biochemical synthesis coefficient, and the biological sludge age. However, this ratio is affected by several variables and makes it difficult to theoretically predict the powdered carbon and biomass responses in a PAC - Activated Sludge system. Moreover, the carbon adsorptive capacities, as affected by sludge age, are influenced by the nature of the adsorbate, the degree of biological regeneration, and the influent concentration of the organic constituents. Empirically derived information is thus required to establish a data base from which PAC process decisions can be made.

Conclusion

The incentives for treating liquid-phase toxic or hazardous constituents using biological methods is overwhelming when considering the process alternatives. However, the process applicability must be proven, the system has to be engineered to enhance biodegradation, and the facility operation must be sensitive to idiosyncracies of the biomass and the organic constituents.

The three major pathways of removal in a biological system have been discussed herein. Biochemical oxidation appears to be the dominant pathway for removing most toxic or hazardous constituents although sorption on the biological floc may be significant when suspended or colloidal organic fractions appear. Air stripping of volatiles may occur in a biological aeration basin, but the evidence indicates this fraction is not significant in the presence of an active biomass. Confirmation of these fractions through material balances may be required if the situation dictates.

The use of powdered activated carbon added to the aeration basin may be considered to enhance the removal of the recalcitrant and persistant constituents should this additional step be required.

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INTRODUCTION

The increasing energy demand over the last four decades has resulted in a corresponding growth and expansion in the refining and processing of crude petroleum. The proliferation of refineries and petrochemical plants around the country, combined with the increasingly stringent quality requirements for effluents discharged from these facilities, has underscored the need for for perfecting existing pollution control technology and developing improved approaches for minimizing the pollution potential in this sector of our production economy.

Although the ideal method in controlling petroleum refining and petrochemical wastewater discharges is to eliminate them at the source, process modifications and in-plant control practices are often rendered impractical from a technological and economic point of view. Therefore, physical, chemical, and biological treatment processes must be perfected and properly utilized to effectively remove the critical pollutants contained within these effluents.

The purpose of this chapter is to consider the spectrum of topics which are pertinent in the control of refinery and petrochemical wastewaters. Although it is difficult to categorize the production facilities which discharge these effluents, applicable Standard Industrial Classification (SIC) numbers include the following(1)(2):

SIC 2911 Petroleum Refining

SIC 2815 Cyclic Intermediates, Dyes, Organic Pigments, and Crudes

SIC 2818 Organic Chemicals

SIC 2819 Inorganic Chemicals Derived From Petroleum

SIC 2821 Plastic Materials and Resins

The American Petroleum Institute also has classified petroleum refineries as follows:

Classification	
A	Topping Plants
B	Topping and Cracking Plants
C	Topping, Cracking, and Petrochemical Plants
D	Integrated Plants (Topping, Cracking, Catalytic Cracking, plus Lube Processing)
E	Integrated and Petrochemical Plants

The first topic discussed is the characterization of wastewaters discharged from these production facilities. Effluent characterization information is used not only as a basis for conceiving and designing treatment systems, but also as the "yardstick" for monitoring and regulating discharge of pollutants and receiving bodies of water.

The second topic considered in this chapter is defining the sources of pollutional output within a refinery or petrochemical complex. As treatment systems must be designed to control all sources of wastewater pollutants which have either an immediate or potential deleterious effect on the receiving environment, a comprehensive understanding of source and magnitude is required. This includes process wastewaters, utility blowdowns, contaminated storm water runoff, ballast handling, and inordinate spills and miscellaneous discharges.

Treatment processes are then discussed within the context of their effectiveness in handling refinery and petrochemical wastewaters. These unit processes are categorized in the general format used by API (2). These are:

Primary Treatment - Gravity Separation

Intermediate Treatment - Neutralization

Chemical Coagulation-Sedimentation

Dissolved Air Flotation

Filtration

Final Treatment (Biological/Physical/Chemical) -

Activated Sludge

Aerated Lagoons

Trickling Filters

Cooling Tower Oxidation

Filtration

Carbon Adsorption

Although the theoretical aspects of these processes and a detailed approach for their design is covered in the references, a description of their concepts, applicability, capacity, and process limitations in treating refinery and petrochemical wastewaters is included in this chapter.

The last segment of this treatise on control of refinery and petrochemical wastewaters is dedicated to water reuse. Although this has always been emphasized in the industrial decision-making process, recently-passed Federal pollution control legislation has underscored the importance of pollution control through recycling and reuse (3).

CHARACTERIZATION AND SOURCE DEFINITION OF REFINERY AND PETROCHEMICAL WASTEWATERS

The characterization of refinery and petrochemical wastewaters in terms of flow, organic constituents, and inorganic constituents is the real basis for in-plant segregation and control, treatment process sizings, system operational control, and effluent regulation. The representativeness of the sampling, the techniques of sample preservation, and the methods of analysis all dictate the overall accuracy of the characterization program. It also should be recognized that the volume of wastewater discharged as well as the analyses indicating the organic and inorganic components require statistical validity before making major process decisions which are predicated on characterization information.

DEVELOPMENT OF WASTEWATER FLOW INFORMATION

The volume and loading of wastewater discharged from industrial production or processing units is of paramount importance in identifying pollution sources, while the flow from the total complex dictates the hydraulic design features of a treatment system and indicates the potential for water conservation.

The most fundamental approach in expressing wastewater flow from a refinery or petrochemical complex is in terms of crude throughput. This flow from a refinery-petrochemical complex or from an individual process unit can be measured using the commonly accepted methods such as weirs, flumes, flow meters, or some less sophisticated approach to flow calculations. This flow can then be expressed in terms of crude throughput

or some applicable measurement of production capacity. The effect of shift change, week-end operation, and process variation should be considered in the flow measurement program to reflect a true picture. It also should be recognized that other flows not involved with process or cooling but which require treatment are common to many refineries. This includes ballast blowdown, storm water runoff, and inordinate dumps, spills, or washdowns. Proper allowance for these wastewaters in terms of treatment capacity should be made. This subject is more thoroughly discussed in subsequent portions of this chapter.

DEFINITION OF WASTEWATER CONSTITUENTS

Parameters used to characterize refinery and petrochemical wastewaters can be categorized into organic and inorganic analyses. The organic content of wastewater is estimated in terms of oxygen demand using biochemical oxygen demand (BOD), chemical oxygen demand (COD), or total oxygen demand (TOD). Additionally, the organic fraction can be expressed in terms of carbon using total organic carbon (TOC). It should be recognized that these parameters do not necessarily measure the same constituents. Specifically, they reflect the following:

BOD - biodegradable organics in terms of oxygen demand

COD - organics amenable to chemical oxidation as well as certain inorganics (such as sulfides, sulfites, ferrous iron, chlorides, and nitrites)

TOD - all organics and some inorganics in terms of oxygen demand

TOC - all organic carbon expressed as carbon

The inorganic characterization schedule for these wastewaters should include those tests which provide information concerning:

1. potential toxicity, such as heavy metals, ammonia, etc.
2. potential inhibitors, such as total dissolved solids (TDS), chlorides, sulfates, etc.
3. contaminants requiring specific pretreatment such as pH, alkalinity, acidity, suspended solids, etc.

A brief discussion of some of the more pertinent aspects of these parameters is included.

Organic Parameters

Biochemical Oxygen Demand (BOD)

The BOD is an estimate of the amount of oxygen required to stabilize biodegradable organic materials in a refinery or petrochemical wastewater by an acclimated microbial population. The general procedures for performing the BOD test are described in Standard Methods for the Examination of Water and Wastewater (4). The BOD, however, is subject to many variables and constraints, particularly when considering complex petrochemical wastes. These are discussed as follows:

1. Time of Incubation - The importance of the incubation time variable is indicated in the basic BOD equation. The usual time is taken as five days although the time for complete stabilization to occur (the ultimate BOD) will depend on the nature of the substrate and the viability of the seed microorganisms. Many hydrocarbons can be substantially degraded in 20 days and the 20-day BOD is considered as the ultimate BOD in various applications. For example, the ultimate oxygen demand in many receiving bodies of water is predicated on 20-day values,

and the effluent quality criteria is therefore expressed in terms of 20-day BOD. It should be recognized, however, that many organic compounds require longer periods of time before the ultimate oxygen demand is satisfied biologically. For example, recently published BOD curves for tertiary butyl alcohol using acclimated seed indicated that two percent of the theoretical yield occurred in five days, approximately 65 percent occurred in 20 days, and the ultimate demand was satisfied in excess of 30 days (5). Based on these data, the oxygen requirement for a long-term biological detention basin receiving substantial quantities of TBA could be underestimated if based on five-day or 20-day BOD values. This underscores the importance of properly assessing the BOD time variable with respect to the ultimate oxygen demand.

2. Nitrification - The oxygen demand is generally exerted by carbonaceous materials during the first five to 10 days with a second stage demand being exerted by nitrogenous materials. The nitrification rate constants are much lower than those for carbonaceous destruction; and, although the two reactions may occur simultaneously, the nitrification demand is not normally conspicuous until the carbonaceous demand has been substantially satisfied. The measurement of oxygen demand exerted by the carbonaceous fraction of the waste can be isolated in one of two ways; namely, by retarding nitrification in the test bottle by the addition of nitrifying inhibitors, or by allowing nitrification to occur and subtracting its demand from the overall result. It should be noted that the nitrogenous oxygen demand is usually a significant portion of the ultimate BOD when considering refinery and petrochemical wastewaters due to the presence of oxidizable nitrogen in the form of ammonia, nitrites, and nitrogen functional groups.

3. Seed Acclimation - The use of a biological seed which is not properly acclimated to the test sample is probably the factor most commonly responsible for erroneous BOD results reported for refinery and petrochemical wastewaters. For example, the five-day BOD value of an acrylamide monomer was determined using a properly acclimated seed and a sewage seed. The BOD_5 value obtained using the sewage seed was only 17 percent of the value reported using the acclimated seed (6). Even a microbial seed which is acclimated to a compound closely related in structure to the test compound may not give the highest possible BOD value. The BOD_5 yield from the acrylamide monomer using a microbial seed acclimated to acrylonitrile was only 22 percent of the value obtained with the monomer acclimated seed. A biological seed should be developed in a continuous or batch laboratory reactor (preferably the former) by feeding the diluted wastewater in question to the initial microbial seed. The waste composition is increased to full strength over a period of time; and, once the organic removal or oxygen uptake in the reactor reaches the maximum level, the seed can be considered as acclimated. The time required to obtain this acclimation depends on the nature of the seed and wastewater. For most refinery wastewaters, this period is less than one week. However, for wastes containing high concentrations of complex organic compounds such as those discharged from petrochemical operations, a period of several weeks may be required.

4. Toxicity - The presence of toxic materials in the wastewater sample may have a biotoxic or biostatic effect on the seed microorganisms. This effect is usually evidenced by "sliding" BOD values

where the BOD yield increases with increasing sample dilution. Once there is the indication of the presence of toxic materials, steps should be taken to identify and remove the toxicants or use dilution values above which the BOD yields are consistent. Constituents in refinery and petrochemical wastewaters which interfere with the BOD test include such substances as chlorinated hydrocarbons and heavy metals.

Chemical Oxygen Demand (COD)

The COD is a measure of the oxygen equivalent of those constituents in a sample which are susceptible to permanganate or dichromate oxidation in an acid solution. Although it is independent of many of the variables which affect the BOD test, there are still factors which influence the COD value of the sample in question. Although many soluble hydrocarbons are completely oxidized by dichromate in the COD test, some of the more stable compounds are not measured. Benzene, for example, is a significant petrochemical pollutant which is resistant to dichromate oxidation. It should be emphasized that the silver sulfate catalyst is necessary for dichromate oxidation of most straight-chain hydrocarbons.

Total Organic Carbon (TOC)

Although TOC is a parameter that has been applied in the field for many years, the advent of the carbon analyzer has provided a rapid and simple method for determining organic carbon levels in aqueous samples, enhancing the popularity of TOC as a fundamental measure of pollution. The organic carbon determination is free of the many variables inherent in COD or BOD analyses, with more reliable and reproducible data being the net result ( )(7). As the analysis time using the

carbon analyzer is only several minutes, the efficacy of using this parameter is apparent particularly when a TOC/COD or TOC/BOD correlation can be established.

Total Oxygen Demand (TOD).

Another analyzer has been developed to measure the amount of oxygen required to combust the impurities in an aqueous sample. This measurement is achieved by providing a continuous analysis of the oxygen concentration present in a nitrogen carrier gas. The oxidizable constituents in the liquid are converted to their stable oxides in a platinum catalyzed combustion chamber. This disturbs the oxygen equilibrium at the platinum surface which is restored by the oxygen in the carrier gas stream. This depletion is detected by a silver-lead fuel cell and is recorded as a negative peak related to the oxygen demand of the sample. The TOD method measures the amount of oxygen consumed in the following chemical reactions (8):

Table 1

TOTAL OXYGEN DEMAND REACTIONS

Reaction	Highest Stable Oxidation State	Percent Reaction Efficiency
$C + O_2$	CO_2	95-100
$H_2 + 1/2\ O_2$	H_2O	95-100
$N^{\pm 3} + 1/2\ O_2$	NO	95
$S^{-2} + 2O_2$	SO_4^{-2}	78
$SO_3^{-2} + 1/2\ O_2$	SO_4^{-2}	72

The TOD and TOC analyzers have similar applications, the output data being correlated to COD and BOD values when possible.

Other Organic Parameters

1. Oil and Grease - One of the more important parameters applied in characterizing refinery and petrochemical wastewaters is the oil and grease measurement. This is particularly true since oils have both a recovery value and a deleterious effect on treatment systems and receiving bodies of water.

The definition of oil and grease is based on the analytical procedure employed and depends on the source, the test solvent, used, the sample to solvent ratio, the pH of the sample, and the analytical inclusion of non-oily material (9). The most widely accepted methods for measurement of oil and grease are tabulated in Table 2. While these methods are recognized within their respective society or institute, the method applied must also conform to the regulatory agency which controls effluent quality in a specific area.

A second definition relating to oil commonly discharged from refinery and petrochemical facilities can be made in terms of its phase. Oil may be free, emulsified, or soluble. A phase separation must take place prior to analyzing the oil using one of the methods cited in Table 2. The methods used to separate these oil phases are discussed as follows:

A. Total Oil - Determine the oil content of the raw wastewater sample.

B. Free Oil - Place a measured amount of wastewater in a separatory funnel and shake vigorously; then let the sample stand quiescently for two hours. Draw off the subnatant (aqueous layer) and determine its oil content. The oil measured is

METHODS FOR DETERMINATION OF OIL IN WATER AND WASTEWATER

Society or Institute	Method Name and Designation	Solvent Used	Solvent Boiling Point °C	Method Description	Interference Material
American Public Health Assn., American Water Works Assn., and Water Pollution Control Federation (2)	Oil and Grease	petroleum ether	35-60	direct extraction	
	Grease	n-hexane	69	soxhlet extraction method	elemental sulfur, a organic dyes
American Society for Testing and Materials (1)	Oily Matter In Industrial Waste Water	benzene, carbon tetrachloride, or chloroform	60-80	distillation of volatile oils followed by direct extraction	phenolic type mate and colloidal sulfu
American Petroleum Institute	Volatile and Nonvolatile Oily Material ------- Method 731-53	benzene	80	distillation of volatile oils followed by direct extraction	alcohols, cresols, and organic acids
	Nonvolatile Oily Material ------- Method 732-53	ethyl ether	35	ferric hydroxide flocculation followed by direct extraction of oil from floc by solvent	elemental sulfur and chlorophyll
Journal WPCF November, 1967	"A Safe Solvent For Oil and Grease Analysis	Freon (CCl_2F-$CClF_2$)	48	direct or soxhlet extraction	

TABLE 2

METHODS FOR DETERMINATION OF OIL IN WATER AND WASTEWATER

Society or Institute	Method name and designation	Solvent used	Solvent boiling point, °C	Method description	Interference material
American Public Health Assn., American Water Works Assn., and Water Pollution Control Federation (2)	Oil and Grease	Petroleum ether	35-60	Direct extraction	
	Grease	n-hexane	69	Soxhlet extraction method	Elemental sulfur, and organic dyes
American Society for Testing and Materials (ASTM) (1)	Oily Matter in Industrial Wastewater	Benzene, carbon tetrachloride, or chloroform	60-80	Distillation of volatile oils followed by direct extraction	Phenolic-type material and colloidal sulfur
American Petroleum Institute (API)	Volatile and Nonvolatile Oily Material, Method 731-53	Benzene	80	Distillation of volatile oils followed by direct extraction	Alcohols, cresols, and organic acids
(3)	Nonvolatile Oily Material, Method 732-53	Ethyl ether	35	Ferric hydroxide flocculation followed by direct extraction of oil from floc by solvent	Elemental sulfur and chlorophyll
(4)	A Safe Solvent For Oil and Grease Analysis	Freon (CCl_2F-$CClF_2$)	48	Direct or soxhlet extraction	

B. continued -

the emulsified and soluble oil fraction. The difference between the total oil content and that measured is the free oil content of the wastewater sample.

C. Soluble Oil - Place a measured amount of wastewater in a separatory funnel and acidify with 10 mls/concentrated hydrochloric acid. Next add 200 gms/l sodium chloride and five gms/l diatomaceous earth. Shake the mixture vigorously and let stand eight hours or more. Filter the mixture through a wet filter paper and measure the oil content of the filtrate. The oil content measured is the soluble oil fraction of the wastewater oil content.

D. Emulsified Oil - The difference between the oil content measured as emulsified and soluble oil, and the soluble oil content is the emulsified oil content.

According to information recently cited, a typical refinery effluent oil concentration would be approximately 70 percent free, 25 percent emulsified, and five percent soluble oil (10).

2. Phenolic Compounds - Phenols and related compounds are generally prevalent in refinery and petrochemical wastewaters and are of particular significance as they are potentially toxic to marine life, create an oxygen demand in receiving waters, and impart a taste to drinking water with even minute concentrations of their chlorinated derivatives. Primary sources of phenolics in wastewaters are from

benzene refining plants, oil refineries, coke plants, chemical operations, and plants which are processing phenols to plastics.

Phenols, or the hydroxy derivatives of benzene, are measured using the distillation approach as per Standard Methods or by other miscellaneous colorimetric, spectroscopic, or chormatographic techniques. A rapid, precise, and selective method using ultraviolet differential adsorption has also been reported recently (11).

Inorganic Parameters

There are many inorganic parameters which are pertinent when determining potential toxicity, general characterization, or process response. Although the evaluation of any number of inorganic analyses may be required for a particular situation, some of the more prevalent analyses are considered herein.

Acidity

The acidity of a wastewater, or its capacity to donate protons, is important because a neutral or near-neutral water is required before biological treatment can be deemed effective, and many regulatory authorities have criteria which establish strict pH limits for final discharges. Acidity in a refinery or petrochemical wastewater can be contributed by both organic and inorganic compound dissociation. Most mineral acids found in petrochemical wastes are typically strong acids such as sulfuric, nitric, or phosphoric. Weaker acids common to these wastewaters include carboxylic acid and carbonic acid.

Alkalinity

Alkalinity of a wastewater is often defined as its acid consuming ability and is measured by titrating a given volume of waste with a

standardized acid until all of the alkaline material has reacted to form salts.

Both organic and inorganic compounds can contribute alkalinity, but the most important alkaline wastes in the petrochemical industry are the spent caustics containing sodium, calcium, and potassium salts. Other process wastes, such as nitrogen in the ammonia form, can contribute to the alkalinity of a solution.

Inorganic Ions

In many cases it is important to measure the inorganic dissolved anions in solution such as chlorides, sulfates, nitrates, and phosphates. This is particularly important in quality control of cooling tower and boiler blowdown waters. Moreover, regulatory agencies are controlling dissolved salt concentrations in effluents, particularly when discharged to fresh receiving waters.

Ammonia Nitrogen and Sulfides

Ammonia nitrogen and sulfides are normally present in refinery effluents resulting from the use of steam in the refining process. The condensation of steam in the presence of a hydrocarbon vapor phase containing NH_3 and H_2S is the primary source of these contaminants depending on the process, feedstock origin, and pressure level at which the steam is condensed (12).

Ammonia nitrogen is usually measured by controlled distillation with titration of the distillate which is held in an acid solution (6). It should be recognized that other constituents common to these wastewaters such as amines, alcohols, and sulfides can interfere with the results.

Sulfide-laden waters, or "sour water," are common in refinery effluents and, if no in-plant control through sulfide stripping is practiced, impart a significant immediate oxygen demand (IOD) to the total discharge. Hydrogen sulfide is also corrosive and causes an objectionable taste and odor in the water.

Sulfides are usually measured colorimetrically although alternative analytical techniques are available (4).

Miscellaneous Parameters

Surface Active Substances

Surface active compounds are those which tend to concentrate at the gas liquid interface, the molecular arrangement being such that a film is formed. Surface active agents contain two important functional groups - one water soluble and the other oil soluble. The water soluble or hydrophilic group may be composed of one or four general types of polar groups: (a) anionic groups consisting of sulfonates, sulfates, and carboxylic acid groups; (b) cationic groups such as amine salts and ammonium compounds; (c) amphoteric groups in which the molecule contains both anionic and cationic groups; and (d) nonionic groups which do not ionize but are water soluble, such as alcohols and glycols which are commonly found in refinery and petrochemical effluents.

Various laboratory procedures are available for the determination of synthetic detergents in water (4). Other surface active chemicals (sulfonic acids, carboxylic acids, etc.) must be determined by laboratory analyses which are not commonly used as pollutional parameters.

Taste and Odor

Methods used to classify and measure taste and odor in wastewaters are strictly arbitrary and most involve the use of human testers who determine the dilution required to make the taste and odor of a particular wastewater satisfactory. Since taste and odor are human senses, this is probably the most suitable method for their determination. Another possibility is the isolation, identification, and measurement of substances which cause taste and odor, but this procedure is currently impractical.

Temperature

Thermal pollution is a serious problem within refinery and petrochemical installations, primarily attributable to blowdown of various condensates and boiler and cooling waters. As maximum water temperatures are established by regulatory agencies because of deleterious effects on receiving waters, cooling is often an integral part of the treatment system requirements.

Heavy Metals

Heavy metallic ions are generally common to refinery and petrochemical wastewaters resulting from corrosion inhibitor additives, catalyst usage, product additives, and laboratory and instrument wastage. As the potential or real impact of these constituents on the receiving environment is significant, there is a continuing emphasis on their detection and control.

Several techniques for heavy metal analysis are given in Standard Methods (4). Atomic absorption flame photometry can also be used quantitatively to detect small quantities of metals. This method is based

on the measurement of light adsorbed at a given wave length (13).

Color and Turbidity

Color and turbidity are physical properties related to the concentration of certain solutes and suspended particles in wastewaters. Many of the wastes produced by the petrochemical industry contain color-producing compounds.

Color in wastewater, true and apparent, can be attributed to two types of physical phemomena. Certain materials in solution or suspension in water will absorb incident light and the wave lengths of visible light absorbed will determine the color of the liquid. The other color effect is caused by the scattering of incident light by colloidal or suspended materials. Liquids which exhibit this light-scattering effect are termed turbid. Both of these effects are highly undesirable in waters receiving waste effluents. Color and turbidity diminish light penetration in natural waters, and also affect the domestic use of water in that they must be removed prior to public acceptance. This removal process often adds great expense to water treatment costs.

Color in water is measured by comparing the sample with a standard cobalt-platinum solution. Turbidity is measured by using several different types of proprietary instruments which measure either scattered or transmitted light. Color which is caused by dissolved contaminants is often termed "true" color and color caused by petrochemical wastes is predominantly of this type. Color caused by suspended or colloidal material is referred to as "apparent" color.

REFINERY AND PETROCHEMICAL SOURCE AND QUALITY ANALYSIS

The first consideration in the evaluation of a plant effluent which leads to conceptualization and engineering of the treatment system is locating source flows and estimating their characteristics. This evaluation must be made not only of current effluent levels but also for future wastewater flows. A logical approach in formulating these estimates is to categorize contributive pollutional inputs into logical source components. These components as defined by the author are:

Normal Process Operations - discharged directly from production units

Utility Operations - blowdown from boiler and cooling systems

Sanitary Sewage - sewage from administrative areas, control houses, and locker and shower facilities.

Contaminated Storm Runoff - runoff from process areas requiring treatment

Ballast Water Blowdown - dirty ballast discharged from tankers receiving product

Miscellaneous Discharges - resulting from inordinate discharges, spills, turnarounds, etc.

Each of these components as graphically depicted in Figure 1 will be discussed individually.

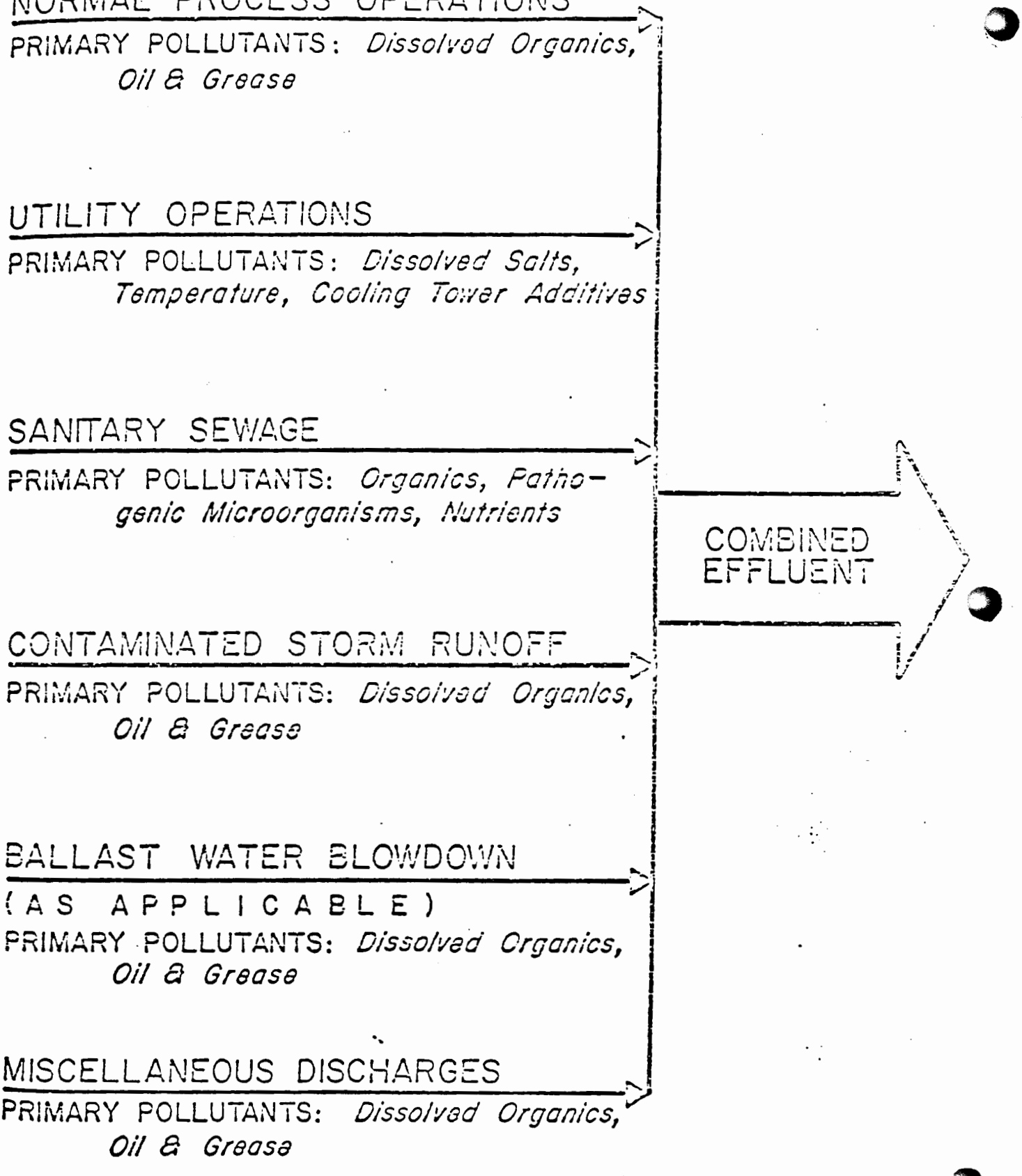

NORMAL PROCESS OPERATIONS
PRIMARY POLLUTANTS: Dissolved Organics, Oil & Grease
UTILITY OPERATIONS
PRIMARY POLLUTANTS: Dissolved Salts, Temperature, Cooling Tower Additives
SANITARY SEWAGE
PRIMARY POLLUTANTS: Organics, Pathogenic Microorganisms, Nutrients
CONTAMINATED STORM RUNOFF
PRIMARY POLLUTANTS: Dissolved Organics, Oil & Grease
BALLAST WATER BLOWDOWN
(AS APPLICABLE)
PRIMARY POLLUTANTS: Dissolved Organics, Oil & Grease
MISCELLANEOUS DISCHARGES
PRIMARY POLLUTANTS: Dissolved Organics, Oil & Grease
COMBINED EFFLUENT

FIGURE 1

PROCESS OPERATIONS

The many combinations of process operation , type of crude charge, and age of plant make it difficult to classify a refinery-petrochemical wastewater as "typical." Intra-plant differences in effluent segregation systems, in-plant treatment systems, and process design, operation, and maintenance also contribute to these variations.

The most commonly used method for predicting the quality of these wastewaters is to relate the quantity and quality of pollutant produced by a unit process to production units. The inherent nature of production and processing, however, mitigates this approach. Nevertheless, this information combined with general effluent characterization data offers an overall knowledge of pollutants which are present and their concentration range.

The American Petroleum Institute Refinery Effluent Profile has tabulated process flow in terms of production units for the five refinery classifications based on questionnaire responses as shown in Table 3.

Table 3

WASTEWATER DISCHARGE AS A FUNCTION OF CRUDE THROUGHPUT

Refinery Classification	No. Refineries Reporting	Gal. Effluent/bbl Crude Throughput		
		Max.	Min.	Avg.
A	15	499.8	0.4	57.5
B	70	1658.6	2.1	116.3
C	20	1399.9	17.6	181.0
D	18	759.4	14.8	143.4
E	4	1700.2	32.8	410.1

The wide range is primarily attributable to water use for cooling purposes as this accounts for approximately 70 percent of refinery water demand (14). Once-through cooling, for example, as practiced in many refineries would keep the effluent volume based on crude throughput on the high side, while water conservation through recycle and reuse would reduce this value to the low side of the spectrum. A similar representation in terms of quality for eight process operations is shown in Table 4 (15).

A general list of pollutants associated with petrochemical processes is tabulated in Table 5 (1). Concentration ranges reported for petrochemical and chemical production are included in Table 6 (1). The wastewater characteristics in terms of the parameters previously cited for selected process operations are given in Table 7 (1). Information such as this is indicative of wastewater characteristics which might be expected from specified operations and can be applied as a basis for programming wastewater surveys and preliminary engineering designs. Information recently obtained in a unit by unit production survey in three refinery-petrochemical installations has indicated the main sources of organic output. The BOD from eight sampling points within a refinery complex representing over 90 percent of the total process BOD contribution is shown in Figure 2 (16). A similar representation of organic output from production units in terms of COD is shown in Figure 3 (16). The relative contribution of COD and oil reported in a comprehensive wastewater survey is shown in Figure 4 (16).

UTILITY OPERATIONS

Utility operations which are an integral part of any refinery-

TABLE 4

WASTE LOADINGS AND VOLUMES PER UNIT OF FUNDAMENTAL PROCESS THROUGHPUT IN OLDER, TYPICAL, AND NEWER TECHNOLOGIES

Fundamental Process	Older Technology				Typical Technology				Newer Technology			
	Flow gal/bbl	BOD lbs/bbl	Phenol lbs/bbl	Sulfides lbs/bbl	Flow gal/bbl	BOD lbs/bbl	Phenol lbs/bbl	Sulfides lbs/bbl	Flow gal/bbl	BOD lbs/bbl	Phenol lbs/bbl	Sulfides lbs/bbl
Crude Oil and Product Storage	4	0.001	*	*	4	0.001	*	*	4	0.001	*	*
Crude Desalting	2	0.002	0.20	0.002	2	0.002	0.10	0.002	2	0.002	0.05	0.002
Crude Fractionation	100	0.020	3.0	0.001	50	0.0002	1.0	0.001	10	0.0002	1.0	0.001
Thermal Cracking	66	0.001	7.0	0.002	2	0.001	0.2	0.001	1.5	0.001	0.2	0.001
Catalytic Cracking	85	0.002	50.0	0.03	30	0.010	20	0.003	5	0.010	5	0.003
Hydrocracking	not in this technology				not in this technology				5	*	*	*
Reforming	9	t	0.7	t	6	t	0.7	0.001	6	t	0.7	0.001
Polymerization	300	0.003	1.4	0.22	140	0.003	0.4	0.010	not in this technology			
Alkylation	173	0.001	0.1	0.005	60	0.001	0.1	0.010	20	0.001	0.1	0.010
Isomerization	not in this technology				not in this technology				*	*	*	*
Solvent Refining	8	*	3	t	8	*	3	t	8	*	3	t
Dewaxing	247	0.52	2	t	23	0.50	1.5	t	20	0.25	1.5	t
Hydrotreating	1	0.002	0.6	0.007	1	0.002	0.01	0.002	8	0.002	0.01	0.002
Deasphalting	*	*	*	*	*	*	*	*	*	*	*	*
Drying and Sweetening	100	0.10	10	*	40	0.05	10	*	40	0.05	10	*
Wax Finishing	*	*	*	*	*	*	*	*	*	*	*	*
Grease Manufacture	*	*	*	*	*	*	*	*	*	*	*	*
Lube Oil Finishing	*	*	*	*	*	*	*	*	*	*	*	*
Hydrogen Manufacture	not in this technology				not in this technology				*	*	*	*
Blending and Packaging	*	*	*	*	*	*	*	*	*	*	*	*

* Data not available for reasonable estimate.
t - Trace.

TABLE 5

PETROCHEMICAL PROCESSES AS WASTE SOURCES

Process	Source	Pollutants
Alkylation: Ethylbenzene		Tar, hydrochloric acid, caustic soda, fuel oil
Ammonia production	Demineralization	Acids, bases
	Regeneration, process condensates	Ammonia
	Furnace effluents	Carbon dioxide, carbon monoxide
Aromatics recovery	Extract water	Aromatic hydrocarbons
	Solvent purification	Solvents + Sulfur dioxide, diethylene glycol
Catalytic cracking	Catalyst regeneration	Spent catalyst, catalyst fines (silica, alumina hydrocarbons, carbon monoxide, nitrogen oxides)
	Reactor effluents and condensates	Acids, phenolic compounds, hydrogen sulfide soluble hydrocarbons, sulfur oxides, fenices
Catalytic reforming	Condensates	Catalyst (particularly Pt. Mo), aromatic hydrocarbons, hydrogen sulfide, ammonia
Crude processing	Crude washing	Inorganic salts, oils, water soluble hydrocarbons
	Primary distillation	Hydrocarbons, tars, ammonia, acids, hydrogen sulfides
Cyanide production	Water scrub	Hydrogen cyanide, unreacted soluble hydrocarbons
Dehydrogenation		
Butadiene prod. from n-Butane and Butylene	Quench waters	Residue gas, tars, oils, soluble hydrocarbons
Ketone production	Distillation slops	Hydrocarbon polymers, chlorinated hydrocarbons, glycerol, sodium chloride
Styrene from ethylbenzene	Catalyst	Spent catalyst (Fe, Mg, K, Cu, Cr, Cs)
	Condensates from spray tower	Aromatic hydrocarbons, including styrene, ethyl benzene, and toluene, tars
Desulfurization		Hydrogen sulfide, mercaptans
Extraction and purification		
Isobutylene	Acid and caustic wastes	Sulfuric acid, C_4 hydrocarbon, caustic soda
Butylene	Solvent and caustic wash	Acetone, oils, C_4 hydrocarbon, caustic soda, sulfuric cid
Styrene	Still bottoms	Heavy tars
Butadiene absorption	Solvent	Cuprous ammonium acetate, C_4 hydrocarbons, oils
Extractive distillation	solvent	Furfural, C_4 hydrocarbons
Halogenation (principally chlorination)		
Addition to olefins	Separator	Spent caustic
Substitution	HCl absorber, scrubber	Chlorine, hydrogen chloride, spent caustic, hydrocarbon isomers and chlorinated products, oils
	Dehydrohalogenation	Dilute acid pollution
Hypochlorination	Hydrolysis	Calcium chloride, soluble organics, tars
Hydrochlorination	Surge tank	Tars, spent catalyst, alkyl halides
Hydrocarboxylation (OXO process)	Still slops	Soluble hydrocarbons, aldehydes
Hydrocyanation (for acrylonitrile, adipic acid, etc.)	Process effluents	Cyanides, organic and inorganic
Isomerization in general	Process wastes	Hydrocarbons; aliphatic, aromatic, and derivative tars
Nitration		
Paraffins		By-product aldehydes, ketones, acids, alcohols, olefins, carbon dioxide
Aromatics		Sulfuric acid, nitric acid, aromatics
Oxidation		
Ethylene oxide and glycol manufacture	Process slops	Calcium chloride, spent lime, hydrocarbon polymers, ethylene oxide, glycols, dichloride
Aldehydes, alcohols, and acids from hydrocarbons	Process slops	Acetone, formaldehyde, acetaldehyde, methanol, higher alcohols, organic acids
Acids and anhydrides from aromatic oxidation	Condensates Still slops	Anhydrides, aromatics, cids Pitch
Phenol and acetone from aromatic oxidation	Decanter	Formic acid, hydrocarbons
Carbon black manufacture	Cooling, quenching	Carbon black, particulates, dissolved solids
Polymerization, alkylation	Catalysts	Spent acid catalysts (phosphoric acid), aluminum chloride
Polymerization (polyethylene)	Catalysts	Chromium, nickel, cobalt, molybdenum
Butyl rubber	Process wastes	Scrap butyl, oil, light hydrocarbons
Copolymer rubber	Process wastes	Butadiene, styrene serum, polymer sludge
Nylon 66	Process wastes	Cyclohexane oxidation products, succinic acid, adipic acid, glutaric acid, hexamethylene, diamine, adiponitrile, acetone, methyl ethyl ketone
Sulfation of olefins		Alcohols, polymerized hydrocarbons, sodium sulfate, ethers
Sulfonation of aromatics	Caustic wash	Spent caustic
Thermal cracking for olefin production (including fractionation and purification)	Furnace effluent and caustic treating	Acids, hydrogen sulfide, mercaptans, soluble hydrocarbons, polymerization products, spent caustic, phenolic compounds, residue gases, tars and heavy oils
Utilities	Boiler blow down	Phosphates, lignins, hool, total dissolved solids, tannins

TABLE 5

WASTEWATER CHARACTERISTICS ASSOCIATED WITH SOME CHEMICAL PRODUCTS

Material	Flow (gal/ton)	BOD (mg/L)	COD (mg/L)	Other Characteristics
Primary Petrochemicals				
Ethylene	50- 1,500	100- 1,000	500- 3,000	phenol, pH, oil
Propylene	100- 2,000	100- 1,000	500- 3,000	phenol, pH
Primary Intermediates				
Toluene	300- 3,000	300- 2,500	1,000- 5,000	
Xylene	200- 3,000	500- 4,000	1,000 8,000	
Ammonia	300- 3,000	25- 100	50- 250	oil, nitrogen
Methanol	300- 3,000	300- 1,000	500- 2,000	oil
Ethanol	300- 4,000	300- 3,000	1,000- 4,000	oil, solids
Buthanol	200- 2,000	500- 4,000	1,000- 8,000	heavy metals
Ethyl benzene	300- 3,000	500- 3,000	1,000- 7,000	heavy metals
Chlorinate hydrocarbons	50- 1,000	50- 150	100- 500	pH, oil, solids
Secondary Intermediates				
Phenol, cumene	500- 2,500	1,200-10,000	2,000-15,000	phenol, solids
Acetone	500- 1,500	1,000- 5,000	2,000-10,000	
Glycerin, glycols	1,000- 5,000	500- 3,500	1,000- 7,000	
Urea	100- 2,000	50- 300	100- 500	
Acetic anhydride	1,000- 8,000	300- 5,000	500- 8,000	pH
Terephtelic acid	1,000- 3,000	1,000- 3,000	2,000- 4,000	heavy metals
Acrylates	1,000- 3,000	500- 5,000	2,000-15,000	solids, color, cyanide
Acrilonitrile	1,000- 10,000	200- 700	500- 1,500	color, cyanide, pH
Butadiene	100- 2,000	25- 200	100- 400	oil, solids
Styrene	1,000- 10,000	300- 3,000	1,000- 6,000	
Vinyl chloride	10- 200	200- 2,000	500- 5,000	
Primary Polymers				
Polyethylene	400- 1,600		200- 4,000	solids
Polypropylene	400- 1,600		200- 4,000	
Polystyrene	500- 1,000		1,000- 3,000	solids
Polyvinyl chloride	1,500- 3,000	50- 500	1,000- 2,000	
Cellulose acetate	10- 200	500- 2,000	1,000- 5,000	
Butyl rubber	2,000- 6,000	800- 2,000	2,500- 5,000	
Dyes and Pigments	50,000-250,000	200- 400	500- 2,000	heavy metals, color, solids, pH
Miscellaneous Organics				
Isocyanate	5,000- 10,000	1,000- 2,500	4,000- 8,000	nitrogen
Phenyl glycine	5,000- 10,000	1,000- 2,500	4,000- 8,000	phenol
Parathion	3,000- 8,000	1,500- 3,500	3,000- 6,000	solids, pH
Tributyl phosphate	1,000- 4,000	500- 2,000	1,000- 3,000	phosphorus

TABLE 7

TYPICAL SPENT CAUSTIC STREAM CHARACTERISICS

Characteristics	Benzene Sulfonation Scrubbing	Ortho-phenyl-phenol Washing	Alkylate Washing	Polymerization
Alkalinity (mg/l)	33,800	18,400	46,250	209,330
BOD (mg/l)	53,600	18,400	256	8,440
COD (mg/l)	112,000	67,600	3,230	50,350
H_2S (mg/l)	-	-	-	-
pH	13.2	9-12	12.8	12.7
Phenols (mg/l)	8.3	5,500	50	22.2
NaOH (wt %)	1	0.2-0.5	-	-
Na_2SO_4 (wt %)	1.5-2.5	-	-	-
Sulfates (mg/l)	3,760	2,440	-	-
Sulfides (mg/l)	-	-	2	3,060
Sulfites (mg/l)	7,100	4,720	-	-
Total Solids	90,300	40,800	-	-

TABLE 7

TYPICAL PROCESS WASTE CHARACTERISTICS OF PRIMARY CONVERSION AND REFINING PROCESSES

Characteristic	Crude Desalting	Catalytic Cracking	Naphtha Cracking	Sour Condensates from Distillation, Cracking, etc.
Ammonia (mg/l)	80	-	-	135-6,550
BOD (mg/l)	60-610	230-440	-	500-1,000
COD (mg/l)	124-470	500-2,800	53-180	500-2,000
Oil (mg/l)	20-516	200-2,600	160	100-1,000
pH (mg/l)	7.2-9.1	-	-	4.5-9.5
Phenols (mg/l)	10-25	20-26	6-10	100-1,000
Salt (as NaCl) (wt.%)	0.4-25	-	-	-
Sulfides (mg/l)	0-13	-	-	390-8,250 (H_2S)

TABLE 7

TYPICAL ACID WASTE CHARACTERISTICS

Characteristic	Acid Wash-Alkylation	Acid Wash-Phenol Still Bottoms	Acid Wash-Orthophenylphenol	Sulfite Wash Liq.OP-phenol Distillation
Acidity (mg/l)	1,105-12,325	-	24,120	675
BOD (mg/l)	31	20,800	13,600	105,000
COD (mg/l)	1,251	248,000	23,400	689,000
Dissolved Solids (mg/l)	-	340,500	81,300	176,800
Oil (mg/l)	131.5	-	-	-
pH	0.6-1.9	1.0	1.1	3.8
Phenols (mg/l)	-	3,800	1,500	16,400
Sulfate (mg/l)	-	-	54,700	-
Sulfite (mg/l)	-	34,800	2,920	74,000
Total Solids (mg/l)	-	403,200	81,600	176,900

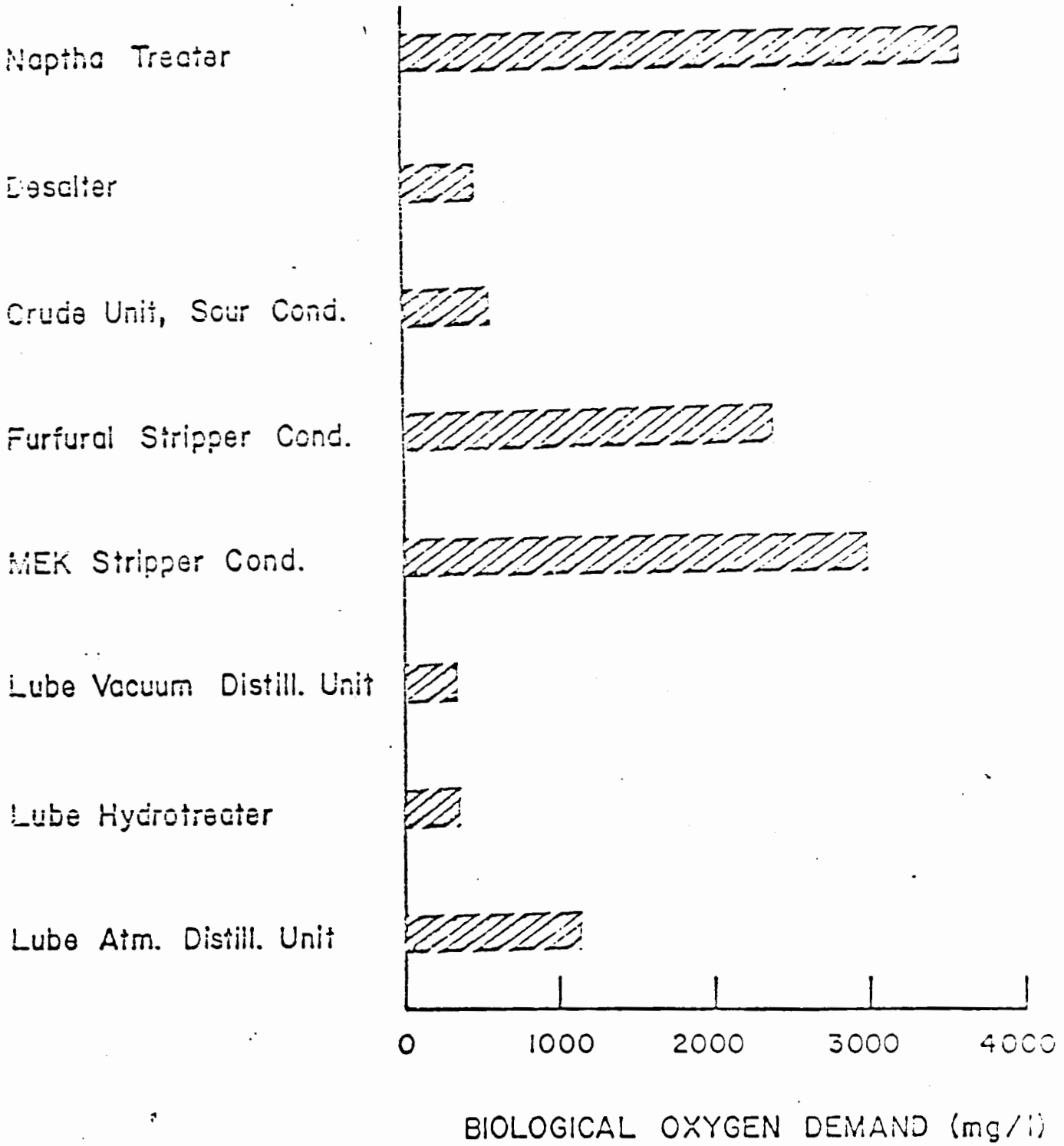

Naptha Treater
Desalter
Crude Unit, Sour Cond.
Furfural Stripper Cond.
MEK Stripper Cond.
Lube Vacuum Distill. Unit
Lube Hydrotreater
Lube Atm. Distill. Unit
0
1000
2000
3000
4000
BIOLOGICAL OXYGEN DEMAND (mg/l)

FIGURE 2

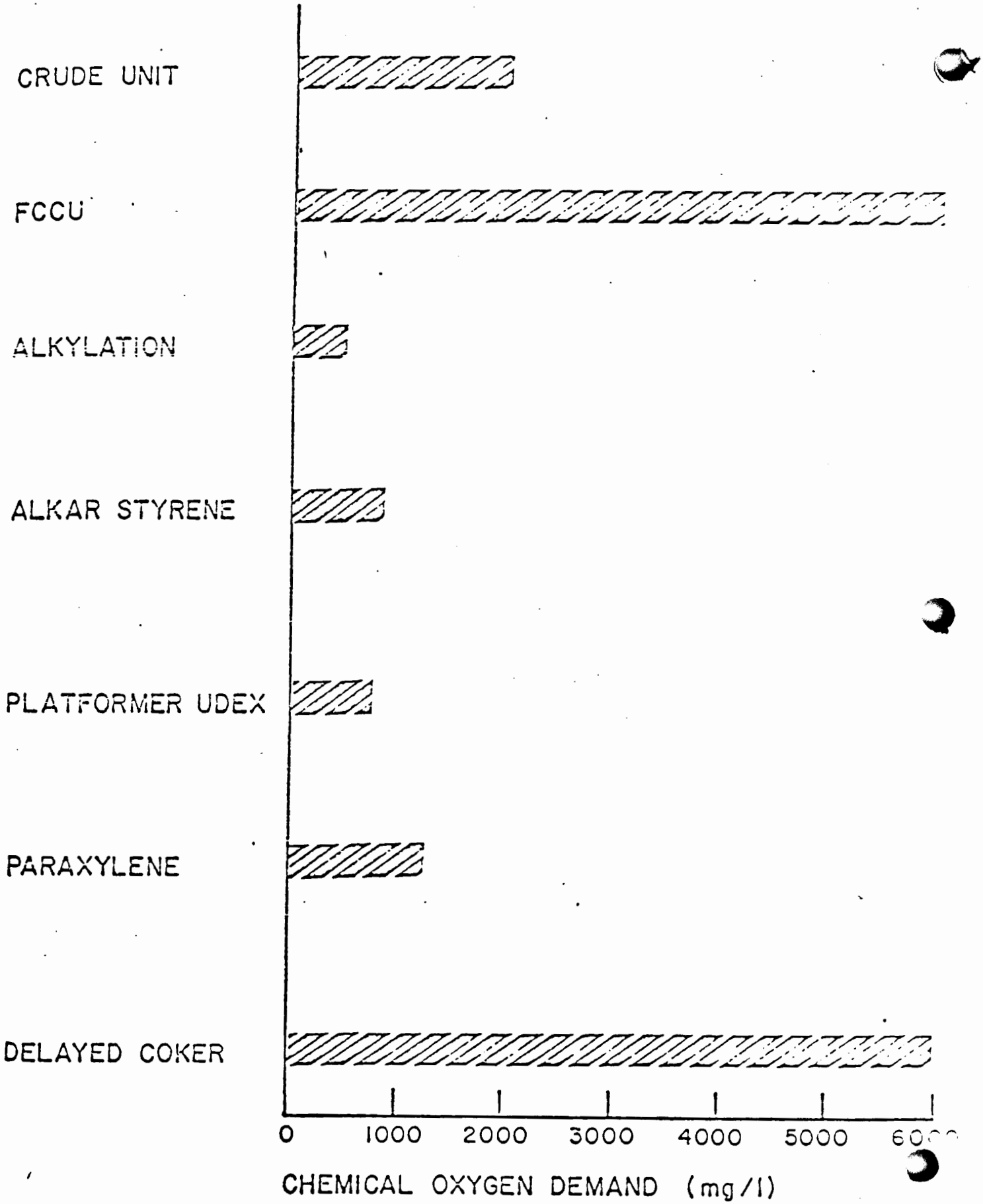

CRUDE UNIT
FCCU
ALKYLATION
ALKAR STYRENE
PLATFORMER UDEX
PARAXYLENE
DELAYED COKER
0
1000
2000
3000
4000
5000
CHEMICAL OXYGEN DEMAND (mg/l)

FIGURE 3

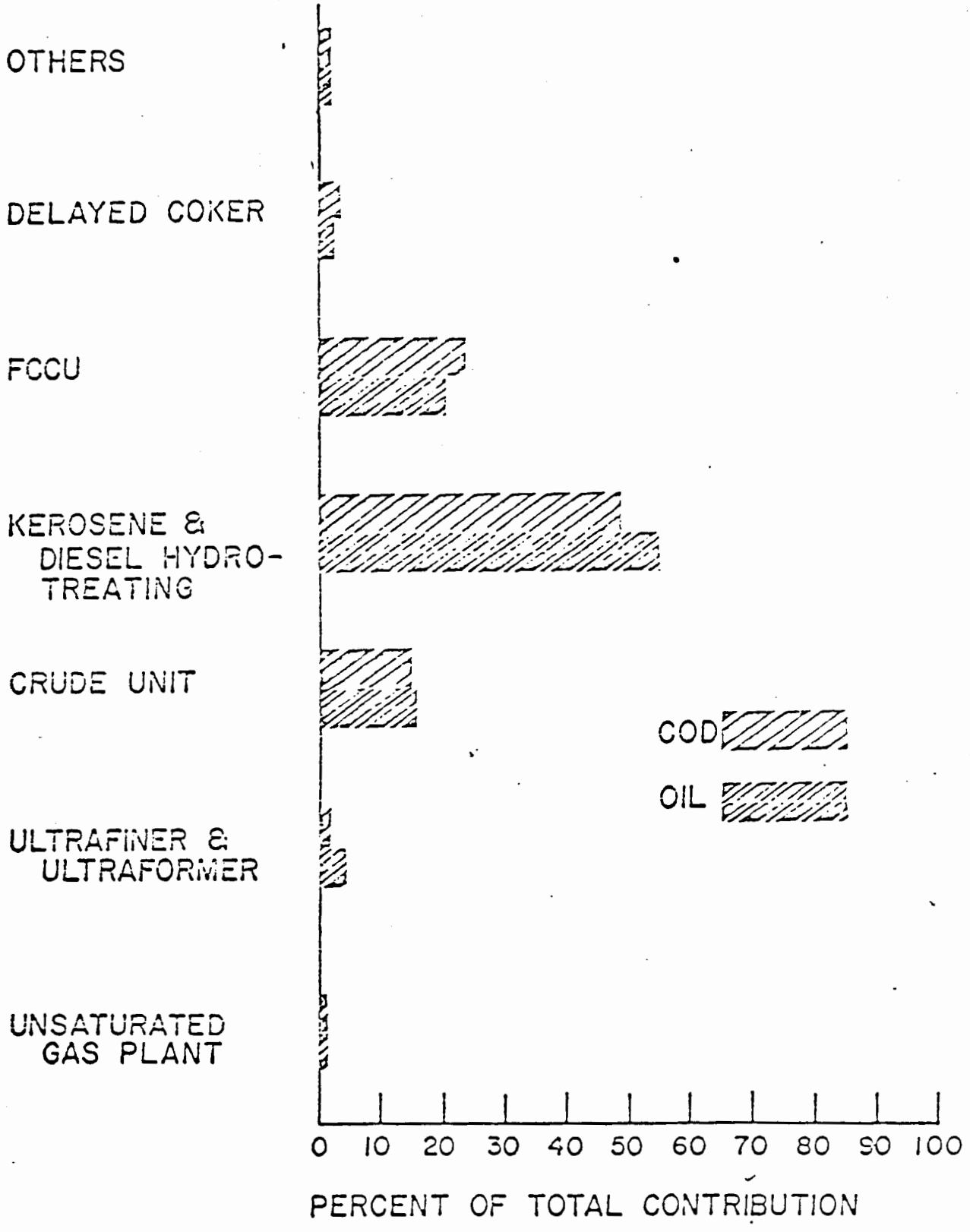

OTHERS
DELAYED COKER
FCCU
KEROSENE & DIESEL HYDRO-TREATING
CRUDE UNIT
ULTRAFINER & ULTRAFORMER
UNSATURATED GAS PLANT
COD
OIL
0 10 20 30 40 50 60 70 80 90 100
PERCENT OF TOTAL CONTRIBUTION

FIGURE 4

petrochemical complex contribute to the wastewater flow in the form of blowdown. The primary sources of this blowdown are from boilers and process steam generators and cooling towers.

It is necessary to control excessive scaling and fouling of tubes in boilers and process steam generators. This is accomplished by limiting the solids and alkalinity concentrations within the boiler or steam generator drums. When treated makeup water is fed to the system, a portion of the water is blown down. Although the volume of blowdown will vary, approximately five percent of the water used to produce the steam can be expected as blowdown flow. Although this generally represents a small part of the utility flow when compared to cooling tower blowdown, their constituents may be significant if the combined flow is marginal in terms of meeting certain quality requirements. The American Boiler Manufacturer's Association recommends that water within steam drums be maintained at the quality limits shown in Table 8 (17).

Table 8

BOILER QUALITY LIMITS

Steam Pressure (psig)	Dissolved Solids (ppm max.)	Suspended Solids (ppm max.)	Alkalinity* (ppm max.)
0-300	3,500	300	700
301-450	3,000	250	600
451-600	2,500	150	500
601-750	2,000	100	400

* Total alkalinity as $CaCO_3$.

Providing these limits are maintained, they represent the quality of the boiler blowdown. Typical quality data of boiler blowdown from a refinery recently surveyed is shown in Table 9.

TABLE 9

STATISTICAL ANALYSIS OF BOILER BLOWDOWN

Parameter	Number of Analysis Reported	Mean	Standard Deviation
pH	22	12 11.6	0.34
Total Suspended Solids (mg/l)	22	40	24.03
Volatile Suspended (mg/l)	22	25 24.9	16
Settleable Matter (mg/l)	22	1918.8	23.4 23
Immediate Oxygen Demand (mg/l)	13	12 12.4	8.3 8
Biochemical Oxygen Demand$_5$ (mg/l)	7	60.9	26.9 27
Chemical Oxygen Demand (mg/l)	22	201	70
Oil and Grease (mg/l)	22	14	5.3
Temperature ($^{\circ}$C)	22	174	8.2
Chromium (mg/l)	3	0.8	0.3 0.2
Phenols (mg/l)	19	0.1	0.2
Fluorides (mg/l)	15	7 6.8	0.4 9
Total Residue (mg/l)	8	4947	300
Ammonia (mg/l)	10	3.3	2.2
Oxygen Demand Index (mg/l)	9	69.3	45.9 46

Blowdown water from cooling towers represents a sizable portion of the combined flow, and certainly the preponderance of the utility blowdown. If a once-through system is used, the cooling tower effluent quality will be the same as the supply water plus treating chemicals that may have been added. When a recirculating system is used, the salts are concentrated as pure water is evaporated from the system cooling tower. Thus TDS, cooling tower additives, and contaminants entering the water via exchanger leaks constitute the contaminants of cooling tower blowdown. With heavy metals and phosphorus being considered by most regulatory agencies as critical pollutants, emphasis of cooling tower additives is of particular significance. Specifically, attention is focused on chromates and phosphates. The most commonly used additives for corrosion and algae control are listed in Table 10 (17). As these chemicals are present in the effluent, their use must be evaluated not only in terms of corrosion and algacide effectiveness but also their impact on effluent quality as related to permissible levels. Quality data from a recirculating cooling tower in a refinery recently surveyed is listed in Table 11.

Blowdown from boilers and cooling towers, if kept segregated from process effluents, are sometimes referred to as "clean streams." This nomenclature is predicated on relative organic content and is valid if the segregation of streams rigidly follows process-utility blowdown lines. It should be recognized, however, that utility blowdown streams still contain organic pollutants, even though they exist at low concentrations. The composition of typical "clean" streams is listed in Table 12 (1). It should again be emphasized that "clean stream" quality

TABLE 10

COOLING TOWER ADDITIVES

ADDITIVE	DESCRIPTION
Sulfuric Acid	Used to prevent scaling by converting insoluble carbonates to the more soluble sulfate salts.
Inorganic Chromate Salts	Used for corrosion control ... concentrations in the circulating water range from 300 mg/l to 2,000 mg/l.
Inorganic and Organic Phosphates and Polyphosphates	Used for corrosion control ... concentration ranges from 2 mg/l to 30 mg/l
Combined Chromate and Phosphate	Used for corrosion control ... concentration for chromate ranges from 10 mg/l to 60 mg/l; concentration for phosphate from 20 mg/l to 50 mg/l.
Organic Chromates	Used for corrosion control ... concentration may be 5 to 20 ppm CrO_4 and 5 to 20 ppm organics.
Chlorinated Phenols	Used for control of algae and bacterial slime. Intermittent dosage may be as high as 300 to 400 ppm.
Chlorine or Bromine	Used for control of algae and bacterial slime. Usually, a chlorine level of one ppm is maintained in the system for at least four hours a day.
Quaternary Ammonium Copper Complexes	Used for algae and bacteria control. Intermittent dosage may be as high as 200 ppm.

TABLE 11

STATISTICAL ANALYSIS OF COOLING TOWER BLOWDOWN

(24 HOUR COMPOSITES)

Parameter	Mean	Standard Deviation
pH	7.3	0.3
Total Suspended Solids (mg/l)	34	-
Volatile Suspended Solids (mg/l)	26	-
Biochemical Oxygen Demand$_5$ (mg/l)	33	35
Chemical Oxygen Demand (mg/l)	141	98
Oil and Grease (mg/l)	7	3
Temperature (^{o}C) (Grab Samples)	27	3
Sulfides (mg/l) (Grab Samples)	0	0
Chromium (mg/l)	12	-
TKN (mg/l)	12	18
Total Phosphate (mg/l)	5	0.9
Total Dissolved Solids (mg/l)	7	
Dissolved Organic Carbon (mg/l)	60	59

TABLE 12

COMPOSITION OF TYPICAL CLEAN WATER EFFLUENT

Water Sources	Total Wastewater %	Flow Range (gpm)	POTENTIAL POLLUTANTS Sources	Type	COD Range (mg/l)
Cooling water (excluding sea water)	40 - 80	100 —10,000 (500 - 200,000 gal. water/ton product)	Process leaks: Bearings, exchangers, etc.	Extractables	1 - 1000
				Mercaptans	
				Sulfides	
				Phenols	0-1000, but
				Cyanide	usually less
				Misc. N. compounds	than 1 mg/l
				Acids	
			Water treatment	Chromate	0-60
				Phosphate	0-60
				Heavy metals	0-30
				Fluoride	0-30
				Sulfate	100-10,000
				Biocides, algacides	0-50
				Misc. organics	0-100
			Scrubbed from air through tower	Hydrogen sulfide	
				Sulfur dioxide	0-1000
				Oxides of nitrogen	
				Ammonia	
				Particulates	0-300
			Make-up water	Total dissolved solids	100-5000
				Particulates	0-100
				Phosphates	0-5
				Fluoride	0-2
Steam equipment	10	50-1,000	Boiler blowdown	Total dissolved solids	500-10,000
				Particulates	5-300
				Extractables	0-10
				Phosphate	1-50
				Sulfite	0-50
				Sulfide	0-5
				Misc. organic compounds	0-200
				Misc. N. compounds	1-100
				Heavy metals	0-10
				Alkalinity	50-500
			Waste condensate	Extractables	0-100
				Ammonia	0-10

concern is centered around TDS, temperature, chromates, and phosphates while process or "dirty" streams contain concentrated organic materials as well as a myriad of inorganic constituents. The decision of segregating or combining these streams is a complex one and is based on their individual or combined impact in the areas of treatment and water reuse. This will be more fully discussed in subsequent sections of this chapter.

SANITARY SEWAGE

Sanitary sewage from process control houses, administrative areas, and locker and shower facilities should be considered as a separate category. Some installations service these areas either by using septic tanks and drainfields or by connecting sewage lines to the process sewers. In other cases, sanitary sewage is collected and treated separately or sent to nearby municipal sewage systems. Although combining sanitary sewage discharged from within the refinery complex with process wastewaters has many advantages, consideration must be given to pathogenic microorganisms commonly found in sewage. Most regulatory agencies require chlorination of industrial effluents which contain sewage. As chlorinating the combined flow is uneconomical, segregating sanitary sewage for separate treatment or prechlorination of this flow before commingling with process waste is usually practiced.

The volume of sanitary sewage can easily be predicted based on the number of personnel employed for each shift. The quality of sewage is well documented but must reflect conditional factors which might affect relative strength such as special shower and cleaning installations, lavatory facilities, etc.

CONTAMINATED STORM RUNOFF

Contaminated storm runoff from industrial production areas has become an area of increasing concern in the development of pollution abatement programs, particularly with respect to regulatory agency policy of definition and control. Storm runoff is intermittent and unpredictable in nature from a quantitative and qualitative point of view. The flow rate and degree of contamination not only vary with time during the course of a storm, but also with each individual area within a refinery-petrochemical complex as each has its own geometric characteristics which influence patterns of surface runoff. This is best illustrated in Figure 5 showing the variable pattern of storm runoff organics (COD) from different process areas within a petrochemical complex (18).

The direct treatment of contaminated storm runoff - being a high-volume, intermittent wastewater stream - is not practical based on economic considerations. Therefore, handling techniques such as storage and/or segregation followed by controlled feeding to treatment must be investigated. An investigation of storm flows must be oriented toward obtaining data to evaluate three salient aspects:

1. probable volume collected;
2. quality characteristics; and,
3. peak flow rates.

If runoff is to be stored or surged prior to eventual treatment, anticipated rainfall volumes must be estimated. Such estimates should be developed statistically from long term precipitation records, for a specific year's precipitation pattern will never occur again in the

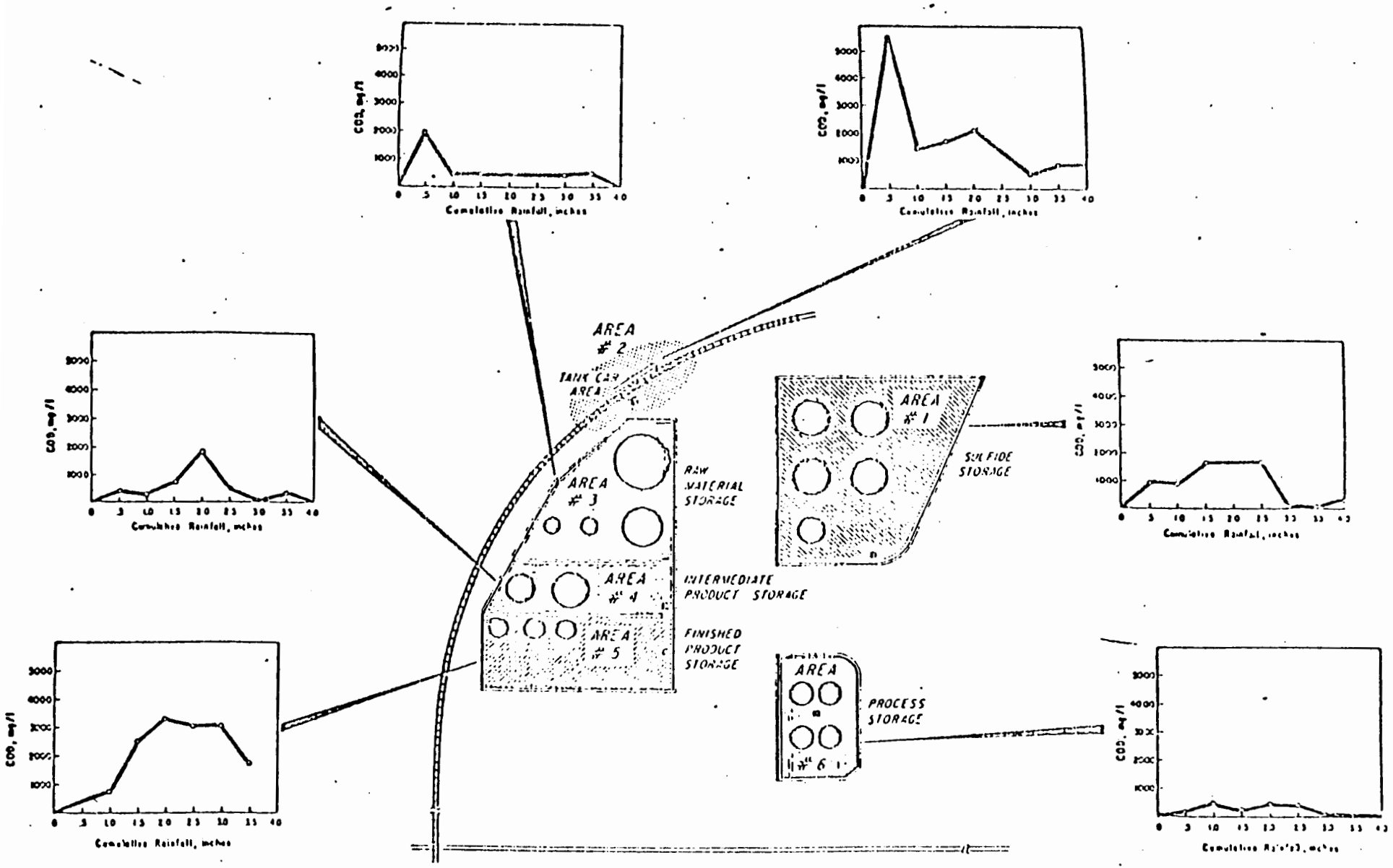

AREA #2
TANK CAR AREA
AREA #3
RAW MATERIAL STORAGE
AREA #4
INTERMEDIATE PRODUCT STORAGE
AREA #5
FINISHED PRODUCT STORAGE
AREA #1
SULFIDE STORAGE
AREA #6
PROCESS STORAGE
COD, mg/l
Cumulative Rainfall, inches

FIGURE 5

same fashion. Fortunately, the Weather Bureau has developed such estimates of probable rainfall for periods up to 10 days in length for many areas. In order to develop estimates for periods of a longer duration, a more sophisticated approach is required. The mathematical properties of the laws of probability are well known and can be used with sufficient accuracy to allow computation of meaningful probability statements concerning future events. An approach using the gamma probability function has been used to approximate the distribution of total rainfall at a given location for a fixed time interval (19). Using this technique, rainfalls for various recurrence intervals can be computed for various periods of time. For example, the inches of rainfall from a specified recurrence interval curve for a stated time period can be interpreted to mean the area in question will receive "x" inches of total rainfall during the specified period of days at least once during the recurrence interval. Based on the projected runoff volume for a design storm, appropriately corrected for precipitation losses not reflected in runoff, volumes of runoff and peak flows can be predicted.

The relationship of organic contaminant concentration to flow for one refinery is shown in Figure 6. As noted, the contaminant mass peaks at the approximate time of maximum flow, but declines more rapidly than flow. The analysis of numerous storm flow COD concentration relationships has indicated between 60 and 80 percent of the COD mass is washed out during a one hour period centered about the peak flow axis.

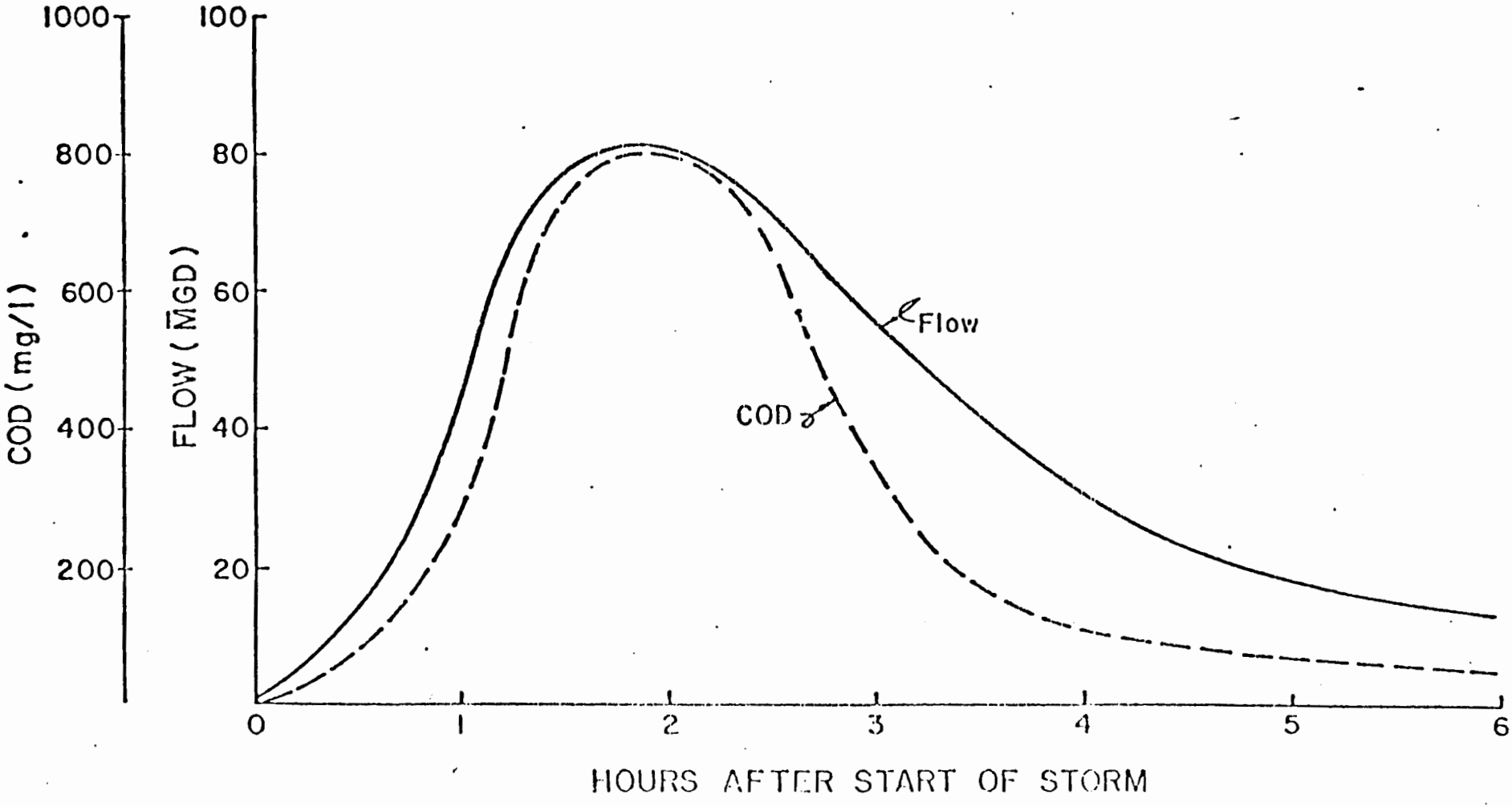

1000
800
600
400
200
COD (mg/l)
100
80
60
40
20
FLOW (MGD)
Flow
COD
0
1
2
3
4
5
6
HOURS AFTER START OF STORM

FIGURE 6

Once the volume and quality of contaminated storm runoff for the design storm is established, a definitive program for handling and treatment can be formulated.

BALLAST WATER BLOWDOWN

Tankers and barges which transport crude or products to and from refinery and petrochemical facilities in coastal areas seldom carry payload on both legs of a journey. This is particularly true of refineries in crude-producing areas which means that tankers are used primarily for exporting finished products, the excess ballast from incoming tankers having to be discharged at the debarkation port. The quantity and quality of ballast water in cases such as this can have a significant impact on the total effluent from an installation requiring treatment.

Ballast is normally taken aboard an empty tanker during its departure from port. The quantity of ballast required during calm weather is usually 1.5 barrels (63 gallons) per ton of tanker deadweight displacement, but is affected to some extent by the judgement of the ship's captain and the individual characteristics of the tanker. Additional ballast is taken aboard at sea as weather conditions warrant. Initially, the ballast has characteristics similar to the body of water from which it was taken. When loaded, however, it is contaminated with the remnants of the previous cargo which remain clinging to the product holds. As only the most modern tankers have separate ballast holds, there is little - if any - truly clean ballast. The degree of ballast contamination is dependent primarily upon the nature of the previous

cargo and the condition of the tanker's holds. Ballast handling procedures at sea vary considerably. Foreign tankers apparently have minimal pollution control discipline. This includes flushing dirty ballast at sea through the seacocks and replacing it with fresh sea water as required. In contrast to the practices of the foreign tankers, domestic tankers follow a more disciplined ballast handling procedure. Ballast tanks are washed at sea; however, an attempt is made to decant the oil-free water underflow by discharging it through the seacocks, consolidating the emulsion and slop oil upper layers in specific dirty ballast tanks. A Butterworth washing head which resembles a high-powered rotary lawn sprinkler is used for the hold cleaning operations. Fresh sea water is then used to flood the emptied ballast tanks and is generally considered clean ballast. Though these procedures are highly efficient, it is difficult to assess the reliability of this practice. However, this procedure does serve a dual purpose; first, by the consolidation of the dirty ballast in one or more special tanks, the volume of ballast to be discharged is reduced, and secondly, sea washings prepare the tanker holds for future product loading.

Ballast unloading operations are also extremely varied. Domestic ships, as a rule, release clean ballast through their seacocks as they proceed toward port. Foreign ships follow a similar procedure, though apparently their discrimination between clean and dirty ballast is generally less discerning. The deballasting operation is by necessity a hurried one, for demurrage charges on even a medium-size tanker are expensive.

In order to ascertain a ballast volume requiring treatment, it is first necessary to estimate the tanker arrival pattern and corresponding ballast volume to be discharged. A typical tanker arrival analysis for one refinery is shown in Figure 7. Using the anticipated volume based on tanker capacity, a surge period can be established to determine ballast storage capacity by constructing a mass curve for the storage time selected. An example of a typical graphical solution using this approach is shown in Figure 8.

The characteristics of ballast water are best described by their organic content in terms of BOD or COD, and the concentration of oil. As ballast is first pumped to a storage tank then sent either to a treatment or to the receiving environment, the characteristics of the underflow from a ballast holding tank are of most interest. The results of ballast water characterization studies conducted at two refineries are tabulated in Table 13.

Table 13

BALLAST WATER CHARACTERISTICS FOR TWO REFINERIES*

	High Value	Low Value	Mean
Refinery No. 1:			
COD, mg/l	472	207	342
BOD_5, mg/l	389	23	168
Oil, mg/l	148	9	44
Chlorides, mg/l	18,500	14,200	16,900
Refinery No. 2:			
COD, mg/l	1,600	1,173	1,456
Oil, mg/l	280	147	183

* Quality of underflow from ballast receiving and holding tank.

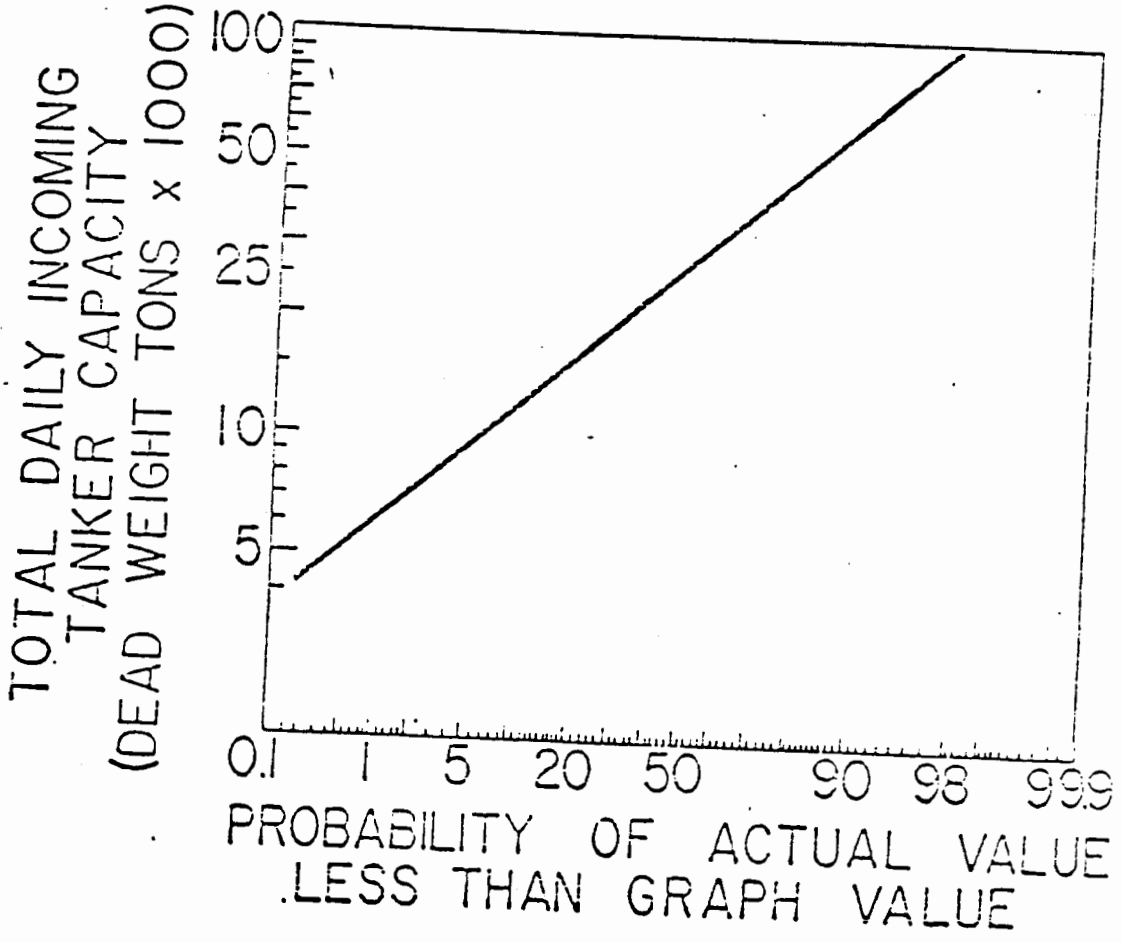
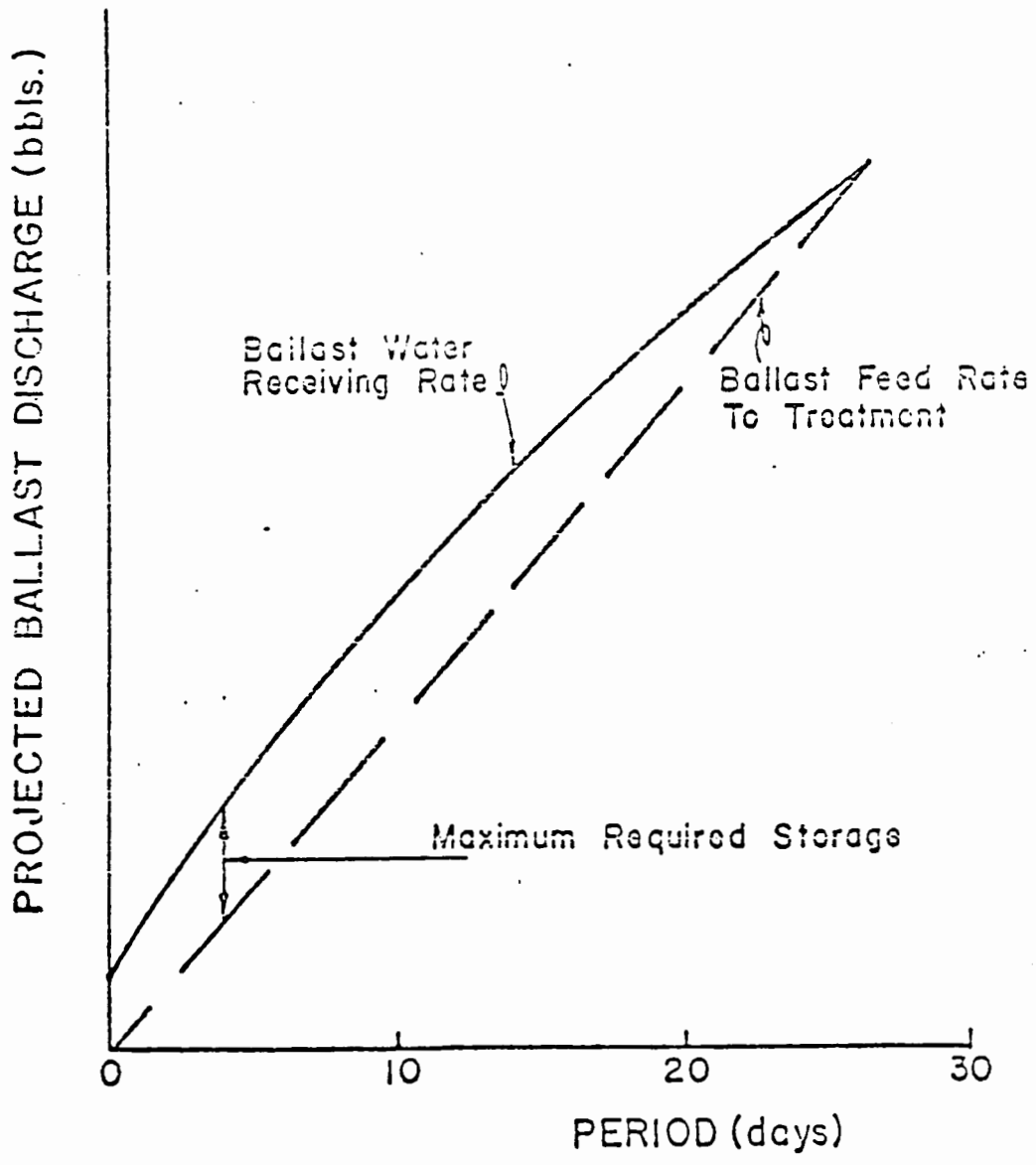

TOTAL DAILY INCOMING
TANKER CAPACITY
(DEAD WEIGHT TONS x 1000)
100
50
25
10
5
0.1
1
5
20
50
90
98
99.9
PROBABILITY OF ACTUAL VALUE
LESS THAN GRAPH VALUE

FIGURE 7


PROJECTED BALLAST DISCHARGE (bbls.)
Ballast Water Receiving Rate
Ballast Feed Rate To Treatment
Maximum Required Storage
0
10
20
30
PERIOD (days)

Although ballast water quality can be expected to vary significantly based on the point of ballast pick-up and handling practices, these data indicate that treatment would be required by most regulatory agencies before this water could be released.

MISCELLANEOUS DISCHARGES

There are many discharges from refinery-petrochemical complexes which are difficult to categorize. These sources result from events such as tank draining or cleaning, product spills, off-spec product dumps, line breaks, and cleaning operations. Wastewaters discharged during turnarounds also can be included in this category.

The pollutional output from a complex which is attributable to most of these sources generally can be reduced through tight management control. The problem areas must first be identified by monitoring specified quality parameters at selected points within the refinery. The best indication of dumps and spills is the geometry of the statistical distribution curve. Significant departures from either an arithmethically or log normal distribution at the higher intervals as illustrated in Figure 9 infers infrequent but unusually severe levels of pollution in terms of effluent COD and oil. Methods of control must be incorporated into a pollution control system by use of alarms, temporary bypass and storage facilities, equalization basins, and treatment capacity for such occurrences.

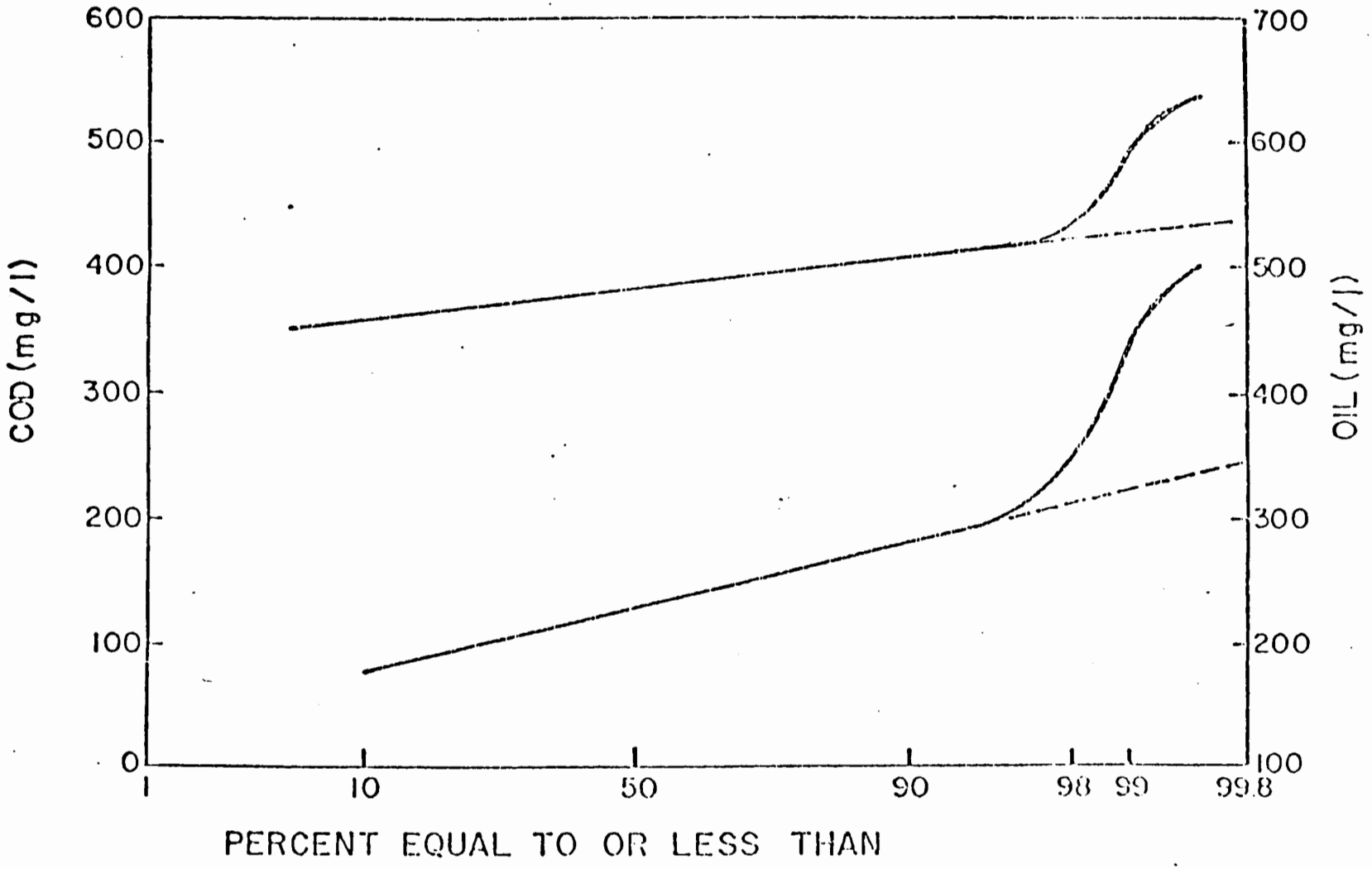

600
500
400
300
200
100
0
COD (mg/l)
700
600
500
400
300
200
100
OIL (mg/l)
1
10
50
90
98
99
99.8
PERCENT EQUAL TO OR LESS THAN

FIGURE 9

SUMMARY

Five categories of refinery-petrochemical wastewater pollution based on source have been cited herein. Process and Utility Operations are common to all refineries and petrochemical installations, but the nature of the wastewater will vary according to process idiosyncrasies, crude charge, and age of the plant. Contaminated Storm Runoff from process areas is a very real source of water pollution and the level of this contribution depends on the cleanliness of the installation, the degree of dikes, curve, and other physical features separating clean or contaminated runoff, and the climatological features of the area. Ballast Water, if applicable, needs to be considered in the pollution control system, as case histories indicate the level of organic contamination is high and allowances for handling and treating miscellaneous spills, dumps, and washdowns should be made in a pollution control program. To put these categories of pollutional output in perspective, an example of the respective hydraulic and organic contributions from two refineries is presented in Table 14.

TREATMENT PROCESSES

The treatment of wastewaters discharged from refinery-petrochemical installations encompasses the removal of diverse pollutants - some rather obvious and standard in nature and some not so obvious. Most of the attention in refinery pollution control is focused on organic removal. Oil and grease is of immediate concern and is usually removed by physical separation processes. Biological treatment, carbon adsorp-

TABLE 14

BASIS FOR TREATMENT FACILITY DESIGN

	Flow (% of total)	BOD (% of total)	COD (% of total)
Refinery No. 1			
Normal Process Operations	21	70	71
Utilities Operations	26	13	14
Contaminated Storm Runoff	20	7	5
Ballast Water Blowdown	23	8	8
Sanitary Sewage	5	1	1
Allowance for Misc. Discharges	5	1	1
	100%	100%	100%
Refinery No. 2			
Normal Process Operations	25	42	
Utility Operations	33	15	
Contaminated Storm Runoff	16	12	
Ballast Water Blowdown	10	15	
Sanitary Sewage	1	<1	
Allowance for Misc. Discharges	15	15	
	100%	100%	

tion, and filtration are currently used in the removal of suspended and dissolved organic constituents, and chemical treatment processes are often required for neutralization, emulsion breaking, and chemical precipitation. Although it is difficult to categorize the treatment processes which constitute a pollution control system in a true generic sense, the processes which are discussed in this chapter are classified as follows:

Primary:	API Separators
	Tilted Plate Separators
	Filtration for Oil Removal
	pH Control
	Stripping Processes
Intermediate:	Dissolved Air Flotation
	Coagulation-Precipitation
	Equalization
Secondary/Tertiary:	Activated Sludge
	Aerated Lagoons
	Trickling Filters
	Waste Stabilization Ponds
	Cooling Tower Oxidation
	Chemical Oxidation
	Filtration
	Carbon Adsorption

In this discussion, general comments about the process and its applicability will be considered as well as process information developed from case histories.

PRIMARY TREATMENT

API Separators

Gravity separation using API separators involves the removal of materials less dense than water, such as free oils and air entrained particulates, and the removal of suspended materials which are more dense than water by sedimentation. The current design principles of the API separator are based on extensive studies and testing programs and include inlet and outlet arrangements, shape factors, and the effect of appurtenances on hydraulic characteristics in separation chambers. The principal factors which affect the design of oil separators are:

A) the specific gravity of the oil;

B) the specific gravity of the wastewater;

C) the temperature of the wastewater stream;

D) the presence or absence of emulsions; and,

E) the suspended solids concentration.

The specific gravities of the oil and water determine the separation rate while they are in turn related to the temperature. These factors determine the allowable overflow rate from the oil separator. Graphical solutions of oil-water separation rates which can be used for separator design have been prepared (20).

As segregation of wastewater streams is a basic principle of refinery waste disposal pracrice, special purpose separators are frequently used for streams containing readily separable oil and low suspended solids concentrations. These units are usually sized on an arbitrary basis. A

schematic showing application of API and special purpose separators within a refinery is shown in Figure 10 (20).

Reported efficiencies of oil separators from refineries around the country are listed in Table 15.

Table 15

TYPICAL EFFICIENCIES OF OIL SEPARATION UNITS

Oil Content Influent (mg/l)	Oil Content Effluent (mg/l)	Oil Removed (%)	Type	COD Removed (%)	SS Removed (%)
300	40	87	Parallel Plate	-	-
220	49	78	API	45	-
108	20	82	Circular	-	-
108	50	54	Circular	16	-
98	44	55	API	-	-
100	40	60	API	-	-
42	20	52	API	-	-
2,000	746	63	API	22	33
1,250	170	87	API	-	68
1,400	270	81	API	-	35

The efficiency, of course, is a function of many design and operating variables. Perhaps the two most significant factors are flow rate and influent oil concentration. Separators must be hydraulically protected to prevent "flushing" during periods of high flow. Bypass or overflow lines are generally used to provide this protection. The effect of flow on separator effluent oil concentration is best illustrated in Figure 11. The oil concentration is significant as higher oil concentrations are removed with greater efficiency than low oil concentrations since the

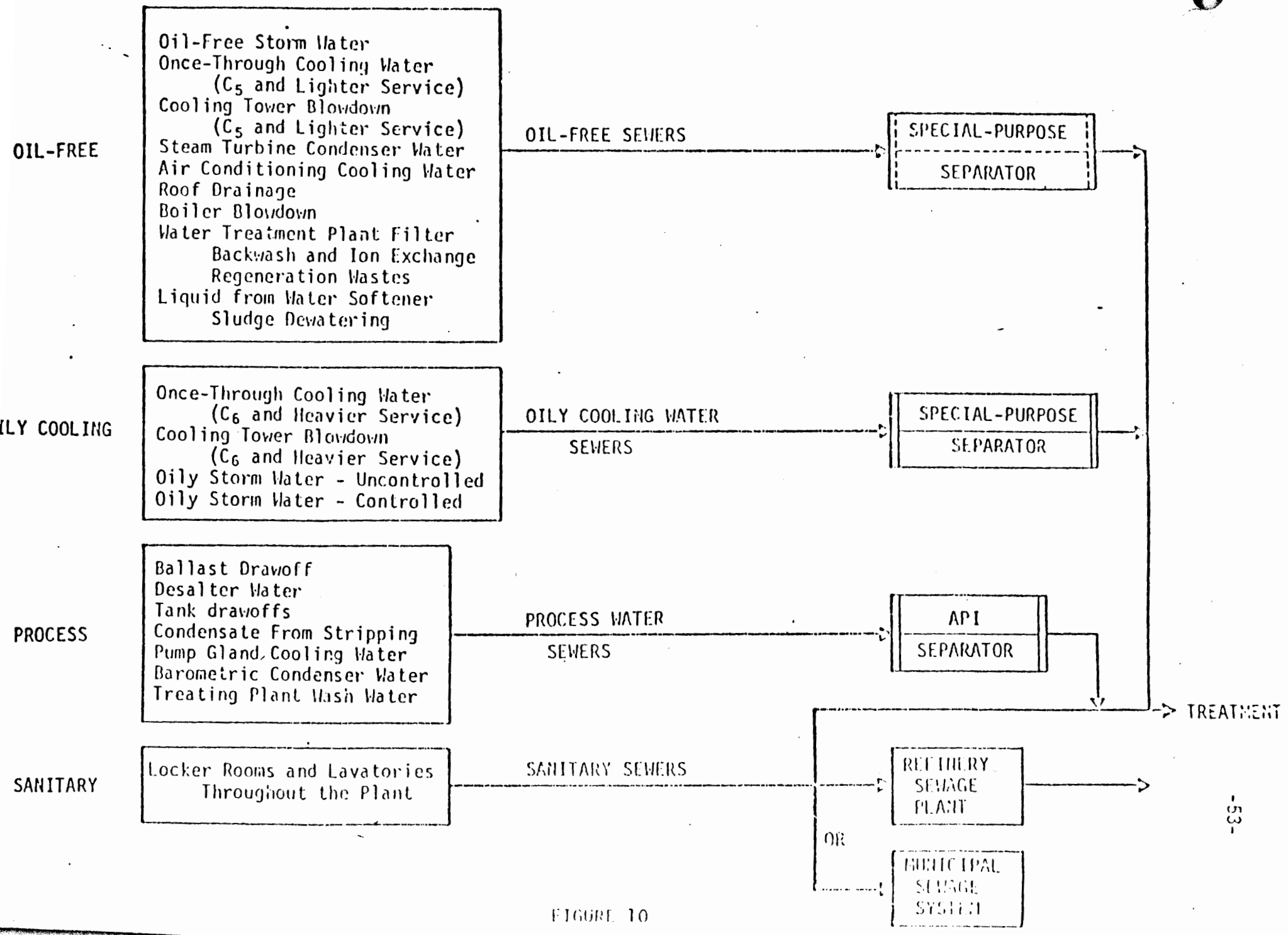

OIL-FREE
Oil-Free Storm Water
Once-Through Cooling Water
(C_5 and Lighter Service)
Cooling Tower Blowdown
(C_5 and Lighter Service)
Steam Turbine Condenser Water
Air Conditioning Cooling Water
Roof Drainage
Boiler Blowdown
Water Treatment Plant Filter
Backwash and Ion Exchange
Regeneration Wastes
Liquid from Water Softener
Sludge Dewatering
OIL-FREE SEWERS
SPECIAL-PURPOSE
SEPARATOR
ILY COOLING
Once-Through Cooling Water
(C_6 and Heavier Service)
Cooling Tower Blowdown
(C_6 and Heavier Service)
Oily Storm Water - Uncontrolled
Oily Storm Water - Controlled
OILY COOLING WATER
SEWERS
SPECIAL-PURPOSE
SEPARATOR
PROCESS
Ballast Drawoff
Desalter Water
Tank drawoffs
Condensate From Stripping
Pump Gland Cooling Water
Barometric Condenser Water
Treating Plant Wash Water
PROCESS WATER
SEWERS
API
SEPARATOR
TREATMENT
SANITARY
Locker Rooms and Lavatories
Throughout the Plant
SANITARY SEWERS
REFINERY
SEWAGE
PLANT
OR
MUNICIPAL
SEWAGE
SYSTEM

FIGURE 10

FIGURE 10

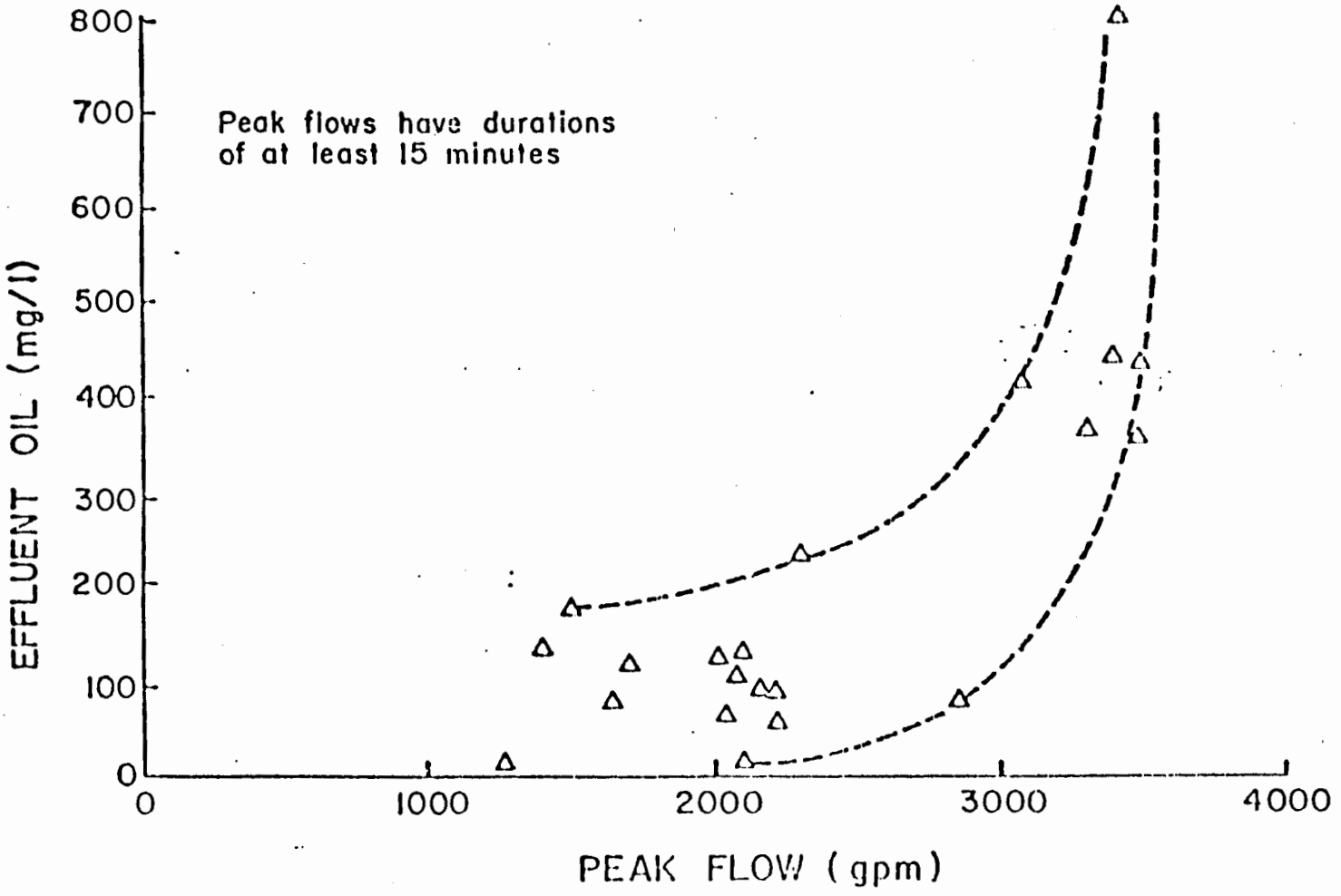


FIGURE 11

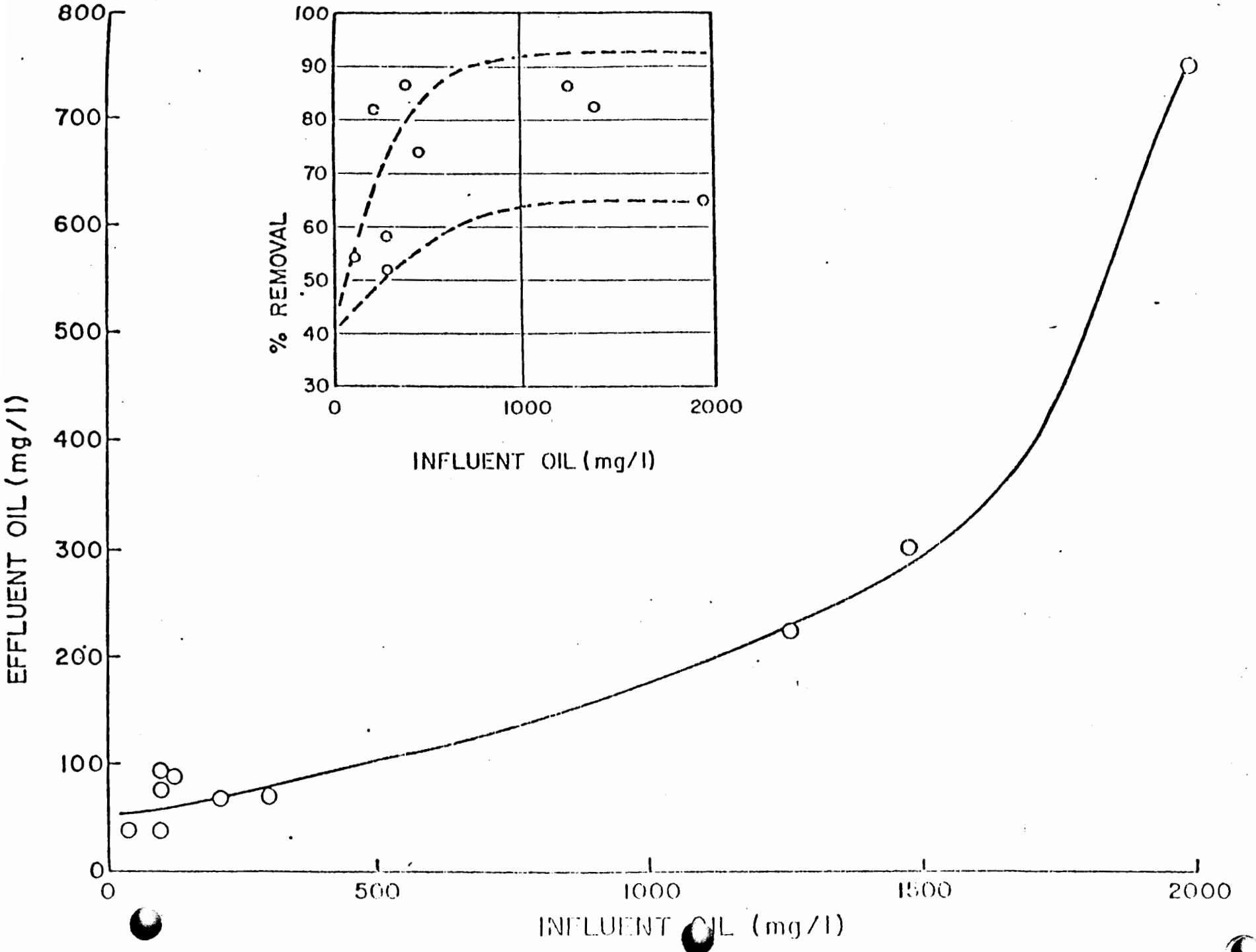
lower limit of oil in the separator effluent is usually around 50 mg/l. The influence of initial oil concentration on separator efficiency is illustrated in Figure 12.

Removal of other contaminants in a separator is highly variable. As indicated in Table 15, COD removal efficiencies vary from 15 to 80 percent and suspended solids removal ranges from 30 to 65 percent. This, of course, depends to a large extent on sampling techniques and analytical procedures.

Tilted Plate Separators

The tilted or parallel plate separator is a recent development for removal of free oils and consists of corrugated plate modules. These modules are installed at an angle of 45 degrees, reducing the separator distance of the lighter-than-water materials and thus the required detention time. The light components coalesce in the trough of the corrugated plate, rise to the top of the module, and are skimmed. Similarly, the settleable particles in the wastewater fall to the bottom of the corrugations and slide to the low end of the module for removal. A schematic diagram of the tilted plate separator is shown in Figure 13 (22).

As tilted plate separators have only recently been applied for the removal of free oil from refinery effluents, little operating data are available. One test program conducted by a manufacturer indicated oil removal as a function of oily water throughput. These data are shown in Table 16 (22). Another refinery survey evaluated a pilot scale tilted plate separator used both in parallel and in series with an existing API separator. The effluent oil concentration as a function of influent levels for three flow rates are shown in Figure 14. A comparison of oil


EFFLUENT OIL (mg/l)
INFLUENT OIL (mg/l)
% REMOVAL
INFLUENT OIL (mg/l)

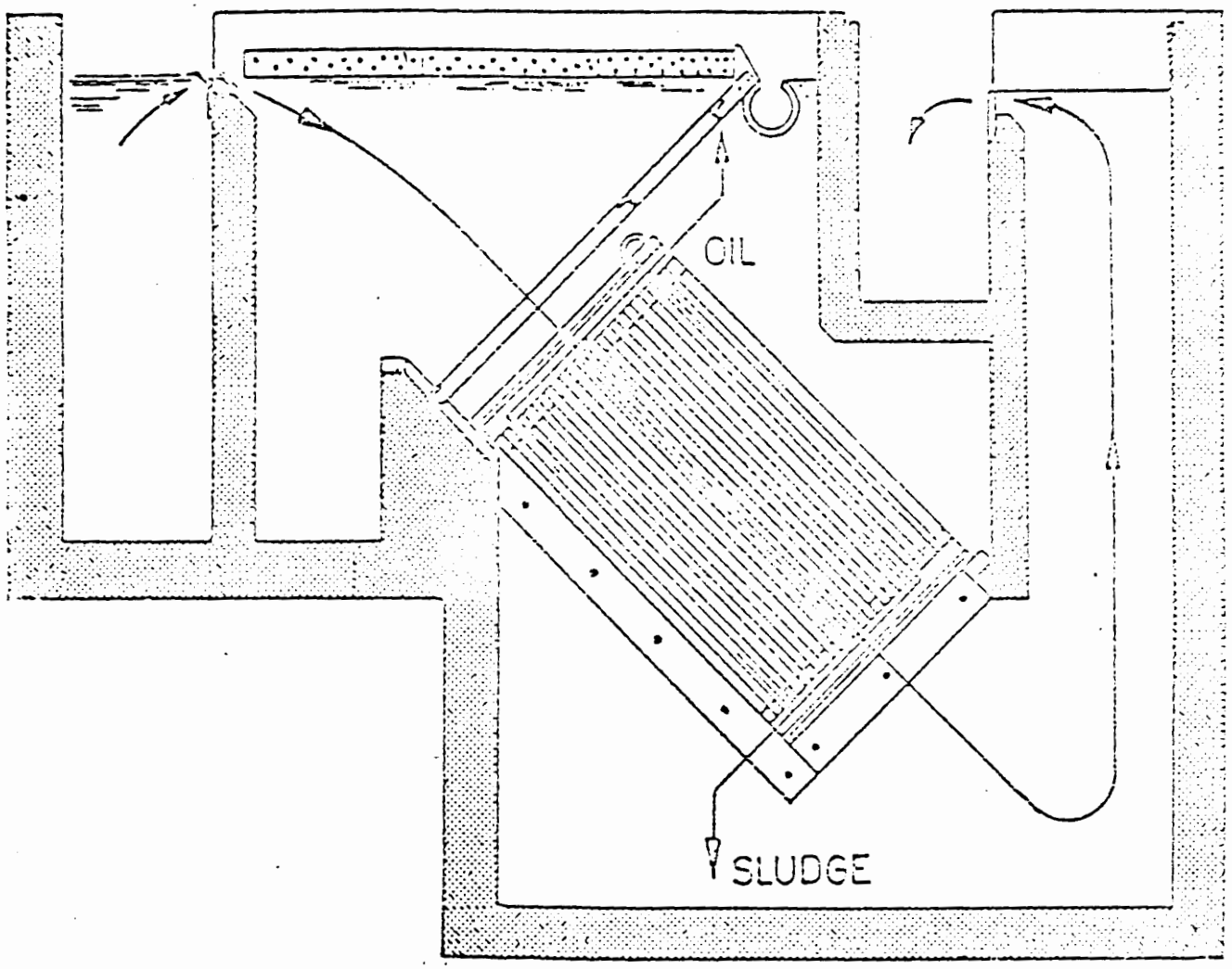
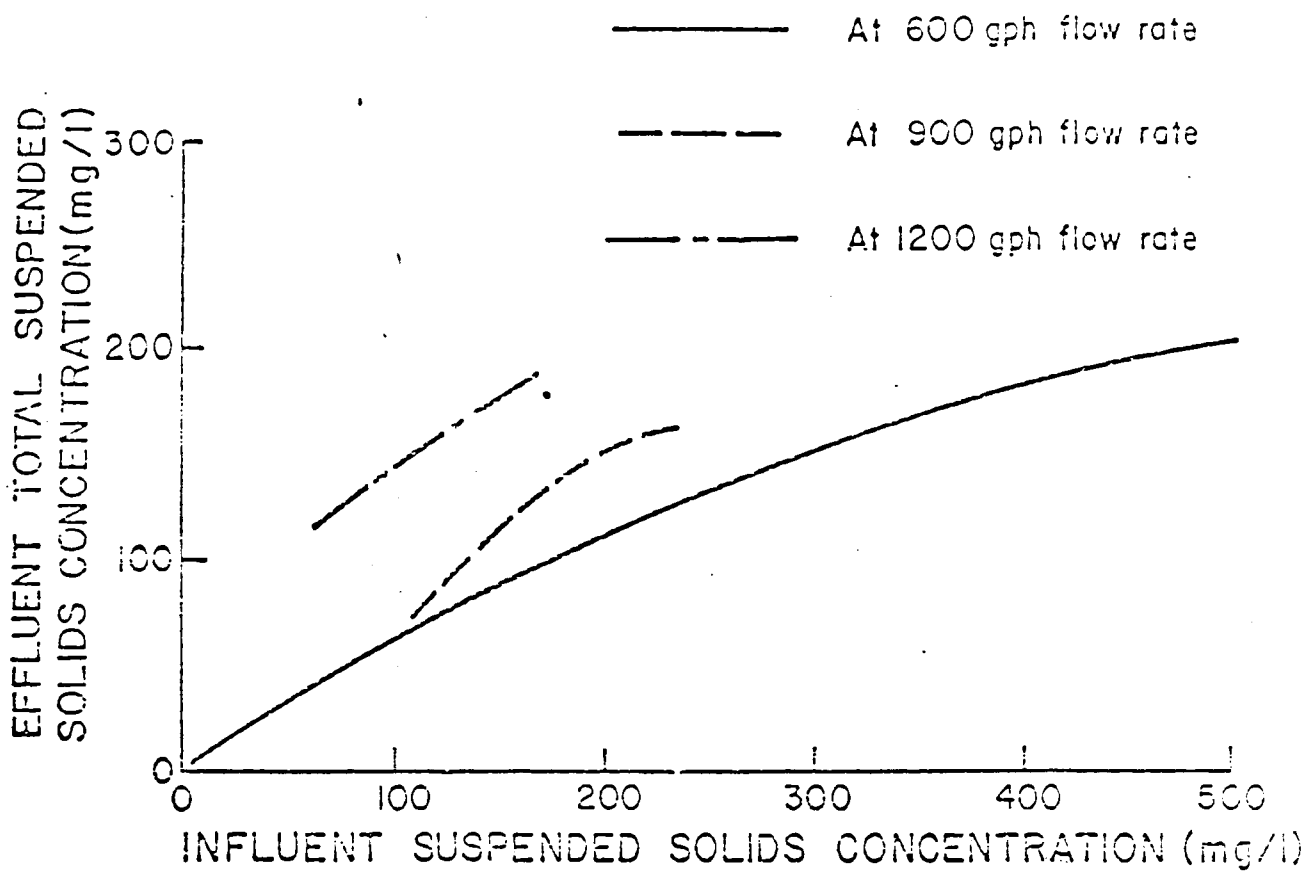


FIGURE 13

TABLE 16

OIL REMOVAL, TILTED PLATE SEPARATOR

Oily Water Throughput (gal/hr)	Influent Oil (mg/l)	Effluent Oil (mg/l)	Percent Percent Removal
8,000	150	50	67
8,000	375	66	82
8,000	500	86	83
16,000	500	178	65
16,600	500	190	62
18,600	570	185	67
18,600	700	330	53


At 600 gph flow rate
At 900 gph flow rate
At 1200 gph flow rate
EFFLUENT TOTAL SUSPENDED SOLIDS CONCENTRATION (mg/l)
300
200
100
0
0
100
200
300
400
500
INFLUENT SUSPENDED SOLIDS CONCENTRATION (mg/l)

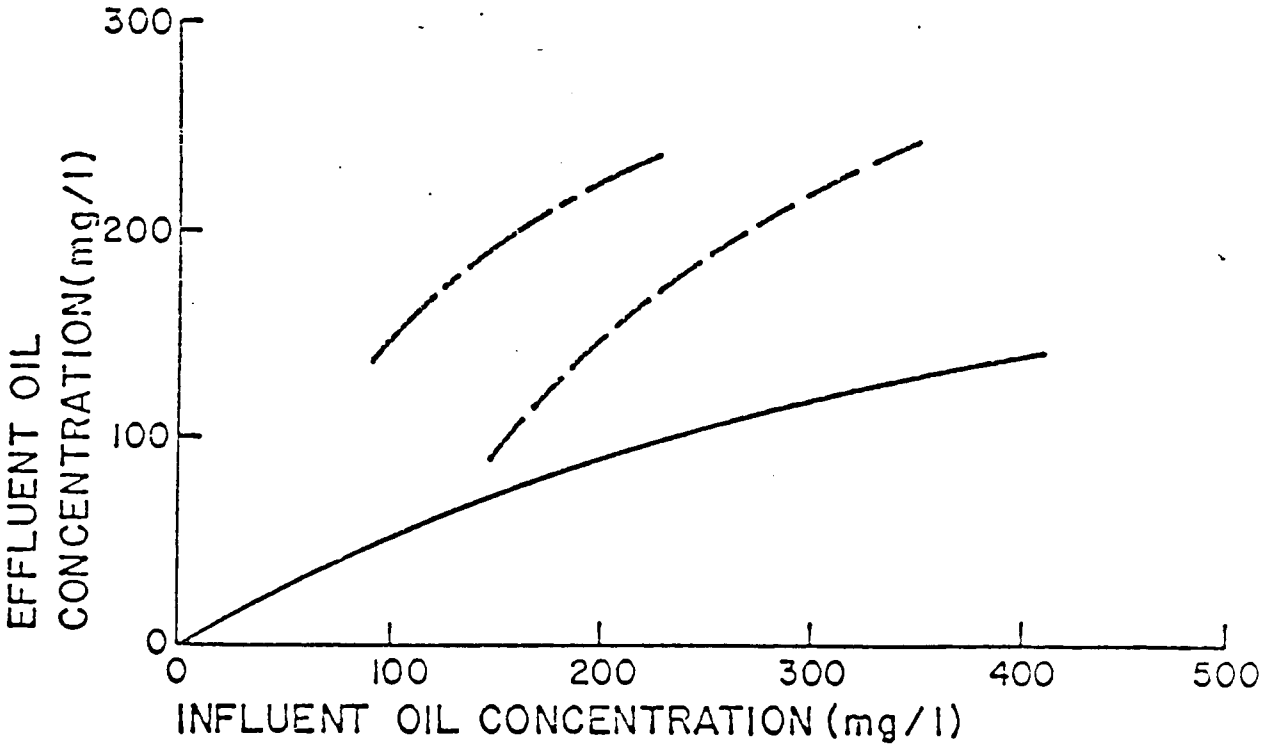

EFFLUENT OIL CONCENTRATION (mg/l)
300
200
100
0
0
100
200
300
400
500
INFLUENT OIL CONCENTRATION (mg/l)

FIGURE 14

removal efficiency achieved by the pilot scale tilted plate separator compared to that achieved in a full scale API separator receiving the same oily wastewater is shown in Figure 15.

There is a broad application for tilted plate separators for the removal of free oil from refinery-petrochemical wastewaters. As little space is required, they can be installed adjacent to an existing API separator which is either overloaded or improperly designed, thereby reducing the effluent oil levels obtained by gravity separation. They also can be installed in parallel with existing separators, reducing the hydraulic load and enhancing the oil removal capacity of the system.

Filtration for Oil Removal

Filtration as a pretreatment step for oil and solids removal is a candidate system which can be used singularly or in conjunction with gravity separators or air flotation systems. Several types of filtration devices have proven effective in removing free and emulsified oils from refinery-petrochemical wastewaters. These vary from filters with sand media to those containing special media which exhibit a specific affinity for oil. One type is upflow using a graded silica media as the filtering and coalescing section. Here, even small particles and globules are separated and retained on the media. The oil particles which flow upward by gravity differential and fluid flow to rise through the coalescent media and through the water phase from which it is separated are collected near the top of the separator. In a solids free stream, the cycle duration is long since the media serves as a coalescer and not as a collector of oil. Regeneration of the bed is accomplished by introducing a rapid rate of wash water and evacuating the solids and remaining oil.

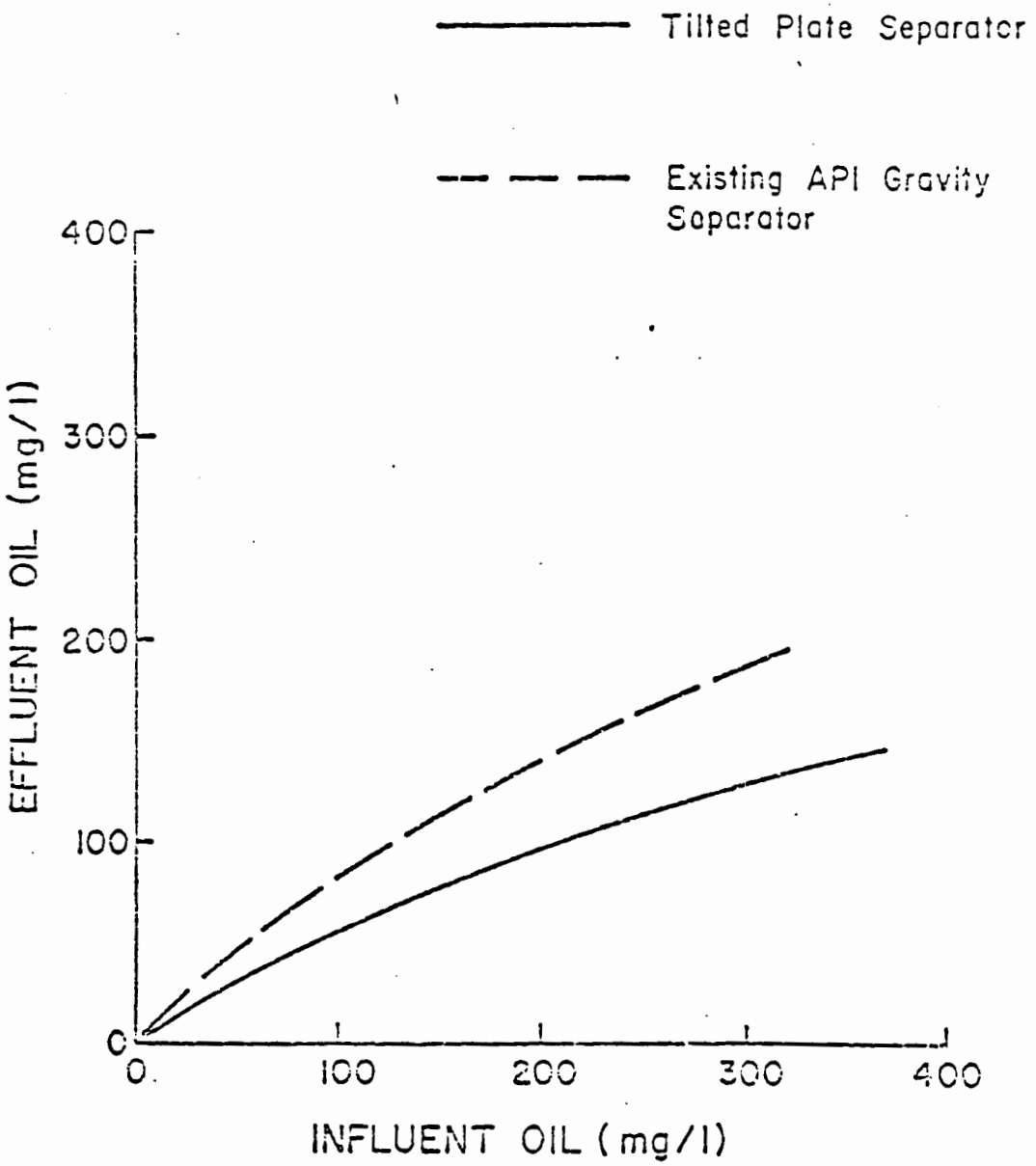

Tilted Plate Separator
Existing API Gravity Separator
EFFLUENT OIL (mg/l)
400
300
200
100
0
0
100
200
300
400
INFLUENT OIL (mg/l)

FIGURE 15

This filtration and coalescing process is often enhanced by the use of polymer resin media.

The advantages of going to filtration as a pretreatment step in oil removal are the compactness of the units, favorable economics in some cases, and flexible operation through control of water and oil draws, flow rate, and backwash regeneration. Some of the disadvantages include reported problems with solids stabilized oil emulsions, dirt and grit collecting rapidly, resulting in higher operational and maintenance costs, and efficiencies which in some cases may be no better than gravity separation units. Manufacturers, however, have reported 90 to 95 percent removal of oils at design flow rates. The application of these units based on most observations is for selected in-plant streams which are dirt-free. Another application would be ballast water treatment following phase separation in a receiving tank.

pH Control

Neutralization is commonly required in the treatment of petrochemical and refinery wastewaters as many process streams are highly acidic or alkaline. Typical neutralization steps are included in the following applications:

(a) emulsion breaking through acidification, and reneutralization following gravity separation;

(b) neutralization prior to biological treatment;

(c) neutralization on specified streams to prevent corrosion;

(d) pH adjustment to prevent unwanted precipitation of certain constituents; and,

(e) pH adjustment to enhance coagulation and sedimentation.

Although refineries and petrochemical installations have many individual streams in the highly acid or alkaline range, the combined effluent generally ranges on the slightly basic side in the pH 7-10 range. There are many installations with primary and secondary steps which do not require any neutralization steps within the treatment complex. Separate discharge of certain streams, however, requires neutralization steps. Such applications include dilute acid or alkaline wash waters, spent caustics from caustic treating operations, acid sludges from alkylation, sulfonation, and acid treating processes, and spent acid catalysts.

Acid streams are neutralized by one of several candidate modes. These include fluidized mixing of the waste with lime slurries, dolomitic lime slurries, caustic, or soda ash. Limestone beds operated either as an upflow or downflow system are occasionally used. Alkaline streams can be neutralized with acid (sulfuric or hydrochloric) or with boiler flue gas (carbon dioxide). Neutralization often can be accomplished by combining internal refinery wastewater streams. For example, spent caustic can often be neutralized with spent acid. Spent caustic neutralization with an acid can be designed as a batch or continuous system. A typical process flow schematic is shown in Figure 16 (1).

Design of a neutralization system is predicated on titration curves which determine the total basicity or acidity of a solution. This curve graphically depicts the pH change per unit addition of reagent. A typical curve for one petrochemical waste is shown in Figure 17, indicating the caustic requirement to obtain a desired effluent of pH 7.5. There are many intricacies in the design and control of a neutralization process,

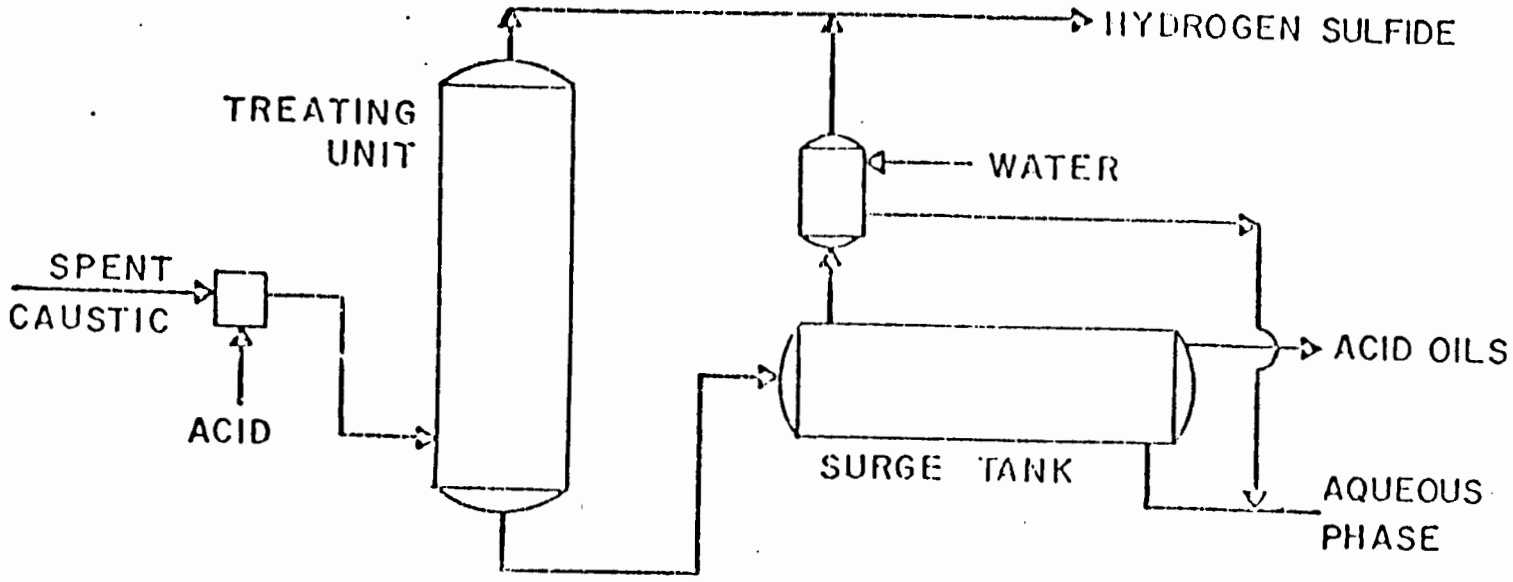

HYDROGEN SULFIDE
TREATING UNIT
WATER
SPENT CAUSTIC
ACID
ACID OILS
SURGE TANK
AQUEOUS PHASE

FIGURE 16

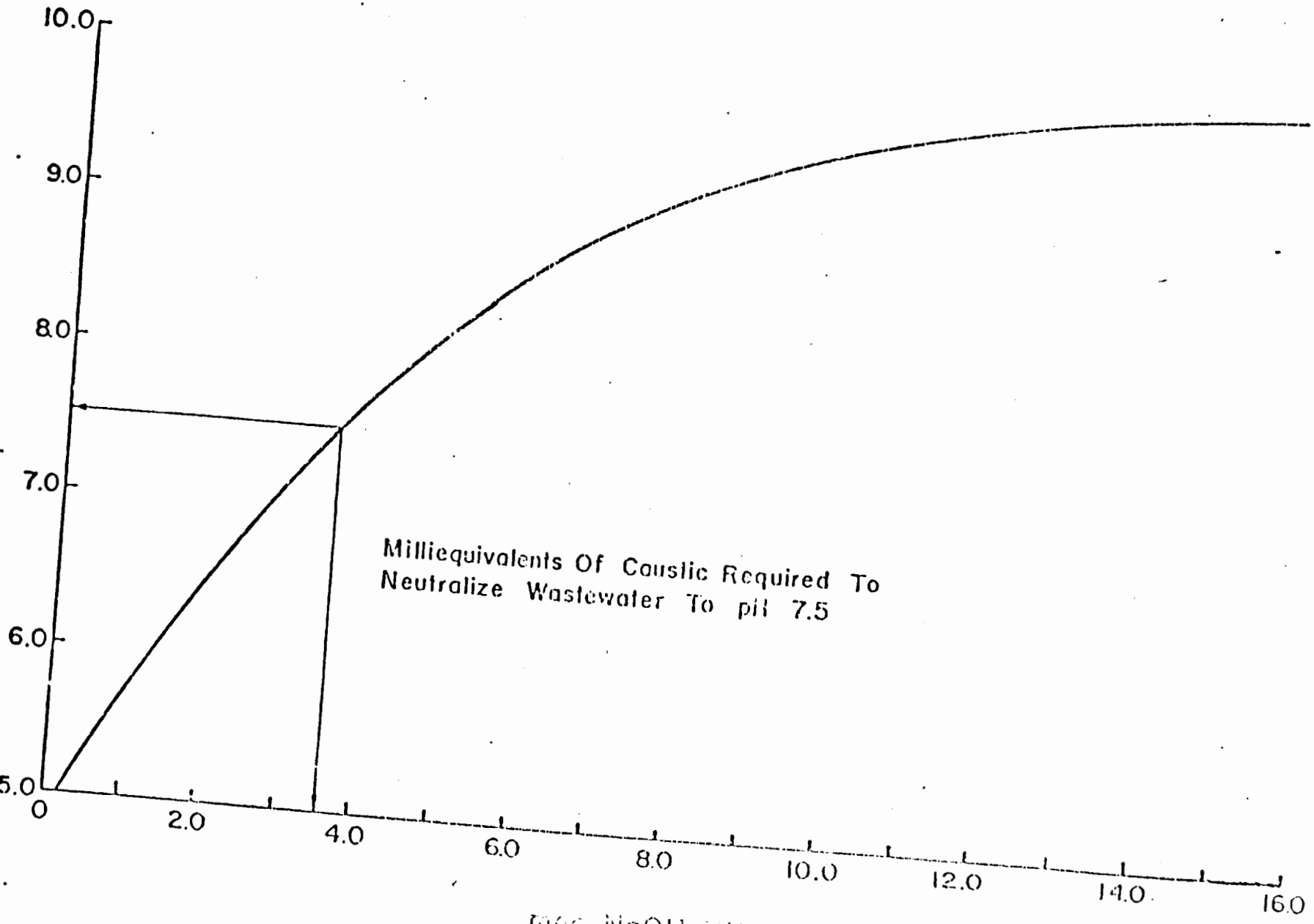

10.0
9.0
8.0
7.0
6.0
5.0
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
Milliequivalents Of Caustic Required To Neutralize Wastewater To pH 7.5
meq NaOH / liter

FIGURE 17

including consideration for mixing, reagent feed systems, and control systems (23). The most economical method of neutralization depends on the characteristics and quantity of the wastewater being neutralized and the source and supply of the neutralizing agent.

Typical applications of neutralization and pH adjustment requirements for treating refinery and petrochemical wastewaters are cited in Table 17 (1).

Table 17

TYPICAL APPLICATIONS OF NEUTRALIZATION OR pH ADJUSTMENT TO PETROCHEMICAL WASTES

Process or Products Manufactured	Waste Components	Agent
Acid treating processes	Spent sulfuric acid	Spent caustic
Adipic acid	Organic acid	Ammonium hydroxide
Alkylation, sulfonation for detergents, etc.	Sulfonic acids Sulfonates	Lime
Amines, amides		
Butadiene	Cuprous ammonium acetate	Spent caustic
Butadiene, olefins		
Catalytic processes	Aluminum chlorid phosphoric acid	Lime
Chemicals for lubricating oils		
Freon	Inorganics	
Herbicides	Chlorinated hydrocarbons	Lime
Many petrochemical operations	Emulsified oils	Lime
Mixed petrochemicals	Aliphatic acids, esters, alcohols, aromatics, amines	Soda ash
Mixed petrochemicals -- olefins, aromatics, nitriles, resins, detergents, etc.	Oily wastes	Lime

cont'd. next page

Table 17 cont'd.

TYPICAL APPLICATIONS OF NEUTRALIZATION OR pH ADJUSTMENT TO PETROCHEMICAL WASTES

Process or Products Manufactured	Waste Components	Agent
Orlon	Mixed organics & inorganics	
Phenol, salycylic acid, rubber chem., aspirin	Mixed organics	Lime
Polyethylene	Hexane, catalyst alcohols	
Polyvinylchloride plastics		Lime
Spent caustics from caustic treating operations	Spent caustic	
Styrene	Acid wastes	Waste alkaline sodium aluminate
Tetraethyl lead	Lead; sodium chlorides, sulfates; ethyl chloride	

Stripping Processes

Stripping processes are used to remove selected constituents from liquid streams. The two most prevalent pollutants found in refinery wastewaters which are susceptible to stripping are hydrogen sulfide and ammonia resulting from the destruction of essentially all the organic nitrogen and sulfur compounds during desulfurization, denitrification, and hydrotreating. The use of steam within the processes is the primary source of conveyance, as the condensation occurs simultaneously with the condensation of hydrocarbon liquids and in the presence of a hydrocarbon vapor phase which contains H_2S and NH_3 (1). Phenols also may be present in these "sour water" condensates and can be stripped from solutions although the ef-

ficiency of removal is less than for sulfide and ammonia. Other aromatics also can be stripped from solution at various levels of efficiency. As the regulatory agencies are imposing increasingly stringent quality standards for refinery wastewater in terms of immediate oxygen demand (sulfide causative) and ammonia, the necessity of in-plant control through stripping towers may be required whether it can be justified in terms of product recovery or not.

The design criteria for sour water strippers is well documented and is outlined in detail elsewhere (1)(2). There are various types of strippers but most involve a single tower equipped with trays or some type of packing. The feed water enters at the top of the tower and steam or stripping gas is introduced at the bottom. As H_2S is less soluble in water than NH_3, it is more readily stripped from solution. High temperatures (230°F +) are required to remove NH_3 where H_2S could be stripped at 100°F if NH_3 were fixed or not present. Therefore, acidification with a mineral acid or flue gas is often used to fix the NH_3 and allow more efficient H_2S removal. Average operating characteristics of some sour water strippers are cited in Table 18 (2). Although acidification enhances sulfide removal, it fixes the ammonia and prevents its removal. This has led to a two stage stripping and recovery process developed by the Chevron Research Company (3). The process flow sheet, as shown in Figure 18, includes a degasser-surge tank combination which allows operational flexibility. Following skimming of any floating hydrocarbon, it is routed to the first column where the H_2S is stripped and sent to a sulfur recovery plant. The water-ammonia mixture than goes to a second fractionator for ammonia stripping. The overhead ammonia,

AVERAGE OPERATING CHARACTERISTICS

OF SOUR WATER STRIPPERS

Type of Stripper	Flow Rate of Stripping Medium (SCF/gal)	Removal		Temperature	
		H_2S (%)	NH_3 (%)	Tower Feed (°F)	Tower Bottom (°F)
Steam					
w/o acidifying[+]	8-32	96-100	69-95	150-240	230-270
w/ acidifying[**]	4-6	97-100	0	200	230-250
Flue Gas					
w/ steam[*]	12.7	88-98	77-90	235	235
w/o steam[*]	11.9	99	8	135	140
Natural Gas					
w/ acidifying	7.5	98	0	70-100	70-100

[+] Data from Eight Towers

[*] Data from Only One Tower

[**] Data from Two Towers

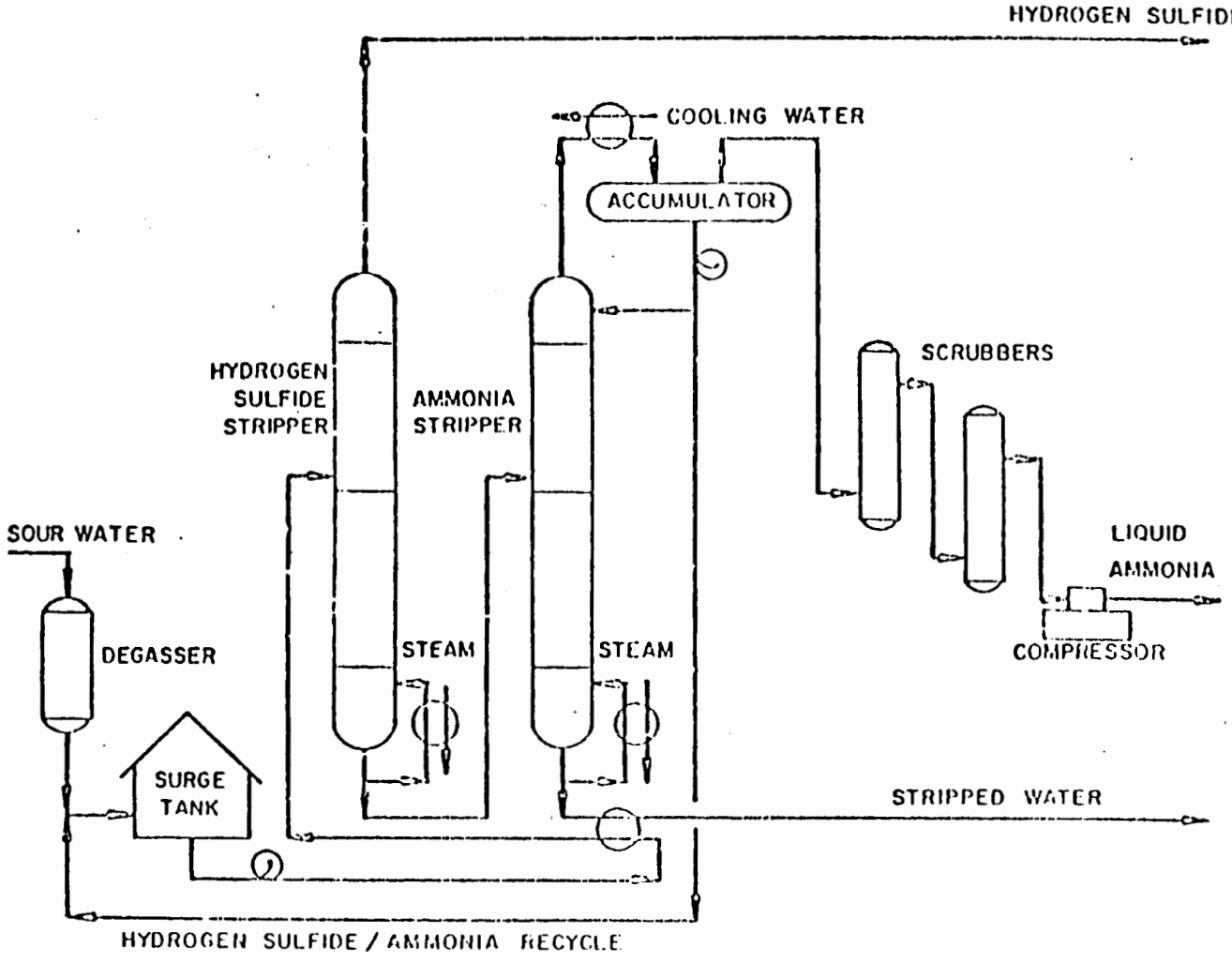

HYDROGEN SULFIDE
COOLING WATER
ACCUMULATOR
SCRUBBERS
HYDROGEN SULFIDE STRIPPER
AMMONIA STRIPPER
SOUR WATER
LIQUID AMMONIA
DEGASSER
STEAM
STEAM
COMPRESSOR
SURGE TANK
STRIPPED WATER
HYDROGEN SULFIDE / AMMONIA RECYCLE

FIGURE 18

approximately 98 percent pure as it leaves the condenser, is further purified by passing it through a scrubber system, and is then liquified as high purity ammonia. The cooled water bottoms from the system are then sufficiently free of H_2S and NH_3 to satisfy most quality criteria containing less than five mg/l H_2S and 50 mg/l NH_3.

Volatile organic compounds can be stripped from aqueous wastes by using air or intense mixing as the stripping agent. The stripping of wastewater containing high concentrations of volatile organics results in a substantial removal of wastewater COD. The amount of BOD removed, however, is questionable. Laboratory tests involving stripping of some biodegradable volatile organic compounds indicated that most of the BOD removal in an aeration tank was due to biological action rather than physical stripping This investigation indicated that the stripping of biodegradable wastes is not usually significant, even if the organics are quite volatile. If an organic compound is non-biodegradable and volatile, however, air stripping may be a significant mechanism for removing this pollutant from a liquid system. For example, benzene and nitrobenzene, both of which are relatively non-biodegradable, can be effectively air stripped from wastewater. Air stripping systems are often not followed by condensation units because of economic considerations, and the practice of releasing volatile compounds to the atmosphere often creates air pollution problems which limit the applicability of this treatment technique.

INTERMEDIATE TREATMENT

Dissolved Air Flotation

Dissolved air flotation (DAF) is a process commonly used in refinery and petrochemical installations to enhance oil and suspended solids removal. It is generally preceded by a gravity oil separator to remove gross quantities of free oil and suspended matter. The process basically involves the pressurization of the influent or recycled wastewater the release of which in either a circular or rectangular tank creates minute bubbles that float the suspended and oily particulates to the surface. The float solids are removed to disposal or recovery by a mechanical surface collector, while the underflow represents the clarified effluent. While DAF units are not as economical as gravity separators, they have the capacity for producing a better quality of effluent and are therefore commonly required to meet the effluent oil levels prior to subsequent treatment or discharge. If a significant portion of the oil is emulsified, chemical addition with rapid mix and flocculation chambers are a part of the flotation unit, breaking the emulsion and enhancing the phase separation. Chemicals normally employed include aluminum, iron, and calcium salts. Polyelectrolytes are frequently added either individually or in combination with these salts.

In order to predict the oil levels in the DAF effluent, it is first necessary to refer to case histories where DAF units are being used to treat refinery oily wastewaters (26). The first case history is graphically represented in Figure 19 where a rectangular DAF unit

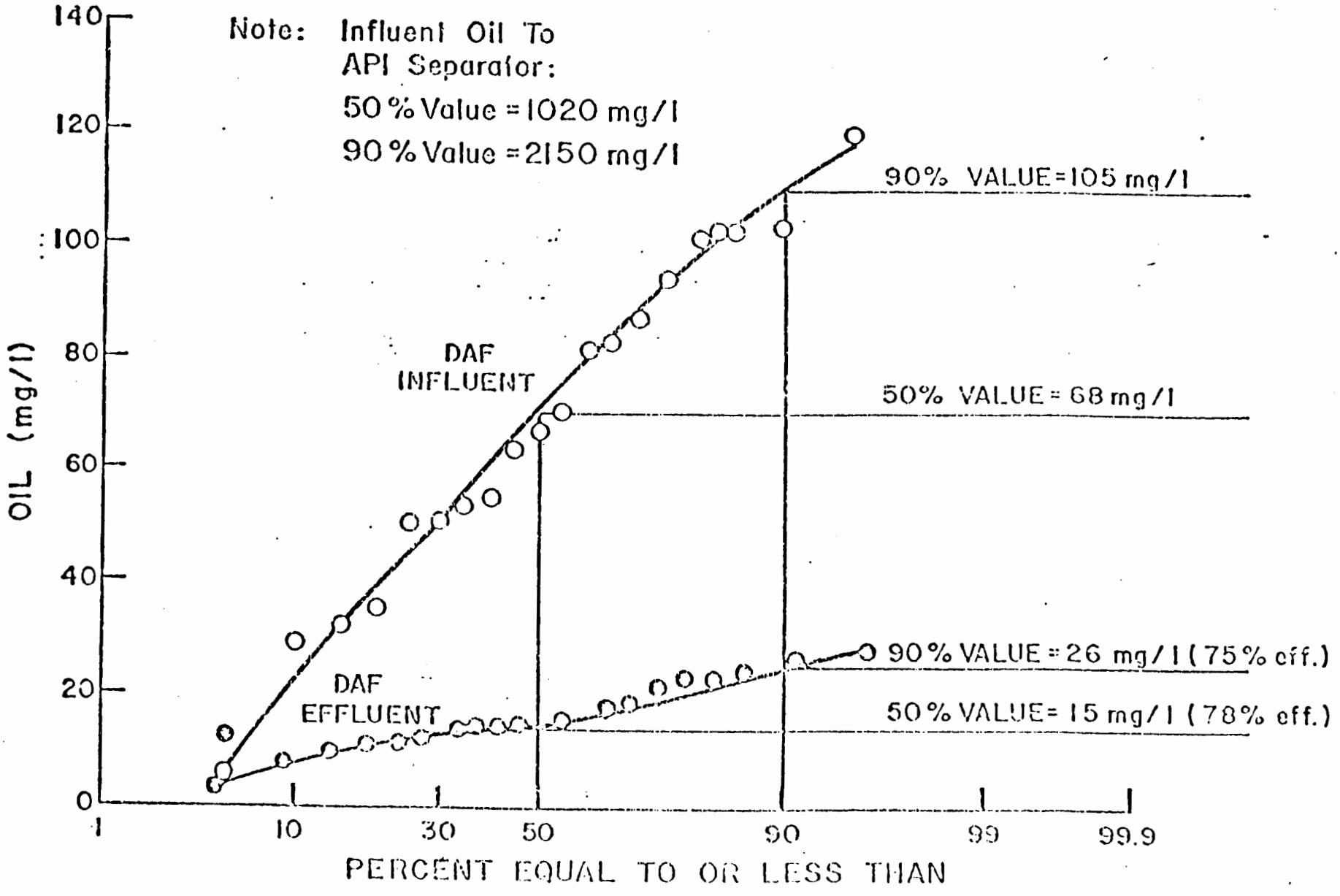

Note: Influent Oil To API Separator:
50 % Value = 1020 mg/l
90 % Value = 2150 mg/l
90% VALUE=105 mg/l
50% VALUE = 68 mg/l
DAF INFLUENT
DAF EFFLUENT
90 % VALUE = 26 mg/l (75 % eff.)
50 % VALUE = 15 mg/l (78% eff.)
OIL (mg/l)
140
120
100
80
60
40
20
0
1
10
30
50
90
99
99.9
PERCENT EQUAL TO OR LESS THAN

FIGURE 19

has been in operation in series with an API separator for several years. As noted, the DAF unit reduces the total oil from 68 mg/l to 15 mg/l at a 50 percent probability and from 105 mg/l to 26 mg/l at a 90 percent probability. The separator influent oil concentration is 1,020 mg/l (50 percent) and 2,150 mg/l (90 percent). The second case history where sufficient data were collected to perform a statistical analysis is shown in Figure 20. This refinery has two circular DAF units preceded by an API gravity separator. Because of in-plant segregation, the oil content in the feed water is higher than would normally be expected. The DAF units reduce the oil from 580 mg/l to 68 mg/l (50 percent) and 1,930 mg/l to 128 mg/l (90 percent). The third case history indicates the variation of oil from a circular DAF unit over two years of analyses as shown in Figure 21. No influent oil concentrations were available, but this plot does indicate 50 percent and 90 percent effluent levels. It should be noted that high oil concentrations which occur 10 percent of the time or less reflect occasional oily dumps or spills which can be expected in most refinery operations.

Although literature reported data is usually insufficient to make a statistical analysis, cited average values are indicative of DAF oil removal capacities over a wide range of influent oil concentrations. A tabulation of this reported data is given in Table 19. DAF efficiency in terms of oil removal is a function of many factors - namely, design overflow rate, retention time, recycle volume, pressurization level, air-solids ratio, type and volume of chemical addition, and the concentration and form of the influent oil. The data tabulated in

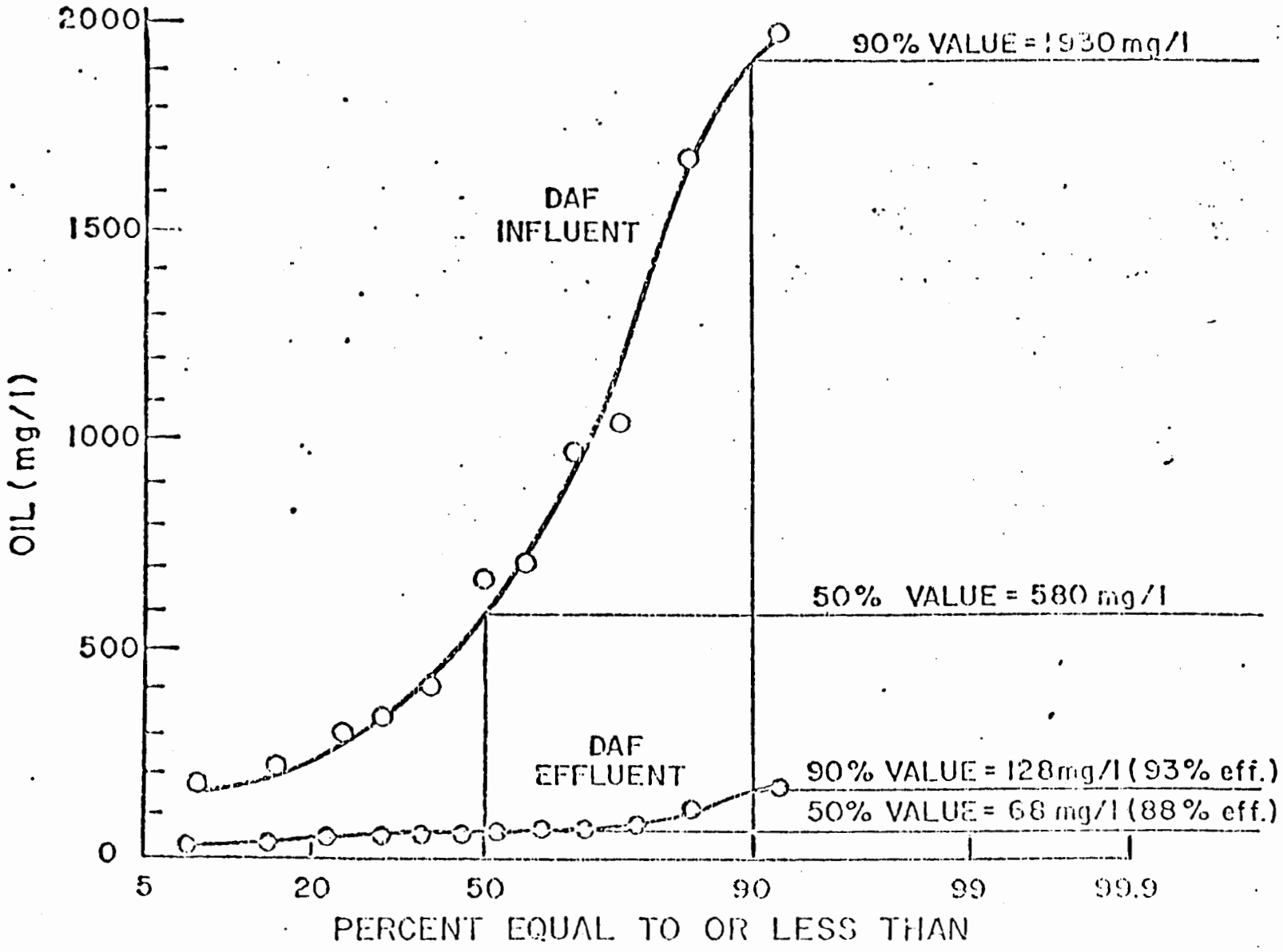

2000
1500
1000
500
0
OIL (mg/l)
90% VALUE = 1930 mg/l
DAF
INFLUENT
50% VALUE = 580 mg/l
DAF
EFFLUENT
90% VALUE = 128mg/l (93% eff.)
50% VALUE = 68 mg/l (88% eff.)
5
20
50
90
99
99.9
PERCENT EQUAL TO OR LESS THAN

FIGURE 20

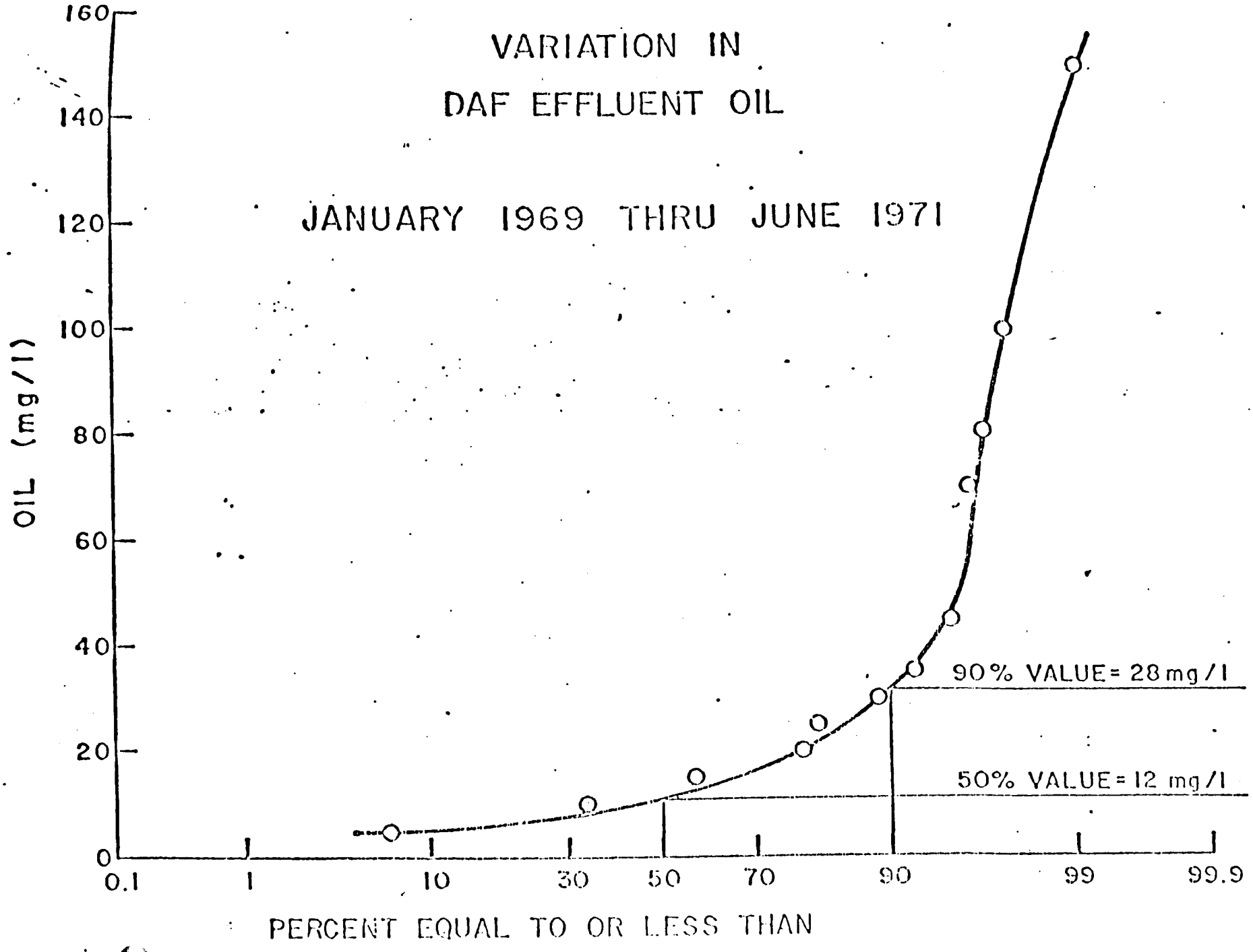

VARIATION IN
DAF EFFLUENT OIL
JANUARY 1969 THRU JUNE 1971
OIL (mg/l)
160
140
120
100
80
60
40
20
0
90% VALUE = 28 mg/l
50% VALUE = 12 mg/l
0.1
1
10
30
50
70
90
99
99.9
PERCENT EQUAL TO OR LESS THAN

FIGURE 2

TABLE 19

DAF PERFORMANCE DATA

Influent oil, mg/l	Effluent oil, mg/l	% removal	Chemicals*	Configuration
1,930 (90%)	129 (90%)	93	Yes	Circular
580 (50%)*	68 (50%)	88	Yes	Circular
105 (90%)*	26 (90%)	75	Yes	Rectangular
68 (50%)	15 (50%)	75	Yes	Rectangular
170	52	70	No	Circular
125	30	71	Yes	Circular
100	10	90	Yes	Circular
133	15	89	Yes	Circular
94	13	86	Yes	Circular
638	60	91	Yes	Rectangular
153	25	83	Yes	Rectangular
75	13	82	Yes	Rectangular
61	15	75	Yes	Rectangular
360	45	87	Yes	Rectangular
315	54	83	Yes	Rectangular

* Alum most common, 100-130 mg/l. Polyelectrolyte, 1-3 mg/l occasionally added.

Table 19 accounts for these variables to the maximum extent possible. For example, all cases cited use chemicals with one exception, design overflow rates fall within the accepted design spectrum of 1.5-3.0 gpm/ft^2, and all use pressurized recycle. Assuming the systems are properly operated, a most significant factor with respect to process capacity and efficiency is the influent oil concentration. This effect is underscored when the data from Table 19 is plotted in a manner which shows effluent oil concentration and oil removal efficiency as a function of influent oil concentration. As shown in Figure 22, the efficiencies of DAF systems range from 60 to 94 percent, depending on the influent oil form and concentration and assuming proper design and operation.

Coagulation-Precipitation

The use of reactor-clarifiers for the coagulation-precipitation removal of suspended and colloidal pollutants in refinery-petrochemical wastewaters is effective for selected streams. The applicability of this process in the removal of these pollutants can be determined through the use of a bench scale jar test noting the change in organics or the critical pollutant in the upper layers of the liquid following chemical addition, rapid mix, flocculation and sedimentation. An assessment of the effect of pH, flocculation time, and chemical selection on pollutant removal can be used to optimize the process. A typical example of the flocculation time influence on the effluent suspended solids concentration is shown in Figure 23.

The conventional coagulation system utilizes a rapid mix tank followed first by slow agitation of the mixture in a flocculation

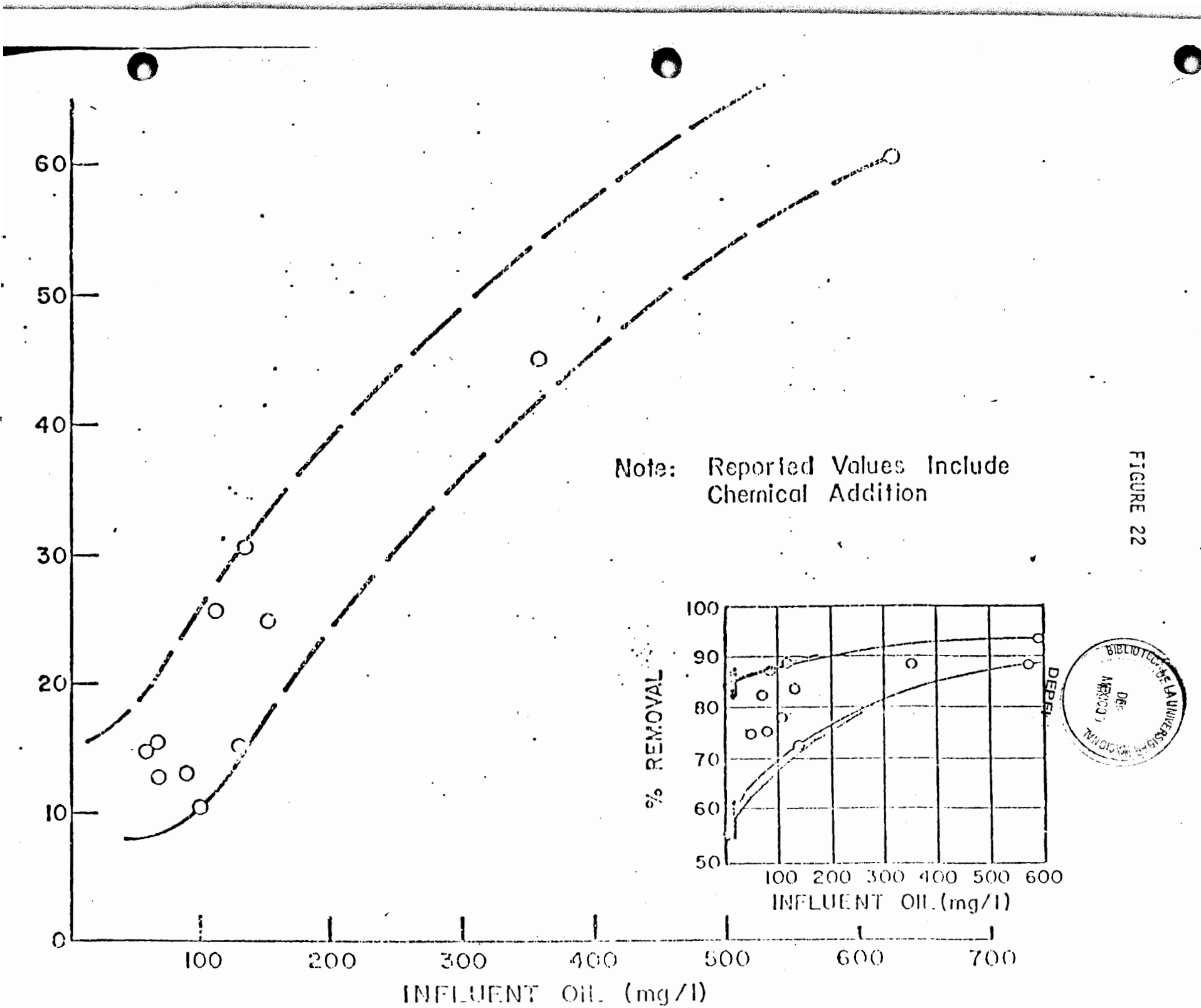


FIGURE 22

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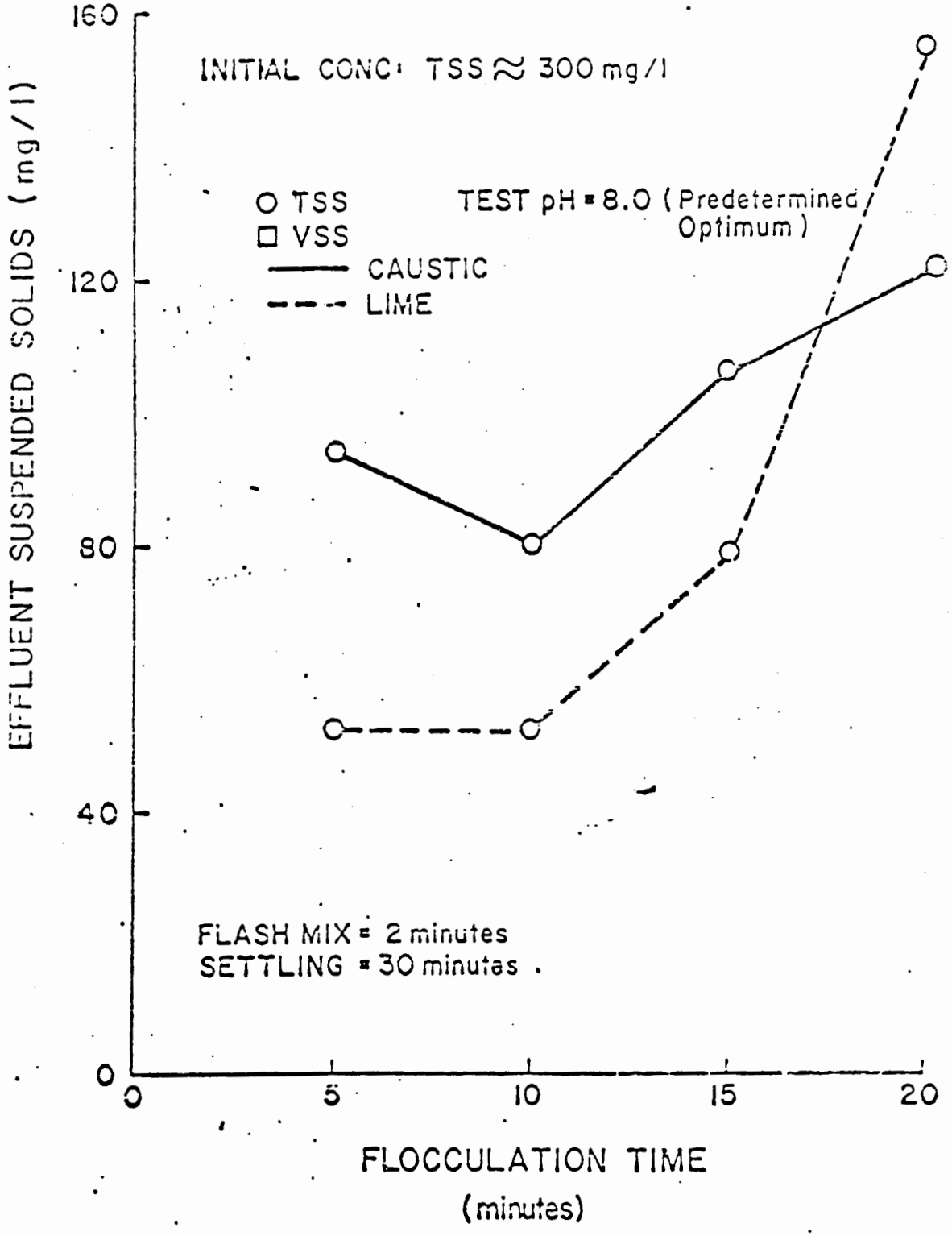

INITIAL CONC: TSS ≈ 300 mg/l
O TSS
□ VSS
CAUSTIC
LIME
TEST pH = 8.0 (Predetermined Optimum)
FLASH MIX = 2 minutes
SETTLING = 30 minutes
EFFLUENT SUSPENDED SOLIDS (mg/l)
160
120
80
40
0
0
5
10
15
20
FLOCCULATION TIME
(minutes)

FIGURE 23

tank to promote the growth of floc particles, then by sedimentation. The sludge blanket clarifier which provides mixing, flocculation, and settling in the same unit has had many industrial applications because of its compact dimensions. This type of unit recycles pre-formed floc which aids in the development of new floc particles and enhances the entrapment of colloids. Occasionally, some form of coagulant aid is required to help form a good settling floc by promoting bridging between floc particles and rendering the floc more settleable. The most common coagulant aids are activated silica and the organic polyelectrolytes. There are three types of these polyelectrolytes: a cationic, which adsorbs on a negative colloid or floc particle; an anionic which replaces the anionic groups on a colloidal particle and permits hydrogen bonding between the colloid and the polymer; and the non-ionic which adsorbs and flocculates by hydrogen bonding between the solid surfaces and the polar groups in the polymer. The most effective coagulant can only be determined through a series of laboratory tests. The chemical compounds most often used in the coagulation-precipitation process are listed in Table 20 (20).

The most common use of reactor-clarifiers in the treatment of refinery and petrochemical wastewaters is the removal of suspended and colloidal material from solution which is pollutional in nature. This process also is effective in reducing nutrients, through the precipitation of phosphates, for example, and heavy metals as most drop out as insoluble metallic hydroxides in the higher pH range. Water soluble alkyl-aryl sulfonates can be removed by coagulation with lime which forms an insoluble precipitate.

TABLE 20

CHEMICAL COMPOUNDS USED IN COAGULATION PROCESSES

Compounds	Formula	Commercial Strength	Grades Available	Weight (Pounds per Cubic Foot)	Remarks
Coagulants:					
Aluminum sulfate	$Al_2(SO_4)_3 \cdot 18H_2O$	17 percent Al_2O_3	Lump Powder Granules	Powder: 38–45 Other: 57–67	Coagulation and sedimentation systems; prior to pressure, filters for removal of suspended matter and oil.
Sodium aluminate	$Na_2Al_2O_4$	55 percent Al_2O_3	Crystals	50–60	Usually added with soda ash to softeners.
Ammonium alum	$Al_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	11 percent Al_2O_3	Lump Powder	60–68	Coagulation systems—not widely used.
Potash alum	$Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$	11 percent Al_2O_3	Lump Powder	64–68	Coagulation systems—not widely used.
Copperas	$FeSO_4 \cdot 7H_2O$	55 percent $FeSO_4$	Crystals Granules	63–66	Suitable coagulant only in pH range of 8.5 to 11.0.
Chlorinated copperas	$FeSO_4 \cdot 7H_2O + \frac{1}{2}Cl_2$	48 percent $FeSO_4$	...	...	Ferrous sulfate and chlorine are fed separately.
Ferric sulfate	$Fe_2(SO_4)_3$	90 percent $Fe_2(SO)_3$	Powder Granules	60–70	Coagulation—effective over wide range of pH, 4.0 to 11.0.
Ferric chloride hydrate	$FeCl_3 \cdot 6H_2O$	60 percent $FeCl_3$	Crystals	...	Coagulation—effective over wide range of pH, 4.0 to 11.0.
Magnesium oxide	MgO	95 percent MgO	Powder	25–35	Essentially insoluble—fed in slurry form.
Coagulant Aids: *					
Bentonite	....	....	Powder	60	Essentially insoluble—fed in slurry form.
Sodium silicate	$Na_2O(SiO_2)_{3.9}$	40 Bé solution	Solution	86	...
pH Adjusters:					
Lime, hydrated	$Ca(OH)_2$	93 percent $Ca(OH)_2$	Powder	25–50	pH adjustment and softening.
Soda ash	Na_2CO_3	99 percent Na_2CO_3	Powder	34–52	pH adjustment and softening.
Caustic soda	NaOH	98 percent NaOH	Flake Solid Ground Solution		pH adjustment, softening, oil removal systems.
[illegible]	[illegible]	[illegible]	Liquid		pH adjustment

It should be recognized that sludge handling and disposal may be the most important component of the reactor-clarifier treatment unit. Landfills are the most common form of inorganic sludge disposal, while organic sludges are generally dewatered and buried or incinerated.

Equalization

The need for equalizing and/or surging wastewaters discharged from refinery and petrochemical processing units as an intermediate step in a treatment system is well established. Biological processes as well as physical-chemical systems operate more effectively if the composition and volume of the wastewater feed is relatively constant. Many wastewater discharges within refinery complexes are from washdowns, tank cleanings, batch operations, and inadvertant spills, necessitating a basin capable of receiving these waters and sequestering their fluctuative nature. Moreover, such basins often permit the neutralization of wastewaters by mixing acidic and alkaline streams which would normally be discharged from the plant at different times. The required size and mixing features of the basin depend on the waste characteristics, the plant operating schedule, and consequent cyclic fluctuations. If sufficient flow and quality information can be obtained from a wastewater survey, a rational basis for designing the equalization facility can be developed. One approach is the use of the following equation (27):

$$x_{(t + \Delta t)} = C_t \left[1 - \exp\left(-\frac{Qt}{V}\right)\right] + x_t \left[\exp\left(-\frac{Qt}{V}\right)\right]$$

where:

t = time increment chosen for the numerical step-by-step calculation

C_t = input concentration averaged over Δt

x_t = basin concentration before addition of the increment of flow at concentration of C_t

$x_{(t + \Delta t)}$ = basin concentration after addition of increment of flow

Q = volumetric flow rate

v = basin volume

t = time, varies between zero and Δt in the equation. The expression need only be evaluated at $t = \Delta t$.

Using this model, the equalization basin concentration of a critical pollutant or that discharged to the treatment process can be calculated at selected time intervals for various equalization volumes. This assumes that the critical pollutant in the industrial discharge was measured at time intervals of sufficient frequency to accurately define the variation. The standard deviation of the equalized concentration will decrease with increasing basin retention time. The relationship then can be used for selecting the retention time which corresponds to the maximum fluctuation that can be tolerated in the biological system. For example, it is recognized that the standard deviation of effluent discharge is a valid statistical parameter for defining the relative degree of the equalization achieved. As shown in Figure 24, the standard deviation for COD loading without equalization for a petrochemical wastewater discharge is approximately 8,000 lb/day. Using two day time increments, the reduction of the standard deviation by virtue of equalization is graphically depicted in Figure 24.

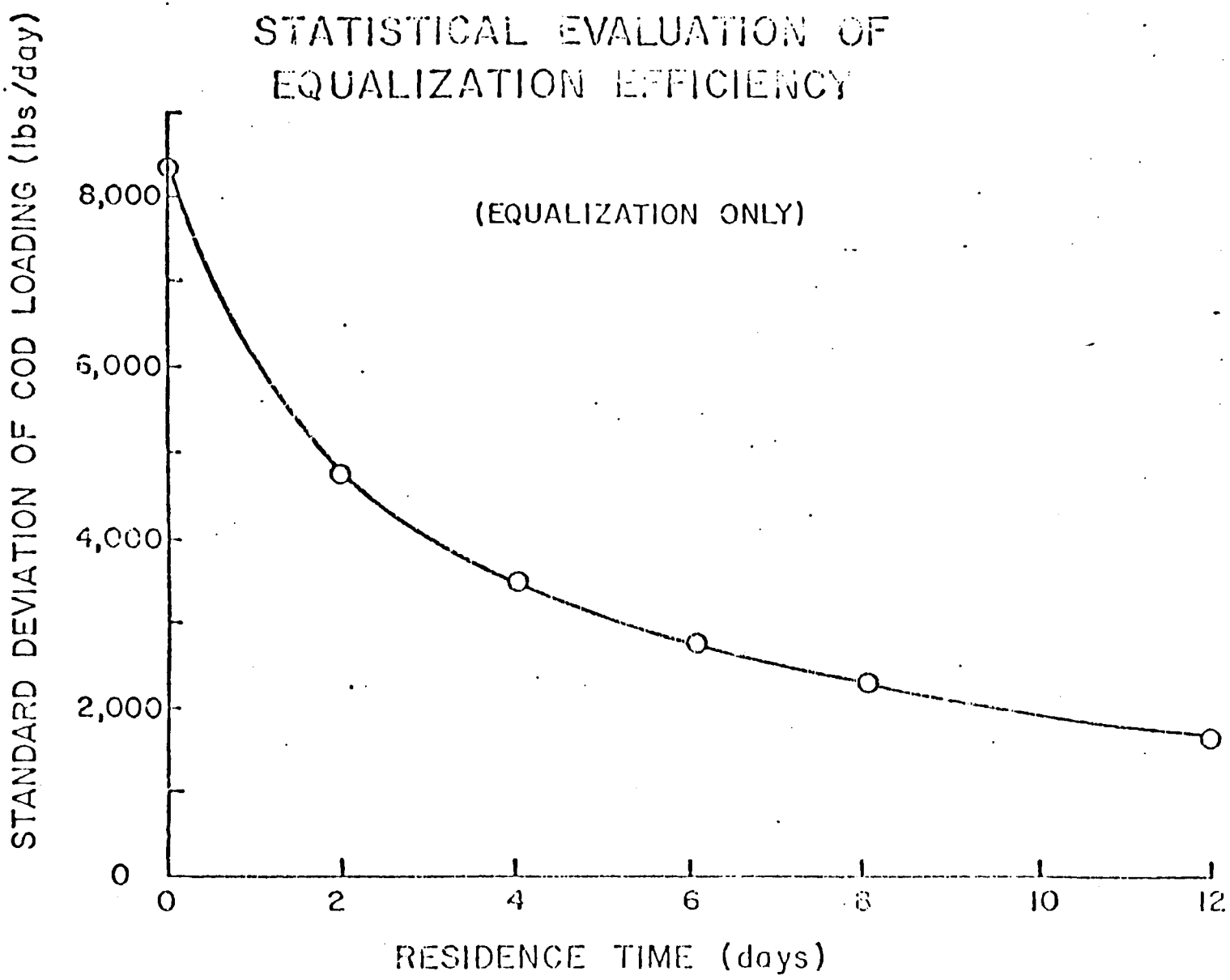

STATISTICAL EVALUATION OF
EQUALIZATION EFFICIENCY
(EQUALIZATION ONLY)
STANDARD DEVIATION OF COD LOADING (lbs/day)
8,000
6,000
4,000
2,000
0
0
2
4
6
8
10
12
RESIDENCE TIME (days)

FIGURE 24

If the transient effect on the treatment system is understood, then the cost effectiveness of an equalization basin can be determined and the optimum size selected.

Various types of construction have been used for equalization basins, including steel tanks, concrete or "shotcrete" basins, earthen lagoons, and vinyl or butyl-rubber lined lagoons. The type of tank selected will depend on the wastewater characteristics, the relative cost of materials and labor, and the land area availability. Mixing equipment such as mechanical mixers or baffling devices are required to insure adequate basin equalization.

SECONDARY-TERTIARY

Activated Sludge

The activated sludge process, a continuous system where a biological population is mixed with wastewater then separated by gravity from the treated liquor, is effective in the treatment of refinery-petrochemical effluents. Although the basic theory and kinetic development is adequately described elsewhere, its special applicability to the treatment of refinery and petrochemical wastewaters is described herein (28)(29).

The basis for the design of an activated sludge system is predicated on producing and maintaining an environment of microorganisms so that their growth and activity are as near optimal as possible. The activated sludge system, by virtue of its high mixed liquor suspended solids (MLSS) concentration accomplished through recycle, is classified as a high rate biological process and can therefore tolerate higher contaminant concen-

tration in the influent wastewater. Major design considerations for the successful activated sludge treatment of refinery-petrochemical wastewaters include:

1. The organic loading in terms of BOD applied per day per unit weight of mixed liquor biological solids;
2. The BOD removal kinetics of a specific refinery-petrochemical wastewater;
3. The organic and inorganic fluctuations of the feed water to the activated sludge system;
4. The free oil loading to the system;
5. The temperature effects of the biological removal capacity of the system;
6. The potential biotoxic or biostatic effects of the refinery-petrochemical effluents on the biological system;
7. The oxygen requirements and biological sludge production rates of the given activated sludge system treating a wastewater of specified quality;
8. The ability of the biological sludge in the system to separate from the treated liquor by gravity in the secondary clarifier, and to concentrate to the point of obtaining the desired MLSS level in the aeration basin through recycle; and,
9. Operational flexibility to maximize process stability and continuity through the inclusion of parallel aeration basins, equalization facilities, off-spec holding basins, complete mixing, etc.

In general, refinery wastewaters are highly amenable to high rate biological treatment using the activated sludge process, thus these systems are widely applied throughout the United States. The exact treatability of a refinery-petrochemical installation is, of course, a function of the effluent quality which depends on the classification of the refinery, the type of crude charge, the age of the facility and nature of its collection system, the relative effluent volume attributed to utility water blowdown, and the degree of in-plant control. For these reasons, design practices of the basic activated sludge process may vary from one installation to another. Treatability studies using bench or pilot scale process simulation techniques are therefore used to formulate the basic design criteria and predict treated effluent quality. It should be recognized, however, that the accuracy of information developed from these treatability studies depends on the accuracy of several assumptions. These include:

1. The characteristics of the wastewater used in the activated sludge tests are representative of those anticipated in field tests.
2. The physical nature of the bench or pilot scale process is similar to the proposed full scale unit.
3. Independent and dependent operational variables are considered.
4. Environmental parameters affecting process efficiency are defined.

It is apparent from these constraints that process simulation techniques can provide predictor relationships and mathematical expressions for the activated sludge treatment process receiving the refinery effluent

in question, but they do not necessarily define a specific model with general applications. However, a treatability study which is properly programmed and judiciously implemented does afford the basis for the logical development of unit process selection, design, and predictive performance.

The design organic load for most activated sludge systems ranges from 0.10 lbs BOD_5/day/lb MLSS (extended aeration) to as high as 0.8 - 1.0 lbs BOD_5/day/lb MLSS. Higher loadings can be imposed, but generally at the expense of poorer efficiency and higher organic levels in the treated effluent.

Oil and grease are of paramount importance when designing activated sludge systems for wastewaters such as those discharged from petroleum refinery and petrochemical installations. Hexane extractables adversely affect a biological system as the concentration in the mixed liquor approaches 50 to 75 mg/l. A recent study conducted for the Environmental Protection Agency indicated that an activated sludge system will perform satisfactorily with a continuous loading of hexane extractables of 0.1 lbs/lb MLSS. It was recommended that the influent to the biological system should contain less than 75 mg/l hexane extractables and preferably less than 50 mg/l. The most significant problem related to oils in biological systems was attributed to lowering floc density to a level where the sludge settling properties were destroyed (30). The removal of free, and to some extent, emulsified oils through gravity separation, air flotation or possibly filtration, as described in the previous sections of this treatise is therefore required in most instances.

Temperature is a particularly important variable in the biological treatment of refinery petrochemical wastewaters. If the combined effluent flow contains a proportionately high volume of cooling tower blowdown, cooling might be required during summer months to satisfy effluent temperature criteria. Conversely, excessive temperature losses through a biological system during winter months in the northern climate might lower biological activity to the point of failing to meet effluent BOD quality standards. As most of the new activated sludge systems are using mechanical aerators to oxygenate and mix the contents of the aeration basin, an approach was developed recently to predict the temperature in activated sludge basins (31). The approach assumes the usual "water warmer than air" case, predicts the basin temperature by calculating the heat balance around the system and plots the calculated aeration basin temperature as a function of the wastewater temperature at the inlet to the aeration basin. An example of this relationship, developed for a refinery in the Midwest using a 10 percent probability basis for the coldest month, is shown in Figure 25. The influence of temperature on biochemical reactions is well documented (32)(33). The most traditional expression for relating the organic removal rate via biochemical oxidation with temperature is the Phelps equation:

$$K_T = K_{20°C}\theta^{(T-20)}$$

where:

K_T = organic (BOD) removal rate at temperature "T"

$K_{20°C}$ = organic (BOD) removal rate coefficient at 20°C

T = liquid temperature, °C

θ = temperature coefficnet

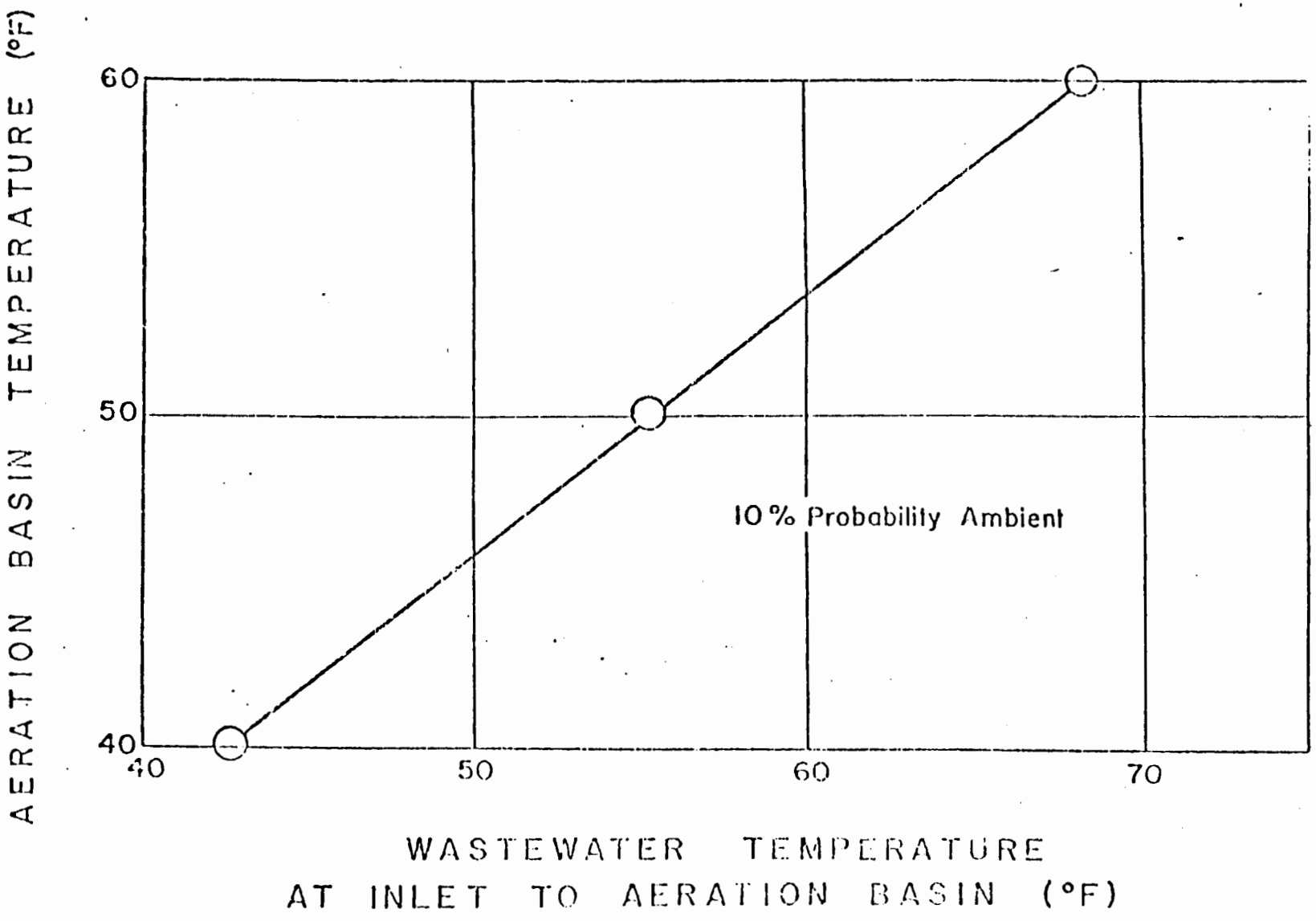

AERATION BASIN TEMPERATURE (°F)
60
50
40
40
50
60
70
10% Probability Ambient
WASTEWATER TEMPERATURE
AT INLET TO AERATION BASIN (°F)

FIGURE 25

The coefficient, θ, is a function of many variables; namely, the nature of the wastewater and type of biological process. Few investigations recognize the significance of the type of wastewater on the temperature effect. For example, an activated sludge process treating an easily degradable potato processing waste as well as a domestic sewage activated sludge plant were not severely affected by basin temperature changes as shown in Figure 26. This is attributed to the fact that both wastes were easily degrable by many biological genera and some removal was undoubtedly the result of "bio-sorption" which is not as temperature-dependent as straight biochemical oxidation. However, activated sludge treatment of a complex chemical petrochemical waste, mostly soluble, was significantly affected by basin temperature. From these plots and other available data, it can be generally stated that the temperature effect is more pronounced with increasing solubility and complexity.

Biotoxicity in an activated sludge process treating refinery and petrochemical wastewaters can be minimized or circumvented by in-plant control, proper equalization, and complete mixing of aeration basins. Most plant upsets - based on experience - result from inadvertent dumps or spills which discharge to the process sewer, shocking the biological system, or by discharging streams to the treatment system containing excessive levels of known biotoxicants such as chromates, sulfides, ammonia, free oil, and other constituents common to refinery-petrochemical effluents.

In order to assess the treatment effectiveness of activated sludge systems in the treatment of refinery-petrochemical wastewaters, a list of performance data has been compiled and is presented in Table 21.

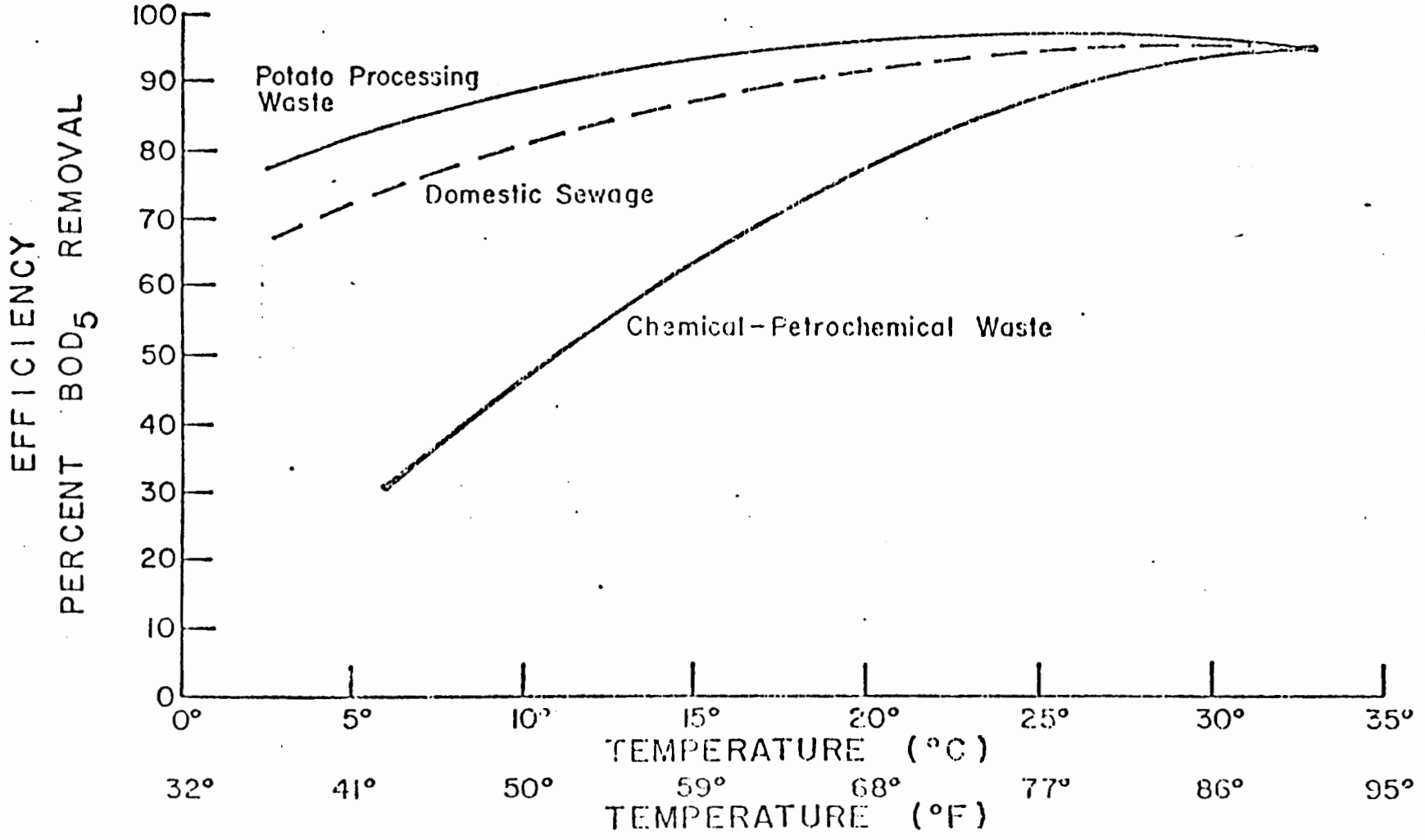

EFFICIENCY
PERCENT BOD5 REMOVAL
100
90
80
70
60
50
40
30
20
10
0
Potato Processing Waste
Domestic Sewage
Chemical-Petrochemical Waste
0°
5°
10°
15°
20°
25°
30°
35°
TEMPERATURE (°C)
32°
41°
50°
59°
68°
77°
86°
95°
TEMPERATURE (°F)

FIGURE 26

TABLE 21

ACTIVATED SLUDGE TREATMENT OF REFINERY-PETROCHEMICAL WASTEWATERS

Product and/or Process	BOD				COD			Organic loading, lb BOD$_5$/(day) (lb MLSS)	Nutrients required	Remarks
	Flow, mgd	In, mg/l	Out, mg/l	Rem, %	In, mg/l	Out, mg/l	Rem, %			
Refinery, natural gas liquids, chemical specialties, sanitary sewage	4.87	90	20	78	200	90	55	0.1	None	Effluent phenol 0.05, = effluent oil 0.5 mg/l
Phthalic anhydride, phenol, salicylic acid, rubber chemicals, aspirin, phenacetin	2.54	45.7	0.1	80.7				0.031	None	Brush aeration, treats trickling filter effluent, 55% sludge return
Refinery, detergent alkylate	2.45	345	50-100	71-85.5	855	150-200	76.0-82.5	0.08	PO_4	Phenols in = 160 mg/l, sulfide in = 150 mg/l, laboratory scale
Butadiene, maleic acid	2.0	2,000	25	98.8	2,090	480	84	0.24	NH_3	
Butadiene, alkylate	1.5	1,000	24	98.8	2,980	477	98.3			
Butadiene, maleic anhydride fumaric acid, tetrahydrophthalic, anhydride, butylene isomers, alkylate	1.5	1,960	24	98.8	2,930	51	81	0.24 (MLVSS)	NH_3	Surface aerators, wastes contain: alcohols, maleic acid, fumaric acid, cetic acid, C_3-C_5 aldehydes, furfural, water-soluble addition products
Ethylene, propylene, benzene	1.44	600	90	85	700	105	85		None	Oily waters: C_5-C_{15} oils 90% phenol removal
Naphthalene, butadiene, phenol, acrylonitrile, soft detergent bases, resins, other aromatics	0.43	500	60	85-90	600	90	80-85	1.5	NH_3 PO_4	Sour waters: oil in = 500 mg/l, phenol in = 65 mg/l, pH adjustment, preceded by trickling filter, phenol removal = 99.9%
Phenol, 2,4-D, aniline, nitrobenzene, rubber, chemicals, polyester resins, misc. chemicals	0.07	370	70	70.2				0.4	NH_3 PO_4	Aerolator pilot-plant sewage added in ratio 1:600 once a week
Ethylene, propylene, butadiene, benzene, polyethylene, fuel oils	0.63	85	10	99	200	200	62.5			Quench waters, polyethylene and benzene wastes: preceded by trickling filter, effluent phenol 0.01 ppm

TABLE 21

ACTIVATED SLUDGE TREATMENT OF REFINERY-PETROCHEMICAL WASTEWATERS (CONTINUED)

Product and/or process	BOD				COD			Organic loading, lb BOD/(day) (lb MLSS)	Nutrients required	Remarks
	Flow, mgd	In, mg/l	Out, mg/l	Rem, %	In, mg/l	Out, mg/l	Rem, %			
Refining processes	0.51-0.03	125	15-25	80-88			65-80	0.28-0.1	PO_4	Phenol removal 85-94%; oil removal 75-85%; effluent phenol 0.5 mg/l; effluent oil 1-2 mg/l; temperature = 30 C
Nylon	0.4	1,540	250	83.8						
Petroleum products	0.27	410	5	98.8	600	60	88			Phenol in = 25 ppm, phenol out = 1 ppm
Acrylic fibers	0.252	2,200	110-220	90-95				0.4		Wastes contain acrylonitrile, dimethylamine, dimethylformamide, formic acid, temperature 15-32 C, return sludge 40-60%, mechanical aeration
Acetone, phenol p-cresol, ditert.-butyl-p-cresol	0.216	3,500-4,400	1,030-750	71-83				0.62-1.1		Waste phenol 600 ppm, waste BOD 7,500-8,000, waste diluted with effluent or water, pilot plant
Resins-formalin, aminoplasts, phenol-formaldehyde, epoxy resins, textile auxiliaries	0.2	890	444-266		50-70			0.8-1.2		Diluted air, domestic waste added; trickling filter follows 100% recycle sludge
Ethylene and propylene oxides, glycols, morpholines, ethylene-diamines, ethers, piperazine	0.15	1,950	20	99	7,070-8,540	5,120-3,050	25-40	0.51	None	Laboratory scale; extended aeration; high nonbiodegradable fraction followed by stabilization ponds

TABLE 21

ACTIVATED SLUDGE TREATMENT OF REFINERY-PETROCHEMICAL WASTEWATERS (CONTINUED)

2,4-D, 2,4,5-T (acid wash wastes)	0.1	1,670	125	92.5	2,500	500	80	0.78 (MLVSS)	NH_3 PO_4	1:1 mixture of acid wash streams diluted 9:1 prior to treatment to reduced chlorides, toxicity. Laboratory scale 90–95% phenol removed; laboratory scale
Cracking, isomerization of butane and naphthene, alkylation, benzene, toluene, alcohols, ketones, cresylic acids		1,100	55–110	90–95				0.5		
Ethylene, acetylene			20					0.23–0.33	PO_4	Effluent phenol 0.1 mg/l, effluent oil 1 ppm
Nylon manufacture				95			85	1.0–3.0	PO_4 NH_3	NH_4OH used as nutrient and neutralizing agent, waste diluted 2:1
Petrochemical plant	2.4	2,850	65	97				0.5	None	Pilot-plant study
Large integrated refinery—Class D incl. once-through cooling water	32.4	270	20	92				0.5	None	Pilot-plant study
Class E refinery	4.6	340	40	88	850	250	71	0.4	None	Pilot-plant study
Class E refinery	2.0	575	50	91	980	200	71	0.4	None	Operating plant
Class C refinery	1.2	205	30	85	544	150	80	0.4	None	Operating plant preceded by API, DAF
Class D refinery	1.8				270	115	58	0.1	None	Operating plant
Class E refinery	25.0	270	25	91	490	150	70	0.4	None	Bench-scale treatability study
Petrochemical complex	7.8				1,500	350	78	0.4	None	Bench-scale treatability study
Petrochemical complex	18.3	600	50	92	1,500	600	60	0.4	None	Bench-scale treatability study

Biological treatment methods, specifically high rate activated sludge systems, are considered to be compatible with the tenets of the Federal Water Pollution Control Act of 1972 (S.B. 2770 as amended). Proven performance of these systems as cited in Table 21 constitute what most interpret as "best practical treatment," particularly when considering "the State of the Art" of alternative non-biological systems. More importantly, activated sludge systems are adaptable to system upgrading by the addition of effluent polishing processes.

Aerated Lagoons

Aerated lagoons are low rate biological systems which provide a "flow-through" basin allowing microorganisms in contact with the wastewater to reduce organic constituents biochemically. Oxygenation and mixing is normally provided by mechanical aeration devices, although power levels are normally too low to maintain dissolved oxygen in all portions of the basin or to completely mix the system. Unlike the activated sludge system, there are no clarification and recycle steps and, therefore, a lower degree of system control. As the operating MLSS level is normally only two to 10 percent of an activated sludge basin, aerated lagoons are more sensitive to transient organic loading, toxic substances, and temperature effects. Aerated lagoons are being used in the treatment of refinery-petrochemical wastewaters in many instances, either as a process preceding waste stabilization ponds or as an interim treatment process which can be converted to an activated sludge system by increasing aeration and mixing and adding secondary clarification and recycle facilities. Recent Federal legislation combined with increasingly stringent effluent quality requirements have mitigated the

attractiveness of aerated lagoons as a "total system." Their application in the treatment of refinery wastewaters is therefore limited to "first stage" or "interim" treatment.

The approach for designing aerated lagoons is outlined elsewhere (28), but basically entails consideration of influent organic levels, the predetermined organic removal rate, the estimated temperature of the lagoon during the critical month, and the anticipated amount of "organic feedback" resulting from any anaerobic decomposition which may occur on the bottom of an incompletely mixed aerated lagoon basin.

Aerated lagoons are operated at high organic loading levels because of the low concentration of microorganisms suspended in the basin. These loadings usually exceed 1.0-2.0 lbs BOD_5/day/lb MLSS. As in activated sludge basins, the organic removal rate is high for most hydrocarbons, such as those discharged from topping plants, but is reduced for wastewaters of increasing complexity such as those discharged from completely integrated facilities. Since the solids level maintained in an aerated lagoon is low, temperature variation will exert a profound effect on the rate of organic (BOD) removal. In order to predict the basin temperature at an extreme summer or winter month, the following aerated lagoon temperature relationship is normally used (28):

$$T_i - T_w = \frac{(T_w - T_a)\, fA}{Q}$$

where:

T_i = influent wastewater temperature (°F)

T_w = basin temperature (°F)

T_a = air temperature (°F)

Q = wastewater flow (MGD)

S = surface area

f = proportionality factor (a function of geographical location)

Another factor which influences aerated lagoon performance is wind, particularly when the basin geometry exhibits a long fetch in the direction of the prevailing wind. Such winds stir up bottom sediments, causing a deterioration of effluent quality in terms of suspended solids, solids stabilized oily material, and settleable solids. Organic feedback is another factor to be considered in design. As large volumes of oily solids tend to settle in the bottom of the basins because of the low mixing levels, subsequent decomposition anaerobically releases byproducts from the bottom sediments back to the overlying water. These by-products are then utilized in the upper layers by aerobic or facultative microorganisms resulting in an additional BOD load to the system. This feedback has been estimated to be as high as 20 percent of the influent organic load in the summer months at one refinery located in the Southwest.

A compilation of aerated lagoons treating refinery-petrochemical wastewater operations at various locations in the United States and the reported operation efficiencies is shown as Table 22.

TABLE 22

AERATED LAGOON TREATMENT OF PETROCHEMICAL WASTES

Product and/or process	Flow, mgd	BOD			COD			Nutrients required	Remarks
		In, mg/l	Out, mg/l	Rem, %	In, mg/l	Out, mg/l	Rem, %		
Refinery butadiene, butyl rubber	19.1	225	100	55	610	350	43	PO_4	Followed by stabilization pond, temperature = 32°C 30% COD is nonbiodegradable, laboratory scale
Refinery	2.45	345	50-100	71-85	855	150-200	77-83	PO_4	Influent phenols 160 mg/l, influent sulfides 150 mg/l, laboratory scale
Petrochemical facility	0.51	100	25	75					Surface aeration, waste is extensively pretreated. Followed by pond
Chemicals for lubricating oils production unit	0.2	465	180	61	1,050	600	43		
Class A refinery	24.0	275	80	71	560	270	52	None	Followed by stabilization pond, power level = 0.08 hp/1,000 gal, detention time = 1 day
Class C refinery	2.0	350	50	84	730	220	70	None	...
Class D refinery	30	200	100	50	700	400	45	None	Followed by small stabilization pond, detention time = 2.5 days

Trickling Filters

Trickling filters have been used in treatment for industrial wastes for many years although the trend is away from filters as high rate secondary treatment facilities in the refinery-petrochemical industry. They do, however, have some application as "roughing" devices preceding other biological or physical-chemical units.

The trickling filter is a packed media bed covered with biological slime through which the wastewater is passed. As the organic-laden waste flows over the slime, organics and oxygen diffuse into the biological mass where they undergo biochemical oxidation to carbon dioxide, water, and metabolic by-products. Granular media is generally used to support the biological mass although the introduction in recent years of synthetic filter media has caused a variety of changes in the design and construction of trickling filters. These media, with low bulk density, have resulted in the use of deeper filters operated at greatly increased organic and hydraulic loading rates.

Most design to date is formulated on empirical standards which must be modified to accommodate the nature of the industrial wastewater. The number of variables which influence trickling filter performance have complicated the development of a dependable model which can be applied or modified to existing conditions. An attempt to quantify some of these variables and verify predictive equations for the trickling filter process performance has recently been published (34).

Some of the variables of design and operation include organic loading, hydraulic loading, nature of organic constituent, temperature,

media type and distribution, and filter geometry and construction. Control of ventilation and plugging is necessary as anaerobic action - which is always present to some extent in a filter - becomes excessive when plugging occurs and ventilation is inadequate.

The recorded performance of trickling filters in the treatment of refinery and petrochemical effluents ranges from 10 to 20 percent removal when used as a roughing device to 50 to 90 percent when applied as a total process for secondary treatment. Performance data for filters using rock media and treating chemical wastes are listed in Table 23. Performance data across a filter using synthetic media for one chemical waste is shown in Table 24. The removal of BOD through a roughing filter using synethetic media is tabulated in Table 25. Additional data for BOD and COD reduction across a trickling filter receiving various petrochemical wastewaters is reported elsewhere (1).

Waste Stabilization Ponds

Waste stabilization ponds depend on the natural aquatic processes of bacterial and algal symbiosis, requiring sunlight as a primary energy source, and have been used successfully in the treatment of refinery and petrochemical wastewaters. Although ponds are often used to provide long term polishing for effluents discharged from upstream biological units, they have been used in some instances as a total treatment system.

Empirical equations which consider organic loading, temperature, and toxic substance effect have been developed and successfully used to design facultative waste stabilization ponds (35). Application of such empirical relationships make certain assumptions, however, and may not apply to the waste stabilization pond treatment of refinery and petro-

TABLE 23

TRICKLING FILTER DATA

Plant	Filter Depth ft	Size of Medium inch	BOD_5 Loading 1000 ft^3/day	% BOD_5 Reduction	Hydraulic loading gal/gd^3/D
Chemical Plant A	9.75	3	25.0	60.0*	590
Chemical Plant B	5** 5***		42.0	91.0****	743
Chemical Plant C	6** 6***	4	35.0	97.5****	257
Chemical Plant D	6** 8***		36.8 18.3	71.0****	1720 1290
Chemical Plant E	14	3-5	94.5	80.0	1000
Chemical Plant F	10	3	44.0	58.3 91.0	492 537

* on gross phenol basis

** first stage treatment

*** second stage treatment

**** overall basis

TABLE 24

TYPICAL PERFORMANCE DATA FOR FILTER USING SYNTHETIC MEDIA

BOD, mg./L		BOD, Lbs./ 1,000 ft.³/day		% Removal
Inf.	Eff.	Loading	Removal	
555	205	586	369	63
567	232	596	348	59
489	233	513	267	52
389	155	408	245	60
428	187	450	252	56
374	157	393	228	58
340	150	357	207	58
450	190	470	275	58

TABLE 25

ROUGHING TREATMENT-GENERAL CHEMICAL WASTE

(Synthetic Biological Oxidation Media)

Flow Rate gpm/ft.^{2}	COD, mg/L		COD Lbs./1000 ft.^{3}/day		% COD Reduction
	Influent	Effluent	Loading	Removal	
1.0	2115	1800	1176	178	16
1.5	2150	1870	1810	237	14
2.0	2010	1780	2258	257	11

System Outline:
Standard Pilot Tower (7 ft.^{3} packed to 21.6 ft. depth).

Waste Description:
Clarified general chemical waste. No recycle. No clarification of tower effluent practiced.

chemical wastewaters. For example, ponds are susceptible to wind action and short-circuiting which would prevent conformance to predictive efficacy and performance. Moreover, the accumulation of emulsions in waste stabilization ponds prevents sunlight penetration resulting in excessive anaerobic action.

The tendency is to construct single ponds although series ponds may be more efficient in that short-circuiting is reduced and overall organic removal is possibly increased. The first pond is usually anaerobic because of the imposed surface loading, and will be odoriferous. It does trap floating organic material, however, and provides for easier removal of these floating materials. The retention time in waste stabilization ponds ranges from one to 90 days. The exact retention time depends on the land available as well as the design requirement. As land is generally quite expensive in areas contiguous to refinery and petrochemical operations, the use of waste stabilization ponds is limited. Additionally, new effluent guidelines are in most cases too stringent for pond capability. The proliferation of algal and bacterial material in ponds, for example, adds to the effluent suspended solids level even though the soluble organic fraction may be reduced to acceptable levels.

As previously mentioned, waste stabilization ponds are not widely used in the United States to treat refinery and petrochemical effluents. Typical waste stabilization pond operation data from five refineries as reported by API is shown in Table 26 (20). Additional operating data from petrochemical plants is found in Table 27 (1).

TABLE 26

TYPICAL OXIDATION POND OPERATING DATA

Refinery:	A		B		C		D	
Retention time, days:	5		7		20		10	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
[illegible], mg per liter	30	12	37	8	105	8	...	...
[illegible]ag per liter	29	22	29	0.2	3.1	0.5	26	0.5
[illegible] per liter	250	175	107	32	...	...	100 to 300	82 to 150
[illegible] solids, mg per liter	...	...	...	...	52	9	...	...
[illegible], mg per liter	...	...	...	...	...	...	58	58
[illegible] mg per liter	...	...	...	...	196	22	...	...
[illegible] bases, mg per liter	...	...	...	...	...	...	...	...
[illegible], mg per liter	...	...	1.2	0.1	...	...	1	0
[illegible]	...	...	10.8	9.5	8.7	8.3	7 to 8	7.1 to 8.6
[illegible]erature, deg F	...	...	...	...	115	38	...	...

TABLE 27

WASTE STABILIZATION POND TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow, mgd	BOD			COD			Organic loading, lb BOD_5/(acre)(day)	Nutrients required	Remarks
		In, mg/l	Out, mg/l	Rem, %	In, mg/l	Out, mg/l	Rem, %			
Refinery butadiene, butyl rubber	19.1	100	50	50	350	200	43	Primary pond 91; total ponds 46	None	Ponds in series after aerated lagoon, laboratory scale
Resins, alcohols,	5	500-1,000	400-700	20-60				96	None	Anaerobic
amines, esters,	5	400-700	25-50	88-96				164	None	Anaerobic
styrene, ethylene	5	25-50	5-30	40-90				5	None	Aerobic
Butane, propane natural gas, ethanol, ethyl chloride, polyethylene, ammonia, H_2SO_4	3.25	150	7-15	90-95	260			75	None	Facultative pond, 18 days detention, influent SO_4 = 650 mg/l
Refinery, detergent alkylate	2.45	50-100	20-50	50-80	150-200	120	20-40	95	None	After aerated lagoon or activated sludge, laboratory scale
Plastics	1.09	680	180		1,681	590	65			Facultative ponds
Ethylene and propylene oxides, glycols, morpholines, ethylenediamines, ethers, piperazine	0.15	20			5,120-5,950	4,610-4,450	10-25	25	None	Laboratory scale Facultative ponds to remove some residual COD. High nonbiodegradable fraction. After activated sludge
Mixed petrochemicals				95-99			75-96	100		Facultative ponds

Cooling Tower Oxidation

The use of cooling towers as biological oxidation systems has been successfully applied in the treatment of refinery wastewaters although there are certain inherent disadvantages in such practices. If the primary drawback of fouling heat exchangers can be resolved, cooling tower organic reduction has been shown to be successful (36)(20). These studies indicated that the use of wooden cooling towers as a combined biological wastewater treatment and cooling system was workable considering biological efficiency, heat transfer efficiency, tower packing disintegration, and solid build-up and sloughing.

The bacterial growth resulting from the organic removal through a tower has been reported as finely dispersed and non-filamentous (20). Even though the predominant microorganisms did not result in a type of sludge mass which caused a fouling or slime problem, daily backwash of the condensers and coolers was required.

Periodic blowdowns are necessary to keep the dissolved and suspended solids in the cooling water at required levels. The BOD of this blowdown will still be high because of the presence of suspended biological sloughing so that subsequent treatment of blowdown is required. Generally, only a few problems associated with additional equipment corrosion have been observed while using this type of system. Although cooling water treatment has been used exclusively in refinery complexes, such systems undoubtedly have application for reuse of specific petrochemical wastewaters.

A simplified schematic of a cooling tower biological oxidation system is shown in Figure 27. Reported operation data from two cooling tower waste treatment systems is shown in Table 28 (20).

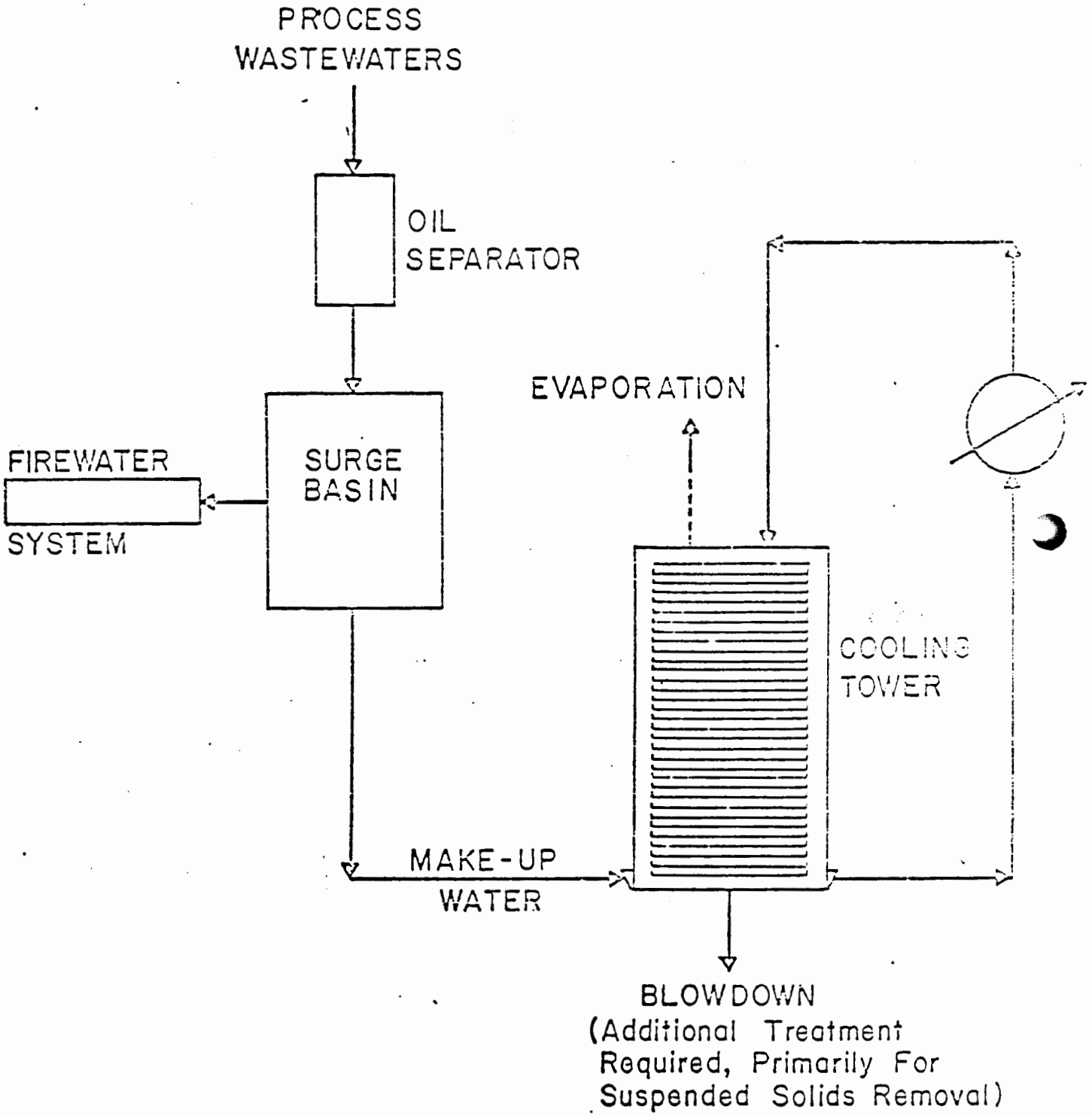

PROCESS
WASTEWATERS
OIL
SEPARATOR
EVAPORATION
FIREWATER
SYSTEM
SURGE
BASIN
COOLING
TOWER
MAKE-UP
WATER
BLOWDOWN
(Additional Treatment
Required, Primarily For
Suspended Solids Removal)

FIGURE 27

TABLE 28

—Average Operating Data from Two Cooling Tower Waste Treatment Systems

	Refinery *A*		Refinery *B*	
	Influent	Effluent	Influent	Effluent
Flow, gpm	2,500	700	...	...
Temperature, deg F	70	75	77	80
Suspended solids, mg per liter	28	100	...	...
Sulfides, mg per liter	0	0	...	...
Phenolics, mg per liter	12	0.09	3	0.05
BOD, mg per liter	158	111	30	15
COD, mg per liter	327	231	...	...
pH	7.5	7	9.2	7.3
Alkalinity, mg per liter as $CaCO_3$	150	75	...	...
Oil, mg per liter	30	30	30	20
Chlorides, mg per liter	...	...	1,300	3,200

Chemical Oxidation

Chemical oxidation of selected waste streams within a refinery or petrochemical complex may be an appropriate method of treatment, depending on the oxidation reaction time, the characteristics of the oxidation products, and overall process economics. Chemical oxidation, raising the oxidation level of a substance or reducing its BOD and COD, can be accomplished using the primary oxidizers of oxygen, ozone, permanganate, chlorine, or chlorine dioxide. Catalytic oxidation offers a practical means of oxidizing small volumes of concentrated organic waste which are not susceptible to other forms of treatment. A brief discussion of each of these oxidation approaches follows.

Gaseous or dissolved oxygen is used both as a stripping agent for such gases as carbon dioxide, hydrogen sulfide, methane, and other low boiling organic compounds as well as for chemical oxidation (37). Although the use of pure oxygen may be applicable from a process point of view, economics may render it impractical. Pure oxygen is, however, being used for biological systems with a reported savings in cost over conventional systems. Air oxidation is used for sulfide oxidation as well as for removal of divalent forms of iron and manganese. The oxidation of iron, however, is strongly pH-dependent.

The chemistry and theory behind the oxidation of sulfides is well documented (17). Most sulfide oxidation units presently used are patented designs. The design criteria and operating conditions for several of these units are listed in Table 29. All of the units mentioned oxidize 100 percent of the influent sulfides, but if large

TABLE 29

DESIGN AND EFFICIENCY OF SELECTED SULFIDE OXIDATION UNITS

Oxid. Products	Tower Temp. (Top) (°F)	Feed ($\frac{\text{lb Sulfide}}{\text{min}}$)	Air Flow ($\frac{\text{lb air}}{\text{lb S oxidized}}$)	Detention Time (hr)	Pressure (Top) (psia)	Sulfur Oxidized ($\frac{\text{lb/hr}}{\text{ft}^3 \text{ tower}}$)	Remarks
100% Thiosulfite	185-250	1.4-11.7	7.3-12.2	1.1-7.9	50-79	0.29-0.39	Concurrent air-water flow, no catalyst
54% Thiosulfite 46% Sulfate	230	0.68	6.8	3.87	75	0.03	"
44% Thiosulfite 56% Sulfate	239	0.17	27.0	3.31	57	0.01	"
37% Thiosulfite 63% Sulfate	239	0.08	57.5	6.62	57	0.05	"
100% Sulfate	265	0.73	28.4	3.52	72	0.035	

quantities of mercaptans or mercaptides are present in the waste, a reoxidizer may be required to insure complete oxidation. The reoxidizer should be operated at a temperature of 130 to 150°F with a pressure of 50 psi to prevent mercaptan stripping. The data in Table 29 indicate that sulfides can be oxidized to thiosulfates more easily than to sulfates. It is possible that some sulfate was produced in the towers but to obtain maximum conversion, low sulfide loadings are required. The oxidation of sulfides in a liquid phase using a typical sulfide oxidation unit is shown in Figure 28. Heavy oils should be eliminated from the waste prior to oxidation since pilot plant studies indicated that five percent of such oil could decrease the oxidation rate by 50 percent.

Ozone is an oxidizing agent used for phenols, cyanides, and unsaturated organics destruction since it is a considerably stronger oxidizing agent than chlorine. It is a powerful oxidant which reacts rapidly with a majority of organic compounds and microorganisms present in wastewaters. The primary disadvantage is the high capital cost associated with the ozone generation equipment. It does, however, effectively oxidize many constituents and is used for color removal, disinfection, iron and manganese removal, phenol oxidation, and cyanide oxidation. The efficiency of ozone destruction of chlorinated hydrocarbons for various ozone dosage levels is indicated in Table 30 (1).

Permanganate oxidation has been and is being used in treating water to remove taste, odor, iron and manganese, but is not generally used for the specific removal of BOD.

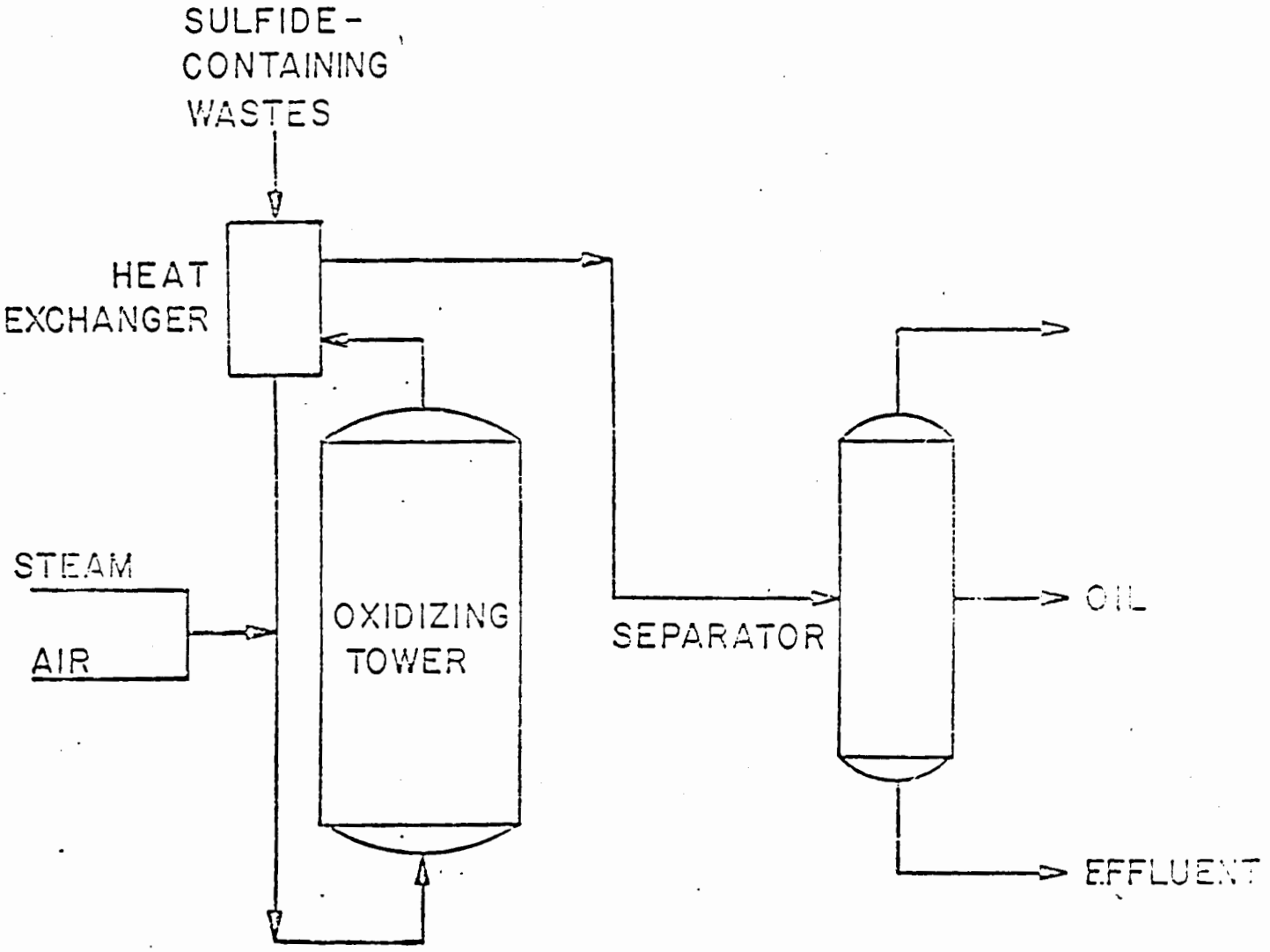

SULFIDE-
CONTAINING
WASTES
HEAT
EXCHANGER
STEAM
AIR
OXIDIZING
TOWER
SEPARATOR
OIL
EFFLUENT

FIGURE 28

TABLE 30

OZONATION OF CHLORINATED HYDROCARBONS

Ozone Dosage (mg/l)	pH Initial	COD Raw Waste (mg/l)	COD Treated Waste (mg/l)	COD Reduction (%)
994	12.2	3,340	1,410	57.8
2,530	12.6	"	900	73
2,700	7.0	"	1,460	56.5
3,920	12.6	"	745	77.5
4,640	12.6	"	450	86.5
5,400	12.6	"	314	90.5

Chlorine has been applied in oxidizing phenol and cyanides in petrochemical wastes. The oxidation of phenols, however, must be carried to completion to prevent the release of chlorophenols which can cause objectionable odors and tastes in drinking water, even at very low concentrations. An excess of chlorine is usually required because of the reaction with various other chemical compounds such as ammonia, sulfides, and various organics which can interfere with the chlorination process. To prevent the formation of chlorophenols, the pH of the waste is kept at seven or higher and the usual reaction time required is one to two hours. Chlorine can be applied either as free chlorine or as hypochlorite. Cyanides can be oxidized to carbon dioxide and nitrogen by chlorination. The wastewater must be kept at a pH value greater than 8.5 during treatment to prevent the release of toxic cyanogen. Ammonia, which is being singled out as an initial pollutant in refinery and petrochemical effluents, can be oxidized by chlorine to free nitrous oxide gas. However,the chlorine demand is high and the process economics should be evaluated. Nevertheless, chemical oxidation of ammonia may be more practical from an economic and process viewpoint than alternate ammonia removal processes.

Chlorine dioxide has gained wide acceptance in water treatment, and can be considered in refinery wastewater treatment for certain applications as phenol oxidation using chlorine dioxide avoids the formation of chlorophenols (37). Like ozone, the instability of gaseous chlorine dioxide necessitates generation in situ and initial capital costs for these systems are quite expensive.

A tabulation of oxidation processes used in petrochemical wastewater treatment is shown as Table 31 (1).

TABLE 31

OXIDATION PROCESSES USED IN PETROCHEMICAL WASTE TREATMENT

Product or Process	Waste Components (If known)	Type of Oxid. Process	Remarks
Acrylic fibers, nitriles	Cyanides	Ozone	Opt. pH 11-12
Acrylic fibers	Dimethylamine Dimethylformamide	Catalytic oxidation	Pt. catalyst, 310°C, combined with direct combustion
Acrylic fibers, nitriles	Cyanides	Chlorination	1-2 hr treatment time pH 8.5 required
Caustic treating operations	Sulfidic Spent Caustics	Air and steam	Oxidizes sulfides to thiosulfates and sulfates
Ethylene glycol	-	Catalytic oxidation	Copper-chromite catal 97% organic destruct
Mixed petrochemicals	Hydrocarbons	Catalytic oxidation	Metal oxide catalysts
Mixed petrochemicals	0.5-1.0% Organic from column heads	Catalytic oxidation	575°C Pt. catal to control oxidat
Mixed petrochemicals	3-5% Organic acids	Thermal cracking	800°C, natural gas
Synthetic Rubber	Probably unsaturated H.C. (some chlorinated)	Ozonation	Opt. pH 12.6, 90.5% COD reduction
Nylon intermediates	16% NaCl, 0.5% metal salts, 1% misc. organics	Air	Converts metals to insoluble hydroxides
Phenol, resins, refining crude	Phenolics	Ferrous salts and hydrogen peroxide	Expensive
Phenol	Sulfite liquors	Chlorine	
Phenol	Sulfite liquors	Ozone	Opt. pH 12
Phenol	Sulfite liquors	Air-iron catalyst in liq.	Aerations in venturi units 99.9% SO_3 removed-11 hr
p-Cresol	Sulfite liquors	Air	Mixco agitator ring
α-Naphthol	Sulfite liquors	Air	Mixco agitator w/ spa ring
Refinery	Petroleum products	Ozonation	75-85% removal of pet prod. 16 hr detention

Filtration

Filtration - having been used for years as a polishing step in treating water for domestic use - is finding application as an effluent treating polishing process. More filtration polishing can be anticipated in the future for industrial treatment facilities as effluent criteria are becoming more stringent and filter units can easily be adapted to existing biological systems. Moreover, a filtration step is usually required before carbon adsorption polishing units can be put on line.

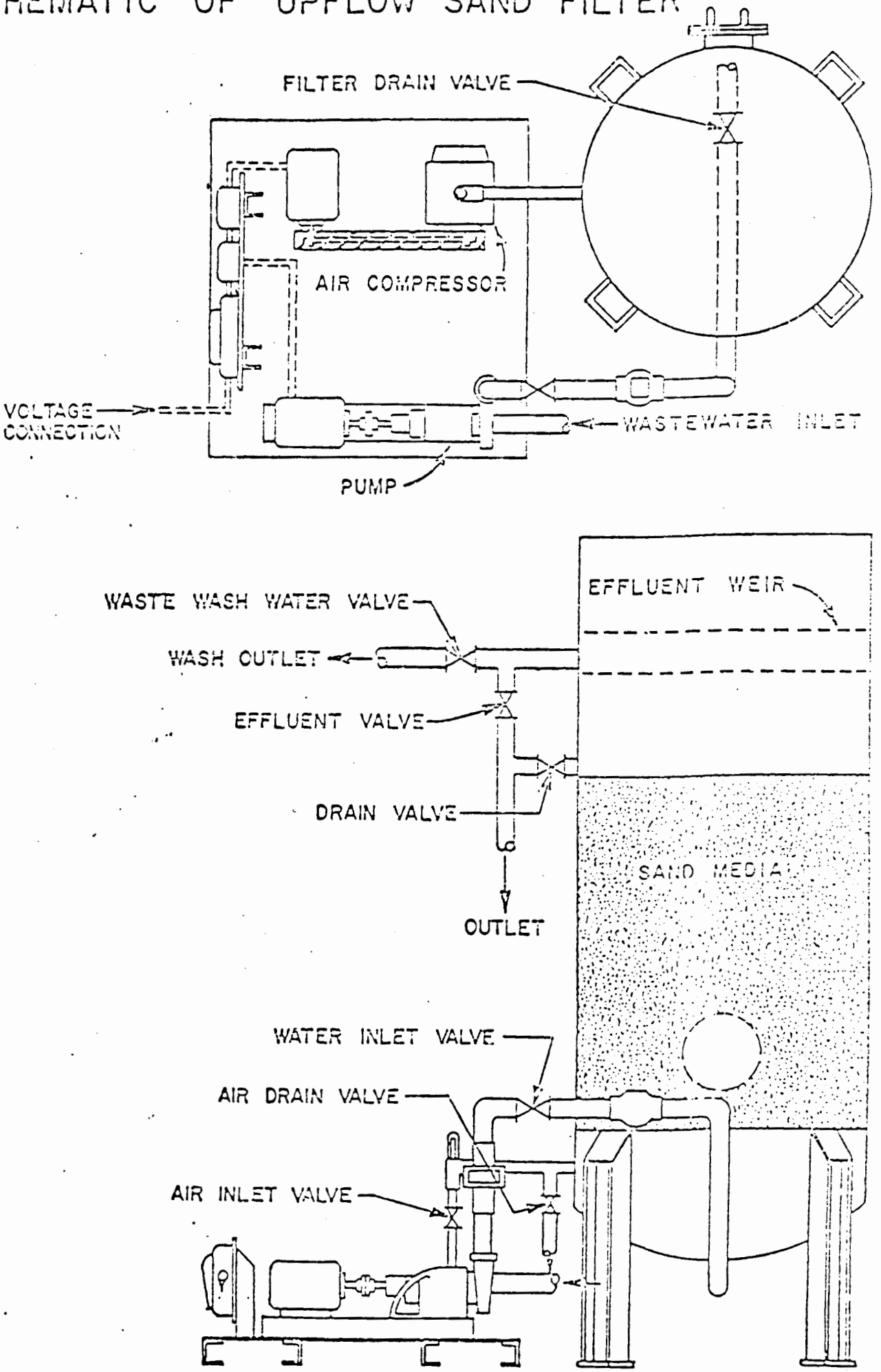
Filtration is particularly applicable for polishing an activated sludge or extended aeration plant receiving refinery or petrochemical wastewaters as much of the effluent organic material is in suspended or colloidal form. Filtration removes most of these constituents, and the backwash can be treated separately or rechanneled back through the biological treatment plant. The filtrate, or effluent, can then be discharged directly to the receiving environment, recycled for reuse, or possibly sent to carbon columns for removal of residual dissolved organic materials.

The design and operating factors for filters include the mode of throughput, the type of media and its distribution, the underdrain system, and the type of backwashing operation. Gravity filters using the downflow or upflow modes of operation are generally used for effluent polishing, although pressure filtration may offer some advantages as part of a tertiary treatment system. The principal advantages of pressure filtration include single pumping requirements, ease of automation, absence of negative pressure, and ability to adsorb higher pressure losses through the sand or anthracite media before backwashing is required.

The efficacy of filtration as an effluent polishing device to a biological plant can first be assessed by measuring the difference between the filtered and unfiltered COD or BOD_5. If this difference is significant and the filtrate samples meet organic concentration criteria, then filtration can be further evaluated using a pilot plant approach for testing. A filtration polishing system was installed behind an extended aeration system at one Midwest refinery - the design criteria based on pilot studies using the upflow filter unit shown in Figure 29. A sand and gravel media was used and water from the existing secondary clarifier was pumped to the pilot filter. Composite samples of the filter influent and effluent were collected throughout each filter run. The operational procedures used for each filter run are listed as follows:

1. The filter was backwashed prior to each test run. The backwash cycle included bumping the filter with 30 cfm of air for three to four minutes. The 100 gpm backwash rate was then continued for an additional six to 10 minutes until a clear effluent was produced.
2. The filtration cycle was initiated controlling the hydraulic flow rate manually with a valve.
3. Turbidity tests were performed on grab samples of the effluent throughout the filter run. The break point was established when the turbidity reached a predefined level.
4. Chemical addition to the discharge side of the feed pump was made with an air operated positive displacement pump.

SCHEMATIC OF UPFLOW SAND FILTER



Pilot tests of the sand filter were performed at surface loadings of four, six, and eight gpm/ft^2. Moreover, filter runs were made at eight gpm/ft^2 using polyelectrolytes as chemical additives.

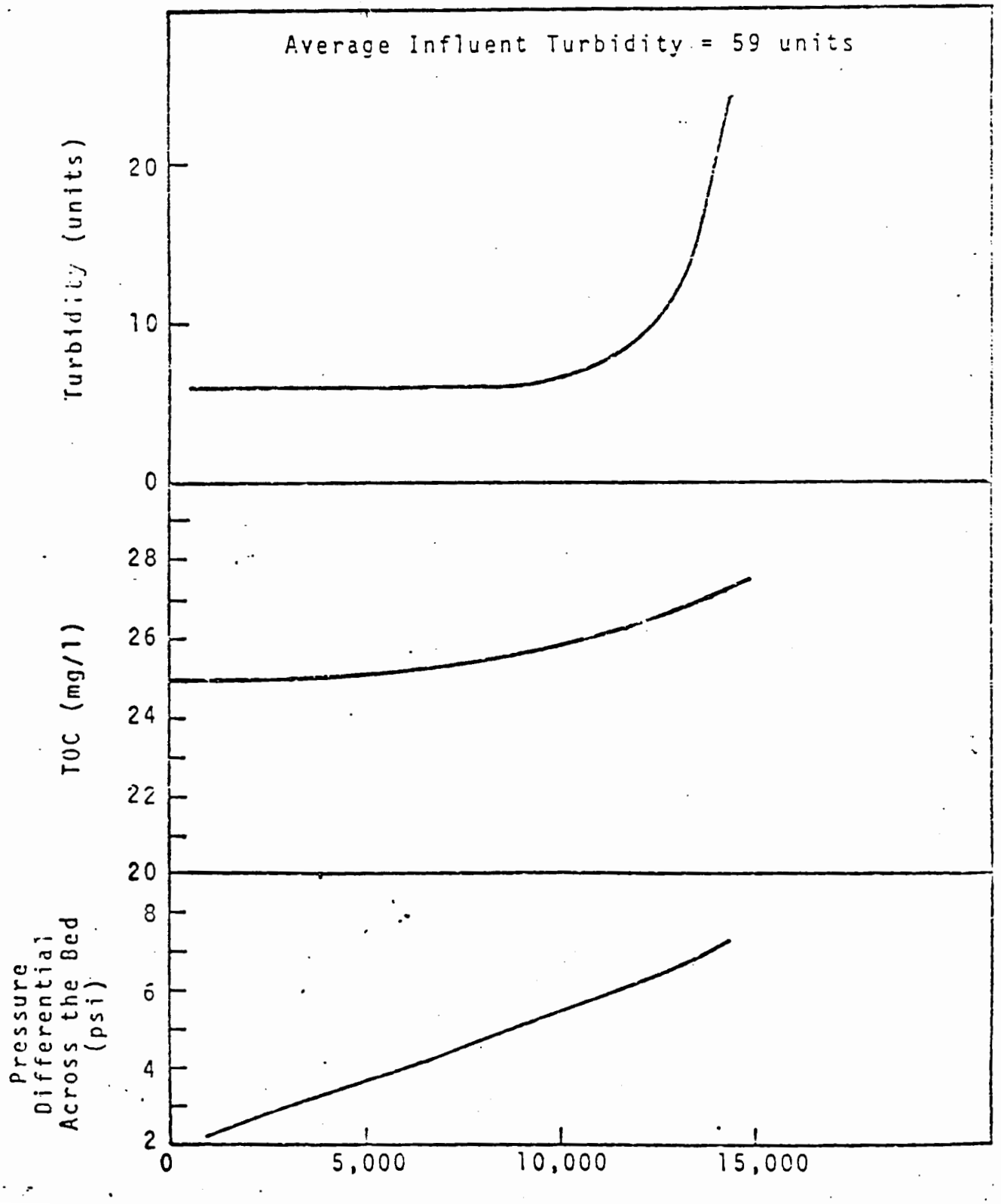
The performance of the pilot filter unit, which was translated into the full scale filter design criteria, is graphically depicted in Figure 30. This figure shows turbidity, total organic carbon (TOC), and pressure differential as a function of throughput volume for one filter run. Based on these pilot scale results, an acceptable effluent could be produced with a filtration system complementing the existing biological facility, and the filtration system was installed.

Carbon Adsorption

Although the carbon adsorption process has not been widely used in the field of refinery and petrochemical wastewater treatment to date, preliminary pilot work and limited experience indicates selected applicability.

The efficacy of utilizing carbon adsorption for the treatment of refinery and petrochemical wastewaters at any point in a process sequence can be determined only after a thorough investigation using continuous flow pilot systems has been performed. There is a tendency for investigators and equipment developers to oversimplify the process adaptability for industrial wastewater applications. Specifically, the translation of data from carbon systems receiving domestic wastes into design criteria for industrial utilization has limited validity and the use of batch isotherm information under any testing condition as a basis for process selection is imprecise. The technical and economic justification for including carbon adsorption as a treatment process in a refinery or petrochemical complex must therefore be predicated on pilot plant simulation, particularly in the absence of case histories

TYPICAL RESULTS FOR
PILOT UPFLOW SAND FILTER EXPERIMENTS



and full scale operational experience. A proper interpretation of the results is then necessary to consummate the process evaluation, determine the economics, and select the most appropriate treatment sequence.

The complexity of refinery and petrochemical wastewaters and the extremes in adsorbability of compound groups further mitigate the applicability of general rate equations. The influence of molecular structure and other factors on adsorbability, for example, are presented in Table 32 (38). This relative adsorbability, combined with unpredictable effects or process variables, forces an empirical approach for investigating carbon process applicability. Breakthrough curves defining contaminant removal rates and residuals (in terms of BOD, COD, TOC, color, etc.), carbon capacities and influence of process variables can therefore be developed using continuous flow columns.

Consideration for placement of the carbon adsorption process includes biological-carbon series treatment, carbon-biological series treatment, and carbon adsorption as a total process. Each of these applications requires primary treatment for the removal of oily substances and suspended matter using gravity separators and, in some instances, dissolved air flotation. A conceptual flow diagram for each of these candidate systems is shown in Figure 31.

Of the applications indicated, the series biological-carbon treatment scheme will probably be most prevalent in the immediate future. This is, by necessity, true for many refineries as they have already made the capital investment in secondary biological plants and require a tertiary process to meet the new quality criteria. In the case of a new facility, this approach lends itself to phase construction by installing biological facilities to meet interim effluent polishing when required.

TABLE 32

INFLUENCE OF MOLECULAR STRUCTURE AND OTHER FACTORS ON ADSORBABILITY

1. Aromatic compounds are generally more adsorbable than aliphatic compounds of similar molecular size.

2. Branched chains are usually more adsorbable than straight chains.

3. Substituent groups affect adsorbability:

Substituent Group	Nature of Influence
Hydroxyl	Generally reduces adsorbability; extent of decrease depends on structure of host molecule.
Amino	Effect similar to that of hydroxyl but somewhat greater. Many amino acids are not adsorbed to any appreciable extent.
Carbonyl	Effect varies according to host molecule; glyoxylic and more adsorbable than acetic but similar increase does not occur when introduced into higher fatty acids.
Double bonds	Variable effect.
Halogens	Variable effect.
Sulfonic	Usually decreases adsorbability.
Nitro	Often increases adsorbability.

4. An increasing solubility of the solute in the liquid carrier decreases its adsorbability.

5. Generally, strongly ionized solutions are not as adsorbable as weakly ionized ones; i.e., undissociated molecules are in general preferentially adsorbed.

6. The amount of hydrolytic adsorption depends on the ability of the hydrolysis to form an adsorbable acid or base.

7. Unless the screening action of the carbon pores intervene, large molecules are more sorbable than small molecules of similar chemical nature. This is attributed to more solute carbon chemical bonds being formed, making desorption more difficult.

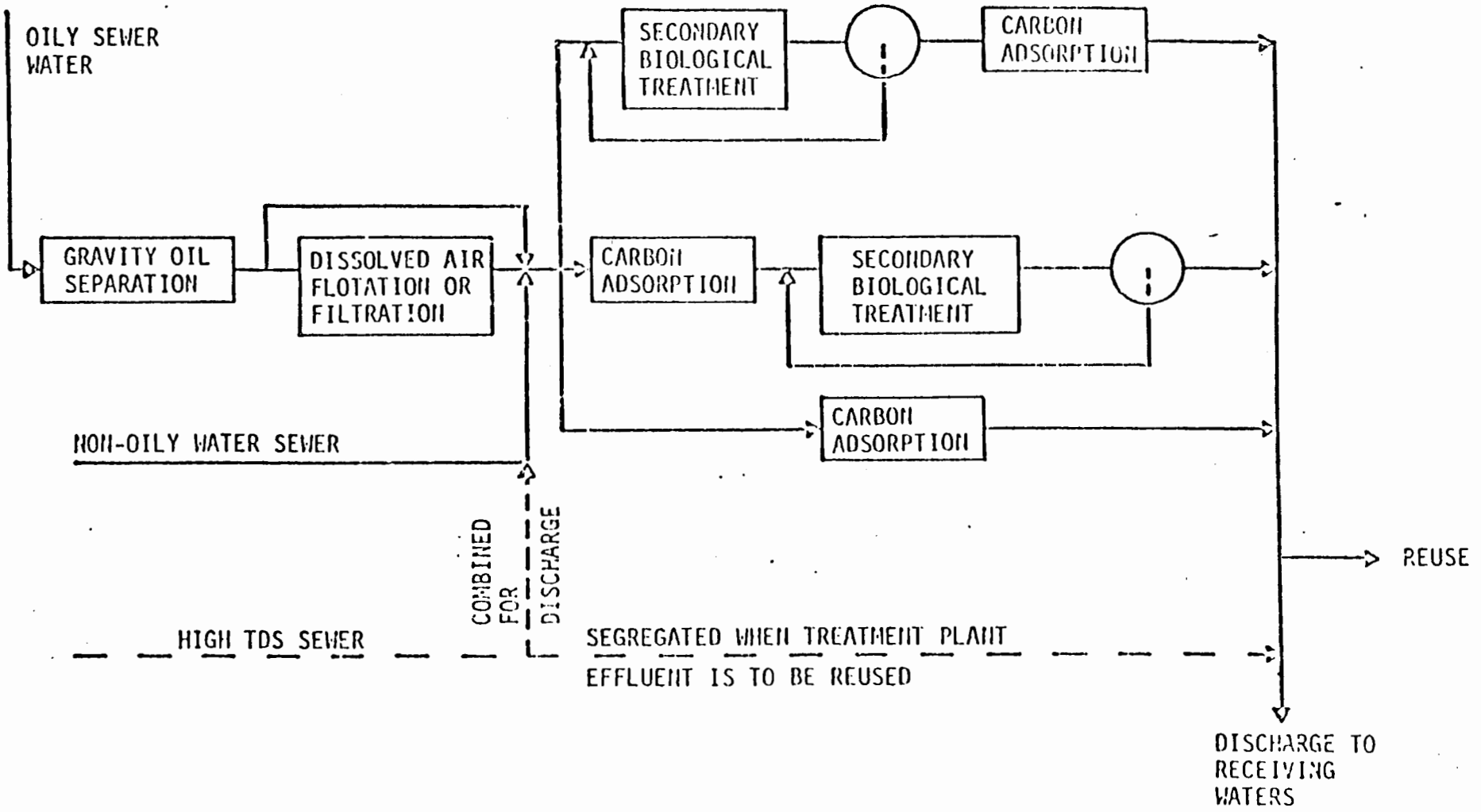

OILY SEWER WATER
SECONDARY BIOLOGICAL TREATMENT
CARBON ADSORPTION
GRAVITY OIL SEPARATION
DISSOLVED AIR FLOTATION OR FILTRATION
CARBON ADSORPTION
SECONDARY BIOLOGICAL TREATMENT
CARBON ADSORPTION
NON-OILY WATER SEWER
COMBINED FOR DISCHARGE
REUSE
HIGH TDS SEWER
SEGREGATED WHEN TREATMENT PLANT EFFLUENT IS TO BE REUSED
DISCHARGE TO RECEIVING WATERS

FIGURE 31

The series carbon-biological system is being considered by some refineries and chemical plants - the apparent advantages being a more effective use of carbon, less chance of biological upset because of carbon removal of biotoxic substances with dampening of organic surges, and a reduction of excess biological sludge inherent with the reduced organic loading. Although these stated advantages merit consideration, one must also recognize the disadvantages; namely, a potential effluent suspended solids and color problem often associated with biological systems, a less efficient biological removal of organics, and the dependence upon a sometimes sensitive biological population to consistently produce an effluent which will meet stringent quality requirements.

Columnar studies have demonstrated some interesting aspects when evaluating performance using primary effluent (from an API separator) for the column feed as compared to using biologically treated effluent as the feed. For example, the carbon appeared to be non-selective with respect to its affinity for adsorbing compounds responsible for BOD and COD respectively. This is evidenced by the fact that the BOD/COD ratio (the fraction of dichromate oxidizable compounds which are biodegradable) remained relatively constant throughout the carbon test series, regardless of the throughput volume. This was true when both the API separator effluent and the activated sludge effluent were applied to the columns. These results are plotted in Figure 32 and illustrate the magnitude of this ratio for both sequences of the biological-carbon series treatment. The reduction of the BOD/COD ratio through an activated sludge system is well documented and has been reported previously. Unfortunately, this ratio stability is responsible for unacceptable effluent BOD levels in many instances when applying

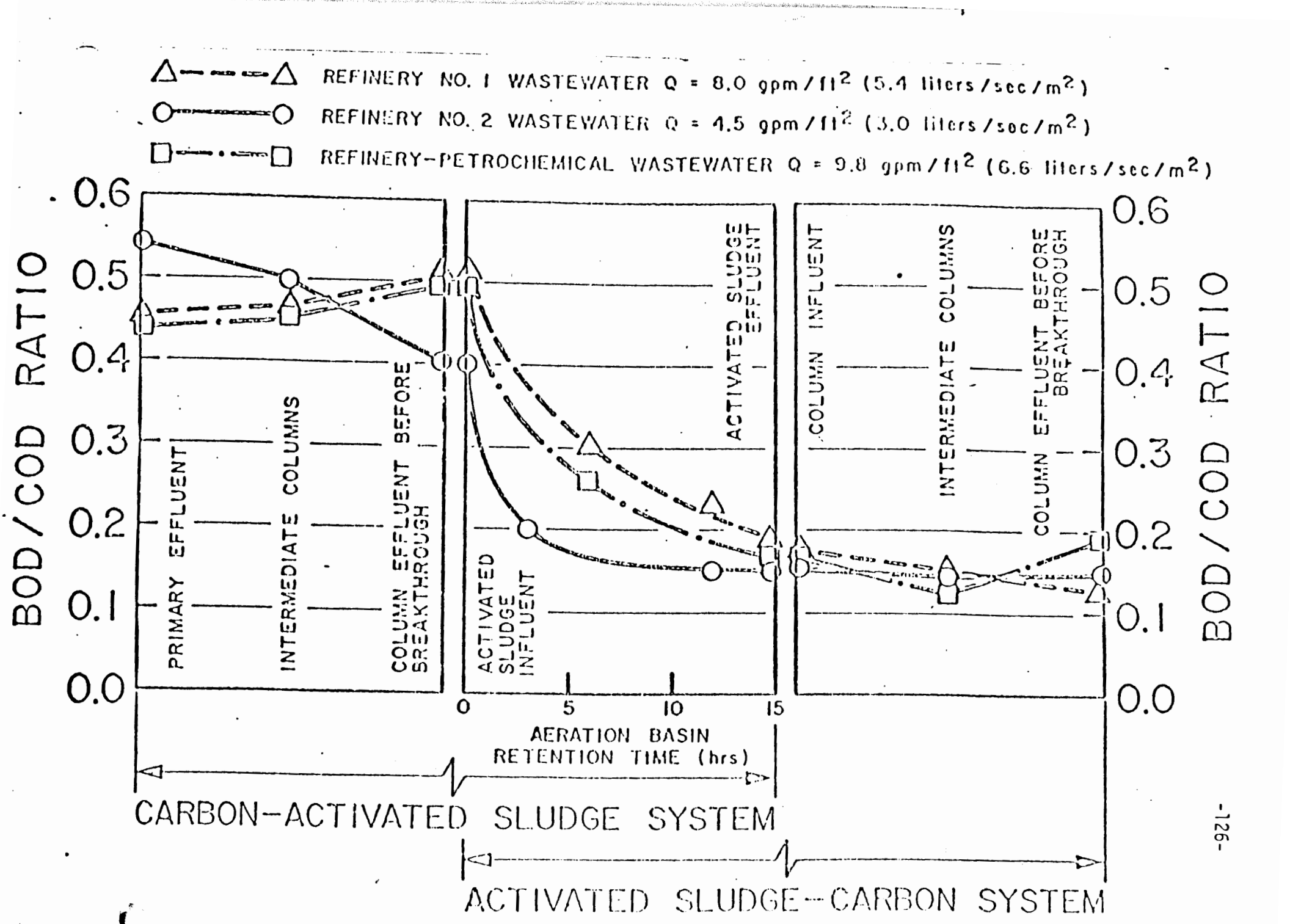

REFINERY NO. 1 WASTEWATER Q = 8.0 gpm/ft² (5.4 liters/sec/m²)
REFINERY NO. 2 WASTEWATER Q = 4.5 gpm/ft² (3.0 liters/sec/m²)
REFINERY-PETROCHEMICAL WASTEWATER Q = 9.8 gpm/ft² (6.6 liters/sec/m²)
BOD/COD RATIO
0.0
0.1
0.2
0.3
0.4
0.5
0.6
PRIMARY EFFLUENT
INTERMEDIATE COLUMNS
COLUMN EFFLUENT BEFORE BREAKTHROUGH
ACTIVATED SLUDGE INFLUENT
ACTIVATED SLUDGE EFFLUENT
COLUMN INFLUENT
INTERMEDIATE COLUMNS
COLUMN EFFLUENT BEFORE BREAKTHROUGH
0
5
10
15
AERATION BASIN RETENTION TIME (hrs)
CARBON-ACTIVATED SLUDGE SYSTEM
ACTIVATED SLUDGE-CARBON SYSTEM

FIGURE 3

the carbon system as a total process. The advantage of using carbon as a tertiary process following biological treatment is therefore apparent when considering stringent effluent BOD criteria.

Based on pilot studies, the anticipated removal of refinery wastewater constituents by activated sludge, total carbon and combined treatment systems is tabulated in Table 33. These levels of removal may not apply in all cases as most of the data presented herein is from integrated refineries (crude distillation, lubes, petrochemicals). However, they are indicative of general treatment effectiveness.

IN-PLANT CONTROL

The genesis of pollution control programs is to minimize and control unavoidable losses at the source. Such practice reduces the cost of waste treatment and, in some cases, may provide an economic plus. Such measures include salvage of unreacted chemicals, recovery of by-products, good housekeeping techniques to reduce leaks and spills, and changes in processing methods. A discussion of some methods of reducing refinery pollution output follows.

Reduction of Raw Material Losses

The losses of raw materials from storage, transport, and processing facilities are an important source of water pollution in the petrochemical industry. Several imporvements can be made by the industry to reduce the magnitude of these losses. The evaporation of light hydrocarbons from storage tanks can be controlled through the use of floating roof tanks. Additionally, vapor recovery lines in tank vents and purge lines used for process start-up and shut-down can be connected to vapor recovery systems. The

TABLE 33

ESTIMATED EFFLUENT QUALITY FOR THE CARBON AND

COMBINED ACTIVATED SLUDGE-CARBON TREATMENT OF REFINERY WASTEWATERS*

itent	Mean Value Range Primary Effluent	Total Carbon Effluent	Combined Activated Sludge-Carbon Effluent	Remarks
	500-700 mg/l	100-200 mg/l	30-100 mg/l	Exact COD residuals vary with complexity of refinery & design contact times in the Act.S. and Carbon Treatment Plants
	250-350 mg/l	40-100 mg/l	5-30 mg/l	BOD residual depends on BOD/COD ratio which characterizes relative biodegradability of wastewater.
ols	10-100 mg/l	<1 mg/l	<1 mg/l	Phenols(ics) are generally amenable to biological and sorption removal.
	8.5-9.5	7-8.5	7-8.5	pH drop in Act.S. systems attributed to biological production of CO_2 and intermediate acids. pH change in carbon columns depends on preferential adsorption of acidic and basic organics.
	50-200 mg/l	<20 mg/l	<20 mg/l	Primary effluent solids depend on design and operation of oil removal units. Act.S. effluent solids depend on effectiveness of secondary clarifier. Low effluent solids characterize carbon column effluent.
	1500-3000 mg/l	1500-3000 mg/l	1500-3000 mg/l	TDS is essentially unchanged through all three treatment systems.
n	15-150 mg/l	10-140 mg/l	2-100 mg/l	Exact concentration depends on pre-stripping facilities, nitrogen content of crude charge, corrosion additive practice and biological nitrification.
	1-10 mg/l	1-10 mg/l	<1-7 mg/l	Only removal attributed to biological synthesis.

* Based on wastewater characterization data and treatability studies conducted by the author at eight refineries and petrochemical installations.

hydrocarbon losses from vacuum jets can be reduced by installing refrigerated condensers ahead of the jets or by connecting the jet exhaust to vapor recovery systems (1).

Pipeline systems should be used to transfer raw materials whenever feasible in order to minimize transfer losses. Many petrochemical industries minimize transport hydrocarbon losses by either having subsidiary companies which supply raw materials or by producing their own. Probably the most important source of hydrocarbon raw material loss is from malfunctioning equipment lines, leakages, pump gland leakage, etc. These losses can be corrected only by careful and persistent in-plant control.

Recovery of Usable Reaction Products

By-products represent a significant pollutional fraction of petrochemical wastewaters and, in many cases, by-product recovery from the process wastes is justified not only in terms of producing a product but also in reducing the pollutional load. The recovery of sulfur from crude oils, for example, minimizes the sulfide and mercaptan pollution. Many petroleum feedstocks contain large amounts of these sulfur compounds which must be removed to prevent the poisoning of process catalysts and products, and it is possible to recover sulfur from these hydrocarbon feedstocks by removing hydrogen sulfide in the form of acid gas using hydrodesulfurization. Hydrodesulfurization consists of removing the hydrogen sulfide from a process stream by stripping with steam or water. The hydrogen sulfide is then stripped from the water or condensate as acid gas.

Other sources of usable materials found in petrochemical wastes are the catalyst complex metals and the tars from catalytic processes. For example, one chemical company has sold a copper-containing tar to a

smelter, which subsequently recovers the copper. Other metals such as nickel may also be present in evaluating quantities in tars and metal complexes. Chemical recovery companies also have reclaimed useful organic materials from tars. Usually the recovery of materials from these tars does not result in a direct profit to the petrochemical plant, but it may prove economically justified in terms of a reduced pollutional discharge.

Alkaline wastes from caustic washes are most significant and there are several methods available utilizing these caustic wastes which may prove more feasible than attempting to treat and discharge them. Some spent caustic solutions containing sulfides, phenolates, cresolates, and carbonates are marketable. Spent caustics containing large amounts of phenols and cresols can be sold to processors who separate and purify the cresylic acid fractions for commercial use. The recovery and marketing of spent caustics is probably the most economical and desirable method for eliminating these wastes.

The recovery and recycle of process effluents containing unreacted raw materials may allow substantial savings in raw material purchases and is common to most petrochemical processes in which the process reaction is incomplete. Many of the secondary reaction by-products are also valuable for use within the petrochemical plant or as marketable products. An example of the in-plant use of a by-product is the use of hydrogen chloride for hydrochlorination processes as one of the reactants in the additional chlorination of olefins. Hydrogen chloride can also be recovered and marketed as a slable product. The removal of phenols from effluents containing recoverable quantities of these compounds is often economical.

For example, the Emscher River Association in Germany recovers large quantities of phenol from wastewater at a substantial profit.

The recovery and reuse of oils is extremely common in the petrochemical industry. Recoverable oils are reprocessed while those which are uneconomical to purify are used as a fuel source. Solvent recovery is also often practiced, especially when the high costs of solvents are considered.

Process Modifications

Process modifications incorporated into the design and operation of petrochemical processing units can often lead to reductions in the pollutional load from the plant. These modifications can be classed as follows: (a) process selection, (b) prevention of product and chemical losses, and (c) modification of operating conditions.

The problems of waste control should be initially considered during the development and design of petrochemical processes since they can often be an important factor in the economics of operation. Pilot plants used in the design of petrochemical processes can be sampled to estimate the process losses and the type of pollutants which will be discharged from the prototype unit. Analyses of these samples will indicate possible process modifications which can be implemented to reduce the pollutional load.

The incorporation of spent caustic regeneration schemes in process and plant design is an example of process selection used to reduce the waste load. The substitution of continuous processes for batch processes also tends to eliminate peak discharges of wastes and to reduce the cost

of treatment required for the waste. Treatment facilities designed to absorb the effects of shock discharges of wastes through equalization basins or overdesigned tanks are considerably more expensive than those which are designed to treat a waste of relatively constant discharge level.

The use of downgraded chemicals in processes which do not require high-quality reactants can facilitate both process and waste control. This type of design utilizes the waste effluents from one process as reactants in another. In the ideal scheme, a chemical could be carried through several processes, each using a slightly lower quality reactant. Caustic washes are often so used in refining operations. For example, caustic washes used to treat light hydrocarbons can later be used as makeup caustic for gasoline treating.

The hydrocarbon losses associated with the use of barometric condensers are an important source of pollution in petrochemical processes. The use of shell and tube heat exchangers rather than barometric condensers can significantly reduce this source of pollution. Process sampling taps connected directly to sewers are a source of pollution which can be avoided by returning drainage to the process unit rather than the sewer. Distillation of waste streams can also be used to eliminate the loss of volatile materials. Furfural, for example, is recovered by azeotropic distillation, eliminating this compound from wastewaters while producing a valuable solvent for use in extraction processes. One example of waste control by process modification has been the elimination of oil emulsion losses from barometric condensers on pipe stills. By rearranging the

interior of the pipe still to reduce friction losses through the trays and by lowering the temperature in the still, losses were reduced to one-sixth of their original quantity.

Reduction of Chemical Cleaning Materials

The chemical cleaning of exchangers, process drums, or fractionating towers can add a significant pollutional load to the refinery effluent. If possible, the cleaning contractor should be required to collect and haul the cleaning chemicals outside of the plant for disposal at contract facilities. If this cannot be accomplished, the deleterious effects of the chemical cleaning agents on the treatment facility can be mitigated by dumping the chemicals as slowly as possible to the sewer system to reduce slug loading. In some instances, neutralization of the chemical cleaners may assist in their subsequent treatment. Additionally, the use of biodegradable detergents would obviously enhance the performance of a biological treatment system.

Handling of Tank Bottoms

Sludges and liquids from tank cleaning operations vary greatly depending on the service of the tank and method of cleanout. The method of cleanout and the mode of disposal can significantly influence the resulting pollution load attributable to this source. For example, the practice of pumping water to the tank and agitating the liquid mixture before opening may free some of the oil from the bottom sludges and tank sides, the upper oil phase and some water then being pumped to the slop oil recovery system. Another practice is to dig a pit within the firewall, convey the sludge to the pit, decant the excess water, and concentrate the sludge. This sludge can then be plowed into the ground, biodegraded by soil bacteria,

or hauled away by vacuum trucks to land farming or contract disposal. The primary considerations for the adoption of methods for tank cleaning or tank bottoms disposal are:

1. The cleaning method should keep as much oil and solids out of the sewer as possible; and,
2. Any solids disposal method should prevent recycling of solids to the sewer separator system.

General Housekeeping

Good housekeeping must be stressed continually. Experience has shown that it can be attained by instilling the proper attitude in all personnel. Experience has also shown that the proper attitude cannot be maintained without a continuing program of re-emphasis and some system of enforcement. This means there must be an inspection system. An operator is less inclined to allow something to be discharged to the sewer if he knows that there is a good chance that the discharge will be detected and management will be informed of it. There must be an enforcement program and an enforcer.

The inspection and policing procedures can be greatly simplified by monitoring instruments that alert the inspector to unusual amounts of any unwanted material in the sewer. The more sophisticated monitoring systems can both identify and quantify material in the sewer. This allows management to inform the operator at a given unit that he lost so many pounds of the material found. This type of instrumental monitoring is very effective, although expensive.

Periodic analysis of composite wastewater samples by gas chromatography can identify many individual contaminants in the water and thus

allow fixing responsibility for them. The frequency of sampling can be adjusted with need. A pH recorder will warn of caustic spills if it is monitored occasionally.

An alert operator at the oil-water separators can - with a little experience - identify many unusual conditions and can notify the proper supervisor immediately.

Whatever the degree of complexity of the policing system that is adopted, the responsibility for use of the data must be assigned to an individual. The data should not only be used for day-to-day policing but also used to establish long range trends. This allows predicting possible difficulties in advance, thus providing time to optimize solutions to the difficulties.

Educational Program

In order to have a successful pollution control program in a refinery, it is essential to get as many employees involved in the effort as possible. For best results, the involvement should include everyone from the plant manager down to the operator who actually turns the valve that discharges an unwanted substance to the sewer, or does not close the valve that causes a drum or tank to overflow to the sewer.

With the current publicity and concern about pollution, it is not as difficult to get poeple involved as it has been in the past when most people were indifferent to the problem. In most refineries, a large number of employees are fishermen or hunters and these persons are easily involved in a conservation program.

The most important step in the involvement process is for upper management to be sincerely dedicated to eliminating pollution as far as is possible.

This dedication must be sincere. Token support of the idea will not fool many people and most employees are only going to be as dedicated as they think management is. Once management is sincerely interested in pollution control, that fact will be obvious and this philosophy will filter down through the organization.

The next step in involvement is to draw the entire plant personnel into the effort. An effort should be made to convince them that each of them has an important part to play in the control effort and that the effort cannot succeed without their help. In order to help develop the feeling of personal responsibility on the employees' part, they should be kept informed on what is taking place. The problems and solutions should be outlined and explained. If they are convinced that management is sincere and that they each have an important role to play, they will provide worthwhile suggestions on methods of achieving the desired goal. How these suggestions are received and acted upon is an important part of the program.

The problem of communication between upper management and the lowest level of operators is a difficult one. One method that does not work is for the plant manager to give the message to the first line of supervisors and hope that they will pass it on down the chain.

If the refinery has a newsletter, a personal message from the manager can be inserted in that media. Short personal messages at Safety Meetings or any other meetings that are attended by all operations employees can be fairly effective.

Although the manpower cost is rather high, the most effective means of getting poeple involved in an all-out pollution control program is to have

.r EDOP, has not yet been clearly defined but is generally construed to mean complete recycle of effluent and the elimination of pollutants discharged from the refinery complex.

Based on the work done by API, the estimated capital costs to obtain Levels I, II, and EDOP are presented in Tables 35, 36, and 37 respectively (39.1). It is noted from these Tables that $907 million (all on 1971 $s required to meet Level I, and an additional $819 million is required to meet Level II. A final increment of $725 million is required to satisfy the EDOP provisions of P.L. 92-500. The cost levels are those required for existing refineries which have a crude refining capacity of approximately 12.4 million barrels per stream day. Including grass-roots refineries to be built between 1972 and 1985 as well as refinery expansions, the capacity should increase to approximately 22 million barrels per stream day. At this capacity, the estimated capital cost to reach the first level treatment is 1.8 billion dollars; to obtain second level treatment, the estimated cumulative total is 3.4 billion dollars; and, to reach EDOP is a cumulative total of 4.8 billion dollars (all expressed as 1972 dollars)(39.1).

The estimated annualized cost, which includes operation, maintenance, and amortization of capital, is 521 million dollars per year for existing U. S. refineries to meet Level I, 597 million dollars per year to achieve Level II treatment, and 795 million dollars per year to obtain EDOP assuming this can be accomplished technically. Assuming the U. S. refining capacity is increased to 22 million barrels per stream day by 1985, these annual costs climb to 620 million dollars for first level, 1.09 billion for second level, and 1.48 billion for EDOP (39.1).

TABLE 35

SUMMARY OF COSTS TO REACH LEVEL I

REFIN. CLASS	NUMBER STUDIED	CAP. MBPD	COST, $/ DAILY BBL I	COST, M$/ REF. I	TOTAL COST, M$
A	8	173	96	2.1	16.6
B	64	3,407	97	5.2	331
C	25	3,201	64	8.2	204
D	11	1,030	104	9.8	107
E	13	3,358	74	19.1	248
	121	11,170	81	7.5	907

TABLE 36

SUMMARY OF COSTS TO REACH LEVEL II

REFIN. CLASS	NUMBER STUDIED	CAP. MBPD	COST, $/ DAILY BBL	COST, MM$/ REFINERY	TOTAL COST, MM$
			II	II	
A	8	173	86	1.9	14.8
B	64	3,407	80	4.3	274
C	25	3,201	71	9.2	239
D	11	1,030	95	8.9	98
E	13	3,358	57	14.8	193
	121	11,170	72	6.8	819

TABLE 57

ADDITIONAL ESTIMATED COST TO MEET NSPS

REFIN. CLASS	NUMBER STUDIED	CAP. M BPD	COST, $/ DAILY BBL	COST, $M/ REFINERY	TOTAL COST, $M
A	9	187	34	0.7	6.4
B	65	3,458	61	3.2	212
C	26	3,361	56	7.2	188
D	11	1,030	64	8.6	66
E	13	3,358	76	19.6	255
	124	11,395	64	5.9	725

NOTES: All costs are in 1972 dollars.

Above costs do not include any wastewater costs for refinery expansions or for new refineries. These costs will be developed in final report.

ECONOMIC IMPACT AND COST EFFECTIVENESS

In order to put these capital and annualized costs in perspective, one can take the 1.7 billion dollars to be spent on U. S. refineries having a crude capacity of 12.4 million barrels per stream day and by assuming current refinery capital investments at around one billion per year, approximately 17 percent of this capital investment would be directed toward water pollution control systems in refineries to meet the Level II requirements. Moreover, assuming the cost of processing crude is one dollar per barrel and considering 600 million dollars of annualized cost to obtain second level treatment, 13 cents per barrel of crude processed, or 13 percent of the processing cost will be required for water pollution control.

REFERENCES

The following references are to be inserted in the original list of references submitted with the chapter by D. L. Ford. The numbering system for the inserts is simply: 1.1 is to be inserted immediately after Reference 1, etc., etc.

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VARIABILITY ASSOCIATED WITH ANALYTICAL TESTS (Ref. V-9)

Constituent	Method	Test Concentration mg/l	Standard Deviation mg/l	99% Probability[3] mg/l
BOD	Bottle @ 20°C	175	±26	±67
		2.1	± 0.7	± 1.8
COD	Regular	270	±17.8	±46.9
	Low Level	12.3	± 4.15	±10.7
	Chloride >1000 mg/l	NOT AVAILABLE		
TOC	Infrared, Combustion	NOT AVAILABLE		
Phenolics	Extraction	0.0096	0.00099	0.0025
		0.0483	0.0031	0.008
		0.0935	0.0042	0.011
	Direct Photometric	4.7	0.18	0.46
		48.2	0.48	1.24
		97.0	1.58	4.08
Oil & Grease	Infrared - Freon	13.86[1](17.5)[2]	1.4	3.6
	Separatory - Freon	13.0 (12.6)	0.9	2.3
	Soxhlet - Freon	12.3 (14.8)	1.1	2.8
Sulfides	Titrametric Iodine	NOT AVAILABLE		
TSS	Gravimetric	STATED PRACTICAL RANGE 10-1000 mg/l		
Ammonia	Distillation	0.21	0.122	0.315
		0.26	0.07	0.18
		[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]
	Selective Ion Electrode	1.00	0.04	0.10
		0.27	0.17	0.044
		0.19	0.007	0.018
		0.13	0.003	0.008
	Automated	0.43-1.41	0.005	0.013
Chromium, Total	Atomic Absorption	0.353 (0.370)[4]	0.105	0.27
		0.380 (0.407)	0.128	0.33
		0.072 (0.074)	0.029	0.075
		0.084 (0.093)	0.035	0.09
		0.0102(0.0074)	0.0078	0.02
		0.016 (0.015)	0.009	0.023
Cyanide, Total	Distillation	0.08	0.005	0.013
		0.13	0.007	0.018
		0.28	0.031	0.08
		0.62	0.094	0.22
Cadmium	Atomic Absorption	0.070 (0.073)[4]	0.021	0.054
		0.074 (0.078)	0.018	0.046
		0.0168 (0.014)	0.011	0.028
		0.0183 (0.018)	0.010	0.026
		0.0033 (0.0014)	0.005	0.013
		0.0029 (0.0025)	0.003	0.008

[1] Represents recovery of 14 mg/l of a known oil mixture from sewage

[2] Represents recovery by each method from a sewage sample

[3] Using two-tailed normal distribution

[4] True concentration in "spiked" synthetic sample

THE USE OF BIOLOGICAL SYSTEMS TO REMOVE TOXIC CONSTITUENTS*

Introduction

With the increasing scrutiny of hazardous and toxic materials present in liquid effluents, their fate through the various treatment methodologies, and their ultimate impact on the environment, it is appropriate to reconsider the applicability of biological systems in treating such constituents.

There are many incentives to engineer biological systems that are capable of removing or reducing constituents with toxic or hazardous implications to acceptable concentration levels. As biological treatment processes are universally applied in many industries, the incentives to modify or retrofit as compared to constructing new facilities are obvious. The capital and annual costs associated with biological systems are normally lower than process alternatives, and as the biochemical reactions proceed toward completion, the toxicity potential of the by-products or end-products is generally far less than that of the reactants. It is, therefore, the purpose of this treatise to discuss some of the major elements of system analysis, biochemical concepts, and performance in terms of toxic constituent removal.

The literature is rather consistent in endorsing the activated sludge process (and its appropriate modifications) as capable of removing the priority pollutants to concentration levels at or below the analytical detection limits (1)(2)(3)(4)(5). By definition, there are approximately 85 toxic organic pollutants on EPA's list of priority pollutants and sub-categorized as volatile, base/-neutral, or acid. Other compounds found in industrial effluents may also have deleterious impacts on the environment as they are discharged to the receiving waters.

It is recognized that there are three major pathways by which these constituents can be removed in a high-rate biological system. These include biochemical oxidation

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(biotic), sorption (abiotic) or volatilization (abiotic). It may then become important to identify the importance and relevance of these pathways so that the proper engineering decisions can be made. The preponderance of evidence points to biodegradation being the dominant removal mechanism when an active biomass is present (6)(7)(8)(9). Each situation is unique, however. The physical constants of the liquid phase such as the vapor pressures, the partition coefficients, and the relative solubilities of the dissolved constituents are important as well as the biodegradability of these organic compounds. Moreover, the mixing intensity of the biological reactor, the air flow, the physical geometry, and the inventory of active bio-mass all play an important role. The complexity of such a system, the process and environmental variables which prevail, and the level of operational control all interrelate and force the engineer to judge and configure each system on its technical merits.

Screening Analyses

The first step in developing the necessary information relative to evaluating the applicability of biological treatment systems in removing specified constituents from the liquid fraction is to review the literature for biodegradability and physical characterization data for specific compounds. The most comprehensive sources for listing compound biodegradation information are cited as references (4) and (10). The next logical step is performing the necessary screening tests. There are three basic approaches presented herein, namely, the Warburg analysis, the EBOD analysis, and the bench-scale batch reactor analysis. Each are briefly discussed:

The Warburg Analysis. The Warburg apparatus consists of a monometer and a reaction flask and is frequently used to screen xenobiotic compounds which may be present in the wastewater. The reaction flasks are connected to a monometer and as biochemical oxidation proceeds, the carbon dioxide produced by the respiring microorgnisms is absorbed in a potassium hydroxide solution which occupies the center well of the reaction flask. The acclimated biological seed, which has been added to the flask along with the desired proportion of the wastewater, biochemically oxidizes this substrate to the extent that conditions allow. As the microorganisms utilize the organic constituents of the wastewater sample, the gas phase oxygen is reduced within the closed system, and a corresponding pressure differential is recorded. The cumulative oxygen utilization values can be plotted

versus time and the toxic or inhibitory thresholds are indicated by significant drops in the relative oxygen uptake rates. The Warburg assembly allows the evaluation of several flasks at one time, and different substrates and/or dilutions can be evaluated concurrently. A detailed procedural analysis in utilizing the Warburg approach is described in reference (11).

The Electrolytic BOD Analysis (EBOD). A screening approach using the same principles of the Warburg analysis but applying a different methodology is the application of the Electrolytic BOD Respirometer System (12). This system consists of a reaction vessel, an electrolysis cell, a proportionately controlled incubator, an electronically operated measuring unit, and a printer. The reaction chamber consists of a one liter stirred vessel, the manometric switch, and an electrolytic oxygen generator mounted on the top. The acclimated biological seed and substrate are added to the reaction chamber using the same approach as the one used with the reaction flasks in the Warburg apparatus. As the dissolved oxygen in the liquid phase is biologically utilized, carbon dioxide is released and absorbed in a potassium hydroxide-filled container. This results in a slight vacuum in the air space being produced, and a manometric switch is triggered and oxygen is produced electrolytically to replace the oxygen consumed. The oxygen generated by electrolysis is related to the current applied and to the length of time the generator is on. Therefore, accumulative oxygen demand may be recorded at any time during the test period and is proportional to the degree of biochemical oxidation that takes place. The relative biological activity can then be recorded.

The Batch Reactor Analysis. The Batch Reactor Analysis can be conducted on the bench-scale using several containers affixed with air sparjers. As in the two methods previously described, aliquots of acclimated seed and the substrate in question are added to each reactor and the aeration commences. The volatile suspended solids (VSS) concentration and soluble organic fractions are recorded and monitored as a function of aeration time. The reduction of the soluble organic fraction in each of the reactors is monitored, and this profile is indicative of the relative biodegradability of the substrate. Although the procedure is tedious and requires considerable time to correctly implement, it can be used successfully to delineate approximate threshold concentrations for constituent toxicity and to develop a bio-

logical seed which can effectively reduce recalcitrant compounds. A detailed approach in utilizing the Batch Reactor Analysis are cited in reference (11).

The Empirical Development of Process Kinetics

The formulation of design criteria for the biochemical oxidation of liquid streams containing toxic or hazardous constituents can be developed through the application of bench and full-scale treatability studies using continuous flow reactors (11). Such studies are normally conducted after the screening tests have been performed and the literature thoroughly researched. There are obviously many variables involved with such studies and one must be careful not to oversimplify the process simulation. However, if the environmental conditions, such as temperature, pH, and dissolved solid concentrations are held relatively constant, then one is able to generally predict the achievable levels of biochemical oxidation at predetermined hydraulic retention time and sludge ages. Representative samples of wastewater should be used and the degree of variability in the raw wasteload would determine how much pretreatment and equalization is required prior to introducing the liquid stream into the biological reactor. This analysis, of course, is complicated when the relative concentrations of the toxic or hazardous constituents in the wastewater vary significantly with time.

If one monitors the biodegradation rates for a single substrate in a controlled reactor using acclimated seed, the biodegradation rate normally approximates zero order (a linear reduction of substrate concentration as a function of aeration time.) The "K" rate of the zero order reaction is a function of the intrinsic properties of the organic compounds as determined by the molecular structure and configuration. When many compounds are present, which is normally the case in an industrial waste stream, then concurrent zero order reactions of varying "K" rates are occurring with the total reaction rate of the soluble organic fraction approximating first order. Most of these biodegradation rates have been interpreted using the Monod equation (13). This is basically an approximation of the Michaelis-Menten equation using enzyme kinetics as basically presented in the following equation:

$$\frac{S_o - S_e}{X_a t} = \frac{\left[\frac{S_o - S_e}{X_a t}\right]_{max}\left[S\right]}{\left[S\right] + \left[K_s\right]} \qquad \text{(Eq.1)}$$

Where:

S_o = initial substrate cocentration
S_e = final substrate concentration
X_a = active biomass
t = substrate contact time
K_s = half velocity coefficient

The more recognized form of this equation is:

$$\frac{dS}{dt} = \frac{KS_e}{K_s + S_e} \qquad \text{(Eq. 1-a)}$$

Where: K = the maximum substrate utilizaton rate

and

$$K = kX_a$$

The K and Ks values can be determined graphically by plotting 1/Se as a function of

$$1 \Big/ \frac{S_o - S_e}{X_a \cdot t}$$

with the intercept equal to 1/K and the slope being K_s/K.

For a continuous stirred-reactor (CSTR) at steady state, then the change of concentration with respect to time is zero and the simplified model as presented in Equation 1 can be solved algebraically. In addition to the steady state assumption, one must further assume that the enzyme amount remains constant throughout the experiment, the substrate concentration does not change appreciably during the measurement, substrate feed is sterile, and monitoring of the substrate concentration represents the soluble fraction only. The development of the kinetic equations for batch are plug-flow reactors involved differential equations and are much more difficult to solve.

It is important to recognize that the development of process kinetics using bench or pilot-scale treatability studies have inherent limitations, but properly conducted, can approximate what will occur in the full-scale application. The key elements of predicting effluent concentrations using these simulation techniques center around the utilization of representative wastewater samples, sequestering the variability of the raw wasteload

through pretreatment and equalization, insuring complete mixing in the biological reactor, and properly defining the effects of process and environmental variables. Of particular importance is the effect of the liquid temperature on the biodegradation of toxic or hazardous constituents. One must recognize that the temperature effects could be much more pronounced for recalcitrant molecules as compared to those which are easily biodegradable. The energies of activation of potentially toxic or hazardous molecules are normally higher than that of other organic compounds. The effect of this energy of activation on the "K" rate of a particular molecule is developed as follows:

$$\frac{d \ln k}{dt} = \frac{E}{RT^2} \qquad \text{(Eq.2)}$$

and

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E(T_2 - T_1)}{RT_1T_2}$$

and

$$\frac{k_1}{k_2} = \theta^{T_2-T_1}$$

Where:

E = energy of activation
R = gas constant
T_1, T_2 = liquid temperatures
k_1, k_2 = organic removal velocities
θ = temperature coefficient

It is noted from this equation that the temperature coefficient, θ, is a direct function of the molecular energy of activation, which generally indicates that the more complex and recalcitrant the molecule, the more significant is the effect of liquid temperature. The implications of this are obvious when trying to biologically treat xenobiotic compounds in cold climates. There are engineering approaches to overcome this problem, such as providing a longer sludge age, a higher inventory of active biomass, or minimizing heat losses, but the system should be engineered in recognition of these effects.

Biotic and Abiotic Pathways In The Biological System

As previously mentioned, there are three major pathways by which a toxic or hazardous constituent can be removed in a biological reactor. These include the

straight biochemical oxidation of water soluble organic substrates, the sorption of these constituents on the biological mass, and the volatilization of these compounds into the atmosphere. Mathematically this can be expressed on a mass balance basis by:

$$dS/dt \cdot V =$$

$$QS_o - \left[QS_e + dS/dt_{bio} \cdot V + dS/dt_{str} \cdot V + dS/dt_{sorb} \cdot V\right] \quad \text{(Eq.3)}$$

The development of the various constants for each component removal is discussed elsewhere (2)(18). The precise delineation of these pathways may or may not be important depending on the particular situation. A brief discussion on each of these pathways is presented as follows:

Biochemical Oxidation. The biochemical degradation of both the readily biodegradable and recalcitrant compounds is generally the dominant removal mechanism as documented in the literature. There are several approaches one can take in order to establish the veracity of this removal mode. The most convenient approach is to establish an oxygen material balance. This can be accomplished by determining the oxygen uptake rate in the biological reactor, dividing this value by the volatile suspended solids concentration to put it on a specific basis, and comparing it to uptake rates of similar systems. Furthermore, the system oxygen demand can be compared to the corresponding removal of organic constituents in the system as measured by BOD_5, TOC, or COD, by assuming the fraction of a theoretical oxygen demand that the BOD, TOC, or COD represents, then calculating the balance. If a relatively good balance is obtained, then removal of the organic constituents via the biochemical oxidation pathway can be presumed. This can further be verified by measuring the gas phase concentration of the organic constituents in a closed system in order to verify the closure. If the results are consistent, namely, a good oxygen material balance is obtained by measuring the liquid phase uptake rate and comparing with the organic removal, combined with the detection of nominal constituent concentration in the gas phase, then the biochemical oxidation pathway is confirmed. If this is not the case, then one needs to further analyze the other removal mechanisms.

Sorption. Sorption is basically a mechanism where the constituent colloidal, suspended, and sometimes sol-

uble fractions are physically sorbed on the biological floc. It is precisely this mechanism that led to the development of the contact stabilization process for the treatment of municipal wastewaters, where a significant fraction of the organic constituents is in the colloidal or suspended form. It also may be responsible for removal of toxic or hazardous constituents in the biological treatment of industrial wastewaters. This can basically be determined by monitoring the soluble and nonsoluble fraction of the organic constituents in question throughout the biological process. If an oxygen balance on the liquid side is not achieved, and the selected constituents are measured in the sludge fraction of the system, then the sorption pathway takes on added significance. If sorption does play a dominant role in the removal process, then the system kinetics based on the soluble fraction would obviously be altered. More attention to handling the sludge fraction, however, may be an issue based on the ultimate disposal methodologies in handling the sludge. For example, one could make the case that a significant biocumulation or sorption of toxic or hazardous constituents onto the biological sludge might affect its classification as a hazardous or nonhazardous sludge. This would have obvious implications in the handling and disposal of this sludge under the Resource Conservation and Recovery Act (RCRA).

Volatilzation. The potential for air stripping high vapor pressure compounds into the atmosphere from biological wastewater treatment facilities has been the subject of many investigations because of air pollution implications. As the theoretical prediction of the air stripping phenomenon in a biological treatment system is difficult because of the many physical and biological variables, the quantification of the stripped component can be estimated by bench or full-scale testing. It is first presumed that the equilibrium between the gas and aqueous phases of the constituent is governed by Henry's law for the organic solids in the dilute concentration range.

$$C_g = H_c C_l \qquad \text{(Eq. 4)}$$

Where:

C_g = mass concentration in the gas phase
C_l = mass concentration in the liquid phase
H_c = the Henry coefficient expressed as a dimensionless mass concentration partition ratio

and

$$H' = H_c RT \qquad \text{(Eq.5)}$$

Where:

H' = the Henry coefficient of a molecule (atm/mol/m_3)
R = the universal gas constant
T = the absolute temperature, °K

The Henry partition ratio can be used to approximate the gas and liquid concentrations of a solute, although this is a simplified approach and must be verified by field testing which incorporates the applicable process variables. Although the kinetics of air stripping are complex, proposed models are (14)(22):

$$\frac{S_e}{S_o} = \frac{1}{1 + (Q_a/Q_l) H_c} \qquad \text{(Eq.6)}$$

Where: Q_a/Q_l = airflow to liquid flow ratio

and

$$K_a{}^a \cdot V/Q = bH_c{}^m \qquad \text{(Eq.7)}$$

Where:

$K_a{}^a$ = stripping rate constant
V = volume of the liquid in the reactor
Q = air flow rate
b,m = power function constants

It is important to note that the stripping rate constant is a direct function of liquid temperature (Equation 5) and air flow rate (Equation 6, 7). Therefore, while the Henry coefficient of the compounds in the liquid phase is important relative to the stripping potential, the air flow rate and liquid temperature also play a major role as to what potential

fraction of the organic constituent can be stripped from solution. The temperature effects are exemplified by biodegradability and volatility studies with selected halogenated aliphatics showing 27 to 34 percent volatilization at 25° C, with no volatilization at 5° C (15). Perhaps the most significant factor relative to air stripping, however, is the presence or absence of active biomass in the liquid phase. Most investigators agree that the presence of an active microbial culture shifts the removal pathway from air stripping to biodegradation, even when conditions favor the stripping mechanism. Consequently, one should carefully analyze the total regime in terms of the physical characteristics of the solute, the liquid temperature range, the sorbability potential, and the level of biological activity in the biological reactor prior to predicting the air stripped fraction. Once this is done, then appropriately measuring the organics in the gas phase can be accomlished in order to verify the liquid phase measurements (such as oxygen uptake and organic reduction) and complete the material balance. The relative importance of the stripped fraction with respect to ambient air quality will dictate the extent to which such tests should be performed.

Summary

In summary, the evidence infers that the preponderance of "priority pollutants" in a waste stream being treated biologically are removed through the biodegradation pathway. A recent study was conducted by EPA to determine the biodegradability of 114 organic priority pollutants cited in the EPA consent Decree list (16). This study was based on static flask screening techniques using enrichment cultures and two concentrations of the test compound. The results of these tests, along with those data observed from a cooperative field study between EPA and the Chemical Manufacturing Association (CMA) are presented in Table 1. (1)(6) Even with the stripping modification of these static tests, the volatilization losses were generally less than 30 percent. More comprehensive testing in terms of delineating the biotic and abiotic pathways for removing benzene, toulene, ethylbenzene and o-xylene were recently conducted. (17)(18)(19) The results of these tests, conducted using bench-scale activated sludge reactors are presented in Table 2.

These results were derived from operating bench-scale activated sludge reactors at a sludge age of 2 to 6 days, an operating temperature of approximately 20° C, and at air

TABLE 1

Comparison of Biodegradability of Toxic Organic Pollutants as Predicted by EPA Study to the Five-Plant Study Results

Volatile Compound	EPA Percent Degradation*	Five-Plant Study Percent Removal**
Acrylonitrile	100	99
Benzene	100	100
Bromomethane	48	100
Bromodichloromethane	67	89
Carbon tetrachloride	100	100
Chlorobenzene	100	56***
Chloroethane	NA	91
Chloroform	100	99
Dibromochloromethane	55	100
1,1-dichloroethane	100	79***
1,2-dichloroethane	100	99
1,1-dichloroethene	100	100
t-1,2-dichloroethene	100	98
1,2-dichloropropane	92	97
1,3-dichloropropane	100	98
Ethylbenzene	100	99
Methylene chloride	100	75
1,1,2,2-tetrachloroethane	36	93
Tetrachloroethene	100	27***
1,1,1-trichloroethane	100	38***
1,1,2-trichloroethane	59	72***
Trichloroethene	100	40***
Toluene	100	100
Vinyl chloride	NA	100

Base/Neutral Compound	EPA Percent Degradation*	Five-Point Study Percent Removal**
Acenaphthene	100	95
Acenaphthylene	98	93
Anthracene	92	97
Benzo(a)anthracene	35	56***
Benzo(b)fluoranthene	100	--***
Benzo(a)pyrene	NA	--***
Bis(2-ethylhexyl)phthalate	95	64
Butylbenzylphthalate	100	87***

Dibenzo(a,h)anthracene	NA	--***
Di-n-butylphthalate	100	99
1,3-dichlorobenzene	35	100***
1,2-dichlorobenzene	29	94
Diethylphthalate	100	99
Dimethylphtnalate	100	99
Dioctylphthalate	94	90
Fluoranthene	100	83***
Fluorene	77	93
Isophorone	100	100
Naphthalene	100	100
Nitrobenzene	100	98
Pyrene	100	84***
1,2,4-trichlorobenzene	24	82

Acid Compound	EPA Percent Degradation*	Five-Plant Study Percent Removal**
2-chlorophenol	100	41
2,4-dichlorophenol	100	91
2,4-dimethylphenol	100	100
2,4-dinitrophenol	100	84
2-nitrophenol	100	77
Pentachlorophenol	100	36
Phenol	100	98
2,4,6-trichlorophenol	100	45

* Includes volatilization losses at 25 C and initial concentration of 5 mg/l

**Based on arithmetic means

***Influent concentration less than 40 ppb

NA = not available

Table 2

Fate of Benzene, Ethylbenzene, Toulene, and Xylene
in Activated Sludge Reactors

Reference		Benzene	Toulene	Ethylbenzene	O-xylene
(17)	% Biodegraded	97.8	94.90	94.6	--
	% Air Stripped	2.0	5.10	5.2	--
	% Sorbed	--	.02	.2	--
(18)	% Biodegraded	83.6	83.8	80.0	78
	% Air Stripped	15.9	15.6	19.5	21
	% Sorbed	0	0	0	0
(19)	% Biodegraded	--	88.4	--	--
	% Air Stripped	--	11.6	--	--
	% Sorbed	--	--	--	--

flow rates in the range of 185 to 400 ml air/liter of reactor volume/min. (2.47 to 5.35 cfm/1000 gal) These data support the removal totals tabulated in Table 1 and confirm dominance of the biological pathway preference even with moderate liquid temperatures and high air flow rates, both of which favor air stripping.

Addition of Powdered Activated Carbon to Biological Systems

The addition of powdered activated carbon (PAC) to the biological treatment systems is receiving considerable attention in the United States today, particularly with respect to the removal of the recalcitrant organic constituents, many of which constitute the "priority pollutants". With emphasis of the State and Federal regulatory authorities on upgrading effluent quality in terms of both the traditional organic pollutants as expressed by BOD, COD, TOC, or TOD, as well as the priority pollutants, both the industrial and municipal sectors of the economy are evaluating this approach based on its potential economic and process advantages over alternative systems.

The applicability of activated carbon in removing specific substrates depends on the molecular weight, solubility, polarity, location of functional groups, and overall molecular configuration. However, many of the organic constituents included in the list of 129 "priority pollutants", as cited by the United States Environmental Protection Agency, are amenable to carbon adsorption as shown in Table 3. (20). This increases the attractiveness of this process, particularly when the removal of priority pollutants becomes the critical requirement for effluent quality control.

Investigations of PAC systems have centered around several process enhancement approaches. These include the enhancement of a system to receive shock loadings or temperature changes, improving non-biodegradable or persistant organics removal, improving removal of priority pollutants, improving color removal, enhancing the resistance to biologically toxic or static substances, improving the organic capacity of existing facilities, improving nitrification, suppressing foam in aeration system, improving sludge handling, and reducing sludge bulking. The emphasis in recent years has been primarily directed toward removal of toxic or hazardous pollutants, and removal of other residual organic compounds.

The applicability of activated carbon in upgrading

TABLE 3

Priority Pollutant Removals Across PACT System*

Compound	Concentration in ug/liter (ppb) Feed	PACT Effluent	Removal (%)
Volatile Organics			
Benzene	105	0.9	98
Carbon Tetrachloride	94	1.4	95
Chlorobenzene	1720	30	98
Chloroethane	280	12	94
Chloroform	201	21	81
Ethylbenzene	41	1.7	94
Methyl Chloride	1770	Nil	99
Tetrachloroethylene	24	1.7	93
Toluene	519	1.7	99
1,1,1-Trichloroethane	13	0.6	89
Trichloroethylene	41	1.9	94
Trichlorofluoromethane	155	3.0	95
Base-Neutral Extractables			
1,2-Dichlorobenzene	259	120	44
2,4-Dinitrotoluene	1900	243	65
2,6-Dinitrotoluene	1640	575	64
Nitrobenzene	454	2	99
1,2,4-Trichlorobenzene	523	169	66
Acid Extractables			
2-Chlorophenol	11	1.6	95
2,4-Dinitrophenol	161	5.0	98
4-Nitrophenol	1020	10	97
Phenol	489	38	94

*Values are averages of data which show significant day-to-day variations in removals. Results were obtained by GC/MS analyses of plant samples and are subject to analytical error.

treatment systems by removing organic and selected inorganic constituents should first be tested using batch reactors in an isotherm approach (21). This involves adding washed, powdered activated carbon to predetermined volumes of wastewater at various concentrations, then measuring the residual constituent concentration at equilibrium. The isotherms can be analyzed in terms of COD, TOC, TOD, or specific compound concentrations. The general equation for such a test can be expressed as follows:

$$\log (C_o - C_f) - \log M = \log K + 1/n \log C_f$$

Where: (Eq.8)

C_o = initial concentration, mg/l
C_f = final concentration, mg/l
K = Freundlich constant, mg/gm
1/n = Freundlich constant
M = carbon dosage, mg/l

A PAC dosage can be estimated from such data, although these requirements should be considered as approximations only.

Following screening tests, bench-scale continuous reactors can be used to develop basic design criteria. These reactors can be used in parallel, using one as a control unit with no PAC addition and adding PAC to the other units controlling operating variables, such as temperature, pH, MLSS, and organic loading. PAC relationships can then be developed for selecting the desired carbon dosage and PAC mixed liquor to achieve the stipulated effluent quality in terms of both conventional parameters and specific toxic constituents. The two are interrelated and are a function of sludge age. By definition, biological sludge age in an activated sludge plant is:

$$\theta = \frac{X_{a_{bio}} V}{Q_w X_u + (Q - Q_w) X_e} \qquad \text{(Eq.9)}$$

Where:

θ = biological sludge age
$X_{a_{bio}}$ = average MLSS concentration (biological)
Q_w = sludge wastage flow
X_u = sludge underflow concentration
Q = total flow
X_e = effluent TSS concentration

The PAC dosage-equilibrium PAC MLSS concentration can then be defined, based on a mass balance, as follows:

$$X_{e_{PAC}} = \frac{X_i \theta}{HRT} \qquad \text{(Eq.10)}$$

Where:

$X_{e_{PAC}}$ = equilibrium PAC MLSS concentration
X_i = PAC dosage
θ = sludge age
HRT = hydraulic retention time

It should be noted that the total MLSS in a PAC aeration basin will normally be half biological and half carbon, the exact ratio depending on the nature of the substrate (or adsorbate), the biochemical synthesis coefficient, and the biological sludge age. However, this ratio is affected by several variables and makes it difficult to theoretically predict the powdered carbon and biomass responses in a PAC - Activated Sludge system. Moreover, the carbon adsorptive capacities, as affected by sludge age, are influenced by the nature of the adsorbate, the degree of biological regeneration, and the influent concentration of the organic constituents. Empirically derived information is thus required to establish a data base from which PAC process decisions can be made.

Conclusion

The incentives for treating liquid-phase toxic or hazardous constituents using biological methods is overwhelming when considering the process alternatives. However, the process applicability must be proven, the system has to be engineered to enhance biodegradation, and the facility operation must be sensitive to idiosyncracies of the biomass and the organic constituents.

The three major pathways of removal in a biological system have been discussed herein. Biochemical oxidation appears to be the dominant pathway for removing most toxic or hazardous constituents although sorption on the biological floc may be significant when suspended or colloidal organic fractions appear. Air stripping of volatiles may occur in a biological aeration basin, but the evidence indicates this fraction is not significant in the presence of an active biomass. Confirmation of these fractions through material balances may be required if the situation dictates.

The use of powdered activated carbon added to the aeration basin may be considered to enhance the removal of the recalcitrant and persistant constituents should this additional step be required.

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DESIGN, OPERATION AND CONTROL OF BIOLOGICAL NITRIFICATION - DENITRIFICATION SYSTEMS

INTRODUCTION

The increasing emphasis on reducing the ammonia nitrogen content of industrial wastewaters discharged to the aquatic environment has necessitated a more introspective analysis of the biological removal of nitrogen. This form of ammonia removal, while subject to many process and operation vagaries, still is generally the most attractive candidate system for ammonia removal in terms of process applicability and cost-effectiveness. It is recognized, however, that the nitrifying and denitrifying microorganisms are environmentally sensitive and subject to many process variables. There is prolific literature addressing this subject, but the process variables and descriptive parameters are often expressed in non-quantitative terms or inadequately interpreted. It is, therefore, the objective of this chapter to discuss the concepts of biological nitrification and denitrification, consider aspects of design, and outline operational techniques necessary for process control.

THE NITROGEN CYCLE

Nitrogen exists in many compounds because of the high number of oxidation states it can assume. In ammonia or organic nitrogen compounds, which is the form most closely associated with plants and animals, its oxidation state is -3. At the other extreme, its oxidation state is +5 when in the nitrate form. In the environment, changes from one oxidation state to another can be biologically accomplished by living organisms. The relationship between the various compounds and transformations which can occur are often presented schematically in a diagram referred to as the nitrogen cycle as illustrated in Figure 5-1. The forms of nitrogen which are most prevalent in wastewaters and which require treatment are ammonia (as NH_4^+), nitrate (as NO_3^-), and organic nitrogen in the form of amines and other nitrogenated compounds.

The biological conversion of ammonia to nitrate (nitrification) and the subsequent reduction to nitrogen and nitrous oxide is illustrated in Figure 5-2. It is this transformation that, when controlled from a process point of view, provides a mechanism for reducing the nitrogen related pollution potential in wastewaters. The discussion will, therefore, relate to this biological transformation process.

NITRIFICATION

Ammonia and organic nitrogen are converted to nitrite and nitrate by the organisms Nitrosomonas and Nitrobacter, respectively. Since an accumulation of nitrite is rarely observed, it has been concluded that the rate of conversion of nitrite controls the rate of overall reaction. The specific reactions illustrated in Figure 5-2 are as follows: Ammonia is first oxidized to nitrite by Nitrosomonas:

$$NH_4^+ + 1.5\ O_2 \xrightarrow{\text{Nitrosomonas}} 2H^+ + H_2O + NO_2^- \qquad (5\text{-}1)$$

Davis L. Ford, Ph.D., P.E.

FIGURE 5-1

THE NITROGEN CYCLE

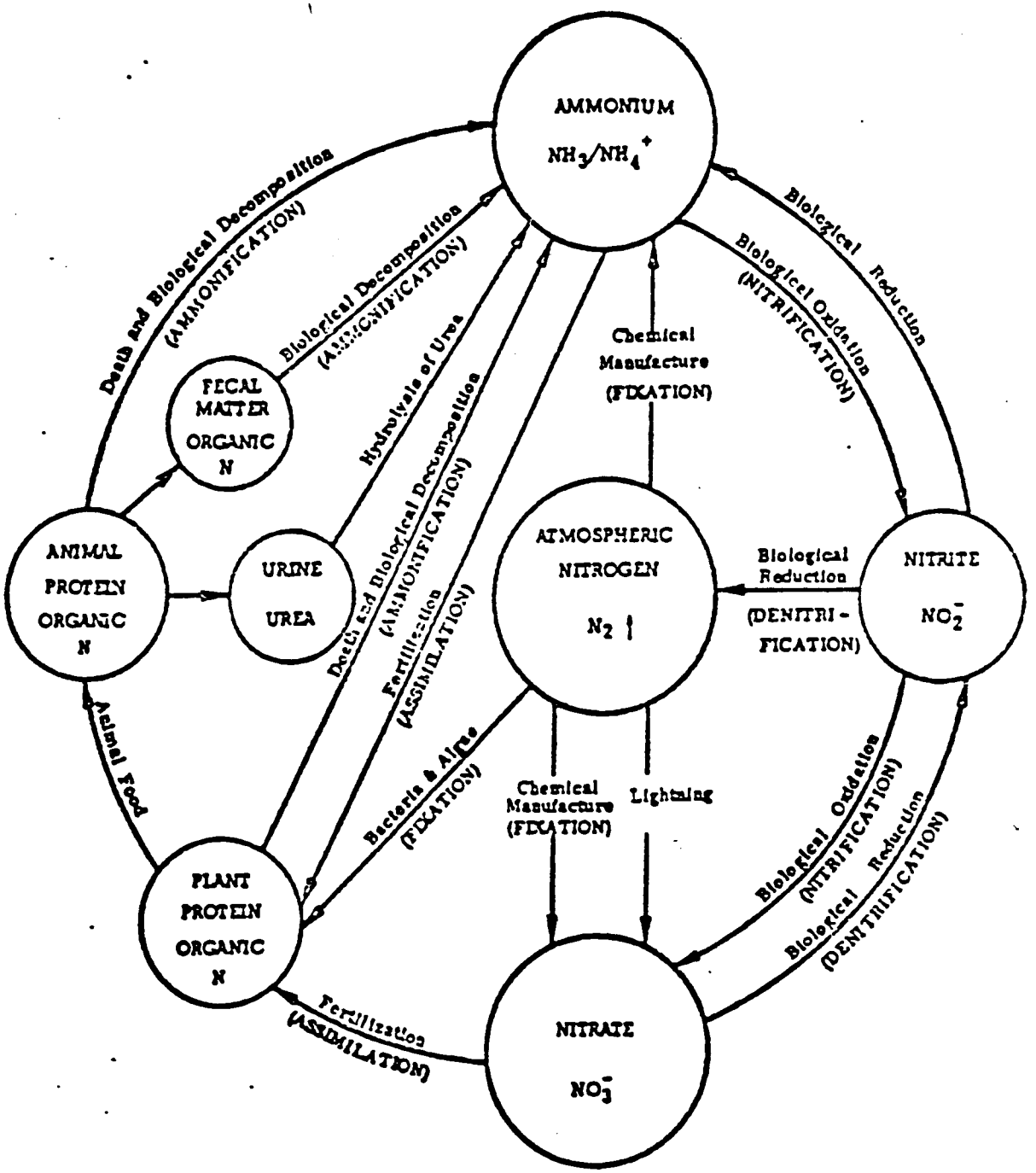
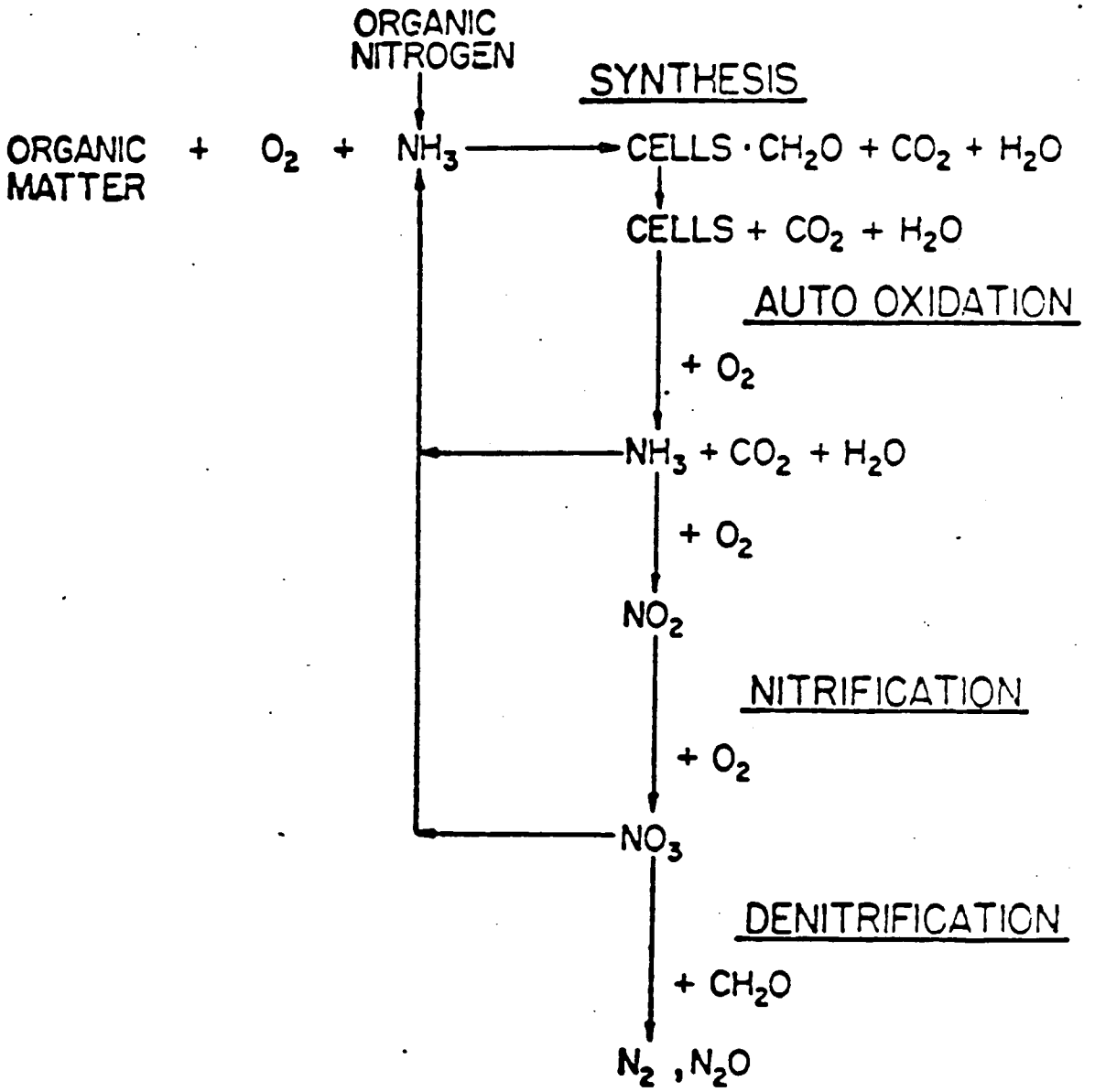


FIGURE 5-2

THE NITROGEN CYCLE BIOLOGICAL PROCESSES



Other organisms capable of oxidizing ammonia to nitrite are Nitrosococc/ Nitrosospima, Nitrosocystis, and Nitrosotloea, although these are probably of secondary importance in wastewater treatment systems. The theoretical demand for the biochemical oxidation of ammonia to nitrite is calculated as 3.43 lb. oxygen per lb. of ammonia oxidized.

The nitrite is then oxidized to nitrate by Nitrobacter:

$$2\ NO_2^- + O_2 \xrightarrow{\text{Nitrobacter}} 2\ NO_3^- \qquad (5\text{-}2)$$

The theoretical demand for the subsequent oxidation to nitrate is calculated as 1.14 lb. oxygen per lb. of nitrite oxidized.

Based on 120 BOD bottle studies evaluating the nitrification oxygen demand, it was concluded that 3.22 parts of oxygen are required per part of NH_4-N oxidized to NO_2-N and that 1.11 parts of oxygen are needed to oxidize to NO_3-N(1). This is slightly less than the theoretical value of 4.57, probably attributable to the fact that some of the reduced nitrogen is assimilated as cellular material in the carbon dioxide fixation reaction:

$$5CO_2 + NH_3 + 2H_2O \longrightarrow C_5H_7NO_2 + 5O_2 \qquad (5\text{-}3)$$

Factors Influencing Nitrification

There are many factors which affect nitrification. It is first pertinent to note the characteristics of nitrifying bacteria as cited in Table 5-1 (2). It is noted that both Nitrobacter and Nitrosomonas are both autotrophic aerobes with a relatively slow generation time. Given this information, some of the more prevalent factors which influence nitrification are cited below:

Temperature - The optimum temperature for nitrification is generally placed in the range of 28 to 32°C. As shown in Figure 5-3, there is a significant reduction as the temperature is reduced. It is generally assumed that for all practical purposes, nitrification ceases to proceed below 5°C or above 45°C. The required detention time for successful nitrification may be several times greater in the winter than in the summer for adequate nitrification. This may necessitate operating at higher sludge ages (or MLSS values) in the winter to maintain the required level of nitrification. Recorded data from a nitrifying tower using redwood slats also indicate a slightly pronounced effect than observed in a fluidized activated sludge system.

Dissolved Oxygen Levels - There has been considerable debate over the optimum dissolved oxygen level for maximum rates of nitrification. Early work by Downing indicated that maximum rates of nitrification proceeded only at dissolved oxygen levels greater than 3 mg/l (3). More recent work has indicated that there is no apparent inhibition of nitrification at D.O. levels exceeding 1.5 mg/l but that D.O. levels below 0.5 mg/l will have a negative influence on nitrification as the microorganisms are obligately aerobic (4).

pH Level - The rate of ammonia oxidation to nitrate declines in the acid range for both unacclimated and acclimated cultures. The rate

TABLE 5-1

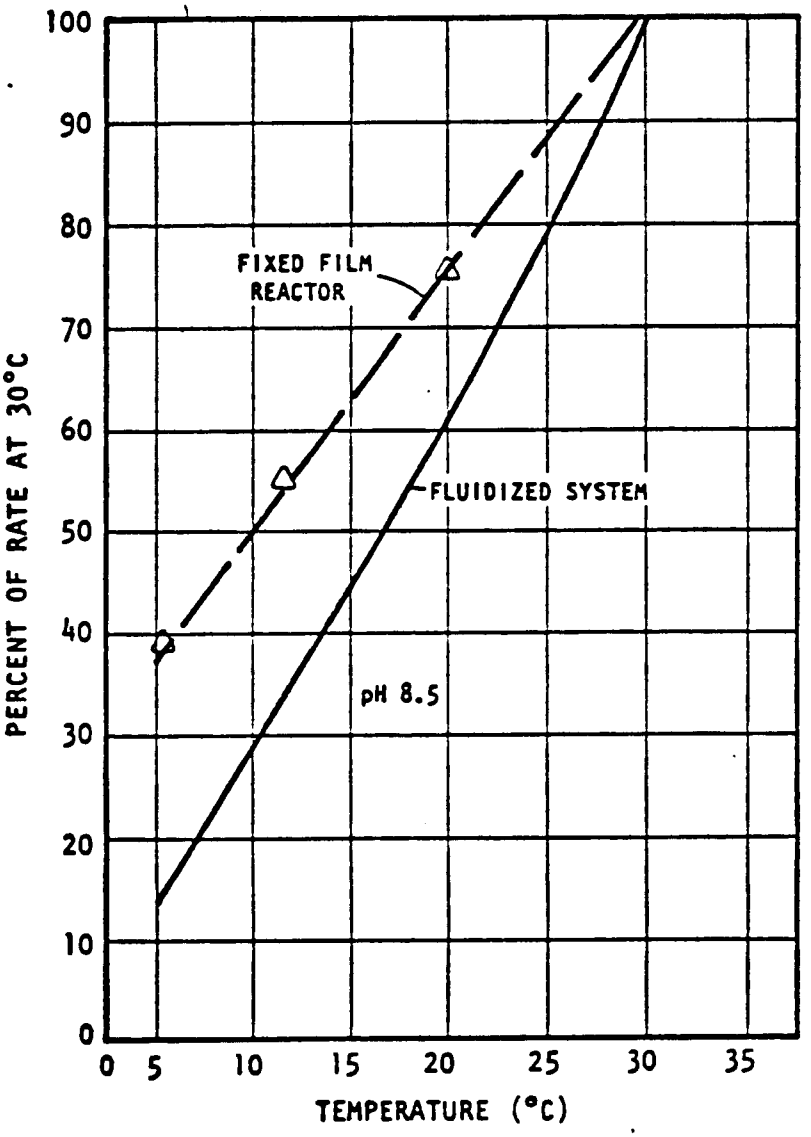
SOME CHARACTERISTICS OF NITRIFYING BACTERIA

	Nitrosomonas	Nitrobacter
Morphology:		
Cell Size	1 x 1.5μ	0.5 x 1μ
Cell Weight	0.12-0.5 x 10^{-12} g	-
Estimated Generation Time (hours)	8 - 36	12 - 59
Autotroph	Obligate	Facultative*
Oxygen Requirement	Strict Aerobe	Strict Aerobe
Yield Coefficient (lb cell/lb N oxidized)	0.04 - 0.13	0.02 - 0.07
Growth Constant (lb cell/lb cell/day	0.33 - 2.2	0.14 - 1.39
Saturation Constant (mg/l)	1.0 mg/l @ 20°C 10 mg/l @ 30°C	5 mg/l @ 25°C 8.4 mg/l @ 32°C

*Nitrobacter may grow on an organic carbon source, although an inorganic source is the preferred medium.

FIGURE 5-3

TEMPERATURE EFFECTS ON NITRIFICATION RATE



of nitrification begins to decrease somewhere at pH of 6.3 to 6.7. Generally, the rate is assumed constant in the range of 7.2 to 8.0. There is a wide range in reported pH optimum for nitrification, the results from most investigators shown in Figure 5-4.

Alkalinity - Alkalinity is destroyed by the oxidation of ammonia by virtue of the release of hydrogen ions as shown in Equation (5-1). Approximately 7.1 mg of alkalinity as $CaCO_3$ is destroyed per mg NH_3-N oxidized although this has been reported to be less at higher BOD-ammonia ratios and shorter sludge age (5). To maintain the optimal pH ranges in a normal activated sludge system, therefore, a highly buffered system is necessary to insure process control.

Substrate Loading and Sludge Age - There is considerable information relative to the effect of organic and ammonia loading on nitrification. The development of thresholds based on such loading possibly can be misleading as other factors may influence the threshold magnitude. However, it has been reported that nitrification is adversely affected in a municipal system once the organic loading exceeds 0.4 to 0.6 lbs. of BOD_5 per day 1 lb. MLVSS or a sludge age of less than four days (6). Industrial wastes may require lower organic loadings and longer sludge ages.

Another way of expressing the effect of substrate loading on nitrification thresholds is in terms of ammonia food to microorganism (F/M) ratio. For example, ammonia removal via nitrification as a function of ammonia loading for a chemical wastewater is shown in Figure 5-5, indicating a threshold of 0.45 to 0.55 lbs. of ammonia applied per day per lb. MLVSS (7).

Inhibition of Nitrifiers - The nitrifiers are extremely sensitive organisms and, although they may thrive and perform successfully under optimum conditions, severe upsets may occur in the presence of very small concentrations of inhibitory substances. Compounds which are most noted for toxicity and nitrifiers include heavy metals, cyanides, halogenated compounds, phenols, mercaptans, and thiourea. The presence of trace amounts of these constituents may not nullify nitrification, but could lower the rate substanially so that "washout" due to retarded growth may occur in the system. A partial list of organic compounds which inhibit nitrifiers is tabulated in Table 5-2 (8). The effect of metallic ions is also of concern. It is difficult to establish precise thresholds, because the chelation and precipitation potential will affect this value. However, it is believed that metal ion concentrations above 0.25 mg/l of copper nickel, or chromium can inhibit nitrification (5).

Two of the most important inhibatory constituents are substrate induced. In an attempt to identify the boundaries of free ammonia (FA) and free nitrous acid (FNA) inhibition on nitrifiers, a series of batch and continuous reactor experiments were conducted with the following results (7):

(1) FA inhibited Nitrosomonas at a concentration of 10 to 150 mg/l and inhibited Nitrobacter at a concentration of 0.1 to 1.0 mg/l; and

FIGURE 5-4

NITRIFICATION AS A FUNCTION OF pH

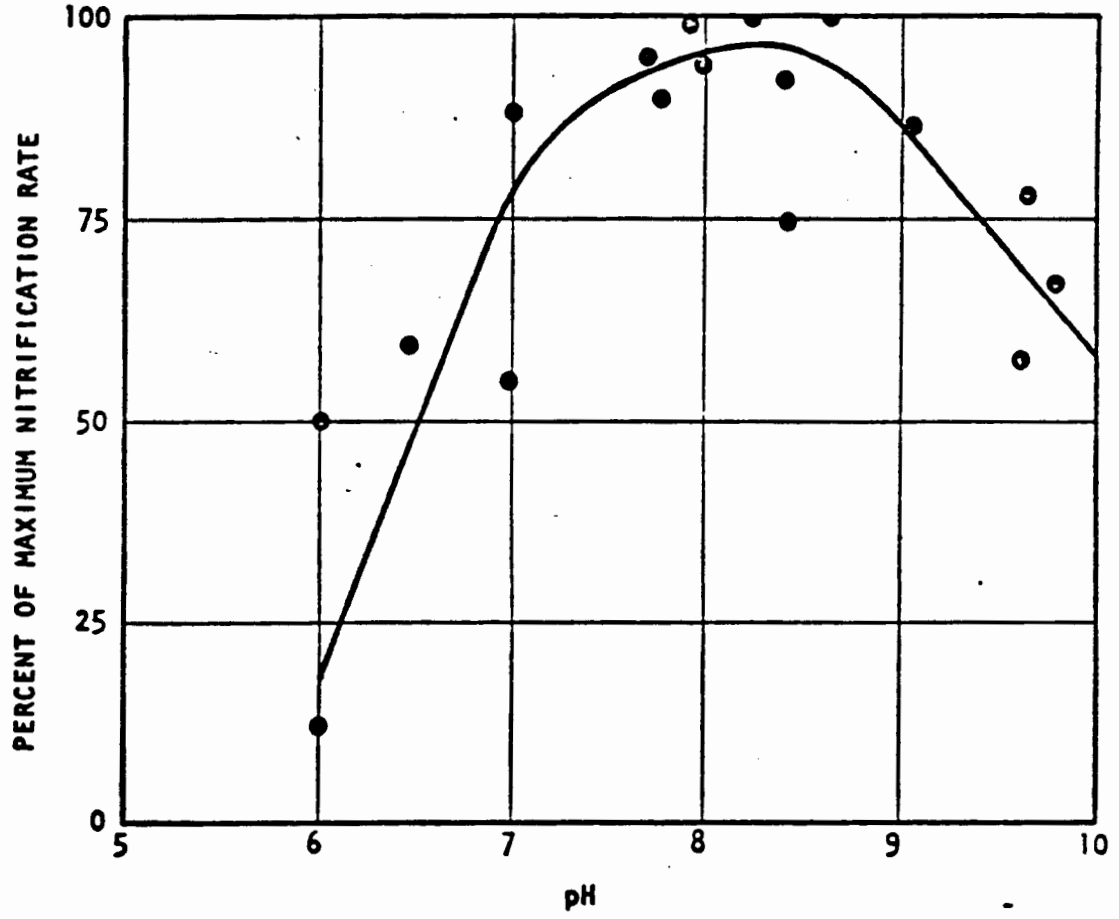


FIGURE 5-5

PHASE I EFFECT OF F/M RATIO ON AMMONIA REMOVAL

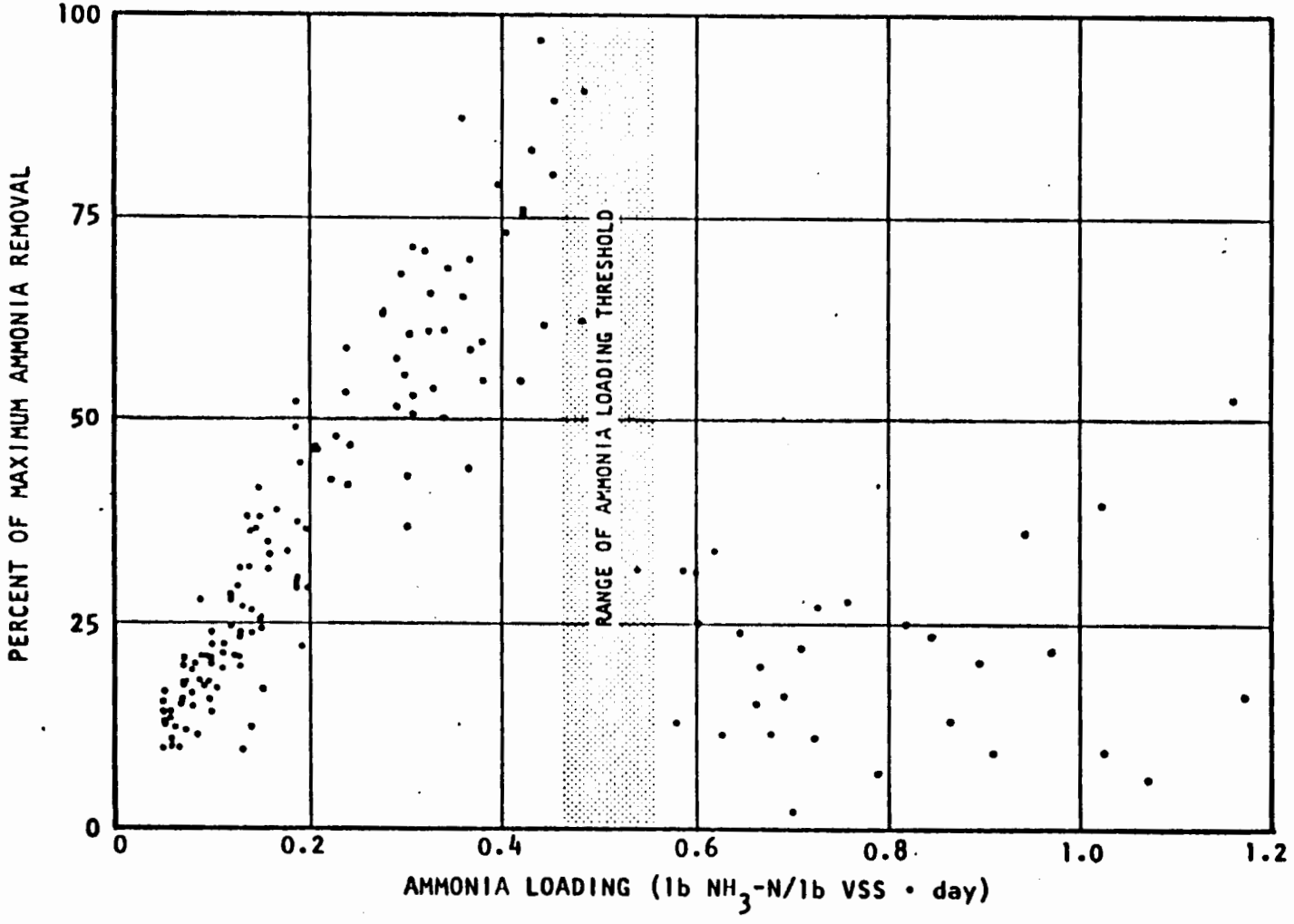


TABLE 5-2
ORGANIC COMPOUNDS THAT INHIBIT ACTIVATED SLUDGE NITRIFICATION

Compound	Concentration* mg/l
Acetone	2,000
Allyl alcohol	19.5
Allyl chloride	180
Allyl isothiocyanate	1.9
Benzothiazole disulfide	38
Carbon disulfide	35
Chloroform	18
o-Cresol	12.8
Di-allyl ether	100
Dicyandiamide	250
Diguanide	50
2,4-Dinitrophenol	460
Dithio-oxamide	1.1
Ethanol	2,400
Guanidine carbonate	16.5
Hydrazine	58
8-Hydroxyquinoline	72.5
Mercaptobenzothiazole	3.0
Methylamine hydrochloride	1,550
Methyl isothiocyanate	0.8
Methyl thiuronium sulfate	6.5
Phenol	5.6
Potassium thiocyanate	300
Skatol	7
Sodium dimethyl dithiocarbomate	13.6
Sodium methyl dithiocarbamate	0.9
Tetramethyl thiuram disulfide	30
Thioacetamide	0.53
Thiosemicarbazide	0.18
Thiourea	0.076
Trimethylamine	118

* Concentration giving approximately 75% inhibition.

(2) The inhibition of nitrifying organisms was first observed at FNA concentrations varying between 0.2 and 2.8 mg/l.

The FA concentration, as a function of pH, is based on the ammonia equilibrium:

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \qquad (5\text{-}4)$$

The FNA concentration, as a function of pH, is based on the nitrous acid equilibrium:

$$NO_2^- + H^+ \rightleftharpoons HNO_2 \qquad (5\text{-}5)$$

The FA concentration can be calculated based on the total ammonia concentration, the pH, and the liquid temperature as follows:

$$FA(\text{as } NH_3, \text{ mg/l}) = \frac{17}{14} \frac{[\text{Total } NH_3 \text{ (as N, mg/l)}][10^{pH}]}{(K_b/K_w + 10^{pH})} \qquad (5\text{-}6)$$

where:

K_b = the ionization constant of the ammonia equilibrium, and

K_w = the ionization constant of water.

$$\text{The ratio } (K_b/K_w) = e^{(6{,}334/273+°C)} \qquad (5\text{-}7)$$

The FNA concentration can be calculated based on the total nitrite concentration, the pH, and the liquid temperature as follows:

$$FNA \text{ (as } HNO_2, \text{ mg/l)} = \frac{46}{14} \frac{[NO_2\text{-N (as } NO_2, \text{ mg/l)}]}{(K_a)(10^{pH})} \qquad (5\text{-}8)$$

where:

K_a = the ionization constant of the nitrous acid equilibrium.

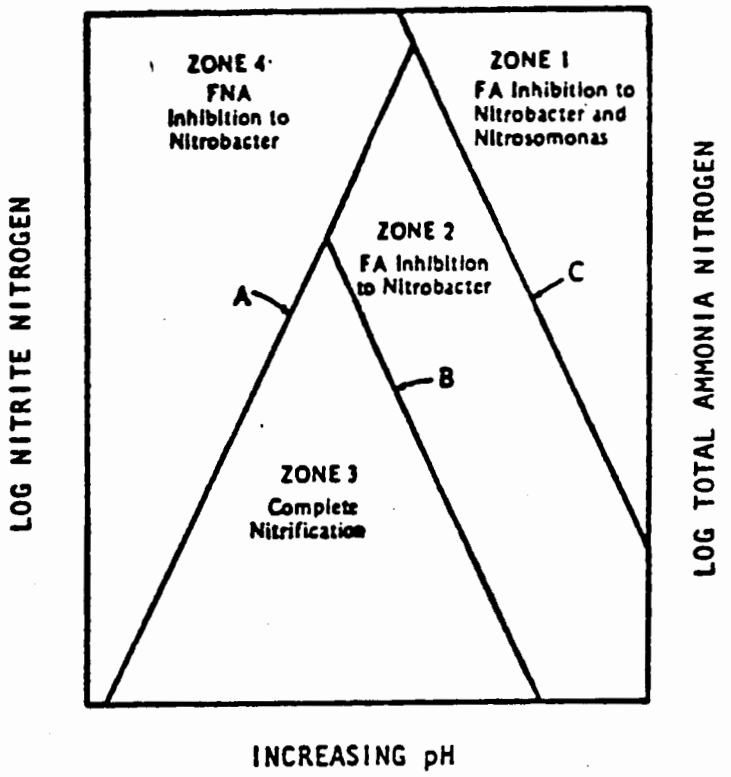
This constant can be related to temperature as follows:

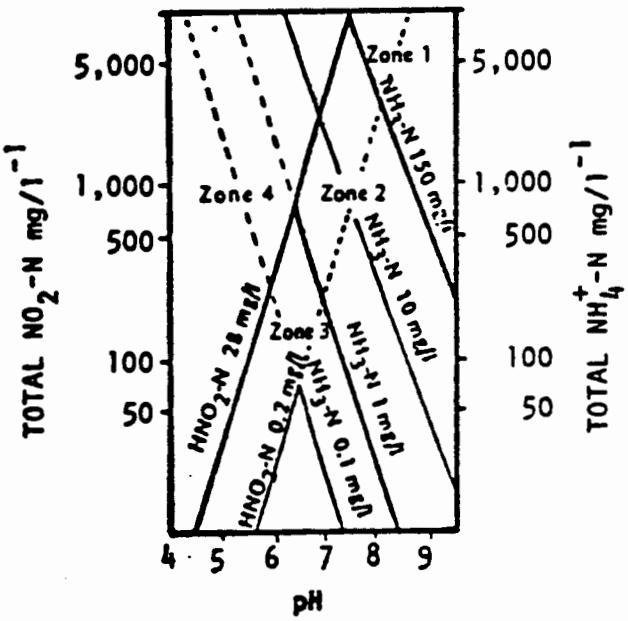
$$K_a = e^{(-2{,}300/273+°C)} \qquad (5\text{-}9)$$

Using these relationships and cognizant of FA and FNA inhibition as previously discussed, the interrelationship between inhibition thresholds, ammonia-nitrogen concentration, nitrite concentration, and pH can be displayed graphically as shown in Figure 5-6 (A) and (B). This graph, in conjunction with a more readable graphical

FIGURE 5-6

NITRIFICATION - TOLERANCE GRAPH





presentation of FA determination (Equation 5-6) as shown in Figure 5-7 and FNA determination (Equation 5-8) as shown in Figure 5-8, enables one to predict the substrate toxicity potential based on total ammonia, total nitrite, and pH conditions in a given nitrification treatment system (2).

It should be noted that biochemical ammonia removal via nitrification is normally independent of heterotrophic capability to remove COD. For example, Ford, et al noticed little effect of the COD removal capacity of an activated sludge system while increasing the ammonia loading to a level that caused the nitrification capacity to fail (7).

FIGURE 5-7

DETERMINATION OF FREE AMMONIA

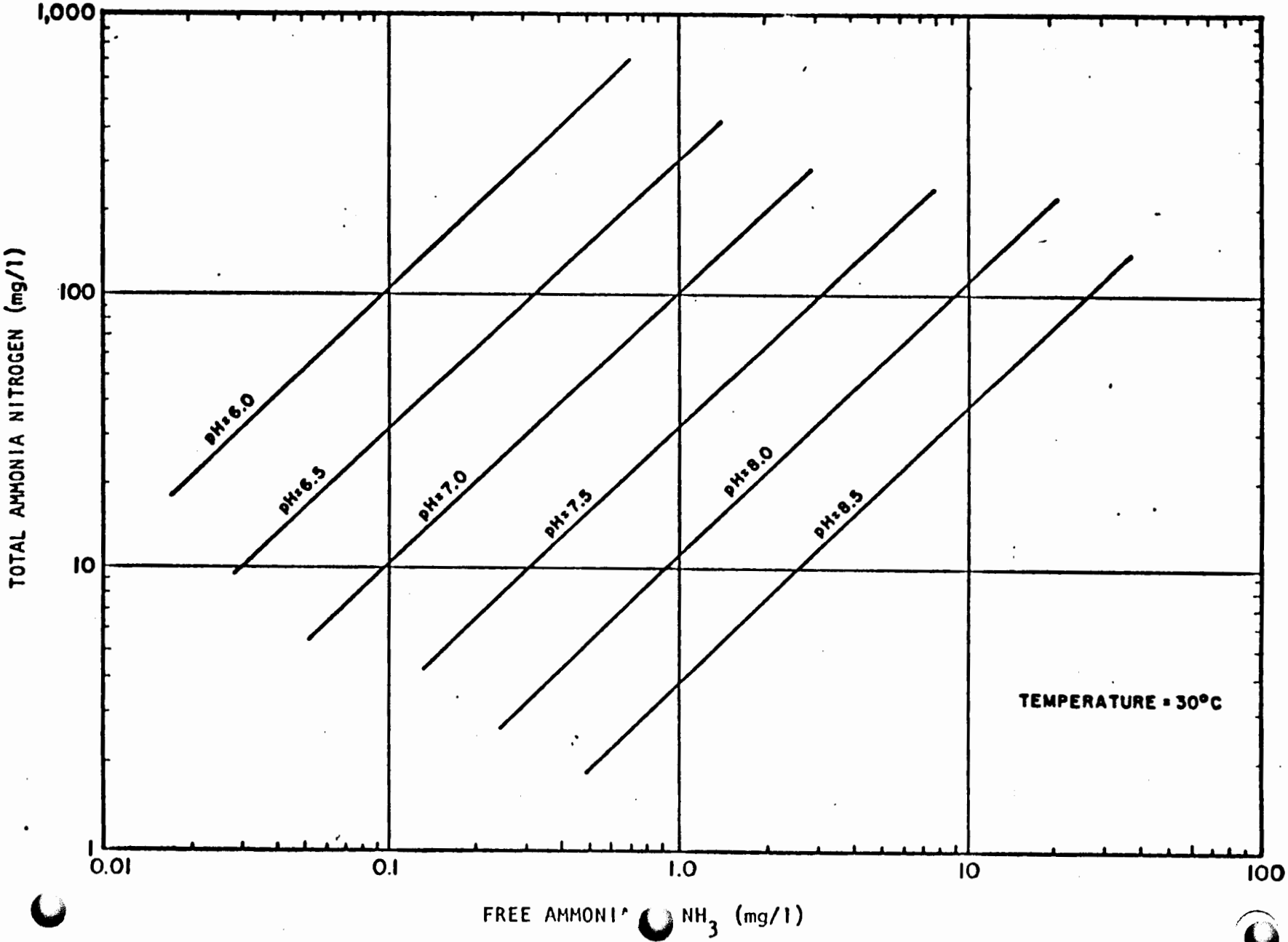
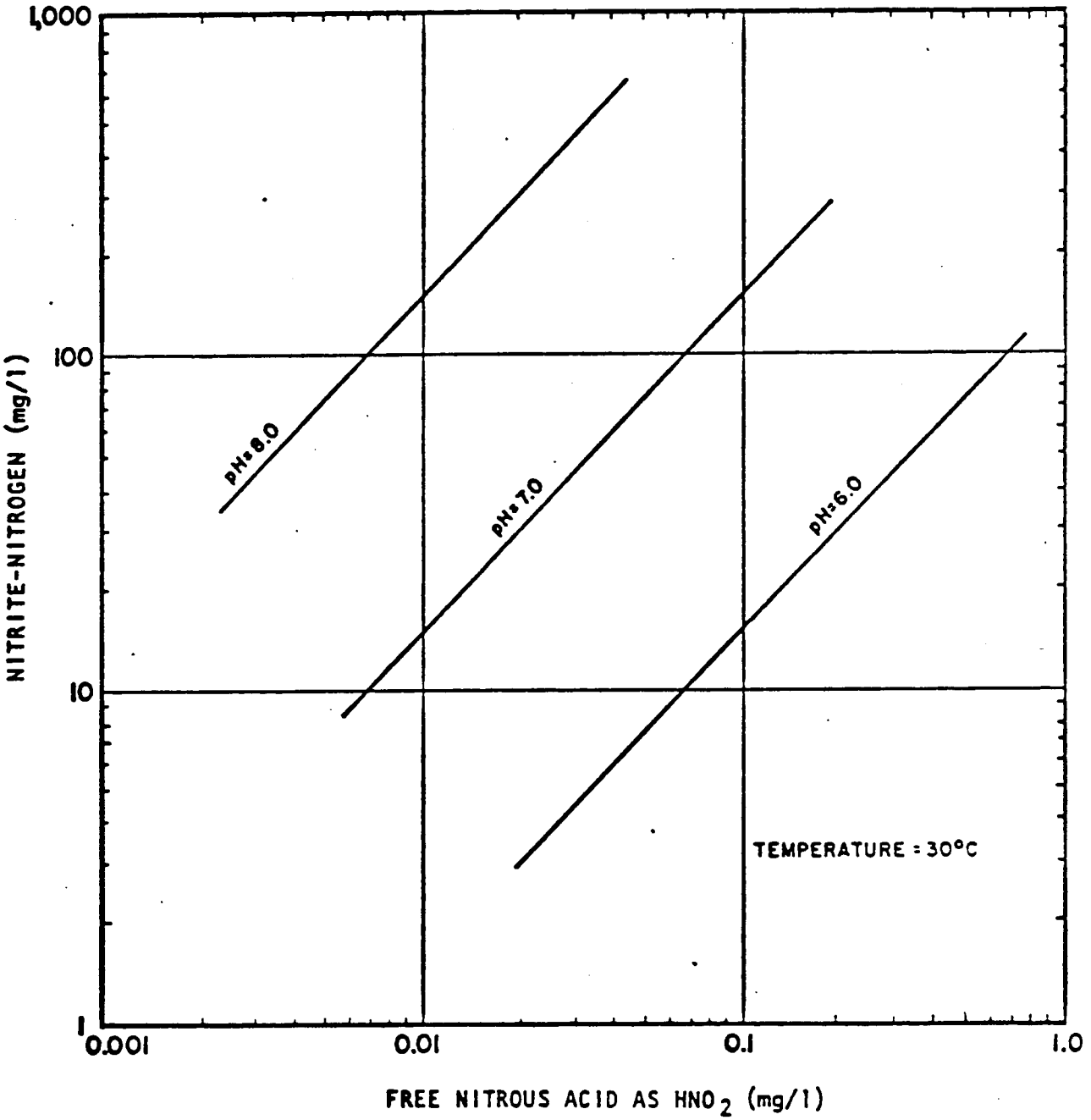


FIGURE 5-8

DETERMINATION OF FREE NITROUS ACID



Design Concepts of Nitrification Systems

Although the emphasis of this discussion is directed toward the operational and process control aspects of nitrification, a brief discussion of the mathematical design relationships and system design concepts are presented herein.

Mathematical Relationships

There have been many approaches proposed in defining nitrification kinetics in order to establish basic design criteria for nitrifying systems. The minimum aeration time to sustain nitrification in an activated sludge system operating at defined organic loading conditions was first defined by Downing et al (3). This relationship is:

$$t_m = \frac{S_o\ (.1 + .9t_m^{-\frac{1}{2}})}{(1 + r)}\ (\frac{1}{\hat{\mu}_n})(\frac{1}{X}) \qquad (5\text{-}10)$$

where:

t_m = minimum aeration time to sustain nitrification

$\hat{\mu}_n$ = maximum net specific growth rate of Nitrosomonas at the design temperature

r = hydraulic recycle ratio

S_o = influent BODs

X = biomass concentration

The overall relationship for substrate removal and bacterial growth as described by Monod can be expressed as:

$$-\frac{dS}{dt} = \frac{\hat{q}\ S}{K_s + S} \quad \text{and} \quad \frac{dX}{dt} = \frac{\hat{\mu}\ S}{K_s + S} \qquad (5\text{-}11)$$

where:

S = substrate concentration in reactor, mg/l

$\hat{q}$ = maximum substrate removal rate (mg N/mg VSS/day)

X = biomass concentration (mg/l)

K_s = saturation constant (mg/l)

$\hat{\mu}$ = maximum growth rate (mg cell/mg cell/day)

This relationship has been shown by several investigators to correspond to the growth of nitrifying organisms and removal of ammonia

nitrogen (3)(9). At low substrate concentrations, a first-order relationship is indicated. At high substrate concentrations, a maximum nitrification rate is approached and the reaction rate becomes zero order. The rate of change in cellular mass per unit cell mass per unit time is defined as the specific growth rate and is defined mathematically in Equation (5-11).

A mass balance for the system yields the relationship as follows assuming the specific growth rate includes both growth and endogenous metabolism.

$$V\,(dX/dt) = QX_o + \mu(V)X \qquad (5\text{-}12)$$

where:

V = reactor volume

X_o = initial biomass concentration

X = biomass concentration in reactor

Q = flow rate

Under steady-state conditions the equation reduces to the following form:

$$\frac{Q(X - X_o)}{X\,V} = \mu = \frac{\hat{\mu}\,S}{K_s + S} \qquad (5\text{-}13)$$

A mass balance can also be constructed for the substrate assuming that ammonia removal is only a result of oxidation by Nitrosomonas:

$$V\,(dS/dt) = Q\,(S_o - S) - q(V)X \qquad (5\text{-}14)$$

where:

S_o = initial ammonia concentration

S = ammonia concentration in reactor

Under steady-state conditions the equation reduces to the following form:

$$\frac{Q\,(S_o - S)}{X\,V} = q = \frac{\hat{q}\,S}{K_s + S} \qquad (5\text{-}15)$$

where:

q = specific removal rate (mg N/mg VSS/day)

A simplified design approach taking a different form has been suggested recently (6):

$$\frac{S}{S_o} = e^{-k_n (X_v t - X_L t)} \qquad (5\text{-}16)$$

where:

S = effluent ammonia concentration, mg/l

S_o = influent ammonia concentration, mg/l

k_n = nitrification rate coefficient, day^{-1}

X_v = MLSS concentration in basin

t = hydraulic retention time, days

$X_L t$ = limiting value of $X_v t$ below which nitrification is negligible

The theoretical oxygen requirements required to oxidize ammonia to nitrate as previously stated is 4.57 lbs per lb or an observed value of 4.3 lbs per lb as some nitrogen is assimilated as cellular material. Recent studies conducted by Ford, et al indicated oxygen uptake values correlated fairly well with ammonia removal as shown in Figure 5-9 (7).

From the trend shown in this Figure, it was estimated that the oxygen requirement ranges from 4.2 to 6.3 lbs per lb of ammonia oxidized including oxygen required for heterotrophic synthesis and respiration. The average requirement was approximately 5.6. When considering a theoretical oxygen requirement of 4.3 pounds to oxidize one pound of ammonia to nitrate and assuming 0.7 pounds of oxygen to satisfy one pound of COD, an approximate oxygen mass balance was calculated when "quasi-state-state" conditions prevailed:

4.3 [NH_3-N removed, mg/day] + 0.7 [COD removed, mg/day]

= [oxygen requirement, mg/day] (5-17)

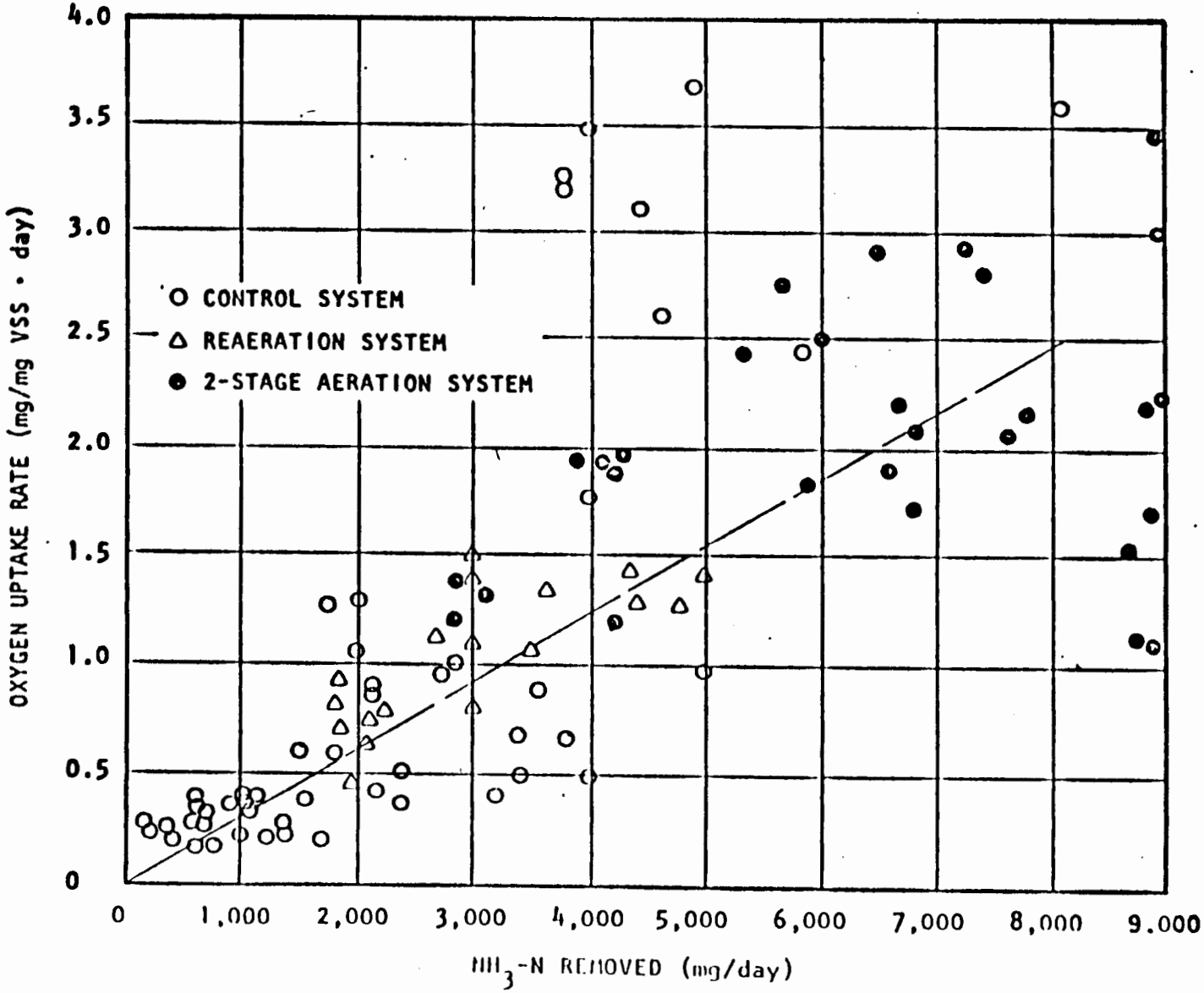
System Design Concepts

There have been many concepts of designing nitrification systems that have developed over the years, most of which have centered around some modification of fluidized activated sludge systems. However, recent work has included the use of rotating biological contactors for nitrifying wastewaters (10).

Nitrification can be achieved in a single stage-carbonaceous/ nitrification system assuming the aforementioned factors which affect nitrification are controlled. Of course, the retention time or sludge age must be sufficient to enable the nitrification reactions to approach completion. The use of side stream aeration (two aeration basins using a single clarifier) and two stage aeration (a series operated system with two clarifiers) have been shown to be nitrification-effective,

FIGURE 5-9

OXYGEN UPTAKE - AMMONIA REMOVAL RELATIONSHIP
(CONTROL SYSTEM)



with perhaps greater process reliability during cold weather periods and upset conditions (6). The use of rotating biological contactors has proven to be an effective nitrification approach, although subject to the same influencing factors that affect fluidized systems. It is interesting to note that altering the flow pattern in a four stage contactor system is reported to enhance the nitrification capacity at yarying temperature ranges. The concept is to design the system allowing the flexibility to operate the discs in parallel during the warmer months, seeding each stage, then using a series mode of operation in the winter.

A flow diagram of each of these nitrifying systems is presented in Figure 5-10.

Operational Control and Troubleshooting

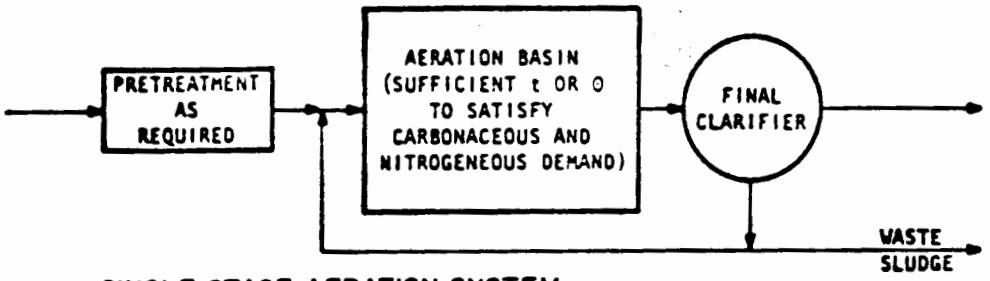
The concepts of nitrification and design approaches have been discussed. Given this background, it is important to understand how such systems can be utilized in an optimal manner through operational control and effective troubleshooting. The most significant factors which relate to operational control and troubleshooting are discussed in the following narrative.

Defining and Maintaining Nitrifying Population

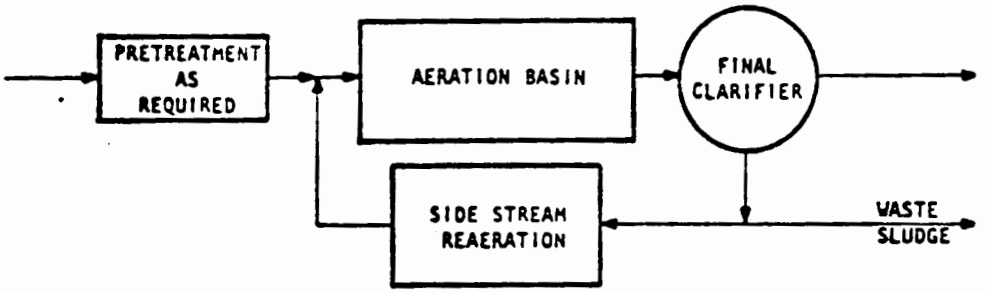
Most of the studies centering around process performance as a function of sludge age and concentration of nitrifiers has been predicated on mixed liquor volatile suspended solids (MLVSS) as an indicator of the nitrifying population. Although this may hold true for certain conditions, MLVSS is an inadequate parameter to express nitrifier concentration as there is no logical basis for correlating nitrifying bacteria and the volatile solids concentration in the mixed liquor. For this reason, the possibility of isolating Nitrosomonas and Nitrobacter in a mixed liquor sample was recently evaluated (7). It was determined that the Nitrosomonas and Nitrobacter could be isolated in a relatively short period of time using straight forward techniques. It is mandatory for these isolation techniques to be simple and rapid if they are to be used as a design or operating control tool. The procedure used for the selective enrichment of Nitrosomonas and Nitrobacter were developed in the latter part of the nineteenth century to isolate certain soil bacteria. The procedure used for this isolation is outlined in Table 5-3 (11)(12)(13). The plate count value of these isolated microorganisms expressed as a percent of the total plate count is indicative of the fraction of active biomass which are actually nitrifiers. As shown in Figure 5-11, it is interesting to note that this value was less than one percent of the active biomass in an activated sludge system successfully nitrifying an industrial waste. This increased to as high as ten percent as the influent ammonia nitrogen was synthetically increased, then diminishing somewhat as a further increase in ammonia nitrogen resulted in FA inhibition. Another expression of the nitrifying fraction of the active biomass is shown in Figure 5-12 where the nitrifiers are related to the ammonia removal. The value of the nitrifiers total plate count ratio can be a valuable aid in determining not only the presence or absence of nitrifiers in a system but also the relative numerical presence of these bacteria in the system. This number can, in turn, be used to determine the corrective action to be taken to upgrade or improve nitrification performance. For example, low values infer reseeding where high relative

FIGURE 5-10

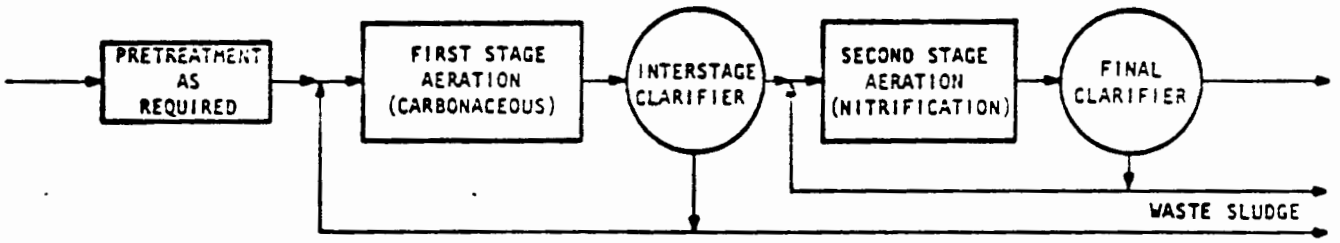
FLOW DIAGRAMS FOR CANDIDATE NITRIFYING SYSTEMS



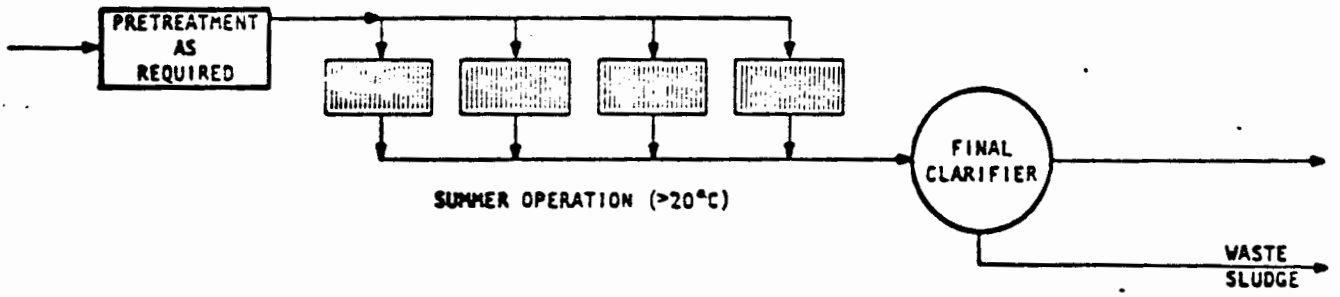
SINGLE STAGE AERATION SYSTEM

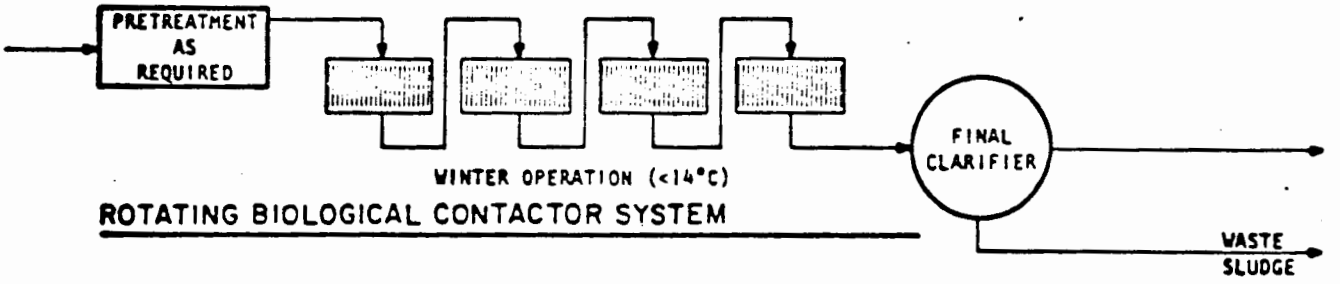


SIDE STREAM REAERATION SYSTEM



TWO STAGE AERATION SYSTEM





ROTATING BIOLOGICAL CONTACTOR SYSTEM

TABLE 5-3
PROCEDURE FOR NITRIFIER ISOLATION

1. Composition of basal medium (all amounts are in grams per liter).

K_2HPO_4	=	1.0 gm
$MgSO_4 \cdot 7H_2O$	=	0.2 gm
$FeSO_4 \cdot 7H_2O$	=	0.05 gm
$CaCl_2$	=	0.02 gm
$MnCl_2 \cdot 4H_2O$	=	0.002 gm
$NaMoO_4 \cdot 2H_2O$	=	0.001 gm

2. Selective medium for isolation of Nitrosomonas: Add NH_4Cl (1.5 gm) and $CaCO_3$ (5 gm) per liter of basal medium.

3. Selective medium for isolation of Nitrobacter: Add $NaNO_2$ (3.0 gm) per liter of basal medium.

4. For solidification of the media, 1.5 percent purified Agar (Difco) was added.

5. Media was autoclaved for 20 minutes (150°C at 20 psi).

6. Water blanks for determining colony counts were prepared as 10 ml volumes in screw-cap tubes and autoclaved as above.

7. Plates were incubated in darkness at 27°C for seven days before counts were determined.

8. Morphology:

   Nitrosomonas: small, compact, sharply-defined colonies, brownish in color.

   Nitrobacter: single colonies are small, compact, irregular in shape and brownish in color. (Note: inhibited by the presence of ammonia. Also the accumulation of nitrate arrests the reaction.)

FIGURE 5-11

PHASE II NITRIFIER PROFILE - CONTROL SYSTEM

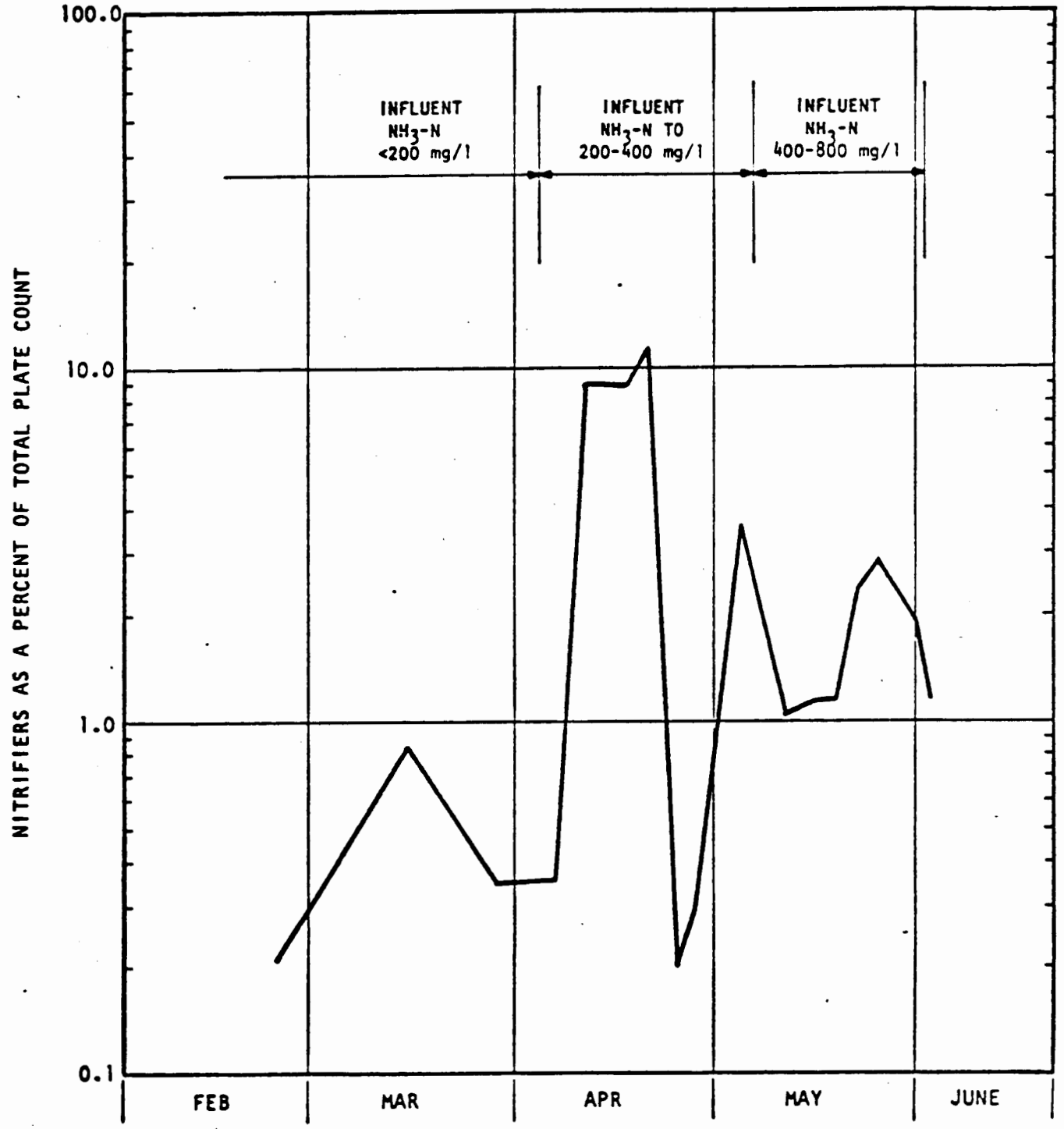
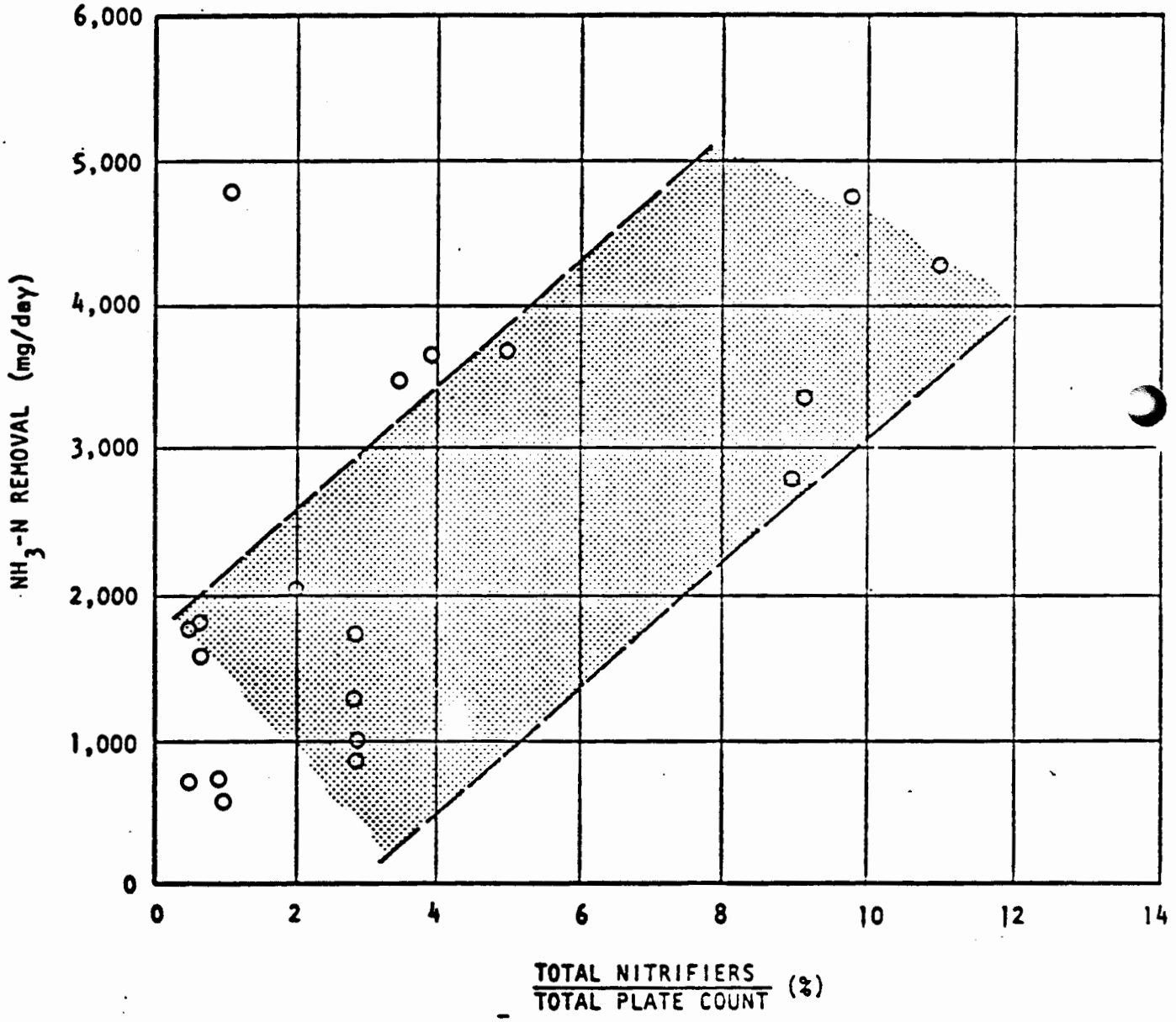


FIGURE 5-12

NITRIFIER - AMMONIA REMOVAL RELATIONSHIP



values coupled with poor nitrification performance indicates inhibition of the existing nitrifiers possibly due to pH, temperature, or the presence of inhibitory constituents.

There are several advantages of maintaining as many nitrifiers in the system as possible. First, the adverse temperature effect as shown in Figure 5-3 can be offsetted as more nitrifiers per unit volume are biochemically oxidizing the same quantity of ammonia nitrogen. The overall nitrification capacity can, therefore, be maintained using this approach. For example, it is noted in Figure 5-3 that a 50 percent reduction in rate is observed when the temperature is reduced from 18°C to 9°C. This is confirmed when comparing the correlation shown in Figure 5-13 between ammonia removal as a function of MLVSS levels (with limitations previously noted) and temperature. For example, the ammonia removal at 18°C with 1,000 mg/l MLVSS is the same at 9°C using 2,000 mg/l MLVSS. This, of course, would indicate the nitrifying fraction at 1,000 and 2,000 mg/l MLVSS remains unchanged. When solids levels are increased, several factors must be considered. First, the increased level of solids will result in an increased solids loading to the secondary clarifier which may cause poor thickening in the clarifier. This constraint might be critical during peak wet weather flow conditions. Secondly, the increased solids levels will result in a rapid depletion of dissolved oxygen in the mixed liquor and in the secondary clarifier. The low D.O. levels could very likely result in denitrification taking place in the secondary clarifier during warm weather operation. This denitrification will result in floating sludge and high effluent suspended solids levels. Consequently, a provision for rapid sludge removal should be incorporated into the clarifier design, also the use of scum weirs which will collect the floating sludge and allow the entrapped nitrogen gas bubbles to escape into the atmosphere should be considered. The sludge will then resettle in the clarifier, if the design is sufficiently conservative.

Dissolved Oxygen Control

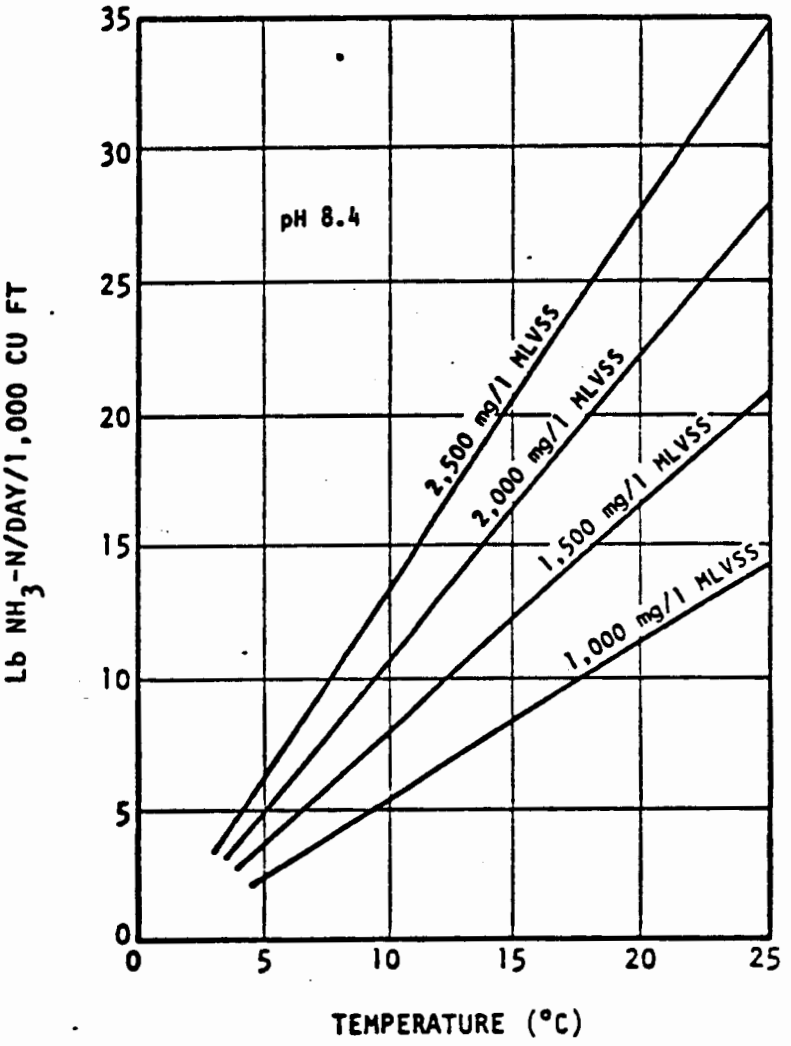
As indicated above, the presence of dissolved oxygen is critical to maintaining nitrification, either in a fluidized activated sludge system or in a fixed-bed reactor such as a nitrification tower or a rotating biological disc. For this reason, the dissolved oxygen level in the liquid should be carefully monitored and never allowed to fall below 1.5 mg/l. Below this value, a diminution of nitrifying activity can be expected.

Alkalinity and pH Control

The effect of alkalinity and pH on nitrifying systems has been discussed, the more salient facts being a drop-off of nitrification occurring when the pH falls below 6.5 to 7.0 and nitrification resulting in the destruction of alkalinity. It is, therefore, imperative that the system be adequately buffered to counteract its tendency to become more acidic through carbon dioxide production (heterotrophic biochemical oxidation) and/or the release of hydrogen ions (autotrophic nitrification). The destruction of alkalinity can be estimated by assuming 0.5 lbs of alkalinity destroyed per lb of BOD_5 removed and up to seven lbs of alkalinity removed per lb of ammonia nitrogen oxidized. This latter value decreases as the sludge age or the quantity of ammonia nitrogen is reduced, although seven lbs is appropriate for estimating purposes.

FIGURE 5-13

SOLIDS AND TEMPERATURE EFFECTS ON OPERATION



Depending on the type of hardness, carbonate, bicarbonate, or hydroxide alkalinity can be added, the form depending on which would be the least likely to precipitate. In the case of a rotating biological contactor, alkalinity can be added between selected stages, depending on the pH profile.

It is important to maintain the proper pH in the system, and residual buffer in the effluent assures pH stability and infers the presence of inorganic carbon for the autotrophic nitrifiers.

Influent Transients

Due to the low growth rate of the nitrifying organisms, the rate of assimilation of ammonia is slow. Consequently, the nitrifying organisms are not capable of rapidly assimilating large transients of ammonia introduced into the aeration basin. Under these conditions, much of the ammonia will pass through the system untreated. Although the nitrifiers are capable of adapting to low concentrations of inhibitory compounds, slight shocks can cause dramatic changes in the performance of the system. For this reason, equalization (or possibly the addition of powdered activated carbon) can sequester these transient inputs and assist in nitrification reliability.

Detection and Control of Inhibitory Substances

Nitrifiers are subject to many inhibitory substances, and when a nitrification process is not performing to the desired level of efficiency the possible presence of biotoxic or biostatic constituents should be investigated. There are several detection approaches and these are discussed briefly:

(a) Check potential nitrification toxicity using the standard BOD test - Monitor ammonia nitrogen during BOD incubation at various dilutions, and note reduction as a function of dilution.

(b) Verify the presence of nitrifiers using the previously cited isolation techniques - The reduction of nitrifiers as a function of total plant count from a "baseline" number indicates the presence of inhibitory or toxic substances.

(c) Check potential nitrification toxicity using a manometric technique (14) - This approach involves the use of a number of electrolytic respirometer sample bottles. During biological activity, oxygen depleted in the liquid sample is replenished by oxygen transfer from the gas phase above the liquid. CO_2 escapes to the gas phase and is absorbed by KOH solution. The corresponding pressure decrease in the gas phase activates a current in the electrolytic cell and oxygen is produced and released to the gas phase to increase the pressure to its normal level. The oxygen produced is recorded and related to the degradation of wastewater.

The nitrification toxicity test involves innoculating wastewater samples with active nitrifying organisms and using the electrolytic respirometer to observe the presence and relative rate of nitrification. If nitrification is not

observed, the wastewater contains toxic substances at sufficient levels to inhibit nitrifying bacteria. Normally, wastewater that is known to be easily nitrified is tested in parallel with wastewater under study. This allows a measurement of the activity of the nitrifying seed and a comparison to the nitrification rate of an easily nitrified wastewater.

Inhibitory substances can be categorized into three general headings, namely, organic inhibitors, some of which are cited in Table 5-2; heavy metals; and substrate ammonia nitrogen and nitrite nitrogen. Once specific constituents are determined to inhibit the nitrification process, candidate pretreatment steps and associated economics can be evaluated. For example, granular activated carbon pretreatment or the direct addition of powdered activated carbon to a fluidized system (or even in the liquid phase of a rotating biological contactor) may reduce the organic toxicants to sub-toxic levels. Chemical reduction and precipitation is commonly used to reduce heavy metal concentrations, and equalization combined with moderate air stripping and/or lowering the pH may reduce free ammonia to sub-inhibitory levels. It is, therefore, necessary to evaluate the applicability of these processes, verify their ability to enhance the nitrification process, and estimate the associated capital and operating costs.

Summary

It is important in any treatment system to detect process problems and offer remedies in the shortest time possible. A troubleshooting guide has been prepared to facilitate this approach and is presented in Table 5-4.

TABLE 5-4

TROUBLESHOOTING GUIDE - NITRIFICATION

Operational Problem	Possible Cause	Troubleshooting Action
Reduction in Nitrification - Increase in effluent ammonia nitrogen concentration	Temperature	Increase nitrifying concentration; alter aeration mode to reduce heat loss if D.O. can be maintained; investigate possibility of modifying waste stream routing or adding heat to maintain liquid temperature during winter months. In rotating biological contactor systems, consider changing flow from a parallel to a series operation.
	Dissolved Oxygen	Insure a minimum of 1.5 mg/l D.O. is in all portions of the basin; increase aeration capacity or reduce MLVSS (if possible from a process point of view) to insure adequate oxygen is available for the nitrifiers.
	pH/Alkalinity	Nitrifiers are sensitive to pH - insure pH in range of 7 to 9 is maintained wherever nitrifiers are in contact with the substrate. System must be buffered as pH will tend to drop as nitrification occurs. Residual alkalinity in effluent of approximately 50-100 mg/l (as $CaCO_3$) desirable to insure a buffer and provide an inorganic carbon source.
	Inadequate Sludge Age	Increase sludge age to the maximum practical level by increasing MLVSS, assuming adequate D.O. can be maintained and solids level to clarifier is not excessive.
	Inadequate Nitrifying Population	Increase MLVSS if possible; verify adequate fraction of MLVSS are nitrifiers using isolation techniques as discussed herein. Reseeding from good nitrifying plants may be required.
	Presence of Toxic or Inhibitory Substances	Verify presence of inhibitory or toxic substances by one o methods discussed in this section. Review efficacy of pretreatment to reduce constituent(s) to sub-toxic or sub-inhibitory levels. Consider the possibility of adding powdered activated carbon directly to the mixed liquor to remove organic precursors. Pre-equalization possibly will help

DENITRIFICATION

Biological denitrification is the dissimilative reduction of nitrate nitrogen into atmospheric nitrogen, with some nitrous oxide (N_2O) and nitric oxide (NO) also evolving. It should be recognized that nitrate nitrogen also can be reduced to the ammonia oxidation level followed by incorporation as nitrogen into the bacterial cellular mass. These assimilative reactions should not be confused with denitrification.

The denitrification process can be carried out in a fluidized or suspended biological system or in fixed film reactors. Anoxic conditions usually prevail, and a carbon and energy source is required with nitrate being the electron acceptor. A broad range of facultative heterotrophic bacteria can accomplish denitrification and these include Psuedomonas, Micrococcus Achromobacter and Bacillus. Some 36 different species of bacteria have been identified as denitrifying (15).

The Mechanisms of Denitrification

Most denitrifying bacteria are chemoorganotrophic or bacteria which utilize organic compounds as electron donors. As many bacteria can denitrify, very little can be concluded from identifying and quantifying bacterial species which are actively denitrifying as has been proposed for their nitrifying counterparts. Design and operation, therefore, has to be based on empirically-derived information.

The first step in the reduction of nitrate is the conversion to nitrite.

$$NO_3^- + 2e \longrightarrow NO_2^- \qquad (5\text{-}18)$$

This reduction from an oxidation level of (+5) to (+3) is well documented, although the subsequent reduction to nitrous oxide, nitric oxide, and nitrogen gas is less defined. The chain of reaction is branched which accounts for the various end-products. Two mechanisms for the production of nitrous oxide, for example, are:

$$2NO_2^- \longrightarrow 2NO + N_2O \qquad (5\text{-}19)$$

and

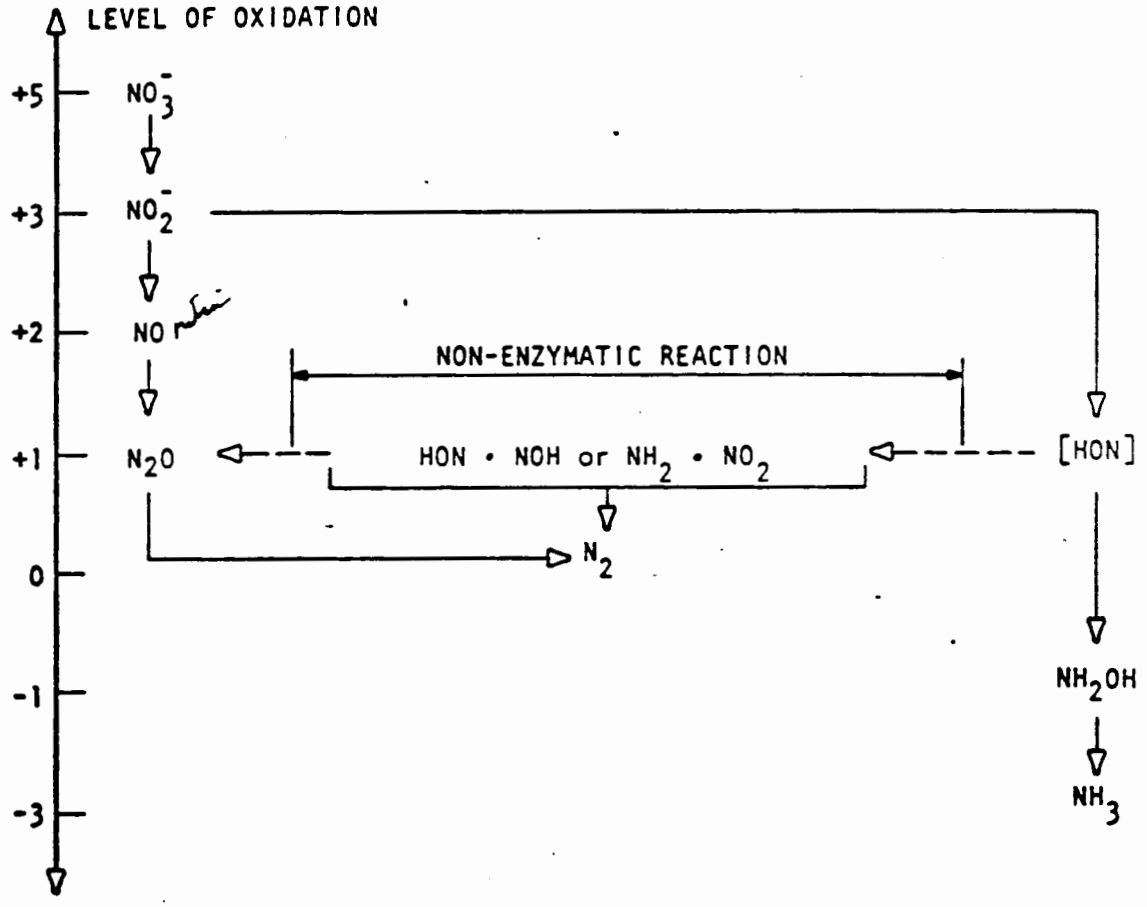
$$2NO_2^- \longrightarrow 2(NOH) \longrightarrow (NOH)_2 + N_2O \qquad (5\text{-}20)$$

Most investigators agree that either nitrous oxide or nitric oxide are obligatory intermediates in the formation of atmospheric nitrogen. The branched reaction assumes a non-enzymatical dimerization to form hyponitrite or nitriamide as shown in the proposed denitrification reaction sequence illustrated in Figure 5-14(15).

As previously indicated, NO_3^- is the final electron acceptor, with some organic carbon source being required as the electron donor. Oxygen competes with nitrate as the electron acceptor, and has a higher affinity for electrons. The presence of oxygen, therefore, will immediately result in the transfer of the transport system electrons from nitrate to oxygen, explaining why denitrification depends on anaerobiosis in order to properly function.

FIGURE 5-14

REACTION SEQUENCE OF NITRATE REDUCTION



Denitrifying microorganisms require an organic electron donor as previously stated, as well as trace mineral nutrients such as calcium, magnesium, potassium, sodium, and phosphate. Nitrate nitrogen can function as the sole nitrogen source in many cases, but some denitrifiers require other nitrogenous compounds such as amino acids or ammonium (16).

Factors Influencing Denitrification

As in nitrification, there are many factors which influence both the rate and extent of denitrification. A discussion of the more prevalent factors is presented herein.

Temperature

As in all biochemical reactions, denitrification is temperature dependent. The temperature effect has been determined to follow the Arrhenius Law which states:

$$k_m = A^{-\frac{E}{RT}} \qquad (5\text{-}21)$$

where:

k_m = maximum growth rate

A = frequency factor

E = energy of activation

R = ideal gas constant

T = temperature

or the more commonly expressed approximation:

$$\mu_{m_T} = \mu_{m_{20}} \theta^{(T-20)} \qquad (5\text{-}22)$$

The θ value as determined by Dawson and Murphy was determined to be 1.12 in the temperature interval between 5°C and 27°C. The results of Mulbarger, et al, evaluating denitrification rates as a function of temperature shown in Figure 5-15 fairly well track this value (17).

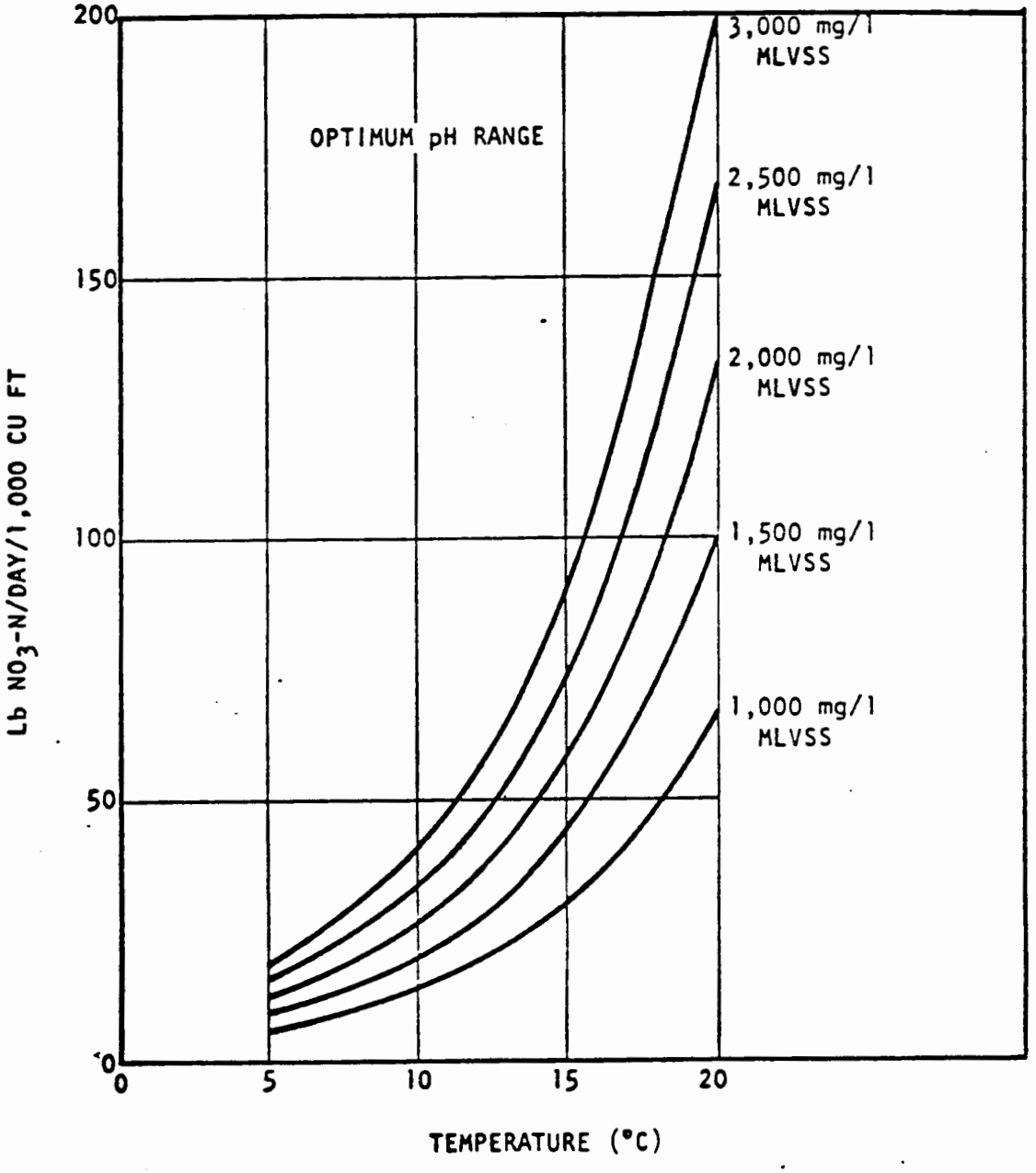
It is important to note that denitrification does occur in the 5 to 10°C range albeit slow, indicating an incentive to operate at the highest possible MLVSS level possible to offset the decreased rate with an increased denitrifying population.

Dissolved Oxygen Levels

As mentioned previously, denitrification is an anaerobic process, primarily based on the fact that oxygen competes with nitrate as an electron acceptor, retarding the actual removal of nitrate. Unlike the anaerobic fermentation processes, the concern of oxygen presence is not toxicity, but competition. First, assimilative nitrate reduction is

FIGURE 5-15

DENITRIFICATION - TEMPERATURE RELATIONSHIP



SOURCE: BASED ON DENITRIFICATION RATES OBSERVED AT MANASSAS, VA. (REF: MULBARGER)

unaffected by the presence of oxygen. The need for anaerobiosis for dissimilative reduction has been demonstrated, although the effect of oxygen is dependent of several factors. Wuhrmann, et al, for example, have shown that the presence of oxygen is more retardant to dissimilative denitrification in the neutral pH range as compared to that in a slightly acidic environment (18). In summary, anaerobiosis should be maintained in a denitrification system, but the effect of oxygen and its mechanism in affecting nitrate reduction should be understood.

pH Level

The pH affects denitrification in accordance with the general knowledge of the influence of pH on biological reactions. The effect of pH on the denitrification rate as reported by several investigators is plotted in Figure 5-16 (17). This infers an optimal pH range from 6.5 to 8.

Denitrification tends to raise the pH of the system by producing alkalinity from the organic electron donor as shown in the following overall reaction:

$$5CH_3OH + 6NO_3^- \longrightarrow 5CO_2 + 3N_2 + 6OH^- + 7H_2O \qquad (5\text{-}23)$$

The production of CO_2 and OH^- leaves a net of 1/6 mole of hydroxyl ions to raise the pH of the liquid. The expression of sequential transformation from nitrate to nitrogen in the presence of an organic electron donor is:

$$3NO_3^- + CH_3OH \longrightarrow 3NO_2^- + H_2CO_3 + H_2O \qquad (5\text{-}24)$$

and

$$2NO_2^- + CH_3OH + H_2CO_3 \longrightarrow N_2 + 2HCO_3^- + 2H_2O \qquad (5\text{-}25)$$

It has been estimated that the alkalinity gain via denitrification is approximately half the loss which occurs during nitrification (19).

Carbon Source for Denitrification

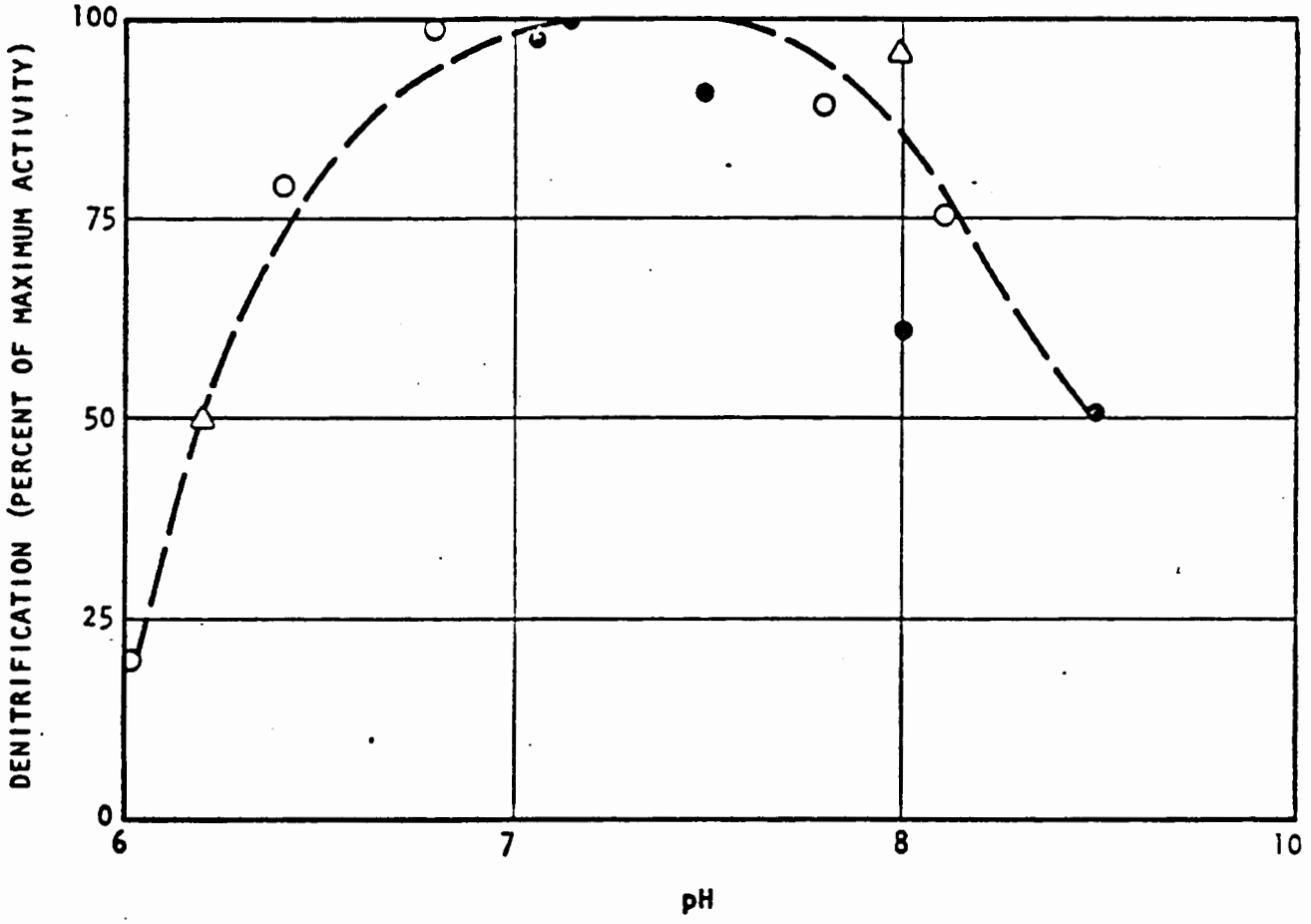
The fact that the organic carbon and energy sources are utilized during nitrification makes it necessary to add a carbon and energy source to the denitrification step. The selection of the electron donor, or carbon source, can greatly influence the configuration of the denitrification process, the success of its operation, and the overall costs. The selection of the organic carbon source depends on reactivity with nitrate, consumption, availability, and cost. Candidate sources of organic carbon are discussed as follows.

Synthetic Carbon Sources

The most common synthetic carbon source is methanol which is one of the more reliable and economical donors in use. The theoretical dissimilative consumption is 1.9 lbs methanol per lb of NO_3-N reduced to nitrogen. Literature values are somewhat higher, and a commonly used equation for

FIGURE 5-16

EFFECT OF pH ON NITRIFICATION



predicting methanol consumption is:

$$C_m = 2.47\ NO_3^-\text{-}N + 1.53\ NO_2^-\text{-}N + 0.87\ D.O. \quad (5\text{-}26)$$

where:

C_m = required methanol concentration, mg/l

NO_3-N = nitrate concentration removed, mg/l

NO_2-N = nitrite concentration removed, mg/l

D.O. = dissolved oxygen depletion, mg/l

The sludge, or biomass production can be predicted similarly:

$$C_b = 0.53\ NO_3^-\text{-}N + 0.32\ NO_2\text{-}N + 0.19\ D.O. \quad (5\text{-}27)$$

where:

C_b = biomass production

Other synthetic carbon sources include glucose, methane, ethanol, acetone, saccharose, and sodium citrate (17).

Excess Sludge

The use of excess sludges from biological processes will provide a source of internal cellular carbon which will provide a carbon source for denitrification during extended periods of time. Excess sludges have been used in Europe but have required long retention periods and are not successful in reducing nitrate levels to low concentrations.

Industrial Wastes

Many industrial wastes are high strength in carbon but low in nitrogen content so that they will provide an adequate source of carbon for denitrification. In specific instances, it is possible to locate a local concentrated industrial source of carbon which may be successfully used for denitrification. This situation is not too common, however.

Raw Organic Wastewater

The use of raw waste for denitrification is probably the most economical and effective way of achieving denitrification in a system where nitrification and denitrification are required. The recycle of nitrified effluent back to the front end of the treatment system will allow contact of nitrate with high strength raw waste. Under anoxic conditions, namely, a stirred reactor with no aeration, a portion of the raw waste BOD will be utilized as a carbon source for denitrification. This recirculation of nitrified effluent reuses the dissolved oxygen

which has already been supplied by mechanical aeration for nitrification, thereby reducing total energy requirements in the system.

Design Concepts for Denitrification Systems

The wide variety of bacteria which can denitrify makes it difficult to formulate specific design relationships, necessitating an empirical approach to establish the required sludge age of hydraulic retention time. Typical operating values for MLVSS in fluidized systems are 4,000 to 6,000 mg/l, 400 to 700 gpd/ft^2 overflow rates for final clarifiers, and sludge synthesis rates of 0.7 lbs VSS produced per pound of nitrate nitrogen reduced.

There are many flow schemes used in denitrifying systems, most being fluidized biological reactors. Anaerobic contact filters also have been successfully applied as denitrifying components in nitrogen removal facilities. There are three main categories for flow schemes, namely, the combined sludge system where the nitrifiers, denitrifiers, and carbonaceous bacteria are commingled, the separate sludge system where interstage clarifiers provide a means of separating these biological populations, and anaerobic filter systems. A brief discussion of each of these concepts is presented.

Combined Sludge Systems

This approach involves a basic configuration where the oxygen supply is controlled to various basin segments, or alternatively turned on and off, allowing the same biomass to perform the nitrification, organic removal, and denitrification functions. Synthetic organic compounds have been used, but raw wastewater and endogenous carbon sources (recycle sludge) are dominating.

Separate Sludge System

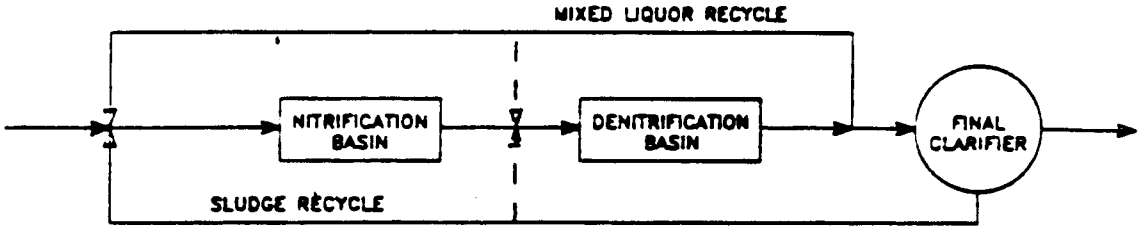
The separate sludge system utilizes separate fluidized reactors which follow the final clarifiers from the conventional activated sludge process. The mixed liquor is kept in suspension with some mixing device, and the external organic carbon source is added directly to this basin. In some cases, a three sludge system is applied with two interstage and one final clarifier. Although cost-intensive, this technique is claimed to give better process regulation due to the separation of the biomass into three separate sludges, namely, a mineralizing, a nitrifying, and a denitrifying sludge.

Anaerobic Filter Systems

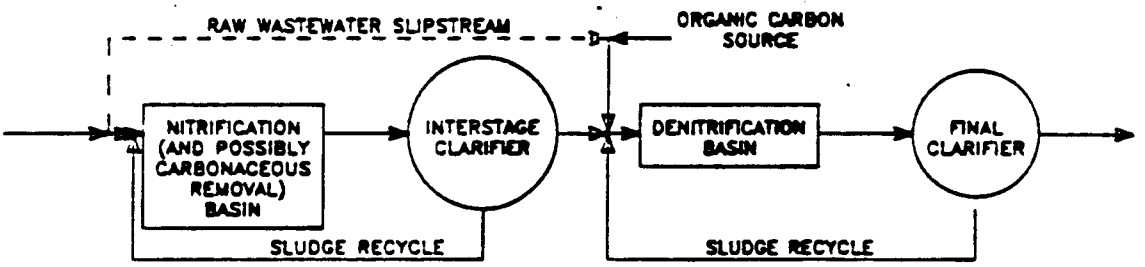
The use of a fixed media to provide denitrification has been applied for the past several years. It involves the attachment of denitrifying microorganisms to a submerged filter media devoid of oxygen, and adding an energy and carbon source at the inlet to the filter. Recirculation is often required to overcome operational problems related to nitrogen gas accumulation in the filter.

Although it is recognized that there are an infinite amount of modifications to the aforementioned systems, a simplified flow diagram for each basic concept is presented in Figure 5-17.

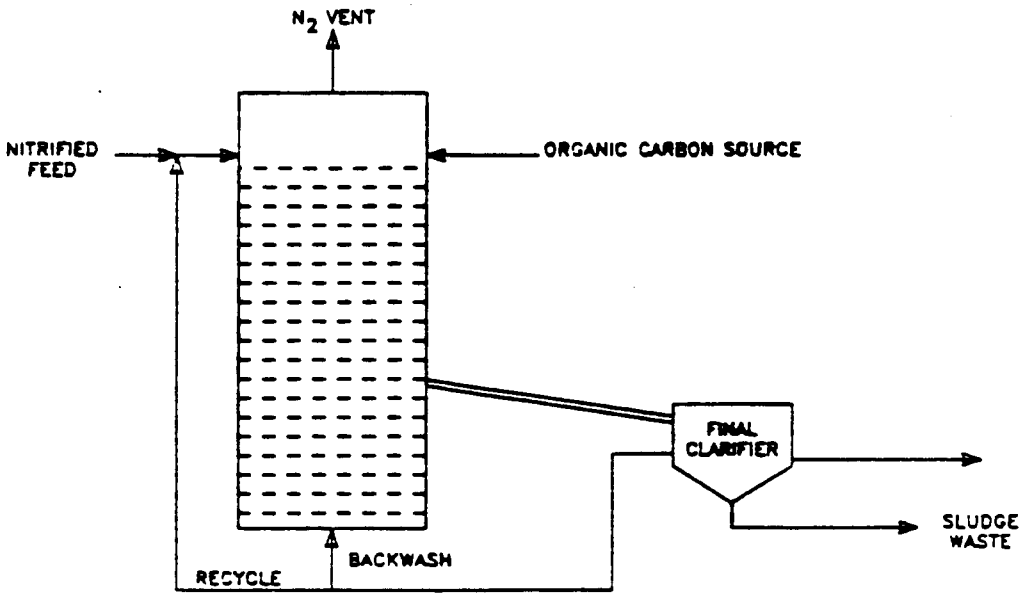
FIGURE 5-17
DENITRIFICATION FLOW SCHEMES



COMBINED SYSTEM



SEPARATE SLUDGE SYSTEM



ANAEROBIC FILTER SYSTEM

Operational Control and Troubleshooting

The concepts of biological denitrification have been presented. Although denitrification systems do not share the many operational vagaries inherent with nitrification systems, there are certain operational and troubleshooting methods which can be used to enhance process efficiency. The primary operational factors include temperature, concentration of denitrifying biomass, pH/alkalinity, dissolved oxygen, and organic carbon source. Because of the wide variety of microorganisms capable of dissimilative denitrification, specific bacterial isolation and identification is practically meaningless.

A summary of operational control techniques as presented in this narrative is outlined in Table 5-5.

TABLE 5-5

TROUBLESHOOTING GUIDE - DENITRIFICATION

Operational Problem	Possible Cause	Troubleshooting Action
Reduction in Denitrification Process - increase in effluent nitrate concentration	Temperature	Increase MLVSS concentration; reseed or partially seed with proven denitrifying biomass; investigate possibility of adding heat to maintain liquid temperature.
Fluidized System	Dissolved Oxygen	Insure oxygen is absent in denitrification tank or during denitrifying cycle. If present, reduce mixer speed if applicable to minimize introduction of oxygen. The addition of oxygen scavenging chemicals on a temporary basis may enhance denitrification if the presence of oxygen is the problem.
	pH/Alkalinity	Insure pH of denitrifying basin is within the 6.5 to 8 range. Adjust as necessary.
	Inadequate Sludge Age	Increasing the sludge age, or, in effect increasing the denitrifying population may be necessary to insure maximum process efficiency. Using the same procedure as outlined to offset temperature effects is a possible remedy. There is a practical limit to the MLVSS concentration based on the capability of the mixer to keep the solids in suspension as well as the maximum allowable solids loading to the clarifiers.
	Insufficient or Unavailable Electron Donor	Dissimilative nitrate reduction will not occur in the absence of an organic carbon source to serve as an electr donor. Check presence of such a source in effluent and add as required.
Submerged Filter System	Inadequate Contact Time, Accumulation of Nitrogen Gas in Filter, Poor Denitrifying Biomass	Increase recycle ratio; increase frequency of backwashing check adequacy of organic carbon source

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REGULATORY CONSTRAINTS ON WASTE TREATMENT

Lial F. Tischler, Ph.D., P.E.*

OVERVIEW

Public Law 92-500, the 1972 Amendments to the Federal Water Pollution Control Act, represented a complete change in federal policy toward water pollution control. Prior to the enactment of P.L. 92-500, treatment requirements for an individual point source were set by the states with federal emphasis basically being on setting water quality standards for surface waters in conjunction with the state or states concerned. P.L. 92-500 changed this emphasis on stream standards to direct control of effluent quality from point sources by means of permits and uniform guidelines specifying required levels of treatment for various classes of point sources. To accomplish this, the Amendments shifted the burden of control from the states to the U.S. Environmental Protection Agency (EPA). EPA was given the responsibility of developing uniform guidelines for required levels of treatment for municipal and industrial point sources and for establishing a nationwide system for permitting discharges from point sources. In addition to these key changes in emphasis on effluent quality control, a number of other significant changes which affect treatment were made in these Amendments.

At the end of December 1977, the President signed the Clean Water Act of 1977. The final version of this legislation is the result of extensive negotiations between House and Senate members and represents the "mid-course correction" provided for in the original version of P.L. 92-500. A number of sections of P.L. 92-500 were modified by the Clean Water Act and the pertinent changes with respect to treatment will be identified and discussed herein. The following outline summarizes the most important aspects of the Act:

TITLE I – Research and Related Programs

Section 105 – Demonstration Grants for New Technology
Grants up to 75 percent total cost to public entities, private industry, etc. to develop advanced treatment techniques.

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TITLE II – Grants for the Construction of Treatment Works

Section 201 – Wastewater Management Planning
Emphasizes regional treatment, evaluation of alternatives; grants are for publicly-owned treatment plants

Section 202 – Federal share is 75 percent

Section 203 – EPA must approve plans and specifications

Section 204 – Prescribes limitations on grants

Section 208 – Areawide planning

TITLE III – Standards and Enforcement

Section 301 – Effluent Limitations

Best Practicable Control Technology Current Available for industry by July 1, 1977

Secondary treatment for municipal wastes by July 1, 1977

More stringent standards in water quality limited streams must be met by July 1, 1977

Best Available Technology Economically Achievable for industry by July 1, 1984, for certain identified toxic pollutants and within three years after limitations are set for other toxic pollutants

Best Conventional Pollution Control Technology (BCT) for "conventional" pollutants by July 1, 1984

Best Available Technology Economically Achievable for all other pollutants not identified by July 1, 1984 or within three years after promulgation of limitations, but in no case later than July 1, 1987

Compliance of municipal plants with 201 plans by July 1, 1983

Review and revision of effluent limitations every five years

Goal of "zero" discharge of pollutants

Provides for a waiver to BATEA under certain conditions

Section 302 – Water Quality Related Effluent Limitations

More stringent than limitations in Section 301 – to be applied if water quality standards are not met by application of 1977-level treatment

Section 303 – Water Quality Standards

Section 304 – Information and Guidelines

Gives EPA authority to set industry/municipal effluent limitations

Pretreatment standards for industrial discharges to publicly-owned treatment works (noncompatible constituents)

EPA is to establish analytical procedures

EPA is to establish monitoring and reporting requirements

Section 306 – National Standards of Performance

Sets effluent limits for new industrial sources – 27 categories as a minimum

New Source -- construction began after publication of proposed regulations

Section 307 -- Toxic and Pretreatment Effluent Standards

EPA to designate toxic substances and set effluent limitations

EPA to set pretreatment standards for industrial dischargers to public systems (noncompatible constituents)

Section 308 – Inspections, Monitoring, and Entry

Requires plant owners to monitor and record operations as designated by EPA

All records are public

TITLE IV – Permits and Licenses

Section 401 – Certification by EPA for any Federal License or Permit that the Proposed Activity is in Accordance with Sections 301, 302, 306, and 307

Section 402 – National Pollutant Discharge Elimination System (NPDES) Permits

Issued to all point sources unless EPA authorizes otherwise

Permit must comply with Sections 201, 203, 306, 307, and 403

States can be authorized to issue NPDES Permits

Section 403 – Ocean Discharge Criteria

EPA shall promulgate guidelines

Section 405 – Disposal of Sewage Sludge

EPA to issue permit for any sludge disposal in navigable waters

The key sections of the Clean Water Act with respect to treatment requirements are Section 301, Effluent Limitations; Section 304, Information and Guidelines; Section 306, National Standards of Performance; and Section 307, Toxic and Pretreatment Effluent Standards. Sections 301, 304, and 306 have been addressed by EPA by preparing "effluent limitations guidelines" for both municipal and industrial point sources. Section 307, dealing with toxic and pretreatment standards, is currently in the process of implementation by EPA. These guidelines and their basis and current status will be discussed in the following sections.

MUNICIPAL GUIDELINES

P.L. 92-500 required EPA to set treatment levels for municipal treatment plants for 1977 corresponding to secondary treatment, which was termed "Best Practicable Control Technology." After studying the performance of a number of municipal treatment plants, EPA arrived at limits which are considered to be attainable by a well-designed and carefully operated waste treatment plant. These limits are shown in Table 1.

TABLE 1

1977 SECONDARY TREATMENT LEVELS
PUBLICLY-OWNED TREATMENT WORKS

Constituent	Maximum 30-day Average	Maximum 30-day Average
BOD_5	30	45
TSS	30	45
pH	6 – 9	6 – 9

The law allows states to set more stringent limitations than the EPA guidelines. Many states have done this and Texas' municipal treatment plant standards are shown in Table 2 as an example. Note that Texas has set limits on grab samples in addition to the averages used by EPA. This is not uncommon since most agencies believe that enforcement actions will be much easier if grab sample limits are used rather than averages over some period of time such as a week or a month. In addition, compliance monitoring by the state agencies is much less costly if samples taken over a short period of time can be compared with some short-term standard.

The basis for all of the different standards (30-day average, 7-day average, grab sample) is essentially the same. A long-term level of performance (usually annual) for a given type of plant is specified as being the "standard" treatment level is set by analyzing data from many operating plants. The shorter-term limits are then set using statistical analyses of the normal variations of effluent quality from these plants. These limits are supposed to be set such that the probability of a plant being found noncompliant with a short-term standard due to "normal" variation is very low, in other words, to exceed the short-term limits, a plant would have to be performing at a level exceeding the long-term (annual) limit for facilities of this type. Obviously, the selection of this variability level is critical to the design of a treatment plant. If the variability used in setting the effluent limitations is not great enough to account for "inherent" variability in treatment systems, it will be necessary to overdesign or add unit processes to improve the long-term performance in order to assure compliance with the short-term standards. Since this same conceptual approach was used by EPA to set limits for both municipal and industrial point sources, the inherent variability in performance as a given treatment system becomes extremely important.

Another important aspect of the municipal treatment guidelines for 1977 can be seen by studying the total suspended solids (TSS) limitations. It is immediately obvious that facultative waste stabilization ponds (FWSP) cannot meet the TSS limits even if they are designed such that they can meet the biological oxygen demand (BOD) levels specified. This is a consequence of the algal cells in these effluents which EPA has designated as a pollutant similar in nature to any other type of biological or organic solids. This is a very controversial issue and will not be discussed herein. However, since an extremely large number of small communities throughout the United States use this low-cost treatment system, the economic ramifications of these requirements are substantial. EPA has been under considerable pressure to change these limits and in 1977 issued new rules for municipal treatment plants which allow use of FWSP in small communities [1]. Basically, these new rules allow the EPA Regions and states to grant variances, on a case-by-case basis, to the TSS limits in Table 1. The plants would still have a TSS limit, but it could be higher than those specified in Table 2 to account for algal

TABLE 2

STATE OF TEXAS
EFFLUENT STANDARDS FOR DOMESTIC WASTEWATER TREATMENT PLANTS

	Effluent Set	30-Day Average BOD	TSS	NH_3 N	P	F.C. (5)	7-Day Average BOD	TSS	NH_3 N	P	F.C. (5)	24 Hr. Composite BOD	TSS	NH_3 N	P	Grab Samples Column I (1) BOD	TSS	NH_3 N	P	Column II (2) BOD	TSS	NH_3 N	P	O_2	Cl_2 (3)	T (4)
gen																										
nand	0	30	30	-	-	-	45	45	-	-	-	70	70	-	-	50	50	-	-	100	100	-	-	-	-	-
	1	20	20	-	-	-	30	30	-	-	-	45	45	-	-	35	35	-	-	65	65	-	-	-	-	-
	2	10	15	-	-	-	15	25	-	-	-	25	40	-	-	20	25	-	-	35	60	-	-	2	-	-
	3	5	10	-	-	-	10	20	-	-	-	20	35	-	-	10	20	-	-	30	60	-	-	4	-	-
	4	5	5	-	-	-	10	10	-	-	-	20	20	-	-	10	10	-	-	30	30	-	-	4	-	-
	2 N	10	15	5	-	-	15	25	10	-	-	25	40	15	-	20	25	15	-	35	60	15	-	2	-	-
	3 N	5	10	5	-	-	10	20	10	-	-	20	35	15	-	10	20	15	-	30	60	15	-	4	-	-
	4 N	5	5	3	-	-	10	10	6	-	-	20	20	10	-	10	10	8	-	30	30	15	-	4	-	-
ifection	A(6)	-	-	-	-	200	-	-	-	-	400	-	-	-	-	-	-	-	-	-	-	-	-	-	1	20
ent	3 P	5	10	-	2	-	10	20	-	4	-	20	35	-	7	10	20	-	4	30	60	-	10	4	-	-
moval	4 P	5	5	-	1	-	10	10	-	2	-	20	20	-	4	10	10	-	2	30	30	-	6	4	-	-

When examining 5 consecutive grab samples randomly collected on separate days by the same entity, the pollutant concentration shall not exceed the specified level.
Single grab sample (instantaneous) limit
Not less than
Detention time in minutes
Log average fecal coliform organisms per 100 ml
Any combination of detention time and chlorine residual where the product of Cl_2 (mg/l) x t (min.) equals or exceeds 20 is satisfactory except that the minimum detention time shall be 20 minutes and the minimum residual shall be 0.5 mg/l. If the required chlorination criteria do not achieve the fecal coliform count required by the permit, a modification of disinfection requirements may be necessary.

tment Process Corresponding to Effluent Set

Set 0 - oxidation ponds (existing ponds only)
1 - secondary (conventional design)
2 - modified secondary (enhanced solids separation)
3 - set 2 with chemical addition
4 - set 3 with filters

Set 2 N - set 2 with biological nitrification
3 N - set 3 with biological nitrification
4 N - set 4 with biological nitrification
3 P - chemical addition in biological process
4 P - chemical precipitation after biological treatment

cells in the effluent. The BOD limits would not be relaxed, however. In addition, the significance of algal cells as a pollutant has still not been resolved and the use of this type of biological treatment system for large municipal and industrial point sources is still not accepted by EPA unless the TSS limits specified in Table 1 can be met.

The Clean Water Act provides that the EPA and/or state can issue a permit for a municipal discharge to marine waters which is less stringent than secondary treatment provided certain conditions are met. These conditions include: the receiving water quality will remain acceptable for fish and wildlife and contact recreation, the applicant will operate a receiving water monitoring program, all pretreatment requirements are met, no other point source will be required to have a higher level of treatment as a result of the designated discharge, and the applicant has developed a program to eliminate toxic pollutants from nonindustrial activities.

INDUSTRIAL GUIDELINES

EPA promulgated effluent limitations guidelines for Best Practicable Control Technology Currently Available (BPT), Best Available Technology Economically Achievable (BAT), and New Source Performance Standards (NSPS) for a number of industrial categories. Those industries for which guidelines have been promulgated to date are listed in Table 3. The basis for these guidelines can be summarized as follows:

(1) Within a given industrial category, types of products/processes which generate similar raw waste loads (flow and quality) are grouped into subcategories.

(2) The raw waste loads for each selected industrial subcategory are established by sampling programs.

(3) Treatment systems which are considered to represent the desired levels of effluent control technology for a specific industrial category are selected. See Table 4 for an example form the organic chemicals industry. Activated sludge was selected as BPT treatment technology model.

(4) Determine the expected long-term effluent quality/performance for the selected type of treatment technology by analyzing

TABLE 3

INDUSTRIAL CATEGORIES FOR WHICH
THE U.S. ENVIRONMENTAL PROTECTION AGENCY
HAS PUBLISHED EFFLUENT GUIDELINES AND STANDARDS

Dairy Products	Grain Mills
Canned and Preserved Fruits and Vegetables	Canned and Preserved Seafood
Sugar Processing	Textiles
Cement Manufacturing	Glass Manufacturing
Feedlots	Asbestos Manufacturing
Electroplating	Rubber Processing
Organic Chemicals	Timber Products
Plastics and Synthetics	Pulp, Paper, and Paper Board
Soaps and Detergents	Builders Paper and Board Mills
Fertilizer Manufacturing	Meat Products
Petroleum Refining	Coal Mining
Iron and Steel Manufacturing	Offshore Oil and Gas Extraction
Nonferrous Metals	Mineral Mining and Processing
Phosphate	Ore Mining and Dressing
Steam Electric Power Generating	Paving and Roofing Materials
Ferroalloy Manufacturing	Paint Formulating
Leather Tanning and Finishing	Ink Formulating
Explosives Manufacturing	Gum and Wood Chemicals Manufacturing
Carbon Black Manufacturing	Hospitals
Inorganic Chemicals	Pesticides Chemicals Manufacturing
Pharmaceutical Manufacturing	Photographic Processing

TABLE 4

ORGANIC CHEMICALS STUDY
TREATMENT TECHNOLOGY SURVEY

Type of Treatment or Disposal Facility	Number of Plants Observed	
	Phase I	Phase II
Activated Sludge	7	9
Activated Sludge-aerated lagoon	2	0
Activated Sludge-polishing pond	0	1
Activated Sludge-solar evaporation pond	0	1
Trickling Filter-activated sludge	1	0
Aerated lagoon-settling pond	3	1
Aerated lagoon-no solids separation	2	1
Facultative Anaerobic lagoon	4	4
Stripping Tower	1	1
No current treatment - system in planning stage	3	7
To Municipal Treatment Plant	5	23
Deep-well disposal	2	6
Physical Treatment, e.g. API Separator	4	3
Activated Carbon	0	6
Incineration	0	1
TOTAL	34	64

[2]

operating data from plants treating the particular wastes in question. See Table 5 for an example of this performance analysis for activated sludge treatment of organic chemicals wastewaters. At higher levels of technology, pilot and laboratory data were often used to set the BAT limits.

(5) Establish the short-term effluent variations by statistically analyzing the performance data used in (4) above.

(6) Set the effluent guidelines for each industrial subcategory by using the short-term performance levels and raw waste loads for each product/process.

Obviously, each industrial category required slight differences in approach to the effluent guidelines. In general, nowever, the above procedure was followed. Table 6 summarizes the basis of the 1977 guidelines for several industrial categories. There are several significant items in this procedure which affect the required level of treatment for a given industrial subcategory: (1) the raw waste load used to define the subcategory; (2) t attainable long-term performance of the specified treatment technology; and (3) the inherent variability of the specified treatment technology.

EPA was forced by the courts to prepare the guidelines hurriedly. Because of this, the data available on all of the above three items were sketchy and not well-documented. In some cases, performance of a given treatment system was extrapolated from one type of industry to another by a process termed "technology transfer." As a result of lawsuits by industry, all of the organic chemicals and plastics and syntnetics guidelines nave been withdrawn by EPA and are currently invalid. Portions of the guidelines for petroleum refining, grain processing, and steel manufacturing industries have also been negated by the courts. Other suits are still pending in various federal courts.

The direction EPA has taken in promulgating the new BAT guidelines and the effluent guidelines which have been remanded can be discerned by referrir to the records of the decisions which have been made by the various appellate courts. Particularly appropriate to this discussion is the decision made t the Tenth Circuit Court [3] on the Petroleum Refining Guidelines which were only partially remanded, as summarized below.

TABLE 6

BASIS FOR INDUSTRIAL EFFLUENT GUIDELINES FOR 1977 (BPT)

Category/Segment	BPT Long-term Effluent Concentration		BPT Allowable Variability Factor	
	BOD_5 (mg/l)	TSS (mg/l)	Monthly	Daily
Major Organic Products	20 - 30[1]	30	2.0	4.5
Synthetic Resins	15 - 75[2]	30	1.6 - 2.2[2]	3.1 - 4.0[2]
Synthetic Polymers	15 - 75[2]	30	1.6 - 2.2[2]	3.1 - 4.0[2]
Grain Processing	100[3]	100[3]	1.0[3]	3.0
Unbleached Kraft and Semichemical Pulp	46 - 97[2]	120	1.0	2.0
Leather Tanning and Finishing	75	75	1.0	2.0
Petroleum Refining	15	10	1.7	3.2 - 2.9[4]
Cane Sugar Refining	60 -100[2]	60 -100[2]	1.0	2.0 - 3.0[5]

[1] Minimum 93 percent removal, maximum 99 percent.

[2] Depends on subcategory for individual process.

[3] Mills with concentrated streams, recirculating cooling water, limits are for maximum 30-day average.

[4] Lower figure is for TSS.

[5] Higher figure is for TSS.

TABLE 5

HISTORIC TREATMENT PLANT PERFORMANCE
50 PERCENT PROBABILITY OF OCCURRENCE

Plant No.	Treatment System	Category	COD		BOD		TOC		SS		Data Base	
			% Removal	Effluent mg/l	% Removal	Effluent mg/l	% Removal	Effluent mg/l	% Removal	Effluent mg/l	Duration (months)	Performance Period
1[1]	AL	D	75	320	97	10	--	--	--	--	6(Sept-Feb)	daily average
2[1,2]	AS-AL	C	96.4	470	--	--	--	--	--	163	12	daily average
3[1]	AS	D	63	700	93.5	16	--	--	--	55	12	monthly average
4[1]	AS	B	64.2	120	--	15	--	--	--	--	14	monthly average
5[1,2]	TF-AS	B	73.5	83	--	--	--	--	--	--	14	monthly average
6	AL	B-C	--	--	--	791	--	--	--	665	12	weekly average
7	AL	C	--	165	--	9.9	--	--	--	81	12	monthly average
8[1]	AL	B	--	75	--	23.5	--	--	--	24.3	12	monthly average
9[1]	AS	C	--	--	83	152	60	170	--	130	7(Aug-Feb	daily average
10[1]	AS	B	74.5	80	90.1	20	--	--	--	--	12	weekly average
11[1,2]	AS-AL	C	--	--	99.7	20	97	100	-370	145	12	daily average
12	AS	A-B	85	97	--	53	--	--	--	--	12	monthly average
13	AS	B-C	--	610	--	294	--	295	--	189	14	monthly average
14	AS	B	--	--	73	410	42	780	--	280	14	monthly average
15	AL		--	226	--	63	--	--	--	--	6(July-Dec)	weekly average
16[1]	AS-	D	--	--	82.5	362	--	--	--	289	8(Aug-Mar	monthly average
17[1]	AS	D	67	1,760	--	--	--	--	--	--	6(June-Oct	daily average
18	AS	D	25.4	1,520	61.6	303	--	--	--	480	12	weekly average
19[1]	AS	D	--	--	97.6	157	--	--	--	--	5(June-Sept)	monthly average
20[1]	AS	C	--	296	98.8	46.9	--	--	--	--	5(June-Sept)	weekly average
Exemplary Plant Average			74	378	93	82.2	79	135	--	134		
Exemplary Single Stage Plants - Average			69		97		60		--	65[3]		

[1] Plants considered to be exemplary in performance.

[2] Multiple-stage biological treatment.

[3] Plant 16 is not included in average.

The American Petroleum Institute and 10 member companies filed suit against EPA in the Tenth Circuit Court of Appeals requesting that the Court set aside in total the regulations promulgated by EPA in 40 CFR, Part 419. The Court made its decision on August 11, 1976, setting aside two major portions of the Petroleum Refining Guidelines and allowing the remainder to stand. The principal arguments set forth by the American Petroleum Institute can be summarized as follows:

(1) EPA cannot impose effluent limitations on existing sources by regulation. The position of API is that only the permit issuer can impose effluent limitations under Section 301 and this section says nothing about "regulations" as described in Section 304(a).

(2) EPA can issue regulations under Section 304 which are guidelines for the permit issuer's information and consideration in writing effluent limitations but are not binding, single-number standards which should be uniformly applied nationwide.

(3) The guidelines published pursuant to Section 304 should be a range of limits, not single-number standards for selected subcategories.

(4) The API attacked the variance provisions which EPA had included in the 1977 Guidelines, apparently since the Act did not explicitly provide this authority as it did for the 1983 step (Section 301(c)). EPA had added a provision to the Guidelines for 1977 (BPT) indicating the permit issuer could deviate from the Guidelines if a discharger could show that its plant was fundamentally different from those used to develop the Guidelines.

(5) Several aspects of the 1977 Guidelines were challenged by API including: the specification of in-plant changes to reduce waste loads; the use of "exemplary plants" to define the required treatment levels; the application of granular-media filtration as end-of-pipe treatment technology when it is not in current widespread use; net versus gross effluent limitations; the treatment of storm water runoff from process

areas and specified limits on "clean" storm water runoff; the variability factors and methodology used by EPA to define the monthly and daily limits from the long-term average performance of the exemplary plants; the data base and guidelines used by EPA for the Class E, petrochemical refineries; and the EPA's supposed failure to adequately assess the total costs of the required treatment technology.

(6) EPA specified technology for 1983 (BAT) which was neither available nor economically achievable when the use of carbon adsorption polishing of BPT effluents was used as the basis for the regulations.

(7) EPA New Source Performance Standards, which are based on BAT flow limitations and 1977 end-of-pipe treatment technology, are void because of the above-mentioned invalidity of the 1977 limitations, the unattainability of the BAT limitations by existing sources, and the use of stale cost figures.

The Tenth Circuit Court's decision set aside all of the BAT limitations and the storm water limitations for 1977 but ruled in favor of EPA on all other issues. It is informative to quote certain passages directly from the Court Record:

(1) With respect to the treatment of storm runoff – "EPA furnishes no record reference to support this regulation. It relies on after-the-fact rationalization in its brief, but such rationalization is no substitute for Agency action not sustained by the record" [3].

(2) Variability Factors – "The whole problem of variability factors presents a practical effort to accommodate for variations in plant operations. As technology for control of pollutant discharges improves, the variations should lessen. The choice of statistical methods lies within the sound discretion of EPA. EPA has acted properly and reasonably in establishing the variability factors before us" [3].

(3) BAT Technology – "Examination of EPA's record citations and appraisal of its shifting and inconsistent rationales makes it

difficult for us to discern upon what, if any, basis EPA promulgated the 1983 limitations. The failure of the BP plant to achieve the limitations when placed in full-scale operation may not be ignored. We can ascertain the 1983 limitations because of their reliance on the carbon adsorption technology....The questions raised, particularly those relating to costs, should be considered by EPA on remand" [3].

(4) New Sources – "Even if the 1983 flow reductions are unattainable by existing refineries, it does not follow that new plants could not be designed so as to incorporate the means of attaining the lower flow rates. There is not record support for the claim that the flow rates for new sources are unattainable" [3].

With respect to the other issues, the Court's opinions were basically in line with those of other courts deciding on similar cases. There is some inconsistency in these decisions which is discussed in depth in the Tenth Circuit Court's opinions. The Court reflects on the causes of these differences as follows: "A cursory glance at the above listed decisions reveals that difficulties which the federal courts of appeals have had with the Act....Perhaps the pressure on Congress to do something was a major cause of the unsatisfactory legislation. The Act is difficult to understand, contrue, and apply." [3]. Nevertheless, this Court and others have construed EPA's authority under the Act to be broad. Provided a sound basis is used for the EPA decisions in question, the courts have generally found in favor of the Agency. The court decisions are quite illuminating in regard to the powers of EPA, and Appendix A includes a list of the relevant cases for reference.

In general then, the Courts have held that EPA could promulgate the industrial guidelines and limitations following the procedures described above. The remands have been due to errors in the application of this procedure. To remedy this, EPA is currently conducting much more detailed studies of raw waste loads and treatment performance for the various point source categories which were found by the Courts to be inadequate. This is being accomplished by sending detailed questionnaires to all known manufacturers in a given industrial category to obtain data on raw waste loads and treatment system performance. In addition, EPA is conducting a substantial

amount of field testing in various industrial categories to establish a basis for the new BAT and pretreatment limitations which they are currently proposing.

Section 308 of the Act requires industries to submit to EPA such data to allow preparation of effluent limitations and guidelines. EPA is currently using the information submitted to the 308 letters to develop raw waste loads and performance levels commensurate with BAT.

The Clean Water Act of 1977 makes substantive changes to Sections 301, 304, and 307 which affect industrial waste treatment requirements. Section 307, which deals with toxic pollutants, will be discussed more fully later in this report. With respect to nontoxic materials, a new category of pollutants, defined as "conventional pollutants," was defined to allow EPA additional flexibility in defining treatment required for the next level of control technology specified in the Act, implementation of which was moved from July 1, 1983, to July 1, 1984. The Act specifically mentions BOD, TSS, pH, and fecal coliform organisms as conventional pollutants and provides EPA latitude to add other pollutants to this category. On July 1, 1979, EPA issued final regulations adding oil and grease to the list of conventional pollutants and designating chemical oxygen demand (COD) and phosphorus as nonconventional pollutants (44 FR 44501). The new rules, promulgated at 40 CFR 401, include a list of all conventional pollutants as well as a list of all currently designated toxic pollutants. A new level of control technology, identified as Best Conventional Pollutant Control Technology (BCT), is specified for these pollutants. EPA is to consider the cost-effectiveness of reducing the conventional pollutants against anticipated improvements in receiving water quality and comparison of the required costs to industry versus the costs for requiring similar levels of treatment by publicly-owned treatment works. The methodology for making this comparison was published on August 23, 1978, by EPA at 43 FR 37570. On July 27, 1981 a Federal Appeals Court remanded the BCT methodology to EPA for review and reissuance as the result of a court challenge to these procedures by industry (American Paper Institute versus EPA). The Court found that the Clean Water Act specifically requires two cost tests for establishing the BCT level of technology: (1) cost comparison with POTW secondary treatment for the BCT treatment technology for a specific industry, and (2) an evaluation of industrywide cost-effectiveness of the proposed BCT technology. The Court found that EPA had

conducted the former cost test but not the latter, and consequently the BCT methodology was invalid. All proposed and promulgated BCT regulations were thus remanded to EPA for review and repromulgation. Industry also argued that the POTW cost comparison methodology was invalid because a level of treatment more stringent than conventional secondary treatment was applied. The Court's review, however, threw out this challenge indicating that this issue was a matter of the Agency's discretion and its basis was valid. This is another indication that the courts will give considerable technical latitude to the Agency in setting specific limits, provided that an adequate data base is available and is used.

It is implicit in these new requirements that the level of control required of industry will be less than that formerly required by BAT for this class of pollutants. This change is in recognition of the fact that the requirement of BAT for all pollutants was extremely cost-ineffective and would provide little additional improvement in receiving water quality on a nationwide basis, as was lucidly pointed out by the National Commission on Water Quality. EPA and the states still retain authority to require more stringent treatment if it is required to maintain receiving water quality.

Another important addition to Section 304 is defined as Best Management Practices (BMP). This section allows EPA to publish supplemental regulations for any specific toxic or hazardous pollutant to control plant site runoff, spills, leaks, solids and waste disposal and drainage from raw materials stock piles. This section provides EPA with broad discretion for establishing regulations for these activities even though they are not an effluent discharge as defined by the Act. EPA promulgated general BMP regulations on June 7, 1979. The Agency plans to revise the BMP regulations and guidance document in the latter part of 1981.

TOXIC MATERIALS GUIDELINES

Section 307 of the Clean Water Act requires EPA to identify toxic pollutants and promulgate effluent limitations for these materials. In 1973, EPA proposed effluent limitations for nine materials under this section (aldrin/dieldrin, benzidine, cadmium, cyanide, DDT (DDE, DDD), endrin, polychlorinated biphenyls, mercury, and toxaphene). Extensive public hearings were held, but the regulations for these toxic pollutants were not

promulgated by EPA until 1979. In 1974, several environmentalist groups filed suit against EPA in the Federal District Court in Washington, D.C. to force promulgation of toxic pollutant standards. In the summer of 1976, the EPA and these groups entered into a stipulation before the Court (the so-called "Consent Decree") in which EPA agreed to take the following actions:

(1) By 1983, the EPA would promulgate BAT effluent limitations, NSPS, and pretreatment standards which would include toxic pollutants. The procedure to be used is the same as that previously used by EPA to establish effluent limitations.

(2) These effluent limitations and pretreatment standards would be applicable to each of a specific list of chemical compounds as shown in Table 7.

(3) The EPA agreed to develop regulations for a list of Standard Industrial Classification (SIC) code numbers encompassing the majority of manufacturing activities. In addition, EPA agreed that the standards which would be promulgated would cover at least 95 percent of all point sources in a particular SIC category.

(4) In the stipulation, EPA agreed to engage the services of contractors to gather and assemble the necessary data to prepare the effluent limitations described above. EPA was to have executed contracts for studying all 21 industrial categories by October 1, 1977, initiating the contracting process for specified categories by June 30, 1976. All contractors were to complete these efforts within one year after contract execution. EPA will then propose regulations not later than six months after each contract completion and promulgate these regulations six months after proposal. The dates for these proposals, by industrial category, are listed in the stipulation.

(5) The stipulation also requires EPA to publish water quality criteria for all of the pollutants shown in Table 7 by June 30, 1978. Furthermore, if the new effluent limitations do not meet the water quality criteria, then the Administrator

TABLE 7

TOXIC POLLUTANTS FOR WHICH EPA WILL PROMULGATE EFFLUENT LIMITATIONS

Acenapthene	Endrin and metabolites
Acrolein	Ethylbenzene
Acrylonitrile	Fluoranthene
Aldrin/Dieldrin	Haloethers
Antimony and compounds	Halomethanes
Arsenic and compounds	Heptachlor and metabolites
Asbestos	Hexachlorobutadiene
Benzene	Hexachlorocyclohexane
Benzidine	Hexachlorocyclopentadiene
Beryllium and compounds	Isophorone
Cadmium and compounds	Lead and compounds
Carbon tetrachloride	Mercury and compounds
Chlordane	Naphthalene
Chlorinated benzenes	Nickel and compounds
Chlorinated ethanes	Nitrobenzene
Chloroalkyl ethers	Nitrophenols
Chlorinated napnthalene	Nitrosamines
Chlorinated phenols	Pentachlorophenol
Chloroform	Phenol
2-chlorophenol	Phthalate esters
Chromium and compounds	Polychlorinated byphenyls
Copper and compounds	Polynuclear aromatic hydrocarbons
Cyanides	Selenium and compounds
DDT and metabolites	Silver and compounds
Dichlorobenzenes	2,3,7,8 - Tetrachlorodibenzo-p-dioxin (TCDD)
Dichlorobenzidine	
Dichloroethylenes	Tetrachloroethylene
2,4-dichlorophenol	Thallium and compounds
Dichloropropane and dichloropropene	Toluene
2,4-dimethylphenol	Toxaphene
Dinitrotoluene	Trichloroethylene
Diphenylhydrazine	Vinyl chloride
Endosulfan and metabolites	Zinc and compounds

is to provide for more stringent treatment requirements as authorized under Section 302 of the Act.

In addition to the above major points, the Consent Decree between EPA and the plaintiffs speaks to many technical and administrative aspects of the development of the new toxic standards. These include provisions for the EPA to exclude a point source category or specific pollutant from coverage under the regulations under certain circumstances. If the EPA elects to do this, they must file statements with the Court and the plaintiffs presenting the reasons for such exclusions.

EPA soon recognized that the list shown in Table 7 represented thousands of compounds and was intractable from the standpoint of issuing specific regulations. Therefore, their first step in complying with the agreement was to review each class of compounds shown in Table 7 with the intent of selecting a smaller group of chemicals which are both the most likely to be present in effluent discharges and also represented the potentially most hazardous materials. A list of 129 "priority pollutants" that meets these criteria was prepared by EPA and is included as Appendix B. EPA has sent out questionnaires and is conducting field tests to develop information on effluent discharges and treatability in conventional industrial waste treatment plants and publicly-owned treatment works for these priority compounds. Simultaneously, additional research into the hazardous levels of these pollutants is being conducted so that effluent limits can be set on the basis of both treatability and toxicity in the environment.

The Clean Water Act specifically incorporates the list of materials in Table 7 into the FWPCA and requires EPA to issue effluent limitations for each. All industrial sources are to implement BAT by July 1, 1984 for the toxic pollutants for which limitations exist on July 1, 1980. All other toxic pollutant limitations are to be met within three years of promulgation. A key addition to the pretreatment requirements (for industrial discharges to publicly-owned treatment works) is the necessity for removal of a toxic material if it contaminates sludge from the publicly-owned works such that they cannot be disposed of by land application.

The complexity of the task of developing guidelines for toxic pollutants has caused EPA to lag considerably behind the court-imposed deadline for

proposal. As of January 1, 1980, EPA had proposed BAT and BCT guidelines and pretreatment standards for only the following industrial point source categories: leather tanning and finishing, electroplating, textiles, timber products, rubber processing, and petroleum refining.

On August 3, 1981, EPA filed a motion with the Federal District Court in Washington to modify the provisions of the Consent Decree. The Agency proposed to reschedule and substantially modify the promulgation of the BAT and pretreatment regulations specified in the agreement. The major provisions of this modification request included rescheduling promulgation of BAT and pretreatment standards as follows: one industrial category in 1981, 14 categories in 1982, and eight in 1983. In addition, EPA proposed to drop rulemaking for 10 industrial categories which have been found to be insignificant sources of toxic pollutants. The reasons cited for the rescheduling are the complexity of the task, which EPA greatly underestimated, and budget and personnel constraints brought on by simultaneous required rulemaking in other environmental areas. The extent of the Agency's problem in issuing the BAT and pretreatment regulations can be seen by the fact that as of August 1981, EPA had promulgated rules for only one industrial category (timber processing) and proposed rules for only 13 others.

EPA's motion also requested some significant modifications to certain provisions of the Consent Decree. The proposed modifications include:

(1) delete the requirement that EPA add additional toxic pollutants to the 65 compounds/classes and write rules for each new pollutant added;

(2) delete the requirement that EPA issue water quality criteria for each of the 65 toxic pollutant classes;

(3) eliminate the requirement for EPA to set special controls for discharge of toxic pollutants to selected bodies of receiving water which are considered severely polluted; and

(4) delete the provision that requires EPA to reissue NPDES permits if BAT limits are promulgated after permit issuance.

Whether or not the Court agrees to these modifications, it is clear that the delays in issuing BAT and pretreatment regulations will delay implementation

of these technologies beyond the July 1, 1984 target. Based on the activities of EPA to date, it seems clear that not only will these regulations be delayed, but they may turn out to be somewhat less stringent than was originally expected.

It can be seen from this brief summary that the coming toxic pollutant guidelines will prove even more complex from a technical standpoint than the existing limitations for the more common wastewater pollutants. Data on the performance of the various types of available treatment technology for removing constituents such as those listed in Table 7 is sparse to non-existent. Even less is known about inherent variability of treatment unit performance in these applications. Substantial efforts will have to be made during the next five to 10 years to define the availability and efficiency of treatment processes for reducing quantities of these trace materials so that designers and operators can respond to the new effluent limitations as they are promulgated.

WATER QUALITY LIMITED SEGMENTS

Section 302 of P.L. 92-500 allows the designation of certain bodies of receiving waters as "water quality limited" segments. A water quality limited segment is one in which the application of the effluent limitations as specified in the EPA effluent guidelines would not be sufficient to attain or maintain water quality at a level that would assure the protection of public water supplies, agricultural and industrial uses, the protection and propagation of a balanced population of shellfish, fish, and wildlife, or would allow recreational activities in and on the water. In this case, the EPA or state can establish effluent limitations more stringent than those specified in the guidelines for point sources discharging to these receiving waters.

In general, the effluent constitutents from POTWs and industrial plants which will normally be controlled in water quality limited segments are ogranic loading (BOD, COD, TOC), ammonia-nitrogen (NH_3-N), and oil and grease.

The procedure for establishing effluent limitations for point sources discharging to a water quality limited segment generally involves the use of some type of mathematical model or allocation procedure to apportion the

allowable loading of a particular constituent to each discharger in the segment. These allocations are generally made by the state regulatory agency. When a procedure of this type is used, the actual waste load allocations could be anywhere between the 1977 level and zero. In general, it is unlikely that effluent limitations more stringent than BCT and BAT (1984) limitations would be applied.

The Agency plans to propose, in late 1981, a regulation which will define its waste load allocation policy. This regulation is designed to assure that uniform procedures are applied nationwide for waste load allocations in water quality limited receiving waters.

EPA has recently issued water quality criteria for the 65 toxic pollutant classes shown in Table 7. In fall of 1981, the Agency plans on proposing regulations which will govern the adoption, revision and approval of State water quality standards. The regulation will set out procedures for the environmental and economic analyses necessary to change designated uses of receiving waters and will describe the process for determining where criteria should be developed for toxic pollutants. The inclusion of toxics in the water quality standards for a specific receiving water body could significantly change the level of treatment technology required for discharges to that water body.

SUMMARY

This brief discussion has indicated the substantial impact of the Clean Water Act on the design and operation of waste treatment plants. The shift in emphasis from stream quality maintenance to uniform point source controls has a great impact on the required levels of treatment plant performance. Although there have been many lawsuits against EPA for improper development of effluent guidelines, the courts have generally found that the concepts and procedures used were acceptable and the only fault lay in their application to specific cases.

The toxic pollutant guidelines will place even more emphasis on the proper selection, design, and operation of treatment processes. Designers, owners, and operators of both municipal and industrial treatment systems would be wise to familiarize themselves with the basis used by EPA for setting

the effluent guidelines applicable to their case and the performance of t relevant treatment processes, with special understanding of inherent (unavoidable) variability in effluent quality. Only in this way can compliance with these new and stringent treatment requirements be assured.

REFERENCES

[1] Federal Register, Volume 41, No. 172, Thursday, September 2, 1976, pages 37221 – 37223.

[2] U.S. Environmental Protection Agency, "Development Document for Effluent Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category." EPA-440/1-74-009-a, Washington, D.C., April 1974.

[3] American Petroleum Institute vs EPA, U.S. Court of Appeals – Tenth Circuit, Environmental Reporter, 9 ERC 1252 – 1265 (1976).

APPENDIX A

COURT DECISIONS OF CASES INVOLVING EPA'S INDUSTRIAL EFFLUENT GUIDELINES

(1) CPC International, Inc. v. Train, 8 Cir., 515 F.2d 1032 [7 ERC 1887] (Corn Wet Milling)

(2) American Iron and Steel Institute v. Environmental Protection Agency, 3 Cir., 526 F.2d 1027 [8 ERC 1321] (Iron and Steel Manufacturing)

(3) American Meat Institute v. Environmental Protection Agency, 7 Cir., 526 F.2d 442 [8 ERC 1369] (Meat Products)

(4) American Petroleum Institute v. Train (API I), 10 Cir., 526 F.2d 1343 [8 ERC 1529] (Jurisdiction)

(5) E.I. duPont de Nemours & Company v. Train [8 ERC 1506] (duPont I), 4 Cir., F.2d, No. 74-2237, opinion filed December 30, 1975, cert. granted 44 LW 3585 (Jurisdiction)

(6) E.I. duPont de Nemours & Company v. Train (duPont II), 4 Cir., F.2d, Nos. 74-1261, etc., opinion filed March 10, 1976, cert. granted 44 LW 3733-3734 [8 ERC 1718] (Inorganic Chemicals)

(7) Tanners' Council of America, Inc. v. Train, 4 Cir., F.2d, Nos. 74-1740 etc., opinion filed March 10, 1976 [8 ERC 1881] (Leather Tanning)

(8) FMC Corporation v. Train, 4 Cir., F.2d, Nos. 74-1386, etc., opinion filed March 10, 1976 [8 ERC 1731] (Plastic and Synthetic Materials)

(9) Hooker Chemicals & Plastics Corp. v. Train, 2 Cir., F.2d, No. 74-1687, opinion filed April 28, 1976 [8 ERC 1961] (Phosphorus Manufacturing - existing sources)

(10) Hooker Chemicals & Plastics Corp. v. Train, 2 Cir., F.2d, No. 74-1683, opinion filed April 28, 1976 [8 ERC 1975] (Phosphorus Manufacturing - new sources)

(11) Natural Resources Defense Council, Inc. v. Environmental Protection Agency, 2 Cir., F.2d, No. 74-1258, opinion filed April 28, 1976 [8 ERC 1988] (Variance Clauses)

(12) American Frozen Food Institute v. Train, D.C., Cir., F.2d, Nos. 74-1464 etc., opinion filed May 11, 1976 [8 ERC 1993] (Frozen Potato Products)

(13) Appalachian Power Co. v. Train, 4 Cir., F.2d, Nos. 74-2096 etc., opinion filed July 16, 1976 [9 ERC 1033] (Steam Electric Power)

APPENDIX B

EPA EFFLUENT GUIDELINES DIVISION
LIST OF PRIORITY POLLUTANTS FOR BAT REVISION STUDIES

1. *acenaphthene
2. *acrolein
3. *acrylonitrile
4. *benzene
5. *benzidine
6. *carbon tetrachloride (tetrachloromethane)
   *chlorinated benzenes (other than dichlorobenzenes)
7. chlorobenzene
8. 1,2,4-trichlorobenzene
9. hexachlorobenzene
   *chlorinated ethanes (including 1,2-dichloroethane, 1,1,1-trichloroethane and hexachloroethane)
10. 1,2-dichloroethane
11. 1,1,1-trichloroethane
12. hexachloroethane
13. 1,1-dichloroethane
14. 1,1,2-trichloroethane
15. 1,1,2,2-tetrachloroethane
16. chloroethane
    *chloroalkyl ethers (chloromethyl, chloroethyl and mixed ethers)
17. bis(chloromethyl) ether
18. bis(2-chloroethyl) ether
19. 2-chloroethyl vinyl ether (mixed)
    *chlorinated naphthalene
20. 2-chloronaphthalene
    *chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)
21. 2,4,6-trichlorophenol
22. parachlorometa cresol
23. *chloroform (trichloromethane)
24. *2-chlorophenol
    *dichlorobenzenes
25. 1,2-dichlorobenzene
26. 1,3-dichlorobenzene
27. 1,4-dichlorobenzene
    *dichlorobenzidine
28. 3,3-dichlorobenzidine
    *dichloroethylenes (1,1-dichloroethylene and 1,2-dichloroethylene)
29. 1,1-dichloroethylene
30. 1,2-trans-dichloroethylene
31. *2,4-dichlorophenol
    *dichloropropane and dichloropropene
32. 1,2-dichloropropane
33. 1,2-dichloropropylene (1,3-dichloropropene)
34. *2,4-dimethylphenol
    *dinitrotoluene
35. 2,4-dinitrotoluene
36. 2,6-dinitrotoluene
37. *1,2-diphenylhydrazine
38. *ethylbenzene
39. *fluoranthene
    *haloethers (other than those listed elsewhere)
40. 4-chlorophenyl phenyl ether
41. 4-bromophenyl phenyl ether
42. bis(2-chloroisopropyl) ether
43. bis(2-chloroethoxy) methane
    *halomethanes (other than those listed elsewhere)
44. methylene chloride (dichloromethane)
45. methyl chloride (chloromethane)
46. methyl bromide (bromomethane)
47. bromoform (tribromomethane)
48. dichlorobromomethane
49. trichlorofluoromethane
50. dichlorodifluoromethane
51. chlorodibromomethane
52. *hexachlorobutadiene
53. *hexachlorocyclopentadiene
54. *isophorone
55. *naphthalene
56. *nitrobenzene
    *nitrophenols (including 2,4-dinitrophenol and dinitrocresol)
57. 2-nitrophenol
58. 4-nitrophenol
59. *2,4-dinitrophenol
60. 4,6-dinitro-o-cresol
    *nitrosamines
61. N-nitrosodimethylamine
62. N-nitrosodiphenylamine
63. N-nitrosodi-n-propylamine
64. *pentachlorophenol
65. *phenol
    *phthalate esters
66. bis(2-ethylhexyl) phthalate
67. butyl benzyl phthalate
68. di-n-butyl phthalate
69. di-n-octyl phthalate
70. diethyl phthalate
71. dimethyl phthalate
    *polynuclear aromatic hydrocarbons
72. benzo(a)anthracene (1,2-benzanthracene)
73. benzo(a)pyrene (3,4-benzopyrene)
74. 3,4-benzofluoranthene
75. benzo(k)fluoranthane (11,12-benzofluoranthene)
76. chrysene
77. acenaphthylene
78. anthracene
79. benzo(ghi)perylene (1,12-benzoperylene)
80. fluorene
81. phenanthrene
82. dibenzo(a,h)anthracene (1,2,5,6-dibenzanthracene)
83. indeno (1,2,3-cd))pyrene (2,3-o-phenylenepyrene)
84. pyrene
85. *tetrachloroethylene
86. *toluene
87. *trichloroethylene
88. *vinyl chloride (chloroethylene)
    pesticides and metabolites
89. *aldrin
90. *dieldrin
91. *chlordane (technical mixture & metabolites)
    *DDT and metabolites
92. 4,4'-DDT
93. 4,4'-DDE (p,p'-DDX)
94. 4,4'-DDD (p,p'-TDE)
    *endosulfan and metabolites
95. a-endosulfan-Alpha
96. b-endosulfan-Beta
    endosulfan sulfate
    *endrin and metabolites
98. endrin
99. endrin aldehyde
    *heptachlor and metabolites
100. heptachlor
101. heptachlor epoxide
    *hexachlorocyclohexane (all isomers)
102. a-BHC-Alpha
103. b-BHC-Beta
104. r-BHC (lindane)-Gamma
105. n-BHC-Delta
    *polychlorinated biphenyls (PCB's)
106. PCB-1242 (Arochlor 1242)
107. PCB-1254 (Arochlor 1254)
108. PCB-1221 (Arochlor 1221)
109. PCB-1232 (Arochlor 1232)
110. PCB-1248 (Arochlor 1248)
111. PCB-1260 (Arochlor 1260)
112. PCB-1016 (Arochlor 1016)
113. *toxaphene
114. *antimony (total)
115. *arsenic (total)
116. *asbestos (fibrous)
117. *beryllium (total)
118. *cadmium (total)
119. *chromium (total)
120. *copper (total)
121. *cyanide (total)
122. *lead (total)
123. *mercury (total)
124. *nickel (total)
125. *selenium (total)
126. *silver (total)
127. *thallium (total)
128. *zinc (total)
129. **2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)

*Specific compounds and chemical classes as listed in the consent degree.

**This compound was specifically listed in the consent degree. Because of the extreme toxicity (TCDD), EPA recommends that laboratories not acquire analytical standard for this compound.

FEDERAL LEGISLATIVE HISTORY
WASTEWATER AND SOLID WASTES

1899 **Rivers & Harbors Act** - Used as a basis to require discharge permits from the Corps of Engineers prior to the 1972 Clean Water Act but "Navigable waterways" was difficult to define and legal battles ensued. This act provided no standards for granting or denying permits, and there was no basis for enforcement with adequate penalties.

1912 **Federal Water Pollution Control Act** - Authorized U.S. Public Health Service to investigate pollution.

1948 U.S. Public Health Service authorized to provide technical services to States and Water Pollution Control Division in U.S. Public Health Service established.

1965 **Solid Waste Disposal Act** - First significant recognition of the Federal Government that solid waste disposal was a national issue. The primary thrust of the Act was to:

(1) initiate and accelerate a National Research and Development program, and

(2) provide technical and financial assistance to State and local governments in the planning, development, and conduct of disposal programs.

Basically, this Act was incomplete, did not provide enforcement, and did not mandate a regulatory authority(s) to deal with the broader issues related to solid waste. At the time of passage of this Act, there were no State-level solid waste agencies in the country and only five states had employees assigned to any phase of solid waste management. By mid-1975, all States but Wyoming, which was still drafting its rules and regulations, had enacted solid waste management statutes (1). This Act was amended in 1970 when Congress passed the Resource Recovery Act. This Act emphasized recycling, resource recovery, and waste to energy, but still lacked enforcement provisions.

Davis L. Ford, Ph.D.

1969 **National Environmental Policy Act (NEPA)** - Established the requirement that an environmental assessment be prepared by the applicant prior to the issuance of a Federal discharge permit for a new source. This assessment is then used as a basis for the Federal regulatory authority to determine if an environmental impact statement is required prior to constructing a new facility.

1970 Formation of Environmental Protection Agency (EPA)

1972 **Clean Water Act** - Congress enacted (CWA) this comprehensive legislation consisting of five main elements:

(1) A system of categorical guideline effluent standards for each industry;

(2) Receiving water quality standards;

(3) A discharge permit program with enforceable limitations;

(4) Special problem provisions including toxic chemicals and oil spills; and

(5) A construction grant and loan program for publically owned treatment works.

Congress significantly amended the Act in 1977 to focus technology-based standards more effectively in the control of toxic pollutants identified pursuant to Sec. 307 of the Act and priority pollutants listed in the NRDC consent decree. Additional significant amendments were passed in 1987, tightening discharge numerical standards to assure compliance of water quality standards for toxic pollutants (2).

In February 1989 new rules were prepared for the management of disposing sewage sludge in response to regulatory requirements imposed in the 1987 amendments. These proposed regulations cover disposal of sludge produced in the treatment of domestic wastewater using any of the following practices:

(1) Land application

(2) Distribution and marketing

(3) Monofilling (sludge-only landfills)

(4) Surface disposal

(5) Incineration

Specific numerical limitations would be imposed for up to 23 toxic pollutants which could significantly alter management practices currently used in the disposal techniques listed above. Specifically, land application rates could be reduced, composted sludge would be more regulated, monofilling would be virtually eliminated, and gas emissions from incinerators would be subject to more scrutiny.

1972 **Marine protection, Research and Sanctuaries Act (MPRSA)** - Act passed by Congress to regulate ocean dumping. This Act has been amended several times, the most significant being in 1988, effectively prohibiting the offshore dumping of industrial wastes and sewage sludge, leaving dredge spoils as the only large volume waste for which ocean dumping is regulated rather than prohibited.

1974 **Safe Drinking Water Act** - EPA was given no direct authority to regulate underground discharges under the Clean Water Act, so it was in the Safe Drinking Water Act that enabled EPA to control such discharges while encouraging States to develop underground injection control programs. This Act also establishes enforceable primary and secondary drinking water standards and was amended in 1986, to include numerical concentration limitations for 83 designated constituents by 1989. Although U.S. Public Health Service drinking water standards evolved through enabling statutes in 1914, 1946, and 1962, they were enforceable only on interstate carriers. This 1974 Act, therefore, dramatically expanded the Federal role in establishing and

enforcing drinking water standards, regulating underground injection, and protecting groundwater quality.

Protection of groundwaters from hazardous wastes was first addressed in the Resource Conservation and Recovery Act of 1976 (RCRA), so this statute and the Safe Drinking Water Act are used in tandom relative to groundwater regulation.

1976 **Resource Conservation and Recovery Act (RCRA)** - The predicate Solid Waste Act of 1965 and 1970, Clean Water Act of 1972, and Safe Drinking Water Act of 1974 led to the passage of the first comprehensive legislation establishing guidelines for the management of hazardous waste. RCRA establishes a permit system that certifies compliance with minimum waste management standards for facilities that treat, store, or dispose of wastes identified as hazardous by EPA. It provides "cradle to the grave" control on generators and transporters of hazardous wastes and upon owners and operators of treatment, storage, and disposal facilities. The basic regulations evolving from this statute were not promulgated until May 19, 1980.

The most important amendment to RCRA was the Hazardous and Solid Waste Amendments of 1984. These amendments were designed to:

(1) close regulatory loopholes;

(2) promote more widespread recycling of hazardous materials; and

(3) reduce industrial use of land disposal technologies.

The most significant provision is the prohibitions on the land disposal of hazardous wastes. Land ban restrictions are in effect by August 1990 for all RCRA listed and characteristic hazardous waste, exempting those wastes which EPA deems to have no adverse effect on human health and the environment. This is based on a reasonable degree of certainty that there will be "no migration" of hazardous

constituents from a land disposal facility taking into account persistance, toxicity, mobility, and propensity to bioaccumulate. Basically, hazardous wastes currently sent to land disposal sites must:

(1) be recycled,

(2) land disposed under a "no migration variance," or

(3) be treated using Best Demonstrated Available Technology (BDAT) before land disposal.

A "hammer" provision is in effect, compelling a land disposal ban for "undetermined" hazardous wastes by statutory deadlines.

A proposed RCRA toxicity characteristic rule, which sets a new test to determine whether a waste is hazardous and subject to RCRA hazardous waste, subtitle C, is currently being considered, and would bring many more hazardous waste sites and activities, such as industrial wastewater treatment plants, under regulation (4).

Proposed changes to Subtitle D of the 1984 RCRA amendments, released by EPA in August 1988, will have a major impact on non-hazardous waste management when enacted, probably in 1991 (5). The stricter requirements are primarily directed toward municipal and industrial non-hazardous solid waste landfills, which EPA has found to have an adverse effect on groundwater and ambient air quality. These changes would require:

(1) groundwater monitoring systems at existing and new landfills, with cleanup of contaminated groundwater;

(2) restrictions on new landfill locations;

(3) more monitoring of methane; and

(4) new requirements for closure and post-closure procedures.

This is the first significant Federal regulation of municipal landfills and will apply to all new and existing sites, but not retroactive to sites closed at the time the rules become effective. Once they become final, States will have 18 months to implement the rules.

1976 **Toxic Substances Control Act (TSCA)** - This Act was designed to enable the Federal government to close significant gaps in the authority to test and regulate problem chemicals before they can reach the environment. It has two main regulatory features:

(1) Acquire sufficient information by EPA to identify and evaluate potential hazards from chemical substances; and

(2) Regulate the production, use, distribution, and disposal of such substances where necessary.

An anomalous provision of TSCA is the specific regulation of polychlorinated biphenyls (PCB's). This led to banning some uses of PCB's in 1977 and most production and use by 1979 (2). Non-liquid PCB's of greater than 50 ppm, for example, can only be disposed of in an approved incinerator or TSCA approved landfill (3).

1980 **Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund)** - The enactment of this legislation basically provided funding and enforcement authority for cleaning up hazardous waste sites, and along with RCRA, provides "wrap around" coverage. Whereas RCRA is a program for present hazardous waste activities, CERCLA provides a comprehensive response program for past hazardous waste activities. Superfund is funded by an excise tax on petroleum and selected chemicals, federal general funds, and fines and recoveries.

In 1986, the Superfund Amendment and Reauthorization Act (SARA) was enacted by Congress which significantly expanded the scope. CERCLA covers all environmental media (air, water, surface water, groundwater, and soil) and has extensive jurisdiction. The "degree of hazard" is broad, and CERCLA can apply to virtually any waste or product. It does not have the "hazardous" specificity of designation that restricts the application of RCRA.

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1. Melosi, M.V. Garbage in the Cities - Refuse, Reforms and the Environment 1880-1980. pp. 200-202, Texas A&M Press (1981).

2. Government Institutes, Inc., Environmental Law Handbook, Tenth Edition, G. I. Inc., Rockvill, Md. (1989).

3. Federal Register, 40 CER 761.60 (July 1987).

4. INSIDE EPA (Dec. 1989).

5. Federal Register, 40 CFR 257 & 258 (August 1988).

ADVANCED WASTEWATER TREATMENT for WATER REUSE

by

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MEXICO CITY, MEXICO
DECEMBER 1991

.....convert biologically treated municipal and industrial wastewaters to usable water resources.

RECOMMENDED FEED WATER LIMITS FOR STEAM GENERATIONS
HIGH-PRESSURE DRUM-TYPE UNITS

TDS	50 ppb max.
Total iron	10 ppb max.
Total copper	10 ppb max.
Total silica	20 ppb max.
Oxygen	5 ppb max.
Hydrazine	10-20 ppb max. residual
pH	8.8-9.2 (copper-alloy system)
	9.2-9.4 (copper-free system)

COMPOSITION OF TREATED EFFLUENTS

CONSTITUENT	CONCENTRATION (mg/L)
BOD_5	15-25
COD	40-80
TOC	13-26
TSS	20-30
TDS	550-1150
P	6-15
N	20-60

PROCESS ALTERNATIVES

CONSTITUENT	PROCESS
Suspended Solids	Chemical coagulation and sedimentation
	Filtration Sand Multi Media
Nitrogen	Biological Nitrification and denitrification
Phosphorus	Chemical Precipitation Biological removal
Dissolved organics (BOD, COD and TOC)	Adsorption on Activated Carbon
Total Dissolved Solids	Reverse Osmosis Ion Exchange Distillation

FACTORS AFFECTING ADSORPTION ON ACTIVATED CARBON

- Adsorbability
- Functionality
- pH
- Temperature

ADSORPTION IS FAVORED BY:

- Increase in number of carbons in chain
- Increase in number of aromatic groups
- Increase in branching
- Decreasing polarity
- Decreasing solubility in water
- Decreasing degree of dissociation

ADSORPTION PREFERENCE

acids > aldehydes > esters > ketones >alcohols > glycols
(Note: number of carbons < 4)

pH EFFECTS

undissociated species are more easily adsorbed

low pH favors adsorption of acids (e.g.volatile acids, phenol)

high ph favors adsorption of basis (e.g. amines)

Other compounds are adsorbed at higher pH

TEMPERATURE

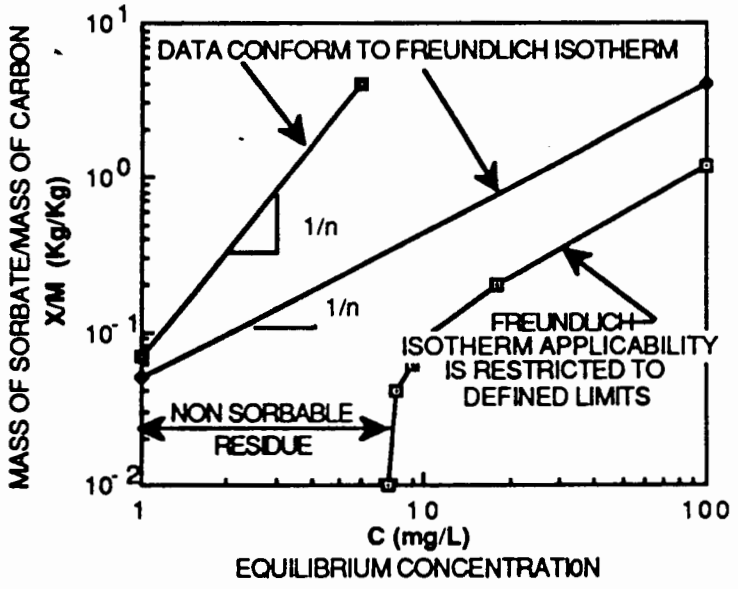
increased temperatures increase adsorption because of viscosity and diffusivity effects

FREUNDLICH ISOTHERM

$$\frac{X}{M} = KC^{1/n}$$

where:

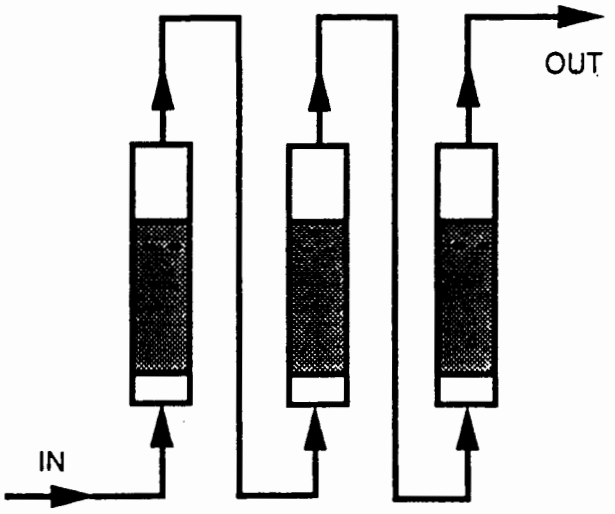
X	=	amount of impurity adsorbed (mg)
M	=	weight of carbon (g)
C	=	equilibrium concentration of impurity in solution (mg/L)
K,n	=	constants characterizing the carbon - adsorbate system



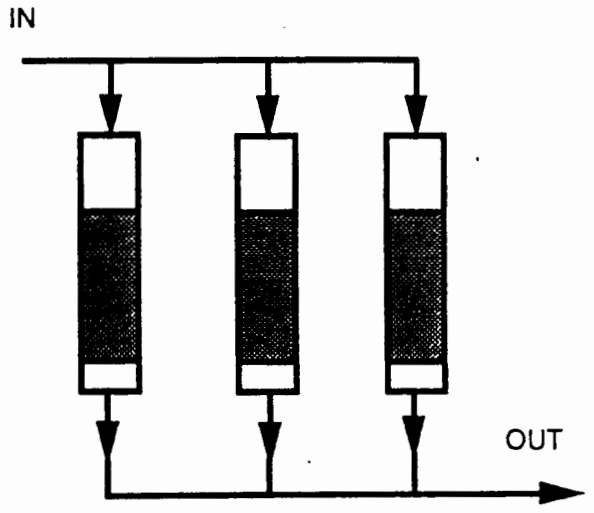
TYPICAL PROPERTIES OF ACTIVATED CARBON (8 X 30 Mesh)

	LIGNITE	COAL*
Total Surface Area (m^2/g)	600-650	950-1050
Bulk Density (lb/ft^3) (backwashed and drained)	22	26
Particle density (g/cm^3) (wetted in water)	1.3-1.4	1.3-1.4
Pore volume (cm^3/g)	1.0	0.85
Effective size (mm)	0.75-0.90	0.80-0.90
Uniformity coefficient	1.9 or less	1.9 or less
Mean particle diameter (mm)	1.5	1.6
Pittsburgh abrasion number	50-60	40-60
Moisture as packed, max. (%)	9	2
Molasses RE (relative efficiency)	100-120	40-60
Ash (%)	12-18	5-8
Mean pore radius (Angstrom)	33	14

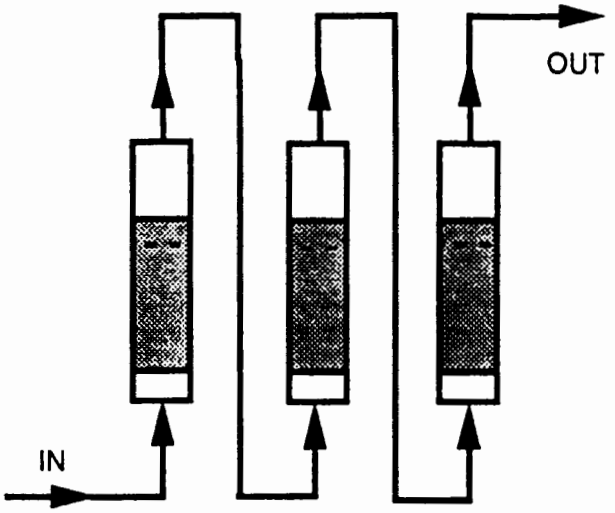
*Bituminous



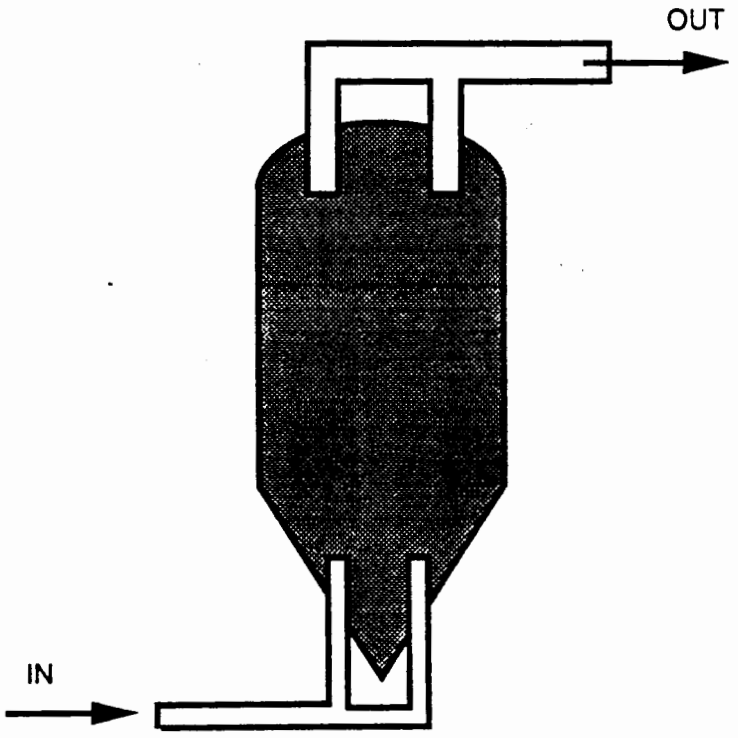
GRANULAR ACTIVATED CARBON
UPFLOW EXPANDED ADSORBERS IN SERIES



GRANULAR ACTIVATED CARBON
DOWNFLOW ADSORBERS IN PARALLEL



GRANULAR ACTIVATED CARBON
UPFLOW EXPANDED ADSORBERS IN SERIES



GRANULAR ACTIVATED CARBON
MOVING-BED ADSORBER

MEMBRANE PROCESSES

PROCESS	FUNCTION	SEPARATION DRIVING FORCE	TYPICAL APPLICATION
Ultrafiltration	Species separation based on physical properties	Hydraulic pressure	By-product recovery from waste streams
Electrodialysis	Ion transport	Electric potential gradient	Brackish water desalination
Reverse Osmosis	Water transport	Hydraulic pressure	Brackish or seawater desalination, ultra-pure water production

REVERSE OSMOSIS

Reverse Osmosis is a process which enables solutes (salts) to be separated from solvents (water) without a phase change.

SUCCESSFUL APPLICATION AREAS

- Brackish and saline water desalination
- Domestic wastewater treatment
- Drug and beverage concentrate
- Product Recovery

REVERSE OSMOSIS DESIGN CONSIDERATIONS

Pressure	pH
Temperature	Turbidity
Flux	Feed Water Velocity
Recovery Factor	Pretreatment
Salt Rejection	Post Treatment
Membrane Fouling	Cleaning
Membrane Life	Power Utilization

Osmotic Pressure

Osmotic Pressure -- Is a function of the dissolved salt concentration and not the membrane.

Modified Van't Hoff Equation:

$$\pi = \phi \frac{n}{v} RT$$

Where:

- π = osmotic pressure, atm.
- ϕ = osmotic pressure coefficient
- $\frac{n}{v}$ = ionic concentration, moles/liter
- T = absolute temperature
- R = universal gas constant, 0.083 $\frac{\text{atm-liters}}{\text{moles}}$

REVERSE OSMOSIS MEMBRANES

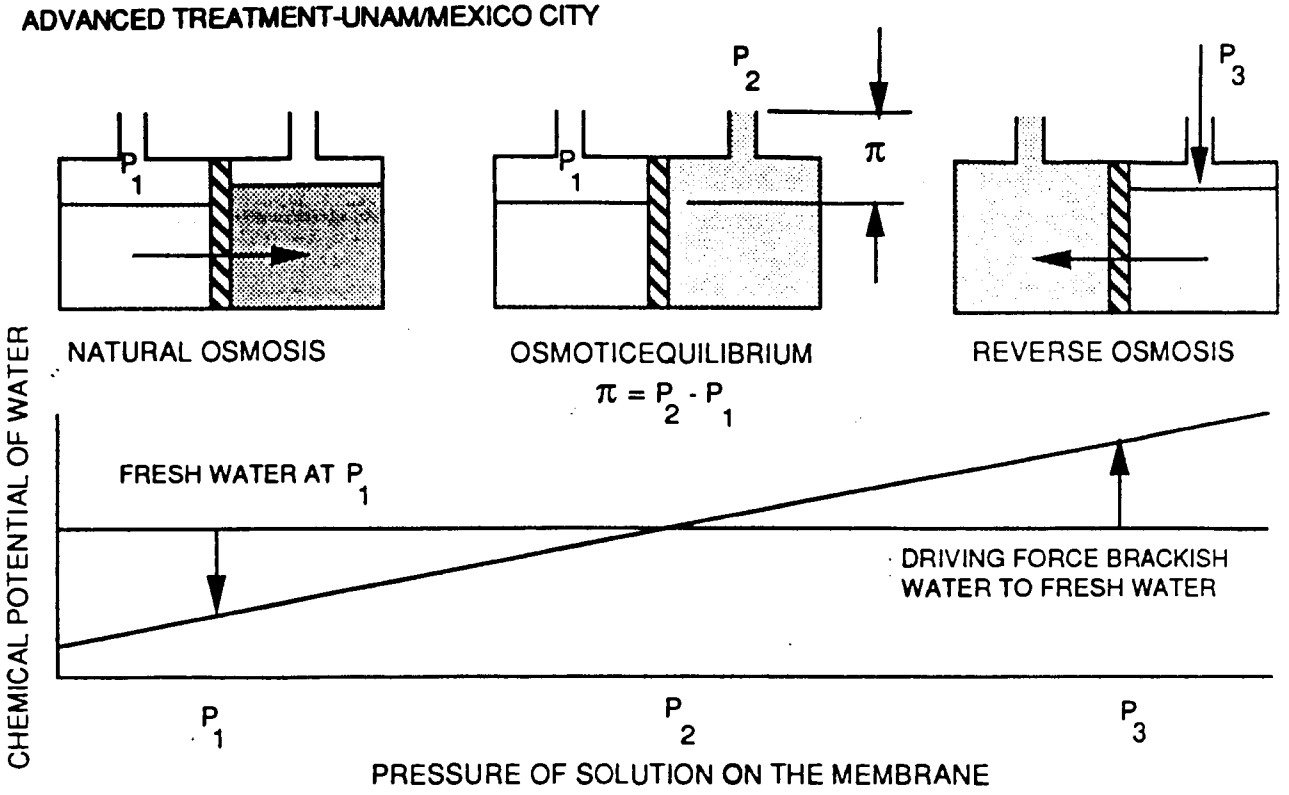
Cellulose Acetate

Aromatic Polyamide - DuPont Hollow Fine Fiber

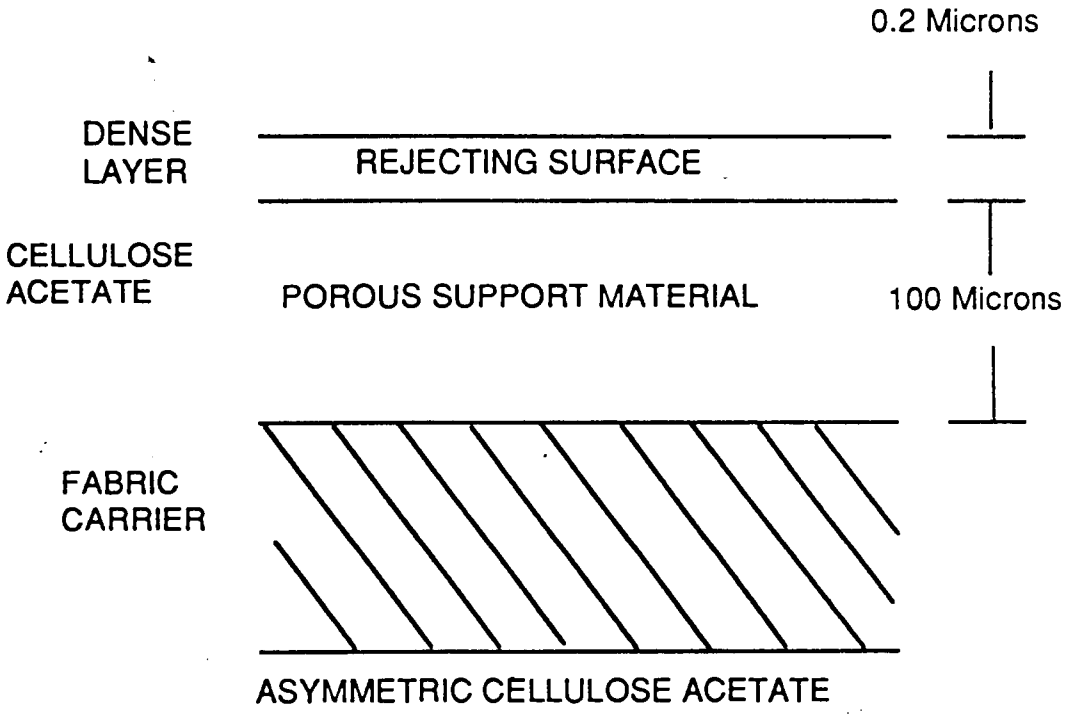
Polysulfone coated with polyethyleneimine crosslinked with tolylene -2,4 disocyanate

REVERSE OSMOSIS FEED WATER PARAMETERS

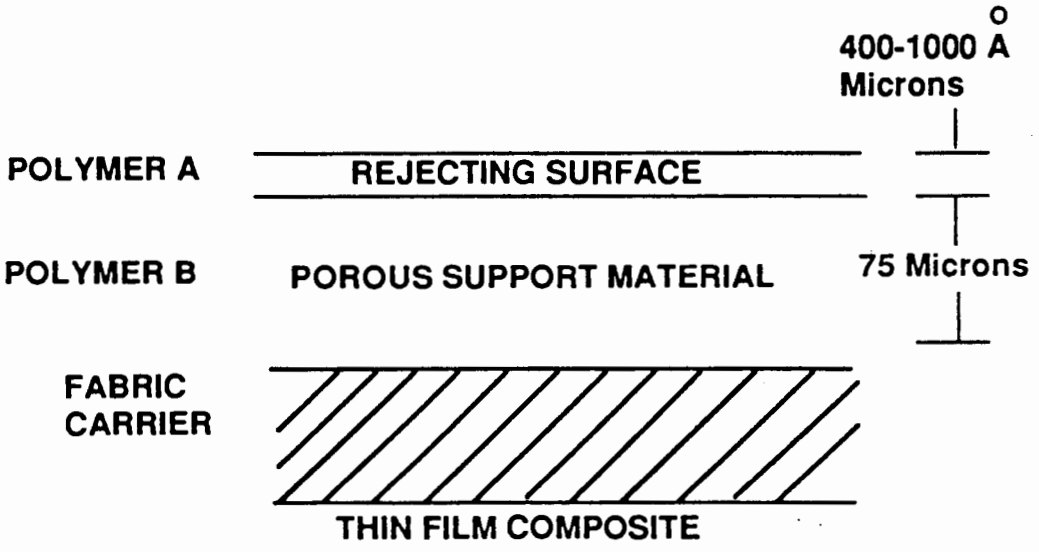
PARAMETER	UNIT	RANGE
Turbidity	JTU	1.5-3.0
Plugging Factor	%	45-90
Chlorine Residual	mg/L	0.1-2.0
Combined Fe & Mg	mg/L	0.1-0.7
pH	----	>6.5
Organics	----	Remove oils,grease and solvents detrimental to membrane
Living Matter	----	----



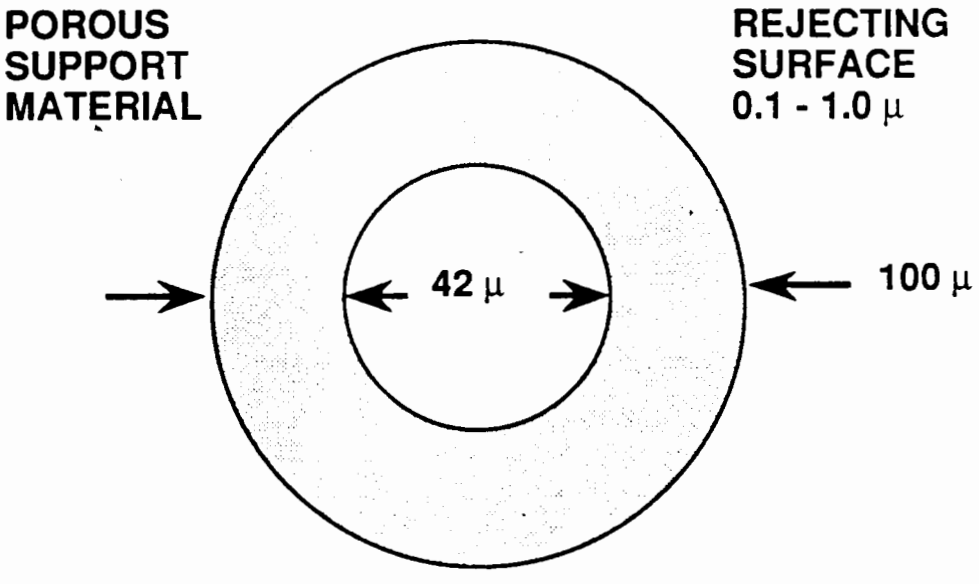
REVERSE OSMOSIS PROCESS ILLUSTRATION



ASYMMETRIC CELLULOSE ACETATE



THIN FILM COMPOSITE



HOLLOW FINE FIBER

REVERSE OSMOSIS PRETREATMENT REQUIREMENTS

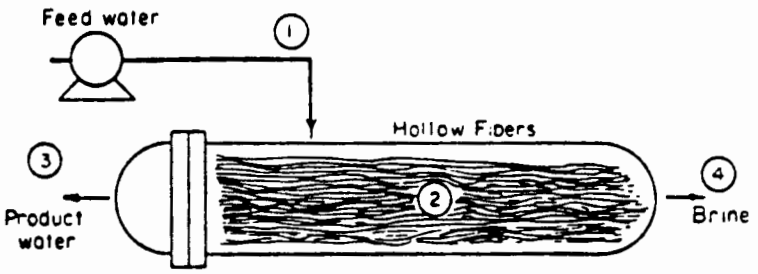
PROCESSES	PARAMETER CONTROLLED
Polishing Filtration	Turbidity
Acid Injection	Membrane hydrolysis calcium salt deposition
Sodium Hexametaphosphate	Calcium sulfate deposition
Prechlorination	Biomass growth
Activated Carbon Filtration	Oil, grease, solvent and dechlorination
Rapid Sand Filtration	Turbidity and organisms
Manganese Zeolite Filtration	Iron and manganese
Partial Lime Softening	Calcium and salt deposition
Ion Exchange	Inorganic ions
Ozone	Organics, iron and manganese

REVERSE OSMOSIS POST TREATMENT

PROCESSES	PARAMETER CONTROLLED
Degasification	Dissolved carbon dioxide
Base addition	Product pH
Disinfection	Pathogenic organisms

MEMBRANE FOULANTS

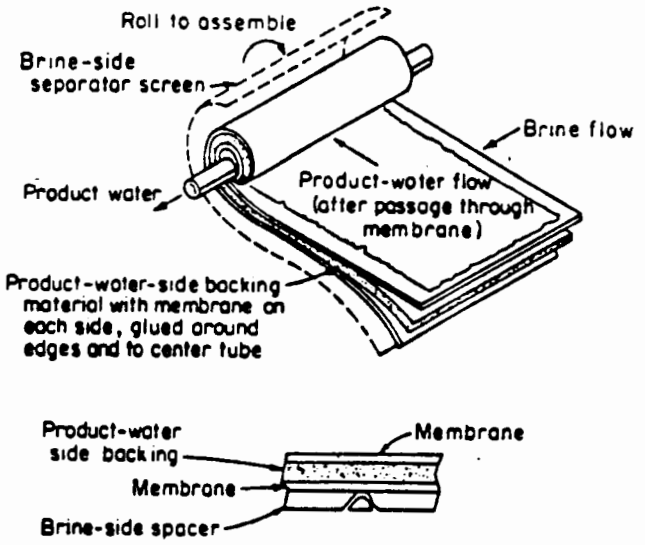
- Scale
  - Calcium carbonate
  - Calcium sulfate
  - Iron oxide hydrates
  - Silicates
- Suspended Solids
- Organics
- Living matter



1. Brackish feed water
2. Product water collected in hollow fibers
3. Product water removed
4. Brine removed

Typical - OD:ID - 44.6μ:24.9μ

RO HOLLOW FINE FIBER MODULE CONFIGURATION



RO SPIRAL WOUND MODULE CONFIGURATION

REVERSE OSMOSIS MODULE CONFIGURATIONS

	Spiral Wound	Hollow Fine Fiber
Membrane Surface Area, ft^2/ft^3	100 - 300	5,000 - 10,000
Product Water Flux, gfd	8 - 25	0.1 - 2
Typical Module Factors		
Brine Velocity, ft/sec	0.7	0.04
Brine Channel Dia., in.	0.05	0.004
Permissible Feed		
pH	5.5 7.5	2 - 10
Temperature, °F	100	100
Method of Membrane		
Replacement	on site	return to factory
Replacement Labor	Medium	Medium
High Pressure Limitation	Membrane Compaction	Fiber Collapse
Pressure Drop		
Product Water Side	Medium	High
Feed to Brine Exit	Medium	Low
Concentration Polarization Problem	Medium	Low
Membrane Cleaning -		
Mechanical	No	No
Chemical	Yes - pH and solvent limited	Yes less restricted

CLARIFIED PRIMARY EFFLUENT TREATMENT BY REVERSE OSMOSIS

	FEED CONCENTRATION (mg/L)	REDUCTION %*
Calcium	54-114	>99.6
Magnesium	13-26	>99.3
Sodium	92-188	92.5
Potassium	17-29	91.5
Ammonia-N	37-57	90.2
Chloride	209-378	90.4
Sulfate	256-388	>99.8
Phosphate	>1-3	>99.4
Total COD	24-109	65.7
COD		
After Aeration	---	85.7
Turbidity, JTU	7.6 (typical)	100
TDS	757-1170	93.3

* Based on feed to reverse osmosis unit only. Total process reduction Based on raw sewage is significantly higher for several species.

CAPITAL COST OF REVERSE OSMOSIS SYSTEMS
(BRACKISH WATER TREATMENT)

Capacity (1000 gpd)	Cost ($1,000)
10	15
50	50
100	90
500	375
1000	600
5000	2750

OPERATING COSTS OF REVERSE OSMOSIS SYSTEMS
(¢/1000 GALLONS)

Capacity (1000 gpd)	Power(2)	Chemicals	O&M	Membrane Replacement	Total
10	15	6-10	54	30	105-109
50	15	5-8	29	25	74-77
100	15	4-7	20	20	59-62
500	15	4-7	11	17	47-50
1000	15	3-6	8	15	41-44
5000	15	3-6	6	12	36-39

(1) Operating at 400 psi at 75% recovery
(2) At 2.5 cents/kw-hr

WATER QUALITY AT VARIOUS STAGES OF TREATMENT
LAKE TAHOE, CA

Quality Parameter	Biological	Chemical Clarifier	Filter	Carbon
BOD (mg/L)	30		3	1
COD (mg/L)	70		25	10
SS (mg/L)	26	10	0	0
Turbidity (JTU)	15	10	0.3	0.3
Phosphorus (mg/L)	6	0.7	0.1	0.1

WATER QUALITY AT VARIOUS STAGES OF TREATMENT COLORADO SPRINGS

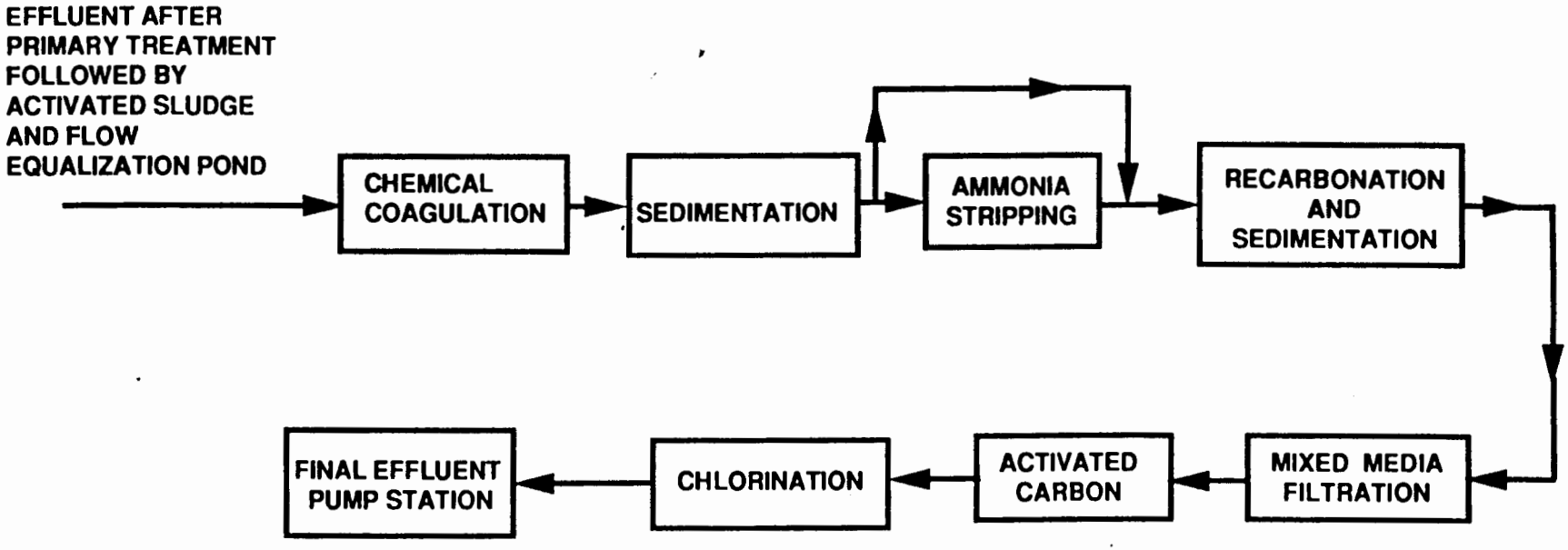
Quality Parameter	Trickling Filter*	Final Effluent
BOD (mg/L)	102	8.0
COD (mg/L)	258	15.7
SS (mg/L)	62	2.2
Turbidity (JTU)	54	2.2
Phosphorus (mg/L)	15	0.5

*Trickling filter plant capacity is 13 MGD (0.57 m^3/s) and was operated at a flow rate of 23 to 25 MGD (1.0 to 1.1 m^3/s).

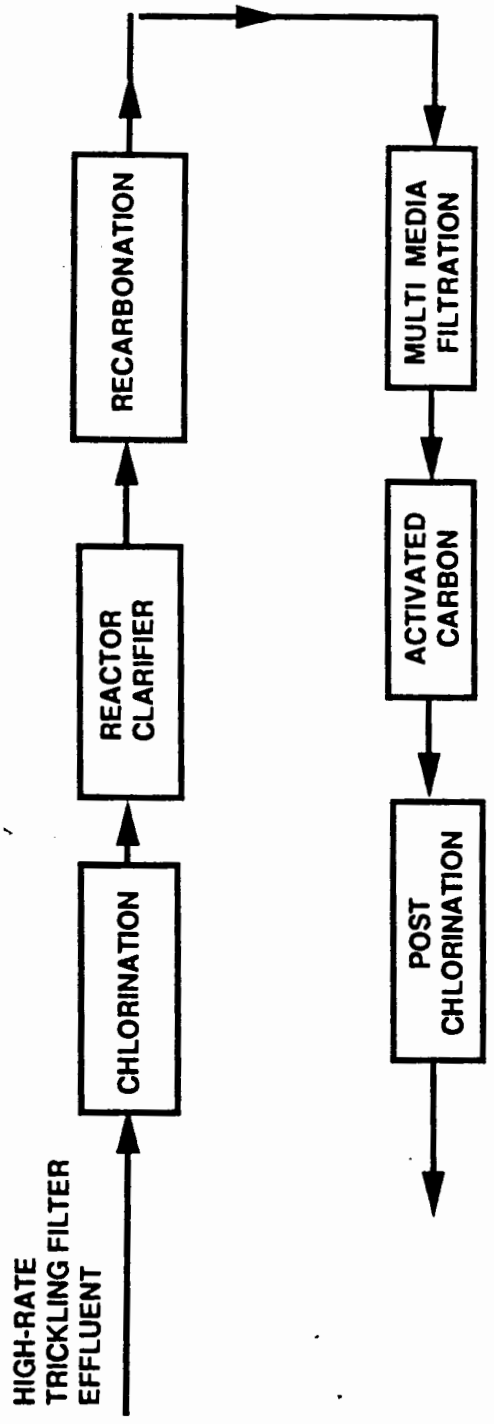
REVERSE OSMOSIS AVERAGE PROCESS REMOVAL

Constituent	Average Concentration		Average Removal (%)[a]
	Influent	Effluent	
Electrical conductivity (μmho/cm)	1460.0	70.0	95
Sodium (mg/L)	196.0	11.0	94
Chloride (mg/L)	280.0	16.0	94
Sulfate (mg/L)	220.0	0.8	99
COD (mg/L)	25.0	1.5	94
Ammonia-N (mg/L)	5.6	0.5	91
Calcium (mg/L)	118.0	2.0	98

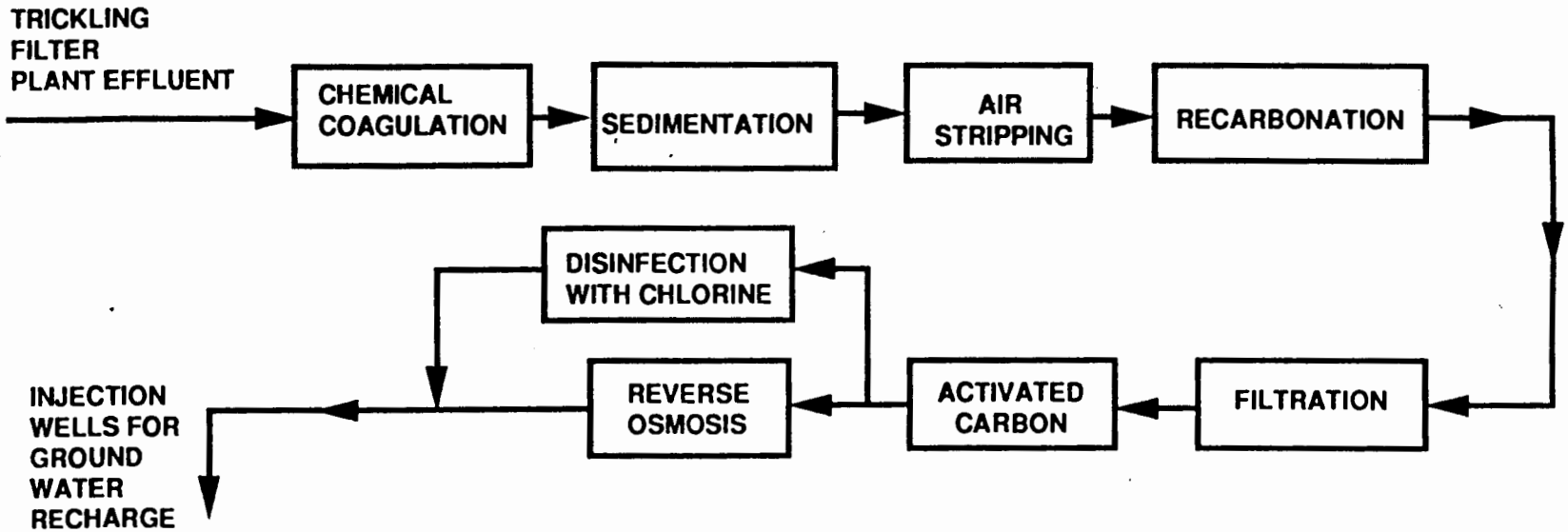
[a]Data from the Orange County (Calif.) Water Factory 21.



LAKE TAHOE ADVANCED WASTEWATER TREATMENT FACILITY



WATER RENOVATION PLANT - COLORADO SPRINGS, CO

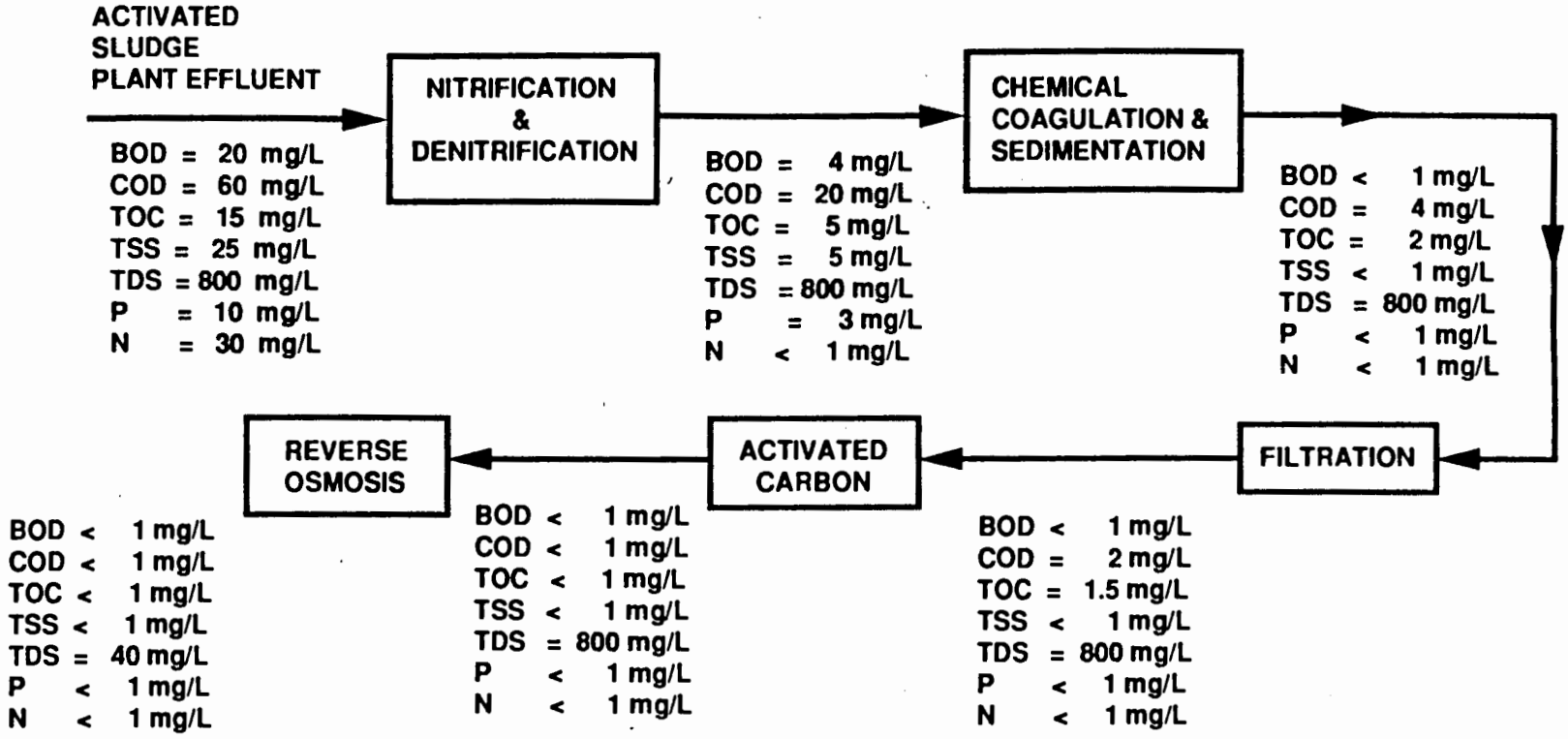


WATER FACTORY 21 - ORANGE COUNTY, CA

WASTEWATER TREATMENT PROCESS EFFICIENCIES
(per cent removal)

PROCESS	BOD	COD	TOC	TSS	NH_3 N	NO_3 N	P	TURB[1]
Activated Sludge[2]	89	72	83	81	63	----	45	86
Nitrification[3]	75	56	73	61	97	----	50	89
Denitrification[3]	47	35	22	42	32	89	52	0
Coagulation-Sedimentation[3] (ferric & lime)	81	81	73	91	----	----	96	69
Filtration								
Biological[3]	39	34	33	73	33	56	57	71
Bio/Chemical[4]	36	22	25	42	----	-----	----	31
Activated Carbon[4]	53	47	64	64	39	5	88	73
Reverse Osmosis								
Act Sludge	----	>96	----	>95[5]	>95	----	>99	----
Bio/Act Carbon[6]	----	>92	----	>95[5]	>96	----	>99	----
Bio/Chemical[4]	----	>66	----	>93[5]	>90	----	>99	----

1 Turbidity
2 Removal from primary effluents
3 Removal from secondary effluents
4 Removal from chemically clarified secondary effluents
5 Total Dissolved Solids (TDS)
6 Removal from activated carbon treated secondary effluents



HYPOTHETICAL ADVANCED WASTEWATER TREATMENT SYSTEM MUNICIPAL WASTEWATER

LOW-COST WASTEWATER TREATMENT--PONDS, SUPPLEMENTAL AERATION, EFFLUENT POLISHING, WETLANDS, AND LAND DISPOSAL

by

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NOTATIONS

NOTATIONS

Symbol	Name
AWSP	anaerobic waste stabilization pond(s)
BOD	biochemical oxygen demand
BOD_R	BOD removal
BOD_u	ultimate BOD
BOD_5	5 day BOD, 20 °C BOD_5 = 65% BOD_u
COD	chemical oxygen demand
°C	degrees Celsius
cal	calorie: cal x 4.186 = joule
cm	centimetre(s)
cm^2	square centimetre
cm/h	centimetres per hour
cm/wk	centimetres per week
f	inhibition factor
f'	sulfide loading factor
FWSP	facultative waste stabilization pond(s)
g	gram(s)
ha	hectare = acres
J/g	joules per gram
J/ha·yr	joules per hectare per year
$k·(day^{-1})$	first order BOD removal coefficient
kg	kilogram(s)
kg/ha	kilograms per hectare
kg/ha·d	kilograms per hectare per day
kJ	kilojoules
kJ/d	kilojoules per day
km	kilometre
km^2	square kilometre
kW	kilowatt
L	litre(s)

Symbol	Name
L_a	BOD_u
L_s	design loading kg COD/ha·d
L/ha·d	litres per hectare per day
m	metre(s)
m^2	square metre
m^3/s	cubic metres per second
MAWSP	mechanically aerated waste stabilization pond(s)
mg	milligram(s)
mg/L	milligrams per litre
Mg (or t)	megagram (metric tonne)
MJ/kg	megajoules per kilogram
MJ/m^3	megajoules per cubic metre
MJ/yr	megajoules per year
N/cm^2	Newtons per square centimetre
pH	hydrogen ion concentration
PWSP	polishing waste stabilization pond(s)
SS	suspended solids
θ	temperature coefficient
T	temperature
TKN	total Kjeldahl nitrogen
TN	total nitrogen
TP	total phosphorus
TSS	total suspended solids
V	pond volume (m^3)
WSP	waste stabilization pond(s)
WSPS	waste stabilization pond system(s)
WWTP	wastewater treatment plant(s)

CONVERSIONS

U.S. Customary Unit				
Name	Abbreviation	Multiplier	Abbrev.	Name
acre	acre	0.405	ha	hectare
acre-foot	acre-ft	1 233	m^3	cubic metre
cubic foot	ft^3	28.32 0.02832	L m^3	litre cubic metre
cubic feet per second	ft^3/s	28.32	L/s	litres per second
degrees Fahrenheit	°F	0.555(°F-32)	°C	degrees Celsius
feet per second	ft/s	0.305	m/s	metres per second
foot (feet)	ft	0.305	m	metre(s)
gallon(s)	gal	3.785	L	litre(s)
gallons per acre per day	gal/acre•d	9.353	L/ha•d	litres per hectare per day
gallons per day	gal/d	4.381×10^{-5}	L/s	litres per second
gallon per minute	gal/min	0.0631	L/s	litres per second
horsepower	hp	0.746	kW	kilowatt
inch(es)	in.	2.54	cm	centimetre(s)
inches per hour	in./h	2.54	cm/h	centimetres per hour
mile	mi	1.609	km	kilometre
miles per hour	mi/h	0.45	m/s	metres per second
million gallons	Mgal	3.785 3 785.0	ML m^3	megalitres (litres x 10^6 cubic metres
million gallons per acre	Mgal/acre	8 353	m^3/ha	cubic metres per hectare
million gallons per day	Mgal/d	43.8 0.044	L/s m^3/s	cubic metres per second cubic metres per second
parts per million	ppm	1.0	mg/L	milligrams per litre
pound(s)	lb	0.454 453.6	kg g	kilogram(s) gram(s)
pounds per acre per day	lb/acre•d	1.12	kg/ha•d	kilograms per hectare per day
pounds per square inch	$lb/in.^2$	0.069 0.69	kg/cm^2 N/cm^2	kilograms per square centimetre Newtons per square centemetre
square foot	ft^2	0.0929	m^2	square metre
square inch	$in.^2$	6.452	cm^2	square centimetre
square mile	mi^2	2.590 259.0	km^2 ha	square kilometre hectare
ton (short)	ton (short)	0.907	Mg (or t)	megagram (metric tonne)
tons per acre	tons/acre	2 240 2.24	kg/ha Mg/ha	kilograms per hectare megagrams per hectare

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INTRODUCTION

Wastewater treatment frequently requires different technological and management approaches. The most sophisticated process, although justifiable for most wastewater treatment systems, may not be justifiable for many urban locations and plant sites.

An alternative low-cost wastewater treatment system may provide equally acceptable or even better quality effluents. The low-cost wastewater treatment and disposal systems discussed herein meet this concept. For example, the initial construction and operating costs are usually much less that an equivalent rated activated sludge facility. Also, the level of technical expertise required to operate the low-cost facility is less.

Obvously, the simpler systems must perform in an acceptable manner. Some of the principal considerations in process selection are:

a. no endangerment to the health of the public;
b. no impairment to the environment;
c. availability of required operator skills;
d. minimization of capital and operating costs; and
e. maximization of available resources.

BASIC CONSIDERATIONS

Wastewaters may contain domestic sewage, industrial discharges, agricultural run-offs, and storm water flows. These are relatively dilute wastes. Domestic wastewaters are composed of 99.9% water and 0.1% impurities, mainly suspended, colloidal and dissolved solids. Additional materials such gases, microoorganisms and other substances are included in the wastes. Unless the wastes contain toxic substances, biological processes will remain the most economical.

The conventional wastewater treatment facility separates the solids and liquids by use of capital-intensive units. In contrast, the lower cost waste stabilization pond systems (WSPS) combine conventional unit operations and thereby reduce the cost. Also, in many cases the low-cost waste management system is frequently more effective in removing pathogens.

NATURAL SYSTEMS

All biological systems and many physical/chemical systems employ some aspect of the natural system. However, natural responses supported by mechanical separation and aeration are ENERGY-INTENSIVE. A natural treatment process would not depend on external energy sources exclusively.

The natural systems encompass three major treatment, reuse and disposal concepts. These are:

a. waste stabilization ponds (anaerobic, facultative and polishing);
b. land application (slow rate, rapid infiltration and overland flow); and
c. wetland treatment (natural, constructed and rush/reed beds).

RATIONALE

Many of the less affluent areas in the U. S. A., predominantly smaller towns in rural areas, and isolated industries share the problems of developing countries. These communities and industries cannot afford the treatment systems utilized by the densely populated cities.

A concerted effort must be made to develop economically achievable pollution control. Unfortunately, if water reuse practices are not properly planned and conducted, future health problems surely will become more burdensome. Estimates indicate that five million people die each year from water-borne diseases (1,2). In addition, there may be as many as one billion cases of gastroenteritis, schistosomiasis, filariasis, malaria, and onchocerciasis. These problems occur because an estimated 1.4 billion people have inadequate sanitary waste disposal facilities. Nearly 30% of the deaths of children in developing countries are attributed to diarrhreal diseases stemming from bad drinking water. The combination of poor quality drinking water and poor sanitation is probably responsible for over 80% of the morbidity and mortality in the developing countries.

Pre-treatment of domestic and most industrial wastewaters is necessary prior to reuse of water through land application. The range of pre-treatment requirements can vary considerably. A properly designed pond system is highly effective in removing biodegradable organic wastes, pathogens, settleable solids, trace amounts of heavy metals, and relatively large amounts of refractory organics. These systems are energy efficient. They are adaptable to an agricultural water reuse operation.

Microbial growth and energy utilization in wastewater biodegradation processes are similar. However, bacteria function differently under anaerobic, facultative, or aerobic environments, and each special unit process must be designed to accommodate the specialized community of microorganisms.

Irrespective of the process used, application of today's wastewater treatment technology requires a thorough characterization of the wastewater. Engineering designs can be made to select the most appropriate treatment systems. Pond systems can be designed to provide almost any level of treatment desired. Typical pond arrangements can readily provide 70% to 90% reduction of the 5-day, 20 °C, biochemical oxygen demand (BOD_5).

WSP can be effective in removing disease-causing agents. Sedimentation can be used effectively to remove ova and cysts (specific gravity about 1.1). Sedimentation has been shown to be responsible for the removal of E. histolytica. According to laboratory tests, anaerobic ponds curtail the hatching and survival of the eggs of S. mansoni. Conversely, facultative ponds do not suppress the hatching of the eggs or affect materially the survival of miracidia of S. mansoni. The vector snails

transplanted into full-scale ponds reportedly die within 10 weeks. The eggs of Ascaris lumbriocoides survive for long periods in septic tank sludges.

As the algal-bacterial environment becomes more complex with the involvement of a greater variety of algal species, the die-off rates of enteric organisms increase. Laboratory and field tests support these conclusions (3). The die-off coefficients for enteric bacteria have been found to be similar in laboratory tests using mixtures of axenic algal cultures and in field studies. Tests conducted with pathogenic bacteria and algal cultures have yielded results similar to those found when enteric bacteria have been used. Escherichia, Pseudomonas, and Serratia have exhibited after-growth potential while Proteus, Alcaligenes, Enterobacter, Salmonella, Shigella, and Vibrio have not.

The disposal of wastewaters on land is not new, and when used effectively is an excellent solution to water reuse and treatment problems. Clearly, treatment of wastewater in ponds followed by beneficial land application accomplishes three important objectives. First, the soil is a living filter and there probably isn't a more cost-effective means of polishing an effluent. Second, the effluents from well-designed WSPS can be used safely for a wide variety of agricultural uses. Third, the entire concept of WSP treatment, land disposal, and water reuse minimizes adverse social, economic, and environmental consequences.

The task of developing a new design or unconventional treatment system is not always easy. There must be a common understanding of the existing body of knowledge that deals with low-cost wastewater treatment. Professionals involved in the wastewater treatment business must be capable of interfacing with the "active" environmentalist, "conventional" designer and "election conscious" decisionmaker.

CHANGING POLICIES

The task of utilizing low-cost systems is becoming easier. At both the national and state levels, there is a growing awareness that some of the natural systems are economical. Frequently, it can be shown that these more natural systems consume less energy, produce less sludge, and require fewer operators.

ECONOMICS OF ALTERNATIVE WASTEWATER TREATMENT SYSTEMS

Energy costs are commensurate with the rate of stabilization and the level of treatment required. The difference in capital cost between secondary biological and tertiary physical-chemical treatment is significant. Seven levels of treatment technology and their corresponding power consumption requirements are tabulated in Table 1. The power requirement for a WSPS is zero. The BOD removal efficiency of each of these systems is approximately the same.

Table 1. Energy Demands for Selected Treatment Processes (Design Flow = 0.7 m3/s)

Process	Power Consumption ($kJ/d \times 10^5$)
Waste Stabilization Pond System	0
Rotating Biological Contactor (no sludge handling)	576
Rotating Biological Contactor (sludge handling)(	1,080
Activated Sludge (no sludge handling)	864
Activated Sludge (sludge handling)*	1,368
Powdered Activated Carbon Treatment**	1,620
Physical-Chemical Treatment***	2,844

* Sludge handling includes aerobic digestion, thickening, dewatering, and multiple hearth incineration.

** System includes basic activated sludge process with carbon feed facilities and multiple hearth incineration/regeneration of carbon-synthesis sludge mix.

*** System includes chemical coagulation-precipitation, ammonia stripping, filtration, activated carbon adsorption, and lime recalcination.

The energy requirements for making the consumables for some treatment systems are given in Table 2. For example, about 6.3 kJ are needed to produce 1,000 kg of lime.

Table 2. Energy Requirements for Wastewater Treatment Plant Consumables (4)

Consumable	Energy Requirement (J/g)
Activated Carbon	28,800 - 39,600
Chlorine	16,200
Alum	720
Lime	2,160 - 2,520
Polymer	720

Methane derived from fermentation of organic waste materials is a direct way of co-generating energy. Some dry biomass contains about half as much energy as

coal--16 MJ/kg. Present use of biomass is equivalent to about 2 x 10^9 to 3 x 10^9 MJ/yr worldwide (less than one percent of world energy production).

The additional energy required to distribute the treated water on the crop land is shown in Table 3. While gravity distribution does not require pumping energy, there are possible costs with other components of land treatment. Also, the cost of managing return flows can become an importnt cost factor.

Table 3. Most Common Unit Energy Requirements for Land Treatment of Municipal Wastewater

Treatment System	Component	Electricity* (MJ/1,000 m^3)	Fuel (MJ/1,000 m^3)	Total Equivalent (MJ/1,000 m^3)
Slow rate	Pumping for distribution	0.50	–	0.50
	Crop planting, cultivation, harvent, drying, transport	–	0.68	0.68
	Energy credit for fertilizer value of wastewater	0.0	(0.50)	(0.50)
Total		0.50	0.18	0.68
Rapid infiltration	Distrbution (gravity)	–	–	–
	Recovery wells	0.18	—	0.18
Total		0.18	–	0.18
Overland flow	Transmission	0.36	–	0.36
	Forage harvest	—	0.22	0.22
Total		0.36	0.22	0.58

1 kWh = 3.60 MJ

WASTE STABILIZATION PONDS

Typical waste stabilization pond configurations are shown in Figure 1. Multiple series-connected or parallel units are possible.

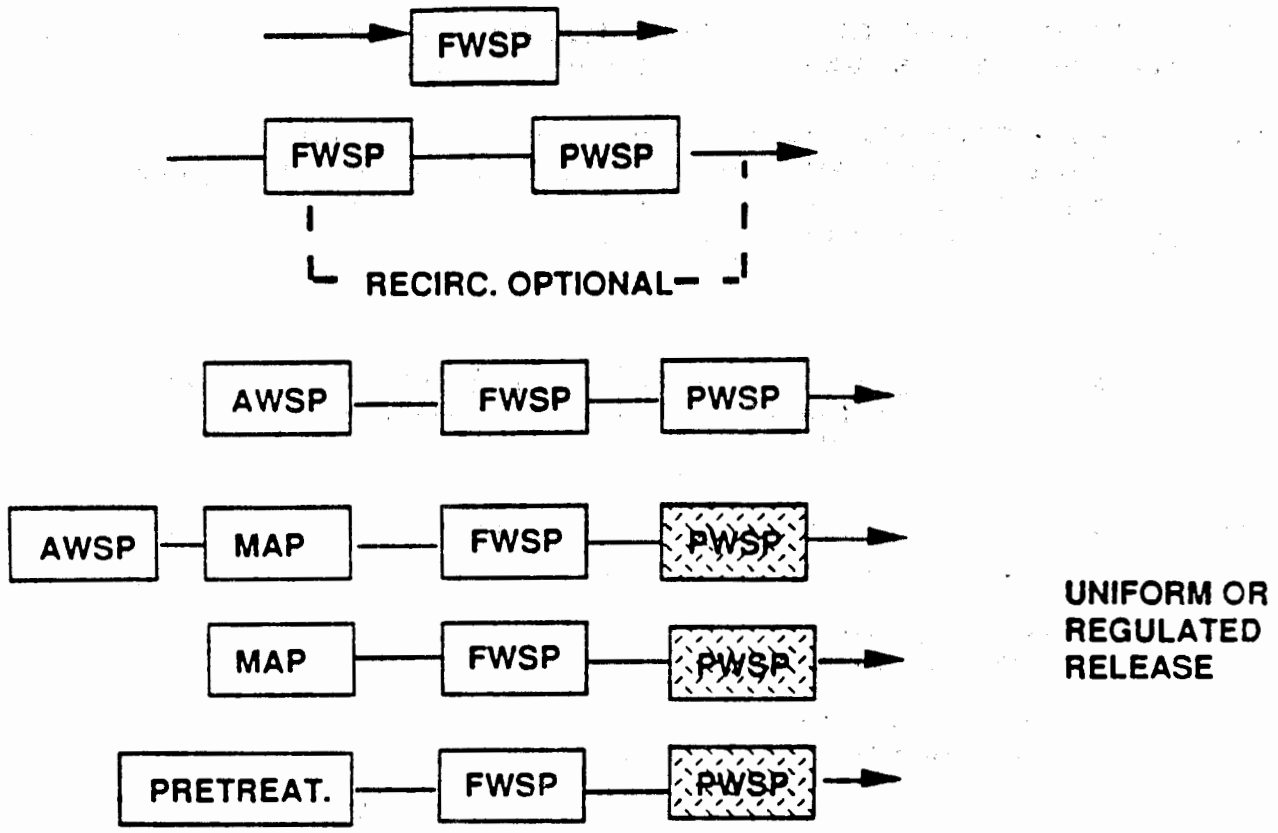


Figure 1. Possible Treatment Trains Associated with Facultative Waste Stabilization Ponds

The facultative waste stabilization pond (FWSP) is the central unit in a low-cost system. The primary source of oxygen is derived from photosynthesis. An anaerobic waste stabilization pond (AWSP) may be utilized to reduce the size of a FWSP. Similarly, a mechanically aerated pond system (MAP) can be used to reduce the space requirements with or without the assistance of an AWSP. The FWSP is usually followed by a polishing waste stabilization pond (PWSP). All pond systems may contain series connected units or be replicated as parallel systems.

ANAEROBIC WASTE STABILIZATION POND (AWSP)

An AWSP is an unmixed, deep basin. Organic removal is accomplished through hydraulic detention and solids sedimentation. In either case anaerobic decomposition of the organic substances reduces the BOD of the waste. A true AWSP is completely devoid of dissolved oxygen with the possible exception of a shallow facultatiave layer near the surface.

When anaerobic treatment processes are used, it is necessary to create an environment in which complex wastes are first hydrolized and then fermented. This process can be accomplished in either the AWSP or the bottom layer of a FWSP. The limiting step in a typical anaerobic process is the rate of fermentation or more specifically, the transformation of organic acids to methane. Of these acetic, propionic, and long-chain fatty acids (palmitic and stearic) are the most limiting.

Anaerobic fermentation is a sequential process. First, facultative organisms hydrolyze complex organic compounds into simpler organic molecules, primarily organic acids. Second, the anaerobic methane forming bacteria transform the organic acids into methane and carbon dioxide. Both processes may take place simultaneously and sychronously in a well-buffered system. The facultative acid producing bacteria also can use molecular oxygen during metabolism and protect the anaerobic methane forming bacteria from dissolved oxygen. These facultative organisms can tolerate a wide variation in pH ranging from a pH = 5.5 to about pH = 8.4. Also, temperature affects the rate of acid fermentation; however, these organisms are active over a temperature range of approximately 5 °C to in excess of 60 °C. During acid fermentation, almost no net reduction in the chemical oxygen demand or biochemical oxygen demand occurs. Carbohydrates such as cellulose and starch are converted to simple sugars which, in turn, are broken down to organic acids, aldehydes, and alcohols. Lipids, fats, and oils are converted to glycerol and fatty acids which subsequently are broken down into alcohols, aldehydes, and organic acids. Proteins are degraded to amino acids which, in turn, are converted to organic acids, mercaptans, and amines. During this conversion step, some carbon dioxide, ammonia, and hydrogen sulfide gas may be released. The principal intermediate compounds released during acid fermentation are the short chain carboxylic acids (volatile acids) primarily acetic, propionic, and butyric acids; however, smaller quantities of formic, valeric, isovaleric, and caprioc acids frequently are found in anaerobic systems. These volatile acids are converted by the methane forming bacteria into methane and carbon dioxide.

The conversion of the volatile acids by the methane forming bacteria results in a marked reduction in the amount of biodegradable material (COD, BOD) in the system. The amount of organic material stabilized during methane fermentation is directly proportional to the amount of methane produced.

A schematic diagram of the mechanism of anaerobic degradation of organic wastes is presented in Figure 2. The environmental factors which affect methane fermentation are summarized in Table 4. Initially, there is a decrease in pH accompanied by a rapid increase in the quality of methane in the off gas. The amount of methane gas produced can be predicted by estimating the degree of waste stabilization achieved, or conversely, the amount of methane gas produced can be used to determine the quantity of COD stabilized in the system. Methane can be expressed in terms of equivalent oxygen as shown in Equation 1. Therfore, one mole of methane is equivalent to two moles of oxygen or for 16 grams of methane produced and released from the system, 64 grams of oxygen equivalents (COD or BOD_u) are removed from the waste.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (1)$$

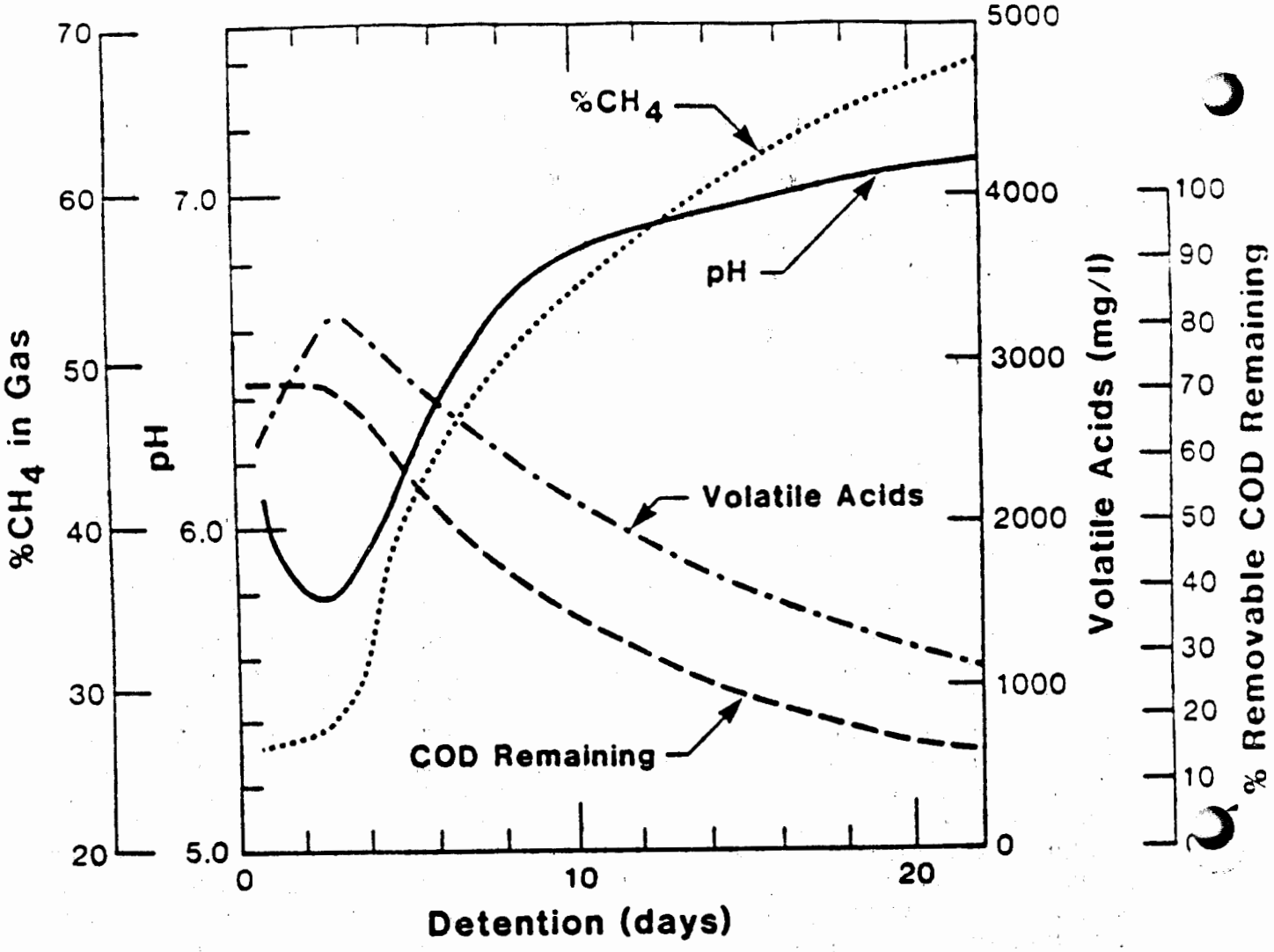


Figure 2. Anaerobic Degradation of Organic Waste

Table 4. Environmental Factors for Methane Fermentation

Variable	Optimum	Extreme
Temperature (°C)	30 to 35	25 to 40
pH	6.8 to 7.4	6.3 to 7.8
Oxidation-Reduction Potential (millivolts)	-520 to -530	-490 to -550
Volatile Acids (mg/L as acetic)	50 to 500	2000
Alkalinity (mg/L as $CaCO_3$)	2000 to 3000	1000 to 5000

Methane formation is precluded by sulfate reduction where sulfate concentrations are high. However, once the sulfates are reduced to H_2S, methane fermentation proceeds, provided the other environmental conditions are appropriate. The H_2S produced diffuses into the upper layers of the digester or pond and may cause odor problems if released into the atmosphere. The reduction of sulfate by organisms such as Desulfuvibrio requires a dissolved oxygen concentration of less than 0.16 milligram per liter (mg/L). Temperature should be greater than 15 °C. The optimum oxidation-reduction potential (ORP) for anaerobic conditions is -100 to -300 millivolts (mv) at pH 7.0. Growth is inhibited at ORP greater than +27 mv.

Sulfides can be toxic to bacteria in anaerobic systems at concentrations in excess of 200 mg/L at a pH near neutral. However, at concentrations between 50 and 100 mg/L, sulfides are tolerated. On the other hand, this anion will react with soluble heavy metal ions to form a metal sulfide precipitate which is relatively insoluble at pH near neutral. Approximately 1.8 to 2.0 mg/L of heavy metals are precipitated as metal sulfides by 1.0 mg/L of sulfide ($S^=$). This phenomenon offers an attractive alternative for the treatment of industrial wastewaters which contain heavy metals.

The alkalinity of the anaerobic system may provide the buffering capacity to the system; and this is essential for proper pH control. Alkalinity, primarily in the form of bicarbonate ions, is derived from the breakdown of organics. This relationship between alkalinity and the carbon dioxide in the gas is pH dependent and may be illustrated by Equations 2 and 3.

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (2)$$

$$H_2CO_3 \rightarrow H + HCO_3 \qquad (3)$$

The hydrogen ion concentration and eventually the pH of the system may be calculated from the following equilibrium equation for the ionization of H_2CO_3, Equation 4.

$$[H^+] = k_1 \frac{[H_2CO_3]}{[HCO_3^-]} \qquad (4)$$

At pH = 5.6 and pH = 7.4, and at normal carbon dioxide content in the gas, namely, 30 to 40 percent by volume, the bicarbonate alkalinity will range between 1,000 and 5,000 mg/L. Concentrations of alkalinity of about 3,000 mg/L are generally preferred rather than attempting to operate the system at the extreme values.

Ammonia is closely related to the alkalinity in the control of the anaerobic process. Ammonia reacts with the carbon dioxide and water resulting in ammonium carbonate which is available to react with the free volatile acids resulting in the formation of volatile acid salts. These reactions may be written as Equations 5 and 6.

$$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3 \quad (5)$$

$$NH_4HCO_3 + RCOOH \rightarrow RCOONH4 + H + HCO_3^- \quad (6)$$

At low volatile acid concentrations, the bicarbonate alkalinity represents approximately the total alkalinity; however, as the volatile acid concentration increases, the bicarbonate alkalinity is much lower than the total alkalinity.

At moderate temperatures, reductions in BOD of 50% to 70% have been reported for anaerobic ponds. The recommended depth for anaerobic ponds are 2 to 4 meters. The advantages of the deeper ponds are: (a) more efficient land utilization; (b) protection of the anaerobic methane bacteria from environmental changes; and (c) adequate storage for sludge and other settleable deposits. However, it must be noted that increasing depths tend to promote thermal stratefication and the average temperature lapse rate in a stabilization pond may be as high as 3 °C per meter. When the temperature decreases from 20 °C to 15 °C near the bottom of the pond, there may be a five-fold decrease in methane production.

The hydraulic detention, as contrasted to the solids retention, for anaerobic ponds need only be sufficient to settle the solids or partially biodegrade the soluble organics anaerobically. In some cases, a hydraulic detention of 3 to 5 days may be adequate, but the solids retention might require weeks or months of storage time. The detention-temperature-biodegradation relationship must be established by laboratory and pilot-scale studies. The minimum surface loading rate necessary for anaerobic conditions in an AWSP is usually between 200 and 600 kg BOD/ha·d; although there is no reason why the surface loading could not be 2000 kg BOD/ha·d.

FACULTATIVE WASTE STABILIZATION POND (FWSP)

Effective design of a FWSP requires considerable judgment (5,6). The size and shape of a FWSP can be estimated through laboratory and pilot studies; however, empirical relationships, based on appropriate temperature values, can be used to estimate the desired surface area, depth, hydraulic detention, sludge retention and other physical characteristics.

FWSP DESIGN PARAMETERS: Important design parameters are:

1. Ultimate Biochemical Oxygen Demand: The design of the FWSP should be conservative, and if solids or industrial wastes are involved the ultimate BOD_u load must be considered. The total oxygen requirement will be the sum of the immediate oxygen demand and the BOD_u or COD of both the soluble and solid fractions of the wastewater. The first-order BOD removal coefficient, K·(day^{-1}), can help in evaluating biological reactions.

2. Temperature: Temperature corrections are typically introduced through Θ. Values of Θ range from 1.036 to 1.085. It is recommended that 1.085 be used. If there is a considerable seasonal variation in temperature, it is important to use the average temperature (°C) of the coldest month of the year. The relationship $\Theta^{(T-35)}$ was developed to accommodate designs based on temperature. If the water temperatures exceed 35 °C, the bacteriological reactions proceed very rapidly and blue-green algae are mostly present. Under such conditions, typical designs for surface areas will not provide sufficient photosynthetic oxygen rapidly enough to maintain a viable aerobic-facultative environment. The pond will become murky, further reducing light penetration and oxygen production.

3. Light: Ponds will fail if there is inadequate light penetration. However, rarely is there inadequate sunlight at the surface of the pond. Excessive turbidity must be avoided because this is the main problem in obtaining adequate light transmission throughout the effective depth of a pond. Radiation energy required for the production of each g of oxygen has been determined to be about 15×10^3 J (3,580 cal). One g of cell material is theoretically equivalent to about 1.6 g of oxygen. Assuming that algal cell substances contain 85% organic matter, the oxygen yield per g of ash is about 1.35 g.

Photosynthetic energy conversion (sunlight) in a pond is subject to the total algae production and the daily insolation:

$$\text{Conversion} = \frac{\text{Production } (\frac{g}{m^2 \cdot d}) \times \text{Heat of Combustion (5.5 kcal/g)} \times 10^{-4} \frac{Cm^2}{m^2}}{\text{Total Insolation } (\frac{g \cdot cal}{m^2 \cdot d}) \times 10\text{-}3 \frac{kcal}{g \cdot cal}}$$

4. Sulfide: An average sulfide concentration of about 7 mg/L will destroy a crop of algae. When the sulfate ion concentration exceeds 500 mg/L, reductions in BOD loadings must be made or surface area increased. Sulfides are responsible for most pond odor and photosynthetic inhibition problems. The chemistry of inorganic sulfur compounds is complex, but usually sulfite and elemental sulfur is formed during the decomposition of thiosulfate when the pH drops below 5. Similarly, the conversion of thiosulfate to sulfate proceeds at pH ranges between 5.6 and 7.9.

5. Chlorophyll Inhibitors: The inhibitory effects of several organic chemicals on Chlorella pyrenoidosa have been documented. In sufficient concentrations, many industrial wastes severely reduce photosynthetic action.

6. Nutrient Utilization: The amount of nitrogen and phosphorus that must be added to pond systems bears no relationship to the amount required for high-rate treatment processes. Much of the nutrient in ponds can be recycled. Typically, BOD to phosphorus and BOD to nitrogen ratios, respectively, are 100:1 and 20:1. Some algal forms can utilize atmospheric nitrogen. In some cases, the concentration of algae can be reduced by appropriate nutrient management.

Generally, series-connected systems (AWSP-FWSP-PWSP) provide the best treatment units for recycling and possibly removing phosphorus. Removal of phosphorus from the liquid substrate occurs mostly in the AWSP and FWSP. Similarly, in the case of phosphorus deficiency in the liquid substrate, the sediments of these ponds can provide short-term phosphorus requirements. In a predominantly aerobic environment, such as provided by a PWSP, the phosphorus may be retained and not released to the overlying water. Models exist that can be used to estimate the amount of phosphorus that may be recycled (9).

7. Special Environmental and Waste Considerations:

a. Wind (magnitude and direction are important considerations in designing outfall weirs);
b. Evaporation and precipitation (data are required to establish the effective hydraulic detention);
c. Flooding (must not be permitted);
d. Groundwater (one or more liners may be required);
e. Soil characteristics (geotechnical data should be obtained to improve the design of clay liners and dikes);
f. Flow (daily average);
g. Chemical (BOD or COD, toxic or inhibitory materials, pH, sulfates and sulfides, and floating oil content should be determined);
h. Physical characteristics (floatable materials, color, and suspended and settleable solids should be determined); and
i. Toxicity (heavy metals should be evaluated).

8. Facilities: The master plan should include a layout sufficiently large to accommodate future expansion. It is best to construct only that portion of the WSPS presently needed. The grounds must be prepared for proper drainage; levees must be graded uniformly before grass is planted; surface water runoff and sediments must not be permitted to enter the pond; roadways must be developed to provide ready access; and embankments must be protected from erosion and animals.

9. Operation and Maintenance: All WSPS must be operated and maintained. Training programs for operators are very cost effective. Mosquito production in ponds is in direct proportion to the amount of emergent vegetation. Larvae of Culex, Anopheles, and other types of mosquitoes have been found in pond systems. Decaying algal mats blown into a corner may cause severe odors. For example, Chlamydomonas can grow rapidly, spread over pond surfaces, and reduce the penetration of light to the remainder of the pond. The entire mass, if not disturbed, may produce intense odors. The solution to the mat problem is immediate dispersement. Agitation of the surface will usually cause the floating mass to disperse and settle to the bottom.

A change in odor and color of the pond forecasts a possible change in the performance. Frequently, odors accompany illicit waste releases which cause a rapid change in the biological culture.

FWSP DESIGN EXAMPLES: Several empirical designs are available to determine the required surface area of a FWSP. The diversity in empirically derived concepts is provided in the following two examples:

1. Empirical Relationship--Example No. 1: Equation 7 was developed after evaluating 150 operating pond systems in tests and conducting several years of laboratory and pilot-plant studies over a wide range of temperatures. The BOD removals should be 80% to 90%. Based on observed fluctuations in pond performance, environmental conditions, and loadings, an appropriate safety factor was incorporated into Equation 5. It is logical to assume that the total BOD of the settled solids and wastewater will be exerted because of the relatively long hydraulic detention. If the influent load is primarily settled sewage or soluble BOD, the the BOD_5 might be used, and thereby reduce the overall volume by about 35%.

$$V = 3.5 \times 10^{-5} \, Q \, L_a \, \Theta^{(35-T)} \, f \, f' \qquad (7)$$

Where:

- V = pond volume (cubic meters)
- Q = flow (liters per day: Nq = No. of people x per person contribution
- L_a = ultimate influent BOD_u (mg/L) or COD
- f = algal inhibition factor, f = 1 for domestic wastes and many industrial wastes
- f' = sulfide or other immediate chemical oxygen demand, f' = 1 for SO_4 equivalent ion concentration of less than 500 mg/L
- Θ = temperature coefficient, usually assumed to be 1.085 for FWSP for domestic or non-toxic industrial wastes

Selection of the depth depends on the type of waste, settleable solids, temperature, and variability of the climate. A minimum depth of one meter is required to control vegetation. A maximum depth of two meters is recommended for a FWSP. Deep ponds are likely to become stratified, resulting in inadequate mixing, poor photosynthetic action, and inadequate oxygen production.

The land requirements can be reduced by providing pre-treatment (AWSP, MAP). Additional treatment and uniformity of effluent can be obtained by adding one or more PWSP.

The following guidelines for depth are suggested when temperatures are moderate and uniformly warm.

Depth	Pretreatment
1 to 1.5 m	Efficient solid removal (AWSP or Septic Tank Effluent)
1.5 to 1.75 m	Modest amounts of settleable solids. Surface area based on effective depths of 1.25 to 1.5 m with additional sludge storage of 0.25 m.

Figures 3 and 4 are used to obtain the detention, volume, and surface areas for the requirements provided below. (Pretreatment is assumed).

Given: Pretreatment with AWSP, septic tank, or leaching tank (60% BOD_u removal).

a. Population (N)	1,000
b. Mean Flow (Q) = Nq	1,000 x 100L/person/d
c. BOD_5	275 mg/L (50 g/person/d)
d. BOD_u (design base)	404 mg/L (BOD_5/0.68)
e. Temperature	28 °C
f. Land	Available
g. Embankment material	Available
h.	Percolation controllable with compacted local clay material and plastic liner
i. Rainfall	About equal to evaporation
j. Inhibition	f = 1
k. Sulfate loading	f' = 1

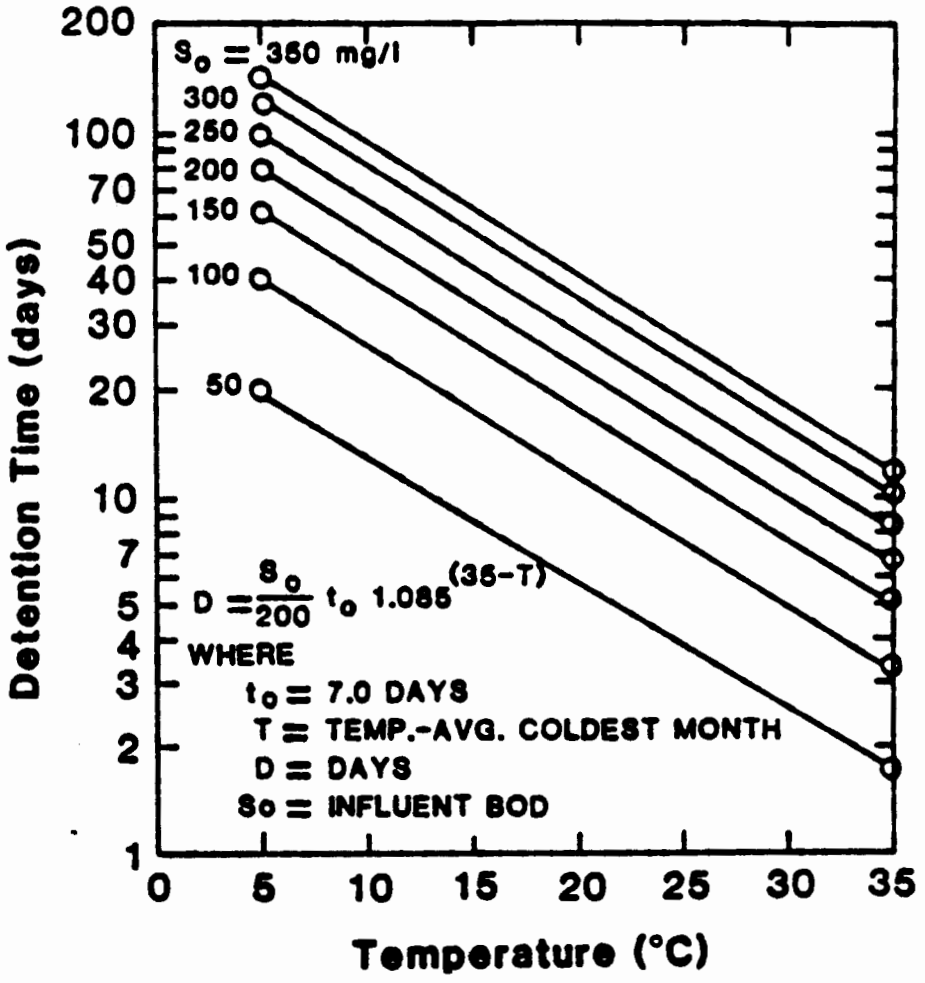


Figure 3. Detention for Facultative Waste Stabilization Pond

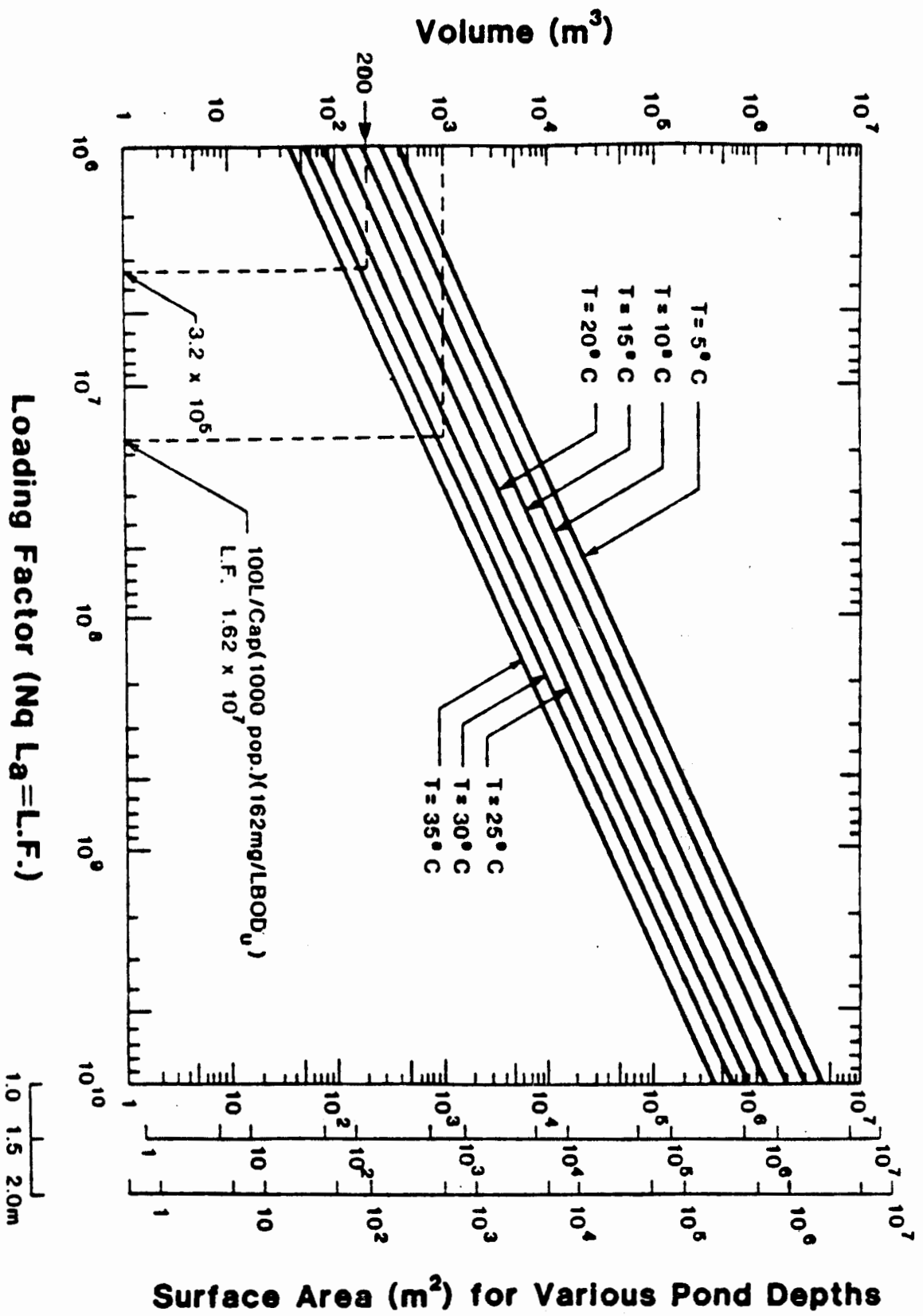


Figure 4. Graph for Calculating the Required Volume and Surface Area of a Facultative Pond

Required: Detention, volume, and surface area of FWSP (80% - 90% BOD_R)

Solution:

a. From Figure 3, using a temperture of 28 °C and a BOD_U load of (404) (0.40) = 162 mg/L, the required detention is 10 days, based on an effective design depth of one m.

b. From Figure 4, the required volume is about 1,000 m^3; the surface areas based on 1, 1.5, and 2.0 m of depth, respectively, are 1,000, 667, and 500 m.

c. From Equation 7, the above numbers may be checked:

(1)	Flow	100 m^3/d
(2)	Organic Load = 40.4 kg/d)	16.2 kg/d
(3)	Volume = $(3.5)\ 10^{-5})\ 0.10 \times 10^6$ L/d) $(404)\ (1\text{-}0.60)\ (1.085)^{(35-28)}$	
	= (567) (1.8)	1021 m^3
(4)	(a) Surface = 1021 m^3/1.0m	1021 m^2 = 0.102 ha
	(b) Surface = 1021 m^3/1.5m	681 m^2 = 0.068 ha
(5)	(a) Surface Loading = (16.2 kg/d/0.102 ha)	158 kg/ha•d
	(b) Surface Loading = (16.2 kg/d)/ 0.068 ha	238 kg/ha•d
(6)	Detention = 1021 m^3)/100 m^3/d)	10.2 d
(7)	BOD_U remaining = 16.2 kg/d (1-0.80)	3.24 kg/d
	BOD_U remaining = (404 mg/L x 0.40) (1-0.80)	32 mg/L

2. Empirical Relationship--Example No. 2: an alternative design, providing 70% to 80% BOD removal, has been proposed by McGarry and Pescod, Equations 8 and 9 (10).

$$L_s = 20T - 120 \quad (8)$$

Where: L_s = design loading (kg BOD/ha•d)
T = temperature (°C)

or

$$BOD_R = 0.725\ BOD_L + 10.25 \quad (9)$$

Where. BOD_R = BOD removal (kg/ha•d)
BOD_L = BOD load (kg/ha•d)

Given: Same as example 1.

Required: Same as example 1 (except BOD_R = 70% - 80%).

Solution:

L_s = 20T - 120

Design Load = 20 x 28 -120 = 440 kg BOD/ha•d

$BOD_R = 0.725\ BOD_L + 10.25$

BOD_R = 0.725 x 440 kg BOD/ha•d + 10.25

BOD_R = 330 kg BOD/ha•d

BOD_R = 75%

These two examples provide different answers, but BOD removals are different. FWSP systems are subject to a vast number of climatic variabilities. When a pond is heavily loaded, small cyclic changes in algal populations, weather, temperature, and waste characteristics can change the oxygen content of the pond dramatically. When ponds are receiving maximum loads, the influent area may become predominatly anaerobic with the usual accompanying odors. These overloading problems do not occur immediately. In most cases ponds do not reach maturity until they have been in operation for one or more years.

When a FWSP undergoes stress there may be rapid changes in pH, turbidity, algal forms, and photosynthetic oxygen production. The alternative to FWSP failure is to increase the size or add an AWSP.

DESIGN PROBLEMS: The major problems noted in FWSP designs are:

- misuse of anaerobic/facultative/aerobic biological principles;
- improper interpretation of physical/chemical requirements;
- unrealistic surface-volume-detention relationships for specific biological requirements; and
- improper designs based on short-term observations.

POLISHING WASTE STABILIZATION PONDS (PWSP)

A single FWSP may not provide uniformly acceptable effluent. Temporary upsets, short circuiting, and a host of other factors interfere in pond performance. Therefore, one or more PWSP may be necessary. The PWSP is not intended to relieve an underdesigned FWSP.

Generally, three to five days detention and a depth of one m are used for PWSP. This detention time and pond volume can be checked against Equation 7. If the BOD_u used in the calculations specifies a longer detention than three to five days, the larger surface area should be used. Also, if protein recovery (fish farming) is desired, additional series-connected PWSP may be utilized.

REMOVAL OF ALGAE

WSPS are generally effective in reducing BOD and total suspended solids (TSS), there can be a problem with excessive algae in the effluent, especially during the warmer seasons. Therefore, sometimes it is necessary to consider techniques for removing algae. Some background information is provided below.

IMPACT OF ALGAE ON RECEIVING ENVIRONMENTS: There are three factors that have to be considered in examining the effect of algae on a receiving water. First, over a relatively long period, some of the algae in an effluent will die and exert an oxygen demand on the receiving waters. Second, algae released to the environment will adjust their generation rates within a matter of days to reflect the new set of environmental constraints. Third, if the receiving system is not light-limiting at the autotrophic level, the resident algal populations may increase as a function of nutrient loadings.

The respiration requirements of viable algae are only about three percent of the body weight. If algae discharged to a stream remain suspended in light and are supplied the needed nutrients, they will grow and produce excess oxygen in the absence of severe salinity and temperature stresses. If the algae settle out, they will respire at a low rate, with oxygen demands of dead algae being approximately 1.4 times the dry weight of freshly destroyed algal cells.

Ample evidence indicates that placement of algae into a dark environment does not cause their immediate death. Rather, algae die at a diminishing rate and require 20 to 30 days to deplete their nutritional reserves. Studies indicate that at least some cells of Chlorella and Scenedesmus have remained sufficiently viable to be recultured after 60 to 90 days in an unheated anaerobic digester.

It has been shown that it is possible to chlorinate at a dosage to kill E. coli and permit survival of certain algae. The maximum dosage permissible for algal survival appears to be about 8 to 10 mg/L. Above this dosage, lysis increases and the BOD of the effluent increases accordingly.

GENERAL ALGAE REMOVAL CONSIDERATIONS: The removal of algal cells from pond effluents has been studied in considerable detail. The removal systems include the use of aquatic plants, predators, dissolved air flotation in conjunction with chemicals, sand and rock filtration, and nutrient control. Table 5 lists reported capital, operation, and maintenance costs associated with three possible treatment methods for removing algae fro pond effluents.

WATER HYACINTHS FOR EFFLUENT POLISHING: Water hyacinths (Eichhornia crassipes) (Mart. Solms-Laubach) were reportedly discovered in 1824 growing throughout the backwaters of the Amazon River Basin in Brazil (15). Characterized by its large glossy green leaves and pale lavender flowers above the water and feather-like, fibrous root system below, the water hyacinth can be found growing in many of the warm regions of the world. Hyacinths can overwhelm a body of water in a short time. However, these plants have proven to be an effective tool in PWSP effluents. The foliage shades the algae from sunlight, the plants remove nutrients from the

wastewater by direct plant uptake, and the root system provides a habitat for various grazing organisms.

Table 5. Algae Removal Costs

Treatment Method	Capital Cost ($/M^3$)	O&M ($/M^3$)	Year/(Ref.)
Microscreens	1.22	0.1	1982/(11)
Sand Filters			
Paired Bed Operation	0.17	0.022	1977/(12)
Modification of Existing Lagoon	0.14	0.022	1977/(12)
Water Hyacinths			
(w/o Greenhouse)			
Favorable	1.15	0.17	1978/(13)
Unfavorable	2.21	0.22	1978/(13)
(w/Greenhouse	0.55	-	1985/(14)

In addition to algae removal, hyacinths are responsible for reducing BOD, nitrogen, and, to a lesser extent, phosphorus. Removal of nutrients occurs primarily by plant uptake and oxidation by bacteria residing on the hyacinth's fibrous root system. Table 6 shows that an average reduction of algae, as represented by suspended solids removal, is on the order of 70% to 80%. Although there are no definitive criteria for the design and operation of a water hyacinth polishing system, general guidelines were published by the United States Environmental Protection Agency (16). Design guidelines are given in Table 7.

Water hyacinths are susceptible to salinity and temperature effects. although salinity is not often a problem when using hyacinths in a polishing pond, temperature can prove to be a serious limitation. Freezing water temperatures can cause plants to die in a matter of hours, and as a result, the use of hyacinths has been restricted to warmer climates (17).

The City of Austin, Texas (U.S.A.) has operated a hyacinth research facility. The greenhouse, 2.06 ha, encloses three hyacinth ponds arranged in parallel, each 265 m long.

UTILIZATION OF DUCKWEED: Duckweed may be used to control algae, because it eliminates light and is a floating aquatic macrophyte with a preference for ammonia. This plant has the advantage of converting degradable pollutants directly into protein. The effluent is suitable for agricultural use, and the nitrogen rich plant provides a bonus.

Table 6. Performance of Hyacinth WSPP

Site Description	SS		BOD_5		TN		TP		Reference
	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	
Williamson Creek WWTP, Austin, Texas									
Phase I (study)	38	5	22.6	5.2	8.2	2.5	-	-	
Phase II (study)	97	6	46.5	5.7	9.9	3.6	-	-	(35)
Full Phase	43.6	7.3	39.6	6.4	-	-	-	-	
National Space Tech. Lab, Mississippi	97	10	110	5	12.0	3.4	3.7	1.6	(36)
Roseville WWTP, Roseville, California									
Winter (Harvested)	10.7	3.0	11.6	3.5	16.7	3.5	-	-	(37)
Summer (Harvested)	7.1	5.4	8.6	2.5	18.2	8.0	-	-	
Coral Springs, Florida	5.6	2.9	13.1	2.9	22.4	1.0	10.9	3.6	(39)
Shreveport WWTP, Shreveport, Louisiana									
Pilot Study	231	16	231	41	35.9	19.5	-	-	(41)

Table 7. Design Guidelines

Parameter	Design Value	Expected Effluent Quality
Hydraulic Residence Time	> 6 days	BOD_5 < 10 mg/L
Hydraulic Loading Rate	800 m^3/ha·day	SS < 10 mg/L
Maximum Depth	0.91 m	TP < 5 mg/L
Area of Individual Basins	0.4 ha	TN < 5 mg/L
Organic Loading Rate	< 50 kg BOD_5/ha·day	
Length to Width Ratio of Hyacinth Basin	> 3:1	
Water Temperature	> 20 °C	
Mosquito Control	Essential	
Diffuser at Inlet	Essential	
Dual Systems, Each Designed to Treat Total Flow	Essential	
Nitrogen Loading Rate	< 15 kg TKN/ha·day	

The nutrients from the wastewater are absorbed by each frond and not from a central stem. The plants are capable of direct assimilation of organic molecules, such as carbohydrates and various amino acids. The specific growth rates may range from 0.10 to 0.35 g/g d. The annual yield on a dry weight basis may be 55 ton/ha. The protein content will be about 30% (18).

DISEASE AGENT REMOVAL: For purposes of disease control, the design of a polishing pond or filter system should be based principally on detention time. A vital feature for efficient reduction of the fecal bacteria is that the ponds be arranged in series. The detention must be determined primarily by the purification required. The die-off of fecal bacteria in aerobic ponds can be estimated, assuming reasonable mixing occurs, by Equation 8.

$$\frac{N}{N_0} = \frac{1}{KR+1} \qquad (8)$$

Where

N = concentration bacteria in a single pond
N_0 = influent concentration of bacteria

R = detention time
K = velocity constant, tentative value assumed to be 2

For a series of ponds, the relationship then becomes:

$$\frac{N}{N_o} = \frac{1}{(KR+1)^n}$$

Where

n = number of ponds in series with equal detention times

Quantitative data have been obtained which demonstrate the effect of representative algal species on selected enteric bacteria. The data show that individual algal species exert little influence on the die-off of enteric bacteria (19).

Both laboratory and field tests showed that anaerobic pretreatment in combination with facultative and polishing ponds, as compared to facultative and polishing ponds in series, resulted in higher die-offs of enteric bacteria.

FACILITIES DESIGN

Facilities design must consider the location and layout of the present and future plant, the interconnections, the physical structures, construction drawings and specifications. Site selection is of great importance. Pretreatment units consisting of grit chambers and bar racks must be considered under some circumstances.

Flow measuring devised are necessary. The piping arrangements must consider all inlets, outlets, transfer systems, and manholes. Inlets must be submerged and may require multiple units. Series-connected ponds require interpond piping, but these should help to minimize short circuiting. The design of the outfall system must consider pond level control, erosion, and mode of discharge. Transfer devised, such as manholes, provide operational flexibility. Earthwork includes clearing, road construction, excavation, embankment construction, dike protection, sealing of the bottom, grassing, fencing, drainage ditches, and associated facilities.

All earthen structures used must be constructed to protect groundwater resources. Typically compacted clay and membrane liners are required. Suggested requirements are as listed below:

- membrane lining with a minimum thickness of 20 mils, and an underdrain leak detection system; and
- in-situ or placed clay soils having the following qualities may be utilized in which clay has the following properties.
    a. more than 30% passing a 200-mesh sieve
    b. liquid limit greater than 30%
    c. plasticity index greater than 15
    d. minimum thickness of 2 feet

OPERATION AND MAINTENANCE

A pond system is an investment. Maintenance (M) and operation (O) is necessary. The following M/O are considered to be minimum requirements.

- Reports and measurements for regulatory agencies
- Enjoyment and structural maintenance
- Dike maintenance
- Insect control
- Odor control
- Tree and vegetation control
- Depth maintenance
- Mixing control
- Startup, shut-down and transfer controls.

MECHANICALLY AERATED WASTE STABILIZATION PONDS (MAWSP)

Aeration and mixing may be accomplished by recirculation of oxygen-rich waters from the effluent of a facultative or polishing pond system to the influent area, or by mechanically induced surface aeration. The two types of MAP are sometimes referred to as completly mixed, aerobic lagoons and partially mixed faculative lagoons. In the later case, the velocities and mixing characteristics permit much of the non-oxidized biological solids to settle to the bottom. These deposits must undergo anaerobic decomposition. In both cases, the effluents can be further treated by FWSP.

Figures 5 and 7 illustrate in summary form the utilization of oxygen and autotrophic growth requirements. Similarly, the associated coeficients relating to cell synthesis and endogenous respiration are shown. The role of the volatile suspended solids (VSS) or accumulated biological sludge mass is illustrated.

Figures 8 through 11, respectively, summarize the thirteen steps required to design an aerobic lagoon, design of facultative lagoon, advantages of series connections, and size relationships between a two-stage aerobic lagoon.

Figures 12 through 15 describe the basis for MAP design: oxygen utilization coefficients, sludge production coefficients, minimum detention, and temperature effects. These coefficients must be obtained through experimentation, usually batch tests.

The relationship between aeration basin temperature and aeration power level for both diffused air and surface aerators is illustrated in Figure 15. This temperature effect is very important. The biological activity is related to temperature and the oxygen transfer rates are also a function of temperature.

Figures 16, 17 and 18, respectively, illustrate oxygen transfer characteristics, influence of power input as related to surface area and power input versus suspended solids. Texas regulation, for example, requires that the mechanical aeration units in aerated lagoons shall have sufficient power to provide a minimum of 1.6 pounds of oxygen per pound of five-day BOD applied with the largest unit out of service.

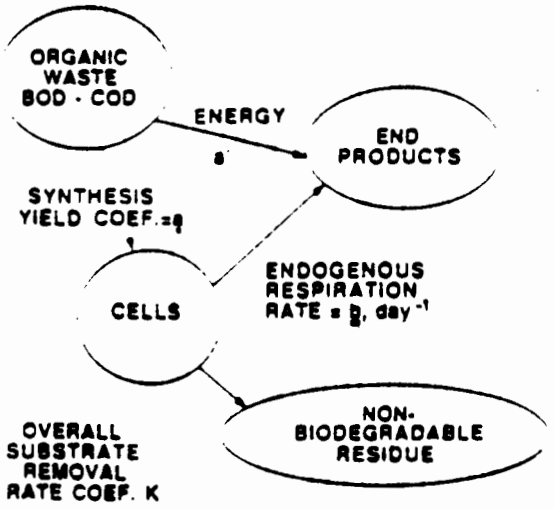
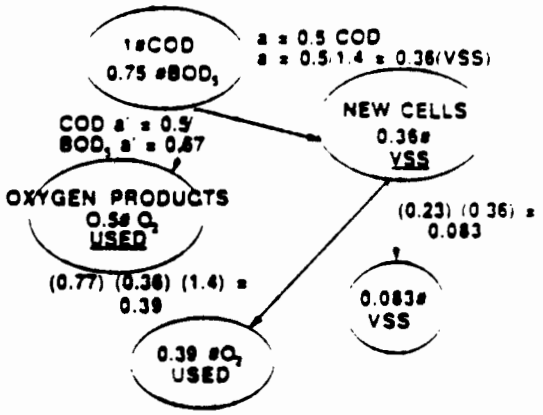


Figure 5. Aerobic Biological Oxidation



a = fraction of (BOD) (COD) REMOVED ⟶ CELLS

a' = fraction of (BOD) (COD) OXIDIZED ⟶ for energy

Waste	a BOD_5	a' BOD_5	b, day^{-1} (VSS BASIS)
REFINERY	0.49 - .62	0.4 - .8	0.10 - 0.160
PETROCHEM.	0.31 - .72	0.31 - .76	0.05 - 0.180

Figure 6. Autotrophic Growth

1. $do/dt = 1.72(S_o - S_e) - 1.37(VSS_1 - VSS_2)\ t$

do/dt = O_2 Uptake rate, mg.l.hr
S_o = Initial BOD_5
S_e = Remaining BOD_5
VSS_1 = Live organisms
VSS_2 = Dead organisms
t = Aeration time, days

2. OXYGEN TRANSFER

$dC/dt = k_L a\ (\beta C_s - C)\alpha$
dC/dt = mg/l/hr
$k_L a$ = OVERALL COEFF. (O_2 TRANSFER)
C_s = D.O. @ SAT., mg/l
C = D.O. @ time t, mg/l
α = O_2 transfer correction factor
β = Salinity - Surface tension correction factor

NOTE: $k_L a$ empirically derived describes O_2 as function of aerator delivery rate & volume of water per aerator.
$do/dt = dc/dt = 1 = k_L a\ (\beta C_s - C)\alpha$

Figure 7. Oxygen Uptake Rate

1. COMPUTE BASIN VOL=V=Qt
2. WINTER BASIN TEMP (USUALLY CONTROLS TERMINAL BOD_5)

$$t/D = \frac{T_i - T_w}{f(T_w - T_a)}$$

3. CORRECT BOD REACTION RATE FOR WINTER

$$k_{T_2} = k_{T_1}\,\theta^{(T_2 - T_1)}$$

4. CALCULATE BOD_5 (WINTER EFFLUENT)

$$\frac{S_e}{S_o} = \frac{1 - bt}{akt}$$

5. REPEAT FOR SUMMER (O_2 Req. & Power Level)
6. CALCULATE AVERAGE V.S.

$$X_v = \frac{aS_r}{1 - bt}$$

7. CALCULATE O_2 REQUIREMENT

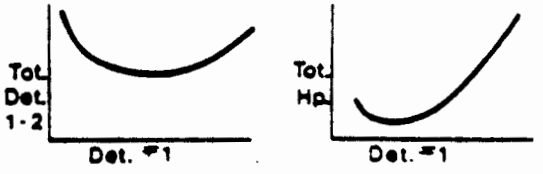
$$R_r = a'S_r - b'X_v$$

8. HORSEPOWER

$$N = N_o \frac{(\beta C_s - C_L)}{C_{s20}}\alpha\theta^{(T-20)}$$

$\frac{R_r}{N}$ = HORSEPOWER

9. CHECK POWER LEVELS
   Min ≅ 14 hp/MG
10. REPEAT USING DIFFERENT DETENTION TIMES
11. DESIGN BASIN II
    a. Min. power level for Fac. Lag.
       84 hp/MG to maintain
       50 mg/l SS in susp.
    b. REPEAT DESIGN
12. OPTIMIZE
    a. MINIMIZE TOTAL DETENTION
    b. OR TOTAL Hp.



13. NUTRIENTS
    a. 12% Nitrogen
    b. 2.6% Phosphorus

Figure 8. Design - Aerobic Lagoon

$$\frac{S_e}{S_o} = \frac{S_o(1-F)}{S_o - k X_v t}$$

F = Coeff. (Feedback from Sediments)

(Temp. DEPENDENT)

= 1.0 – 1.4 (Winter – Summer)

NOTE:

O_2 REQ. NOT COMPUTED DIRECT

EMPIRICALLY

$R_r = F'S_r$

F = OVERALL O_2 UTILIZATION

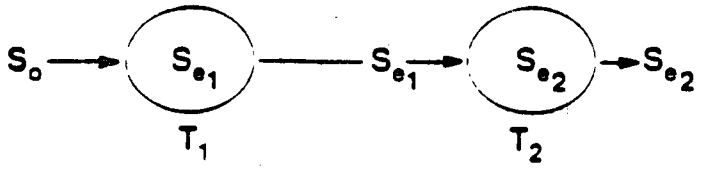
= 0.8 – 1.1 (Winter)

= 1.2 – 1.5 (Summer)

Figure 9. Design Facultative Lagoon

1. ADVANTAGES
   a. USES LESS SPACE
   b. MIN. TOTAL BASIN VOLUME
   c. MAINTAIN THERMAL BALANCE
      BASIN #1 - Maintain high temp.
      High VSS
      High reaction rate
   d. BASIN #2 - Low power level
   e. Assume = k valves series connected lagoons require 50% volume
   f. Well mixed reactors, connected in series are intermediate between plug flow and well mixed

Figure 10. Series Connections



$$\frac{S_{e_1}}{S_o} = \frac{1}{1 + kT_1} \; ; \; \frac{S_{e_2}}{S_o} = \frac{1}{1 + kT_2}$$

$$\frac{S_{e_2}}{S_o} = \frac{1}{(1 + kT_1)(1 + kT_2)}$$

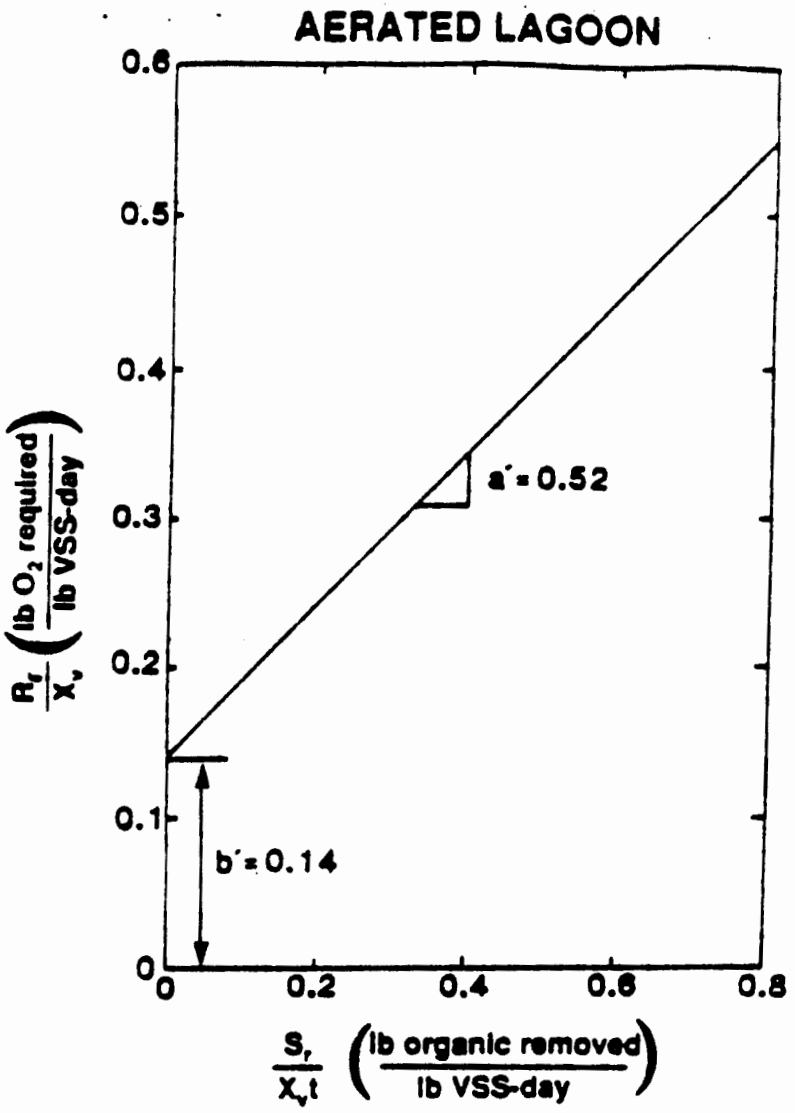
$$T_T = T_1 + T_2 \; ; \; T_1 = T_T - T_2$$

$$\frac{S_{e_2}}{S_o} = \left[\frac{1}{1 + k(T_T - T_2)}\right]\left[\frac{1}{1 + kT_2}\right]$$

Diff. & Eq. to 0; $\frac{dS_{e_2}}{dT_2}$

$$T_T - T_2 = T_2 \qquad \text{or} \qquad T_1 = T_2$$

Figure 11. Two Stage Aerobic



Determination of Oxygen Utilization Coefficients

$R_r = a'S_r + b'\psi X_v$

$R_r = O_2$ Reqd.

S_r = BOD removed

X_v = MLVSS

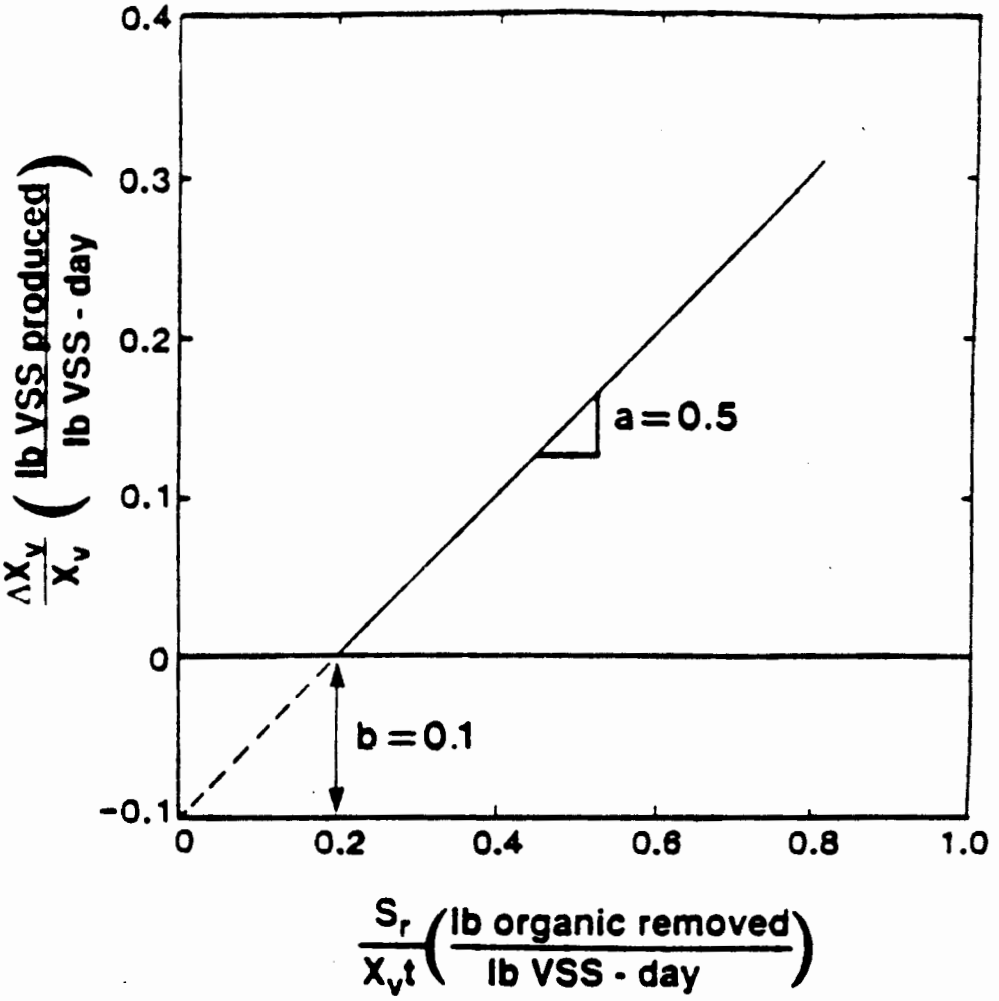
ψ = Biodegradable fraction MLVSS

$a' = O_2$ utilization coeff.(cell)

$b' = O_2$ utilization coeff (endog.)

Figure 12. Determination of Oxygen Utilization Coefficients

AERATED LAGOON



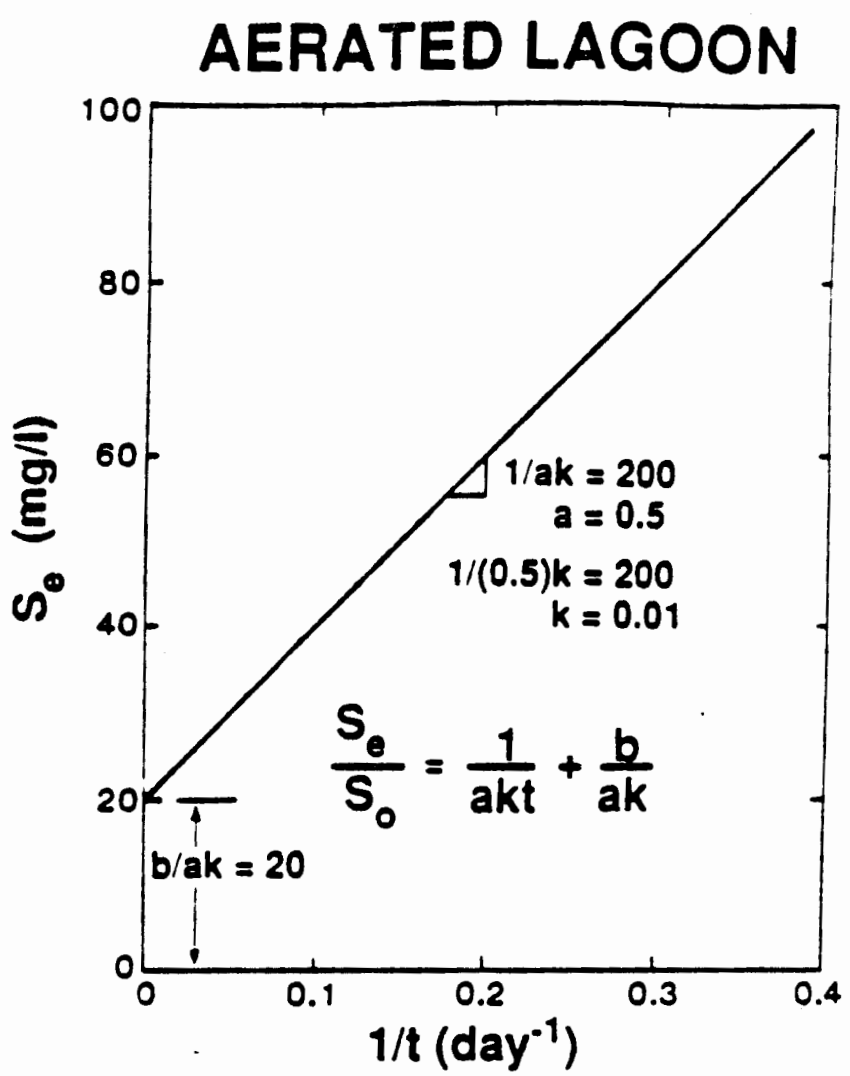
SLUDGE PRODUCTION COEFFICIENTS

$$\Delta X_v = fsi + aS_r - b\psi X_v$$

f = influent solids not biodegradable

ψ = biodegradable fraction of MLVSS

Figure 13. Sludge Production Coefficients



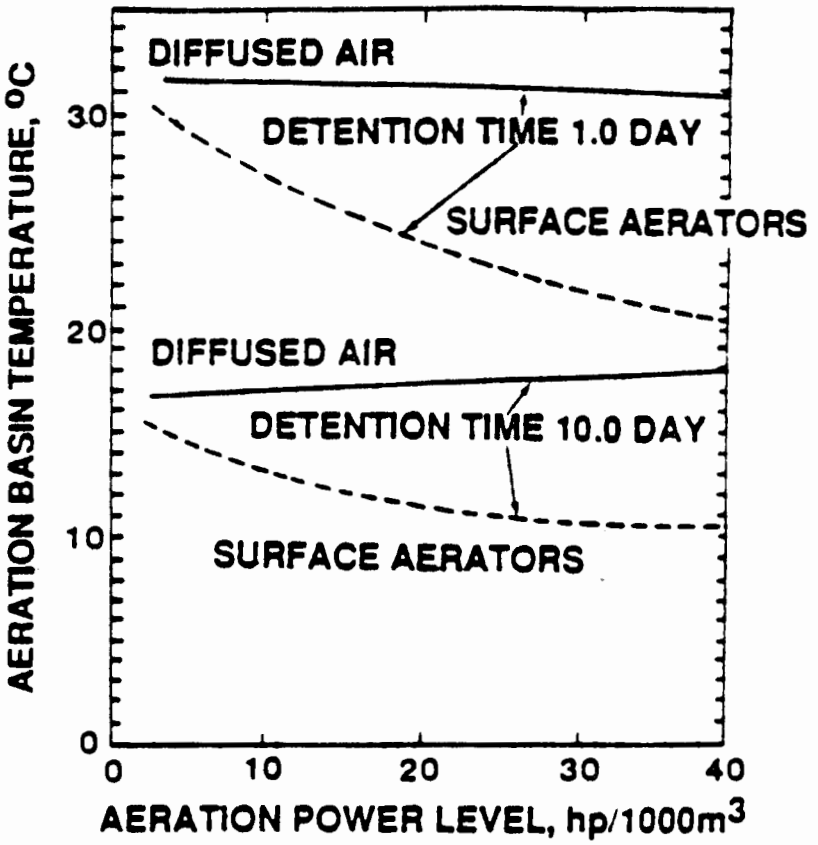
MINIMUM DETENTION

$$t_m = \frac{1}{ak-b}$$

k = <u>Temp. Depend.</u>

Figure 14. Minimum Detention

Cooling Effect of Surface Aerators and Diffused Air System



TEMPERATURE EFFECTS

$$\frac{t}{D} = \frac{T_i - T_w}{f(T_w - T_a)}$$

t = Detention, days

D = Depth, ft

T_i = Influent (^oF)

T_a = Mean air (^oF) (Weekly)

T_w = Basin temp, ^oF

$f \cong 90$

Figure 15. Temperature Effects

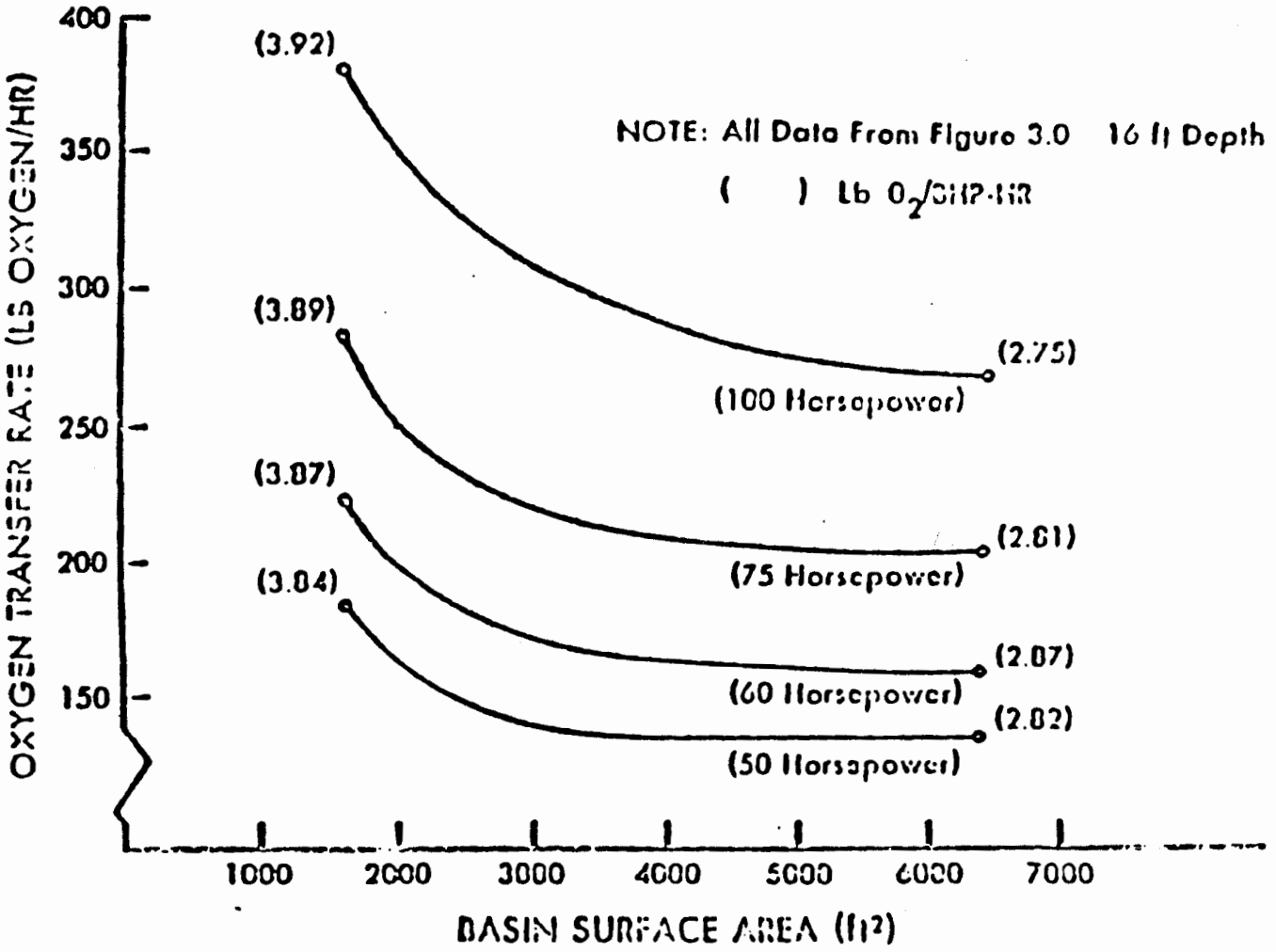


Figure 16. Oxygen Transfer Rate vs. Basin Surface Area for Low-Speed Surface Aerators

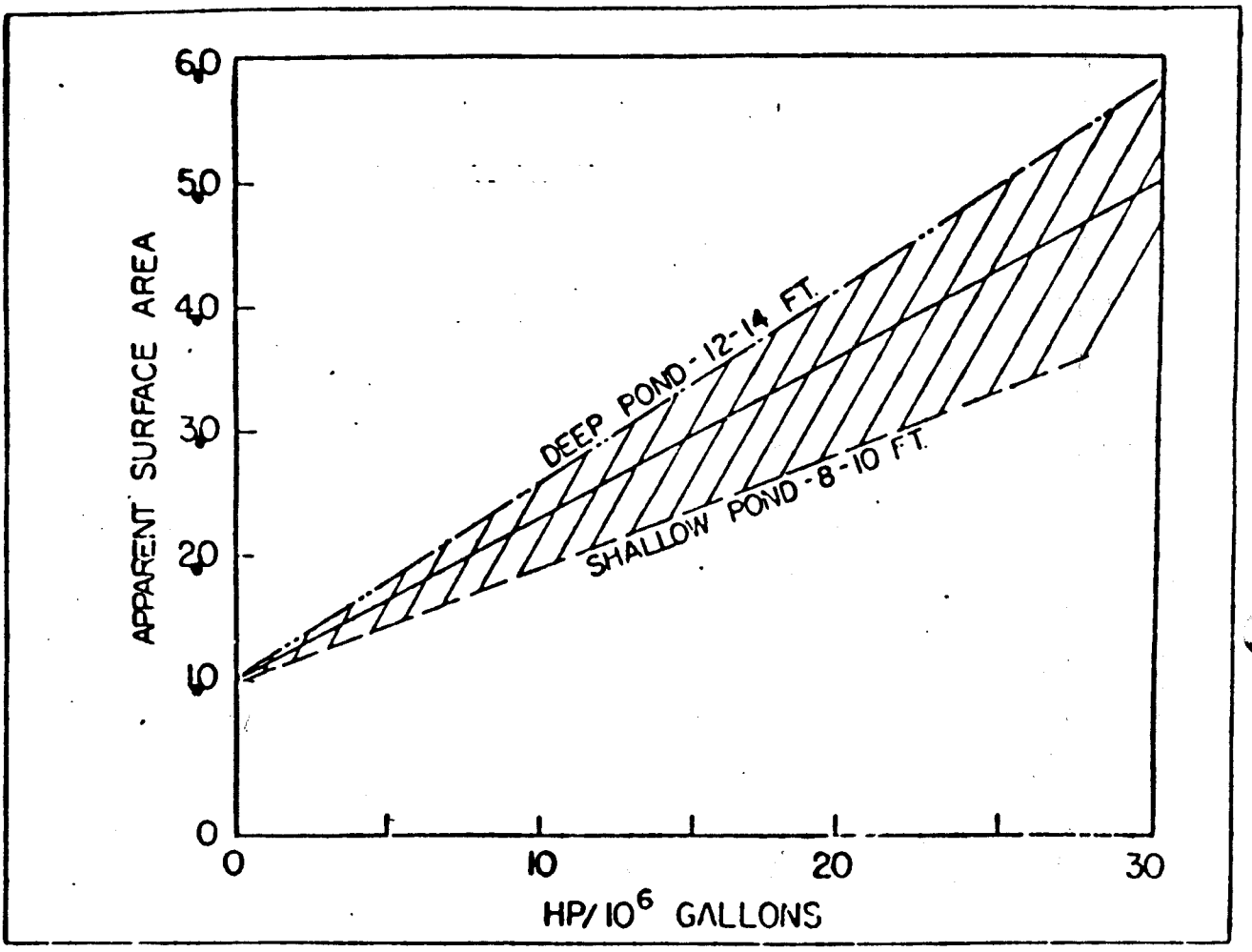


Figure 17. Influence of Power Input--Apparent Surface Area

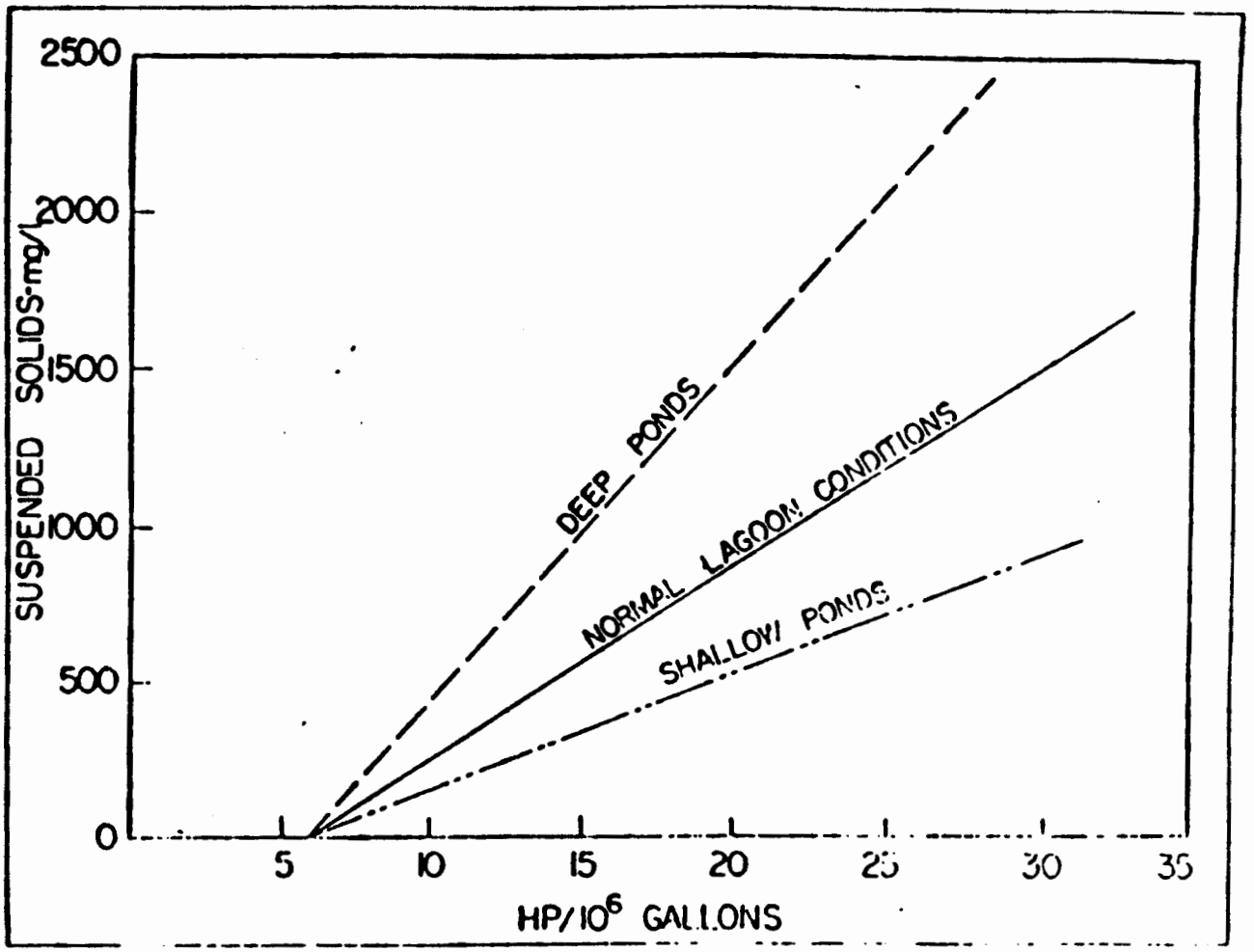


Figure 18. Influence of Power Input--Solids Suspension

LAND APPLICATION

The disposal of wastewaters by land treatment provides an attractive alternative for solving costly waste management problems. The earth's mantle has been described as a "living filter" and the most ecologically appropriate treatment system for man-made wastes.

For clarity of definition, land treatment is not necessarily wastewater spreading, wastewater farming, disposal of partially treated effluents on the land or even the use of effluents for irrigation purposes. The difference is in what aspect of the management plan is being maximized. If crops are used as a part of a land treatment system, the objective is to apply as much wastewater as possible without decreasing plant growth.

EXAMPLES OF WASTEWATER REUSE VIA LAND DISPOSAL

Land disposal of wastewater predates modern civilization. More recent historical experiences describing the use of wastewaters to irrigate cropland are fairly well documented (23). For example, it is known that use of wastewater for irrigation purposes was common practice in Bunzlau, Germany, as early as 1559 (1). Selected wastewater reuse and land disposal projects are described below:

Werribbee Farm, Melbourne, Australia, discharges 4.4×10^5 cu m/day to several thousand acres of crop land supporting 30,000 sheep and 22,000 beef cattle. The concentration of heavy metals in the harvested herbage falls within acceptable ranges although N, P, and K show increases, the BOD_5 and SS removal rates are around 95%. all of this is remarkable since 30% of the flow and 75% of the organic loading is contributed by industrial wastes.

The municipal wastewater farms of Paris have been in operation since 1880, and these farms have been very successful. These farms are receiving about 100 million cu m/yr of wastewater. Application rates are 4 m per year over a mixture of sand, clay, and gravel.

At Braunschweig, Germany, cereal crops, potatoes, sugar beets, and asparagus have been irrigated by wastewater application for many decades (1).

At present, Israel utilizes most of its fresh water potential of 1,500 million cu m per year. About 75% is supplied to agriculture. It is planned that by 1985, 10% of the agricultural water requirements will be supplied through wastewater reclamation.

In Poland during dry years, sewage represents 50% of all surface flow. The Wroclaw Farm, 1,500 ha, receives 170,000 cu m/day. It has been in operation for 100 years.

The King Khalid Military City, Saudi Arabia, a city of 70,000 people and one of the world's largest and costliest construction projects, will reuse all water. Sewage effluents will be used for agricultural purposes.

About 3% (31,000 ha) of the total area under irrigation is irrigated with wastewater. Municipalities provide about 85% of this wastewater.

The U.S. nearly a decade ago registered about 600 municipalities and 1,300 industrial facilities discharging wastewaters on land. Most of these sites were located in the dryer western states. The 1972 amendments to the U.S. Federal Water Pollution Control Act indicate that it is a national goal to minimize discharge of waste to surface waters.

The State of California leads the U.S. in reuse with a history of irrigation and reuse that dates back to 1929. The volume of wastewater reused in 1977 was about 227 billion cu m. Of the 200 projects in operation, 150 were classified as nonsensitive crop irrigation and 50 were used to water golf courses, recharge groundwater, industrial reuse, and other purposes.

At the billion dollar Disney World complex in Florida, a secondary treatment plant with tertiary holding poind provides water for tree farms, agricultural usage, aquaculture, and wetlands-land treatment systems.

The largest agricultural water reuse project is located in Muskegon County, Michigan. This single project involves about 4,000 ha.

Lubbock, Texas, can now enjoy one of the largest parks in the U.S. because of innovative water reuse planning. The park covers 620 ha and a recreational greenbelt that is 10 km long. To insure a water supply, reclaimed wastewater will be withdrawn from stored groundwater produced through irrigation of 1800 ha of farm land with municipal wastewater.

On a smaller scale, a turf farmer rented 13.4 ha near the wastewater treatment plant of Tolleson, Arizona. The farmer guarantees the city a minimum rent of $3,500 per year. The farmer uses chlorinated secondary effluent.

POTENTIAL WASTEWATER CONTAMINANTS AND NUTRIENTS

Wastewater, particularly industrial wastes, contain various amounts of contaminants such as salts, nitrogen, nontoxic organics, toxic elements, and microorganisms.

SALTS: The extent and severity of injury caused by salt are influenced by soil characteristics. Dissolved solids will leach out of the water and sludges and accumulate in a soil. Sandy soils permit rapid leaching but at the same time, the amount of salt per unit volume of waste available to plants is greater in a sandy soil.

Sodium ions present a major problem. The sodium absorption ratio (SAR) expresses the degree of sodium absorption from a solution in equilibrium with the soil. The SAR is defined as follows by Equation 12:

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{++} + Mg^{++}}{2}}} \qquad (12)$$

Irrigation water with a SAR value of less than 10 (ion concentrations in milliequivalents per liter) constitutes a low hazard. At high levels, sodium causes deflocculation of clay soils and subsequent sealing. Serious problems occur when the exchange sodium percentage reaches a value of 15% (23).

NITROGEN: Land application of municipal wastewaters on land has a number of advantages. Nearly all soils respond to additions of nitrogen by increasing production; however, for optimum crop production, the nitrogen application must be in balance with the need. Furthermore, if the nitrogen is applied to the soils in amounts greatly in excess of crop needs and is allowed to percolate to the groundwater, nitrate contamination may occur. The important process involved in nitrogen removal during land application of wastewater involve:

a. ammonia volatilization
b. crop removal
c. soil adsorption of ammonia
d. incorporation into the soil organic fraction, and
e. denitrification

The relative impact of any of the above processes on nitrogen removal is highly dependent on soil characteristics, climate, and wastewater management practices.

Fertilizer value of municipal wastewaters is readily evident in that a five centimeter per week application might provide commercial fertilizer constituents equivalent to approximately 233 kg/ha of nitrogen, 224 kg of phosphate (P_2O_5) and 254 kg of potash (K_2)). These data are equivalent to an annual application of about 2,200 kg of a ten-ten-ten fertilizer per hectare. This is more than twice as much as a generally acceptable application of commercial fertilizer. Some crops are highly effective in removing nitrogen and phosphorus.

Waste management is the key to excess nitrogen in industrial wastes. This control process may involve crop selection, amount of waste applied in relation to soil, drainage, infiltration, and other factors such as pH, moisture, temperature, and carbon content. Average uptake of nitrogen by crops ranges from about 27 kg for wheat to as much as 270 kg for well-mamaged Bermuda grass (24). Generally, low application rate systems should be designed for nitrogen uptake by crops. The time-movement scale for the soluble inorganic forms of nitrogen is the same as that for the percolation of the water. The critical C:H ratio affecting mineralization and immobilization is between 15 and 33, and the critical N(%) in an inorganic waste is between 1 and 3% for mineralization. A high BOD waste may enhance reducing conditions and cause denitrification.

PHOSPHORUS: Municipal wastewaters may contain 1.0 to 40 mg/L of phosphorus. Since phosphorus is essential for all forms of life, it may be possible to

increase agricultural productivity by applying municipal wastewater on the land. Unfortunately, phosphorus is highly reactive and reactions involving phosphorus with soils are complex. The capacity of a soil to sorb phosphorus is dependent on the concentration of phosphorus in solution, pH of the soil, temperature, time, total amount of phosphorus added, and the concentrations of various constituents in the wastewater that directly react with phosphorus. Also, the downward movement of phosphorus in a soil profile is diffuse.

Removal of phosphorus in harvested crops is typically 10% or less of the fertilizer phosphorus added during the season in which the crop is grown, although recoveries may be as high as 50% to 60%. Phosphorus removed by the usual harvested portions of selected agronomic, vegetable, and fruit crops ranges from a low of 11 kg/ha•yr to as high as 95 kg/ha•yr.

NONTOXIC ORGANICS: Biodegradable, nontoxic organics do not present a potential hazard, but soil clogging may occur. This restriction in flow results in decreased infiltration and percolation. Wastes having a high C:N ratio appear to induce clogging.

TOXIC ELEMENTS: Wastewaters containing heavy metals may produce a major long-term hazard. Of greatest concern are boron, cadmium, cobalt, chromium, mercury, nickel, lead, and zinc; however, other metals such as copper may present a problem. Some metals in wastewaters such as zinc are essential to life and may provide an environmental benefit, but these also can accumulate and post potential long-term hazards.

Conditions that favor low pH, sandy soils, high metal sludges, and metal sensitive crops require most supervision. Generally, the concentration of a metal in soil is the most important factor to consider. Since most metals are relatively immobile in soils, there are only two major factors that must be assessed to evaluate the status of a metal in soil: (a) the total mass input to a soil, and (b) the vertical distribution of that mass when it is in a relatively steady state condition in the soil.

Identification of metal species is very important. Metal species differ in chemical properties and these classes incude complexes, ion pairs, and chelates.

MICROORGANISMS: Removal of microorganisms, particularly human pathogens from wastewaters applied to soils, is an important consideration in land disposal of municipal wastes. More than 90% of the bacteria are removed in the upper one centimeter of a good soil. Yet, several meters of soil may be necessary for nearly complete removal of bacteria. The rate of movement is dependent upon such characteristics as type of soil, porosity, and channeling. Longevity of organisms such as Salmonella depends on a number of factors including temperature, organic matter content, and aerobic state. These organisms have been observed in some instances to survive in soil from six months to a full year. Salmonella survive in frozen soil for longer periods than in unfrozen soil, while E. coli survive longer in sterile than in non-sterile soils.

Survival of pathogenic organisms in and on the soil and on vegetable crops has received considerable attention. Table 8 gives survival times of various pathogens in the different media.

HYDRAULIC CAPACITY

The capacity of the soil to accept and transmit water is crucial to the design of both rapid and slow rate land application systems. Hydraulic parameters of importance are:

a. infiltration
b. vertical permeability (percolation), and
c. horizontal permeability

The hydraulic properties of a soil (flow or retention of water within the soil profile) include:

a. soil-water characteristic curve
b. percent moisture at saturation
c. permeability
d. infiltration rate
e. ability to drain
f. specific yield
g. specific retention, and
h. transmissivity.

It should be noted that water held in soil is roughly inversely proportional to the pore diameter.

LAND TREATMENT

The controlled application of wastewater onto the land surface can provide a high degree of treatment. The three major land treatment processes are:

a. slow rate
b. rapid infiltration; and
c. overland flow

There are various types of land application. Irrigation by spraying or spreading provides controlled discharge of effluent. The application method depends upon the soil, the type of crop, the climate, and topography. Overland flow is controlled discharge in which a large portion of the wastewater becomes runoff; whereas in the infiltration-percolation process the major portion of the waterwater enters the groundwater.

TABLE 8. SURVIVAL TIMES OF PATHOGENS

Organism	Media	Survival Time
Anthrax bacteria	In water and sewage	19 days
Ascaris eggs	On vegetables	27-35 days
	On irrigated soil	2-3 years
	In soil	6 years
B.dysenteriae flexner	In water containing humus	160 days
B.typhosa	In water	7-30 days
	In soil	29-70 days
	On vegetables	31 days
Cholera vibrios	On spinach, lettuce	22-29 days
	On cucumbers	5 days
	On nonacid vegetables	2 days
	On onions, garlic, oranges, lemons, lentils, grapes, rice and dates	Hours to 3 days
Coliform	On grass	14 days
	On clover leaves	12-14 days
	On clover at 40-60% humidity	6 days
	On lucerne	34 days
	On vegetables (tomatoes)	35 days
	On surface of soil	38 days
	At -17°C	46-73 days
Entamoeba histolytica	On vegetables	3 days
	In water	Months
Enteroviruses	On roots of bean plants	At least 4 days
	In soil	12 days
	On tomato and pea roots	4-6 days
Hookworm larvae	In soil	6 weeks
Leptospira	In river water	8 days
	In sewage	30 days
	In drainage water	32 days
Liver fluke cysts	In dry hay	Few weeks
	In improperly dried hay	Over a year
Poliovirus	In polluted water at 20°C	20 days
Salmonella	On grass (raw sewage)	6 weeks*
	On clover (settled sewage)	12 days
	On vegetables	7-40 days
	On beet leaves	3 weeks
	On grass	Over winter
	On surface of soil and potatoes	40 days*
	On carrots	10 days*
	On cabbage and gooseberries	5 days*
	In sandy soil - sterilised	24 weeks
	In sandy soil - unsterilised	5-12 weeks
	On surface of soil (raw sewage)	46 days
	In lower layers of soil	70 days
	On surface of soils (stored sewage)	15-23 days
	In air dried, digested sludge	17 weeks*
Schistosoma ova	In digestion tanks	3 months
	In sludge at 60-75°F (dry)	3 weeks
	In septic tank	2-3 weeks
Shigella	On grass (raw sewage)	6 weeks
	On vegetables	7 days
Streptococci	In soil	35-63 days
	On surface of soil	38 days
S. typhi	In water containing humus	87-104 days
Tubercle bacteria	On grass	10-14 days
	In soil	6 months*
	In water	1-3 months
Typhoid bacilli	In loam and sand	7-17 days
	In muck	40 days
Vibrio comma	In river water	32 days
	In sewage	5 days

Figure 19 illustrates the relationship between liquid loading rate and soil type for the three land application approaches (12). Applications may vary. In the spray method, effluent is applied through nozzles or sprinkler heads. Costs of this system are relatively high because of pump and piping costs and power for operation of pumps. In the ridge and furrow method, application is by gravity flow. Relatively flat land is required for this method and care must be taken to avoid clogging up soil pores. Flooding requires level land so that a uniform inundation depth can be maintained. Crops must be able to tolerate the periodic flooding; "drying out" of the soil between applications is necessary to avoid clogging.

Overland flow is used with low infiltration and/or percolation capacities. Generally, close growing grasses are utilized. Rapid infiltration/percolation designs may be used where deep permeable soil materials are available. Crop irrigation land treatment applies treated effluents by spray applications or by flooding through furrows or borders.

PLANNING AND TECHNICAL ASSESSMENT

Several factors determine the utility of each site. They should be evaluated both individually and collectively when assessing the requirements of any treatment site; i.e., (a) climate conditions, (b) size of the facility, (c) land characteristics, (d) effluent characteristics, and (e) methods of distribution.

A direct relationship exists between climate and in such cases where sprayed effluent supplements agriculture or silviculture. Similarly, availability of land and size of facility are interrelated. Waste characteristics determine the degree of pretreatment required. Finally, climatic conditions and mode of distribution are closely interrelated. For example, spray irrigation is more generally used in humid areas, while surface applications, i.e., overland flow and ridge furrow irrigation are more adaptable to more arid regions. It seems that the latter technique is utilized more for larger sites, 400 ha. (1,000 acres) (14).

A critical feasibility study will assist in identifying significant problem areas. Such a study should include: (a) land location and mode of acquisition; (b) groundwater contamination assessments; (c) soil characteristics and eutrophication enhancement. Land procurement may be an expensive and difficult problem. Groundwater must be carefully monitored. As to soil characteristics, some soils possess large adsorption capacity. Phosphorus saturation and clogging are frequently limiting factors in the life span of a disposal site. Control of heavy metals is necessary. However, crop rotation can eliminate some of the above problems.

The overall planning process should include the following steps:

a. waste characterization
b. land treatment system suitability
c. land requirement
d. site identification
e. site screening

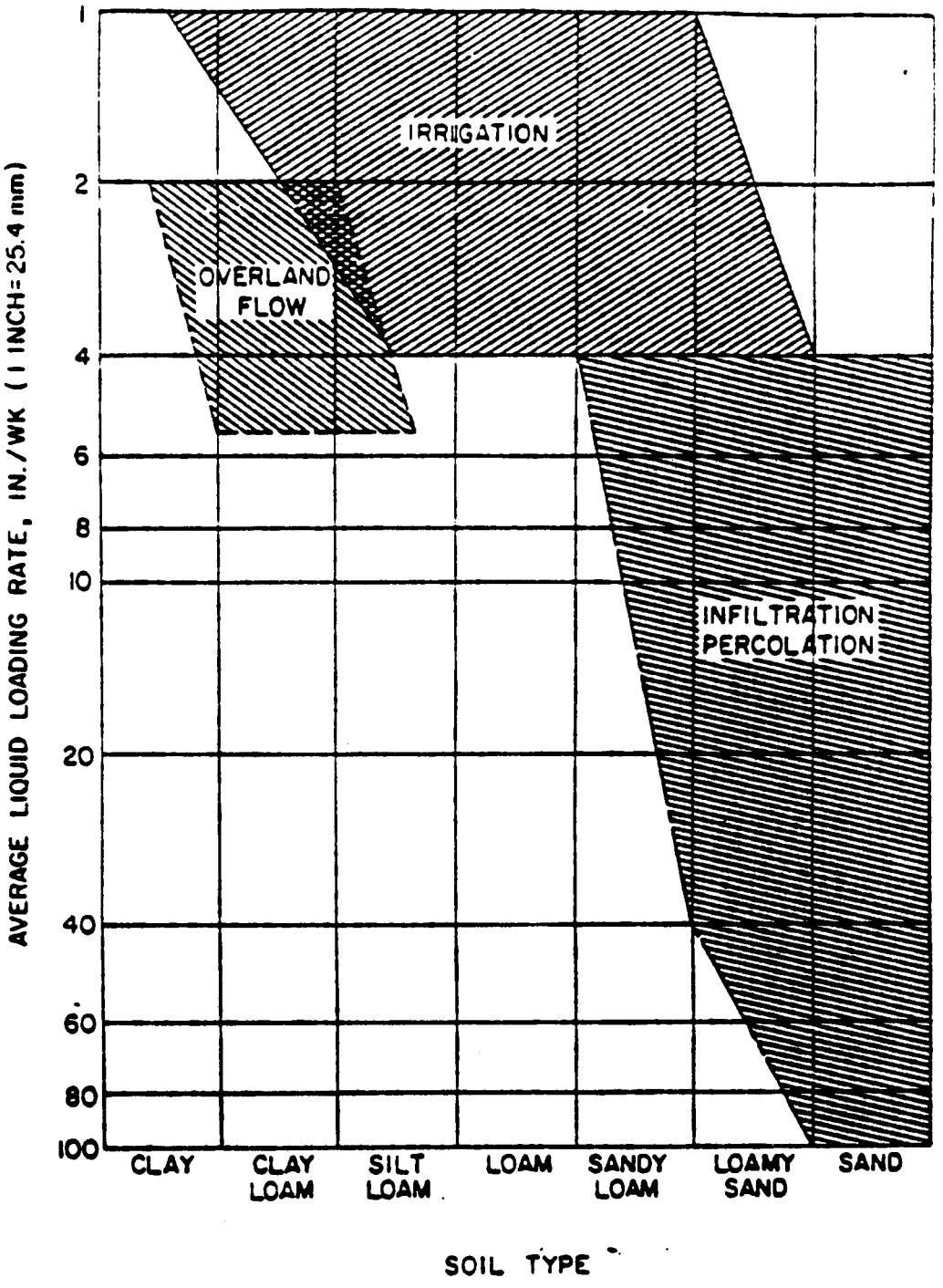


Figure 19. Soil Type Versus Liquid Loading Rates for Different Land Application Approaches

Table 9. Field Investigations (25)

	Test Pits	Bore Holes	Infiltration Rate	Soil Chemistry
Remarks	Usually with a backhoe, includes inspection of existing SCS reports, road cuts, etc.	Drilled or augered, includes inspection of driller's logs for local wells, water table levels	Match the expected methods of application, if possible	Includes review of SCS survey
Information to Obtain	Depth of profile, texture, structure, soil layers restricting percolation	Depth to groundwater, depth to impermeable layer(s)	Expected minimum infiltration rate	Specific data relating to crop and soil management, phosphorus and heavy metal retention
Estimates Now Possible	Need for vertical conductivity testing	Groundwater flow direction	Hydraulic capacity based on soil permeability (subject to drainage restrictions)	Crop limitations. Soil amendments. Possible preapplication requirements.
Additional Field Tests	Vertical conductivity (optional)	Horizontal conductivity	--	--
Additional Estimates	Refinement of loading rates	Mounding analysis, dispersion, need for drainage	--	Quality of percolate
Number of Tests	Depends on size, soil uniformity, needed soil tests, type of system. Typical minimum of 3 to 5 per site.	Depends on system type (more for RI than SR), soil uniformity, site size. Typical minimum of 3 per site.	Depends on size of site, uniformity of soil. Typical minimum of 2 per site.	Depends on uniformity of soil types, type of test, size of site

*f. potential site selection
g. field investigation
h. preliminary design criteria and costs
i. evaluation of alternatives
*j. plan selection, and
k. initiation of land treatment design

*Check points which may indicate that land treatment is not feasible.

Field tests are very important. A typical order of testing progressing from exploratory test pits to laboratory tests is given in Table 9. A general interpretation of the chemical tests is summarized in Table 10.

SMALL SYSTEMS

The design of small systems (generally less than 3,785 cu m/d) includes special cost and operational considerations. While slow rate, rapid infiltration or overland flow systems can be used, it must be recognized that experts will not be available on a daily basis. Therefore, the design and operating criteria are most important.

In addition to pretreatment requirements, selection of a hydraulic loading rate is most important. The permeabiity of the soil usually controls the loading rate; however, when slow rate or rapid infiltration systems overlie potential drinking water aquifers, nitrogen loading may be the limiting factor.

WETLAND TREATMENT

Wetlands are natural systems (20). These systems are those areas that are natural marshes, constructed wetlands and rush/reed beds. The rush/reed beds are designed to follow ponds or other types of treatment. The water table is near or above the ground surface long enough each year to maintain saturated soil conditions and growth of native vegetation.

Generally, the full capacity of the native wetlands is not fully utilized because regulatory requirements specify that the wastewaters must meet discharge requirements. The assumption is made that the wetlands are part of the receiving body of water.

Constructed wetlands provide more specific control over the hydraulic and loading regimes (21). These systems are not considered to be part of the U. S. waterways. The limiting design parameters for the constructed wetlands can be devided into two categories as listed below:

a. free-water surface -- BOD, SS, and N removal
b. subsurface flow -- BOD, SS, N, P, and metals removal

The vegetation excludes sunlight and the soil, as well as the plant surfaces, provide a surface for nitrifying bacteria. The removal efficiencies of BOD, TSS and nitrogen may be greater than 80%. Long-term phosphorus removal may be more variable.

Initially, it must be made crystal clear that the constructed wetlands is designed to serve a wastewater treatment purpose. It is not likely that it can serve effectively as a treatment facility and at the same time become a critical habitat to be protected.

Constructed wetlands will probably require three or more years to mature. Any existing consent order to achieve compliance in an existing treatment facility must recognize this time constraint.

The training required for the operator may require some specialized effort. For example, thorough knowledge of nitrification/denitrification is required, and this necessitates specialized understanding of dosing rates which controls the aerobic/anaerobic environment.

Table 11 lists the construction and ongoing costs for natural systems. These units are clearly some of the least expensive systems to manage and construct.

Table 10. Interpretation of Soil Chemical Tests

Test Result	Interpretation
pH of saturated soil paste	
<4.2	Too acid for most crops to do well
5.2-5.5	Suitable for acid-tolerant crops
5.5-8.4	Suitable for most crops
>8.4	Too alkaline for most crops, indicates a possible sodium problem
cation exchange capacity (CEC), meq/100 g	
1-10	Sandy soils (limited adsorption)
12-20	Silt loam (moderate adsorption)
>20	Clay and organic soils (high adsorption)
exchangeable cations, % of CEC	Desirable range
Sodium	≤5
Calcium	60-70
Potassium	5-10
exchangeable sodium percentage, % of CEC	
<5	Satisfactory
>10	Reduced permeability in fine-textured soils
>20	Reduced permeability in coarse-textured soils
electrical conductivity, mmhos/cm at 25°C of saturation extract	
<2	No salinity problems
2-4	Restricts growth of very salt-sensitive crops
4-8	Restricts growth of many crops
8-16	Restricts growth of all but salt-tolerant crops
>16	Only a few very salt-tolerant crops make satisfactory yields

Table 11. Construction and Ongoing Costs for Natural Systems (21)

Concept	Capital cost, dollars/$m^3 \cdot d$	Ongoing management costs dollars/m^3
On-site[a]	1000-3000	0.01-0.10
Slow rate[b]	800-2000	0.10-0.20
Rapid infiltration[c]	450-900	0.05-0.10
Overland flow[d]	450-900	0.05-0.10
Facultative pond[e]	600-1000	0.08-0.15
Aerated pond[f]	600-1200	0.10-0.16
Hyacinth pond[g]	500-1000	0.12-0.14
Constructed wetland[h]	500-1000	0.03-0.09

a for daily flow rates up to 40 m^3/d.

b includes an allowance for pretreatment and storage, flow rate = 400 m^3/d,crop harvest included.

c with pretreatment to primary, at a flow rate = 400 m^3/d

d pretreatment screening or settling at a flow rate = 400 m^3/d, crop harvest included

e No pretreatment, at a flow rate = 400 m^3/d

f Partial mix aeration, at flow rate = 400 m^3/d, no pretreatment

g Pretreatment: screening or settling, flow rate = 400 m^3/d, with plant harvest

h Free water surface type; pretreatment: screning or settling, flow rate = 400 m^3/d, no regular harvest

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DRAFT

TEXAS WATER COMMISSION
WETLAND FILTER DESIGN

Summary:

The Water Utilities Division proposes the attached rules for the design and construction of constructed wetland filters for use in municipal wastewater treatment. The Plans and Specifications Review Section has noted a dramatic increase in the number of projects considering constructed wetland filters as a viable treatment unit. Given the right application these units have the potential to provide a reliable low cost method of treating municipal wastewater to secondary standards. Presently, there are not any comprehensive criteria addressing the design and construction of these units. Since there is a desperate need for low cost wastewater treatment in certain disadvantaged regions of the State, the use of these units will likely increase. The purpose of the proposed rules is twofold; first, to facilitate the proper sound design of these units, and second, to promote a low cost reliable wastewater treatment alternative to Texas communities.

The proposed rules will be included in Section §317 as "Appendix G" (§317.15) and reflect guidelines for the design and construction of constructed wetlands filter units. The rules are divided into four subsections. The first subsection §317.15(a) defines constructed wetlands terminology. The second subsection §317.15(b) states general design considerations, prohibits the use of natural wetlands as treatment units, identifies typical vegetation, and states requirements for primary treatment, liners, flood protection, configuration, flow distribution, and total suspended solids removal. Subsection §317.15(c) concentrates on submerged flow filter design, media sizing, organic loading, and natural aeration capacity. The final subsection §317.15(d) concentrates on free water surface filter design, organic loadings, and vector control.

The proposed rules have been routed internally. Comments received through this routing have been incorporated into the rules. Most of these comments addressed typographical errors in tense, meaning, and punctuation. One comment recommended a narrower scope of purpose for the definition subsection. Consequently, some items previously contained in the definition subsection have been transferred to the general considerations subsection. Finally, one comment addressed the use of pesticides to control vectors in Freewater Surface filters. Language addressing the limited use of such vector controlling methods has been added.

31 TAC §317.15

Preamble:

The Texas Water Commission proposes the addition of new §317.15, concerning design of sewerage systems. The section establishes minimum design standards for facilities which use constructed wetlands filters to treat and dispose of primarily domestic wastewater. The section proposes to define minimum acceptable standards and recommended guidelines which must be met in order to obtain construction approval and where applicable rate the capacity of the previously mentioned facilities. This section is proposed as a new section to the existing 31 TAC §317. The authority vested in this chapter has been granted to the Texas Water Commission by 70th Legislature under the Texas Water Code §26.034.

The propose rules will be included in Section §317 as "Appendix G" and reflect guidelines for the design and construction of constructed wetlands filter units. The section provides design requirements and recommended guidelines for the utilization of constructed wetlands filters as municipal wastewater treatment units. Subsection §317.15(a) defines constructed wetlands terminology, prohibits the use of natural wetlands as treatment units, identifies typical vegetation, and states acceptable uses. Subsection §317.15(b) states general design considerations and requirements for primary treatment, liners, flood protection, configuration, flow distribution, and total suspended solids removal. Subsection §317.15(c) concentrates on submerged flow filter design, media sizing, organic loading, and natural aeration capacity. Subsection §317.15(d) concentrates on free water surface filter design, organic loadings, and vector control.

31 TAC §317.15: APPENDIX G - GENERAL GUIDELINES FOR THE DESIGN OF CONSTRUCTED WETLANDS FILTERS FOR USE IN MUNICIPAL WASTEWATER TREATMENT

(a) DEFINITIONS

(1) Constructed Wetlands. Constructed Wetlands are designed and man-made complexes of saturated substrates, emergent and submergent vegetation, animal life, and water that simulates natural wetlands. Constructed wetlands as described in these rules are meant to function exclusively as wastewater treatment units. They consist of two (2) varieties: Submerged Flow Systems and Free Water Surface Systems. Combinations of these varieties may also be acceptable methods of treatment. Constructed Wetlands are constructed treatment units that are inundated or saturated by wastewater flows at a frequency and duration sufficient to support, and under normal circumstances do support, a prevalence of flora and fauna typically adapted for life in saturated or inundated soil conditions, i.e., a wetland. Terms that are considered synonymous with constructed wetlands are manmade wetlands, engineered wetlands, artificial wetlands, rock reed filters, vertical bio-reactor, submerged flow systems, freewater surface systems, artificial marsh, marsh reed filter, botanical reactor, and rooted emergent wetland filters.

(3) Submerged Flow. A Submerged Flow System (SFS) consists of a lined basin or channel filled with a granular rock media. The media supports the growth of both emergent vegetation on the surface and fixed bio-film on the subsurface. The wastewater flows horizontally, vertically, and transverses the subsurface of the filter through interstices of the media and vegetation root structure. Wastewater levels are nominally maintained at least three (3) inches below the filter surface.

(4) Free Water Surface. The Free Water Surface System (FWS) consists of a lined basin or channel partially filled with soil or other media suitable for supporting rooted emergent and/or submergent vegetation. Wastewater flows over the top of the media and through the stalks and detritus of the emergent and/or submergent vegetation at a shallow depth no greater than 36-inches.

(b) GENERAL CONSIDERATIONS

These guidelines are intended for an exemplary basis. The criteria for design, construction, and operation should be based on data collected from operational data of similar facilities, pilot-plant and bench-scale studies, and/or proper engineering and scientific investigations which should be submitted at the time of review.

(1) Natural Wetlands. The Commission will prohibit the use of any land defined as a wetland by the U.S. Army Corp of Engineers in 40 CFR §122.2 and subject to regulations found in §404 of The Clean Water Act for use in wastewater treatment. Any subsequent construction activity located in a natural wetland may require a permit from the U.S. Army

Corp of Engineers.

(2) Typical Wetlands Vegetation. Suggested flora for constructed wetlands in the State of Texas include the following:

(A) Emergent aquatic vegetation - such as Typha spp. (catails), Scirpus spp. (bulrush), Sagittaria spp. (arrowhead), Phragmites spp. (reeds), Juncus spp. (rushs), Eleocharis spp. (spikerush), Iris spp. (water iris), etc...

(B) Floating aquatic vegetation - such as Lemna spp. (duckweed), Hydrocotyle umbellata (water pennywort), Limnobium spongia (frogbit), Nymphaea spp. (water lily), Wolffia spp. (water meal), etc...

(C) The use of indigenous plants is strongly recommended provided that these species have been proven suitable for use in wastewater treatment. Procurement of these seed plants from natural wetlands should insure the natural wetlands are not significantly impacted.

(D) The use of all harmful or potentially harmful wetlands plants and organisms, as described in 31 TAC §§57.111-57.118 and 31 TAC §§57.251-57.258, must first be approved by the Texas Parks and Wildlife Department.

(3) Allowed Uses. Constructed wetlands can be used as a:

(A) Secondary treatment unit, or

(B) Tertiary polishing unit.

(4) Primary Treatment. All systems shall be preceded by primary treatment. Systems may be preceded by secondary treatment. Primary treatment can include septic tanks, Imhoff tanks, facultative lagoons, aerated lagoons, stabilization ponds, and any other treatment process which removes the settleable solids and floating material. The design of these pretreatment units shall conform with applicable State design criteria.

(5) Liners. When required in the facility's permit or by the Commission, basins shall be lined with an impermeable liner, either soil or synthetic, as described below.

(A) Soil.

(i) All placed clay or in-situ soils used for basin liners shall be certified by adequate geotechnical test results. For all in-situ soils, the design engineer shall present adequate soil borings information which insures the homogeneousness of the selected soil. Placed clay or in-situ soils shall have a measured permeability of less than 10^{-7} cm/sec. and/or the following characteristics:

(I) More than 30 % passing a #200 mesh sieve;

(II) Liquid limit greater than 30%;

(III) Plasticity index greater than 15;

(IV) No clods larger than two (2) inches;

(V) Minimum compacted thickness of two (2) feet for placed clay liners and four (4) feet for in-situ soils.

(ii) All placed clay liners shall be installed according to the following criteria. However, when using in-situ soils for the required liner only the upper six (6) inches should be reworked as follows:

(I) Maximum loose lift of eight (8) inches, six (6)

inches compacted;

(II) Minimum compaction effort of 95 percent Standard Proctor (ASTM D-698);

(III) Liners shall be keyed into the existing in-situ soils.

(B) Synthetic. All synthetic liners shall have a minimum thickness of 30 mils and contain underdrain leak detection which shall consist of leachate collection and detection systems. Proper installation of the above mentioned materials shall be described in the project's specifications. The liner material shall be resistant to or protected from ultra-violet (UV) light degradation.

(6) Flood hazard analysis. The 100-year flood plain elevation shall be provided. Proposed treatment units which are to be located within the 100-year flood plain will not be approved for construction unless protective measures satisfactory to the Commission (such as levees or elevated treatment units) are included in the project design. If construction inside the 100-year flood plain is necessary, authorization from the proper coordinating authority must be obtained. All units must either be three (3) feet above the 100 year flood plain or have a berm with at least three (3) feet of freeboard above the 100 year flood plain.

(7) Berms. Berms shall have side slopes of no steeper than 3:1. Berms shall be lined or constructed of impermeable clay as described in the preceding section pertaining to soil liners. All clay berms shall be keyed into the clay liner.

(8) Configuration. Facilities with permitted average daily flows over 100,000 gallons per day shall conform with the following configuration standards.

(A) Multiple Cells. The treatment units shall be divided into cells that can be operated separately. Each cell shall have the ability to be completely drained.

(B) Parallel Trains. Design considerations may include parallel treatment streams or trains which can be operated independently of each other.

(C) The cells shall be designed to operate as plug flow channels. A proper length to width ratio to achieve this condition should be considered in the design of each system.

(D) Switching Capability. The design shall allow for each cell to be taken out of service at any time and its flows routed to another cell.

(E) Wind Protection. All FWS filters shall be situated so as to minimize the adverse effects of the prevailing winds.

(F) All filters should maintain a minimum slope along the bottom of at least 0.25 % to facilitate draining.

(9) Flow Distribution.

(A) Inlets. All treatment units shall have multiple inlets (a minimum of 3) and provide a method to mitigate erosion of the media.

(B) Outlets. All treatment units shall have multiple outlets (a minimum of 3). FWS outlets shall be submerged and be able to exclude floating detrital material and scum.

(C) The design should allow inlets and outlets to be raised and lowered, so that water levels within the basin can similarly be varied and provide the ability to flood the

beds when necessary.

(D) Basin Hydraulic Design.

(i) Submerged Flow Systems: SFS Filters should be designed to prevent surface ponding of wastewater. The hydraulic loading of these filters should be limited to the effective hydraulic capacity of the media in place. This effective hydraulic capacity will be a function of the clean media's hydraulic capacity reduced by root intrusion, slime layer, detritus, algae, and other blockages.

(ii) Free Water Surface Systems: FWS Filters should be designed to prevent scour, erosion, and plant damage during peak flow periods. The hydraulic loading of these filters should be limited to the open channel carrying capacity of the filter at full growth.

(10) Flow Equalization. Flow to the filters shall provide for a uniform environment and growth conducive to wetlands.

(11) Initial Vegetation Spacing. Plants should be placed no greater than 36-inches apart (center to center). All plants to be used should be healthy, insect free, and undamaged. A broad diversity of plant species within any unit is recommended.

(12) TSS Removal. The Total Suspended Solids (TSS) removal efficiency of the filters may be as high as 95%. However, this removal efficiency is dependent on the quiescence of the filter. These filters should be able to attain permitted TSS effluent concentrations of less than 10 mg/l. However, if the facility is unable to meet its permitted parameters, alternate means of solids removal must be pursued.

(13) Nitrification. Nitrification in the filter will be considered on a case by case basis.

(c) SUBMERGED FLOW FILTER DESIGN

(1) Basic design parameters. SFS wetlands are sized according to primary and/or secondary treatment efficiency preceding the units, i.e. fraction of remaining BOD_5, and the permitted 30-day average effluent discharge concentration of BOD_5. The following factors shall be considered in the selection of the design hydraulic and organic loadings: strength of the influent sewage, effectiveness of primary and/or secondary treatment, type of filter media, ambient wastewater temperature for winter conditions, and treatment efficiency required.

(A) Rock/Media Design. The following are minimum requirements for material specifications of the rock media:

(i) Crushed rock, slag or similar media should not contain more than five percent by weight of pieces whose longest dimension is three times its least dimension. The rock media should be free from thin, elongated and flat pieces and should be free from clay, sand, organic material, or dirt.

(ii) Rock media, except for the top planting layer, should conform to the following size distribution and gradation when mechanically graded over a vibrating screen with square openings:

(I) Passing six inch sieve - 100 % by weight;

(II) Retained on two inch sieve - 90-100 % by weight;
(III) Passing two inch sieve - 0.2 % by weight;
(IV) Passing one inch sieve - > 0.1 % by weight;
(V) The media should have a Mohs hardness of at least 5.0.

(B) Installation of the rock media:

(i) Rinsing or washing of media to remove sediment is recommended. This washing should be sufficient to remove any significant amounts of dirt or accumulated debris.

(ii) The proper placement and installation of media is vital to the success of the filter. Undue compaction exerted on the media's surface, as it is installed and after its installation, can fracture and consolidate the media. The introduction of foreign fine particles and fracturing can adversely affect the filter's hydraulic conductivity. Therefore, the following guidelines are recommended:

(I) A layer of smaller rock (0.5 - 1.0 inches) may be used on the top of the filter to ease planting of the vegetation and aid in vector control.
(II) Media should be gently put in place, avoiding excessive dropping, jostling, and abusive handling.
(III) Heavy machinery should not be allowed on the surface of the media after final placement. If machinery is allowed on the surface all tire ruts should be smoothed over to prevent ponding in ruts.
(IV) Provisions should be made after planting to provide water and nutrients to the plants if the filters start-up will be delayed.

(2) Organic Loadings. The following tables present typical ranges for detention time within the filters in days. Each detention time represents combinations of different classes of secondary and tertiary treatment and different effluent parameters. These times are recommendations, only. Design engineers may submit sufficient operating data for similar installations, and/or actual field conditions to justify their efficiency calculations. These times represent the theoretical detention time of wastewater within the basin. Therefore, the amount of detention volume available is equal to the basin's volume multiplied by the average porosity of the media. Evapotranspiration and precipitation should also be considered when calculating detention time. The tables are based on the following assumptions: (1) An average effective porosity of the media of 32%, (2) An average wastewater treatment plant influent BOD_5 of 200 mg/l.

(A) Secondary and Tertiary Treatment. The detention times in Table No. 1 are based on the fractional BOD_5 remaining in the filter's influent and the permitted effluent limits. For permitted effluent BOD_5 concentration and removal efficiencies that fall between the listed quantities, linear interpolation is permissible.

Table No. 11

DETENTION TIME (days)
SUBMERGED FLOW SYSTEM

Permitted BOD_5 mg/l	Fractional BOD_5 Remaining After Initial Treatment						
	0.70	0.60	0.50	0.40	0.30	0.20	0.10
30	2.5	2	1.7	1.3	1	1	n/a
20	3.5	3	2.7	2	1.5	1	n/a
10	5	4.7	4.3	3.8	3	2	1

(B) Tertiary Treatment Following Pond Systems Only: The detention time is based on the assumption that the treatment facility is composed of a facultative lagoon followed by two stabilization ponds each sized according to the current State design criteria found in 31 TAC §317. For applications where pond effluent is to be polished to meet an effluent BOD_5 concentration of 30 mg/l a minimum of one (1) day detention time through the filter will be required.

(3) Oxygen Loadings. Since SFS should function in an aerobic environment, the wastewater dissolved oxygen level is critical.

(A) The following equation gives the recommended filter surface area needed to maintain sufficient oxygen transfer through fully developed plant roots:

$$A_s = 361\ [BOD_{5(i)}]$$

Where: A_s - required filter surface area to maintain aerobic conditions in wastewater in ft^2.

$[BOD_{5(i)}]$ - amount of BOD_5 in the unit's influent in lb/day.

(B) Other means of introducing oxygen into the wastewater will be considered.

(d) FREE WATER SURFACE FILTER DESIGN

(1) Basic design parameters. FWS wetlands are sized according to primary and/or secondary treatment efficiency, i.e. fraction of remaining BOD_5, and the permitted 30-day average effluent discharge concentration of BOD_5. The following factors are considered in the selection of the design hydraulic and organic loadings: strength of the influent sewage, effectiveness of primary and/or secondary treatment, type of filter media, ambient wastewater temperature for winter conditions, and treatment efficiency required.

(2) The following tables present typical ranges for detention time within the filters in days. Each detention time represents combinations of different classes of primary and secondary treatment and the different effluent parameters. These times are suggested for illustrative purposes, only. Design engineers may submit sufficient operating data for similar installations, and/or actual field conditions to

justify their efficiency calculations for the filters. The tables are based on the following assumptions: (1) Specific surface area of the media (stems, roots, detritus, etc...) 15.7 m^2/m^3, (2) Ambient winter conditions wastewater temperature of 7.5°C (45.5°F), and (3) An average wastewater treatment plant influent BOD_5 of 200 mg/l.

(A) Secondary Treatment. These detention times are based on the type and efficiency of the primary treatment unit which precede the FWS wetlands.

(i) Septic Tank or Facultative Pond as Primary Treatment Method:

Table No. 2:

Effluent BOD_5 Concentration (mg/l)	Required Detention Time (days)
30	8
20	11
10	15

(ii) Imhoff Tank or Clarification as Primary Treatment Method:

Table No. 3:

Effluent BOD_5 Concentration (mg/l)	Required Detention Time (days)
30	10
20	13
10	17

(B) Tertiary Treatment. The detention times given in Table No. 4 are based on the fraction of BOD_5 remaining after secondary treatment. Table No. 4 assumes a wastewater treatment plant influent BOD_5 of 200 mg/l. For percentages that fall between the listed quantities, linear interpolation is permissible.

Table No. 4:

DETENTION TIME (days)
TERTIARY TREATMENT FREE WATER SURFACE SYSTEM

Permitted BOD_5 mg/l	Fractional BOD_5 Remaining After Secondary Treatment								
	0.50	0.45	0.40	0.35	0.30	0.25	0.20	0.15	0.10
30	8	7	7	6	5	3	2	n/a	n/a
20	11	10	9	8	7	6	5	3	n/a
10	15	15	14	13	12	11	9	7	5

(3) Vector Control. The presence of mosquitos and other vectors has been associated with open water. Since the FWS filters will have open water surfaces, vector control must be a priority. Vector control mechanisms using natural controlling agents such as introduction of Gambusia spp. (mosquito fish) have been proven effective. However, if the predatory fish are used to control vectors, provisions must be made within the basin for designated open water areas so the fish can surface for oxygen. At least 20 percent of the basin's surface should be open to the atmosphere. Other methods of vector control are acceptable. However, the introduction of chemicals (such as pesticides) should be carefully evaluated so that there are no adverse effects on effluent water quality.

SUPERCRITICAL WATER OXIDATION OF WASTEWATERS

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Introduction

The long-term pollution prevention goals must be to minimize waste production and reduce risk. In the case of toxic wastewaters and sludges, the objective might be to achieve two further goals: (a) total destruction of toxic substances; and (b) perform this task in a totally enclosed system.

Magnitude of the Problem

Hazardous wastes in the USA continue to grow (Gloyna 1987). Industrial contributions amount to about 280 MMT. Chemicals and allied products account for 30% of this total. There are about 70,000 and 125,000, respectively, large and small hazardous waste generators.

The amount of industrial and municipal sludge production is about 36 million metric tons per year, equally divided between the two sources. By year 2000, the municipal contribution may double.

Regulations

Society has reacted to the hazardous waste problem by passing increasingly complex legislation and creating massive regulatory requirements. Figure 1 illustrates the rapid increase in major Federal Laws.

Wastewater Treatment and Disposal Options

Wastewaters require some form of treatment. The alternatives for treatment and disposal of residual wastewaters are shown in Table 1.

Supercritical Fluids

Much has been written about supercritical fluids (SCF), supercritical extraction, and supercritical water oxidation (SWO). Special SCFs are too attenuated to be true liquids and too dense to be true gases. SCFs occur when both temperatures and pressures within the fluid exceed the critical point (Tc and Pc). Under these conditions the density, dielectric constant, hydrogen bonding, and some other physical properties are altered such that the water behaves as a moderately polar organic liquid under ambient conditions. For example, benzene under supercritical water conditions becomes miscible in all proportions, and similarly, some types of wood completely dissolve. However, under the same conditions the solubility of NaCl and CaCl, respectively, might be as low as 100 mg/L and 10 mg/L. The changes in the characteristics of water as it is subjected to supercritical conditions are shown in Fig. 2.

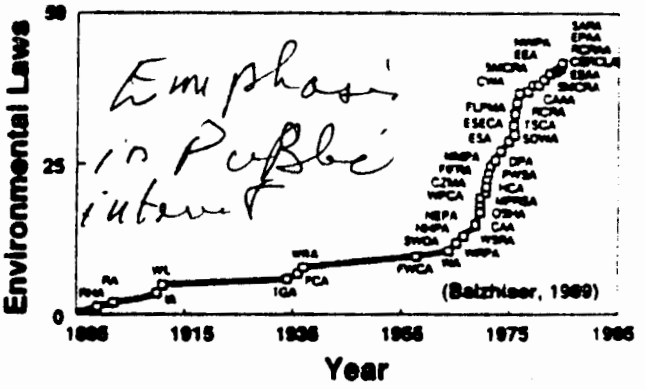


Figure 1. Growth of U.S. Environmental Laws

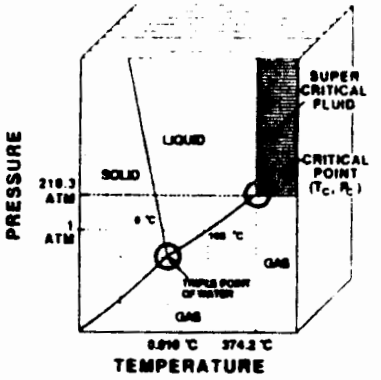


Figure 2. Phases of Water at Moderate Pressures (Josephson 1982)

At elevated temperature and pressure, a fluid has much greater ability to act as a solvent because the internal energy of the SCF is sufficient to overcome the internal bonding of the fluid molecules (hydrogen bonding disappears in the case of water). The great solvent properties of SCF at low density provides high diffusivity and rapid mass transfer (Johnston, 1982).

Table 1. Alternatives for Treatment and Disposal of Wastewaters

Technology	Acceptability/Potential Problems
1. Dilution	Not a substitute for treatment
2. Biol./Phys./Chem	Economical and efficient for removal of dilute organic wastes
3. Deep-Well Injection	Technically feasible, costly, but increasingly unacceptable
4. Solar Evaporation	Technically feasible, but alledged air pollution and groundwater problems.
5. Land Disposal	Potential groundwater pollution and crop contamination
6. Oxidation-Regener.	For waste concentrations below 1%, relatively expensive
7. Incineration	For concentrated organic wastes (>20%); temperatures of 900°C to 1,100°C and residence time of 2 sec.
8. Ozonation	Limited by rate of mass transfer and produces refractory residual low-molecular weight compounds
9. Wet Air Oxidation	Off gases and effluent may require additional treatment
10. Subcritical, (WAO)	Applicable for biological sludges and organic liquid wastes
11. Supercritical Water	Potentially totally enclosed and system applicable to wide range of organic compounds and waste characteristics

Supercritical Water Oxidation

The SCWO process embraces the oxidation of organics, in the presence of high concentrations of water under temperatures and pressures above the critical point (C.P.) values of water, 374°C (705.5°F) and 22,120 KN/M^2 (3206 psia or 218 atm). The C.P. lies on the vapor-liquid saturation dome, 374°C and density of 0.1 to 0.5 g/cm^3, a dielectric constant of 3 to 10, and nearly 100% solubility of organics. The surface tension of water under these conditions becomes zero. The thermal energy contained in the water molecules reduces hydrogen bonding, and therefore SCW becomes an excellent solvent for non-polar organic substances.

The conversion of organic materials in a waste to CO_2, H_2O, and acids or oxyacids of heteroatoms and metals under SCWO conditions is a function of the reaction temperature and residence time. The products of organic nitrogen and ammonia, below 650°C, are primarily N_2 and N_2O. The latter decomposes to N_2 and O_2. SCWO at about 400°C (750°F) does not destroy ammonia. Heteroatoms (chlorine, sulfur, and phosphorus) are oxidized to the respective acid forms or corresponding salts if sufficient cations are present.

The SCWO process provides a very strong oxidizing environment. It is expected that 80% of the metals in a waste stream are likely to be incorporated in the ash. Calcium sulfate is expected to form. Calcium passing the reactor may be divided equally between ash and liquid. Sulfates may be split between ash and liquid. In supercritical water (SCW) conditions (374°C to 450°C) salts may remain dissolved or condense as a concentrated brine solution or as a solid particulate (>450°C). The heavy metals may form carbonates or oxides and depending on their volatility may precipitate. The organics are converted to CO_2 and H_2O during the oxidation stage. Char will most likely oxidize slowly.

Physicochemical Properties of SCWO

One of the key characteristcs illustrating the structure of water in the supercritical region is the static dielectric constant. This constant is a measure of the extent of hydrogen bonding and polarity of water. The static dielectric constant of water under normal conditions is about 80

(Uematsu, et al., 1980). The unusually high dielectric constant value is due to the strong hydrogen bonding between water molecules. In the critical region, as the density of water decreases, the extent of hydrogen bonding decreases since hydrogen bonding is a short range force.

Another important solvation characteristic of supercritical water is that many gases that are only sparingly soluble in normal liquid water are completely miscible with supercritical water. Phase behaviors of H_2O-O_2 and H_2O-Air (Japas, et al., 1985a) and H_2O-N_2 (Japas, et al., 1985b) systems at supercritical conditions show that both gases are completely miscible with supercritical water. Carbon dioxide and argon are also completely miscible with supercritical water.

Supercritical water is a very poor solvent for inorganic salts. The solubilities of salts gradually increase over the temperature range of 200 °C to 450 °C with a few exceptions (potassium sulfate, sodium sulfate, sodium phosphate, sodium carbonate, and lithium sulfate) (Marshall, 1975). At temperatures above 450 °C and densities less than 0.3 g/cm^3, however, supercritical water exhibits dielectric constant values less than 2. The low density substantially reduces the solubilities of inorganic salts in supercritical water.

Experimental Apparatus

The SCWO facility, located at the Balcones Research Center at The University of Texas at Austin, contains a number of reactor systems. These are used to conduct basic kinetic studies, materials performance, heat transfer, corrosion, erosion, encrustation material balances, liquid-solid separations, mixing, and treatability tests. The equipment list includes the following units:

a. Mark I Batch Reactor System (liquid or sludges)
b. Mark II Batch Reactor System (liquid or sludges)
c. Mini-Tubular, Plug-Flow Reactor System
d. Vertical, Concentric-Tube Reactor System (hydrogen peroxide and liquid)
e. Vertical Concentric Tube Reactor System (H_2O_2 or O_2, liquid or sludges)
f. Pilot-Scale Reactor System (Complete SCWO Reactor Facility)

The Mark I reactor system, Figure 3, consists of a frame in which the various components are housed. The frame occupies a space roughly 9.2 m x 1.2 m x 1.5 m. Major components include a reactor vessel assembly, a fluidized sand bath, a water bath, a wrist action shaker, and a reactor vessel assembly transfer system. The fluidized sand bath (Techne, Model SBL-2, 2.9 kW) is capable of rapidly increasing the reactor temperature. The wrist action shaker enhances mixing and heat transfer.

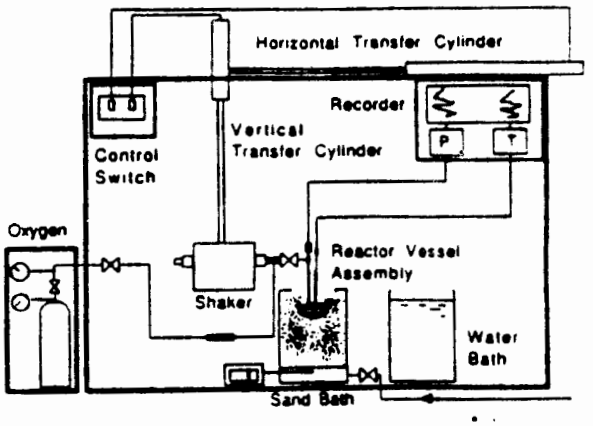


Figure 3. Batch Reactor System (Mark I)

A typical reactor vessel assembly consists of a coiled tube reactor vessel, a high-pressure tee (Swagelok), a type-J thermocouple (sheathed with inconel 600) with adapter, a pressure transducer (Viatran Model 345BH3DHA20), and an oxygen connector. The coiled tube reactor vessel is made from Stainless Steel 316, 0.36 cm I.D. (0.64 cm O.D.) tubing, and accommodates relatively large volumes of sample (25 mL). Either pure oxygen gas or hydrogen peroxide may be used. Temperatures up to 550 °C and pressures up to 410 atm may be imposed.

A second generation microreactor system, Figure 4, is capable of simulating temperature-depth profiles of a deep-well, subcritical and SCWO operation. The reactor is made of SS 316 tube, the outside diameter (O.D.) of the tube is 9.5 mm, the inside diameter (I.D.) is 6.5 mm and the length is 1.22 m. The volume of this tubular reactor was 40 mL. The reactor accommodates either manual or computerized control.

A miniature, tubular, plug-flow reactor system is used to evaluate oxidation kinetics. This continuous-flow reactor system achieves reasonable turbulent plug-flow and isothermal conditions.

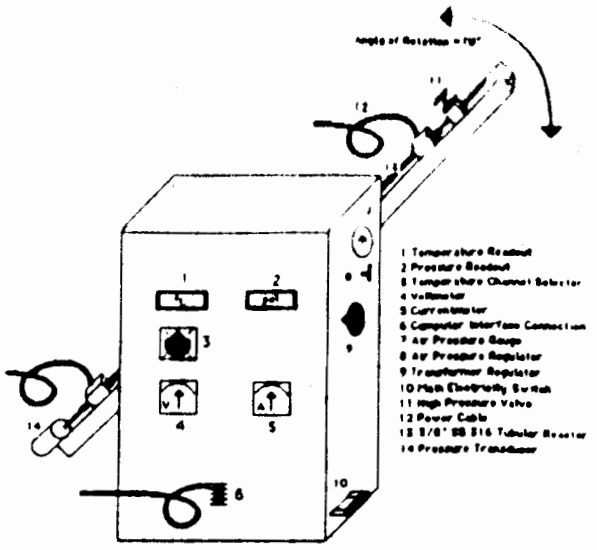


Figure 4. Schematic of the Batch, Heat-Simulator Reactor (Mark II)

Vertical, Concentric Tube Reactors

Two continuous-flow SCWO systems utilize the concentric-tube reactor configuration. These units are modifications of a patented device (Welch, 1989). One of these reactors, (UTVR#1), consists of vertically mounted concentric tubes. Both tubes are 4.57 m in length. The inner tube, 0.953-cm outside diameter and 0.165-cm wall thickness, is made of SS 316. The top 3.05 m section consists of SS 316 while the bottom 1.53 m section contains Hastelloy C-276. The outside diameter and wall thicknesses, respectively, are 2.69 cm and 0.554 cm. The total internal volume of the tubing assembly, including core and annular sections is 690 cm^3. The reactor volume in the lower section is 230 cm^3. The unit is electrically heated with 4.25 KW band heaters and heating tapes. The SCWO zone at the bottom is maintained at near isothermal conditions (±5°C). The maximum temperature and pressure, respectively, are 500°C and 350 bar. The maximum flow rate at a temperature of 500°C is about 130 gm/min. The residence time in the reaction zone is subject to the operating conditions but may range from 0.5 min to 5 min.

The second vertical reactor (UTVR#2) incorporates a number of special features for studying sludge volume reduction, corrosion, encrustation, and solid-fluid separation. This unit accepts either hydrogen peroxide or oxygen. The configuration of this reactor system is shown in Figure 5. Both tubes are 5.74 m in length and are made of SS 316. The inner tube dimension can be varied from 0.635 cm to 1.27 cm outside diameter and from 0.0889 cm to 0.165 cm wall thickness. The size of the inner tube depends on specific task requirements. The outside diameter and wall thickness, respectively, of the outer tube are 5.08 cm and 1.27 cm. The total internal volume of this SCWO reactor, including core and annular sections, is about 3 L. Nine band heaters provide a total of 9 KW. The heaters are evenly spaced in the bottom two-third of the concentric-tube assembly. A wattmeter monitors total electrical power input for heat balance around the reactor. Seventeen thermocouples at seven different locations are attached to the surfaces of the outer tube, annular section, and inner core of the reactor. The temperature profile of the reactor assembly can be monitored continuously by a Fisher-Porter Computer Work Station. In addition, digital readout capability exists for temperature, pressure, and weight of feed tank. A Lewa Diaphragm Pump (Model HLM-1) is capable of delivering up to 130 cm^3/min at a pressure of 276 bar. Sludge particles up to 100 microns in size and solid concentrations up to 6 wt % are acceptable. The maximum design temperature and pressure, respectively, are 450 °C and 241 bar. The residence time in the reaction zone may range from 5 min to 30 min.

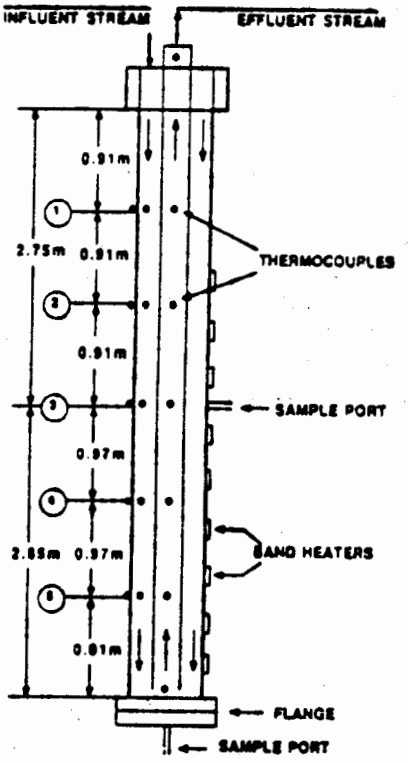


Figure 5. Configuration of Thermocouples and Band Heaters in the Continuous-Flow Concentric-Tube SCWO Reactor (UTVR#2)

A fully instrumented SCWO pilot plant has been assembled to demonstrate the effectiveness of all applicable components required for a SCWO prototype. This unit (patent pending) is capable of accepting an influent flow of about 150 L/hr (40 gal/hr). This unit is sponsored by EcoWaste Technologies, Austin, Texas.

Organic Matter

Data describing the destruction of an industrial sludge using batch and continuous-flow reactors operating under a variety of environmental conditions are presented. The results include kinetics of sludge destruction, production and transformation of intermediate products, metals concentration in the liquid effluent, ash leachability, and sludge mass-volume reduction (Shanableh, 1990)

Figure 6 illustrates the destruction of excess activated sludge. In this case, the temperatures varied from 300°C to 450°C. The TS concentration was 5%. The TCOD, combined COD of the liquid and solid fraction of the sludge, was 46,500 mg/L. The 20 mL capacity reaction vessel contained 5 mL of sludge and the initial oxygen pressure was 82 bar. The resulting density of water at supercritical conditions was approximately 0.25 g/mL. When the temperature increased from 300°C to 400°C, TCOD destruction increased at all residence times. Supercritical water temperatures with appropriate residence times were required to achieve complete TCOD destruction. At 20 min residence time, TCOD removals increased from about 84% at 300°C, to more than 99.8% at 425°C. As the temperatures approached SCWO conditions, the organic destruction was virtually complete. TCOD destruction was not significantly affected by the TS concentrations in the influent (1.1% and 3%). The destruction of sludge in the continuous-flow reactor was achieved through both oxidation and thermal decomposition. Below the critical temperature, 374°C, TCOD destruction increased significantly as the temperature increased. However, above the critical temperature, TCOD destruction increased gradually as the temperature increased.

The formation and destruction of volatile acids are important aspects of the treatment of wastewaters and sludges. At subcritical temperatures and short residence times, considerable acetic acid is produced, Figure 7. At temperatures of 300°C and 343°C, respectively, acetic acid concentrations increase from 2,450 mg/L to 3,540 mg/L and 2,250 mg/L to 2,810 mg/L then decrease to 2,250 mg/L and 750 mg/L. At SCWO temperatures, 400°C to 450°C, acetic acid shows no initial increase and the amounts produced are lower as compared with subcritical temperatures. The acetic acid, as a transformation product, is oxidized rapidly at SCWO.

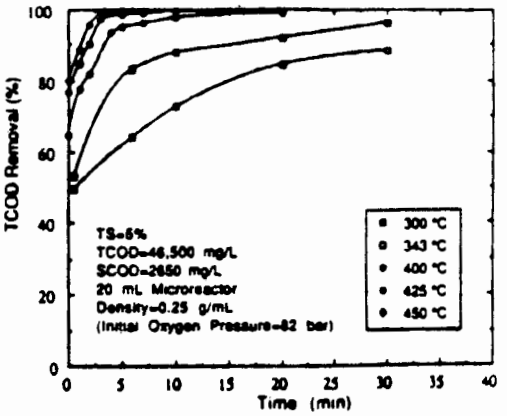


Figure 6. Destruction of Sludge.

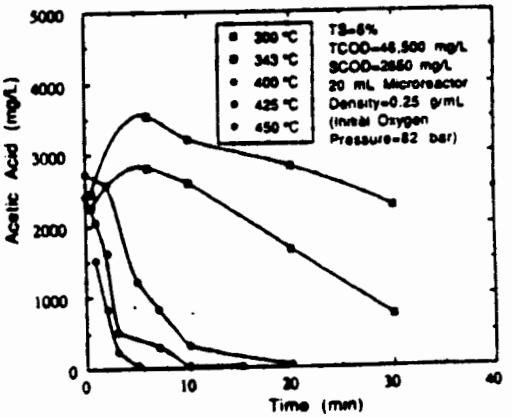


Figure 7. Production and Transformation of Acetic Acid

The production and transformation of ammonia are important aspects of sludge destruction. As shown in Figure 8, ammonia production at 300°C increased with longer residence times. As the temperature increased, the ammonia levels stabilized. At temperatures between 343°C to 400°C, ammonia concentrations increased initially, then decreased as the residence times increased. When the residence time was less than 10 min, ammonia production increased with increased reaction temperatures between 300°C and 425°C. However, at higher temperatures the initial increase in ammonia concentration was followed by a reduction as the residence time increased. The pH of the effluent ranged from 6.5 to 8. The ratio of the initial oxygen charge to

the COD was more than 3. Helling and Jefferson (1988) reported that at oxidation temperatures below 525°C, ammonia did not oxidize at a measurable rate. At a TS concentration of 3%, ammonia in the effluent did not vary when the flow rate was increased from 50 g/min to 100 g/min. At a TS level of 3%, ammonia in the effluent increased gradually from 330 mg/L to 470 mg/L as the temperature increased from 300°C to 450°C. The effluent pH increased gradually as the ammonia concentration increased. At a TS concentration of 3% and a flow rate of 50 g/min, pH increased from a pH = 5.5 (300°C) to pH = 7.5 (450°C).

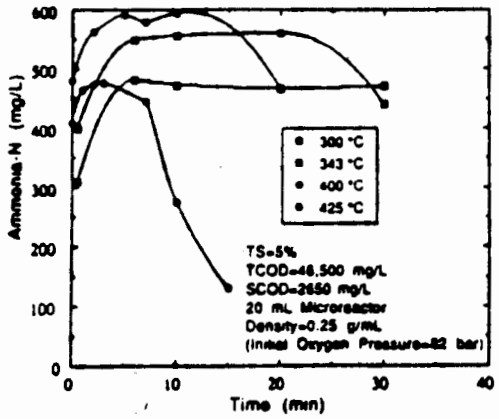


Figure 8. Production and Transformation of Ammonia

The size distribution of the suspended particles in the influent and ash is shown in Figure 9. The reactor temperatures varied from 280°C to 455°C. The influent particles' diameters ranged from 0.8 μm to 8 μm. The particles in the effluent ranged from 0.9 μm to 3 μm. Most of the influent particle diameters ranged between 2μm to 40μm.

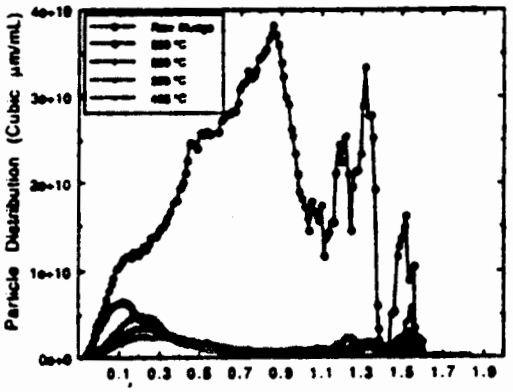


Figure 9. Relative Change in Particle Size Distribution

The solid residues were analyzed for compliance with the EPA Toxicity Characteristics Leaching Procedure, TCLP. The results are presented in Table 2. The data indicate that at subcritical and supercritical temperatures, the concentrations of leachable metals in the TCLP extract of the ash were lower than the requirements.

Table 2. Metals Leachability (conc. in mg/L).

	AS	Ag	Ba	Cd	Cr	Hg	Pb	Se
TCLP Limit	5	5	100	1	5	0.2	5	1
Raw Sludge(1)	<1	<1	1.8	<1	<1	<0.2	<2	<1
Ash(2) (331°C)	<1	<1	<1	<1	<1	<0.2	<1	<1
Ash(2) (351°C)	<1	<1	<1	<1	<1	<0.2	<1	<1
Ash(2) (396°C)	<1	<1	<1	<1	<1	<0.2	<1	<1

Oxidation of Acetamide

Acetamide and ammonium acetate provide examples of typical kinetic studies (Lee 1990). Since ammonium acetate is a stable by-product of acetamide hydrolysis, the destruction of ammonium acetate probably is the rate controlling step in the destruction of acetamide. Acetamide is subject to hydrolysis as well as oxidation, whereas ammonium acetate is subject only to oxidation.

Hydrolysis is more significant than oxidation in the destruction of acetamide in supercritical water, indicating that water functions as an active reactant as well as a reaction medium. The hydrolysis kinetics for acetamide is first-order with respect to the acetamide concentration. The effect of water density on the hydrolysis is negligible in the experimental conditions. The by-products from the hydrolysis of acetamide in supercritical water conditions are acetic acid and ammonia. The suggested two-step mechanism for the hydrolysis of acetamide involving the nucleophilic attack of the water molecule is consistent with the experimental observations on the kinetics and the by-product formation.

The overall reaction (hydrolysis + oxidation) kinetics for acetamide in supercritical water conditions is close to first-order (1.2) with respect to the acetamide concentration. The effect of the hydrogen peroxide concentration on the reaction rate is negligible. Similarly, the water density exhibits a negligible effect on the overall reaction rate. The oxidation kinetics for acetamide in supercritical water conditions has been derived by subtracting the hydrolysis rate from the overall reaction rate. The oxidation kinetics is again first-order with respect to the acetamide concentration. The oxidation is more sensitive to the reaction temperature as compared

to the hydrolysis. The effect of the hydrogen peroxide concentration on the oxidation rate is negligible. Three oxidative destruction paths have been suggested for acetamide in supercritical water with hydrogen peroxide or oxygen as the oxidant.

Typical conversion of acetamide into acetic acid and ammonia is shown in Figure 10. The dotted line represents the expected concentration for both acetic acid and ammonia. Since the experimental data are close to the calculated values, these results imply that there are no other significant parallel reactions.

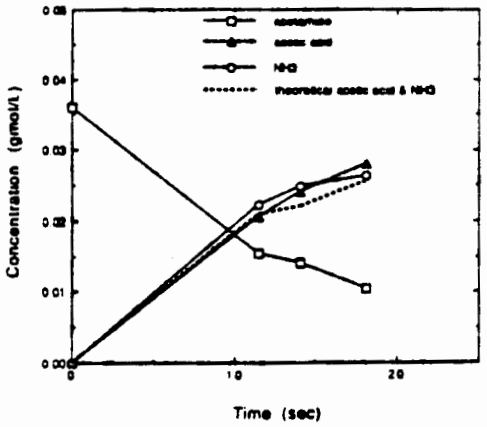


Figure 10. Conversion of Acetamide to Acetic Acid and Ammonia by Hydrolysis; T=475 °C, P=314 atm.

The conversion trends of acetamide and acetic acid are presented in Figure 11. The acetic acid formation rate at 400 °C, (acetamide hydrolysis), is much faster than the oxidation of acetic acid. At a retention time of 300 seconds, 99.6% conversion can be achieved. However, under these test conditions, about 80% (molal base) of the initial acetamide is converted into and remains as acetic acid. Therefore, at 400 °C, the oxidation of acetic acid is the rate controlling step. However, at 500 °C, the destruction of acetic acid is so rapid that the oxidation of acetic acid is no longer rate controlling.

Toxic Organic Compounds

Test results for selected compounds are summarized in Table 3. Efficiencies greater than 99.999% were obtained for 2,4-dichlorophenol with temperatures of 450 °C and reaction times of 3 to 4 min. The destruction efficiencies for other compounds were greater than 99.5%.

Heat Transfer

Due to the high heat of combustion, reactions with relatively low concentrations of organics in supercritical water can become self-sustaining. Heat transfer to water in countercurrent flow within a vertical, concentric-tube SCWO reactor (UTVR#2) is shown in Figure 12 (Michna and Gloyna, 1990). Temperatures in the reactor ranged from 300 °C to 450 °C. The system pressure was held constant at a gauge pressure of 248 bar (3600 psig). Three mass flow rates were used in the course of the experimental work. The

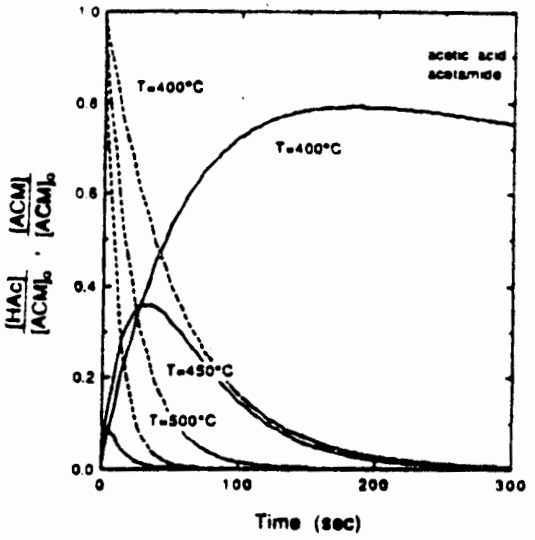


Figure 11. Concentration Change of Acetamide and Acetic Acid

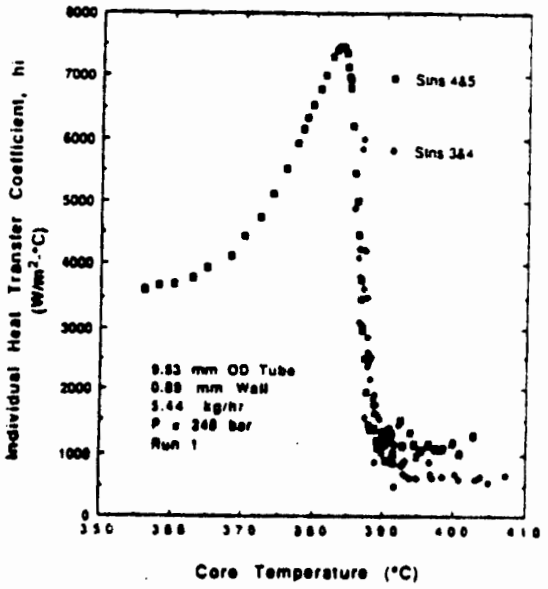


Figure 12. Individual Heat Transfer Coefficient as a Function of Core Temperature for Run 1

Table 3. Destruction Efficiency for Toxic Organic Compounds

Compound	Temp* (°C)	Time (min.)	Concentration in (mg/L)	Concentration out (mg/L)	D.E. (%)
p-chlorophenol	450	3	1000	<0.1	>99.99
2,4-dichlorophenol	450	4	1000	<0.01	>99.999
2,4,6-trichlorophenol	500	2	200	<0.01	>99.995
2,4-dinitrotoluene	450	1	200	<1.0	>99.5
ethylene glycol	450	2	1000	<1.0	>99.9
diethylene glycol-diethyl ether	450	2	1000	<1.0	>99.9

* Hydrogen peroxide Water density = 0/2 mg/L

low rates were 4.00, 5.44, and 8.00 kg/hr. Maximum values occurred as the bulk temperature reached the pseudocritical point. Immediately beyond the pseudocritical point, the heat transfer coefficient dropped rapidly to values of less than three to four times those in the subcritical region.

Summary

Subcritical and supercritical water oxidation present attractive alternatives for the destruction of biological sludges and toxic organic wastes. Complete destruction in a totally enclosed system is possible. Typical engineering problems such as erosion, corrosion, heat transfer, and kinetics require further attention.

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WASTE STABILIZATION PONDS

Special Slides

E. F. Gloyna

BACTERIA

- AEROBIC BACTERIA
- ACID FORMING BACTERIA
- CYANOBACTERIA
- PURPLE SULFUR BACTERIA
- PATHOGENIC BACTERIA

AEROBIC BACTERIA

- *Beggeatoa alba*
- *Sphaerotilus natans*
- *Achromobacter*
- *Alcaligenes*
- *Flavobacterium*
- *Pseudomonas*
- *Zoogloea* spp.

1. ACID FORMING BACTERIA
(HETEROTROPHS)

COMPLEX ORGANIC ⟶ ALCOHOLS AND ACIDS
ACIDS (ACETIC - PROPIONIC - BUTYRIC)

2. ACID FORMING BACTERIA

ACIDS VIA METHANOGENIC BACTERIA = METHANE

CYANOBACTERIA
(BLUE GREEN ALGAE)

SIMPLE ORGANIC
CARBON DIOXIDE
INORGANIC MEDIUM } LIGHT { OXYGEN }

NITROGEN MAY BE ATMOSPHERIC

PURPLE SULFUR BACTERIA
(Chromatiaceae)

PURPLE OR ORANGE - BROWN - PINK - RED
NEED PROPER WAVELENGTH
ANAEROBIC LAYER
$H_2S \longrightarrow S$ or SO_4

PATHOGENIC BACTERIA

Salmonella
Shigella
Escherichia
Leptrospira
Francisella
Vibrio

ALSO: VIRUSES & PROTOZOA

ALGAE

AUTOTROPHIC

INORGANIC NUTRIENTS

MOST REQUIRE INORGANIC NITROGEN

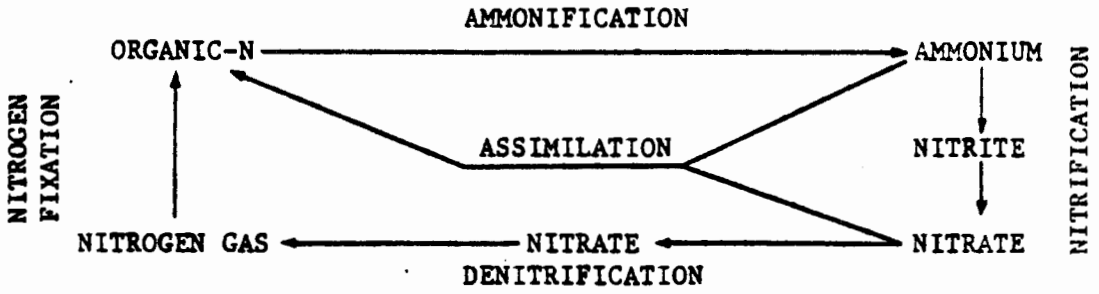
ANIMALS

- PLANTONIC Cladocera
- BENTHIC Chironomidae

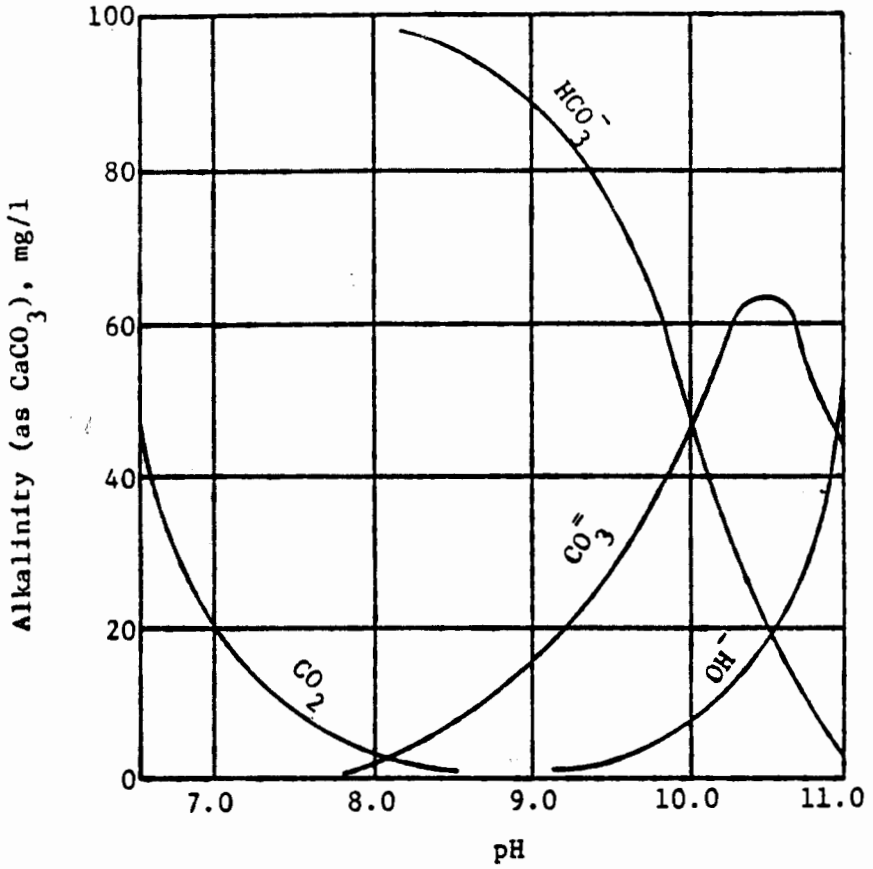
PHOTOSYNTHESIS

- OXYGENIC $H_2O \xrightarrow{\text{sunlight}} \frac{1}{2}O_2 + 2H^+ + 2e^-$
- ANOXYGENIC $H_2S \longrightarrow S^o + 2H^+ + 2e^-$

SIMPLIFIED NITROGEN CYCLE



CALCULATED RELATIONSHIP BETWEEN pH, CO_2, $CO_3^=$, HCO_2^-, and OH^-



LIGHT

500 to 5,000 FOOT CANDLES

(5380 to 53,800 lumen/m^2)

TKN

AMMONIA, AMMONIUM, ORGANIC NITROGEN

- AMMONIA STRIPPING
- AMMONIA ASSIMILATION IN BIOMASS
- BIOLOGICAL NITRIFICATION
- BIOLOGICAL DENITRIFICATION
- SEDIMENTATION OF INSOLUBLE ORGANIC NITROGEN

NITROGEN REMOVAL
(FACULTATIVE WASTE STABILIZATION PONDS)

- GASEOUS AMMONIA STRIPPING TO THE ATMOSPHERE
- AMMONIA ASSIMILATION IN ALGAL BIOMASS
- BIOLOGICAL NITRIFICATION - DENITRIFICATION

AMMONIA REMOVAL

$$NH_3^o + H_2O \rightleftharpoons NH_4^+ + OH^-$$

AMMONIA REMOVAL

For temperatures to 20°C:

$$\frac{C_e}{C_o} = 1/1 + \frac{A}{Q}(0.0038 + 0.000134T)\exp[(1.041 + 0.044T)(pH - 6.6)]$$

AMMONIA REMOVAL

For temperatures of 21°C to 25°C:

$$\frac{C_e}{C_o} = \frac{1}{1 + [5.035 \times 10^{-3} \frac{A}{Q} e^{1.540\ (pH-6.6)}]}$$

where:

C_o = influent concentration of $(NH_4^+ + NH_3^o)$, mg/l as N

C_e = effluent concentration of $(NH_4^+ + NH_3^o)$, mg/l an N

A = surface area of the pond, m^2

Q = flow rate, m^3/d

T = temperature, °C

PHYSICAL CONSTRUCTION

- O DIKE CONSTRUCTION
- O WAVE PROTECTION
- O WEATHER PROTECTION
- O RODENT PROTECTION
- O SEEPAGE PROTECTION

POND SEALING

- O BENTONITE LINEARS
- O ASPHALT LINEARS
- O SOIL CEMENT LINEARS
- O THIN MEMBRANE LINEARS

POND HYDRAULICS

- INLET & OUTLET
- TRANSFER OUTLETS
- BAFFLING
- WIND EFFECTS
- STRATIFIED PONDS

AQUACULTURE

- INVERTEBRATES
  (Daphnia, Artemia, bivalve mollusks)
- WATER HYACINTH
- FISH

AEROBIC RESPIRATION

$$C_6H_{12}O_6 + 6O_2 \xrightarrow{\text{enzymes}} 6CO_2 + 6H_2O + \text{new cells}$$

NITRIFICATION REACTION

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O$$

DENITRIFICATION REACTION

$$6NO_3^- + 5CH_3OH \longrightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^-$$

CARBONATE BUFFERING SYSTEM

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

$$M(HCO_3)_2 \rightleftharpoons M^{++} + 2HCO_3^-$$

$$HCO_3 \rightleftharpoons CO_3^= + H^+$$

$$CO_3^= + H_2O \rightleftharpoons HCO_3^- + OH^-$$

$$OH^- + H^+ \rightleftharpoons H_2O$$

PROPER POND DESIGN PROVIDES

- O HIGH BOD REMOVAL
- O HIGH PATHOGEN REMOVAL
- O HEAVY METALS REMOVAL
- O REFRACTORY ORGANICS REMOVAL
- O ENERGY SAVING
- O SAVING IN NUTRIENT COST

TO MEET LOW COST TREATMENT OBJECTIVES

- O WASTEWATER CHARACTERIZATION
- O ESTABLISH ALTERNATIVES
- O EVALUATE DESIGN CRITERIA
- O INTEGRATE POND DESIGNS INTO TREATMENT TRAIN
- O ASSESS ECONOMIC AND ENVIRONMENTAL FACTORS

PROBLEMS IN DESIGNING PONDS

- O INADEQUATE UNDERSTANDING OF COMPLEXITIES
- O BASIC PRINCIPLES NOT FOLLOWED
- O DEFINITIONS LOOSELY APPLIED (i.e. FWSP)
- O EXTRAPOLATION OF SHORT-TERM OPERATIONAL EXPERIENCES
- O PHYSICAL, CHEMICAL, BIOLOGICAL PARAMETERS NOT ADEQUATELY APPLIED
- O INADEQUATE COMPARISONS BETWEEN TYPES

BASIC TERMINOLOGY

- O AWSP
- O MAP
- O FWSP
- O PWSP
- O COMBINATION

ECONOMIC EVALUATION

Detention			POND CHARACTERISTICS				COST			
AWSP	FWSP	PWSP	AREA	PERIMETER	VOL.	LENGTH				
			A	D	V	L	A	V	L	E#
(DAYS)	(DAYS)	(DAYS)	(M^2)	(M)	(M^3)	(M^2)				

E = % OF V & L TO COVER APPURTENANCES

PWSP

AFTER GROWTH POTENTIAL

1. ESCHERICHIA
2. PSEUDOMONAS
3. SERRATIA

NO AFTERGROWTH

1. PROTEUS
2. ALCALIGENES
3. ENTERABACTER
4. SALMONELLA
5. SHIGELLA
6. VIBRIO

AWSP

1. OPEN ANAEROBIC DIGESTERS
2. TEMPERATURE SENSITIVE
3. SUBJECT TO THERMAL STRATIFICATION
4. SERIES CONNECTION O.K.
5. SULFUR PRESENTS PROBLEM
6. REQUIRES M&O

FWSP

- CRITICAL PARAMETER
  1. SURFACE AREA
- DESIGN MUST CONSIDER
  1. TEMPERATURE
  2. TOTAL OXYGEN REQUIREMENTS
  3. VOLUMETRIC LOAD
  4. TOXICITY AND INHIBITION
  5. NUTRIENT RECYCLE
  6. GEOTECHNICS
  7. EFFECTIVE DEPTH
  8. RECEIVING WATERS

EMPIRICAL DESIGN FOR FWSP

$$V = 3.5 \times 10^{-5} \, QL \, [\theta^{35-T)}]f \cdot f'$$

A CONSERVATIVE CONCEPT FOR A SINGLE POND

FUTURE DEVELOPMENTS

NEED TO KNOW IMPACT OF:

- DEGRADATION OF COMPLEX ORGANICS
- RECYCLE OF NUTRIENTS
- NITRIFICATION AND DENITRIFICATION
- RECYCLE OF SULFUR COMPOUNDS
- CONTROL OF DOMINANT SPECIES
- ECONOMICAL REMOVAL OF ALGAE

FOR BETTER UTILIZATION

1. IMPROVE PREDICTABILITY OF PERFORMANCE
2. UPDATE REGULATORY CRITERIA
3. UNDERSTAND DESIGN LIMITATIONS
4. MANDATE M&O
5. ELIMINATE SHORT CIRCUITING

WASTEWATER REUSE THROUGH LAND APPLICATION

Earnest F. Gloyna[1]

Abstract

Clearly, disposal of wastewater on land and the use of land treatment systems for renovating wastewaters and crop management can be cost effective. However, the planning, design, and construction of each system must be site specific. Wastewater disposal, crop management, water reclamation, complexities of the soil continuum, and plant ecosystem enter into the technical assessment of wastewater disposal on agricultural land.

Wastewater reuse through land application is not new, and there have been many successful systems. However, in today's environment, the level of potential contaminants in wastewaters is increasing. Salts, fertilizers, nontoxic organics, toxic elements, and objectionable microorganisms contribute to the problems associated with treatment and land disposal of wastewaters and sludges.

Low-cost pretreatment of municipal wastewaters and most industrial effluents is usually necessary. Pretreatment systems employing physical, chemical, biological, or combination treatment processes are viable alternative processes. In many cases, the waste stabilization pond system presents an ideal alternative.

Following pretreatment, there are several land application systems that are available. Land application involves irrigation, overland flow, and infiltration-percolation. Basic methods of application embrace sprinkler, flooding, and ridge and furrow. The utility of each site depends on climate, effluent characteristics, size of facility, methods of distribution, and land characteristics.

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Introduction

The disposal of wastewaters by land treatment provides an attractive alternative for solving costly waste management problems. The earth's mantle has been described as a "living filter" and the most ecologically appropriate treatment system for man-made wastes.

Frequently, the earth's soil is capable of being engineered into a condition whereby large amounts of treated wastewaters can be discharged onto the land. Yet, the engineering and overall planning associated with wastewater collection, treatment, and disposal is a very complex problem.

For clarity of definition, land treatment is not necessarily wastewater spreading, wastewater farming, disposal of partially treated effluents on the land or even the use of effluents for irrigation purposes. The difference is in what aspect of the management plan is being maximized. If crops are used as a part of a land treatment system, the objective is to apply as much wastewater as possible without decreasing plant growth.

In most cases, wastewaters will require some form of treatment prior to land application. Each wastewater, soil condition, and cover crop will require individual evaluation and a specific application procedure. Once these basic requirements have been established, then it is possible to design an efficient treatment unit that satisfies the necessary public health requirements.

It is the objective of this presentation to review some of the successful land disposal systems with due consideration to the historical successes of wastewater reuse via land disposal, potential wastewater contaminants, low-cost pretreatment, land application practices, and assessment of planning considerations.

Examples of Wastewater Reuse Via Land Disposal

Land disposal of wastewater predates modern civilization. More recent historical experiences describing the use of wastewaters to irrigate cropland

are fairly well documented. For example, it is known that use of wastewater for irrigation purposes was common practice in Bunzlau, Germany, as early as 1559. (1) Selected early land application systems are shown below in Table 1.

TABLE 1. Selected Early Land Application Systems

Location	Date Started	Type of System	Area (ha)	Flow (cu m/day)
International				
Croydon-Beddington, England	1860	Sewage farm	250	20,000
Paris, France	1869	SR[a]	6,500	300,000
Leamington, England	1870	Sewage farm	160	3,000
Berlin, Germany	1874	Sewage farm	2,800	--
Wroclaw, Poland	1882	Sewage farm	1,500	170,000
Melbourne, Australia	1893	SR	4,000	180,000
		OF[b]	1,400	260,000
Braunschweig, Germany	1896	Sewage farm	4,000	60,000
Mexico City, Mexico	1900	SR	45,000	2,000,000
United States				
Calumet City, Michigan	1888	RI[c]	5	4,500
Woodland, California	1889	SR	100	16,000
Fresno, California	1891	SR	1,620	98,000
San Antonio, Texas	1895	SR	1,620	76,000
Vineland, New Jersey	1901	RI	6	3,000
Ely, Nevada	1908	SR	570	5,700

[a]SR = slow rate

[b]OF = overland flow

[c]RI - rapid infiltration

Today the disposal of wastewater on land and the utilization of land treatment processes have developed into a well-defined technology. Added emphasis is placed on pretreatment, overall planning, and efficient reuse of water. Selected wastewater reuse and land disposal projects are described below:

Australia: Werribbee Farm, Melbourne, Australia, discharges 4.4×10^5 cu m/day to several thousand acres of crop land supporting 30,000 sheep and 22,000 beef cattle. (2) The concentration of heavy metals in the harvested

herbage fall within acceptable ranges although N, P and K show increases, the BOD_5 and SS removal rates are around 95%. All of this is remarkable since 30% of the flow and 75% of the organic loading is contributed by industrial wastes.

France: The municipal wastewater farms of Paris have been in operation since 1880, and these farms have been very successful. These farms are receiving about 100 million cu m/yr of wastewater. Application rates are 4 m per year over a mixture of sand, clay, and gravel. (1)

Germany: At Braunschweig, Germany, cereal crops, potatoes, sugar beets, and asparagus have been irrigated by wastewater application for many decades. (1)

Israel: At present, Israel utilizes most of its fresh water potential of 1,500 million cu m per year. About 75% is supplied to agriculture. It is planned that by 1985, 10% of the agricultural water requirements will be supplied through wastewater reclamation. (4)

Poland: In Poland during dry years, sewage represents 50% of all surface flow. The Wroclaw Farm, 1,500 ha, receives 170,000 cu m/day. It has been in operation for 100 years. (1)

Saudi Arabia: The King Khalid Military City, Saudi Arabia, a city of 70,000 people and one of the world's largest and costliest construction projects, will reuse all water. Sewage effluents will be used for agricultural purposes. (3)

South Africa: About 3% (31,000 ha) of the total area under irrigation is irrigated with wastewater. Municipalities provide about 85% of this wastewater. (5)

United States: The U.S. nearly a decade ago registered about 600 municipalities and 1,300 industrial facilities discharging wastewaters on land. Most of these sites were located in the dryer western states. The 1972 Amendments to the U.S. Federal Water Pollution Control Act indicate that it is a national goal to minimize discharge of waste to surface waters.

The State of California leads the U.S. in reuse with a history of irrigation and reuse that dates back to 1929. The volume of wastewater reused in 1977 was about 227 billion cu m. Of the 200 projects in operation, 150 were classified as nonsensitive crop irrigation and 50 were used to water golf courses, recharge groundwater, industrial reuse and other purposes. (6)

At the billion dollar Disney World complex in Florida, a secondary treatment plant with tertiary holding ponds provides water for tree farms, agricultural usage, aquaculture, and wetlands-land treatment systems.

The largest agricultural water reuse project is located in Muskegon County, Michigan. This single project involves about 4,000 ha. (7)

Lubbock, Texas, can now enjoy one of the largest parks in the U.S. because of innovative water reuse planning. The park covers 640 ha and a recreational greenbelt that is 10 km long. To insure a water supply, reclaimed wastewater will be withdrawn from stored groundwater produced through irrigation of 1800 ha of farm land with municipal wastewater. (8)

On a smaller scale, a turf farmer rented 13.4 ha near the wastewater treatment plant of Tolleson, Arizona. The farmer guarantees the city a minimum rent of $3,500 per year. (9) The farmer uses chlorinated secondary effluent.

Potential Wastewater Contaminants and Nutrients

Wastewater, particularly industrial wastes, contain various amounts of contaminants such as salts, nitrogen, nontoxic organics, toxic elements, and microorganisms.

Salts: The extent and severity of injury caused by salt is influenced by soil characteristics. Dissolved solids will leach out of or accumulate in a soil. Sandy soils permit rapid leaching but at the same time the amount of salt per unit volume of waste available to plants is greater in a sandy soil. Dissolved solids in industrial wastes depends largely on the recycle practices,

but Table 2 gives some relative concentrations in different industrial effluents. (10)

TABLE 2. Industrial Wastes (9)

Process	Total Dissolved Solids (mg/L)
Oil Refinery	2,000 - 3,000
Metal Processing	12,000
Leather Tanning	3,800 - 36,500
Poultry Processing	350 - 3,200
Pulp and Paper	2,000
Vegetable Processing	2,000 - 6,000

Sodium ions present a major problem. The sodium absorption ratio (SAR) expresses the degree of sodium absorption from a solution in equilibrium with the soil. The SAR is defined as follows:

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{++} + Mg^{++}}{2}}}$$

Irrigation water with a SAR value of less than 10 (ion concentrations in milliequivalents per liter) constitutes a low hazard. At high levels, sodium causes deflocculation of clay soils and subsequent sealing. Serious problems occur when the exchange sodium percentage reaches a value of 15%. (11)

Nitrogen: Land application of municipal wastewaters on land has a number of advantages. Nearly all soils respond to additions of nitrogen by increasing production; however, for optimum crop production, the nitrogen application must be in balance with the need. Furthermore, if the nitrogen is applied to the soils in amounts greatly in excess of crop needs and is allowed to percolate to the groundwater, nitrate contamination may occur. The important processes involved in nitrogen removal during land application of wastewater involve:

a. ammonia volatilization,
b. crop removal,
c. soil adsorption of ammonia,
d. incorporation into the soil organic fraction, and
e. denitrification.

The relative impact of any of the above processes on nitrogen removal is highly dependent on soil characteristics, climate, and wastewater management practices.

Fertilizer value of municipal wastewaters is readily evident in that a five centimeter per week application might provide commercial fertilizer constituents equivalent to approximately 233 kg/ha of nitrogen, 224 kg of phosphate (P_2O_5) and 254 kg of potash (K_2O). (2) These data are equivalent to an annual application of about 2,200 kg of a ten-ten-ten fertilizer per hectare. This is more than twice as much as a generally acceptable application of commercial fertilizer. Some crops are highly effective in removing nitrogen and phosphorus. The full nitrogen cycle in soil is given in Figure 1.

Waste management is the key to excess nitrogen in industrial wastes. This control process may involve crop selection, amount of waste applied in relation to soil, drainage, infiltration, and other factors such as pH, moisture, temperature, and carbon content. Average uptake of nitrogen by crops ranges from about 27 kg for wheat to as much as 270 kg for well-managed Bermuda grass. (12) Generally, low application rate systems should be designed for nitrogen uptake by crops. The time-movement scale for the soluble inorganic forms of nitrogen is the same as that for the percolation of the water. The critical C:H ratio affecting mineralization and immobilization is between 15 and 33, and the critical N (%) in an inorganic waste is between 1 and 3% for mineralization. A high BOD waste may enhance reducing conditions and cause denitrification.

Phosphorus: Municipal wastewaters may contain 1.0 to 40 mg/L of phosphorus. Since phosphorus is essential for all forms of life, it may be possible to increase agricultural productivity by applying municipal wastewater

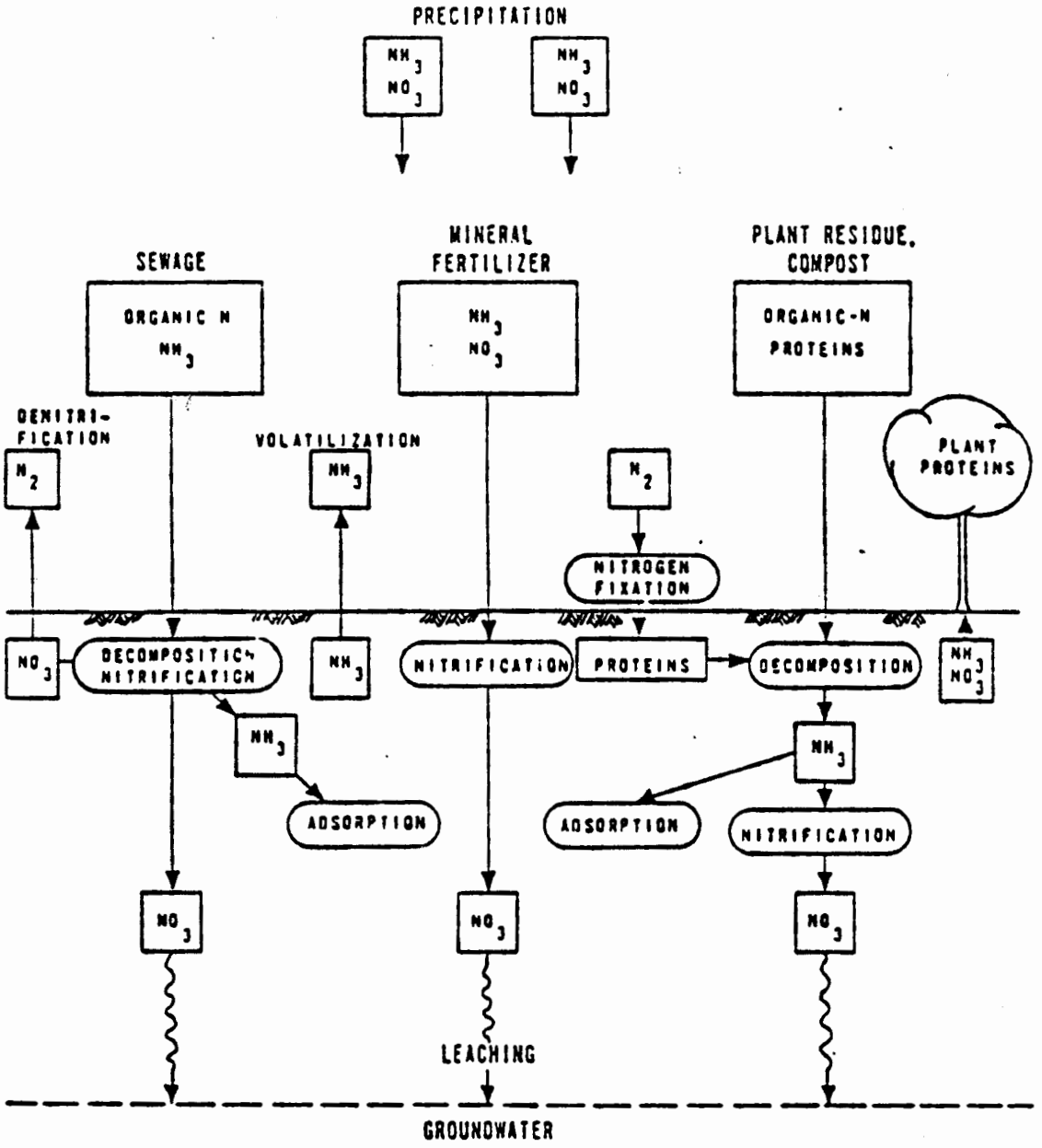


FIGURE 1. NITROGEN CYCLE IN SOIL

on the land. Unfortunately, phosphorus is highly reactive and reactions involving phosphorus with soils are complex. The capacity of a soil to sorb phosphorus is dependent on the concentration of phosphorus in solution, pH of the soil, temperature, time, total amount of phosphorus added, and the concentrations of various constituents in the wastewater that directly react with phosphorus. Also, the downward movement of phosphorus in a soil profile is diffuse.

Phosphorus, as a solid phase, (a) consists of organic phosphorus, the amount of which is highly dependent on the amount of organic matter in the soil; (b) inorganic compounds; and (c) phosphorus adsorbed on various types of surfaces in the soil. Orthophosphate, PO_4, is the most stable configuration in soil movement. Soluble inorganic phosphorus introduced into a soil is chemically adsorbed on surfaces, and also it can be precipitated. The adsorption reaction is with iron, aluminum, or calcium ions exposed on solid surfaces.

Removal of phosphorus in harvested crops is typically 10% or less of the fertilizer phosphorus added during the season in which the crop is grown, although recoveries may be as high as 50% to 60%. Phosphorus removed by the usual harvested portions of selected agronomic, vegetable, and fruit crops ranges from a low of 11 kg/ha·yr to as high as 95 kg/ha·yr. (13)

Nontoxic Organics: Biodegradable, nontoxic organics do not present a potential hazard, but soil clogging occur which results in decreased infiltration and percolation. Wastes having a high C:N ratio appear to induce clogging. In general, the rate of organic decomposition must be carefully considered.

Toxic Elements: Wastewaters containing heavy metals may produce a major long-term hazard. Of greatest concern are boron, cadmium, cobalt, chromium, mercury, nickel, lead, and zinc; however, other metals such as copper may present a problem. Some metals in wastewaters such as zinc are essential to life and may provide an environmental benefit, but these also can accumulate and pose potential long-term hazards.

Conditions that favor low pH, sandy soils, high metal sludges, and metal sensitive crops require most supervision. Generally, the concentration of a metal in soil is the most important factor to consider. Since most metals are relatively immobile in soils, there are only two major factors that must be assessed to evaluate the status of a metal in soil: (a) the total mass input to a soil, and (b) the vertical distribution of that mass when it is in a relatively steady state condition in the soil.

Identification of metal species is very important. Metal species differ in chemical properties, and these classes include complexes, ion pairs, and chelates. Table 3 provides a listing of substances with which metals may form chemical and/or physical associations.

TABLE 3. Classification of Substances with Which Metals May Form Chemical and/or Physical Associations in Fresh Waters and Wastewaters (14)

Complex and Ion Pair Formers	Chelates	Precipitants	Adsorbents
H_2O	$R(COO^-)_x$	OH^-	Clay minerals
NH_3	Fulvates	CO_3^{2-}	Hydrous oxides (Al, Fe, Mn, Si)
OH^-	Humates	PO_4^{3-}	Humates
Cl^-	Polypeptides	S^{2-}	Fulvates
HCO_3^-	Polyaminosaccharides	SO_4^{2-}	Bio-remnants
CO_3^{2-}	Polyuronides		Calcium carbonates
SO_4^{2-}	Proteins		Iron sulfides
$RCOO^-$	Polyphosphate		Calcium phosphates
RSO_3^-			

Microorganisms: Removal of microorganisms, particularly human pathogens from wastewaters applied to soils, is an important consideration in land disposal of municipal wastes. More than 90% of the bacteria are removed in the upper one centimeter of a good soil. Yet, several meters of soil may be

necessary for nearly complete removal of bacteria. The rate of movement is dependent upon such characteristics as type of soil, porosity, and channeling. Longevity of organisms such as Salmonella depends on a number of factors including temperature, organic matter content, and aerobic state. These organisms have been observed in some instances to survive in soil from six months to a full year. Salmonella survive in frozen soil for longer periods than in unfrozen soil, while E. coli survive longer in sterile than in non-sterile soils.

Survival of pathogenic organisms in and on the soil and on vegetable crops has received considerable attention. Table 4 gives survival times of various pathogens in the different media. Table 5 is a summary of factors that affect the survival of enteric bacteria and viruses in soil. In land application, control of insects and rodents is an important operational control.

Hydraulic Capacity

The capacity of the soil to accept and transmit water is crucial to the design of both rapid and slow rate land application systems. Hydraulic parameters of importance are:

a. infiltration;
b. vertical permeability (percolation); and
c. horizontal permeability.

The hydraulic properties of a soil (flow or retention of water within the soil profile) include:

a. soil-water characteristic curve;
b. percent moisture at saturation;
c. permeability;
d. infiltration rate;
e. ability to drain;
f. specific yield;
g. specific retention; and
h. transmissivity.

It should be noted that water held in soil is roughly inversely proportional to the pore diameter.

TAPLE 4. Survival Times of Pathogens (15)

Organism	Media	Survival Time
Anthrax bacteria	In water and sewage	19 days
Ascaris eggs	On vegetables	27-35 days
	On irrigated soil	2-3 years
	In soil	6 years
B.dysenteriae flexner	In water containing humus	160 days
B.typhosa	In water	7-30 days
	In soil	29-70 days
	On vegetables	31 days
Cholera vibrios	On spinach, lettuce	22-29 days
	On cucumbers	7 days
	On nonacid vegetables	2 days
	On onions, garlic, oranges, lemons, lentils, grapes, rice and dates	Hours to 3 days
Coliform	On grass	14 days
	On clover leaves	12-14 days
	On clover at 40-60% humidity	6 days
	On lucerne	34 days
	On vegetables (tomatoes)	35 days
	On surface of soil	38 days
	At -17°C	46-73 days
Entamoeba histolytica	On vegetables	3 days
	In water	Months
Enteroviruses	On roots of bean plants	At least 4 days
	In soil	12 days
	On tomato and pea roots	4-6 days
Hookworm larvae	In soil	6 weeks
Leptospira	In river water	8 days
	In sewage	30 days
	In drainage water	32 days
Liver fluke cysts	In dry hay	Few weeks
	In improperly dried hay	Over a year
Poliovirus	In polluted water at 20°C	20 days
Salmonella	On grass (raw sewage)	6 weeks+
	On clover (settled sewage)	12 days
	On vegetables	7-40 days
	On beet leaves	3 weeks
	On grass	Over winter
	On surface of soil and potatoes	40 days+
	On carrots	10 days+
	On cabbage and gooseberries	5 days+
	In sandy soil - sterilized	24 weeks
	In sandy soil - unsterilized	5-12 weeks
	On surface of soil (raw sewage)	46 days
	In lower layers of soil	70 days
	On surface of soils (stored sewage)	15-23 days
	In air dried, digested sludge	17 weeks+
Schistosoma ova	In digestion tanks	3 months
	In sludge at 60-75°F (dry)	3 weeks
	In septic tank	2-3 weeks
Shigella	On grass (raw sewage)	6 weeks
	On vegetables	7 days
Streptococci	In soil	35-63 days
	On surface of soil	38 days
S. typhi	In water containing humus	87-104 days
Tubercle bacteria	On grass	10-14 days
	In soil	6 months+
	In water	1-3 months
Typhoid bacilli	In loam and sand	7-17 days
	In muck	40 days
Vibrio comma	In river water	32 days
	In sewage	5 days

TABLE 5. Factors that Affect the Survival of Enteric Bacteria and Viruses in Soil

Factor		Remarks
pH	Bacteria	Shorter survival in acid soils (pH 3 to 5) than in neutral and alkaline soils
	Viruses	Insufficient data
Antagonism from soil microflora	Bacteria	Increased survival time in sterile soil
	Viruses	Insufficient data
Moisture content	Bacteria and viruses	Longer survival in moist soils and during periods of high rainfall
Temperature	Bacteria and viruses	Longer survival at low (winter) temperatures
Sunlight	Bacteria and viruses	Shorter survival at the soil surface
Organic matter	Bacteria and viruses	Longer survival (regrowth of some bacteria when sufficient amounts of organic matter are present)

Land Treatment

The controlled application of wastewater onto the land surface can provide a high degree of treatment. The three major land treatment processes are:

a. slow rate;
b. rapid infiltration; and
c. overland flow.

Various types of land application are illustrated in Figure 2. Irrigation by spraying or spreading provides controlled discharge of effluent. The application method depends upon the soil, the type of crop, the climate, and topography. Overland flow is controlled discharge in which a large portion of the wastewater becomes runoff; whereas in the infiltration-percolation process, the major portion of the wastewater enters the groundwater.

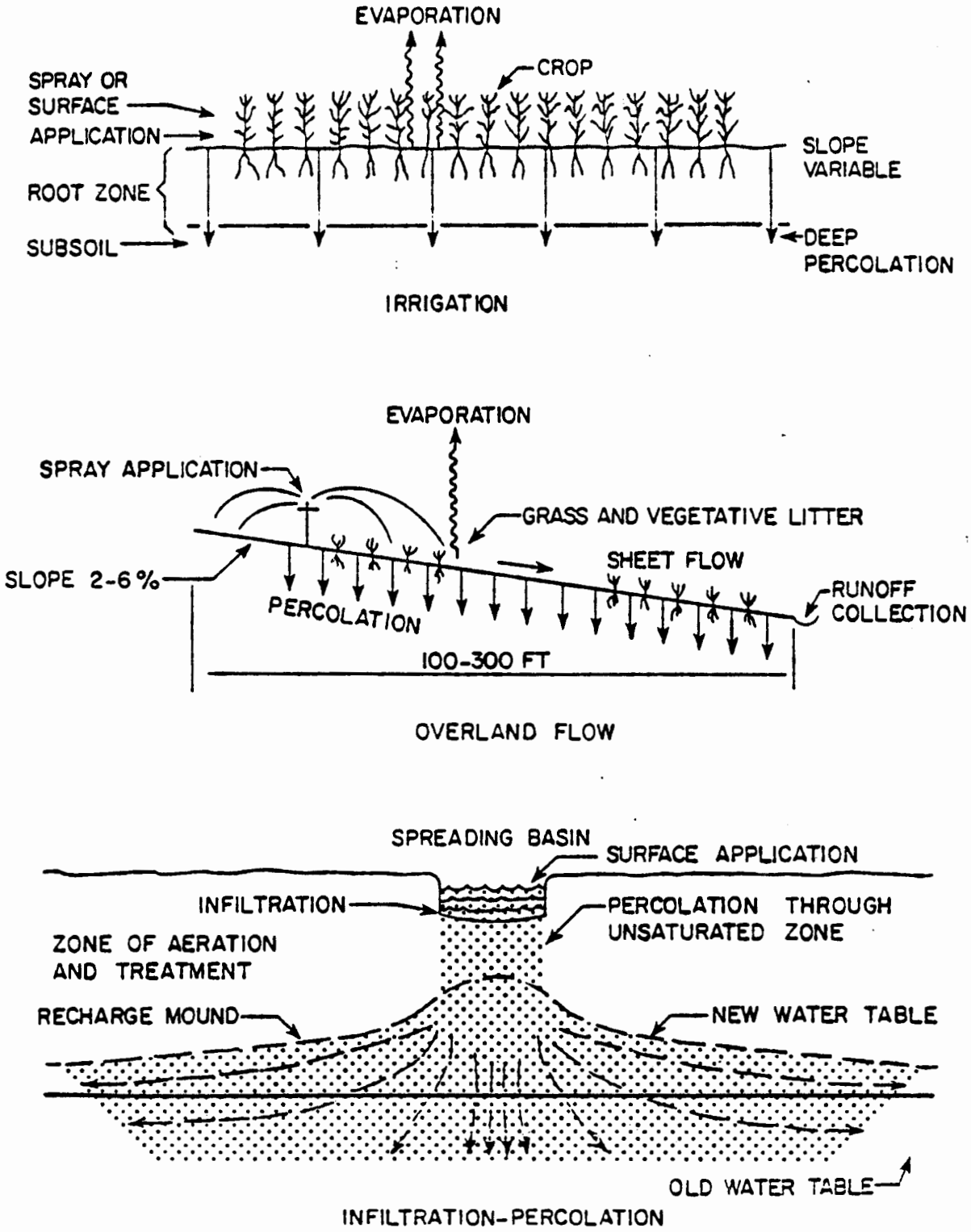


FIGURE 2. LAND APPLICATION APPROACHES

Figure 3 illustrates the relationship between liquid loading rate and soil type for the three land application approaches. (3) Application methods for wastewater disposal on land are illustrated in Figure 4. In the spray method, effluent is applied through nozzles or sprinkler heads. Costs of this system are relatively high because of pump and piping costs and power for operation of pumps. In the ridge and furrow method, application is by gravity flow. Relatively flat land is required for this method and care must be taken to avoid clogging up soil pores. Flooding requires level land so that a uniform inundation depth can be maintained. Crops must be able to tolerate the periodic flooding; "drying out" of the soil between applications is necessary to avoid clogging.

Where land treatment is desired, overland flow is used with low infiltration and/or percolation capacities. Generally, close growing grasses are utilized. Rapid infiltration/percolation designs may be used where deep permeable soil materials are available. Crop irrigation land treatment applies treated effluents by spray applications or by flooding through furrows or borders.

Comparisons of site characteristics, design features of land treatment systems, and expected quality of treated water are presented in Tables 6, 7, and 8. Because of site specific characteristics, the site characteristics and design features are not limits that should be considered to be absolute. Similarly, the expected quality can vary.

Planning and Technical Assessment

Several factors determine the utility of each site. They should be evaluated both individually and collectively when assessing the requirements of any treatment site; i.e., (a) climate conditions, (b) size of the facility, (c) land characteristics, (d) effluent characteristics, and (e) methods of distribution.

A direct relationship exists between climate and in such cases where sprayed effluent supplements agriculture or silviculture. Similarly, availability of land and size of facility are interrelated.

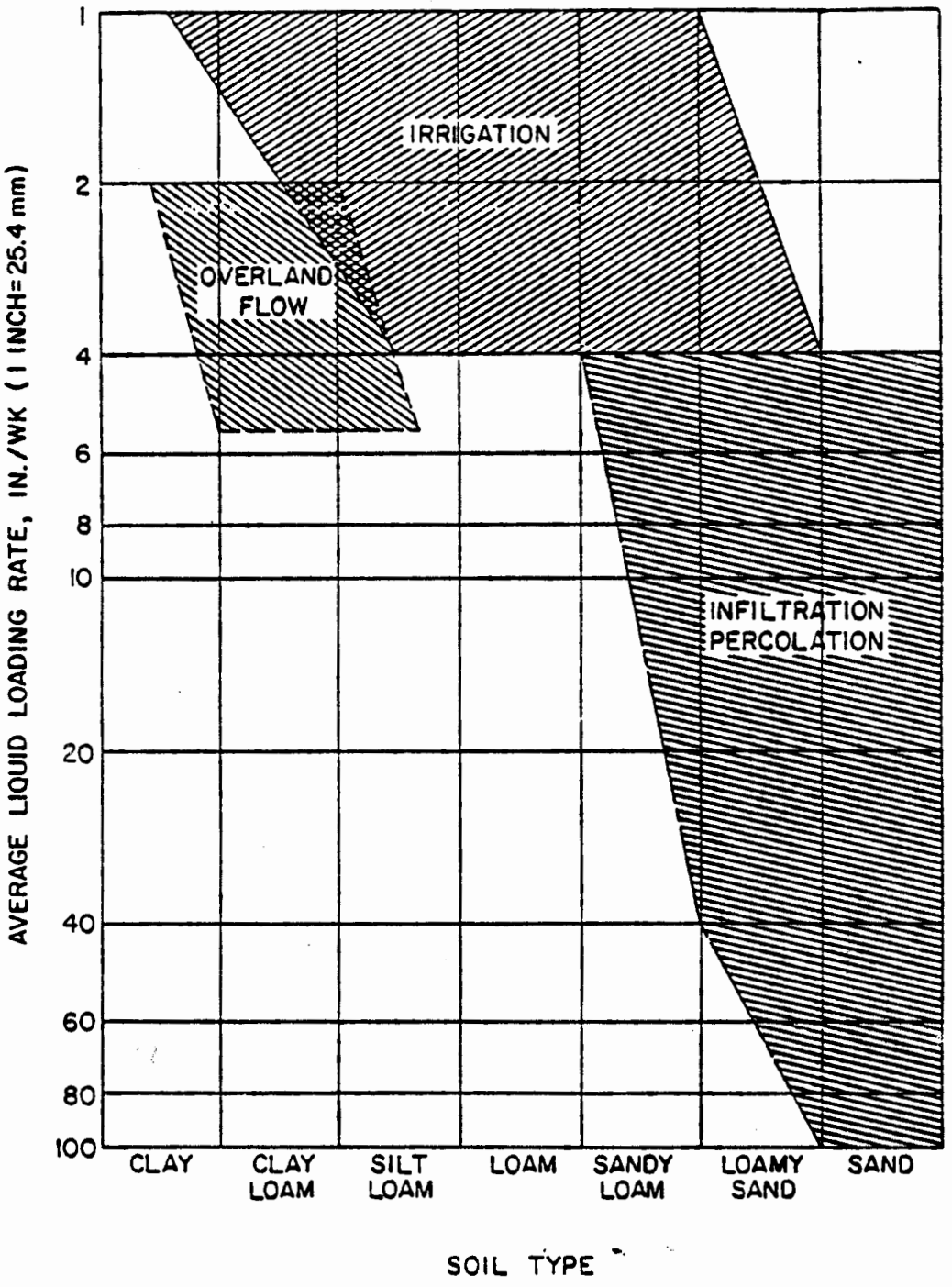
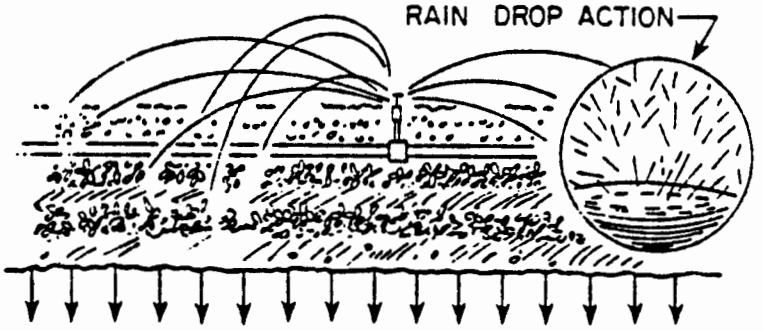
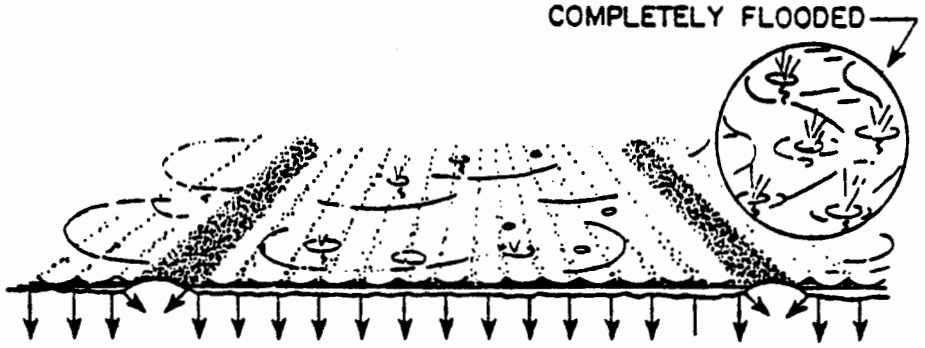


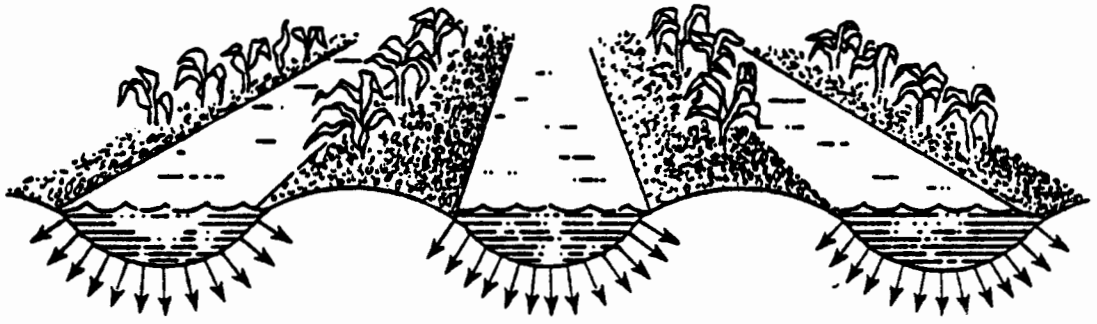
FIGURE 3. SOIL TYPE VERSUS LIQUID LOADING RATES FOR DIFFERENT LAND APPLICATION APPROACHES



SPRINKLER



FLOODING



RIDGE AND FURROW

FIGURE 4. BASIC METHODS OF APPLICATION

TABLE 6. Comparison of Site Characteristics for Land Treatment Processes (15)

	Slow Rate	Rapid Infiltration	Overland Flow
Grade	Less than 20% on cultivated land; less than 40% on noncultivated land	Not critical; excessive grades require much earthwork	Finish slopes 2-8%[a]
Soil permeability	Moderately slow to moderately rapid	Rapid (sands, sandy loams)	Slow (clays, silts, and soils with impermeable barriers)
Depth to groundwater	0.6-1 m (minimum)[b]	1 m during flood cycle;[b] 1.5-3 m during drying cycle	Not critical[c]
Climatic restrictions	Storage often needed for cold weather and during heavy precipitation	None (possibly modify operation in cold weather)	Storage usually needed for cold weather

[a]Steeper grades might be feasible at reduced hydraulic loadings.

[b]Underdrains can be used to maintain this level at sites with high groundwater table.

[c]Impact on groundwater should be considered for more permeable soils.

TABLE 7. Comparison of Typical Design Features for Land Treatment Processes (15)

Feature	Slow Rate	Rapid Infiltration	Overland Flow
Application techniques	Sprinkler or surface[a]	Usually surface	Sprinkler or surface
Annual loading rate, m	0.5-6	6-125	3-20
Field area required, ha[b]	23-280	3-23	6.5-44
Typical weekly loading rate, cm	1.3-10	10-240	6-40[c]
Minimum preapplication treatment provided in the United States	Primary sedimentation[d]	Primary sedimentation[e]	Grit removal and comminution[e]
Disposition of applied wastewater	Evapotranspiration and percolation	Mainly percolation	Surface runoff and evapotranspiration with some percolation
Need for vegetation	Required	Optional	Required

[a]Includes ridge-and-furrow and border strip.

[b]Field area in hectares not including buffer area, roads, or ditches for 3,785 m^3/d (1 Mgal/d) flow.

[c]Range includes raw wastewater to secondary effluent, higher rates for higher level of preapplication treatment.

[d]With restricted public access; crops not for direct human consumption.

[e]With restricted public access.

TABLE 8. Expected Quality of Treated Water from Land Treatment Processes[a] mg/L Unless Otherwise Noted (15)

Constituent	Slow Rate[b]		Rapid Infiltration[c]		Overland Flow[d]	
	Average	Upper Range	Average	Upper Range	Average	Upper Range
BOD	<2	<5	5	<10	10	<15
Suspended solids	<1	<5	2	<5	10	<20
Ammonia nitrogen as N	<0.5	<2	0.5	<2	<4	<8
Total nitrogen as N	3[e]	<6[e]	10	<20	5[f]	<10[f]
Total phosphorus as P	<0.1	<0.3	1	<5	4	<6
Fecal coliforms, No./100 mL	0	<10	10	<200	200	<2,000

[a]Quality expected with loading rates at the mid to low end of the range.

[b]Percolation of primary or secondary effluent through 1.5 m (5 ft) of unsaturated soil.

[c]Percolation of primary or secondary effluent through 4.5 m (15 ft) of unsaturated soil; phosphorus and fecal coliform removals increase with distance.

[d]Treating comminuted, screened wastewater using a slope length of 30-36 m (100-120 ft).

[e]Concentration depends on loading rate and crop.

[f]Higher values expected when operating through a moderately cold winter or when using secondary effluent at high rates.

Waste characteristics determine the degree of pretreatment required. Finally, climatic conditions and mode of distribution are closely interrelated. For example, spray irrigation is more generally used in humid areas, while surface applications--i.e., overland flow and ridge furrow irrigation--are more adaptable to more arid regions. It seems that the latter technique is utilized more for larger sites, 400 ha. (1,000 acres). (14)

A critical feasibility study will assist in identifying significant problem areas. Such a study should include: (a) land location and mode of acquisition; (b) groundwater contamination assessments; (c) soil characteristics and eutrophacation enhancement. Land procurement may be an expensive and difficult problem. Groundwater must be carefully monitored. As to soil characteristics, some soils possess large adsorption capacity. Phosphorus saturation and clogging are frequently limiting factors in the life span of a disposal site. Control of heavy metals is necessary. However, crop rotation can eliminate some of the above problems.

The overall planning process should include the following steps:

a. waste characterization,
b. land treatment system suitability,
c. land requirement,
* d. site identification,
e. site screening,
* f. potential site selection,
g. field investigation,
h. preliminary design criteria and costs,
i. evaluation of alternatives,
* j. plan selection, and
k. initiation of land treatment design.

* Check points which may indicate that land treatment is not feasible.

Field tests are very important. A typical order of testing progressing from exploratory test pits to laboratory tests is given in Table 9. A general interpretation of the chemical tests is summarized in Table 10.

TABLE 9. Field Investigations (15)

	Test Pits	Bore Holes	Infiltration Rate	Soil Chemistry
Remarks	Usually with a backhoe, includes inspection of existing SCS reports, road cuts, etc.	Drilled or augered, includes inspection of driller's logs for local wells, water table levels	Match the expected methods of application, if possible	Includes review of SCS survey
Information to Obtain	Depth of profile, texture, structure, soil layers restricting percolation	Depth to groundwater, depth to impermeable layer(s)	Expected minimum infiltration rate	Specific data relating to crop and soil management, phosphorus and heavy metal retention
Estimates Now Possible	Need for vertical conductivity testing	Groundwater flow direction	Hydraulic capacity based on soil permeability (subject to drainage restrictions)	Crop limitations. Soil amendments. Possible preapplication requirements.
Additional Field Tests	Vertical conductivity (optional)	Horizontal conductivity	--	--
Additional Estimates	Refinement of loading rates	Mounding analysis, dispersion, need for drainage	--	Quality of percolate
Number of Tests	Depends on size, soil uniformity, needed soil tests, type of system. Typical minimum of 3 to 5 per site.	Depends on system type (more for RI than SR), soil uniformity, site size. Typical minimum of 3 per site.	Depends on size of site, uniformity of soil. Typical minimum of 2 per site.	Depends on uniformity of soil types, type of test, size of site

TABLE 10. Interpretation of Soil Chemical Tests (15)

Test Result	Interpretation
pH of saturated soil paste	
<4.2	Too acid for most crops to do well
5.2-5.5	Suitable for acid-tolerant crops
5.5-8.4	Suitable for most crops
>8.4	Too alkaline for most crops, indicates a possible sodium problem
cation exchange capacity (CEC), meq/100 g	
1-10	Sandy soils (limited adsorption)
12-20	Silt loam (moderate adsorption)
>20	Clay and organic soils (high adsorption)
exchangeable cations, % of CEC	**Desirable range**
Sodium	≤5
Calcium	60-70
Potassium	5-10
exchangeable sodium percentage, % of CEC	
<5	Satisfactory
>10	Reduced permeability in fine-textured soils
>20	Reduced permeability in coarse-textured soils
electrical conductivity, mmhos/cm at 25°C of saturation extract	
<2	No salinity problems
2-4	Restricts growth of very salt-sensitive crops
4-8	Restricts growth of many crops
8-16	Restricts growth of all but salt-tolerant crops
>16	Only a few very salt-tolerant crops make satisfactory yields

Overload flow is generally used when the surface soils are slowly permeable or have a restrictive layer of clay at depths of 0.3 to 0.6 m. Also, overland flow can be used on more permeable soils using higher loading rates than would be possible with a slow rate system. The treated water leaving an overland flow system may be through surface runoff if there are heavy clays below the surface. Overload flow design criteria shown in Table 11 for fall, spring, and summer application have provided BOD and suspended solids concentrations less than 20 mg/L, total nitrogen less than 10 mg/L, ammonia nitrogen less than 5 mg/L, and total phosphorus less than 6 mg/L. (15)

Process performance of an overland flow system may involve the following considerations:

1. BOD removal
2. Suspended solids removal
3. Nitrogen removal
4. Phosphorus removal
5. Trace element removal
6. Microorganism removal
7. Trace organics removal
8. Effect of rainfall
9. Effect of slope grade
10. Performance during start-up

TABLE 11. Overland Flow Design Guidelines (15)

Preapplication Treatment	Hydraulic Loading Rate, (cm/d)	Application Rate, (cu m/m·ha)	Application Period, (hr/d)	Application Frequency (d/wk)	Slope Length (m)
Screening	0.9-3	0.07-0.12	8-12	5-7	36-45
Primary Sedimentation	1.4-4	0.08-0.12	8-12	5-7	30-36
Stabilization Pond	1.3-3.3	0.03-0.10	8-18	5-7	45
Complete Secondary Biological	2.8-6.7	0.10-0.20	8-12	5-7	30-36

Small Systems

The design of small systems (generally less than 3,785 cu m/d) includes special cost and operational considerations. While slow rate, rapid infiltration or overland flow systems can be used, it must be recognized that

experts will not be available on a daily basis. Therefore, the design and operating criteria are most important.

In addition to pretreatment requirements, selection of a hydraulic loading rate is most important. The permeability of the soil usually controls the loading rate; however, when slow rate or rapid infiltration systems overlie potential drinking water aquifers, nitrogen loading may be the limiting factor. The following equation may serve as a guideline for calculating the maximum allowable nitrogen loading rate:

$$L_{w(n)} = \frac{C_p(Pr - ET) + 10U}{(1 - f)(C_n - C_p)}$$

where $L_{w(n)}$ = wastewater hydraulic loading rate based on nitrogen limits, cm/yr

C_p = percolate nitrogen concentration, mg/L, limited to = 10 mg/L at the project boundary (or the background nitrate concentration, if it is greater than 10 mg/L)

Pr = precipitation rate, cm/yr

ET = evapotranspiration rate, cm/yr

U = crop nitrogen uptake rate, kg/ha·yr

C_n = nitrogen concentration in applied wastewater, mg/L (after losses in preapplication treatment)

f = fraction of applied nitrogen removed by dentrification and volatilization

Conservative nitrogen uptake values are given in Table 12.

Energy Requirements

Possible energy needs for land treatment systems involve pretreatment, pumping to site, distribution over the site, and tailwater recovery. Typical energy requirements are shown in Table 13.

TABLE 12. Nitrogen Uptake Rates for Selected Crops

Crop	Nitrogen Uptake Rate, kg/ha·yr
Forage	
Alfalfa	300
Bromegrass	130
Coastal bermudagrass	400
Kentucky bluegrass	200
Quackgrass	240
Reed canarygrass	340
Ryegrass	200
Sweet clover	180
Tall fescue	160
Field	
Barley	70
Corn	180
Cotton	80
Milomaize (sorghum)	90
Potatoes	230
Soybeans	110
Wheat	60

TABLE 13. Most Common Unit Energy Requirements for Land Treatment of Municipal Wastewater (15)

Treatment System	Component	Electricity, kWh/1,000 m^3	Fuel, MJ/1,000 m^3	Total Equivalent, kWh/1,000 m^3
Slow rate	Pumping for distribution	0.14	--	0.14
	Crop planting, cultivation, harvest, drying, transport	--	0.68	0.20
	Energy credit for fertilizer value of wastewater	--	(0.50)	(0.14)
Total		0.14	0.18	0.20
Rapid infiltration	Distribution (gravity)	--	--	--
	Recovery wells	0.05	--	0.05
Total		0.05	--	0.05
Overland flow	Transmission	0.10	--	0.10
	Forage harvest	--	0.22	0.06
Total		0.10	0.22	0.16

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CONVERSION FACTORS
U.S. Customary to SI (Metric)

U.S. Customary Unit			SI	
Name	Abbreviation	Multiplier	Syrbol	Name
acre	acre	0.405	ha	hectare
acre-foot	acre-ft	1 234	m^3	cubic metre
cubic foot	ft^3	28.32 0.0283	L m^3	litre cubic metre
cubic feet per second	ft^3/s	28.32	L/s	litres per second
degrees Fahrenheit	°F	0.555(°F-32)	°C	degrees Celsius
feet per second	ft/s	0.305	m/s	metres per second
foot (feet)	ft	0.305	m	metre(s)
gallon(s)	gal	3.785	L	litre(s)
gallons per acre per day	gal/acre-d	9.353	L/ha•d	litres per hectare per day
gallons per day	gal/d	4.381×10^{-5}	L/s	litres per second
gallon per minute	gal/min	0.0631	L/s	litres per second
horsepower	hp	0.746	kW	kilowatt
inch(es)	in.	2.54	cm	centimetre(s)
inches per hour	in./h	2.54	cm/h	centimetres per hour
mile	mi	1.609	km	kilometre
miles per hour	mi/h	0.45	m/s	metres per second
million gallons	Mgal	3.785 3 785.0	ML M^3	megalitres (litres x 10^6 cubic metres
million gallons per acre	Mgal/acre	8 353	m^3/ha	cubic metres per hectare
million gallons per day	Mgal/d	43.8 0.044	L/s m^3/s	cubic metres per second cubic metres per second
parts per million	ppm	1.0	mg/L	milligrams per litre
pound(s)	lb	0.454 453.6	kg g	kilogram(s) gram(s)
pounds per acre per day	lb/acre•d	1.12	kg/ha•d	kilograms per hectare per day
pounds per square inch	$lb/in.^2$	0.069 0.69	kg/cm^2 N/cm^2	kilograms per square centimetre Newtons per square centemetre
square foot	ft^2	0.0929	m^2	square metre
square inch	$in.^2$	6.452	cm^2	square centimetre
square mile	mi^2	2.590 259.0	km^2 ha	square kilometre hectare
ton (short)	ton (short)	0.907	Mg (or t)	megagram (metric tonne)
tons per acre	tons/acre	2 240 2.24	kg/ha Mg/ha	kilograms per hectare megagrams per hectare

IN SITU BIODEGRADATION

ADVANCED WASTEWATER TREATMENT for WATER REUSE

by

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UNIVERSIDAD NACIONAL AUTONOMA DE MEXICO

MEXICO CITY, MEXICO
DECEMBER 1991

.....convert biologically treated municipal and industrial wastewaters to usable water resources.

RECOMMENDED FEED WATER LIMITS FOR STEAM GENERATIONS
HIGH-PRESSURE DRUM-TYPE UNITS

TDS	50 ppb max.
Total iron	10 ppb max.
Total copper	10 ppb max.
Total silica	20 ppb max.
Oxygen	5 ppb max.
Hydrazine	10-20 ppb max. residual
pH	8.8-9.2 (copper-alloy system)
	9.2-9.4 (copper-free system)

COMPOSITION OF TREATED EFFLUENTS

CONSTITUENT	CONCENTRATION (mg/L)
BOD_5	15-25
COD	40-80
TOC	13-26
TSS	20-30
TDS	550-1150
P	6-15
N	20-60

PROCESS ALTERNATIVES

CONSTITUENT	PROCESS
Suspended Solids	Chemical coagulation and sedimentation
	Filtration Sand Multi Media
Nitrogen	Biological Nitrification and denitrification
Phosphorus	Chemical Precipitation Biological removal
Dissolved organics (BOD, COD and TOC)	Adsorption on Activated Carbon
Total Dissolved Solids	Reverse Osmosis Ion Exchange Distillation

FACTORS AFFECTING ADSORPTION ON ACTIVATED CARBON

- Adsorbability
- Functionality
- pH
- Temperature

ADSORPTION IS FAVORED BY:

- Increase in number of carbons in chain
- Increase in number of aromatic groups
- Increase in branching
- Decreasing polarity
- Decreasing solubility in water
- Decreasing degree of dissociation

ADSORPTION PREFERENCE

acids > aldehydes > esters > ketones >alcohols > glycols
(Note: number of carbons < 4)

pH EFFECTS

undissociated species are more easily adsorbed

low pH favors adsorption of acids (e.g.volatile acids, phenol)

high ph favors adsorption of basis (e.g. amines)

Other compounds are adsorbed at higher pH

TEMPERATURE

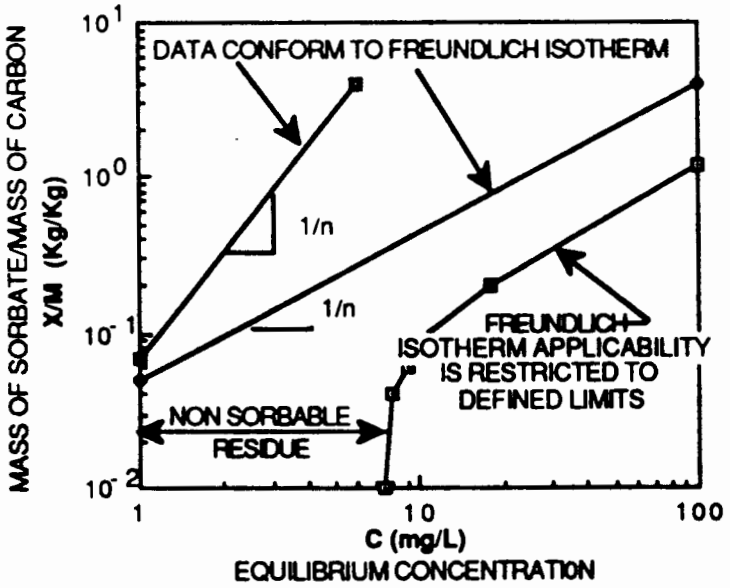
increased temperatures increase adsorption because of viscosity and diffusivity effects

FREUNDLICH ISOTHERM

$$\frac{X}{M} = KC^{1/n}$$

where:

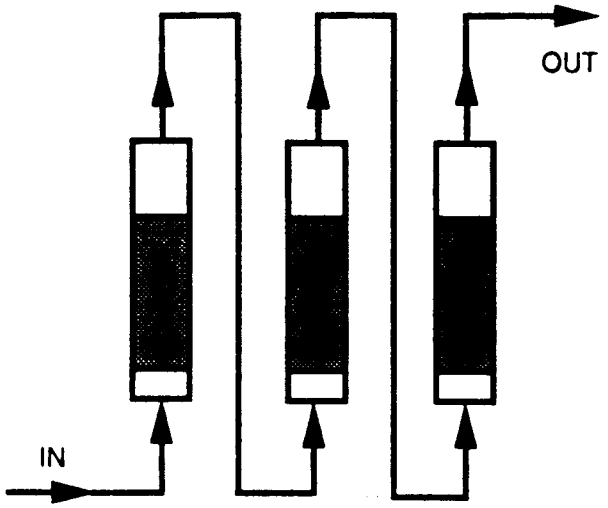
X	=	amount of impurity adsorbed (mg)
M	=	weight of carbon (g)
C	=	equilibrium concentration of impurity in solution (mg/L)
K,n	=	constants characterizing the carbon - adsorbate system



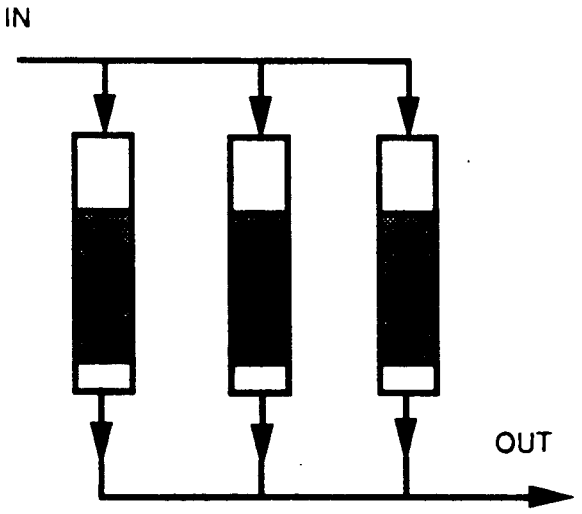
TYPICAL PROPERTIES OF ACTIVATED CARBON
(8 X 30 Mesh)

	LIGNITE	COAL*
Total Surface Area (m^2/g)	600-650	950-1050
Bulk Density (lb/ft^3) (backwashed and drained)	22	26
Particle density (g/cm^3) (wetted in water)	1.3-1.4	1.3-1.4
Pore volume (cm^3/g)	1.0	0.85
Effective size (mm)	0.75-0.90	0.80-0.90
Uniformity coefficient	1.9 or less	1.9 or less
Mean particle diameter (mm)	1.5	1.6
Pittsburgh abrasion number	50-60	40-60
Moisture as packed, max. (%)	9	2
Molasses RE (relative efficiency)	100-120	40-60
Ash (%)	12-18	5-8
Mean pore radius (Angstrom)	33	14

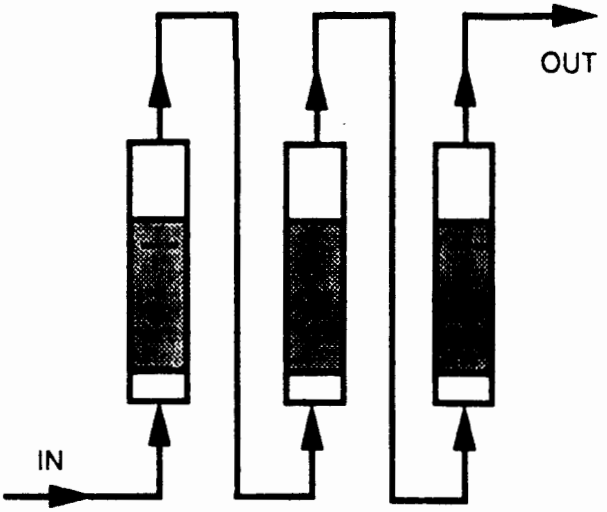
*Bituminous



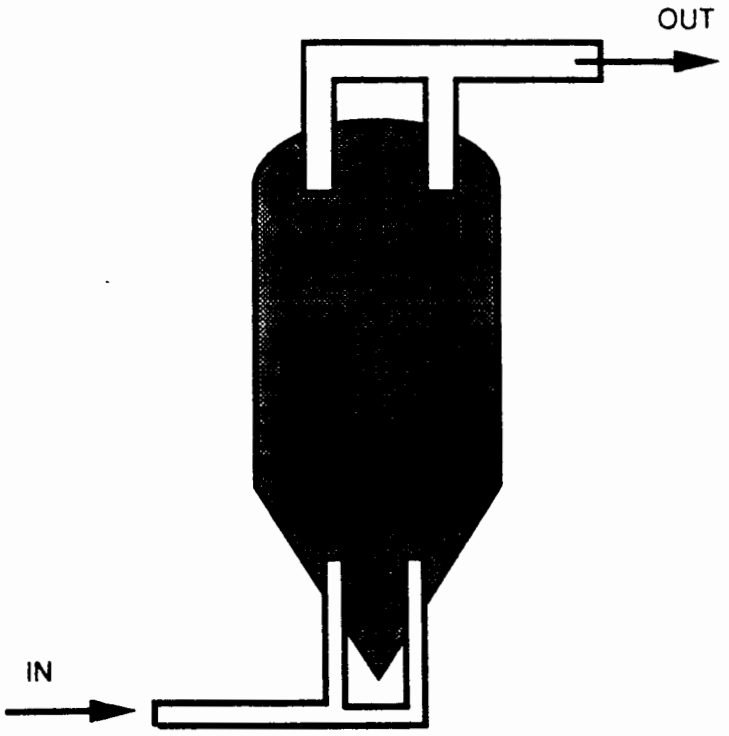
GRANULAR ACTIVATED CARBON
UPFLOW EXPANDED ADSORBERS IN SERIES



GRANULAR ACTIVATED CARBON
DOWNFLOW ADSORBERS IN PARALLEL



GRANULAR ACTIVATED CARBON
UPFLOW EXPANDED ADSORBERS IN SERIES



GRANULAR ACTIVATED CARBON
MOVING-BED ADSORBER

MEMBRANE PROCESSES

PROCESS	FUNCTION	SEPARATION DRIVING FORCE	TYPICAL APPLICATION
Ultrafiltration	Species separation based on physical properties	Hydraulic pressure	By-product recovery from waste streams
Electrodialysis	Ion transport	Electric potential gradient	Brackish water desalination
Reverse Osmosis	Water transport	Hydraulic pressure	Brackish or seawater desalination, ultra-pure water production

REVERSE OSMOSIS

Reverse Osmosis is a process which enables solutes (salts) to be separated from solvents (water) without a phase change.

SUCCESSFUL APPLICATION AREAS

- Brackish and saline water desalination
- Domestic wastewater treatment
- Drug and beverage concentrate
- Product Recovery

REVERSE OSMOSIS DESIGN CONSIDERATIONS

Pressure	pH
Temperature	Turbidity
Flux	Feed Water Velocity
Recovery Factor	Pretreatment
Salt Rejection	Post Treatment
Membrane Fouling	Cleaning
Membrane Life	Power Utilization

Osmotic Pressure

Osmotic Pressure -- Is a function of the dissolved salt concentration and not the membrane.

Modified Van't Hoff Equation:

$$\pi = \phi \frac{n}{v} RT$$

Where:

- π = osmotic pressure, atm.
- ϕ = osmotic pressure coefficient
- $\frac{n}{v}$ = ionic concentration, moles/liter
- T = absolute temperature
- R = universal gas constant, 0.083 $\frac{\text{atm-liters}}{\text{moles}}$

REVERSE OSMOSIS MEMBRANES

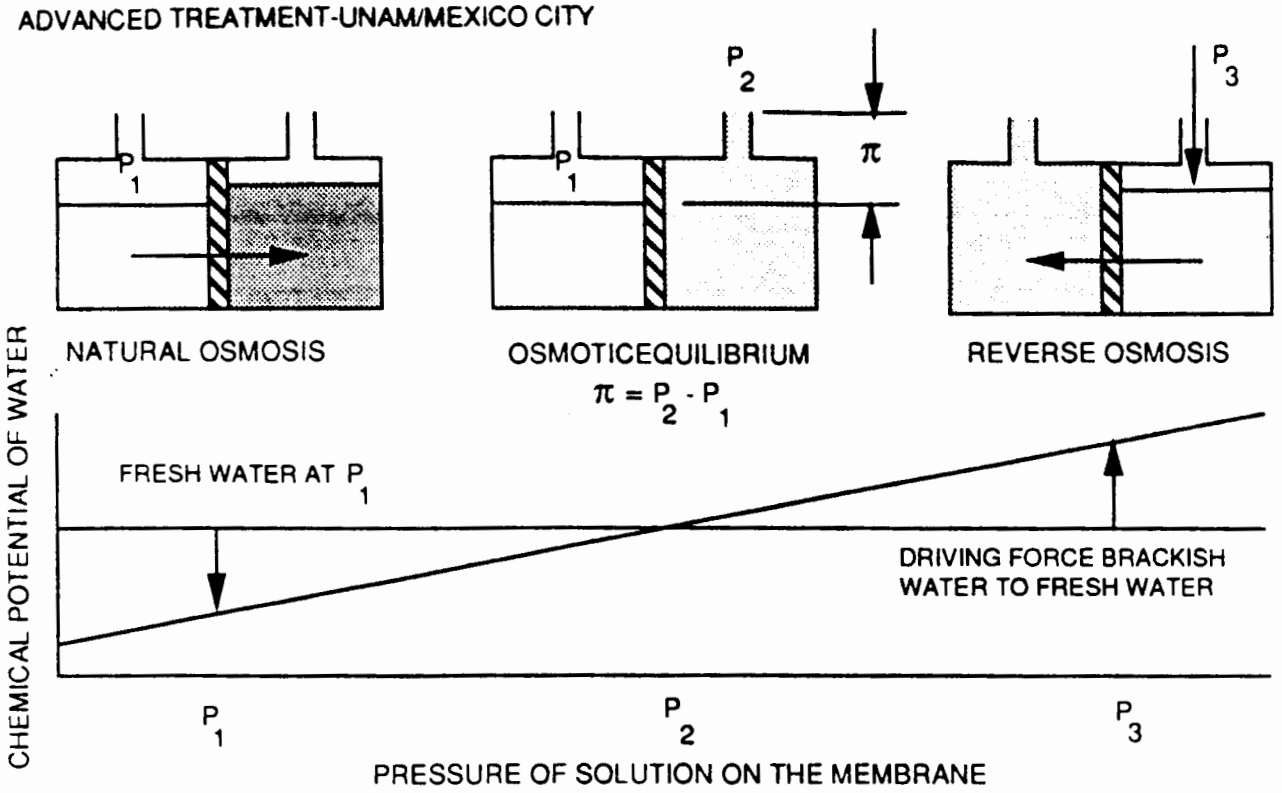
Cellulose Acetate

Aromatic Polyamide - DuPont Hollow Fine Fiber

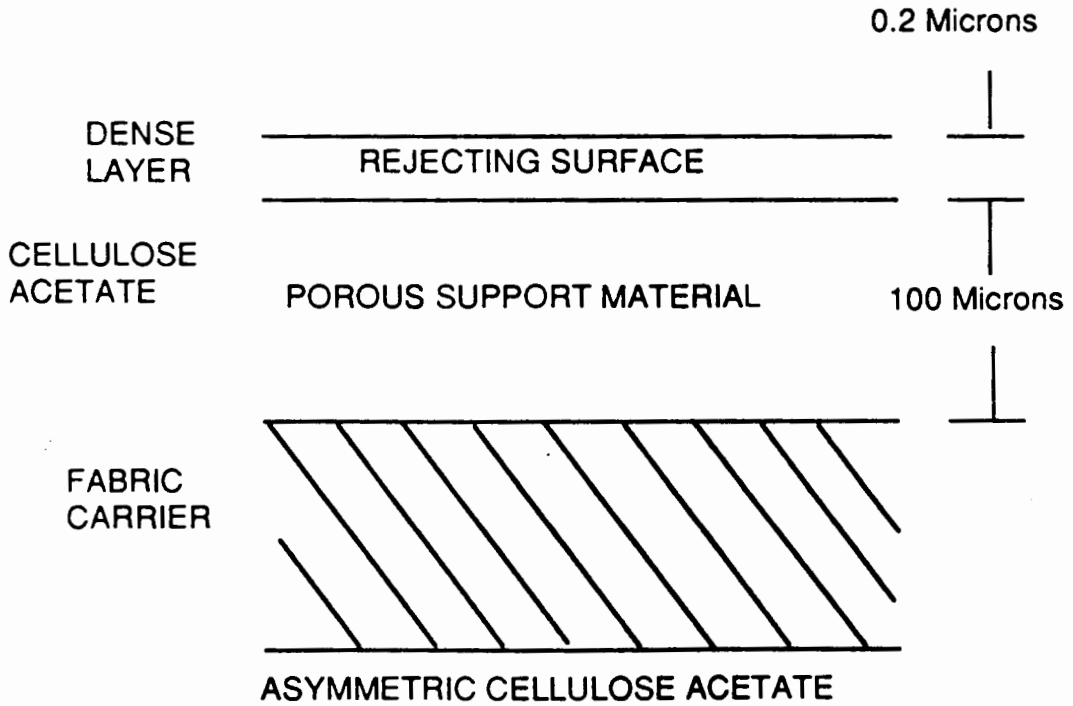
Polysulfone coated with polyethyleneimine crosslinked with tolylene -2,4 disocyanate

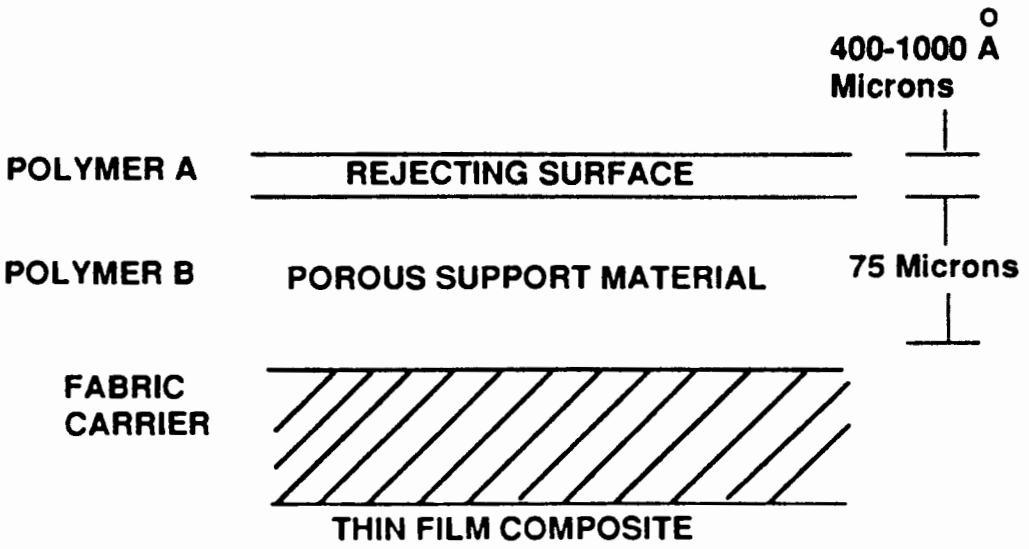
REVERSE OSMOSIS FEED WATER PARAMETERS

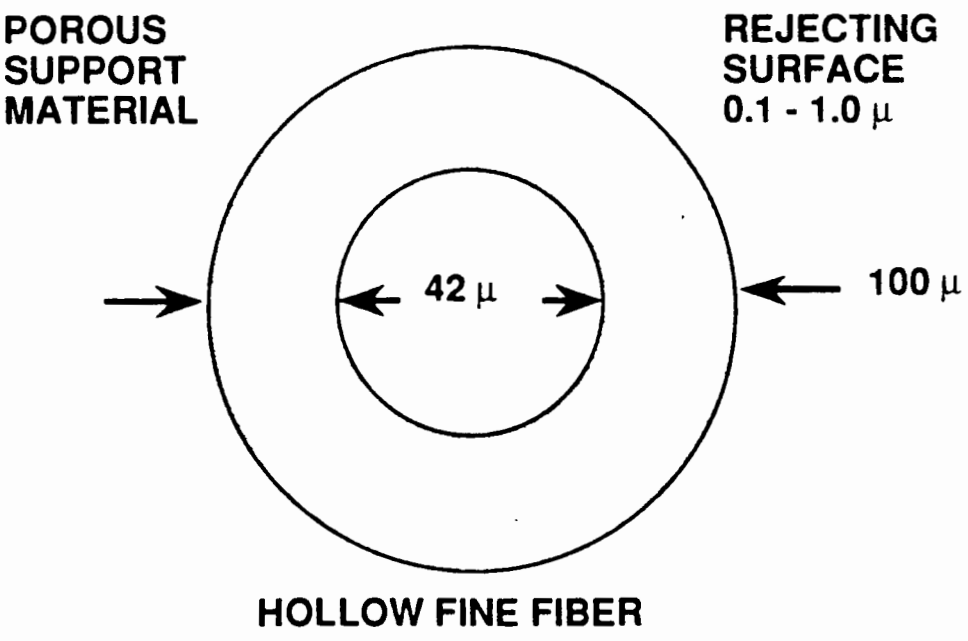
PARAMETER	UNIT	RANGE
Turbidity	JTU	1.5-3.0
Plugging Factor	%	45-90
Chlorine Residual	mg/L	0.1-2.0
Combined Fe & Mg	mg/L	0.1-0.7
pH	----	>6.5
Organics	----	Remove oils,grease and solvents detrimental to membrane
Living Matter	----	----



REVERSE OSMOSIS PROCESS ILLUSTRATION




400-1000 A
Microns
POLYMER A
REJECTING SURFACE
POLYMER B
POROUS SUPPORT MATERIAL
75 Microns
FABRIC
CARRIER
THIN FILM COMPOSITE


POROUS
SUPPORT
MATERIAL
REJECTING
SURFACE
0.1 - 1.0 μ
42 μ
100 μ
HOLLOW FINE FIBER

REVERSE OSMOSIS PRETREATMENT REQUIREMENTS

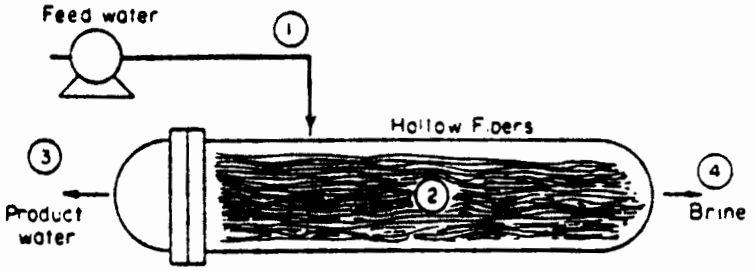
PROCESSES	PARAMETER CONTROLLED
Polishing Filtration	Turbidity
Acid Injection	Membrane hydrolysis calcium salt deposition
Sodium Hexametaphosphate	Calcium sulfate deposition
Prechlorination	Biomass growth
Activated Carbon Filtration	Oil, grease, solvent and dechlorination
Rapid Sand Filtration	Turbidity and organisms
Manganese Zeolite Filtration	Iron and manganese
Partial Lime Softening	Calcium and salt deposition
Ion Exchange	Inorganic ions
Ozone	Organics, iron and manganese

REVERSE OSMOSIS POST TREATMENT

PROCESSES	PARAMETER CONTROLLED
Degasification	Dissolved carbon dioxide
Base addition	Product pH
Disinfection	Pathogenic organisms

MEMBRANE FOULANTS

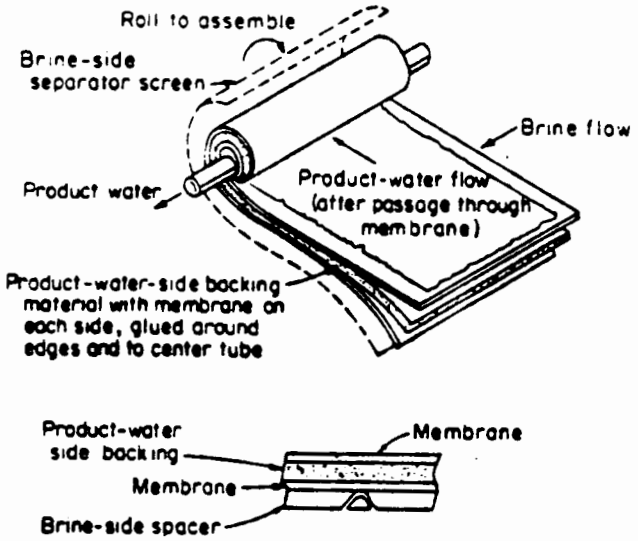
- Scale
  - Calcium carbonate
  - Calcium sulfate
  - Iron oxide hydrates
  - Silicates
- Suspended Solids
- Organics
- Living matter



1. Brackish feed water
2. Product water collected in hollow fibers
3. Product water removed
4. Brine removed

Typical - OD:ID - 44.6u:24.9u

RO HOLLOW FINE FIBER MODULE CONFIGURATION



RO SPIRAL WOUND MODULE CONFIGURATION

REVERSE OSMOSIS MODULE CONFIGURATIONS

	Spiral Wound	Hollow Fine Fiber
Membrane Surface Area, ft^2/ft^3	100 - 300	5,000 - 10,000
Product Water Flux, gfd	8 - 25	0.1 - 2
Typical Module Factors		
Brine Velocity, ft/sec	0.7	0.04
Brine Channel Dia., in.	0.05	0.004
Permissible Feed		
pH	5.5 7.5	2 - 10
Temperature, °F	100	100
Method of Membrane		
Replacement	on site	return to factory
Replacement Labor	Medium	Medium
High Pressure Limitation	Membrane Compaction	Fiber Collapse
Pressure Drop		
Product Water Side	Medium	High
Feed to Brine Exit	Medium	Low
Concentration Polarization Problem	Medium	Low
Membrane Cleaning -		
Mechanical	No	No
Chemical	Yes - pH and solvent limited	Yes less restricted

CLARIFIED PRIMARY EFFLUENT TREATMENT BY REVERSE OSMOSIS

	FEED CONCENTRATION (mg/L)	REDUCTION %*
Calcium	54-114	>99.6
Magnesium	13-26	>99.3
Sodium	92-188	92.5
Potassium	17-29	91.5
Ammonia-N	37-57	90.2
Chloride	209-378	90.4
Sulfate	256-388	>99.8
Phosphate	>1-3	>99.4
Total COD	24-109	65.7
COD		
After Aeration	---	85.7
Turbidity, JTU	7.6 (typical)	100
TDS	757-1170	93.3

* Based on feed to reverse osmosis unit only. Total process reduction Based on raw sewage is significantly higher for several species.

CAPITAL COST OF REVERSE OSMOSIS SYSTEMS
(BRACKISH WATER TREATMENT)

Capacity (1000 gpd)	Cost ($1,000)
10	15
50	50
100	90
500	375
1000	600
5000	2750

OPERATING COSTS OF REVERSE OSMOSIS SYSTEMS
(¢/1000 GALLONS)

Capacity (1000 gpd)	Power(2)	Chemicals	O&M	Membrane Replacement	Total
10	15	6-10	54	30	105-109
50	15	5-8	29	25	74-77
100	15	4-7	20	20	59-62
500	15	4-7	11	17	47-50
1000	15	3-6	8	15	41-44
5000	15	3-6	6	12	36-39

(1) Operating at 400 psi at 75% recovery
(2) At 2.5 cents/kw-hr

WATER QUALITY AT VARIOUS STAGES OF TREATMENT
LAKE TAHOE, CA

Quality Parameter	Biological	Chemical Clarifier	Filter	Carbon
BOD (mg/L)	30		3	1
COD (mg/L)	70		25	10
SS (mg/L)	26	10	0	0
Turbidity (JTU)	15	10	0.3	0.3
Phosphorus (mg/L)	6	0.7	0.1	0.1

WATER QUALITY AT VARIOUS STAGES OF TREATMENT COLORADO SPRINGS

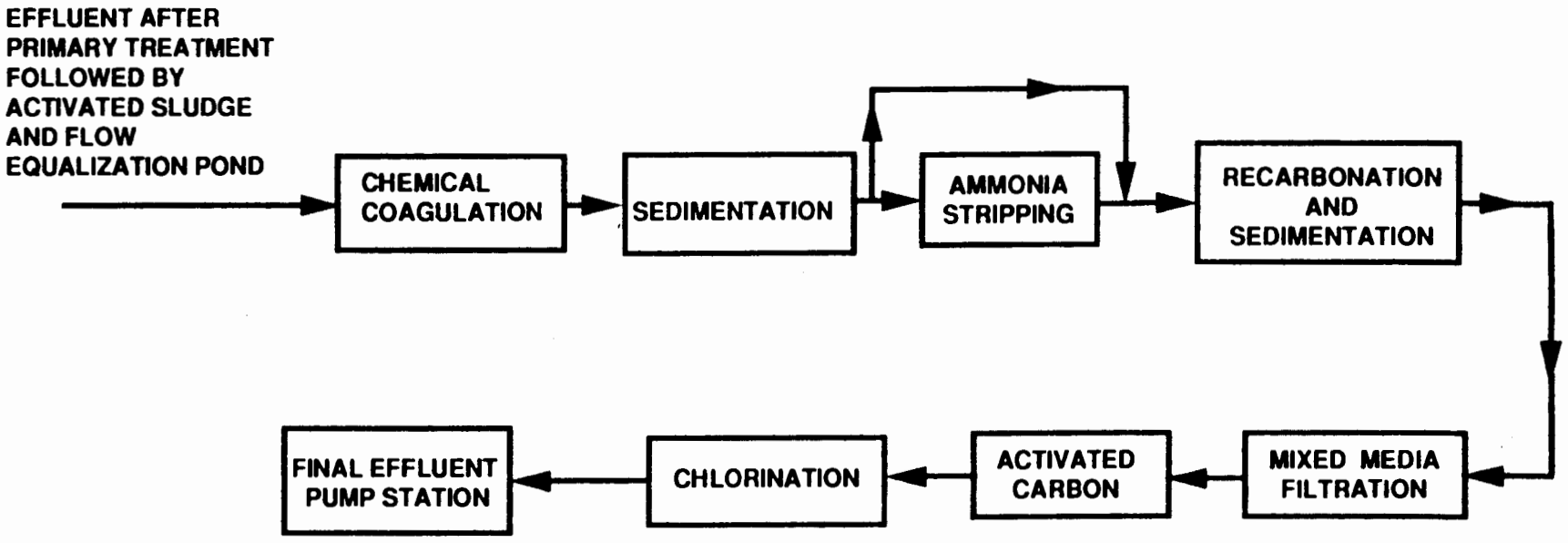
Quality Parameter	Trickling Filter*	Final Effluent
BOD (mg/L)	102	8.0
COD (mg/L)	258	15.7
SS (mg/L)	62	2.2
Turbidity (JTU)	54	2.2
Phosphorus (mg/L)	15	0.5

*Trickling filter plant capacity is 13 MGD (0.57 m^3/s) and was operated at a flow rate of 23 to 25 MGD (1.0 to 1.1 m^3/s).

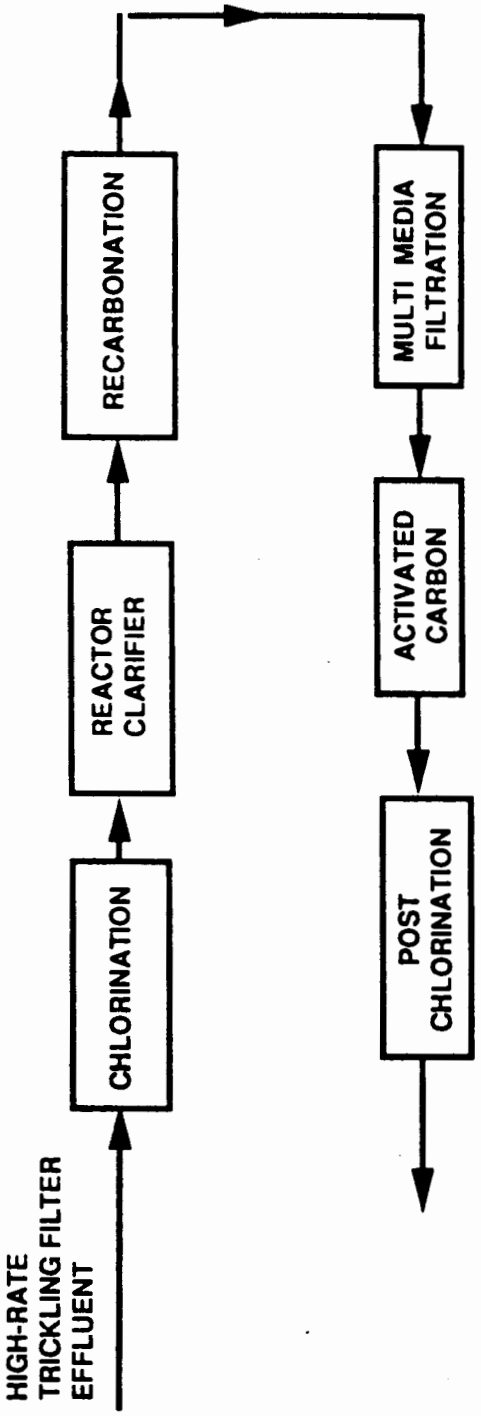
REVERSE OSMOSIS AVERAGE PROCESS REMOVAL

Constituent	Average Concentration		Average Removal (%)[a]
	Influent	Effluent	
Electrical conductivity (µmho/cm)	1460.0	70.0	95
Sodium (mg/L)	196.0	11.0	94
Chloride (mg/L)	280.0	16.0	94
Sulfate (mg/L)	220.0	0.8	99
COD (mg/L)	25.0	1.5	94
Ammonia-N (mg/L)	5.6	0.5	91
Calcium (mg/L)	118.0	2.0	98

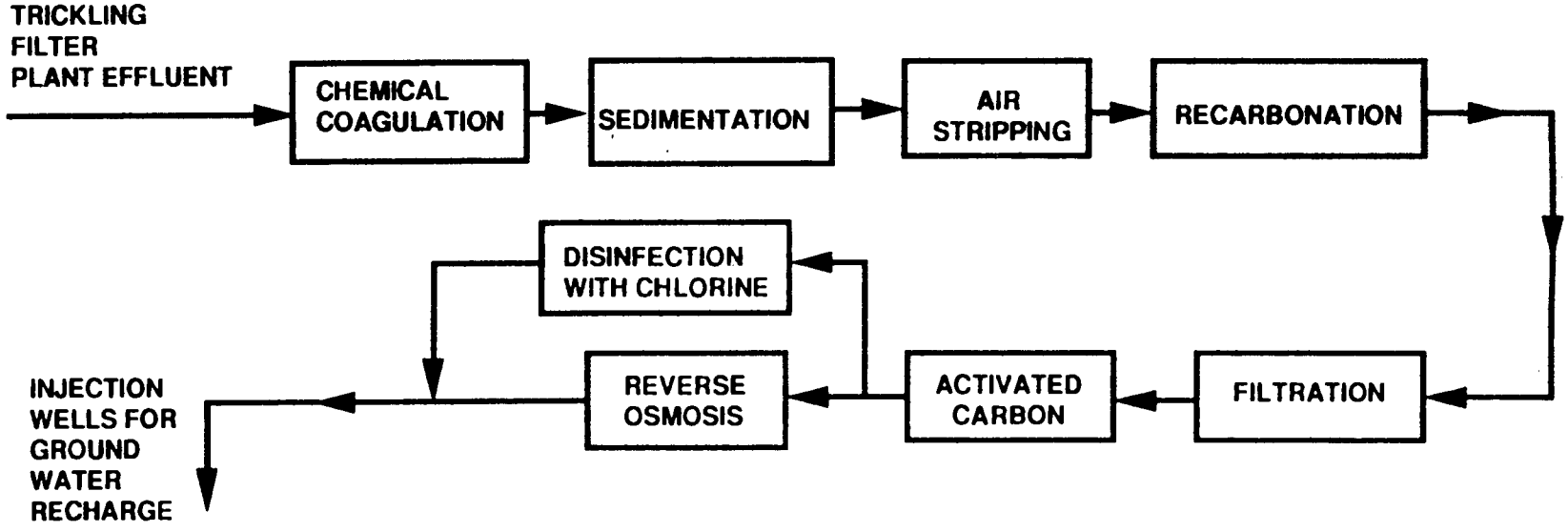
[a]Data from the Orange County (Calif.) Water Factory 21.



LAKE TAHOE ADVANCED WASTEWATER TREATMENT FACILITY



WATER RENOVATION PLANT - COLORADO SPRINGS, CO

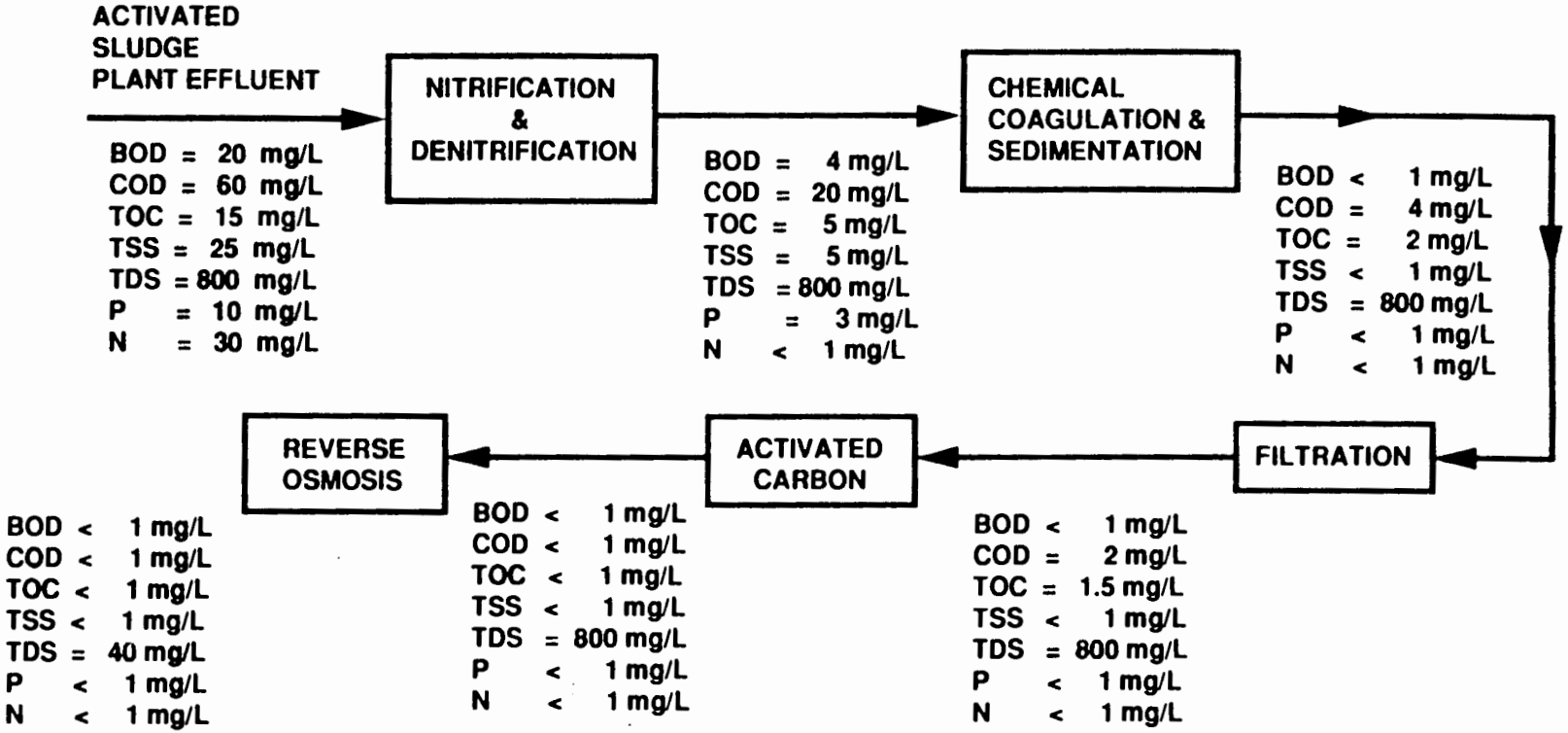


WATER FACTORY 21 - ORANGE COUNTY, CA

WASTEWATER TREATMENT PROCESS EFFICIENCIES (per cent removal)

PROCESS	BOD	COD	TOC	TSS	NH_3 N	NO_3 N	P	TURB[1]
Activated Sludge[2]	89	72	83	81	63	----	45	86
Nitrification[3]	75	56	73	61	97	----	50	89
Denitrification[3]	47	35	22	42	32	89	52	0
Coagulation-Sedimentation[3] (ferric & lime)	81	81	73	91	----	----	96	69
Filtration								
Biological[3]	39	34	33	73	33	56	57	71
Bio/Chemical[4]	36	22	25	42	----	-----	----	31
Activated Carbon[4]	53	47	64	64	39	5	88	73
Reverse Osmosis								
Act Sludge	----	>96	----	>95[5]	>95	----	>99	----
Bio/Act Carbon[6]	----	>92	----	>95[5]	>96	----	>99	----
Bio/Chemical[4]	----	>66	----	>93[5]	>90	----	>99	----

1 Turbidity
2 Removal from primary effluents
3 Removal from secondary effluents
4 Removal from chemically clarified secondary effluents
5 Total Dissolved Solids (TDS)
6 Removal from activated carbon treated secondary effluents



HYPOTHETICAL ADVANCED WASTEWATER TREATMENT SYSTEM MUNICIPAL WASTEWATER

6.4 IN SITU BIODEGRADATION

Process Description

In situ biodegradation is a process that uses existing indigenous aerobic bacteria, or introduced cultured strains of bacteria, to biodegrade organic compounds in soil or groundwater. Since the biodegradation process occurs below water or ground surface, precise process control is not feasible. However, the biological process may be accelerated by introducing supplemental materials, including:

- Nutrients (phosphorous, nitrogen),
- Oxygen, and
- Cultured bacterial strains.

In situ biodgradation is often used in conjunction with a groundwater pumping and reinjection system to circulate nutrients and oxygen through a contaminated aquifer and associated soils. It can provide substantial reduction in contaminant levels in soils and groundwater at a fraction of the cost of soil excavation and/or above-ground pump and treat systems. Such a system is depicted on Figure 6.4.

Waste Types Handled

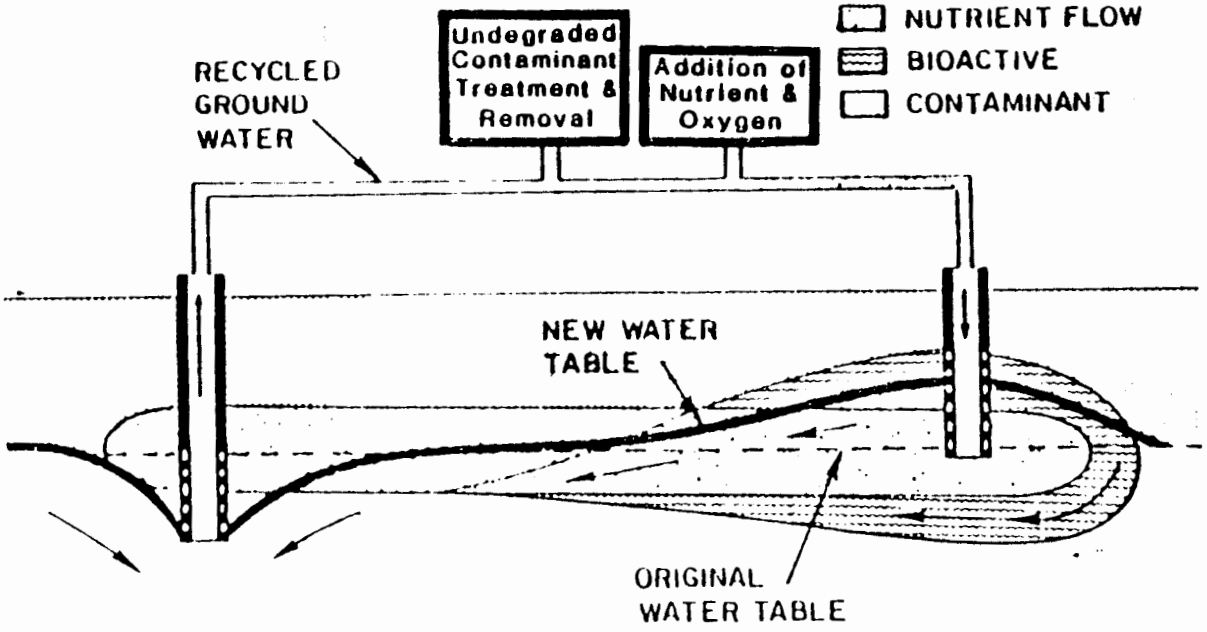
To date, in situ biodegradation has been applied to sites contaminated with readily biodegradable nonhalogenated organics, primarily gasoline. Applications can include the following waste types:

- Gasoline and fuel oils,
- Hydrocarbon solvents (e.g., benzene, toluene, xylene),
- Nonhalogenated aromatics (e.g., ethylbenzene, stryene, phenol, cresol), and
- Alcohols, ketones, ethers and glycol.

The most common applications have been at gasoline spill sites where conventional excavation and/or treatment methods are very costly.

Before in situ biodegradation can be used, wastes must be evaluated for:

- Biodegradability,
- Oxygen requirement,
- Nutrient requirement for biodegradation,
- Solubility,



Source: FMC Aquifer Remediation Systems

FIGURE 6.4

SCHEMATIC DIAGRAM OF IN SITU BIODEGRADATION

- o Inhibitory effects at various concentrations, and
- o Total quantity contained on site.

Waste Restrictive Characteristics

In situ biodegradation is generally inhibited by:

- o Halogenated organics,
- o Elevated levels of metals, and
- o Elevated levels of inorganics such as chlorides, acids, or caustics.

Site Requirements

A number of site-specific factors are critical in evaluating the potential for use of in situ biodegradation on that site. These include:

- o Site geology,
- o Soil characteristics, including
  - permeability
  - pH
  - moisture content
  - organic content
- o Aquifer characteristics and hydrogeology,
- o Water quality parameters, including
  - dissolved oxygen
  - pH
  - alkalinity
  - available nutrients
- o Subsurface temperatures.

In general, suitable sites would meet the following criteria:

- o Site geology and hydrology allowing for ready pumping and extraction of contaminated water, followed by reinjection and recirculation,
- o Soils with neutral pH, high permeability and moisture content of 50 to 75 percent, and
- o Water quality parameters in ranges such that inhibition of biological activity does not occur.

Required Onsite Facilities/Capabilities

Following positive evaluation of site environmental factors and waste characteristics, systems for introduction of nutrients and oxygen into

groundwater and soil must be developed. These may include pumping and recirculation or infiltration galleries.

Soil and water quality characteristics must be monitored at regular intervals, and nutrient/oxygen supplies adjusted. Biodegradation may continue for several months, and final results may not be apparent for one to two years. Contaminant levels in soil and water may or may not drop below designated action levels.

Environmental Impacts

The long-term effects of nutrient introduction on groundwater must be evaluated. Another environmental concern is that the final contaminant reduction is generally not predictable. In spite of these concerns, in situ biodegradation is a simple process, requiring minimal site preparation and producing less site disruption.

Costs

In situ biodegradation may produce acceptable results at costs far below conventional treatment systems.

While costs are difficult to generalize, examples cited by vendors suggested costs could be as low as 10 percent of excavation and/or pump and treat costs. The potential for use in remediation of subsurface gasoline tank leaks merits serious consideration.

Commercial Applications

Several firms listed in the Table 6-1 and below offer complete in situ biodegradation systems and services.

Bio Systems, Inc.
FMC-Aquifer Remediation Systems
Geraghty and Miller
O.H. Materials
Polybac Corp.

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ES&T SERIES

In situ biorestoration of organic contaminants in the subsurface

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Rice University
Houston, TX 77251

In situ biorestoration of subsurface materials contaminated with organic compounds is being evaluated by EPA and by industry as one technique for managing hazardous wastes. The process usually involves stimulating the indigenous subsurface microflora to degrade the contaminants in place, although microorganisms with specialized metabolic capabilities have been added in some cases. The ultimate goal of biodegradation is to convert organic wastes into biomass and harmless byproducts of microbial metabolism such as CO_2, CH_4, and inorganic salts.

In contrast to many remedial techniques that simply transfer the waste from one part of the environment to another *(1)*, in situ biorestoration may offer a better solution through partial or complete destruction of the contaminants. Although there are several technologies—such as land treatment; composting; and treatment in bioreactors, pits, lagoons, and soil biofilters—that use biodegradation as a tool in hazardous waste management *(2)*, this paper will focus largely on existing and potential applications of in situ biorestoration of contaminated subsurface materials.

The potential use of subsurface microorganisms to degrade a variety of groundwater contaminants evolved in the 1980s *(3)*, although the technique was patented and used for hydrocarbons by R.L. Raymond as early as the 1970s *(4–7)*. The process is similar to some conventional wastewater treatments in that nutrients and a terminal electron acceptor for microbial metabolism, usually oxygen, are added to the organic waste to facilitate biodegradation in a bioreactor. However, the bioreactor in this case is the subsurface, which is not as defined and controllable as the bioreactors used in wastewater treatment. Rather than treating the concentrated source of a spill, in situ biorestoration treats contamination sorbed to the formation matrix and dissolved in the groundwater. The majority of subsurface spills that have been remediated using this technique have been hydrocarbons *(3)*.

Requisites for application

Two essential criteria must be met before the in situ biorestoration process can be implemented. First, the subsurface matrix must be permeable enough to allow perfusion with a solution of oxygen and nutrients. Second, contaminant-degrading microorganisms must be present. The first criterion is deter-

Series update: Looking behind, looking ahead

We are now midway through this series of five articles on remedial action technologies. The first part was in the May issue on page 504. Wayne Chudyk of Tufts University discussed field instruments for assessing hazardous waste sites. These instruments are useful on-site and involve in situ measurements. Gone are the days of getting samples, sending them to an analytical laboratory, and waiting for analyses. Established on-site techniques include field gas chromatography for volatile organic compounds and specific conductance electrode screening for monitoring for ionic contaminants. Emerging techniques that are being used in the field include remote laser-induced fluorescence for analysis of aromatic organics and X-ray fluorescence (XFR) for analysis of organics.

The second part was in the June



issue on page 630. Douglas Mackay of UCLA and John Cherry of the University of Waterloo discussed the limitations of pump-and-treat technology, an above-ground technique for cleaning up groundwater contaminated by industrial solvents and aromatic hydrocarbons from petroleum products. Cleanup of groundwater proceeds slowly using this technology. These authors said that pump-and-treat technology is best thought of as a management tool to prevent, by hydraulic manipulation of the aquifer, continuation of contaminant migration.

This third part of the series involves the in situ biorestoration of organic contaminants in the subsurface.

The fourth part, written by Peter Daley of Chemical Waste Management, will discuss technologies for remediation of aqueous streams, sludges, and solids—including membrane processes, thermal separations, catalytic methods, and pyrolyzers.

The last part, written by James Patterson of the Illinois Institute of Technology, will discuss waste minimization. Less technical than the other four articles, it will discuss the genesis of the waste reduction concept in the Resource Conservation and Recovery Act and the challenge of this concept for industry.

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mined by measuring the hydraulic conductivity (K) of the formation. Formations with hydraulic conductivities of 10^{-4} cm/sec or greater are most amenable to in situ biorestoration. Because the subsurface can be heterogeneous, it is important to know the hydraulic conductivity at several locations in the treatment site. Analysis of most subsurface materials has indicated that microorganisms are present and that they can biodegrade a variety of contaminants *(3, 8)*; however, biodegradation in the subsurface will most likely be site-specific and even microsite-specific.

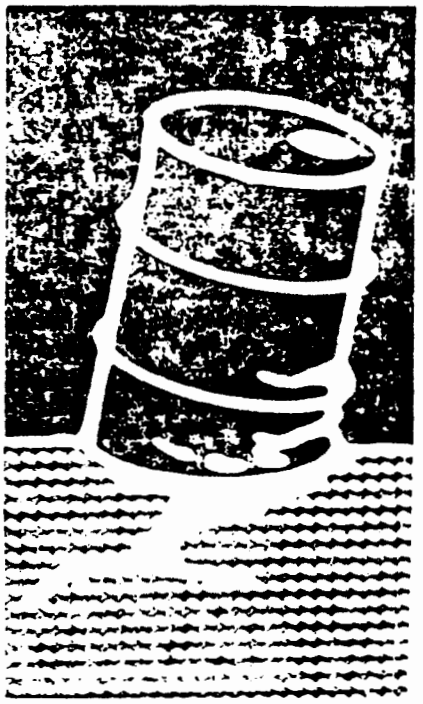
Feasibility studies for the biodegradation of the contaminants are usually conducted in the laboratory using subsurface material collected from the site. Biodegradation should be studied in subsurface samples from several locations because of the potential for variability in contaminant biodegradation in the subsurface *(9)*. The use of groundwater to determine biodegradation potential in the subsurface may produce erroneous results because nonnative microorganisms are often associated with wells *(10)*.

Application: Subsurface contamination

Provided that the subsurface is permeable enough and contaminant degrading microorganisms are present and active, several steps should be taken to characterize and prepare a site for in situ biorestoration. The steps include: a thorough site investigation with regard to hydrogeology and contaminant regime, free product recovery (physically recoverable unaltered phase of contaminant such as liquid fuel), laboratory tests to determine the nutrient requirements of the microflora, laboratory tests to determine the compatibility of the nutrient formulation determined in the third step with the subsurface formation, system design, and system operation and monitoring.

In the site investigation, hydrogeological parameters other than hydraulic conductivity that should be determined include depth to the water table and zone of contamination, the specific yield of the aquifer, the rate and direction of groundwater flow, and the types and extent of contamination. Where it is applicable, free product must be removed before implementation of a bioremedial system. The addition of oxygen and nutrients to a site containing a physically removable phase of contamination would waste time and capital *(11)*. There are several well systems and vacuuming techniques available for removal of the free phase which have been discussed by Thomas et al. *(1)*.

Because of the highly carbonaceous



nature of organic waste, the addition of an electron acceptor (usually oxygen) and essential nutrients such as nitrogen, phosphorus, and trace elements to the groundwater may be required to enhance biodegradation. Oxygen has been the terminal electron acceptor used in most in situ subsurface biorestoration efforts. The rate of bioremediation in the subsurface is usually limited by the amount of oxygen that can be transported to the organisms in the zone of contamination *(12, 13)*. In addition to serving as a terminal electron acceptor in microbial metabolism, molecular oxygen is required in the major degradative pathway for saturated aliphatic and aromatic hydrocarbons *(14)*.

Several methods can be used to supply oxygen to the subsurface, including the addition of air, pure oxygen, or hydrogen peroxide. Sparging the ground water with air and pure oxygen can supply only 8 and 40 mg dissolved oxygen/L, respectively, depending on the temperature of the injection fluid *(3)*. Hydrogen peroxide, which dissociates to form water and 1/2 molecule of oxygen, is infinitely soluble in water; however, the oxidant can be toxic to microorganisms at concentrations as low as 100 ppm *(15)*.

The hydrogen peroxide and the inorganic nutrient formulations that are determined to best enhance contaminant biodegradation must be tested for compatibility with the subsurface material at the site. Precipitation of the inorganic nutrients and complexation these nutrients with subsurface constituents may plug the aquifer or render essential nutrients unavailable for microbial consumption. The rate of hydrogen peroxide decomposition will be affected by the organic matter and mineral content of the subsurface; decomposition of hydrogen peroxide may be controlled artificially using several methods *(7)*.

After the removal of any free product and completion of laboratory feasibility studies, the bioremediation system is implemented. The nutrient solution is added through injection wells or infiltration galleries and is recovered using production wells. The solution is percolated through the unsaturated zone into the saturated zone by infiltration galleries, whereas it may be directly injected into the saturated zone by injection wells. Wells are installed between the injection and production points to monitor the concentrations of contaminants, nutrients, microbial cells, and other indicators of bioremediation. The solution produced can be recirculated in a closed-loop system or treated and disposed at the surface. Schematic diagrams of both types of injection and production systems are shown in Figure 1.

The inorganic nutrients are usually added first, followed by the oxygen source. Simultaneous addition of oxygen and inorganic nutrients could result in excessive microbial growth around the injection point and consequently plug the formation. The inorganic nutrients may be added by batch or continuous feed; however, oxygen is usually added continuously because oxygen transport is rate-limiting in subsurface contaminant biodegradation *(12, 13)*. When hydrogen peroxide is used, toxicity problems can be minimized by starting with concentrations around 50 mg/L, which are then increased step-wise to levels as high as 1000 mg/L.

Monitoring of the operation is critical for determining the progress of in bioremediation. A decrease in cell number may indicate peroxide toxicity; however, an unexplained decline in microbial numbers is often observed in



...biodegration in the subsurface will most likely be site-specific and even microsite-specific.



well water at the beginning of the injection process before peroxide is added (16). In general, breakthrough of oxygen or peroxide in samples of water from monitoring wells indicates contaminant removal in that area.

Pilot-scale field demonstration

A pilot-scale field demonstration of the Raymond technique for hydrocarbon bioremediation was initiated in February 1988 at the site of an aviation fuel spill in Traverse City, Michigan (16). The overall objective of the test, a quantitative demonstration of the method, will provide a basis for process design. The model BIOPLUME II (17), developed at Rice University to predict contaminant transport affected by oxygen-limited biodegradation, was used to design the well system and estimate the time required for bioremediation. The aquifer was pretreated initially with pure oxygen to acclimate the subsurface microflora to higher than normal oxygen concentrations and then was perfused with hydrogen peroxide (16). To avoid peroxide toxicity, the initial dose of peroxide was 50 mg/L; this dose was increased step-wise to 750 mg/L. Although the project has not been completed as of June 1989, partial bioremediation has occurred throughout much of the test area.

Variations to standard practices

Although the majority of applications of in situ biorestoration has involved remediation of hydrocarbon spills using oxygen as the electron acceptor, several innovative variations to the method have been investigated in the laboratory and the field. These variations include the use of alternate electron acceptors, the enhancement of aerobic biodegradation of chlorinated aliphatic solvents, and the addition of microorganisms with specialized metabolic capabilities.

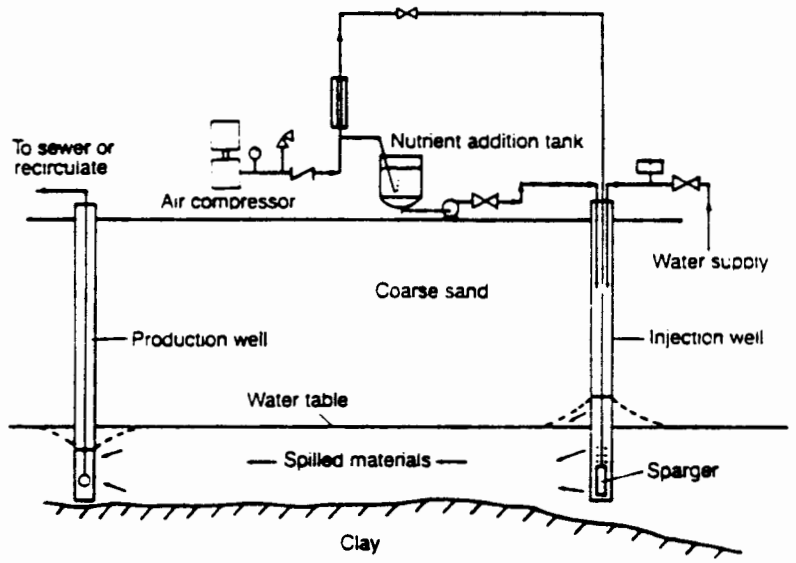
Alternate electron acceptors. Although oxygen is required in the major biodegradative pathways for many organic contaminants, especially hydrocarbons, several investigators have shown that the alkylbenzenes can be degraded under anaerobic conditions (18–26). The use of nitrate as a terminal electron acceptor, or denitrification, involves the reduction of nitrate in the following sequence: NO_3^- (nitrate), NO_2^- (nitrite), N_2O (nitrous oxide), N_2 (nitrogen gas). Although denitrification is thought to occur under strict anaerobic conditions, the use of combinations of nitrate and oxygen, termed aerobic denitrification, may be possible (26, 27). During aerobic denitrification, nitrate could serve as the terminal electron acceptor so that oxygen would be available for catabolism of the organic contaminant.

The use of nitrate in subsurface bioremediation is an attractive alternative or supplement to oxygen because nitrate is more soluble in water and could allow for more efficient and cost-effective remediation; however, high concentrations of nitrate in drinking water can pose serious health threats. Nitrate as an electron acceptor in the biodegradation of gasoline components and phenolics has been demonstrated in the field (28–32). In addition to nitrate, nitrous oxide may serve as an electron acceptor in the biodegradation of m-xylene (25). Compared to nitrate, the implications for nitrous oxide use in bioremediation schemes are noteworthy because nitrous oxide is not a groundwater pollutant and does not form toxic intermediates such as nitrite upon reduction.

Cometabolism by methanotrophs. The ubiquity of the chlorinated aliphatic solvents, such as 1,1,1-trichloroethane and 1,1,1-trichloroethylene, in aerobic aquifers suggests that they are biologically recalcitrant in the presence of oxygen; however, enrichment of environmental samples with natural gas or methane and air selects for microbial populations that can effect the cometabolism of these compounds. (Cometabolism is the biodegradation of an organic substance by a microbe that cannot use the compound for growth and hence must rely on other compounds for carbon and energy.) Exposure of the samples to methane and air selects for methanotrophs, or methane-utilizing microorganisms, which possess a monooxygenase enzyme that oxidizes methane as well as several alkanes, alkenes, and halogenated methanes (33, 34). Methane provides both carbon and energy for microbial growth, while the chlorinated solvent is

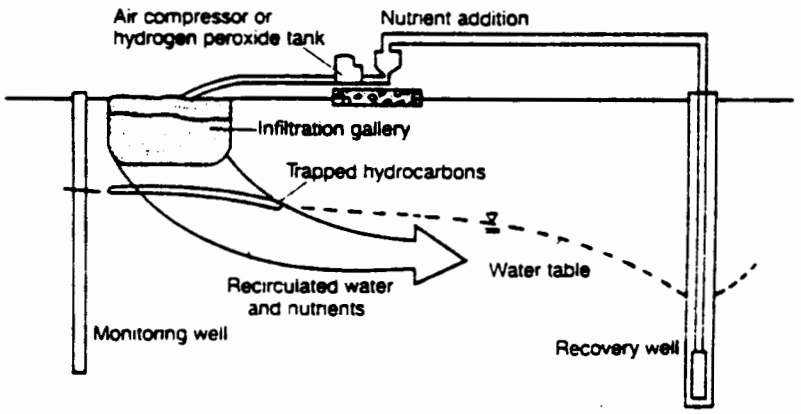
FIGURE 1
Biorestoration systems

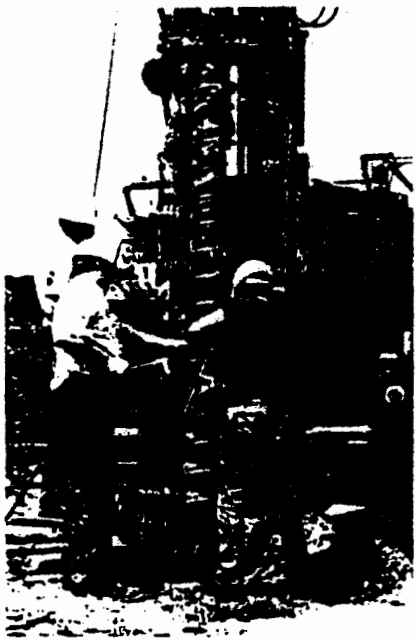
(a) Schematic of typical aerobic subsurface biorestoration



Source: Reference 5.

(b) Infiltration gallery for recirculation of water and nutrients





Drilling stage of biorestoration process

coincidentally metabolized.

Chlorinated aliphatic solvents that have been cometabolized under these conditions include tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1-dichloroethane, 1,2-dichloroethane, *cis*- and *trans*-1,2-dichloroethylene, 1,1-dichloroethylene, vinyl chloride, dichloromethane, carbon tetrachloride, and chloroform *(35–40)*. However, the heavily chlorinated compounds such as tetrachloroethylene, 1,1,1-trichloroethane, carbon tetrachloride, and chloroform are degraded more slowly than their less chlorinated analogues or not at all in some samples *(36, 39, 40)*.

Trichloroethylene biodegradation by induction of an aromatic pathway. Trichloroethylene has been reported to be aerobically biodegraded by induction of an aromatic pathway in several species of bacteria. Researchers at Technology Applications and EPA in Gulf Breeze, Florida, tested the biodegradation potential of trichloroethylene in soil and water samples with histories of prior exposure to organochlorine compounds *(41)*. Of the samples tested, one biodegraded trichloroethylene; however, it was discovered that a component in the water from the sampling site was required for trichloroethylene biodegradation to occur. An isolate that degraded trichloroethylene was obtained from this sample, designated strain G4, and tentatively ascribed to the genus *Acinetobacter*. The organism was able to convert trichloroethylene to CO_2 and nonvolatile products in the presence of water from the site and oxygen.

Further work by these researchers indicated that the component in the water that was required for trichloroethylene biodegradation was phenol; the phenol could be substituted with toluene, o-cresol, and m-cresol *(42)*. Their results indicated that trichloroethylene degradation by strain G4 occurred via an enzyme, most likely a dioxygenase, in an inducible aromatic pathway that uses *meta* fission.

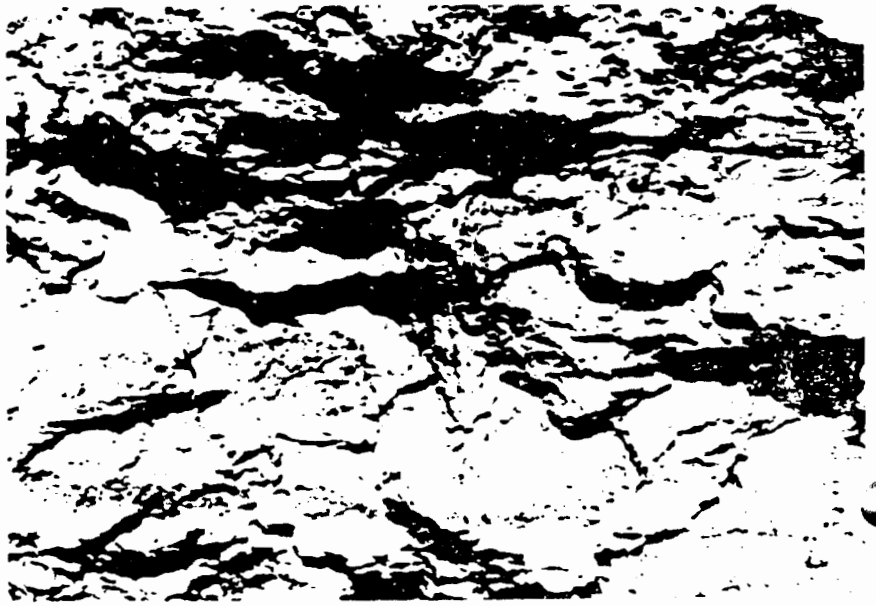
Toluene dioxygenase was demonstrated to be required in trichloroethylene degradation by another organism, *Pseudomonas putida* PpF1, which was shown to degrade toluene by the *meta* fission pathway *(43)*. Additional experiments indicated that trichloroethylene was biodegraded in samples of estuarine and river waters and groundwaters to which phenol or toluene had been added–but not in those without an inducer. The authors concluded that trichloroethylene persists in the environment because the enzyme inducers, and not the organisms, are absent.

Field demonstrations of biodegradation. Methane-enhanced cometabolism of a spill of chlorinated aliphatic solvents has been applied at the Moffett Naval Air Station, Mountain View, California *(44, 45)*. In the first field experiment, about 20 mg/L methane and 32 mg/L oxygen were alternately injected to stimulate the methanotrophs and evenly distribute their growth throughout the test plot. Additional nutrients were not added. After biostimulation, trichloroethylene was continuously injected at a concentration of 100 μg/L, decreased later to 60 μg/L, while methane and oxygen were alternately injected into the test plot for three months.

It was estimated that 20–30% of the trichloroethylene was biodegraded. It was speculated that the low removal efficiency for trichloroethylene in this demonstration could have resulted from the high degree of chlorination of the trichloroethylene molecule, the limited amounts of methane and oxygen that can be dissolved in water and transported to the methanotrophs, and competition by both methane and trichloroethylene for the methane monooxygenase enzyme.

Bioremediation of trichloroethylene, and *cis*- and *trans*-dichloroethylene was investigated in the same test plot in a second field trial eight months after methane addition had been terminated *(45)*. In contrast to the first experiment, the aquifer was not pretreated with methane and oxygen to stimulate growth of the methanotrophs. The biotransformation of *trans*-dichloroethylene, *cis*-dichloroethylene, and trichloroethylene added at 50, 110, and 130 μg/L was 65, 45, and 25%, respectively, which suggests that the less-chlorinated compounds are more readily degraded than are the highly chlorinated compounds. The same amount of trichloroethylene was biotransformed in both experiments, suggesting that either the degradative ability of the organisms was not significantly enhanced or enhancement was not maintained by repeated biostimulation.

In addition to the field demonstration of methane-enhanced biodegradation of the chlorinated aliphatic solvents Lawes and Litchfield *(46)* have obtained a patent for the aerobic biodegradation of chlorinated aliphatic solvents in soils and water by adding only oxygen and nutrients. In their process, it is claimed that compounds such as 1,1,1- and 1,1,2-trichloroethane, 1,1- and 1,2-dichloroethane, trichloroethylene, carbon tetrachloride, tetrachloroethylene, chloroform, 1,1-dichloroethylene, *cis*- and *trans*-1,2-dichloroethylene, and vinyl chloride can be



Section of subsurface with discontinuities



Collecting subsurface sample for bioremediation studies

biodegraded in situ by indigenous microorganisms by adding inorganic nutrients and oxygen in the form of hydrogen peroxide. The evidence for this process relies on laboratory experiments conducted with groundwater from a site contaminated with trichloroethylene, tetrachloroethylene, and *trans*-1,2-dichloroethylene; microbial growth in the presence of trichloroethylene and several combinations of nitrogen sources, hydrogen peroxide, and acetate was assessed under aerobic and anaerobic conditions.

Addition of microorganisms. The addition, or inoculation, of microorganisms with specialized metabolic capabilities to degrade organic wastes is not a new concept. Seed microorganisms have been used for decades to start up new wastewater treatment operations. More recently, pure and mixed cultures of microorganisms have been added to on-site surface operations to degrade hazardous waste. Mixed cultures are added when several organisms are required to provide the entire array of enzymes needed to degrade a recalcitrant compound or mixture of diverse waste.

Microorganisms with specialized degradative capabilities may be obtained by selective enrichment techniques and genetic manipulation. Although microorganisms that have been manipulated by selective enrichment techniques are often added to soils and water in hazardous waste remediation, the use of genetically engineered organisms in the environment is illegal without prior government approval.

The success of inoculation depends on several criteria: the organisms must retain their specialized metabolic capability, the organisms must come into contact with the contaminant, and nutrient and environmental conditions must be conducive to contaminant biodegradation. Usually, such criteria can be controlled in bioreactors, such as wastewater treatment plants, but cannot be easily controlled in in situ confined areas such as treatment ponds and lagoons. Goldstein et al. *(47)* suggested that the success of inoculation depends on providing a concentration of the target contaminant that will support growth, the presence of toxins or predators that may reduce the viability of the inoculum, the presence of substrates other than the contaminant that may be preferentially used, and the accessibility of the contaminant.

Understandably, inoculation of uncontrolled areas such as soil, surface waters, and the subsurface for hazardous waste remediation has been met with varying success or is undemonstrated. Atlas *(48)* indicated that hydrocarbon degrading microoorganisms exist in most environments and that the addition of seed cultures is probably unnecessary to effect biodegradation of these compounds. However, environmental pollutants other than hydrocarbons may not be as biologically labile and their biodegradation may require or be enhanced by inoculation.

The results of several laboratory investigations have indicated that the biodegradation of specific compounds such as phenols, pesticides, and several chlorinated compounds can be enhanced by inoculation with specialized cultures of microorganisms *(49–55)*. Several pentachlorophenol (PCP)-degrading cultures of bacteria have been inoculated into soil and have removed PCP successfully *(49, 50)*. The obligately anaerobic dehalogenating bacterium, DCB-1, holds promise for initiating the biodegradation of highly chlorinated compounds such as the polychlorinated biphenyls (PCBs) *(56, 57)*. Chlorine substituents can be removed by DCB-1 to allow further metabolism of the compound to innocuous products by other organisms.

In addition, the white rot fungus, *Phanerochaete chrysosporium*, has been found to biodegrade several highly recalcitrant compounds such as DDT, 1,2,3,4,5,6-hexachlorocyclohexane (Lindane), the chlorinated phenols, PCBs, polycyclic aromatic hydrocarbons with more than three rings, and chlorinated dioxins *(58, 59)*. Mixtures of chloro- and methyl-aromatics have been simultaneously biodegraded by a genetically engineered *Pseudomonas* sp. B13 possessing a single catabolic pathway that cleaves both types of aromatic compounds *(60)*.

Contaminant-degrading microorganisms are often injected into the subsurface during attempts at in situ bioremediation *(61–63)*. Although the addition of microorganisms to bioreactors and surface treatments such as lagoons and landfarming is easily accomplished, the injection of microorganisms into the subsurface presents a more difficult problem. The injected organisms must be transported through the subsurface to the zone of contamination, colonize the subsurface matrix, and grow to be effective in contaminant removal. Whether these criteria are met will depend on the hydraulic conductivity of the subsurface material *(64, 65)*, the composition of the solid matrix *(66)*, and the biological and physical properties of the organisms *(65, 67–70)*.

Obviously, microbial transport will not occur in subsurface materials with average pore diameters that are smaller than the organism. Provided that the pore spaces are large enough to allow such passage, organic matter and clay may affect transport by sorbing the cells out of solution. In addition, the size, shape, condition, and stickiness of the cells will affect their transport. However, in situ microbial transport through subsurface materials has been demonstrated *(70, 71)*.

Surface treatments using microbes. In addition to subsurface contamination, many hazardous waste sites have surface contamination that needs remediation. The contamination may be present in the surface soil or in waste pits. Such wastes are often treated in aerobic or anaerobic lagoons. The waste is present as a slurry, suspended solid, or sludge *(2)*. The purpose of the system is first to dissolve and then biodegrade the contaminants into innocuous materials. The first step, dissolution, can be achieved by microbial, chemical, or mechanical action. Adequate mixing is essential for maximum dissolution.

Under aerobic conditions, mixing and aeration may be provided by sparging with air or by using submerged or floating aerators. In some cases, seed microorganisms and nutrients such as

nitrogen and phosphorus could be added for the biodegradation of a highly recalcitrant compound.

A field application of in situ biodegradation of sludges and contaminated soils in a lagoon will be initiated in the summer of 1989 at an abandoned industrial waste site in Crosby, Texas (*72*). The site is contaminated with petrochemical and other industrial wastes. In situ feasibility studies indicated that significant biodegradation of the lagoon sludge occurred after aeration and the addition of inorganic nutrients.

Summing up

In situ biorestoration is a promising technique for the remediation of subsurface contamination. The process involves injecting an electron acceptor, usually oxygen, and inorganic nutrients to stimulate contaminant biodegradation by the indigenous subsurface microflora. Essential criteria for its implementation include the presence of contaminant-degrading microorganisms and subsurface materials that are permeable enough to allow adequate transport of a nutrient solution.

Surface microorganisms that degrade hydrocarbons are most likely ubiquitous; however, finding indigenous subsurface microorganisms that degrade the more recalcitrant compounds such as polycyclic aromatic hydrocarbons and highly chlorinated aromatic compounds is more difficult. Remediation of sites contaminated with such compounds may require the addition of microorganisms with specialized degradative capabilities. Although seeding microorganisms into above-ground bioreactors and surface impoundments for contaminant biodegradation has succeeded, injection of microorganisms into the subsurface to degrade contamination is an undemonstrated technique.

When applicable, the biodegradation of organic compounds into inorganic constituents and cell mass offers a better solution to hazardous materials disposal instead of simply transferring the contamination from one medium of the environment to another.

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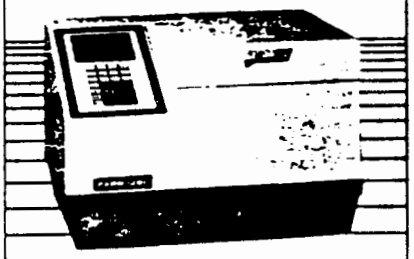
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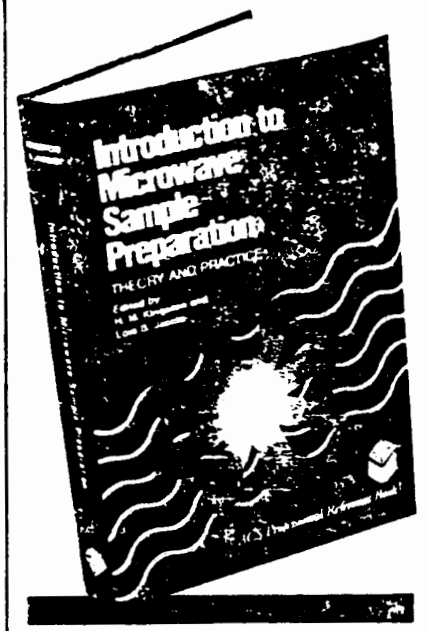
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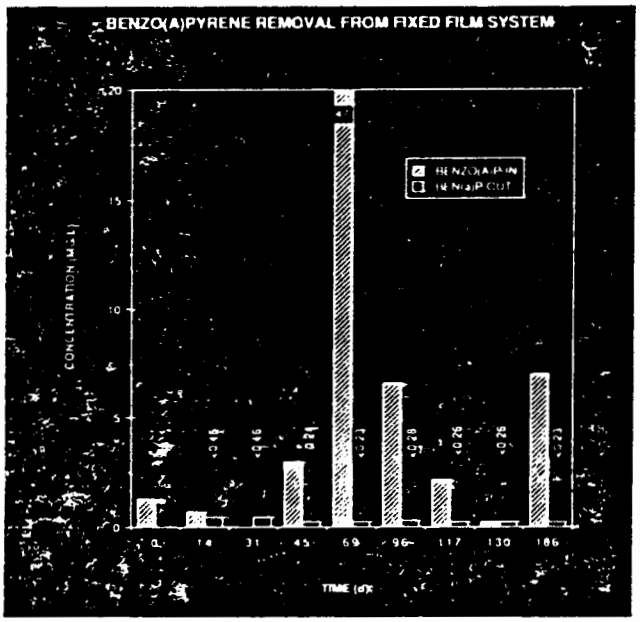
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biologically degradable materials can be removed from a site more cheaply than they can be treated by biological methods. In other cases, biological treatment is uneconomical because of climatic factors such as temperature and rainfall. Finally, the issue of volatilization and its control at hazardous waste sites is becoming a more prominent issue to be addressed. While many volatile materials are known to be biodegradable, transfer to the air is often more rapid than biodegradation. However, creative and established methods in biotreatment are being developed to minimize volatile emissions and associated control costs.

Summary

Biological treatment has a wide range of applications in hazardous waste treatment, and is becoming increasingly prominent because it offers a cost-effective method of cleanup, and produces terminal destruction of contaminants. There is an increasing understanding of mixed culture systems and an increasing array of novel applications of well founded microbial concepts. At many sites, bioremediation will be most advantageously applied in conjunction with other technologies, such as thermal destruction or physical or chemical pretreatment, but there are many cases where closure of a hazardous waste site can be accomplished strictly with biological treatment. Biological treatment is versatile, the organisms used in treatment systems are resilient, and sound engineering concepts have proven to be appropriate in effecting contaminant destruction. Experience with various methods of biological treatments is increasing, and their potential for reducing both remediation costs, and latent liability resulting from non destructive technologies, causes many to reconsider their choices for site remediation.



Removal of benzo(a)pyrene from contaminated groundwater during treatment in a fixed-film bioreactor. These results demonstrate stability over a wide range of loading rates.

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Biological treatment of hazardous waste

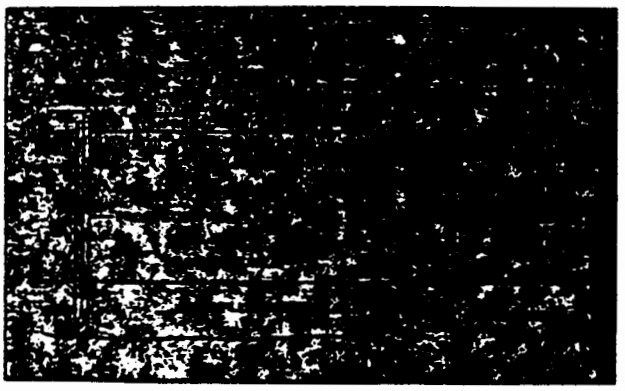
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The controlled destruction of hazardous materials by natural methods in biological treatment offers unique and extremely diverse opportunities for the cleanup of contaminated environments. Biological treatment of hazardous materials is important because the results of treatment are usually innocuous materials such as biological cell mass and carbon dioxide, thus eliminating potential latent liability of the "treated" waste. Applications of biological treatment are becoming increasingly important in the field of hazardous waste treatment. This article discusses some basic concepts of biological treatment, and reviews some of the more prominent techniques applied to hazardous waste site cleanup. The article also discusses some of the significant non-biological issues which must be addressed to understand the feasibility of using biological treatment.

Biological treatment is not a novel technology, and usually relies on the idigenous populations of the site, or enrichment with other naturally occurring organisms to accomplish successful treatment. The concepts of biological treatment are well founded, and often implemented through simple enrichment of appropriate nutrients and by increasing oxygen transfer within the contaminated environment. In more complex physical environments, biological activity is stimulated and maintained by implementing established engineering practices, coupled with the management of otherwise constraining physical barriers (such as geological and hydrological).

Basic concepts — Nature of the organism

All living systems require sources of energy to develop and sustain their populations. In biological treatment, the contaminant is usually one of the sources of food and energy for single species and/or consortia of organisms thriving in the contaminated environment. The activity of organisms responsible for contaminant destruction is controlled by several environmental factors, notably nutrients, water and oxygen availability, temperature, and pH. In addition, activities can be inhibited by the presence of toxic organic compounds, metals, or high salt contents.



Schematic diagram of a typical in situ bioremediation project.

During the microbial growth process, organisms incorporate certain amounts of nutrients, such as nitrogen and phosphorous, particularly during growth of their populations to produce biomass. Available nitrogen and phosphorous must be maintained as sufficient concentrations with respect to the available organic carbon in the contaminated environment to assure that only the contaminant is the limiting nutrient. Generally, the range of carbon:nitrogen:phosphorous is between about 100:10:1 to 100:1:0:5 depending on the type of treatment used, and the phase (liquid or solid) in which the contaminant is found. Control of the particular physical environment is usually resolved by maintaining adequate moisture (for as an example, the optimal is approximately 1 bar), the pH in the range of 6-8, the temperature as near the optimum for the degrading organisms as can be reasonably achieved (to a limit, the higher the temperature, the faster the degradation process), and the dissolved oxygen content in aerobic systems at near saturation with air (approximately 8 mg/L). In many cases, other potentially limiting factors such as salinity or toxicity must also be recognized and addressed if bioremediation is to be successful. Organisms can survive and thrive in otherwise inhibitory and toxic environments because of changes in their metabolic or physical characteristics developed during a process of acclimation, but in extreme cases biological treatment must be coupled with physical and chemical treatment methods. Finally, it must be recognized that organisms require a final sink for the electrons transferred during metabolic processes. In aerobic digestion, the electron acceptor is usually oxygen, while in anaerobic systems, the electron acceptors are organic acids, carbon dioxide or other oxides such as sulfates and nitrates.

Nature of the Contaminant: The complexity of the organic material often determines the likelihood of the molecule to be degraded. For example, long-chained aliphatic hydrocarbons, aldehydes, and ketones are rapidly degraded to end-products of carbon dioxide and water. In contrast, polynuclear aromatic (PNA) compounds with 4 or more rings are degraded only slowly, if at all, when they are the only hydrocarbons present although their concentrations can be lowered in the presence of structurally related compounds. Heterocyclic compounds containing nitrogen, sulphur, and oxygen are also often difficult to degrade. The extent to which degradation of the important halogenated compounds occurs varies depending on the structure of the molecule and the degree to which it is halogenated. By-products of partial degradation can result from cer-

tain chlorinated compounds such as some chlorinated pesticides and solvents. The classic example for this type of problem is the partial degradation of trichloroethene, resulting in the formation of vinyl chloride, a compound known to be more toxic than its parent compound. Some compounds including, notably some of the polychlorobiphenyls (PCBs) and their congeners are not known to be biodegradable under any conditions tested.

Treatment methods — 1. Conventional treatment

Conventional treatment processes for contaminated soils and waters rely on aerobic processes which have been developed for landfarming of wastes and for wastewater treatment. In simple terms, this process consists of enriching an environment with a source of oxygen in the presence of the appropriate microorganisms to mineralize the contaminants to carbon dioxide and water. There are many treatment options which rely on this concept, and several are established with adequate understanding of engineering and control. The most important of these options using aerobic processes are land treatment, liquid/solids (soil slurry) treatment, above-ground water treatment systems, and in situ bioremediation. These options are discussed in detail below.

Solid phase land treatment: Organic contaminants in soils are susceptible to aerobic digestion, and this process occurs naturally to a limited degree. The rates may be greatly enhanced by fertilizing, irrigating, and tilling the soil to increase the availability of nutrients, moisture oxygen and to the soil microorganisms, a process also described as landfarming, or solids treatment. In this process, the organisms used are most often the indigenous population, unless the environment is too severe. In these cases, parameters of the soil matrix can often be adjusted, and organisms known to degrade the contaminant can then be mixed into the soil matrix. Through scheduled tilling and maintenance of the moisture content, pH, and nutrients, decomposition and immobilization of the contaminants occur within both the upper soil layer (zone of incorporation), and the underlying layers. This type of treatment is one of the older and most widely used treatment technologies for hazardous waste treatment. In particular, the technology has been used successfully throughout the United States, especially at petroleum refinery sites treated under RCRA, and also with creosote-contaminated sludges and soils. Typical costs for this type of treatment are in the range of $50-$80/yd^3, depending on the need for a liner, and on the extent of excavation required.

A variation of the solid phase land treatment is composting, in which waste decomposition is achieved at high temperatures which result from the high biological activity occurring within the process. This type of treatment has been shown effective for the treatment of highly contaminated material, and consists of piling the contaminated soil, mixed with a bulking agent, at heights of three to six feet. Aeration is provided by either forcing air through a contained system, or by mechanically turning the pile. The bulking agents increase the total volume of the treated material, and facilitate mixing requirements and oxygen transfer. The system is amenable to moisture, pH, and nutrient control by simple irrigation techniques, and to volatile emission control, when the system is enclosed. Where temperature is critical to increasing removal rates, the compost pile can be amended with other sources of organic matter to increase the biological activity, and the temperature of the system. Typically, the cost of this type of process is about $100/cubic yard.

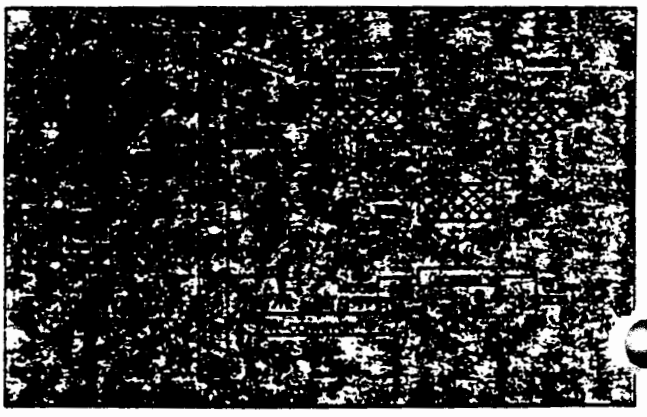
Liquid/Solids Treatment (LST): This type of system offers the significant control of important operating parameters resulting in rapid and effective treatment. The system relies on efficient mass transfer controlled by adequate mixing and aeration conditions. This type of treatment is similar in concept to conventional activated sludge treatment, but is usually conducted in batch mode, resulting in the discharge of active organisms at the same time as the cleaned soil is discharged from the treatment tank. The time required to reestablish an acclimated microbial population in subsequent batches can be minimized by recycling portions of the previous batch of solids and/or the decant.

Liquid phase treatment requires entirely different equipment for materials handling than solid phase treatment, and the issue of how best to promote mass transfer of oxygen and soluble contaminants is a major concern for engineering design. The solids content of the resulting slurry depends on several factors including the type of soil, the type of mixing and aeration equipment available, and the rates of removal to be achieved. The two rate limiting steps in an ideal system are the degree of solubilization of the organic contaminant, and the level at which active microbial populations can be maintained during the treatment.

The sophistication of the treatment tank can range from lined lagoons constructed with earth materials at the site, to carefully designed and engineered reactors, depending on the objectives of treatment. While the cost of treatment with LSTs is highly influenced by the conditions of the site, the associated capital costs are 30%-50% less than alternative technologies such as incineration, and an estimated cost for the treatment is in the range of $100-$150/yd^3. The use of LSTs potentially could provide control of volatile emissions when they are of concern, and may also eliminate some statutory concerns related to contaminant migration.

Liquids: Contaminated liquids resulting from soil washing or groundwater recovery can be treated in

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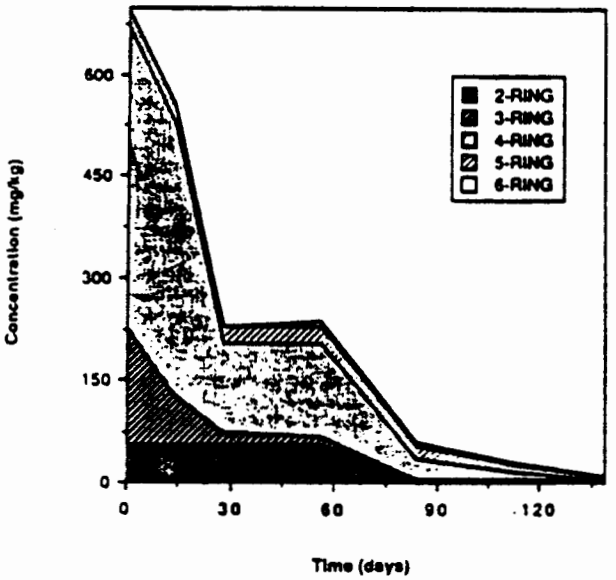
Schematic diagram of a white rot fungus treatment system.

Continued from page 81)

aboveground bioreactors. Generally, this type of treatment relies on conventional techniques developed for aerobic digestion, and include activated sludge, sequencing batch, and fixed-film bioreactors. The method of operation can be either continuous or batch, depending on the variation in the contaminant concentrations and the nature of the contaminants. Engineering design and control is most established with this type of treatment, because they are the same as those for conventional aerobic digestion. Essentially, the goal of this type of treatment is to maximize the kinetics of degradation and minimize the hydraulic detention times by providing maximum mass transfer opportunities, and highly active populations of acclimated organisms. Some of the problems associated with formation of pinpoint flocs (and subsequent washout of biomass) in activated sludge processes have been alleviated by elaborate schemes of biomass recovery and recycle, with Sequencing Batch Reactors, and with Fixed-Film processes.

In situ Treatment: There are many cases where in situ biological treatment should be considered, and especially where soil excavation would be difficult or extremely expensive. The most common type of in situ treatment involves the biodegradation of contaminants which are adsorbed onto soils within the saturated zone of a site. The process involves the addition of small amounts of ammonia and phosphate, and large quantities of an oxygen source, typically (but not limited to) hydrogen peroxide. This is accomplished by injecting nutrient-enriched solutions into the contaminated zone through a series of wells or trenches, and recovering groundwater down gradient.

In order for the process to be effective, the injection/recovery system must provide for the transport of nutrients throughout the entire contaminated region, following the pathway taken by the contaminant, if possible. This is particularly difficult at sites where the geology is highly irregular, or has been disturbed because of past construction, and at sites with multiple or unknown sources of contamination. The in situ remediation process is usually accompanied by surface treatment of the recovered groundwater.



Loss of polycyclic aromatic hydrocarbons during land treatment of creosote-contaminated soil.

The engineering parameters associated with this process are highly dependent on soil permeability, which becomes the rate-limiting step for mass transfer of oxygen to the aerobic organisms. In a few instances, in situ bioreclamation has been used for treatment in unsaturated soils. However, these cases are limited to fairly shallow depths over groundwater which is already contaminated. These treatment situations are difficult to control, and rely on introducing nutrient-rich water through percolation, or through pressure injection with multiple injection points. Air is then drawn through the soil, using vacuum pumps, to enhance the air exchange in the soil matrix. In situ treatment is most cost-effective with contaminants which are easily degraded, but which have very low solubilities in water. Costs of treatment with this type of in situ process are highly varied, but the costs for sites amenable to this type of treatment range from $8-$15 lb of contaminant.

2. Anaerobic treatment methods

Methanogenic environment: In conventional anaerobic digestion, organic material is solubilized and converted to organic acids by one set or organisms (acetogens), and then to methane by another and distinct set of organisms (methanogens) in a subsequent but highly interrelated metabolic step. The environment in which the methanogenic bacteria survive is quite specific and rigorous. Free oxygen must be practically absent and the redox potential must be lower than 330mV. Without these conditions, the more sensitive methanogens become inactive, causing the accumulation of organic acids and finally resulting in the loss of biological activity in both groups of organisms. The conversion of energy from the organic contaminant to cell mass is as much as 20 times less than in aerobic digestion and therefore considerably less biological sludge is produced. During the methanogenic process, unique reactions can also occur, notably the dechlorination of certain recalcitrant organic compounds.

While anaerobic digestion is not established for the hazardous waste treatment industry, it may become particularly useful in at least three cases. These cases are:

(1) Where the organic content of the contaminant is extremely high, and aerobic digestion is too expensive for these concentrations of contamination;
(2) where the degradation of biological sludges generated in a separate aerobic treatment is significant, and disposal of the sludges is of considerable concern and/or expense; and

(3) where dechlorination of particular compounds is required and occurs slowly, if at all, under aerobic conditions.

3. Other promising technologies

Aerobic White Rot Fungus: The application of the fungus, *Phanerochaete chrysosporium*, has been shown effective in the degradation of compounds resisting conventional treatment using bacterial (procaryotic) systems. This organism is eucaryotic, and secretes enzymes which are active outside the cell, thus eliminating the need for transporting the contaminants across the cell membrane. The active enzyme system consists of several related enzymes and peroxide, and is secreted under nitrogen limiting conditions. The enzyme system is non-specific, and attacks a wide range of organic molecules, resulting in mineralization of otherwise slowly degraded compounds such as pentachlorophenol, benzo(a)pyrene, and chlorinated pesticides, such as DDT (see Table 1). The organism is capable of degrading a wide range of compounds, and may be especially suitable for treating recalcitrant, and large or complex molecules. The essential features of an engineered process for this organism may include the following:

1. Growth of the fungus on a non-contaminant growth substrate (i.e. wood, straw, corn cobs).
2. Incorporation of the growth substrate, inocula and contaminated soil;
3. Treatment by composting the mixture;
4. Separation of the substrate from the contaminated soil; and
5. Re-use of the growth substrate, and return of the decontaminated soil to the site.

Table 1. Organics Reported to be Degradable by White Rot Fungus.

Napthalene	p-cresol
2-Methylnaphthalene	Benzoic Acid
Phenanthrene	2,3,7,8 TCDD
Benzo(a)pyrene	Chlordane
PCBs (Aroclors 1254 & 1242)	Lindane
	Atrazine
Pentachlorophenol	DDT

Co-metabolism: Aerobic and anaerobic microorganisms are known to degrade certain organic pollutants when the organisms are grown in the presence of the pollutants with other organic compounds which become the primary energy source for growth. The process is carried out by various groups of bacteria including methanotrophs (organisms which utilize methane), methanogens, and denitrifiers. Occurrences of these metabolic activities are well-documented, and in some situations, have been controlled with engineered systems. Table 2 lists some of the contaminants shown to be degraded under co-metabolic conditions. The concept of co-metabolism is thought by many to be one of the more promising concepts of biological treatment that can be exploited to broaden the range of applications in pollution control.

Table 2. Compounds known to be degradable through co-metabolic conditions.

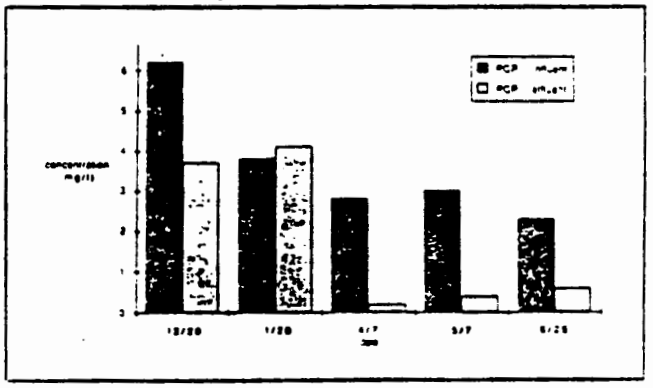
Trichloroethylene	tetrachloroethylene
dichloroethylene	carbon tetrachloride
dichloroethane	chloroform
vinyl chloride	DDT
chloroform	Lindane
1,1,1-Trichloroethane	Polychlorinated biphenyls

Denitrification: An increasing number of compounds are found to be degraded under anaerobic denitrifying conditions. In this process, nitrate becomes the electron acceptor, being converted to N_2 and N_2O gases. Under such conditions, benzene and a wide range of related compounds can be completely mineralized to CO_2 and cell mass. More recently, PAH compounds such as napthalene and acenapthene were shown to be degraded by this process.

Denitrification has several potential advantages in bioremediation, depending on the range of contaminants to which this technology can be applied. This process may be especially promising in in situ treatment of some groundwater environments where the supply of free oxygen is difficult.

Limitations of microbial treatment

Like any single type of technology, biological treatment is not one which can be applied to all circumstances. Living systems require specific living conditions, and the presence of metals, salts, and some organics are sometimes present at inhibitory or toxic concentrations. Like any method of on-site treatment, site-specific concerns must be addressed, requiring time and expertise from a broad range of scientific and engineering disciplines. As has already been mentioned, harmful by-products can occasionally result from biologically mediated reactions. In some cases,



Loss of pentachlorophenol during aerobic treatment of groundwater. Results show increasing effectiveness due to temperature increases and acclimation by the microbial community in the fixed-film bioreactor.

BIOLOGICAL WASTE TREATMENT

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TYPES OF MICROBIAL REACTIONS

Organism Type	Source of energy	Source of carbon
Heterotrophic	Organic Substrate	Organic Substrate
Autotrophic	Inorganic Substrate	CO_2 usually
Photosynthetic	Sunlight	CO_2

Organism Type	Dissolved Oxygen	No Dissolved Oxygen
Aerobic	Required D.O. End Products → $CO_2 + H_2O$	
Facultative	D.O. Present End Products → $CO_2 + H_2O$	Anoxic Conditions End Products → $CO_2 + H_2O$ + Intermediates
Anaerobic		D.O. is inhibitory and toxic End Products → $CO_2 + CH_4 + H_2O$

Biological treatment is applicable to wastewaters containing biodegradable organic materials. A The conversion of organic substrate to end products and cell biomass may be represented schematically in the following illustration.

Bacterial growth can be defined by the following equations for the **aerobic heterotrophic** decomposition of an organic substrate. Glucose is used as the substrate

Substrate oxidation:

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + H_2O$$

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Cell synthesis can be represented as:

$$20\ C_6H_{12}O_6 + 24\ NH_4^+ + 2\ H_2PO_4^- + O_2 + \text{Bacteria} \rightarrow C_{60}H_{87}O_{23}N_{12}P + 83\ H_2O + \text{Residual Non Degradable Organics}$$

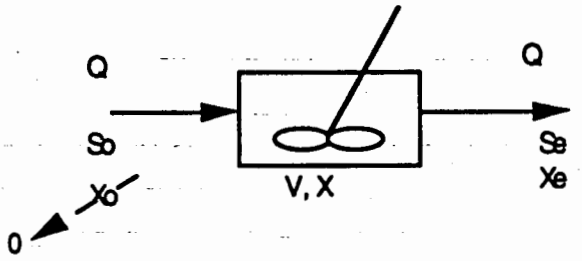
A simpler representation of the cell composition commonly used is $C_5H_7O_2N$

Cell oxidation (auto oxidation) (endogenous respiration) can be written as:

$$C_5H_7O_2N + 5O_2 \rightarrow 5CO_2 + NH_4^+ + H_2PO_4^- + 2H_2O + \text{Non-Degradable Residue}$$

$$\frac{5\ O_2}{C_5H_7O_2N} = \frac{5(32)}{113} = 1.42\ \frac{\text{gm } O_2}{\text{gm biomass}}$$

Referring to the attached figure,



the net biomass produced is:

$r_g' = Yr_{su} - k_dX$

r_g' = net rate of biomas produced [mg/L-day]

$Y = \frac{\text{mg/L biomass}}{\text{mg/L substrate utilized}}$

rsu = substrate removal rate [mg/L-day]

k_d = endogenous respiration or decay rate [day^{-1}]

X = concentration of biomass [mg/L]

MASS BALANCE

Biomass

$$V\frac{dX}{dt} = QX_o - QX + V(r_g')$$

but at steady state $\frac{dX}{dt} = 0$, and there is no biomass in the influent; therefore, $X_o = 0$.

The equation reduces to:

$$QX = Vr_g'$$

However, substituting for r_g'

$$QX = V(Yr_{su} - k_dX) = VYr_{su} - k_dVX$$

A mass balance on substrate is

$$V\frac{dS}{dt} = QS_o - QS_e + V(-r_{su})$$

but at steady state $\frac{dS}{dt} = 0$, and the equation reduces to

$Q(S_o - S_e) = V(r_{su})$, and solving for the rate of substrate removal

$$r_{su} = \frac{Q(S_o - S_e)}{V}$$

Substituting into the above equation

$$QX = YQ(So - Se) - k_dVX.$$

This equation can be rewritten as:

$$\frac{QX}{VX} = YQ\frac{(S_o - S_e)}{VX} - k_d$$

where

$$\frac{QX}{VX} = \frac{\text{biomass produced/day}}{\text{biomass in the reactor}}$$

The reciprocal of $\frac{QX}{VX} = \frac{\text{biomass in the reactor}}{\text{biomass produced/day}}$ is the average time that the biomass is in the reactor and is called the mean cell residence time or sludge age = θ_c [days].

The equation can be rewritten as:

$$\frac{1}{\theta_c} = YU - k_d$$

where:

$$U = \text{Specific Substrate Utilization} \frac{Q(S_o - S_e)}{VX} \quad [\frac{\text{kg BOD}_5 \text{ removed}}{\text{kg MLSS-day}}]$$

This expression describes a straight line relationship in which

the slope = Y (Cell Yield Coefficient) $[\frac{\text{g biomass}}{\text{g substrate removed}}]$ and

at U = 0 , the vertical intercept = k_d $[day^{-1}]$

However,

$$U = \frac{k\ S}{K_s + S}$$

where:

k = maximum substrate removal rate per unit biomass per day $\frac{\text{mg/L BOD}_5}{\text{mg/L MLVSS-day}}$

Taking the reciprocal of both sides of the equation results in

$$\frac{1}{U} = \frac{K_s + S}{k\ S} = \frac{K_s}{k}\frac{1}{S} + \frac{1}{k}$$

DESIGN CONSIDERATIONS

Kinetic Parameters	Design Variables	
Y	θ_c	
k_d	X	interdependent
K_s	S	
k	θ_h	

Sludge Produced (P_x)

$$P_x = Y\ Q(So - S) - k_d VX$$

dividing by biomass in the reactor (VX)

$$\frac{P_x}{VX} = YQ\frac{(S_o - S_e)}{VX} - k_d = \frac{1}{\theta_c}$$

rewriting this equation as:

$$\frac{1 + k_d\theta_c}{\theta_c} = YQ\frac{(S_o - S_e)}{VX}$$

the hydraulic detention time in the reactor is

$$\frac{V}{Q} = \theta_c$$

solving for the biomass concentration;

$$X = \frac{Y(So - Se)\theta_c}{(1 + k_d\theta_c)\theta_h}$$

for system with no recycle

$$\theta_c = \theta_h$$

and

$$X = \frac{Y(S_o - S_e)}{1 + k_d\theta_c}$$

The substrate concentration, S, may be calculated using the following relationship:

$$U = \frac{Q(S_o - S_e)}{VX} = \frac{kS}{K_s + S}$$

Substituting for X with:

$$X = \frac{Y(S_d - S_e)}{(1 + k_d\theta_c)}$$

the substrate concentration, S, is:

$$S = \frac{K_s(1 + k_d\theta_c)}{\theta_c(Yk - k_d) - 1}$$

OPERATIONAL CONSIDERATIONS INCLUDE:

SLUDGE VOLUME INDEX

SVI is the volume occupied (mL) by one gram of MLSS (dry weight) after settling for 30 minutes in a one-liter graduate cylinder.

$$SVI = \frac{\text{volume occupied (mL)}}{\text{mass of solids (gm)(dry wt.)}}$$

OXYGEN REQUIREMENTS

$$O.U.R. = \frac{Q(S_o - S_e)}{f} - 1.42\ P_x$$

or

$$O.U.R. = a'\ Q(S_o - S_e) + b'\ VX$$

and the specific oxygen utilization rate is:

$$\frac{O.U.R.}{VX} = \frac{a'Q(S_o - S_e)}{VX} + b'$$

NUTRIENT REQUIREMENTS

Nitrogen requirement is 12% to 13% of the dry weight of the biomass produced

$N(kg/d) = (0.12 \text{ to } 0.13)\ P_x$

Phosphorus requirement is 2% to 3% of the dry weight of the biomass produced

$P(kg/d) = (0.02 \text{ to } 0.03)\ P_x$

FOOD/MICROORGANISM

$$\frac{F}{M} = \frac{QS_o}{VX} \qquad \text{and} \qquad U = \frac{Q(S_o - S_e)}{VX}$$

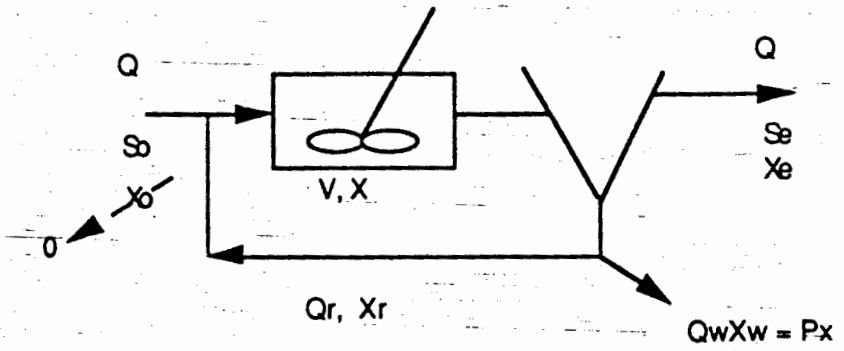
but

$$E(\%) = \frac{(S_o - Se)}{S_o}(100)$$

therefore,

$$U = \frac{Q(S_o - S_e)F/M}{QS_o} = \frac{(F/M)(E)}{100}$$

BIOLOGICAL SYSTEM WITH BIOMASS RECYCLE



Mass balances of the solids and substrate would result in the same design equation and expressions for biomass concentration and substrate concentration:

$$\frac{1}{\theta_c} = YU - k_d$$

$$\frac{P_x}{VX} = \frac{YQ\,(S_o - S_e)}{VX} - k_d \text{ and}$$

$$P_x = Y\,Q(So - S) - k_d VX$$

$$X = \frac{Y(So - Se)\theta_c}{(1 + k_d\theta_c)\theta_h}$$

$$S = \frac{K_s(1 + k_d\theta_c)}{\theta_c(Yk - k_d) - 1}$$

$$O.U.R. = a'\,Q(S_o - S_e) + b'\,VX$$

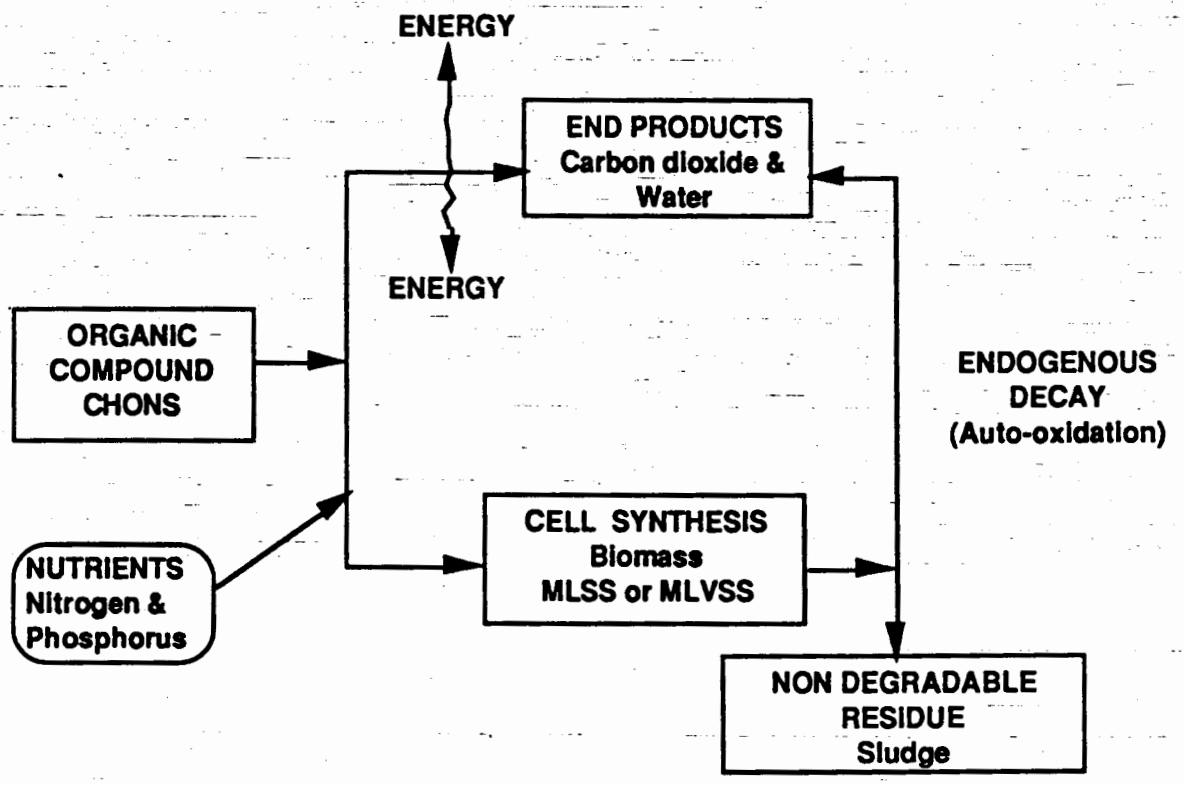
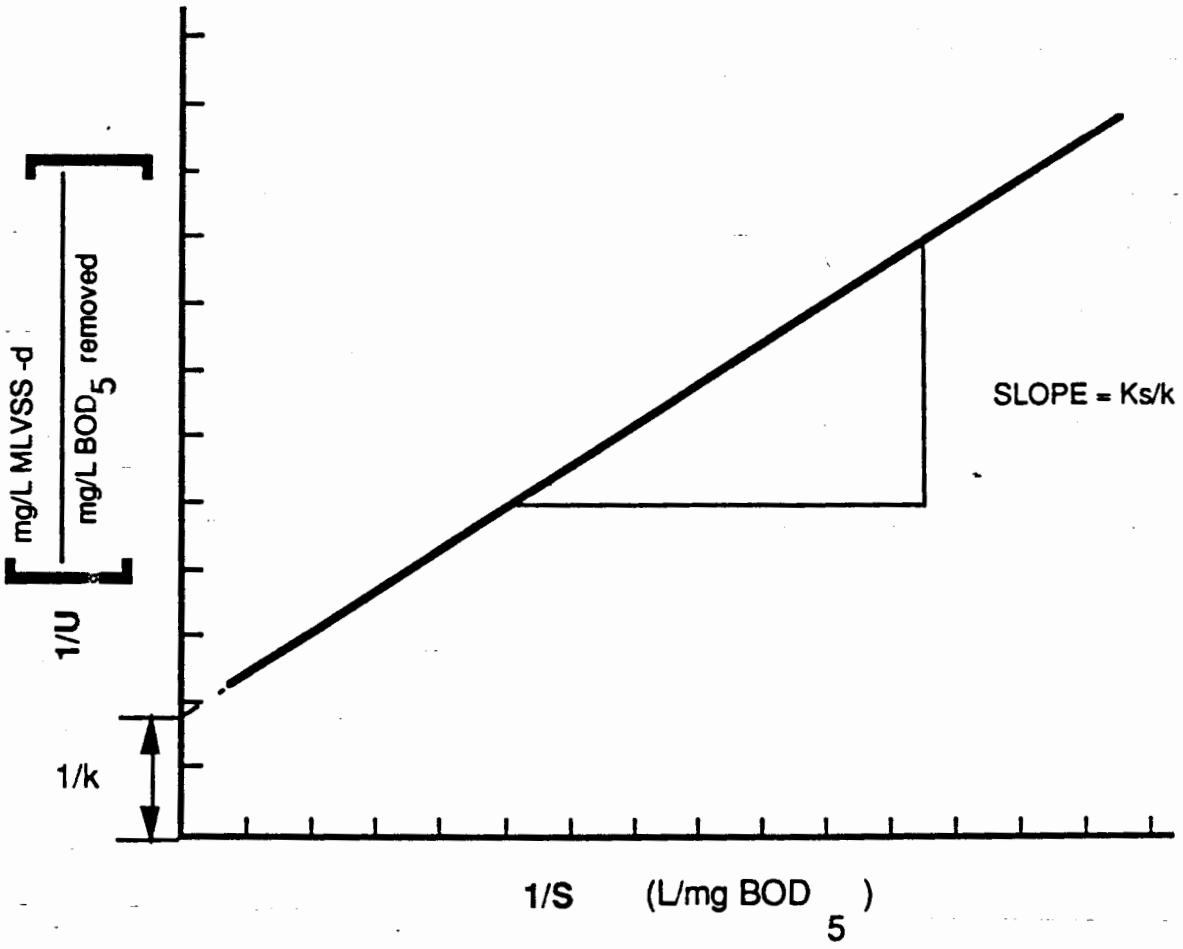
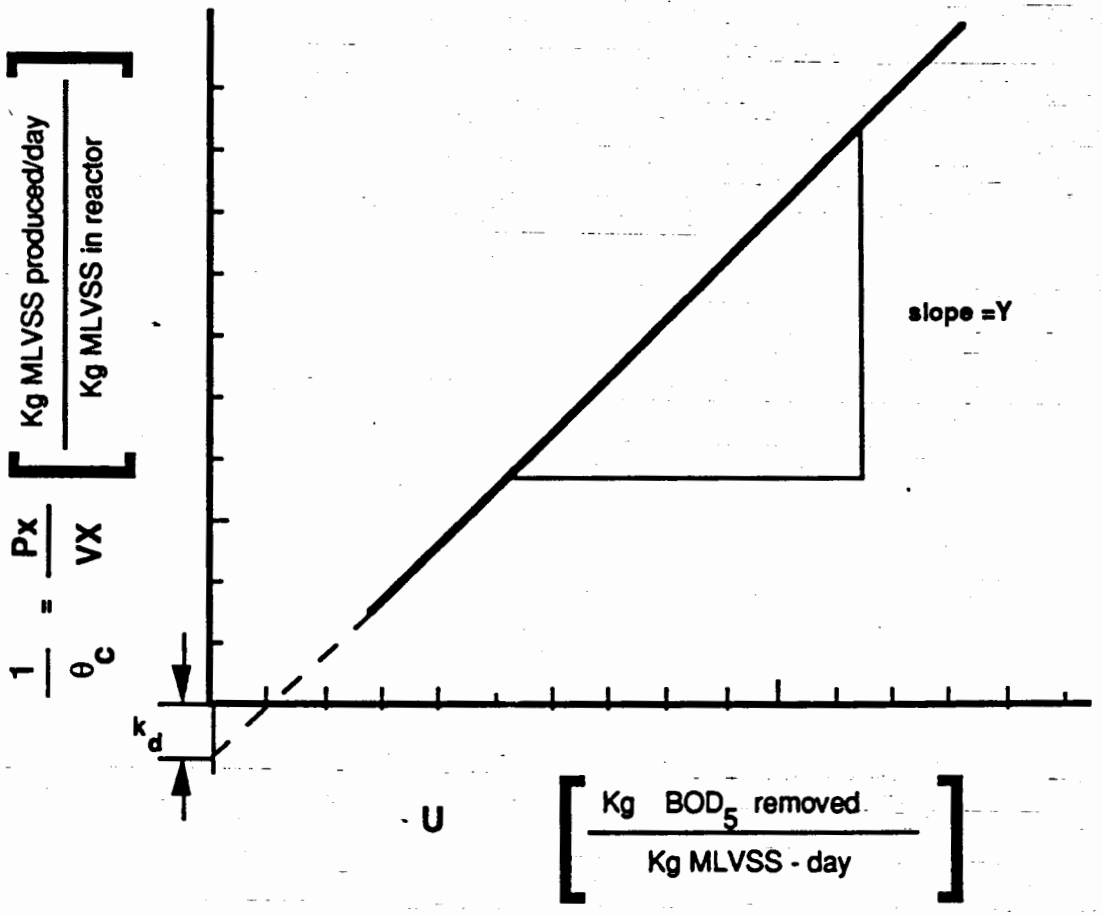


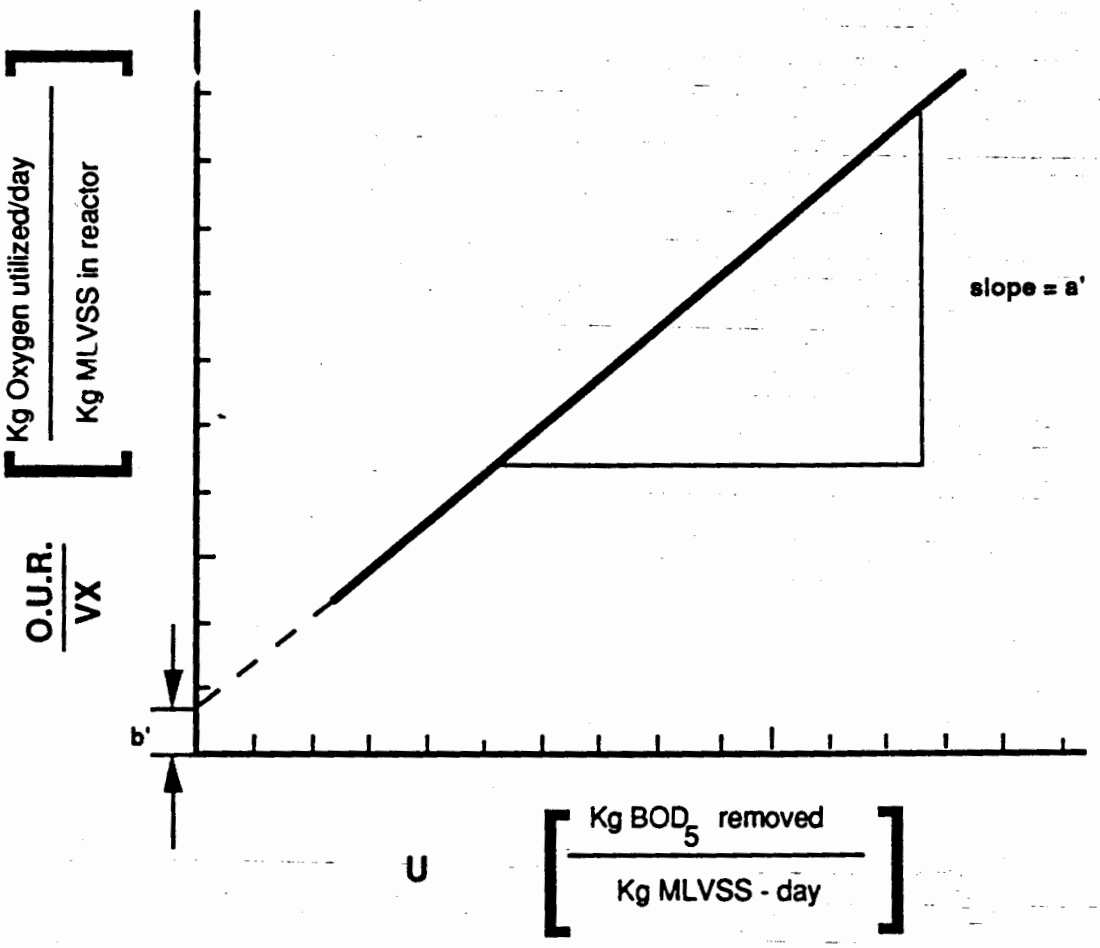
FIGURE 1. Heterotrophic degradation of organic chemicals



DATA FOR EVALUATION OF KINETIC PARAMETERS



DATA FOR EVALUATION OF KINETIC PARAMETERS



DATA FOR EVALUATION OF KINETIC PARAMETERS

OVERVIEW OF MICROBIOLOGICAL CONCEPTS

Joseph F. Malina, Jr., P.E.

Objectives of Biological Treatment are:

stabilize organic matter
incorporate non-settleable colloidal solids into biomass (sludge) - type of coagulation

Role of Microorganisms

Variety of microorganisms - primarily - **BACTERIA** (some fungi, molds, yeast and protozoa)
organic material is oxidized and used to meet requirements for energy and cell maintenance resulting in oxidized (aerobic) or reduced (anaerobic) end products and some of the organic material is converted into new cells and biomass.

Microbial Metabolism

Need to understand microbial biochemical activities before selection of treatment process

- general nutritional requirements
- microbial metabolism - molecular oxygen requirements

Nutritional Requirements for Microbial Growth

- Energy
- Carbon
- Inorganic macronutrients
  - Nitrogen
  - Phosphorus
- Inorganic micronutrients
  - Sulfur
  - Potassium
  - Calcium
  - Magnesium
  - Iron
- Organic growth factors
  - vitamins

Carbon and Energy Sources

TYPES OF MICROBIAL REACTIONS

Organism Type	Source of energy	Source of carbon
Heterotrophic	Organic Substrate	Organic Substrate
Autotrophic	Inorganic Substrate	CO_2 usually
Photosynthetic	Sunlight	CO_2

Typical electron acceptors in biological wastewater treatment

Environment	Electron Acceptor	Process
Aerobic	Oxygen, O_2	Aerobic metabolism
Anaerobic	Nitrate, NO_3^-	Nitrification
	Sulfate, $SO_4^=$	Sulfur reduction
	Carbon dioxide, CO_2	Methanogenesis

Nutrient and Growth Factors
- Principal : N,P S,K, Mg, Ca, Fe, Na, and Cl
- Minor: Zn, Mn,Mo, Se, Co, Cu, Ni, V, and W
- Organic: amino acids, purines, pyrimidines and vitamins

Microbial Nutrition and Biological Treatment

Types of Microorganisms in biological wastewater treatment

Heterotrophs (chemoheterotrophic)

- enzyme mediated reactions
- respiratory metabolism - external electron transfer
- fermentative metabolism - does not involve external electron acceptor
  - less energy produced, less growth
- aerobic respiration - molecular oxygen is the electron acceptor
  - obligately aerobic
- anoxic respiration - oxidized inorganics are electron acceptors

Anaerobic respiration - generates energy by fermentation
- obligately anaerobic - no molecular oxygen is present
- facultative anaerobes - can grow either in the presence or absence of molecular oxygen
- aerotolerant anaerobes

Bacteria morphology
- spheres - cocci 0.5 - 1.0 μm diameter
  - streptococcus
  - staphylococcus
  - sarcina
- cylinders - bacillus 0.5 to 1.0 μm in width and 1.5 to 3.0 μm in length
- helix - spirllum 0.5 to 5 μm in width and 6 to 15 μm in length (spiral)

Schematic of bacterial cell

Cell composition $C_5H_7O_2N$ or $C_{60}H_{87}O_{23}N_{12}P$

N content ≈ 12% to 13% wt of biomass

P content ≈ 2% to 3% wt of biomass

Function of Cell Wall - provide structure and shape (morphology)
protein/polysaccharide composition

Function of Cell membrane

Osmotic regulator - controls transport of water

Transport regulator - gases (O_2, CO_2, N_2)
fat solvents (alcohols, ether, chloroform, etc.)
Glucose, amino acids, glycerol, fatty acids, etc.
strong electrolytes (inorganic salts, acids, and bases)
Large molecules (disaccharides: sucrose, maltose, lactose, etc.)

Enzymes - organic catalysts, proteinaceous compounds (-ase) compound specific and reaction specific

Nuclear Area - DNA and RNA

Glycogen - starch storage

Volutin - Pentosenucleic acids storage

Slime capsule (polysaccharide)

Factors Affecting Biodegradation

Substrate - type and concentration
Bacterial population- acclimated
Nutrients - N & P
Oxygen - Aerobic
- - - - - - - - - - - - - - - - - - -
pH
Temperature
Toxicity/Inhibitory materials

Other organisms of importance

Fungi

Algae

Protozoa and Rotifers

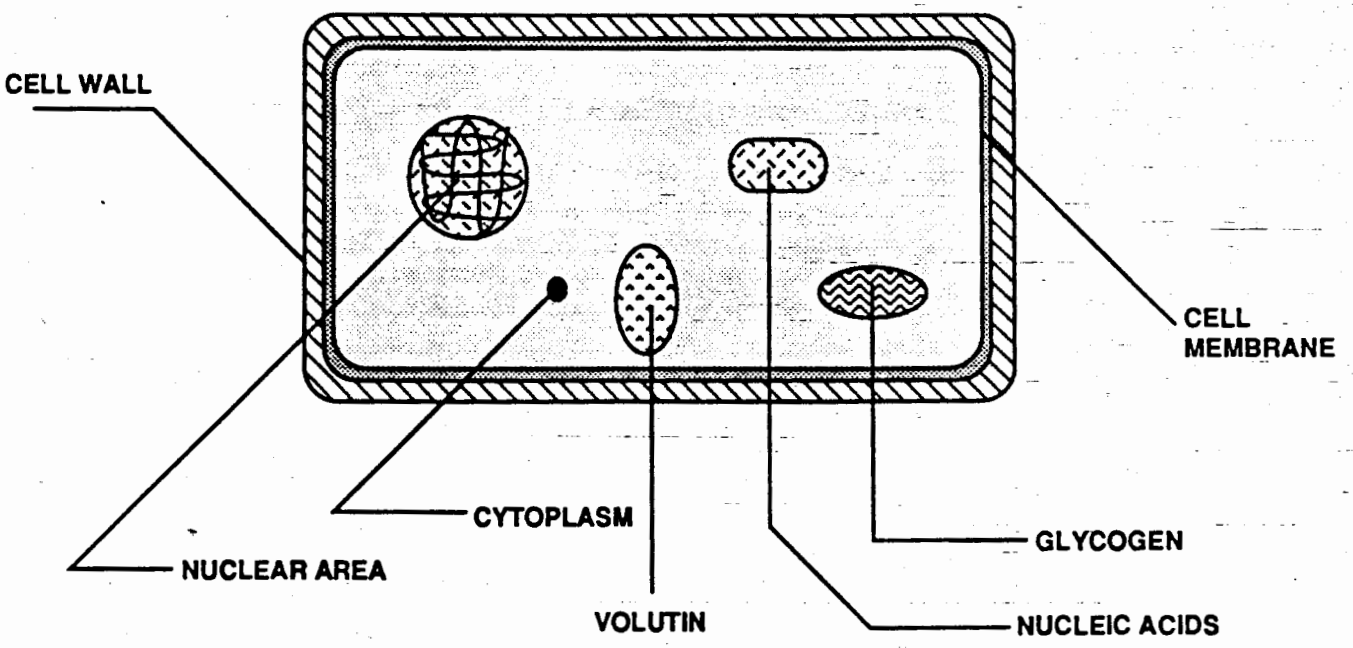
Bacterial Growth

General Growth Patterns in Pure Cultures

Number vs biomass

Kinetics

"TYPICAL" BACTERIAL CELL



Design Consideration for Biological Carbon, Nitrogen and Phosphorus Removal

Joseph F. Malina, Jr. P.E.

BIOLOGICAL CARBON REMOVAL

For specific wastewater, microbial population and environmental conditions (aerobic vs anaerobic, etc.)

The kinetic coefficients and parameter : Y, k_d, k, and K_s are fixed,

Therefore, **S**, effluent substrate concentration is a direct function of the specific substrate utilization rate, **U**, and therefore, the mean cell residence time, θ_c

Setting one operational variable, **S** or θ_c or **U** fixes (establishes) the other two and the efficiency of performance also is established for a given type and concentration of substrate S_o

Minimum sludge age

at minimum sludge age S_o=S

and $\frac{1}{\theta_c{}^m} = Yk - k_d$

Design relationship requires:

- mean cell residence time, θ_c
- Specific Substrate utilization rate, U
- yield coefficient, Y
- endogenous decay rate, k_d
- food to microorganism ratio, F/M
- settleability of the sludge, ZSV or SVI
- oxygen requirements, kg O_2/hr
- nutrient requirements, N & P

BIOLOGICAL NUTRIENT (N & P) REMOVAL

Control of nutrients is important since nitrogen (ammonia) effects streams and water quality and phosphorus may be the limiting nutrient in accelerating the eutrophication process

Nutrient control strategies are dictated by the:

- characteristics of untreated wastewater
- type of existing wastewater treatment facility
- level of nutrient control required
- seasonal versus year round control

Alternatives removal strategies include:

chemical precipitation of P (alum or iron salts)
integration of nitrogen oxidation in biological treatment
biological removal of P
combined nitrification/denitrification
combined N & P removal

Nitrification

$$NH_4^+ + 1.5\ O_2 \xrightarrow{Nitrosomonas} NO_2^- + 2H^+ + H_2O + \text{New Cells}$$

$$HNO_2 + 0.5\ O_2 \xrightarrow{Nitrobacter} HNO_3 + \text{New Cells}$$

These reactions are energy yielding

The overall reaction is:

$$NH_4^+ + 2\ O_2 = NO_3^- + 2H^+ + H_2O$$

Cell synthesis also takes place

$$4\ CO_2 + HCO_3^- + NH_4^+ + H_2O = C_5H_7O_2N + 5\ O_2$$

The overall oxidation and synthesis reaction is

$$NH_4^+ + 1.83\ O_2 + 1.98\ HCO_3^- = 0.021\ C_5H_7O_2N + 0.98\ NO_3^- + 1.041\ H_2O + 1.88\ H_2CO_3$$

During nitrification for each g NH_3-N oxidized

4.33 g of O2 are consumed

7.15 g of alkalinity as CaCO3 are destroyed

0.15 g of new cells are formed and

0.08 g of inorganic carbon are consumed

Nitrification Processes may be classified as:

Single stage carbon oxidation and nitrification
Separate stages for carbon oxidation and for nitrification

Nitrification capabilities are a affected by BOD_5/TKN

BOD_5/TKN = 1 to 3 are typical of separate nitrification systems and the fraction of nitrifiers in the MLSS is 0.21 to 0.083 as the ratio increases from 1 to 3

BOD_5/TKN > 5 (nitrifier fraction = 0.054) represents a combined carbon oxidation/nitrification system

Single Stage for Carbon Oxidation and Nitrification

suspended growth activated sludge
environment must be optimum for nitrifiers, i.e.

minimum DO in MLSS = 2 mg/L

pH = 7.2 to pH = 9.0

Design approach

select safety factor to handle peak, diurnal and transient loads (usually SF = 2 applied to SRT)

estimate maximum growth rate of nitrifiers based on lowest operating temperature, DO and pH

determine minimum cell-residence time (SRT)based on adjusted growth rate

determine design cell-residence (SRT) time using safety factor

determine N concentration

determine hydraulic retention time for effluent N concentration

determine organic substrate utilization rate (U) where a single stage carbon oxidation/nitrification process is used.

Typical 0verall Nitrification Design Parameters

Coefficient	Basis	Range	Typical
Y	mg VSS/mg NH_4^+ - N	0.1-0.3	0.2
k_d	d^{-1}	0.03-0.06	0.05

Attached growth nitrification

Typical loading rates for nitrification

Process	Percent Nitrification	Loading Rate lb $BOD_5/10^3 ft^3 \cdot d$
Trickling filter, rock medium	75-85	10-6
	85-95	6-3
Tower trickling filter, plastic medium	75-85	18-12
	85-95	12-6
Rotating Biological Contactors	90	1-3*

*$gal/ft^2 \cdot d$

DENITRIFICATION

Stoichiometry

Energy Reaction

$$6\ NO_3^- + 2\ CH_3OH = 6NO_2^- + 2\ CO_2 + 4H_2O$$

Energy Reaction

$$6\ NO_2^- + 3\ CH_3OH = 3N_2 + 3\ CO_2 + 3\ H_2O + 6\ OH^-$$

Overall Energy Reaction (Denitrification)

$$6\ NO_3^- + 5\ CH_3OH = 3N_2 + 5\ CO_2 + 7\ H_2O + 6\ OH^-$$

Synthesis

$$3\ NO_3^- + 14\ CH_3OH + 3\ H^+ = 3\ C_5H_7O_2N + H_2O$$

Overall Nitrate reduction

$$NO_3^- + 1.08\ CH_3OH + H^+ = 0.065\ C_5H_7O_2N + 0.47\ N_2 + 0.76\ CO_2 + 2.44\ H_2O$$

The following empirical equation may be used to calculate the methanol requirements

$$C_m = 2.47\ N_o + 1.53\ N_1 + 0.87\ D_o$$

where:

C_m = required methanol concentration, mg/L
N_o = initial nitrate-nitrogen concentration, mg/L
N_1 = initial nitrite-nitrogen concentration, mg/L
D_o = initial dissolved-oxygen concentration, mg/L

During denitrification, for each g of NO_3^- reduced to N_2

3.7 g COD are consumed

0.45 g new cells are produced, and

3.57 g alkalinity are formed

Typical Denitrification Kinetic Coefficients

Coefficient	Basis	Range	Typical
Y	mg VSS/mg NO_3^- - N	0.4-0.9	0.8
k_d	d^{-1}	0.04-0.08	0.04

Design approach

determine minimum cell-residence time (SRT)based on adjusted growth rate
select safety factor to handle peak, diurnal and transient loads (usually SF = 2 x SRT)
determine design cell-residence (SRT) time using safety factor
determine organic substrate (NO_3^- - N) utilization rate (U)
determine effluent NO_3^- concentration
determine hydraulic retention time for effluent NO_3^- concentration

Typical design parameters for biological phosphorus removal

Design	Units	Process A/O	Process PhoStrip	Process SBR
F/M	lb BOD5/lb MLVSS·d	0.2-0.7	0.1-0.5	0.15-0.5
SRT, θ_c	d	2-25	10-30	
MLSS	mg/L	2,000-4,000	600-5,000	2,000-3,000
HRT, θ	h			
Anaerobic zone		0.5-1.5	8-12	1.8-3
Aerobic zone		1-3	4-10	1.0-4
Return Activated sludge	% of Influent	25-40	20-50	
Internal recycle Stripper underflow	% of Influent		10-20	

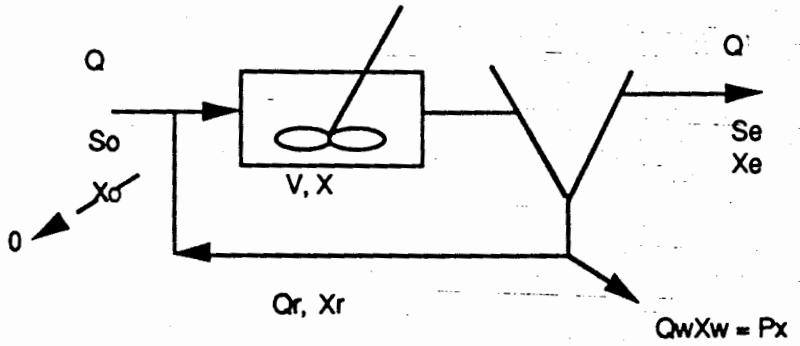
CURRENT CONCERNS

VOC
Heavy Metals
Priority Pollutants
Aquatic Toxicity

DESIGN OF BIOLOGICAL WASTEWATER TREATMENT SYSTEMS

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C.W. Cook Professor in Environmental Engineering
The University of Texas at Austin

DEFINITION OF TERMS



Q = Flow Rate of Influent
(gal/day) (m^3/sec)

Q_W or Q_W' = Flow Rate of Wasted Sludge
(gal/day) (m^3/sec)

Q_R = Flow Rate of Return Sludge
(gal/day) (m^3/sec)

S_o = concentration of soluble substrate [BOD, COD, or TOC] (mg/L) Entering reactor (influent)

S_e = concentration of soluble substrate in effluent [BOD, COD or TOC] mg/L

X_o = concentration of suspended solids in influent (mg/L)

X_e = concentration of suspended solids in effluent (mg/L)

X = concentration of suspended solids in the reactor {MLSS - mixed liquor suspended solids} or MLVSS ~ mixed liquor volatile suspended solids} (mg/L) - ?

X_R = concentration of suspended solids in the settled sludge (mg/L)

V = volume of the reactor (gal), (ft^3), (m^3)

θ_h = hydraulic detention time $\frac{V}{Q}$ = (days)

θ_c = cell residence time or sludge age = $\frac{\text{mass of solids in the reactor}}{\text{mass of solids wasted/day}}$

= $\frac{VX}{Q_W X_R}$ OR $\frac{VX}{Q_W{}^1 X}$

Y = cell (sludge sythesis coefficient, fraction of substrate (BOD, COD or TOC) converted to cells (sludge) (sometimes referred to as a)

k_d = cell decay coefficient or rate also call endogenous respiration rate (sometimes referred to as b)

$\frac{F}{M}$ = food to microorganism ratio mass of substrate (BOD, COD, or TOC) applied to the reactor daily divided by the mass of suspended solids (MLSS or MLVSS) in the reactor

$$\frac{Q\,S_o}{V\,X} = \frac{S_o}{\theta_h\,X}$$

U = specific substrate utilization rate (BOD, COD or TOC) removal ? divided by the mass of suspended solids in the reactor

$$\frac{Q(S_o - S_e)}{V\,X} = \frac{S_o - S_e}{\theta_h X}$$

$$U = \frac{(F/M)\,E}{100} \qquad E = \frac{S_o - S}{S_o}(100)$$

Design Equation

$$\frac{1}{\theta_c} = YU - k_d$$

Sludge Production

$$P_x = YQ(S_o - S_e) - k_d V X \quad (kg/d)$$

Oxygen Requirements for Activated Sludge Process

$$OUR = a' Q(S_o - S_e) - b' V X \quad (kg/d)$$

a' = oxygen utilization required for cell synthesis

b' = oxygen utilization rate during endogenous respiration

$$OUR = \frac{Q(S_o - S_e)}{f} - 1.42\,P_x$$

where $f = \frac{BOD_5}{BOD_u}$

1.42 kg O_2/kg Cells

DESIGN CONSIDERATIONS

F/M = 0.05 → 1.0

θ_c = 6 d → 15 d

θ_h = 4 hr → 8 hr

Organic Loading

$0.3 \rightarrow 3$ kg/m^3

$20 \rightarrow 190 \frac{\text{lb BOD}}{1000 \text{ Ft}}$ or $0.25 \rightarrow 25 \frac{\text{lb BOD}}{1000 \text{ Gal}}$

Air Requirements

F/M ≥ 0.3

$30 \rightarrow 55$ m^3/kg BOD removed
$500 \rightarrow 900$ ft^3/lb BOD removed

F/M < 0.3

$75 \rightarrow 115$ m^3/kg BOD removed
$1200 \rightarrow 1800$ ft^3/kg BOD removed

Diffused Air

$3.75 \rightarrow 15$ m^3/m^3 (7.5 m^3/m^3)
$0.5 \rightarrow 2.0$ ft^3/gal (1.0 ft^3/gal)

PRE- OR PRIMARY TREATMENT REQUIREMENTS
for
BIOLOGICAL TREATMENT

Constituent	Limiting or inhibitory concentration	Treatment
Suspended Solids	> 125 mg/L	Loagooning, flotation
Oil or Grease	> 50 mg/L	Skimming tank or separator
Heavy Metals	< 1 - 10 mg/L	Precipitation or ion exchange
Alkalinity	0.5 lbs. alkalinity as $CaCO_3$ per lb. BOD removed	Neutralizatin for excesive alkalinity
Acidity	Free mineral acidity	Neautralization
Organic Laod Variation (Based on 4 hours composite)	> 4:1	Equalization
Sulfides	> 100 mg/L	Precipitation or stripping
Chlorides	> 8,000 - 15,000 mg/L	Dilution, ion exchange
Phenols	> 70 - 160 mg/L	Stripping, provide complete mixing
Ammonia	> 1,600 mg/L	Dilution, pH adjustment and stripping
Dissolved salts	> 16,000 mg/L	Dilution, ion exchange

Cell-Synthesis Coefficient Y $\left(\frac{\text{mg MLVSS synthesized}}{\text{mg soluble COD removed}}\right)$

Temperature (°C)	Organic Chemicals Industrial Wastewater	Petrochemical Industrial Wastewater
4	—	0.49
10	0.28	0.42
15	0.33	—
20	0.23	0.43
30	0.31	0.21
31	—	—

Dissolved Oxygen Uptake Coefficient a'
$\left(\frac{\text{mg dissolved oxygen utilized}}{\text{mg soluble COD removed}}\right)$

Temperature (°C)	Organic Chemicals Industrial Wastewater	Petrochemical Industrial Wastewater
4	—	0.382
10	—	0.823
15	0.227	—
20	0.408	0.467
30	0.184	0.151
31	—	—

Economic Comparison - Deep Well vs. Biological Route

	Biological System	Deep Well System
Capital Cost	$140,000	$300,000
Operating Costs	$/Year	$/Year
Power Costs	11,400	13,000
Waste Neutralization Costs	119,500	16,800
Filter Element Replacements	—	1,400
Nutrient Costs	28,100	—
Dilution Water Costs	6,600	—
Labor Costs	7,500	10,200
Maintenance (3.5% of capital)	4,900	10,500
Depreciation (10% of capital)	14,000	30,000
Total Operating Expenses	$192,000	$ 82,000
Differential Capital Cost	$160,000	
Gross Operating Cost Savings	$110,000/Year	
Direct Earnings Rate on Incremental Disposal Well System Capital	69%	
Payout Period	2.2 years	

REFINERY WASTE WATER TREATMENT RESULTS

Parameter	API Separator mg/L	Bio-Treated mg/L	Carbon Treated mg/L	Bio-Carbon Treated mg/L
BOD_5	97	7	48	3
COD	234	98	103	26
TOC	56	30	14	7
Oil & Grease	29	10	10	7
Phenols	3.4	0.01	0.004	0.001
Chromium	2.2	0.9	0.2	0.2
Copper	0.5	0.1	0.05	0.05
Iron	2.2	3.0	0.3	0.9
Lead	0.2	0.2	0.2	0.2
Zinc	0.7	0.4	0.08	0.15
Sulfide	33	0.2	39	0.2
Ammonia	28	27	28	27
Cyanides	0.25	0.2	0.2	0.2
Turbidity*	26	17	11	5
Color**	30	15	15	1

ANAEROBIC TREATMENT

$$\frac{1}{\theta_c} = YU - K_d$$

$$\theta_c = \frac{VX}{QX}$$

$$\frac{QX}{VX} = Y\frac{(S_o - S_e)\,Q}{XV} - k_d$$

$$QX = Y\,Q\,(S_o - S_e) - k_d\,VX$$

$$X = Y\,(S_o - S_e) - k_d\,\theta_c X$$

$$X = \frac{Y(S_o - S_e)}{1 + k_d\theta_c}$$

Gas Production

$$G = 5.63\,[(e(S_o - S_e)\,Q) - 1.42\,P_x]$$

$$e = 0.80 \rightarrow 0.90$$

$$P_x = YQ\,(S_o - S_e) - k_d\,VX$$

For systems without recycle $P_x = QX$

$$QX = Y\,Q(S_o - S_e) - k_d\,\theta_c X$$

Divide both sides of the equation by QX

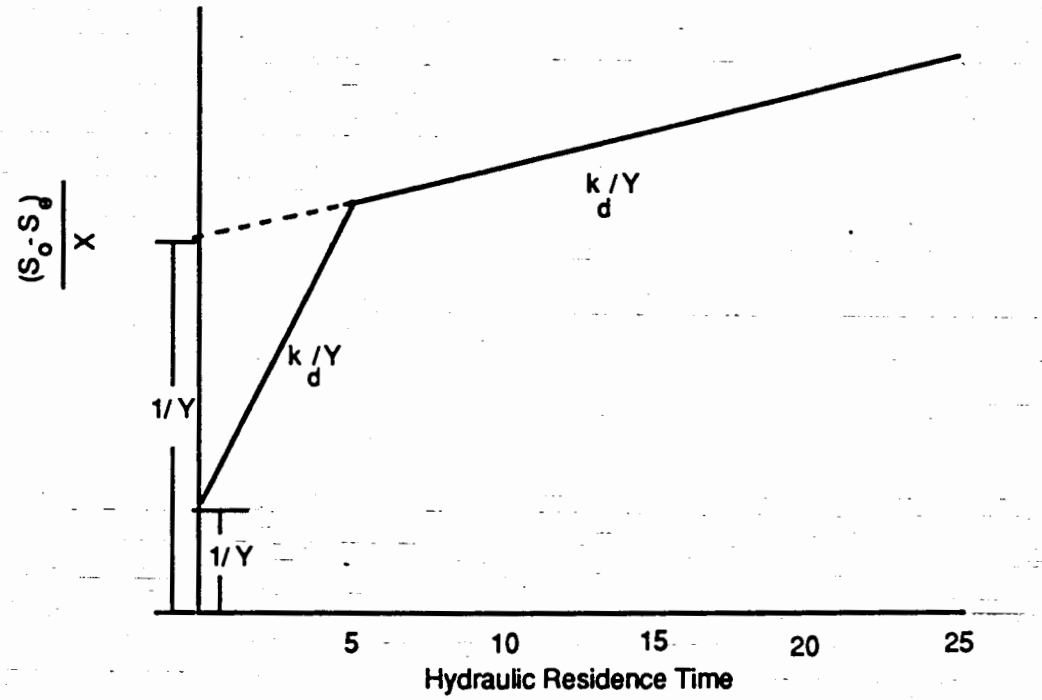
$$1 = \frac{Y\,(S_o - S_e)}{X} - k_d\,\theta_c$$

Rearrange terms results in

$$1 + K_d\,\theta_c = Y\frac{(S_o - S_e)}{X}$$

$$\frac{1}{Y} + \frac{k_d\theta_c}{Y} = \frac{S_o - S_e}{X}$$

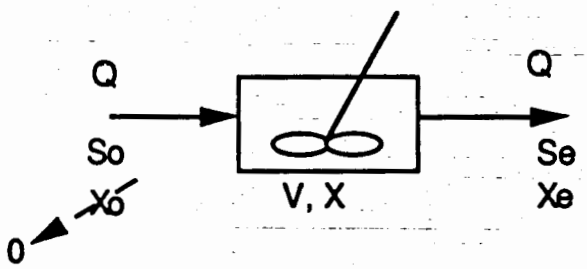
A Plot of $\frac{S_o - S_e}{X}$ vs θ_c results in a straight line with slope $= \frac{k_d}{Y}$ and intercept $= \frac{1}{Y}$



PROBLEMS

BIOLOGICAL WASTEWATER TREATMENT
DESIGN EXAMPLE
DETERMINING KINETIC COEFFICIENTS

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Observed operating data are presented below.

$\frac{V}{Q}$	$\frac{1}{\theta}$	S_o	S	X vss	$\frac{1}{S}$	$\frac{S_o-S}{\theta X}$	$\frac{\theta X}{S_o-S}$	$\frac{S_o-S}{S_o}$
days	$days^{-1}$	mg/L	mg/L	mg/L		$\frac{mg/L}{mg/L\text{-}d}$		
3.2	0.313	300	7	128	0.143	0.725	1.379	0.977
2.0	0.500	300	13	125	0.077	1.148	0.871	0.957
1.6	0.625	300	18	133	0.056	1.325	0.755	0.949
1.1	0.909	300	30	129	0.033	1.903	0.526	0.900
1.1	0.909	300	41	121	0.024	1.946	0.514	0.863

To determine kinetic coefficients K_S and k use:

$$\frac{\theta X}{S_o - S} = \frac{K_S}{k}\frac{1}{S} + \frac{1}{k}$$

Plot $\frac{\theta X}{S_o - S}$ vs $\frac{1}{S}$ Figure 1

To determine Y & k

Use $\frac{1}{\theta_c} = YU - k_d$

Plot $\frac{1}{\theta_c}$ vs U Figure 2

If effluent required is S = 15 mg/L

$\frac{1}{S} = 0.067$ and at $\frac{1}{S} = 0.067$ from Figure 1

$$\frac{\theta X}{S_o - S} = 0.825 \quad \text{or} \quad \frac{S_o - S}{\theta X} = 1.212 \frac{\text{mg/L}}{\text{mg/L-day}}$$

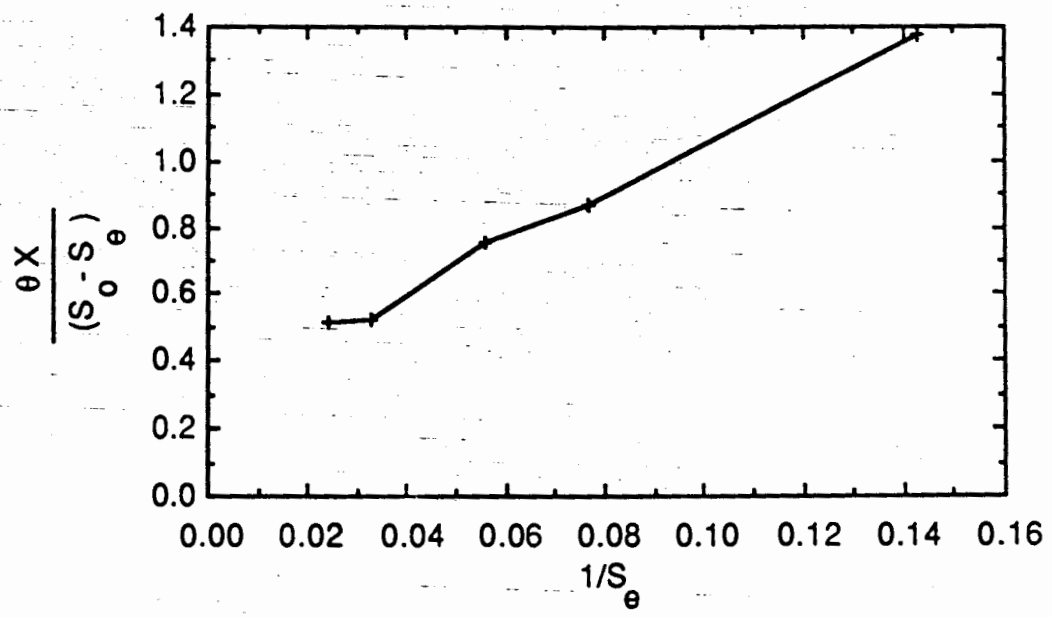


FIGURE 1

at U = 1.212 From FIGURE 2

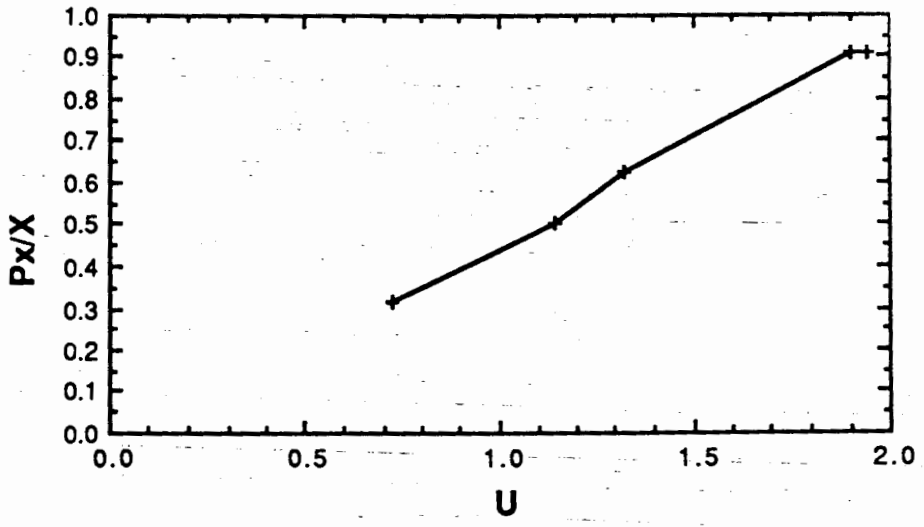


FIGURE 2

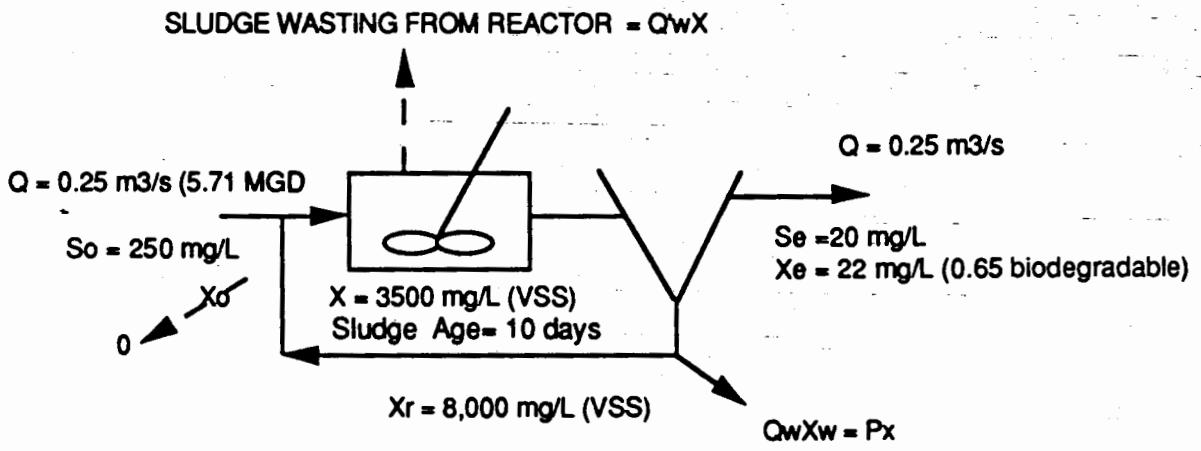
$$\frac{P_x}{X} = \frac{1}{\theta_c} = 0.55 \quad \text{or} \quad \theta_c = 1.82 \text{ days}$$

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BIOLOGICAL WASTEWATER TREATMENT
ACTIVATED SLUDGE DESIGN EXAMPLE

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A schematic of an activated sludge plant & pertinent design information include:



Kinetic Coefficients

$Y = 0.5$ mg/mg

$\frac{BOD_5}{BOD_u} = 0.68$

$k_d = 0.06\ day^{-1}$

$\frac{MLrss}{MLSS} = 0.8$

Calculate:

a) Effluent Soluble BOD
b) Aeration Tank Volume
c) Sludge Wasted (Quantity & Volume)
d) Recirculation Rates
e) Oxygen Requirements

a)Biodegradable Solids = 0.65 (22) = 14.3 mg/L

Ultimate BOD of Solids = 14.3 (1.42) = 20.3 mg/L

BOD_5 of Effluent = 0.68 (20.3) = 13.3 mg/L

Soluble Effluent BOD

$S_e = 20 - 13.8$

$S_e = 6.2$ mg/L

$$E = \frac{S_o - S_e}{S_o} (100) = \frac{250 - 6.2}{250} (100) = 97.5\%$$

b.) Using $X = \frac{\theta_c}{\theta} \frac{Y(S_o - S)}{(1 + k_d\theta_c)}$

and $\theta = \frac{Y}{Q}$

$$V = \frac{\theta_c Q Y (S_o - S)}{X (1 + k_d\theta_c)}$$

$$V = \frac{10d(0.5)(0.25\ m^3/s)(250-6.2)\frac{mg}{L}\ 3600\ \frac{sec}{hr}\ \frac{24\ hr}{day}}{3500\ mg/L\ (1 + \frac{0.06}{day}\ 10\ day)}$$

$V = 4702\ m^3$

c) Sludge Production

$$P_x = Y(S_o - S)\ Q - k_d V X$$

$$= \frac{0.5\ (250-6.2)g/m^3(0.25)m^3/s(3600)s/hr(24)hr/d}{10^3\ g/kg}$$

$$\frac{((0.06)(4702m^3)(3500\ mg/L))}{10^3\ g/kg}$$

$= 2,633 - 988$

$= 1,645$ kg/day MLVSS

OR $\frac{1645}{0.8} = 2,056$ kg/day MLSS

Volume of sludge

$Q_{wr}\ X_R = P_X VSS$

$$Q_{wr} = \frac{1645\frac{kg}{d}}{8000\frac{g}{m^3}\ \frac{kg}{1000g}}$$

$= 206\ m^3/day$ (0.054 MGD)

OR

$$\theta_c = \frac{VX}{Q_{wr}X_R}$$

$$Q_{wr} = \frac{4702\ m^3(3500\ mg/L)}{10\ d\ (8000\ mg/L)} = 206\ \frac{m^3}{day}$$

d) Recirculation Rate

$$QX_o + Q_R X_R = (Q + Q_R)X$$

$$Q_R(X_R - X) = QX$$

$$Q_R = Q\left(\frac{X}{X_R - X}\right)$$

$$Q_R = 0.25\left(\frac{3500}{4500}\right) = 0.19\ \frac{m^3}{sec}$$

$$q = \frac{V}{Q} = \frac{4702\ m^3}{0.25\ \frac{m^3}{sec}\ \frac{3600\ sec}{h}} = 5.22\ hr\ (0.22\ day)$$

Including recirculation

$$q = \frac{V}{Q + Q_R} = \frac{V}{1.78Q}$$

$$q = 2.93\ hr.\ (0.122\ day)$$

e) Oxygen Requirements

$$KgO_2/day = \frac{Q(S_0 - S)}{10^3\ (0.68)} - 1.42\ P_{x(vss)}$$

$$= \frac{0.25\ (250-6.2)(3600)24}{10^3(0.68)} - 1.42\ (1646)$$

$$= 7744 - 2337 = 5407\ KgO_2/day$$

$$\frac{O_2}{BOD_5\ removed} = \frac{5407\ Kg\ O_2/day}{0.25\ (250-6.2)\ (3600)\ 24\ (10^{-3})}$$

$$= \frac{5407}{5266} = 1.027\ \frac{Kg\ O_2}{Kg\ BOD_5}$$

Check:

$$F/M = \frac{Q\,S_o}{VX} = \frac{S_o}{\theta X}$$

$$= \frac{250\ mg/L}{(0.22\ day)\ (3500\ mg/L)}$$

$$= 0.325\ day^{-1}$$

$$\text{Volumetric Loading} = \frac{S_o Q}{V\ 10^3} = \frac{S_o}{q\ 10^3}$$

$$= \frac{250}{0.22\ (10^3)} = 1.14\ \frac{kgBOD_5}{m^3\text{-day}}$$

Air Requirements

Basis O_2 = 23.2% Weight and Oxygen Transfer Efficiency is 8%

$$\frac{1.027\ kg\ O_2}{kg\ BOD_5\ removed\ \frac{1.021\ kg}{m^3\ air}\ (0.232)\ 0.08} =$$

$$46.1\ \frac{m^3\ air}{kg\ BOD_5\ removed}$$

The settleabilty of the sludge controls the return sludge recycle rate; therefore the settling characteristics and the ability to concentrate the sludge must be evaluated.

OBSERVED SETTLING DATA

CONCN MLSS MG/L	1600	2500	2600	4000	5000	8000
Initial Settling Velocity (m/h)	3.353	2.438	1.524	0.610	0.305	0.091

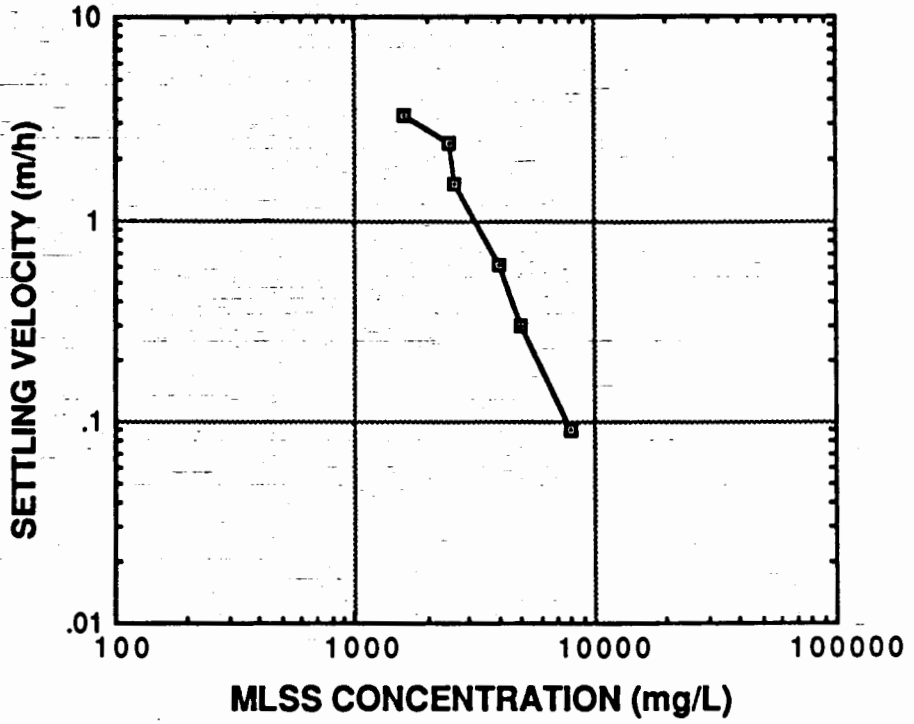


Figure 1 Initial Settling Velocities - Activated Sludge

Figure 1 is a plot of initial settling velocity vs MLSS concentration. The curve yields the following data and solids flux values are developed in the table below.

MLSS CONC'N gm/m^3	INITIAL SETTLING VELOCITY V (m/h)	SOLIDS FLUX $XV = \frac{(gm/m^3)(m/h)}{10^3 gm/kg} = kg/m^2 - h$
1000	3.6	3.6
1500	3.5	5.25
2000	2.8	5.60
2500	1.8	4.50
3000	1.15	3.45
4000	0.55	2.20
5000	0.30	1.50
6000	0.18	1.08
7000	0.125	0.875

The solids flux data can be plotted vs the initial MLSS concentrations resulting in the Solids Flux Curve presented in Figure 2.

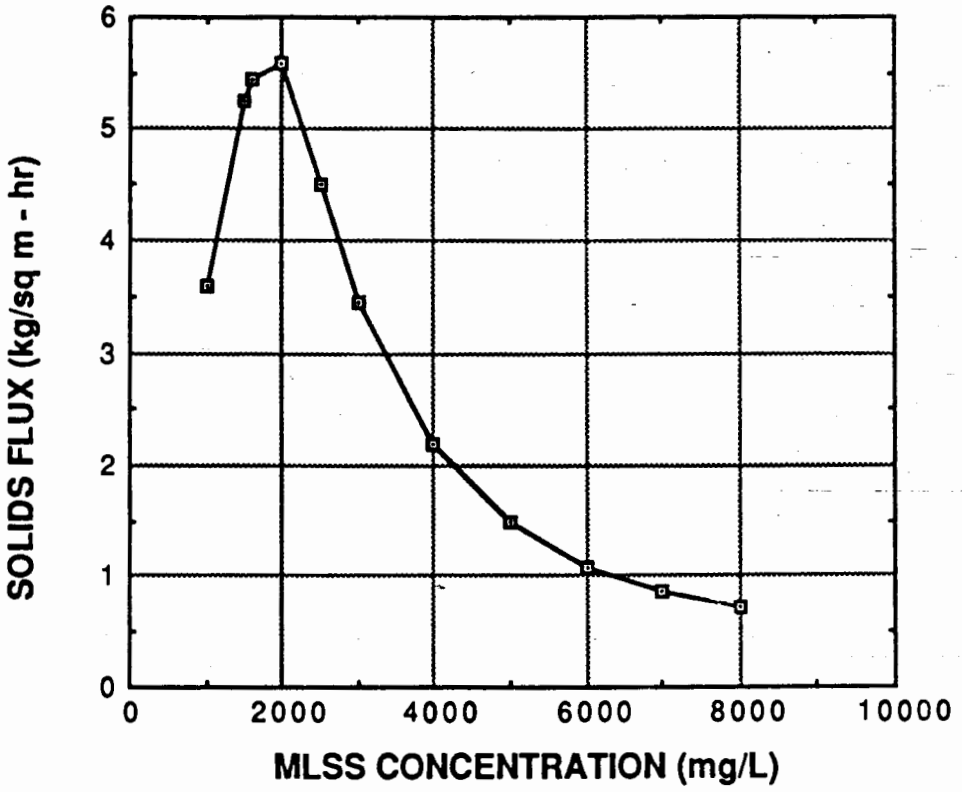


Figure 2 Solids Flux Curve

By drawing a line tangent to the Solids Flux Curve and passing through the desired underflow concentration on the horizontal ordinate, the limiting solids flux can be read from the vertical ordinate. The data are presented in the table below.

Limiting solids values are listed below (y-intercept)

Underflow Conc'n gm/m^3	Limiting Solids Flux SF_L $(kg/m^2 - L)$	X_0 - 4375	$X = \frac{Q_R}{Q}$
8000	3.95	3625	1.21
9000	3.10	4625	0.95
10000	2.70	5625	0.78
11000	2.25	6625	0.66
12000	1.95	7625	0.57

TSS in aeration Tank $= \frac{3500}{0.8} = 4375 \frac{gm}{m^3}$

Recycle ratio for different underflow concentrations.

$$Q X_o + Q_R X_u = (Q + Q_R)\, 4375$$

$$\alpha = \frac{Q_R}{Q} \text{ or } Q_R = \alpha Q$$

$$\alpha = \frac{4375}{X_U - 4375}$$

The surface area required can be calculated for different sludge recycle rates

$$SF_a = SF_L = \frac{(1 + \alpha)QX\ 3600\ sec/hr}{A(m2)\ 10^3 gm/kg}$$

X_u mg/L	SF_L kg/m^2-hr	α	Area m^2	Overflow rate m^3/m^2 - day
8000	3.95	1.21	2203	9.81
9000	3.10	0.95	2477	8.72
10000	2.70	0.78	2596	8.32
11000	2.25	0.66	2905	7.44
12000	1.95	0.57	3170	6.81

For underflow concentration = 10,000 mg/L overflow rate is 8.32 m^3/m^2 - day or settling rate of 0.366 m/hr

From plot of settling velocity vs concentration at 0.366 m/hr X mg/L = 4600 mg/L since concentration at interface will be less than 4600 mg/L design is conservative.

Depth for thickening

Assume: Minimum depth for clarification = 1.5 m and that 30% solids in aeration tank are retained in secondary clarifier

Average concentration in sludge zone is approximately 7000 mg/L

Solids in clarifier

$$0.3\ (V)X_{SS} = 0.3\ (4702\ m^3)\frac{4375\ gm - kg}{10^3\ gm\ m^3} = 6171\ kg$$

(Area) (depth)(Concentration) = Mass

$$\frac{2596\ m^2\ (m)\ (7000\ gm/m^3)}{10^3\ gm/kg}$$

depth = 0.34 m

Total minimum depth required for normal operations = 1.5 + 0.34= 1.84 m

Must include additional depth to accommodate peak flow and increased sludge volumes.

DESIGN EXAMPLE
COMPLETELY-STIRRED-TANK REACTORS
WITH SOLIDS RECYCLE
INDUSTRIAL ORGANIC CHEMICALS WASTEWATER

Joseph F. Malina, Jr., PhD, P.E.
C.W. Cook Professor in Environmental Engineering
The University of Texas at Austin

OPERATING DATA

Unit No.	Reactor Volume (V) (L)	Flow Rate (Q) (L/d)	θ_c (days)	S_o COD (mg/L)	S_e COD (mg/L)	X MLVSS (mg/L)	OUR (mg/day)
1	10.3	8.7	2.2	3,545	950	1,120	17,365
2	10.3	9.4	2.0	3,680	1,140	1,090	18,110
3	9.6	7.8	3.2	3,675	480	1,850	20,070
4	9.6	7.8	3.3	3,625	470	1,890	19,955
5	10.1	9.0	4.65	3,675	290	2,900	26,040
6	10.1	9.5	4.6	3,680	295	3,025	27,500

TABLE 2

$\frac{1}{\theta_c}$ (day^{-1})	$\frac{Q(S_o - S_e)}{VX}$ (day^{-1})	$\frac{R_r V}{VX}$ (day^{-1})	E_s (%)
0.46	1.96	1.51	73
0.50	2.12	1.61	69
0.31	1.40	1.13	87
0.30	1.36	1.10	87
0.22	1.04	0.89	92
0.22	1.05	0.90	92

An organic chemicals industrial wastewater completely mixed activated sludge with recycle

1. Influent to aeration basin has an average soluble COD of 3650 mg/L.
2. Average hydraulic detention time based on influent flow only is 1.16 day.
3. A 90% soluble COD removal efficiency is required.
4. Average daily flow is 1.5 mgd (5,678 m^3/d).
5. Results of treatability studies are presented in Tables I and II, and plotted in Figures 1, 2 and 4.

6. Design 2 aeration basins.

7. Volume of each aeration basin

= 0.75 mgd x 1.16 d
= 0.870 million galls
= 116,310 ft^3

$$= \frac{5678\ m^3/d}{2} \times 1.16\ d = 3{,}293\ m^3$$

8. Design sludge age θc

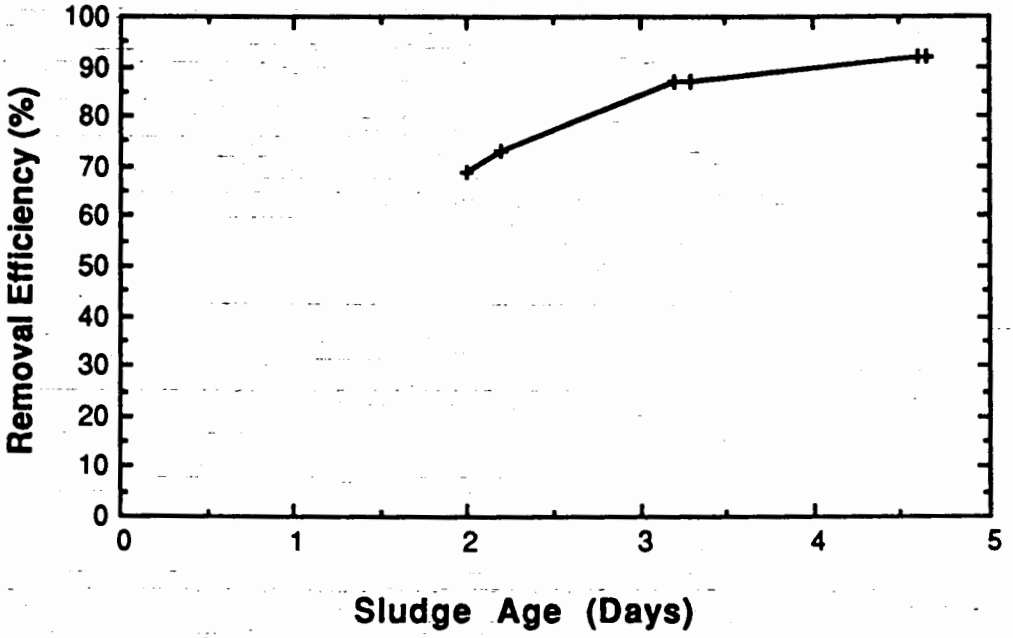


Figure 1

From Figure 1:

for $E_s = 90\% \rightarrow \theta_c = 4$ days

9. From Figure 2:

the cells-synthesis coefficient $Y = 0.26 \frac{\text{mg MLVSS synthesized}}{\text{mg soluble COD removed}}$

the micro-organism decay coefficient $k_d = 0.05\ day^{-1}$

10. The specific micro-organism growth rate $\frac{1}{\theta_c} = 0.25\ day^{-1}$

11. The design specific utilization (Figure 2)

$$U = \frac{Q(S_o - S_e)}{VX} = 1.17 \frac{\text{mg soluble COD removed}}{\text{mg MLVSS - day}}$$

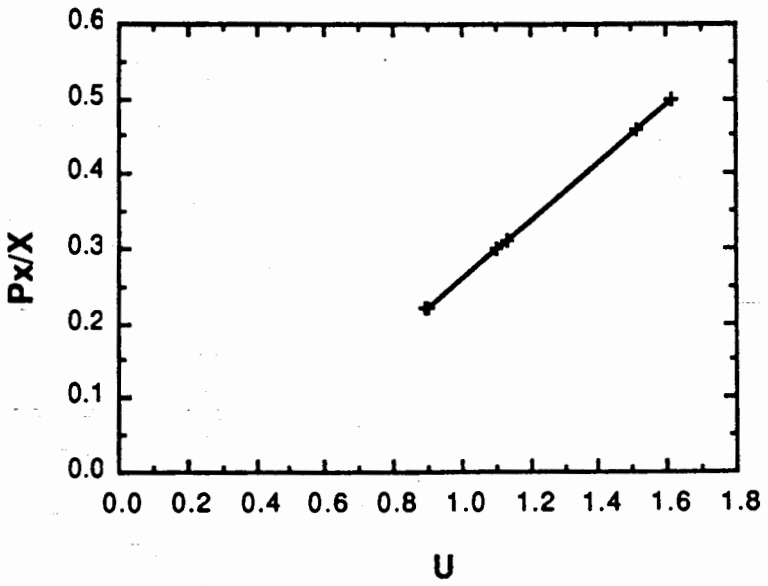


Figure 2

12. The steady state MLVSS concentration X

$$U = \frac{Q(S_o - S_e)}{VX} = 1.17$$

$$X = \frac{Q(S_o - S_e)}{1.17V}$$

$$\frac{Q}{V} = \frac{1}{1.16}\ day^{-1}\ (given)$$

S_o = 3650 mg/L (given)

S_e = 365 mg/L (90% required efficiency)

$$X = \frac{(3650 - 365)}{1.17 \times 1.16} = 2420\ mg/L\ MLVSS,\ or\ 3361\ mg/L\ MLSS$$

$$X = \frac{Y(S_o - S_e)\,\theta_c}{(1 + k_d\theta_c)\,\theta_h}$$

$$X = \frac{0.26\,(3650-365)(4)}{[1 + 0.05\,(4)]\,1.16}$$

X = 2454 mg/L MLVSS, or 3408 mg/L MLSS

13. Recycled sludge has 1.2 % suspended solids (volatile fraction = 0.72)

$Q_r X_r = (Q + Q_r)X$ Figure 3

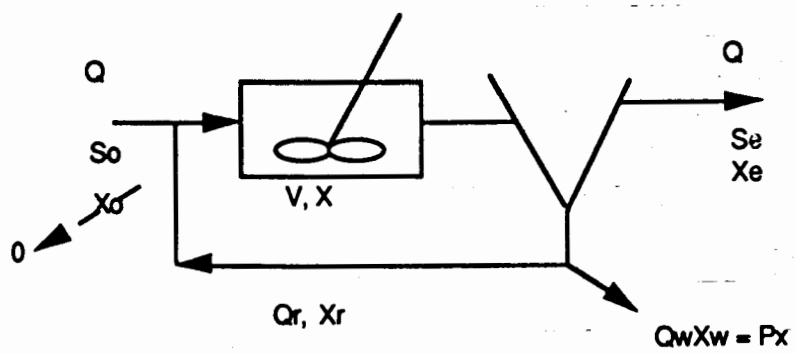


Figure 3

$Q_r X_r = QX + Q_r X$

$Q_r(X_r - X) = QX$

$\frac{Q_r}{Q} = \frac{X}{X_r - X}$ = Recycle ratio

$\frac{Q_r}{Q} = \frac{2420}{12500 \times 0.72 - 2420} = 0.37$

total $Q_r = 0.37 \times 1.5$ mgd = 0.55 mgd

or = 0.37 x 5,678 m^3/d = 2,100 m^3/d

14. Mass of sludge (MLVSS) wasted daily:

From each aeration basin

$P_x = \frac{VX}{\theta_c} = \frac{0.870 \times 8.34 \times 2420}{4}$

P_x = 4390 lb/day

$P_x = \frac{3293\ m^3\ (2420\ g/\ m^3)}{4\ d\ (1000\ g/kg)}$ = 1,992 kg/d

total wastage from both aeration basins

P_x = 4390 x 2 = 8780 lb/day (MLVSS)

= 12194 lb/day (MLSS)

P_x = 1,992 x 2 = 3,984 kg/day (MLVSS)

= 5,533 kg/d (MLVSS)

An alternate method of calculating sludge production is:

$P_x = YQ(S_o - S_e) - k_d VX$

= 0.26 (1.5)(3650 - 365) 8.34 - 0.05 (1.74) (2454) 8.34

= 10685 - 1781

= 8904 lb/day (MLVSS)

OR 12367 lb/day (MLSS)

= {0.26 (5,678 m^3/d) (3650 - 365) g/m^3 - 0.05 (2) (3,293 m^3) (2454) g/m^3} (kg/1000 g)

= 4,042 kg/day (MLVSS)

OR 5,613 kg/day (MLSS)

15. Volume of sludge wasted daily if wastage is to be done from the recycle line:

$$Q_w = \frac{8780}{9000 \times 8.34} = 0.117 \text{ mgd (12500 mg/L) MLSS}$$

(0.058 mgd from each aeration basin)

$$Q_w = \frac{4042 \text{ kg/day}}{9000 \text{ g/m}^3 \text{(kg/1000g)}} = 450 \text{ m}^3\text{/day (at 12,500 mg/L MLSS)}$$

16. Volume of sludge wasted daily if wastage is to be done from the aeration basin:

$$\theta_c = \frac{VX}{Q_w X}$$

$$Q_w = \frac{2 \times 0.87}{4} = 0.435 \text{ mgd (3400 mg/L)}$$

(0.218 mgd from each aeration basin)

$$Q_w = \frac{2 (3{,}293 \text{ m}^3)}{4\text{day}} = 1{,}646 \text{ m}^3\text{/day}$$

17. From Figure 4:

the dissolved oxygen utilization coefficient

$$a' = 0.67 \frac{\text{mg dissolved oxygen utilized}}{\text{mg soluble COD removed}}$$

the endogenous respiration coefficient

$b' = 0.2 \text{ day}^{-1}$

mass of oxygen utilized daily in each aeration basin is:

$$R_r V = a' Q (So - Se) + b' VX$$

$$R_r V = 0.67 \times 0.75 (3650 - 365) \times 8.34 + 0.2 \times \frac{1.5}{2} \times 1.16 \times 2420 \times 8.34$$

R_rV = 13766 + 3512 = 17,278 lbs/day

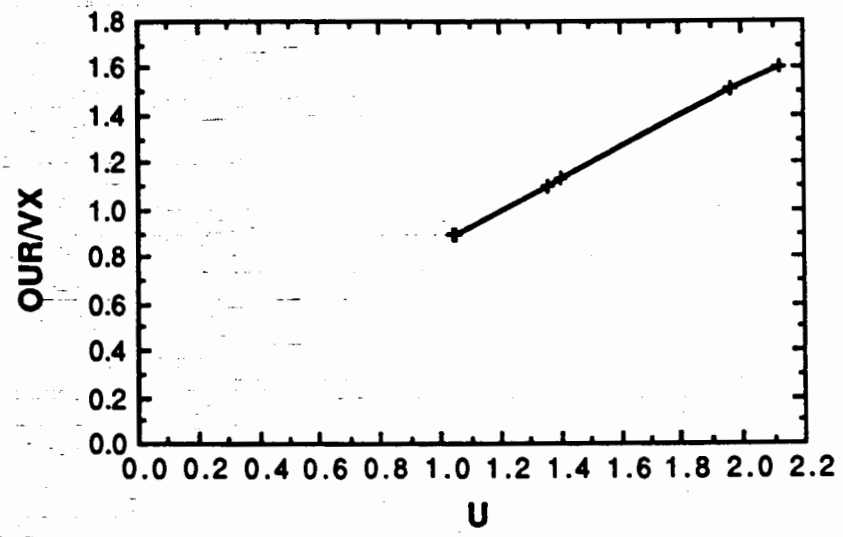


Figure 4

total mass of oxygen utilized daily

= 17278 x 2

= 34,556 lb/day

R_rV = {0.67 (5,678 m^3/d) (3650 - 365)g/m3 + 0.2 (2)(3,293 m^3) (2420) g/m3) (kg/1000 g)

= 12,497 kg/ day + 3,188 kg/day

= 15,685 kg/day

17. Nutrient Requirements

Average total nitrogen (N) concentration in influent = 200 mg/L

Total phosphorus (P) concentration in influent is negligible.

Nitrogen Requirements = 12.5% = mass of MLVSS wasted daily

Phosphorus Requirements = 2.5% x mass of MLVSS wasted daily

Nitrogen Requirements = $\frac{12.5}{100}$ x 8780 = 1098 lb/day

= 0.125 (4,042 kg/day) = 505 kg/day

Nitrogen Concentration required = $\frac{1098}{1.5 \times 8.34}$ = 88 mg/L

= $\frac{505 \text{ kg/day}}{5678 \text{ m}^3\text{/day(kg/1000g)}}$ = 89 mg/L

∴ Nitrogen is available in excess.

Phosphorus Requirements = $\frac{2.5}{100}$ x 8780 = 220 lb/day

= 0.25 (4,042 kg/day) = 101 kg/day

Phosphorus Concentration required = $\frac{220}{1.5 \times 8.34}$ = 18 mg/L

= $\frac{101}{5678/1000}$ = 18 mg/L

18 mg/L P should be added to influent.

ACTIVATED SLUDGE PROCESS

PROCESS DESCRIPTION

The activated sludge process is probably the most commonly used system for the biological treatment of municipal and industrial wastewaters. The essential components of the activated sludge plant are an aeration tank with the necessary aeration equipment, a final clarifier in which the biological solids can be separated from the liquid effluent, and the necessary pumps to recycle the concentrated solids to the aeration tank. The incoming wastewater is mixed with the returned sludge solids in the aeration tank and this mixture is aerated for about two to six hours. The intensity of aeration must be sufficient to mix the tank contents. The mixture of incoming wastewater and the activated sludge solids is commonly called the mixed liquor. Most of the settled sludge is returned from the clarifier to the aeration tank; however, a portion of the sludge is wasted. This excess sludge is a result of bacterial growth as well as the accumulation of nonbiodegradable suspended solids which enter the system.

The activated sludge contains a mixture of a wide variety of microorganisms which are capable of degrading different organic compounds. Inactive suspended materials also accumulate in the biological floc which forms during the aeration. The bacteria and other microorganisms in the activated sludge are generally found in most municipal wastewaters. The mass of activated sludge increases as the microorganisms degrade the organic material in the wastewater and grow in the aerobic environment of the aeration tank. The bacterial growth rate during the initial stages is very high because the substrate concentration is relatively high compared to the bacterial population. After a week or two of operation of the activated sludge treatment plant, the desired mixed liquor suspended solids concentration and the desired degree of treatment are attained.

The activated sludge process has been modified in numerous ways since 1914 when the process was first applied to wastewater treatment. In the original process which is called the conventional activated sludge process, the wastewater and return sludge entered at one end of a long narrow tank. The mixed liquor flowed in the longitudinal direction and with the help of the diffused air aeration system, a spiral flow resulted. The mixed liquor left the other end of the long narrow tank.

A number of the modifications in the activated sludge process are illustrated in Figure 3-1. The basic differences occur in the point at which the incoming

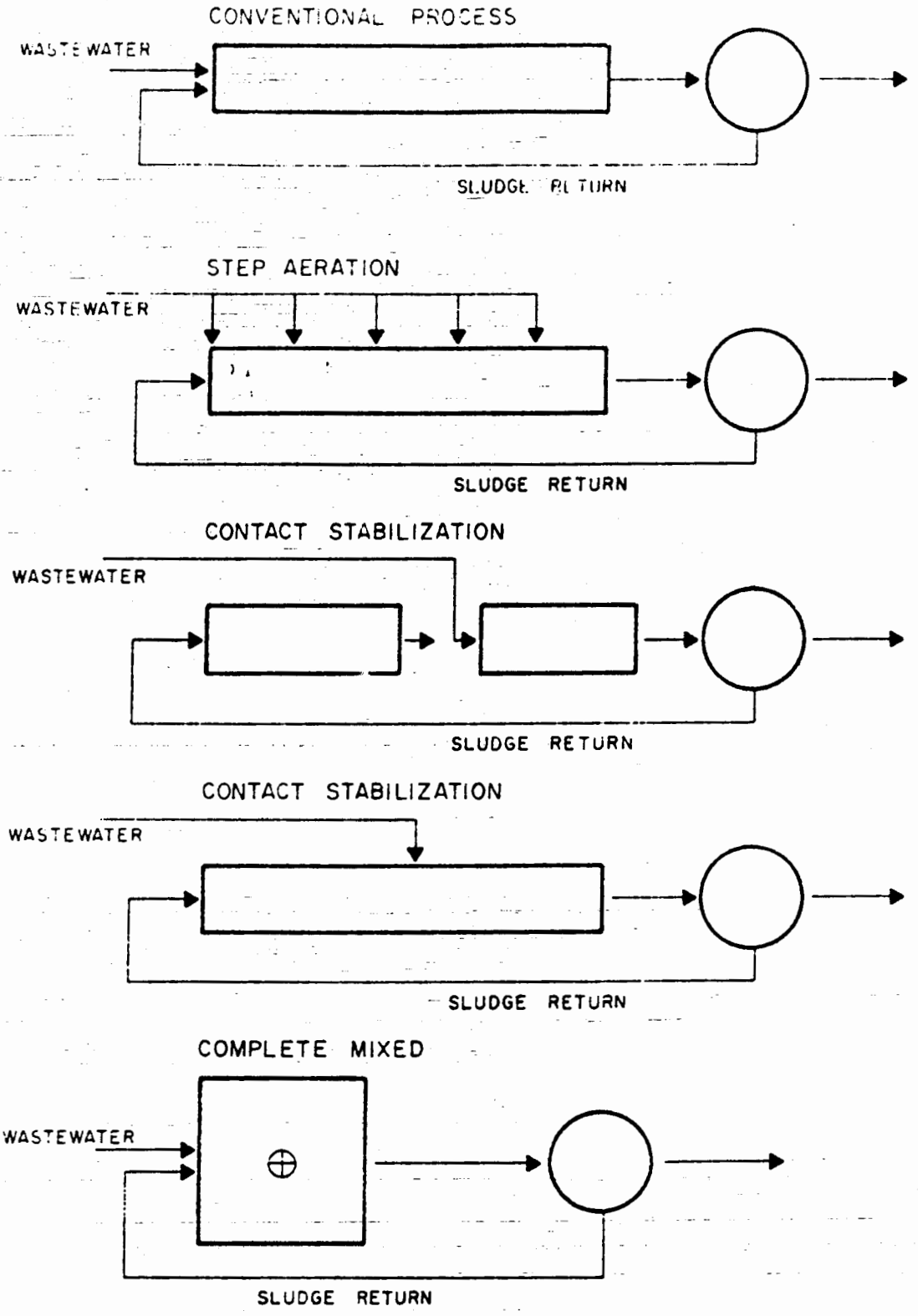


FIG. 3-1 AERATION TANK ARRANGEMENTS

wastewater is introduced into the aeration tank and mixed with the return sludge, the reaeration of the return sludge prior to coming into contact with the incoming wastewater and the type of flow pattern that might be typical of the system and operation.

Aeration of the return sludge has been practiced for many years. The original purpose for reaeration was to maintain the return sludge aerobic because the sludge would turn anaerobic in the final clarifier since the quantity of return sludge was relatively small. Kraus (1945) and Hatfield (1931) pumped anaerobic digester supernatant into the reaeration tank and effectively treated the supernatant with the return sludge. In both cases the concentration of mixed liquor suspended solids was high and a long aeration time was maintained. This type of system also minimized the shock loads to the aeration tank since the flow of digester supernatant was distributed more uniformly throughout the day and a higher concentration of solids was available to utilize the organic material in the supernatant.

The contact stabilization process was introduced independently by Ullrich and Smith (1951) as well as by Eckenfelder and Grich (1956). This process was based on observations made in the conventional activated sludge system which indicated that the soluble fraction of the organic material in wastewater was almost entirely removed after very short aeration times. Therefore in the contact stabilization process, the incoming wastewater is mixed with the return reaerated sludge for very short times of about 30 minutes to two hours. The sludge solids are then separated from the liquid and the concentrated sludge is reaerated prior to being mixed with the incoming wastewater. The aeration times in the contact zone must be long enough to permit a reduction of the concentration of soluble organics to the predetermined effluent concentration. However, in the contact zone, the nonsoluble colloidal and particulate materials are also incorporated in the activated sludge floc particles and are removed in the final clarifier. The sludge is aerated for an additional two to four hours in the stabilization or reaeration tank. In many plants, the stabilization zone and the contact zone are not physically separated; therefore, it is difficult to calculate the exact time which may be attributed to contact and to stabilization.

The completely mixed system has been used extensively in laboratory-scale units in evaluating the various parameters which affect the activated sludge process. However, this process has only been recently installed for the treatment of municipal and industrial wastewaters. The development of surface and mechanical aerators which may be used separately or in conjunction with diffused air systems has made the use of completely mixed tanks more popular. In the completely mixed tanks, the concentration of oxygen and of the substrate is constant at each point throughout the entire tank volume. The system permits automatic control of oxygen transfer and

is relatively resistant to shock loading since the influent wastewater is distributed uniformly throughout the entire tank volume.

The extended aeration process is a modification of the activated sludge process and is characterized by relatively low organic loadings; therefore, the sludge which is produced during biodegradation is also stabilized to some extent in the aeration tank. However, in the extended aeration process the nonbiodegradable solids tend to accumulate and must be removed periodically.

The activated sludge process can be operated as the conventional activated sludge process and the contact stabilization process. The flow pattern in the aeration tanks can be categorized as the plug flow or the completely mixed. The performance of the various process modifications and flow schemes can only be compared if each system is operated at an identical organic loading and with identical wastewater. The results of laboratory-scale experiments comparing contact stabilization and the conventional activated sludge processes indicated that the effluent BOD concentration for each process was almost identical at organic loading rates of 0.40 to 1.90 pounds of BOD/pound of mixed liquor suspended solids -day (Water Pollution Research Laboratory, 1967, 1968).

PERFORMANCE OF THE ACTIVATED SLUDGE PROCESS

The first order substrate removal model does not normally apply for the organic loadings at which most activated sludge plants are operated. Therefore, data are compared on the basis of detention time, BOD volume load (pounds of BOD per 1000 gallons of tank volume per day) and organic loading (pounds of BOD per pound mixed liquor suspended solids or per pound of mixed liquor volatile suspended solids per day). However, neither the MLSS nor MLVSS concentrations define the inert fraction of the solids present in the mixed liquor. The nonbiodegradable solids in the mixed liquor include the inert suspended solids in the influent and in the return sludge and may be represented as Equation 3-1 which can be modified and used to calculate the nonbiodegradable suspended solids.

$$QX_{on} = WX_n + QX_{en} \qquad 3\text{-}1$$

$$X_n = X_{on} \cdot \frac{G}{t} \qquad 3\text{-}2$$

in which:

X_{on}, X_{en} = influent and effluent nonbiodegradable suspended solids (mg/l)

X_n = nonbiodegradable suspended solids in the aeration tank (mg/l)

G = sludge age (days) (total suspended solids in the system divided by the total suspended solids leaving the system per day)

t = theoretical detention time (days) (aeration tank volume divided by wastewater flow rate)

The interrelationship between the concentration of nonbiodegradable suspended solids in the mixed liquor, the sludge age, and the theoretical aeration time are shown in Figure 3-2. These curves are based on an influent nonbiodegradable suspended solids concentration of 50 mg/l. Therefore, at a sludge age of four days and a theoretical detention time of six hours the accumulation of nonbiodegradable suspended solids in the mixed liquor is about 750 mg/l.

The relationship of the nonbiodegradable fraction of the mixed liquor suspended solids and the ratio of the influent BOD to influent suspended solids is presented in Figure 3-3. These data are from pilot-scale studies conducted by Wuhrmann (1964) and from the experimental work conducted at the Govalle Treatment Plant in Austin, Texas, and the Hyperion Treatment Plant in Los Angeles, California. The accumulation of nonbiodegradable suspended solids in the mixed liquor range from 40 to 70 percent of the total mixed liquor suspended solids and was affected by the ratio of influent BOD to influent suspended solids (S_o/X_o) which ranged from 0.5 to 1.75.

The curves in Figure 3-3 reflect the efficiency of primary clarification at the particular treatment plant. The relatively high percentage of nonbiodegradable solids in the mixed liquor at the Govalle Plant is indicative of no primary clarification. The relatively low ratio reported for the Hyperion Plant is typical of efficient primary treatment. The data reported by Wuhrmann (1964) for the operation of a pilot plant reflect the different analytical procedures used for determining suspended solids. The Wuhrmann data are based on a membrane filtration technique which captures about 10 to 15 percent more of the suspended solids than the glass fiber or paper filter techniques used at the Govalle and Hyperion Plants. If the results reported by Wuhrmann are adjusted, the data would compare quite favorably.

The operating conditions under which these data were collected were influent BOD of 90 to 200 mg/l, and influent suspended solids concentrations of 70 to 250 mg/l. The mixed liquor suspended solids concentrations was 600 to 6000 mg/l and the BOD loading rate varied from 0.17 to 2.0 lb BOD/lb MLSS-day. The curves indicate that the influence of the loading is relatively

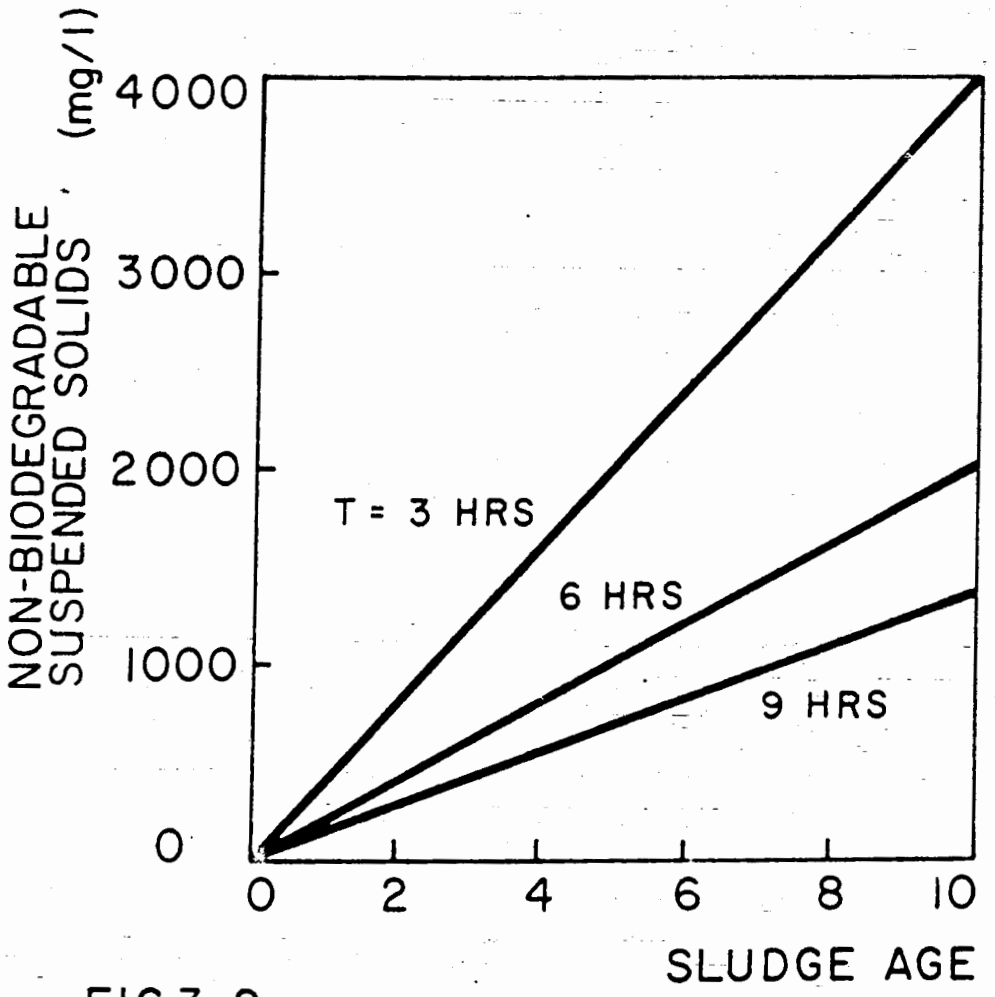


FIG.3-2
NON-BIODEGRADABLE SUSPENDED SOLIDS IN MIXED LIQUOR

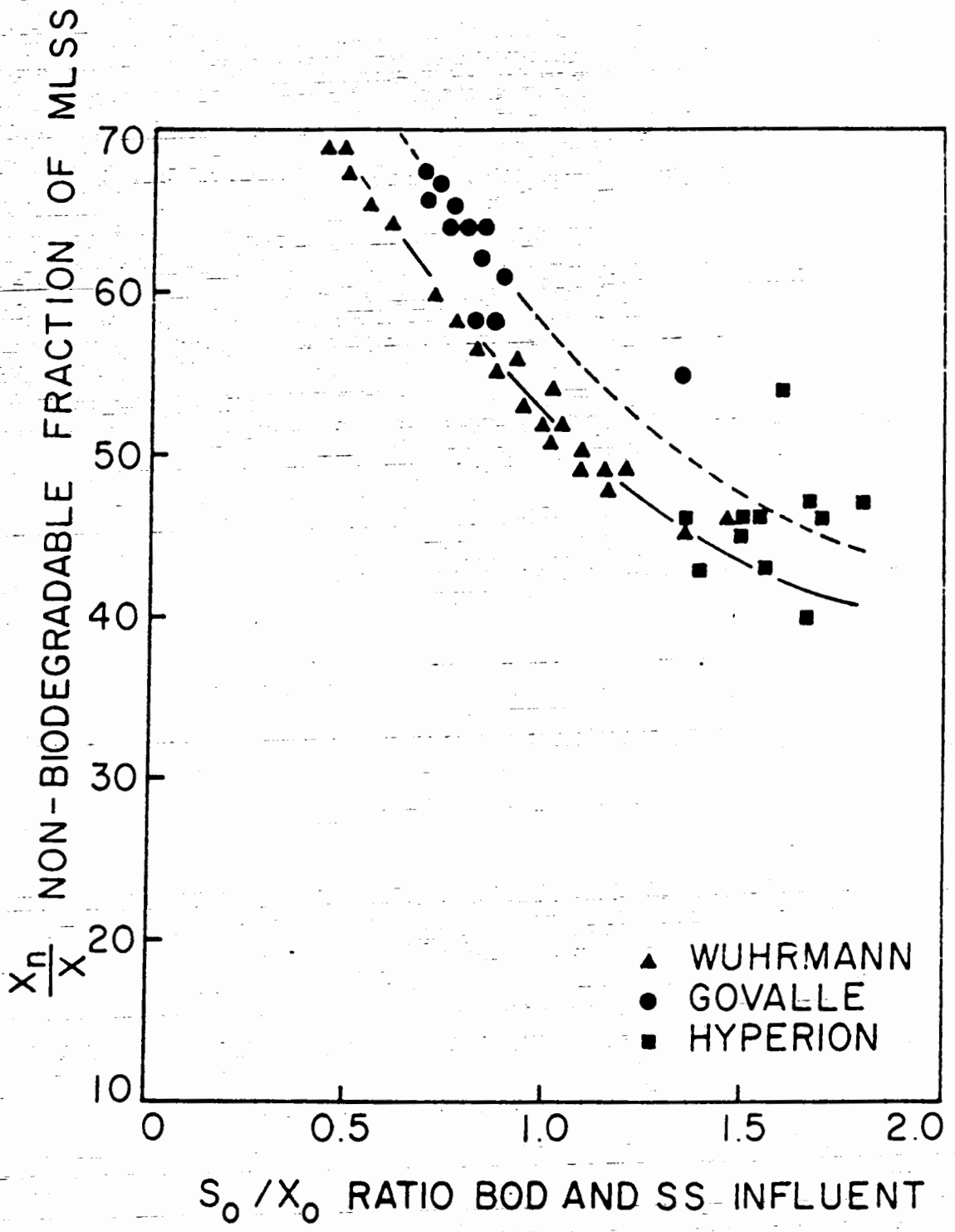


FIG.3-3
NON-BIODEGRADABLE SOLIDS OF MIXED LIQUOR

negligible At times, it may be useful to compare data based on the mixed liquor active suspended solids concentration (MLASS) which can be obtained by subtracting the nonbiodegradable fraction from the total suspended solids concentration. For example, at a loading rate of 0.3 lb BOD/lb MLSS - day, the rates of BOD removal based on the active mixed liquor suspended solids concentration would be 0.55 and 0.85 lb of BOD/lb MLASS - day, respectively. The ratio of MLASS to MLSS for Hyperion and Govalle were 0.55 and 0.35, respectively. These data indicate that the loading rate at the Govalle Plant is about 60 percent higher at the Hyperion Plant. Loading based on volatile suspended solids would exhibit similar differences. However, the mixed liquor suspended solids (MLSS) concentration is generally the only measure of the solids in the aeration tank at most plants; therefore, a comparison of performance data for various plants must be based on the total mixed liquor suspended solids.

The relationship between the effluent filtered BOD and the BOD loading (lb BOD/lb MLSS - day) is illustrated in Figure 3-4. The BOD loading ranged from 0.2 to 1.0 lb BOD/lb MLSS - day. The effluent filtered BOD of the Govalle samples scattered widely from about three mg/l to over 11 mg/l for loadings of less than 0.2 to about 0.5 lb BOD/lb MLSS - day. The scatter in the data from these experiments was considerably greater than that for the data observed at Hyperion which indicated a slight increase in the effluent BOD as the loading increased from 0.2 to almost 1.4 lb BOD/lb MLSS - day. The Hyperion data seemed to indicate a linear relationship between the effluent filtered BOD and the BOD loading range.

It should be pointed out that data presented in Figure 3-4 are not comparable theoretically since the Hyperion Plant and one of the three plants at the Govalle Plant were operated as the conventional activated sludge process whereby the other two plants at the Govalle Plant were operated as the contact stabilization process. If one considers that the removal rate of soluble substrate is not affected by the nonsoluble organic material, the relationship which results comparing the soluble BOD loading rates and the effluent soluble BOD concentration can be calculated and plotted as shown in Figure 3-5. The curves indicate that there is a linear relationship between the effluent soluble BOD and the soluble BOD loading. The loading rates for the contact stabilization plant were based only on the volume of the contact zone, the MLSS in the contact zone, and the incoming wastewater flow. These data indicate that the concentration of soluble material in the effluent increases as the loading expressed as soluble BOD also increases. In general, at the same soluble BOD loading the residual BOD at the Govalle Plant was higher than that reported at the Hyperion Plant. The results of laboratory-scale experiments at the Govalle Plant indicate that the soluble BOD in the effluent of contact stabilization process was between three and six mg/l at soluble organic loading rates of 0.3 to 2.3 lb BOD/lb MLSS - day

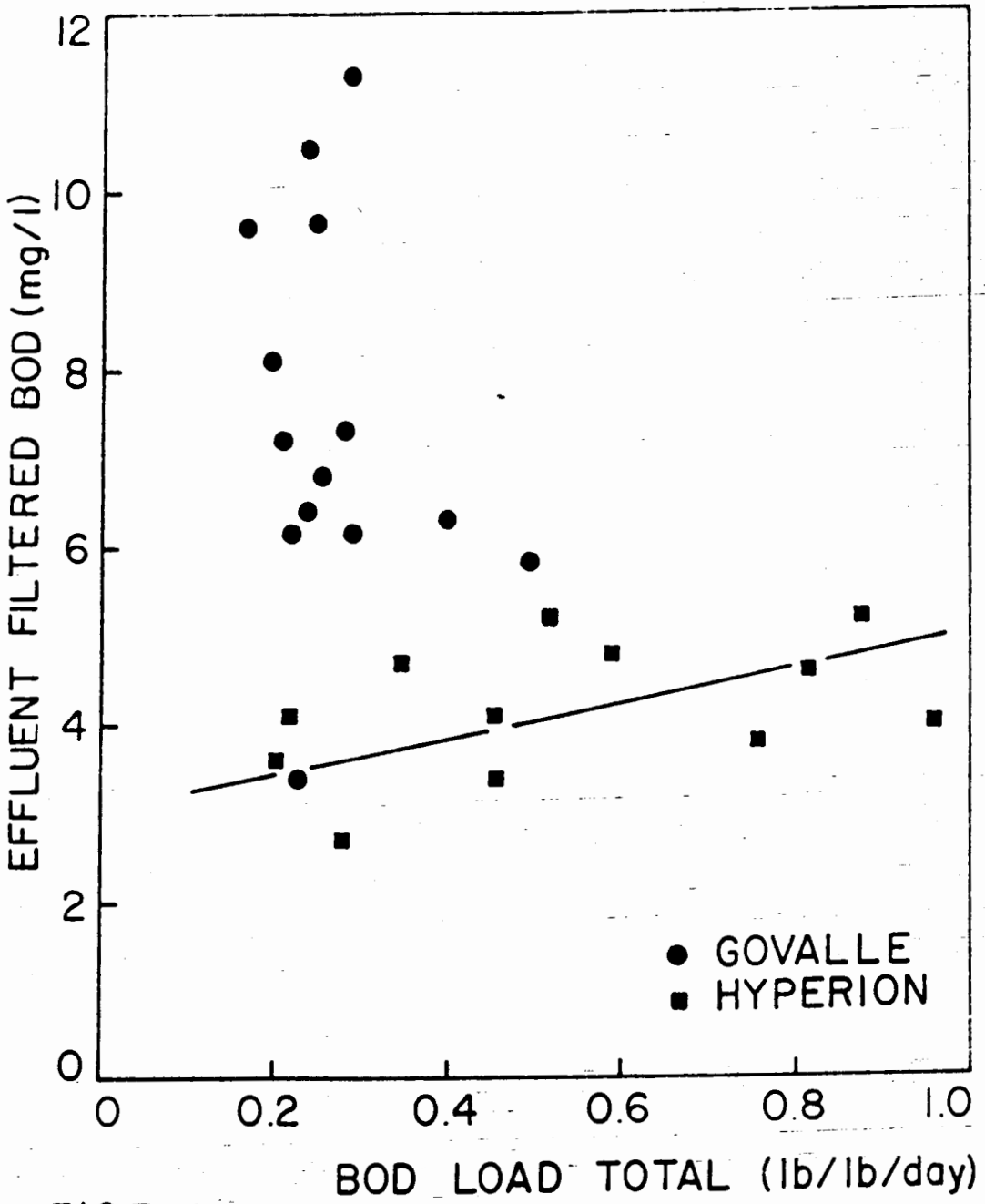


FIG.3-4

TOTAL LOAD AND SOLUBLE EFFLUENT

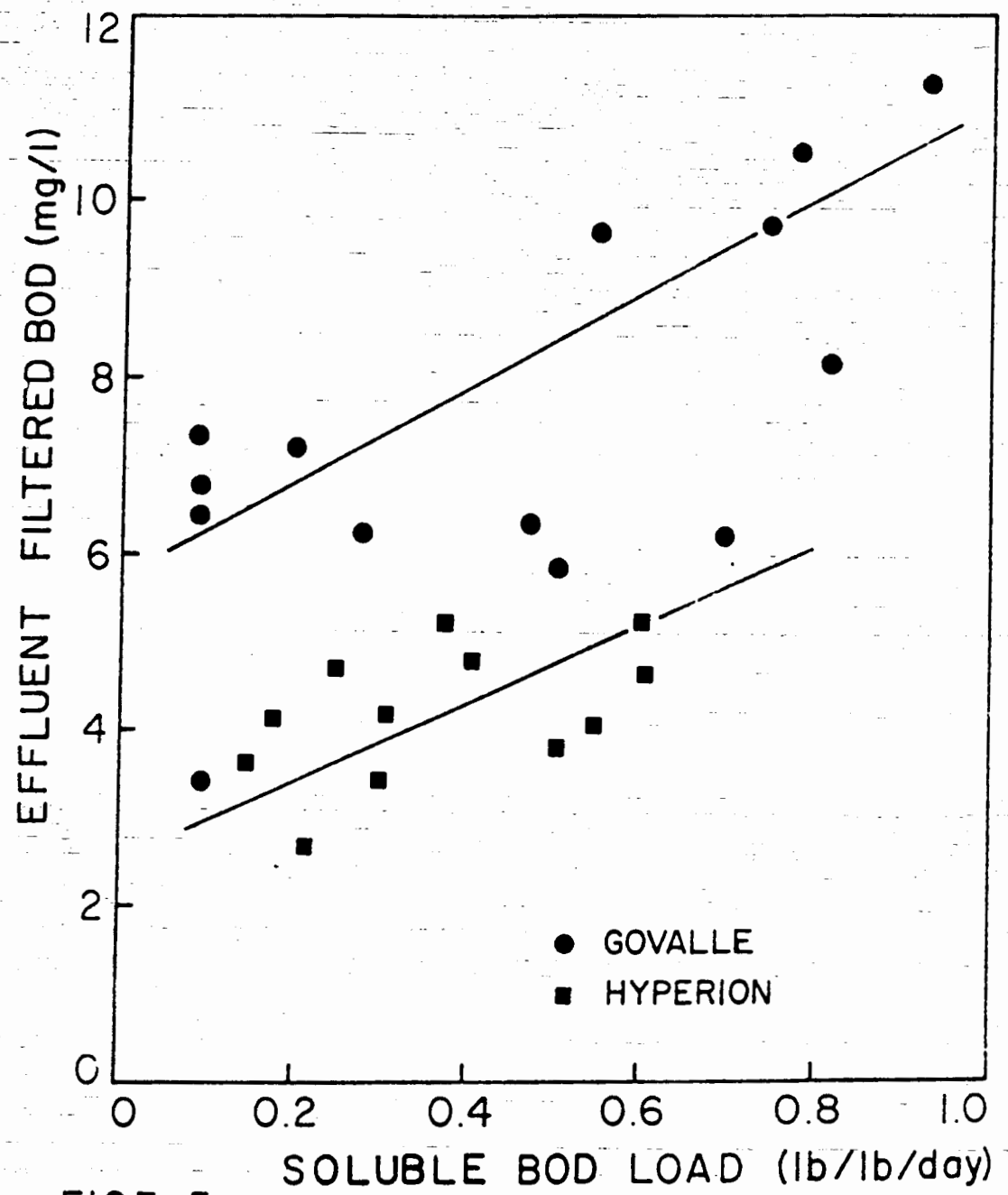


FIG.3-5

SOLUBLE LOAD AND EFFLUENT

(Berryhill, 1970). These residual BOD concentrations are in the same range as that reported for the Hyperion Plant effluent. The relationship between the effluent soluble COD and the soluble COD loading rates are presented in Figure 3-6. These data indicate that the effluent soluble COD increases at a much more rapid rate with increasing soluble COD loading at the Hyperion Plant than at the Govalle Plant.

The discrepancy between the laboratory-scale data and the full-scale data observed at the Govalle Plant may be explained by the fact that the laboratory-scale runs were performed about six months after the full-scale experiments, and the composition of the wastewater was different. The relatively high effluent BOD at the Govalle Plant indicate that these residual organic materials are degradable but at an extremely show rate.

The more useful presentation of data for practical purposes is the relationship between the total effluent BOD and the loading rate expressed in terms of total BOD entering the plant. This relationship is presented in Figure 3-7, for data observed at the Hyperion Plant, the Govalle Plant, and the pilot-plant studies by Wuhrmann (1964). These data scatter considerably over a loading rate of about 0.1 to almost 2.0 lb BOD/lb MLSS - day. The results of the three different experiments should be discussed individually.

The results for the Hyperion Plant were reported by Smith and Eilers (1969). The wastewater flow for all the experiments was 50 MGD. The theoretical aeration times were four, five, and six hours, respectively, and were maintained by using different numbers of aeration tanks. The loading rate was changed by varying the mixed liquor suspended solids concentration in the aeration tank from 600 to 3500 mg/l. The surface area of the settling tanks were constant for all experiments and provided an overflow rate of about 530 gallons/sq ft-day. The increase in total BOD in the effluent was the result of the increased effluent suspended solids concentration caused by the increased loading rates.

During the Govalle experiments, the wastewater flow varied slightly and the organic loading was changed by controlling the mixed liquor suspended solids concentration in the aeration tanks. The overflow rates for the clarifiers fluctuated from 750 to 1000 gallons/sq ft - day. Therefore, part of the scatter of the effluent BOD is caused by the suspended solids in the effluent. However, during most of the runs, partial nitrification took place. It is therefore safe to assume that the nitrification continued in the BOD bottle resulting in higher BOD concentrations than would be expected for only carbonaceous material.

Wuhrmann, on the other hand, used three pilot plants in parallel in the experiments in Zurich, Switzerland. The detention times used were 25, 50,

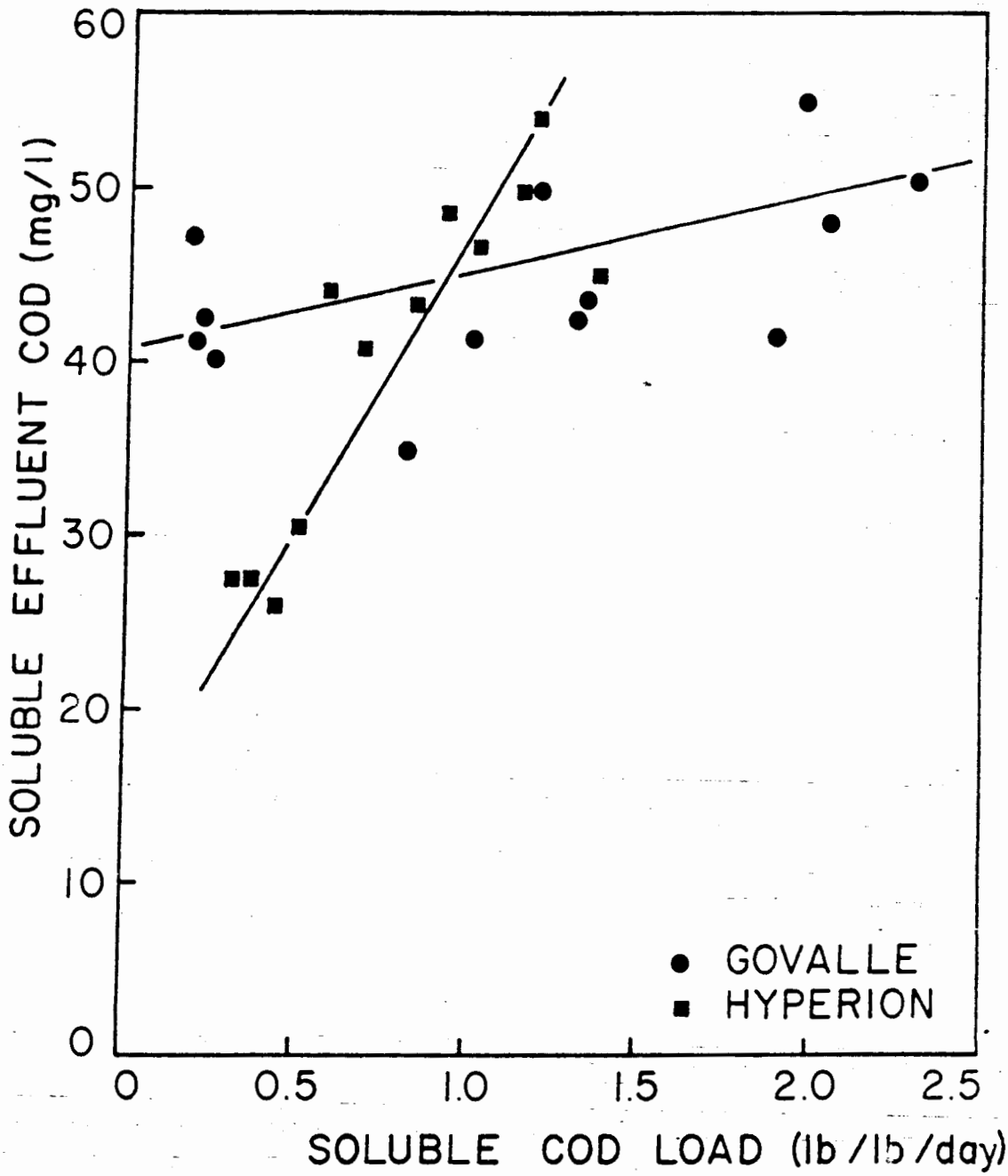


FIG.3-6
SOLUBLE COD LOAD AND EFFLUENT

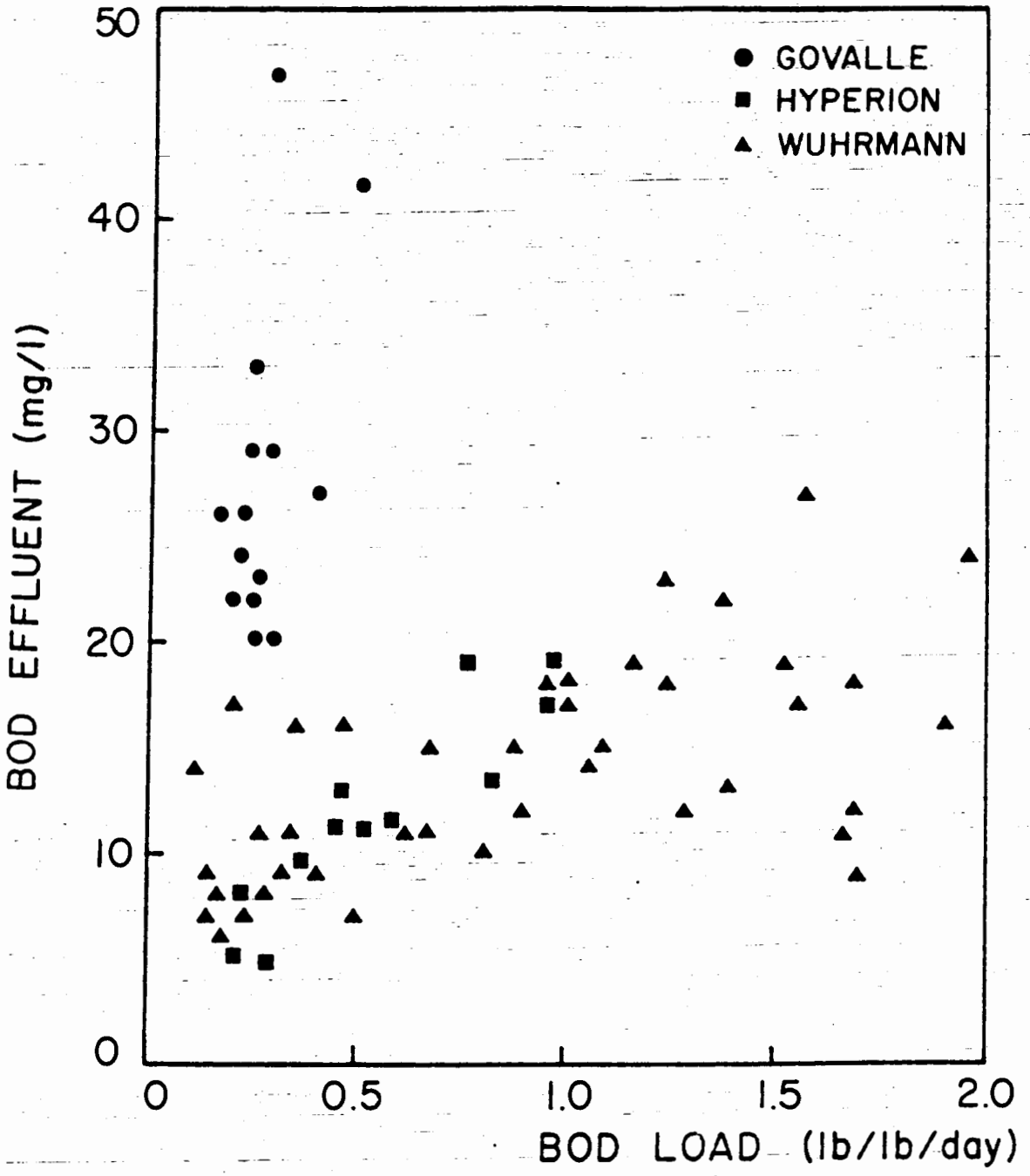


FIG.3-7
BOD LOAD AND BOD EFFLUENT

and 125 minutes, respectively. The mixed liquor suspended solids concentrations were maintained at 3300 and 6000 mg/l, respectively. The overflow rates to the clarifiers were about 530 gallons/sq ft - day which was about the same as that reported for the Hyperion experiments. Therefore, the data reported by Wuhrmann compare favorably with that reported by Hyperion.

The data presented in Figure 3-5 indicated that the soluble effluent BOD concentrations only increased slightly with increasing loading. Therefore, it can be expected that the higher total effluent BOD concentrations are caused primarily by the increased suspended solids concentrations in the effluent. The effluent suspended solids are plotted versus the effluent BOD in Figure 3-8. These data indicate that the effluent BOD concentration increases as the suspended solids concentration increases. The scatter in this particular plot is caused by the number of factors including nitrification in the BOD bottle which results in a relatively high BOD at relatively low suspended solids concentration and the activity of the suspended solids. The suspended solids of a highly loaded plant will exert a higher BOD in the effluent than those solids from a relatively lightly loaded plant. For these data the ratio of the concentrations of total BOD to the suspended solids (BOD/SS) is in the range of 0.55 to 1.10.

The concentration of suspended solids in the clarifier effluent is affected by the hydraulic overflow rate, the solids loading rate to the clarifier, and the settling and flocculation characteristics of the sludge. At a constant overflow rate and initial suspended solids concentration, the settling and flocculation of the sludge are the only factors which influence the effluent concentration. These sludge properties can be related to sludge age. Therefore, the effluent concentration of suspended solids were plotted against sludge age for the data reported by Wuhrmann and for the experiments at the Hyperion Plant since the overflow rate for these experiments was the same (530 gpd/sq ft). These data are presented in Figure 3-9 and indicate that the effluent suspended solids concentration increases as the sludge age decreases. However, the effluent suspended solids concentration would increase sharply for a longer sludge age typical of the extended aeration systems. Temperature is also a factor as indicated by higher effluent suspended solids concentrations at lower temperatures as reported by Wuhrmann.

The performance of the activated sludge process treating municipal wastewater is controlled in some respect by the concentration of suspended solids in the effluent. The suspended solids in the effluent of a well operated secondary clarifier are essentially small floc particles (pin flocs) and single microbial cells. As a concentration of ciliated protozoa increases, the effluent suspended solids decrease. These protozoa are predators of bacteria and consume the fine floc particles. The growth rate of the protozoa in most cases is much lower than that for the bacteria. Therefore, as the sludge age increases, there is a better chance for the protozoa concentration to

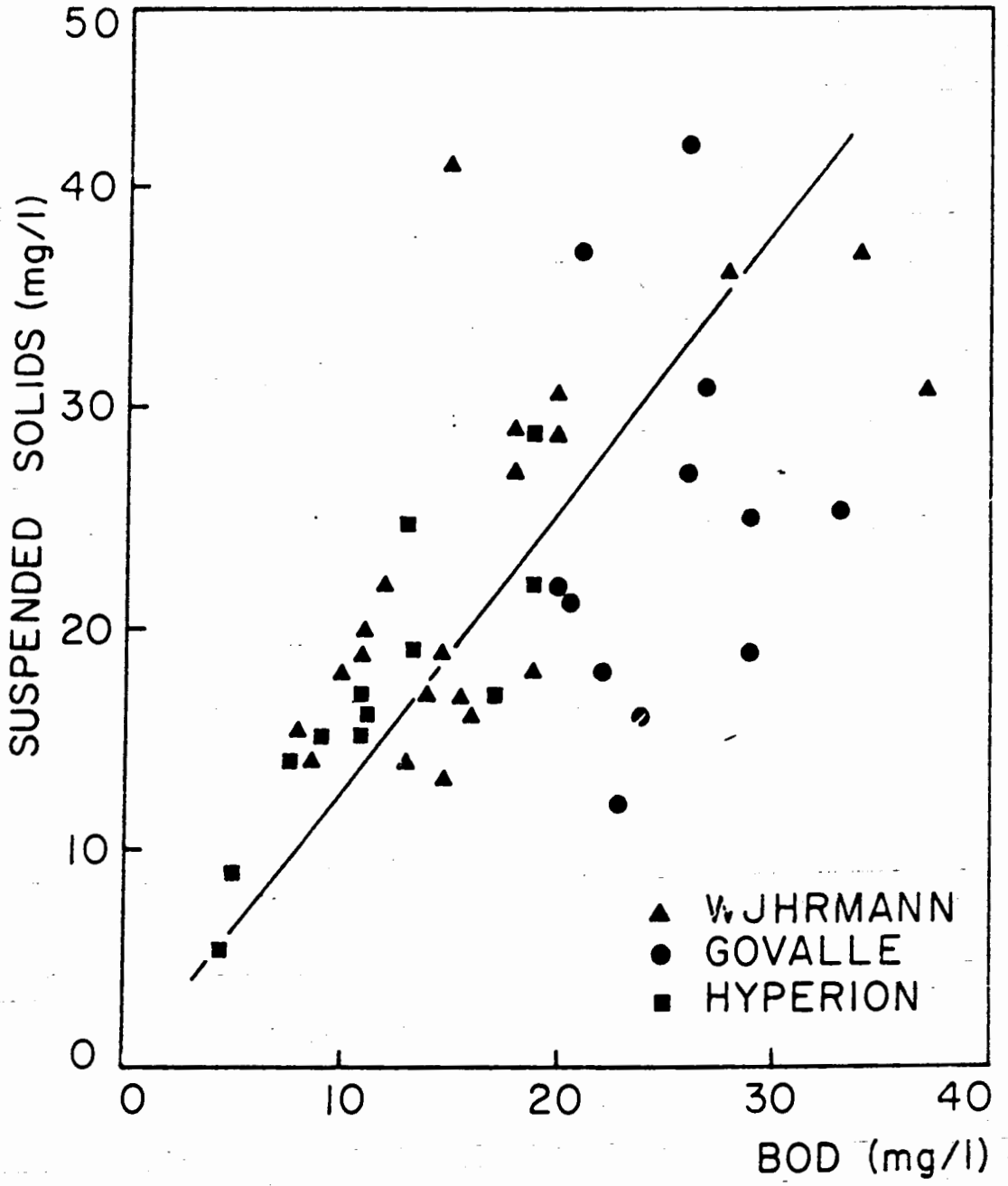


FIG.3-8
BOD AND SUSPENDED SOLIDS
EFFLUENT

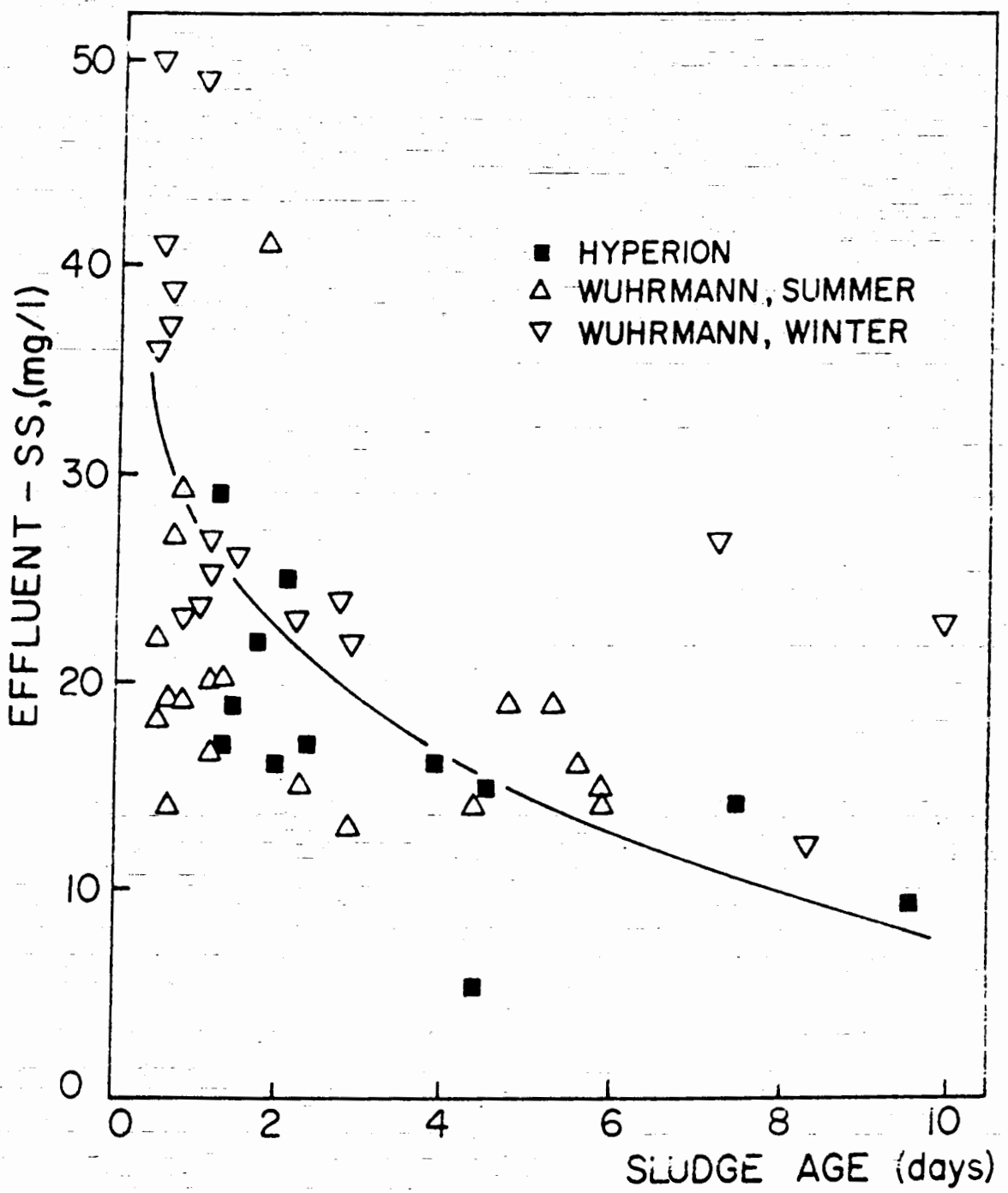


FIG.3-9
EFFLUENT SS AND SLUDGE AGE

increase resulting in a reduction in the concentration of suspended solids in the effluent and an improved effluent quality. Temperature also affects the performance of a clarifier. As the temperature decreases, the viscosity of the water increases and thereby reduces the settling rate of the floc particles. Therefore, a higher concentration of suspended solids in the effluent is observed at low temperatures.

Lower overflow rates in the final clarifier did not seem to be the only solution to increasing the efficiency of the final settling process. Other remedial procedures may be dictated by the characteristics of the sludge. In some cases, flocculating agents may be required to produce a more stable and more settleable floc. The gases resulting from denitrification or from the capture of air bubbles may cause floating floc particles, and some way of releasing the gas is required to improve settling. Final clarifiers may be plagued with density currents which affect the efficiency of solids removal by possibly carrying suspended solids from the sludge blanket up over the effluent weirs.

The mathematical model presented in Equation 3-3 may be used to calculate oxygen requirements if no nitrification takes place.

$$\frac{R}{X} = a' \left(\frac{S_o - S_e^*}{Xt}\right) + b' \qquad 3\text{-}3$$

In practice the oxygen requirements per unit volume may be more useful. This equation may be modified to include the oxygen requirements for nitrification.

$$R = \frac{8.34}{1000}\, a' \frac{24\,(S_o - S_e^*)}{t} + b'X + 4.60 \frac{24 \Delta NH_3}{t} \qquad 3\text{-}4$$

in which:

R	=	oxygen uptake per unit volume (lb/1000 gal/day)
t	=	theoretical aeration time (hours)
S_o	=	influent BOD (mg/l)
S_e^*	=	soluble effluent BOD (mg/l)
X	=	MLSS (mg/l)
ΔNH_3	=	ammonia removal (mg/l)

a' = constant relating to the oxygen required for sludge synthesis (for municipal wastewater = 0.53 lb/lb)

b' = endogenous oxygen uptake rate (for municipal wastewater = 0.15 lb/lb/day).

In most municipal biological treatment plants the residual soluble effluent BOD is three to seven mg/l which in fact is about five percent of the influent concentration, and $S_o - S^* = 0.95S_o$. Therefore, a' = 0.53 lb/lb, and $a'(S_o - S^*) = 0.05S_o$. Therefore, equation 3-4 may be rewritten as Equation 3-5.

$$R = \frac{8.34}{1000}\left[0.5\frac{24S_o}{t} + 0.15X + 4.6\frac{24\Delta NH_3}{t}\right] \qquad 3\text{-}5$$

These equations can be used to calculate the total oxygen requirements per unit volume of aeration tank per day. However, the distribution of oxygen required to satisfy the oxygen uptake rates which vary throughout the aeration tank and throughout the course of the day is not provided. The maximum oxygen uptake rate was observed in laboratory and full-scale experiments to occur at the end of the daily peak loading. Therefore, the oxygen uptake rate reaches a peak normally in late afternoon when the rate of flow and the strength of the incoming wastewater begin to decrease. The ratio of the peak oxygen uptake rate to the daily average oxygen uptake rate is much higher in those plants which are highly loaded than in the plants which have a low organic loading. In the low loaded plants, the endogenous oxygen uptake rate tends to equalize the peak oxygen uptake rates which may develop. The ratio of oxygen uptake rates is also lower than the ratio of the peak organic loading to the average organic loading for a given day. The results of laboratory-scale studies indicate that some of the suspended solids which accumulate in the mixed liquor undergo degradation after the peak organic loading has passed through the plant (Berryhill, 1970). This oxygen requirement caused by the degradation of the insoluble organic material may be attributable to the fact that these organic solids undergo degradation at a much lower rate than the dissolved organic material. Therefore, for design purposes, it can be assumed that the distribution of oxygen uptake rates at a treatment plant is similar to the distribution of incoming wastewater flow. The oxygen uptake rate also varies with the length of longitudinal tanks. The biodegradation of soluble organic material is high compared to that for the nonsoluble material. Therefore, the oxygen uptake rate in the aeration tank is almost always higher in the first part of the tank. The oxygen uptake rate will then decrease as the concentration of soluble organic material decreases. The results of experimental studies point to this variation in oxygen uptake rates and the peaks that can occur. These data presented in Figure 3-10 indicate the relationship of oxygen uptake rate to aeration time for a batch contact

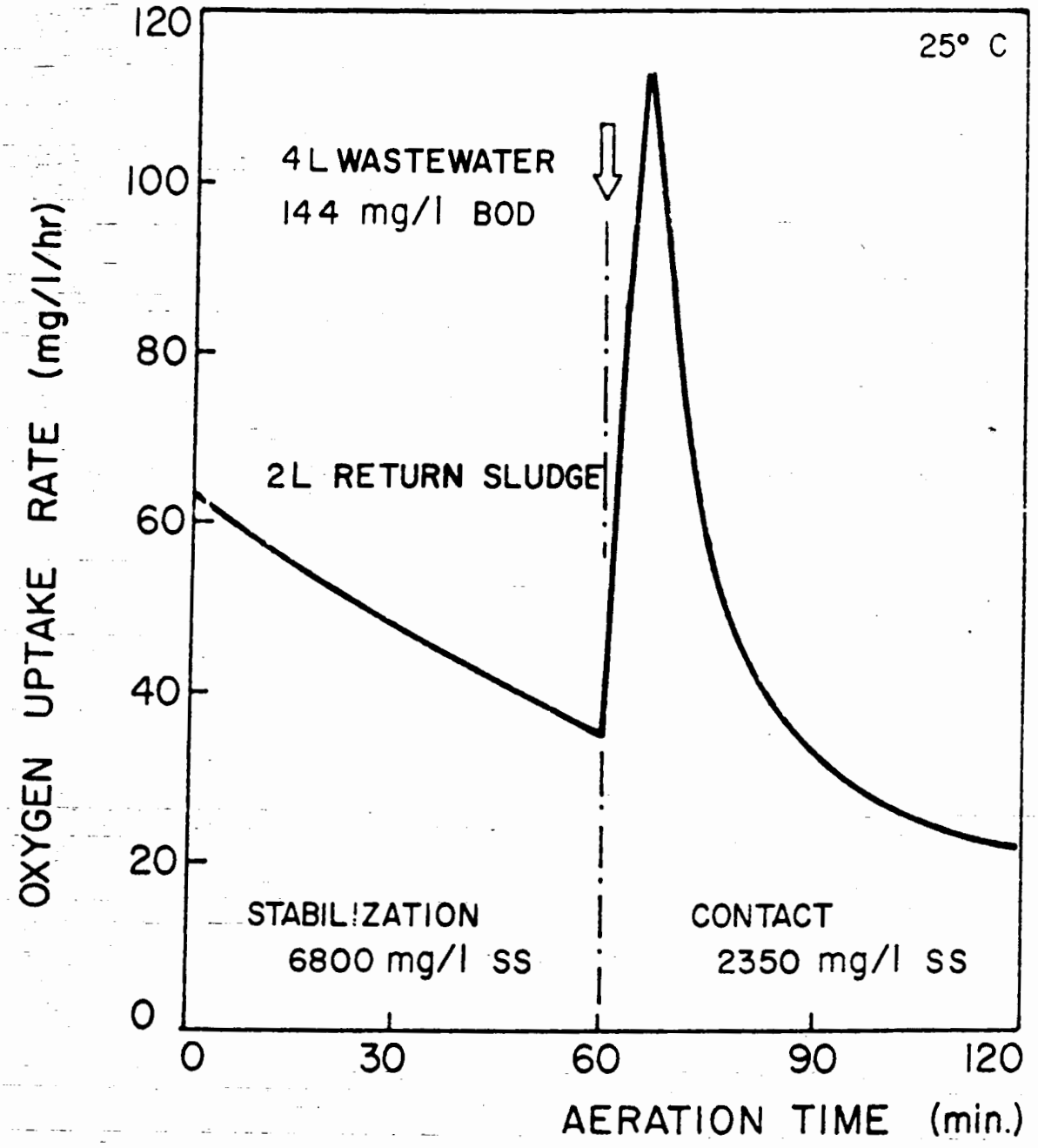


FIG.3-10
OXYGEN UPTAKE RATES (BATCH)

stabilization system. After the wastewater is introduced, the oxygen uptake rate increases sharply until a peak is reached and decreases markedly with time. This peak coincides with the rate of utilization of the soluble organic material. In the full-scale plant where the contact and stabilization zones were not physically separated, this peaking of oxygen uptake rate was reduced since some degree of backmixing was observed. This backmixing causes mixing of the influent with a larger volume of mixed liquor and tends to equalize the oxygen uptake rate.

The distribution of incoming wastewater to various points in the aeration tank in the step aeration process also tends to maintain a relatively constant oxygen uptake throughout the entire length of the tank. The results of oxygen uptake profiles determined in the contact stabilization plant and the conventional activated sludge system at the Govalle Treatment Plant in Austin, Texas are shown in Figure 3-11. These results indicate a similar pattern, namely that the oxygen uptake rate is highest shortly after the influent wastewater is mixed with return sludge and decreases rapidly to an equilibrium level. After this point, the oxygen uptake rate decreases slightly to a minimum rate at the effluent of the aeration basin.

AERATION

The oxygen required for biodegradation of organic material in wastewaters is usually introduced into the aeration tank as diffused air or by mechanical equipment. The aeration equipment is normally evaluated under standard conditions of a water temperature of 20°C and an oxygen concentration of zero. The aeration equipment is classified according to oxygenation capacity (OC) expressed in units of pounds of oxygen per unit volume of aeration tank (lb O_2/1000 gal-day). At times, the aeration efficiency (N_o) is also provided in terms of pounds of oxygen per horsepower hour (lb/HP-hr). However, the oxygen transfer is different under process conditions than under standard conditions. An oxygen concentration of about two mg/l is generally maintained in the aeration basin although it may be possible to operate at lower dissolved oxygen concentrations.

The oxygen transfer rate constant ($k_L a$) is related to the oxygenation capacity by Equation 3-6.

$$OC = (k_L a)\ (C_s) \qquad 3\text{-}6$$

in which:

C_s = concentration of oxygen in water at saturation

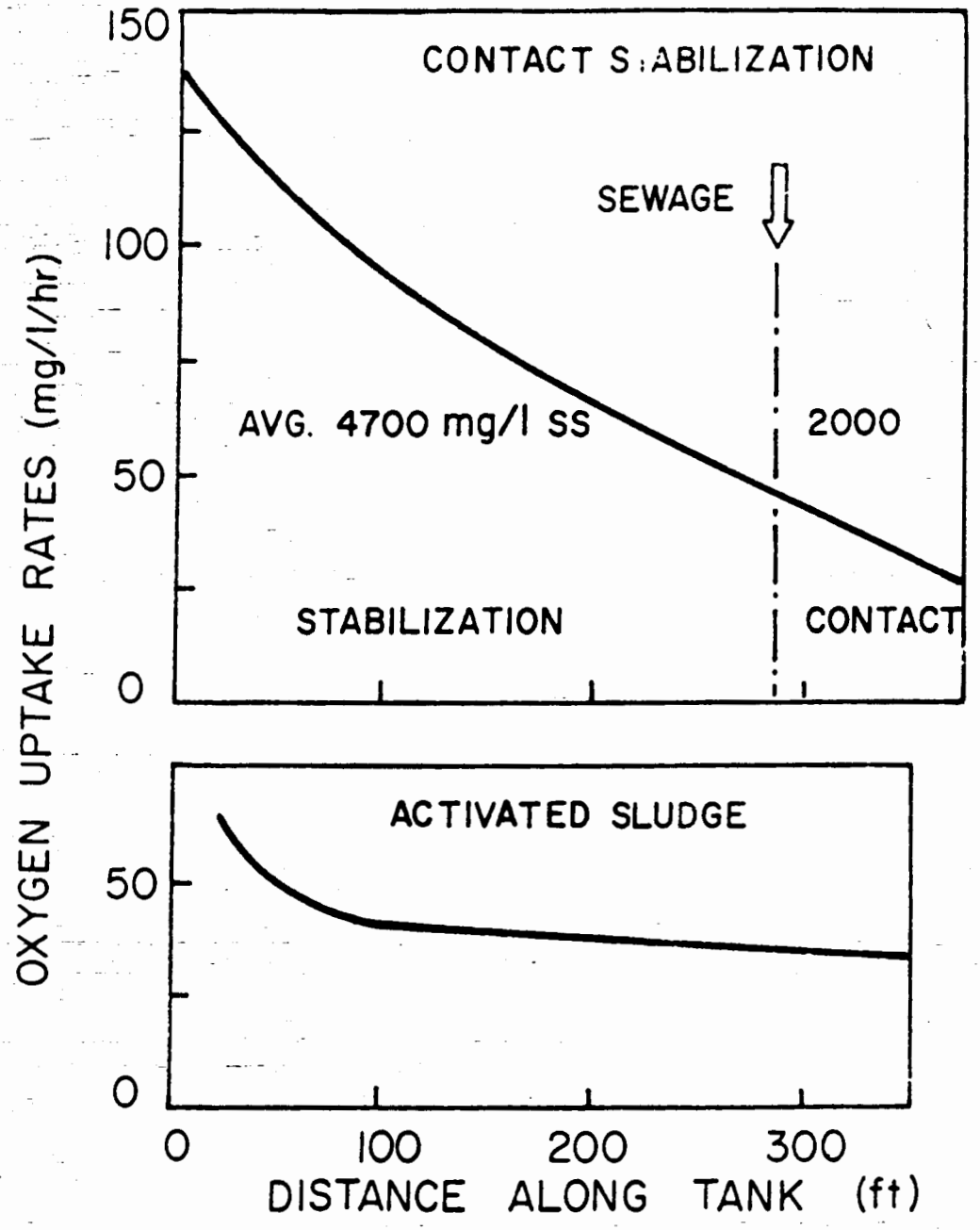


FIG.3-11
OXYGEN UPTAKE PROFILES

The oxygen transfer rate constant increases as the temperature increases, but the oxygen concentration at saturation decreases at higher temperatures. Therefore, although these two parameters are affected by temperature, the oxygenation capacity is relatively independent of temperature. The oxygenation capacity decreases by about six percent when the temperature increases from five degrees to 30°C.

The oxygen transfer is different for wastewater, for mixed liquor and for tap water under comparable conditions. The actual oxygen transfer rate, therefore, can be expressed by Equation 3-7:

$$OT_T = OC \frac{C_{s_T} - C}{C_{s_{20}}} \alpha \, 1.02^{(20-T)} \qquad 3\text{-}7$$

in which:

OT_T = oxygen transfer rate at temperature T in °C (lb/1000 gal-day)

OC = oxygenation capacity at T = 20°C (lb/1000 gal-day)

C = concentration of oxygen in liquid (mg/l)

C_{s_T} = concentration of oxygen in liquid at saturation at T°C (mg/l)

$C_{s_{20}}$ = concentration of oxygen in liquid at saturation at T=20°C

α = ratio of oxygen transfer under process conditions to the oxygen transfer in tap water at the same temperature

The effect of temperature on the oxygenation capacity is presented in Figure 3-12. The curve shows that temperature changes have a more noticeable effect at the lower temperatures than at the higher temperatures.

The concentration of oxygen at saturation in a diffused air aeration system must be corrected for the increased pressure that occurs as the air is released at the bottom of the tank. The saturation concentration of dissolved oxygen can be adjusted for the partial pressure at the mid-depth of the tank by using Equation 3-8.

$$C_{sm} = C_s \left(\frac{P_b}{29.4} + \frac{O_t}{42}\right) \qquad 3\text{-}8$$

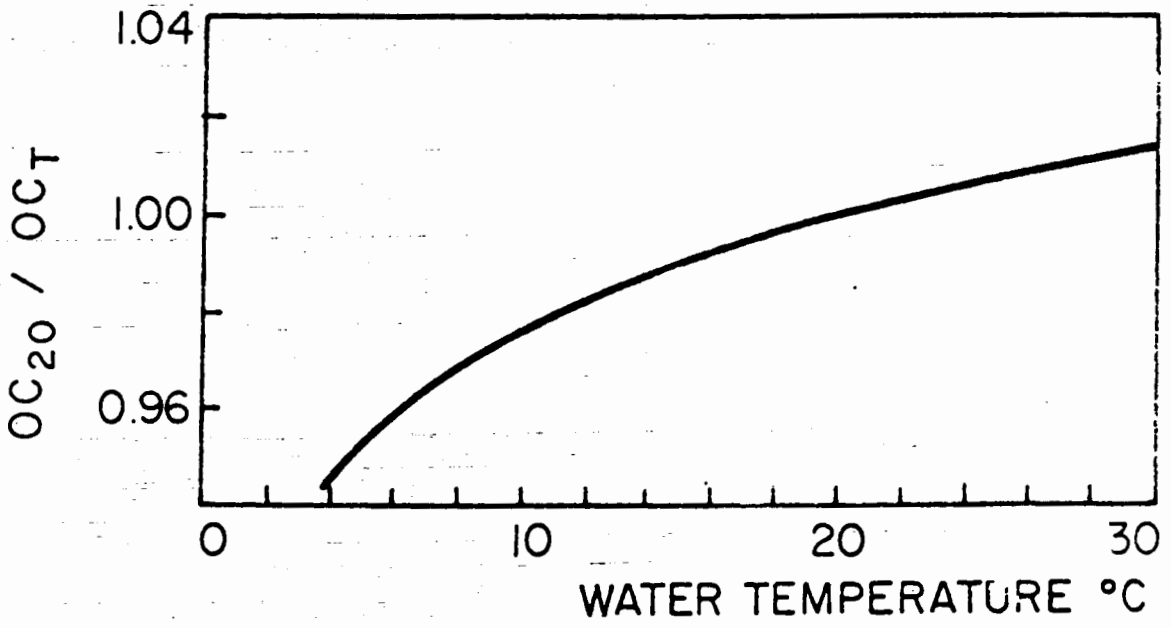


FIG.3-12 INFLUENCE OF TEMPERATURE ON OXYGENATION CAPACITY

in which:

C_{sm} = concentration of oxygen at saturation at mid-depth (mg/l)

C_s = concentration of oxygen at saturation under standard conditions (mg/l)

P_b = absolute pressure at depth of air release (lb/sq in)

O_t = oxygen in air leaving the aeration tank (percent)

The concentration of oxygen at saturation at mid-depth (C_{sm}) therefore depends on the depth of the diffuser as well as the percentage of oxygen in the air leaving the aeration tanks. The effect of the depth at which the diffusers are located on the ratio of the concentration of oxygen at saturation at mid-depth to the concentration of dissolved oxygen at saturations under standard conditions is presented in Figure 3-13. This curve was calculated for an oxygen transfer efficiency of five percent and indicates a linear relationship between the ratio C_{sm}/C and depth.

Various values of alpha used in Equation 3-7 have been reported for municipal wastewater. In bubble aeration systems, alpha has been reported to be equal to between 0.60 and 0.80 whereas in surface aeration systems, this value ranged from 0.80 to 1.10.

The interaction between oxygen transfer, depth and rate of air flow are presented schematically in Figure 3-14. A linear relationship between the oxygen transfer and the rate of air flow at a constant depth exists. However, at the extremely high air flow rates, the rate of oxygen transfer tends to level off at some equilibrium value. There is also a linear relationship between oxygen transfer and depth at a constant air flow rate. The exact value of the oxygen transfer at different depths and air flow rates is controlled to a large extent by the type of diffuser or bubble introduction device used. The aerator configuration and tank geometry influence the oxygen transfer rate. In a spiral flow tank, the actual velocity of the water increases with increasing air flow rates; therefore, the water air bubble contact time and the shear of the bubbles decrease resulting in a lower oxygen transfer per unit of volume of air. The ratio of the depth to width of the aeration tank also influences the oxygen transfer rate. The aeration device controls the diameter of the bubbles which are released. The oxygen transfer decreases as the diameter of the bubble increases. The oxygen transfer for a specific aeration device can be expressed as the oxygen transfer per 1000

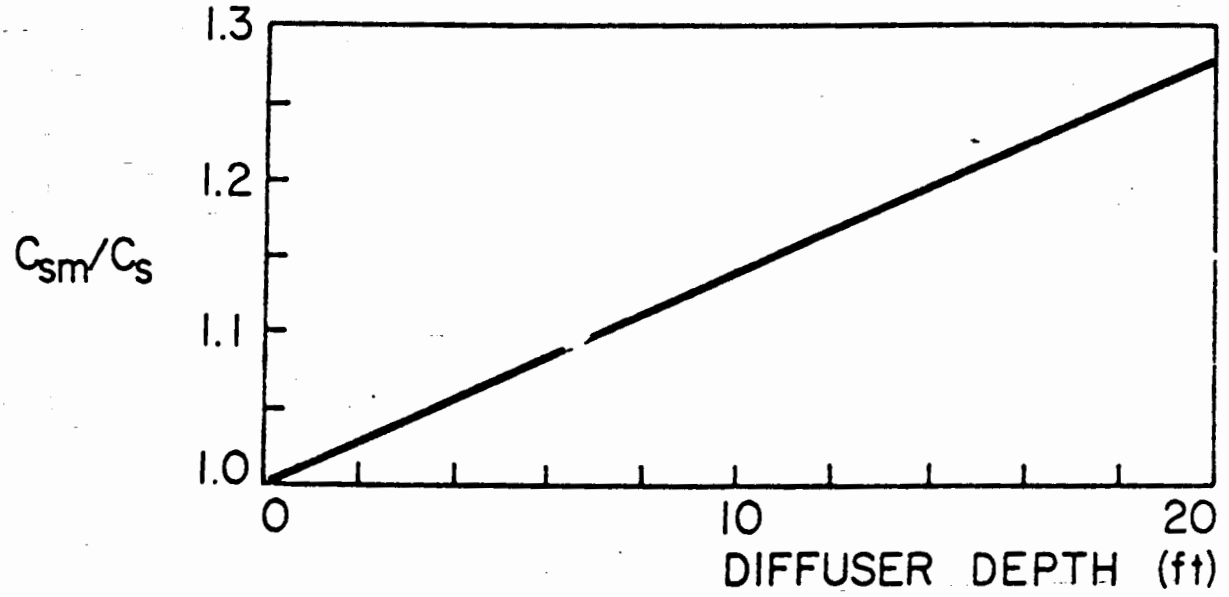
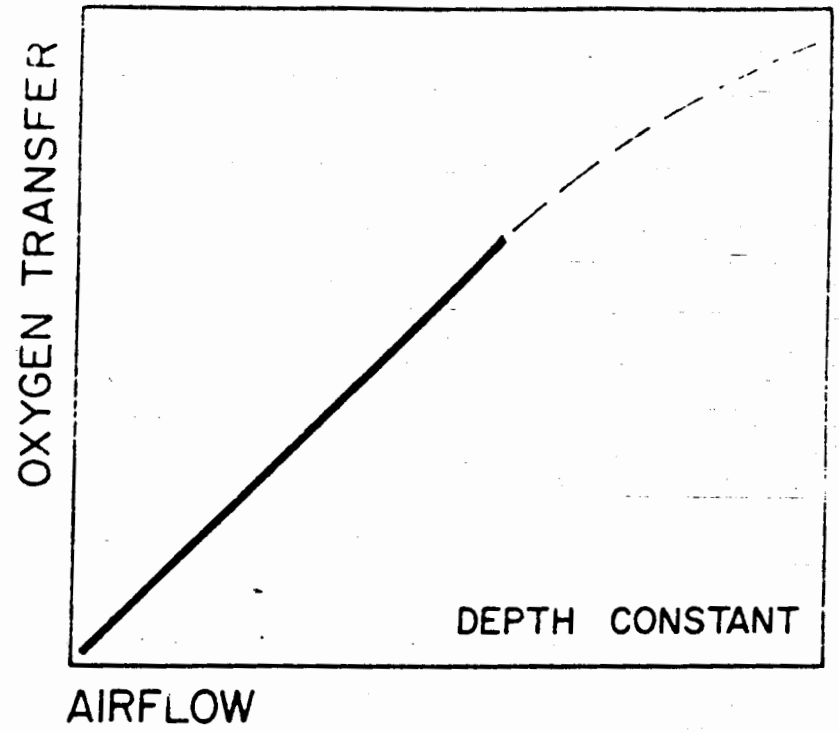


FIG.3-13 OXYGEN SATURATION AND DEPTH OF AIR RELEASE



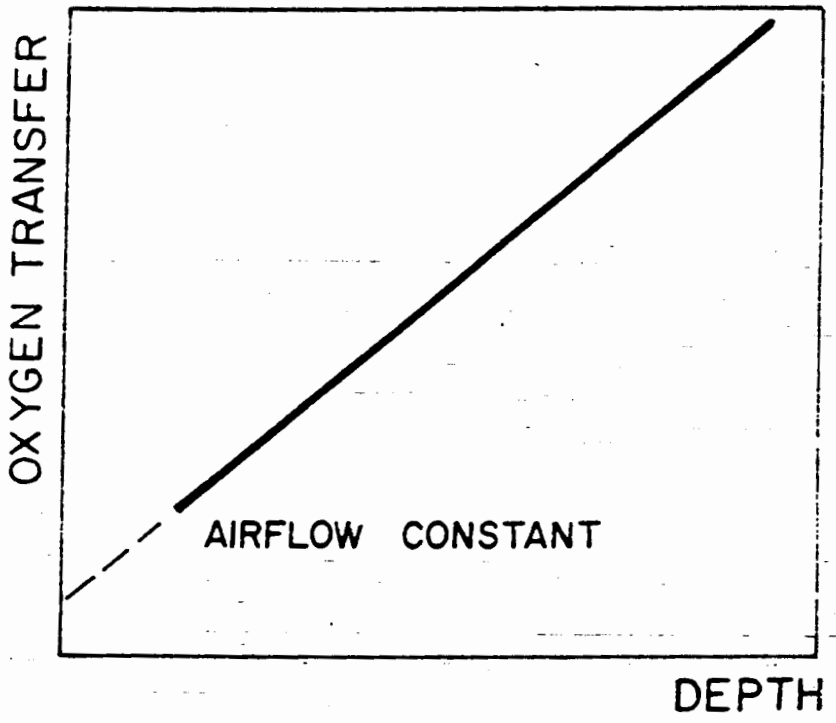


FIG.3-14

BUBBLE AERATION — OXYGEN TRANSFER (SCHEMATIC)

cubic feet of air flow per foot of depth of the air release. Each aeration device has optimum air flow rate beyond which the aeration efficiency decreases.

Mechanical aerators which are located at or near the surface of the liquid in the aeration tank are being used to a large extent. These aerators can be categorized as:

(a) cone aerators with or without draft tubes

(b) pump-type aerators which operate at high speeds, and

(c) brush aerators.

Schematic diagrams of the various types of surface aerators are shown in Figure 3-15.

Pump-type aerators are directly coupled to the motor and no gear box for speed reduction is required. The oxygen transfer can be controlled by introducing air into the suction portion of the aerators. However, less water is pumped.

The oxygen transfer of cone aerators increases within a given range with the depth of immersion of the aerator and with increasing peripheral velocity. Available data indicate that the increase in oxygen transfer is proportional to the third power of the peripheral velocity. The oxygen transfer also increases as the tank volume is reduced. Therefore, the oxygenation efficiency expressed as lb/HP-hr increases with increasing power level expressed as HP/1000 gallons. The general relationships between oxygen transfer and depth of immersion and the peripheral speed are illustrated in Figure 3-16. The relationship between oxygen transfer efficiency and power level is also illustrated schematically. The characteristics of aeration device determine the need for a draft tube. Draft tube aerators usually can be used only in very shallow tanks.

Sludge deposits may develop in the aeration tank when mechanical aerators are used. Knop and Kalbskopf (1968) indicate that the velocity at the bottom of an aeration tank in which cone or turbine-type aerators were used is a function of a power level. It has been observed that sludge deposits could not be found in tanks where the bottom velocity was much lower than one ft/sec. These reports indicate that turbulent conditions exist in the bottom of the tanks and that the velocities cannot be effectively measured by the common propeller-type meters.

Brush aerators which were developed by Kessener were initially mounted on the walls of aeration tanks in which spiral flow was maintained. However,

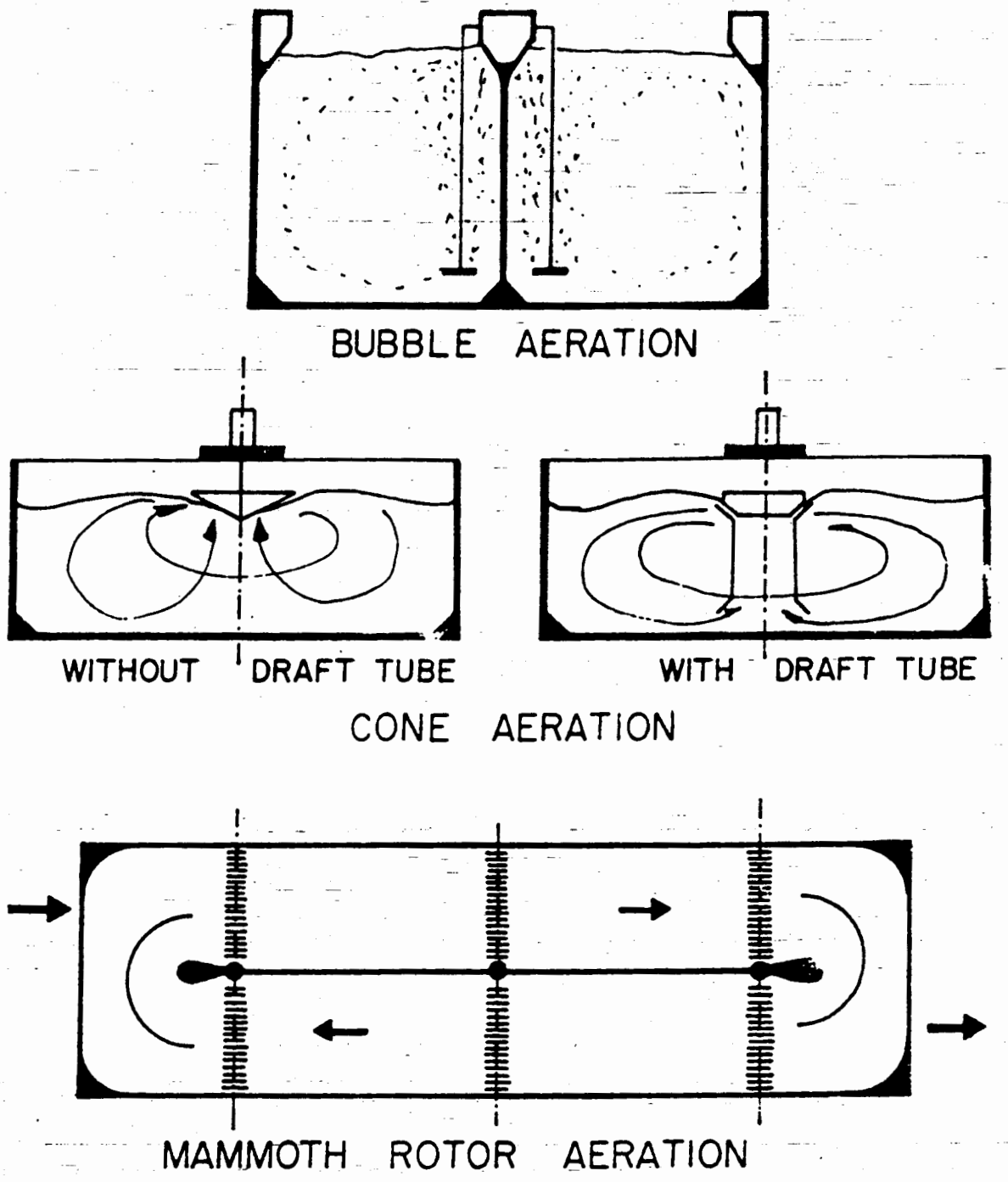


FIG.3-15
TYPICAL AERATION TANKS

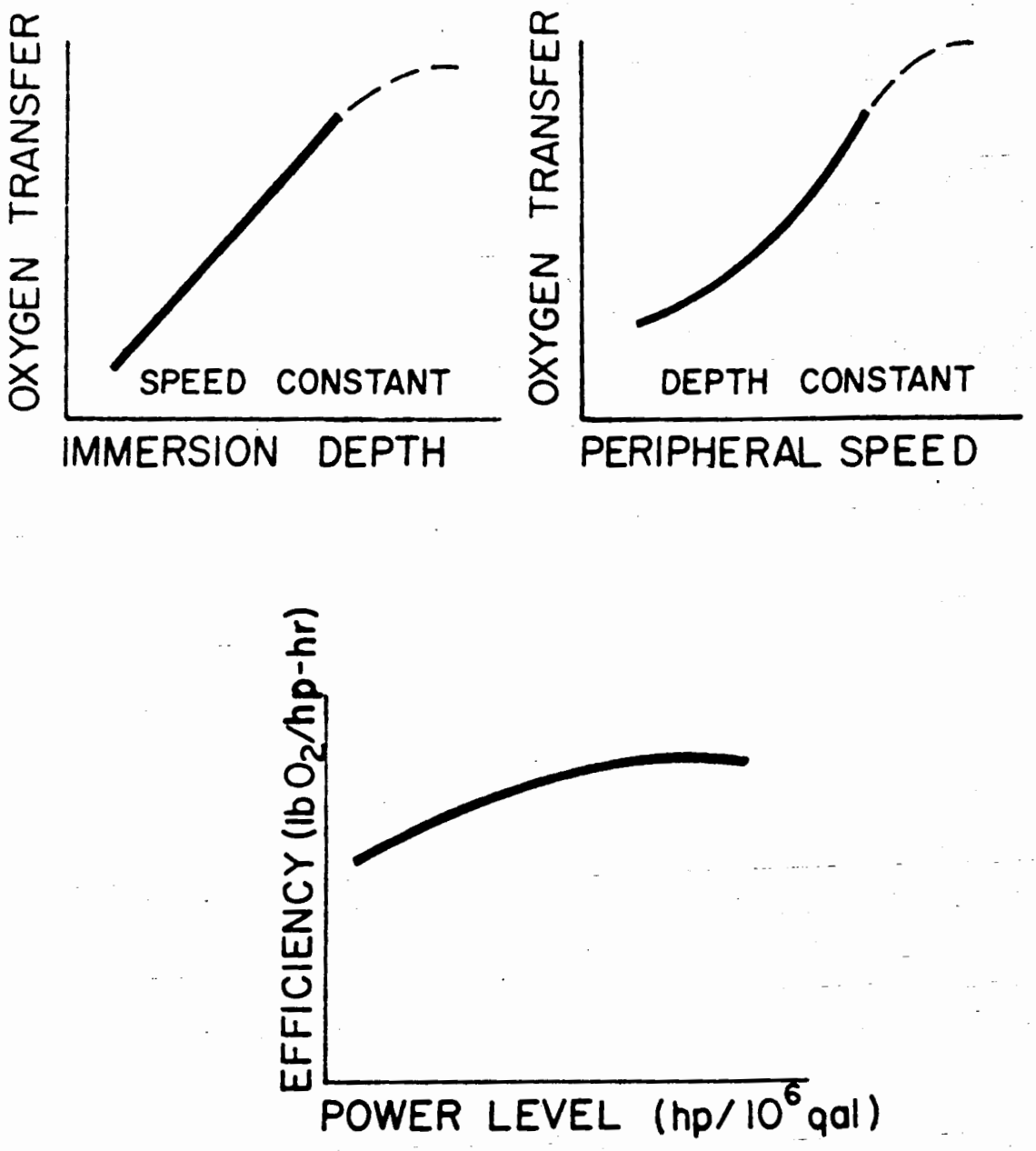


FIG.3-16
MECHANICAL AERATOR CHARACTERISTICS

the development of the cage-rotor and the mammoth rotor has eliminated the use of wall mounted brushes. Brushes are now mounted in a horizontal position perpendicular to the direction of flow. If more than one pair of rotors is operated in a single tank, baffles must be installed near the rotors to enhance mixing and maintain higher oxygen transfer rates. The oxygen transfer for brush aerators increases linearly with the depth of immersion and with the peripheral speed raised to the 2.5 power. The brushes are usually operated at a fixed speed and the oxygen transfer can be controlled by the depth of immersion. The rate of oxygen transfer to an aeration system of a specific surface area can be reported as pounds of oxygen per hour per unit or pounds of oxygen per HP/hour. The operating range must be given and the dimensions of the tank must be provided in order to effectively design a system using brush aerators.

Von der Emde and Kayser (1969) reported the oxygenation capacity and oxygen transfer efficiency of various aeration devices under process conditions. These data indicate that for bubble aeration systems in which nozzles with 0.28-inch diameter orifices were used, the value for OC = 0.95 lb O_2/1000 cu ft air/ft of depth of air release and a value of N = 1.30 lb O_2/HP-hr. The data reported for ceramic tube-type diffused aeration systems was OC = 0.2 lb O_2/1000 cu ft air/ft of depth of air release and N = 1.85 lb O_2/HP-hr. The oxygen transfer efficiency for surface aerators of the cone-type was reported as N = 2.0 to 3.5 lb O_2/HP-hr.

The above discussion of aeration equipment indicates that each aeration device requires a specific and different tank geometry, and the selection of aeration equipment must include the cost of the tanks as well as the aeration efficiency under process conditions. More detailed discussion of the design of aeration equipment may be found in Gloyna and Eckenfelder (1968) and in Eckenfelder and Ford (1970).

Recently the use of pure oxygen for aeration has been investigated by Albertson (1970). Two full-scale activated sludge treatment plants were operated in parallel in which one system was aerated with pure oxygen and the other with diffused air. However, some of the operating conditions such as sludge age and mixed liquor volatile suspended solids concentration were different in the air and oxygen systems operating in parallel. The oxygen system operated at a higher sludge age and mixed liquor volatile suspended solids concentration than the air system. The increased sludge age results in a lower production of cells, a greater destruction of volatile solids and an overall lower sludge yield. The quantity of soluble BOD removed per unit tank volume increases as the concentration of mixed liquor volatile suspended solids increases. These factors partially explain the higher rate of BOD removal and a lower sludge yield reported for the oxygen system when compared with the aerated activated sludge system. Ball and

Humenick (1971) prepared a review and analysis of oxygen systems for municipal wastewater treatment and concluded that although oxygen systems may provide some real advantages over air systems, the benefits may not outweigh the costs.

The greatest savings for the pure oxygen system in total annual cost were based on the low production of solids and the reduced sludge handling costs. A comparison of the pure oxygen system with surface aerators which in fact have on the average about a 50 percent higher efficiency of oxygen transfer than the diffused air system may have resulted in different results.

WASTE SLUDGE AND RETURN SLUDGE

The quantity of sludge produced during the activated sludge process is a function of the sludge age as well as the quantity of BOD removed and can be expressed mathematically as:

$$\frac{1}{G} = a^*\left(\frac{S_o - S^*_e}{xt}\right) - b + \frac{X_{on}}{Xt} \qquad 3\text{-}9$$

Typical values of a* and b are 0.63 and 0.075, respectively. The soluble BOD in the effluent is equal to about five percent of the initial BOD or $S^*_e = 0.05\ S_o$. The results of two studies using municipal wastewater indicate that the nonbiodegradable influent suspended solids represented 60 percent of the influent suspended solids. Introducing these values into Equation 3-9 results in Equation 3-10 which can be further reduced to Equation 3-11.

$$\frac{1}{G} = 0.63\left(\frac{0.95\ S_o}{Xt}\right) - 0.075 + \frac{0.6\ X_o}{Xt} \qquad 3\text{-}10$$

$$\frac{1}{G} = \frac{0.6\ (S_o + X_o)}{Xt} - 0.075 \qquad 3\text{-}11$$

The relationship presented in Equation 3-11 between the sludge age and the summation of the influent BOD and suspended solids is presented in Figure 3-17. The data points are those reported by Wuhrmann (1964) for pilot plant studies as well as for the Hyperion and Govalle full-scale experiments. The line drawn through the points has a slope of 0.60 and provides a basis for estimating the amount of sludge produced in a somewhat better fashion than the growth models which depend on the composition of the wastewater and for which different values of the coefficients a and b must be determined. The scatter in the data, especially in the results reported

for the operations at the Covalle Treatment Plant may be explained partially by the fact that the quantity of sludge wasted at this plant is merely an estimate and is not based on any specific flow measurements. There is also a greater percentage of nonbiodegradable solids in the effluent to the Covalle Plants, since no primary clarification preceeds the aeration tank. However, the data reported by Hyperion are described quite well by the line shown on Figure 3-17. This closeness of fit may be explained by the fact that at the Hyperion Plant, primary treatment preceeds the aeration tank and much of the nonbiodegradable suspended solids are removed in the primary clarifier. The scatter of the Wuhrmann data can be attributed to difficulties encountered in attempting to measure waste sludge flows in pilot plant operations.

The excess sludge calculated as the reciprocal of sludge age is the total mass of solids leaving the activated sludge system. Therefore, the flow of waste sludge may be calculated.

$$G = \frac{VX}{WX_{RS} + QX_e} \qquad 3\text{-}12$$

$$W = \frac{1}{X_{RS}} \left(\frac{VX}{G} - QX_e \right) \qquad 3\text{-}13$$

The sludge wasting facility should be able to discharge the total amount of sludge wasted per day during a 10 - 14 hour period if we assume that the effluent suspended solids concentration is zero and that the concentration of return sludge is the lowest which can be obtained with the total return sludge pump capacity and a mixed liquor suspended solids concentration of 2,000 mg/l. The return sludge concentration depends on the flow rates of return sludge and of incoming wastewater as well as the concentration of mixed liquor suspended solids maintained in the aeration tank. This relationship can be expressed in Equation 3-14 and 3-15.

$$X_{RS} Q_{RS} = X(Q + Q_{RS}) \qquad 3\text{-}14$$

$$X = X_{RS} \frac{Q_{RS}}{(Q + Q_{RS})} \qquad 3\text{-}15$$

in which:

X = mixed liquor suspended solids concentration (mg/l)

X_{RS} = concentration of suspended solids in the return sludge (mg/l)

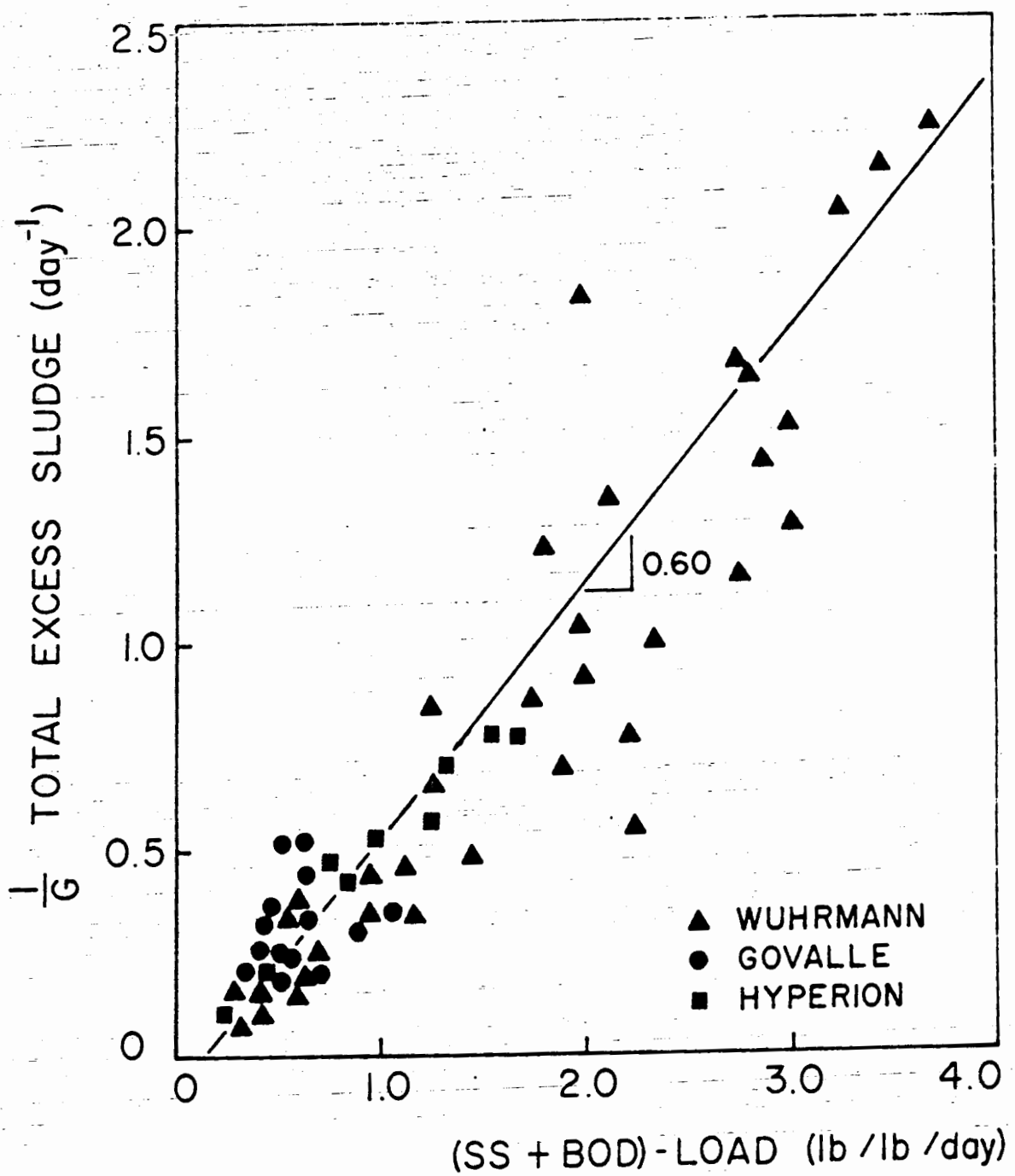


FIG.3-17
EXCESS SLUDGE AND (SS + BOD) - LOAD

Q_{RS} = return sludge flow rate (1000 gal/hr)

Q = wastewater flow rate (1000 gal/hr)

The concentration of suspended solids in the mixed liquor in the aeration tank will decrease as the incoming wastewater flow increases, if the rate of flow of return sludge and the concentration of suspended solids in the return sludge remain constant. However, the variations in the concentration of mixed liquor suspended solids will decrease as the ratio of return sludge flow to incoming wastewater flow increases. It is from this point of view that the return sludge flow rate should be maintained at some reasonable level or not be permitted to be very low.

The concentration of suspended solids in the return sludge is generally estimated by using the concentration of activated sludge which results after 30 minutes of settling. The reciprocal of this concentration of solids in the settled sludge is the sludge volume index. Therefore, the concentration of suspended solids in the return sludge may be expressed as Equation 3-16.

$$X_{RS} = \frac{10^6}{SVI} \qquad 3\text{-}16$$

in which:

X_{RS} = concentration of suspended solids in the return sludge in mg/l

SVI = sludge volume index (milliliters per gram) and represents the volume occupied by one gram of sludge after settling for 30 minutes in a one liter cylinder.

The sludge volume index for a municipal activated sludge plant is about 150. The limiting concentration of suspended solids in the return sludge will therefore be about 6,700 mg/l. At a return sludge flow equal to the incoming wastewater flow, a mixed liquor suspended solids concentration of about 3500 mg/l could be maintained. Therefore, in general the capacity of the return sludge pumps should be about equal to the average wastewater design flow. The aeration tank should be designed based on a concentration of suspended solids in the mixed liquor of about 3,000 mg/l.

The energy required for pumping the return sludge is negligible compared to the energy required for aeration. Therefore, the return sludge pumps could be operated at a constant flow rate of the entire 24-hour period. By operating continuously at a predetermined flow rate, the return sludge system would

not require any elaborate flow control devices. Two or three return sludge pumps having the same capacity should provide enough flexibility to handle the variations of return sludge flow required. In most municipal treatment plants, it is common practice to have more than one return sludge pump. Screw pumps are preferred in the newer plants in Europe. In many cases, a single screw pump is installed and is capable of returning the quantity of sludge required at the large treatment plants.

It is difficult to maintain and control the concentration of suspended solids in the mixed liquor by changing the rate of return sludge flow. A more effective way of controlling the concentration of mixed liquor suspended solids is by wasting sludge. Unfortunately, this method provides for only a decrease in the concentration of the mixed liquor suspended solids. Therefore, wasting sludge should be carefully controlled. An alternate system is to waste sludge continuously; however, if semi-continuous wastage is required, this waste can be controlled by pumps which are operated on a time cycle or by using some other suitable flow control device.

EXTENDED AERATION PROCESS

The extended aeration process is a modification of the activated sludge process in which the sludge age is maintained at a relatively high value providing time for a portion of the sludge to be stabilized. An extended aeration plant normally consists of an aeration tank, followed by a final clarifier and the necessary pumps for sludge return. The excess sludge is generally wasted in the form of suspended solids in the effluent.

The extended aeration process is widely used for relatively small communities in the United States and Europe. The basic difference in the operation of extended aeration plants in the United States and Europe is that in Europe the excess sludge is removed from the system in order to maintain effluent which contains a BOD of five to 15 mg/l. At the small plants serving communities of 100 to 500 people, the sludge is dewatered on the sludge drying beds. At the larger plants, the excess sludge is stored and subsequently trucked to the agriculture areas. The basic design parameter is the degree of stabilization of the waste sludge. At organic loadings of about 0.05 lb BOD/lb of MLSS-day, the sludge is reported to be well stabilized. Storage of this material under anaerobic conditions does not cause any severe odor problems. A number of plants are operated at organic loadings of 0.1 lb BOD/lb MLSS-day in order to reduce the volume of aeration that is required. The excess sludge from these plants is partially stabilized. The organic loading rate expressed in terms of initial suspended solids concentration as well as initial BOD concentration can be calculated using Equation 3-11. If one assumes that the wasted sludge is well stabilized at a sludge age of 30 days, this equation can be modified.

$$\frac{1}{30} \quad 0.6 \left(\frac{X_o + S_o}{Xt} \right) - 0.075 \qquad 3\text{-}17$$

therefore

$$\frac{X_o + S_o}{Xt} = 0.18 \qquad 3\text{-}18$$

The BOD loading rate would therefore be 0.065 lb BOD/lb MLSS-day based on the assumption that the ratio of influent suspended solids to BOD is about 1.75. The volume of the aeration tank for an extended aeration plant can be based on a load of influent BOD and suspended solids of 0.15. This value would give a somewhat larger aeration volume compared to the value calculated from the theoretical equations.

FINAL CLARIFIERS

The final clarifiers represent an important unit process in the activated sludge plant. The suspended solids are separated from the effluent liquid in the final clarifier and the degree to which the sludge concentrate in the final clarifier will control to some extent the rate at which return sludge must be pumped to the aeration tank.

Clarifiers can be divided into two characteristic groups depending on the hydraulics, namely upflow clarifiers and horizontal clarifiers. The clarifiers may be circular or rectangular and exhibit either flow pattern. Deep clarifiers with a relatively small surface area are generally the upflow types whereas the shallow basins with large surface areas are more likely to be horizontal flow types. The design of final clarifiers is generally based on the overflow rate and the detention time. Theoretical conditions, however, indicate that the overflow rate is far more important than the detention time.

The method by which the settled sludge is withdrawn from the clarifier also affects the performance of the clarifier. The preferred sludge collection mechanism is a vacuum or suction type draw off. The plow type collectors with the chain and flight mechanism in rectangular basins or the bridge with attached plows in circular basins are not very effective in concentrating the waste activated sludge. The sludge tends to flow over the plow as the plow moves through the sludge blanket and very little movement of the sludge to the concentrating compartment takes place. The vacuum or suction type draw off actually draw the solids into the collection pipe under the force of the hydraulic head in the tank. Schematic diagrams of center feed and peripheral feed circular clarifiers and rectangular clarifiers are illustrated

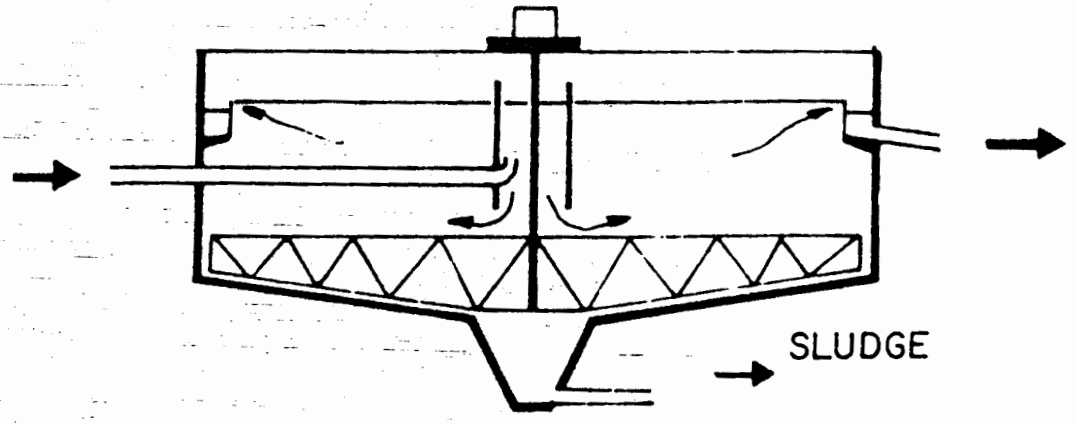
in Figure 3-18. The center feed clarifier and the rectangular clarifier illustrate the plow-type collectors whereas the peripheral feed clarifier indicates the suction draw off. Suction draw off equipment can also be installed in the center feed circular clarifier or a rectangular clarifier.

The results of recent investigations by Pflanz (1968) indicate that the effluent suspended solids concentration from final clarifiers operated at constant overflow rates, increased as the concentration of mixed liquor suspended solids increased. The results also indicate that at a constant overflow rate and a constant concentration of mixed liquor suspended solids, the effluent suspended solids concentration increased as the sludge volume index increased. The effluent suspended solids also increased as the temperature decreased.

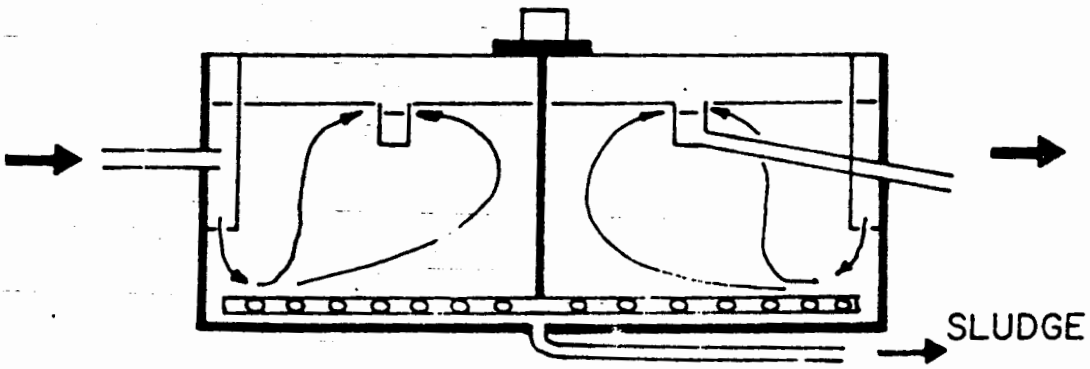
The interdependency of the mixed liquor suspended solids and the sludge volume index indicate that a relationship also exists between effluent suspended solids concentration and the sludge volume surface load. The sludge volume surface load is the product of the overflow rate (gallons per square foot per day) and the fraction of the initial volume occupied by the sludge solids after settling for 30 minutes. Therefore, the sludge volume surface load in a final clarifier with an overflow rate of 1000 gal/sq ft-day, and a sludge which occupies 1/10 the volume of the initial sludge after settling 30 minutes would be 100 gal/sq ft-day.

The relationship between the sludge volume surface load and the effluent suspended solids concentration are presented in Figure 3-19. This plot is based on the data presented by Pflanz (1969). The data show considerable scatter primarily at the higher values of sludge volume surface loading, and effluent suspended solids concentration. However, at the lower range of values, there is a fairly good correlation. The scatter seems to be the result of errors in determining the sludge volume index, which is generally determined under quiescent conditions. However, the conditions in the settling tank are far from quiescent and a good degree of the turbulence in the full-scale tank may actually promote flocculation of the sludge particles. Therefore, in the laboratory determination of the sludge volume index a slow stirring device which is placed in the cylinder would more closely simulate the conditions in the field and may give much more reliable results.

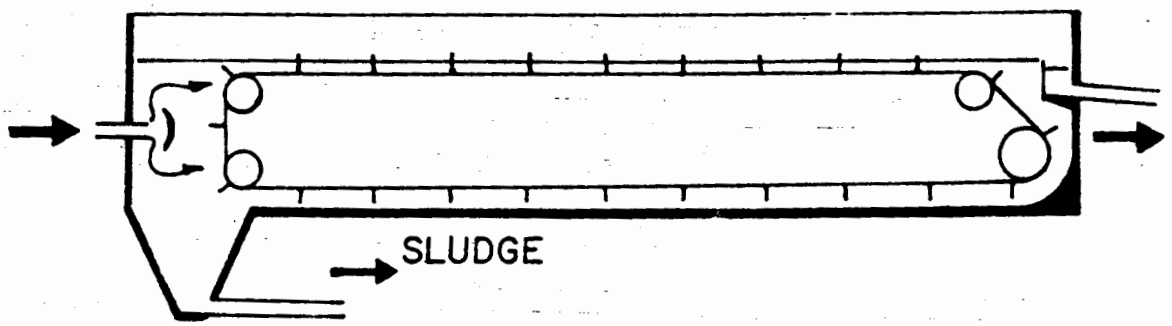
Much of the sludge settles near the inlet zone of the final clarifier under normal overflow flow rates of about 500 gal/sq ft-day and a mixed liquor suspended solids concentration of about 3000 mg/l. A thin layer of diluted sludge may result in a density current. This diluted layer will move along the bottom of the tank, rise to the effluent weirs and result in high effluent suspended solids concentrations. Prevention of these density currents



CIRCULAR CLARIFIER WITH CENTER FEED



CIRCULAR CLARIFIER WITH PERIPHERAL FEED



RECTANGULAR CLARIFIER

FIG.3-18
DIFFERENT TYPES OF FINAL CLARIFIERS

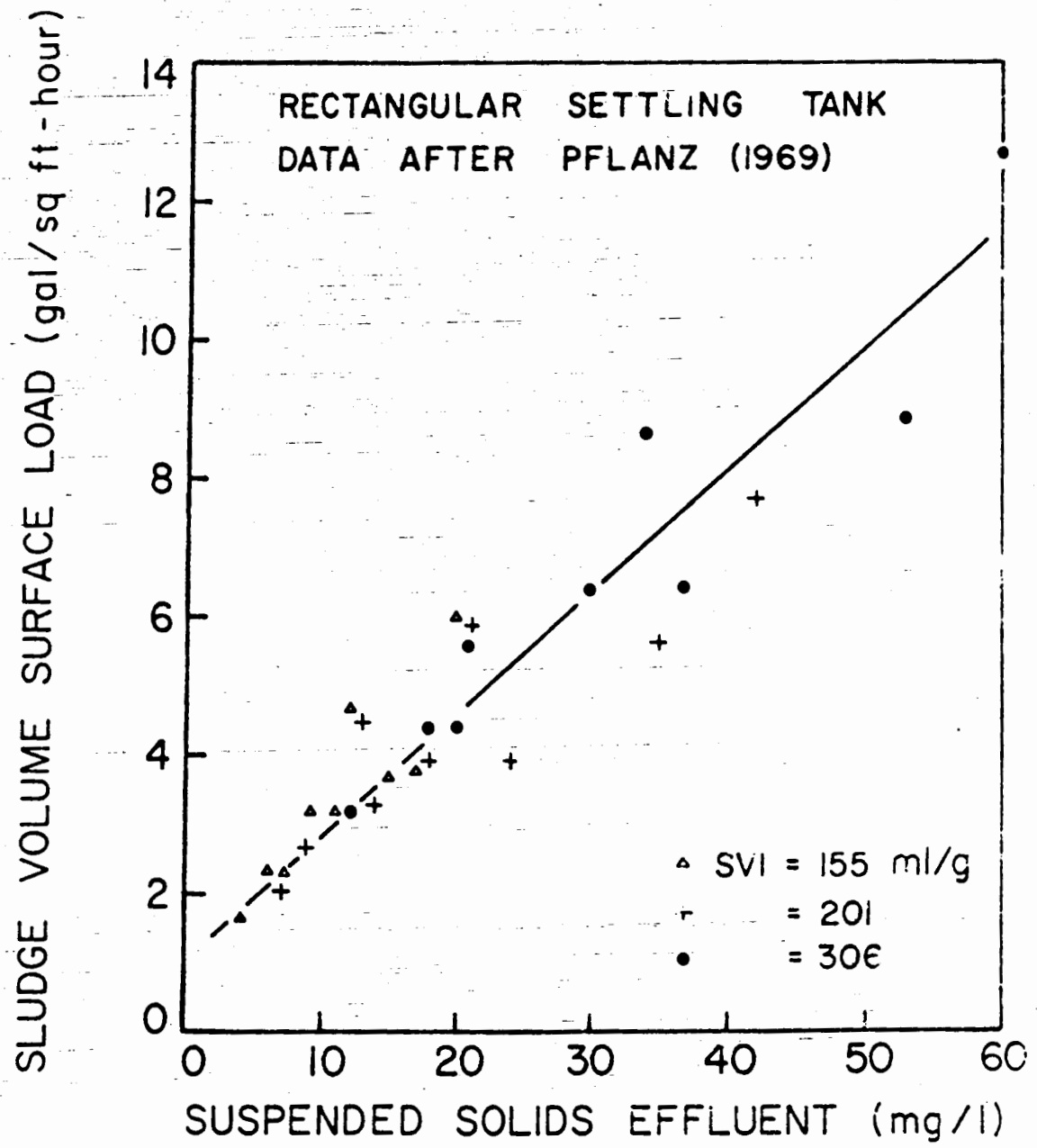


FIG.3-19
SLUDGE VOLUME SURFACE LOAD
AND EFFLUENT SUSPENDED SOLIDS

would reduce the concentration of suspended solids in the effluent. Density currents were minimized at rectangular final clarifiers which were eight to ten feet deep at three plants in Europe. The method used for minimizing the density currents are illustrated in Figure 3-20.

The settling tanks at the treatment plant at Nordhorn, Germany, had a single effluent weir across the entire width of the tank. However, high effluent suspended solids concentrations were observed and attributable primarily to density currents. A vertical plastic sheet was placed at a point about 1/4 the total tank length and essentially divided the tank into two separate parts. Most of the solids settled in the first part. The increased velocity of flow over the top of the sheet caused the remainder of the suspended solids to become well mixed. Therefore, no density currents were observed in the second part of the tank. This procedure reduced the concentration of suspended solids observed in the effluent.

The results of experiments conducted at the treatment plant at Baden, Austria, indicated that if the weirs at the end of the tank were closed and the effluent was only taken off by the weirs along the side of the tank as illustrated in Figure 3-20, the concentration of suspended solids in the effluent was much less than when all weirs were operated. Similar results were reported at the treatment plant in Ergolz, Switzerland. In this case, six weirs were originally used as those illustrated in Figure 3-20. However, when the weirs 1, 3, and 5 were closed, the concentration of suspended solids in the effluent was markedly reduced.

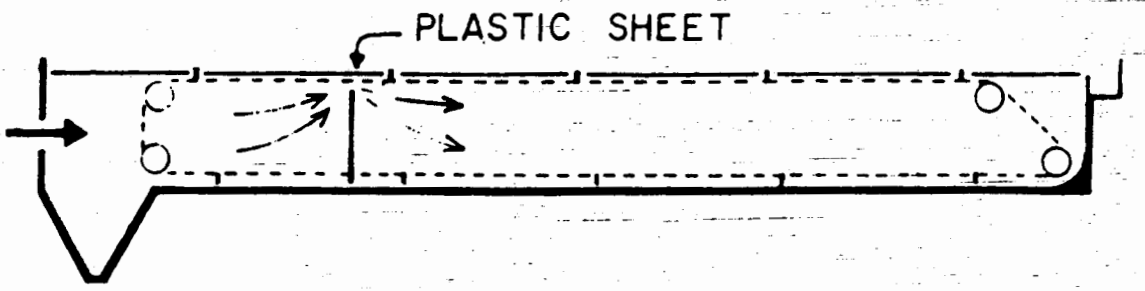
The withdrawal of sludge from secondary clarifiers for return to the aeration basin takes place at a point very near the inlet to the tank with the exception of the peripheral feed tanks. Therefore, the required area of the final clarifier is calculated using the incoming wastewater design flow and the return sludge flow rate is not included. The overflow rate for a clarifier may be calculated based on the sludge volume surface load and desired effluent suspended solids concentration. For example, for an effluent suspended solids concentration of 25 mg/l the sludge volume surface load is five gal/sq ft-hr (120 gal/sq ft-day) based on the curve in Figure 3-19. At a mixed liquor suspended solids concentration of 3000 mg/l and a sludge volume index of 100 ml/g, the volume occupied by the settled sludge after 30 minutes of settling is 30 percent of the initial volume. This calculation is shown in Equation 3-19.

$$3000 \text{ mg/l} \frac{100 \text{ ml}}{\text{gm}} \times \frac{\text{gm}}{1000 \text{ mg}} \times \frac{\text{L}}{1000 \text{ ml}} = 0.3 \qquad 3\text{-}19$$

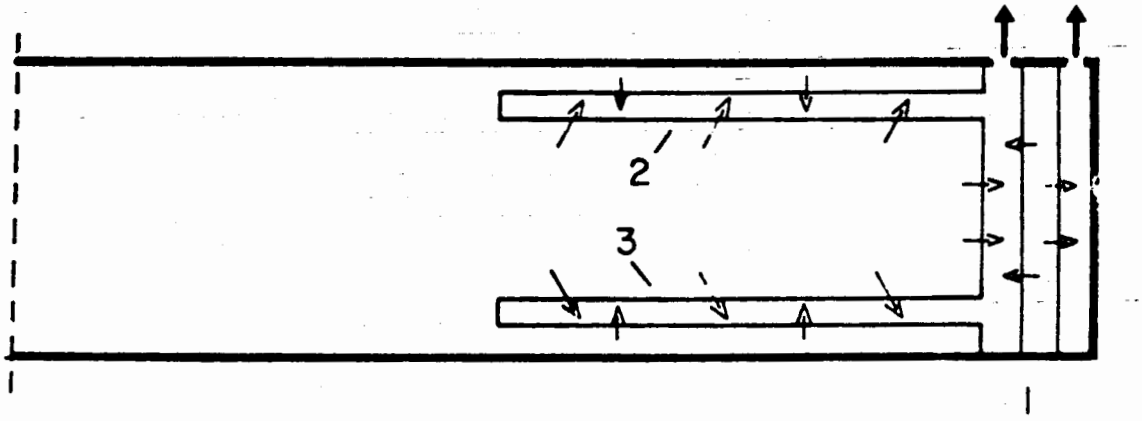
Therefore, the required overflow rate is equal to 400 gal/sq ft-day as shown by the calculation in Equation 3-20.

$$\frac{120 \text{ gal/sq ft-day}}{0.3} = 400 \text{ gal/sq ft-day} \qquad 3\text{-}20$$

NORDHORN



BADEN



ERGOLZ

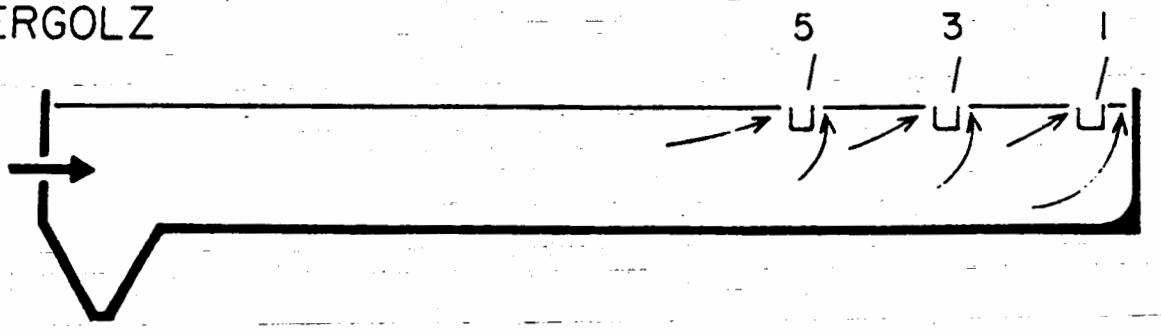


FIG.3-20
IMPROVEMENTS OF FINAL CLARIFIERS

The calculated overflow rate is somewhat lower than that frequently used for design valves of 600 to 800 gal/sq ft-day. This lower value based on the data presented by Pflanz (1968) may be attributed to the fact that in the particular secondary clarifier used by Pflanz only one effluent weir across the entire width of the rectangular basin was used at relatively low temperatures, namely between 13° - 15°C. Therefore, at newly designed plants, the overflow rate of the secondary clarifier of 600 gal/sq ft-day can be used for smaller plants up to a total of one MGD, and up to 700 gal/sq ft-day for the larger plants. The design calculations should not be based on the daily design flow but rather on the peak flow. Therefore, if the design is based on the peak hourly flow, the overflow rates for smaller plants should be 25 gal/sq ft-hour and 30 gal/sq ft-hr for the larger plants.

NITRIFICATION AND DENITRIFICATION

Nitrification and denitrification have been reported to occur in the activated sludge process. These processes remove nitrogen from the effluent from the activated sludge process.

Nitrification involves a conversion of ammonia to nitrite and nitrate. The reactions are presented in Equations 3-21 and 3-22.

$$2NH_4 + 3O_2 \xrightarrow{\text{Nitrosomonas}} 2NO_2^- + 2H_2O + 4H^+ + \text{New } \underline{\text{Nitrosomonas}} \text{ Cells} \qquad 3\text{-}21$$

$$2NO_2 + O_2 \xrightarrow{\text{Nitrobacter}} 2NO_3^- + \text{New } \underline{\text{Nitrobacter}} \text{ cells} \qquad 3\text{-}22$$

The conversion of ammonia to nitrite is accomplished by the microorganism Nitrosomonas, and the conversion of nitrite nitrogen to nitrate nitrogen is accomplished by Nitrobacter organisms. The rate of growth of Nitrosomonas is described by Equation 3-23 for nitrification.

$$\mu = \mu_{max} \frac{(NH_4)}{k_m + (NH_4)} \qquad 3\text{-}23$$

in which:

μ = growth rate of Nitrosomonas (day^{-1})

μ_{max} = maximum growth rate (day^{-1})

(NH_4) = concentration of ammonia (mg/l)

k_m = concentration of ammonia when $\mu = 0.5\mu_{max}$ (mg/l)

Downing (1964) reported the growth constants for Nitrosomonas at 20°C to be $\mu_{max} = 0.33$/day and $k_m = 1.0$ mg/l of ammonia nitrogen. The maximum growth rate for the Nitrobacter at 20°C reported by Downing was $\mu_{max} = 0.14$/day. These data indicate that the maximum growth of Nitrosomonas and Nitrobacter probably occur at an ammonia concentration of about 3.0 mg/l. At concentrations of ammonia above this minimum concentration, the rate of nitrification is independent of the ammonia concentration and the nitrification reactions are zero order. The growth rate constants for the nitrifying bacteria are relatively low compared to those reported for heterotrophs. For example, Schulze (1964) reported that the maximum growth rate for Escherichia coli and a glucose substrate was 18 per day. Therefore, the detention time in the activated sludge system must be greater than the generation time of the nitrifying bacteria, otherwise these bacteria would be washed out of the system. Since the nitrifying bacteria are associated with the mixed liquor the sludge age should be sufficiently long to provide active growth of the nitrifying bacteria if nitrification is to take place. On the other hand, the amount of nitrification which occurs can be calculated from the sludge age.

The maximum growth rate of the nitrifying bacteria is markedly affected by changes in temperature. The result of investigations at the Water Pollution Laboratory (Anon., 1967) indicate that the rate constant increases about seven percent per degree centigrade. The effect of temperature on the growth of nitrifying bacteria is presented in Figure 3-21 Nitrification will take place if the reciprocal sludge age (1/G) is lower than the maximum growth rate of the nitrifying bacteria.

Aerobic conditions must be maintained for nitrification. Downing (1964) and Wuhrmann (1964) reported that a minimum concentration of dissolved oxygen of one mg/l is required in order to achieve nitrification. The maximum rate of nitrification requires dissolved oxygen concentrations of more than 200 mg/l.

Nitrification will occur to some extent in activated sludge treatment plants operated at organic loading rates of about 0.25 lb BOD/lb MLSS-day or lower. If nitrification does occur, a higher oxygen uptake rate will be exerted than that calculated for the removal of carbonaceous matter only. Therefore, nitrification should be included in calculating oxygen requirements.

Partial nitrification is possible in the contact stabilization process, since the sludge age is relatively high in this process. However, since the contact time is relatively short, only a partial nitrification is possible. In the

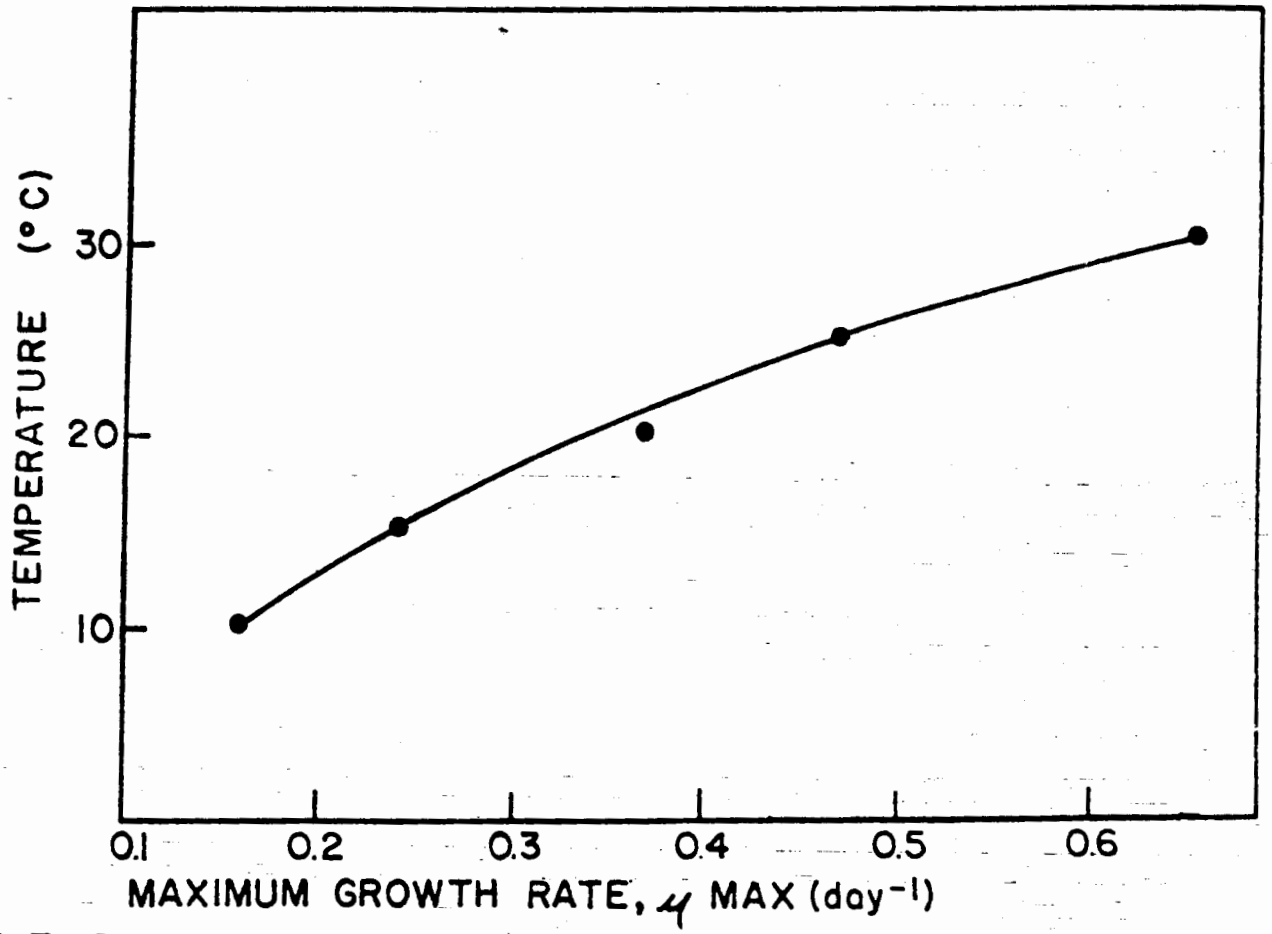


FIG. 3-21
TEMPERATURE EFFECTS ON GROWTH RATE OF NITRIFYING BACTERIA (Downing 1964)

stabilization tanks where the concentration of nitrifying bacteria is high, the concentration ammonia is the limiting factor. The ammonia removal in the contact stabilization process will be increased at higher return sludge flow rates and lower contact times.

Denitrification can take place once the ammonia has been converted to the nitrite or nitrate form. If the dissolved oxygen concentration in the mixed liquor is at a concentration less than one mg/l heterotrophic bacteria can utilize the oxygen associated with the nitrites and nitrates for metabolism, and the nitrogen is released as nitrogen gas. A denitrified effluent can be obtained by placing a denitrification tank between the aeration basin and the final clarifier. The denitrification tank should be equipped with a mixing device to maintain the solids in suspension but not to introduce any oxygen. The time required for total denitrification can be estimated from the initial dissolved oxygen concentration in the mixed liquor and the quantity of oxygen present in the form of nitrites or nitrates as well as the oxygen uptake rate of the mixed liquor. Wuhrmann (1964) indicated that the time required for denitrification can be calculated from the mass balance which is presented in Equation 3-24:

$$VR_N = Q\,(C_o + C_N) \qquad 3\text{-}24$$

$$t_D = \frac{V}{Q} = \frac{C_o + C_N}{R_N} \qquad 3\text{-}25$$

in which:

t_D = detention time of the mixed liquor in the denitrification basin (hrs)

C_o = dissolved oxygen concentration in the mixed liquor entering the denitrification basin (mg/l)

C_N = oxygen in the form of nitrite and nitrates (mg/l)

R_N = oxygen uptake rate of the mixed liquor in denitrification basin (mg/l-hr)

The oxygen uptake rate in the denitrification basin is very similar to the endogenous rate. If nitrification takes place in the aeration tank an no denitrification is provided, partial denitrification may take place in the final clarifier and the released nitrogen gas may cause a portion of the settled sludge to float. Therefore baffles should be located near the effluent weirs in the final clarifiers to reduce the carryover of suspended solids into the effluent.

PROCESS CONTROL

The practical control of the activated sludge process involves:

(a) control of the concentration of dissolved oxygen in the aeration tank, or

(b) control of the mixed liquor suspended solids concentration.

The dissolved oxygen concentration in the aeration basin should usually be maintained between 1.0 and 2.0 mg/l. The amount of oxygen transferred in the aeration basin therefore should be capable of satisfying variations in the oxygen uptake rate. The automatic control of the oxygen transfer to the system may be realized by monitoring the concentration of dissolved oxygen at the point in the aeration tank where the oxygen uptake rate is at a maximum. If the concentration of dissolved oxygen in the aeration tank falls below a minimum desirable level the aeration equipment can be called upon to provide additional oxygen. On the other hand, if the dissolved oxygen concentration in the aeration basin exceeds the desired level, the amount of oxygen introduced can be reduced. The savings in power costs over a number of years of operation would probably be sufficient to cover the capital cost of the automatic control system. A single oxygen probe would be required for a completely mixed aeration tank or the tank in a step aeration system, since the oxygen uptake rate should be the same throughout the entire volume of the tank. In longitudinal spiral flow tanks generally used for the conventional activated sludge process, the oxygen probe should be installed near the wastewater inlet since it is at this point that the oxygen uptake rate is the highest.

The concentration of mixed liquor suspended solids in the aeration tank can be decreased by increasing the quantity of sludge wasted. An increase in the mixed liquor suspended solids concentration is practically impossible; therefore, the quantity of sludge wasted should be carefully controlled. Generally, continuous wasting at a predetermined rate is preferred to the practice of wasting sludge periodically.

Guarino and Carpenter (1970) indicated that the control of the loading rate is possible, by storing return sludge to provide the necessary sludge to maintain a constant loading rate. This procedure is essential since the incoming BOD is very difficult to control. Therefore, by controlling the concentration of mixed liquor suspended solids, the loading rate can be maintained relatively constant. Sludge is pumped to storage tanks during the night time hours when the loading rates are relatively low and introduced into the system during the day time when the organic loading reaches its peak. This system would provide savings in power required for accommodating the oxygen uptake rate.

All municipal wastewater treatment plants operate under transient loading conditions. The ratio of the daily peak to the minimum flow is in a range of 3-1 to 10-1 or more. In most treatment plants, the effluent BOD is practically not affected by the fluctuating transient conditions provided the organic loading was equal to or less than 0.5 lb BOD/lb MLSS-day. Observations at treatment plants indicate that the biological processes require some time for recovery. Generally the recovery occurs during the night time hours when the organic load to the plant is low or on the weekends when loadings are also lower than during the work week. The recovery time could be required for stabilization of the biological solids and/or for the biodegradation of other particulate material which accumulate in the mixed liquor.

DESIGN FACTORS

Design and layout of an activated sludge plant for the treatment of municipal wastewater is based on the following design data:

(a) wastewater flow (MGD) daily peak wastewater flow (1000 gal/hr)

(b) average influent BOD (mg/l)

(c) average influent suspended solids (mg/l)

The basic data should also include any industrial waste and information relating to type, source of wastewater, and quantity of discharge. This information is required to minimize the possibility of shock loadings to the activated sludge system. If more than 1/2 the total BOD load to the plant is contributed by a single industry, it is conceivable that laboratory or pilot-scale treatability studies should be performed to effectively select the proper design parameters.

A number of other factors must be considered in the design of a biological treatment plant since other variables might affect the performance and operation of the overall plant. The need for primary sedimentation prior to biological treatment is sometimes questioned. The characteristics of the wastewater and the manner in which the solids are to be ultimately disposed of should be considered carefully prior to deciding on whether a primary clarifier is required. The removal of suspended solids in the primary sedimentation tank would minimize the load on the biological treatment process since some of the biodegradable solids would be removed and the oxygen uptake requirements would be considerably lower. In this case, the primary solids would more than likely be treated in an anaerobic digestion system prior to disposal on the sludge drying beds. However, it is also possible for the primary solids to be mixed with the waste activated sludge and treated by

aerobic digestion provided the quantity of waste activated sludge is at least equal to the quantity of primary sludge requiring disposal.

Generally, the final decision is based on a cost estimate. However, other factors should also be included before a final decision. Primary sedimentation is preferable in those cases where the incoming suspended solids are mainly inorganic such as might be found in a treatment plant handling combined wastewater. Primary clarification also permits the removal of floating materials. Therefore, if primary clarification is not installed prior to the aeration tank, it is essential that the secondary clarifiers be equipped with skimming equipment.

The layout of the biological treatment plant is also important. Any layout of the processes should provide for flexible operation under a variety of conditions. Most municipal waste treatment plants have a number of aeration basins and final clarifiers operating in parallel. This requirement is generally established by the regulatory agency in the particular state or region. However, pipes and channels connecting the various units should be so designed that taking any one unit process out of operation does not affect the use of the remaining unit processes. For example, it should be possible to take an aeration tank out of service and operate all clarifiers by distributing the incoming wastewater, and return sludge to the remaining aeration units. On the other hand, if a final clarifier is out of operation, it should be possible to continue operating the plant with all unit aeration tanks being utilized. With this type of design and plant layout a single blower station and a single sludge return pumping station could be included in the design. Some additional piping might be required to maintain this flexibility, but the cost of the piping is recovered in terms of the ability of having continuous operation of the plant.

An estimate of the ultimate organic load and wastewater flow must be determined at the time of the initial design, although it is extremely difficult to estimate what might happen 25 to 50 years after the plant is in operation. The future program of operation of a treatment plant is helpful in the design of the various components so that the plant can be expanded as organic and hydraulic loads increase. The initial construction phase of the treatment plant should be designed for ease of expansion.

herbage fall within acceptable ranges although N, P and K show increases, the BOD_5 and SS removal rates are around 95%. All of this is remarkable since 30% of the flow and 75% of the organic loading is contributed by industrial wastes.

France: The municipal wastewater farms of Paris have been in operation since 1880, and these farms have been very successful. These farms are receiving about 100 million cu m/yr of wastewater. Application rates are 4 m per year over a mixture of sand, clay, and gravel. (1)

Germany: At Braunschweig, Germany, cereal crops, potatoes, sugar beets, and asparagus have been irrigated by wastewater application for many decades. (1)

Israel: At present, Israel utilizes most of its fresh water potential of 1,500 million cu m per year. About 75% is supplied to agriculture. It is planned that by 1985, 10% of the agricultural water requirements will be supplied through wastewater reclamation. (4)

Poland: In Poland during dry years, sewage represents 50% of all surface flow. The Wroclaw Farm, 1,500 ha, receives 170,000 cu m/day. It has been in operation for 100 years. (1)

Saudi Arabia: The King Khalid Military City, Saudi Arabia, a city of 70,000 people and one of the world's largest and costliest construction projects, will reuse all water. Sewage effluents will be used for agricultural purposes. (3)

South Africa: About 3% (31,000 ha) of the total area under irrigation is irrigated with wastewater. Municipalities provide about 85% of this wastewater. (5)

United States: The U.S. nearly a decade ago registered about 600 municipalities and 1,300 industrial facilities discharging wastewaters on land. Most of these sites were located in the dryer western states. The 1972 Amendments to the U.S. Federal Water Pollution Control Act indicate that it is a national goal to minimize discharge of waste to surface waters.

The State of California leads the U.S. in reuse with a history of irrigation and reuse that dates back to 1929. The volume of wastewater reused in 1977 was about 227 billion cu m. Of the 200 projects in operation, 150 were classified as nonsensitive crop irrigation and 50 were used to water golf courses, recharge groundwater, industrial reuse and other purposes. (6)

At the billion dollar Disney World complex in Florida, a secondary treatment plant with tertiary holding ponds provides water for tree farms, agricultural usage, aquaculture, and wetlands-land treatment systems.

The largest agricultural water reuse project is located in Muskegon County, Michigan. This single project involves about 4,000 ha. (7)

Lubbock, Texas, can now enjoy one of the largest parks in the U.S. because of innovative water reuse planning. The park covers 640 ha and a recreational greenbelt that is 10 km long. To insure a water supply, reclaimed wastewater will be withdrawn from stored groundwater produced through irrigation of 1800 ha of farm land with municipal wastewater. (8)

On a smaller scale, a turf farmer rented 13.4 ha near the wastewater treatment plant of Tolleson, Arizona. The farmer guarantees the city a minimum rent of $3,500 per year. (9) The farmer uses chlorinated secondary effluent.

Potential Wastewater Contaminants and Nutrients

Wastewater, particularly industrial wastes, contain various amounts of contaminants such as salts, nitrogen, nontoxic organics, toxic elements, and microorganisms.

Salts: The extent and severity of injury caused by salt is influenced by soil characteristics. Dissolved solids will leach out of or accumulate in a soil. Sandy soils permit rapid leaching but at the same time the amount of salt per unit volume of waste available to plants is greater in a sandy soil. Dissolved solids in industrial wastes depends largely on the recycle practices,

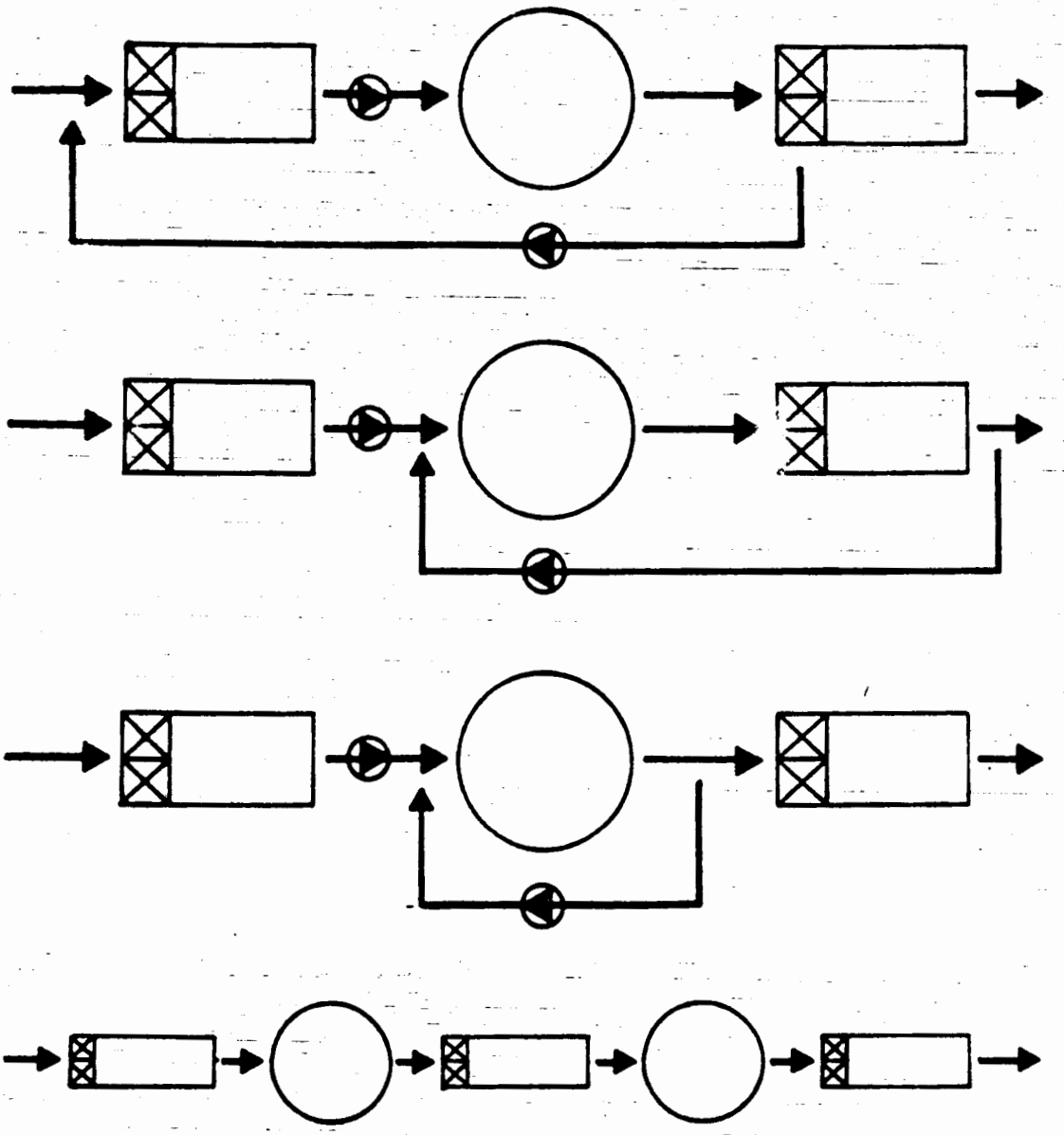


FIG. 5-1

TRICKLING FILTER; FLOW DIAGRAMS

The applicability of the trickling filter process may be summarized by the following statement from the Manual of Design of Sewage Treatment Plants (1967) as follows: "They are capable of providing adequate treatment of such wastes where the production of a plant effluent of 20 to 30 milligrams per liter of BOD is acceptable or where partial treatment is acceptable."

5-2. Performance of Trickling Filters

5-2.1 General

The flow pattern of the wastewater in a trickling filter is generally assumed to be plug flow. However the results of tracer studies indicate that mixing does take place in the filter. However, no backmixing is possible. Some particles of liquid will pass through the filter at a much more rapid rate than others. However, in spite of this mixing the mechanism of biodegradation of the soluble fraction of the wastewater in a trickling filter can be described by first order reaction kinetics applied to a plug flow process.

The overall performance of a trickling filter involves a number of processes including coagulation, flocculation, and/or biodegradation of the particulate organic matter as well as the performance of the final clarifier in separating the suspended solids from the liquid. Eckenfelder (1961) correlated data from a trickling filter using a retardant reaction which, in essence, is a first order reaction applied to a completely mixed tank. Other more recently published material which will be discussed later used similar reactions.

5-2.2 Kinetics of Soluble Organic Removal

The basic mathematical model describing the biodegradation of soluble substrate in a plug flow system were developed in Chapter 2 and presented as equation 2-13. This equation is rewritten as equation 5-1:

$$\frac{S_e^*}{S_o^*} = e^{-kXt} \qquad 5\text{-}1$$

in which

S_e^*	=	effluent concentration of soluble substrate (mg/L)
S_o^*	=	influent concentration of soluble substrate (mg/L)
k	=	rate constant ($time^{-1}$)
X	=	concentration of active microorganisms (mg/L)
t	=	time of flow through the filter

If it is assumed that the entire filter medium is covered with a uniform layer of microorganisms, the total microbial population is a function of the available surface and can be expressed as equation 5-2.

$$X = c_1 A_v \qquad 5\text{-}2$$

in

X	=	active microbial population per unit volume of filter
A_v	=	specific surface of medium (sq ft/cu ft)
c_1	=	constant

The factor c_1 is a function of the thickness of the film, the density of the microbial population in the film, the penetration of oxygen into the film, and the transport of substrate into the film. Oxygen and substrate are transported into the film by means of diffusion processes. The aerobic surface of a thin film is normally underlain by an anaerobic layer. Therefore, a very thick film does not necessarily indicate that the number of active aerobic microorganisms is very large. The soluble organic compounds released during anaerobic degradation will be transported into the aerobic film.

The flow-through time is a function of the real flow per unit area of nominal surface area of the filter medium. Therefore, the flow-through time can be calculated from equation 5-3, if the flow velocity is assumed to be independent of the depth of the filter medium.

$$t = c_2 \, DQ^{-n} \qquad 5\text{-}3$$

in which

t	=	time of flow to travel the depth of the filter
Q	=	hydraulic surface loading (million gallons per acre per day (MGAD)
D	=	filter depth (feet)
c_2, n	=	constants which characterize the medium

The constants n, and c_2, characterize the filter medium and are a function of the size and configuration of the medium. The value of n is relatively constant for several filter media, however, the coefficient c_2 is a function

of the specific surface areas ($c_2 = c_3 A_v^m$). However, in practice it is very difficult to independently evaluate the exponents m and n. Therefore equation 5-3 can be used to describe the flow-through time and can be rewritten as equation 5-4.

$$t = c_3 D A_v^m Q^{-n} \qquad 5\text{-}4$$

The biodegradation rate constant, k, the coefficient, c_1, which describes the relationship between the active microbial population and the specific surface area are interdependent; therefore, cannot be effectively evaluated separately. The coefficient c_2 which relates the time of flow through the filter with the depth and the hydraulic loading can be determined from tracer studies using the tracer response techniques discussed in Chapter 2. However, when these constants and coefficients are determined from biological experimentation, a single constant is developed which can be described by equation 5-5.

$$k^* = k c_1 c_2 \qquad 5\text{-}5$$

Equation 5-1 can be rewritten as equation 5-6 which can be used to calculate the effluent substrate concentration.

$$S_e^* = S_o^* e^{-(k^* A_v DQ^{-n})} \qquad 5\text{-}6$$

This first order reaction is widely used to describe the performance of trickling filters. Unfortunately the substrate removal rate constant, k* is

a function of the configuration of the filter medium, the thickness of the active film, and the characteristics of the influent wastewater as well as temperature. Therefore, this rate constant is different for various types of wastes and types of filter medium. The exponent, n, has been reported to range in value from 0.30 to 0.90. The numerical value of this exponent decreases as the slime thickness increases, and the flow-through time increases as the slime thickness increases. Therefore, it is essential that the exponent, n, is evaluated under process conditions in which a slime layer has been developed rather than using tap water and clean filter medium.

Eckenfelder (1966) reported a method for the determination of a rate constant, k*, and the exponent, n. The exponent in equation 5-6 can be simplified as shown in equation 5-7 and used for the evaluation of experimental data. At a constant flow rate using the same wastewater, the same filter medium, and at a constant temperature, the exponent can be reduced to

$$k^* A_v Q^{-n} = 2.303\, k_Q \qquad 5\text{-}7$$

Equation 5-6 can be rewritten in logarithmic form as shown in equations 5-8 and 5-9.

$$\log_e (S_e^*/S_o^*) = 2.303\, k_Q D \qquad 5\text{-}8$$

$$\log_{10} (S_e^*/S_o^*) = k_Q D \qquad 5\text{-}9$$

The rate constant k_Q is the slope of the line resulting from a plot of the fraction of BOD remaining (S_e/S_o) at various depths of filter medium. This particular plot is shown in Figure 5-2. The data indicate that the rate constant, k_Q, is a function of the hydraulic loading to the filter since the slope of the line describing the fraction remaining data are different for different flow rates. Rearranging and rewriting equation 5-7, the relationship between the k_Q and the hydraulic loading rate is represented by equation 5-10.

$$\log k_Q = \log \left(\frac{k^* A_v}{2.303}\right) - n \log Q \qquad 5\text{-}10$$

The plot of equation 5-10 is also shown in Figure 5-2. The exponent, n, is the slope of the resulting line from the plot of k_Q and the hydraulic loading, Q. The rate constant of k* can be calculated from equation 5-10 since at a hydraulic loading of one the log of Q equals zero then equation 5-10 can be reduced to equation 5-11.

$$\log k_Q = \log \left(\frac{k^* A_v}{2.303}\right) \qquad 5\text{-}11$$

Therefore by extrapolating the line to a hydraulic loading of one the numerical value for k_Q can be graphically determined from the graph. The specific surface area is constant for the particular filter medium, therefore, the rate constant, k*, can be determined from equation 5-11 or graphically. The graphical method is shown by the third plot in Figure 5-2 in which the fraction of substrate remaining (S_e/S_o) is plotted versus the quantity ($A_v\ DQ^{-n}$). The slope of the line resulting from this plot is the rate constant, k*.

are presented as exponential functions to the base e. Therefore, in order to effectively provide information on which comparisons can be made the rate constant, k^*, should be expressed in terms of the base e along with the units in which the hydraulic loading were calculated. The numerical value of the exponent, n, should also be included with the other data.

The influence of the exponent, n, on the rate constant, k^*, is illustrated graphically in Figure 5-3. Experimental data at two different hydraulic loadings to a 20 foot deep filter are used to calculate the rate constant. The exponent, n, was evaluated from tracer studies and n = 0.70. Using this value of the exponent the hydraulic loading rate did not markedly effect the performance of the filter and the slope of the line through the data resulted in a single rate constant, $k^* = 0.056$. However, if the exponent, n = 0.4 as indicated by the literature was used a separate line would fit the data observed at each of the two different hydraulic loadings. These curves are also illustrated in Figure 5-3. The slopes of the lines were $k^* = 0.0121$ and 0.0168, respectively when the exponent was n = 0.40. This illustration may provide a partial explanation for the relatively wide range of values reported in the literature for the rate constant k^*.

Data observed during pilot-scale trickling filter studies using various filter media in a three foot diameter filter are presented in Figure 5-4. An exponent n = 0.50 was used in calculating the data for presentation in this figure. The specific surface area of the medium was 10 sq ft/cu ft of fresh limestone which had an effective size of four to six inches, 27 sq ft/cu ft

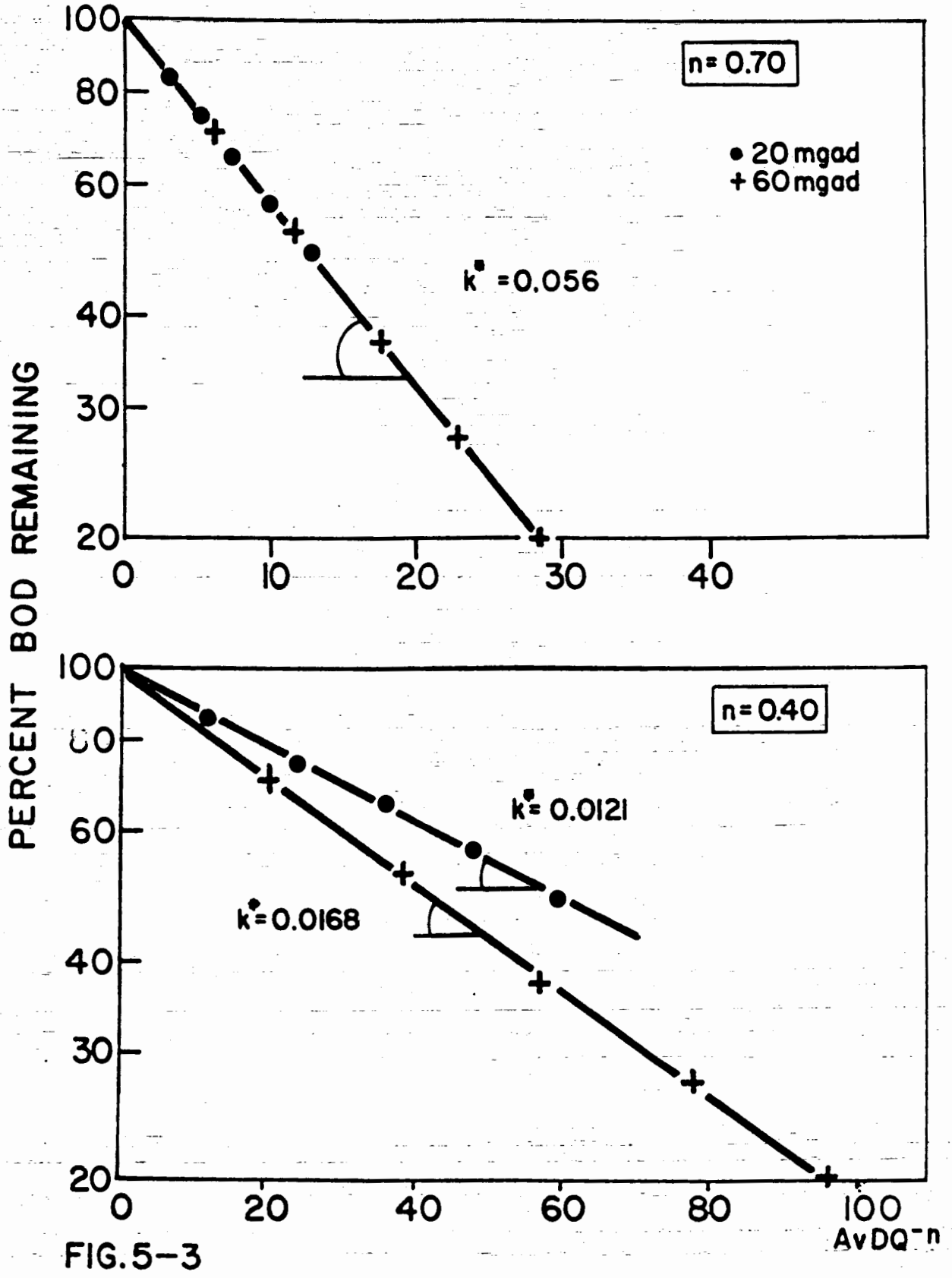


FIG. 5-3

INFLUENCE OF n ON k*

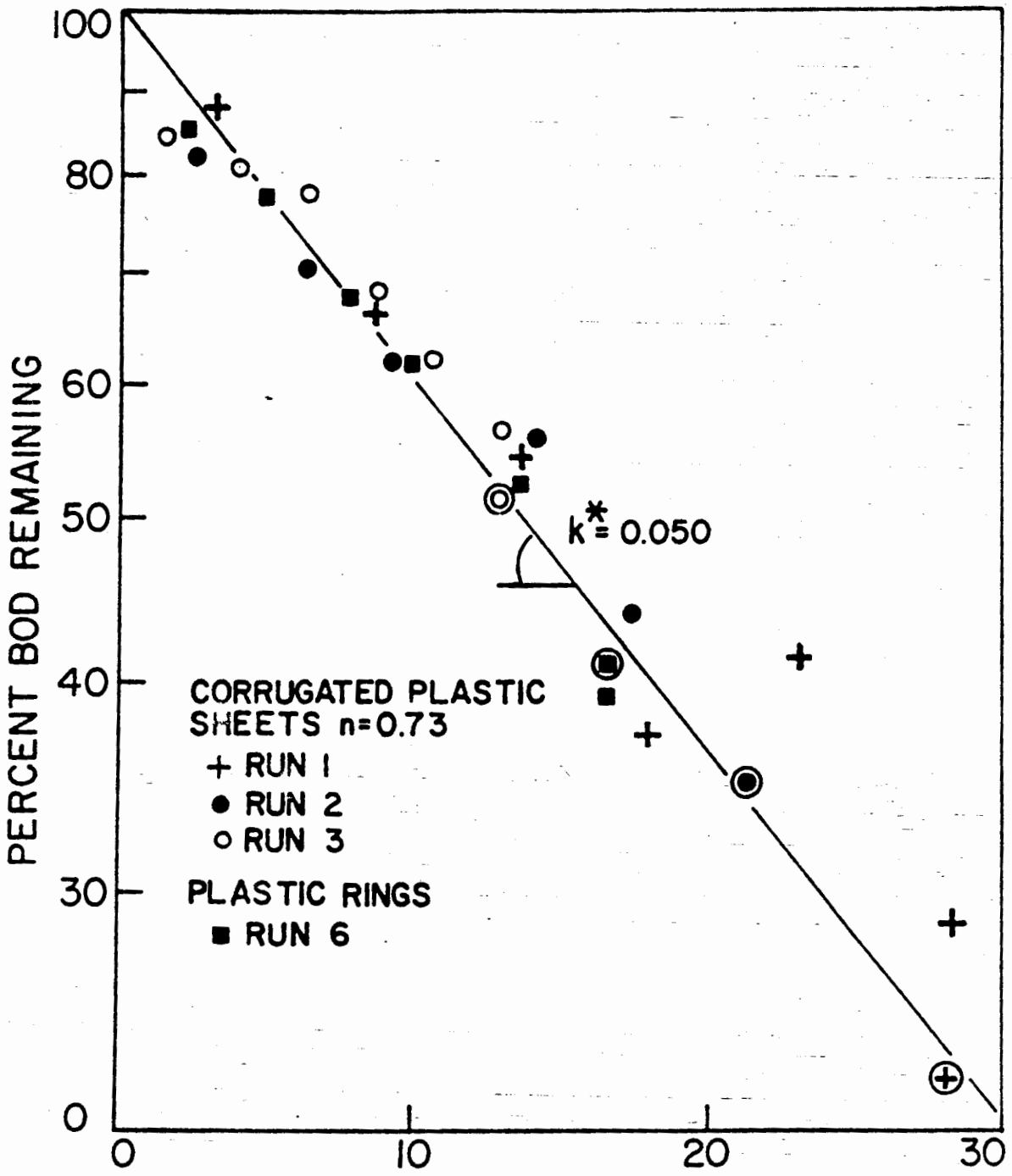


FIG.5-4
DETERMINATION OF $k^* A_V D Q^{-n}$
PILOT PLANT DATA: GOVALLE, AUSTIN

of corrugated plast sheets and 30 sq ft/cu ft of plastic rings. The data observed in the experiments in which the filter medium was either the corrugated plastic sheet or the plastic rings compare quite well. However, it is interesting to note that the slope of line drawn through the data will vary and depends on which data points might be selected. The composite sample data were used to draw the line of best fit because of the scatter among the data observed for the grab samples. The average rate constant for the plastic media was k^*, = 0.017. The data observed for the rock filter medium result in a line which had a slope considerably different than those for the plastic media. The exponent n for corrugated plastic medium was evaluated using data from three experimental runs. The data reported by Gromiec and Malina (1970) indicate that n = 0.73. The value of the exponent n = 0.70 is used for evaluating the data observed when the filter medium was plastic rings. The data compare very well with the data observed for corrugated plastic sheets. The composit sample data observed for the rock medium will be comparable to the plastic medium data only if the exponent n = 0.36. These data are presented in Figure 5-5 and the slope of the line indicates that the rate constant k^* = 0.050. This rate constant is approximately three times that calculated based on an exponent, n = 0.50.

These illustrations indicate the difficulty encountered when correlations of data from different experiments are attempted. The two procedures discussed have limited applications because the exponent, n, is affected by the hydraulic loading rate, however, the value does not reflect the effects of the detention time. The detention time in the trickling filter was expressed in equation 5-3. The coefficient c_2 used in this equation can be assumed

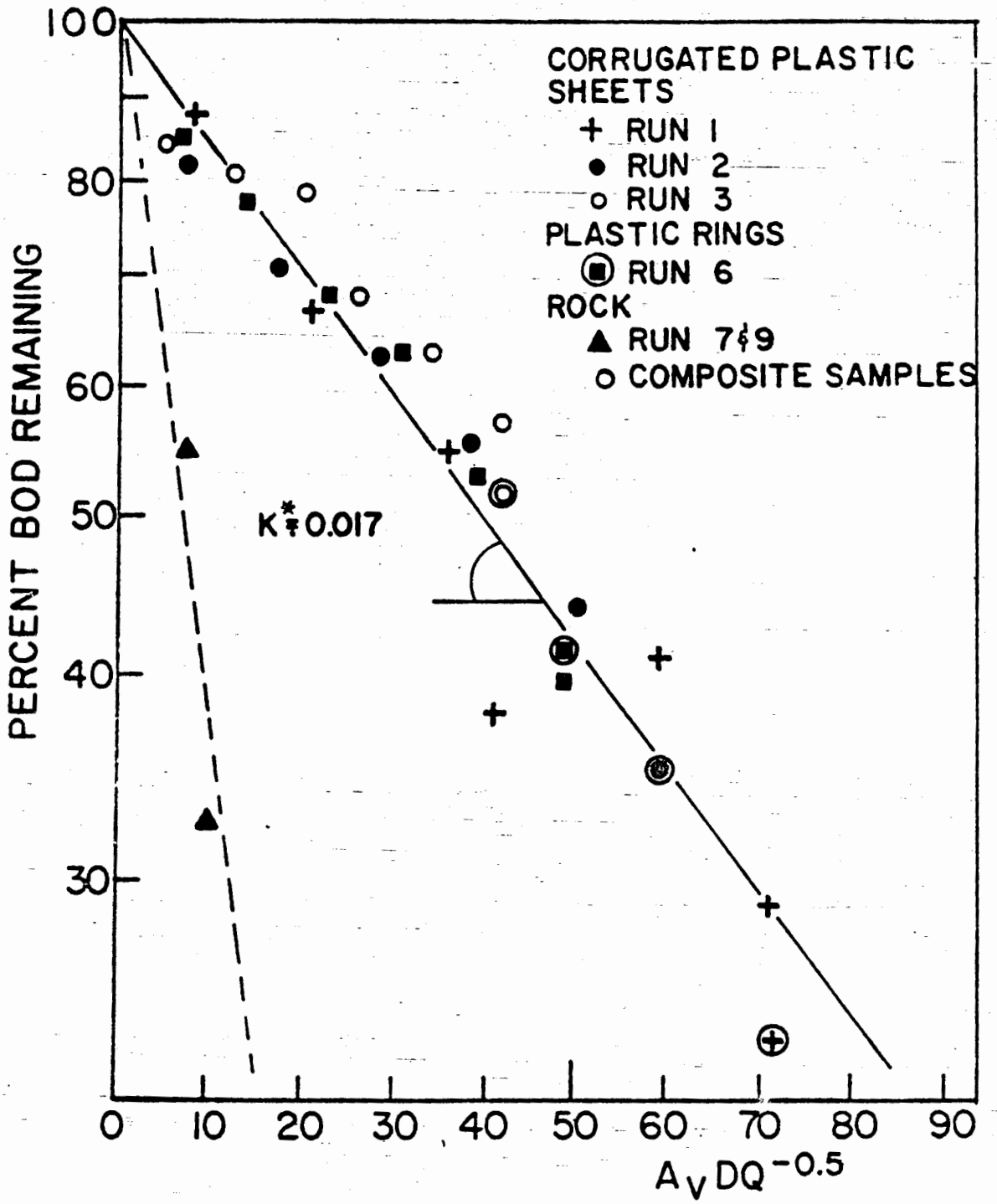


FIG.5-5

DETERMINATION OF k^*

PILOT PLANT DATA, GOVALLE, AUSTIN

to be different for different filter medium and is included in the overall rate constant, k*. Therefore, the rate constant can also be expected to vary with the type of filter medium.

The flow-through time is also a function of the configuration of the filter medium and the hydraulic surface load. Therefore, the flow-through time for different types of filter medium can be characterized and the rate constant can be calculated independent of the detention time.

5-2.3 Factors Affecting Performance

The overall performance of trickling filters traditionally has been related to the hydraulic surface loading and the organic loading. The performance could be correlated to either parameter when the concentration of BOD of the wastewater and the depth of the filter remain relatively constant.

The use of plastic media in place of rocks has led investigators to evaluate other parameters which might be correlatable to the performance of trickling filters. Attempts to correlate the quantity of filter slime to the actual surface area and in turn determine the organic load in terms of pounds of BOD per unit area of slime have been reported by Rincke and Wolters (1970) as well as by Lamb and Owen (1970). The effects of depth of the overall performance of trickling filters which were operated under identical conditions were reported by Keefer and Meisel (1952), Audion et al. (1970),

Chipperfield (1967), and Bruce and Merkens (1970). Trickling filters were packed with medium to depth of up to 25 feet and the specific surface area of the media ranged from 12.2 square feet per cubic foot up to 67 square feet per cubic foot of corrugated or tubular plastic medium. The influent concentration of BOD of the wastewater was 200 to 400 mg/l. The results of studies using settled municipal wastewater applied to corrugated plastic medium indicated that the volumetric BOD removal rate (lb BOD/1000 cu ft-day) was dependent only on the volumetric BOD loading (lb BOD applied/ 1000 cu ft-day) and was independent of the depth.

The relationship between BOD removal and the specific surface area is presented in Figure 5-6. The data indicate that the BOD removal increases as the specific surface area increases. The results of tracer studies conducted by Bruce (1970) are plotted in Figure 5-7. These data indicate that the relationship between the detention time in the filter and the specific surface area of the filter medium is approximately linear. The data observed at higher specific surface areas deviate somewhat from linearity. This deviation from linearity may be partially attributable to the geometric configuration of the particular medium.

The performance of trickling filters is therefore related to the volumetric BOD loading as well as the specific surface area of the filter medium. The volume of filter medium required for effective treatment is considerably less for plastic media which have higher specific surface areas than for rock. Theoretically, the relationship between the volume required and the specific surface area may be presented as Equation 5-13.

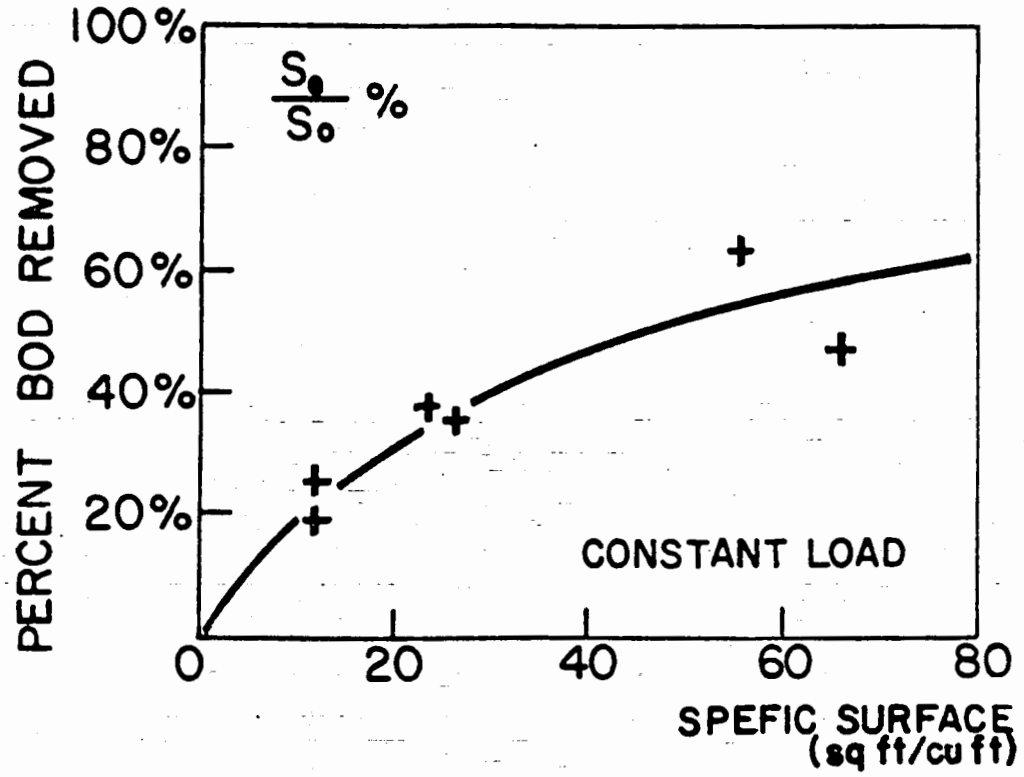


FIG.5-6
BOD REMOVAL VERSUS SPECIFIC SURFACE

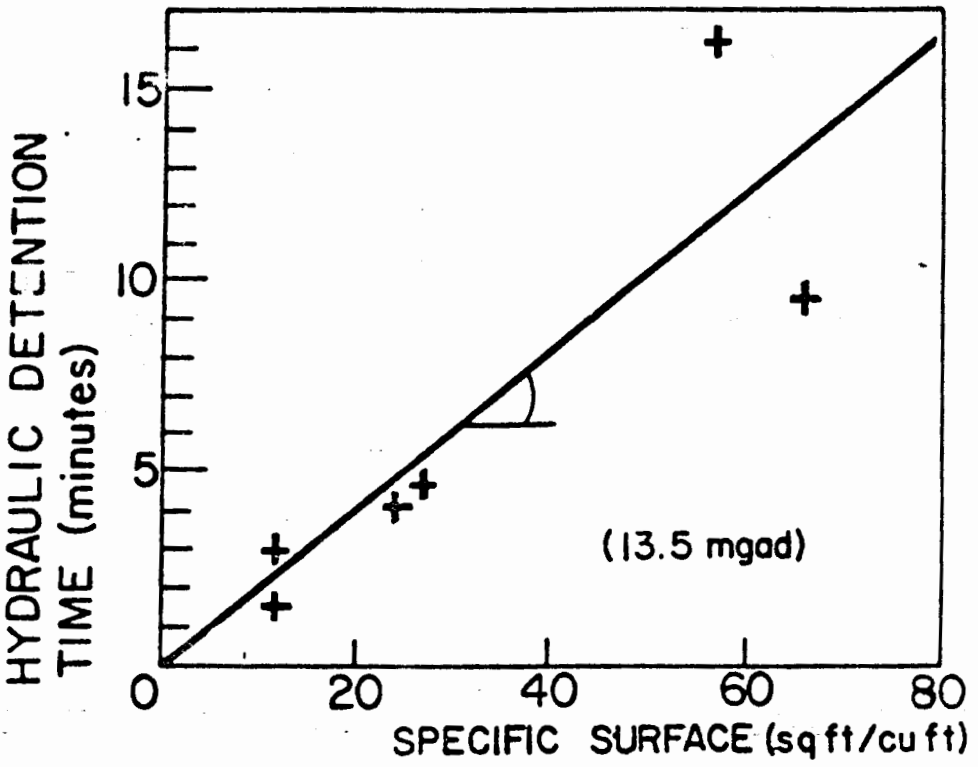


FIG.5-7

BOD REMOVED AND HYDRAULIC DETENTION TIME OVER SPECIFIC SURFACE

$$\frac{V_x}{V_o} = \frac{A_{vx}}{A_{vo}} \qquad 5\text{-}13$$

in which:

V_x = required volume of plastic filter medium (cu ft)

V_o = required volume of rock filter medium (cu ft)

A_{vx} = specific surface area of plastic medium (sq ft/cu ft)

A_{vo} = specific surface area of rock filter medium (sq ft/cu ft)

This relationship has not been completely verified; however, some of the results of the more recent experiments indicate that this relationship is valid. A safety factor in the relationship to reflect the effective slime area is incorporated when filter medium other than rock is used. Equation 5-14 represents this relationship in which it is assumed that only 70 percent of the difference in the specific surface area of the plastic medium and the conventional rock medium is effective and that the specific surface area of rock filter medium, A_v = 12 sq ft/cu ft.

$$\frac{V_x}{V_o} = \frac{1}{1 + 0.7\left(\frac{A_v - 12}{12}\right)} \qquad 5\text{-}14$$

The relationship between the fraction of volume required for plastic filter medium compared to conventional rock filter medium and the specific surface area are presented in Figure 5-8. The required volume can be reduced by 50 percent when filter medium which has a specific surface area of

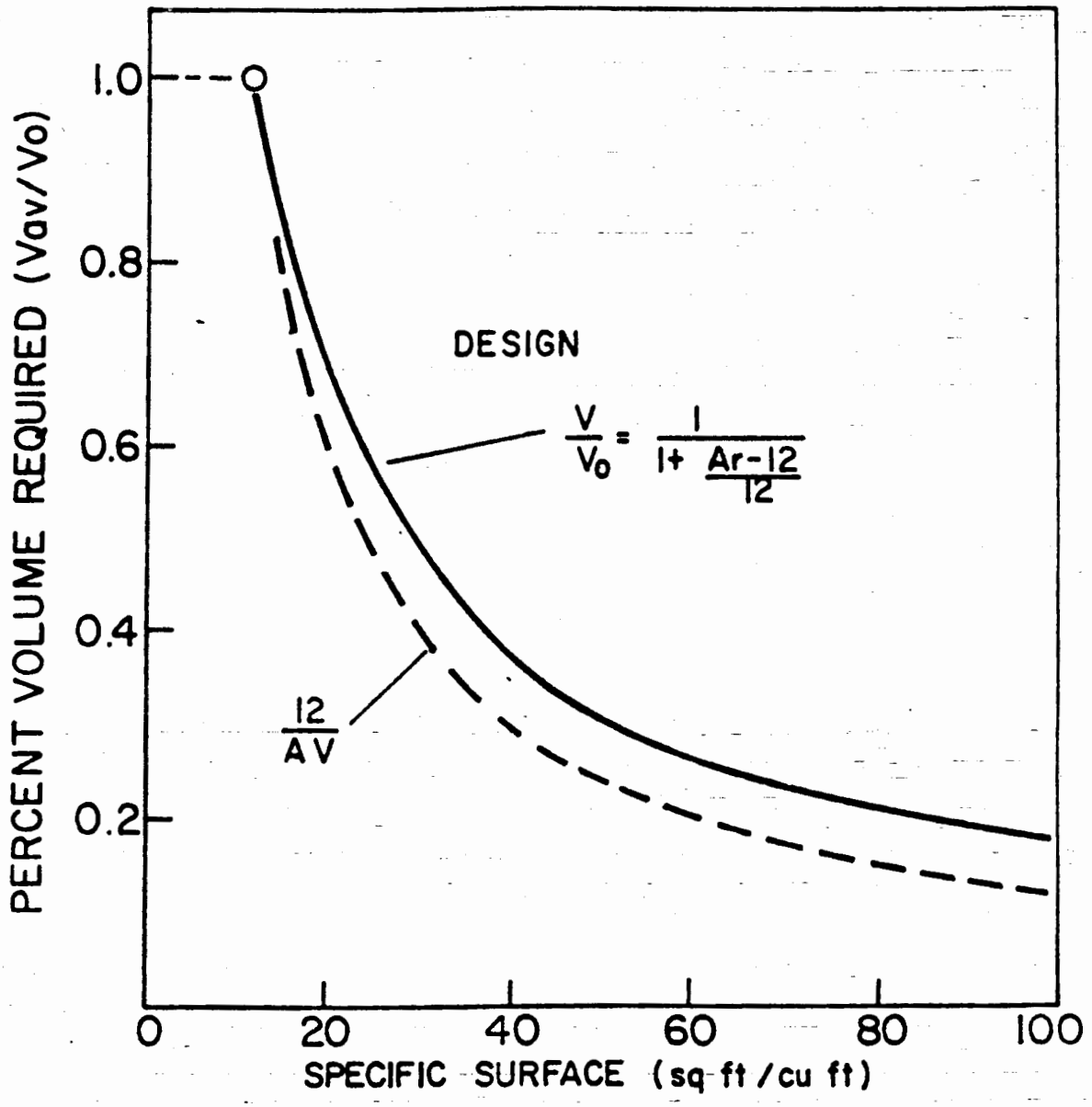


FIG. 5-8
RELATIONSHIP BETWEEN FRACTION OF VOLUME REQUIRED AND SPECIFIC SURFACE

30 sq ft/cu ft is used and the volume requirement is further reduced to 25 percent of the volume required for conventional rock filter material medium when the specific surface area of the filter medium is increased to 60 sq ft/cu ft. However, increasing the specific surface area of the medium beyond 60 sq ft/cu ft does not markedly reduce the volume requirements. Therefore, the removal of BOD by trickling filters should increase as the specific surface area increases. Bruce (1970) has demonstrated this relationship through experimental studies.

The performance of trickling filters expressed in terms of BOD removal can be improved by increasing the specific surface area of the filter medium. This relationship is illustrated in Figure 5-9. The series of curves indicate that the efficiency of a high-rate rock trickling filter can be increased from 50 to 75 percent by replacing the rock medium with a plastic medium with a specific surface area of 60 sq ft/cu ft. However, as the efficiency of the rock filter increases, the improvement in the performance of the filter resulting from increasing the specific surface of the medium is less. For example, increasing the specific surface area of a high rate rock trickling filter operating at an efficiency of 95 percent would result in an efficiency of 98 percent. The specific surface area of 60 sq ft/cu ft seems to be the limiting value since negligible changes in the efficiency and performance of the filter are observed at higher values. Other data indicate that problems with clogging are more common when the filter medium has specific surface area of greater than 60 sq ft/cu ft.

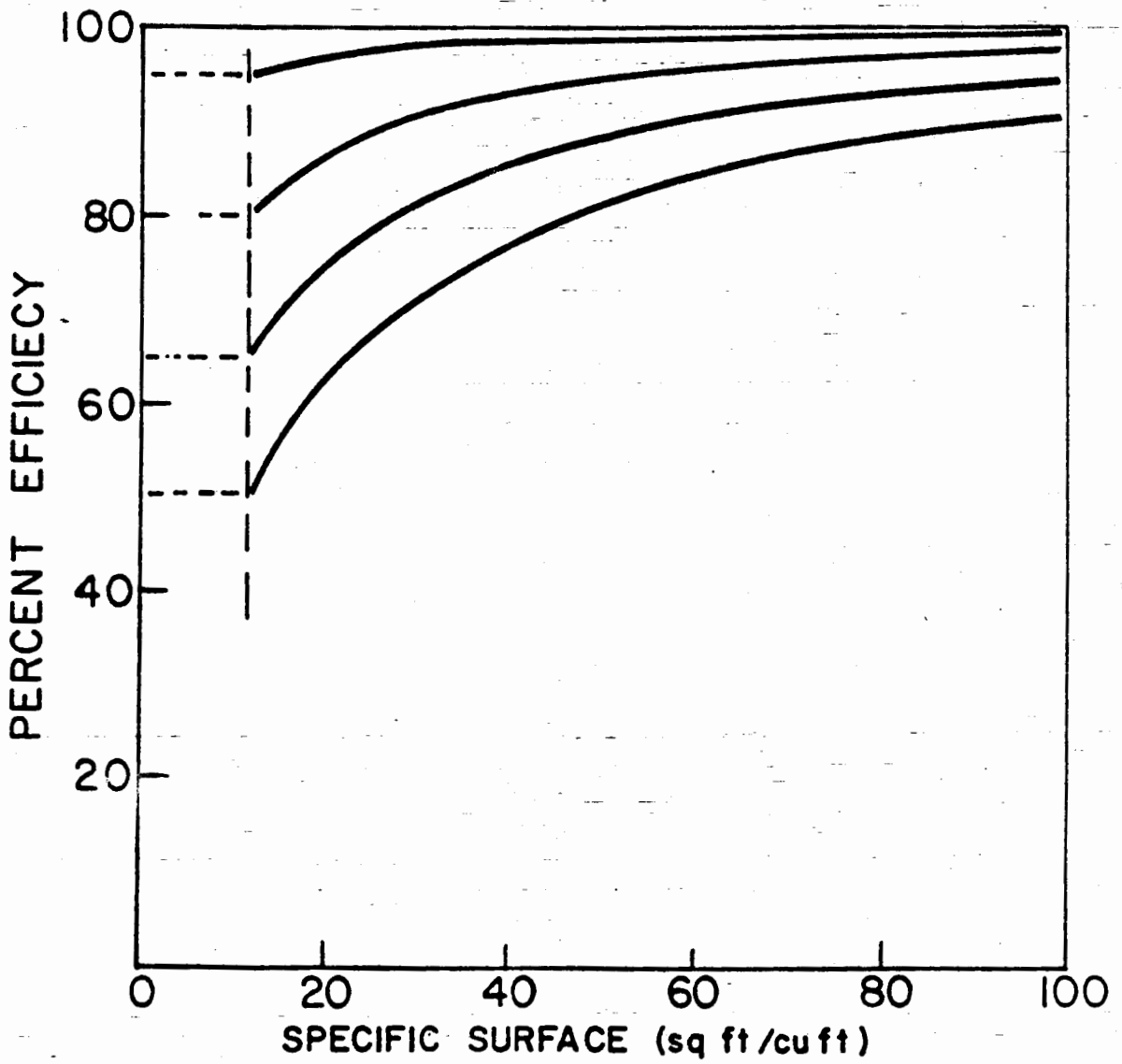


FIG.5–9
PERFORMANCE AND SPECIFIC SURFACE

Theoretically, the efficiency of BOD removal by low-rate trickling filters can also be increased by using a filter medium which has a higher specific surface area than the rock medium. However, the results of investigations by Audion, et al (1970) indicate that the increase in efficiency was negligible at various loadings rates. This phenomenon may be explained by the fact that at low hydraulic loading rates the slime surface is not uniformly wet; therefore, only a small portion of the slime is actually in contact with the wastewater. This uneven wetting is even more noticeable when corrugated or tubular medium is used since the wastewater flows vertically downward with very little lateral distribution. The results of tracer studies reported by Bruce and Merkens (1970) indicate that in a 7.5-foot deep trickling filter with corrugated plastic medium, about 90 percent of the tracer was recovered within an eight-inch diameter circle and that 95 percent of the tracer was recovered within a 16-inch diameter circle. These data indicate that uniform wetting of the surfaces of the filter medium is a very important design consideration. Bruce and Merkens (1970) indicated that the minimum hydraulic loading for a corrugated plastic medium for complete wetting of the surfaces was 10.5 gallons per square foot per hour.

The minimum hydraulic surface loading can be calculated based on the assumption that the wetting or the thickness of the liquid film varies linearly with the specific surface area. Equation 5-15 can be used to calculate the minimum required hydraulic service loading, based on the assumption

that the specific surface area of rock medium A_v = 12 sq ft cu ft and that the rock is uniformly wet at a hydraulic loading of 5 gal/sq ft-hour.

$$q_A = 5\frac{A_v}{12} = 0.42\,A_v \qquad 5\text{-}15$$

q_A = hydraulic surface loading (gal/sq ft-hour)

A_v = specific surface area of filter medium (sq ft/cu ft)

The removal of soluble BOD is a function of the depth of the filter medium, however, the overall performance of a trickling filter was not affected by depth beyond some minimal depth required for the removal of soluble organics. The BOD of the effluent of the final clarifier following a trickling filter is a function of the concentration of suspended solids in the effluent. Bruce and Merkens (1970) reported that the non-soluble BOD of the trickling filter effluent was equal to 60 to 80 percent of the concentration of suspended solids in the effluent. Therefore, the concentration of BOD in the effluent of a trickling filter when the suspended solids concentration is 30 mg/l would be at least 18 mg/l. Therefore, the overall performance of a trickling filter plant can be improved by increasing the efficiency of removal of suspended solids in the final clarifier. This relationship between the BOD and suspended solids in the effluent of biological processes has also been noted for the activated sludge process.

The minimum depth required for trickling filters should be based on the desired effluent concentration of soluble BOD. The significance of depth of the filter in connection with soluble BOD is illustrated in the following example. Equation 5-6 can be used to calculate the hydraulic surface loading which would result in a 95 percent reduction in the concentration of soluble BOD for corrugated plastic filter medium at depths of ten and 20 feet, respectively, assuming that the rate constant, $k = 0.05$, the specific surface area, $A_v = 27$ sq ft/cu ft and the exponent, $n = 0.73$. Using these numerical values, equation 5-6 can be reduced to the relationship between the hydraulic surface loading and the depth as shown in equation 5-16.

$$Q^{-0.73} = \frac{2.21}{D} \qquad 5\text{-}16$$

The calculated hydraulic surface loading for a ten foot and a 20-foot deep filter are 8.0 MGAD and 20.8 MGAD, respectively. Therefore, the volume of trickling filter required for 95 percent removal of soluble BOD for a 20-foot deep filter is approximately one-half the volume required for a ten foot deep filter. Applying a hydraulic load of 20.8 MGAD to a ten foot deep trickling filter would result in an efficiency of removal of soluble BOD of only 78 percent. Therefore, trickling filters should be designed to be deep enough to produce an effluent which has the desired concentration of soluble BOD. The overall performance of trickling

filters is affected to some extent by recirculation of the effluent. Recirculation is recommended in high-rate filters in order to minimize clogging and ponding caused by growth of the slime. The problem of clogging is minimized to some extent by using corrugated plastic filter media which have a relatively high fraction of void spaces. The effect of recirculation on removal of soluble organic material can be determined by developing a massed balance, as indicated in Equation 5-17.

$$\frac{Q\,S_o + Q(RC)S_e}{Q\,(1 + RC)} = \text{effluent concentration} \qquad 5\text{-}17$$

The rate of recirculation is included in the term RC which is equal to the ratio of the recirculated flow to the incoming wastewater flow. Equation 5-17 can be combined with Equation 5-6 and re-written as Equation 5-18, which can be rearranged and expressed as Equation 5-19.

$$\frac{S_e^*\ [1 + (RC)]}{S_o^* + (RC)\,S_e^*} = e^{-kA_vD[(1 + RC)Q]^{-n}} \qquad 5\text{-}18$$

$$\frac{S_e^*}{S_o^*} = \frac{e^{-kA_vD\,[(1 + RC)\,Q]^{-n}}}{(1 + RC) - (RC)\,e^{-kA_vD\,[(1 + RC)\,Q]^{-n}}} \qquad 5\text{-}19$$

in which:

S_o^*, S_e^*	=	concentration of soluble influent and effluent BOD (mg/l)
Q	=	hydraulic surface loading without recirculation (MGAD)
RC	=	Recirculation ratio = (rate of flow of recycle/ rate of flow of influent)

The efficiency of BOD removal using recirculation can be calculated using Equation 5-19 and the parameters for corrugated plastic media. The efficiency for a ten foot deep filter with a hydraulic surface loading rate without recirculation of 20.8 million gallons per day is approximately 78 percent. At a recirculation ratio RC = 1 and RC = 2 the efficiency was about the same, namely 74 percent. In this example, theoretically the performance of the trickling filter is not improved by using recirculation. Similar results were also reported for experiments using corrugated plastic medium at the Govalle Wastewater Treatment Plant in Austin, Texas. These data were observed at hydraulic surface loading rates of 94.5 MGAD without recirculation and with 100 percent recirculation. The effluent soluble BOD in both cases was approximately the same.

Recirculation can improve the efficiency of soluble BOD removal of a trickling filter in those cases where the exponent, n, is relatively low and when the soluble effluent BOD is relatively high without recirculation. The quality of the effluent of trickling filters has usually been reported to be improved when recirculation is practiced. This improved effluent quality is more than likely the result of more uniform wetting of the filter medium and the result of washing out of the accumulated solids from the medium. Therefore, general design practice should include recirculation pumps for conventional (rock) trickling filters. The overall effect of recirculation on performance of a trickling filter plant should be evaluated for each particular installation.

The trickling filter effluent rather than the effluent of the secondary clarifier should be recycled either directly to the filter or through the primary clarifier. This practice is preferred over the normal practice of recirculation from the effluent of the final clarifier, since in many plants chemical flocculating agents would be added to the secondary clarifier in order to improve the efficiency of solids separation.

The operating temperature has an effect on the overall performance of a trickling filter plant in two ways. The biological processes responsible for removal of soluble organic material are temperature dependent and the settling velocity of the suspended material is affected by the change in viscosity resulting from temperature changes. The effect of temperature on the rate of biodegradation is expressed in equation 5-20.

$$k_T = k_{20}\theta^{(T - 20)} \qquad 5\text{-}20$$

The temperature coefficient, θ, has been reported to vary from 1.035 to 1.072 (Eckenfelder 1966). The discrepancy in the value of the temperature coefficient may be attributable to the difference in the depth of penetration of oxygen and the rate of oxygen uptake at different temperatures. Eckenfelder (1966) indicated that the effects of temperature changes would be much more marked at higher loading rates. Bruce (1970) indicated that the temperature coefficient, θ, for the overall performance of a trickling filter plant, ranged from 1.1 to 1.35 with an

average value of 1.21. The average monthly temperature during these experiments varied from 9° C to 18°C. During these studies, the efficiency in some of the filters dropped from 80 percent to 40 percent and in other filters from 55 percent to 20 percent as the temperature dropped. The effect of temperature on high-rate trickling filters must be considered in evaluating the performance of these treatment units.

5-2.4 Rock Trickling Filters

The conventional trickling filter contains a rock medium whi has a relatively narrow range of specific surface areas; therefore, the performance of these trickling filters are not affected by the specific surface area. Various mathematical models have been developed to describe the performance of the trickling filters in terms of hydraulic surface load or organic loading. Fairall (1966) developed the mathematical model expressed in Equation 5-21.

$$\frac{S_e}{S_o\ S_e} = \frac{1}{k}\ \frac{Q}{V} \qquad 5\text{-}21$$

This equation is illustrated graphically in Figure 5-10 in which the rate of substrate removal is related to the volumetric hydraulic loading. The slope of the line through the data is equal to the reciprocal of the rate constant, 1/k. The rate constant ranges from k = 1 to k = 10 (day^{-1}). This wide range indicates that the rate constant is a function of the concentration of substrate in the incoming wastewater or is a function of the BOD volume

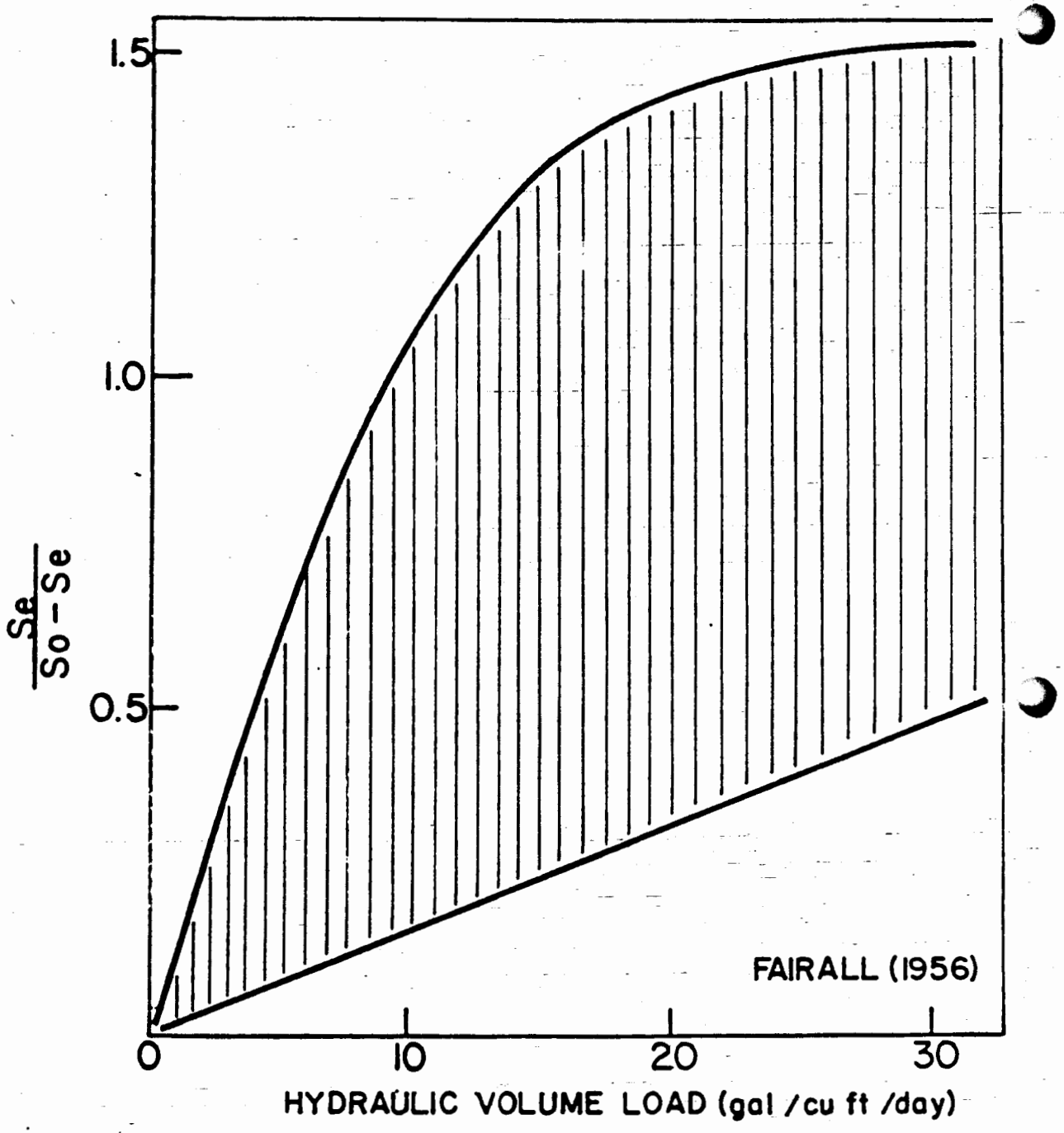


FIG. 5-10
RANGE OF RATE CONSTANTS

load. The data presented by Bruce (1970) also indicate that the BOD volume load affects the rate constant. Therefore, the correlation of the BOD volume load to the efficiency of substrate removal is the preferred method of evaluating data.

The National Research Council (1946) compiled data for 34 operating trickling filters over an eight month period. The range of BOD removal was between 75 and 95 percent for organic loading of up to 2000 lb BOD/acre-day. These data are presented graphically in Figure 5-11 and the average performance of a trickling filter based on these data can be expressed by the model presented in Equation 5-22.

$$\frac{S_e}{S_o} = \frac{1}{1 + 0.0085 \frac{S_o Q}{VF}} \qquad 5\text{-}22$$

in which:

$S_o Q$ = BOD applied (lb/day)

V = volume of medium (acre-feet)

F = number of effective passes = $\frac{1 + RC}{[1 + 0.1\ (RC)]^2}$

The effect of BOD volumetric load on the efficiency of trickling filters has also been reported by Keefer and Meisel (1952) and Rincke (1967) and these data are presented graphically in Figure 5-12. These data indicate that with increasing organic loading rates, the overall performance of trickling filters decreases. The average performance of trickling

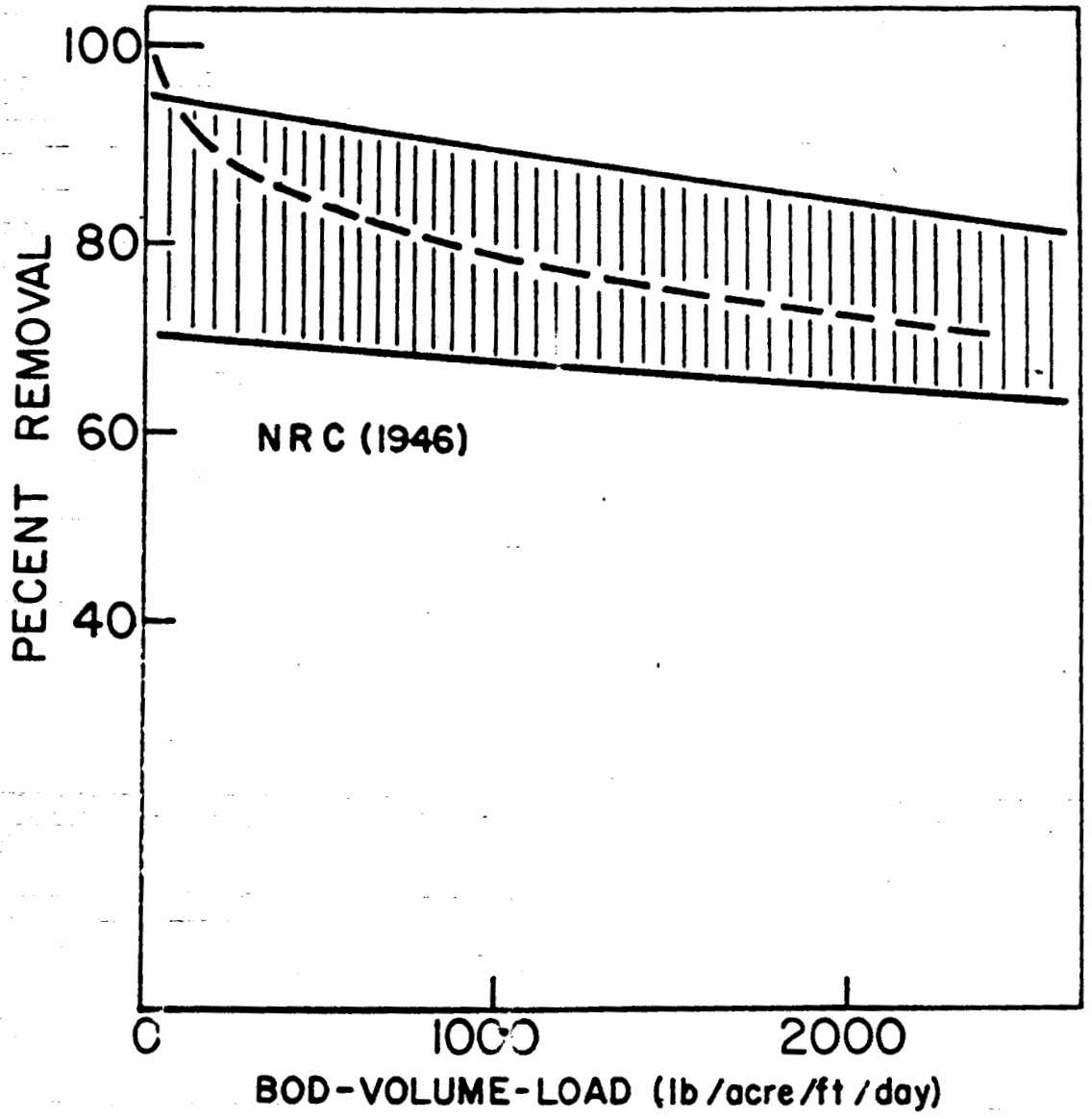


FIG.5-11
REMOVAL AND BOD VOLUME – LOAD

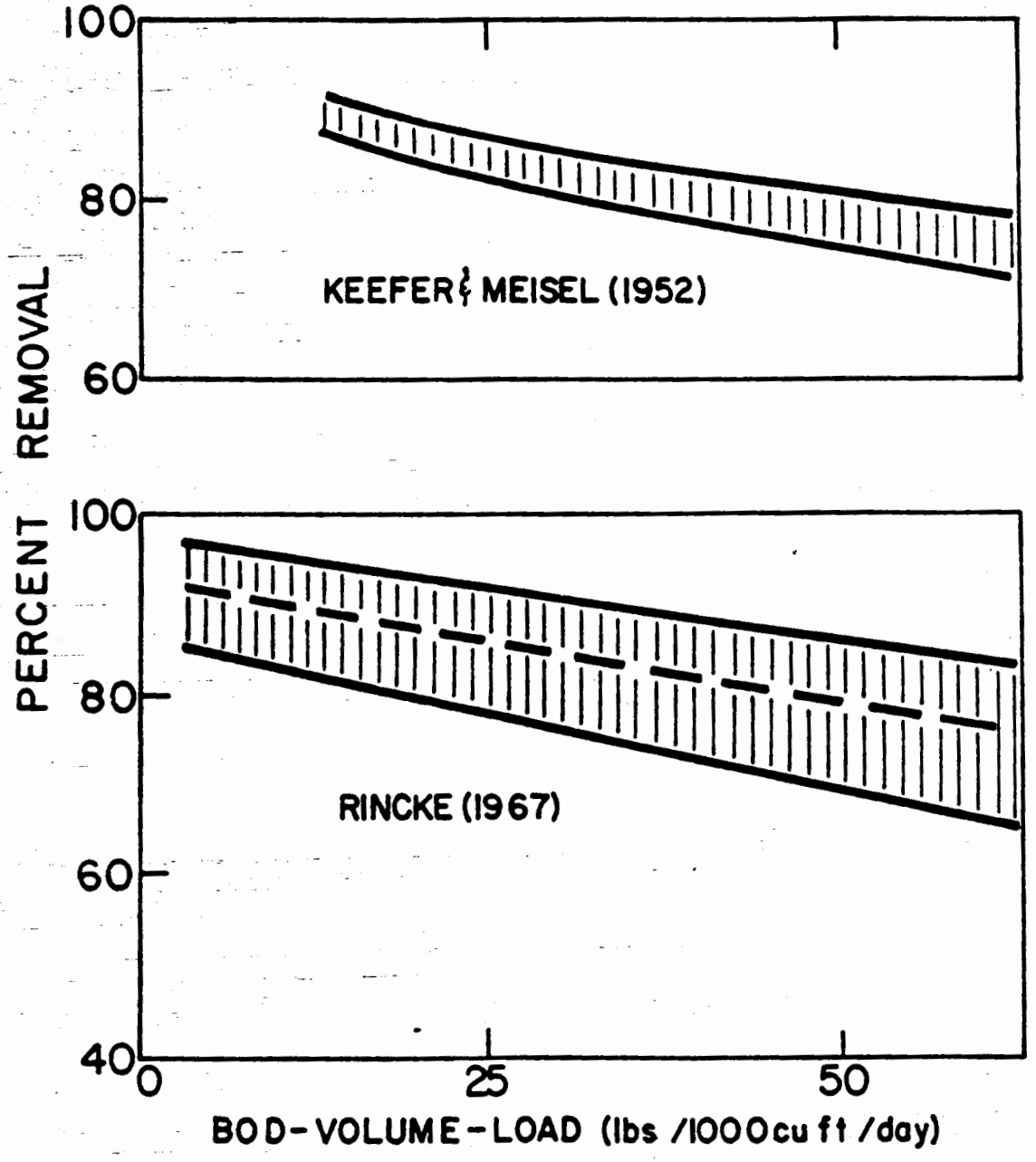


FIG.5-12
REMOVAL AND BOD-VOLUME-LOAD

filters which have a depth between ten and 14 feet has been developed by Rincke (1967) and is expressed in the form of a mathematical model as Equation 5-23.

$$100\,\frac{S_o - S_e}{S_e} = 93 = 0.272\ \frac{QS_o}{V} \qquad 5\text{-}23$$

in which:

$\frac{QS_o}{V}$ = BOD volume load (lb BOD/1000 cu ft - day)

The NRC (1946) data cover a much broader spectrum of operating conditions than the data reported by Keefer and Meisel (1952) or by Rincke (1967). The data reported by Keefer and Rincke are much more comparable and cover a much narrower range, since these data were collected under relatively similar operating conditions.

5-2.5 Excess Sludge

The excess sludge produced in a trickling filter is a function of the rate of conversion of substrate to cell material and the endogenous respiration rate as well as the accumulation of non-biological solids in the filter slime. Sludge production in trickling filters is much similar to that developed in the activated sludge process. The quantity of excess sludge in a trickling filter plant can be determined by a mass balance presented as Equation 5-24.

$$QX_e = Q\,a\,(S_o - S_e^*) - bVX + QX_{on} \qquad 5\text{-}2$$

in which:

Q	=	wastewater flow (MGD)
V	=	filter volume (cu ft)
X_e	=	effluent suspended solids from filter (mg/l)
X_{on}	=	influent nonbiodegradable suspended solids (mg/l)
S_o	=	influent BOD (mg/l)
S_e^*	=	effluent soluble BOD (mg/l)
X	=	biological sludge mass per unit volume (lb/cu ft)
a, b	=	constants

The sludge mass in a trickling filter can be related to the specific surface area by Equation 5-25.

$$VX = f(VA_v) \qquad 5\text{-}25$$

Combining 5-24 and 5-25 and rearranging the terms results in Equation 5-26.

$$\frac{Q}{VA_v} X_e = \frac{Q}{VA_v} [a(S_o - S_e^*) + X_{on}] - b \qquad 5\text{-}26$$

The constants in this equation can be evaluated graphically as illustrated in Figure 5-11 which represents a plot of the (BOD + SS) loading versus the excess sludge. The data in the plot are based on the assumptions

that the effluent soluble BOD concentration is approximately zero and that the influent non-biodegradable suspended solids equal the total suspended solids entering the system. The data presented in Figure 5-13 represent experimental results reported by Bruce and Merkens (1970) and data observed at the Govalle Wastewater Treatment Plant in Austin, Texas for rock and plastic rings filter media, respectively.

The data indicate that the slope for the data reported for the Austin plant is somewhat higher than that for the other data. The wastewater at the Austin plant has a lower ratio of BOD to suspended solids which might account for the higher slope. The slope of the lines tend to decrease at the higher loading rates and is possibly the result of a lower rate of solids biodegradation at the higher loadings than at lower loadings. An estimate of the excess sludge from a high-rate trickling filter can be generally determined by Equation 5-27 which is derived from the data plotted in Figure 5-13.

$$\frac{Q}{VA_v} X_e = 0.5 \frac{Q}{VA_v} (BOD + SS) - 0.5 \qquad 5\text{-}27$$

The excess solids are expressed in terms of pounds of solids per thousand square feet of filter medium per day in this equation. Equation 5-27 can be written as Equation 5-28:

$$X_e = 0.5 (BOD + SS) - 0.5\left(\frac{VA_v}{Q}\right) \qquad 5\text{-}28$$

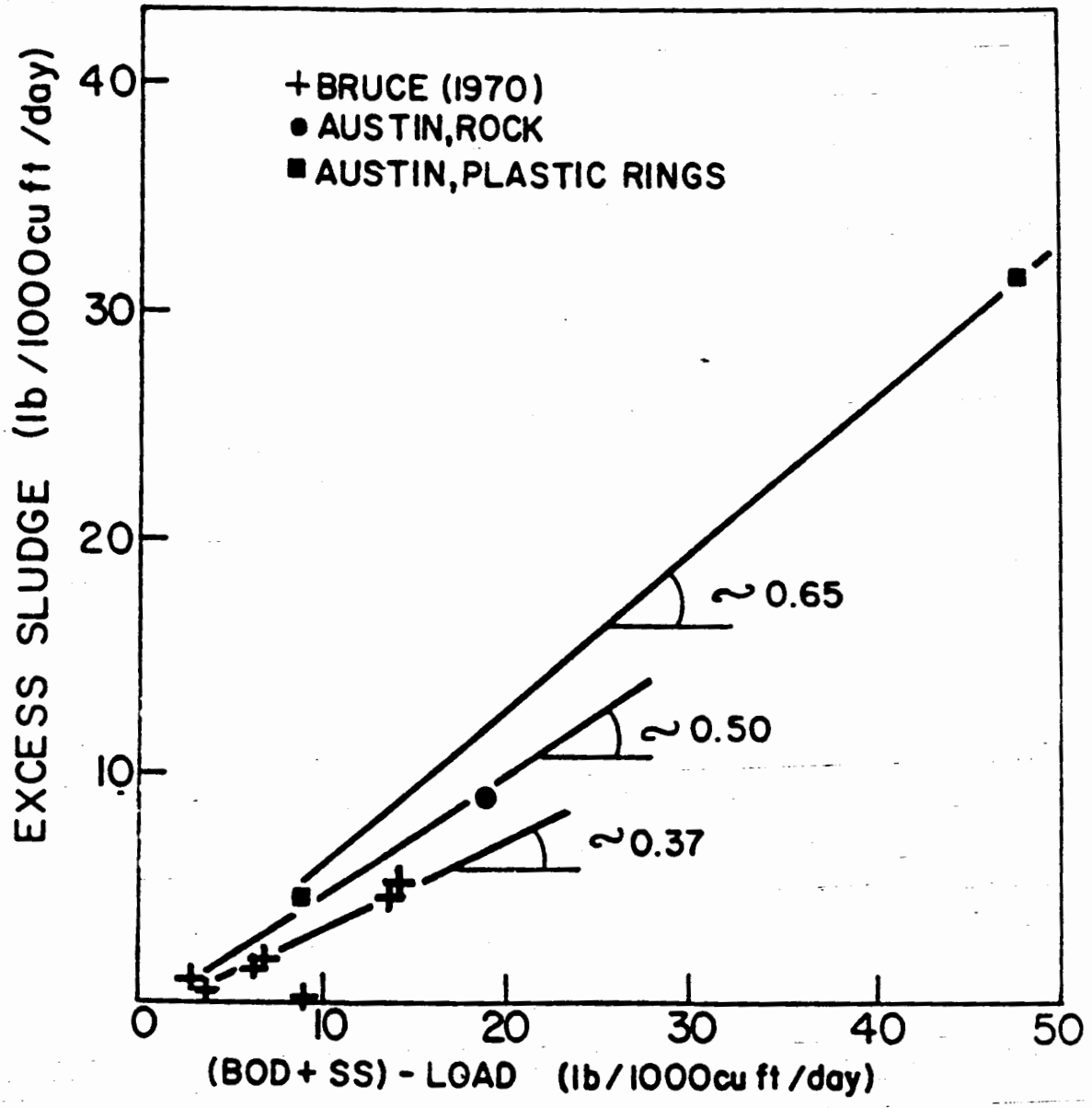


FIG.5-13
EXCESS SLUDGE FROM TRICKLING FILTERS

This equation indicates that 50 percent of the (BOD + SS) is converted to suspended solids which remain in the filter effluent. This conversion factor is somewhat lower than that reported for activated sludge systems.

The quantity of excess sludge produced in a low-rate trickling filter is much lower than that reported for high-rate filters or for the activated sludge process. The lower rate of solids accumulation may be attributable to the grazing activities of microorganisms. The activity of the protozoa is reduced considerably at low temperatures. Therefore, slime tends to accumulate in the trickling filter during winter operation and the filter tends to unload the slime in the spring when the activity of the microorganisms is once again increased.

5-3 Design Factors

5-3.1 Basic Design Data

The data required for design of trickling filter plants is the same information as is necessary for the design of activated sludge plants.

5-3.2 Design Considerations

Conventional trickling filters which contain rock require excellent primary clarification of the incoming wastewater in order to avoid clogging of the filter medium and ponding of the wastewater. Filters in which plastic corrugated or tubular medium which has relatively high void spaces is used can tolerate much more suspended solids than the rock medium,

therefore, very efficient clarification of the wastewater is not a prerequisite. However, a primary clarifier should precede any trickling filter treating municipal wastewater. Slag and other similar materials tend to clog in a similar fashion, as does rock filter medium.

Recirculation of the effluent of the trickling filter to the primary clarifier or to the trickling filter may be practiced. The primary advantage of recirculation is to maintain uniform wetting of the slime on the filter medium and possibly to improve the removal of soluble BOD when high effluent concentrations result without recirculation.

5-3.3 Filter Volume and Filter Medium

The volume of the filter medium required and the cost can be calculated for conventional rock filters. This cost then can be compared with the cost of other filter media. The cost estimate should include the medium, the structure for the various filter media, and pumping. A conventional rock-like material has specific surface area which ranges between ten and 20 sq ft/cu ft whereas the plastic filter media have specific surface areas that range from 25 to 70 sq ft/cu ft. The filter medium can be classified as follows:

(a) randomly packed material (rocks, stones, plastic rings, raschid rings, etc.)

(b) self-supporting modules or corrugated plastic sheets

(c) suspended corrugated sheets

(d) self-supporting plastic pipe or tubular materials

The main advantage of the plastic filter media is a high percentage of void spaces which is between 90 and 97 percent of the total volume compared to 30 to 50 percent of the volume for conventional rock filters. The void space provides for circulation of air as well as minimizes the potential clogging problems. As the specific surface area increases, the void space decreases.

The relationship between the clear space openings and the specific surface areas for various types and configurations of synthetic filter media are presented in Figure 5-14. It is interesting to note that square pipes, honeycomb pipes, spheres and corrugated sheets which have the same diameter of open space or distance between sheets have about the same specific surface area. Circular pipes exhibit the highest specific surface area if the inside and outside surfaces of the pipe are included. However, at relatively small pipe diameters, the void space between the pipes becomes clogged with solids and the specific surface will decrease to about one-half the theoretical value. Corrugated plastic sheets have specific surface areas which are about twice that of a plain sheet. Calculation of the specific surface area for corrugated plastic sheets which are placed 2.1 inches apart indicate a theoretical specific surface area of 27.5 sq ft/cu ft. This value compares favorably with the value of 27 sq ft/cu ft reported by the manufacturers. Therefore, the curves in Figure 5-12 can be used to give preliminary estimates of the relationship of specific surface area and the distance between sheets or clear diameters. A

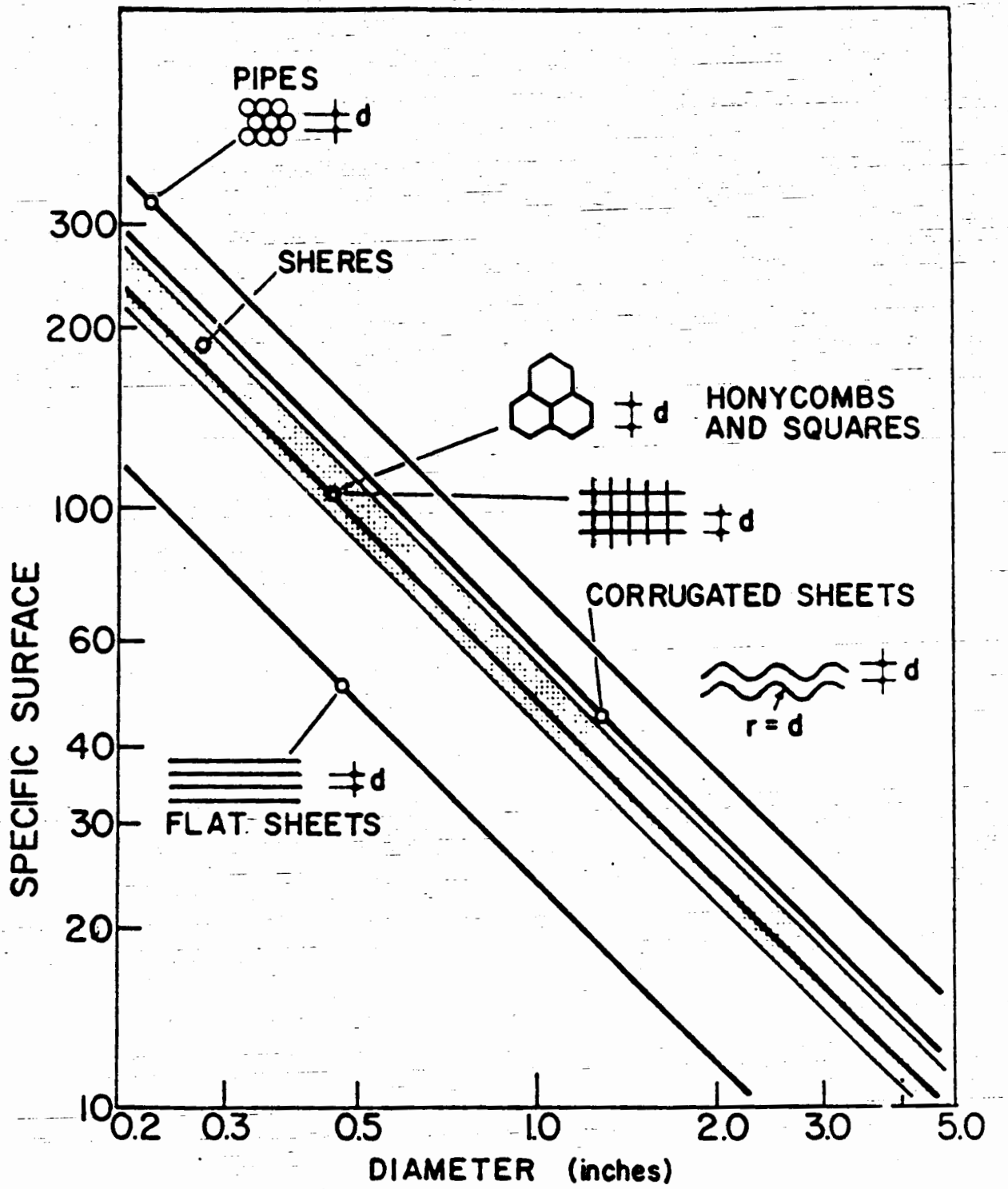


FIG.5-14
RELATIONSHIP OF SPECIFIC SURFACE AND DIAMETER FOR VARIOUS MEDIA

clear opening of 0.7 - 0.8 inches is required to avoid clogging of the medium by slime. This limitation therefore also limits the maximum specific surface area to about 70 sq ft/cu ft.

5-3.3 Operating Factors

There are two operational techniques of improving the efficiency of a trickling filter system which is already installed. Recirculation may be employed or the dosing frequency can be changed. Recirculation can minimize ponding and clogging by washing out the accumulated slime and solids. Hawks and Shepherd (1970) reported that the dosing frequency also can affect the operation of a trickling filter. Dosing frequencies of 0.3 and 14 minutes were used over a five-year period of operation. The results indicate that in the summer, the performance of the trickling filter was better at high dosing frequencies and in the winter the performance was better at the low dosing frequencies. At the lower dosing frequency, a high hydraulic loading is applied to relatively small areas of the filter and the washout effect is therefore greater. At the low dosing frequency in the wintertime, less slime tends to accumulate than at the high dosing frequencies. Variation of dosing frequency might be considered to improve the operation of low-rate trickling filters as well.

5-3.4 Design Formulation

Various design formulations have been developed and various standards of design have been recommended. The Ten State Standards

(1968) recommended design loading rates of up to 50 lb BOD/1000 cu ft - day. The efficiency of BOD removal at this range of organic loadings is between 67 and 75 percent. These efficiencies are at the lower end of the range reported in Figures 5-9 and 5-10. These standards do not include any temperature effects and it seems that the design performance includes winter conditions. Other published information indicates that the efficiency is limited to about 80 to 85 percent regardless of the type of filter medium and depth of medium used. Low-rate trickling filters can be operated at higher efficiencies than the high-rate trickling filters.

The results of studies conducted in England with smaller size graded rocks and slags indicate that detention times in these filters are relatively long and that high efficiencies of BOD removal are possible. Eden (1964) reports that for a five-foot deep trickling filter detention time of one to two hours are possible depending on the rate of hydraulic application. Therefore, a higher efficiency can be obtained at these longer detention times.

Trickling filters which are packed with plastic media require uniform wetting and the flow of the wastewater is essentially vertically downward. Therefore, long detention times are not possible with this type of filter medium. In England, two stage filtration is employed for many industrial wastes. The first-stage trickling filter is operated as a high-rate filter with a plastic medium. The second-stage trickling filter is operated at a low-rate using conventional rock or slag media.

The performance of single stage conventional rock filters at different BOD volume loads are presented in Table 5-2. The efficiency is expressed as the average as well as the recommended design values. At the lowest BOD volume loading, the effluent BOD concentration should average about 20 mg/l although values of 25 mg/l can be expected.

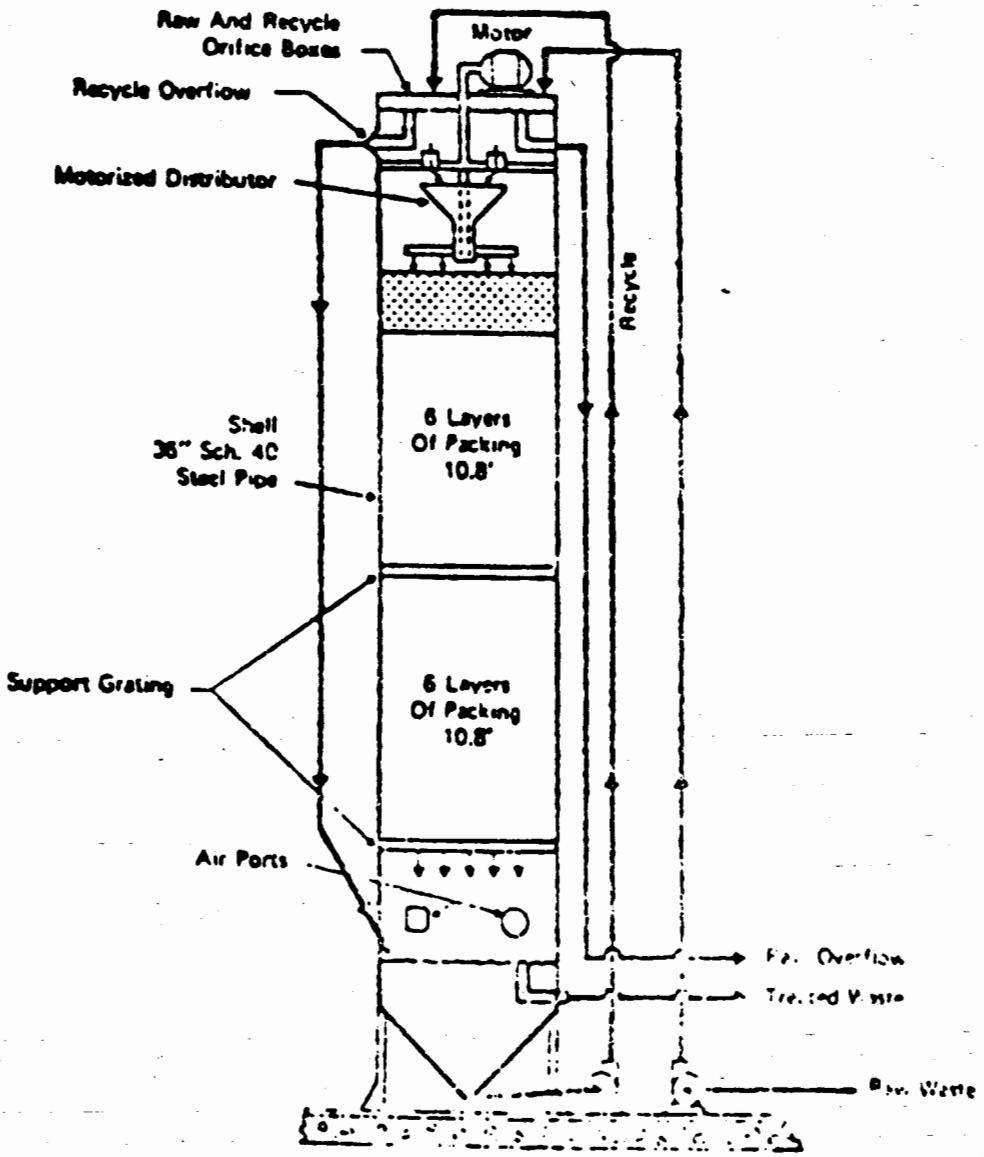
The required volume of filter medium can be reduced when plastic corrugated or tubular material is used. The reduction in volume required can be calculated using Equation 5-14. However, in order to maintain uniform wetting of the medium, the hydraulic surface load required can be computed from Equation 5-15. The excess sludge produced during high rate trickling filtration can be calculated from Equation 5-27.

TABLE 5-2

TRICKLING FILTER DESIGN

Conventional Filling Material
($A_v \sim 12$ sq ft/cu ft)

BOD Volume Load lb/10^3 cu ft/day	Efficiency Average	Design
10	~ 82%	75%
50	~ 77%	67%
75	~70%	60%



PILOT SCALE TRICKLING FILTER CROSS SECTION

FIGURE 1

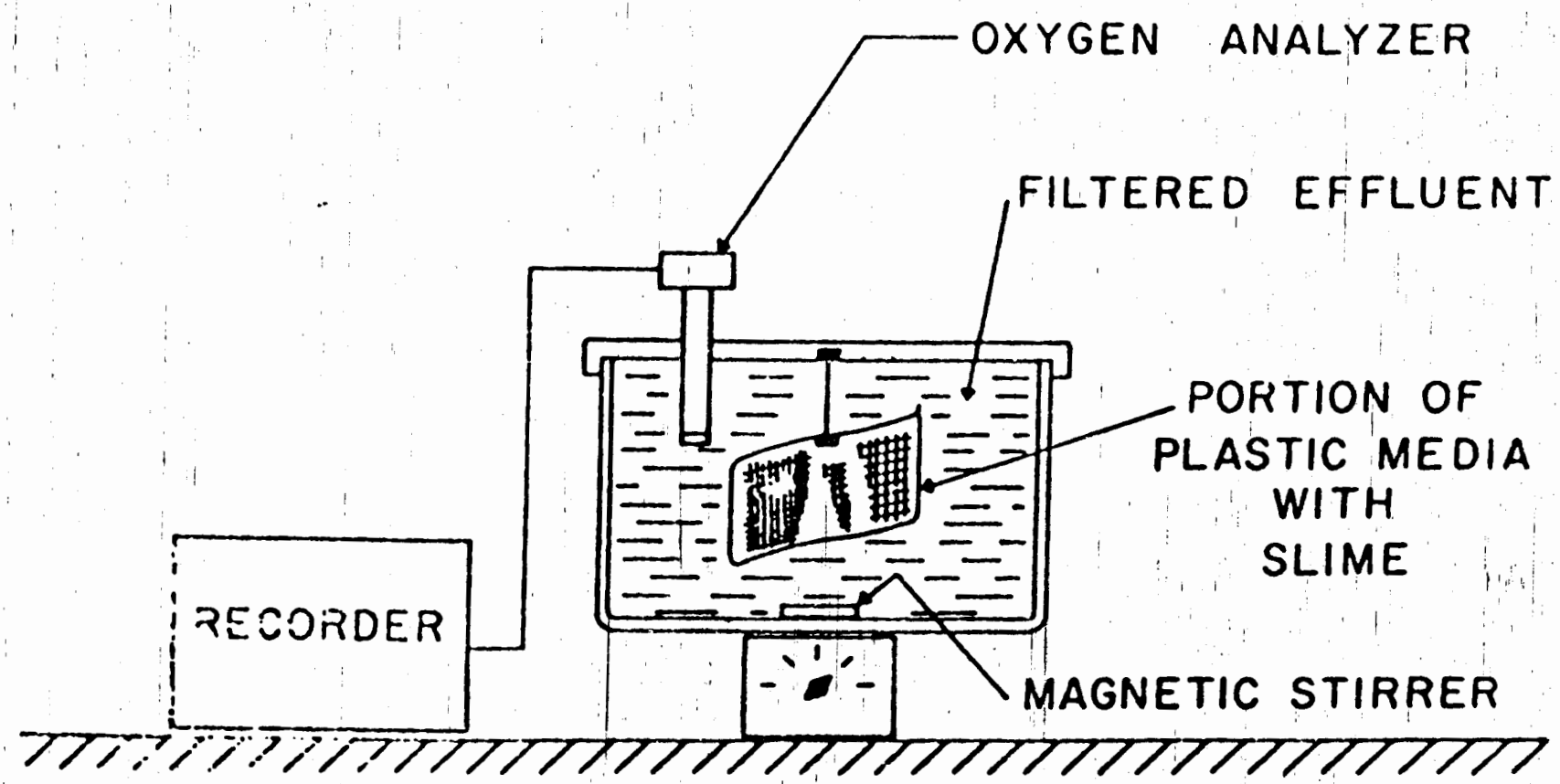


FIG. 3-4 SCHEMATIC OF LABORATORY APPARATUS FOR MEASUREMENT OF OXYGEN UPTAKE RATES FOR FILTER SLIMES

TABLE 4-3 SURFACE OXYGEN - UTILIZATION RATES*

Organic loading (lb BOD/day/1000 cu ft)	Hydraulic loading (gpm/sq ft)	Temp. (°C)	Depth from top of filter (feet)	k_r (T) (mg O_2/hr/sq cm)	$k_{r(20)}$ (mg O_2/hr/sq cm)
69	1.5	30	10.5	0.074	0.034
			17.6	0.061	0.028
161	3.0	24	10.5	0.076	0.056
			17.6	0.066	0.049

*Average of four sets of data

TABLE 4-4 SUMMARY OF BOD REMOVAL CHARACTERISTICS OF VARIOUS MEDIA TREATING SETTLED SEWAGE

Medium Description	Specific Surface ft^2/ft^3	Average Influent BOD_5 mg/l	$k_{s(20)}$	Date Source
2.5 inch Rounded Gravel	19.7	272	0.583	Water Pollution Research 1959, 1960
1.0 inch Slag	59.8	272	0.769	
Surfpac	27	100*	0.357	Germain, 1966
1.5 Polypropylene Flexirings	40	78	0.460	Anon, Bulletin KF-3 of Koch Eng. Co., 1968
Surfpac	28	200	0.395	Balakrishnan et al., 1968
2.5-4.0 inch Rock	15	200	0.275	(Personal Communication
Surfpac	28	200	0.330	with Dow Chemical Co.)
Flocor	27	162	0.486	Jank, 1969
Surfpac	27	53	0.359	This Research

* Estimated value

BIODISC TREATMENT

by

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I. INTRODUCTION

A biodisc is analogous to a fixed film reactor. Bacterial slime grows on discs rotating through wastewater. The discs are mounted to a horizontal shaft. The advantages of biodisc system include

a. Simplicity
b. Reliability - with adequate pretreatment
c. Low energy Consumption -
d. Modular construction

Removal Kinetics

The biodisc is considered a single stage reactor. The assumptions on which the Kinetic model is based include

a) uniform biochemical reaction over the entire disc surface
b) the concentration in the tank is the same throughout (complete mix)

A simplied illustration of the biodisc model is presented in Figure 1.

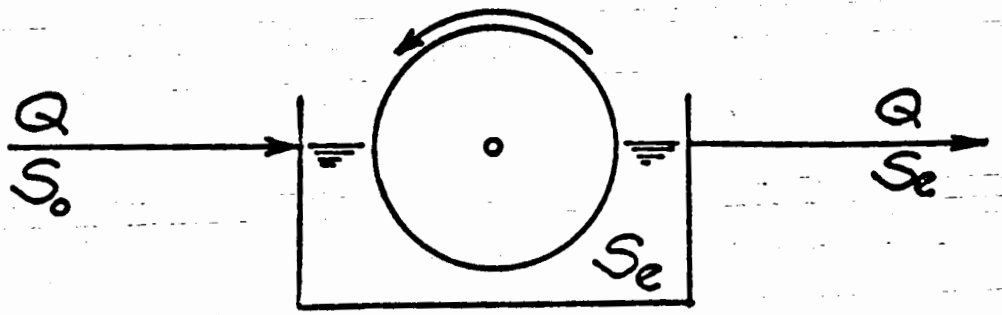


Figure 1 - Simplified Biodisc Model

The specific BOD removal rate may be defined as

$$R = \frac{Q}{A}(S_o - S_e)$$

Where R = Rate of BOD removal per unit area of disc
Q = Wastewater flow rate
A = Disc area
S_o = influent BOD
S_e = effluent BOD

The relationship between (R) Sepcific BOD removal rate and (S_e) the BOD concentration is illustrated in Figure 2.

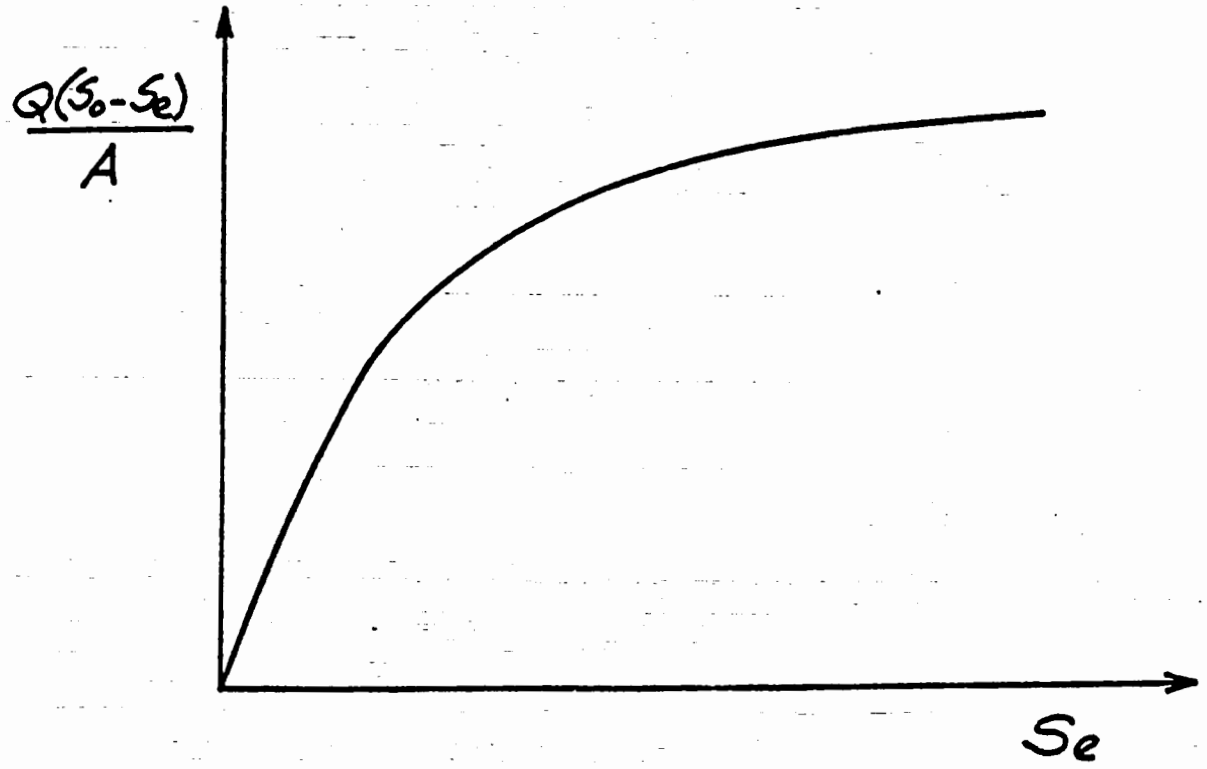


Figure 2 - The relationship between Specific BOD removal and effluent BOD concentration.

The shape of the curve indicated first order Kinetics at low BOD Concentrations and Zero order at high BOD Concentrations. Therefore

$$R = f(S_e) = P\left(\frac{S_e}{K + S_e}\right)$$

Where

P = maximum specific BOD removal rate
K = BOD Concentration (s) at which the specific BOD removal rate is exactly one-half the maximum rate

BIOLOGICAL TREATMENT AS BDAT

FOR PETROLEUM WASTES

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ABSTRACT

The April 8, 1988 Federal Register identified EPA's proposed BDAT standards for treatment of petroleum wastes. Research on the liquid/solids biological treatment of petroleum oily wastes in a controlled tank environment coupled with land treatment is shown to minimize harm to human health and the environment. The University of Texas version of the Regulatory and Investigative Treatment Zone (RITZE) Model is used to analyze the migrational rate of hazardous constituents in biological treated petroleum wastes applied to land farms especially in terms of groundwater protection. Results to date indicate that biological treatment may be able to meet BDAT criteria for some wastes. The use of liquid/solids biological treatment followed by land treatment and RITZE model analysis can be used to support a no migration petition showing such treatment as minimizing potential harm to groundwater, human health and the environment.

INTRODUCTION

On August 17, 1988, the U.S. Environmental Protection Agency issued specific treatment standards for hazardous wastes from the petroleum refining industry (40CFR, Section 268, Subpart D). The wastes are prohibited from land disposal unless these treatment standards are met by use of best demonstrated available technology (BDAT). For petroleum wastes, EPA has been determined that fluidized bed incineration or solvent extraction represents BDAT. Because of inadequate treatment capacity for these BDAT technologies, EPA has granted a two year national variance for petroleum wastes. This means the treatment standards do not have to be met until 1990. Since

many petroleum refineries rely on land treatment (land farm) for their wastes, the two year variance allows time for these refineries to develop treatment alternatives or to demonstrate that their land treatment facilities allow "no migration" of hazardous constituents.

Research is currently directed towards developing a biological liquid/solids treatment (LST) system, i.e., slurry phase which will treat refinery waste to the greatest achievable standards. The original objective of the LST research was to demonstrate a process that could meet BDAT criteria. However, based on laboratory results to date, it appears that biological LST may meet BDAT criteria for organics only under rigorous process constraints. A more realistic approach is the application of biological LST as a pretreatment step prior to land treatment. This paper discusses such an approach utilizing laboratory data on treated residuals from bench scale LST reactors as input to the RITZE (Regulatory and Investigative Treatment Zone, Expanded) model. The model is then used to successfully demonstrate that this combined treatment approach achieves no migration of hazardous constituents.

BACKGROUND

BDAT for Petroleum Wastes

On August 17, 1988, the Environmental Protection Agency (EPA) finalized specific treatment standards for the following hazardous wastes from the petroleum refining industry--dissolved air flotation float (K048), slop oil emulsion solids (K049), heat exchanger bundle cleaning sludge (K050), API separator sludge (K051) and leaded tank bottoms (K052).

The Hazardous and Solid Waste Amendments (HSWA), enacted on November 8, 1984, require EPA to promulgate regulations that restrict the land disposal of hazardous wastes. Specifically, the HSWA specify dates when particular groups of hazardous wastes are prohibited from land disposal unless it has been demonstrated to the EPA Administrator that there will be no migration of hazardous constituents from the disposal unit or injection zone for as long as the wastes remain hazardous.

Land disposal is defined as the placement of hazardous waste in a landfill, surface impoundment, waste pile, injection well, land treatment facility, salt dome formation, salt bed formation or underground mine or cave.

Best demonstrated available technologies (BDAT) are technologies that can be used with a specific hazardous waste to substantially diminish the toxicity of the waste or substantially reduce the likelihood of migration of hazardous constituents from the waste so that short- and long-term threats to the environment are minimized. Wastes that meet

treatment standards established by EPA are not prohibited and may be land disposed in a Subtitle C hazardous waste facility.

EPA identifies full-scale technologies that are practical and whose performance has been 'demonstrated'. Such technologies are evaluated to determine whether they: (a) are commercially available, (b) do not present a clear increase in risk to human health and the environment when compared to land disposal of the untreated wastes and (c) substantially diminish the toxicity of the waste or substantially reduce the likelihood of migration of hazardous constituents from the waste.

The performance data from such technologies are then evaluated to determine whether the data is representative of well-designed and well-operated treatment systems. Only data from well-designed and well-operated systems are included in determining BDAT. The performance data on such systems are statistically analyzed to determine the performance level representative of treatment by BDAT.

EPA may establish treatment standards as either a specific technology, or as a performance level of treatment monitored by measuring the concentration of hazardous constituents in the waste or treatment residual or in an extract of the waste or treatment residual. When possible, EPA prefers to establish treatment standards as performance levels, allowing industry flexibility in meeting the treatment standard. Under such conditions, industry may use any technology not otherwise prohibited, e.g., impermissible dilution, to meet the treatment standard.

EPA has determined that for BDAT organics in the K048-K052 wastes, fluidized bed incineration achieves a level of performance that represents treatment by BDAT. EPA also believes that a well-designed and well-operated rotary kiln incinerator will achieve the applicable treatment standards for K048-K052. For metals in the incinerator ash, EPA has determined that stabilization using a lime/flyash binder achieves a level of performance that represents BDAT. For metals in the wastewater, EPA identified chromium reduction followed by chemical precipitation and vacuum filtration as BDAT for metals.

These technologies were judged to be demonstrated and available because they are commercially available and provide substantial reduction of the organic and metal hazardous constituents. Table 1 presents the BDAT standards for the listed refinery wastes.

Biological Liquid/Solids Treatment Systems

Biological LST systems are analogous to conventional biological suspended growth processes such as activated sludge, extended aeration and aerobic digestion. LST is used to reduce the

TABLE 1
BDAT TREATMENT STANDARDS FOR PETROLEUM WASTES
(NON-WASTEWATERS)

Constituent	K048		K049		K050		K051		K052	
	Total (mg/kg)	TCLP (mg/l)	Total (mg/kg)	TCLP (mg/l)	Total (mg/kg)	TCLP (mg/l)	Total (mg/kg)	TCLP (mg/l)	Total (mg/kg)	TCLP (mg/l)
Anthracene	*	*	6.2	*	*	*	6.2	*	*	*
Benzene	9.5	*	9.5	*	*	*	9.5	*	9.5	*
Benzo(a)anthracene	*	*	*	*	*	*	1.4	*	*	*
Benzo(a)pyrene	0.84	*	0.84	*	0.84	*	0.84	*	0.84	*
Bis(2-ethylhexyl) phthalate	37	*	37	*	*	*	37	*	*	*
Chrysene	2.2	*	2.2	*	*	*	2.2	*	*	*
o-Cresol	*	*	*	*	*	*	*	*	2.2	*
p-Cresol	*	*	*	*	*	*	*	*	0.9	*
Di-n-butyl phthalate	4.2	*	*	*	*	*	4.2	*	*	*
Ethylbenzene	67	*	67	*	*	*	67	*	67	*
Naphthalene	**	*	**	*	*	*	**	*	**	*
Phenanthrene	7.7	*	7.7	*	*	*	7.7	*	7.7	*
Phenol	2.7	*	2.7	*	2.7	*	2.7	*	2.7	*
Pyrene	2	*	2	*	*	*	2	*	*	*
Toluene	9.5	*	9.5	*	*	*	9.5	*	9.5	*
Xylenes	**	*	**	*	*	*	**	*	**	*
Cyanides (total)	1.8	*	1.8	*	1.8	*	1.8	*	1.8	*
Arsenic	*	0.004	*	0.004	*	0.004	*	0.004	*	0.004
Chromium (total)	*	1.7	*	1.7	*	1.7	*	1.7	*	1.7
Nickel	*	0.048	*	0.048	*	0.048	*	0.048	*	0.048
Selenium	*	0.025	*	0.025	*	0.025	*	0.025	*	0.025

*Not Applicable
**Reserved

quantity and toxicity of hazardous organic wastes. These processes treat wastes that are in a suspended solid, slurry or sludge form. The process relies upon the mobilization of the contaminants into the aqueous phase where they are then susceptible to microbial degradation and volatilization. The mobilization or dissolution step can be a result of microbial action and/or physical-chemical action. In either case, this is an important step in the overall process. Another way to view the LST concept is a combination of the phenomenon which occur in land treatment and in conventional suspended growth systems.

The ability of LST to significantly reduce the level of contaminants in a waste stream involve the following primary phenomena: (1) the extraction (solubilization) of the organics into the aqueous phase, (2) biodegradation of the extracted organics into less toxic and less environmentally significant forms, and (3) the volatilization of the contaminants from both the hydrocarbon and the aqueous phases. It is important to realize that regardless of the chosen flow regime, LST require sufficient mixing of the liquid and solids to achieve effective mass transfer of (1) the organics to the aqueous phase and (2) the terminal electron acceptor (in most cases oxygen) to the microorganisms, and the suspension of solids in solution.

The most frequently used process configuration is a single, batch reactor system in which the extraction and biodegradation occur concomitantly in a heterogeneous liquid/solids reactor (i.e., tank, pit, lagoon). The reactor is loaded with the contaminated organic material and air is introduced to provide both mixing for the extraction process and oxygen for the biological reactions. Aeration and mixing may be provided by submerged aerators, floating aerators or compressors and spargers (lances). It is important to provide both adequate mixing and good oxygen transfer. The dissolution/extraction of the contaminants is directly related to the mass transfer of the contaminants from the solid/hydrocarbon phase into the aqueous phase. Generally speaking, the more energy provided for mixing, the higher the rate of mass transfer. In addition, since the aqueous phase degradation will occur by microbial action, adequate quantities of oxygen must be supplied for microbial treatment. Additional factors influencing the rate of microbial degradation include temperature, pH and available nutrients such as nitrogen, phosphorous.

At the completion of the treatment, the aeration and mixing are discontinued and the solids are allowed to settle. The treated liquid is decanted and discharged while the treated solids are further treated by conventional land treatment or disposed of on site. If the process is applied to a lagoon or surface impoundment, it may be possible to decant the liquid and leave the solids in place.

LST is a relatively new approach for the remediation of contaminated organic materials. There have been several applications of LST for the treatment of wood treating, coal tar and most recently petroleum wastes. The success of these systems combined with the historically successful land treatment of petroleum, wood preserving and coal tar wastes point to the fact that LST can be technically and economically feasible for the treatment of emulsified tars, soils, hydrocarbon sludges and highly contaminated soils.

No Migration Issues

A no-migration variance is a decision that can be rendered by EPA to allow the land disposal, at a particular facility, of specific, prohibited wastes not meeting the treatment (BDAT) standards established by EPA for those wastes. Anyone that desires a no-migration variance must demonstrate "to a reasonable degree of certainty that there will be no migration of hazardous constituents from the disposal unit or injection zone for as long as the waste remains hazardous".

Generally, the term "to a reasonable degree of certainty" is interpreted to mean that hazardous constituents applied to a land disposal unit will not exceed human health-based or environmentally protective levels beyond the edge of the disposal unit. In most cases, the disposal unit is defined as the limit of the engineered components. Both interpretations may be defined differently in some site-specific cases. This definition of no migration does not allow for fate and transport of hazardous constituents above acceptable levels outside the boundary of the unit.

Land treatment units are subject to all of the general provisions of the land disposal restrictions program, since they are considered to be disposal units under RCRA. To apply restricted wastes which do not meet the BDAT performance standards, an owner or operator of a land treatment unit must apply for a no-migration variance.

The petition must demonstrate that the no-migration standard is met for all media. Many wastes that are currently land-treated contain significant amounts of organic constituents and/or metals. Therefore, the petition must demonstrate a sufficient level of degradation and/or immobilization or waste constituents and metals within the treatment zone. For the volatile constituents, the applicant must demonstrate that the health-based or environmental standards are not exceeded by air emissions.

For land treatment units, the information included in a land treatment demonstration and in a Part B permit application should include most, if not all, of the technical information needed for a no-migration petition. Some additional information and predictive modeling results, particularly for

air emissions may be needed for specific sites.

Such a demonstration can be made by using site-verified emission models, emission monitoring and/or ambient air monitoring. Another means of meeting no migration requirements for air emissions is to remove the volatile constituents from the waste prior to land treatment. A variety of processes are capable of reducing volatile constituents to extremely low concentrations. These processes include solvent extraction, thermal treatment, composting and biological liquid/solids treatment. Although these processes represent an additional compliance cost, they can represent significant cost savings over meeting BDAT performance standards.

Accurate and representative modeling of waste constituent modeling will be an integral part of most petitions. The models used and the assumptions underlying them must be thoroughly explained. It may necessary to use several models to evaluate the various contaminant transport routes. For land treatment systems, several models exist to evaluate contaminant degradation and mobility in the unsaturated zone as well as to estimate air emissions.

Land Treatment

Land treatment has been the most widely used technology for the treatment and disposal of hazardous waste. The technology has been used for over 30 years for the treatment of oily wastes primarily from the petroleum refining industry. An extensive data base exists with this technology which has been applied to the development of other biological processes.

Land treatment uses the assimilative capacity of the soil to decompose and contain the applied waste in the surface soil layer (usually the top 6 to 12 inches). This upper soil layer is the zone of incorporation. The incorporation zone, and the underlying soils where additional treatment and immobilization of the applied waste constituents occurs, is referred to as the treatment zone. The treatment zone depth in the soil may be as much as five feet. However, most of the immobilization will occur in the zone of incorporation.

As shown in many studies (API, 1983, 1984; Brown et.al., 1984, Loehr and Malina, 1986), land treatment systems used for oily wastes do degrade and immobilize the waste applied at such sites. Oil, metals and other constituents of environmental concern are successfully controlled by such systems.

An extensive data base on the degradation of hazardous constituents in land treatment systems has been gathered over the past several years (API, 1987; Sims et.al., 1987). Most of the data has centered on the loss rates associated with aromatics and polynuclear aromatics. The use of land treatment under controlled and well designed and operated conditions

should continue to be available to meet the mandates of RCRA and CERCLA.

RESULTS AND DISCUSSION

A laboratory study is currently underway to develop biological LST systems for the treatment of specific K wastes. Results from this study are preliminary and are not available for publication at this time. However, results from another phase of this study, the biological LST of mixed, weathered K wastes, are presented here and used as input to the RITZE model.

Bench Scale Biological LST

Several 20 liter reactor vessels were used to evaluate the aerobic, biological treatment of petroleum wastes. These wastes were a mixture of slightly weathered wastes. The wastes were treated in batch (or in one case, semi-continuous) reactors with the addition of nutrients (nitrogen and phosphorous) for a period of up to 100 days. Several loading rates (as percent initial Oil and Grease) were studied and fate of volatile organic constituents (specifically BTEX) and polynuclear aromatic compounds (PAH) were monitored over the time of the study. BTEX was also monitored in the off gas from the reactors.

This study was performed as the screening and technology development study prior to the in-depth studies currently in progress. As such, only summary results from these reactors will be presented here. Table 2 presents a summary of the initial characteristics of the wastes (PAH and BTEX) and the characteristics of the residuals from the LST reactors. These reactors averaged 100 percent removal of BTEX. Off gas analyzed showed that most of BTEX were volatilized. This is an important finding, pointing to the possible need for volatiles capture.

It is important to note that the wastes used in this screening study had a high O&G and high PAH content. Additional research includes treatment of a K waste for an operating refinery with an O&G content <10 percent, individual PAH concentrations <10 ppm and total BTEX of <500 ppm. It is expected that much higher levels of treatment will be achieved on this waste than were achieved on the wastes used in the screening study. The results from the screening study were used as input to the RITZE Model as described in the next section.

RITZE Model Application

A mathematical model was used to assess the fate of the organic constituents remaining in treated LST residuals following further treatment in a solid phase/land treatment system. The model is extensively discussed in the Permit Guidance Manual on

CASE STUDIES

Numerous bioremediation case studies exist that identify the performance that can be achieved. The following illustrate specific applications:

Case Study A: On-site treatment was chosen[1] as the closure alternative for a creosote impoundment at a Superfund site in Minnesota. This alternative was identified in the feasibility study as the most cost-effective source control measure for the site. The effectiveness of the bioremediation technology to detoxify contaminated soils at the site was demonstrated in pilot-scale studies. Results of these studies were used to develop design criteria for a full-scale treatment facility.

A lined, 3-acre land treatment facility was constructed in 1985 to treat 10,000 cubic yards of contaminated soil and sludges from the creosote impoundment. The facility has operated successfully since 1986, achieving greater than 90 percent reduction of polynuclear aromatic hydrocarbons (PAH's).

Before the on-site treatment alternative was implemented, bench-scale and pilot-scale studies were conducted to define operating and design parameters for the full-scale facility. Several performance, operating and design parameters were evaluated:

- soil characteristics
- climate
- treatment supplements
- reduction of gross organics and PAH compounds
- toxicity reduction
- effect of initial loading rate
- effect of re-application

Three different loading rates were evaluated in the test plot studies: 2, 5 and 10% benzene extractable (BE) hydrocarbons. The soils used in the pilot study consisted of a fine sand collected from the upper 2 feet of the impoundment. The soil was contaminated with creosote constituents consisting primarily of PAH compounds. Total PAH's in the soil ranged from 1000 to 10,000 ppm, and BE hydrocarbons ranged from approximately 2 to 10% by weight.

Because the natural soils were fine sands and extremely permeable, the full-scale system included a liner and leachate collection system. To simulate the proposed full-scale conditions, the pilot studies consisted of five lined, 50 square foot test plots with leachate collection. The studies were designed to maintain conditions which promote the degradation of hydrocarbons. These included:

- maintain a pH of 6.0 to 7.0 in the media,
- maintain soil carbon to nitrogen ratios between 50:1 and 25:1, and
- maintain soil moisture near field capacity.

Hydrocarbon losses in the test plots were measured using benzene as the extraction solvent. The analysis of BE hydrocarbons provided a general parameter well suited to wastes containing high molecular weight aromatics such as creosote wastes. Reductions of BE hydrocarbons were fairly similar between all the field plots. Average removals in these plots over four months were approximately 40%.

Decreases in the following 16 PAH compounds were monitored:

2-Ring Compounds	4-, 5- and 6-Ring Compounds
Naphthalene	Fluoranthene
Acenaphthylene	Pyrene
Acenaphthene	Benzo(a)anthracene
	Chrysene
3-Ring Compounds	Benzo(j)fluoranthene
Fluorene	Benzo(k)fluoranthene
Phenanthrene	Benzo(a)pyrene
Anthracene	Dibenzo(a,h)anthracene
	Benzo(g,h,i)perylene
	Indeno(1,2,3,c,d)pyrene

Greater than 62 percent removals of PAH's were achieved in all test plots over a four-month period. Table I summarizes first order rate constants and half-life data for BE hydrocarbons and PAH compounds for the 5 and 10 percent BE hydrocarbon test plots. With the exception of the 4- and 5-ring PAH's, the table shows that the kinetic values were about equal for the two loading rates.

Table I. Pilot Scale Kinetic Data at Two Loading Rates

ITEM	Half-life (days)	
	5% Plot	10% Plot
Benzene Extractables	231	231
2-Ring PAH	30	30
3-Ring PAH	43	43
4+Ring PAH	173	693
TOTAL PAH's	77	87

The pilot-scale studies identified operating and design criteria for a full-scale system:

- treatment period was able to be extended through October
- soil moisture should be maintained near field capacity
- soil pH should be maintained between 6.0 and 7.0
- soil carbon:nitrogen ratios should be maintained between 25:1 and 50:1
- fertilizer applications should be in small, frequent doses
- initial benzene extractable hydrocarbon concentrations of 5 to 10% are feasible
- waste re-application should occur after initial waste concentrations have been degraded
- waste re-application rates of 2 to 3 pounds of benzene extractable organics per cubic foot of soil per every three months are feasible during months which degradation can occur.

The full-scale system was constructed and operated. BE hydrocarbons and the PAH compounds were monitored. BE hydrocarbon concentrations decreased approximately 60 percent over the first year of operation. Most of the decrease occurred during the first 120 days (May through September). Little decrease in BE hydrocarbon concentrations occurred during the fall and winter months.

Table II shows average PAH removals in the pilot-scale and in the full-scale studies. Full-scale removal efficiencies were higher than test plot removal efficiencies for every PAH ring class and for BE hydrocarbons. However, it must be noted that the full-scale facility operated for 360 days compared to 126 days for the test plots. Full-scale half-lives were consistently in the low end of the range of half-lives reported for the test plots.

Table II. Comparison of Full-Scale and Test Plot Removals

	Average Percent Removal		Average Half-Life (days)	
Parameter	Full Scale[1]	Test Plots[2]	Full Scale	Test Plots
2-Ring PAH	95	93-95	<45	29-33
3-Ring PAH	95	83-85	45	46-49
4- and 5-Ring PAH	72	32-60	115	95-226
Total PAH's	90	65-76	65	61-83
BE Hydrocarbons	60	35-56	150	106-200

[1] *Removal efficiency calculated after 193 days of treatment*

[2] *Removal efficiency calculated after 126 days of treatment*

In summary, the rate and amount of PAH degradation was proportional to the number of rings contained by the PAH compounds. The 2-ring and 3-ring PAH's degraded most rapidly. The 4-ring and 5-ring PAH's degraded at slower rates. However, these compounds are strongly adsorbed to soils and were immobilized in the treatment zone of the facility. Table III summarizes water quality data for the leachate collection

Table III. Underdrain Water Quality

	CONCENTRATION ppb		
Compound	June 1986	August 1986	October 1986
Naphthalene	<1	<1	<1
1-Methylnapthalene	<1	<1	<1
2-Methylnaphthalene	<1	<1	<1
Acenaphthylene	<1	<1	<1
Acenaphthene	<1	3.7	2.7
Fluorene	<1	<1	<1
Phenanthrene	<1	<1	<1
Anthracene	<1	<1	<1
Fluoranthene	<1	2.1	1.4
Pyrene	<1	<1	<1
Benzo(a)anthracene	<1	<1	<1
Chrysene	<1	<1	<1
Benzofluoranthenes	<5	<1	<1
Benzopyrenes	<5	<1	<1
Indeno(1,2,3,c,d)pyrene	<5	<1	<1
Dibenzo(a,h)anthracene	<5	<1	<1
Benzo(g,h,i)perylene	<5	<1	<1

system of the facility. Only acenaphthene and fluoranthene were detected in the drain water samples. Concentrations for these two compounds were near analytical detection limits.

The full-scale unit has matched or surpassed the performance of the pilot-scale unit in degrading creosote organics. The advantages of on-site treatment are that it reduces the source of contaminants at the site in a very cost-effective manner. It also meets the approach of regulatory agencies toward on-site remedies and reduces the liability of the owner/operator due to off-site disposal.

Case Study B: On-site bioremediation was evaluated, using laboratory treatability studies, to decontaminate soil containing petrochemical wastes[2]. The objective was to identify the use of this technology as a viable closure alternative for the contaminated soils from ponds, impoundments and storage lagoons that contained waste industrial sludges. Toxicity screening analyses estimated the potential impact of the material on soil biota, the relative toxicity of the contaminated soil, the initial application rates to be used, and the detoxification that occurred during bioremediation. Six detailed treatability studies evaluated the effect of: (a) loading rates, (b) moisture level, and (c) need for amendments. The primary emphasis was on determining degradation (loss) rates of representative polyaromatic (PAH) hydrocarbons.

The results of the treatability studies indicated that the moisture level in the bioremediation of contaminated soil was a critical parameter for the degradation of 2-, 3- and 4-ring PAH's. With the moisture content maintained at 80 percent of field capacity, degradation rates were considerably greater than at drier conditions, such as 40 percent of field capacity. For contaminated soil alone, maintaining the moisture content at 80 percent of field capacity did not result in adequate PAH degradation. Other parameters, such as acclimated organisms and nutrients, also played an important role in achieving degradation of PAH compounds. When a 1% dry waste activated sludge amendment was added to the contaminated soil, degradation of 2- and 3-ring PAH's occurred. The waste activated sludge supplied acclimated microorganisms, nutrients and other factors that enhanced PAH degradation.

Uncontaminated soil contained indigenous microorganisms that quickly initiated degradation of PAH compounds when the environmental factors were appropriate for microbial activity. Specially developed strains of microorganisms to degrade PAH's were not necessary.

The results indicated that bioremediation was an appropriate closure alternative for these contaminated soils from lagoons containing waste industrial sludges. A pilot-scale study to obtain larger-scale technical and economical feasibility data is being planned.

Case Study C: This study[3] is an on-going RCRA land treatment demonstration for a proposed full-scale land treatment facility in Montana. The wastes evaluated are creosote-contaminated soils and sludges resulting from the closure of a RCRA surface impoundment. The proposed full-scale land treatment facility will be used to treat and detoxify the wastes removed from the impoundment at closure.

The soils at the site are loamy silts and silty sands and have an organic matter content of about 1.5%. The climate is semi-arid. Annual evapotranspiration exceeds annual precipitation and there is limited recharge to the groundwater. Monthly ambient temperatures exceed 50° F approximately six months of the year.

Waste application rates were 2% and 5% benzene extractable (BE) hydrocarbons. The 2% plot included subsequent bi-monthly applications of 2% BE to evaluate the effect

of waste re-applications. The 5% plot did not include re-application in order to evaluate the effect of one batch loading.

To minimize replicate plots and analytical costs, certain management practices were selected and were applied consistently to all the plots. These practices were anticipated to optimize treatment:

- maintaining a surface soil pH between 6.0 and 7.0
- maintaining a soil carbon:nitrogen ratio of 25:1
- maintaining soil moisture near field capacity through irrigation
- applying organic amendments to provide nutrients and increase the organic carbon content of the surface soil
- tilling the soil once every two weeks
- preventing storm water run-on from entering the plots and capturing run-off

The field plots were 12' x 50' with a defined treatment depth of 5'. The plots were surrounded by earthen berms to prevent run-on from entering the plots. Each plot was graded to a 1% slope, and a lined run-off collection sump capable of handling two, 25-year, 24-hour storm events was present at the toe of the slope. The entire study area was fenced.

Three types of soil-pore water collection devices were installed in each plot: (a) a vacuum lysimeter, (b) a pan lysimeter constructed from a hollow glass block, and (c) a trench lysimeter consisting of a 10-foot long, 6-inch diameter PVC drain, placed at the bottom of the treatment zone. Monitoring at the site included monthly sampling of the zone of incorporation to evaluate the degradation of specific organic constituents and biannual sampling of soil cores, soil pore water and groundwater to evaluate contaminant immobilization. The principal hazardous constituents being evaluated are polyaromatic hydrocarbons. Other constituents that are monitored include indicator parameters such as BE hydrocarbons and total phenols. Soil moisture is checked on a weekly basis to evaluate the need for supplemental irrigation.

The land treatment demonstration was successful. The soil core, lysimeter and groundwater analyses did not detect migration of hazardous constituents from the treatment zone.

SUMMARY

These and similar case studies indicate bioremediation is a feasible method for the degradation of organics in contaminated soils and in residues from industrial processes. Exploitation of the versatility of microorganisms for the treatment of inorganic and organic chemicals in such soils and residues can provide alternative and environmentally compatible treatment technologies. The application of bioremediation processes has resulted from understanding the mechanisms by which microorganisms metabolize chemicals in complex mixtures. It is possible to use naturally occurring microorganisms and further enhance their activity by modifying and controlling their environment. Specially developed microorganisms have not been shown to be necessary.

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2. Jacques, R.B. and R.C. Loehr (July 1988). "Biological Detoxification of a Contaminated Soil". In *Proceedings*, Environmental Engineering Conference, Vancouver, B.C. American Society of Civil Engineers.

3. Ryan, J.R. and J. Smith (1986). "Land Treatment of Wood Preserving Wastes". In *Proceedings*, National Conference on Hazardous Waste and Hazardous Materials, HMCRI Institute, Silver Springs, Maryland.

- inadequate type or numbers of microorganisms, such as due to toxic conditions
- conditions too acid or alkaline
- lack of nutrients such as nitrogen, phosphorus, potassium, sulfur or trace elements (petrochemical residues, for example, are not nutritionally balanced)
- unfavorable moisture conditions (too wet or too dry)
- lack of oxygen or other electron acceptors

Bioremediation processes are biological treatment processes that improve or stimulate the metabolic capabilities of microbial populations to degrade organic residues. The processes take into consideration the factors that affect microbial activity and modify the existing conditions so that microbial degradation can occur. For example, if inadequate nitrogen or phosphorus are available, such nutrients can be added to assure satisfactory microbial degradation. If the residues are too toxic, addition of other chemicals or uncontaminated soil may reduce the toxicity to the point that microbial degradation can occur. If inadequate type or numbers of microorganisms are present, acclimated organisms can be added.

TREATABILITY STUDIES

Treatability studies are used to determine the feasibility of bioremediation processes. The basic concepts of a treatability and feasibility evaluation are identified in Figure 1. The evaluation proceeds through defined logic decisions. Problem definition, in terms of the performance objectives to be met, and the type of data that is needed to meet regulatory, feasibility and design needs, occurs and a general idea or vision of the better technical approaches are important first steps. Another important early step is to adequately characterize the waste, residue or contaminated soil to determine the type and concentration of contaminants that must be dealt with. Waste characterization can identify the parameters that need to be monitored to determine performance, to assure protection of human health and the environment, and to establish technical and economic feasibility.

With such information, appropriate laboratory treatability studies can be devised. A preliminary assessment of the site conditions can identify the general conditions that are likely to limit microbiological degradation. Laboratory treatability studies are used to establish the fundamental and operational factors that are conducive to bioremediation and that can overcome the existing limitations.

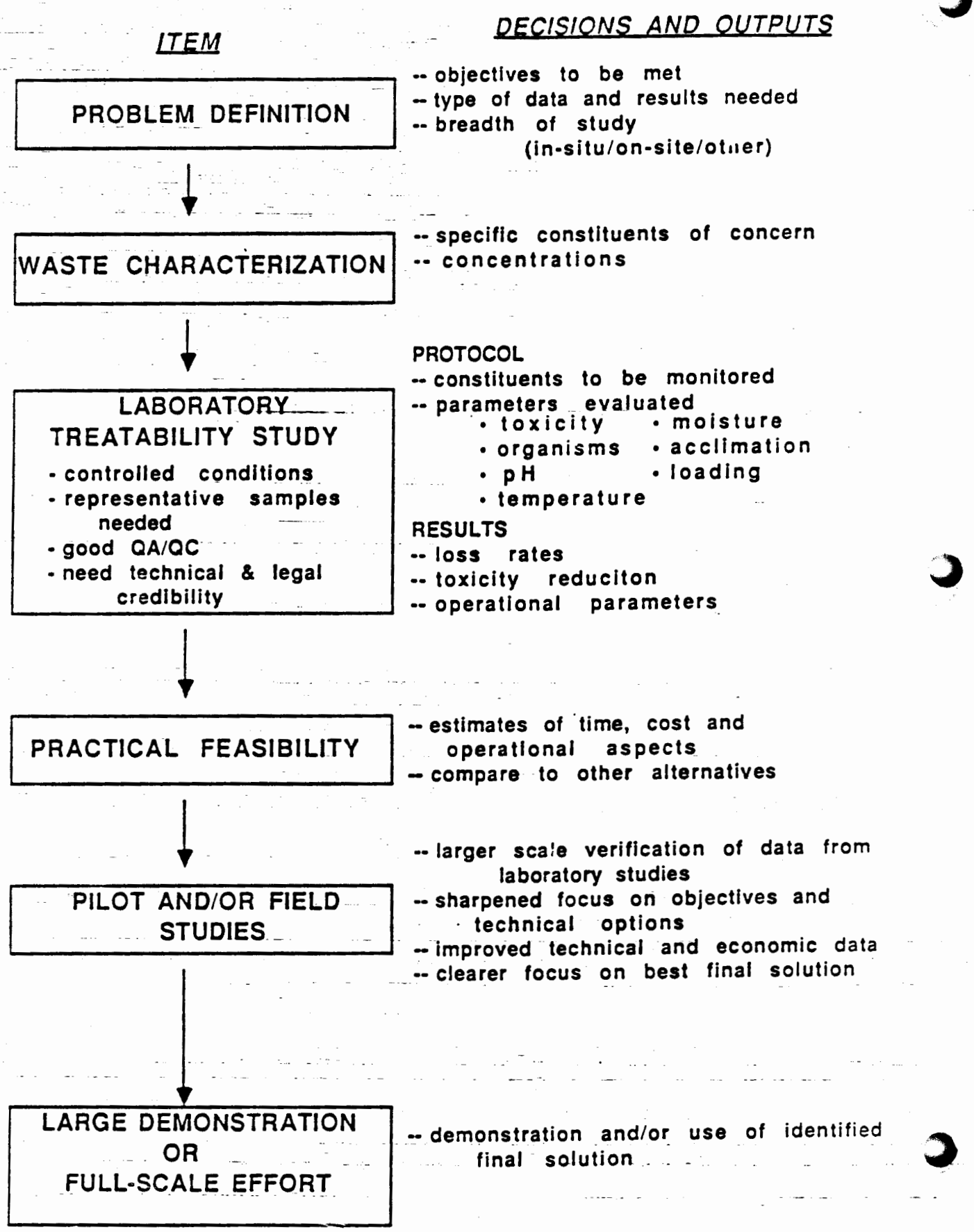
These treatability studies are conducted under controlled laboratory situations so that the specific parameters that optimize microbial degradation can be identified. Experience with similar wastes guides the treatability studies which are conducted using established protocols and analytical techniques.

Naturally occurring microorganisms, such as those which have developed at a contaminated site or in specific residues, commonly are effective. Genetically engineered microorganisms have not been shown to be needed.

If one or more processes are shown to be technically and economically feasible based on the laboratory treatability studies, pilot-scale treatability studies are used to extend the "optimum" laboratory results and to obtain better size, operational and economic data. In addition, field demonstration studies are used to further evaluate large-scale process configurations before full-scale bioremediation is initiated.

FIGURE 1

BIOREMEDIATION TREATABILITY EVALUATION -- BASIC CONCEPTS



The numerical valves of k & K_s may be obtained graphically after rearranging the above equation and solving for the reciprocal of the specific BOD removal rate

$$\frac{1}{R} = \frac{K}{P}\left(\frac{1}{S_e}\right) + \frac{1}{P}$$

A plot of $(\frac{1}{R})$ vs $(\frac{1}{S_e})$ results in a straight line with a slope (K/P). This This relationship is presented in Figure 3.

DETERMINATION OF RBS CONSTANTS

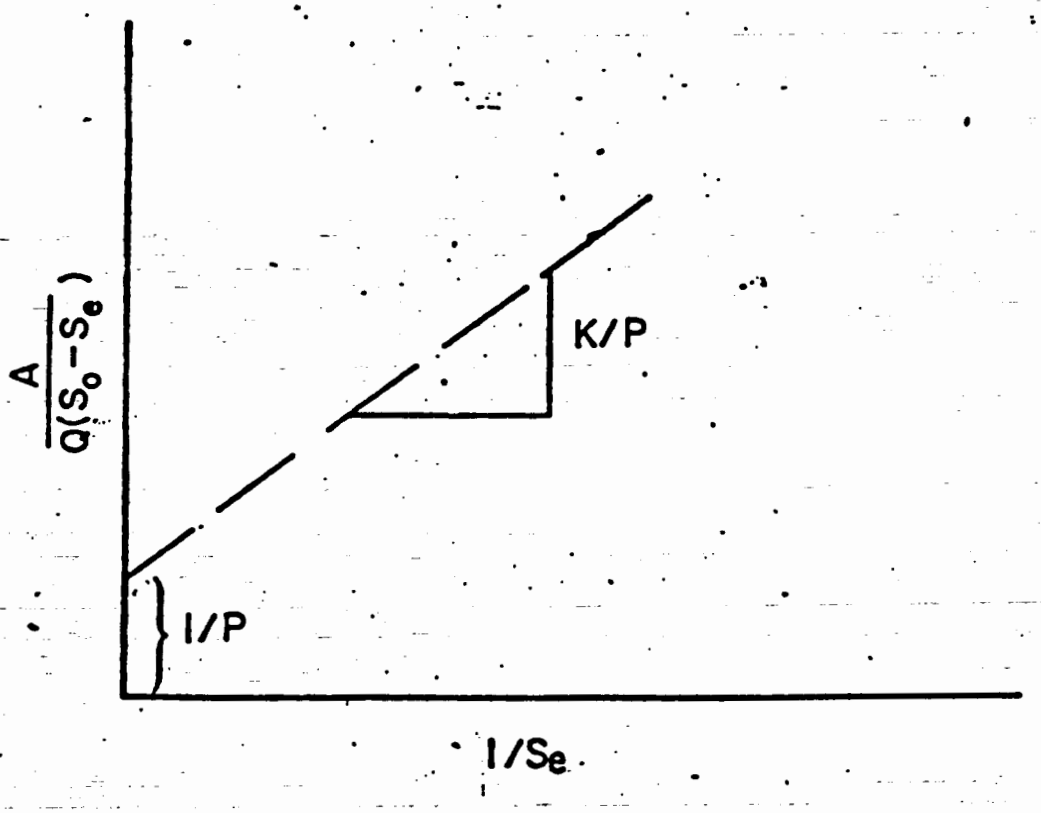


Figure 3

At $\frac{1}{S_e} = 0$; $\frac{1}{P}$ = Y Axis intercept

and at

$\frac{1}{R} = 0$; $-\frac{1}{K}$ = X Axis intercept

The BOD removal rate is a function of the hydraulic loading as illustrated in Figure 4.

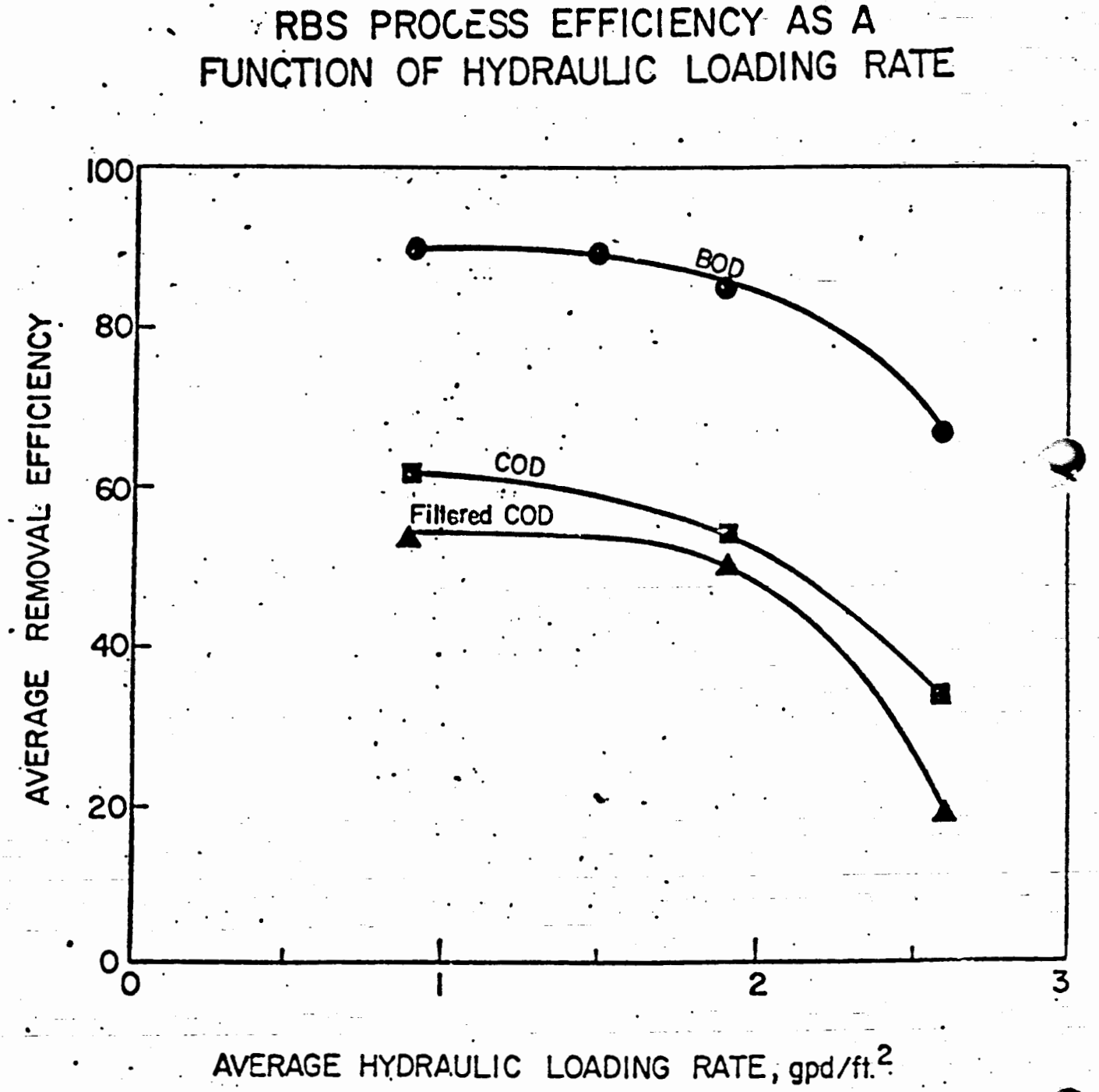
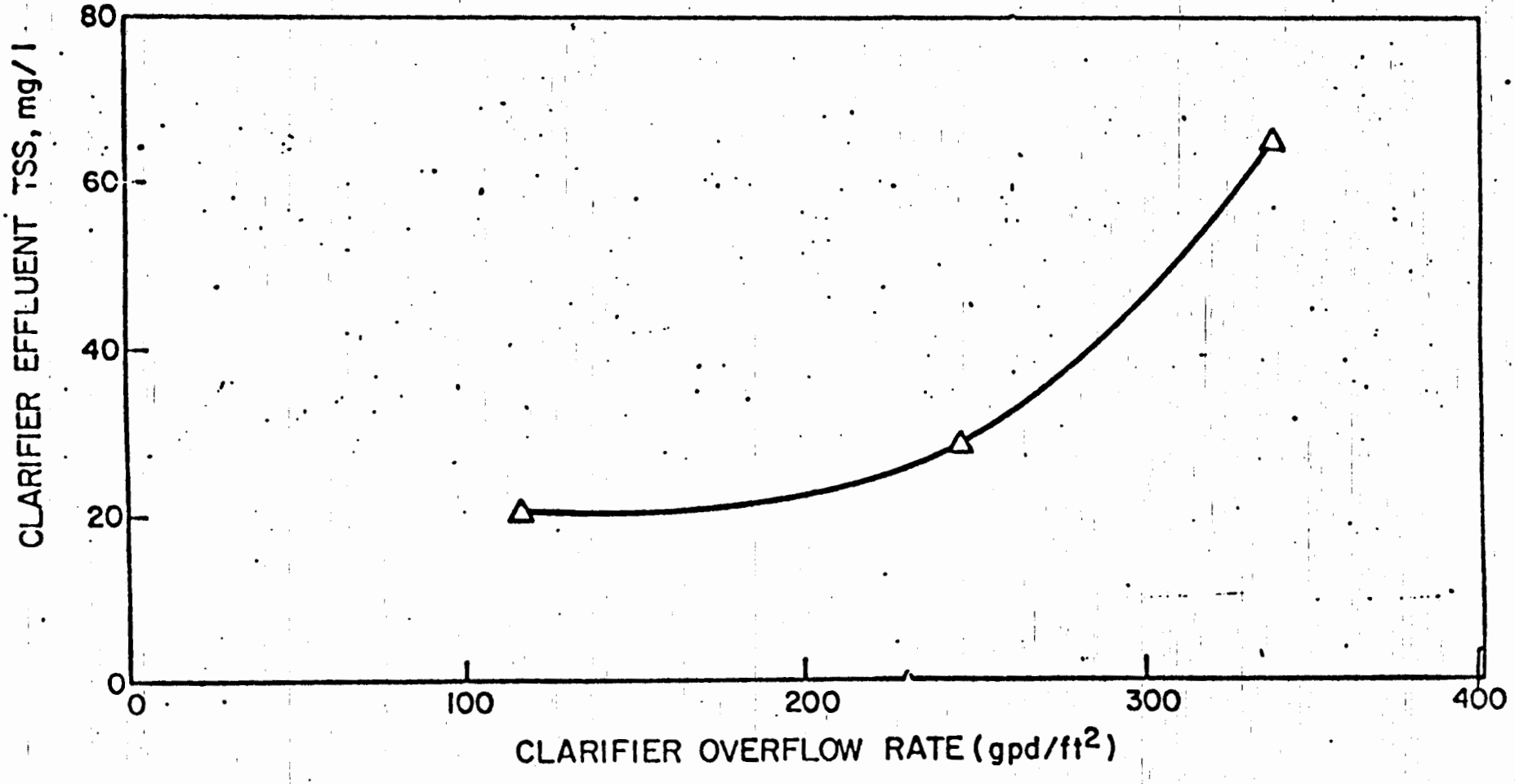


Figure 4

Design Parameters

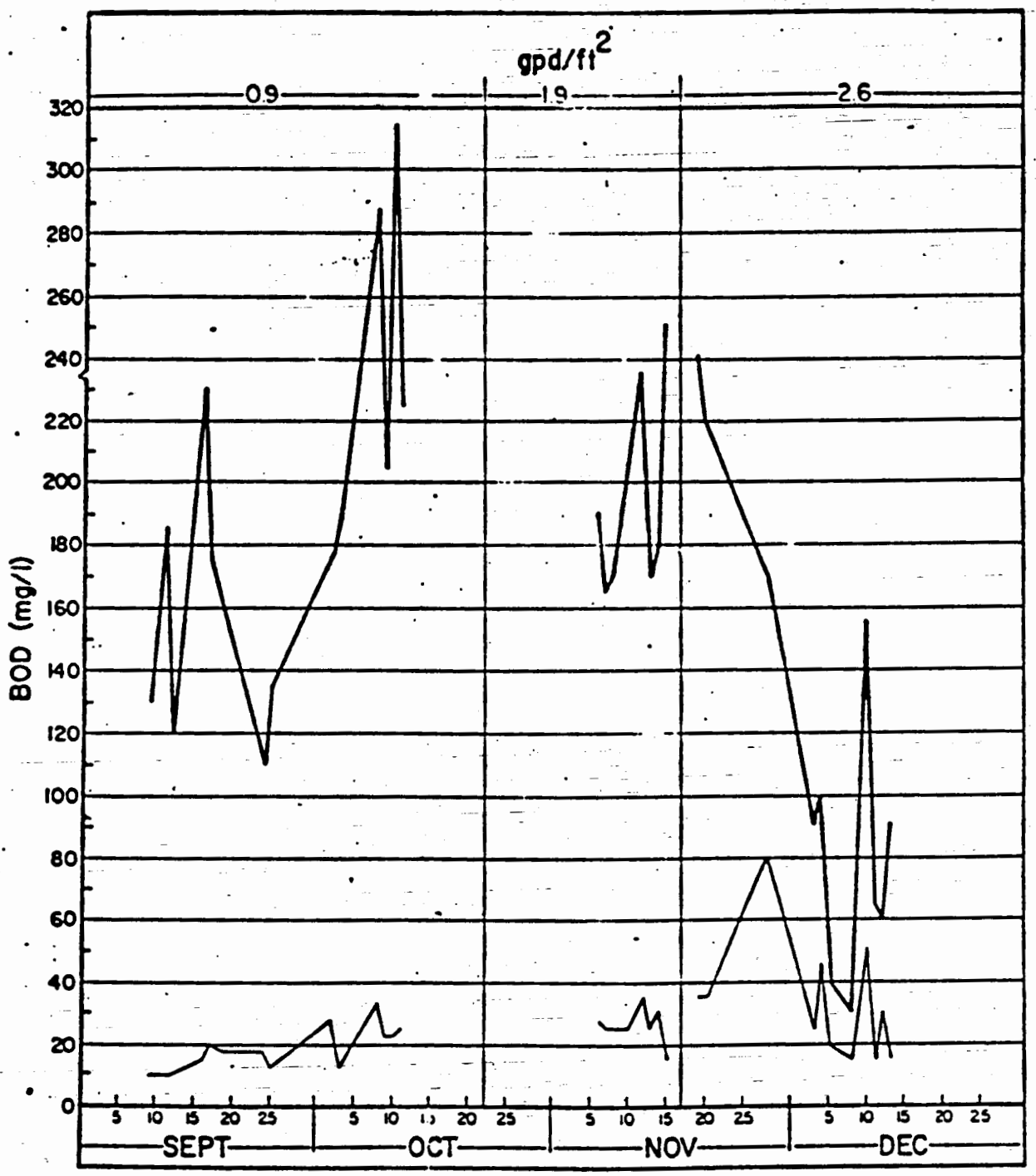
Rotational Speed	40 - 60 fpm
BOD Removal	2 - 4 lb/1000 sq ft
Energy Requirements	7.5 hp (connected)/100,000 sq ft
Cost	$0.30 $0.50/sq ft

CLARIFIER EFFLUENT TSS VS. OVERFLOW RATE



PILOT PLANT OPERATION VARIATIONS

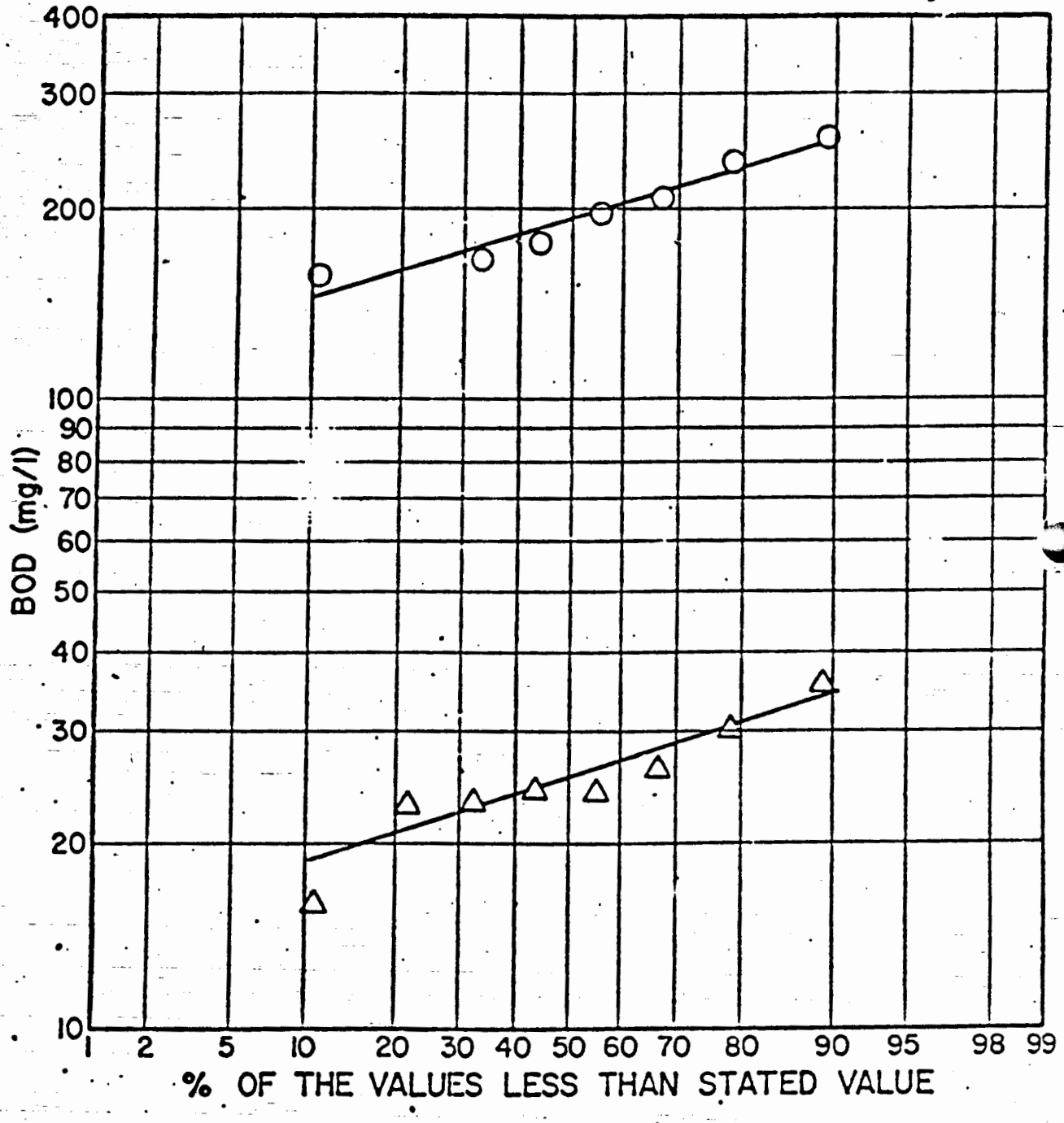
BOD



— PILOT UNIT INFLUENT
— CLARIFIER EFFLUENT

BOD PROBABILITY DISTRIBUTION

L9 gpd/ft^2



○ Influent
△ Effluent

MIDLAND, MICHIGAN, WASTEWATER TREATMENT
EFFLUENT CHARACTERISTICS

		Avg. Secondary Effluent (mg/l)
BOD_5		15 - 20
Suspended Solids		15 - 20
pH		7 - 8
NH_3-N		8 - 18
NO_3-N		0.3 - 0.5
Organic-N		1.5 - 4.0
Temperature:	Winter	44°F (7°C)
	Summer	68°F (20°C)

TABLE 2

PLASTIC MEDIA CHARACTERISTICS

Available Surface Area	27 sq ft/cu ft
Void Space	94%
Sheet Thickness	30 mil
Weight	2.6 lb/cu ft
Material	Polyvinyl Chloride

TABLE 17

DESIGN GUIDELINES

Basis:

A. Waste stream contains no significant nitrification inhibitors.

B. Influent NH_3-N concentration <25 mg/l.

C. Carbonaceous loading <15 lbs BOD_5/1000 cu ft media/day

D. Media depth = 21.5 feet

E. Relatively constant total hydraulic flow.

F.

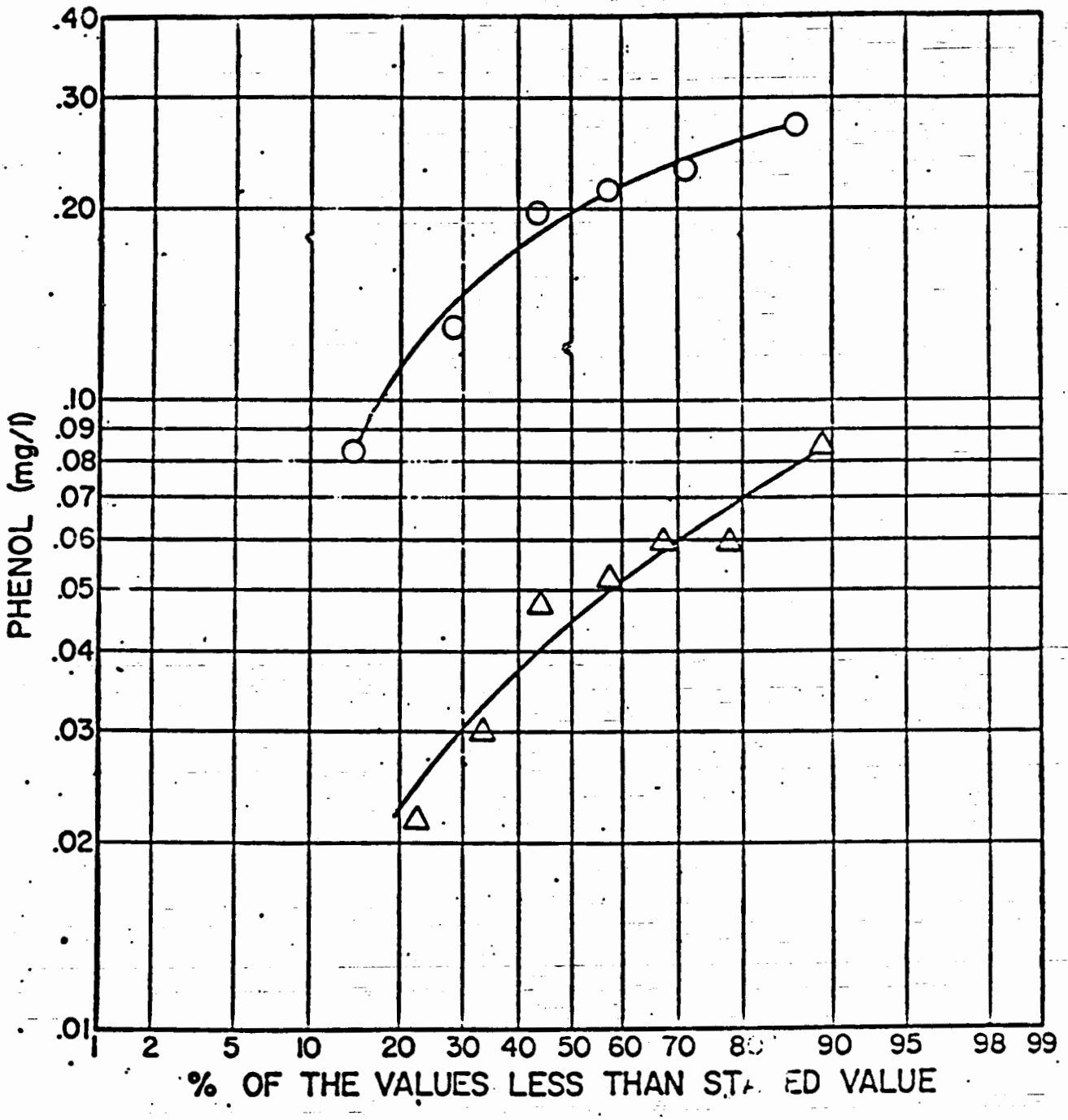
Influent Feed Rate (gpm/sq ft)	Nitrification Performance (%)
0.5	90
0.75	85
1.0	80
1.5	75

G. These values are valid for wastewater temperatures >60°F. Figure 15 illustrates the effect of wastewater temperature on these guidelines.

H. Media: 27 sq ft/cu ft
94% void volume

PHENOL PROBABILITY DISTRIBUTION

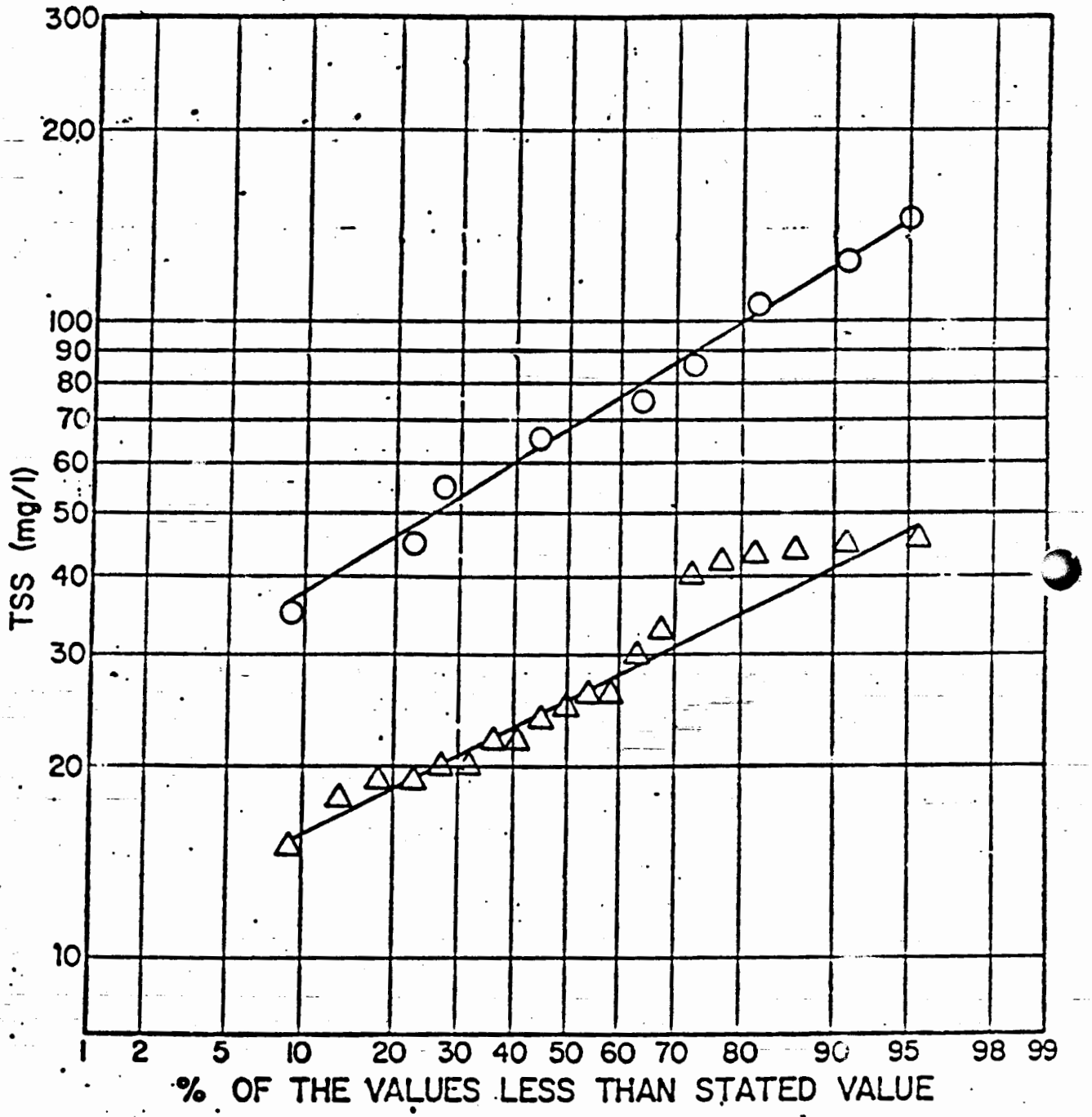
0.9 gpd/ft^2



○ Influent
△ Effluent

TSS PROBABILITY DISTRIBUTION

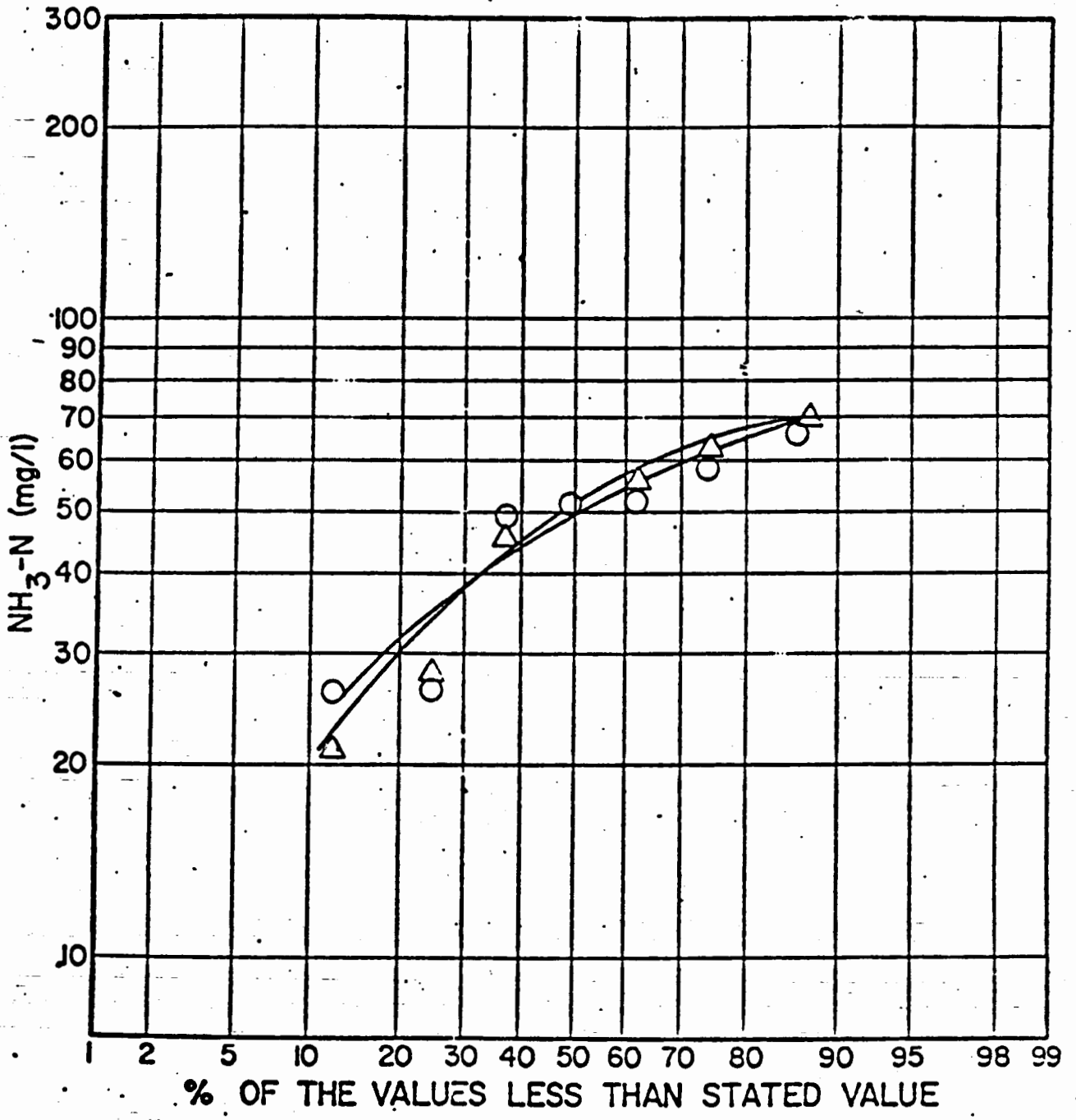
1.9 gpd/ft^2



○ Influent
△ Effluent

AMMONIA-NITROGEN PROBABILITY DISTRIBUTION

1.9 gpd/ft^2



○ Influent
△ Effluent

2.1 LAND TREATMENT

2.1.1 Technology Description

Land treatment is a managed technology that involves controlled application of a waste on the soil surface and the incorporation of the waste into the upper soil zone. It is not the indiscriminate dumping of waste on land, and it is not landfilling. Landfills store wastes in man-made or natural excavations and use a combination of liners and leachate collection systems to control the migration of the landfilled waste or resultant byproducts. Liners are not a part of a land treatment system. Land treatment technology relies on the dynamic physical, chemical and biological processes occurring in the soil. As a result, the constituents in the applied wastes are degraded, immobilized or transformed to environmentally acceptable components.

The terms, "land farm", "land farming", "biodisposal farming", "soil incorporation", "land application", "soil cultivation", or "land spreading" also have been used to describe this technology. The term "land treatment" is more appropriate for this treatment and disposal technology since it better describes the end results of the technology – oxidation, immobilization and containment.

The design and operation of a land treatment facility is based on sound scientific and engineering principles as well as on extensive practical field experience. A land treatment site is designed and operated: (a) to maximize waste degradation and immobilization, (b) to minimize release of dust and volatile compounds as well as percolation of water-soluble waste compounds, and (c) to control surface water runoff. Land treatment can be a viable management practice for the treatment and disposal of non-hazardous wastes as well as some types of hazardous wastes. The applied wastes can be liquid, semi-solid, or solid.

Land treatment uses the assimilative capacity of the soil to decompose and contain the applied waste in the surface soil layer (usually the top 6 to 12 inches). This upper soil layer is the zone of incorporation. The incorporation zone, and the underlying soils where additional treatment and immobilization of the applied waste constituents occurs, is referred to as the treatment zone. The treatment zone depth in the soil may be as much as 5 feet. Most of the transformations, biological oxidation, and immobilization will occur in the zone of incorporation.

2.1.2 Technology Status

Land Treatment has been used at over 100 petroleum refinery sites and an additional 100 sites in other industries, including chemical production, metal products production, wood production, textile manufacturing, and paper production. To date, emphasis has been largely on RCRA facilities and closures with little examination of

CERCLA (Comprehensive Environmentail Response Compensatison and Liability Act) issues.

2.1.3 Technical Applicability

As shown in many studies (API, 1983, 1984; Brown et al., 1984; Loehr and Malina, 1986), land treatment systems used for oily wastes do degrade and immobilize the waste applied at such sites. Oil, metals, and other constituents of environmental concern are successfully controlled by such systems.

Land treatment is suitable for use on a broad spectrum of wastes. Wastes which have been land treated include:

- petroleum refinery sludges,
- creosote sludges and wastewaters;
- municipal sludges and wastewaters,
- food processing sludges and wastewaters,
- chemical plant wastes,
- wood and paper process sludges, and
- textile mill sludges.

The characteristics of the wastes to be treated in a land treatment system will affect the development of the appropriate waste loading rates for a particular site.

2.1.4 Typical Application

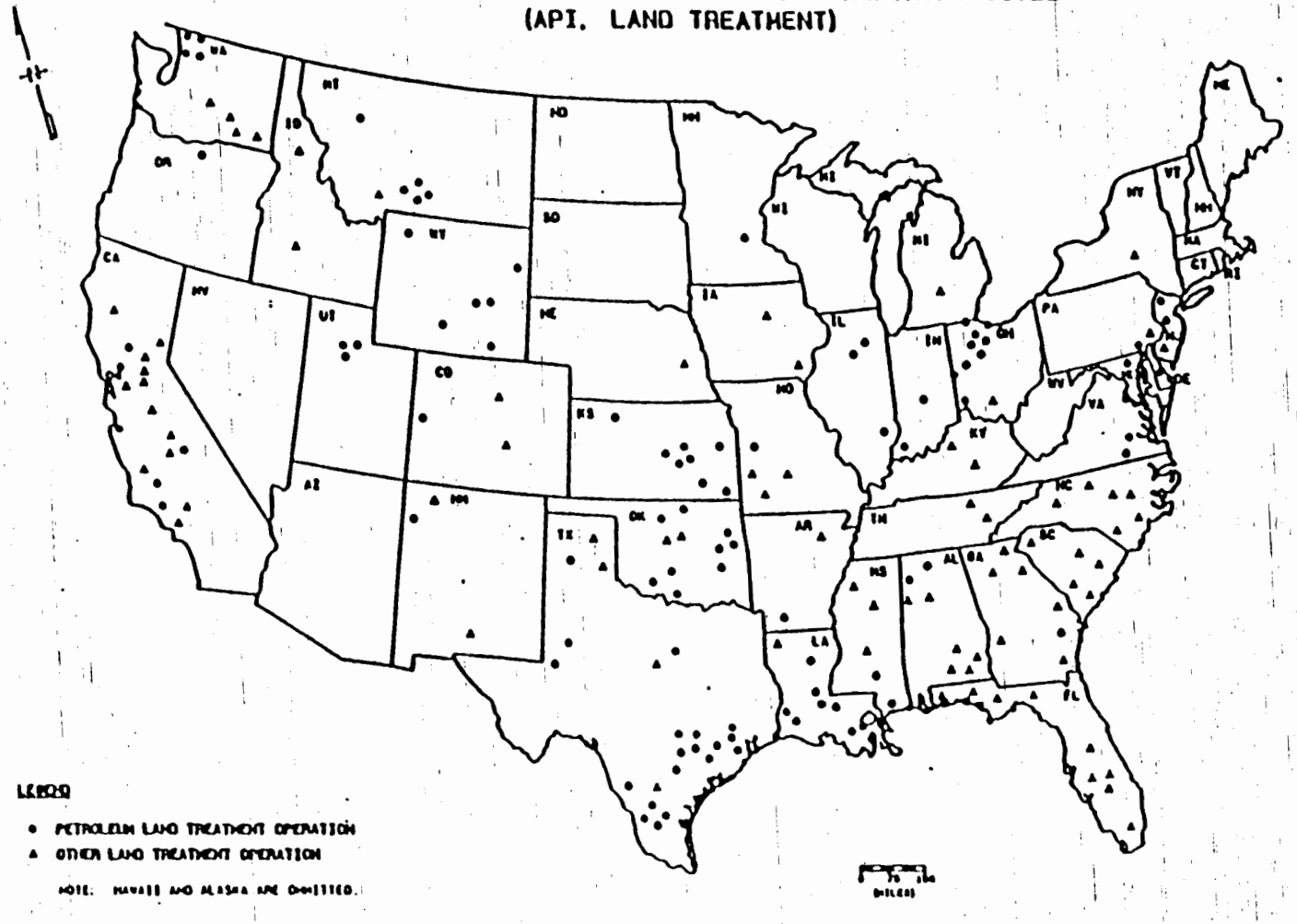
Land treatment has been successfully practiced in all major climatic regions of the United States, Europe, and Canada under a wide range of hydrogeologic conditions. In the U.S., approximately 200 land treatment systems are in operation, including over 100 at petroleum refining facilities. Figure 2-1.1 shows the geographical distribution of these land treatment sites. This figure suggests that there are very few site limitations which cannot be overcome with the appropriate design and operation of a land treatment facility. Rules specifying "ideal" site characteristics are not very realistic. It is more important to consider how critical site factors are addressed in the design and management of the facility.

2.1.5 Process Description

Land treatment is a process which relies on naturally occurring physical, chemical, and biological interactions within the soil to degrade, transform, or immobilize waste components. Wastes to be treated are physically applied to the surface layer of the soils, either directly or just below the surface at a controlled rate. Following the application of the wastes, some type of cultivation method is used to mix the waste and the soils to provide a uniform treatment zone. Operating conditions within the treat-

Figure 2-1.1

GEOGRAPHICAL DISTRIBUTION OF LAND TREATMENT SITES
(API, LAND TREATMENT)





ment zone are monitored and controlled in order to enhance the efficiency of the system.

In order to design and operate a land treatment system, three sets of factors must be considered: waste factors, site factors and operational factors (Table 2-1.1). The waste and site factors are used to develop the soil site assimilative capacity (SSAC), which is the principal design factor for the treated waste. The SSAC defines the appropriate waste loading rates and land requirements. Models can be used to define the SSAC when appropriate soil/waste degradation rate constants and partition coefficients have been developed. The following sections present a brief description of the factors which influence the design and operation of land treatment systems.

2.1.6 Key Design Considerations

A set of important site factors for several full scale land treatment facilities which will influence the design of systems is provided in Table 2-1.2. As previously stated, a wide variety of climate, hydrogeological, and waste conditions can be included in successful applications for land treatment technologies.

Climate is a particularly significant site factor which affects the design and operation of a land treatment facility. Climate has an impact on: (a) appropriate application rates, (b) frequency of waste application, (c) storage requirements, (d) runoff system design, and (e) system performance.

Laboratory studies have indicated that the optimal soil temperature for biodegradation of oily wastes are 20°C or greater. Biological activity decreases as the temperature decreases below this point. Little degradation takes place in soil with a temperature near freezing; however, with proper design and operation land treatment can be successful in colder climates as well as in humid and warm climates.

Soil temperature for bare surface soils are commonly greater than ambient air temperatures by 2 to 5°C during daylight hours. Surface soil temperatures at land treatment sites may exceed ambient temperatures by 5 to 8°C due to increased microbial respiration and the increase in radiant energy due to the darker soils which result from oil applications. For the purpose of developing general design parameters, the term degradation month has been developed. A degradation month is defined as a month which the average air temperature exceeds 10°C. This concept permits useful comparisons to be made between land treatment facilities with significantly different climatic conditions. The concept was developed for comparison purposes only and does not imply that degradation will not occur during months when the average air temperature is less than 10°C.

Site preparation activities at most facilities include: (a) removal of site vegetation, (b) the separation of the site into several plots, and (c) the construction of an elevated roadway/dike around the facility to control surface runoff and permit site access. Many land treatment facilities are graded to promote surface drainage and collect site runoff. The types of site modifications instituted at land treatment facilities vary depending on the existing site characteristics. Examples of modifications which may be required at a site are provided in Table 2-1.3.

2.1.7 Key Operating Considerations

Operating plans for land treatment facilities must be developed for each specific site and application. These facilities will vary in terms of waste application rates, method of waste application, soil amendments used, and storm water management practices. The operating plan which is developed must consider these factors as well as economic factors.

Waste application methods vary from subsurface injection of fluid sludges to surface application of liquid and semi-solid sludges. The depth of cultivation defines the zone of incorporation for the facility which applies wastes only to the soil surface. The most common cultivation equipment used are disk harrows and rototillers. Rototillers are preferred by some facilities because they are thought to accomplish more thorough mixing of the waste and soil. However, rototillers are considered more difficult and expensive to maintain and operate. If harrows are used, several passes are required over a field to provide a homogeneous soil waste mixture. The frequency of cultivation for most facilities is once per waste application event. Facilities which operate with high organic loading rates may cultivate 2 or 3 times per waste application event to enhance soil aeration and waste/soil contact. Less frequent cultivation is reported for land treatment sites which receive sludges or wastewaters with low organic content.

The use of soil amendments varies considerably among land treatment facilities and is extremely site and waste specific. Agricultural lime or waste lime sludges are applied at facilities where surface soil has low pH. Nutrient applications (in particular nitrogen) may enhance degradation rates in the initial period of operation. However, many facility operators, particularly those who use low waste application rates, do not consider nutrients necessary to optimize the performance of their facilities. Moderate amounts of fertilizers have been applied at a few facilities to enhance degradation. Supplemental irrigation has been used on a limited basis at some facilities located in semi-arid areas.

Site runoff must be contained and managed at all waste treatment operations. The runoff water which is collected may be allowed to evaporate on site, or it may be discharged to a wastewater treatment system.

Monitoring is a particularly important aspect of land treatment operations. Most facilities are routinely monitored for pH, soil moisture content, oil and grease content, and nutrients in order to schedule waste application events and determine the need for supplemental soil amendments. In addition, if listed hazardous wastes are applied at a facility, the operators are required to monitor the soil and soil pore water in and beneath the treatment zone, and the ground water under the facility to evaluate the performance of the facility.

2.1.8 Prior Applications

The treatability of oily wastes by land treatment has been investigated extensively in bench-scale and pilot-scale studies. This section summarizes the results of several recent studies with petroleum refining wastes and creosote wastes in field test plots, bench-scale reactors, and soil columns. These studies provide information with respect to the following land treatment considerations:

degradation rates and immobilization of hazardous waste constituents;

appropriate loading rates; and

optimum conditions for degradation, detoxification and immobilization of hazardous waste constituents in land treatment systems.

The results of these studies show that hazardous constituents can be successfully controlled by land treatment when appropriate design criteria and management practices are used.

Land treatment is viable technology for reducing

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Land treatment can protect human health and the environment from wastes as diverse as liquid municipal waste water, liquid and dewatered municipal sludge, and petroleum industry wastes.

The basic technology also can be used for bioremediation of contaminated soils at Superfund and other sites. The use of land treatment under controlled and well-designed and operated conditions should continue to be available to the petroleum and other industries.

Land treatment is a managed technology that involves the controlled application of a waste on the soil surface and the incorporation of the waste into the upper soil. It is not the indiscriminate dumping of waste on land, and differs significantly from landfilling, waste piles, and surface impoundments. These methods store wastes in man-made or natural excavations and use a combination of liners and leachate collection systems to control the migration of the waste or resultant by-products.

Land treatment relies on the dynamic physical, chemical, and biological processes occurring in the soil. As a result, the constituents in the applied wastes are degraded, immobilized, or transformed to environmentally acceptable components.

The land-treatment process uses the assimilative capacity of the soil to degrade, immobilize, and contain the applied waste. The upper soil layer (the top 6-12 in.) in which the waste is incorporated is the zone of incorporation (ZOI).

This zone, in conjunction with the underlying soils where additional treatment and immobilization of the applied waste constituents occurs, is referred to as the treatment zone. For hazardous wastes, the treatment zone depth is defined as 5 ft. The transformations, biological oxidation, and immobilization occur primarily in the upper part of the treatment zone.

Land-treatment technology has been used successfully for the treatment and disposal of: Petroleum industry wastes; other industrial wastes such as from the wood preserving, pulp and paper, and food processing industries; and municipal wastewater and sewage sludges. It is also used for remediation of contaminated soil and is a suitable closure process at specific sites.

When the technology is designed and operated using proper procedures and methods, land treatment has been shown to be protective of human health and the environment.

The design and operation of a land-treatment facility is based on sound scientific and engineering principles as well as on extensive practical field experience. A land-treatment site is designed and operated to: Maximize waste degradation and immobilization, minimize release of dust and volatile compounds as well as percolation of water soluble waste compounds, and control surface water runoff.

Land treatment can be a viable management practice for the treatment for disposal of nonhazardous wastes as well as some types of hazardous wastes. The applied wastes can be liquid, semi-solid, or solid.

At some point, wastes may no longer be applied at a site and the site must be closed. A closure and post-closure plan must be prepared and approved by the appropriate regulatory agency. This plan can utilize degradation and immobilizaton as a closure mechanism.[1]

Land treatment is an important technology for the treatment and disposal of oily wastes from U.S. refineries. About 100 land treatment facilities treating petroleum industry wastes, primarily from the refining sector, exist in the United States.[2]

In addition, 26 of 38 Canadian refineries and at least 10 refineries in Europe use land treatment as an environmentally sound, cost-effective waste-disposal technology. At these sites, the constituents in the applied wastes have been degraded and immobilized successfully. At many petroleum industry land treatment sites, water balances indicate that there is little or no net percolation as a result of the small amount of water added with the applied waste, the low precipitation, and the high transpiration due to evaporation.

Table 1

Types of wastes applied to full-scale refinery land-treatment facilities

Oil-water separator sludge
Dissolved air flotation sludge
Induced air flotation sludge
Tank bottoms
Slop oil emulsion solids
Oily sludge
Filter cakes
Biological sludges
Cooling tower sludge
Lime sludge
Coker blowdown sludge

Land treatment of refinery wastes has been successfully practiced in all of the major climatic regions of the United States, Europe, and Canada under a wide range of hydrogeologic conditions. The data suggest that there are very few site limitations which cannot be overcome with the appropriate design and operation of land treatment facilities.

Regulatory framework. On Nov. 8, 1984, the U.S. Congress passed amendments to the Resource Conservation and Recovery Act (RCRA) that specifically prohibit land disposal of hazardous wastes beyond specified dates unless the U.S. Environmental Protection Agency (EPA) determines that a land disposal method is protective of human health and the environment. The EPA was required to set a schedule for land restriction decisions for all hazardous waste listed as of Nov. 8, 1984.

The schedule for the land disposal restriction decisions was published in the Federal Register on May 28, 1986. Petroleum refining industry-listed wastes such as K048 DAF float and K051 API separator sludge are to be evaluated and have decisions made by Aug. 8, 1988.

Under Section 3004(K) of RCRA, land disposal of hazardous waste is defined to include "...any placement

Based on a paper presented at HAZMACON [illegible] Atlantic City, N.J.

petroleum-waste toxicity and migration potential

Table 2

Organic compounds detected in soil collected from below ZOI of a controlled land-treatment study

COMPOUND	Depth below ZOI, ft 0-1.5		1.5-2.5		2.5-3.5
	Column A	All other columns	Column A	All other columns	All columns
VOLATILES					
Benzene	<0.91	<0.91	<0.18	<0.18	<0.18
Toluene	<0.90	<0.90	<0.18	<0.18	<0.18
Ethyl Benzene	<0.90	<0.90	<0.18	<0.18	<0.18
p-Xylene	<0.89	<0.89	<0.18	<0.18	<0.18
m-Xylene	<0.90	<0.90	<0.18	<0.18	<0.18
o-Xylene	<0.91	<0.91	<0.18	<0.18	<0.18
Naphthalene	<0.78	<0.78	<0.16	<0.16	<0.16
2-Methylnaphthalene	0.77	<0.54	<0.11	<0.11	<0.11
1-Methylnaphthalene	4.68	<1.02	<0.20	<0.20	<0.20
PAH					
Naphthalene	<5.0	<5.0	<5.0	<5.0	<5.0
Acenaphthylene	<7.5	<7.5	<7.5	<7.5	<7.5
Acenaphthene	<2.5	<2.5	18.40	<2.5	<2.5
Fluorene	<0.5	<0.5	<0.5	<0.5	<0.5
Phenanthrene	4.125	<0.5	<0.5	<0.5	<0.5
Anthracene	<0.5	<0.5	<0.5	<0.5	<0.5
Fluoranthene	4.6	<0.5	<0.5	<0.5	<0.5
Pyrene	110.0	<1.0	<1.0	<1.0	<1.0
Benzo(a)anthracene	<0.5	<0.5	<0.5	<0.5	<0.5
Chrysene	<0.5	<0.5	<0.5	<0.5	<0.5
Benzo(b)fluoranthene	<0.5	<0.5	<0.5	<0.5	<0.5
Benzo(k)fluoranthene	13.28	<0.5	<0.5	<0.5	<0.5
Benzo(a)pyrene	<0.5	<0.5	<0.5	<0.5	<0.5
Dibenzo(a,h)anthracene	<0.5	<0.5	<0.5	<0.5	<0.5
Benzo(g,h,i)perylene	15.58	<1.0	<1.0	<1.0	<1.0
Indeno(1,2,3-cd)pyrene	6.42	<0.5	<0.5	<0.5	<0.5
Oil and grease	13,600	<600	<600	<600	<600
Microtox (% luminescence)	NT*	NT	NT	NT	NT

Source: API, 1987; data are from soil columns that had petroleum industry wastes applied at realistic land treatment rates to the ZOI; all units are of compound per kg of dry soil except for Microtox.

*NT, nontoxic

of such hazardous waste in a...land treatment facility..." As a result, land treatment facilities for hazardous wastes are subject to the banning decisions. Land treatment is "disposal" for purposes of 3004(K) restrictions, but it is also RCRA "treatment" as the term is defined under RCRA 1004(34). Land treatment of hazardous wastes involves the incorporation of the waste into the ZOI in order to degrade, transform, or immobilize hazardous constituents.

After this in situ treatment occurs, the long-term disposal of the remaining residues begins. This dual aspect—treatment and disposal—makes land treatment unique among land disposal alternatives. These unique aspects have been recognized by EPA (51 FR 1710, Jan. 14, 1986).

The amendments specify that a method of land disposal may not be protective of human health and the environment unless upon application by an interested person it has been demonstrated to the administrator that there will be no migration of hazardous constituents from the disposal unit or injection zone for as long as the wastes remain hazardous."

The statute also requires EPA to set "levels or methods of treatment, if any, which substantially diminish the toxicity of the waste or substantially reduce the likelihood of migration of hazardous constituents from the waste so that short-term and long-term threats to human health and the environment are minimized."

Properly designed and operated land treatment facilities achieved this requirement. This results from the degradation, immobilization, and transformations that occur at a land-treatment site.

Wastes that meet the treatment standards established by EPA are not subject to the land disposal prohibitions. If EPA fails to set treatment standards (best demonstrated available technologies-BDAT) for any of the scheduled listed hazardous wastes by May 8, 1990, all such wastes are prohibited from land disposal unless EPA grants a case-by-case petition.

In the Federal Register of Nov. 7, 1986, EPA identified procedures that it will use to establish treatment standards for hazardous wastes, evaluate petitions for a variance from the treatment standard, and evaluate petitions demonstrating that continued land disposal of hazardous wastes is protective of human health and the environment.[4] These procedures indicate how BDAT will be considered for hazardous wastes such as those from the petroleum industry.

RCRA specified that BDAT may be expressed as either a performance standard or a method of treatment. EPA decided to establish BDAT treatment standards as performance standards rather than adopting an approach that would require the use of specific treatment methods because of a belief that performance standards offer the regulated community greater flexibility to develop and implement compliance strategies, provide an incentive to develop innovative treatment technologies, and ensure that a technology is operated properly.

Even though specific technologies are identified in the Nov. 6 notice as being able to meet the indicated performance standards, and other technologies will be so identified for additional wastes in future notices, it is not necessary that those technologies actually be used to meet the indicated performance standards.[5]

The most economical technology, or combination of technologies, that can achieve the identified performance standards can be used. The advantage of meeting the promulgated performance standards is that the residues from such treatment are not subject to the land-disposal prohibitions and can be disposed of in an RCRA subtitle C land disposal facility that has been fully permitted and that has an approved waste management plan.

The terms "demonstrated" and "available" were defined in the Nov. 7 notice. To be considered a demon-

strated treatment technology for the purposes of this final rule, a full-scale facility must be known to be in operation for the waste or similar wastes.

In order to be considered "available," a demonstrated technology must substantially diminish the toxicity of the waste or substantially reduce the likelihood of migration of hazardous constituents from the waste. This ensures that all wastes are adequately treated. Treatment will always be deemed substantial if it results in nondetectable levels of the hazardous constituents in the toxicity characteristic leaching procedure (TCLP) extract.

EPA will evaluate the risks associated with treatment technologies and land-disposal methods. Based on a comparative risk assessment, those technologies that are found to represent greater total risks than land disposal of the untreated waste will be considered as "unavailable" and will be excluded as a basis of establishing treatment standards.

EPA recognizes that treatment standards need to incorporate a variability factor. This factor is intended to account for variations that arise from mechanical limitations in the equipment, from variations in waste characteristics, and from variations in analytical test methods. The variability factor was established as the ratio of the calculated 99th percentile concentration, C_{99}, to the mean concentration.

BDAT examples. BDAT processes applicable to petroleum industry wastes have not been defined as yet and probably will not be known for awhile because the land disposal restriction decisions for such wastes do not have to be promulgated until August 1988. The Nov. 7 notice did, however, identify BDAT for solvents and, therefore, provides an indication of how EPA intends to make performance standard decisions. A similar approach is likely to define BDAT for petroleum industry wastes.

The majority of the data used in developing BDAT for solvents were from full-scale treatment facilities. Some pilot and bench-scale data from treatment facilities, which also were demonstrated on a full-scale basis, were included. For biological treatment, for example, full-scale treatment data from 28 plants in the organic chemicals, plastics, and synthetic fiber industries were analyzed.

Nine demonstrated treatment technologies for the spent solvents were identified: batch distillations, thin film evaporation, fractionation, incineration, steam stripping, biological treatment, carbon adsorption, air stripping, and wet air oxidation. The performance data from these technologies were evaluated.

Analyses of variance were performed to determine if one of the technologies performed significantly better. Where a particular technology performed better, the treatment standard was based on that technology. Within a treatability group, the highest treatment value reflecting well-designed and operated treatment facilities were used.

As a result of this evaluation, three technologies were found to perform best—steam stripping, biological treatment, and carbon adsorption—and the performance standards were based on the performance of these technologies. The standards ranged from 0.05 to 5.0 mg/l. in the effluent from the noted processes. The table of standards appears on page 40610 of the Nov. 7 notice.[3]

A note in the table indicates that, although the noted technologies are the basis of the standards, those technologies are not required to be used in meeting the standards. This agrees with the discussion presented earlier.

Compliance with the land disposal requirements and the treatment standards does not relieve hazardous waste disposal facilities of the obligation to comply with all other federal, state, and local environmental requirements.

Achieving the treatment standards may cause cross-media transfer of pollutants, such as from air stripping and from incinerator emissions. Such transfers may be restricted or controlled by other environmental regulations.

In the Feb. 5, 1987, Federal Register notice, EPA proposed standards to limit emissions of volatile organics at hazardous waste treatment, storage, and disposal facilities.[4] These proposed standards require 95% reduction in volatile organic emissions from product accumulator vessels, including process vents and surge-control vessels.

Product accumulator vessels include units to distill and steam or air strip volatile components from hazardous waste. The proposed standards will apply to BDAT facilities that intend to generate a disposable residue.

Stream stripping is an acceptable BDAT for solvents but the volatile organics from the steam stripper must be reduced by 95% by air emission control technologies such as incinerators, scrubbers, and carbon adsorbers. Therefore, such BDAT technologies are permitted to release 5% of the volatile organics.

It is very clear that dilution, such as simply mixing wastes with soil, will not be allowed as a method to comply with the restrictions and standards. This is a generic emphasis that applies to all media-surface waters, the atmosphere, and soil.

A new section, part 268.3, has been added to the federal regulations to cover this point.[3] This part states that, "No generator, transporter, handler, or owner or operator of a treatment, storage, or disposal facility shall in any way dilute a restricted waste or the residual from treatment of a restricted waste as a substitute for adequate treatment."

An active treatment process is re-

The authors...



Loehr



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Rucker

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Rucker joined API in 1975 as technical advisor in the Office of General Counsel, after spending 4 years with Mobil Research & Development Corp., and 6 years with Union Carbide Corp.'s chemical division. He has a BS in civil engineering and an MS in environmental engineering from Virginia Polytechnic Institute and State University, and he is a member of the National Society of Professional Engineers and the Water Pollution Control Federation.

quired to diminish the toxicity of a hazardous waste and substantially reduce the migration of hazardous constituents.

Land treatment and BDAT. Although no BDAT's have yet been established for petroleum industry wastes, the general approach for establishing such BDAT's by EPA is clear, and example performance standards are available. This allows a comparison of land treatment as used in the petroleum industry to the approach being used by EPA to assure that land disposal methods are protective of human health and the environment. To be considered a demonstrated facility, full-scale facilities must be known to be in operation for a waste or similar waste. To be available, a demonstrated technology must substantially diminish the toxicity of a waste or substantially reduce the likelihood of migration of hazardous constituents from the waste.

Air stripping, biological treatment, and carbon adsorption are acceptable BDAT's for solvents. Ninety-five percent reduction of volatile organics is judged an acceptable performance standard. An active treatment process is required.

Available data indicate that land treatment, as practiced by the petroleum industry, meets the definition of a demonstrated technology and achieves the equivalent or greater performance of BDAT's as summarized previously. Land treatment for petroleum wastes has been used for several decades at locations throughout the world, with a variety of wastes (Table 1) and for small and large facilities. Thus, petroleum waste land treatment is a demonstrated technology.

Land treatment is an active treatment process that accomplishes degradation of organics, immobilization of inorganics, and results in the transformation of hazardous constituents to less and nonhazardous constituents. Land treatment results in biological treatment of organics, such as occurs in a conventional waste treatment system; sorption of organics to the organic carbon in the soil, such as occurs in more conventional carbon adsorption processes; immobilization of metals in the soil; and small quantities of volatile emissions, such as occur in air stripping and biological treatment.

Thus, land treatment consists of the processes that have been identified as BDAT for constituents (solvents and organics) that are part of petroleum industry wastes.

Land treatment of petroleum industry wastes substantially reduces the migration of hazardous constituents from the soil. Table 2 illustrates results from a detailed laboratory petroleum industry land-treatment study that evaluated average as well as extreme rainfall events.[3]

Most of the compounds did not migrate below 0.5 ft. Leachate collected from these columns indicated that no PAH or volatile compounds leached during the study, nor did the leachate exhibit any toxicity. Similar results have been obtained in field studies as well as other laboratory studies. Land treatment of petroleum industry wastes reduces the toxicity of the applied wastes. Table 2 indicates that the soil samples below the zone of incorporation did not exhibit any toxicity using the standard "Microtox" procedure. Other examples of toxicity reduction are noted in the following paragraphs.

Mutagenicity determinations used to evaluate the detoxification of petroleum wastes indicated a reduction from mutagenic to nonmutagenic activity when API separator sludge slop oil emulsion solids were incubated with clay loam and sand loam soils, respectively.[6] When the land treatment of an oily waste was evaluated, waste application and soil tilling did reduce the number of earthworms at a field site.[7] However, no long term toxicity resulted. As the waste constituents were degraded and immobilized, the soil biota were able to recover and return to background conditions.

Considerable data exist on the immobilization of metals at petroleum industry land-treatment facilities. The metals in the applied waste are immobilized in the treatment zone, primarily in the upper soil layers.[2]

Soils from petroleum industry land-treatment facilities have been evaluated using the EPA extraction procedure (EP). The metal concentrations in the EP extract were significantly lower than the EP limits used to define a hazardous material.[2] Thus, although the metals are immobilized and do accumulate, they do not appear to be of environmental concern.

Industry studies have shown that such emissions do occur at petroleum industry land treatment facilities.[2] However, there has been no indication that such emissions have caused adverse impacts on human health and the environment.

Available information demonstrates that land treatment is an active treatment process that differs from other hazardous waste land disposal methods. Land treatment is not merely dilution nor merely storage; it is a treatment process that accomplishes degradation, immobilization, and transformation.

Land treatment of petroleum industry wastes reduces the toxicity of the applied waste and significantly reduces the migration of hazardous constituents. Numerous studies have shown that such constituents do not migrate deep into the treatment zone and, therefore, do not migrate through the 5-ft treatment zone.

Land treatment of petroleum wastes can meet performance standards such as those being established for BDAT.

Regulatory agencies, as well as Congress, should recognize the differences between land treatment and other land disposal methods when land disposal restrictions and regulations are developed. Land treatment does reduce the risk to human health and the environment from constituents in petroleum industry wastes and achieves the performance standards similar to those now being established for BDAT.

Because the statutory definition of land disposal includes land treatment, decisions by EPA relative to overall prohibitions for various methods of land disposal will affect future operations. Options that could be considered in such decisions include allowing land treatment to be evaluated along with other technologies as BDAT or acceptance of land treatment demonstrations as the functional equivalent of the petition process.

Facilities may petition EPA for a variance from the land disposal prohibition determination. A longer-term option could be a redefinition of land treatment in RCRA so that it is not included with techniques which constitute only storage and disposal.

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Biological Remediation of Petroleum Hydrocarbons

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ABSTRACT

This paper describes biological remediation operations at a petroleum products terminal in New England. Remediation activities commenced in 1988, initially at bench-scale and subsequently at full-scale. The laboratory study consisted of a volatilization phase to model soil handling activities and, subsequently, a bench-scale biological treatment operation conducted in beaker-scale microcosms. Full scale biological treatment operations were conducted between May and October 1988. Approximately 19,000 yd^3 of contaminated soil were completely treated during this period.

The half-life of o-xylene was determined to be 1.4 days from the laboratory study. As o-xylene is the least volatile of the constituents monitored, its half-life was used to represent the half-lives of total BTEX. Calculations of the kinetics for degradation of BTEX from the field data indicate an average half-life of 6.2 days. A first order kinetic model gave TPH half-lives of 3.6 days. Calculation of the kinetic parameters from field data indicates the half-life for TPH is approximately 23 days. Selection of appropriate analytical methods and critical interpretation of test results is fundamental in evaluation and optimization of the bioremediation process.

INTRODUCTION

This paper describes biological remediation operations at a petroleum products terminal in New England. The 22-ac riverfront site was used to store primarily gasoline and No. 2 fuel oil from the 1920s through 1982. In 1987, the 14 storage tanks, with capabilities up to 3.5 million gals each, were dismantled. Figure 1 presents a site map.

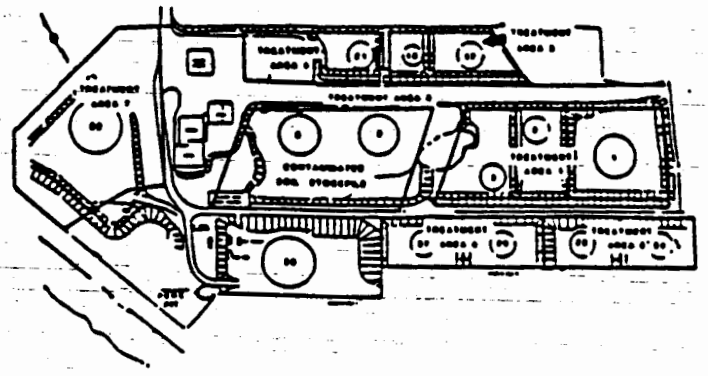


Figure 1
Site Operations Map

Remediation activities commenced in 1988, initially at bench-scale and subsequently at full-scale. The laboratory study consisted of a volatilization phase to model soil handling activities and, subsequently, a bench-scale biological treatment operation conducted in beaker scale microcosms. Full-scale biological treatment operations were conducted between May and October 1988. Approximately 19,000 yd^3 of contaminated soil were completely treated during this period. Treatment operations were initiated on an additional 14,000 yd^3 near the end of the construction season. This material remains in treatment throughout the winter months. Treatment operations will resume in 1989.

This paper describes not only the biological treatment of soils contaminated by petroleum products, but also problems associated with approved analytical protocols for this technology.

PROJECT DESCRIPTION

Remediation Criteria

Plans for redevelopment of the sloping site as a residential condominium complex include significant regrading and construction of townhouses and multistory residential structures. The state regulatory agency having jurisdiction over this site imposed low level cleanup criteria for the final remediation given the residential end use. Extensive negotiations were required to establish criteria not only in terms of absolute numbers, but also analytical protocols and procedures. These criteria are shown in Table 1.

Table 1
Contamination Criteria

	BTEX(1)		TPH(2)		Napthalene(3)	
	Maximum (ppm)	Average (ppm)	Maximum (ppm)	Average (ppm)	Maximum (ppm)	Average (ppm)
End of Treatment	1.0	0.25	100	50	<1.0	NA
Limit of Excavation	1.0	0.25	100	50	<1.0	NA

(1) Measured by EPA method 8020.
(2) End of Treatment - measured by GC method (modified EPA method 8100)
Limit of Excavation - measured by IR method (EPA method 418.1)
(3) Measured by EPA method 8100.

Cleanup criteria were established for discrete constituents including benzene, toluene, ethylbenzene and xylenes (BTEX), and naphthalene. To characterize fuel oil constituents, as well as other components of gasoline, cleanup criteria were established for total petroleum hydrocarbons (TPH). Both gas chromatography (GC) and infrared (IR) methods were used. Additionally, some GC/MS analyses were performed to identify specific compounds reported as TPH by the various methods.

Note that the limits of excavation criteria are listed separately from end-of-treatment criteria. Initially, this designation was included due to different requirements of analytical frequency; however, after initial operations, this designation was required to differentiate analytical protocols. Note, too, the differentiation between the site wide average criteria and the allowable maximum. Given the nature of the problem and the inherent variability in this project (i.e., analyses of an index chemical parameter in variable geologic and humic matrices) it is believed the difference in the two criteria is too narrow.

The TPH analytical method uses a chemical standard against which specific analytical results are compared to determine the concentration of contaminant. The TPH method was originally developed to assist in the characterization and remediation of petroleum spills. Typically, a sample of the spilled product would be available for use as a standard. At this site, all product had been removed prior to initiation of the project so that no known standard was available. Split samples were analyzed using both GC and IR methods to evaluate various potential standards for quantifying petroleum hydrocarbons.

Although the laboratory study indicated some variation between GC and IR data, the limited data we had were not sufficient to allow us to evaluate the impact of the analytical procedures. Cleanup criteria were established based upon the IR protocol, following the U.S. EPA approved method (From U.S. EPA Method 418). The large analytical data base generated during full-scale operations quickly indicated problems with the IR method, particularly as applied to biological treatment projects.

Treatability Study

The first phase of the laboratory study was designed to model volatilization of BTEX associated with excavation and handling of gasoline-contaminated soil. The second phase modeled biodegradation of BTEX and TPH during full-scale operations. Using our knowledge of previous site investigations, we obtained soil samples from former tank areas with typical BTEX and TPH concentrations.

Volatilization was evaluated in a sealed, glove-box chamber which the air was passed through at predetermined rates (Fig. 2). A mixing fan inside the glove-box kept the chamber air well mixed to assure uniform air sample. The gloved portals allowed a technician to turn, aerate and sample of the soil.

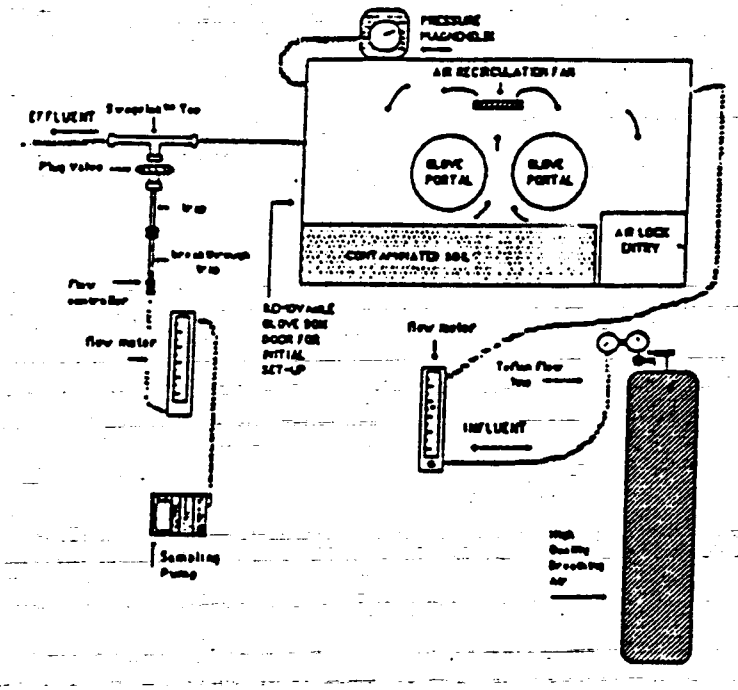


Figure 2
Glove-Box Apparatus

Air leaving from the glove-box contained gasoline-contaminated soil was sampled over the course of Phase I of our study. Two Tenax traps were used in parallel to assure adequate capture of volative contamina with no breakthrough. The downstream end of the trap was connect to a flow controller, in-line air flow meter and low flow (50 ml/min) sample pump. After the required sampling time had elapsed, the valve and sample pump were turned off and the Tenax traps were removed and placed in labeled containers. The samples were subsequently submitted to the laboratory and stored frozen until analyzed.

Within the glove-box, soils were aerated to simulate material handling activities at 90 and 190 hrs following the start of each run. Soils in the glove-box were first tilled/aerated thoroughly and then sampled in triplicate. Soil samples were collected in triplicate at time zero (t$_0$), 90, 190 and 240 hrs to monitor BTEX removals in soil within the glove-box and at 38 and 60 days once emission sampling was complete.

Following the volatilization study, the contaminated soil was removed from the glove-box and simulated full-scale biotreatment operations were undertaken. This stimulation included maintaining the soil at approximately 20% moisture content by weekly watering, mixing and tilling. Soil concentrations of BTEX and TPH were monitored to evaluate biodegradation under conditions similar to field treatment operations anticipated for full-scale remediation. Soil nitrogen and phosphorus concentrations were monitored to assess the nutrient status at study initiation and completion.

Field Operations

Full-scale treatment operations began with the loading of treatment areas with contaminated soils. Soils were dumped into the windrow location and leveled with a bulldozer. Cobbles and boulders exposed on the surface were removed, initially by hand and subsequently with a mechanical rock picker.

A tire driven horizontally mounted auger, produced by Brown Bear Co. (Brown Bear), made a pass through the contaminated soils and seed, mixing the materials and forming a windrow approximately 2 feet high and 4 ft wide. Windrows were placed toe to toe without travel lanes between, allowing the ratio of soils in treatment to the size of the treatment area to be 2,500 yd^3/ac.

Cobbles and boulders varied significantly from as much as 40% to 50% in the fills to 10% to 20% in the sand and gravel. The size of the boulders occasionally exceeded 2 ft. A rock-picking operation was initiated, initially consisting of two laborers manually removing rocks into the back-hoe. Subsequently, a mechanical rock picker, towed through the treatment area behind an agricultural tractor, was used.

Soils were aerated approximately every other day by turning with the Brown Bear. Aeration operations began at a 10 ft wide travel lane at the edge of the treatment area. The windrow, originally at the right side of the equipment, was moved by the horizontal auger to the left, across the travel lane. During this operation, the soils were thoroughly mixed and aerated.

Numerous samples of the contaminated soils were obtained throughout the treatment operations and analyzed for carbon, nitrogen and phosphorous. These analyses indicated that the C:N:P ratio averaged 12:1:0.5, significantly below the target maximum of 25:1:0.5. Therefore, no nutrients were added during the season's operations.

Measurements of pH were regularly performed in the field with a pH meter. These measurements showed the soils were initially slightly acidic, typically in the range of 6.0 to 6.5. As treatment progressed, the soils became more acidic requiring the addition of lime. Agricultural lime was added at a rate of 80 to 160 pounds per 100 cubic yards to restore the pH to between 6.0 and 8.0. Lime was manually spread over the surface of the windrows and subsequently mixed into the soils by the Brown Bear.

Irrigation of the contaminated soils was required throughout the summer to maintain the proper soil moisture content for optimum microbial activity. Prior to aeration, water, directly from the fire hydrants or from the water truck, was sprayed over the treatment areas until run-off was observed or the surface of the windrows appeared saturated. Watering generally was performed on a weekly basis depending upon the amount of precipitation.

Once analytical results indicated the cleanup criteria had been achieved, the treated soils were excavated with a loader, placed in trucks and hauled to backfill areas at the site. Typically, this material was used to regrade previous excavations, allowing these areas to be used as treatment areas. The material was also used to build access roads in various locations at the site.

BIOTREATMENT RESULTS

BTEX

Volatilization data collected from analysis of the Tenax traps during the laboratory study were used to calculate an emission flux rate. Emission flux results demonstrate what can be expected to occur during volatilization and materials handling events:

- Constituent flux rapidly decreases with time
- Constituent flux increases during handling events

Maximum flux rates, as measured at study initiation, varied from 0.61 ug/cm²/hr for benzene to 8.74 ug/cm²/hr for xylenes. Emission flux is strongly dependent on constituent soil concentrations. Although benzene is more volatile then xylenes, flux was lower due to the low concentrations of benzene present in the soil (<0.01 mg/kg) as compared to xylenes (0.14 mg/kg).

Figure 3 shows the variation of flux rates with time for O-xylenes. Constituent flux rapidly decreased to approximately 10% of the initial flux in 90 hrs. Following the first materials handling event at 90 hrs, flux increased to between 15 and 40 % of the initial flux and then again rapidly decreased to approximately 2% of the initial flux at 190 hrs. The second materials handling event (190 hrs) caused flux to increase slightly (3 to 15 % of initial flux). No assessment of volatilization was undertaken during field operations, with the exception of perimeter air quality monitoring.

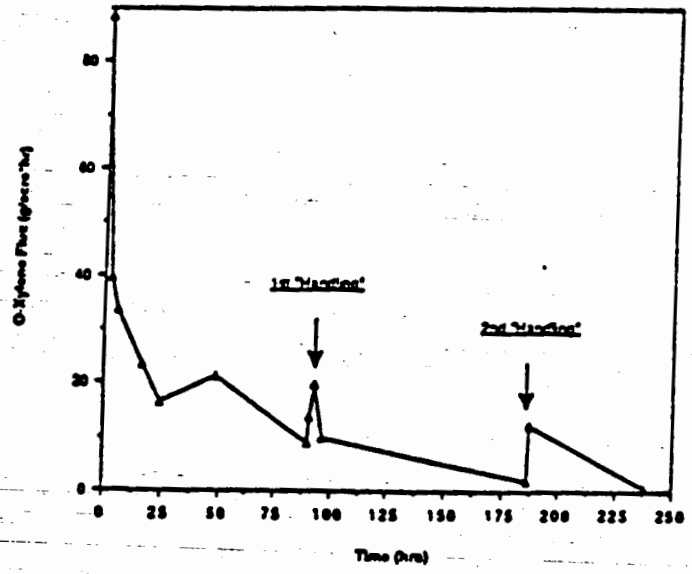


Figure 3
O-xylene Flux vs. Time

As xylene is the least volatile constituent of the BTEX constituents monitored, o-xylene data were used to evaluate the worst case soil loss associated with biological treatment. The first 24 hr soil concentration data for o-xylene were subsequently used to determine soil loss kinetics using both zero and first order kinetic models. Both gave good fits to the data, with an R^2 value of 0.976 and 0.986 for zero and first order equations, respectively. Using zero and first order kinetic models, the half-life of o-xylene was determined to be 1.5 and 1.4 days, respectively. As o-xylene is the least volatile of constituents monitored, its half-life should represent the half-lives of total BTEX.

Calculations of the kinetics for degradation of BTEX from the field data indicate an average half-life of 6.2 days. Reports by the American Petroleum Institute indicate half-lives of from 6 to 10 days for toluene and p-xylene. Cleanup criteria for BTEX were generally achieved within 21 days of initiation of treatment.

TPH

Soil samples were obtained at times 0, 90, 190 and 240 hrs and at 38 and 60 days. Triplicate analyses of TPH concentration by the GC method were performed during the laboratory study. Results show that concentrations decrease with time. The initial TPH concentration measured by GC was 405 mg/kg; this value was reduced to 50 mg/kg in 10 days. Soil TPH concentration by GC was further degraded to less than 10 ppm in 38 days. Final (60 day) triplicate sampling was performed to assure that no detectable TPH was present in the soil. This lack of detection standard indicated that concentrations were less than the analytical detection limit of 10 ppm.

Soil TPH data were used to evaluate soil loss kinetics using both first and zero order kinetic models. The first order model gave a better fit to the data than the zero order model (R^2 of 0.688 and 0.592, respectively). Zero and first order kinetic models gave TPH half-lives of 5 and 3.6 days, respectively. Figures 4a and 4b show regression plots for the zero and first order relationships between TPH concentration and time, as determined in the treatability study.

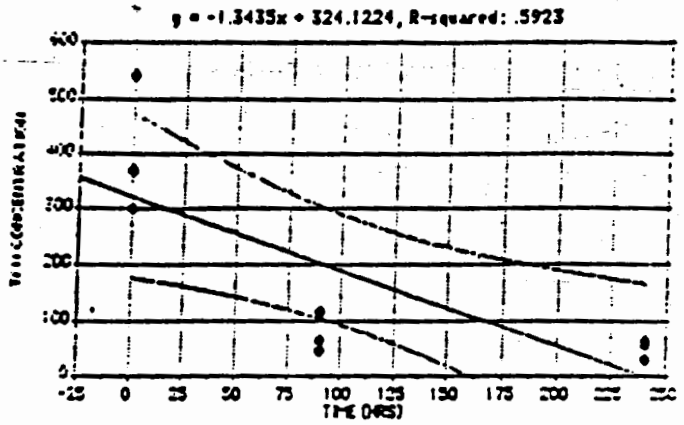


Figure 4a
Zero Order Regression

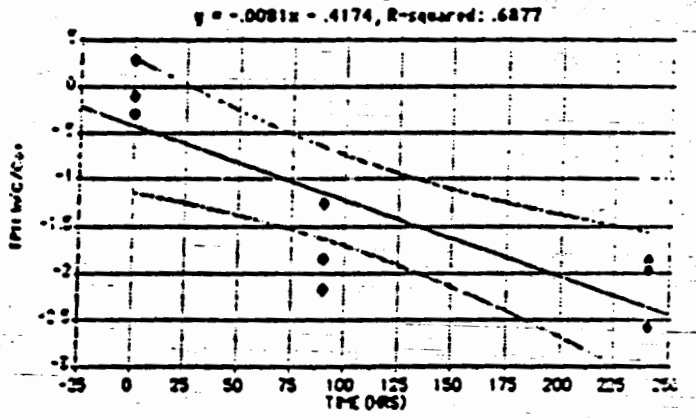


Figure 4b
First order regression

The results of treatment during 1988 full-scale operations show soils at the initiation of treatment are contaminated at average levels of from 300 to 500 ppm TPH, although significant variation was found. The average time for biological treatment to achieve end-of-treatment criteria was 60 days.

Figure 5 presents a plot of the TPH data versus time of treatment for 1988 operations. Our calculations of the kinetic parameters from this data indicate the half life for the TPH compounds is approximately

23 days. Loehr, et al., report that half-lives for C_0 through C_9 vary significantly from as low as 7 days to as much as 45 days, averaging approximately 20 days. Given the 60 days required to achieve TPH clean-up criteria, the TPH criteria control treatment operations at the site.

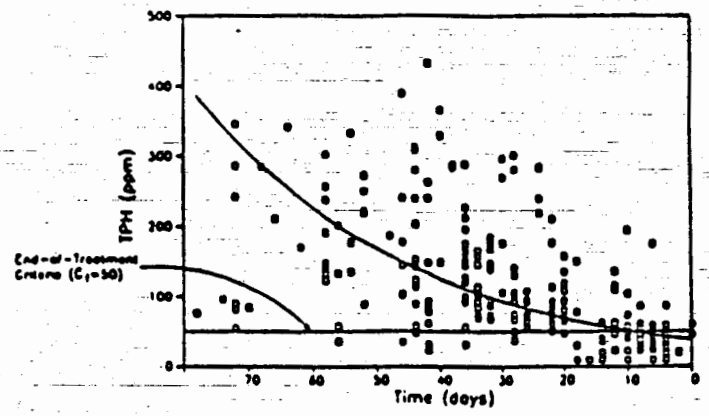


Figure 5
TPH Degradation Kinetics

TPH ANALYTICAL METHODOLOGY

Selection of appropriate analytical methods and critical interpretation of test results are fundamental in evaluation and optimization of the bioremediation process. The analytical method selected for process monitoring must provide reliable and complete petroleum hydrocarbon quantification. The method should also provide qualitative contaminant information for supporting process development in complex treatment systems.

Analyses for TPH during full-scale operations were initially conducted by the IR method (U.S. EPA Method 418.1) using a laboratory standard of 3:3:2 mixture of n-hexadecane, isooctane and chlorobenzene. Initial results showed significant data scatter but a trend toward decreasing TPH. Subsequent analyses, however, showed an apparent trend of increasing TPH. This anomaly led to a review of the analytical protocols and to numerous duplicate analyses of split samples.

Research into the IR method showed this method measured compounds having a carbon hydrogen bond linearly oscillating at a specific frequency. Prior to analyzing the sample extract, the extract was passed through a silica gel column in an attempt to remove organic acids generated by the degradation process containing the carbon hydrogen bond and therefore measured by the method as TPH. Replicate analyses using different amounts of silica gel showed no change in TPH concentrations. Analysis by GC/MS identified many of the compounds identified as TPH by the IR method as organic acids, indicating the silica gel cleanup was unable to remove these compounds. Therefore the analytical method was reporting incorrect concentrations of TPH.

Duplicate analysis of treated soil samples by the GC and IR methods showed significantly lower TPH concentrations when measured by GC as opposed to IR. Additionally, background soil samples with significant organics obtained from off-site locations (an adjacent park) had significant TPH contamination as measured by the IR method but no significant TPH contamination as measured by GC. Table 2 shows a comparison between TPH as measured by IR and by GC for soil samples taken from the off-site location and treatment windrows. Therefore, the analytical method used to determine the end-of-treatment was changed to the GC method (modified U.S. EPA Method 8200).

The infrared quantification employs a measurement of absorbance at approximately 2930 cm^{-1}, produced by the carbon-hydrogen bond. The method will measure any freon extractable, non-silica gel removable compound containing carbon-hydrogen groups. This method does not provide any qualitative contaminant information other than the presence of the carbon-hydrogen bond.

The IR method generally is useful in site investigation studies where a gross indicator of contamination is needed. This method becomes ineffective when used to monitor the progress of bioremediation, particularly when the treatment process is near completion. At that stage in treatment, the presence of interferences will falsely indicate a healthy treatment process has stalled near its end.

Table 2
Comparison of TPH Analyses
IR and GC Methods

Sample	Location	TPH by IR	TPH by GC
1-AB.1.5	Treatment windrow	317	69
1-CD.1.5	Treatment windrow	148	109
1-EF.1.5	Treatment windrow	136	48
1-GH.1.5	Treatment windrow	160	65
1-IJ.1.5	Treatment windrow	167	105
1-K.1.5	Treatment windrow	172	60
1-L.1.5	Treatment windrow	110	67
1-M.1.5	Treatment windrow	153	114
5-A.1.1	Treatment windrow	250	75
5-B.1.1	Treatment windrow	144	109
PBGD-4	Park adjacent to site	76	9
PBGD-5	Park adjacent to site	nd	10
PBGD-6	Park adjacent to site	33	10

Quantification of hydrocarbons by flame ionization gas chromatography involves a component separation technique followed by a component detection and quantification technique. This method enables the analyst to obtain a component profile for the sample. Observation of this profile and how it changes throughout the process, together with quantitative results obtained using this method, provides detailed process data. Analysis of samples from the contaminated soil prior to treatment will produce a petroleum hydrocarbon profile which can be reasonably well matched with available standards. Analysis of treatment standards will reveal changes in the component profile. In general, the profile shifts to approximate an increasingly higher boiling range distillate. Quantification of the hydrocarbon components indicates a reduction in TPH. As the process nears completion, the profile no longer indicates petroleum hydrocarbon components. Instead, a relatively broad, poorly resolved response is observed. The composition of these unresolved components is assumed to be the same as the material producing the interference in the IR analysis. With the GC method, this response can be eliminated from quantification of petroleum components.

Choosing an appropriate standard for TPH quantification is essential to obtaining realistic results. U.S. EPA Method 418.1 calls for using a reference blend of hexadecane, isooctane and chlorobenzene. Although using this standard will generate method defined results with good laboratory-to-laboratory reproducability, the values obtained will frequently vary significantly from actual petroleum distillate levels. Table 3 shows a comparison between analyses of duplicate samples from contaminated soils. One analysis used the 3:3:2 mixture as a standard and the other used No. 6 fuel oil.

Table 3
Comparison of Calibration Standards
for TPH by IR Analysis

Sample #	TPH by IR: 3:3:2 Mixture	TPH by IR: #6 Fuel Oil
2-AD.1.6	92	71
2-AD.1.7	169	130
2-J.1.5	221	170
2-J.1.6	162	125
2-K.1.5	212	163
2-K.1.6	166	128
2-L.1.6	155	119
2-L.1.7	186	143
2-M.1.6	237	182
2-M.1.7	152	117

Ideally, the standard used for quantification should match the distillate pattern in the sample as closely as possible, but the complexity of typical weathered contaminated soil prohibits exact matching. In an effort to obtain conservative estimates of TPH levels when an exact match is not possible, standards should be chosen with the distillation ranges higher rather than lower than the range observed in the samples.

BIOLOGICAL TREATMENT OF HAZARDOUS WASTE

(preprint of an article which appeared in the February 1988 issue of Civil Engineering)

J.R. Ryan, R. Kabrick and R. Loehr

Biological treatment processes have received increased attention over the past several years as a safe and cost effective means of treating a wide variety of hazardous wastes. Biological treatment involves the application of sound engineering and scientific principles to the treatment of solid, aqueous or gaseous waste streams composed principally of degradable organics. In the hazardous waste field, most full scale applications have been with non-halogenated petroleum derived waste although recently there has been bench through full scale applications with various solvents, wood preserving chemicals and coal tar wastes.

Most biological treatment systems are variants of the technologies identified in Figure 1. Each technology is applicable to a specific set of waste matrices as illustrated in the figure. This paper provides a brief description of the technologies suitable for treatment of sludges and contaminated soils; land treatment, composting and liquid solids treatment.

LAND TREATMENT

Land treatment has been the most widely used technology for the treatment and disposal of hazardous waste. The technology has been used for over 30 years for the treatment of oily wastes primarily from the petroleum refining industry. An extensive data base exists with this technology which has been applied to the development of other biological processes.

Technology	Solids	Aqueous wastes	Gaseous Emissions
LAND TREATMENT	•	•	
COMPOSTING	•		
LIQUID/SOLIDS	•	•	
IN-SITU		•	
SOIL FILTERS			•
CONVENTIONAL		•	

FIGURE 1

Land treatment uses the assimilative capacity of the soil to decompose and contain the applied waste in the surface soil layer (usually the top 6 to 12 inches). This upper soil layer is the *zone of incorporation*. The incorporation zone, and the underlying soils where additional treatment and immobilization of the applied waste constituents occurs, is referred to as the *treatment zone*. The treatment zone depth in the soil may be as much as five feet. However, most of the transformations, biological oxidation and immobilization will occur in the zone of incorporation.

Liners are generally not a part of a land treatment system. Land treatment technology relies on the dynamic physical, chemical and biological processes occurring in the soil. As a result, the constituents in the applied wastes are degraded, immobilized or transformed to environmentally acceptable components.

As shown in many studies (API, 1983, 1984; Brown et. al., 1984; Loehr and Malina, 1986), land treatment systems used for oily wastes do degrade and immobilize the waste applied at such sites. Oil, metals and other constituents of environmental concern are successfully controlled by such systems.

Land treatment is suitable for use on a broad spectrum of wastes. Wastes which have been land treated include:

- contaminated soils,
- petroleum refinery sludges,
- creosote sludges and wastewaters,
- municipal sludges and wastewaters,
- food processing sludges and wastewaters,
- chemical plant wastes,
- wood and paper process sludges, and
- textile mill sludges.

Land treatment has been successfully practiced in all major climatic regions of the United States, Europe and Canada under a wide range of hydrogeologic conditions. In the U.S. approximately 200 land treatment systems are in operation, including over 100 at petroleum refin-

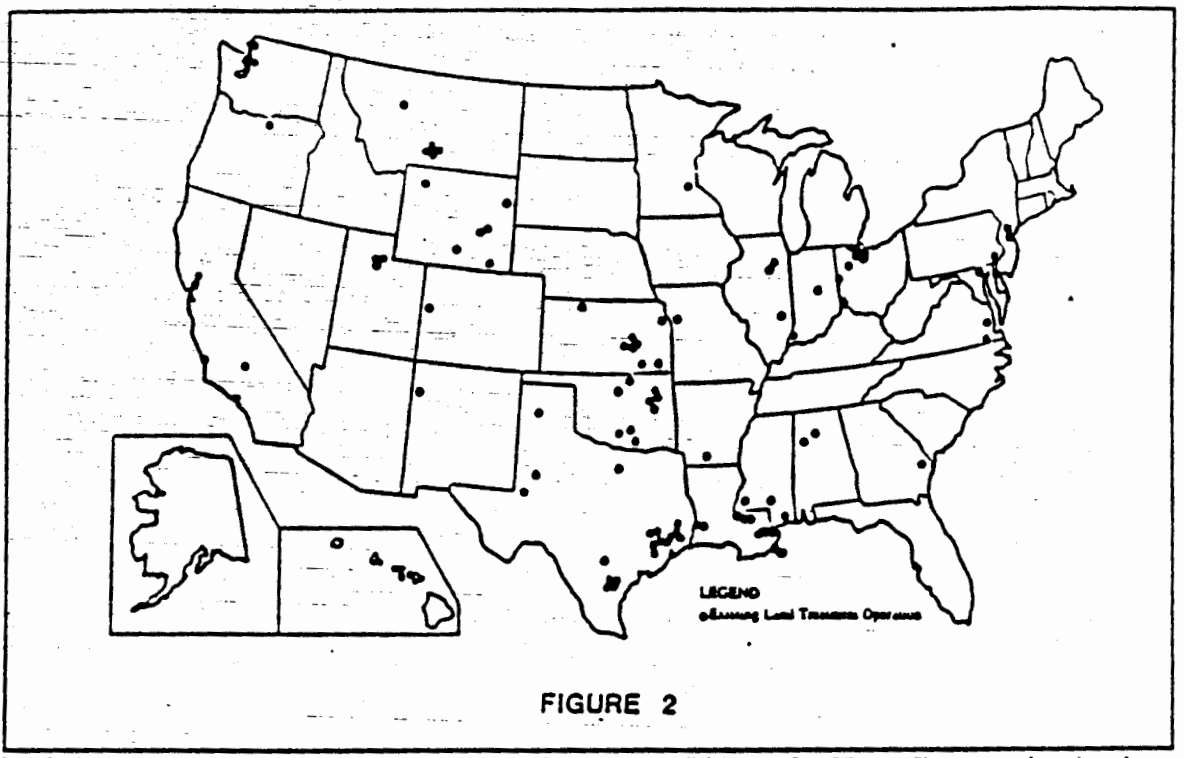


FIGURE 2

ing facilities. Figure 2 shows the geographical distribution of these land treatment sites. This figure suggests that there are very few site limitations which cannot be overcome with appropriate design.

An extensive data base on the degration of hazardous constituents in land treatment systems has been gathered over the past several years (API, 1987; Sims et. al., 1987). Most of the data has centered on the loss rates associated with aromatics and polynuclear aromatics. Table 1 provides a brief summary of the half lives of certain aromatics and PAH compounds in land treatment systems.

As noted earlier, most application of hazardous waste land treatment have involved petroleum refining wastes treated under RCRA. Land treatment, however, has been approved and implemented at at least one CERCLA site involving the closure of a wood preserving lagoon (Linkenheil, 1987). At this site, a pilot test was run for one year which demonstrated that the creosote constituents could be degraded by acclimated soil microorganisms. Approximately 12,000 yards of contaminated soils and sludges were removed from an impoundment and temporarily stored. A lined treatment area was then constructed over the former impoundment and the stored wastes applied to the treatment area. Total cleanup cost including excavation of the waste and construction and operation of the treatment area were approximately $80/yard. Costs for unlined land treatment systems are in the range of $50/yd. Extensive site testing is necessary to obtain RCRA permits. Land treatment is currently considered a land disposal method and is subject to the land disposal ban prohibitions of RCRA. The extensive data base gathered over the past few years, however, has shown that land treatment can be protective of human health and the environment with wastes having characteristics as diverse as liquid municipal wastewater, liquid and dewatered municipal sludge, and petroleum and other industry wastes. The basic technology also can be used for bioremediation of contaminated soils at Superfund and other sites. The use of land treatment under controlled and well designed and operated conditions should continue to be available to meet the mandates of RCRA and CERCLA.

COMPOSTING

Composting is a batch biological process typically used to treat wastes with high concentrations of biodegradable organic solids. Waste destruction and conversion is achieved by thermophilic aerobic microorganisms which occur naturally in decaying organic matter. The basic objective of this process is to maximize microbial activity while at the same time decreasing waste volume, odors and aqueous side streams. Composting is an adaption of conventional biological waste management methods. As such, the factors that affect the performance of biological treatment processes (adequate nutrients, satisfactory pH and temperature, nontoxic conditions, adequate oxygen and satisfactory moisture conditions) also will affect the performance of composting.

TABLE 1

SUMMARY OF HALF LIVES
FOR
SELECTED AROMATIC AND PAH COMPOUNDS
(API, 1987)

COMPOUND	NUMBER OF RINGS	HALF LIFE (days)
TOLUENE*	1	5.8 - 6.5
P-XYLENE*	1	8.6 - 10.2
NAPHTHALENE*	2	9.1 - 13.9
ANTHRACENE	3	<9 - 53
PHENANTHRENE	3	<6 - 43
BENZO(a)ANTHRACENE	4	63 - 231
CHRYSENE	4	41 - 116

* = corrected for volatilization loss.

The composting process is generally completed in piles three to six feet high. Aeration is provided by either periodically turning the piles mechanically or through a forced aeration system. Bulking agents such as wood chips are commonly added to facilitate mixing and oxygen transfer. These bulking agents are typically screened out at the completion of the composting process and mixed in with a subsequent batch loading of waste.

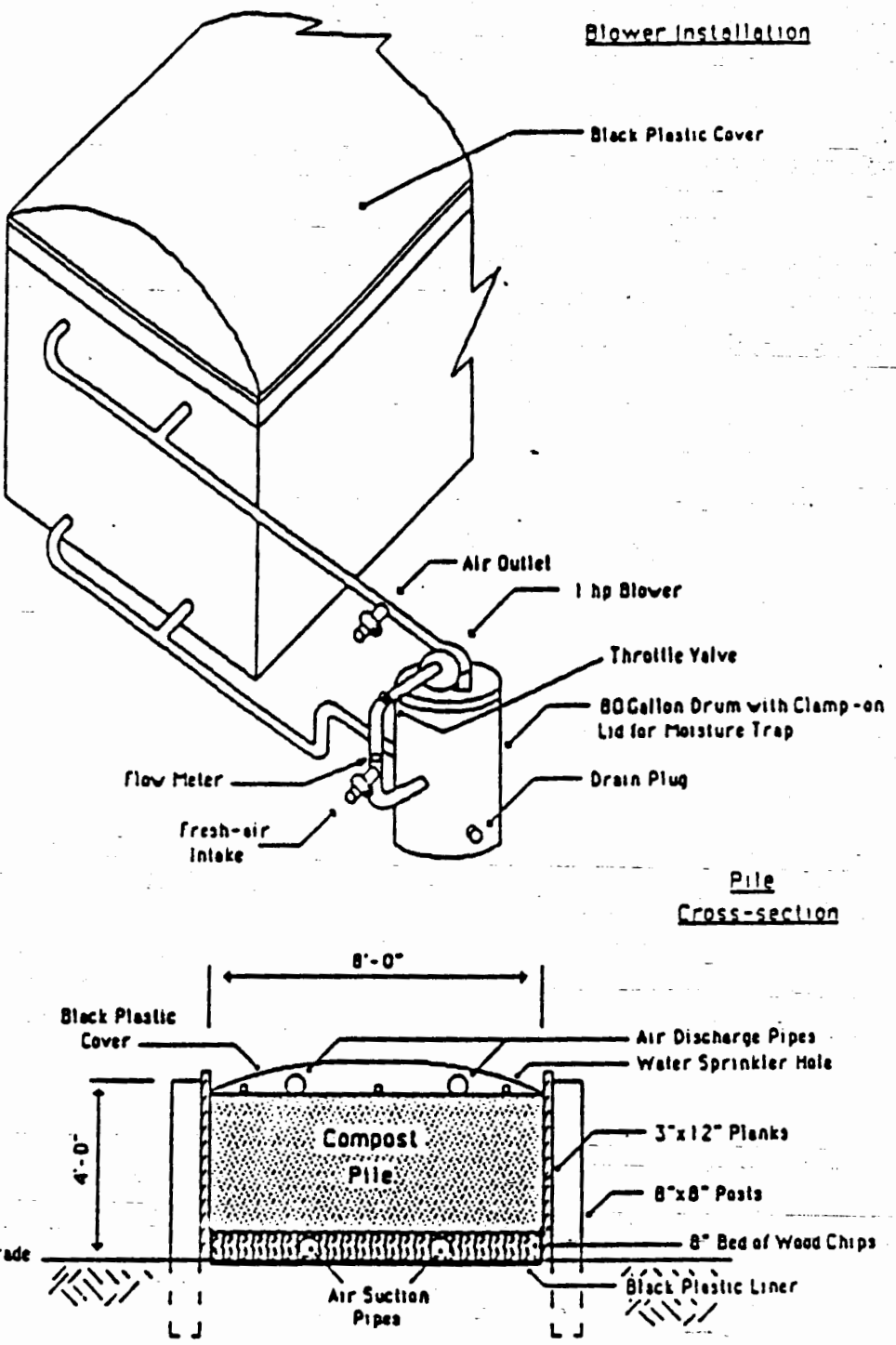
The largest use of composting technology has been in the municipal sector for sewage sludge. This technology has also been used to treat a variety of industrial solid wastes, including industrial wastewater treatment sludges, food processing wastes, and some industrial wastes containing low levels of pesticides.

A significant amount of published data is available in support of the composting process, however, much of the data deals only with the composting of wastewater treatment sludges. The application of composting to sludges/soils contaminated with hazardous wastes has only recently been attempted. Research by numerous private and public institutions is now beginning to address this issue. For instance, in Great Britain, a proprietary and successful town gas site remediation has recently been completed. The firm which completed work at the site claims that significant coal tar waste degradation was achieved by composting. This success was based on reduction of coal tars to below a one percent (10,000 ppm) target level, and it is not known whether lower levels were achieved. For many wastes, the concentration of such organics may be less than 10,000 ppm at the beginning of a bioremediation process.

Another study is being conducted at Rutgers University where the degradation of hazardous industrial compounds during composting is being investigated. Preliminary results from the study are available (Hunter and Finstein, 1986). Aliphatic hydrocarbons were degraded to a significant extent, although the degradation of the polycyclic aromatics, in particular chrysene, was noticeably less. This study does show that the microbial degradation of these compounds is possible by composting.

Bench scale composting studies are currently being conducted with the use of a white rot fungus. This organism produces a non-selective enzyme which is capable of degrading recalcitrant organics. Studies have shown that this organism is capable of completely degrading complex PAH, pentachlorophenol, DDT and certain PCB's in relatively short time periods. The enzyme activity is enhanced in high carbon to nitrogen ratio environments, therefore the organism is compatible with the bulking agent requirements of most compost systems.

Figure 3 shows a pilot scale compost system constructed by ReTeC for treatment of diesel contaminated soils and shows a cross section of the unit. Aeration is provided by an air compressor which draws a vacuum at the bottom of the pile and returns the air at the top. Make up air is



PILOT-SCALE COMPOST SYSTEM

FIGURE 3

added as necessary as oxygen is depleted. Nutrients and water are provided through an irrigation system located at the top of the pile.. The studies completed to date have shown that the diesel contaminants have half lives in the range of 30 to 60 days. Full scale costs are estimated to be less than $100/yd.

A major difference in the use of composting for such remediations is that the organic content of such sites probably will not support thermophilic conditions. The organics are much less biodegradable than those in municipal sewage sludge or food processing wastes and are present in much lower concentrations. However, temperatures above ambient are likely to occur even if thermophilic temperatures are not attained. It is possible to add amendments that are more biodegradable, such as sewage sludge or manure, to achieve higher temperatures in the composting process. This could cause greater loss and degradation rates due to the higher temperatures and possibly co-metabolism of less biodegradable organics.

The practical advantage of composting for bioremediation of hazardous waste sites may be the increased loss rates that occur because of the greater oxygen transfer capabilities of the process and the above-ambient temperatures. In addition, the system is amendable to design as a closed loop system to control air emissions and leachate generation.

BIOREMEDIATION WITH LIQUID/SOLIDS SYSTEMS

Liquid/solids treatment systems (LSTS) are biological treatment systems analogous to conventional biological suspended growth processes such as activated sludge, extended aeration and aerobic digestion. LSTS are used to reduce the quantity and toxicity of hazardous organic wastes. These processes treat wastes that are in a suspended solid, slurry or sludge form. The process relies upon the mobilization of the contaminants into the aqueous phase where they are then susceptible to microbial degradation and volatilization. The mobilization or dissolution step can be a result of microbial action and/or physical-chemical action. In either case, this is an important step in the overall process. Another way to view the LSTS concept is a combination of the phenomenon which occur in land treatment and in conventional suspended growth systems.

The ability of LSTS to significantly reduce the level of contaminants in a waste stream involve the following primary phenomena: (1) the extraction (solubilization) of the organics into the aqueous phase, (2) biodegradation of the extracted organics into less toxic and less environmentally significant forms, and (3) the volatilization of the contaminants from both the hydrocarbon and the aqueous phases. There are two basic flow regimes for LSTS as shown in Figure 4. It is important to realize that regardless of the chosen flow regime, LSTS require sufficient mixing of the liquid and solids to achieve effective mass transfer of (1) the organics to the aqueous phase and (2) the terminal electron acceptor (in most cases oxygen) to the microorganisms, and the suspension of solids in solution.

The most frequently used process configuration is a single, batch reactor system in which the extraction and biodegradation occur concomitantly in a heterogeneous liquid/solids reactor (i.e. tank, pit, lagoon). The reactor is loaded with the contaminated organic material and air is introduced to provide both mixing for the extraction process and oxygen for the biological reactions. Aeration and mixing may be provided by submerged aerators, floating aerators or compressors and spargers (lances). It is important to provide both adequate mixing and good oxygen transfer. The dissolution/extraction of the contaminants is directly related to the mass transfer of the contaminants from the solid/hydrocarbon phase into the aqueous phase. Generally speaking, the more energy provided for mixing, the higher the rate of mass transfer. In addition, since the aqueous phase degradation will occur by microbial action, adequate quantities of oxygen must be supplied for microbial treatment. Additional factors influencing the rate of microbial degradation include temperature, pH and available nutrients such as nitrogen, phosphorus.

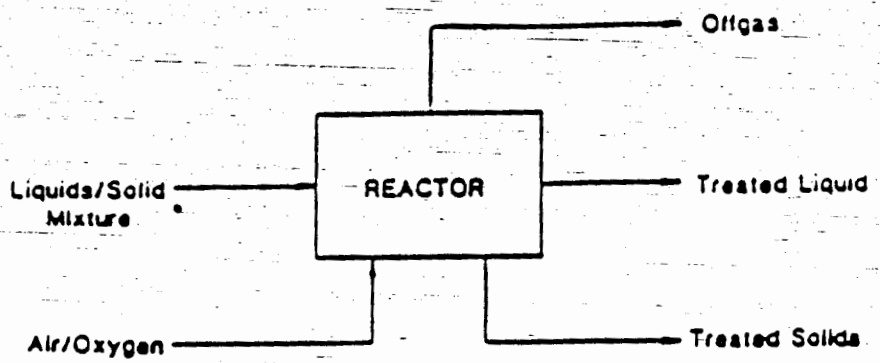
At the completion of treatment, the aeration and mixing are discontinued and the solids are allowed to settle. The treated liquid is decanted and discharged while the treated solids are further treated by conventional land treatment or disposed of on site. If the process is applied to a lagoon or surface impoundment, it may be possible to decant the liquid and leave the solids in place.

LSTS are a relatively new approach for the remediation of contaminated organic materials. There have been several applications of LSTS for the treatment of wood treating, coal tar and most recently petroleum wastes. The success of these systems combined with the historically successful land treatment of petroleum, wood preserving and coal tar wastes point to the fact that LSTS can be technically and economically feasible for the treatment of emulsified tars, soils, hydrocarbon sludges and highly contaminated soils.

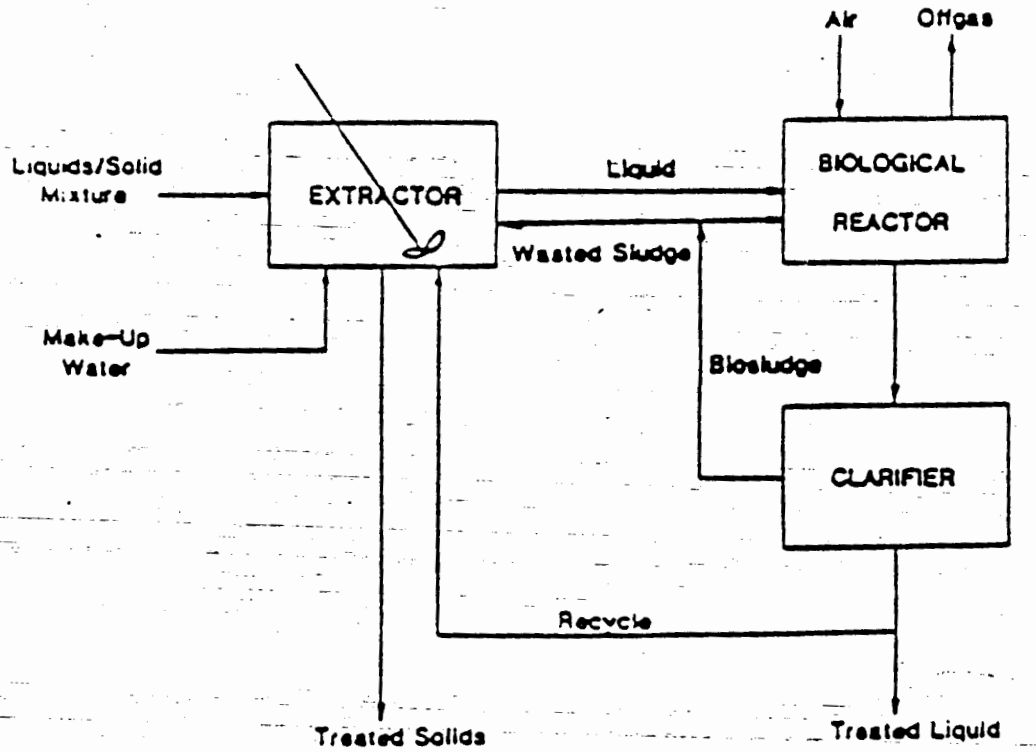
LSTS have been applied in at least two instances to coal tar materials. These materials were present in a gas holder (approximately 600,000 gallons) and in a concrete structure (approximately 2000 cubic yards). Both treatments were applied in-situ with air provided using lances in the

PROCESS FLOW DIAGRAM : LIQUID/SOLIDS SYSTEMS

SINGLE REACTOR SYSTEM



TWO STAGE SYSTEM



LIQUID/SOLID TREATMENT SYSTEMS	FIGURE
FLOW REGIMES	4

holder and surface aerators in the concrete structure. Significant reduction in tar volume, phenol concentration and flash point were achieved in the gas holder over a period of nine months.

Extensive applications (on the order of 20 to 30) of this technology have occurred within the wood treating industry. Most of these applications are directly related to the closure of open lagoons which contain creosote sludge. Air is typically provided using surface aerators. The residuals from the process have generally required additional treatment before closure of the lagoon was approved. This treatment was often provided in the form of conventional land treatment. Although documentation is not available, it is known most of these sites are in EPA Regions IV and VI.

LSTS are on-site treatment technologies that have the potential to oxidize, stabilize and immobilize organic constituents of hazardous wastes. A limited number of studies have shown LSTS capable of 99% reduction in phenolics and up to 85% reduction of polynuclear aromatic hydrocarbons in as short as eight months.

The economic benefits of LSTS are influenced by site characteristics as are other treatment and disposal costs. However experience has shown that when biological treatment is applicable at the site, the associated capital costs are 30 to 50% less than those of alternative technologies such as incineration. While LSTS costs are not readily available they are estimated at $100 to $150 per yard of material processed. Operating costs associated with LSTS are largely due to the energy cost for mixing and aeration.

Relative to other on-site biological treatment approaches (i.e. land treatment and composting), LSTS has the potential to achieve the treatment goals in a shorter time using less land area. LSTS utilizing tank reactors may eliminate regulatory obstacles or concerns related to the land ban or to contaminant migration to the groundwater.

SUMMARY

A variety of biological technologies are available for the treatment of hazardous wastes (sludges and contaminated soils). The most widely used technology is land treatment which has been applied in the petroleum refining industry for over 30 years. Recently there have been applications of land treatment for the remediation of CERCLA sites contaminated with wood preservatives and petroleum distillates.

A variant of land treatment is composting. The treatment is carried our in aerated piles thereby minimizing land area requirements. Although slightly more expensive than land treatment, composting offers greater process control and can be designed as a closed loop system to control air emissions and leachate generation. Most applications of composting have been in the municipal sector, although considerable bench and pilot work is being conducted with coal tar and petroleum derived waste.

Liquid/solid systems offer a potentially cost effective means of treating sludges in a slurry form. These systems may provide more rapid treatment of certain wastes than composting or land treatment. The technology is an adaptation of conventional suspended growth systems although energy requirements for mixing are considerably greater. These systems are a relatively new approach for the remediation of hazardous wastes. However, several full scale systems are currently in use for the treatment of coal tar and petroleum derived wastes arising from site closures.

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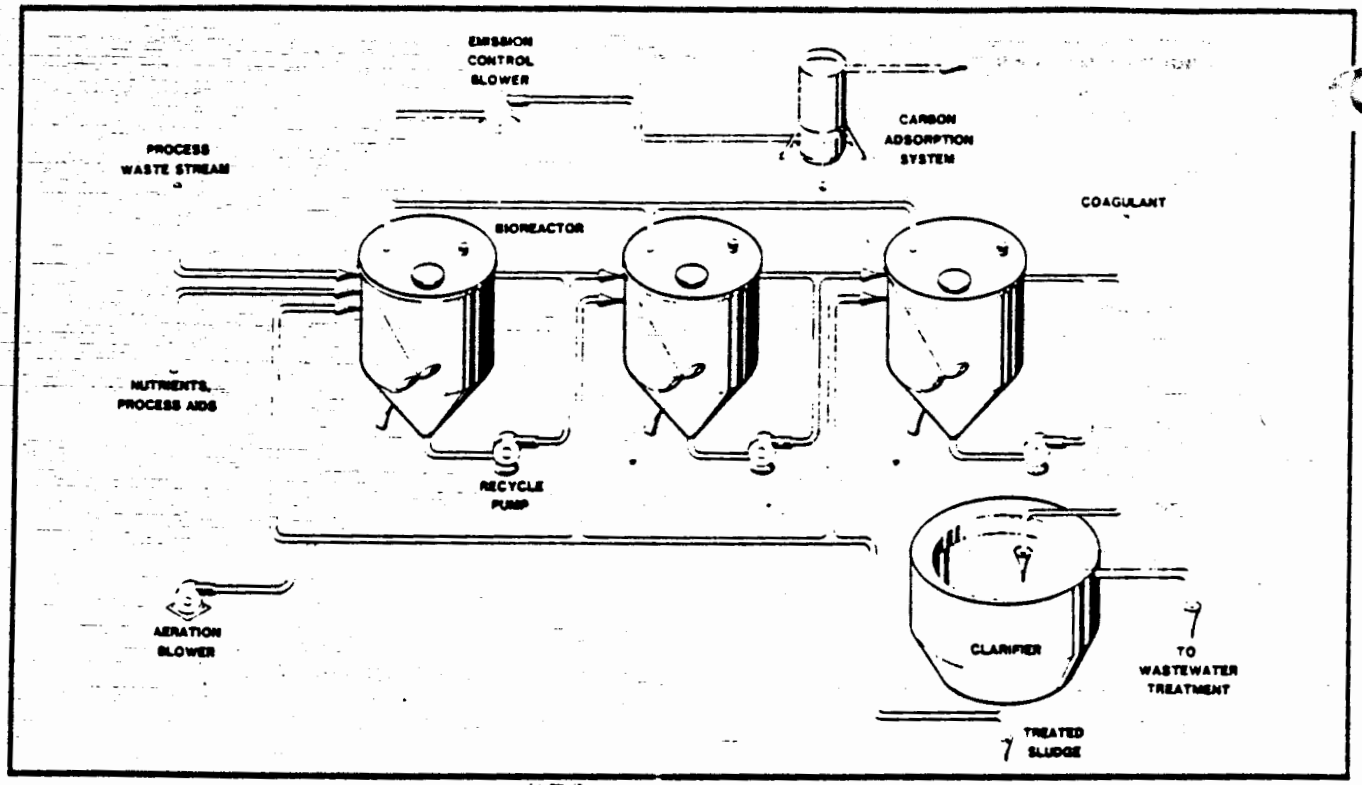
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Configuration for Liquid/Solids Contact Biostabilization

Loss of Polycyclic Aromatic Hydrocarbons (PAH)
During Liquid Solids Treatment of Petroleum Refinery Sludges

Sludge Origin	Solids Loading(%)[1]	PAH Mass (mg) Initial	PAH Mass (mg) Final	Treatment Time (days)	Percent Reduction[2]
Lagoon	5	191	35	60	82 (76)
Lagoon	10	393	37	60	91 (87)
Impoundment A	5	393	40	60	90 (75)
Impoundment A	30	1315	100	60	92 (89)
Impoundment A	11	64 Kg	15 Kg	60	81 (60)
Impoundment B	6	28 Kg	5.4 Kg	90	76 (25)

[1] Loading on a material dry weight basis

[2] Total PAH (Carcinogenic PAH)

BIOREMEDIATION OF CONTAMINATED SOILS

by

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ABSTRACT

Bioremediation is a managed, demonstrated active treatment process that uses microorganisms to degrade and transform the chemicals in contaminated soil and industrial sludges and residues. The process also reduces the toxicity of the organics and the migration potential of hazardous constituents in such material. On-site and in-situ bioremediation processes have been used for the treatment of residues from the petroleum and wood preserving industries and for soils contaminated by contents of lagoons and storage impoundments.

The fundamentals of biological treatment, as applied to these methods to achieve clean-up, closure and treatment objectives, are the key to the proper design and operation of bioremediation processes. Treatability evaluations determine the technical and economical feasibility of alternative process configurations. Such evaluations include: (a) waste and residue characterization, (b) problem and performance definition, (c) controlled laboratory studies, (d) pilot and/or field studies, and (e) large-scale demonstrations.

The application of bioremediation processes has resulted from understanding the factors that affect the microbial metabolism of chemicals in complex mixtures. It is possible to use naturally occurring microorganisms and further enhance their activity by modifying and controlling their environment.

INTRODUCTION

Increasingly, complex mixtures of chemicals, many defined as hazardous and toxic, enter the environment. The need for remedial action has resulted in legislation and regulations that require action be taken to identify and reduce or eliminate these hazards in a cost-effective and environmentally sound manner. The existing regulations are the result of several legislative mandates:

- the Safe Drinking Water Act (SDWA) -- protecting and restoring aquifers
- the Resource Conservation and Recovery Act (RCRA) -- destroying or detoxifying hazardous wastes
- the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) -- restoring Superfund sites and decontaminating soils
- the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) -- waste pesticide disposal

The regulatory and technical challenge is to use cost-effective control technologies that can treat complex mixtures and reduce the threat to human health and the environment. Bioremediation can be such a technology.

Bioremediation is a managed, demonstrated, active treatment process that uses the known capacity of the microbial environment to degrade and transform chemicals, reduce the toxicity of organics and reduce the migration of hazardous constituents in contaminated soils and industrial sludges and solids. This technology can meet the mandates of current pollution control, hazardous waste and abandoned site regulations.

Bioremediation has been used for the treatment of residues from the petroleum, wood preserving and pulp and paper industries and for remediation of contaminated soil. The advantages of on-site or in-situ bioremediation processes include:

- is accomplished where the problem is located
- does not require transporting large quantities of contaminated material off-site
- destroys the problem rather than moving it somewhere else
- minimizes long-term liability
- is ecologically sound and is an extension of a natural process
- generally is cost-effective and competitive with other decontamination technologies for organics

BIOREMEDIATION PROCESS FUNDAMENTALS

In practice, bioremediation encompasses a broad spectrum of configurations and operating conditions that are needed to achieve the performance required by the goals and circumstances of each situation. Actual remediation results from a wide range of physical, chemical and biological processes. In bioremediation, the microbiological processes predominate. Properly designed and managed, bioremediation can: (a) degrade the biodegradable organics, and (b) result in the recalcitrant organic molecules being incorporated into the residual organic pool of humic substances in the environment.

Natural microorganisms, such as those found in the soil, degrade a large variety of organic compounds, thereby obtaining energy for their growth. Under aerobic conditions when there are no inhibitory compounds, the end products of the degradation are oxidized compounds such as water, carbon dioxide, nitrate and sulfate. Under anaerobic conditions, degradation (fermentation) also can occur. However, the end products are reduced compounds such as methane, volatile acids, ammonia and hydrogen sulfide. These reduced end products can be oxidized under aerobic conditions. The organics that can be degraded aerobically and anaerobically include many that are found in petrochemical and petroleum industry residues and wood preserving residues as well as those found in municipal sludges and food processing residues.

If bioremediation can occur and is effective, why do some organics, such as contaminated soils, persist in the environment? This is a reasonable question that is answered by identifying the factors that affect microorganisms and therefore bioremediation processes. Even biodegradable organics may persist if adverse factors and non-optimum conditions exist. The factors that may prevent microbial degradation and bioremediation include:

- chemical concentrations that are toxic to microorganisms

TABLE 2

RESULTS FOR BIOLOGICAL LST OF PETROLEUM WASTES
(CONCENTRATIONS ARE BASED ON A WET WEIGHT BASIS)

COMPOUND	INITIAL CONCENTRATION (MG/KG)	FINAL CONCENTRATION (MG/KG) AVG	ST. DEV
BENZENE	88	BDL	--
TOLUENE	4.8	BDL	--
ETHYLBENZENE	210	BDL	--
XYLENE (TOTAL)	450	BDL	--
NAPHTHALENE	350	BDL	--
ACENAPHTHYLENE	15U	BDL	--
ACENAPHTHENE	15U	BDL	--
FLUORENE	700	BDL	--
PHENANTHRENE	15U	30	20
ANTHRACENE	15U	65	48
FLUORANTHENE	190	45	3
PYRENE	190	174	69
BENZ(A)ANTHRACENE	100	168	176
CHRYSENE	210	314	9
BENZO(B)FLUORANTHENE	28	101	12
BENZO(K)FLUORANTHENE	20	96	82
BENZO(A)PYRENE	20	189	51
DIBENZO(A,H)ANTHRACENE	32	BDL	--
BENZO(G,H,I)PERYLENE	15U	BDL	--
INDENO(1,2,3-C,D)PYRENE	15U	BDL	--

U - Constituent searched for but not detected at the indicated level.

Hazardous Waste Land Treatment Demonstrations (EPA 1986). Extremely conservative assumptions were used regarding constituent degradation rates and partitioning coefficients.

Model Description

The model describes a soil column one meter square with depth specified by the user. The column consists of a plow zone or upper treatment zone and a lower treatment zone. The soil environment within the column is made up of four phases: soil grains, pore water, pore air, and pore oil. The waste is applied to the plow zone at loading rates and frequencies specified by the user.

Once applied to the land and mixed into the plow zone, a constituent may be mobilized by three mechanisms: migration between phases, dispersion and advection. Movement between phases is controlled by partitioning coefficients. Three types of partitioning occur in the model: soil/water (Kd), oil/water (Kow), and air/water (Kh). Dispersive transport is caused by molecular diffusion and turbulence within the phase. The water phase and its dissolved constituents are advected at the average soil pore water velocity. This velocity is calculated from the site infiltration (recharge) rate and soil properties such as soil type, porosity and bulk density.

The constituents may be decomposed by biochemical processes which are represented in the model by first-order rate kinetics. Different rate coefficients may be assigned to different phases and to different depths within the soil column.

Model Input Variables

Input parameters used in the modeling scenario reflect both measured values and literature reported values as well as some general assumptions concerning a typical land treatment site. LST residual concentrations of PAH constituents as measured in a laboratory (on a dry-weight basis) study following two months of treatment were used as initial concentrations (Table 3). Only those compounds which were found in detectable concentrations were evaluated in the modeling scenario.

First order rate constants were selected from a review of the literature for complex waste soil studies (Table 3). The lowest reported values were used as input parameters to the RITZE model to assess a worst case land treatment scenario. Table 3 summarizes first order rate constants as measured in a solid phase system using identical waste materials as treated in a liquid/solids system. Due to the rapid loss of parent compound, 2 and some 3-ring PAH compounds could not be characterized. As indicated in Table 3, the laboratory values are one to two orders of magnitude higher than the low range of literature reported values and demonstrates the conservative

TABLE 3

INITIAL CONCENTRATION AND FIRST ORDER DECAY RATE

COMPOUND	INITIAL CONCENTRATION (b) AVG. (ST.DEV.) mg/kg dry wt.	LABORATORY (1) k (per day)	LITERATURE (2) HIGH	LITERATURE (2) LOW	# OBSERVATION
Naphthalene	<20.8	-	0.1107	0.0094	11
Acenaphthylene	<26.6	-	0.0500	0.0089	2
Acenaphthene	<20.8	-	0.0154	0.0072	2
Fluorene	<2.9	-	0.0383	0.0008	16
Phenanthrene	42 (15)	-	>0.1200	0.0004	26
Anthracene	96 (39)	-	0.0870	0.0011	22
Fluoranthene	47 (20)	0.140	0.0470	0.0006	21
Pyrene	183 (90)	-	0.0339	0.0001	24
Benzo(a)anthracene	167 (162)	0.035	0.0130	0.0003	20
Chrysene	413 (19)	0.016	0.0170	0.0001	20
Benzo(b)fluoranthene	156 (29)	0.020	0.0107	0.0006	9
Benzo(k)fluoranthene	141 (66)	0.036	0.0114	0.0006	8
Benzo(a)pyrene	240 (45)	0.212 (a)	0.0496	0.0018	11
Dibenzo(a,h)anthracene	<0.3	0.411 (a)	0.0099	0.0003	5
Benzo(g,h,i)perylene	<0.8	-	0.0165	0.0015	4
Indeno(1,2,3-cd)pyrene	<0.4	-	0.0165	0.0021	7
Oil and Grease	313,000 (17,388)	0.013			

(1) as measured for a complex petroleum waste.
(2) complex waste mixtures only.
(a) zero order kinetics used to estimate rate of loss.
(b) as measured in liquid/solids treatment residuals following two months of treatment.

assumption used in the modeling scenario. Degradation rates were assumed the same in all phases (oil, soil and water) and at all depths in the treatment zone. No degradation was assumed to take place in the unsaturated pore space (air phase). The decay rate of oil was set equal to the laboratory measured oil and grease decay rate (Table 3).

Partitioning coefficient data were selected from a review of the literature as summarized in Table 4 for oil/water and Table 5 for soil/water. Soil/water partitioning is highly correlated to soil organic content. Koc values reported in Table 5 are independent of soil organic carbon. Soil specific partitioning coefficients can be determined by the following equation:

$$Koc * (\text{organic carbon fraction}) = Kd \qquad (1)$$

Specific site information and waste application information used in the model include:

- 5% oil and grease loading to the soil,
- 30% oil content in the waste,
- No water in the waste (allowed to dry prior to tilling),
- Upper treatment zone depth of six inches,
- Lower treatment zone depth of five feet,
- Sandy clay loam soil,
- 20 inches of rainfall per year, and
- Average ambient temperature of 20° C.

It was assumed that the soil did not contain initial concentrations of the constituents. In addition, no air/water partitioning or dispersion were allowed to occur. The waste residuals were applied in one application. Input values for the RITZE model application are summarized in Table 6.

Modeling Results

The RITZE model was used to predict soil and water concentrations as well as mass degraded, remaining and leached following ten years of treatment under the scenario previously described. Because of the extremely low decay rates used in the modeling effort, constituent mass was still present in the treatment zone after 10 years. However, soil and water concentrations at the bottom of the treatment zone were below one part per billion detection. Trace amounts of mass were lost from the system over the 10 year period totalling less than 0.00005% of

TABLE 4

RANGE OF VALUES FOR LOG (Kow) FOR SELECTED PAH COMPOUNDS

COMPOUND	REFERENCE NUMBER 1	2	3	4	RANGE upper	lower
Naphthalene	3.36	3.35	3.29		3.36	3.29
Acenaphthylene						
Acenaphthene		3.92			3.92	3.92
Fluorene		4.18	4.18		4.18	4.18
Phenanthrene	4.57	4.57	4.45	4.46	4.57	4.45
Anthracene	4.54	4.54	4.45	4.45	4.54	4.45
Fluoranthene		5.22	4.90	5.33	5.33	4.90
Pyrene	5.18	5.18	4.90	4.88	5.18	4.88
Benz(a)anthracene						
Chrysene		5.79		5.61	5.79	5.61
Benzo(b)fluoranthene				6.57	6.57	6.57
Benzo(k)fluoranthene				6.84	6.84	6.84
Benz(a)pyrene				6.04	6.04	6.04
Dibenzo(a,h)anthracene				5.97	5.97	5.97
Benzo(g,h,i)perylene		7.10			7.10	7.10
Indeno(1,2,3-cd)pyrene				7.66	7.66	7.66

* All units for partition coefficients are g/m3 / g/m3

REFERENCES:
(1) Karickhoff et al, 1979
(2) Miller et al, 1985
(3) Abdul and Gibson, 1986
(4) Mahmood and Sims, 1986

TABLE 5

RANGE OF VALUES FOR LOG (Koc) FOR SELECTED PAH COMPOUNDS

COMPOUND	REFERENCE NUMBER 1	2	3	4 lower	4 upper	5	6 upper	RANGE 6 lower	upper	lower
Naphthalene	3.11	2.66	3.15	3.11		2.94	3.05	2.97	3.15	2.66
Acenaphthylene										
Acenaphthene			4.11				3.60	6.30	6.30	3.60
Fluorene		3.51					3.86	3.86	3.86	3.51
Phenanthrene	4.36	3.77	4.36	4.36		4.08	4.25	4.13	4.36	3.77
Anthracene	4.41	4.44	4.24			4.20	4.22	4.13	4.44	4.13
Fluoranthene		4.71	5.12				5.01	4.58	5.12	4.58
Pyrene	4.92	4.79	4.67	4.04	5.11	4.83	4.86	4.56	5.11	4.04
Benz(a)anthracene				6.27			5.29	5.29	6.27	5.29
Chrysene			5.40				5.47	5.29	5.47	5.29
Benzo(b)fluoranthene			5.36				6.25	6.25	6.25	5.36
Benzo(k)fluoranthene			5.63				6.52	6.52	6.52	5.63
Benz(a)pyrene			5.83	6.65			5.72	5.72	6.65	5.72
Dibenzo(a,h)anthracene			5.76	5.75	6.49	6.22	5.65	5.65	6.49	5.65
Benzo(g,h,i)perylene							6.78	6.78	6.78	6.78
Indeno(1,2,3-cd)pyrene			6.45				7.34	7.34	7.34	6.45

* All units for partition coefficients are ml/g
** Data from reference 2 was derived from Kd data.
Kd = Koc * (organic carbon fraction)

REFERENCES:

(1) Karickhoff et al, 1979
(2) Abdul and Gibson, 1986 (Flint Sample)
(3) Mahmood and Sims, 1986
(4) API Treatability Data, 1986
(5) Karickhoff, 1981
(6) Calculated from Table 2 using:
log (Koc) = log (Kow) - 0.317 (1,7)
(7) Hassett et al., 1980

TABLE 6

INPUT VALUES FOR RITZE MODEL APPLICATION

SOURCE:	Table 1	Table 1	Table 2	Table 3	
	initial conc.	DECAY		Kd x10^6	
COMPOUND	in residuals ug/g waste	RATE per day	Kow g/m3/g/m3	UTZ(1)	LTZ(2) g/g/g/m3
PHENANTHRENE	42	0.0004	28184	58.9	29.4
ANTHRACENE	96	0.0011	28184	134.9	67.5
FLUORANTHENE	47	0.0006	79433	380.2	190.1
PYRENE	183	0.0001	75858	109.7	54.8
BENZO(a)ANTHRACENE	167	0.0003	407380	1949.8	974.9
CHRYSENE	413	0.0001	407380	1949.8	974.9
BENZO(b)FLUORANTHENE	156	0.0006	3715352	2290.9	1145.4
BENZO(k)FLUORANTHENE	141	0.0006	6918310	4265.8	2132.9
BENZO(a)PYRENE	240	0.0018	1096478	5248.1	2624.0

(1) = upper treatment zone, assuming 1% organic carbon content.
(2) = lower treatment zone, assuming 0.5% organic carbon content.

INPUT VALUES USED FOR ALL COMPOUNDS

FACTOR	UNITS	VALUE
Loading Rate	g residual/100 g soil	16.7
Residual oil content	g/g residual	0.3
Residual water content	g/g residual	0.0
Residual density	g/cc	1.1
Oil density	g/cc	0.9
Soil Porosity	m3/m3	0.4
Bulk Density	g/cc	1.3
Moisture Coefficient		7.12

the mass applied for all compounds except phenanthrene. RITZE modeling results are summarized in Table 7.

Under the conditions of this modeling study, the PAH constituents of concern were successfully treated and Table 4 immobilized. Land treatment can be considered a viable alternative for treatment and ultimate disposal of LST residuals.

CONCLUSIONS

Preliminary research on biological LST has shown that this process (as a pretreatment step) in combination with land treatment can successfully treat petroleum wastes to meet no migration criteria. Current research is being conducted on the treatment of specific, individual K wastes by biological LST. Biological LST is being evaluated as a BDAT option of these wastes. Given the current status of K wastes, it is recommended that biological LST be considered as a pretreatment step for petroleum wastes currently being land farmed.

Acknowledgements

J. R. Coover performed all RITZE modeling. M. R. Coover was responsible for the design and operation of the bench scale reactors. Dean Kinney performed all monitoring and sampling of the reactors.

TABLE 7

RITZE MODELING RESULTS

COMPOUND	CONCENTRATION (a) WATER	SOIL	MASS DEGRADED	MASS LEACHED
Phenanthrene	BDL	BDL	76.8%	0.0002%
Anthracene	BDL	BDL	98.2%	0.0000%
Fluoranthene	BDL	BDL	88.8%	0.0000%
Pyrene	BDL	BDL	30.6%	0.0000%
Benzo(a)anthracene	BDL	BDL	66.6%	0.0000%
Chrysene	BDL	BDL	30.6%	0.0000%
Benzo(b)fluoranthene	BDL	BDL	88.8%	0.0000%
Benzo(k)fluoranthene	BDL	BDL	88.8%	0.0000%
Benzo(a)pyrene	BDL	BDL	99.9%	0.0000%

(a) as predicted at the bottom of the treatment zone (5 feet) following 10 years of treatment.
BDL = below detection limit of 1 ppb.

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THE HAZARDOUS AND SOLID WASTE AMENDMENTS OF 1984

POLICY ON THE MINIMIZATION OF HAZARDOUS WASTE:

"THE CONGRESS HEREBY DECLARES IT TO BE THE NATIONAL POLICY OF THE UNITED STATES THAT, WHEREVER FEASIBLE, THE GENERATION OF HAZARDOUS WASTE IS TO BE REDUCED OR ELIMINATED AS EXPEDITIOUSLY AS POSSIBLE. WASTE THAT IS NEVERTHELESS GENERATED SHOULD BE TREATED, STORED OR DISPOSED OF SO AS TO MINIMIZE THE PRESENT AND FUTURE THREAT TO HUMAN HEALTH AND THE ENVIRONMENT."

- AFTER SEPTEMBER 1, 1985, MANIFESTS MUST CONTAIN A CERTIFICATION THAT WASTE VOLUME OR QUANTITY AND TOXICITY HAS BEEN REDUCED TO THE MAXIMUM DEGREE ECONOMICALLY PRACTICAL;

- AFTER SEPTEMBER 1, 1985, ALL ON-SITE TSD PERMITS MUST REQUIRE GENERATORS TO CERTIFY ANNUALLY TO THE SAME REDUCTIONS AS REQUIRED ON THE MANIFEST

- BIENNIAL REPORTS MUST INDICATE EFFORTS TO REDUCE WASTE VOLUME AND TOXICITY AND DOCUMENT ACTUAL REDUCTION ACHIEVED

- SMALL QUANTITY GENERATORS ARE TO HAVE A "GOOD FAITH EFFORT" FOR MINIMIZATION

WASTE MINIMIZATION

BENEFITS

- LIABILITY REDUCTION
  -- REDUCES THE RISK OF FUTURE LIABILITIES

- COST REDUCTION
  -- REDUCES COSTS OF CURRENT POLLUTANT CONTROL AND COSTS OF FUTURE CLEANUP AND REMEDIATION

- WASTE INVENTORY DEVELOPED
  -- PROVIDES DATABASE FOR MANAGEMENT DECISIONS

- SOCIETAL CONCERN
  -- DEMONSTRATES CORPORATE COMMITMENT TO RESPONSIBLE ENVIRONMENTAL MANAGEMENT

- COMPLIANCE
  -- MEETS REGULATORY COMPLIANCE REQUIREMENTS

- REGULATORY AVOIDANCE
  -- HELPS REDUCE NEED FOR ADDITIONAL FEDERAL AND LOCAL REGULATIONS AND THE COST OF COMPLIANCE

WASTE MINIMIZATION TECHNIQUES

- MATERIAL CHANGE
- PROCESS MODIFICATIONS
- VOLUME REDUCTIONS

WASTE MINIMIZATION

MYTHS

- OPERATOR AWARENESS IS HIGH
- ECONOMICS ALREADY FORCE MINIMUM WASTE PRODUCTION
- PRODUCTION PROCESSES ARE MATURE, THERE IS LITTLE OPPORTUNITY FOR CHANGE
- CURRENT TECHNOLOGICAL KNOWLEDGE IS ADEQUATE FOR SAFE LONG-TERM WASTE MANAGEMENT
- ECONOMICS WILL NOT ALLOW RECAPITALIZATION
- WASTE MINIMIZATION WILL PAY FOR ITSELF OR WILL NOT COST MUCH MONEY

CURRENT WASTE MINIMIZATION INCENTIVES

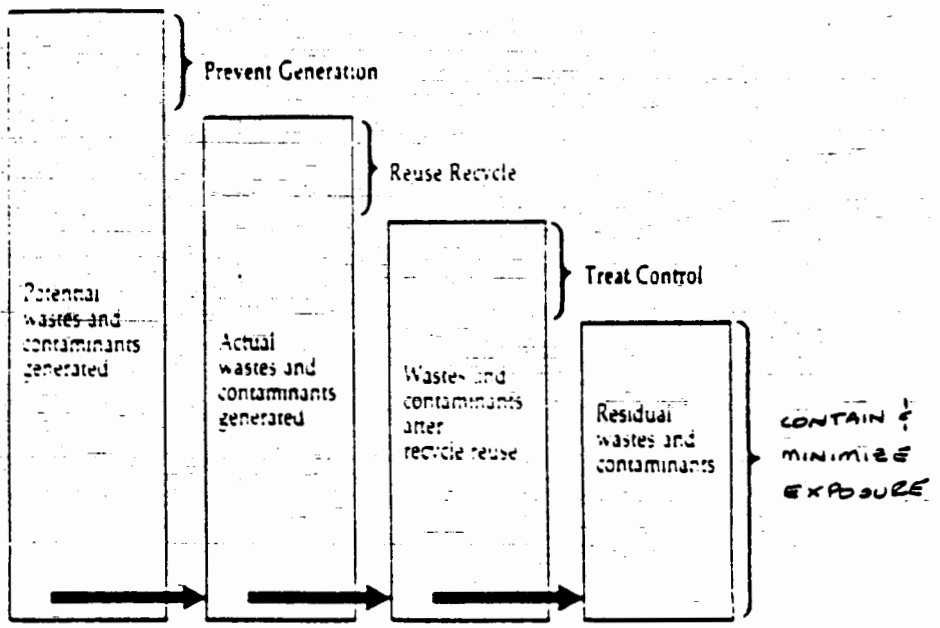
- INCREASED COST OF HAZARDOUS WASTE DISPOSAL (CAUSED IN PART BY FEDERAL AND STATE STANDARDS)
- INCREASED COST AND DECREASED AVAILABILITY OF COMMERICIAL LIABILITY INSURANCE
- PUBLIC PRESSURE
- DIFFICULTIES IN SITING HAZARDOUS WASTE MANAGEMENT FACILITIES

WASTE REDUCTION

Basic Steps

- Conduct waste audit in plant or around specific processes
- Attempt a total materials balance taking into account: (a) the raw materials and other inputs that are used, (b) the products produced, (c) gaseous, liquid and solid wastes generated, and (d) infrequent process operations
- Identify "unaccounted for" losses and attempt to locate the source of such losses from the material balance data
- Identify routine and non-routine leaks and losses
- Evaluate experience at other plants and processes
- Identify regulations related to waste minimization and reduction at the source
- Identify financial incentives for waste reduction, such as tax benefits, reduced liability, reduced treatment and disposal costs, reduced raw material purchases, etc.
- Working with industry, indicate:
  - (a) possibilities for reducing losses, i.e., spill protection plans, gasket replacement maintenance, vapor loss control, etc.
  - (b) possibilities of product or solvent substitution or other process change
  - (c) possibilities for waste separation and recycle and reuse

Hierarchy for Risk Reduction



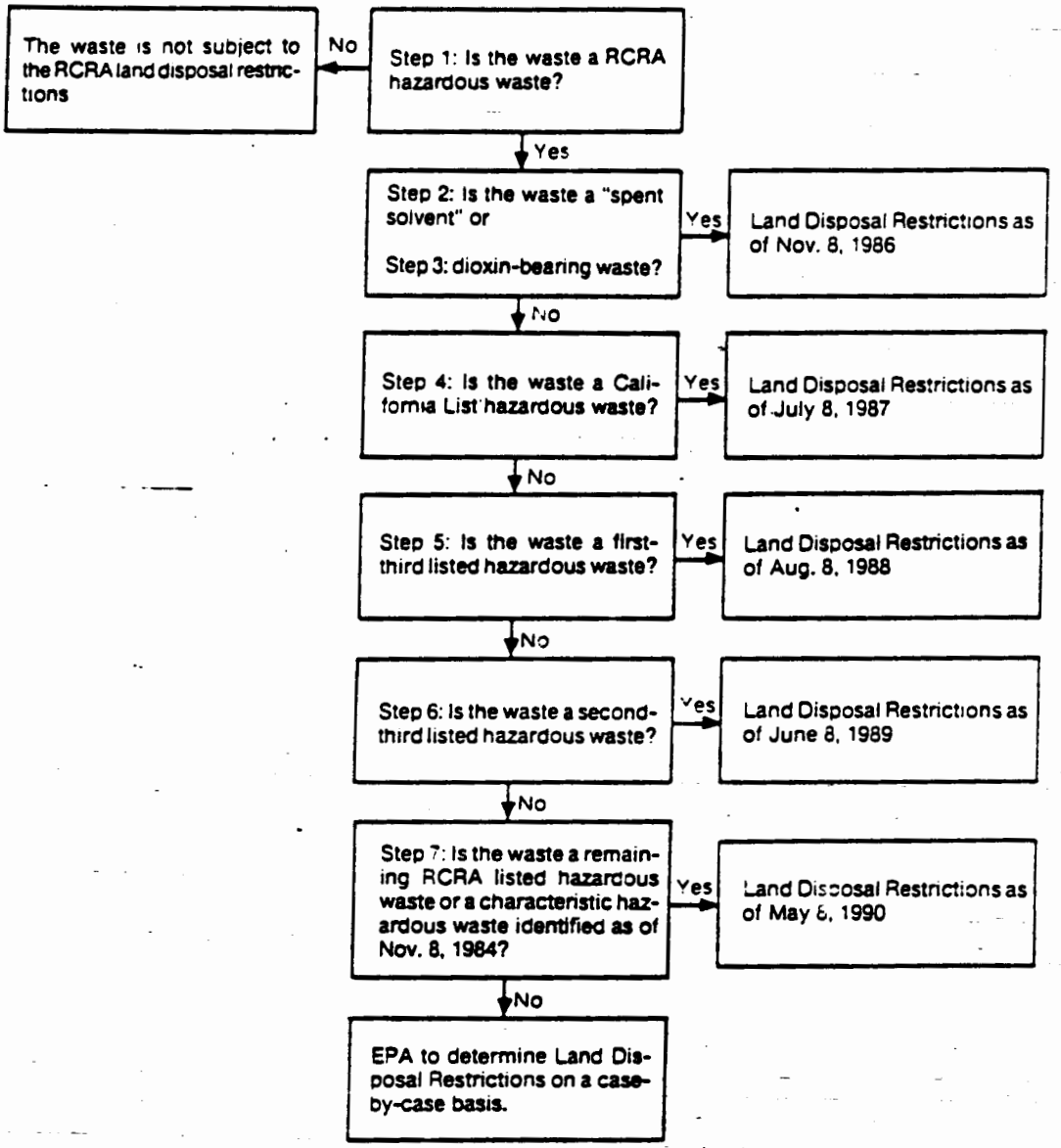
Suggested Steps of a Waste Minimization Assessment

- Prepare background material for the assessment.
- Conduct a preassessment visit to identify candidate waste streams.
- Select waste streams for detailed analysis.
- Conduct a detailed site visit to collect data on selected waste streams and controls and related process data.
- Develop a series of potential waste minimization options.
- Undertake preliminary option evaluations (including development of preliminary cost estimates).
- Rank options by:
  - waste reduction effectiveness;
  - extent of current use in the industry;
  - potential for future application at the facility.
- Present preliminary results to plant personnel along with a ranking of options.
- Prepare a final report, including recommendations to plant management.
- Develop an implementation plan and schedule.
- Conduct periodic reviews and updates of assessments.

Case Study of a Waste Minimization Assessment

In 1986, EPA sponsored a waste minimization assessment at an electric arc furnace steel-making facility. The assessment team examined waste minimization options, including source reduction and resource recovery, for the company's corrosive and heavy metal wastes. The assessment revealed that calcium fluoride (fluorspar) in the sludge generated during neutralization of the pickling line wastewater could be economically recovered. Previously, the company had disposed of the sludge and purchased 1,000 tons of fluorspar per year as flux material for the steel-making process. The waste minimization option identified by the assessment team will save the company $100,000 per year in costs avoided to purchase fluorspar, and a further $70,000 per year because of a 30 percent reduction in the volume of sludge to be disposed of.

Figure 1
RCRA Land Disposal Restrictions Overall Logic Diagram



BEST DEMONSTRATED AVAILABLE TECHNOLOGIES (BDAT)

- EPA IS REQUIRED TO SET "LEVELS OR METHODS OF TREATMENT, IF ANY, WHICH SUBSTANTIALLY DIMINISH THE TOXICITY OF THE WASTE OR SUBSTANTIALLY REDUCE THE LIKELIHOOD OF MIGRATION OF HAZARDOUS CONSTITUENTS FROM THE WASTE SO THAT SHORT AND LONG TERM THREATS TO HUMAN HEALTH AND THE ENVIRONMENT ARE MINIMIZED"

- WASTES THAT MEET SUCH TREATMENT STANDARDS ARE NOT SUBJECT TO THE HAZARDOUS WASTE LAND DISPOSAL PROHIBITIONS

- PERTINENT TECHNOLOGIES ARE THOSE THAT (A) HELP RESULT IN NO MIGRATION AND (B) INDICATE THAT ANY RESIDUES WILL NOT BE HAZARDOUS

- BDAT ESTABLISHED AS PERFORMANCE STANDARDS

- ANY TECHNOLOGY THAT ACHIEVES THE IDENTIFIED STANDARDS IS ACCEPTABLE

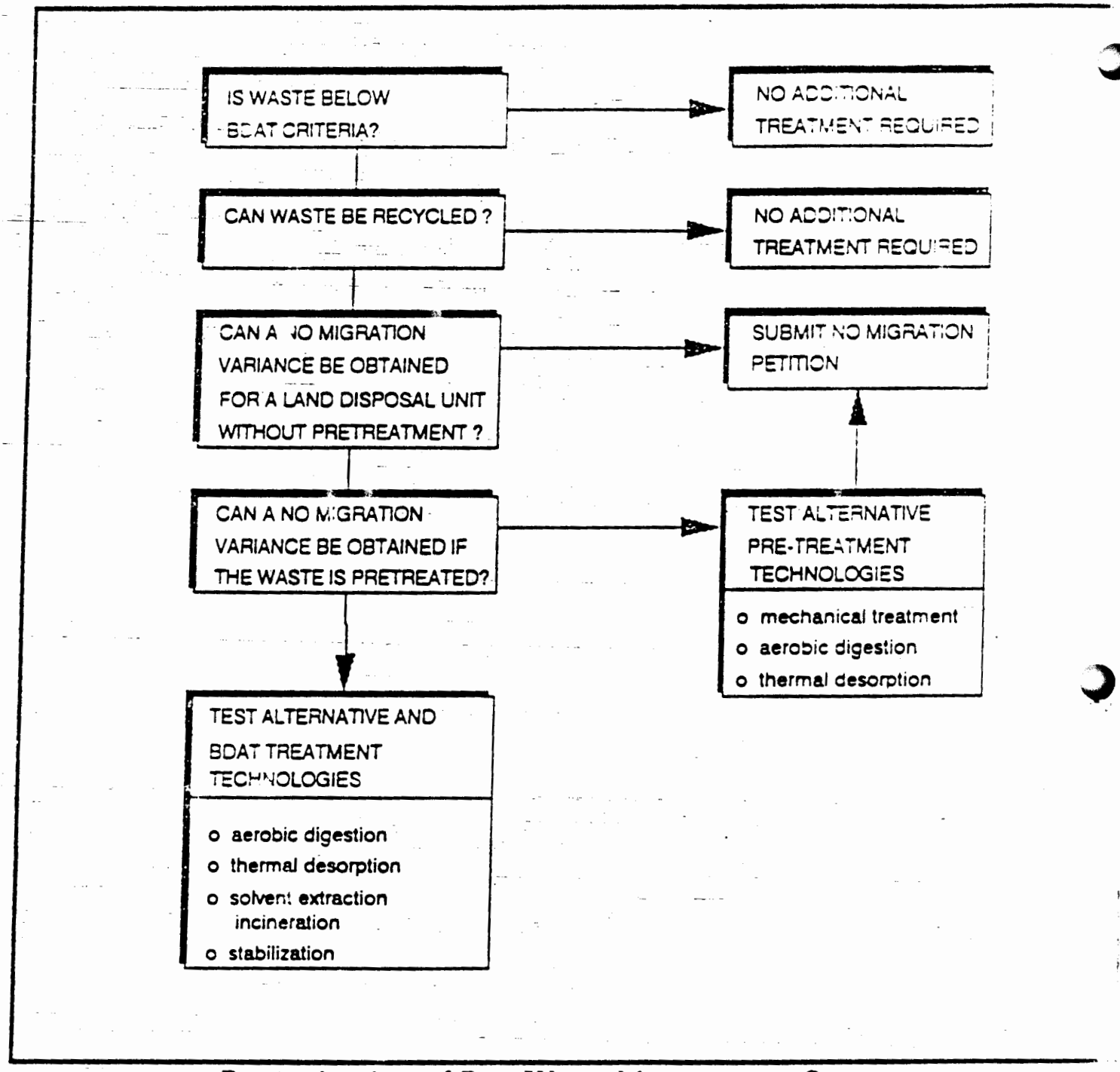
HAZARDOUS WASTES



BDAT PROCESSES



LAND DISPOSAL
(SUBTITLE C)



Determination of Best Waste Management Strategy

BDAT DEFINITIONS

- DEMONSTRATED -- A FULL SCALE FACILITY MUST BE KNOWN TO BE IN OPERATION FOR THE WASTE OR SIMILAR WASTES

- AVAILABLE -- A DEMONSTRATED TECHNOLOGY MUST SUBSTANTIALLY DIMINISH THE TOXICITY OF THE WASTE OR SUBSTANTIALLY REDUCE THE LIKELIHOOD OF MIGRATION OF HAZARDOUS CONSTITUENTS FROM THE WASTE

- SUBSTANTIAL - NO DEFINITIVE DEFINITION - EPA WILL DEFINE INITIAL BDAT PROCESSES. TREATMENT ALWAYS WILL BE DEEMED SUBSTANTIAL IF IT RESULTS IN NONDETECTABLE LEVELS OF THE HAZARDOUS CONSTITUENTS IN THE TCLP EXTRACT

BDAT - DILUTION?

- DILUTION WILL NOT BE ALLOWED AS A METHOD TO COMPLY WITH THE RESTRICTIONS AND STANDARDS
- A GENERIC BAN - APPLIES TO ALL MEDIA - ATMOSPHERE, WATER AND SOIL
- AN ACTIVE TREATMENT PROCESS IS REQUIRED

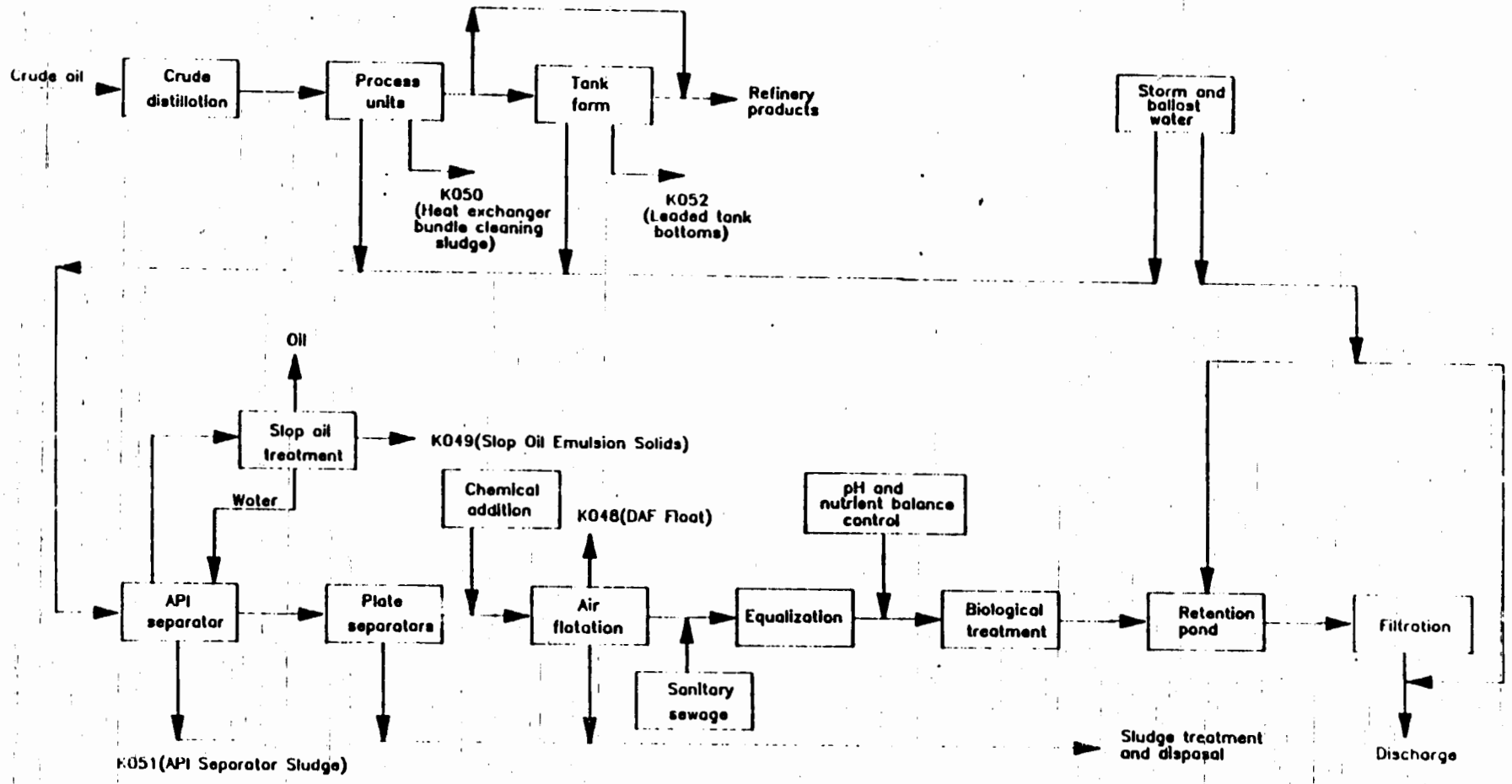


Figure 2-2

Generation of K048, K049, K050, K051 and K052

FINAL TREATMENT STANDARDS FOR FIRST-THIRD WASTES

Hazardous waste description	Constituents of concern	Nonwastewater: Total composition, mg/kg	Nonwastewater: TCLP, mg/L	Wastewater: total composition, mg/L	Effective date
K048 – Dissolved air flotation (DAF) float from the petroleum refining industry	Benzene	9.5	—	0.011	8/8/90
	Benzo(a)pyrene	0.84	—	0.047	
	Chrysene	2.2	—	0.043	
	Cyanides (total)	1.8	—	—	
	Di-n-butyl phthalate	4.2	—	0.060	
	Ethylbenzene	67	—	0.011	
	bis(2-Ethylhexyl) phthalate	37	—	0.043	
	Fluorene	—	—	0.050	
	Naphthalene	—	—	0.033	
	Phenanthrene	7.7	—	0.039	
	Phenol	2.7	—	0.047	
	Pyrene	2.0	—	0.045	
	Toluene	9.5	—	0.011	
	Xylenes	—	—	0.011	
	Arsenic	—	0.004	—	
	Chromium (total)	—	1.7	0.20	
	Lead	—	—	0.37	
	Nickel	—	0.048	—	
	Selenium	—	0.025	—	
K049 – Slop oil emulsion solids from the petroleum refining industry	Anthracene	6.2	—	0.039	8/8/90
	Benzene	9.5	—	0.011	
	Benzo(a)pyrene	0.8-	—	0.047	
	Carbon disulfide	—	—	0.011	
	Chrysene	2.2	—	0.043	
	Cyanides (total)	1.8	—	—	
	2,4-Dimethyl phenol	—	—	0.033	
	Ethylbenzene	67	—	0.011	
	bis(2-Ethylhexyl) phthalate	37	—	0.043	
	Naphthalene	—	—	0.033	
	Phenanthrene	7.7	—	0.039	
	Phenol	2.7	—	0.047	
	Pyrene	2.0	—	0.045	
	Toluene	9.5	—	0.011	
	Xylenes	—	—	0.011	
	Arsenic	—	0.004	—	
	Chromium (total)	—	1.7	0.20	
	Lead	—	—	0.037	
	Nickel	—	0.048	—	
	Selenium	—	0.025	—	

FINAL TREATMENT STANDARDS FOR FIRST-THIRD WASTES

Hazardous waste description	Constituents of concern	Nonwastewater: Total composition, mg/kg	Nonwastewater: TCLP, mg/L	Wastewater: total composition, mg/L	Effective date
K050 — Heat exchanger bundle cleaning sludge from the petroleum refining industry	Benzo(a)pyrene	0.84	—	0.047	8/8/90
	Cyanides (total)	1.8	—	—	
	Phenol	2.7	—	0.047	
	Arsenic	—	0.004	—	
	Chromium (total)	—	1.7	0.20	
	Lead	—	—	0.037	
	Nickel	—	0.048	—	
	Selenium	—	0.025	—	
K051 — API separator sludge from the petroleum refining industry	Acenaphthene	—	—	0.050	8/8/90
	Anthracene	6.2	—	0.039	
	Benzene	9.5	—	0.011	
	Benzo(a)anthracene	1.4	—	0.043	
	Benzo(a)pyrene	0.84	—	0.047	
	Chrysene	2.2	—	0.043	
	Cyanides (total)	1.8	—	—	
	Di-n-butyl phthalate	4.2	—	0.060	
	Ethylbenzene	67	—	0.011	
	bis(2-Ethylhexyl) phthalate	37	—	0.043	
	Fluorene	—	—	0.050	
	Naphthalene	—	—	0.033	
	Phenanthrene	7.7	—	0.039	
	Phenol	2.7	—	0.047	
	Pyrene	2.0	—	0.045	
	Toluene	9.5	—	0.011	
	Xylenes	—	—	0.011	
	Arsenic	—	0.004	—	
	Chromium (total)	—	1.7	0.20	
	Lead	—	—	0.037	
	Nickel	—	0.048	—	
	Selenium	—	0.025	—	
K052 — Total bottoms (leaded) from the petroleum refining industry	Benzene	9.5	—	0.011	8/8/90
	Benzo(a)pyrene	0.84	—	0.047	
	o-Cresol	2.2	—	0.011	
	p-Cresol	0.90	—	0.011	
	Cyanides (total)	1.8	—	—	
	2,4-Dimethyl phenol	—	—	0.033	
	Ethylbenzene	67	—	0.011	
	Naphthalene	—	—	0.033	
	Phenanthrene	7.7	—	0.039	
	Phenol	2.7	—	0.047	
	Toluene	9.5	—	0.011	
	Xylenes	—	—	0.011	

CLOSURE OPTIONS

- REMOVAL OF CONTAMINATED SOIL
- COVER SITE - VEGETATIVE COVER OR CLAY OR SYNTHETIC CAP
- NO ACTION -- CONTINUED MONITORING
- CONTINUED TREATMENT WITH AMENDMENTS AS REQUIRED
- COMBINATION OF THE ABOVE

NO MIGRATION PETITIONS

What is a No-Migration Variance?

A no-migration variance is a decision that can be rendered by EPA to allow the land disposal, at a particular facility, of specific, prohibited wastes not meeting the treatment (BDAT) standards established by EPA for those wastes. Anyone that desires a no-migration variance must demonstrate "to a reasonable degree of certainty that there will be no migration of hazardous constituents from the disposal unit or injection zone for as long as the waste remains hazardous." Generally, the term "to a reasonable degree of certainty" is interpreted to mean that hazardous constituents applied to a land disposal unit will not exceed human health-based or environmentally protective levels beyond the edge of the disposal unit. In most cases, the disposal unit is defined as the limit of the engineered components. Both interpretations may be defined differently in some site-specific cases. This definition of no migration does not allow for fate and transport of hazardous constituents above acceptable levels outside the boundary of the unit.

Why are No-Migration Variances Needed?

The Hazardous and Solid Waste Amendments of 1984 (HSWA) prohibits the land disposal of all listed and characteristic hazardous wastes unless they are treated. Wastes included in the EPA's land disposal prohibitions will have to be treated by best demonstrated available technology (BDAT) or to equivalent levels to meet the treatment standard established by the EPA, unless a no-migration variance is obtained. Prohibited wastes cannot be stored on the land (unless storage is for the purpose of accumulating sufficient quantities to facilitate proper recovery, treatment or disposal) without a no-migration variance. The land disposal prohibitions become effective at varying dates over the period of 1986 through 1990. With only a few exceptions, all

untreated RCRA hazardous wastes will be banned from land disposal unless a no-migration variance is received from the EPA.

What is the Procedure to Obtain a No-Migration Variance?

Owners or operators of land disposal unit should submit no-migration petitions directly to EPA, Washington, D.C. Prior to preparing a petition, petitioners are strongly encouraged to participate in meetings with EPA personnel to determine the nature and extent of information that must be included in the site-specific petition.

Petitions received by EPA are reviewed to determine if they are complete. If the petition is incomplete, EPA may either dismiss the petition or request additional information which must be provided before further review of the petition occurs. If the additional information is not submitted in a timely manner or is not sufficient, EPA will dismiss the petition.

Complete petitions will be subjected to an in-depth technical review to determine if a variance should be issued. The petitioner will be notified if EPA intends to deny the variance and given the opportunity to withdraw the petition. Unless the petition has been withdrawn or dismissed, the decision to either issue or deny a variance will be noticed in the Federal Register and public comments on that decision will be accepted for 30 days after the notice date. At the end of the public comment period, the EPA will make a final determination on variance issuance and publish its decision in the Federal Register.

Who Should be Contacted in EPA?

Specific information on no-migration variances, including the information that is required in the no-migration demonstration and the level of detail appropriate for the petition can be obtained from:

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Solid Wastes
Permits and State Programs Division
401 M Street, S.W.
Washington, D.C. 20460

The current telephone number of the Division can be obtained by calling the EPA-RCRA Hotline, 800-424-9346.

Can No-Migration Variances be Obtained for Land Treatment Units?

Land treatment units are subject to all of the general provisions of the land disposal restrictions program, since they are considered to be disposal units under RCRA. To apply restricted wastes which do not meet the BDAT performance standards, an owner or operator of a land treatment unit must apply for a no-migration variance.

The petition must demonstrate that the no-migration standard is met for all media. Many wastes that are currently land-treated contain significant amounts of organic constituents and/or metals. Therefore, the petition must demonstrate a sufficient level of degradation and/or immobilization of waste constituents and metals within the treatment zone. For the volatile constituents, the applicant must demonstrate that the health-based or environmental are not exceeded by air emissions.

How Can Air Emission Requirements be Met?

Such a demonstration can be made by using site-verified emission models, emission monitoring and/or ambient air monitoring. Another means of meeting no migration requirements for air emissions is to remove the volatile constituents from the waste prior to land treatment. A variety of processes are capable of reducing volatile constituents to extremely low concentrations. These processes include solvent extraction, thermal treatment, composting and biological liquid/solids treatment. Although these process represent an additional compliance cost, they can

represent significant cost savings over meeting BDAT performance standards.

What Information Should be Included in a Petition?

No-migration petitions will vary considerably. The petition content will be strongly influenced by the type of facility for which a variance is sought and the methods chosen to demonstrate that the facility will adequately protect human health and the environment. The petition must provide site-specific information as well as generic and national information for certain requirements. The specific level of detail required for each petition can be identified by individuals and organizations familiar with such petitions and in pre-petition conferences between EPA and land disposal owners and operators and/or their consultants.

The type of information needed includes the following:

- waste descriptions
- waste types and sources
- waste characteristics
- waste incompatibilities
- transformation and immobilization mechanisms
- facility description
- background environmental quality
- waste mobility modeling
- environmental impacts
- site characterization
- geology
- ground-water hydrology
- surface-water hydrology
- climatology
- meteorology
- monitoring plan
- compliance with federal, state and local laws
- consideration of infrequent events
- quality assurance and control

For land treatment units, the information included in a land treatment demonstration and in a Part B permit application should include most, if not all, of the technical information needed for

a no-migration petition. Some additional information and predictive modeling results, particularly for air emissions, may be needed for specific sites.

A successful petition must meet the following criteria which form the basis of the EPA evaluation:

(1) Waste and environmental sampling, testing and analysis data are accurate and reproducible;

(2) Sampling, testing and estimation methods for determining chemical and physical properties of wastes and environmental parameters are explained;

(3) Simulation models used in the demonstration must be calibrated for specific waste and site conditions;

(4) A quality assurance and quality control plan must be submitted that addresses all aspects of the demonstration; and

(5) An analysis must be performed to identify and quantify any aspects of the demonstration that contribute significantly to uncertainty.

The petition also must verify that the petitioner is familiar with all information in the petition and that the data and information is true, accurate and complete to the extent possible.

for measuring emissions and the data evaluation procedures used to establish "no migration".

ReTeC has the experience with: (a) land disposal processes, particularly with land treatment design and operation, (b) pre-treatment processes to remove volatiles from wastes and residues, (c) contaminated soil bioremediation processes, and (d) permitting requirements and other legal and regulatory issues. ReTeC can help land disposal owners and operators develop and submit no-migration petitions.

For further information, contact any ReTeC office or Mr. John R. Ryan at 22419 72nd Avenue, South, Kent, WA, 98032, (206) 872-0247

CLEAN UP GOALS AT CERCLA SITES

I. SOIL CLEAN UP GOALS AT CERCLA SITES

A. Soil clean up goals must generally satisfy two criteria. First, the concentrations of chemicals in soil must be set at levels which protect people from direct contact exposure, which includes:

- o ingestion
- o dermal contact
- o inhalation of gaseous constituents volatilized from the soil
- o inhalation of fugitive dust

B. The concentrations of chemicals in soil must be kept at levels which protect groundwater supplies from excessive leaching. TCLP can be useful in evaluating the acceptability of different levels of residual contamination with respect to leachability. If TCLP data are not available, the potential for leaching can be evaluated from the equilibrium partitioning of chemicals between soil water and soil organic carbon.

The next two subsections review clean up goals for PAHs and PCP in soil. Each subsection is divided into three parts. The first part reviews clean up goals of action levels published in Superfund RODs. The second part presents a range of clean up goals based on potential direct contact exposures to soils. The third part presents the results of TCLP tests on soils.

II. CLEAN UP GOALS FOR PAHs IN SOIL AT CERCLA SITES

A. Superfund RODs

- o CDC stated that 100 ppm total carcinogenic PAHs in soil should not pose a risk exceeding the 10^{-6} level; suggested a limit of 100 ppm total PAH as an action level.
- o Other RODs use 5-100 ppm total carcinogenic PAH.

B. Levels Based on Direct Contact Exposure

Method

- ingestion of soil
- dermal contact
- inhalation of fugitive dust
- inhalation of volatiles

Typical Values

- ingestion of soil
  range: 25, 50, 100, 250, 480 mg/day
- dermal contact (equivalent soil ingestion rates)
  range: 1.0, 8.5, 10, 40, 165 mg/day
- fugitive dust
  ambient dust concentration 70 ug/m^3, 75% respirable and 50% from outside soil
- volatiles
  depends on chemical
- exposure 5 days/wk, 50 wks/yr for 40 years

Risk Based Values for Potential Carcinogenic PAHs

1. ingestion: 25 mg/day
   dermal: 8.5 mg/day
   BaP
   w/ soil deg 17 ppm @ 10^{-6}
   w/o soil deg .9 ppm @ 10^{-6}

2. ingestion: 50 mg/day
   dermal: 40 mg/day
   BaP
   w/soil deg 6. ppm @ 1^{-6}
   w/o soil deg 3. ppm @ 10^{-6}

3. ingestion 100 mg/day
   dermal: 40 mg/day
   BaP
   w/soil deg 4 ppm @ 10^{-6}
   w/o soil deg .2 ppm @ 10^{-6}

Risk based Values for Potential Non-Carcinogenic PAHs
mg/kg in soil

	1	2	3
Naphthalene	7340.	7220.	7120.
Acenaphthylene	190.	187.	184.
Acenaphthene	985.	900.	835.
Fluorene	1250.	1120.	1020.
Phenanthrene	1330.	1180.	1070.
Anthracene	550.	525.	500.
Fluoranthene	7140.	4235.	3110.
Pyrene	7670.	4410.	3210.
Benzo(k)fluoranthene	9250.	4900.	3460.
Benzo(g,h,i)perylene	17100.	6470.	4200.

1 ingestion: 25 mg/day
dermal: 8.5 mg/day

2 ingestion: 50 mg/day
dermal: 40 mg/day

3 ingestion: 100 mg/day
dermal: 40 mg/day

C. Levels Based on Leachate

Sample	O&G Soil	Naphthalene Soil	Naphthalene Water	Non Carc PAHs Soil	Non Carc PAHs Water	Pot Carc PAHs	
1	BDL	BDL	BDL	.2	BDL	BDL	BDL
2	160	BDL	BDL	.4	BDL	BDL	BDL
3	300	BDL	BDL	25.0	10	10	BDL
4	630	BDL	BDL	9.0	BDL	6	BDL
5	1,250	BDL	11	18.0	BDL	9	BDL
6	3,000	BDL	BDL	160.0	3	72	BDL
7	5,300	BDL	BDL	210.0	0.2	75	BDL
8	12,900	200	255	1,000.0	71	100	BDL
9	17,500	170	BDL	3,000.0	17	620	BDL
10	20,400	180	BDL	3,900.0	36	680	BDL
11	43,300	170	BDL	14,300.0	25	2,900	BDL
12	46,700	130	BDL	8,700.0	1	2,000	0.02
13	55,700	3,000	32	21,000.0	100	1,200	BDL
14	73,600	5,400	8	30,100.0	BDL	1,400	BDL
15	92,400	5,700	1042	35,300.0	56	1,500	0.01
	(mg/kg)	(mg/kg)	(mg/l)	(mg/kg)	(mg/l)	(mg/kg)	(mg/l)

III. CLEAN UP GOALS FOR PCP IN SOIL

A. Superfund RODs

- CDC stated that 150 ppm in soil should be acceptable.
- Other RODs use a value of 10 ppm.

B. Levels Based on Direct Contact Exposure

For the routes previously described, the allowable concentration is greater than 1,000 mg/kg.

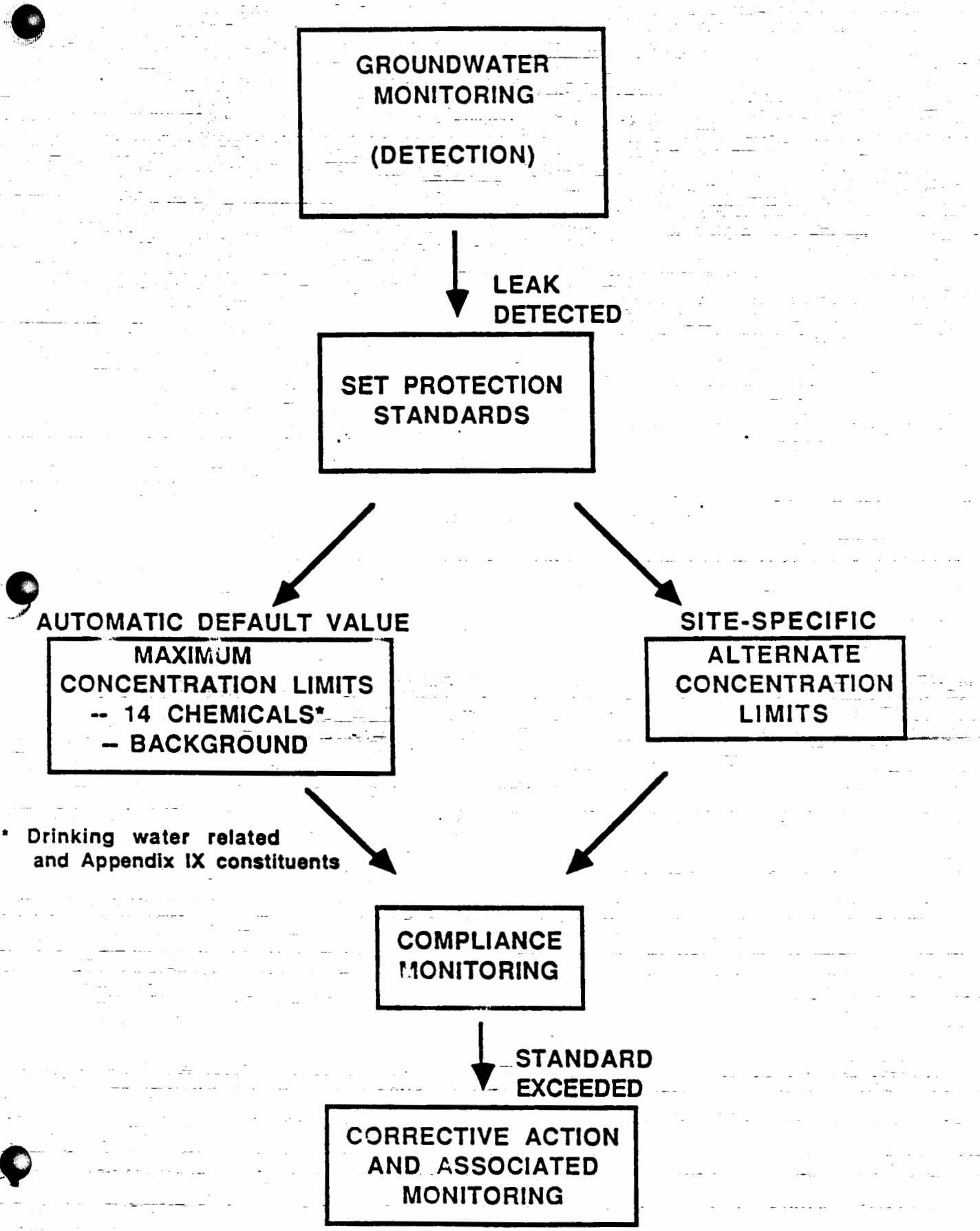
ingestion (mg/day)	25	50	100
dermal (mg/day)	8.5	40	40
PCP (mg/kg)	50,000	25,000	17,800

C. Levels Based on Leachate

To evaluate leachability we should look at results of TCLP.

Sample	Org Soil	PCP Soil	PCP Water
1	BDL	BDL	BDL
2	160	BDL	BDL
3	300	.3	.005
4	630	.1	BDL
5	1,250	.1	BDL
6	3,000	2.0	BDL
7	5,300	1.0	BDL
8	12,900	190.0	.096
9	17,500	190.0	.168
10	20,400	3.0	BDL
11	43,300	14.0	BDL
12	46,700	24.0	BDL
13	55,700	220.0	.054
14	73,600	270.0	.038
15	92,400	240.0	.029
	(mg/kg)	(mg/kg)	(mg/l)

RCRA GROUNDWATER PROTECTION PROCESS



GROUNDWATER MONITORING REQUIREMENTS

BACKGROUND

On July 26, 1982, EPA promulgated RCRA regulations that implemented a strategy for groundwater protection for land-based hazardous waste management units operating under RCRA permits. Once groundwater contamination is suspected, the strategy requires an analysis to determine the nature of the contamination. This information is used to assess the problem, determine the appropriate remedy, determine when the remedy is effective, and insure that no new problems arise during the time the remedy is being applied. In an attempt to be totally comprehensive, the initial regulations provided that contaminated groundwater be analyzed for all constituents contained in Appendix VIII to Part 261.

That decision has been changed. While appropriate for hazardous waste listing purposes, the Appendix VIII list has presented a host of problems when used for purposes of groundwater monitoring. These include practical analytical problems such as listings which are large categories of chemicals, the dissociation or actual decomposition of many Appendix VIII constituents when placed in water, and the lack of analytical standards or suitable analytical methods for many constituents.

EPA had been aware of potential analytical problems with Appendix VIII analyses, although the magnitude of the difficulties was not apparent until the analyses were actually attempted. At the time of promulgation of the 1982 regulations, EPA acknowledged that it lacked analytical methods for several of the Appendix VIII constituents. When owners and operators of hazardous waste facilities began to attempt Appendix VIII analyses, EPA learned that such analyses would be extremely difficult or impossible for a large number of constituents.

EPA took several actions to mitigate the problems. For example, EPA recommended the use of enforcement discretion for some of the most intractable problems that had been identified. In 1984, EPA proposed to eliminate 22 Appendix VIII constituents from the groundwater analysis requirements. (49 FR 38786 (October 1, 1984).

Now, based on the evaluation of the analytical and other problems with the use of Appendix VIII constituents for groundwater monitoring, EPA has replaced the use of Appendix VIII for this purpose with a different list of over 200 specific chemicals. This list was proposed as Appendix IX to Part 264 (51 FR 26632-26642, July 24, 1986).

EPA received comments about the proposed Appendix IX and the proposed changes to the groundwater monitoring requirements until September 1986, after which the comments and other pertinent information were carefully considered before promulgating the final regulations. These changes became final on July 9, 1987 (52 FR 25942-25953).

The final rule replaced the existing requirements to analyze for all Appendix VIII constituents with new requirements to analyze for a specific core list of chemicals plus those chemicals specified by the Regional Administrator on a site-specific basis. This list is required only for groundwater monitoring at RCRA land-based hazardous waste treatment, storage and disposal facilities.

CURRENT REQUIREMENTS

Regulations in Parts 264 and 270 establish a progressive sequence of groundwater monitoring requirements for land-based hazardous waste treatment storage, or disposal facilities. At specified points in the sequence, the owner or operator of any facility known or suspected to be leaking must analyze groundwater for all Appendix IX constituents to determine the nature and extent of the contamination.

Where no groundwater contamination has been detected prior to permit issuance, the operating standards of Subpart F of Part 264 require the owner/operator to sample for selected indicator parameters under a detection monitoring program. If the owner/operator observes an increase in any indicator parameter, he must analyze immediately for all hazardous constituents listed in Appendix IX. 40 CFR 264.98(h)(2). The EPA Regional Administrator will then set "groundwater protection standards" based on the hazardous constituents found in this analysis. 40 CFR 264.92, 264.93, 264.99(a). The owner/operator must change to a compliance monitoring program focused on measuring increases in constituents for which groundwater protection standards were set. A separate provision in the compliance monitoring program, however, also requires the owner/operator to sample each monitoring well annually for all constituents on the Appendix IX list. 40 CFR 264.99(f). The purpose of this annual scan is to allow EPA to consider setting additional groundwater protection standards for any new hazardous constituents found. Finally, if the level of a constituent exceeds a groundwater protection standard, the owner or operator must undertake corrective action. 40 CFR 264.100.

The third requirement for a complete Appendix IX scan appears in the permit application requirements. If a plume of contamination has entered groundwater prior to permit issuance, the permit application rules for land-based hazardous waste units require the owner or operator to conduct a full scan for "each" Appendix IX constituent. 40 CFR 270.124(c)(4). If the scan detects hazardous constituents, the owner or operator must submit all data needed to establish a compliance monitoring or corrective action program. 40 CFR 270.14(c)(7), (c)(8).

APPENDIX LIST

A copy of the final Appendix IX is attached. The final list differs slightly from the proposed list. Based on the comments received on the proposed list and additional detailed evaluation, a few compounds were added and a number of chemicals were removed from the proposed list. In making the changes, the fundamental concern of EPA was that all constituents on the list be readily amenable to EPA standard analytical methods for screening, i.e., methods to determine whether hazardous constituents are present in groundwater samples containing unknown amounts of unidentified chemicals.

In the final Appendix IX, two columns of helpful information have been added. The fourth column identifies suggested analytical methods for the chemical. The methods are from "Testing Methods for Evaluating Solid Waste" (SW-846). This document (SW-846) is the general RCRA analytical methods manual. EPA notes that the suggested list of SW-846 methods is not part of the regulations and EPA is not requiring the use of these methods for Appendix IX analyses. The noted methods are only suggestions.

The last column in Appendix IX contains estimates of a practical quantitation limit (pql) for the particular constituent by a method. The pql is defined in SW-846 and is EPA's current best estimate of the practical sensitivity of the applicable method for RCRA

groundwater monitoring purposes. The pql column is included for guidance purposes only.

The intent of the fourth and fifth columns is to assist laboratories in performing the necessary analyses.

Appendix IX is to be a "living" list and may change over time with the development and standardization of new analytical methods. Therefore, it is possible that there will be revisions to the current Appendix IX. Such revisions will be announced in the Federal Register.

PART 264—AMENDED

1. The authority citation for Part 264 is revised to read as follows:

Authority: Secs. 1008, 2002(a), 3001, 3004, and 3005 of the Solid Waste Disposal Act, as amended, 42 U.S.C. 6905, 6912(a), 6924 and 6925.

2. Section 264.98 is amended by revising paragraphs (h)(2), (h)(3) introductory text and (h)(4)(i) introductory text to read as follows:

§ 264.98 Detection monitoring program.

* * * * *

(h) * * *

(2) Immediately sample the ground water in all monitoring wells and determine whether constituents identified in the list in Appendix IX of Part 264 are present and, if so, at what concentration.

* * * * *

(3) Establish a background value for each constituent that has been found at the compliance point under paragraph (h)(2) of this section, as follows:

* * * * *

(4) * * *

(i) An identification of the concentration of each constituent found in the ground water at each monitoring well at the compliance point:

* * * * *

3. Section 264.99 is amended by revising paragraph (f) to read as follows:

§ 264.99 Compliance monitoring program.

* * * * *

(f) The owner or operator must analyze samples from all monitoring wells at the compliance point to determine whether constituents identified in the list in Appendix IX to Part 264 of this chapter are present and, if so, at what concentration. The analysis must be conducted at least annually to determine whether additional Appendix IX constituents are present in the uppermost aquifer. If the owner or operator finds constituents from Appendix IX in the ground water that are not already identified in the permit as monitoring constituents, the owner or operator must report the concentration of these additional constituents to the Regional Administrator within seven days after completion of the analysis.

* * * * *

Appendix VII and VIII [Reserved]

4. A new Appendix VII and Appendix VIII are added to Part 264 and reserved as follows:

Appendix VII (reserved)
Appendix VIII (reserved)

5. A new Appendix IX is added to Part 264 as follows:

APPENDIX IX—GROUND-WATER MONITORING LIST [1]

Common name [2]	CAS RN [3]	Chemical abstracts service index name [4]	Suggested methods [5]	(µg/L)
Acenaphthene	83-32-9	Acenaphthylene, 1,2-dihydro-	8100	200
			8270	10
Acenaphthylene	208-96-8	Acenaphthylene	8100	200
			8270	10
Acetone	67-64-1	2-Propanone	8240	100
Acetophenone	98-86-2	Ethanone, 1-phenyl-	8270	10
Acetonitrile; Methyl cyanide	75-05-8	Acetonitrile	8015	100
2-Acetylaminofluorene; 2-AAF	53-96-3	Acetamide, N-9H-fluoren-2-yl-	8270	10
Acrolein	107-02-8	2-Propenal	8030	5
			8240	5
Acrylonitrile	107-13-1	2-Propenenitrile	8030	5
			8240	5
Aldrin	309-00-2	1,4:5,8-Dimethanonaphthalene, 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro- (1α,4α,4aβ,5α,8α,8aβ)-	8080	0.05
			8270	10
Allyl chloride	107-05-1	1-Propene, 3-chloro-	8010	5
			8240	100
4-Aminobiphenyl	92-67-1	[1,1'-Biphenyl]-4-amine	8270	10
Aniline	62-53-3	Benzenamine	8270	10
Anthracene	120-12-7	Anthracene	8100	200
			8270	10
Antimony	(Total)	Antimony	6010	300
			7040	2,000
			7041	30
Aramite	140-57-8	Sulfurous acid, 2-chloroethyl 2-[4-(1,1-dimethylethyl)phenoxy]-1-methylethyl ester	8270	10
Arsenic	(Total)	Arsenic	6010	500
			7060	10
			7061	20
Barium	(Total)	Barium	6010	20
			7080	1,000
Benzene	71-43-2	Benzene	8020	5
			8240	
Benzo[a]anthracene; Benzanthracene	56-55-3	Benz[a]anthracene	8100	200
			8270	10
Benzo[b]fluoranthene	205-99-2	Benz[e]acephenanthrylene	8100	200
			8270	10
Benzo[k]fluoranthene	207-08-9	Benzo[k]fluoranthene	8100	200
			8270	10
Benzo[ghi]perylene	191-24-2	Benzo[ghi]perylene	8100	200
			8270	10
Benzo[a]pyrene	50-32-8	Benzo[a]pyrene	8100	200
			8270	10
Benzyl alcohol	100-51-6	Benzenemethanol	8270	20
Beryllium	(Total)	Beryllium	6010	3
			7090	50
			7091	2
alpha-BHC	319-84-6	Cyclohexane, 1,2,3,4,5,6-hexachloro-,(1α,2α,3β,4α,5β,6β)-	8080	0.05
			8250	10
beta-BHC	319-85-7	Cyclohexane, 1,2,3,4,5,6-hexachloro-,(1α,2β,3α,4β,5α,6β)-	8080	0.05
			8250	40
delta-BHC	319-86-8	Cyclohexane, 1,2,3,4,5,6-hexachloro-,(1α,2α,3α,4β,5β,6β)-	8080	0.05
			8250	30
gamma-BHC; Lindane	58-89-9	Cyclohexane, 1,2,3,4,5,6-hexachloro-,(1α,2α,3β,4α,5α,6β)-	8080	0.05
			8250	10
Bis(2-chloroethoxy)methane	111-91-1	Ethane, 1,1'-[methylenebis (oxy)]bis[2-chloro-	8270	10
Bis(2-chloroethyl)ether	111-44-4	Ethane, 1,1'-oxybis[2-chloro-	8270	10
Bis(2-chloro-1-methylethyl) ether; 2,2'-Dichlorodiisopropyl ether	108-60-1	Propane, 2,2'-oxybis[1-chloro-	8010	100
			8270	10
Bis(2-ethylhexyl) phthalate	117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl)ester	8060	20
			8270	10
Bromodichloromethane	75-27-4	Methane, bromodichloro-	8010	1
			8240	5
Bromoform; Tribromomethane	75-25-2	Methane, tribromo-	8010	2
			8240	5

APPENDIX IX—GROUND-WATER MONITORING LIST [1]—Continued

Common name [2]	CAS RN [3]	Chemical abstracts service index name [4]	Suggested methods [5]	PQL (µg/L) [6]
4-Bromophenyl phenyl ether	101-55-3	Benzene, 1-bromo-4-phenoxy-	8270	10
Butyl benzyl phthalate; Benzyl butyl phthalate	85-68-7	1,2-Benzenedicarboxylic acid, butyl phenylmethyl ester	8060	5
			8270	10
Cadmium	(Total)	Cadmium	6010	40
			7130	50
			7131	1
Carbon disulfide	75-15-0	Carbon disulfide	8240	5
Carbon tetrachloride	56-23-5	Methane, tetrachloro-	8010	1
			8240	5
Chlordane	57-74-9	4,7-Methano-1H-indene, 1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-	8080	0.1
			8250	10
p-Chloroaniline	106-47-8	Benzenamine, 4-chloro-	8270	20
Chlorobenzene	108-90-7	Benzene, chloro-	8010	2
			8020	2
			8240	5
Chlorobenzilate	510-15-6	Benzeneacetic acid, 4-chloro-α-(4-chlorophenyl)-α-hydroxy-, ethyl ester	8270	10
p-Chloro-m-cresol	59-50-7	Phenol, 4-chloro-3-methyl-	8040	5
			8270	20
Chloroethane; Ethyl chloride	75-00-3	Ethane, chloro-	8010	5
			8240	10
Chloroform	67-66-3	Methane, trichloro-	8010	0.5
			8240	5
2-Chloronaphthalene	91-58-7	Naphthalene, 2-chloro-	8120	10
			8270	10
2-Chlorophenol	95-57-8	Phenol, 2-chloro-	8040	5
			8270	10
4-Chlorophenyl phenyl ether	7005-72-3	Benzene, 1-chloro-4-phenoxy-	8270	10
Chloroprene	126-99-8	1,3-Butadiene, 2-chloro-	8010	50
			8240	5
Chromium	(Total)	Chromium	6010	70
			7190	500
			7191	10
Chrysene	218-01-9	Chrysene	8100	200
			8270	10
Cobalt	(Total)	Cobalt	6010	70
			7200	500
			7201	10
Copper	(Total)	Copper	6010	60
			7210	200
m-Cresol	108-39-4	Phenol, 3-methyl-	8270	10
o-Cresol	95-48-7	Phenol, 2-methyl-	8270	10
p-Cresol	106-44-5	Phenol, 4-methyl-	8270	10
Cyanide	57-12-5	Cyanide	9010	40
2,4-D; 2,4-Dichlorophenoxyacetic acid	94-75-7	Acetic acid, (2,4-dichlorophenoxy)-	8150	10
4,4'-DDD	72-54-8	Benzene 1,1'-(2,2-dichloroethylidene)bis[4-chloro-	8080	0.1
			8270	10
4,4'-DDE	72-55-9	Benzene 1,1'-(dichloroethylidene)bis[4-chloro-	8080	0.05
			8270	10
4,4'-DDT	50-29-3	Benzene 1,1'-(2,2,2-trichloroethylidene)bis[4-chloro-	8080	0.1
			8270	10
Diallate	2303-16-4	Carbamothioic acid, bis(1-methylethyl)-, S-(2,3-dichloro-2-propenyl) ester	8270	10
Dibenz[a,h]anthracene	53-70-3	Dibenz[a,h]anthracene	8100	200
			8270	10
Dibenzofuran	132-64-9	Dibenzofuran	8270	10
Dibromochloromethane; Chlorodibromomethane	124-48-1	Methane, dibromochloro-	8010	1
			8240	5
1,2-Dibromo-3-chloropropane; DBCP	96-12-8	Propane, 1,2-dibromo-3-chloro-	8010	100
			8240	5
			8270	10
1,2-Dibromoethane; Ethylene dibromide	106-93-4	Ethane, 1,2-dibromo-	8010	10
			8240	5
Di-n-butyl phthalate	84-74-2	1,2-Benzenedicarboxylic acid, dibutyl ester	8060	5
			8270	10
o-Dichlorobenzene	95-50-1	Benzene, 1,2-dichloro-	8010	2
			8020	5
			8120	10
			8270	10

APPENDIX IX—GROUND-WATER MONITORING LIST [1]—Continued

Common name [2]	CAS RN [3]	Chemical abstracts service index name [4]	Suggested methods [5]	(μg/L)
m-Dichlorobenzene	541-73-1	Benzene, 1,3-dichloro-	8010	5
			8020	5
			8120	10
			8270	10
p-Dichlorobenzene	106-46-7	Benzene, 1,4-dichloro-	8010	2
			8020	5
			8120	15
			8270	10
3,3'-Dichlorobenzidine	91-94-1	[1,1'-Biphenyl]-4,4'-diamine, 3,3'-dichloro-	8270	20
trans-1,4-Dichloro-2-butene	110-57-6	2-Butene, 1,4-dichloro-, (E)-	8240	5
Dichlorodifluoromethane	75-71-8	Methane, dichlorodifluoro-	8010	10
			8240	5
1,1-Dichloroethane	75-34-3	Ethane, 1,1-dichloro-	8010	1
			8240	5
1,2-Dichloroethane; Ethylene dichloride	107-06-2	Ethane, 1,2-dichloro-	8010	0.5
			8240	5
1,1-Dichloroethylene; Vinylidene chloride	75-35-4	Ethene, 1,1-dichloro-	8010	1
			8240	5
trans-1,2-Dichloroethylene	156-60-5	Ethene, 1,2-dichloro-, (E)-	8010	1
			8240	5
2,4-Dichlorophenol	120-83-2	Phenol, 2,4-dichloro-	8040	5
			8270	10
2,6-Dichlorophenol	87-65-0	Phenol, 2,6-dichloro-	8270	10
1,2-Dichloropropane	78-87-5	Propane, 1,2-dichloro-	8010	0.5
			8240	5
cis-1,3-Dichloropropene	10061-01-5	1-Propene, 1,3-dichloro-, (Z)-	8010	20
			8240	5
trans-1,3-Dichloropropene	10061-02-6	1-Propene, 1,3-dichloro-, (E)-	8010	5
			8240	5
Dieldrin	60-57-1	2,7:3,6-Dimethanonaphth[2,3-b]oxirene, 3,4,5,6,9,9-hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-, (1aα,2β,2aα,3β,6β,6aα,7β,7aα)-	8080	0.05
			8270	10
Diethyl phthalate	84-66-2	1,2-Benzenedicarboxylic acid, diethyl ester	8060	5
			8270	10
O,O-Diethyl O-2-pyrazinyl phosphorothioate, Thionazin	297-97-2	Phosphorothioic acid, O,O-diethyl O-pyrazinyl ester	8270	10
Dimethoate	60-51-5	Phosphorodithioic acid, O,O-dimethyl S-[2-(methylamino)-2-oxoethyl] ester	8270	10
p-(Dimethylamino)azobenzene	60-11-7	Benzenamine, N,N-dimethyl-4-phenylazo)-	8270	10
7,12-Dimethylbenz[a]anthracene	57-97-6	Benz[a]anthracene, 7,12-dimethyl-	8270	10
3,3'-Dimethylbenzidine	119-93-7	[1,1'-Biphenyl]-4,4'-diamine, 3,3'-dimethyl-	8270	10
alpha, alpha-Dimethylphenethylamine	122-09-8	Benzeneethanamine, α,α-dimethyl-	8270	10
2,4-Dimethylphenol	105-67-9	Phenol, 2,4-dimethyl-	8040	5
			8270	10
Dimethyl phthalate	131-11-3	1,2-Benzenedicarboxylic acid, dimethyl ester	8060	5
			8270	10
m-Dinitrobenzene	99-65-0	Benzene, 1,3-dinitro-	8270	10
4,6-Dinitro-o-cresol	534-52-1	Phenol, 2-methyl-4,6-dinitro-	8040	150
			8270	50
2,4-Dinitrophenol	51-28-5	Phenol, 2,4-dinitro-	8040	150
			8270	50
2,4-Dinitrotoluene	121-14-2	Benzene, 1-methyl-2,4-dinitro-	8090	0.2
			8270	10
2,6-Dinitrotoluene	606-20-2	Benzene, 2-methyl-1,3-dinitro-	8090	0.1
			8270	10
Dinoseb; DNBP; 2-sec-Butyl-4,6-dinitrophenol	88-85-7	Phenol, 2-(1-methylpropyl)-4,6-dinitro-	8150	1
			8270	10
Di-n-octyl phthalate	117-84-0	1,2-Benzenedicarboxylic acid, dioctyl ester	8060	30
			8270	10
1,4-Dioxane	123-91-1	1,4-Dioxane	8015	150
Diphenylamine	122-39-4	Benzenamine, N-phenyl-	8270	10
Disulfoton	298-04-4	Phosphorodithioic acid, O,O-diethyl S-[2-(ethylthio)-ethyl] S-[2-ethyl]ester	8140	
			8270	
Endosulfan I	959-98-8	6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-, 3-oxide, (3α,5aβ,6α,9α,9aβ)-	8080	0.05
			8250	10

APPENDIX IX—GROUND-WATER MONITORING LIST [1]—Continued

Common name [2]	CAS RN [3]	Chemical abstracts service index name [4]	Suggested methods [5]	PQL (µg/L) [6]
Endosulfan II	33213-65-9	6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro- 1,5,5a,6,9,9a-hexahydro-, 3-oxide, (3α,5aα,6β,9β,9aα)-	8080	0.05
Endosulfan sulfate	1031-07-8	6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro- 1,5,5a,6,9,9a-hexahydro-, 3,3-dioxide.	8080 8270	0.5 10
Endrin	72-20-8	2,7:3,6-Dimethanonaphth[2,3-b]oxirene, 3,4,5,6,9,9-hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-, (1aα, 2β,2aβ,3α,6α, 6aβ,7β,7aα)-	8080 8250	0.1 10
Endrin aldehyde	7421-93-4	1,2,4-Methenocyclopenta[cd]pentalene-5-carboxaldehyde, 2,2a,3,3,4,7-hexachlorodecahydro-, (1α,2β,2aβ,4β ,4aβ,5β,6aβ,6bβ,7R*)-	8080 8270	0.2 10
Ethylbenzene	100-41-4	Benzene, ethyl-	8020 8240	2 5
Ethyl methacrylate	97-63-2	2-Propenoic acid, 2-methyl-, ethyl ester	8015 8240 8270	10 5 10
Ethyl methanesulfonate	62-50-0	Methanesulfonic acid, ethyl ester	8270	10
Famphur	52-85-7	Phosphorothioic acid, O-[4-[(dimethylamino)sulfonyl]phenyl]-O,O-dimethyl ester	8270	10
Fluoranthene	206-44-0	Fluoranthene	8100 8270	200 10
Fluorene	86-73-7	9H-Fluorene	8100 8270	200 10
Heptachlor	76-44-8	4,7-Methano-1H-indene, 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-	8080 8270	0.05 10
Heptachlor epoxide	1024-57-3	2,5-Methano-2H-indeno[1,2-b]oxirene, 2,3,4,5,6,7,7-heptachloro-1a,1b,5,5a,6,6a,-hexahydro-, (1aα,1bβ,2α,5α ,5aβ,6β,6aα)	8080 8270	1 10
Hexachlorobenzene	118-74-1	Benzene, hexachloro-	8120 8270	0.5 10
Hexachlorobutadiene	87-68-3	1,3-Butadiene, 1,1,2,3,4,4-hexachloro-	8120 8270	5 10
Hexachlorocyclopentadiene	77-47-4	1,3-Cyclopentadiene, 1,2,3,4,5,5-hexachloro-	8120 8270	5 10
Hexachloroethane	67-72-1	Ethane, hexachloro-	8120 8270	0.5 10
Hexachlorophene	70-30-4	Phenol, 2,2'-methylenebis[3,4,6-trichloro-	8270	10
Hexachloropropene	1888-71-7	1-Propene, 1,1,2,3,3,3-hexachloro-	8270	10
2-Hexanone	591-78-6	2-Hexanone	8240	50
Indeno(1,2,3-cd)pyrene	193-39-5	Indeno[1,2,3-cd]pyrene	8100 8270	200 10
Isobutyl alcohol	78-83-1	1-Propanol, 2-methyl-	8015	50
Isodrin	465-73-6	1,4,5,8-Dimethanonaphthalene,1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a- hexahydro-(1α,4α,4aβ,5β,8β,8aβ)-	8270	10
Isophorone	78-59-1	2-Cyclohexen-1-one, 3,5,5-trimethyl-	8090 8270	60 10
Isosafrole	120-58-1	1,3-Benzodioxole, 5-(1-propenyl)-	8270	10
Kepone	143-50-0	1,3,4-Metheno-2H-cyclobuta- [cd]pentalen-2-one, 1,1a,3,3a,4,5,5,5a,5b,6-decachlorooctahydro-	8270	10
Lead	(Total)	Lead	6010 7420 7421	40 1,000 10
Mercury	(Total)	Mercury	7470	2
Methacrylonitrile	126-98-7	2-Propenenitrile, 2-methyl-	8015 8240	5 5
Methapyrilene	91-80-5	1,2,Ethanediamine, N,N-dimethyl-N'-2-pyridinyl-N'-(2-thienylmethyl)-	8270	10
Methoxychlor	72-43-5	Benzene, 1,1'-(2,2,2,trichloroethylidene)bis[4-methoxy-	8080 8270	2 10
Methyl bromide; Bromomethane	74-83-9	Methane, bromo-	8010 8240	20 10
Methyl chloride; Chloromethane	74-87-3	Methane, chloro-	8010 8240	1 10
3-Methylcholanthrene	56-49-5	Benz[j]aceanthrylene, 1,2-dihydro-3-methyl-	8270	10
Methylene bromide; Dibromomethane	74-95-3	Methane, dibromo-	8010 8240	15 5
Methylene chloride; Dichloromethane	75-09-2	Methane, dichloro-	8010 8240	5 5

APPENDIX IX—GROUND-WATER MONITORING LIST [1]—Continued

Common name [4]	CAS RN [5]	Chemical abstracts service index name [6]	Suggested methods [3]	(µg
Methyl ethyl ketone; MEK	78-93-3	2-Butanone	8015	10
			8240	100
Methyl iodide; Iodomethane	74-88-4	Methane, iodo-	8010	40
			8240	5
Methyl methacrylate	80-62-6	2-Propenoic acid, 2-methyl-, methyl ester	8015	2
			8240	5
Methyl methanesulfonate	66-27-3	Methanesulfonic acid, methyl ester	8270	10
2-Methylnaphthalene	91-57-6	Naphthalene, 2-methyl-	8270	10
Methyl parathion; Parathion methyl	298-00-0	Phosphorothioic acid, O,O-dimethyl O-(4-nitrophenyl) ester	8140	5
			8270	1
4-Methyl-2-pentanone; Methyl isobutyl ketone	108-10-1	2-Pentanone, 4-methyl-	8015	5
			8240	5
Naphthalene	91-20-3	Naphthalene	8100	2
			8270	1
1,4-Naphthoquinone	130-15-4	1,4-Naphthalenedione	8270	10
1-Naphthylamine	134-32-7	1-Naphthalenamine	8270	10
2-Naphthylamine	91-59-8	2-Naphthalenamine	8270	10
Nickel	(Total)	Nickel	6010	5
			7520	40
o-Nitroaniline	88-74-4	Benzenamine, 2-nitro-	8270	50
m-Nitroaniline	99-09-2	Benzenamine, 3-nitro-	8270	50
p-Nitroaniline	100-01-6	Benzenamine, 4-nitro-	8270	50
Nitrobenzene	98-95-3	Benzene, nitro-	8090	40
			8270	10
o-Nitrophenol	88-75-5	Phenol, 2-nitro-	8040	5
			8270	10
p-Nitrophenol	100-02-7	Phenol, 4-nitro-	8040	10
			8270	5
4-Nitroquinoline 1-oxide	56-57-5	Quinoline, 4-nitro-, 1-oxide	8270	10
N-Nitrosodi-n-butylamine	924-16-3	1-Butanamine, N-butyl-N-nitroso-	8270	
N-Nitrosodiethylamine	55-18-5	Ethanamine, N-ethyl-N-nitroso-	8270	
N-Nitrosodimethylamine	62-75-9	Methanamine, N-methyl-N-nitroso-	8270	
N-Nitrosodiphenylamine	86-30-6	Benzenamine, N-nitroso-N-phenyl-	8270	
N-Nitrosodipropylamine; Di-n-propylnitrosamine	621-64-7	1-Propanamine, N-nitroso-N-propyl-	8270	
N-Nitrosomethylethylamine	10595-95-6	Ethanamine, N-methyl-N-nitroso-	8270	10
N-Nitrosomorpholine	59-89-2	Morpholine, 4-nitroso-	8270	10
N-Nitrosopiperidine	100-75-4	Piperidine, 1-nitroso-	8270	10
N-Nitrosopyrrolidine	930-55-2	Pyrrolidine, 1-nitroso-	8270	10
5-Nitro-o-toluidine	99-55-8	Benzenamine, 2-methyl-5-nitro-	8270	10
Parathion	56-38-2	Phosphorothioic acid, O,O-diethyl-O-(4-nitrophenyl) ester	8270	10
Polychlorinated biphenyls; PCBs	See Note 7	1,1'-Biphenyl, chloro derivatives	8080	50
			8250	100
Polychlorinated dibenzo-p-dioxins; PCDDs	See Note 8	Dibenzo[b,e][1,4]dioxin, chloro derivatives	8280	0.0
Polychlorinated dibenzofurans; PCDFs	See Note 9	Dibenzofuran, chloro derivatives	8280	0.0
Pentachlorobenzene	608-93-5	Benzene, pentachloro-	8270	10
Pentachloroethane	76-01-7	Ethane, pentachloro-	8240	
			8270	10
Pentachloronitrobenzene	82-68-8	Benzene, pentachloronitro-	8270	10
Pentachlorophenol	87-86-5	Phenol, pentachloro-	8040	5
			8270	50
Phenacetin	62-44-2	Acetamide, N-(4-ethoxyphenyl)	8270	10
Phenanthrene	85-01-8	Phenanthrene	8100	200
			8270	10
Phenol	108-95-2	Phenol	8040	1
			8270	10
p-Phenylenediamine	106-50-3	1,4-Benzenediamine	8270	10
Phorate	298-02-2	Phosphorodithioic acid, O,O-diethyl S-[(ethylthio)methyl] ester	8140	2
			8270	10
2-Picoline	109-06-8	Pyridine, 2-methyl-	8240	1
			8270	10
Pronamide	23950-58-5	Benzamide, 3,5-dichloro-N-(1,1-dimethyl-2-propynyl	8270	10
Propionitrile; Ethyl cyanide	107-12-0	Propanenitrile	8015	60
			8240	
Pyrene	129-00-0	Pyrene	8100	
			8270	
Pyridine	110-86-1	Pyridine	8240	5
			8270	1

APPENDIX IX—GROUND-WATER MONITORING LIST [1]—Continued

Common name [2]	CAS RN [3]	Chemical abstracts service index name [4]	Suggested methods [5]	PQL (µg/L) [6]
Safrole	94-59-7	1,3-Benzodioxole, 5-(2-propenyl)-	8270	10
Selenium	(Total)	Selenium	6010	750
			7740	20
			7741	20
Silver	(Total)	Silver	6010	70
			7760	100
Silvex; 2,4,5-TP	93-72-1	Propanoic acid, 2-(2,4,5-trichlorophenoxy)-	8150	2
Styrene	100-42-5	Benzene, ethenyl-	8020	1
			8240	5
Sulfide	18496-25-8	Sulfide	9030	10,000
2,4,5-T; 2,4,5-Trichlorophenoxyacetic acid	93-76-5	Acetic acid, (2,4,5-trichlorophenoxy)-	8150	2
2,3,7,8-TCDD; 2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746-01-6	Dibenzo[b,e][1,4]dioxin, 2,3,7,8-tetrachloro-	8280	0.005
1,2,4,5-Tetrachlorobenzene	95-94-3	Benzene, 1,2,4,5-tetrachloro-	8270	10
1,1,1,2-Tetrachloroethane	630-20-6	Ethane, 1,1,1,2-tetrachloro-	8010	5
			8240	5
1,1,2,2-Tetrachloroethane	79-34-5	Ethane, 1,1,2,2-tetrachloro-	8010	0.5
			8240	5
Tetrachloroethylene; Perchloroethylene; Tetrachloroethene	127-18-4	Ethene, tetrachloro-	8010	0.5
			8240	5
2,3,4,6-Tetrachlorophenol	58-90-2	Phenol, 2,3,4,6-tetrachloro-	8270	10
Tetraethyl dithiopyrophosphate; Sulfotepp	3689-24-5	Thiodiphosphonic acid [(HO)$_2$P(S)]$_2$O), tetraethyl ester	8270	10
Thallium	(Total)	Thallium	6010	400
			7840	1,000
			7841	10
Tin	(Total)	Tin	7870	8,000
Toluene	108-88-3	Benzene, methyl-	8020	2
			8240	5
o-Toluidine	95-53-4	Benzenamine, 2-methyl-	8270	10
Toxaphene	8001-35-2	Toxaphene	8080	2
			8250	10
1,2,4-Trichlorobenzene	120-82-1	Benzene, 1,2,4-trichloro-	8270	10
1,1,1-Trichloroethane; Methylchloroform	71-55-6	Ethane, 1,1,1-trichloro-	8240	5
1,1,2-Trichloroethane	79-00-5	Ethane, 1,1,2-trichloro-	8010	0.2
			8240	5
Trichloroethylene; Trichloroethene	79-01-6	Ethene, trichloro-	8010	1
			8240	5
Trichlorofluoromethane	75-69-4	Methane, trichlorofluoro-	8010	1
			8240	5
2,4,5-Trichlorophenol	95-95-4	Phenol, 2,4,5-trichloro-	8270	10
2,4,6-Trichlorophenol	88-06-2	Phenol, 2,4,6-trichloro-	8040	5
			8270	10
1,2,3-Trichloropropane	96-18-4	Propane, 1,2,3-trichloro-	8010	10
			8240	5
O,O,O-Triethyl phosphorothioate	126-68-1	Phosphorothioic acid, O,O,O-triethyl ester	8270	10
sym-Trinitrobenzene	99-35-4	Benzene, 1,3,5-trinitro-	8270	10
Vanadium	(Total)	Vanadium	6010	80
			7910	2,000
			7911	40
Vinyl acetate	108-05-4	Acetic acid, ethenyl ester	8240	5
Vinyl chloride	75-01-4	Ethene, chloro-	8010	2
			8240	10
Xylene (total)	1330-20-7	Benzene, dimethyl-	8020	5
			8240	5
Zinc	(Total)	Zinc	6010	20
			7950	50

[1] The regulatory requirements pertain only to the list of substances; the right hand columns (Methods and PQL) are given for informational purposes only. See also footnotes 5 and 6.

[2] Common names are those widely used in government regulations, scientific publications, and commerce; synonyms exist for many chemicals.

[3] Chemical Abstracts Service registry number. Where "Total" is entered, all species in the ground water that contain this element are included.

[4] CAS index names are those used in the 9th Cumulative Index.

[5] Suggested Methods refer to analytical procedure numbers used in EPA Report SW-846 "Test Methods for Evaluating Solid Waste", third edition, November 1986. Analytical details can be found in SW-846 and in documentation on file at the agency. CAUTION: The methods listed are representative SW-846 procedures and may not always be the most suitable method(s) for monitoring an analyte under the regulations.

[6] Practical Quantitation Limits (PQLs) are the lowest concentrations of analytes in ground waters that can be reliably determined within specified limits of precision and accuracy by the indicated methods under routine laboratory operating conditions. The PQLs listed are generally

stated to one significant figure. CAUTION: The PQL values in many cases are based only on a general estimate for the method and not on a determination for individual compounds. PQLs are not a part of the regulation.

* Polychlorinated biphenyls (CAS RN 1336-36-3), this category contains congener chemicals, including constituents of Aroclor-1016 (CAS RN 12674-11-2), Aroclor-1221 (CAS RN 11104-28-2), Aroclor-1232 (CAS RN 11141-16-5), Aroclor-1242 (CAS RN 53469-21-9), Aroclor-1248 (CAS RN 12672-29-6), Aroclor-1254 (CAS RN 11097-69-1), and Aroclor-1260 (CAS RN 11096-82-5). The PQL shown is an average value for congeners.

* This category contains congener chemicals, including tetrachlorodibenzo-p-dioxins (see also 2,3,7,8-TCDD), pentachlorodibenzo-p-dioxins, and hexachlorodibenzo-p-dioxins. The PQL shown is an average value for PCDD congeners.

* This category contains congener chemicals, including tetrachlorodibenzofurans, pentachlorodibenzofurans, and hexachlorodibenzofurans. The PQL shown is an average value for PCDF congeners.

PART 270—AMENDED

1. The authority citation for Part 270 is revised to read as follows:

Authority: Secs. 1006, 2002(a), 3001, 3004, and 3005, of the Solid Waste Disposal Act, as amended, 42 U.S.C. 6905, 6912(a), 6924 and 6925.

2. Section 270.14 is amended by revising paragraph (c)(4)(ii) to read as follows:

§ 270.14 Contents of Part B: general requirements.

* * * * *

(c) * * *

(4) * * *

(ii) Identifies the concentration of each Appendix IX, of Part 264 of this chapter, constituent throughout the plume or identifies the maximum concentrations of each Appendix IX constituent in the plume.

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BILLING CODE 6560-50-M

ANAEROBIC WASTE TREATMENT*

INTRODUCTION

Anaerobic treatment of wastewaters involves numerous biochemical and microbiological reactions resulting in an orderly and controlled dissimilation of the substrate, without molecular oxygen acting as the hydrogen acceptor. This microbial decomposition of complex organic substrates provides a source of energy and building materials to the bacterial cells which convert a portion of the organic material to carbon dioxide and methane. The microbial population is composed of facultative and anaerobic bacteria which utilize chemically-bound oxygen in the form of carbon dioxide, nitrates, sulfates, or organic molecules as the final hydrogen acceptor resulting in the production of methane, ammonia, hydrogen sulfide, or reduced organic molecules. The facultative microorganisms can also use molecular oxygen during metabolism, and this group of organisms usually prefers aerobic conditions; therefore, these microbes protect the strictly anaerobic bacteria from any small amounts of free dissolved oxygen which may be introduced into the system accidentally during the addition of substrate.

The synthesis of excess bacterial cells during anaerobic treatment is much less than during aerobic treatment; therefore, the disposal of excess biological sludge is minimized and the requirements for biological nutrients such as nitrogen and phosphorus are reduced.

Historically, anaerobic treatment was used for the stabilization of concentrated municipal and industrial sludges. However, recently, anaerobic treatment processes have been applied to the treatment of dilute and concentrated dissolved wastes. Various "anaerobic contact processes" have been developed in which a high concentration of microorganisms is maintained in a reactor, by means of returning settled biologically-active solids or by means of fixed microbial growths. These processes provide relatively rapid and efficient treatment of dissolved organic wastes.

MECHANISM OF ANAEROBIC TREATMENT

The anaerobic treatment of complex wastes resulting in the production of methane involves sequential processes including two distinct stages, each of which is dependent on a different group of bacteria which is specific to the particular stage. The two stages are "acid fermentation" followed by "methane fermentation." Although the mechanism of anaerobic treatment is sequential in nature, both the acid and methane fermentations take place simultaneously and synchronously in a well-buffered and active system.

During "acid fermentation" (Figure 1) waste conversion takes place and the waste is stabilized when methane is produced. Complex organic compounds are converted to simpler organic molecules. Since almost all organic matter may be classified as either carbohydrates, lipids, or proteins, these general types of compounds will be used for illustrative purposes. The conversion of complex carbohydrates such as polysaccharides is shown by a simplified equation:

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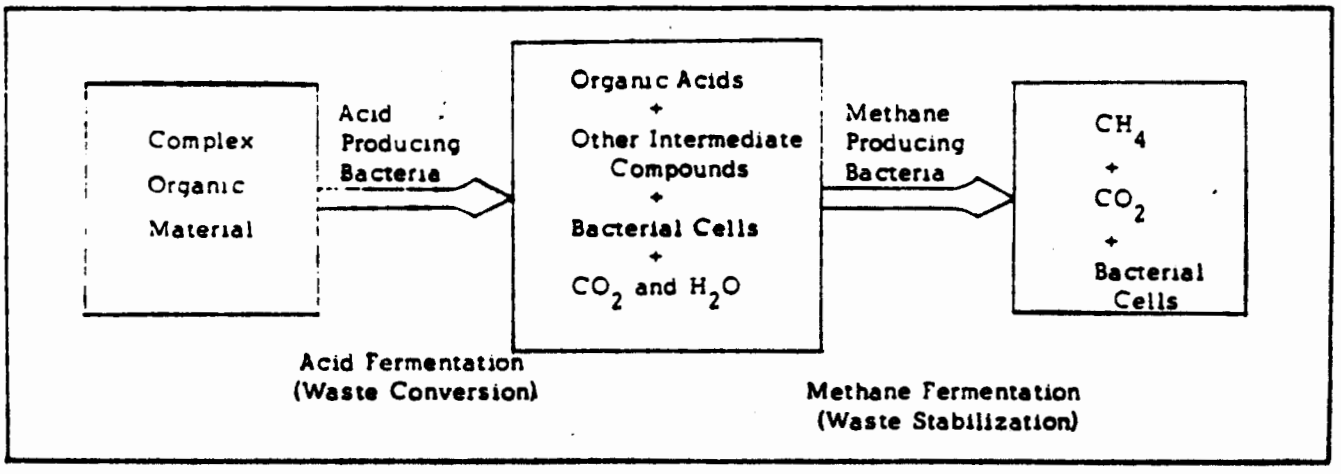


Figure 1. Sequential Mechanism of Anaerobic Waste Treatment

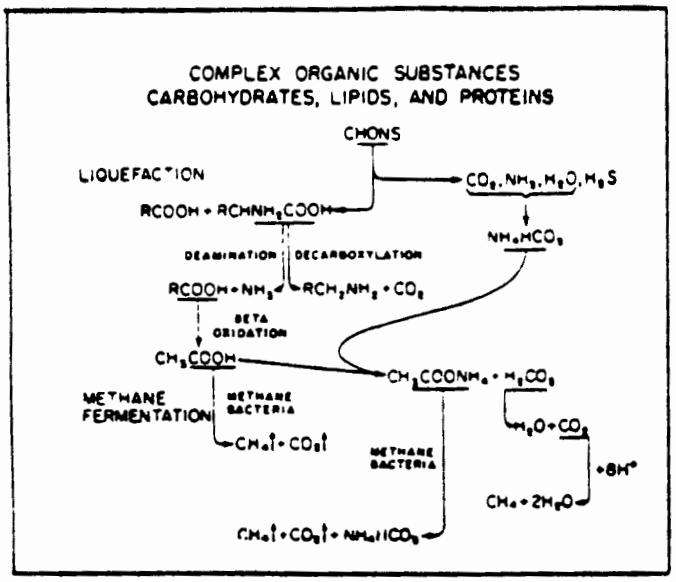


Figure 2. Anaerobic Degradation of Complex Organic Substances

$$\left.\begin{matrix}\text{cellulose}\\ \text{hemicellulose}\\ \text{starch}\end{matrix}\right\}\xrightarrow{H_2O}\text{simple sugars}$$

$$\longrightarrow\left\{\begin{matrix}\text{organic acids}\\ \text{aldehydes}\\ \text{alcohols}\end{matrix}\right\}+CO_2+H_2$$

Wastewaters discharged from the pulp and paper, textile, and food processing industries are typical of wastes which contain complex carbohydrates. Lipids, fats, and oils undergo anaerobic conversion as follows:

$$\text{Triglyceride}\xrightarrow{H_2O}\text{Glycerol - Fatty Acids}$$

$$\longrightarrow\left\{\begin{matrix}\text{alcohols}\\ \text{aldehydes}\\ \text{organic acids}\end{matrix}\right\}+CO_2+H_2O$$

Meat packing, slaughterhouse, and soap manufacturing plant effluents generally contain fats and oils. Proteins are nitrogenous compounds which release amino acids during microbial decomposition. The amino acids are anaerobically converted to numerous compounds as illustrated below:

$$\text{Proteins}\xrightarrow{H_2O}\text{Amino Acids}\xrightarrow[CO_2\quad H_2S]{-NH_2}$$

$$\left\{\begin{matrix}\text{Organic acids}\\ \text{Mercaptans}\\ \text{Amines}\end{matrix}\right\}+CO_2+NH_3+H_2S$$

The principal intermediate compounds resulting from conversion of the substrate during "acid fermentation" are the organic acids. Short-chain carboxylic acids, i.e., volatile acids, are the major product of acid fermentation, and these volatile acids provide substrate for the methane-forming bacteria (Figure 2). The volatile acids commonly found during anaerobic treatment are listed in Table I. The primary acids produced are acetic, propionic, and butyric acids; however, smaller quantities of formic, valeric, isovaleric, and caproic are frequently found during anaerobic treatment.

Acid fermentation is characterized by a drop in pH from near neutral to about 5.0; however, in a balanced system, the subsequent conversion of the acids, as they are formed, to methane and carbon dioxide results in a pH of 6.8 to 7.4 (Figure 3). It is important to note that during acid fermentation there is no appreciable reduction in COD or BOD. The organic content of the waste is relatively unchanged. There is a redistribution among the various types of simpler organic compounds and some loss of carbon and hydrogen which are released as carbon dioxide, and hydrogen gas or hydrogen sulfide, respectively. No stabilization of organic material takes place during the first stage.

The microbial population which converts the heterogeneous substrate to simpler compounds and organic acids is classified as "acid formers." These bacteria are generally facultative, although some are strict anaerobes, and represent a wide variety of microbial genera, some of which are: Aerobacter, Alcaligenes, Clostridium, Escherichia, Flavobacterium, Lactobacillus, Micrococcus, Pseudomonas, and Streptococcus. The "acid formers" are relatively tolerant to changes in pH and temperature, and grow at a much more rapid rate than the "methane bacteria".

The organic acids produced during "acid fermentation" are converted to methane and car-

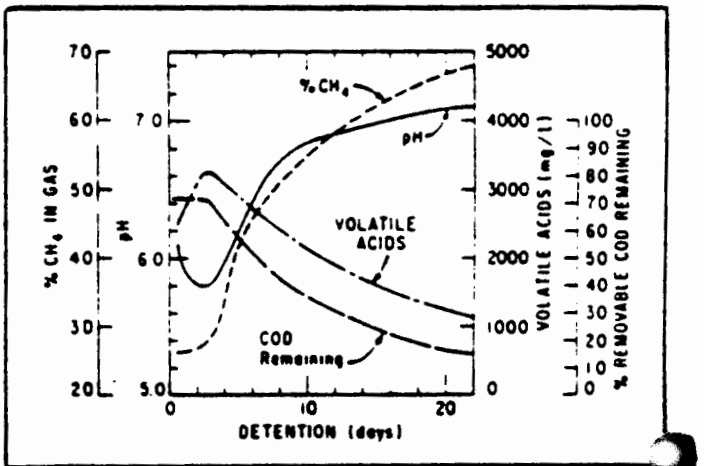


Figure 3. Anaerobic Degradation of Organic Waste (After Andrews)

bon dioxide during "methane fermentation" resulting in a marked reduction in the amount of organic material (COD or BOD) in the system. It is in the second stage of anaerobic treatment that stabilization of the oxidizable organic material is accomplished and the amount of stabilization of organics is directly proportional to the amount of methane produced. Occasionally, hydrogen will be formed or inorganic sulfates, nitrates, or nitrites will be reduced during waste stabilization.

The methane-forming bacteria are strict anaerobic organisms. The various species of methane bacteria which have been isolated and the specific substrates used by each species are listed in Table II. These bacteria have one major similar characteristic, besides being strict anaerobes, namely, all these organisms produce methane from the anaerobic fermentation of simple organic compounds. However, each species of methane bacteria can ferment only a relatively restricted group of simple compounds to methane, therefore a number of different species of methane formers may be necessary to completely stabilize some wastes anaerobically.

The substrate specificity of the methane bacteria is illustrated by the following example in which three species of methane bacteria are required for the complete fermentation of valeric acid. The valeric acid is oxidized by Mbact. suboxydans to acetic and propionic acids. It is interesting to note that Mbact. suboxydans specializes in oxidizing four-carbon and six-carbon fatty acids to acetate and propionate, but cannot break down these compounds any further. The propionate is converted by Mbact. propionicum to acetate, carbon dioxide and methane; however, since Mbact. propionicum cannot utilize the acetate, a third species, Mc. mazei would be necessary to ferment the acetate to methane and carbon dioxide.

The principal organic compound utilized by methane bacteria is acetic acid, although almost all volatile acids can be used by specific species of methane bacteria. The two major pathways to methane are the biological decomposition of acetic acid and the microbial reduction of carbon dioxide, namely:

a) $C^*H_3COOH \longrightarrow C^*H_4 + CO_2$, and
b) $CO_2 + 8H^- \longrightarrow CH_4 + 2H_2O$

Propionic acid on the other hand requires a two-step microbial degradation, namely:

Step I $4CH_3CH_2COOH + 2H_2O \longrightarrow 4CH_3COOH + CO_2 + 3CH_4$

Step II $4CH_3COOH \longrightarrow 4CH_4 + 4CO_2$

Overall $4CH_3CH_2COOH + 2H_2O \longrightarrow 5CO_2 + 7CH_4$

Two different species of bacteria are required for the complete fermentation of propionic acid. Butyric acid is similarly microbially decomposed anaerobically through a series of steps as illustrated below:

Step I $2CH_3CH_2CH_2COOH + 2H_2O + CO_2 \longrightarrow 4CH_3COOH + CH_4$

Step II $4CH_3COOH \longrightarrow 4CH_4 + 4CO_2$

Overall $2CH_3CH_2CH_2COOH + 2H_2O \longrightarrow 5CH_4 + 3CO_2$

Each of the longer-chained organic acids will be degraded microbially to either butyric or propionic

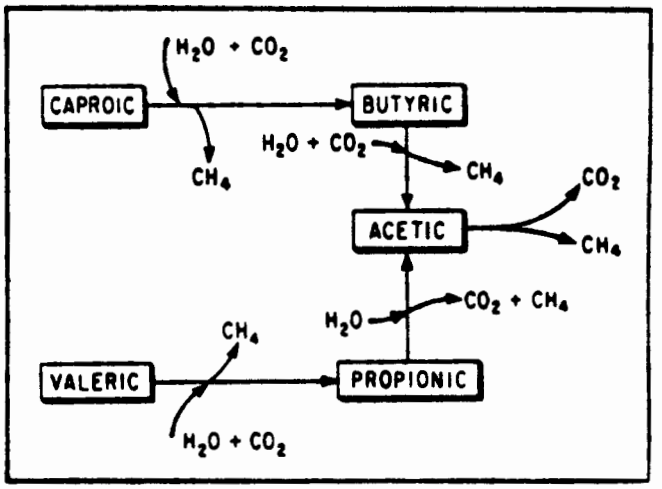


Figure 4. Methane Fermentation From Volatile Acids.

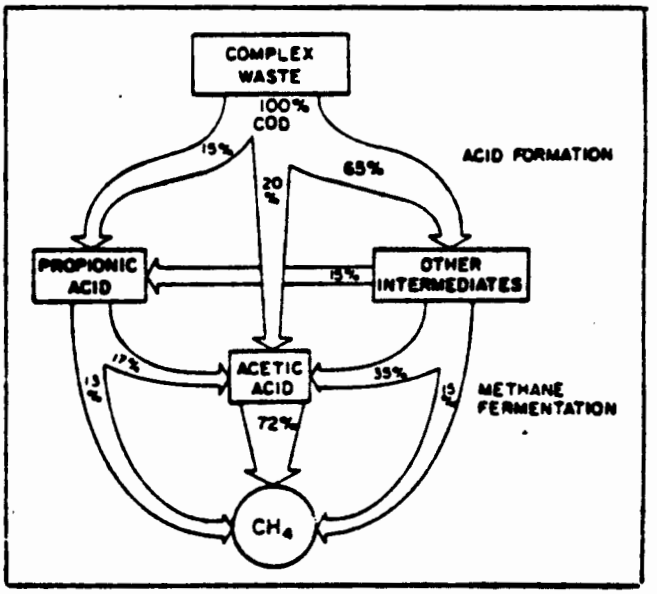


Figure 5. Pathways in methane fermentation of complex wastes such as municipal waste sludges. Percentages represent conversion of waste COD by various routes (McCarty, 1965).

acid and then to acetic acid and methane. This mechanism of methane fermentation is schematically, but not stoichiometrically illustrated in Figure 4. One mole of propionic acid is formed per mole of odd-numbered carbon long chain fatty acid during methane fermentation; however, no propionic acid is formed when long chain even-numbered carbon fatty acids are fermented.

Figure 5 (after McCarty) illustrates the significance of acetic and propionic acids as precursors of methane during the anaerobic decomposition of a complex organic material. The percentages are based on the conversion of COD of municipal sludge to methane gas. The anaerobic treatment of other complex wastes would result in different numerical values for the pathways to methane. The methane fermentation of the propionic and acetic acids resulting from the anaerobic decomposition of a complex waste accounts for approximately 85 percent of the methane produced. The remainder of the methane results from fermentation of formic acid, from reduction of carbon dioxide by hydrogen and from methane fermentation of long-chained fatty acids which undergo "beta-oxidation." The theory of "beta-oxidation" involves a split between the number 2 and number 3 carbon atoms of a long-chain fatty acid, followed by the addition of a water molecule, resulting in the production of one molecule of acetic acid and one molecule of a fatty acid which contains two fewer carbon atoms, i.e., the loss of a $-CH_2CH_2-$ fragment.

The methane bacteria are strict anaerobes which are extremely sensitive to changes in temperature and pH. These bacteria are active in two temperature zones, namely, in the mesophilic range (30°-35°C) and in the thermophilic range (50°C-60°C). However, anaerobic processes have been operated at 25°C successfully when sufficient residence time for the methane bacteria was provided.

Methane bacteria have relatively long generation times ranging from just less than two days to greater than twenty days. At temperatures above 40°C and below 50°C, methane production is inhibited.

The optimum pH range for methane bacteria is 6.4 to 7.2, although in many anaerobic systems treating complex wastes pH values have been reported between 1.2 to 7.8. Above pH 8 and below pH 6 of the growth of the methane bacteria falls off rapidly.

The stabilization of complex wastes anaerobically is directly related to the amount of methane produced. The amount of methane that is anticipated can be determined from the equations for methane production presented above if the substrate, the mechanism, and the biochemistry were known. If the composition of the waste is known, the following formula presented by Buswell may be used to predict the amount of methane which will be produced:

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right)H_2O \longrightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)CO_2 + \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)CH_4$$

The ultimate oxygen demand of the waste being treated is equal to the ultimate oxygen demand of the methane formed. Therefore the amount of methane gas produced from a particular waste can be predicted by estimating the degree of stabilization that will be attained. The amount of methane can be expressed in terms of equivalent oxygen, namely:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

One mole of methane is equivalent to two moles of oxygen. For each 16 grams of CH_4 produced and released from the system, 64 grams of oxygen equivalents (COD or ultimate BOD) are removed from the wastes. In terms of volume of methane gas produced, the relationship is 5.64 ft^3 of methane gas (at standard temperature and pressure) are produced for each lb of COD or ultimate BOD stabilized.

KINETICS OF TREATMENT AND BACTERIAL GROWTH

The relationship between the rate of microbial utilization of components of a waste and the rate of bacterial growth can be expressed in terms of a mathematical model developed by McCarty. This particular expression has some theoretical basis and describes conditions of bacterial growth in both a substrate-limited and a substrate-unlimited environment. The equation is as follows:

$$\frac{dX}{dt} = a\frac{ds}{dt} - bX$$

in which:

$\frac{dX}{dt}$ = microbial growth rate (mass/unit time)

$\frac{ds}{dt}$ = waste utilization rate (mass/unit time)

X = microbial mass

a = growth constant

b = microbial decay rate (1/time)

However, the waste utilization rate can be approximated by the following expression which relates the concentration of nutrients to the microbial growth:

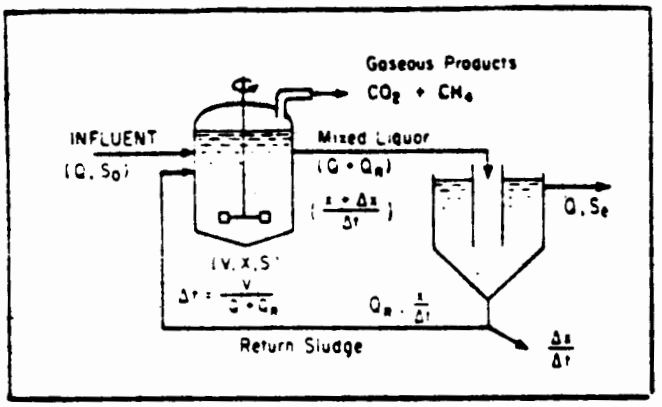


Figure 6. Anaerobic Treatment System with Separate Return Sludge

$$\frac{dF}{dt} = \frac{kXs}{K_s + S}$$

in which:

k = maximum waste utilization rate at a high concentration of waste

K_s = concentration of waste at which dF/dt 1/2 maximum rate

S = concentration of waste surrounding the microorganisms

By combining these two relationships, the microbial growth rate can be expressed as a function of waste concentration:

$$\frac{dX/dt}{X} = \frac{akS}{K_s + S} - b$$

in which:

$\frac{dX/dt}{X}$ = specific growth rate
fractional growth per unit time

For a continuously-fed completely mixed system (Figure 6), the average quantity of microbial mass wasted daily from the total system is $\frac{(\Delta X/\Delta t)}{X}$, i.e., the ratio of the microbial mass wasted per day to the microbial mass in the system. The concentration of waste in the effluent will equal S, the concentration of waste surrounding the microorganisms.

A more usable term, however, is the reciprocal of the specific growth rate, which is the average residence time of the microbial mass in the system or the biological solids retention time (SRT) which is defined as:

$$SRT = \frac{X}{(\Delta X/\Delta t)} =$$

$$\frac{\text{suspended solids in the system}}{\text{suspended solids removed per day}}$$

The use of suspended solids to estimate the microbial mass is adequate because the average detention time of the microorganisms will be approximately the same as that of the mixed liquor suspended solids. The term $(\Delta X/\Delta t)$ should include all the suspended solids removed from the system, namely, the solids accidentally lost in the effluent stream as well as those solids intentionally wasted from the system as excess sludge.

The rate of waste treatment for a continuously fed completely mixed system is:

$$\frac{\Delta S}{\Delta t} = S_o - S_e \; Q$$

in which:

S_o = influent waste concentration (mg/1)
S_e = effluent waste concentration (mg/1)
Q = volumetric rate of flow

The efficiency of anaerobic treatment therefore is equal to:

$$\frac{S_o - S_e}{S_o} \quad (100)$$

The relationship of the solids retention time (SRT) to the concentration of waste in the effluent and to the efficiency of treatment are presented in Figure 7. These curves are based on the as-

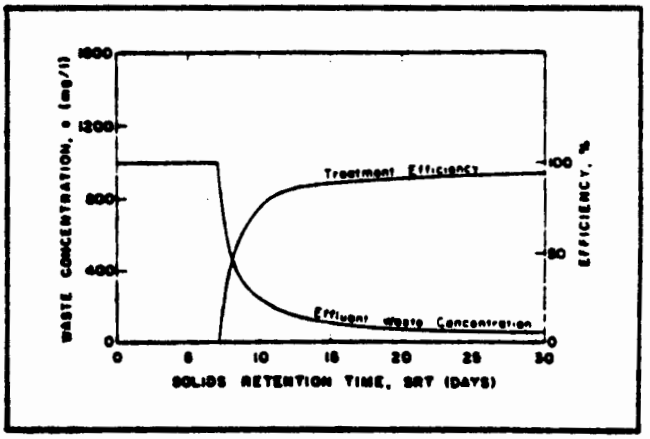


Figure 7. Relationship of the Solids Retention Time to Effluent Waste Concentration and to Treatment Efficiency. (After McCarty, 1965).

sumptions that S_o = 1000 mg/1, K_s = 100 mg/1, a = 0.05, b = 0.04/day, and k = 4 lb/lb-day.

There is a minimum SRT below which no treatment takes place and $S_e = S_o$. The minimum SRT therefore, is that solids retention time which is equal to the generation time of the bacteria responsible for anaerobic treatment. Below the minimum SRT bacteria are removed from the system at a rate faster than that required for microbial reproduction and "washout" of the microbial population occurs. The minimum SRT may be approximated by assuming that b, the rate of decay of the microbial mass, is negligible and the equation becomes:

$$SRT_{min} = \frac{1}{ak}\left[\frac{K_s + S_o}{S_o}\right]$$

The minimum SRT for the anaerobic stabilization of a particular substrate depends on the concentration of the substrate (S_o), the rate at which the substrate is utilized (k) and the fraction of the substrate which is synthesized into bacterial cells (a). The fraction of the waste synthesized into cells is much lower in anaerobic systems because much of the energy released during anaerobic metabolism is lost from the system as methane and is not available for cell synthesis; therefore, the minimum SRT for anaerobic treatment is longer than for aerobic systems, if all other factors are equal.

Generally, the anaerobic stabilization of complex substrates proceeds through methane fermentation of propionic and/or acetic acids. The minimum SRT, therefore, is between 3 to 5 days at a temperature of 25° to 35°C, although some investigators indicate that a minimum SRT of less than two days is possible for the fermentation of propionic acid. The minimum SRT also varies with temperature from 4 days at 35°C to 8 days at 25°C. Methane fermentation ceases at temperatures below 20°C. The efficiency of waste stabilization increases and the amount of sludge accumulation decreases as the SRT is increased (Figure 8). Inorganic nutrients (primarily phosphorus and nitrogen) are required for bacterial growth and cell synthesis. These nutrients are available in sufficient quantities in some wastes, but must be added in the treatment of wastes which lack the necessary nitrogen and phosphorus. The amount of nitrogen required may be calculated based on the empirical formulation of the bacterial cell in an anaerobic system, namely, $C_5H_9NO_3$. In this case the nitrogen requirement is about 11 percent of the volatile fraction of the bacterial cells synthesized during treatment. The phosphorus requirement is about 15 to 25 percent of the nitrogen requirement. Theoretically the nutrients should be based on the amount of substrate stabilized during treatment; however, in anaerobic systems the acid-forming bacteria would utilize the nutrients for growth and sufficient nutrients would not be available for the methane bacteria; therefore, in most cases the nutrient requirement is based on the ultimate BOD or COD entering the system rather than on the fraction removed during treatment.

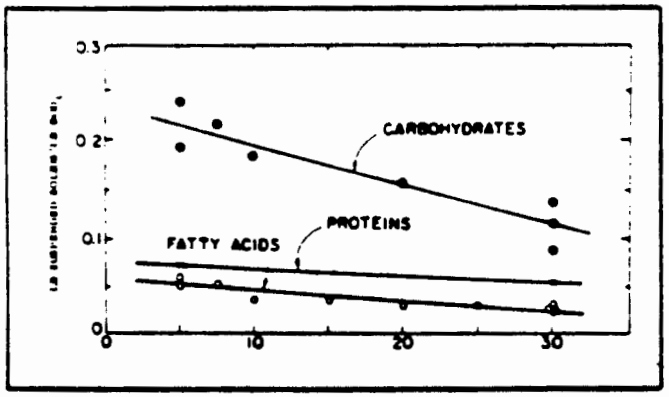


Figure 8. Biological solids production resulting from methane fermentation

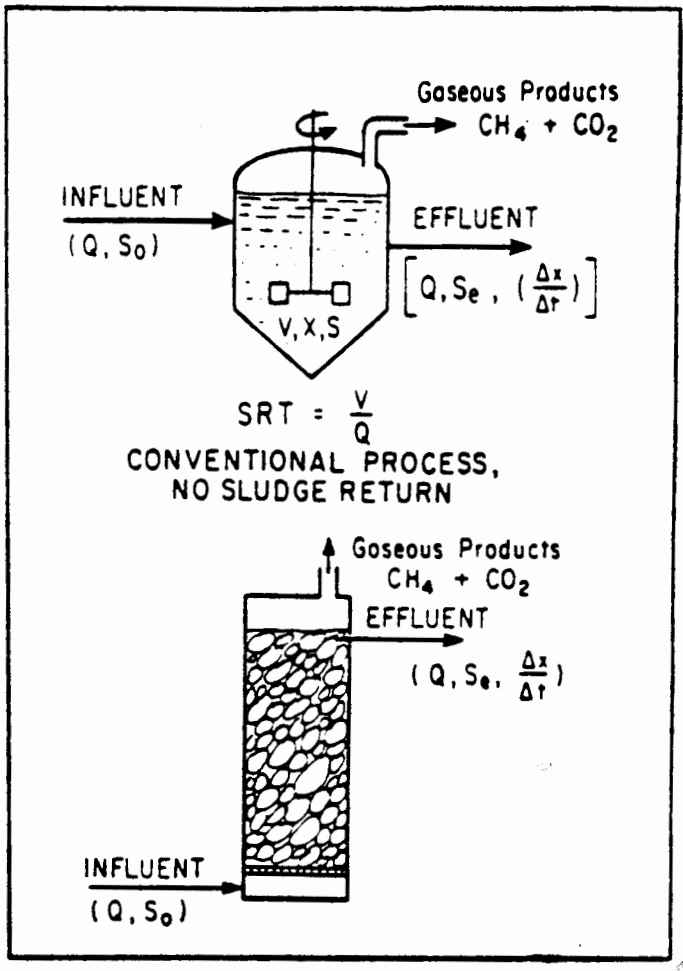


Figure 9. Anaerobic Treatment Processes

Anaerobic systems other than the completely-mixed system with separate sludge return include the conventional system in which there is no separate sludge return and the anaerobic filter.

In the conventional system the SRT equals the hydraulic retention time, namely, V/Q. This system is illustrated in Figure 9. The kinetic and bacterial growth calculations are the same as those presented earlier in this discussion. The anaerobic filter (illustrated in Figure 9) is a process which has only recently been applied to anaerobic treatment. Relatively long values of SRT are possible because the bacteria tend to grow on the walls of the confining structure as well as on the solid media in the filter. Therefore, a rigorous mathematical evaluation of the kinetics of treatment and of bacterial growth is much more complicated and will not be attempted at this time.

ENVIRONMENTAL CONTROL

The environment which will result in maximum efficiency of anaerobic stabilization of wastes is dictated by the tolerance of the methane-forming bacteria, which are more sensitive than the acid-forming bacteria to changes in the environment. Failure to maintain an environment which is conducive for maximum methane production will result in the accumulation of intermediate compounds, primarily organic acids.

The environmental factors which are considered to be optimum for anaerobic treatment besides anaerobic conditions and sufficient nutrients including nitrogen, phosphorus, iron, and others yet undefined are tabulated in Table III.

Toxic materials include a variety of substances. Historically, it has been felt that the accumulation of volatile acids to concentrations in excess of 2000 mg/l resulted in the retardation of methane fermentation; however, the accumulation of volatile acids indicates that the methane forming bacteria are not active; therefore, the build-up of volatile acids is the result of an environment which is not conducive or inhibitory for the methane-forming bacteria rather than the cause of this inability of the methane bacteria to tolerate the environment.

The alkalinity of the anaerobic system is important because it provides a buffer to the system; therefore, sufficient alkalinity is essential for proper pH control. Alkalinity is derived from the breakdown of organics and is present primarily in the form of bicarbonate ions, which are in equilibrium with the carbon dioxide in the gas. This relationship between alkalinity and the carbon dioxide in the gas is pH dependent and may be illustrated by the following equations:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

The hydrogen ion concentration and eventually the pH of the system may be calculated from the following equilibrium equation for the ionization of H_2CO_3:

$$[H^+] = k_1 \frac{[H_2CO_3]}{[HCO_3^-]}$$

At pH's between 6.6 and 7.4 and at normal carbon dioxide content in the gas, namely, 30 to 40 percent by volume, the bicarbonate alkalinity will range between 1000 and 5000 mg/l. Concentrations of alkalinity of about 3000 mg/l are generally preferred rather than attempting to operate the system at the extreme values.

The bicarbonate alkalinity is approximately equal to the total alkalinity of the anaerobic system. A portion of the alkalinity appears as "volatile acid salts" alkalinity which result from the reaction of volatile acids with the bicarbonate present, yielding carbon dioxide. At low volatile acid concentrations, the bicarbonate alkalinity represents approximately the total alkalinity; however, as the volatile acids concentration increases, the bicarbonate alkalinity is much lower than the total alkalinity. About 83.3 percent of the volatile acids concentration contributes to the alkalinity as "volatile acid salts" alkalinity and the following equation may be used to estimate the concentration of bicarbonate alkalinity:

$$BA = TA - (0.85)(0.833)TVA$$

in which:

BA = bicarbonate alkalinity, mg/l as $CaCO_3$
TA = total alkalinity, mg/l as $CaCO_3$
TVA = total volatile acids mg/l as acetic acid.

The factor (0.85) is included to account for the fact that on 85 percent of the "volatile acid salts" alkalinity is measured by titration to pH 4.0.

The different chemical parameters which characterize the anaerobic environment are interrelated and one variable may directly or indirectly affect the others. Therefore, a thorough understanding of these interrelationships and an accurate estimate of the pH, alkalinity, volatile acid concentration and carbon dioxide content of the gas are essential to the control of the anaerobic system.

TOXICITY IN ANAEROBIC TREATMENT

It has been shown that the cation concentration affects the rate reaction of anaerobic organisms to a greater extent than the concentration of organic material.

The effects of salt concentration upon the rate of biological reaction are presented in a general manner in Figure 10. This indicates that at some low concentration the salts may have some stimulatory effect on the system until

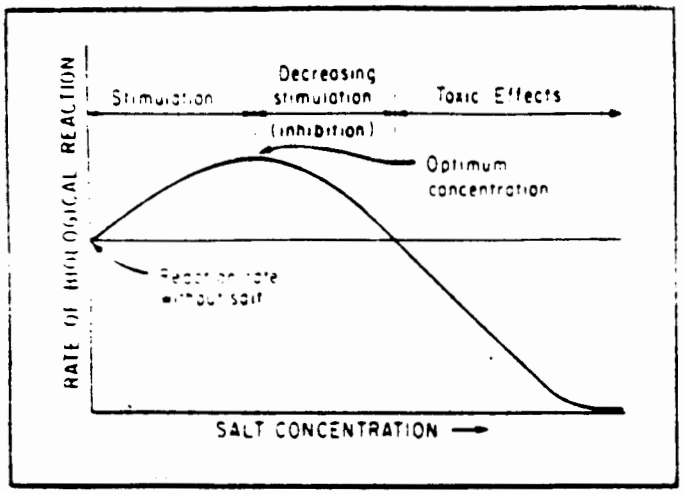


Figure 10. Effects of Salts on Biological Reactions

the concentration reaches a level at which the salt is no longer stimulatory but begins to reduce the rate of reaction below the observed maximum, or is somewhat inhibitory; and eventually, by continuously increasing the concentration of salt the biological activity finally ceases completely. The stimulatory and inhibitory concentrations of some of the common cations are shown in Table IV. The antagonistic and synergistic effects of various combinations of the different salts at different concentrations must be evaluated for the particular waste in question. The data presented in Table IV are indicative of the range of values that may be tolerated in a system. Sodium and potassium are the best antagonists, i.e., will reduce the toxic or inhibitory effects of other cations, if these cations (sodium and potassium) are added up to concentrations within the range at which these cations are stimulatory.

It should be pointed out at this time that the stimulatory or toxic effects of various cations, anions or organic materials to an anaerobic system treating a particular waste is much more complicated than may have been indicated above. Therefore, if the specific waste to be treated anaerobically may be suspect of containing toxic materials the tolerable concentrations of the particular toxic material must be evaluated.

Ammonia, which is essential as a source of nitrogen in nitrogen-deficient wastes and which is released during the anaerobic degradation of organic substrates containing nitrogen, may become toxic to anaerobic bacteria at certain concentrations. The effects of ammonia nitrogen on anaerobic systems are presented in Table V. Ammonia concentrations in excess of 1250 mg/l at high organic loadings resulted in failure of the system; however, at low organic loadings a concentration of ammonia of 5000 mg/l was tolerated. The pH of the environment influences the effects of ammonia, since the equilibrium between ammonia and the ammonium ion is pH sensitive. Free ammonia which is toxic to anaerobic systems is favored at high values of pH.

Sulfides can be toxic to bacteria in an anaerobic system at concentrations in excess of 200 mg/l at a neutral pH near. However, at concentrations between 50 to 100 mg/l, sulfides are tolerated with little or no acclimation. Sulfides may be introduced into the system as a component of the waste or may be produced by the biological reduction of sulfates or degradation of proteins which contain sulfur. Part of the sulfides leave the system as hydrogen sulfide gas, while a portion of the sulfides will be precipitated as heavy metal salts if these metals are present. However, a portion of the sulfides remain dissolved as a weak acid which ionizes depending on the pH of the solution. The dissolved sulfides may have a toxic effect on the bacterial population.

Heavy metals have a toxic effect on the bacteria responsible for anaerobic treatment. Hexavalent chromium may exert a toxic effect on the system, but this metal is normally reduced under anaerobic conditions to the trivalent state which is relatively insoluble at the pH levels encountered in anaerobic systems; therefore, not very toxic. The heavy metals which are quite toxic to bacteria at relatively low concentrations are copper, zinc, and nickel. Iron and aluminum are insoluble at the pH levels in question; therefore, these metals are not toxic.

The concentration of the relatively toxic heavy metals, namely copper, zinc, and nickel which can be tolerated in an anaerobic system is dependent on the concentration of soluble sulfides in the environment. Although soluble sulfides in sufficient concentrations are by themselves toxic to the anaerobic system, this anion will react with the soluble heavy metal ions to form a metal sulfide precipitate which is relatively insoluble. Therefore, in evaluating the tolerance of anaerobic treatment systems to heavy metals, the concentration of anaerobically reducible sulfur compounds must be considered. Approximately 1.8 to 2.9 mg/l of heavy metals are precipitated as metal sulfides by 1.0 mg/l of sulfide ($S^{=}$). This relationship is illustrated by the data presented in Table VI.

TREATMENT UNBALANCE — CAUSES AND CONTROL

The anaerobic waste treatment system may become unbalanced, i.e., operating at less than normal or maximum efficiencies. The cause of these unbalances may be:

a) A sudden change in the environmental conditions, and/or
b) The introduction of toxic substances into the system with the waste to be treated.

The unbalanced anaerobic treatment operation is generally indicated by various parameters including:

a) An increase in the carbon dioxide content of the gas produced and a corresponding decrease in the methane content;
b) A decrease in the total quantity of gas produced daily;
c) An increase in the concentration of volatile acids in the system;
d) A decrease in the pH; and
e) An overall decrease in the efficiency of waste stabilization.

The anaerobic treatment system may be unbalanced temporarily or for a relatively prolonged period. Temporary imbalance may be caused by sudden change in temperature, organic loading, and/or composition of the waste. This type of imbalance can generally be remedied by providing sufficient time to permit the microbial population to adjust to the new environment. Frequently, pH control to a level near neutral, will aid the microbial system to adjust to the new environment. Prolonged or relatively permanent unbalances of the anaerobic system may be the result of the introduction of materials which are toxic to the methane forming bacteria and/or an extreme drop in pH generally caused by improper control. Prolonged imbalance is frequently encountered in starting up a new anaerobic treatment system because in these situations at times the population of methane-forming bacteria does not develop sufficiently to convert the intermediate volatile acids to gaseous end products, and the pH of the system drops to below the minimum level tolerated by the methane bacteria. If the prolonged imbalanced condition is caused by toxic material, the toxic substance must be removed from the waste or the introduction of the toxic agent must be controlled at a level which is not toxic to the system. The imbalances caused by extreme drops in pH may be remedied by providing sufficient time and control of the pH to a level near neutral until the treatment returns to normal efficiency.

Lime is frequently used for pH control; however, one should remember that the pH of the anaerobic system is a function of the carbon dioxide content of the gas as well as the bicarbonate alkalinity and the volatile acids concentrations of the environment. Control of pH is generally desired as the pH drops below pH 6.5 or 6.6. The addition of lime at this pH results in an increase in the bicarbonate alkalinity as shown by the following equation:

$$Ca(OH)_2 + CO_2 \longrightarrow Ca(HCO_3)_2$$

However, the resulting calcium bicarbonate is relatively insoluble, and as the concentration of bicarbonate alkalinity approaches 500 to 1000 mg/l, the continued addition of lime results in the precipitation of the insoluble calcium carbonate, namely:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow + H_2O$$

Therefore, although lime is effective in the control of the pH of an anaerobic treatment system to near neutral, careful control of the addition of lime is imperative because of the interrelationship among the lime added, dissolved carbon dioxide, pH, bicarbonate alkalinity, and the concentration of volatile acids.

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TABLE 1
Volatile Acids Commonly Found During Anaerobic Treatment

Common Name	Formula
Formic Acid	$HCOOH$
Acetic Acid	CH_3COOH
Propionic Acid	CH_3CH_2COOH
Butyric Acid	$CH_3CH_2CH_2COOH$
Valeric Acid	$CH_3CH_2CH_2CH_2COOH$
Isovaleric Acid	$(CH_3)_2CHCH_2COOH$
Caproic Acid	$CH_3CH_2CH_2CH_2CH_2COOH$

TABLE 4
Effects of Cations On Anaerobic Biological Activity

Cation	Stimulatory Concentration mg/l	Moderately Inhibitory Concentration mg/l	Strongly Inhibitory Concentration mg/l
Calcium	100-200	2500-4500	8000
Magnesium	75-150	1000-15000	3000
Potassium	200-400	2500-4500	12,000
Sodium	100-200	3500-5500	8000

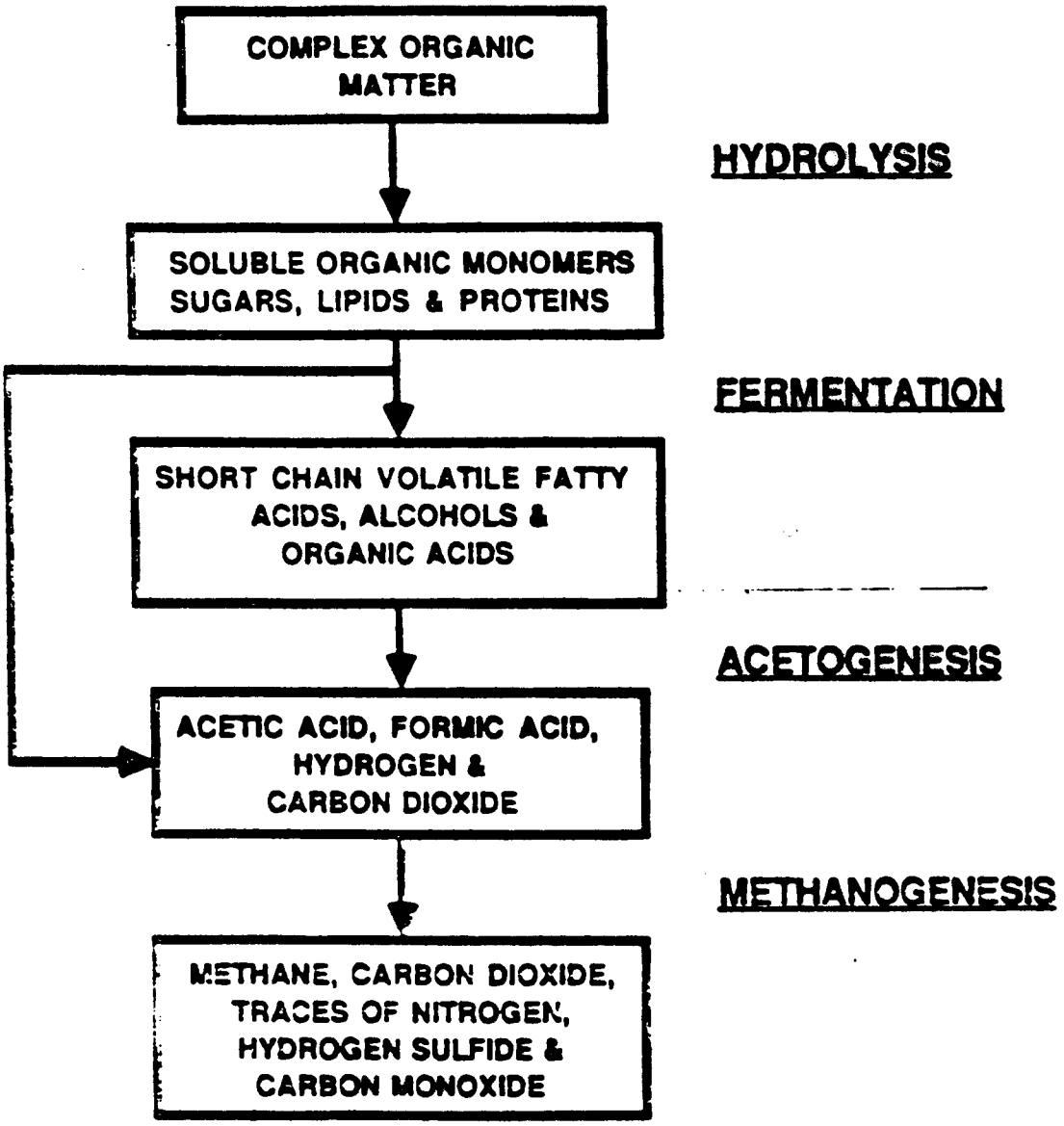
TABLE 5
Effects of Ammonia On Anaerobic Biological Activity

Observed Effect	Ammonia Concentration, mg/l
Beneficial	50-200
No adverse Effects	200-1000
Inhibitory at high values of pH	1500-3000
Toxic	Above 3000

TABLE 6
Precipitation Of Heavy Metal Sulfides

Sulfide Salt	Concentration Of Heavy Metals Precipitated mg/l
Sulfides ($S^{=}$)-- 1 mg/l	1.8-2.0
Sodium Sulfide (Na_2S)-- 1 mg/l	0.75-0.84
Sodium Sulfide ($Na_2S \cdot 9H_2O$)-- 1 mg/l	0.24-0.27

ANAEROBIC DEGRADATION MECHANISM



ADVANTAGES

*LOW ENERGY REQUIREMENTS
*LOW BIOMASS PRODUCTION
*LOW NUTRIENT REQUIREMENTS
*OPERATIONAL ON A SEASONAL OR SWITCH OFF/SWITCH ON BASIS
*ENERGY RECOVERY POSSIBLE
*HEAVY METAL SULFIDES ARE INSOLUBLE IN REDUCING ENVIORONMENT AND NEUTRAL pH

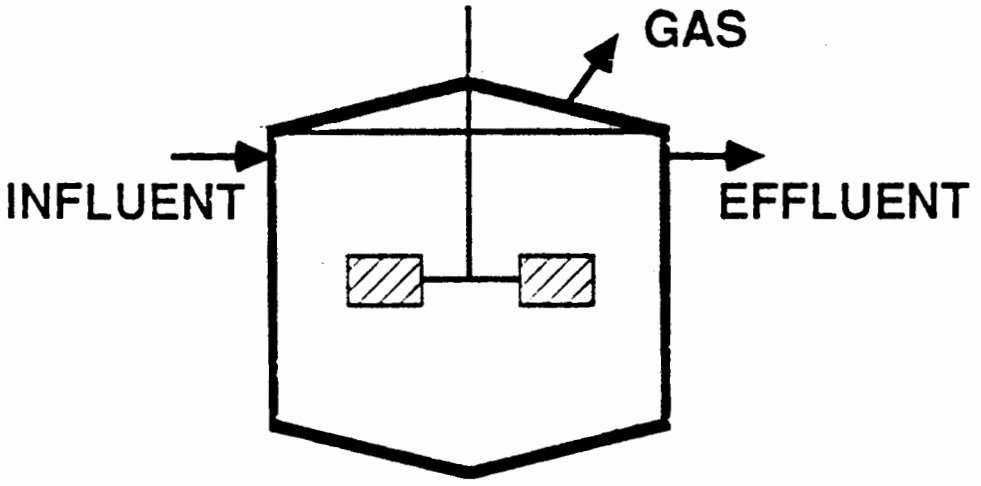
DISADVANTAGES

METHANOGENS GROW SLOWLY
- GENERATION TIMES = 2-30 DAYS

METHANOGENS ARE SENSITIVE TO:
- CHANGES IN TEMPERATURE
- CHANGES IN pH
- CHANGES IN WASTE COMPOSITION

CONTROL PARAMETERS

TEMPERATURE	30-40 C
	50-60 C
ORP	-500 mv
pH	
METHANOGENESIS	6.7-7.7
ACETOGENESIS	as low as 4.5
ALAKALINITY	2,000-3000 mg/L as $CaCO_3$
NUTRIENTS	
HYDRAULIC RETENTION TIME	
SOLIDS RETENTION TIME	

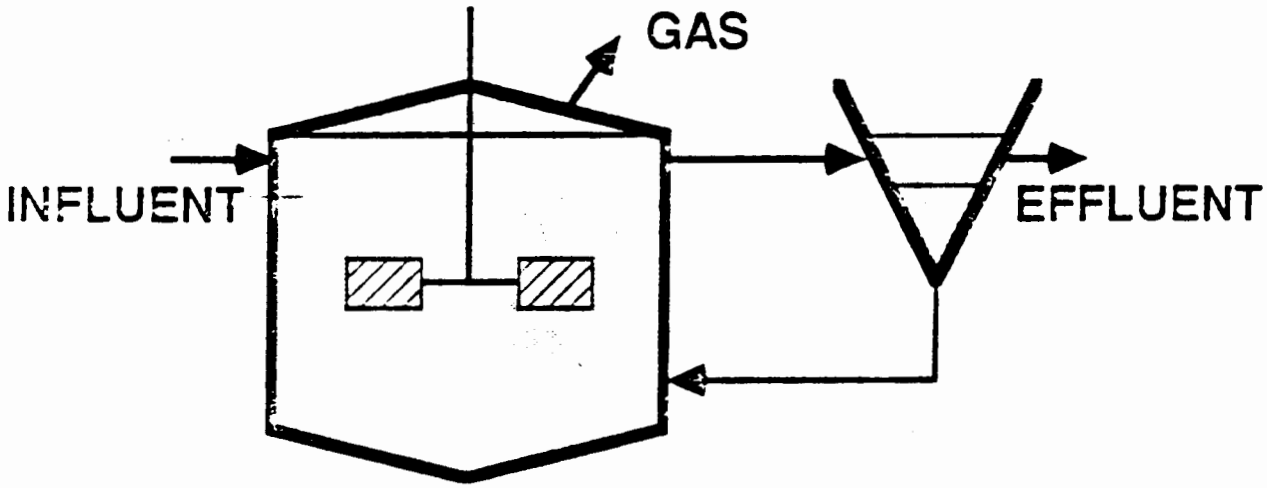


COMPLETELY MIXED REACTOR

ANAEROBIC TREATMENT PERFORMANCE
COMPLETELY MIXED, NO RECYCLE

WASTE SOURCE	INFLUENT BOD mg/L	ORGANIC LOADING RATE kg/cu m-d	HRT days	REMOVAL %
Molasses	15,000	0.7	20.0	99
Beer	22,600*	1.5	15.0	55
Distillery	9,500	1.9	5.0	89
Sugar Beet	32,000	3.2	10.0	96
Wine	22,000	3.2	6.9	97
Molasses	18,000	3.6	5.0	82
Molasses	31,000	3.8	8.0	92
Malt Whiskey	25,000	4.0	6.2	95
Distillery	84,000	8.9	10.0	93
Molasses	100,000*	6.0	16.7	72
Grain Sorghum	67,000*	6.7	10.0	66
Cane Sugar	2,480	0.6	4.0	60
Yeast	6,950	1.7	3.9	70
Palm Oil	65,000*	3.3	20.0	65

*COD

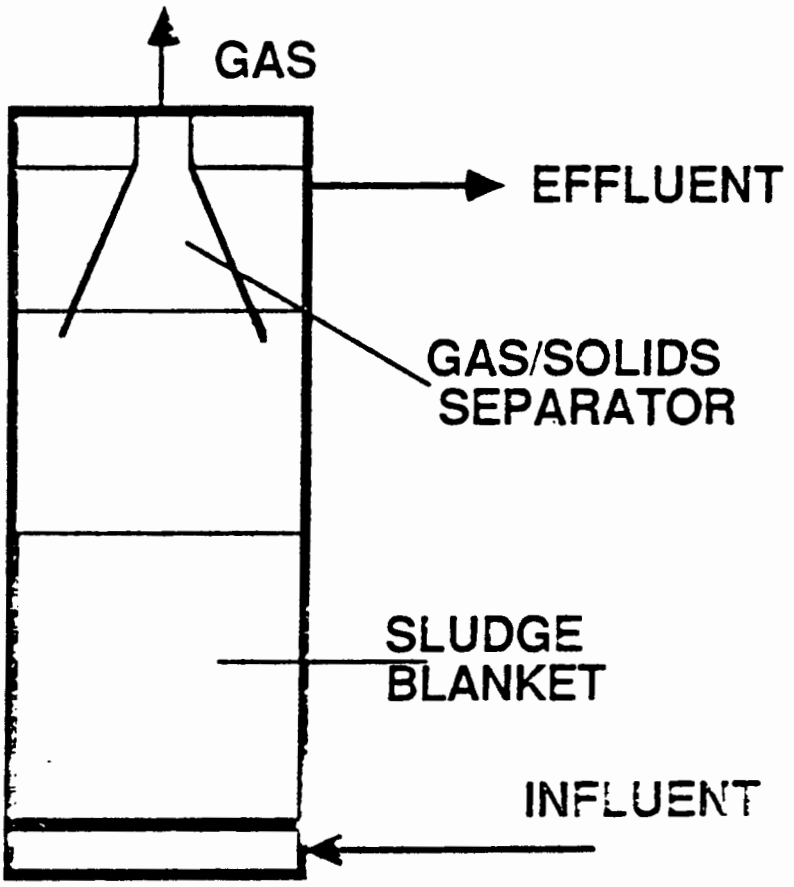


COMPLETELY MIXED REACTOR
WITH RECYCLE

TREATMENT PERFORMANCE
ANAEROBIC CONTACT STABILIZATION PROCESS

WASTE SOURCE	INFLUENT BOD_5 mg/L	ORGANIC LOADING RATE kg/m^3-d	HRT Days	REMOVAL %
Maize Starch	6,280	1.76	3.3	88
Whiskey Distillery	25,000	4.00	6.2	95
Cotton Kiering	1,600*	1.18	1.3	67
Citrus	4,600	3.42	1.3	87
Brewery	3,900	2.04	2.3	96
Meat-Packing	2,000	1.76	1.3	95
Meat-Packing	1,380	2.50	0.5	91
Meat-Packing	1,480	2.63	0.5	95
Meat-Packing	1,310	2.44	0.5	94
Meat-Packing	1,110	2.10	0.5	91
Meat-Packing	1,600	3.20	0.5	95
Wine	7,300	1.50	5.0	99
Distillery	15,000	7.50	2.0	90
Distillery	20,000*	8.30	2.0	85
Rum	55,000*	10.00	5.5	80
Beet Sugar	1,200*	1.20	1.0	
Beet Sugar	1,200*	2.00	1.0	

*COD



ANAEROBIC UPFLOW SLUDGE
BLANKET REACTOR

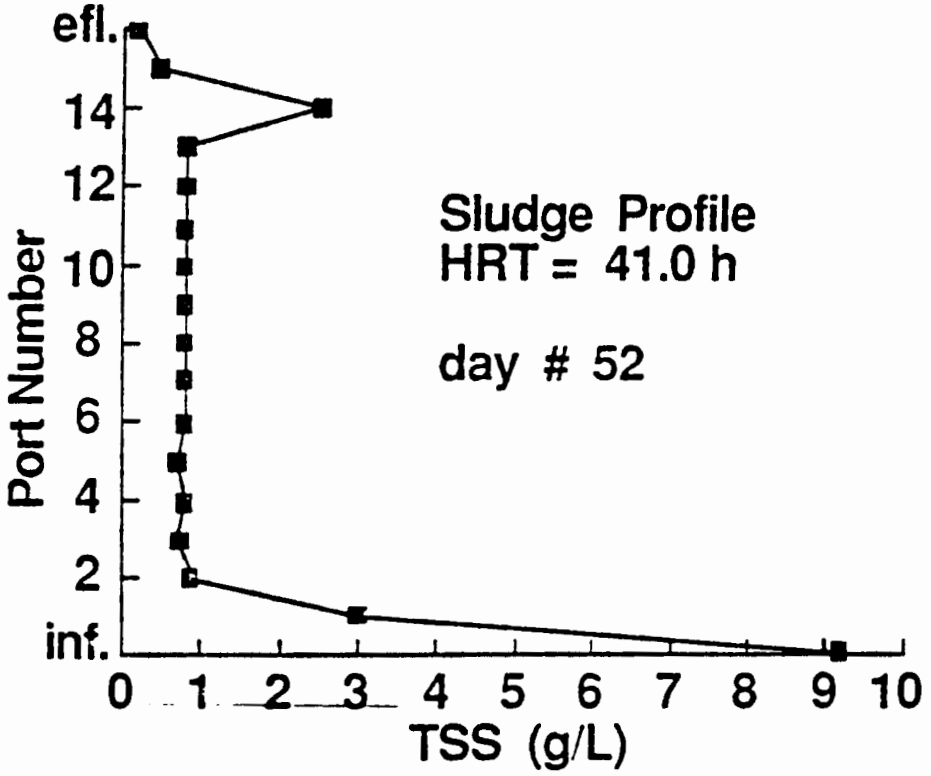
ANAEROBIC TREATMENT PERFORMANCE
UPFLOW SLUDGE BLANKET

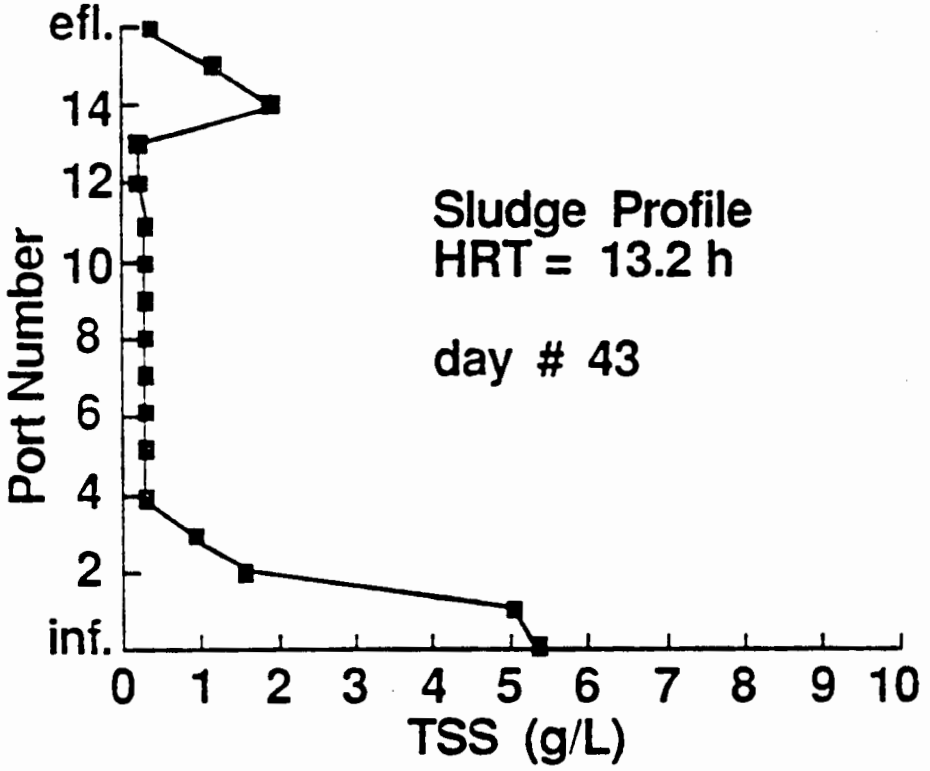
WASTE SOURCE	INFLUENT COD mg/L	ORGANIC LOADING RATE kg/m^3-d	HRT hrs	REMOVAL %
Wheat Starch	2,740	5.5	22	85
Potato	4,300	6.0	18	80
Potato	11,670	7.0	40	94
Barley Starch	5,200	7.8	15	80
Potato Starch	22,000	11.0	47	85
Sugar	17,000	13.3	24	94
Beer	2,500	14.1	5	80
Beet Sugar	3,000	16.2	4	88
Molasses	66,000	18.3	31	45

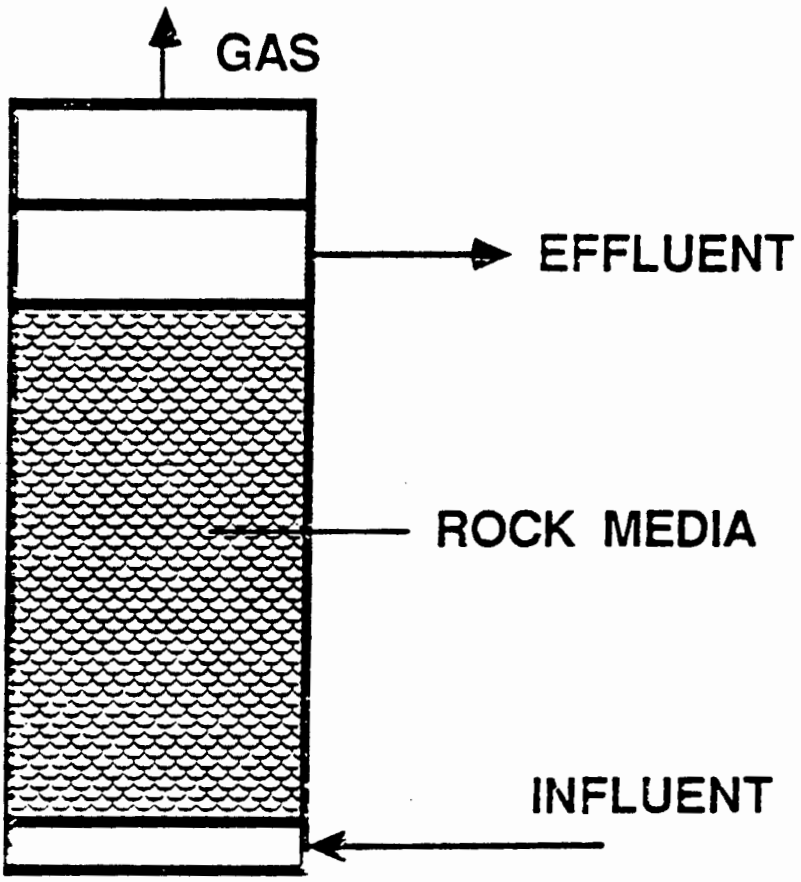
PERFORMANCE OF UASB REACTOR
($T = 35^{o}C$)

HRT (Hours)	27.2	13.2	41.0
Flow (L/d)	21.5	44.2	14.2
Infl COD (g/L)	3.3	2.4	8.3
COD Load (g/d)	29.2	43.6	48.5
COD Removal (%)	95	50	90
Gas Production (L/d)	29.0	19.5	41.6
m^3/kg COD	0.43	0.36	0.39

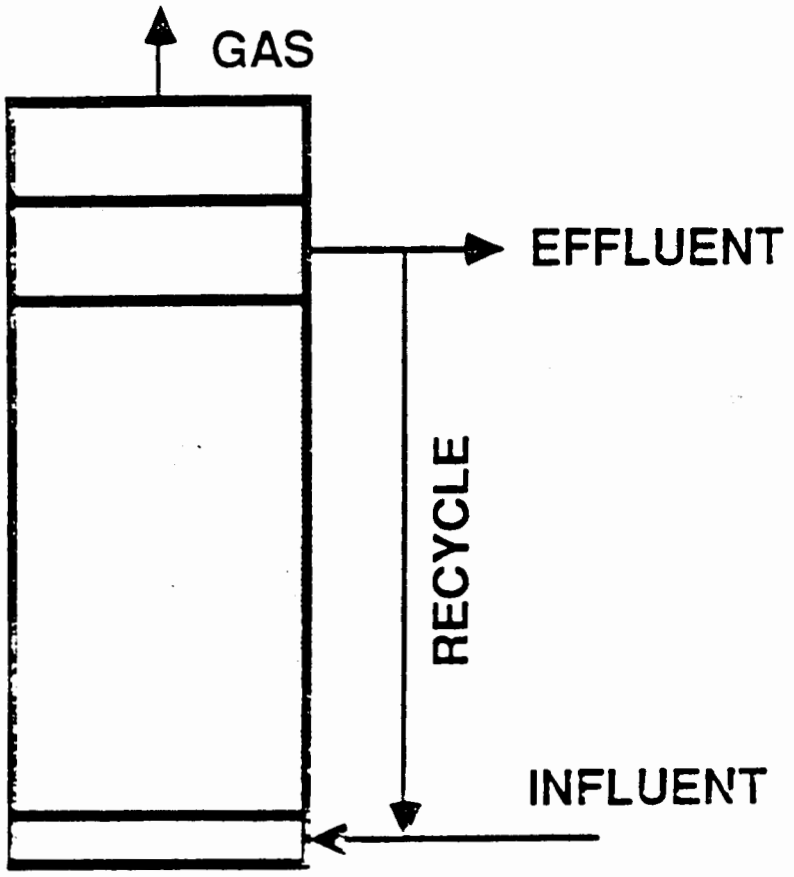
(Craveiro and Malina, 1985)


efl.
14
12
10
8
6
4
2
inf.
Port Number
0 1 2 3 4 5 6 7 8 9 10
TSS (g/L)
Sludge Profile
HRT = 41.0 h
day # 52

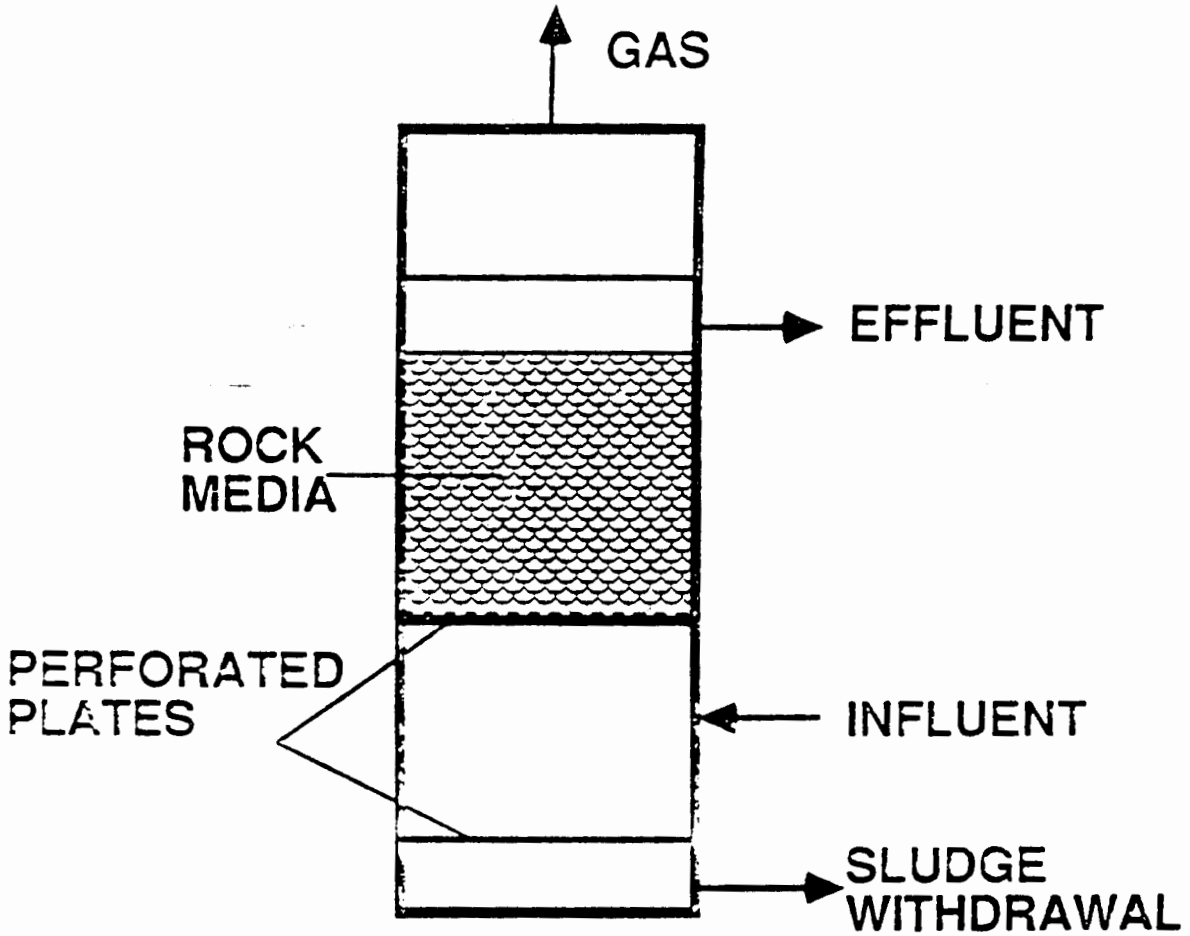

efl.
14
12
10
8
6
4
2
inf.
Port Number
0 1 2 3 4 5 6 7 8 9 10
TSS (g/L)
Sludge Profile
HRT = 13.2 h
day # 43



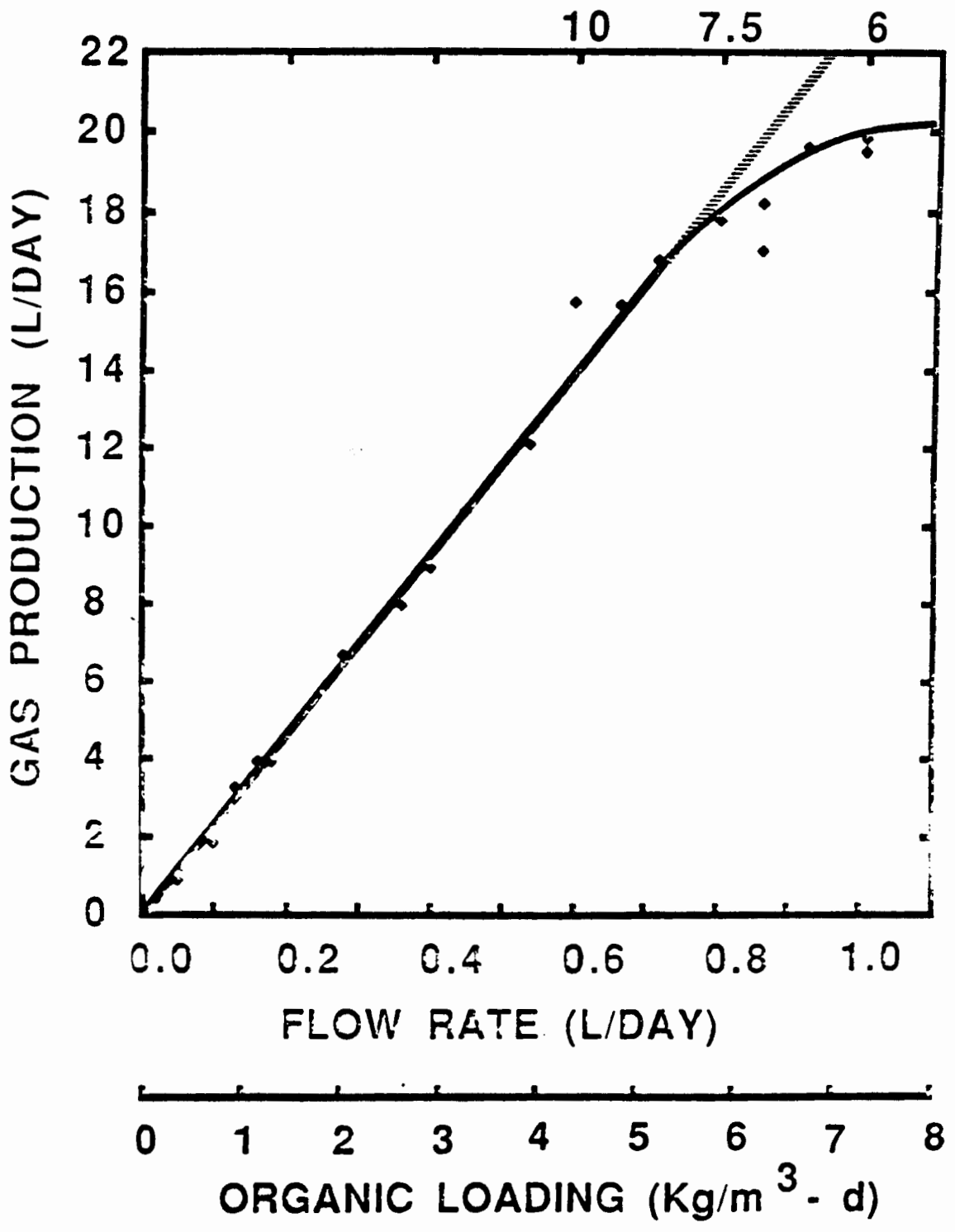
ANAEROBIC UPFLOW PACKED
BED REACTOR



ANAEROBIC FLUIDIZED BED REACTOR



ANAEROBIC UPFLOW PLUG/PACKED
BED REACTOR


HYDRAULIC RETENTION TIME (days)
10
7.5
6
22
20
18
16
14
12
10
8
6
4
2
0
GAS PRODUCTION (L/DAY)
0.0
0.2
0.4
0.6
0.8
1.0
FLOW RATE (L/DAY)
0
1
2
3
4
5
6
7
8
ORGANIC LOADING (Kg/m 3 - d)

ECONOMICS OF ENERGY RECOVERY

DESIGN FACILITY	
ALOCHOL PRODUCTION	550,000 L/Yr
PRODUCTION COSTS	$0.62/Liter
WASTEWATER PRODUCTION	9,000 Gal/Day
	34 m^3/Day
COD	45,000 mg/L
ANAEROBIC PACK BED REACTOR	
HYDRAULIC RETENTION TIME	6 Days
REACTOR VOLUME	54,000 Gallons
	205 m^3
COD REMOVAL	65%
METHANE PRODUCTION	15,000 FT^3/D
	425 m^3/Day
ENERGY VALUE	$5.5X10^9$ BTU/Yr.
CAPITAL COST	
$120,000	
OPERATING COSTS	$1,250/Yr
TOTAL AMORTIZED COSTS	$20,650/Yr
13% INTEREST	
PLANT LIFE = 15 Years	
COST RECOVERY	
$27,500/Yr	
GAS VALUE = $5/$10^6$ BTU	
NET PROFIT	$6,850/Yr
CAPITAL COSTS RECOVERED IN 4.4 Years	

AEROBIC POST TREATMENT
ANAEROBIC PACKED BED EFFLUENTS
MUNICIPAL SEWAGE

TREATMENT	COD (mg/L) INFLUENT TOT	INFLUENT FILT	EFFLUENT TOT	EFFLUENT FILT
30 MIN AERATION	93	69	87	59
TRICKLING FILTER	106	85	75	54
	91	68	71	41

(MITZUTANI AND MALINA, 1985)

PERFORMANCE COMPARISON ANAEROBIC PROCESSES*

REACTOR TYPE	COD LOADING $Kg/m^3.d$	COD REMOVAL %
Contact	1 - 6	80 - 95
Upflow Packed Bed	1 - 10	80 - 90
Fluidized/expanded Bed	1 - 20	80 - 87
Downflow Packed Bed	5 - 15	75 - 88
Upflow Sludge Blanket	5 - 30	85 - 95

* van den Berg & Kennedy, 1983

ANAEROBIC TREATMENT OF DOMESTIC SEWAGE

PROCESS	BOD_5 mg/l	COD mg/l	REFERENCE
Packed Bed	40	---	Genung (1985)
	38	78	Kobayashi (1983)
UASB	15-100	40-360	Lettinga (1983) Grin(1985) Shellinkout (1985)
Expanded/ Fluidized Bed		40	Jewell (1981)
		100-120	Bowker (1981)
	20-30		Yoda (1985)
		40-80 (Activated Carbon)	Jeris(1985)
		80-90 (Sand)	

ANAEROBIC TREATMENT
MUNICIPAL SEWAGE
UPFLOW PLUG/PACKED BED REACTOR

COD (mg/L)					
INFLUENT		EFFLUENT		GAS	TIME*
TOT	FILT	TOT	FILT	PROD cu m/kg	day
232	75	93	69	0.07	18
223	104	106	85	0.17	30
183	102	91	68	0.30	38
236	118	242	205		1**
211	106	89	75		***

* TIME FROM START OF OPERATIONS
** AFTER 15-DAY RESTING PERIOD
*** AVERAGE FOR DAYS 3 THROUGH 13 AFTER 15-DAY RESTING PERIOD

(MITZUTANI AND MALINA, 1985)

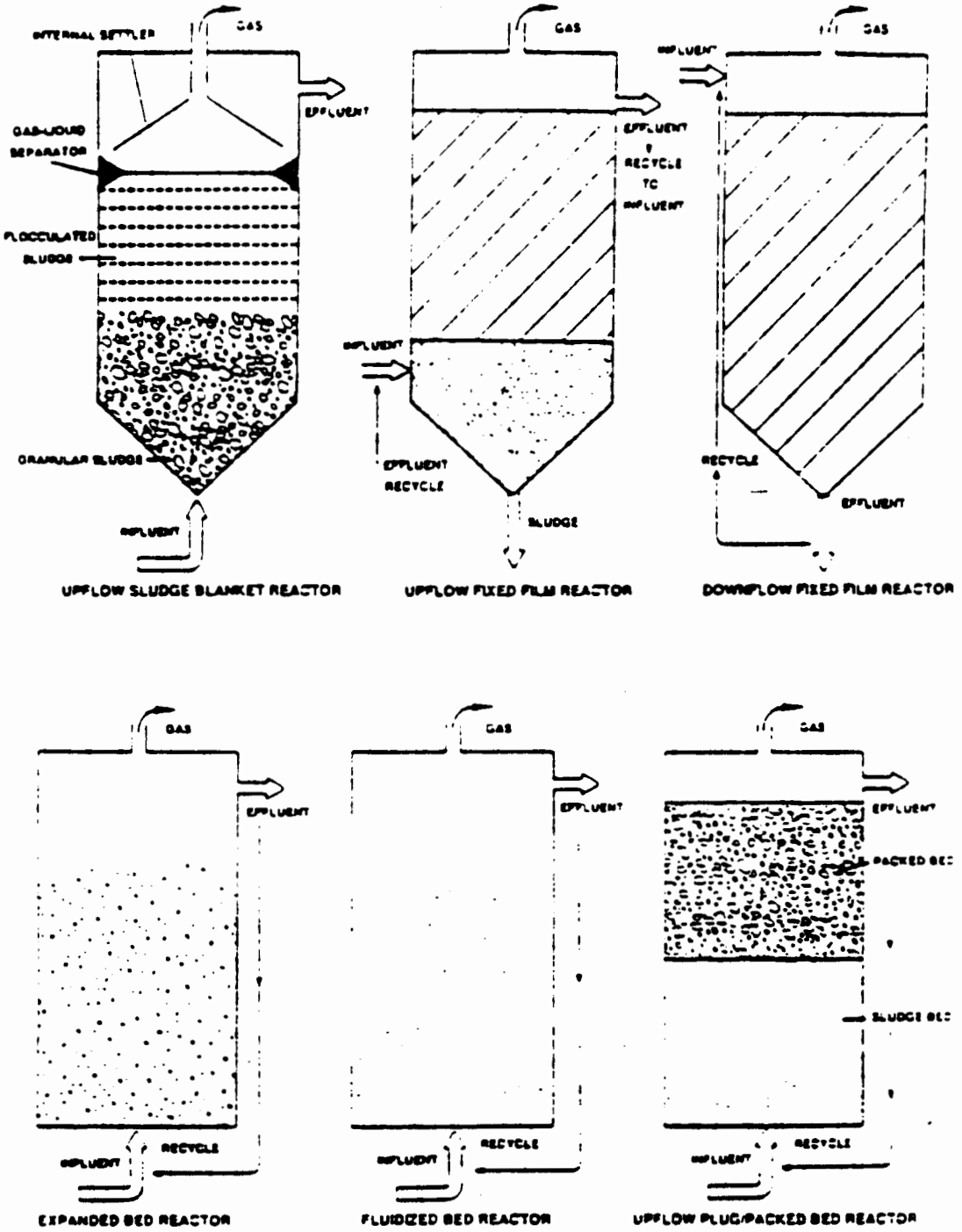


FIGURE 2.4: VARIOUS TYPES OF ANAEROBIC REACTORS - PART :

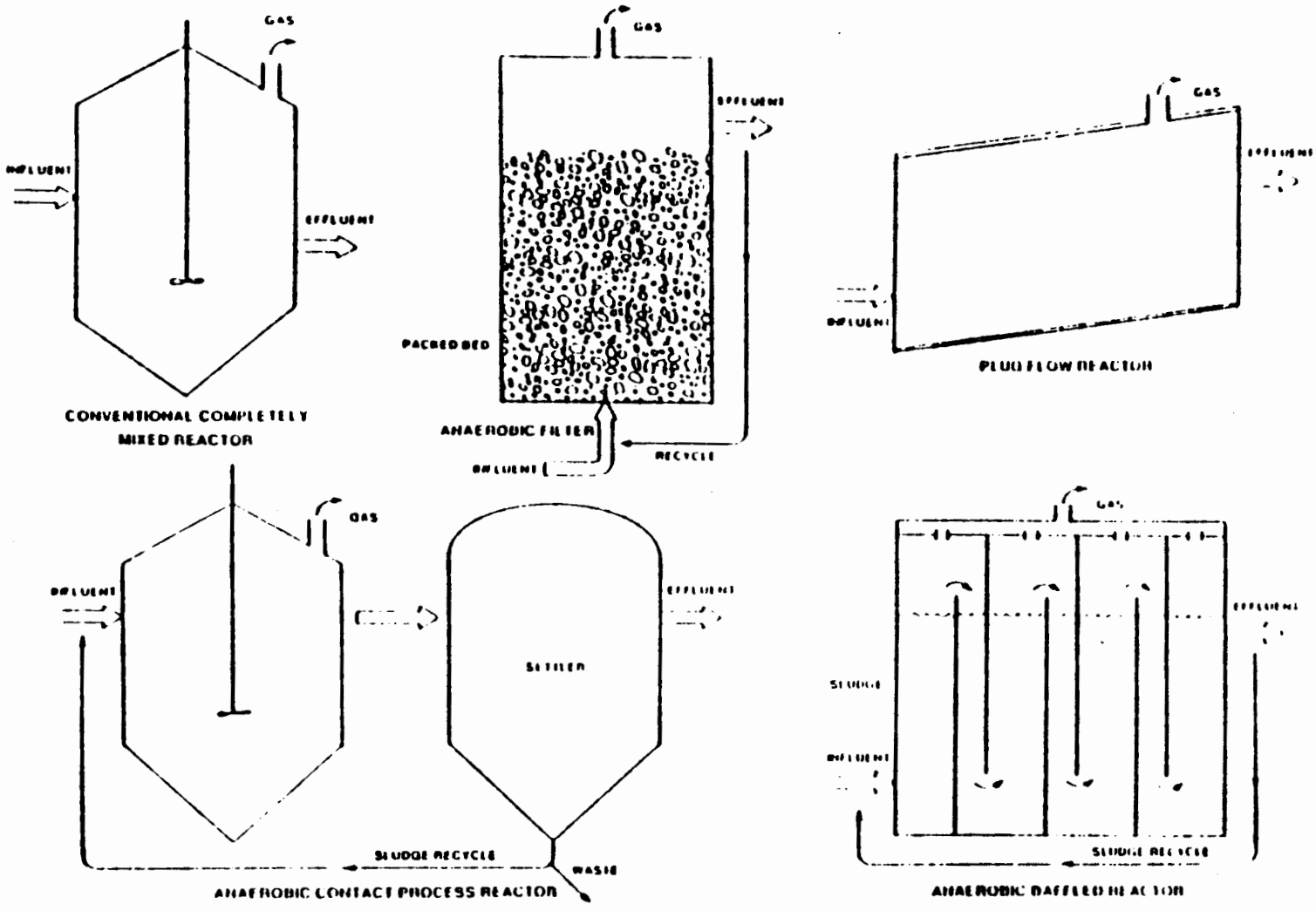


FIGURE 2.5: VARIOUS TYPES OF ANAEROBIC REACTORS PART II

a series of meetings encompassing all shift workers in operations. All technical and engineering personnel that could be involved in design of pollution control facilities or new operating units also should be included.

WATER REUSE

It has been estimated that the petroleum refining and petrochemical industry of the United States today would require more than 12 billions of gallons of water per day if none of the water was used more than one time. The actual water intake of U. S. refineries, however, is only slightly in excess of 20 percent of this amount. A graphical depiction of this water use delineation is shown in Figure 33.

The bulk of the water in the refinery is composed of recirculated water. Recycle of cooling water over cooling towers and back through heat exchangers is one of the most widely applied reuse practices and accounts for approximately 90 percent of the reused water. It has a lower quality requirement than most process applications and therefore provides an excellent opportunity for water reuse and conservation.

Steam condensate provides a high quality of water and this source can be used for recycle. This condensate can be collected and returned to boiler feed systems, then thermal conservation and water saving results in substantial cost reductions. In some cases, steam which is used for heating or other uses can be reused in a lower pressure system.

The use of air fans can result in a 25-fold decrease in the volume of contaminated cooling water used in barometric condensers. Boiler feed water requirements may be reduced by reusing intermediate and high pressure

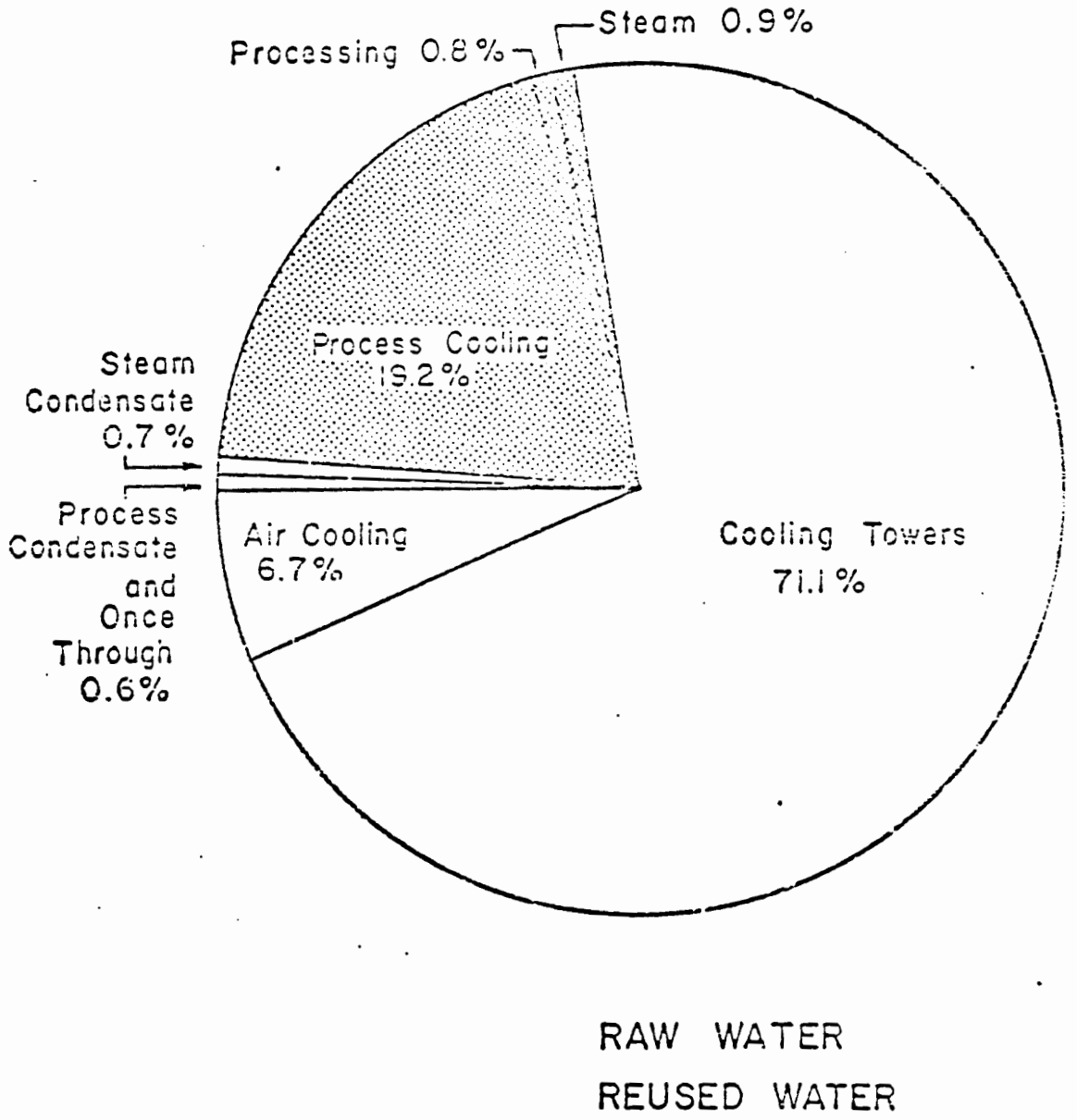

Steam 0.9%
Processing 0.8%
Process Cooling 19.2%
Steam Condensate 0.7%
Process Condensate and Once Through 0.6%
Air Cooling 6.7%
Cooling Towers 71.1%
RAW WATER
REUSED WATER

FIGURE 33

boiler blowdown in low pressure boilers. Additionally, the approach of recycling boiler blowdowns and using them for stripping operations has been practiced at several petrochemical installations.

Many refineries are charging used water to electrical crude oil distillers, a process designed to remove salts, solids, and formation water from unrefined crude before the crude is given subsequent processing. Process condensate and sour water stripper bottoms are often used as desalter makeup. Phenolic laden water is often recycled back to desalters as phenols tend to be taken up by the crude.

Water reuse is often practiced in cokers where large volumes of high pressure water are required to cut coke from the coke drums. This water can be recycled through a gravity separator to remove floating oil and settleable coke fines, then back to the coking unit. As some water leaves with the bulk coke, makeup water is required. This makeup has a low quality tolerance and provides an excellent opportunity to bring in used water from another source within the refinery.

It has been estimated that there is an approximate loss of four percent volume as cooling water makes one pass through the tower. The primary water quality constraint for makeup water to offset this loss is total dissolved solids (TDS). If selected waste streams containing low dissolved solids can be treated for oil removal, they provide an excellent source for cooling tower makeup. This practice will not only reduce the plant water consumption, but also provide organic removal biochemically in the tower as previously discussed.

Another application of used water is storage as a firewater source. The quality requirements for this water are relatively lax and treated

refinery effluent is commonly used for this purpose. Moreover, this water can be used for wash down operations and other similar applications.

Reuse can be better applied if a segregated wastewater collection system exists. Segregation systems used by the petrochemical industry vary widely depending on the reuse requirements, effluent quality requirements, and undesirable effects of commingling specific streams. The bases for the segregation of waste streams are outlined as follows.

1. Uncontaminated Sewers:

   Sewers and drains carrying low or non-organic wastewaters, such as cooling tower and boiler blowdown, uncontaminated storm runoff, etc. This stream may be segregated further into low TDS and high TDS sewers.

2. Contaminated Sewers:

   Sewers and drains receiving contaminated wastewater primarily discharged from process operations. The flow from dumps, spills, and cleaning operations are normally conveyed to this system. It should also have capacity for storm runoff from dirty process areas. Further segregation of contaminated waters may be on an oily and non-oily basis.

3. Sanitary Sewage System:

   This system receives water from sanitary facilities in the process areas, administration facilities, and central shower and locker room buildings.

An example of a segregation system at one refinery and the treatment facilities is illustrated in Figure 34.

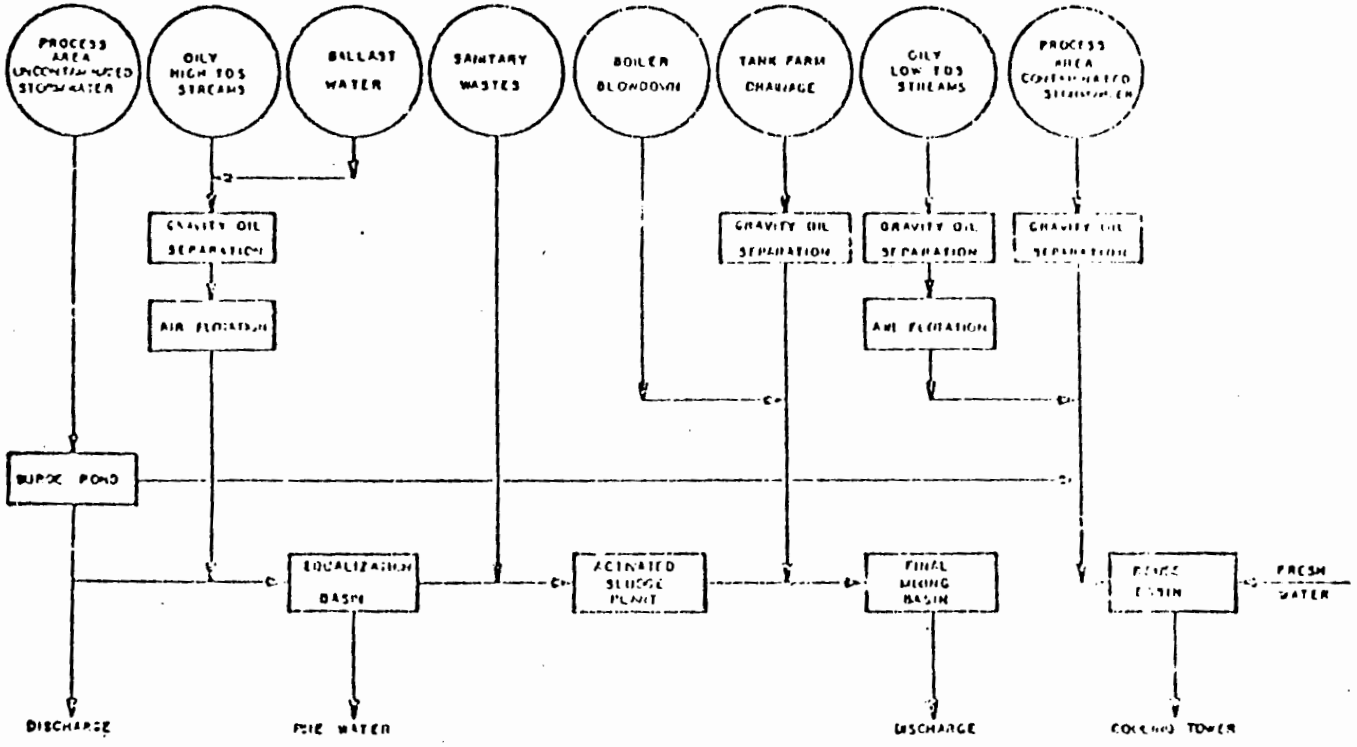

PROCESS AREA UNCONTAMINATED STORMWATER
OILY HIGH TDS STREAMS
BALLAST WATER
SANITARY WASTES
BOILER BLOWDOWN
TANK FARM DRAINAGE
OILY LOW TDS STREAMS
PROCESS AREA CONTAMINATED STORMWATER
GRAVITY OIL SEPARATION
GRAVITY OIL SEPARATION
GRAVITY OIL SEPARATION
GRAVITY OIL SEPARATION
AIR FLOTATION
AIR FLOTATION
SURGE POND
EQUALIZATION BASIN
ACTIVATED SLUDGE PLANT
FINAL MIXING BASIN
FRESH WATER
DISCHARGE
FIRE WATER
DISCHARGE
COOLING TOWER

FIGURE 34

Most water reuse schemes also require additional waste stream segregation and the design of the segregation system will depend upon the type of water reuse being employed at the individual plant. If biological treatment is used to stabilize petrochemical wastes, the sanitary sewage is usually added to it prior to treatment as a source of biological nutrients. However, many regulatory agencies require effluent chlorination when sewage is added, making such a combination unfeasible.

Treatment, reuse, and economics are, of course, all interrelated. The higher the quality demand for reuse, the more costly the treatment processes required to produce this quality. This is illustrated in Figure 35. As noted in this illustration, there is a surcharge associated with reuse when the corresponding water quality requirements are more stringent than those for discharge to the receiving environment. This is not expected to occur frequently, however, as quality levels for final discharge as imposed by the EPA and State regulatory agencies are becoming increasingly stringent. Conversely, when the quality requirements for reuse are less stringent than for final discharge, there is a direct saving involved. The incentive for reuse in light of increasingly stringent effluent quality requirements is therefore apparent. This emphasis should be tempered, however, by a recognition of the relative difficulty associated with treating reused waters. There is a treatment penalty caused by increased water losses through conveyance and evaporation coupled with increasing levels of TDS, residual organics, inert or benign inorganics, and heat. The application of control measures and/or treatment processes required for reuse or disposal of refinery effluents are summarized in Table 34. Contrary to the tenets of the 1972 Water

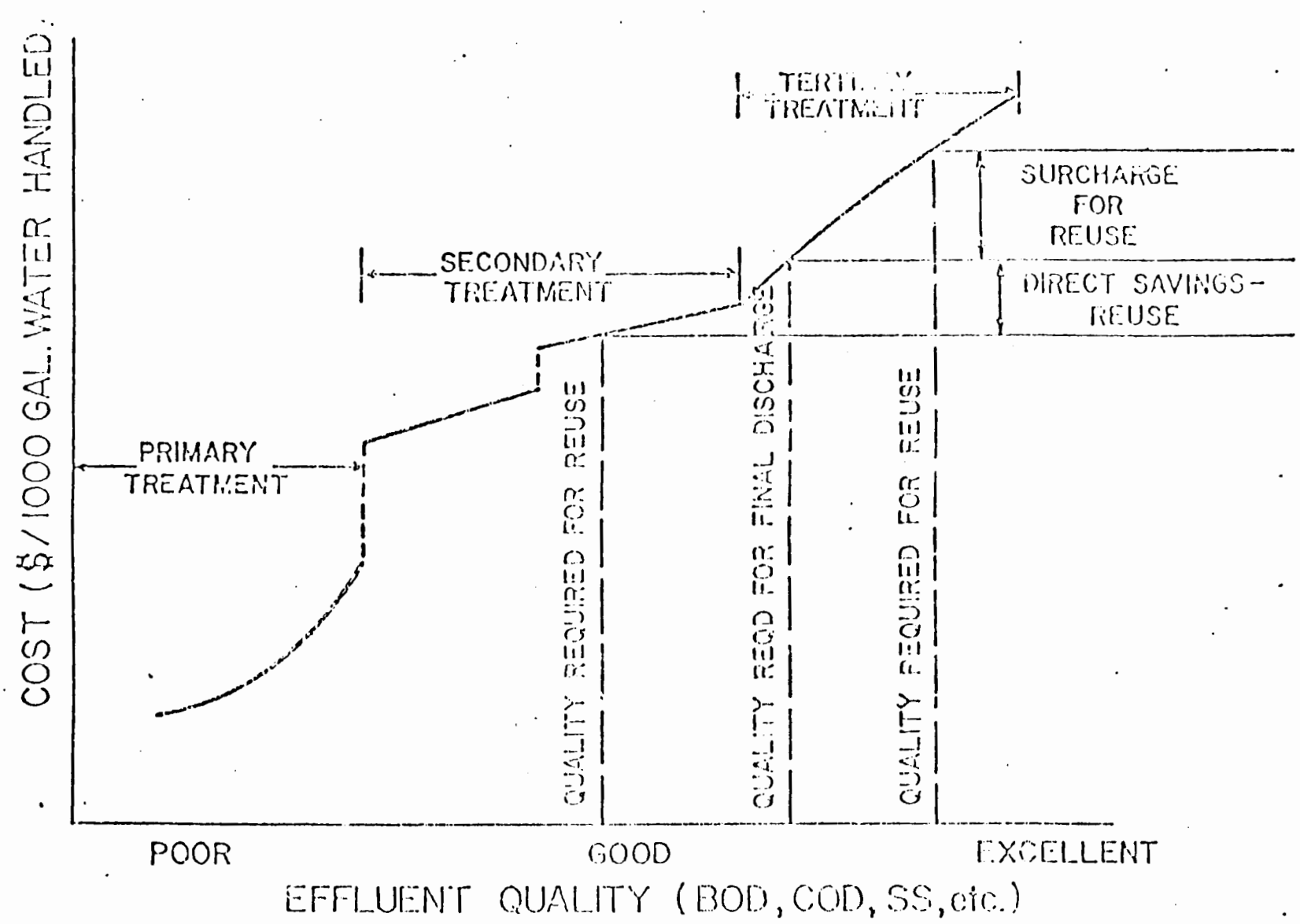

COST ($/1000 GAL. WATER HANDLED)
TERTIARY TREATMENT
SURCHARGE FOR REUSE
SECONDARY TREATMENT
DIRECT SAVINGS - REUSE
PRIMARY TREATMENT
QUALITY REQUIRED FOR REUSE
QUALITY REQD FOR FINAL DISCHARGE
QUALITY REQUIRED FOR REUSE
POOR
GOOD
EXCELLENT
EFFLUENT QUALITY (BOD, COD, SS, etc.)

FIGURE 35

TABLE 34

TREATMENT REQUIRED FOR REUSE AND/OR DISCHARGE OF REFINERY EFFLUENTS

Contaminants	In-Plant	Primary	Intermediate	Secondary	Tertiary	Quaternary
Oil	Segregation, concentration, housekeeping	API separator, tilted-frame separator, filtration	Air flotation, mechanical flotation, media filtration			
Soluble COD	Housekeeping		Chemical precipitation, flotation or gravity separation, equalization	Activated sludge, aerated lagoon, chemical oxidation	Media filtration, carbon adsorption	Reverse osmosis
Hardness	Segregation				Chemical precipitation	Ion exchange
Other TDS	Segregation					Ion exchange, reverse osmosis, electrodialysis
Phosphorus	Segregation, substitution			Activated sludge, aerated lagoon	Chemical precipitation	
Heavy metals	Housekeeping, substitution, segregation	Ponding			Chemical precipitation, chemical oxidation, media filtration	Ion exchange
Sulfides	Segregation, steam stripping				Chemical oxidation	
Ammonia	Substitution, segregation, steam stripping		Trickling filter	Activated sludge	Denitrification	Ion exchange

Bill (3), blowdown at some point within a refinery-petrochemical water system will have to occur, and this stream will be highly contaminated. Moreover, the solids generation rates will still prevail and are not reduced proportionately to water reduction through reuse.

An estimate of blowdown from a water use/reuse system within a refinery-petrochemical complex can only be accomplished by calculating a water and constituent mass balance. A simplified diagram for a refinery reuse scheme such as the one shown in Figure 33 can first be prepared to facilitate the mass balance circulation.

ECONOMICS OF REFINERY WASTEWATER TREATMENT

Implementation of the water pollution control objectives as set forth in the Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500) will have an express economic impact on the petroleum refining and petrochemical industry. A comprehensive economic analysis was recently conducted by the American Petroleum Institute to predict the cost of reaching the three incremental levels of effluent quality objectives as stated in the aforementioned legislation. The first level of treatment generally corresponds to "Best Practicable Technology Currently Available," the second level is the "Best Available Technology," and the third level is the complete Elimination of Discharge of Pollutants (EDOP).

The first level of treatment has been defined elsewhere (1.4) but is generally interpreted as including pretreatment, activated sludge, and effluent polishing using filtration. The second level of treatment includes the additional steps of elimination of once-through cooling water, reuse of treated effluent, and the addition of carbon adsorption. The third level,

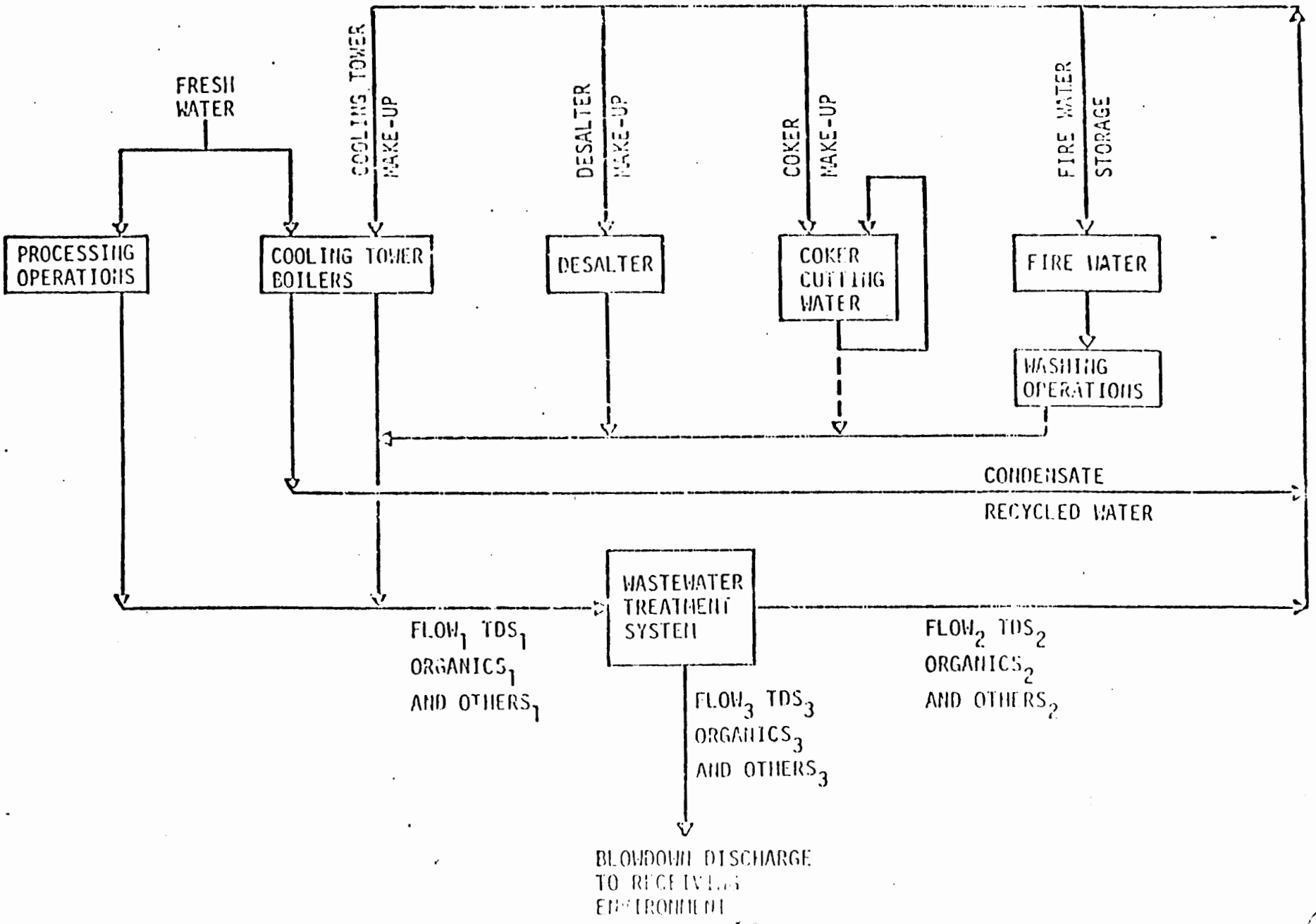

FRESH WATER
COOLING TOWER MAKE-UP
DESALTER MAKE-UP
COKER MAKE-UP
FIRE WATER STORAGE
PROCESSING OPERATIONS
COOLING TOWER BOILERS
DESALTER
COKER CUTTING WATER
FIRE WATER
WASHING OPERATIONS
CONDENSATE
RECYCLED WATER
WASTEWATER TREATMENT SYSTEM
FLOW1 TDS1
ORGANICS1
AND OTHERS1
FLOW2 TDS2
ORGANICS2
AND OTHERS2
FLOW3 TDS3
ORGANICS3
AND OTHERS3
BLOWDOWN DISCHARGE
TO RECEIVING
ENVIRONMENT

FIGURE 3

TREATMENT PROCESSES AND RESIDUALS

TABLE 1. TREATMENT PROCESSES AND RESIDUALS

Classification	Processes	Residuals
Water Treatment	Softening, coagulation sedimentation	Calcium carbonate, sludge and aluminum hydroxide sludge
Preliminary Treatment	Screening and Grit Removal Neutralization, oil water separation	Screening (rags, sticks, etc.) Grit (sand, silt, cinders) Chemical sludge, oil, oily solids
Primary Treatment	Sedimentation or Dissolved Air Flotation	Organic sludge and skimmings (grease and other floating materials)
Intermediate Treatment (Chemical)	Coagulation and Sedimentation	Sludge containing organic solids and chemical precipitate and skimmings
Secondary Treatment	Activated sludge, contact stabilization, extended aeration, trickling filters, rotating bio-discs, etc. followed by secondary clarification	Biological Sludge
	Stabilization Pond	Algae in the effluent
Disinfection	Chlorination Ozonation	
Land Application of Effluents	Pretreatment by primary and biological treatment or chemical treatment	Suspended solids in the effluent applied to the land
Advance Treatment	Coagulation and Sedimentation	Chemical Sludge (aluminum, hydroxide and Ferric hydroxide)
	Sand Filtration	Suspended solids in backwash water
	Adsorption on activated carbon	Spent activated carbon which can be regenerated
	Ion Exchange	Spend regenerant
	Membrane Processes (Reverse osmosis, electrodialysis, etc.)	Concentrated brine
Sludge Treatment	Anaerobic Digestion Aerobic Digestion	Organic material which is partially stabilized, usable gas (methane)
Sludge Concentration	Gravity or Flotation thickening	More concentrated sludge
Sludge Dewatering	Vacuum Filtration Filter press, centrifuge	Sludge Cake
Sludge Disposal	Incineration Pyrolysis Land disposal Ocean disposal	Ash Various products Sludge

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TABLE 2
RESIDUALS FROM MUNICIPAL TREATMENT

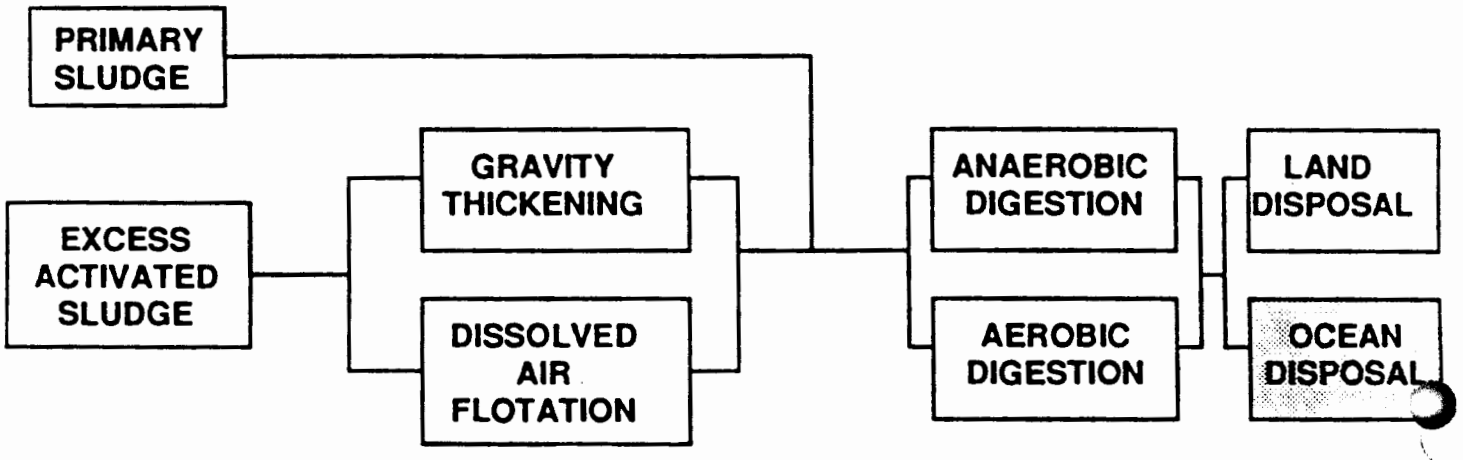
TREATMENT	RESIDUE lb/MG	RESIDUE Gal/MG	RESIDUE cuft/MG
PRELIMINARY			
Screening			0.17-11.7 (1.5)
Grit			0.39-10.5 (2.61)
PRIMARY			
Sludge	1,250	3,675	
Skimmings			0.05-29.78 (7.03)
BIOLOGICAL			
Activated Sludge	1,025	12,300	
Trickling Filter	475	750	
THICKENING			
Gravity/flotation	2,275	4,410*	
SLUDGE DIGESTION			
Primary & Biological	1,262	2,500** (4,000)***	
ADVANCED			
Coagulation & Sedimentation			
Alum****	(2,000)	(12,000)	
Iron****	175-781 (507)	6,000-36,000 (22,000)	
Lime****	3,100-6,800 (4,650)	50,000-63,000 (53,400)	

* Combined primary and waste activated sludge are thickened to 6% TS
** Stabilized sludge solids concentrate to 6% TSS
***Total volume of sludge solids and supernatant
****Numbers in () are typical values

UNIT PROCESSES	FUNCTIONS
Thickening gravity flotation	Water Removal Volume Reduction Blending
Biological Stabilization Aerobic Digestion Anaerobic Digestion Composting	Pathogen Destruction Volume and Weight Reduction Odor Control Putrescibility Control Gas Production (Anaerobic Digestion)
Conditioning	Improve Dewatering Rate Improve Solids Capture Improve Compactability
Belt Filters	Water Removal Solids Capture Change to Damp Cake Volume and Weight Reduction
Dewatering Vacuum Filter Filter Press Centrifuge	Water Removal Volume and Weight Reduction Change to Damp Cake Reduces Fuel Requirements for Incineration/Drying
Drying Beds or Heat Drying	Water Removal
Incineration	Destruction of Solids Water Removal Conversion Sterilization
Final Disposal	Irrigation Cropland Energy Land Reclamation Landfill Ocean Disposal Incineration

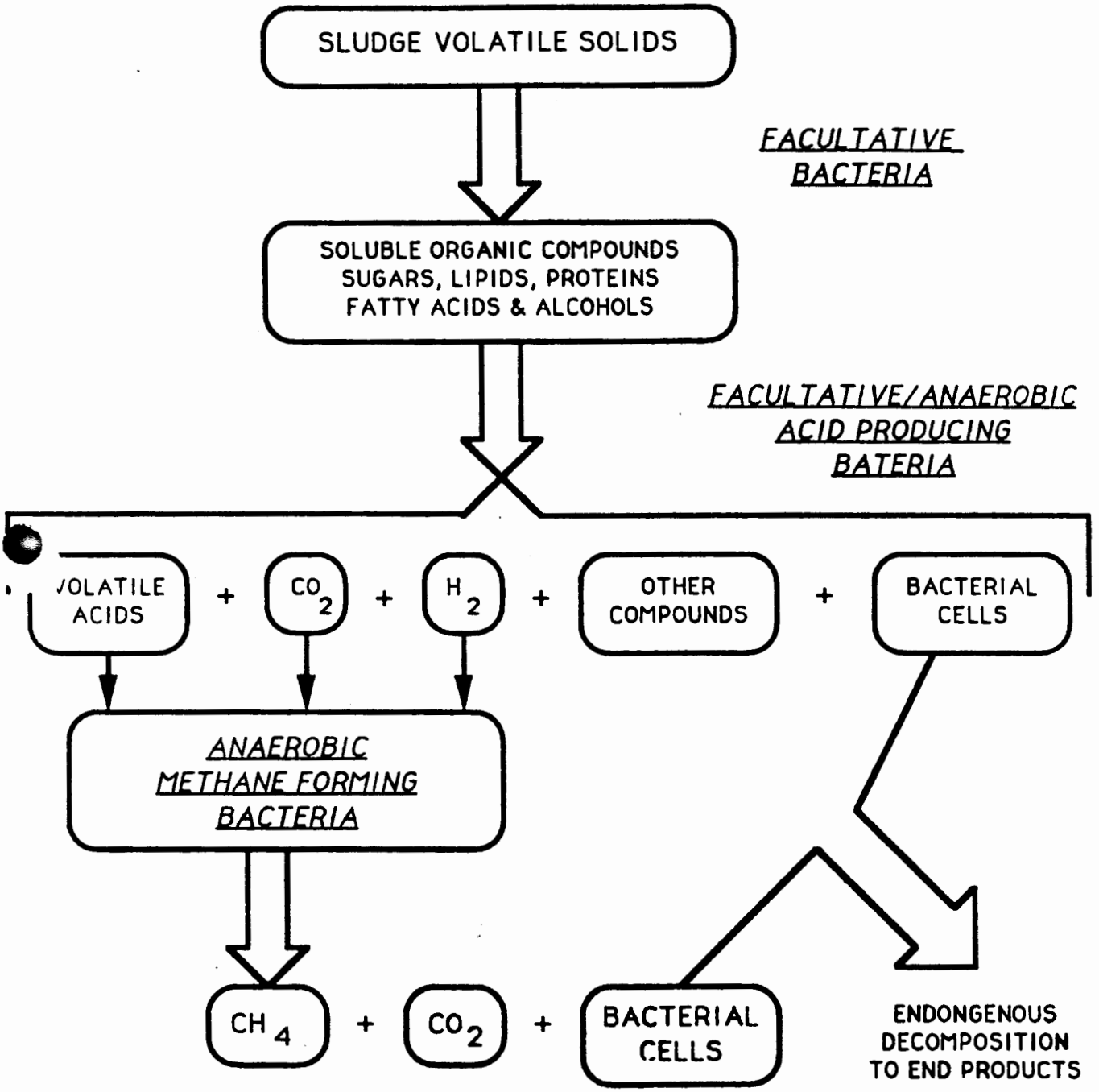
FIGURE 1
SLUDGE TREATMENT PROCESSES AND THEIR FUNCTIONS

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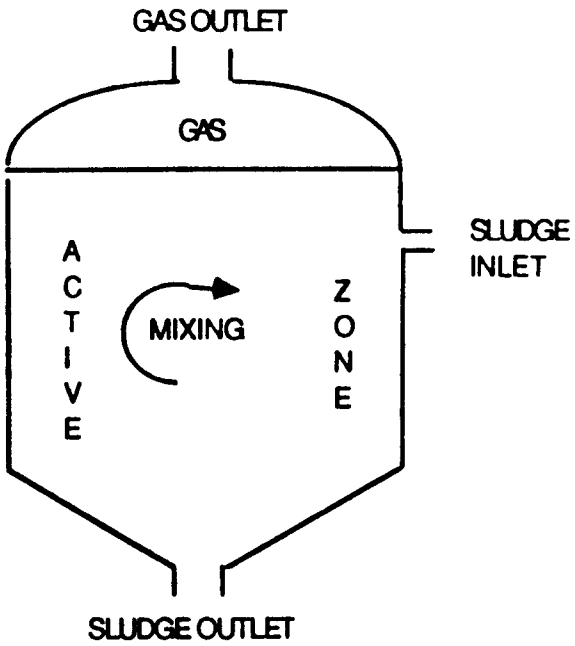
SLUDGE DISPOSAL ALTERNATIVES
BIOLOGICAL TREATMENT

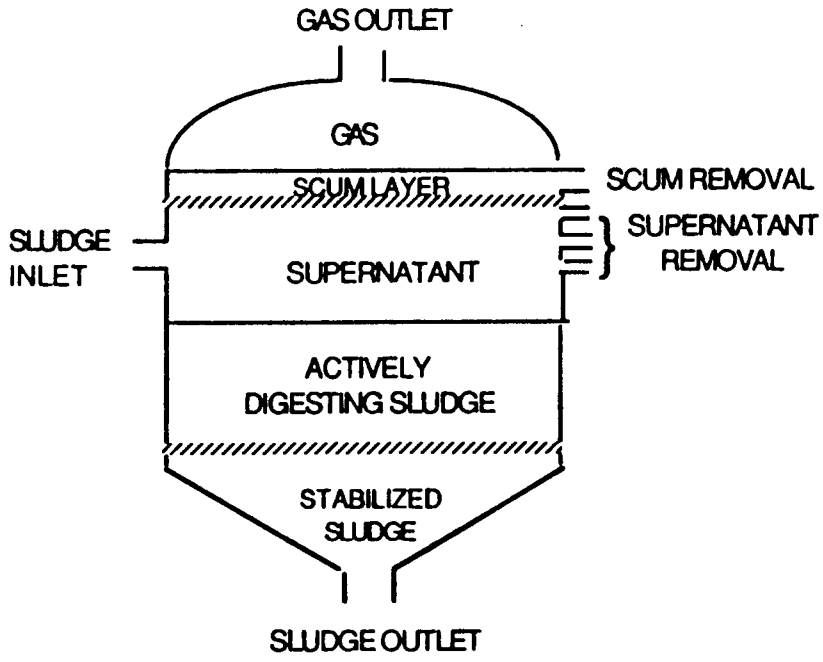
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MECHANISM OF ANAEROBIC SLUDGE DIGESTION

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FIRST STAGE

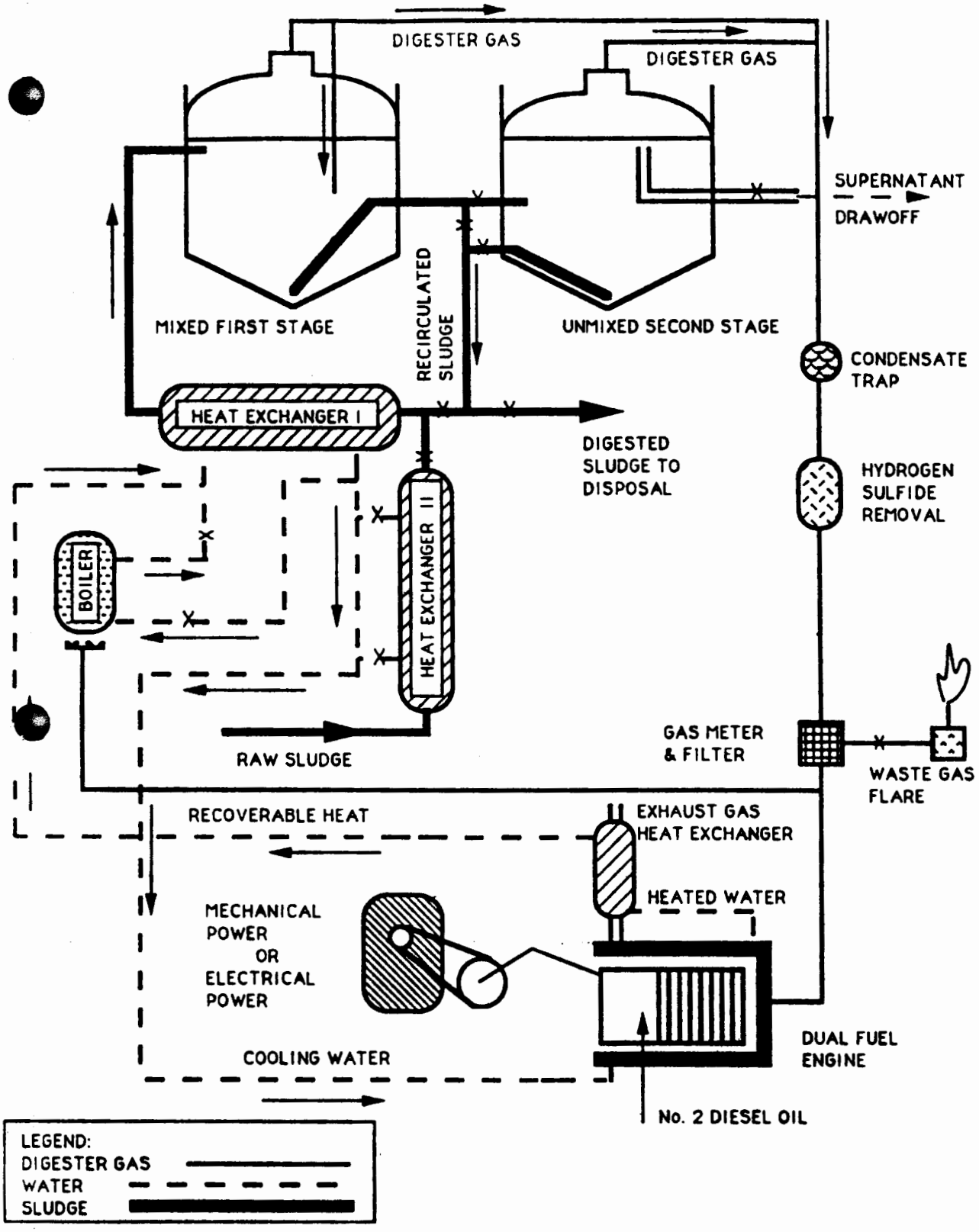
1. Heated to 85° - 95 °F
2. Detention time 15 days or less
3. Continuous or intermittent feeding and withdrawal

SECOND STAGE

1. Unheated
2. Detention time 15 days or less
3. Intermittent feeding and withdrawal
4. Stratification

FIGURE 4
ANAEROBIC DIGESTION

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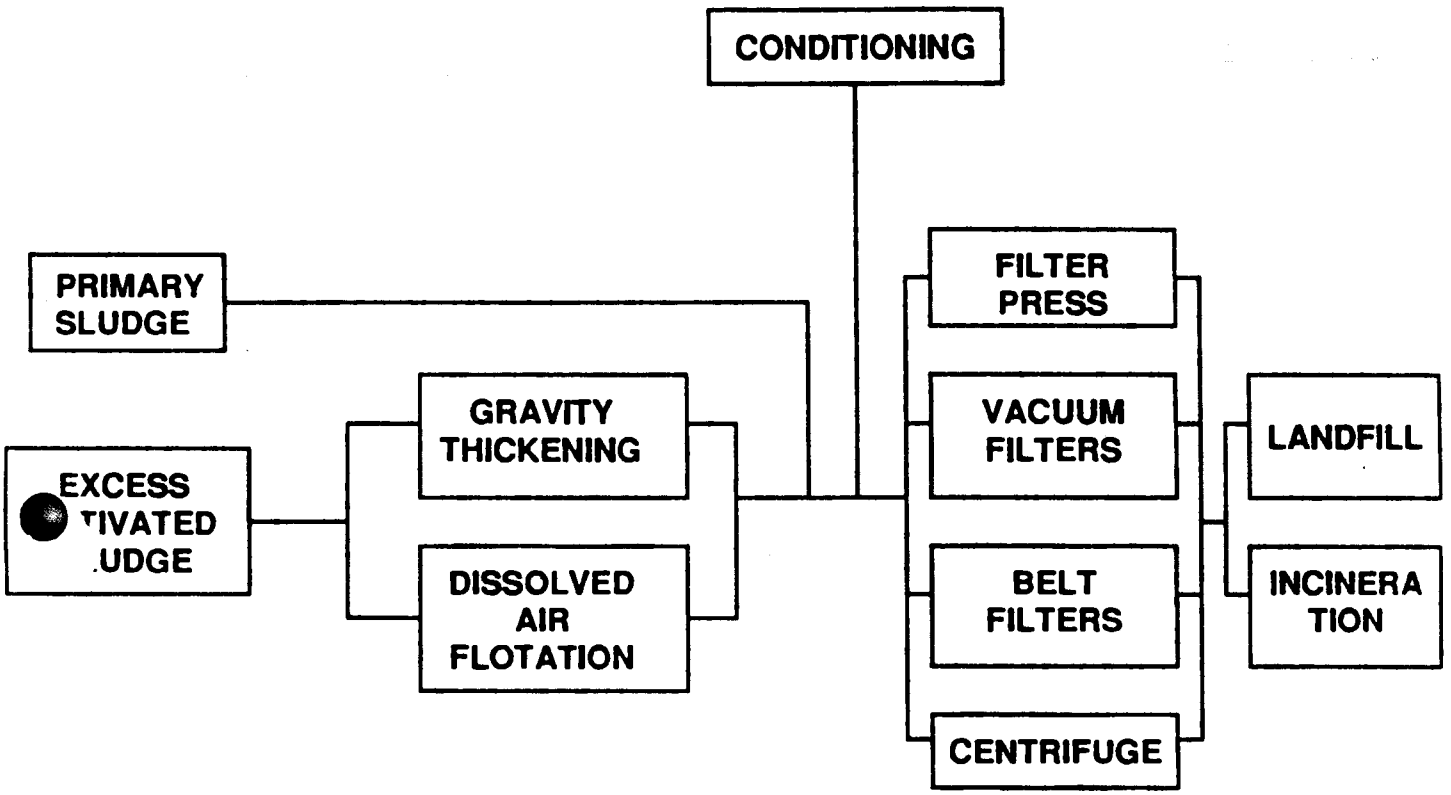


ANAEROBIC DIGESTION SYSTEM WITH GAS RECOVERY AND REUSE

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TABLE 3
TYPICAL CHEMICAL COMPOSITION OF DIGESTED SLUDGE

CHARACTERISTIC	RANGE	TYPICAL
Total dry solids (TS), %	6 -12	10
Volatile solids (% of TS)	30-60	40
Grease and fats (ether-soluble, % of TS)	5-20	...
Protein (% of TS)	15-20	18
Nitrogen (N, % of TS)	1.6-6.0	4.0
Phosphorus (P_2O_5, % of TS)	1.5-4.0	2.5
Potash (K_2O, % of TS)	0.0-3.0	1.0
Cellulose (% of TS)	8 -15	10
Iron (not as sulfide)	3 -8	4
Silica (SiO_2, % of TS)	10 -20	...
pH	6.5-7.5	7.0
Alkalinity (mg/L as $CaCO_3$)	2,500-33,500	3,000
Organic acids (mg/L as HAc)	100-600	200
Thermal content (MJ/kg)	6-14	9



SLUDGE DISPOSAL ALTERNATIVE
DEWATERING AND DISPOSAL

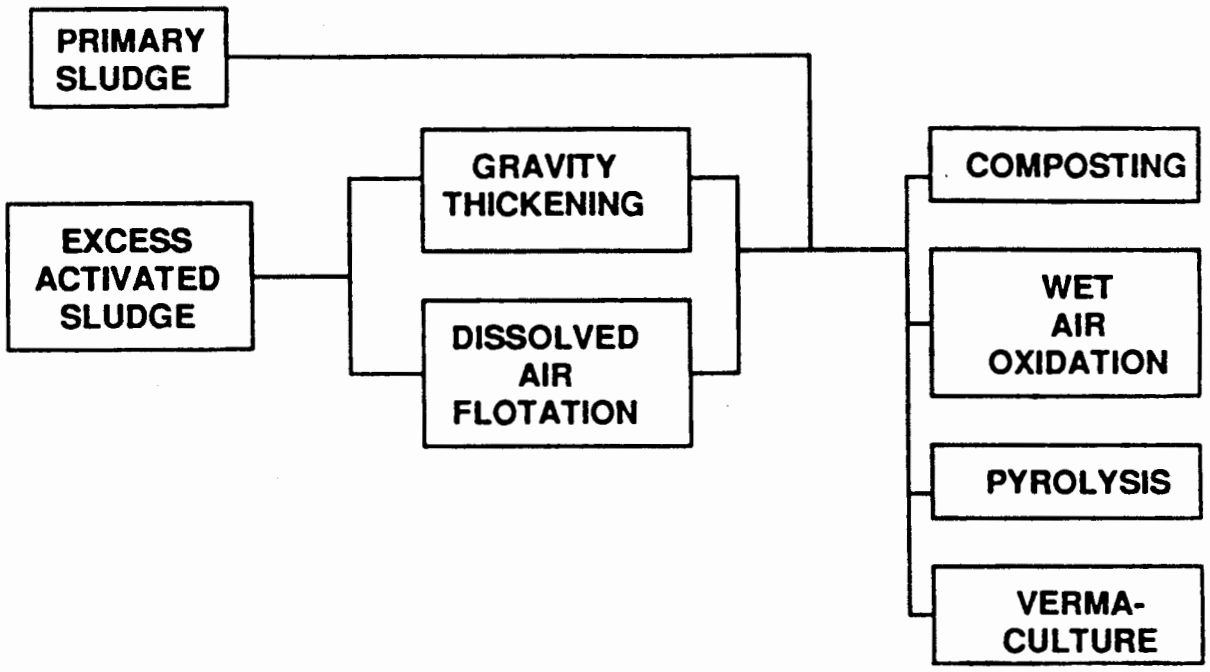
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TABLE 4
TYPICAL CHARACTERISTICS OF A PRIMARY-ACTIVATED SLUDGE MIXTURE AFTER HEAT TREATMENT

	Before Oxidation	After Oxidation		
		Slurry	Filtrate	Filter Cake
Volume (L)	1.00	1.05	1.00	0.05
COD gm	43	36.6	12.9	23.7
COD Reduction %	0	15	--	--
BOD gm	--	--	4.5	--
Total solids gm	35.1	29.8	8.2	21.6
Volatile Solids gm	23.4	18.1	5.2	12.9
Ash gm	11.7	11.7	3.0	8.7
Phosphorus as P gm	0.61	0.61	0.18	0.43
Total Nitrogen gm	1.49	1.49	1.15	0.34
Ammonia Nitrogen gm	0.57 0.03		0.75	0.72
pH	6.0	5.2	--	--
Volume after 4 hr setling %	100	37	--	--
Filtration Resistance ($sec^2/g \times 10^7$)	3500	6	--	--
Moisture Cake %	--	--	--	64

TABLE 5
HEAT-VALUES OF SLUDGES AND FUELS

	Combustibles (percent)	Heat-Value Fuel (BTU/lb)
Fine Screenings	86.4	8,990
Grit	33.2	4,000
Grease and scum	88.5	16,750
Fresh sewage solids	74.0	10,285
Primary sewage sludge	---	7,820
Activated sewage sludge	---	6,540
Digested sludge	59.6	5,290
Digested sewage and garbage solids	49.6	8,020
Waste sulfite liquor solids	---	7,900
Semi-chemical pulp solids	--	5,812
Lignite	89.0	10,850
Wood	89.5	8,675
Newsprint	91.8	7,825
Coal	---	10,000-14,000
Petroleum	---	19,000-20,000



SLUDGE DISPOSAL ALTERNATIVES

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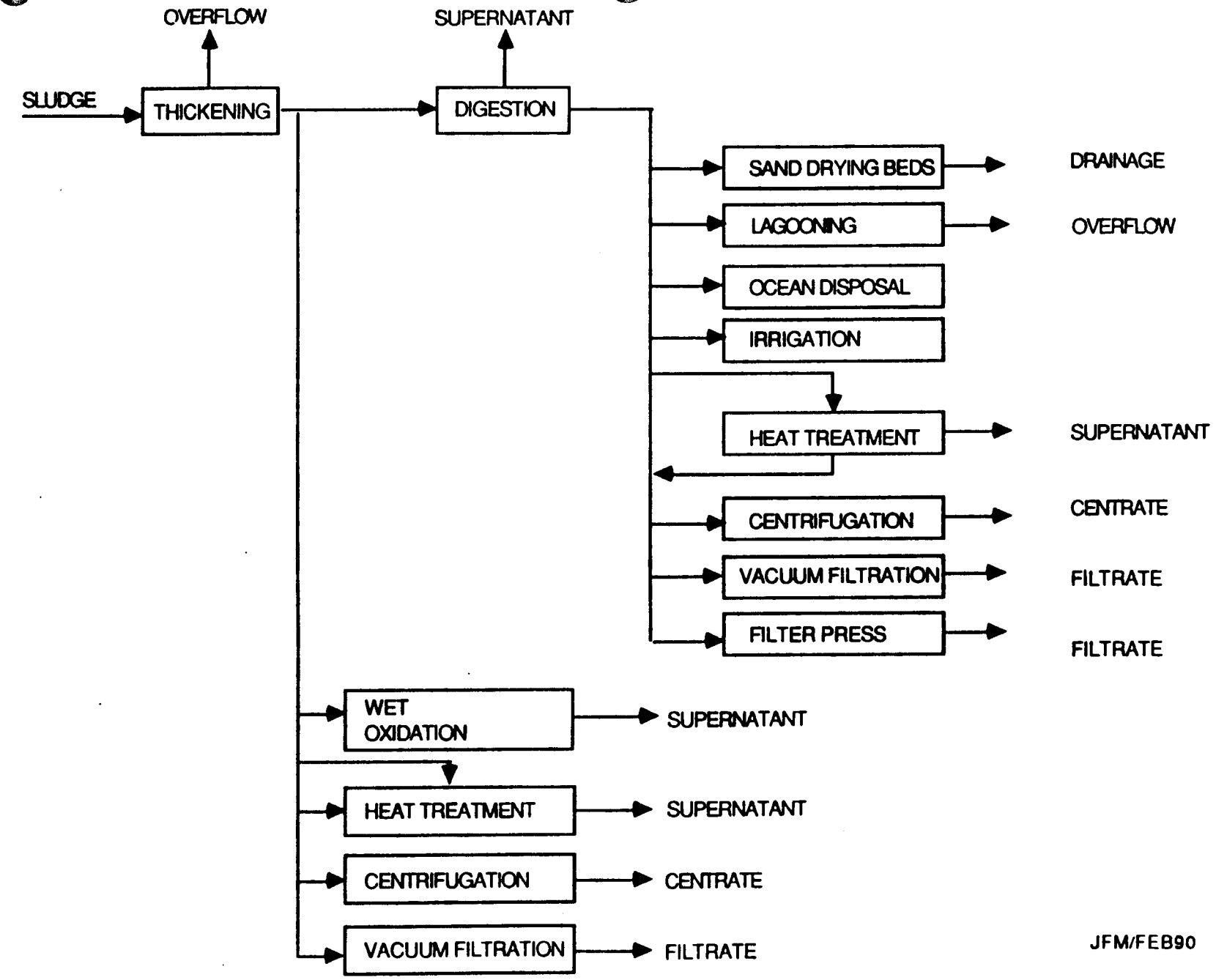


FIGURE 2

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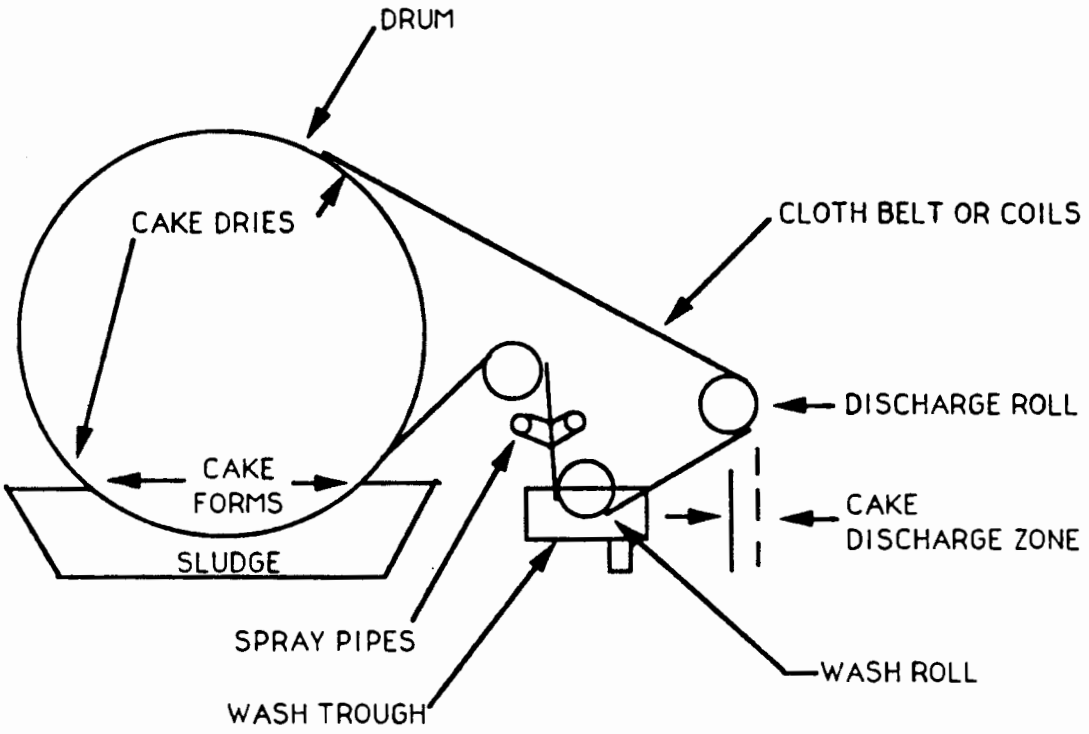


FIGURE 5
CROSS SECTION OF A VACUUM FILTER

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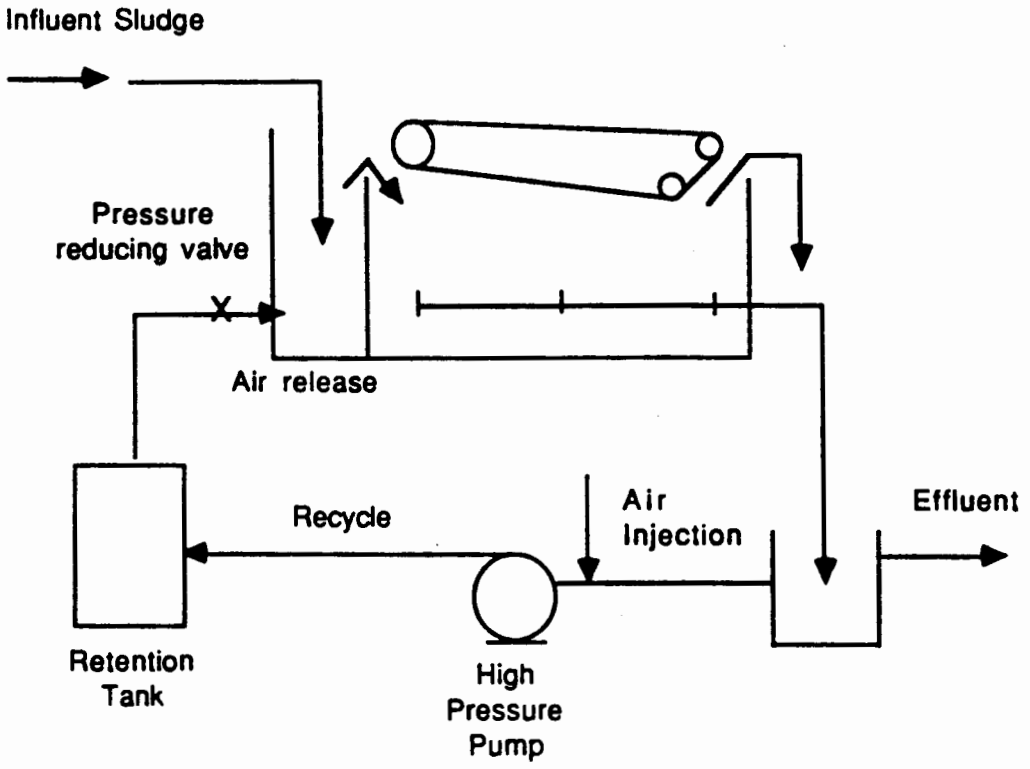


FIGURE 3

SCHEMATIC REPRESENTATION OF FLOTATION SYSTEM WITH EFFLUENT RECYCLE

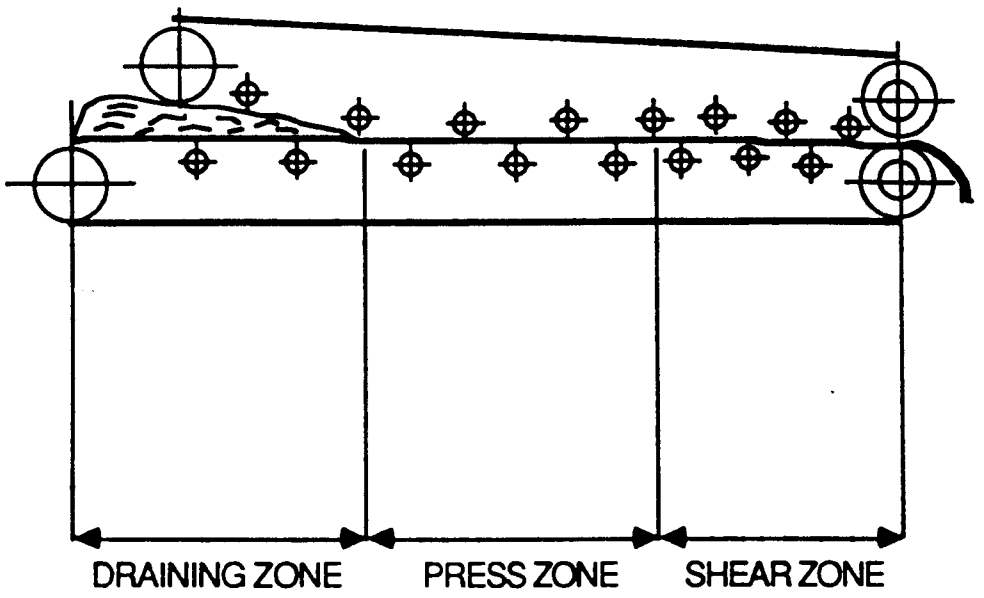
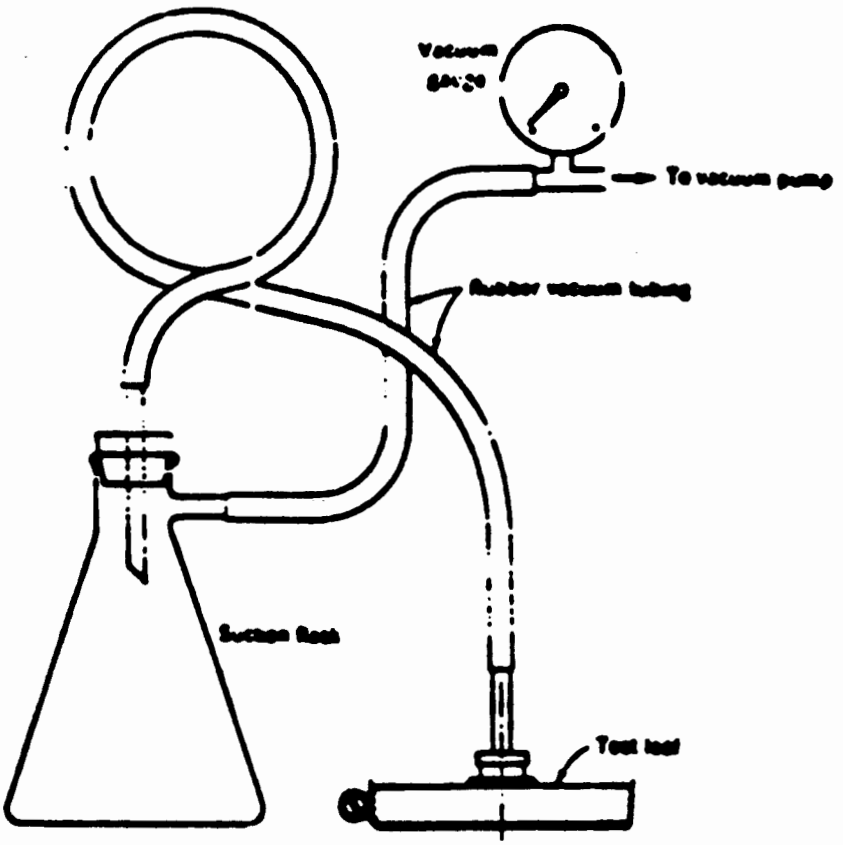
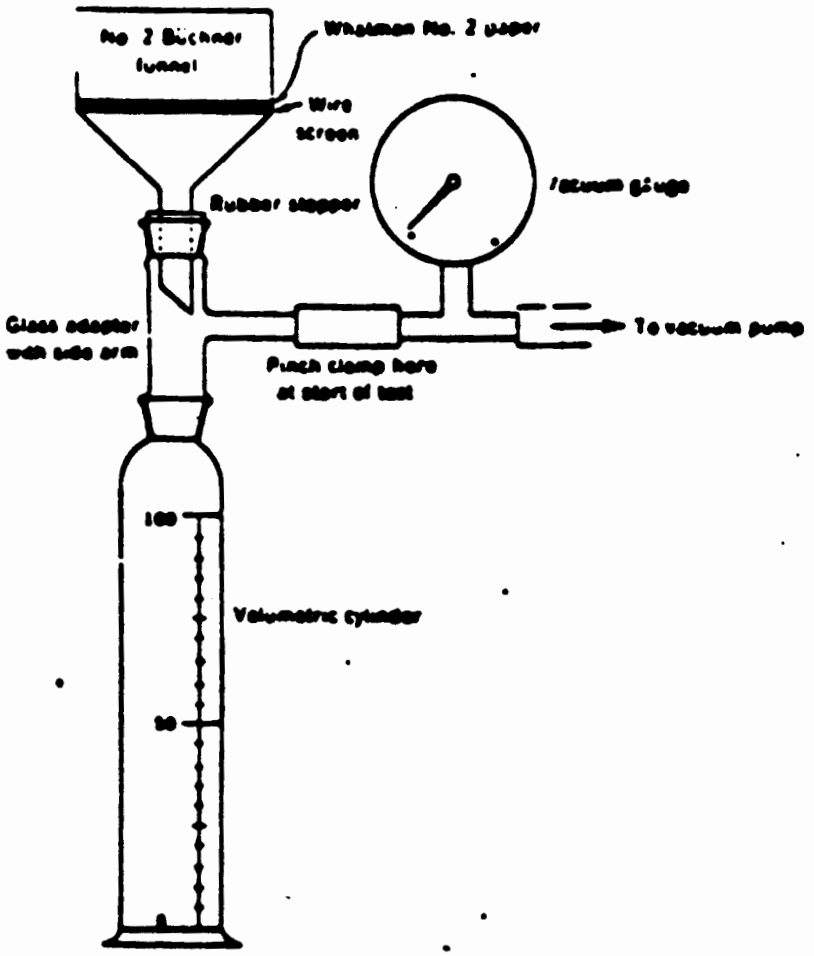


FIGURE 3. Schematic of belt filter

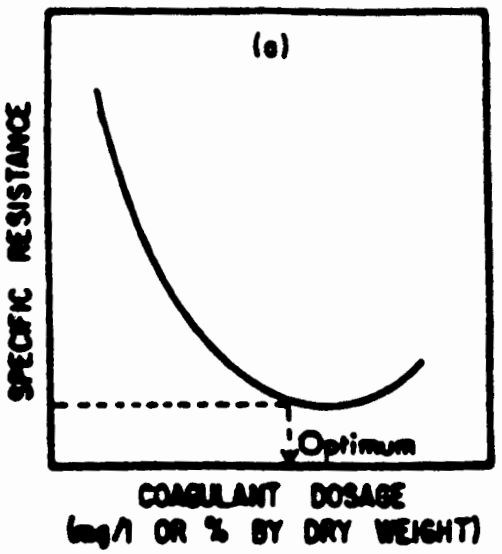


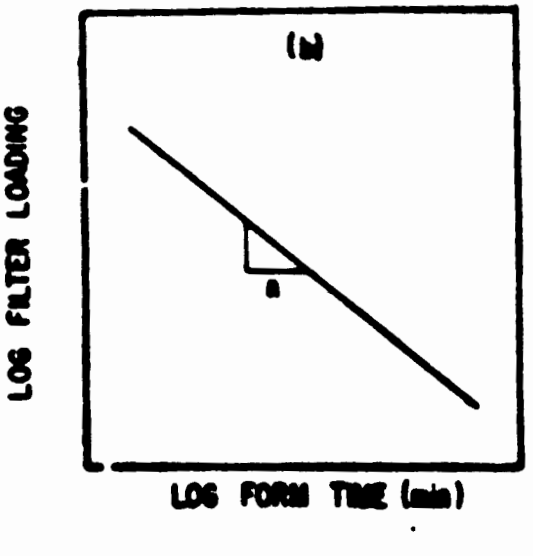
Leaf-test assembly (Eimco Corp.)

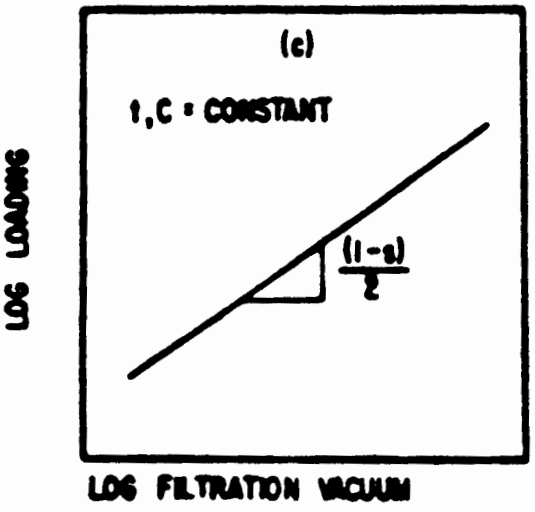


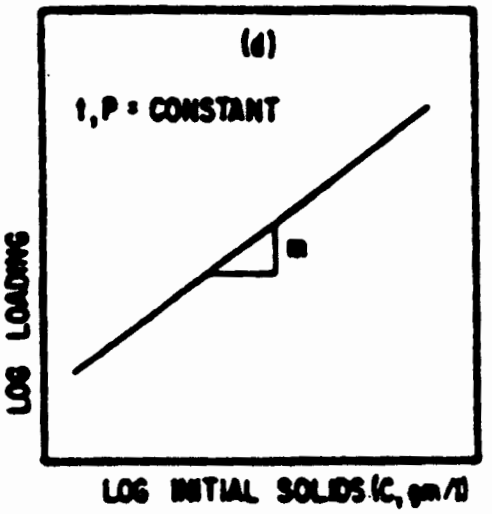
Buchner-funnel assembly for determination of sludge filterability.

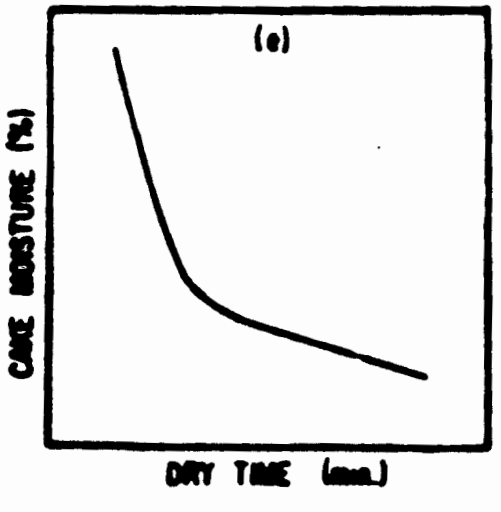
EXPERIMENTAL PLOTS FOR VACUUM FILTRATION DESIGN

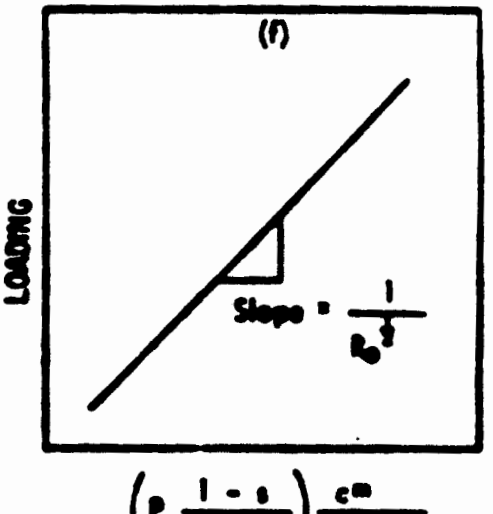


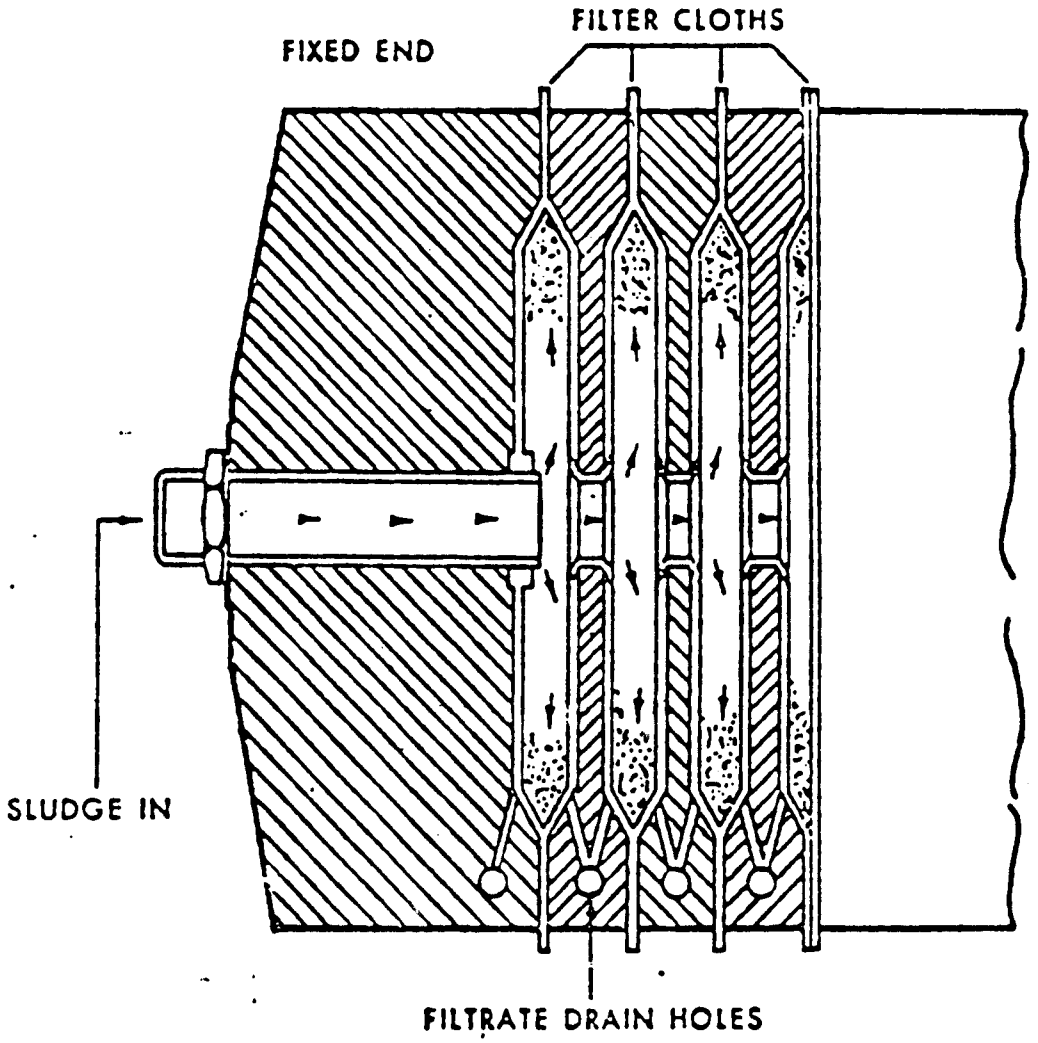




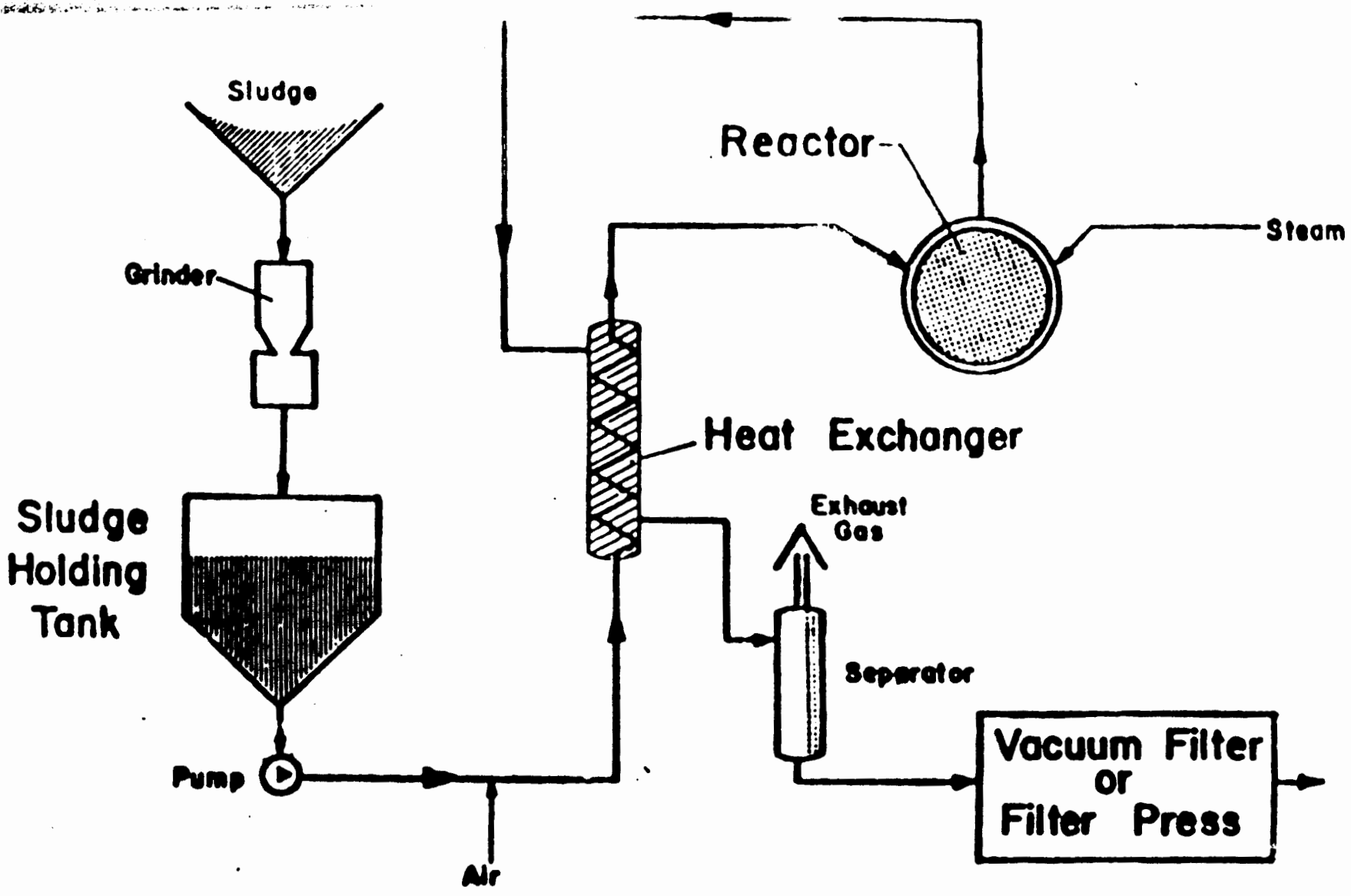




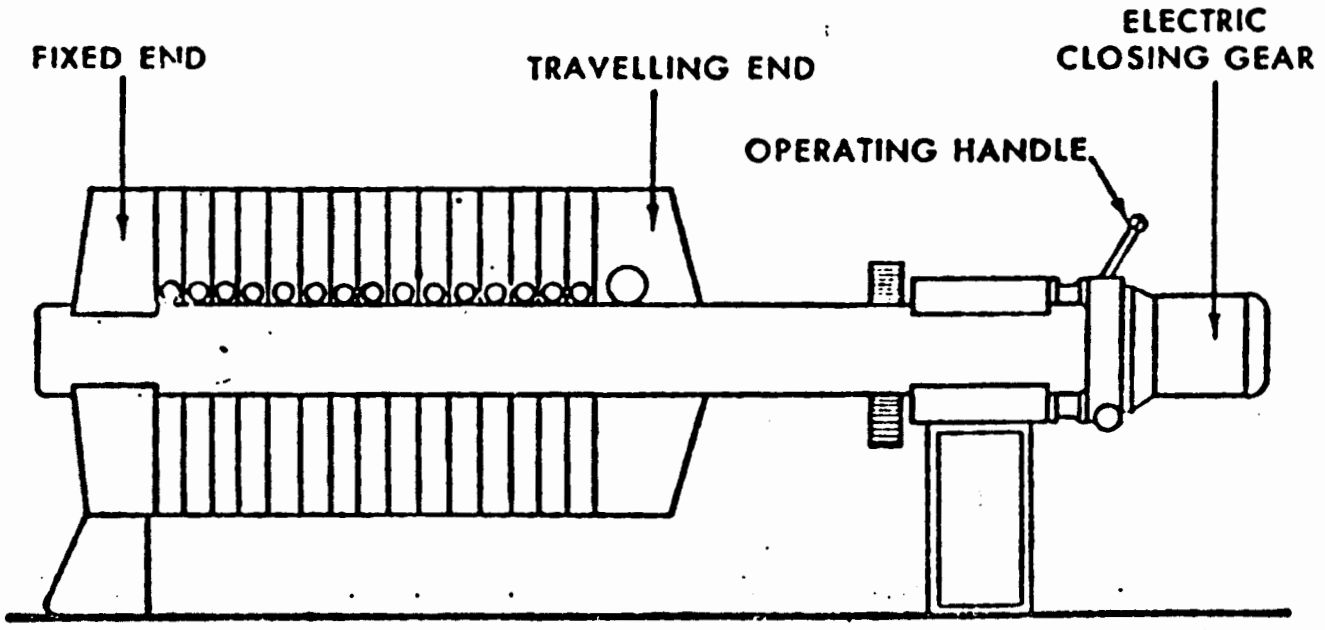




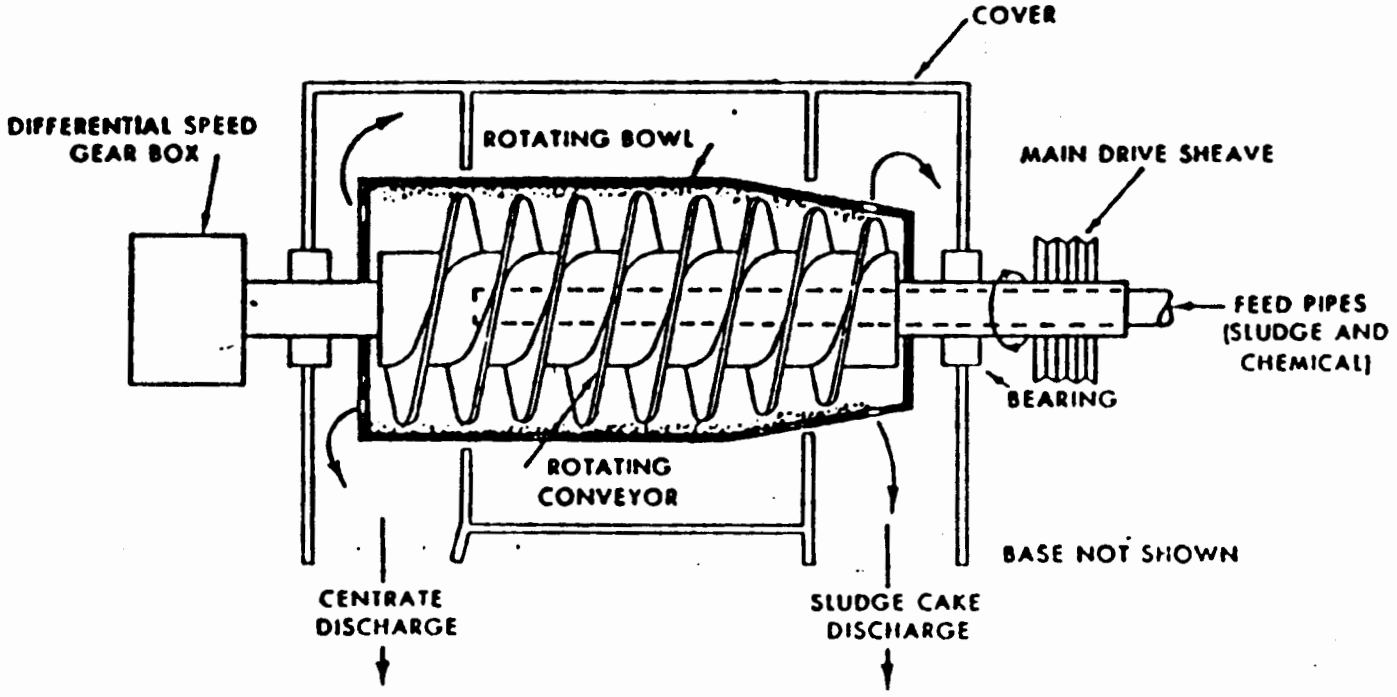
Cutaway view of a filter press



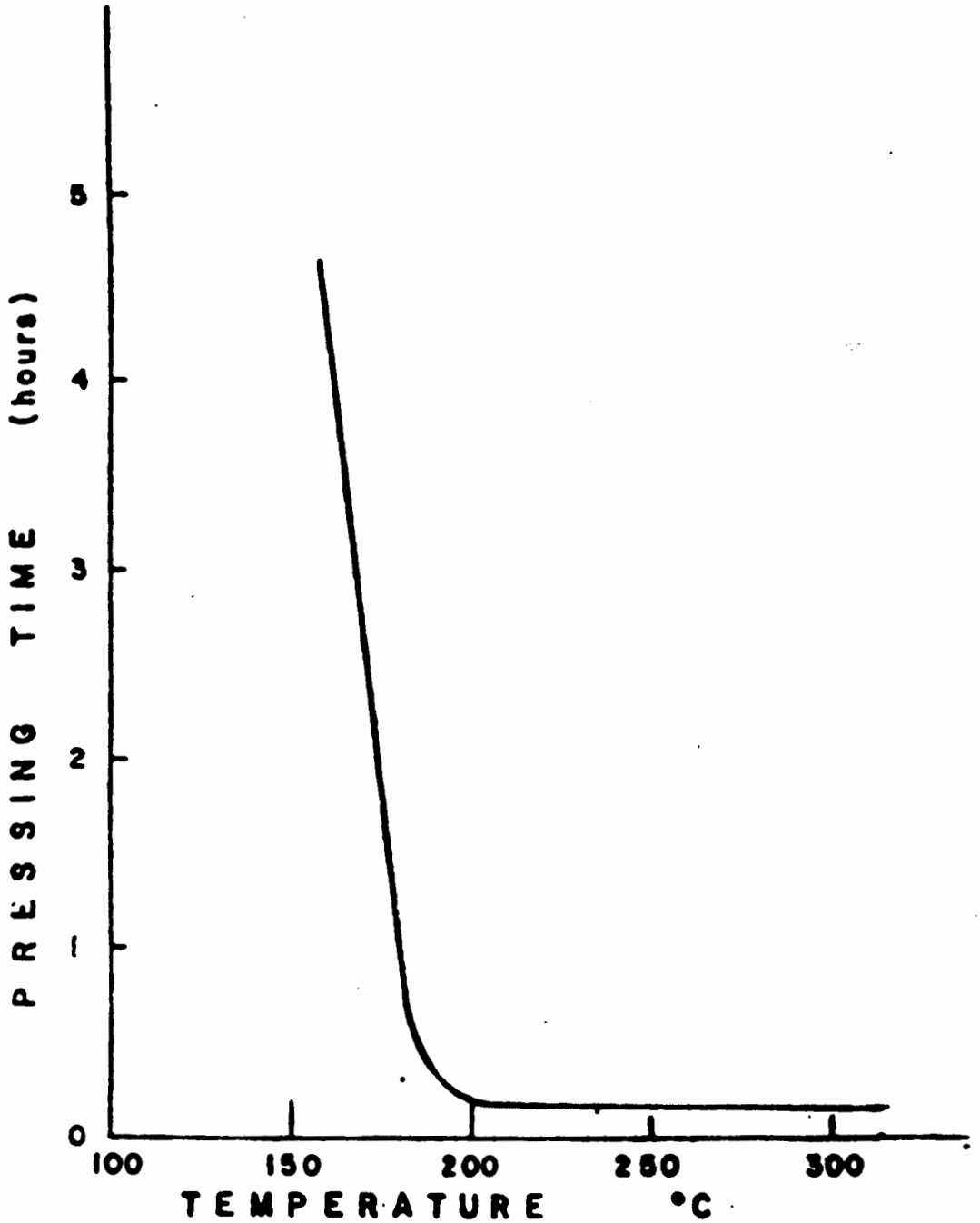
SCHEMATIC FLOW DIAGRAM OF THE ZIMPRO WET AIR OXIDATION SYSTEM



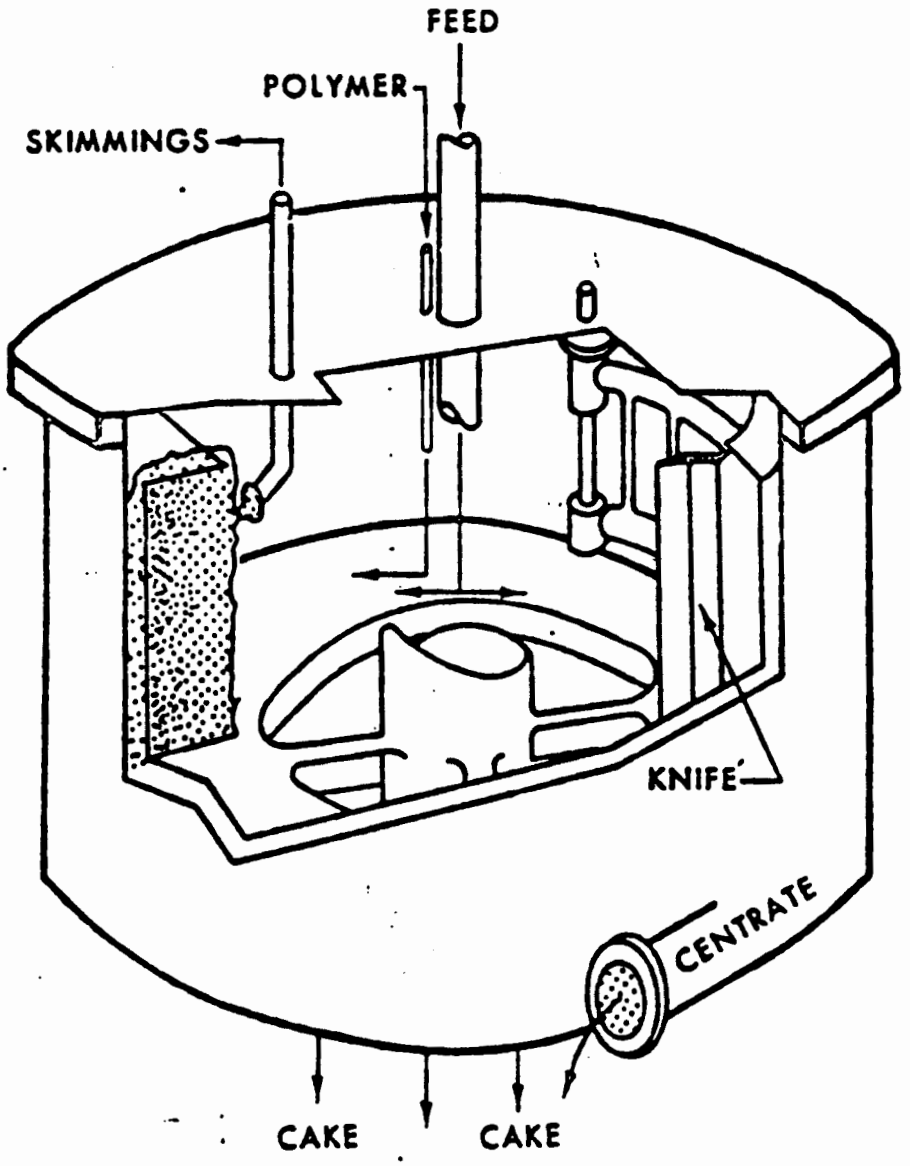
Filter Press



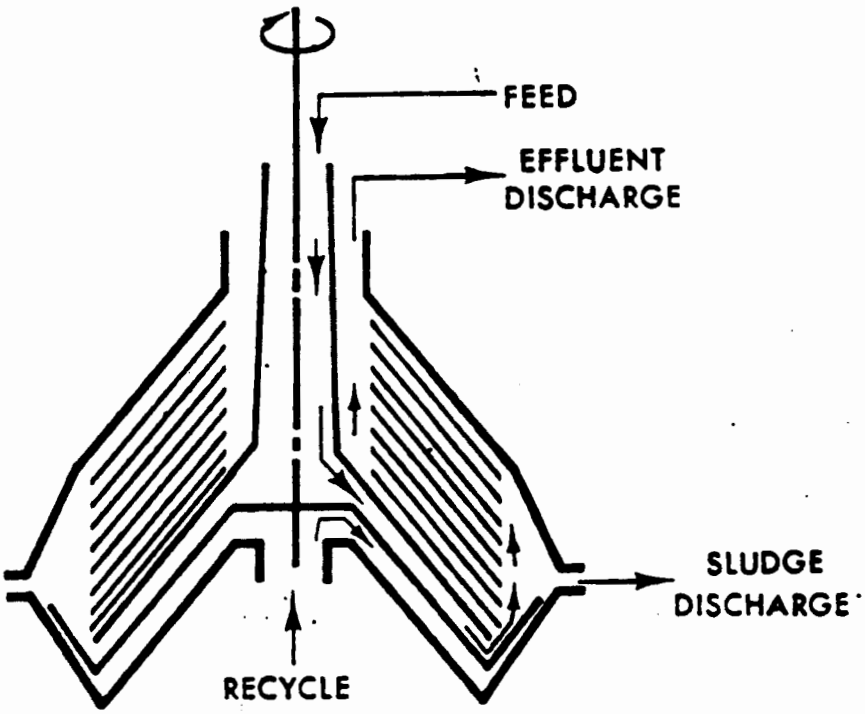
Continuous countercurrent solid bowl conveyor discharge centrifuge.



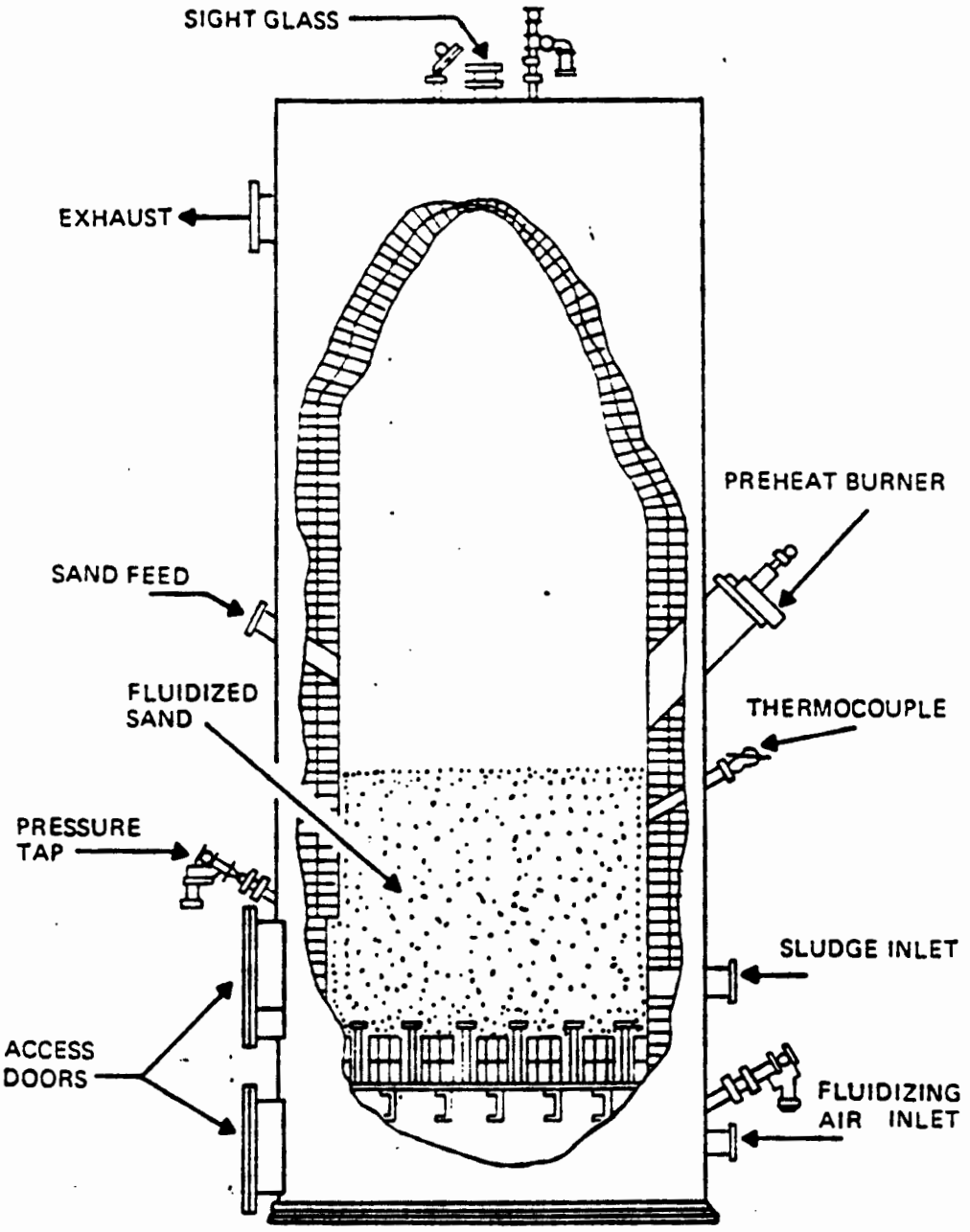
TEMPERATURE EFFECTS ON REQUIRED PRESSING TIME



Schematic diagram of a basket centrifuge.



Disc type centrifuge.



Cross section of a fluid bed reactor.

SOLID WASTES AND SLUDGE TREATMENT AND DISPOSAL

Joseph F. Malina, Jr., P.E.
C.W. Cook Professor in Environmental Engineering
Department of Civil Engineering
The University of Texas at Austin

Introduction

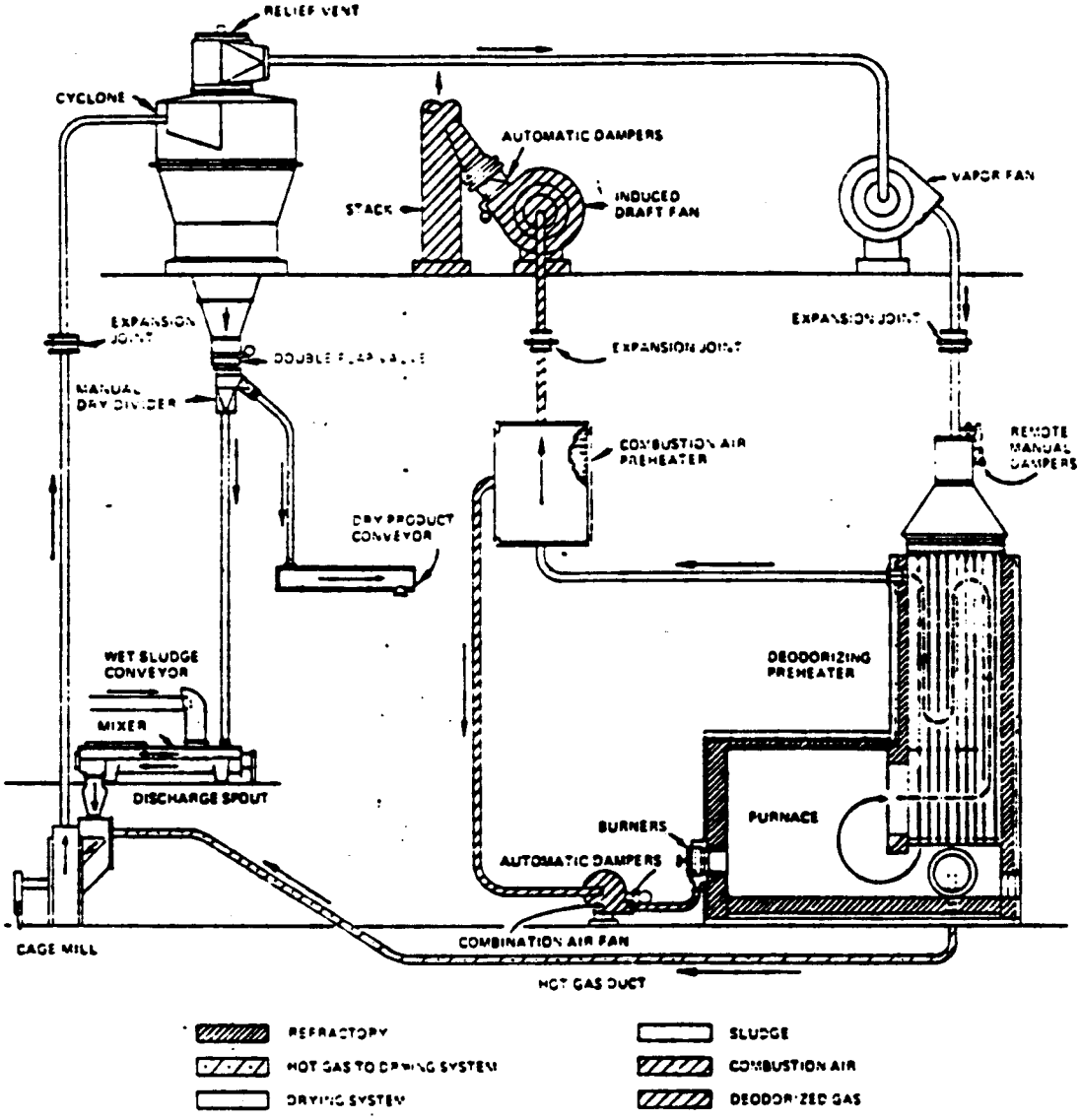
Solid wastes include all waste materials which are not normally airborne or carried in water. Municipal solid wastes include ordinary refuse (garbage; grass and yard trimmings; paper and cardboard; glass, plastic, aluminum and steel containers; wood; scrap metal; plastics; etc.), and bulky items (abandoned vehicles, furniture, appliances, etc. as well as sludges from water and wastewater treatment facilities. The disposal of municipal solid wastes are addressed by the Solid Wastes Act of 1965 and the Resource Recovery Act of 1970.

Waste solids in industry occur in diverse forms. These solid wastes may occur as solids such as scrap wood, paper, or metal, cafeteria refuse, or catalysts; as semi solid tars and resins; as suspended solid monomers and polymers in waste streams; as organic and organic sludges resulting from water and wastewater treatment; or as oily sludges. These materials may be characterized as combustible or non combustible, organic or inorganic, inert or biodegradable, dry or mixed with aqueous or non aqueous solvents, or a combination of several of these components. Some industrial wastes also are classified as hazardous wastes.

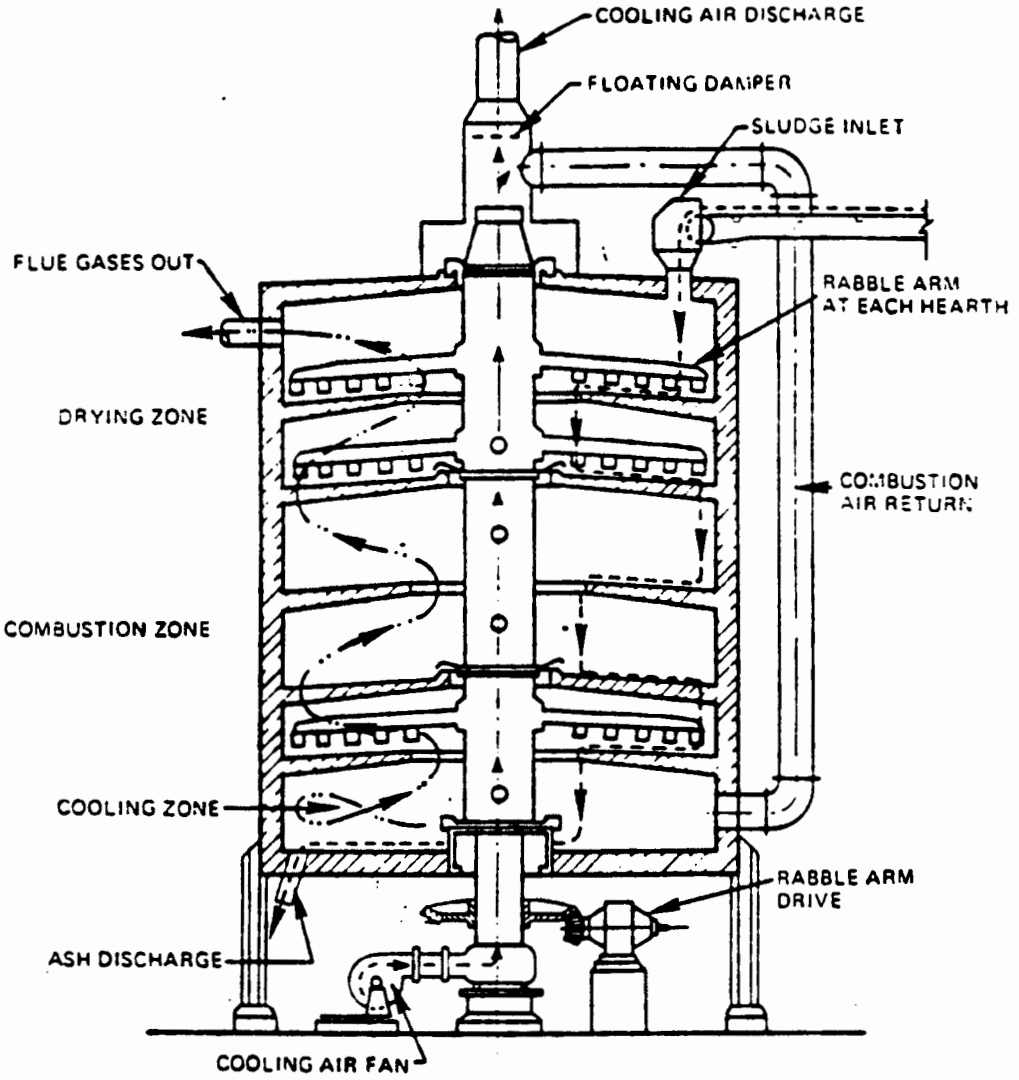
The Resource Conservation and Recovery Act of 1976 (RCRA) and the reauthorization in 1984 affect the disposal of industrial solid wastes and some municipal solid wastes. The overall objective of RCRA the development of

management plans and facilities for the recovery of energy and other resources from waste and for the disposal of the residuals. RCRA also regulates the management and disposal of hazardous wastes. These regulations specifically focus on the "cradle to grave" control of hazardous waste and address the control of hazardous waste generation, transportation from the point of generation to the processor and storage, treatment and disposal at the processing site. RCRA defines solid wastes as any discarded material in any form other than industrial wastewaters which are regulated by the Water Pollution Control Act (PL 92-500). Hazardous wastes are solid wastes which may be liquids, solids or slurries which a) cause or significantly contribute to an increase in mortality or an increase in serious or incapacitating illness; or b) pose substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, disposed of, or managed. Major characteristics of hazardous wastes include: a) flammability (e.g. flash point less than 60 celsius); b) corrosivity (e.g. pH less than pH = 3 or above pH = 12); c) reactivity; d) toxicity (e.g. acute toxicity, bioaccumulation, persistence, ability to damage genetic material); e) radioactivity; f) infectivity (e.g. pathogens).

Many specific and non specific wastes and commercial products and intermediates have been "listed" as hazardous wastes by the U.S. Environmental Protection Agency (EPA). Generators need to be concerned with a) preparation of manifests for each shipment of residuals including immediate response procedures in case of an emergency; b) reporting manifest information periodically to the EPA; and c) developing and implementing acceptable containerization and labeling procedures.



Flash dryer system



Cross section of a typical multiple hearth incinerator.

Municipal Solid Wastes

The municipal solid waste management problem can be defined in terms of storage, collection, and processing. These components are interrelated and interdependent. However, this discussion will focus on the treatment and disposal of solid wastes.

Characteristics

The composition of municipal refuse varies markedly from city to city and from season to season. Typical physical and chemical characteristics of refuse are presented in Tables 1 and 2. Paper is the major component and accounts for about 50 percent of the weight while garbage from food preparation makes up less than 15 percent. The chemical analysis indicates that carbon and oxygen are the major components. The sulfur content is extremely low, which makes refuse a desirable fuel from air pollution considerations. However, the variability of the heat content and moisture content make refuse an unpredictable fuel. The average rate of municipal refuse generation exceeds 7 pound per capita per day.

Handling, Recycling, and Disposal

The majority of the municipal refuse generated in the United States is disposed on or in the land. Many of the sites are open dumps at best. However, low cost land is not available in most urban/industrial complexes and incineration of refuse is an alternative. Typical incinerator use heat generated from the combustion of refuse for the production of steam and hot water for industrial uses. Electric energy is generated at waste to energy incineration facilities. Refuse is mixed with coal in cogeneration plants for the production of electricity. Composting of municipal refuse can convert

refuse into a soil conditioner, but composting has not been economically successful in the United States. Recycling of reusable constituents of refuse is practiced on a limited basis.

Sanitary Landfill

Sanitary landfill includes the placement of the refuse on the ground or in a prepared trench, compaction with heavy equipment and covering daily with about six inches of compacted soil. A sanitary landfill can be used to disposed of municipal solid wastes in a satisfactory, nuisance free, and efficient manner at a low cost provided adequate land is available at relatively short hauling distances (e.g. less than 20 miles round trip for vehicles used to collect refuse). In southern California where the atmospheric condition and the physical environment (mountains which limit atmospheric circulation and dispersion) preclude the use of incineration because of air pollution problems, transfer stations are used to off load refuse from collection vehicles into large semi trailer trucks which haul the refuse to remote sites 50 miles or more from the source.

The type of sanitary landfill operation selected depends on: a) locality, b) topography, c) soil type, and d) the proposed use of the completed fill. Three procedures commonly employed are: a) trench method, b) area method, and c) ramp method. (Figure 1) Large natural depressions also may be used for sanitary landfills. The volume required for a sanitary landfill can be calculated:

$$V = C[(R/D)(1-P)]$$

where:

V = volume (cubic yards per year)
R = refuse production (pounds per year)

D = average density (pounds per cubic yard)
(usually 200 to 400 lb/cu yd)

P = percent reduction in volume resulting from compaction
(usually 0.5 to 0.67 for 2:1 and 3:1 compaction ratios respectively)

C = constant which accounts for the fraction of volume occupied by cover material (usually 1.2 to 1.33)

The geology, topography and ground and surface water resources at a proposed site must be evaluated carefully. The site which has the least potential for water pollution should be selected.

Various chemical and biological reaction take place within a sanitary landfill resulting in the production of methane gas and leachate. The methane gas generated in deep landfills in California is collected, processed to remove carbon dioxide and moisture and sold. Typical leachate composition is presented in Table 3. Leachates could contaminate ground water sources, if not controlled. Therefore, an impervious liner should be installed to isolate the refuse and leachates in landfills from ground water resources. Landfill liners and sealants that can be used to control the movement of leachate and gas include: a) a 6 to 48-inch thick compacted layer of bentonite, illite or kaolonite clay; or b) synthetic membranes (polyvinyl chloride, butyl rubber, hypalon, polyethylene, and nylon reinforced liners); or c) modified asphalt (rubber impregnated asphalt, asphalt covered polypropyiene fabric, and asphalt concrete). Clay liners must be continuous and not allowed to dry and crack. Synthetic membranes are expensive and usually are placed over a bed of compacted sand to insure integrity of the liner which easily can be punctured by sharp edged rocks in the soil. Asphalt liners must be thick enough to maintain continuity under differential settling conditions, particularly if used as cover material to control gas movement.

In lined sanitary landfills a leachate collection system consisting of a main drain and perforated laterals should be installed prior to depositing refuse.

The chemical and biological degradation of the refuse in a landfill results in a reduction in the volume of the refuse and in the settlement of the landfill surface. The total settlement that will occur is a function of a) the total depth of refuse, b) the degree of compaction, c) the composition of the refuse, and d) the moisture content of the fill material. Most of the settlement takes place in the first 12 months and by the end of two years most of the settlement, which is between 10 percent and 30 percent of the initial depth, is completed.

Completed sanitary landfill sites can be used for green areas such as parks, recreational areas, playing fields, and golf courses. Careful planning is essential and the future use should be integrated into the design and operation of the landfill. The use of a completed sanitary landfill for buildings is not recommended. The fill itself is a poor foundation material. Improper compaction and the incorporation of large bulky items in the fill will result in differential settling. Buildings must be built on pilings or caissons to carry the load through the fill material to a solid foundation material. Solid-fill islands may be incorporated into the sanitary landfill to accommodate future building sites or green of a golf course.

Incineration

Incineration is a controlled process for the oxidation of solid wastes. Incineration of refuse also is an effective volume reduction process in which the combustible components are burned by controlled combustion. The

volume reduction is about 80 to 90 percent while the net weight reduction usually is 75 to 80 percent. However, complete burn out of refuse results in a weight reduction of 98 to 99 percent of the combustibles entering the incinerator. The residue remaining after incineration requires disposal and the ash usually is placed/spread on the land at the site or in a sanitary landfill depending on the degree of burn out and the amount of putrescible material in the residue.

The combustibility and heat content of municipal refuse or other solid wastes dictate the feasibility of incineration and the requirement for auxiliary fuel to sustain combustion. The heat content of municipal refuse as received at the incinerator ranges from 3,000 to 6,000 BTU/lb depending on the moisture content. The heat contents of various components of refuse are presented in Table 4.

A modern incinerator is a complex facility requiring skilled operating personnel. The essential components of an incinerator are illustrated schematically in Figure 2. These components are integrated in systems similar to those presented in Figures 3 and 4. The water walled furnace incorporated in the incinerator illustrated in Figure 3 is typical of the design used in waste to energy facilities. The inputs into an incinerator include refuse, auxiliary fuel, air, and water. The residues include unburned refuse, fly ash, gases, dust, and odor. A schematic diagram illustrating the inputs and residue sources is presented in Figure 5. The physical and chemical composition of the residues are presented in Tables 5 and 6, while the quench water characteristics are summarized in Table 7.

The furnace or primary chamber is the heart of the incinerator. Effective burn out requires sufficient time, temperature and turbulence. The time and turbulence are controlled by the method of moving the burning refuse through the furnace. In typical furnaces three types of grates are used to move and agitate the refuse providing the turbulence necessary to enhance combustion. (Figure 5) The rotation of the rotary kiln furnace moves the refuse and causes the turbulence.

The residue after combustion in the primary chamber usually is quenched with water. The ash is separated from the water and hauled to disposal. The unburned airborne particulate material and gases are burned in the secondary chamber where the temperature is sufficient to oxidize all combustible solids and gases. The gaseous constituents of the flue gas are not significant since the oxides of sulfur are minimal. The fly ash in the exit gas must be removed to minimize potential air pollution. The performance and relative costs of some equipment used for air pollution control at municipal incinerators are summarized in Table 8.

Recovery of heat as a by-product of incineration is receiving increasing emphasis because of the cost of fossil fuels. Recovered heat is use for the production of steam which could be used for industrial purposes or for the generation of electricity. Hot water produced also could be used for heating of municipal and industrial buildings. Two general furnace designs are used in waste to energy incinerators: a) water wall furnaces or b) refractory lined furnaces. The water wall furnaces are more efficient heat recovery systems than refractory lined furnaces.

Composting

Composting is a controlled aerobic biological process in which the degradable organic solid wastes are stabilized or digested. The end product of composting is a humus like nuisance free soil conditioner. Air is introduced to provide the oxygen required to maintain aerobic conditions. The aerobic conditions minimize odors and maintains a relatively high rate of biological activity. The temperature in the compost increases to approximately 150 F.

Composting systems can be categorized as: a) mechanical digestion and b) windrow. A schematic diagram of the elements of a typical composting facility is presented in Figures 6 and 7. Size reduction accelerates microbial digestion of the organics by providing a larger surface area for biological activity. The moisture content is maintained between 50 to 60 percent for optimum microbial activity, although biological decomposition takes place at moisture contents of about 30 percent. Water, municipal wastewater, or sludge from municipal wastewater treatment facilities commonly is added to refuse to maintain the proper moisture content. The optimum C/N ratio for composting municipal refuse is 30:1 to 35:1. Municipal wastewater and municipal wastewater treatment plant sludges can be used to increase the nitrogen content of the compost. The initial period of high rate of degradation in the composting process is about five days. However, a much longer aging period, 30 to 60 days is required prior to applying the finished compost to soil. After aging the finishing processes include: a) screening, b) grinding, c) separation of glass and plastics. The extent of finishing of the compost is dictated by the desired quality of the final product.

Composting of municipal refuse has not been successful in the United States. A summary of U.S. composting experience is presented in Table 9.

Recycle Potential

Recycling may be considered a refuse volume reduction process. The technical feasibility of separating reusable components has been established; however other factors dictate the economic feasibility. Specifically, the market potential for the products, projected revenues from sales, total capitol and operating costs, and the scientific, engineering and commercial value of the salvaged material relating to marketability. The salvage potential for municipal refuse and for incineration residues are illustrated in Figures 8 and 9. The primary candidates for salvage and recycle are paper, ferrous metals, non ferrous metals (e.g. aluminum), and possibly glass. The market prices for these components of refuse fluctuates widely. Therefore, recycling cannot be used to the exclusion of other disposal methods, since all of the refuse cannot be reused. Recycling should be an integral part of the overall refuse disposal system.

Current recycling efforts require separation of the reusable constituents at the point of generation. Newspaper, and clean glass, steel and aluminum containers are sorted by the hand at individual residences and collected separately by the municipal agency. In some cases aluminum can be sold at recycle centers, usually established by beverage companies.

Markets for secondary materials must exist for any reclamation system to be economically feasible. the secondary materials industry is a multi-billion dollar establishment. Most of the recycled material is sold and delivered to

the processing facility by industry. The reclaimed material is purchased by other industries which can profit by blending recycled material with virgin material, e.g. scrap iron and steel, ferrous containers, newspaper, textile; etc. The ultimate user of the reclaimed material controls the market. Recycle of industrial solid wastes is more commonplace, because of the consistency of the quality and quantity of the material to be recycled. A municipality intent on recycling components of refuse must become established as a primary supplier of materials of consistent quality and quantity.

Energy savings resulting from recycle and reuse are illustrated in Table 10. However, the cost of transportation of secondary material in most cases is higher than for virgin material. Typical data are presented in Table 11. Therefore, these costs serve as a disincentive for using reclaimed materials.

Any recycling scheme is subject to interruption resulting from price fluctuations and in some special circumstances to severe wet weather, particularly affecting recycling paper. The results of a study on recycling published by the City of Los Angeles, California are presented in Table 12.

The most effective method of separating constituents of refuse is hand sorting. Mechanical, ballistic, gravitation, magnetic, flotation, electrical and chemical methods of sorting are available but size reduction and in some cases separation of paper and organic material are required for efficient performance. One scheme for separating recyclable materials from mixed refuse with maximum flexibility is illustrated in Figure 10. The flexibility lies in the fact that the facility is only one component of the

overall refuse disposal system and is located at a transfer station and can be operated when there is a market for the salvaged material.

Municipal and Industrial Sludges

The treatment of municipal and industrial waters and wastewaters results in the production of sludges are dilute slurries containing relatively low concentrations of inorganic and organic solids (1 to 5 percent by weight). Some industrial sludges may contain oily solids. The final disposal of sludges is either on or in the land, in the air, or in the water. Once the final disposal site is identified the required sludge handling, treatment and/or concentration sequence can be designed.

Sludge Characteristics

A summary of the residuals resulting from water and wastewater treatment is presented in Table 13. Each individual treatment facility will include some combination the processes listed in the table. Chemical sludges from water treatment contain primarily calcium carbonate and aluminum hydroxide. The sludges produced during the treatment of municipal and industrial wastewaters contain organic solids and the principal source of sludge is biological treatment. The biological sludges usually contain about 1 to 2 percent solids by weight and are difficult to concentrate. The characteristics of typical wastewater treatment plant sludges are presented in Tables 14 and 15. The biological sludges from industrial treatment facilities have the same characteristics as municipal activated sludge; therefore, the treatment and disposal methods used are the same. Some industries (e.g. petroleum refining and petrochemical production) also are the source of oily

solids and sludges. Characteristics of oily sludges are summarized in Table 16.

Sludge Treatment and Disposal

Water treatment plant sludges can be recycled. Calcium carbonate sludges can be recalcined by thermally driving off the carbon dioxide resulting in the production of calcium oxide. The recovery and reuse of alum from aluminum hydroxide sludges using sulfuric acid have been successful on a limited scale in the United States. The quantity of sludge produced and the cost of fresh lime or alum affect the economic feasibility of recycling the sludges. The principal methods of disposal of these sludges is the application of the concentrated sludge on the land or the dewatering of the sludge and placing the sludge cake in a sanitary landfill.

The sequence of wastewater sludge processing and the functions of the various categories of sludge treatment are summarized in Figure 11. The liquid separated from the sludge during conditioning, treatment and dewatering (Figure 12) requires treatment. The ultimate disposal of the sludge solids dictates the extent to which the sludge must be treated prior to disposal. For example if disposal is by incineration, the amount of water in the sludge must be minimal to reduce the requirement for auxiliary fuel. However, if the dilute sludge is to be disposed of at sea or on the land, the organic fraction of the sludge must be stabilized usually by anaerobic or aerobic digestion prior to disposal. Other disposal schemes will require varying degrees of treatment and conditioning.

Thickening

Thickening is a concentration process in which water is released from the sludge solids. Thickening may be by gravity or by dissolved air flotation. A gravity thickener resembles a gravity sedimentation tank in which a moving arm with pickets is the mechanism by which some of the water is released. Gravity thickening of waste activated sludge will increase the solids concentration from 1 to 2 percent to 2 to 3 percent. Thickened primary municipal sludge may be reach concentrations as high as 8 percent.

Dissolved air flotation is used primarily for waste activated sludges and involves the recycling of an air saturated pressured stream to be mixed with the influent sludge. (Figure 13) Float concentrations of as high as 4 percent have been reported. The required air/solids ratio ranges from 0.025 to 0.05 pounds of air per pound of dry weight solids.

Stabilization

Stabilization usually involves the anaerobic digestion of the sludge. During anaerobic digestion a portion of the organic matter in the sludge is converted to methane gas resulting in a reduction in the volume of sludge solids requiring disposal. Approximately 12 to 16 cu ft of gas is produced per pound of volatile solids destroyed. This gas contains between 65 and 75 percent methane by volume. The digested sludge dries readily in sand drying beds and liquid digested sludge can be applied to the land or disposed of at sea. Liquid digested sludge is an excellent solid conditioner (Table 17).

Anaerobic digestion tanks are covered and maintained at a temperature of 30 to 35 Celsius. (Figure 13) Under these conditions the required detention time for effective digestion (volatile solids content of the sludge is reduced to 50 percent or less) is approximately 10 to 15 days depending on the degree of operational control. A single stage anaerobic digestion system could be used if the digested sludge is to be disposed of on the land or at sea. However, if other disposal systems are to be used a two-stage anaerobic digestion system is desirable. The second stage is covered but usually is not mixed or heated. The gas produced can be used to heat the incoming sludge or may be converted to mechanical or electrical energy for use at the plant site ((Figure 15). One use for mechanical energy is compressing air for use in diffused air activated sludge systems. The electricity generated can be used for mechanical aerators in the activated sludge process or to drive the influent wastewater pumps or recirculation pumps. Gas recovery and reuse are economically feasible for plants handling about 5 dry tons of wastewater solids per day. The economics are controlled to a large extent by the price of fossil fuel.

Aerobic digestion is applicable to the stabilization of waste activated sludge. The biomass undergoes endogenous respiration or degradation. The detention time and air requirements are 10 to 20 days and 0.5 to 1.2 pounds of oxygen per pound of volatile solids destroyed, respectively. Air requirements for diffused air systems range from 20 to 35 cfm/1000 cu ft for waste activated sludge and up to 60 cfm/1000 cu ft or more for mixtures of primary and activated sludge. If mechanical aeration systems are used the power required ranges from 1 to 1.5 hp per 1000 cu ft. The higher values are typical of aerobic digestion of a mixture of equal parts of primary

and waste activated sludge. The aerobically digested sludge can be disposed of on the land and in the ocean without further treatment.

Conditioning

Wastewater treatment plant sludges do not concentrate well above 4 to 6 percent for waste activated sludge and a mixture of waste activated and primary sludges, respectively, without conditioning. Lime and ferric chloride are the principal inorganic chemical conditioners used. The concentrations of these chemicals required range from 5 to 15 percent by weight or 100 to 300 pounds per dry tons of solids. Synthetic polymers (20 to 60 pounds per dry ton of solids) also have been used to condition sludge.

Fly ash also is an effective conditioner, especially if the sludge is to be incinerated. Fly ash additions of 1 to 4 pounds of fly ash per pound of dry solids have been used to condition primary and activated sludges, respectively.

Heating the sludge to approximately 200 Celsius changes the structure of the sludge matrix and enhances the release of water. Heat treatment of the sludge results in a reduction of the volume occupied by the sludge solids by as much as 100 percent. However, during the heat treatment a portion of the organic material in the sludge is dissolved. Typical filtrate characteristics are presented in Table 18. These filtrates are recycled to the wastewater treatment facility and the additional dissolved organic load must be included in determining aeration requirements.

Conditioning is essential for effective dewatering of sludges by vacuum filters, filter presses or centrifuges. The performance of belt filters also is improved with sludge conditioning.

Belt Filters

Belt filters are devices which increase the solids content of thickened sludges by allowing for gravity drainage of free water and squeezing additional water from the sludge by pressing the sludge between two belts. One belt is made of a woven metal or synthetic fabric and the other is solid usually made of rubber. A schematic diagram of the mechanisms involved is illustrated in Figure 16. Many different configurations and arrangements of the belts characterize the various types of equipment on the market. The reported performance data for different types of equipment indicate cakes solids contents ranging from 10 percent to 30 percent dry solids by weight. Synthetic polymers are used most commonly to increase the solids capture and the solids content of the sludge cake.

Dewatering

Sludge dewatering equipment fall into three general categories: vacuum filters, belt presses, and centrifuges. Dewatering equipment must be preceded by sludge conditioning to be effective. Typical solids contents of dewatered sludge cakes are between 20 percent and 50 percent by weight. The degree of dewatering required is dictated by the processes to follow. If the dewatered sludge cake is to be hauled by dump truck to a land disposal site, the solids content should be increased so that no water is released during hauling. However, if the sludge cake is to be incinerated, the sludge should

be as concentrated as possible for efficient combustion without requiring auxiliary fuel.

Vacuum Filtration Vacuum filters consist of a perforated drum which is covered with a filtering medium, usually a synthetic polymer fabric or stainless steel coils. Figure 17. The medium covered drum is partially submerged in the conditioned sludge. The applied vacuum draws the sludge to the filtering medium. The sludge solids are retained by the medium as the liquid (filtrate) passes through. Through special valving the drum is divided into a filtering zone where the solids are picked up to form the cake, a drying zone in which additional water is drawn from the cake and air is passed through the cake by the vacuum, and a dead zone in which the cake is discharged and the medium is cleaned. The ratio of the form time to the total cycle time is called the submergence which can vary from 25 to 60 percent. Typical cycle times are between 1 to 4 minutes. Other operating variables include: a) conditioning of the sludge, b) agitation of the sludge in the storage trough, c) filtration medium used, and d) vacuum applied. The solids contents of vacuum filter cakes range from 20 percent to 35 percent on a weight basis.

Pressure Filtration Filter presses are designed to allow sludge to be pumped between adjacent plates covered with filter fabric. (Figures 18 and 19) The filter cloth retains the solids as the filtrate is forced through the medium into collection channels. When sludge solids fills the space between the plates, the plates are separated and the filter cake is removed. Although the cycle is automatic operators usually are present to ensure the complete removal of the filter cakes. The operating pressures vary from 100 to 250

psig and the pressing cycle usually is between 30 minutes and one hour. Solids contents of filter cakes range from 35 percent to over 50 percent.

Centrifugation Centrifuges increase the gravitational forces acting on the solids in the sludge resulting in the separation of the solids from the carrier liquid. Three types of centrifuges are used for sludge dewatering: a) solid bowl, b) nozzle or disc centrifuge and c) basket centrifuge. The solid bowl centrifuge (Figure 20) has been used most commonly to dewater sludges. However, in the recent past, basket centrifuges (Figure 21) also have proved to be effective in dewatering waste activated sludge. The nozzle centrifuge (Figure 22) has had limited application to sludge dewatering because of plugging of the nozzles with grit and large particles of solids. However, nozzle centrifuges have been effective is separating oil from oily solids.

The solid bowl centrifuge consists of a bowl and a scrowl each rotating in the same direction. The bowl rotates at speeds of 3,000 to 6,000 rpm while the scrowl rotates approximate 50 to 100 rpm slower. The cake dryness and solids capture are controlled by the pool depth (depth of centrate maintained in the unit. As the pool depth is increased the cake solids decrease and the solids capture increases. The higher capture of fine solids and the associated water account for the decrease in the cake solids content. Conversely, at reduced pool depths the solids capture is lower and the solids content in the cake increases. The addition of polymers to the centrifuge increases solids capture as the mass flow rate is increased. Typical cake solids contents range from less than 20 percent to 30 percent by weight with the addition of conditioning polymers. Without the addition of polymers solid

bowl centrifuges are capable of yielding cake with solid contents of 8 to 12 percent when influent activated sludge was at a concentration of 1 to 2 percent solids by weight.

Basket centrifuges are continuous operating machines which have intermittent influent of sludge. The major components are metal bowl or basket with a lip and a doctor blade to remove the accumulated sludge cake. Sludge is pumped into the rotating basket until the portion of the basket defined by the lip is filled with dewatered solids. At that time the feed sludge pump is stopped, the rotating speed of the basket is reduced, free liquid (centrate) is discharged from the basket, and the doctor blade is positioned to scrape the solids from the side wall of the basket. After removal of the sludge cake is complete the speed is increased and the sludge pumping resumes. Typical solids contents in the cake range from 10 percent to 25 percent without the use of conditioning polymers. Solids capture reported ranged from 80 percent to 98 percent.

Sludge Drying

Aerobically or anaerobically digested sludges can be dried in sand drying beds. Conditioned and dewatered sludges may be dried in mechanical drying systems. Waste activated sludge at times in heat dried without prior digestion.

Sand Drying Beds

Digested sludge is applied to sand drying beds in depths of 6 yo 8 inches. Most of the free water drains from the sludge through sand and gravel into underdrains. The quality of the drainage is similar to that of the

sludge solids and cannot be discharged into receiving streams but must be returned to the wastewater treatment plant. Water bound with the sludge solids evaporates. When the surface of the drying sludge cracks the solids can be removed from the sand. In small drying beds the solids can be removed manually or with a front end loader. However, in large systems special equipment is used to apply the liquid sludge and to remove the dried sludge. The dried sludge can be applied to the land as a soil conditioner.

Heat Drying Mechanical drying systems (Figure 23) require a source of heat. Heated air is mixed with the sludge cake to evaporate some of the water in the sludge. The relatively dry (80 % solids by weight) air borne solids are separated in a cyclone separator. The carrier air passes through an heat exchanger to preheat the incoming air and is deodorized before discharge to the atmosphere. Heat dried sludge usually is sold commercially as a soil conditioner.

Incineration

The heat content of municipal and industrial wastewater treatment sludges and other conventional fuels are presented in Table . The heat content of the sludges offsets the need for auxiliary fuel. In fact, the combustion of dewatered sludge cake (solids content of about 35 percent by weight) can be sustained by the heat released by the sludge solids without the addition of auxiliary fuel. Equipment used for sludge incineration includes: a) multiple hearth furnaces (Figure 24) and b) fluidized bed incinerators (Figure 25).

The products of incineration can be recovered and used to condition the sludge. The heat released can be used to heat treat the sludge and the fly ash can be used as a sludge conditioner prior to vacuum filtration or filter presses. These applications were discussed earlier under sludge conditioning.

Composting

Sludge composting is similar in principle as refuse composting discussed earlier. Wastewater sludges have been mixed with municipal refuse and composted. However, the difficulty in marketing composted refuse has resulted in separate composting of wastewater sludges. Sawdust, wood chips and shreded rubber tires are mixed with the sludge to reduce the overall moisture content of the mixture to between 40 and 70 percent by weight and to provide a matrix to support the sludge solids and enhance the flow of air through the composting sludge. Excessive moisture inhibits the flow of air and the transfer of oxygen required for aerobic biological activity. Fungi and bacteria decompose the organic constituents of the sludge solids and the finished compost is a relatively stable humus like material. Composted sludge is an excellent soil conditioner and has some value as a fertilizer. The nitrogen and phosphorus content of the composted sludge reduces the requirement for these nutrients in fertilizers which might be added for agricultural purposes. Composted activated sludge contains about 12 percent by weight of nitrogen and about 2 percent phosphorus. Compost increases the field moisture content and the organic content of soils and promotes soil aggregation thus inhibiting soil erosion potential.

The shreded rubber tires and the wood chips can be recovered from the composted sludge by ballistic separation. However, sawdust is not easily separated from the composted sludge.

Land Disposal

There are a number of methods for applying sludge to the land. Liquid sludges (0.5 to 12 percent by weight) can be dispensed by: a) sprinkler irrigation, b) injection techniques, c) tanker application, and c) ridge and furrow irrigation. Sludge cakes (15 to 50 percent by weight)can be: a) placed in trenches and covered, b) put in a sanitary landfill, or c) spread on the land and incorporated into the soil. In some areas, anaerobically digested sludge, is applied to green areas such as median strips of highway systems.

Each land application technique must be evaluated in terms of the local climate, topography, and soil conditions. Net evaporation rates also dictate the rate of application of liquid sludge. In areas where the net annual evaporation rate is negative, i.e. the annual rainfall exceeds the annual evaporation, sludge application may be limited to 100 days per year. However, in the southwestern area of the U.S. where the annual evaporation exceeds the rainfall by as much as 70 inches, application periods of 200 to 300 days per year may be possible. Soil properties that must be considered include: a) depth, b) infiltration and percolation capacity (permeability), c) texture, d) aerobic zone, e) alkalinity and acidity, f) pH, and g) exchange capacity.

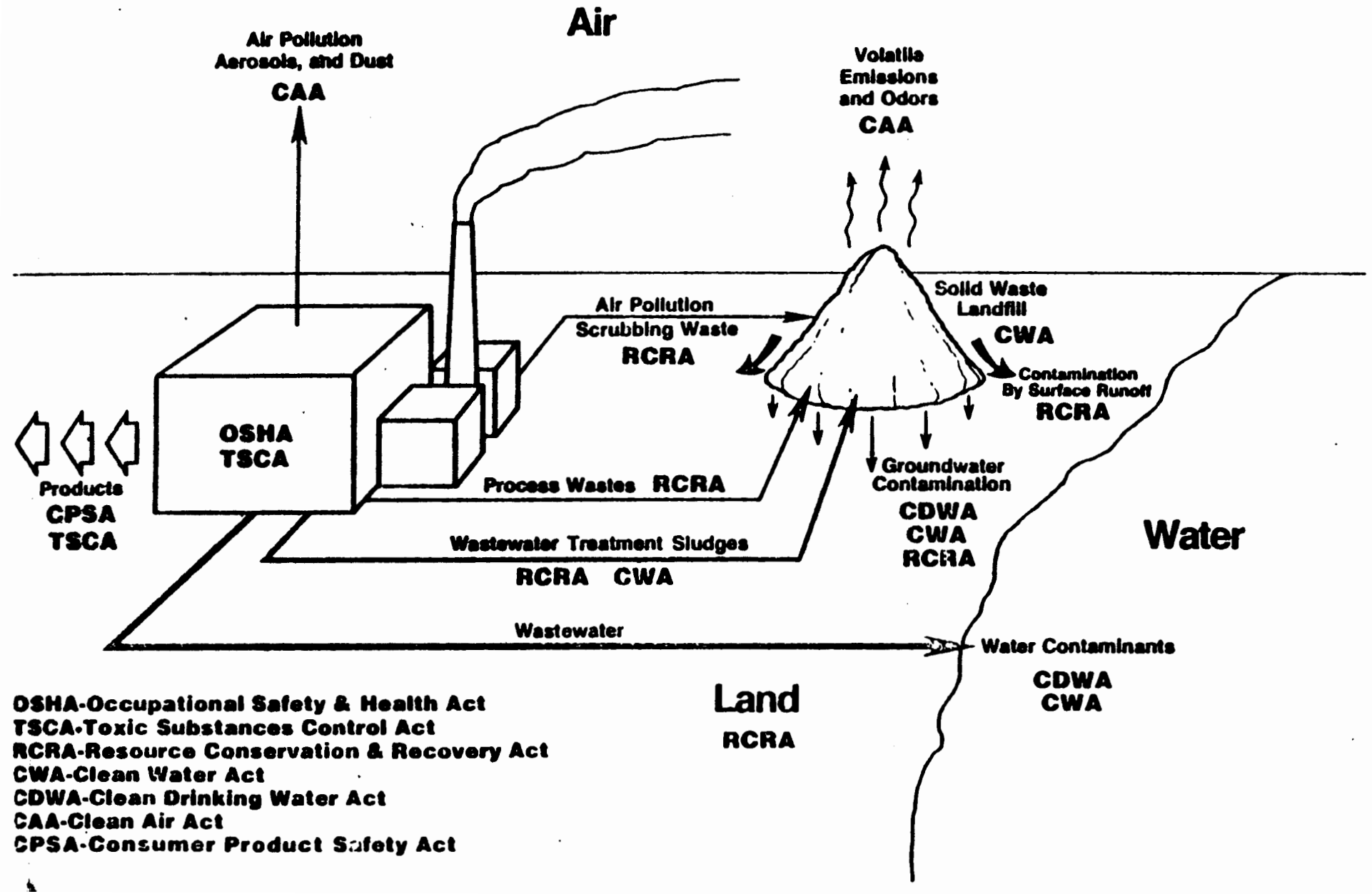
Composted sludge, and liquid and air dried digested sludges can be applied to green areas, recreational areas and parks, and used in the

production of grasses, ornamental plants and other vegetation not normally eaten raw by people. Sludges also have been applied to reclaim land such as abandoned strip mines, and filled areas. The organic content in the sludge helps to stabilize the soil and enhance the growth of ground cover.

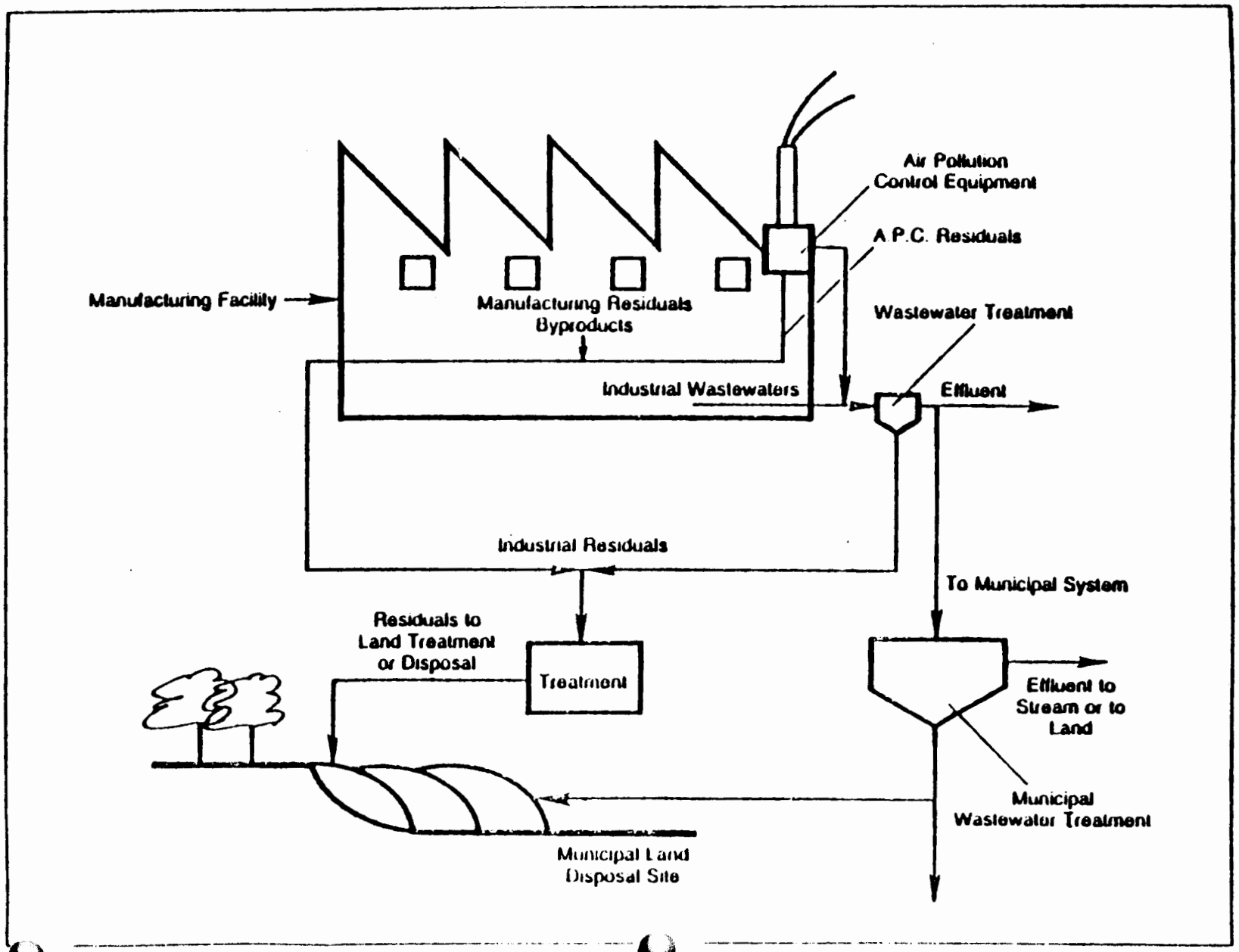
Ocean Disposal

The U.S. Environmental Protection Agency discourages ocean disposal. However, ocean dumping of wastewater sludges using pipelines and barges is used by some coastal cities. Philadelphia, Pennsylvania, and New York City are the two largest cities utilizing barging of wastewater sludges to ocean disposal. Los Angeles, California, is the largest city utilizing an ocean outfall for wastewater sludge disposal.

DISPOSAL ALTERNATIVES



DISPOSAL ALTERNATIVES



Definition Of A Solid Waste

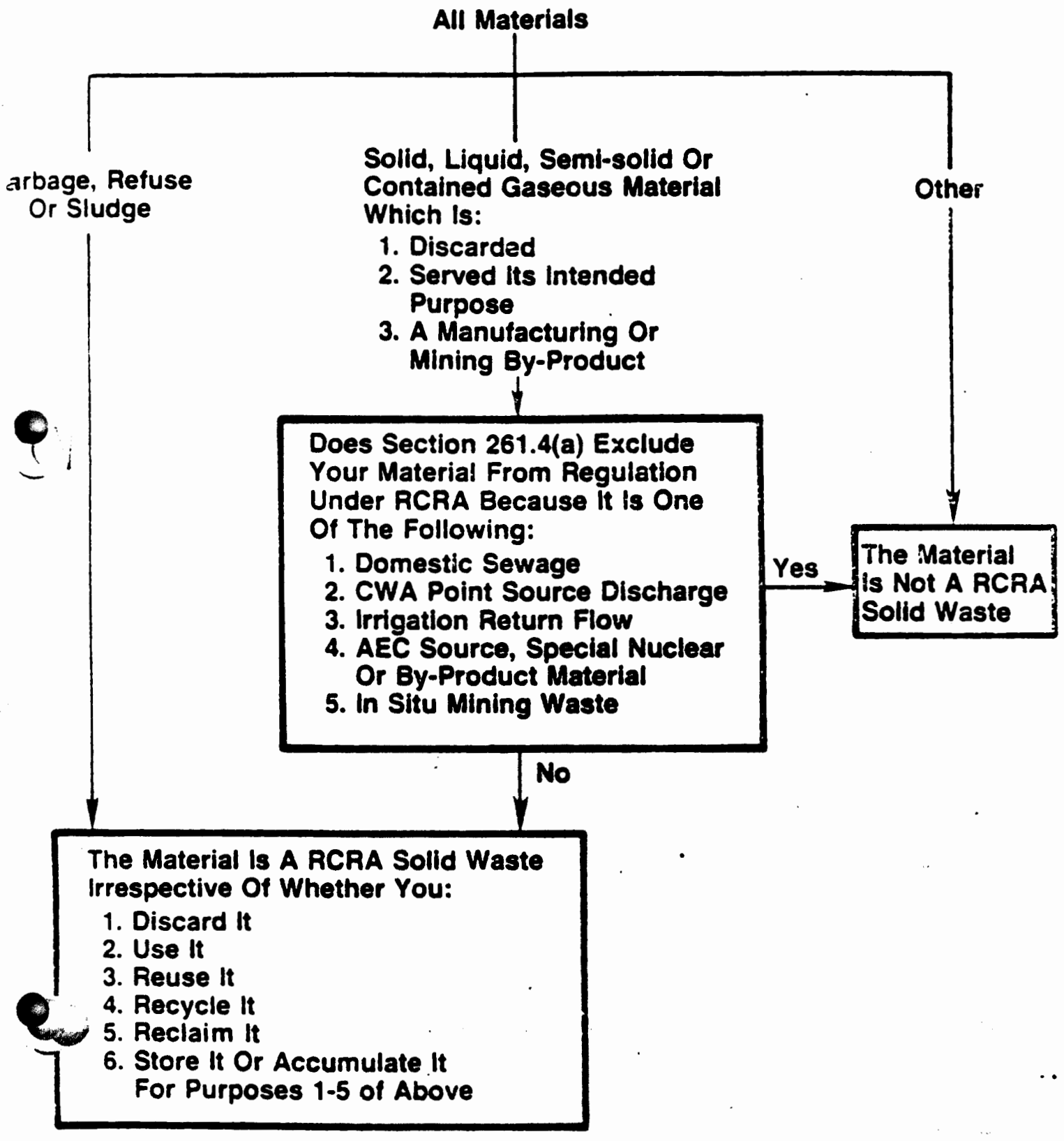


TABLE 1

EXPECTED RANGES IN MIXED MUNICIPAL REFUSE COMPOSITION (1)

Component	Percent composition as received (dry weight basis) Anticipated range	Nominal
Paper	37-60	55
Newsprint	7-15	12
Cardboard	4-18	11
Other	26-37	32
Metallics	7-10	9
Ferrous	6-8	7.5
Nonferrous	1-2	1.5
Food	12-18	14
Yard	4-10	5
Wood	1-4	4
Glass	6-12	9
Plastic	1-3	1
Miscellaneous	< 5	3
Moisture Content:		100
Range (percent) 20-40		
Nominal (percent) 30		

TABLE 2

PHYSICAL AND CHEMICAL CHARACTERISTICS
OF MUNICIPAL SOLID WASTE (4)

Constituents	Percent by Weight (as received)
Proximate Analysis	
Moisture	15-35
Volatile Matter	50-65
Fixed Carbon	3-9
Noncumbustibles	15-25
Ultimate Analysis	
Moisture	15-35
Carbon	15-30
Oxygen	12-24
Hydrogen	2-5
Nitrogen	0.2-1.0
Sulfur	0.02-0.1
Noncombustibles	15-25
Higher Heating Value	BTU per lb (as received) 3,000-6,000

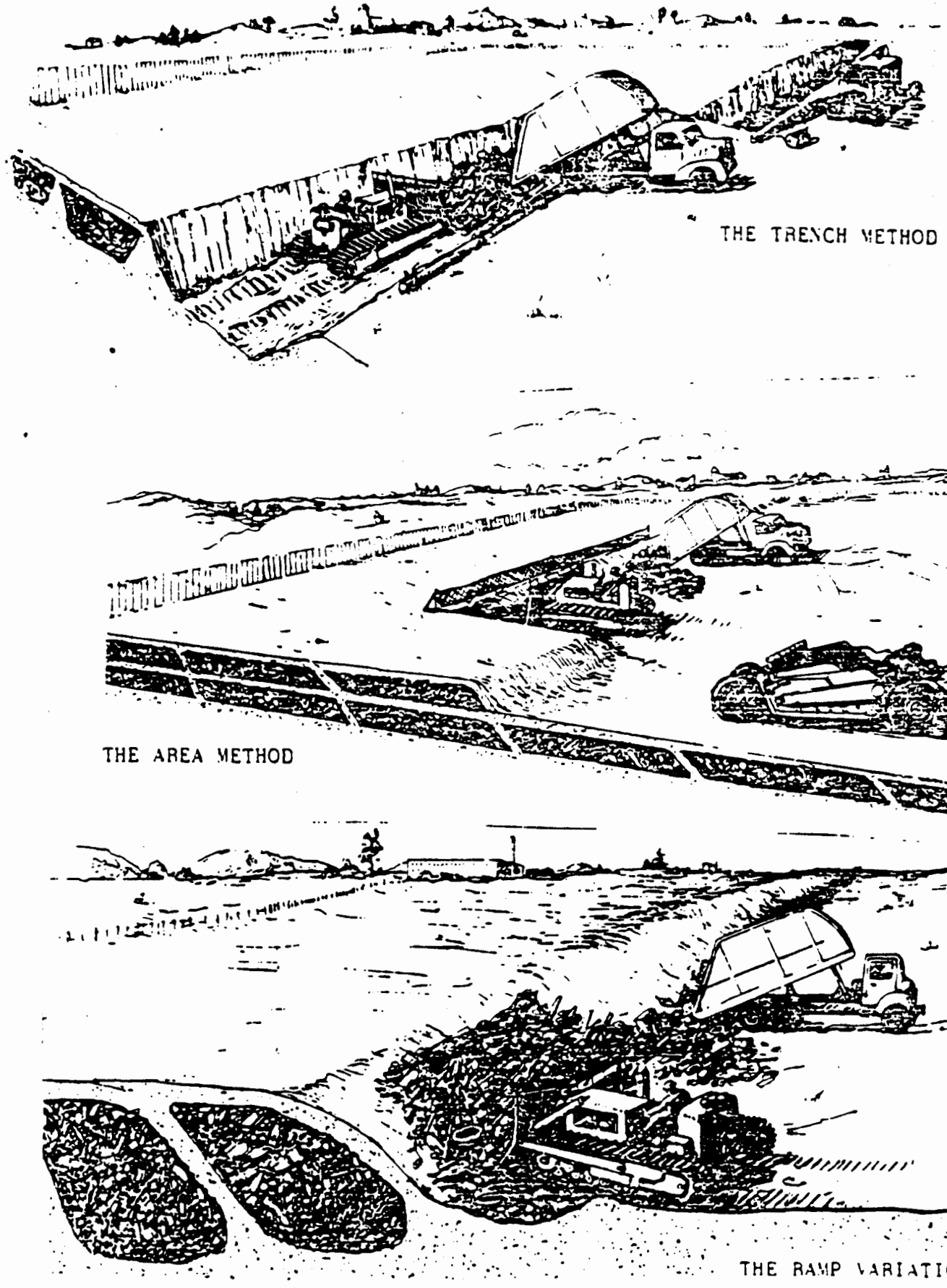


FIGURE 1
SANITARY LANDFILL PROCEDURES (29)
(courtesy US Public Health Services)

TABLE 3

COMPOSITION OF TYPICAL LEACHATES (33)(30)

Constituent	Concentration Range
Iron (mg/L)	200-1,700
Zinc (mg/L)	1-135
Nickel (mg/L)	0.01-0.8
Copper (mg/L)	0.10-9.0
Sodium (mg/L)	100-3,800
Potassium	655-1,860
Phosphate (mg/L)	5-130
Sulfate (mg/L)	25-1,220
Chloride (mg/L)	100-2,400
Total Nitrogen (mg/L)	152-550
Ammonia nitrogen (mg/L)	141-845
Hardness (as $CaCO_3$) (mg/L)	200-8,700
Alkalinity (as $CaCO_3$) (mg/L)	
COD (mg/L)	100-750,000
BOD (mg/L)	7,000-720,000
Total Residue (mg/L)	1,000-45,000
pH	4.00-8.5

TABLE 4

HEAT CONTENT OF COMPONENTS OF MUNICIPAL REFUSE (4)

	Higher Heating Value BTU/pound moisture and ash free basis
Brush, California (8.87% ash**)	8,518
Carbon	14,093
Carbon Monixide	4,347
Cellulose, $C_6H_{10}O_5$	7,526
Cellulose flock, unground	7,490
Charcoal, willow	14,270
Cork	10,410
Dextrin, a gum	7,398
Excelsior (0.77% ash**)	8,625
Fats	
Lipids (ether soluble oils, greases, and waxes)	16,700
Oleic acid	17,009
Stearic acid	17,072
Suet	16,200
Garbage, California (6.53% ash**)	7,280
Greens, California (10.57% ash**)	
Hydrogen	61,100
Leather (10.09% ash**)	9,974
Leaves, dry, California (8.48% ash**)	7,588
Lignin	10,530
Linoleum	11,450
Metals	
Aluminum to Al_2O_3	13,350*
Copper to CuO	1,085*
Iron to Fe_3O_4	2,870*
Iron to Fe_2O_3	3,160*
Lead to PbO	450*
Magnesium to MgO	10,640*
Tin to SnO_2	2,105
Zinc to ZnO	2,295

TABLE 4 (cont'd)

Paper Products	
Books and magazines (24.05% ash**)	7,557
Cardboard (7.79% ash**)	8,373
Mixed paper (6.55% ash**)	8,078
Newsprint (3.93% ash**)	8,550
Waxed paper	11,000
Waxed cartons	12,000
Rags	
Cotton	7,200
Mixed (2.19% ash**)	7,540
Wool	8,900
Residue, California (92.4% ash**)	6,628
Rubber (48% ash**)	12,800
Rubber	12,400
Shellac	13,580
Starch	7,522
Sugars	
d-Glucose (dextrose)	6,724
l-fructose	6,744
Sucrose	7,097
Sulfurs to SO_2	3,983
Synthetics	
Cellulose acetate	8,000
Nylon polymer	13,190
Phenol formaldehyde	11,190
Polyethylene, malt index = 6.0	19,950
Polypropylene, 0.3 - 0.4 antioxidant	19,950
Polystyrene, clear	17,830
Polyurethane foam, not fire retardant	10,260
Rayon flock	7,490
Styrene-butadiene latex copolymer	17,700
Vinyl chloride-vinyl acetate copolymer	8,830
Wood, California (1.13% ash**)	8,420
Wood, Washington, D.C. (1.65% ash**)	8,865

* Indicates BTU/pound of metal
** Indicates ash on a dry basis

FIGURE 2
ESSENTIAL COMPONENTS OF AN INCINERATOR

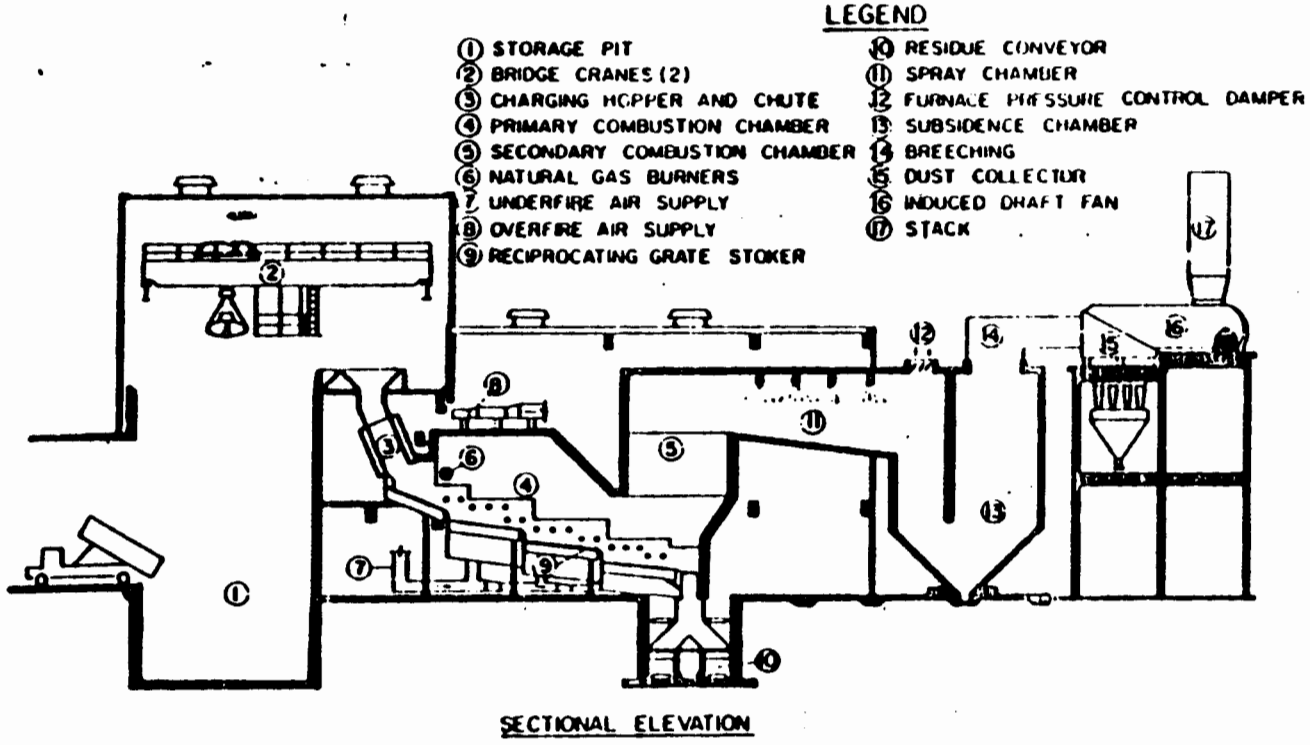


FIGURE 3
CROSS SECTION OF A MUNICIPAL REFUSE INCINERATOR

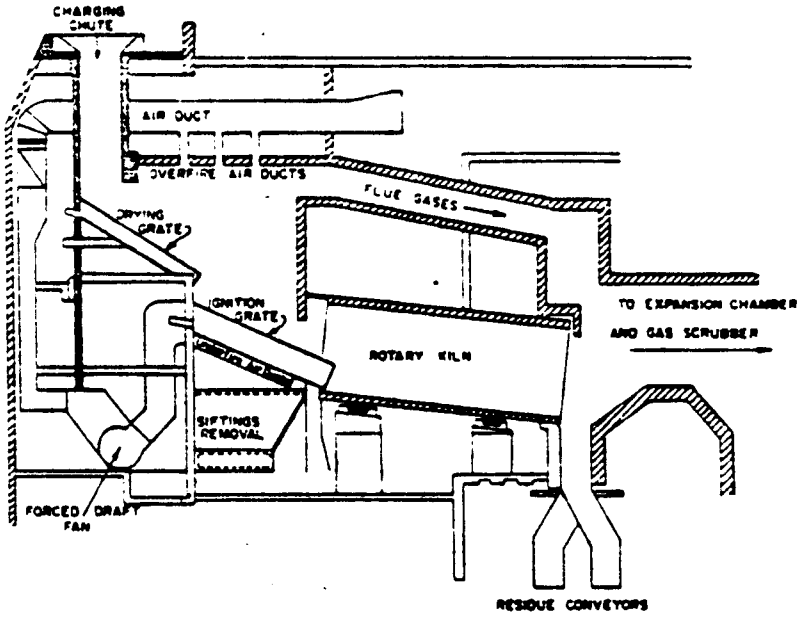


FIGURE 4
ROTARY KILN FURNACE

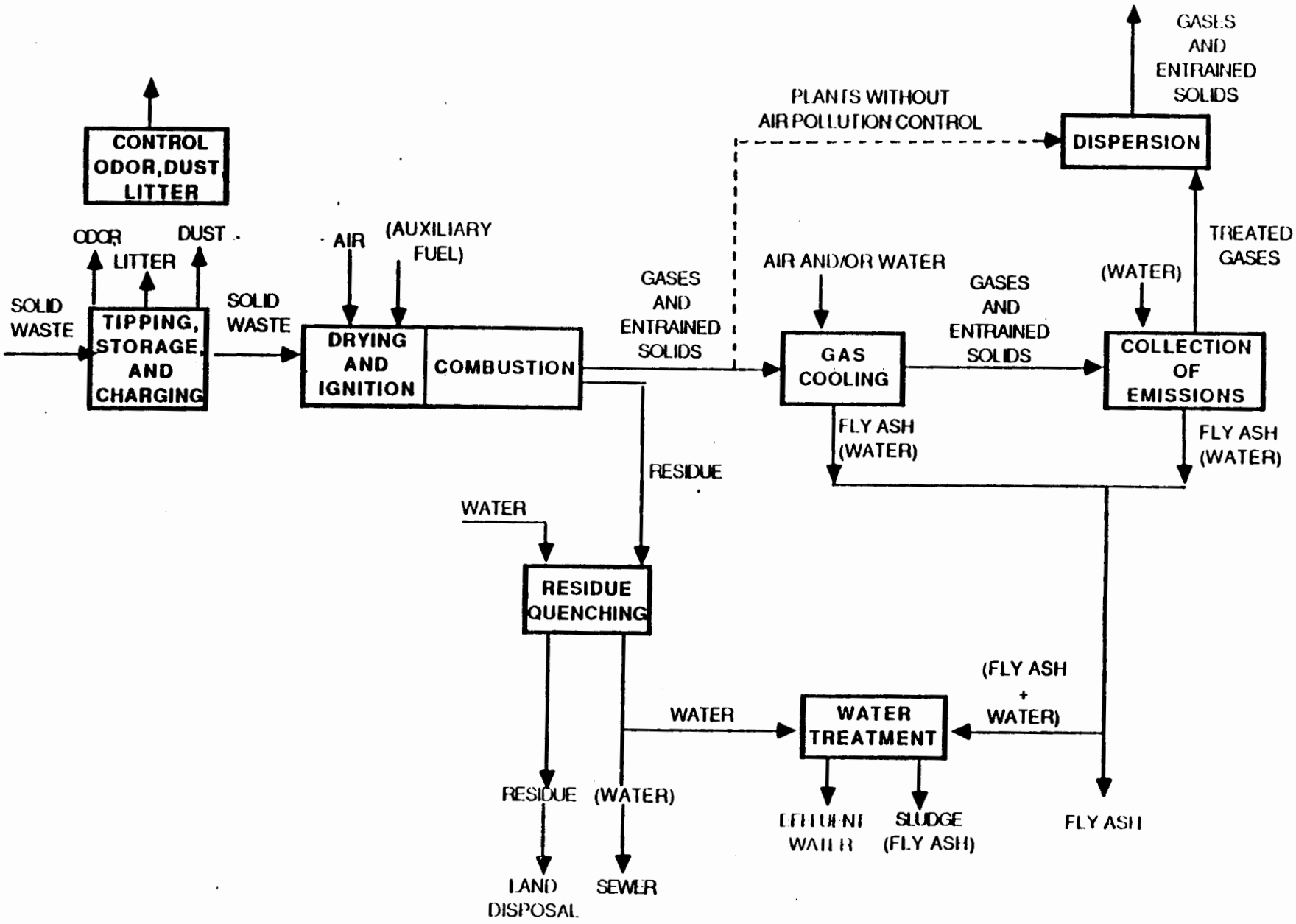


FIGURE 5
INPUTS AND RESIDUE SOURCES AT AN INCINERATOR

TABLE 5

TYPICAL PHYSICAL COMPOSITION OF INCINERATOR RESIDUES (4)

Wet Bulk Density, lb/cu yd	943
Dry Bulk Density, lb/cu yd	575
Moisture, percent	33
Tin Cans, percent*	17
Mill Scale and Small Iron, percent*	7
Iron Wire, percent*	1
Massive Iron, percent*	4
Nonferrous Metals, percent*	2
Stones and Bricks, percent*	1
Ceramics, percent*	1
Unburned Paper and Charcoal, percent*	8
Partially Burned Organics, percent*	1
Ash, percent*	15
Glass, percent*	44

*Dry Wet Basis

TABLE 6

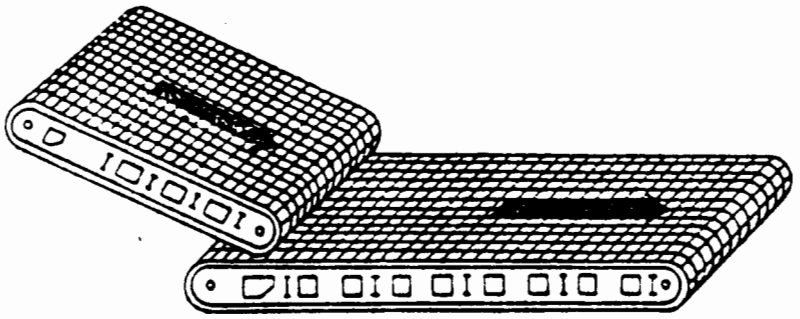
CHEMICAL COMPOSITION OF RESIDUE (4)

Test	Range %
Non-Combustible	50-100
Volatile Material	0-50
Organic	3-15
Inorganic	97-85
Water Soluble	1-8
Ether Soluble	0-5
Calorific Value	0-5000
Protein	0-1
Phosphorus	0-0.5
Carbon	0-20
Hydrogen	0-5
Nitrogen	0-2
Silicon as SiO_2	36-50
Aluminum as Al_2O_3	23-28
Iron as Fe_2O_3	6-10
Calcium as CaO	7-8
Magnesium as MgO	2-3
Sodium as Na_2O	5-6
Potassium as K_2O	
Sulfur as SO_3	3-10
Apparent Specific Gravity	2.6

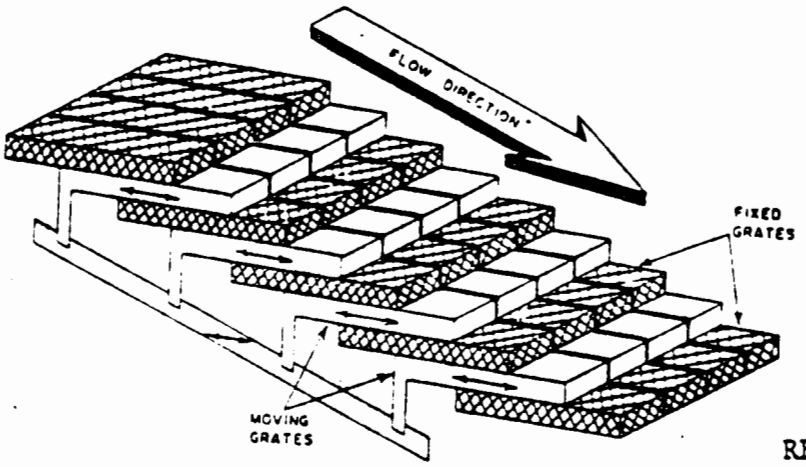
TABLE 7

CHARACTERISTICS OF INCINERATOR WASTEWATER (37)

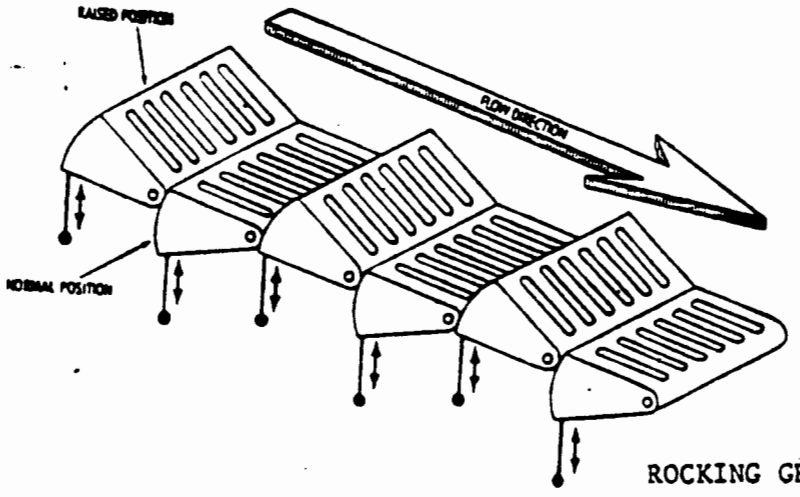
	Residue Quench Water	Flyash Effluent
pH	6.0-11.8	4.5-6.4
Total Dissolved Solids (mg/L)	597-9,005	5,660-9,364
Suspended Solids (mg/L)	7-5,476	208-2,010
Volatile Solids (percent)	10.5-57.6	23.3-24.7
Hardness ($CaCO_3$) (mg/L)	112-1,574	2,440-3,780
Sulfates (SO_4) (mg/L)	110-830	6225-1,350
Phosphate (PO_4) (mg/L)	0-225	11.5-76.2
Chloride (Cl) (mg/L)	50-3,650	2,155-3,821
Alkalinity ($CaCO_3$) (mg/L)	192-1,290	0-28
BOD_5	-	6.2-13.5



TRAVELING GRATE



RECIPROCATING GRATE



ROCKING GRATE

FIGURE 5
FURNACE GRATES

TABLE 8

AIR POLLUTION CONTROL FOR MUNICIPAL INCINERATOR

Collectors	Comparative Space Requirements	Relative Cost of Gas Cleaning per CFM	Collection Efficiency	Gas Temperature Inlet	Gas Temperature Outlet	Water to Collector Per 1000 CFM Gas Treated Evaporated	Water to Collector Per 1000 CFM Gas Treated Total	Gas Conditioning Prior to Collector
Wetting Chamber with Sprays	60%	0.20	40-60%	1800°F	500°F	1.0 GPM	2-3 GPM	None Required
Scrubber								
Spray Type	50%	0.35	75-85%	1800°F	200°F	1.7 GPM	4-8 GPM	None Required
Flooded Plate	30%	0.65	90-95%	1800°F	200°F	1.7 GPM	3-5 GPM	None Required
Venturi	25%	0.40	92-97%	1800°F	200°F	1.7 GPM	4-8 GPM	None Required
Cyclone								
Multi-Cyclone Spinner Vane	25%	0.27	80-92%	500°F-700°F	500°F-700°F	None	None	1. Waste heat boiler cooling to 600°F 2. Evaporative spray cooling to 700°F 3. Air dilution cooling to 700°F
Cyclones to 60" dia. Tangential Inlet	30%	0.30	75-90%	500°F-700°F	500°F-700°F	None	None	Same as for Multi-Cyclone
Wet Wall Cyclones	25%	0.32	85-94%	600°F-1000°F	400°F-600°F	0.2-0.5 GPM	2-4 GPM	Evaporative spray cooling to 1000°F
Fabric Collector								
Glass Cloth	100%	1.00	99%	500°F	500°F	None	None	1. Evaporating spray cooling to 700°F plus air dilution cooling to 500°F 2. Waste heat boiler cooling to 600°F plus air dilution to 500°F
Electrostatic Precipitator								
Dry Precipitator	90%	1.20	95-98%	600°F	600°F	None	None	1. Evaporative spray cooling to 600°F 2. Waste heat boiler cooli[illegible] 500°F

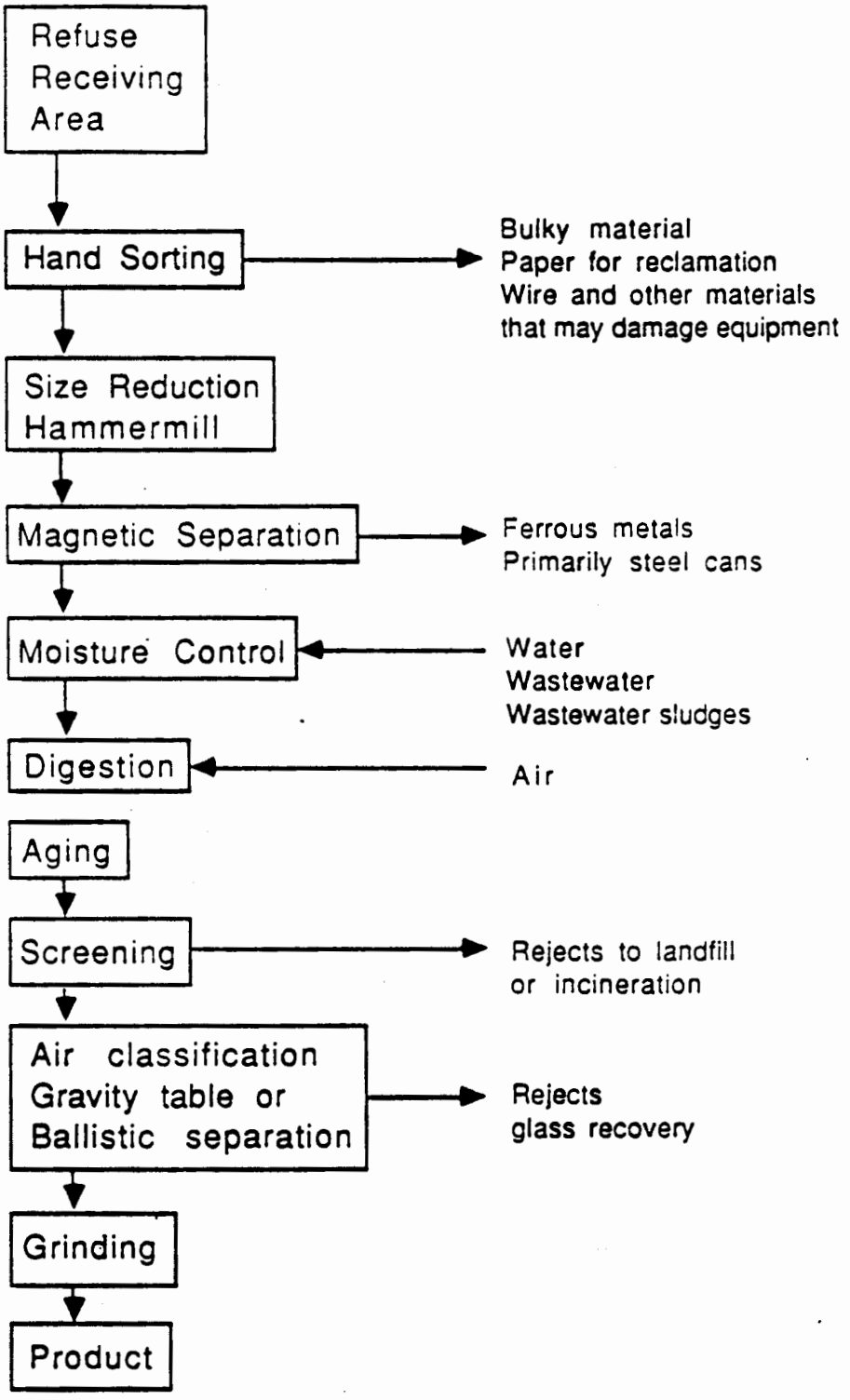


FIGURE 6
SCHEMATIC FLOW DIAGRAM OF A COMPOST PLANT

FIGURE 7
SCHEMATIC DIAGRAM OF A COMPOSTING SYSTEM

MUNICIPAL REFUSE COMPOSTING PLANTS IN THE UNITED STATES (45)

Location	Process	Capacity Ton/Day	Wastes	Began Operation	January 1971 Status
Altoona, Pennsylvania	Fairfield-Hardy	45	Garbage, paper	1963	Operating intermittently
Boulder, Colorado	Windrow	100	Mixed refuse	1965	Operating on demand basis
Gainesville, Florida	Metro Waste Conversion	150	Mixed refuse, digested sludge	1968	Closed 1971
Houston, Texas	Metro Waste Conversion	360	Mixed refuse, raw sludge	1966	Operating on demand basis*
Houston, Texas	Snell	300	Mixed refuse	1966	Closed 1966
Johnson City, Tenn.	Windrow	52	Mixed refuse, raw sludge	1967	Closed 1971
Norman, Oklahoma	Naturizer	35	Mixed refuse	1959	Closed 1964
Mobile, Alabama	Windrow (formerly briquetting process)	300	Mixed refuse, digested sludge	1966	Operating on demand basis
New York, New York	Varro	150	Mixed refuse	1971	Operating
Phoenix, Arizona	Dano	300	Mixed refuse	1963	Closed 1965
Sacramento, Calif.	Dano	40	Mixed refuse	1956	Closed 1963
San Fernando, Calif.	Naturizer	70	Mixed refuse	1963	Closed 1964
San Juan, P.R.	Fairfield-Hardy	150	Mixed refuse	1969	Closed 1971
Springfield, Mass.	Frazer-Eweson	20	Garbage	1954;61	Closed 1962
St. Petersburg, Fla.	Naturizer	105	Mixed refuse	1966	Operating on demand basis
Williamston, Mich.	Riker	4	Garbage, raw sludge, corn cobs	1955	Closed 1962
Wilmington, Ohio	Windrow	20	Mixed refuse	1963	Closed 19

*closed in 1972

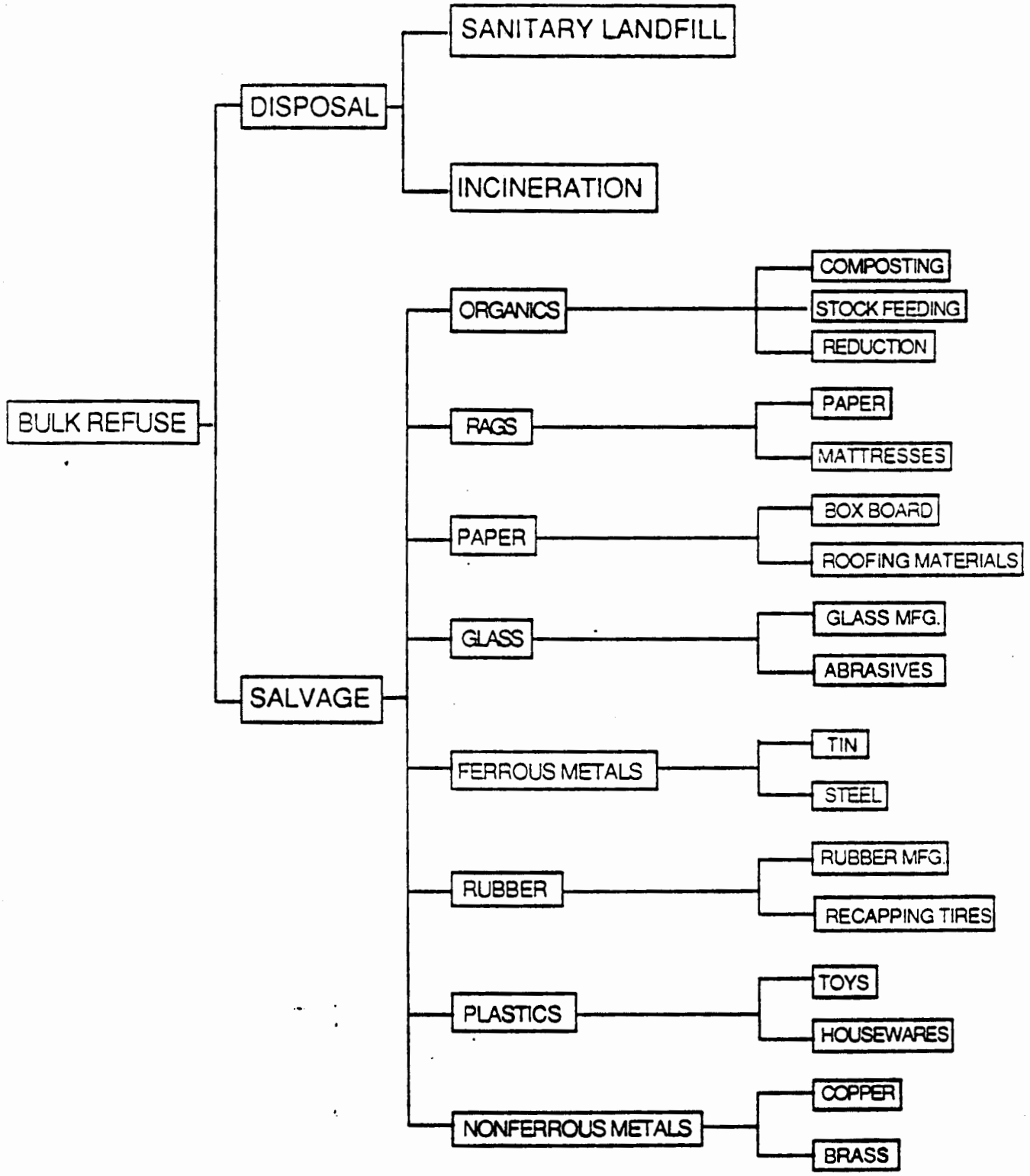


FIGURE 8
SALVAGE POTENTIALS FOR MUNICIPAL REFUSE

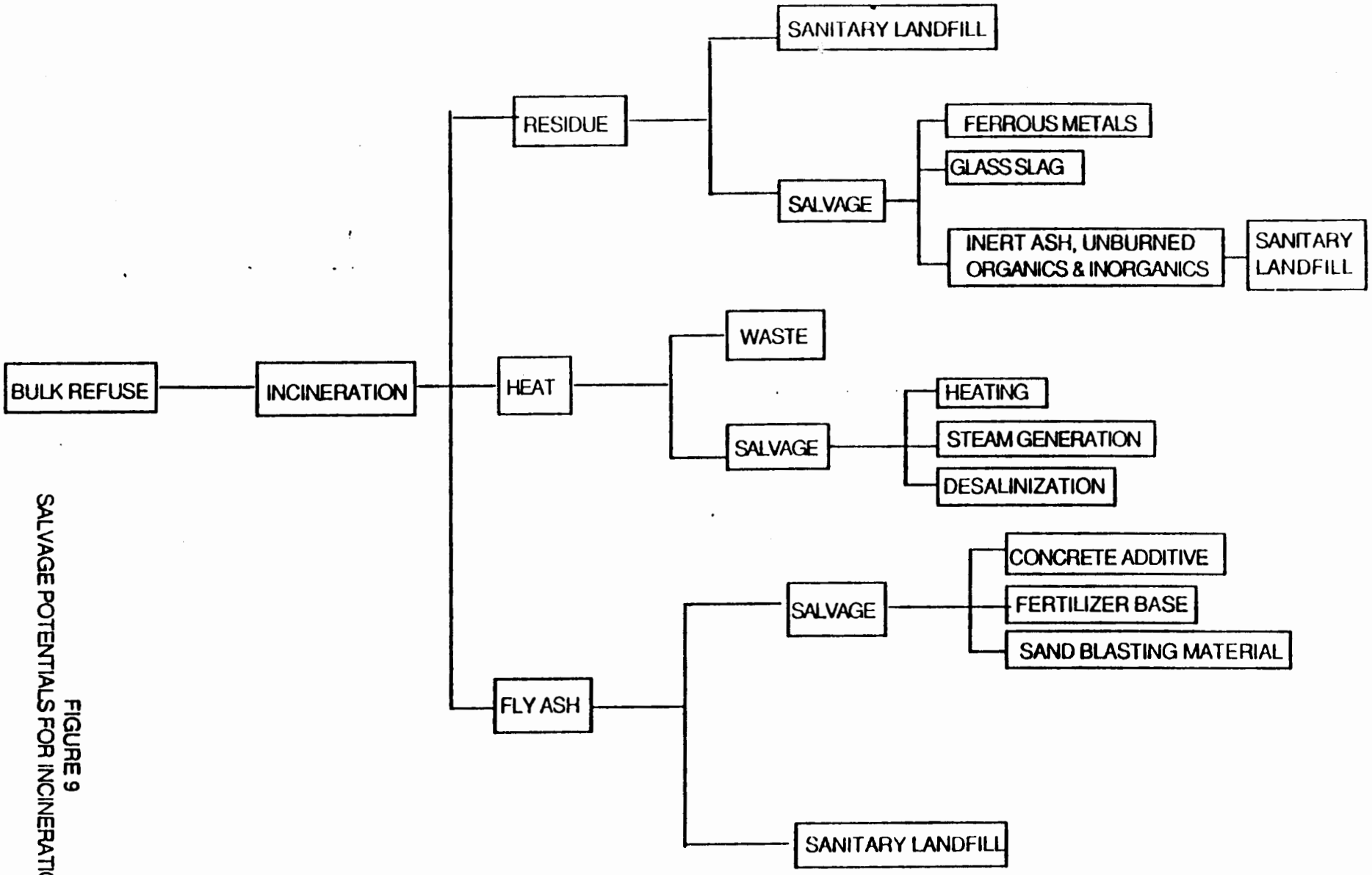


FIGURE 9
SALVAGE POTENTIALS FOR INCINERATION RESIDUE

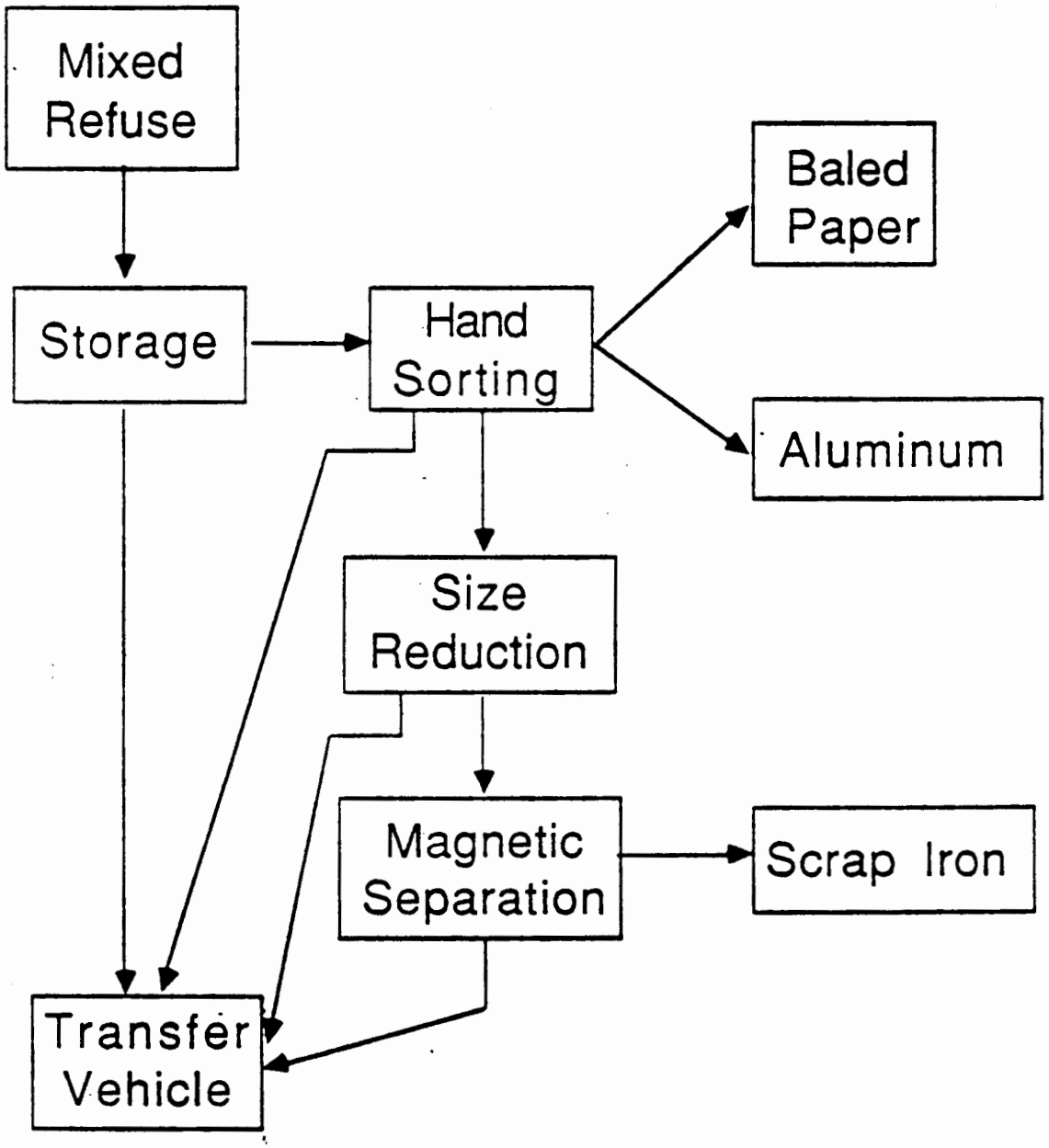


FIGURE 10
SCHEMATIC DIAGRAM OF A CENTRAL SEPARATION FACILITY

TABLE 10. ENERGY REQUIREMENTS - VIRGIN vs. RECYCLE

	ENERGY REQUIREMENTS		Barrels of Oil
	Virgin Material (kwh/ton)	Recycled Material (kwh/ton)	Saved/Ton Recycled Material
Aluminum	51,379	2000	29.1
Iron	4270	1666	1.5
Paper	6730	2520	2.5

TABLE 11. TRANSPORTATION COSTS (1970) - SCRAP vs. VIRGIN MATERIAL

Mode	Virgin Material ($/net ton)	Secondary Material ($/net ton)
Rail Transport		
iron ore vs. ferrous scrap	2.31	4.83
roundwood vs. waste paper	1.92	8.01
woodchips and residue vs. waste paper	2.58	8.01
Motor Transport		
woodchips and residue vs. waste paper	2.44	9.68
pulp vs. waste paper	5.10	9.68

TABLE 12. SOURCES AND CHARACTERISTICS OF OILY REFINERY SOLIDS

	Typical Weight % Composition		
	Water	Solids	Oil
Crude Oil Tank Bottoms	15	45	40
Slop Tank Bottoms	64	4	32
API, CPI Separator Bottoms	36	47	17
Coker Blowdown Solids	20	40	40
Water Impoundment Pond Bottoms	40	40	20

TABLE 12

CONSTITUENCY AND MARKET PRICE OF HOUSEHOLD REFUSE IN THE LOS ANGELES AREA (51)

Category	Fraction Percent	Market Price* Per Ton $	Recovery Factor	Resource Value Per Ton $
Corrugated paper	3.6	10.00	0.8	0.29
Newspaper	10.7	7.00	0.8	0.60
Miscellaneous paper	27.0	-	-	-
Plastic film	0.9	-	-	-
Molded plastics	1,2	-	-	-
Leather, rubber	0.5	-	-	-
Textiles	2.0	50.00	0.7	0.70
Tree trimmings	21.5	-	-	-
Lumber	1.6	-	-	-
Glass	7.3	15.00	0.9	0.99
Ceramics, stone	0.8	-	-	-
Non-ferrous metals	0.8	215.00	0.9	1.55
Ferrous metals	0.8	15.00	0.9	0.70
Grass, dirt	11.6	-	-	-
Miscellaneous	9.7	3.60	0.9	0.17
	100.0			5.00

*These are market prices quoted by various industries at the time this article was prepared.

TABLE 13. TREATMENT PROCESSES AND RESIDUALS

Classification	Processes	Residuals
Water Treatment	Softening, coagulation sedimentation	Calcium carbonate, sludge and aluminum hydroxide sludge
Preliminary Treatment	Screening and Grit Removal Neutralization, oil water separation	Screening (rags, sticks, etc.) Grit (sand, silt, cinders) Chemical sludge, oil, oily solids
Primary Treatment	Sedimentation or Dissolved Air Flotation	Organic sludge and skimmings (grease and other floating materials)
Intermediate Treatment (Chemical)	Coagulation and Sedimentation	Sludge containing organic solids and chemical precipitate and skimmings
Secondary Treatment	Activated sludge, contact stabilization, extended aeration, trickling filters, rotating bio-discs, etc. followed by secondary clarification	Biological Sludge
	Stabilization Pond	Algae in the effluent
Disinfection	Chlorination Ozonation	
Land Application of Effluents	Pretreatment by primary and biological treatment or chemical treatment	Suspended solids in the effluent applied to the land
Advance Waste Treatment	Coagulation and Sedimentation	Chemical Sludge (aluminum, hydroxide and Ferric hydroxide)
	Sand Filtration	Suspended solids in backwash water
	Adsorption on activated carbon	Spent activated carbon which can be regenerated
	Ion Exchange	Spend regenerant
	Membrane Processes (Reverse osmosis, electrodialysis, etc.)	Concentrated brine
Sludge Treatment	Anaerobic Digestion Aerobic Digestion	Organic material which is partially stabilized, usable gas (methane)
Sludge Concentration	Gravity or Flotation thickening	More concentrated sludge
Sludge Dewatering	Vacuum Filtration Filter press, centrifuge	Sludge Cake
Sludge Disposal	Incineration Pyrolysis Land disposal Ocean disposal	Ash Various products Sludge

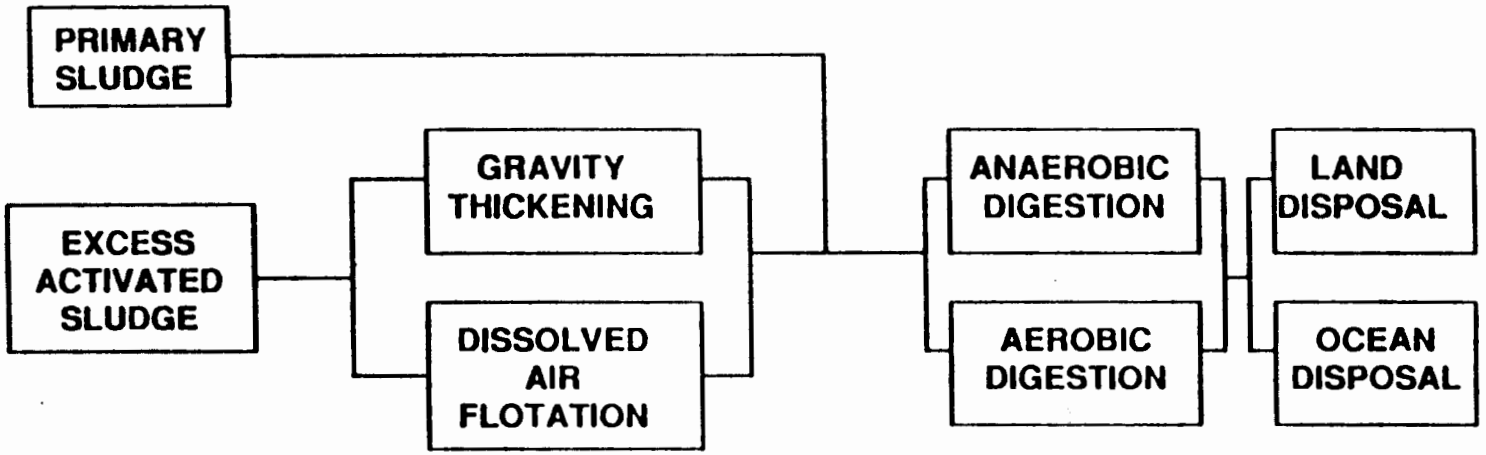
TABLE 14. RESIDUALS FROM MUNICIPAL TREATMENT

TREATMENT	RESIDUE lb/MG	Gal/MG	cuft/MG
PRELIMINARY			
Screening			0.17-11.7 (1.5)
Grit			0.39-10.5 (2.61)
PRIMARY			
Sludge	1250	3675	
Skimmings			0.05-29.78 (7.03)
BIOLOGICAL			
Activated Sludge	1025	12300	
Trickling Filter	475	750	
THICKENING	2275	4410*	
SLUDGE DIGESTION			
Primary & Biological	1262	2500** (4000)***	
ADVANCED			
Coagulation & Sedimentation			
Alum****	(2000)	(12000)	
Iron****	175-781 (507)	6000-36000 (22000)	
Lime****	3100-6800 (4650)	50000-63000 (53400)	

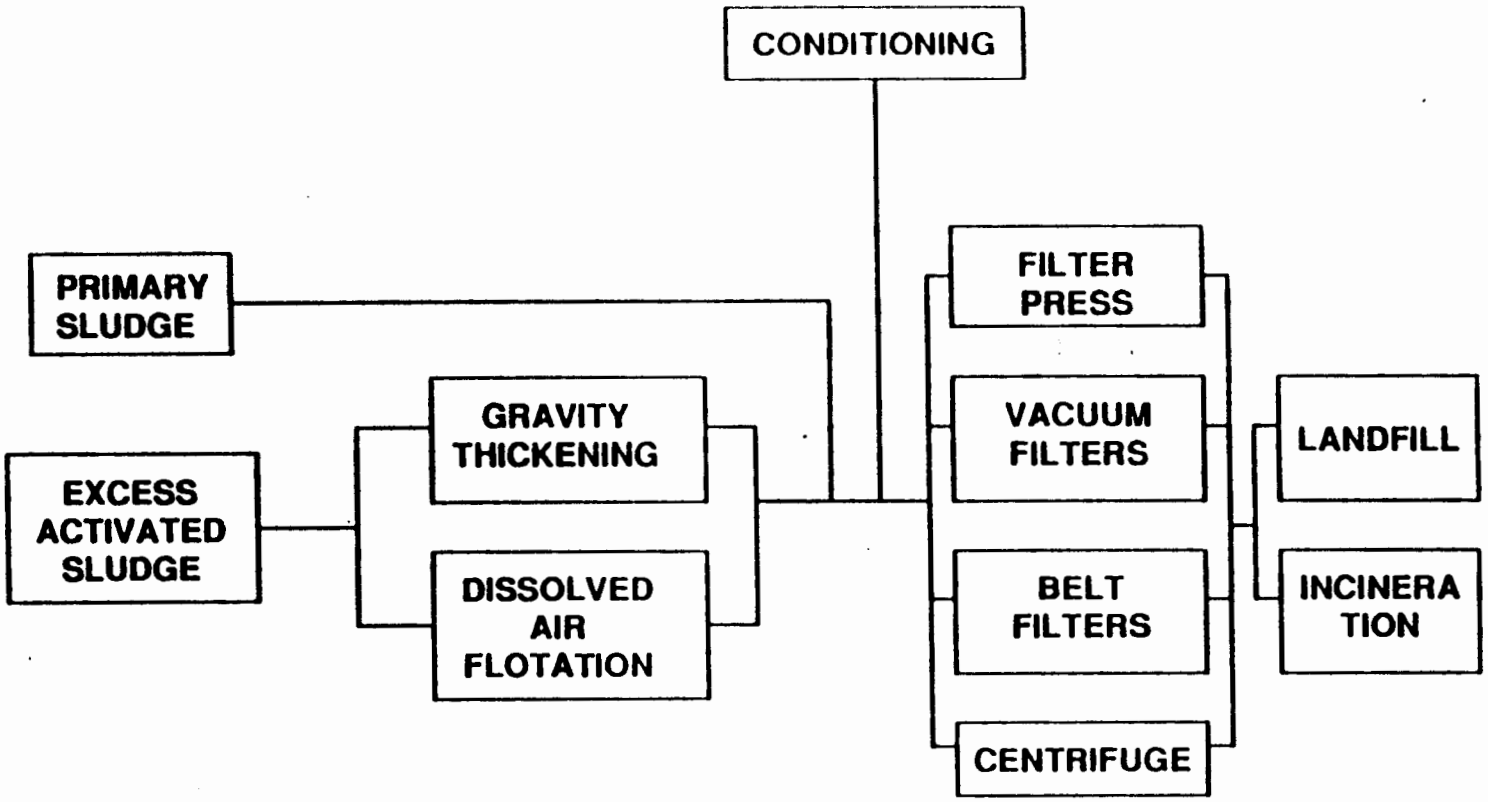
* Combined primary and waste activated sludge are thickened to 6% TS
** Stabilized sludge solids concentrate to 6% TSS
*** Total volume of sludge solids and supernatant
**** Numbers in () are typical values

TABLE 15 TYPICAL CHARACTERISTICS OF MUNICIPAL SLUDGE*

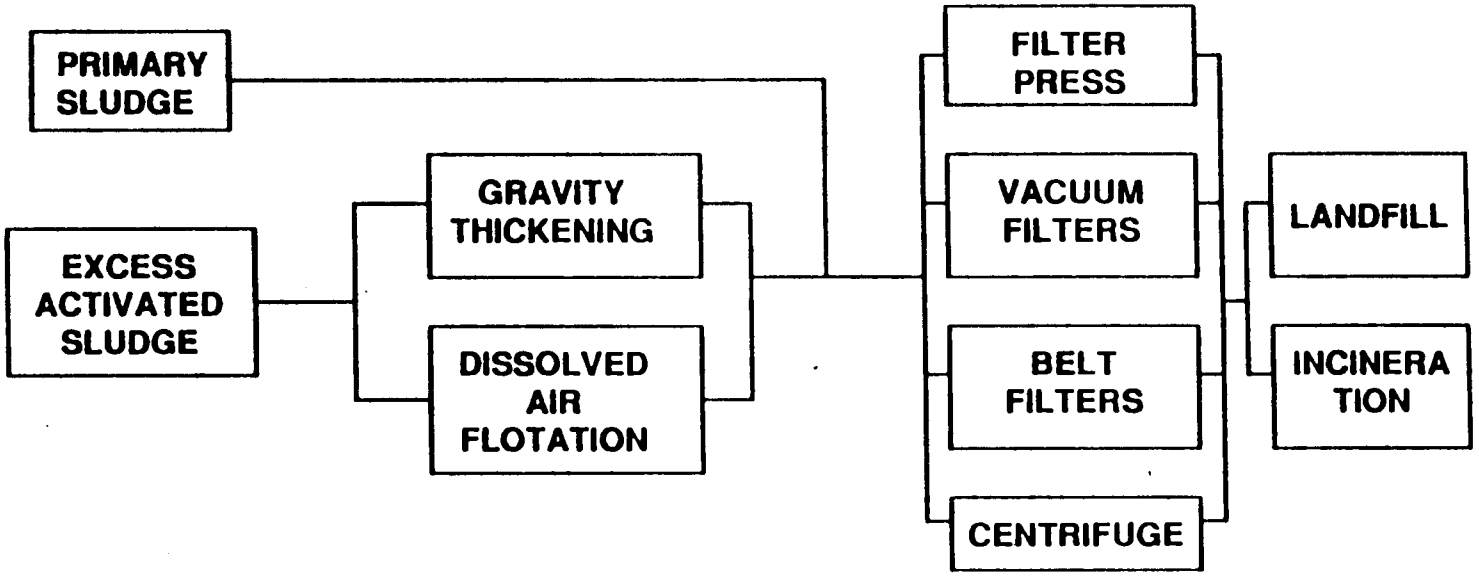
	PRIMARY SLUDGE		ACTIVATED SLUDGE		DIGESTED SLUDGE	
	Range	Typical	Range	Typical	Range	Typical
Total Dry Solids Content (%)	2-7	4	0.5-2	1	2-10	6
Volatile solids (%)	60-80	70	60-80	75	40-60	50
Nitrogen (N) % TS	1.5-8	3.0	4.8-6	5.6	1.6-6.0	3.7
Phosphorus (P_2O_5) % TS	0.8-2.8	1.6	3.0-7.4	5.7	0.9-6.1	1.67
Boron (ppm)					15-11,000	100
Cadmium (ppm)					5-2000	15
Chromium (ppm)					50-30,000	1000
Copper (ppm)					250-17,000	1000
Lead (ppm)					100-10,000	1000
Mercury (ppm)					1-100	10
Nickel (ppm)					25-8,000	200
Zinc (ppm)					500-50,000	2000
PCB (ppm)						


PRIMARY SLUDGE
EXCESS ACTIVATED SLUDGE
GRAVITY THICKENING
DISSOLVED AIR FLOTATION
ANAEROBIC DIGESTION
AEROBIC DIGESTION
LAND DISPOSAL
OCEAN DISPOSAL

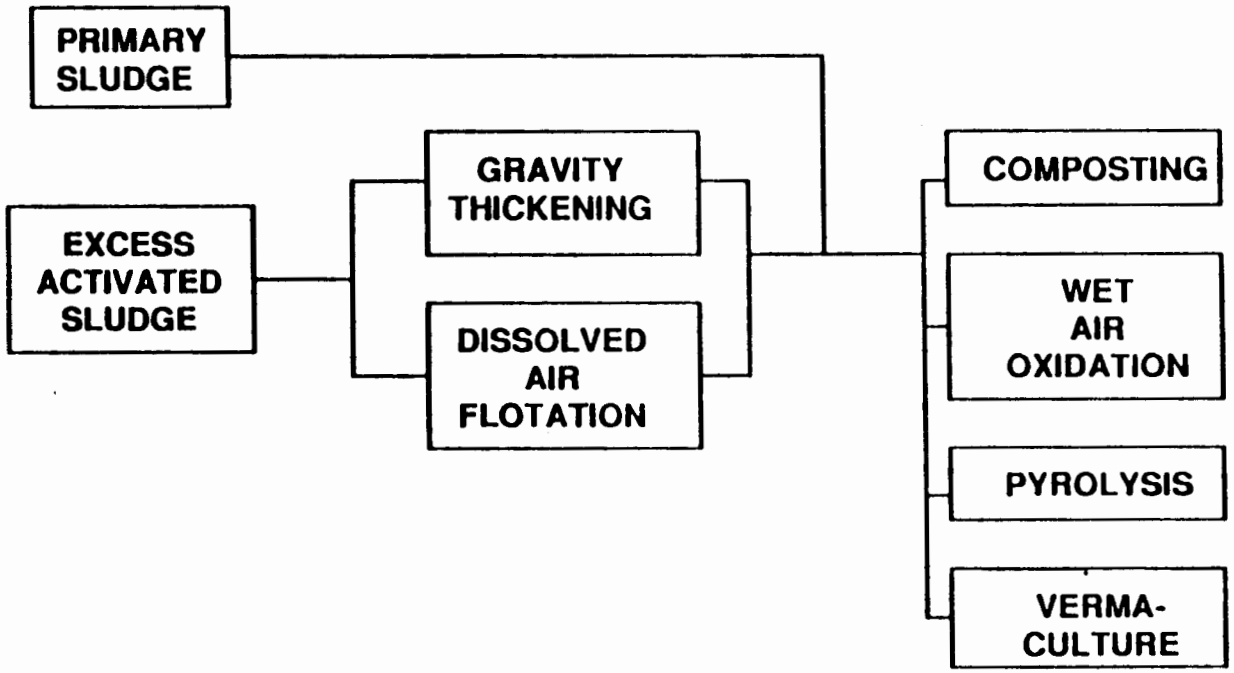
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CONDITIONING
PRIMARY SLUDGE
EXCESS ACTIVATED SLUDGE
GRAVITY THICKENING
DISSOLVED AIR FLOTATION
FILTER PRESS
VACUUM FILTERS
BELT FILTERS
CENTRIFUGE
LANDFILL
INCINERATION

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PRIMARY SLUDGE
EXCESS ACTIVATED SLUDGE
GRAVITY THICKENING
DISSOLVED AIR FLOTATION
FILTER PRESS
VACUUM FILTERS
BELT FILTERS
CENTRIFUGE
LANDFILL
INCINERATION

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PRIMARY SLUDGE
EXCESS ACTIVATED SLUDGE
GRAVITY THICKENING
DISSOLVED AIR FLOTATION
COMPOSTING
WET AIR OXIDATION
PYROLYSIS
VERMA-CULTURE

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UNIT PROCESSES	FUNCTIONS
Thickening gravity flotation	Water Removal Volume Reduction Blending
Biological Stabilization Aerobic Digestion Anaerobic Digestion Composting	Pathogen Destruction Volume and Weight Reduction Odor Control Putrescibility Control Gas Production (Anaerobic Digestion)
Conditioning	Improve Dewatering Rate Improve Solids Capture Improve Compactability
Belt Filters	Water Removal Solids Capture Change to Damp Cake Volume and Weight Reduction
Dewatering Vacuum Filter Filter Press Centrifuge	Water Removal Volume and Weight Reduction Change to Damp Cake Reduces Fuel Requirements for Incineration/Drying
Drying Beds or Heat Drying	Water Removal
Incineration	Destruction of Solids Water Removal Conversion Sterilization
Final Disposal	Irrigation Cropland Energy Land Reclamation Landfill Ocean Disposal Incineration

FIGURE 11
SLUDGE TREATMENT PROCESSES AND THEIR FUNCTIONS

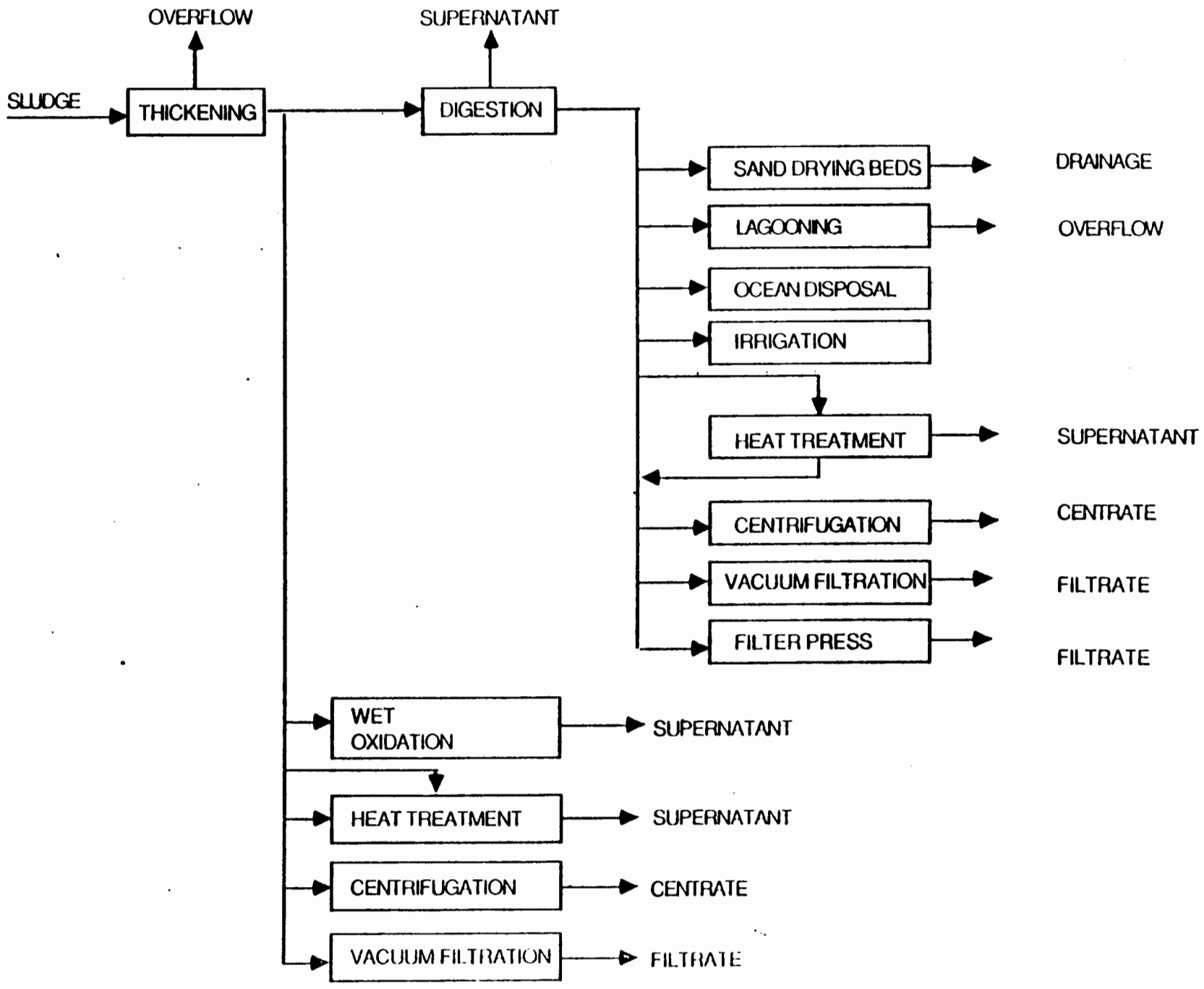

OVERFLOW
SUPERNATANT
SLUDGE
THICKENING
DIGESTION
SAND DRYING BEDS
DRAINAGE
LAGOONING
OVERFLOW
OCEAN DISPOSAL
IRRIGATION
HEAT TREATMENT
SUPERNATANT
CENTRIFUGATION
CENTRATE
VACUUM FILTRATION
FILTRATE
FILTER PRESS
FILTRATE
WET OXIDATION
SUPERNATANT
HEAT TREATMENT
SUPERNATANT
CENTRIFUGATION
CENTRATE
VACUUM FILTRATION
FILTRATE

FIGURE 12

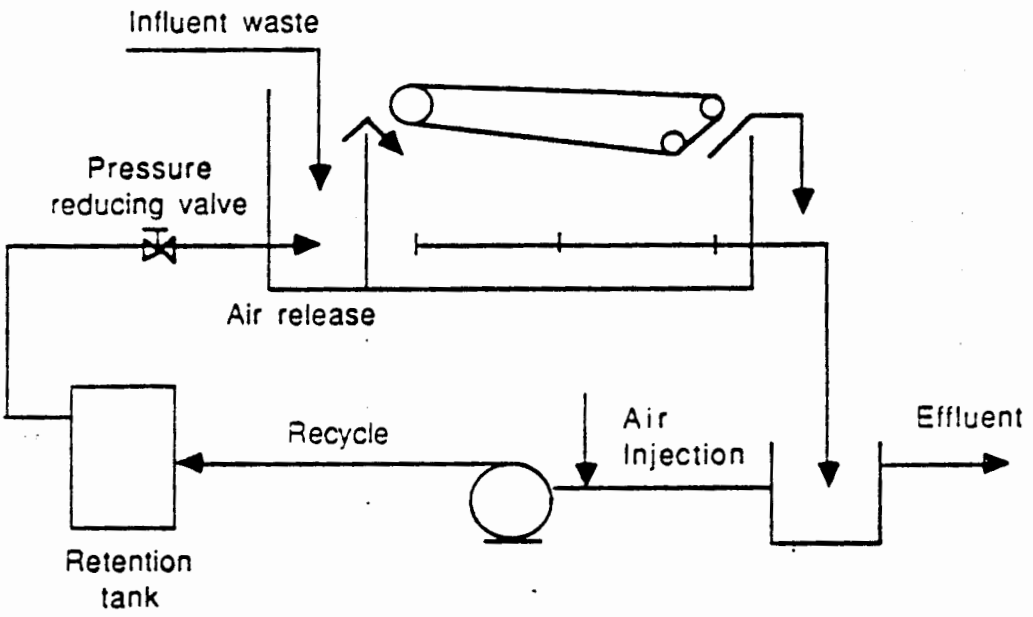
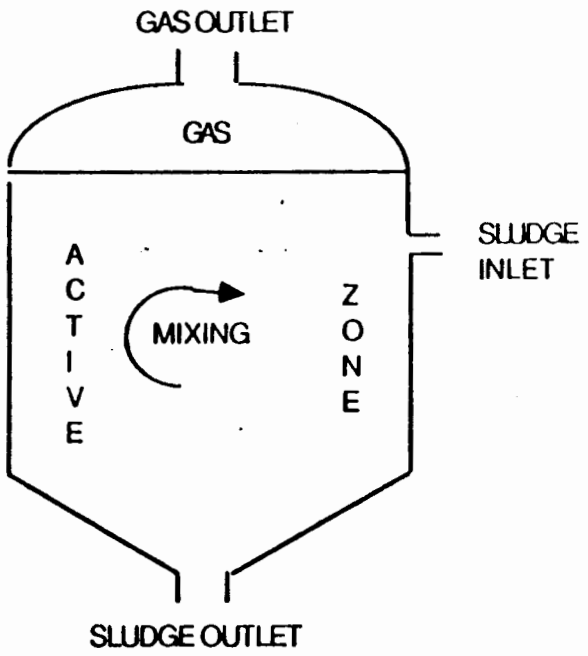
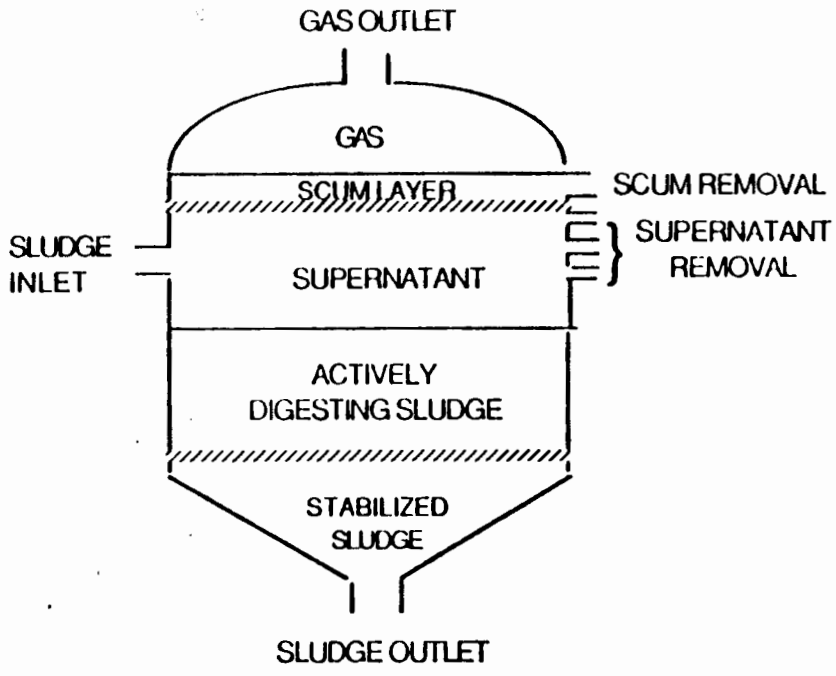


FIGURE 13

SCHEMATIC REPRESENTATION OF FLOTATION SYSTEMS
(a) FLOTATION SYSTEM WITHOUT RECIRCULATION
(b) FLOTATION SYSTEM WITH RECIRCULATION





FIRST STAGE

1. Heated to 85° - 95°F
2. Detention time 15 days or less
3. Continuous or intermittent feeding and withdrawal

SECOND STAGE

1. Unheated
2. Detention time 15 days or less
3. Intermittent feeding and withdrawal
4. Stratification

FIGURE 14
ANAEROBIC DIGESTION

TABLE 17. TYPICAL CHEMICAL COMPOSITION OF DIGESTED SLUDGE

ITEM	DIGESTED SLUDGE RANGE	TYPICAL
Total dry solids (TS), %	6.0-12.0	10.0
Volatile solids (% of TS)	30-60	40.0
Grease and fats (ether-soluble, % of TS)	5.0-20.0	...
Protein (% of TS)	15-20	18
Nitrogen (N, % of TS)	1.6-6.0	4.0
Phosphorus (P_2O_5, % of TS)	1.5-4.0	2.5
Potash (K_2O, % of TS)	0.0-3.0	1.0
Cellulose (% of TS)	8.0-15.0	10.0
Iron (not as sulfide)	3.0-8.0	4.0
Silica (SiO_2, % of TS)	10.0-20.0	...
pH	6.5-7.5	7.0
Alkalinity (mg/L as $CaCO_3$)	2500-33500	3000
Organic acids (mg/L as HAc)	100-600	200
Thermal content (MJ/kg)	6-14	9

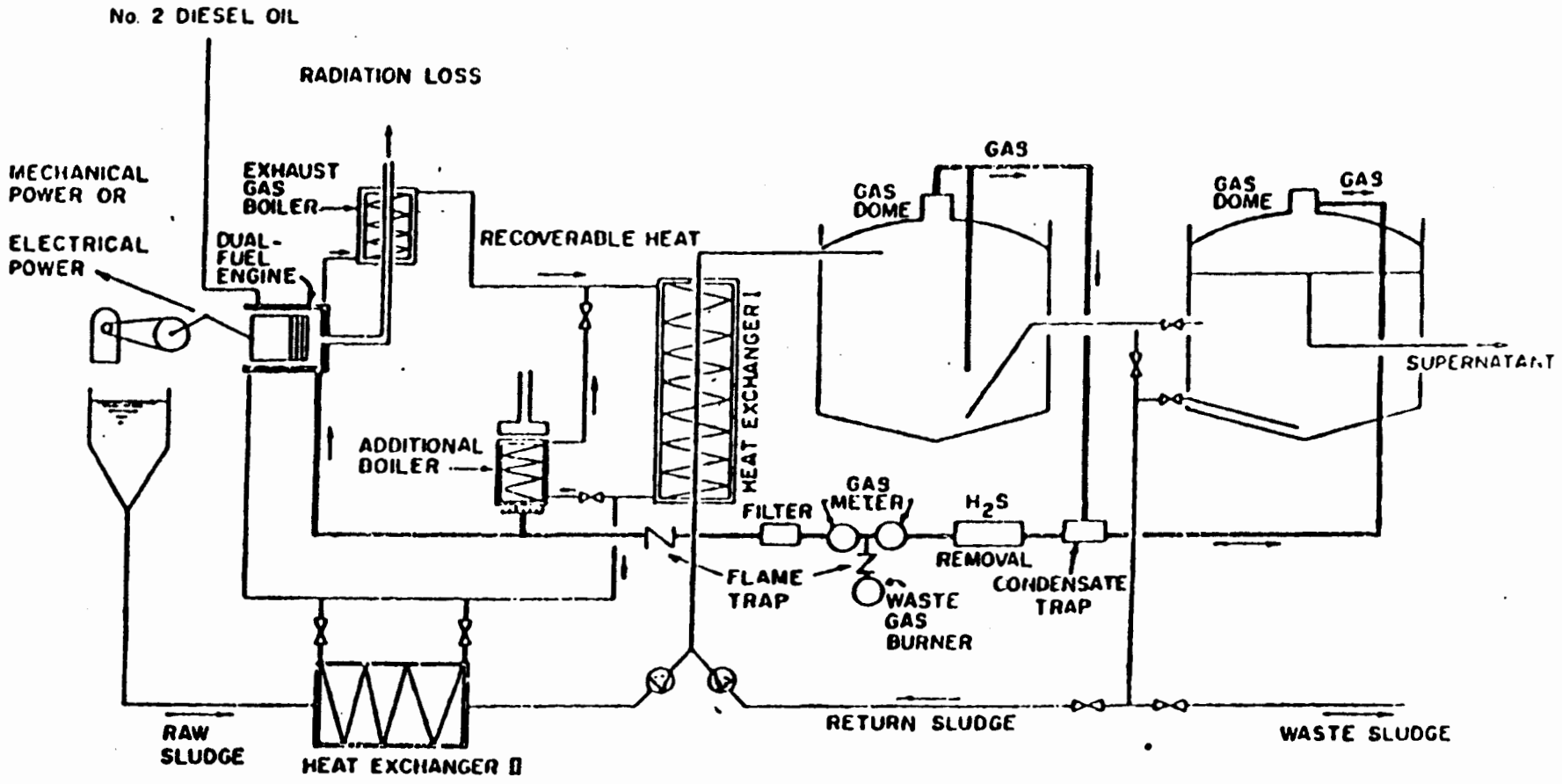


FIGURE 15 - TWO STAGE ANAEROBIC DIGESTION SYSTEM WITH GAS RECOVERY AND UTILIZATION

TABLE 18
TYPICAL CHARACTERISTICS OF A PRIMARY-ACTIVATED SLUDGE MIXTURE AFTER HEAT TREATMENT

	Before Oxidation	After Oxidation		
		Slurry	Filtrate	Filter Cake
Volume (L)	1.00	1.05	1.00	0.05
COD gm	43	36.6	12.9	23.7
COD Reduction %	0	15	--	--
BOD gm	--	--	4.5	--
Total solids gm	35.1	29.8	8.2	21.6
Volatile Solids gm	23.4	18.1	5.2	12.9
Ash gm	11.7	11.7	3.0	8.7
Phosphorus as P gm	0.61	0.61	0.18	0.43
Total Nitrogen gm	1.49	1.49	1.15	0.34
Ammonia Nitrogen gm	0.57	0.75	0.72	0.03
pH	6.0	5.2	--	--
Volume after 4 hr setling %	100	37	--	--
Filtration Resistance ($sec^2/g \times 10^7$)	3500	6	--	--
Moisture Cake %	--	--	--	64

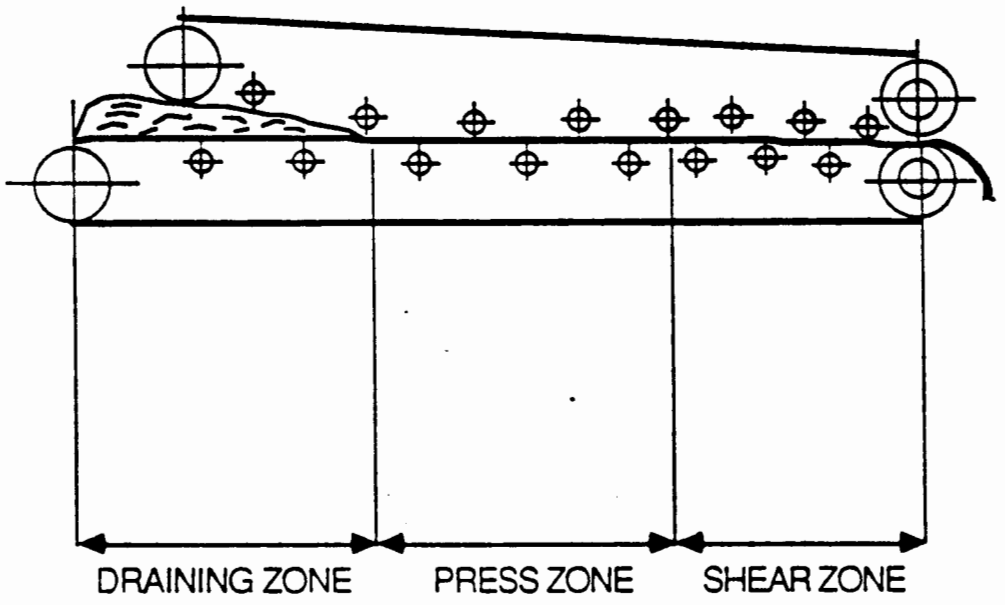


FIGURE 16. Schematic of belt filter

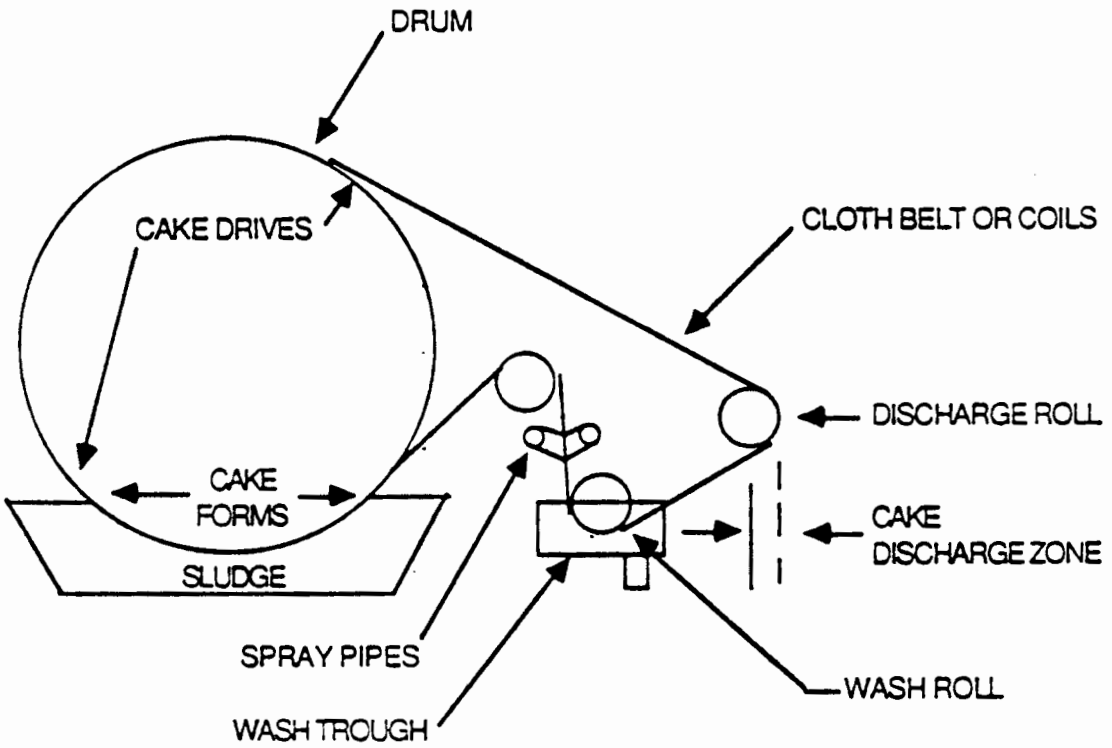


FIGURE 17
CROSS SECTION OF A VACUUM FILTER

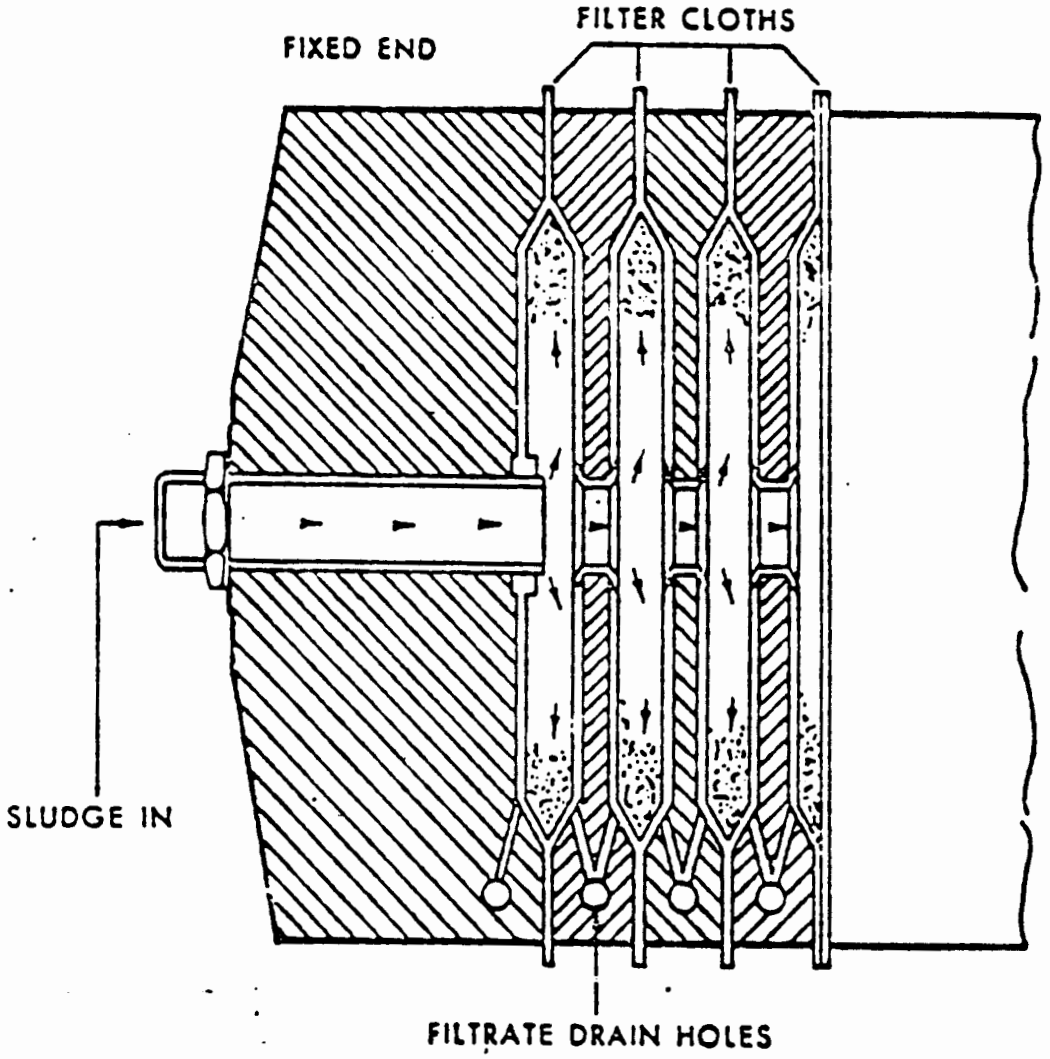


FIGURE 18

Cutaway view of a filter press

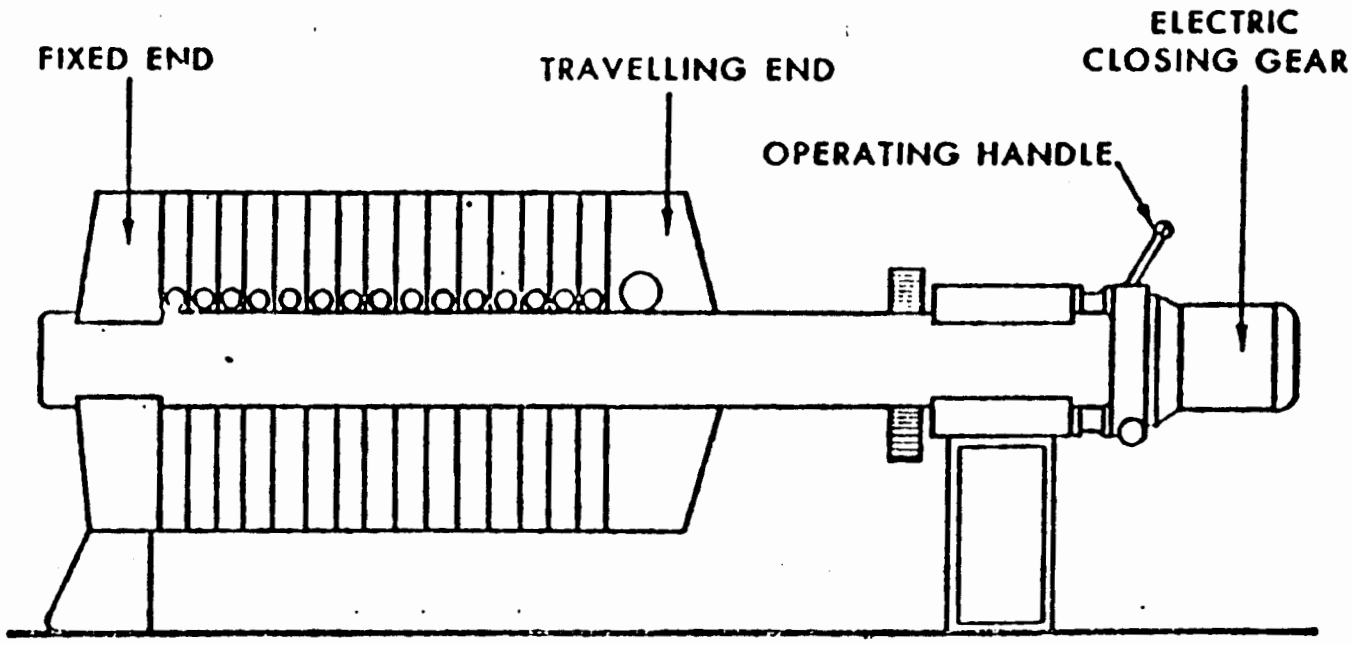


FIGURE 19

Filter Press

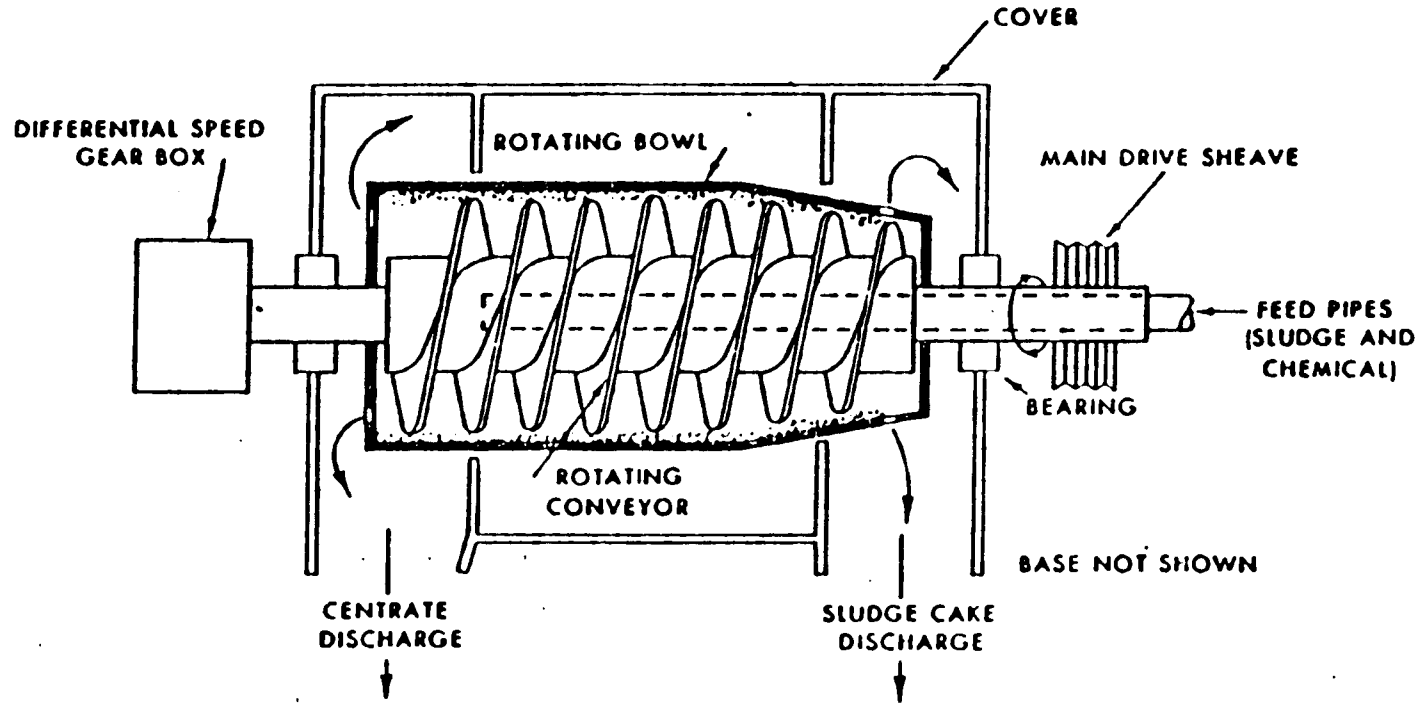


FIGURE 20 Continuous countercurrent solid bowl conveyor discharge centrifuge.

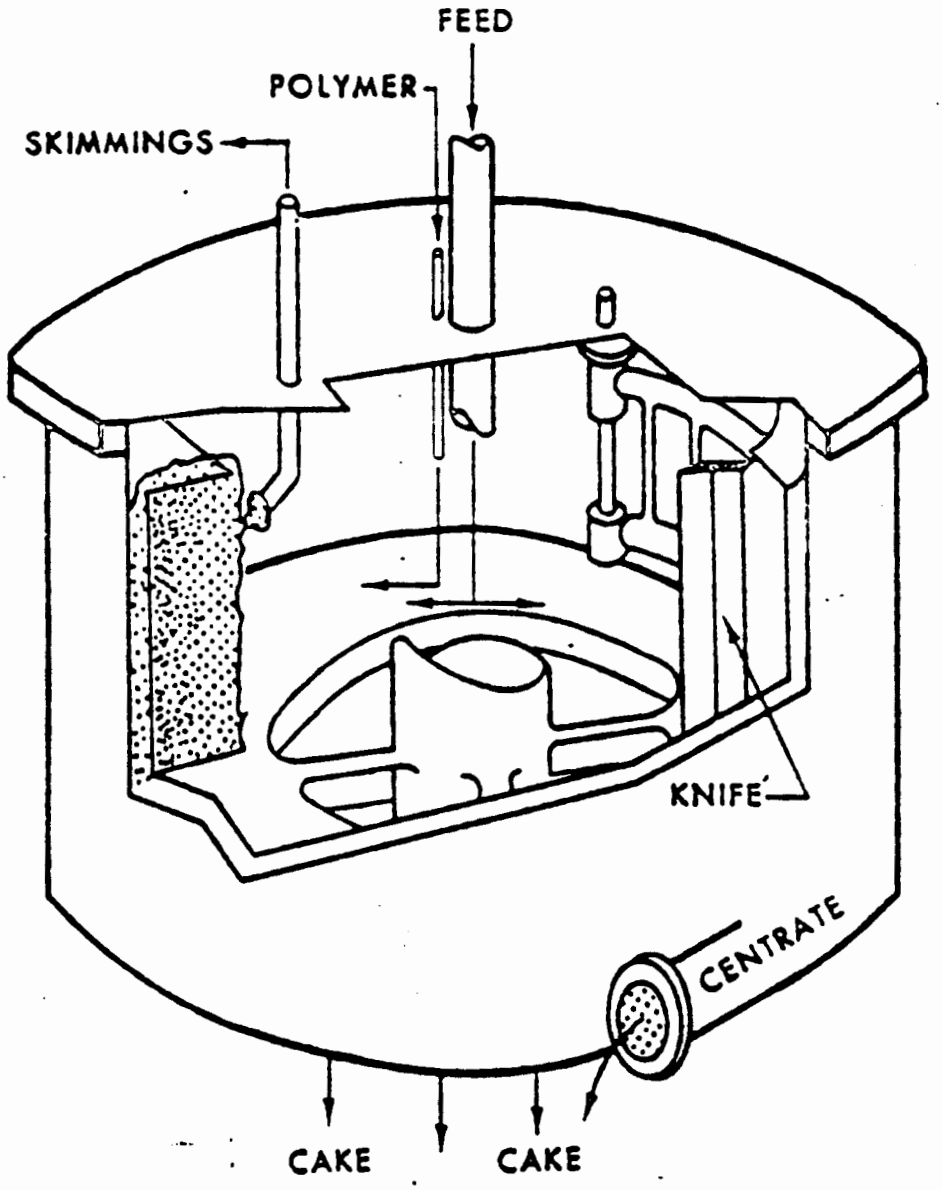


FIGURE 21 Schematic diagram of a basket centrifuge.

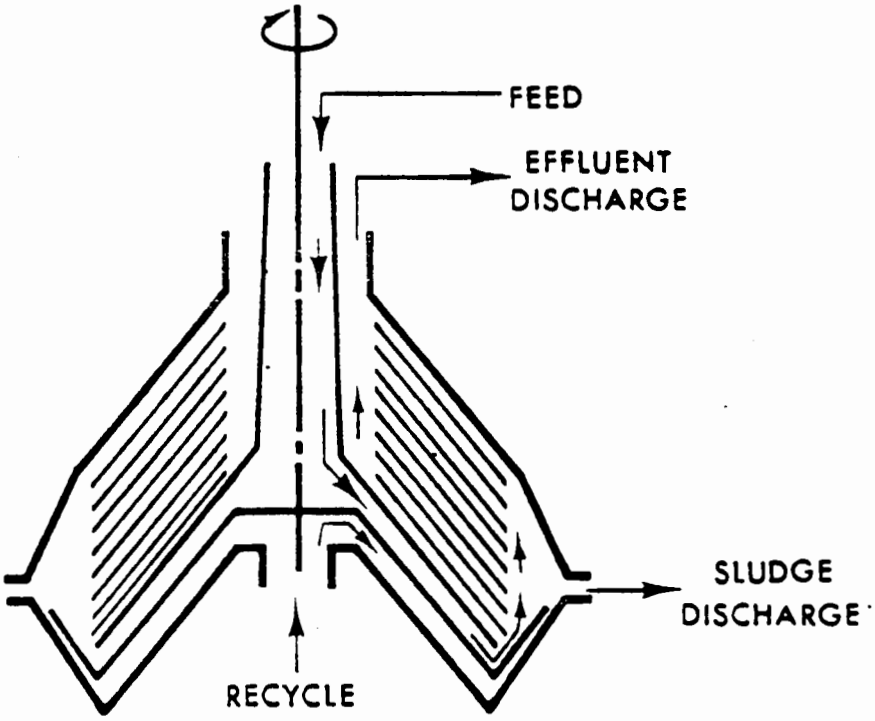


FIGURE 22 Disc type centrifuge.

TABLE 19. HEAT-VALUES OF SLUDGES AND FUELS

Fuel	Combustibles (percent)	Heat-Value (BTU/lb)
Fine Screenings	86.4	8,990
Grit	33.2	4,000
Grease and scum	88.5	16,750
Fresh sewage solids	74.0	10,285
Primary sewage sludge	---	7,820
Activated sewage sludge	---	6,540
Digested sludge	59.6	5,290
Digested sewage and garbage solids	49.6	8,020
Waste sulfite liquor solids	---	7,900
Semi-chemical pulp solids	--	5,812
Lignite	89.0	10,850
Wood	89.5	8,675
Newsprint	91.8	7,825
Coal	---	10,000-14,000
Petroleum	---	19,000-20,000

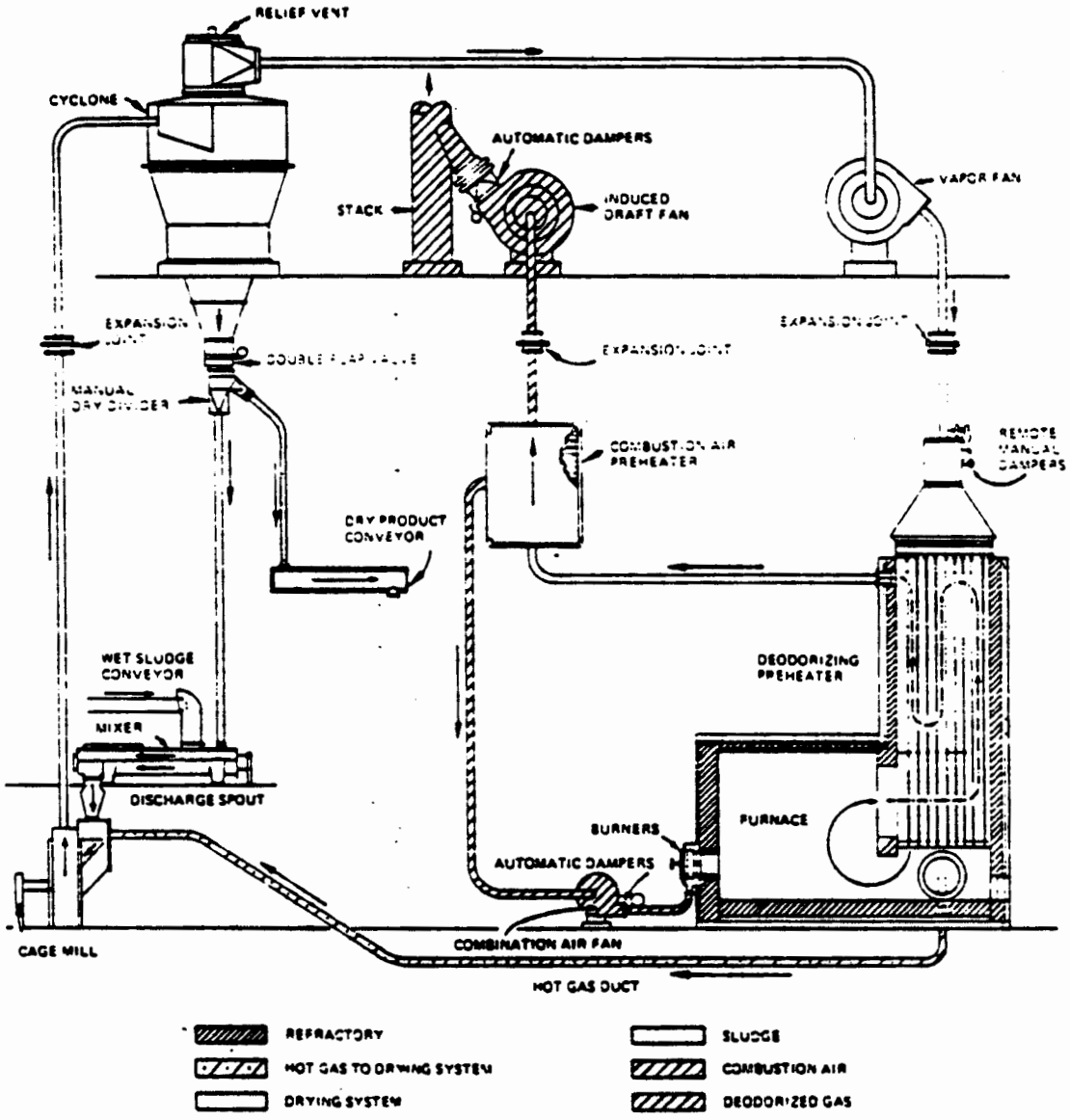


FIGURE 23 Flash dryer system [19].

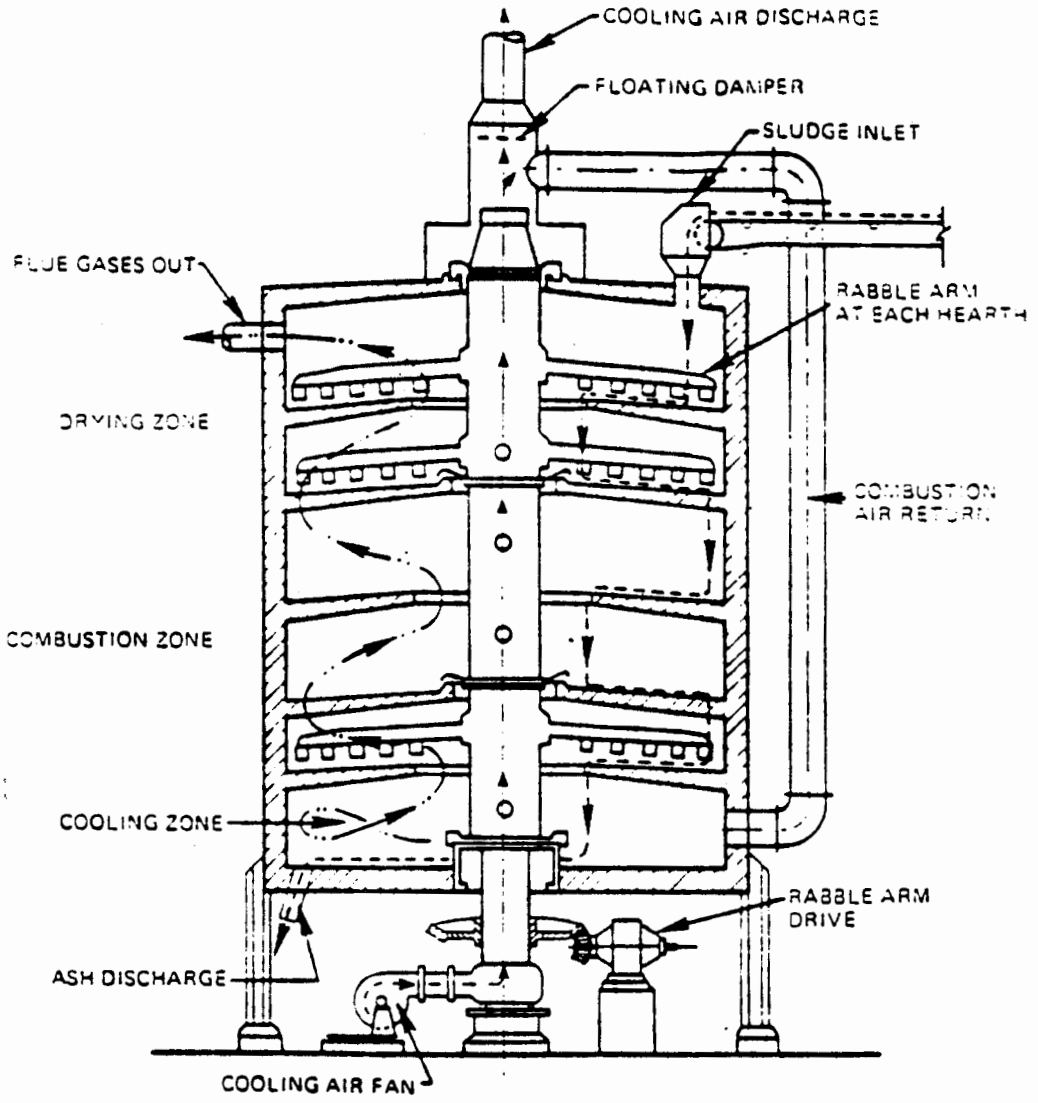


FIGURE 24 Cross section of a typical multiple hearth incinerator.

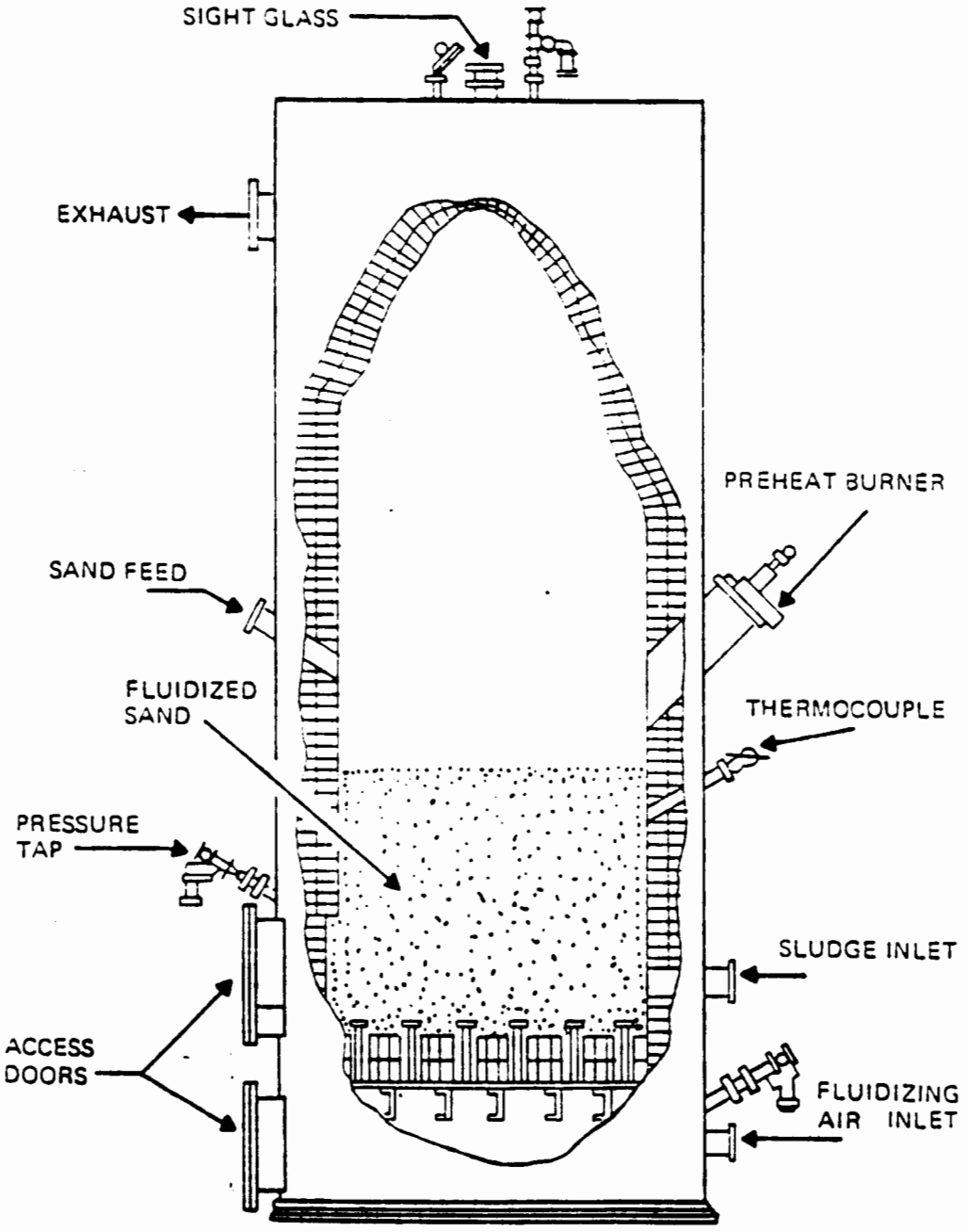


FIGURE 25 Cross section of a fluid bed reactor.

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