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Biological Treatment of High Strength Petrochemical Wastewater

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BIOLOGICAL TREATMENT OF HIGH STRENGTH PETROCHEMICAL WASTEWATER

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U,S. Environmental Protection Agency

FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in ground water; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control, or abate pollution from the petroleum refining and petrochemical industries; and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

This report contributes to the knowledge essential if the EPA is to meet the requirements of environmental laws that it establish and enforce pollution control standards which are reasonable, cost effective and provide adequate protection for the American public.

W. C. Galegar

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Director
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ABSTRACT

The biological treatment of a complex petrochemical wastewater containing high concentrations of organic chlorides, nitrates and amines was initially studied using a sequence of anaerobic methanogenesis and oxygen activated sludge. Bench scale and pilot plant treatability studies were conducted using various composite samples and process wastewater blends. The results of preliminary studies indicated the need for stream segregation and waste reduction programs at the petrochemical plant. Segregation of components of the combined plant waste stream was required to eliminate nonbiodegradable materials and pretreatment minimized the concentration of substances which were toxic or inhibitory to biological treatment.

Nitrates inhibited methanogenesis in the anaerobic system but quantitative removal of nitrates was accomplished. Only partial removal of chemical oxygen demand (COD) was achieved during anaerobic denitrification because of the relatively low nitrate/COD ratio. Anaerobic methanogenic treatment also was unsuccessful in reducing the COD concentration to any great extent, even after pretreatment by anaerobic denitrification.

The activated sludge system was effective in removing the biodegradable portion expressed as biochemical oxygen demand (BOD) of the pretreated combined wastewater stream; but the yellow color of the effluent was unacceptably dark. The activated sludge system performed equally well when high purity oxygen, or air was used for aeration.

Therefore, the final treatment sequence included anaerobic denitrification, and activated sludge using air for aeration and produced an effluent with the following characteristics; essentially no nitrates, BOD $\sim$ 50 mg/l, COD $\sim$ 1200 mg/l, suspended solids 200 mg/l, and yellow in color. The average influent composition was BOD $\sim$ 6000 mg/l, COD $\sim$ 8000 mg/l, nitrates $\sim$ 1000 mg/l, and yellow in color.

This effluent does not meet the limitations imposed for discharge to surface waters.

This report was submitted in fulfillment of Project 12020 EPH by Celanese Chemical Company under the partial sponsorship of the U.S. Environmental Protection Agency. This report covers a period from September 23, 1969 to February 20, 1976 and work completed July 20, 1978.

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SECTION 1

INTRODUCTION

The Bay City plant of the Celanese Chemical Company located in Matagorda County, Texas produces a wide variety of petrochemicals. Wastewaters generated within the plant contain significant quantities of nitrates, amines, chlorinated organics, organic carbon, cyclic compounds, high molecular weight polymers, and heavy metals. In the early years of plant operation, the wastewater treatment and disposal scheme consisted of several hundred acres of waste stabilization and evaporation ponds. The organic loads to the ponds exceeded the design loading and the facultative ponds became anaerobic resulting in the production of odors. This anaerobic biological process indicated that the anaerobic treatment had been effective in reducing the COD (chemical oxygen demand) by more than 90%. However, the anaerobic samples were taken as portions of large pond areas which did not represent actual effectiveness of the entire shallow anaerobic ponds and the results were not duplicated in laboratory anaerobic studies.

Initial treatability studies of the process wastewaters in laboratory activated sludge units resulted in less than 50% removal of the COD concentration. These early observations indicated that some combination of anaerobic and aerobic processes could possibly produce a high quality effluent treating a complex petrochemical wastewater. Therefore, bench scale and pilot scale studies involving combinations of anaerobic and aerobic biological processes were initiated at the Bay City plant and the Corpus Christi Technical Center of the Celanese Chemical Company under the partial support of a demonstration grant funded by the Federal Water Pollution Control Administration (FWPCA).

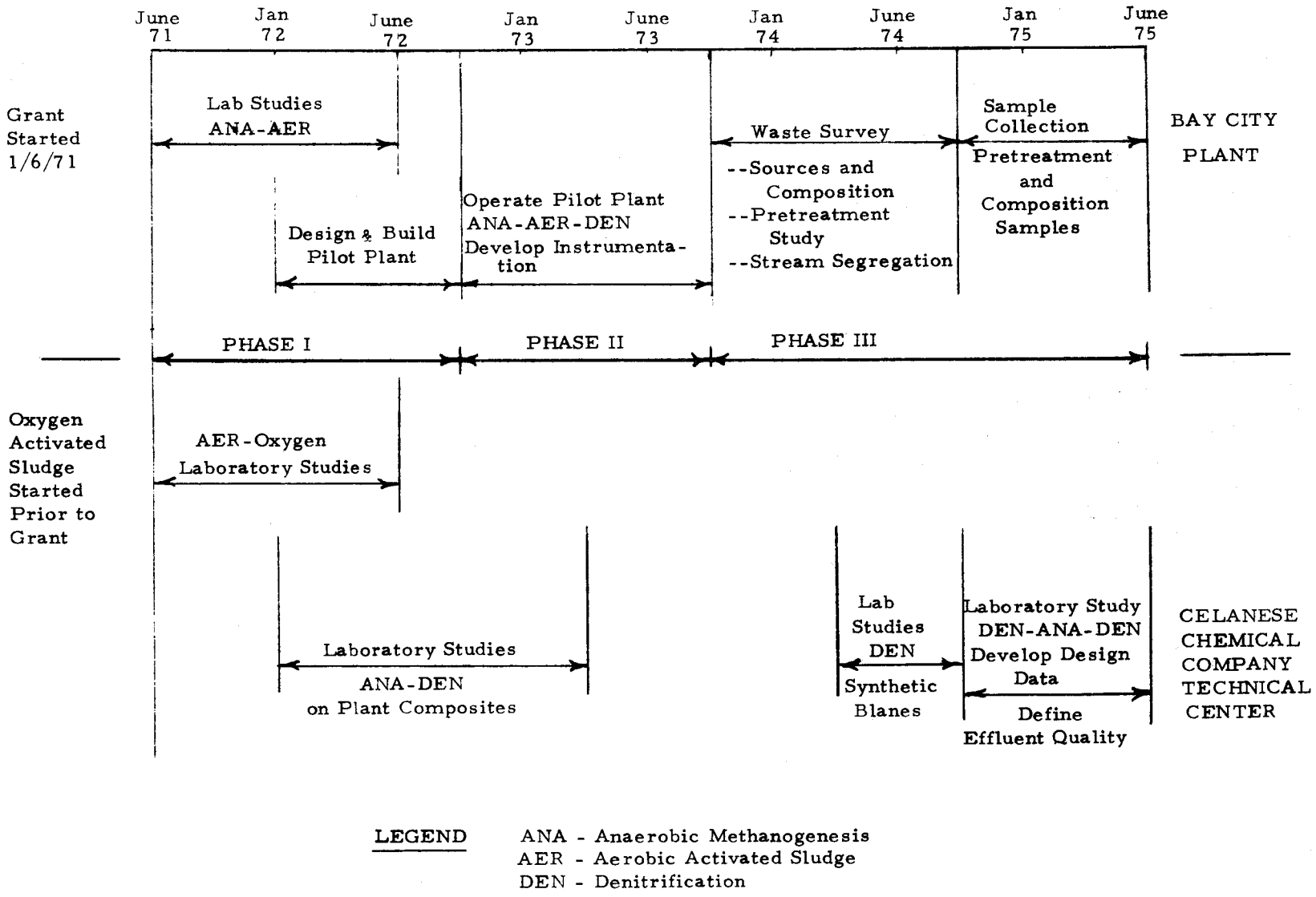
The objectives of the studies included: (a) the investigation of the anaerobic/aerobic treatability of high strength petrochemical waste to produce a water of reusable quality or suitable for discharge; (b) investigation of the effects of high purity oxygen on the aerobic process, specifically the activated sludge system; (c) demonstration of the total process in a pilot scale system; and (d) comparison of the economics of the anaerobic/aerobic system with injection wells.

The project was divided into three phases. The first two phases overlapped. Phase I included bench scale studies conducted at the Celanese Chemical Company Technical Center in Corpus Christi and at the Bay City plant. Phase II included the design, construction and operation of a pilot plant located at the Bay City plant using continuous flow of process wastewaters. The development of design parameters and definition of effluent quality attainable were completed in bench scale studies conducted at the Technical Center as Phase III. The sequence of events through which the project evolved are illustrated in Figure 1.

Several observations made during the early stages of Phase I helped to define the process sequence. Denitrification occurred under anaerobic conditions resulting in reduction in nitrates from about 300 mg/l (milligrams per liter) to less than 5 mg/l with a corresponding reduction in organic carbon. Some of the wastewater streams which were inhibitory or toxic to the anaerobic system were quite readily degradable under aerobic conditions. Other streams which were not amenable to aerobic biodegradation, however, were treatable in the anaerobic systems. Therefore, the wastewater streams at the Bay City plant were segregated into three components, namely the high nitrate containing streams which were amenable to denitrification, wastewaters which were anaerobically degraded and those which could be treated in an aerobic activated sludge system.

The initial biological system used in the bench scale and pilot plant studies included anaerobic denitrification followed by anaerobic methane production, and finally followed by treatment in the aerobic activated sludge system. Bench scale units were operated at the Bay City plant as well as at the Technical Center. The denitrification system operated with a packed bed as well as the fluidized bed containing either sand or activated carbon. Anaerobic methanogenic units were submerged packed beds. The aerobic process was a complete mixed activated sludge system. Individual wastewater streams and various composites of different process waste streams were fed to each of the individual units. Composite samples were routinely collected at the Bay City plant and shipped to the Technical Center. The composition of these composite samples varied as the project progressed reflecting changes in the wastewater characteristics resulting from in-plant waste reduction, waste segregation and proposed pretreatment of specific waste streams prior to biological treatment.

The pilot plant (Phase II) constructed at the Bay City plant included two parallel systems to minimize downtime resulting from potential bacterial inactivation caused by shock loads of specific components in the waste stream. The pilot plant was designed to be portable. This placed some constraints on the selection of equipment. Each of the pilot plants consisted of a three-process system including submerged packed bed denitrification



LEGEND
ANA - Anaerobic Methanogenesis
AER - Aerobic Activated Sludge
DEN - Denitrification

Figure 1. Sequence of events in evolution of project.

unit, a submerged packed bed anaerobic methanogenic unit and completely mixed activated sludge system with a separate clarifier. The activated sludge system was designed to be operated with high purity oxygen using a down flow bubble contact aerator for oxygen transfer and auxiliary mixing. A wastewater storage tank was used to blend the feed for the pilot plant. On-line instrumentation also was included in the pilot plant to continuously monitor dissolved oxygen, organic carbon, and copper concentration. The pilot plant design was based on data from limited bench scale studies. As a result, pilot plant operations were unstable and produced unsatisfactory results.

SECTION 2

CONCLUSIONS

1. Effective biological treatment of a complex petrochemical wastewater requires waste reduction and stream segregation to eliminate non-biodegradable wastewater streams. Pretreatment is essential for removal of heavy metals and other compounds which may be toxic to or inhibit biological treatment processes.

2. Nitrates inhibit methane production in anaerobic treatment systems. However, nitrates are quantitatively converted to nitrogen gas during anaerobic denitrification resulting in the oxidation of 2.85 parts of COD for each part of nitrate N reduced.

3. A treatment sequence including anaerobic denitrification and activated sludge produced an effluent which contained essentially no nitrates (100% removal), BOD ~ 50 mg/l (> 99% removal), COD ~ 1200 mg/l (~ 85% removal), suspended solids ~ 200 mg/l, and yellow in color. This effluent does not meet the limitations imposed for discharge to surface water.

4. Data obtained from glassware (bench scale) units simulate the biological and chemical processes well and provide useful performance data for various operating conditions. The major difficulty is with hydraulic scale-up.

5. The design of a pilot plant should be based on complete glassware (bench scale) data which define process performance and the variables affecting process performance.

6. Reliable instrumentation which continuously monitor flows and other parameters which characterize the various influent and effluent streams is essential to pilot plant operations. However, during the pilot plant phase of this study such instrumentation was not available and a considerable effort was directed toward improving on-line instrumentation to monitor the characteristics of wastewater streams.

7. The results of these studies indicate that the activated sludge process performed equally well when air or high purity oxygen was used for aeration. Therefore, the choice of high purity oxygen versus air is an economic standoff that should be evaluated for each particular application.

SECTION 3

WASTE CHARACTERISTICS AND PROCESS SELECTION

The Celanese Chemical Company Bay City plant produces a wide variety of petrochemicals including acetaldehyde, acetic acid, vinyl acetate, butanol, butyraldehyde, crotonaldehyde, nitric acid, adipic acid, cyclohexanone, hexamethylenediamine, 1, 6-hexanediol, nylon salt and several other minor by-products. Organic compounds including cyclic organics and high molecular weight polymers contribute to the high concentrations of total organic carbon. Nitrogen is present as nitrates, nitrites and amines. Heavy metals, primarily copper, with small amounts of nickel, chromium, cobalt and vanadium may be found. The overall composition of the process wastewaters is presented in Table 1. The combined wastewater is made up of numerous streams; however, six major contributing streams are identified in Table 2. The flow rate percent of total flow and the total organic carbon contribution of the individual streams are also presented in Table 2. It is interesting to note that Stream 3 contributes only 8.6% of the total flow but contains 75.2% of the total organic carbon. The data presented in Tables 1 and 2 represent only gross averages of the composition of the total process wastewater, as well as the average of the flows and total organic carbon of the six individual streams.

The composition and flow vary during the course of the day and from day to day. Analysis for metals indicate a range of copper concentration from less than 0.5 mg/l to as high as 17 mg/l, although surges of heavy metals in excess of 100 mg/l have been recorded. These surges of heavy metals usually occur during the shutdown and clean out of a process reactor. The variability in the composition of the combined process wastewater is also illustrated in the data presented in Table 3. Although the pH indicates that the wastewater is primarily acidic, alkaline values of pH occur. The total organic carbon concentration varied from 1,200 to 22,000 mg/l. The average total organic carbon (TOC) for the 25 samples reported is 15,680 mg/l.

The variations in the flow of the combined process wastewater is illustrated in Figure 2. Flow variations of approximately 600 gpm are not uncommon. The range of flow of the combined process wastewater is

TABLE 1. COMPOSITION OF COMBINED PROCESS WASTEWATER
BAY CITY PLANT

	Concentration mg/l
Total Organic Carbon	15,000
Biochemical Oxygen Demand	33,000
Chemical Oxygen Demand	48,000
Nitrate-Nitrogen	780
Nitrite Nitrogen	27
Ammonia-Nitrogen	770
Phosphate-Phosphorus	130
Chloroaldehydes	2,085
Inorganic Chlorides	35-400
Sodium	400
Copper	2-100
Iron	0.06
Chromium	0.02
Manganese	<0.2
Palladium	<0.2
Nickel	<0.4
Cobalt	<0.02
pH	3.1[a]
Color, APHA	≈ 10,000[b] dark brown

(a) pH units

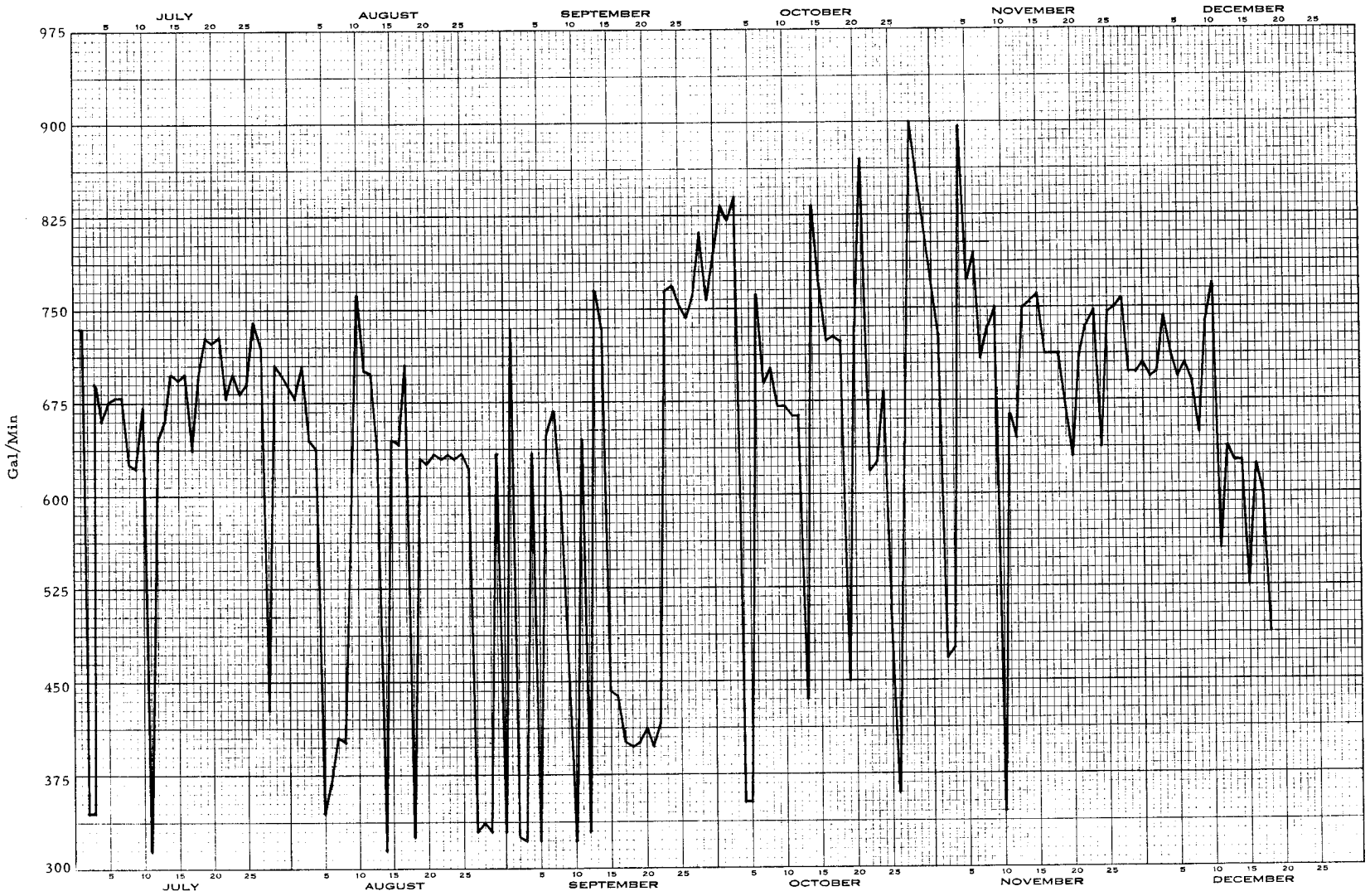
(b) color units

TABLE 2. COMPOSITION OF THE PROCESS WASTEWATER STREAMS AT THE BAY CITY PLANT BEFORE SEGREGATION

Stream No.	Composition	Flow		Total Organic Carbon	
		GPM	Percent of Total Flow	mg/l	Percent of Total TOC
1	Acid stream. Organic chlorides, and chlorinated acetaldehydes	244	38.8	2700	3.7
2	Acid stream. Phosphoric acid, volatile organic acids, sodium hydroxide, low molecular weight aldehyde, aldol products, low molecular weight alcohols	41	5.7	1760	2.4
3	Acetic acid through hexanoic acid Sodium hydroxide C_1-C_6 esters	62	8.6	54300	74.2
4	Alkaline stream. Amines, ammonia, alcohols, oils and copper laden solids	49	6.8	3500	4.8
5	Acetic acid through hexanoic acid, 0-7% nitric acid, succinic, glutaric, adipic acids, cyclic organics, copper and vanadium (0-100 mg/l)	215	29.8	1650	2.1
6	Nylon salt, adipic acid, succinic acid, glutaric acid, copper and vanadium	110	15.3	9200	12.8

TABLE 3. VARIATIONS IN COMPOSITION OF COMBINED PROCESS WASTEWATER
BAY CITY PLANT

Sample No.	pH	Total Organic Carbon, mg/l
1	5.2	12,000
2	9.0	9,300
3	6.9	3,500
4	9.4	15,000
5	3.0	49,000
6	5.7	11,000
7	8.3	1,200
8	5.1	21,000
9	5.2	15,000
10	5.4	12,000
11	4.7	10,000
12	5.5	16,000
13	5.5	14,000
14	6.6	10,000
15	5.0	20,000
16	7.2	20,000
17	5.1	16,000
18	3.7	14,000
19	5.1	15,000
20	5.3	17,000
21	7.5	22,000
22	5.5	17,000
23	5.0	20,000
24	5.1	15,000
25	4.5	17,000
Mean		15,680



Bay City - 1973

Figure 2. Daily variation in volume of plant effluent make.

between 300 and 900 gpm. Variability of the flow and composition coupled with the toxic nature of several compounds in the process wastewater indicate that difficulties with the biological treatment of the combined process wastewater stream can be anticipated.

A number of physical and chemical processes were considered as alternative schemes for treatment and/or disposal of the combined process wastewater at the Bay City plant but each was rejected as a viable alternative for any one of a number of reasons. Severe corrosion problems and inability to oxidize acetic acid which is a major constituent of the waste or its precursors eliminated wet air oxidation from consideration. Fractional distillation was considered but rejected because of the cost entailed in distilling essentially all of the water away from the heavy ends which make up the bulk of the TOC in the process wastewater. In addition, the distillate contained a high organic concentration which precluded the reuse of the water without additional biological treatment. The residue also contained high salt concentration which would cause reboiler fouling and also lead to difficulties in incinerating the residue. Two problems were apparent with reverse osmosis; namely, poor rejection of the relatively low molecular weight fraction of the organic compounds and the presence of tarry fractions which cause rapid deterioration of the membrane resulting in extremely low flux rates. Solvent extraction with removal of chloraldehyde showed some promise, but extremely high solvent recycle requirements rendered the process impractical in terms of solvent losses and complete removal of the chloraldehydes was not possible. Adsorption on activated carbon was technically possible, but was not evaluated during these studies.

A. STREAM SEGREGATION

An initial treatment scheme was developed which included anaerobic denitrification followed by anaerobic methanogenesis and final treatment with an activated sludge system. This treatment sequence is illustrated in Figure 3-B. Several attempts to treat the combined process wastewater in the anaerobic/aerobic series of processes indicated the necessity of stream segregation. The complex mixture of chemicals in the process wastewater posed antagonistic restraints on the stability and efficiency of the biological treatment system. Figure 3-A presents a modified process flowscheme that was developed to utilize the potential benefits of the constituents in the process wastewater.

This initial segregation resulted in three composite wastewater streams (Phase I). The composite "A" included all the nitrate containing wastewater. Composite "B" was a blend of wastewater streams which contained no nitrates or chlorinated organics. Composite "C" was a composite of the other wastewater streams containing organics as well as

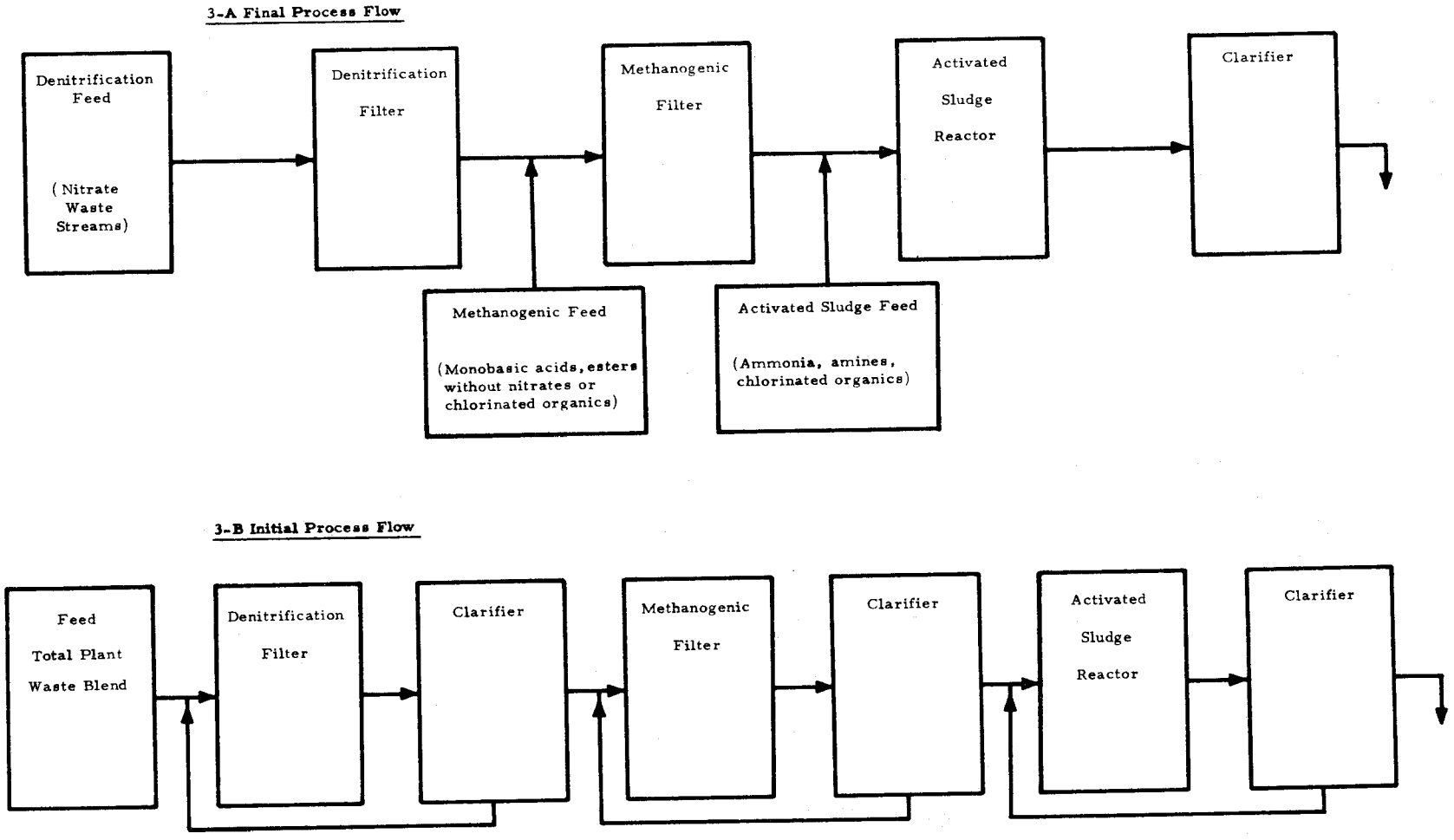


Figure 3. Process schematic evolution.

ammonia, amines, alcohols, nylon salts and chlorinated aldehydes. Each of these three blends of wastewater was fed to the denitrification, methanogenic and activated sludge units, respectively. A number of preliminary tests (Appendix A) were performed to define the design limitations and process components compatibility.

The analyses of the various wastewater streams indicated that effective biological treatment would be possible only if the following remedial measures and pretreatment schemes to control future variations in the composition of the feed were installed. The proposed controls include: a) incineration of streams containing chlorinated organics, amines, and high carbon concentrations with the appropriate post combustion recovery/abatement system; b) reduction of carbon losses by in-unit process changes to minimize wastewater production and reduce the ash content of waste to be incinerated; c) process modifications to eliminate continuous discharge of wastewater into unit sumps; and d) a centralized physical/chemical treatment system to handle the intermittent flows of all unit sumps, to reduce variations in carbon, and eliminate heavy metals from the biological systems.

B. WASTE REDUCTION PROGRAMS

This waste reduction program resulted in significant changes in the composition of the wastewater streams. The overall wastewater disposal and treatment system is illustrated in Figure 4. The proposed treatment or disposal scheme for each of the respective types of wastewater is described in Appendix B.

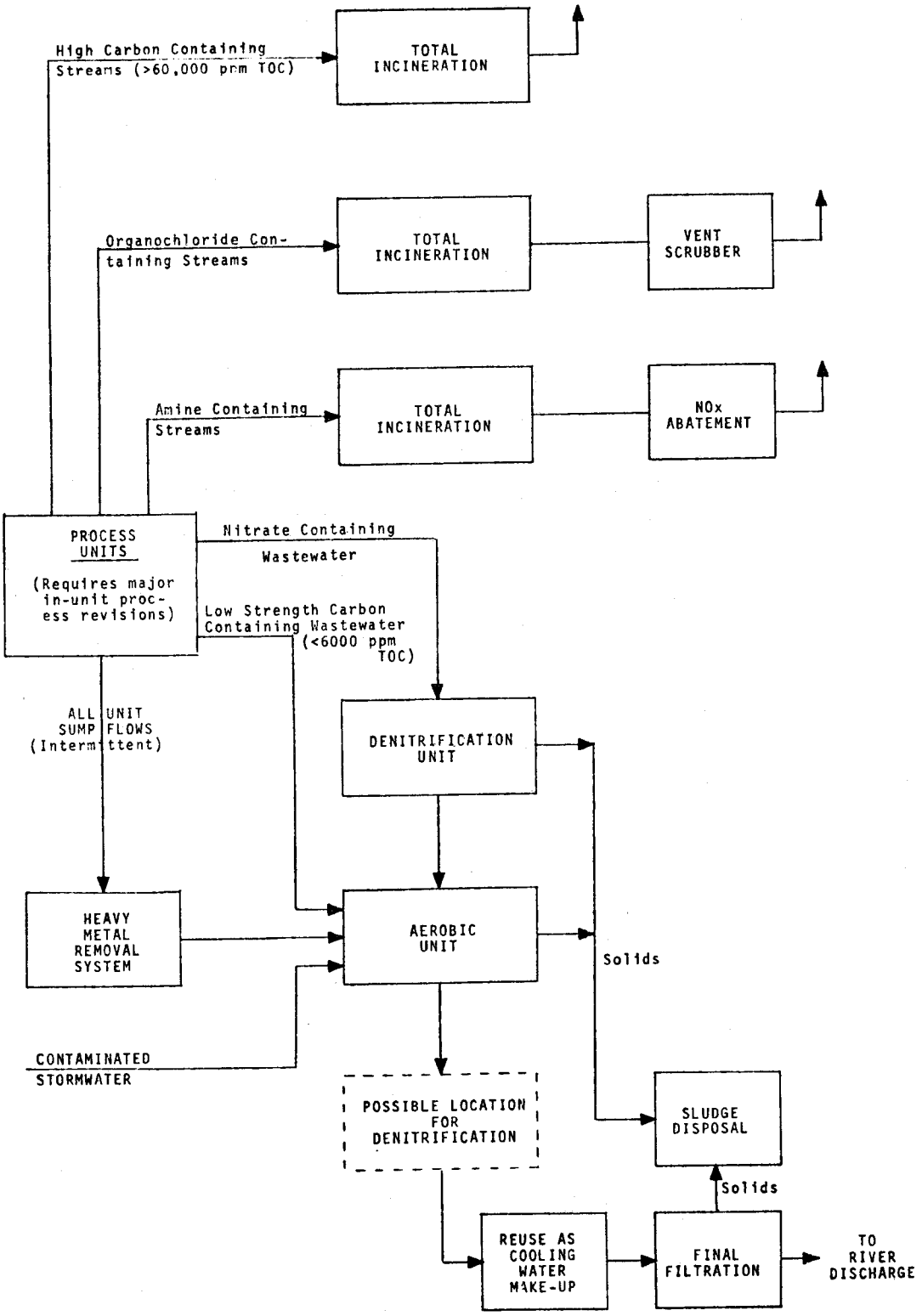


Figure 4. Proposed sequence.

SECTION 4

EXPERIMENTAL AND ANALYTICAL PROCEDURES

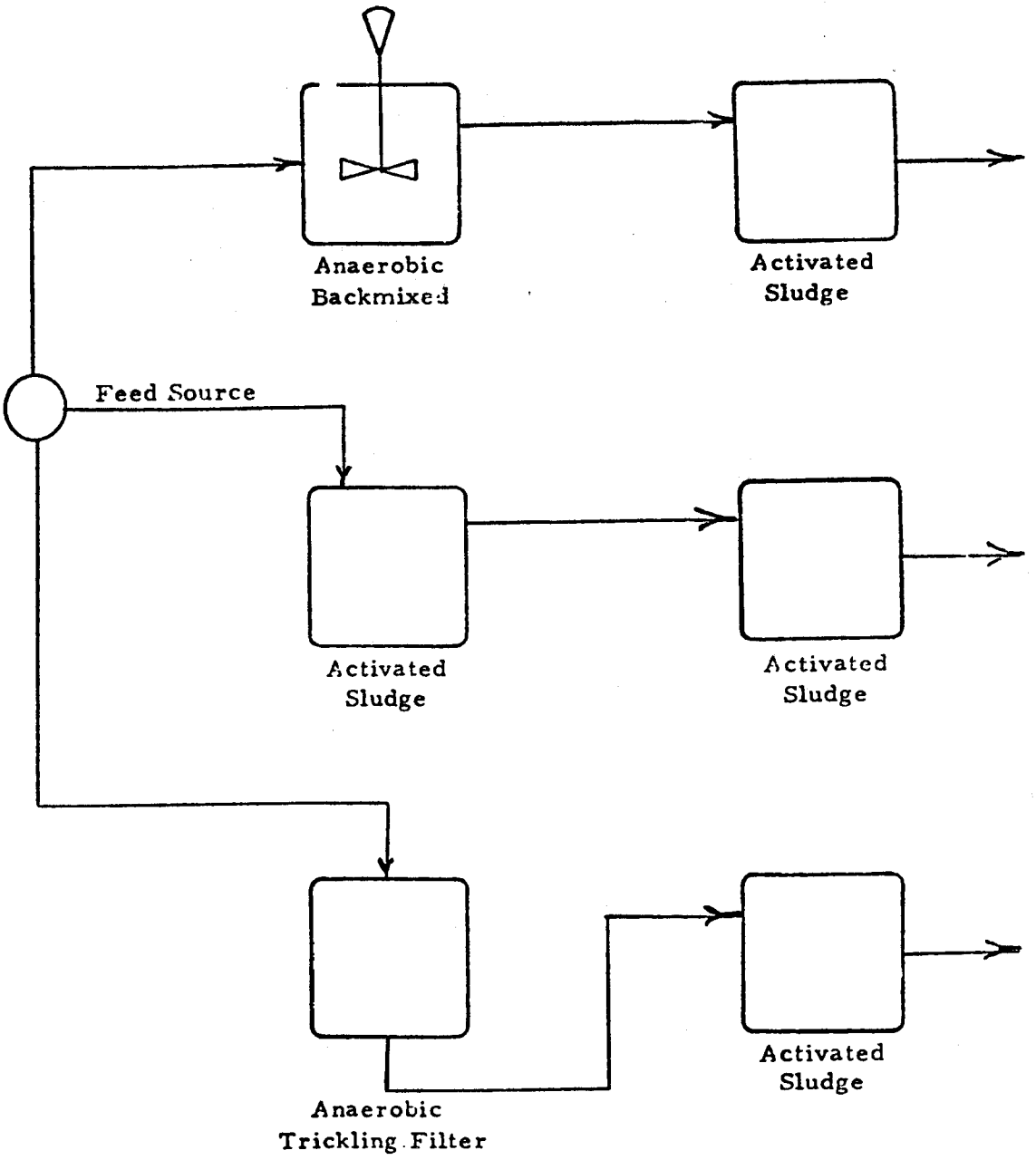
A. BENCH SCALE STUDIES

Bench scale treatability of aerobic and anaerobic biological treatment processes was conducted at the Bay City plant and the Technical Center (Phase I). The original objective of these studies was to evaluate the treatability of the combined plant wastewater; however, as the project progressed, modifications of the systems were necessary until the following proposed treatment sequence evolved. Detailed descriptions of the bench scale reactors are included in Appendix C.

Three bench scale units were operated at the Bay City plant and included: a) a backmixed anaerobic reactor followed by an activated sludge unit; b) a biological control unit that consisted of two activated sludge units in series; and c) anaerobic filter followed by activated sludge system. These three systems and the typical composition of the wastewater blends fed to each system are illustrated schematically in Figure 5.

The initial bench scale studies at the Technical Center concentrated on aerobic biological treatment using high purity oxygen as well as air. These systems included: a) two-stage oxygenated activated sludge system; b) conventional activated sludge system using air; and c) long-term aeration of activated sludge. A schematic representation of the three systems operated at the Technical Center and typical wastewater feed blends to each system are presented in Figure 6.

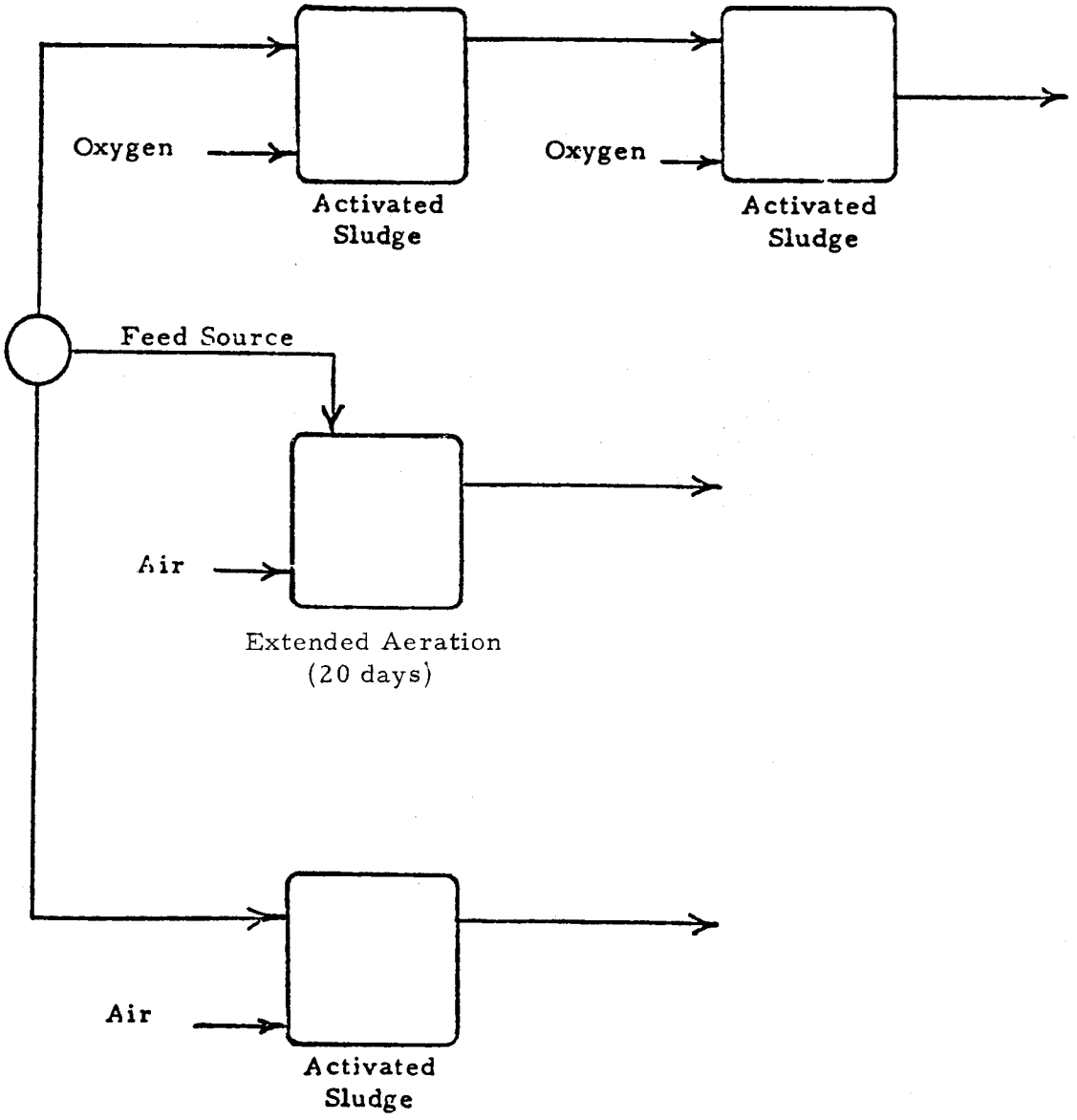
The bench scale studies at the Technical Center expanded and evolved to develop design parameters and criteria for anaerobic denitrification, anaerobic methanogenesis and activated sludge systems. These modifications were based on results of initial laboratory studies and stream segregation (Figure 7).



Typical Feed Composite, mg/l

TOC	15,000
COD	48,000
BOD	33,000

Figure 5. Initial Bay City laboratory studies (October, 1971)



Typical Feed Composite, mg/l	
TOC	15,000
COD	48,000
BOD	33,000

Figure 6. Initial Celanese Chemical Company Technical Center Laboratory Studies.

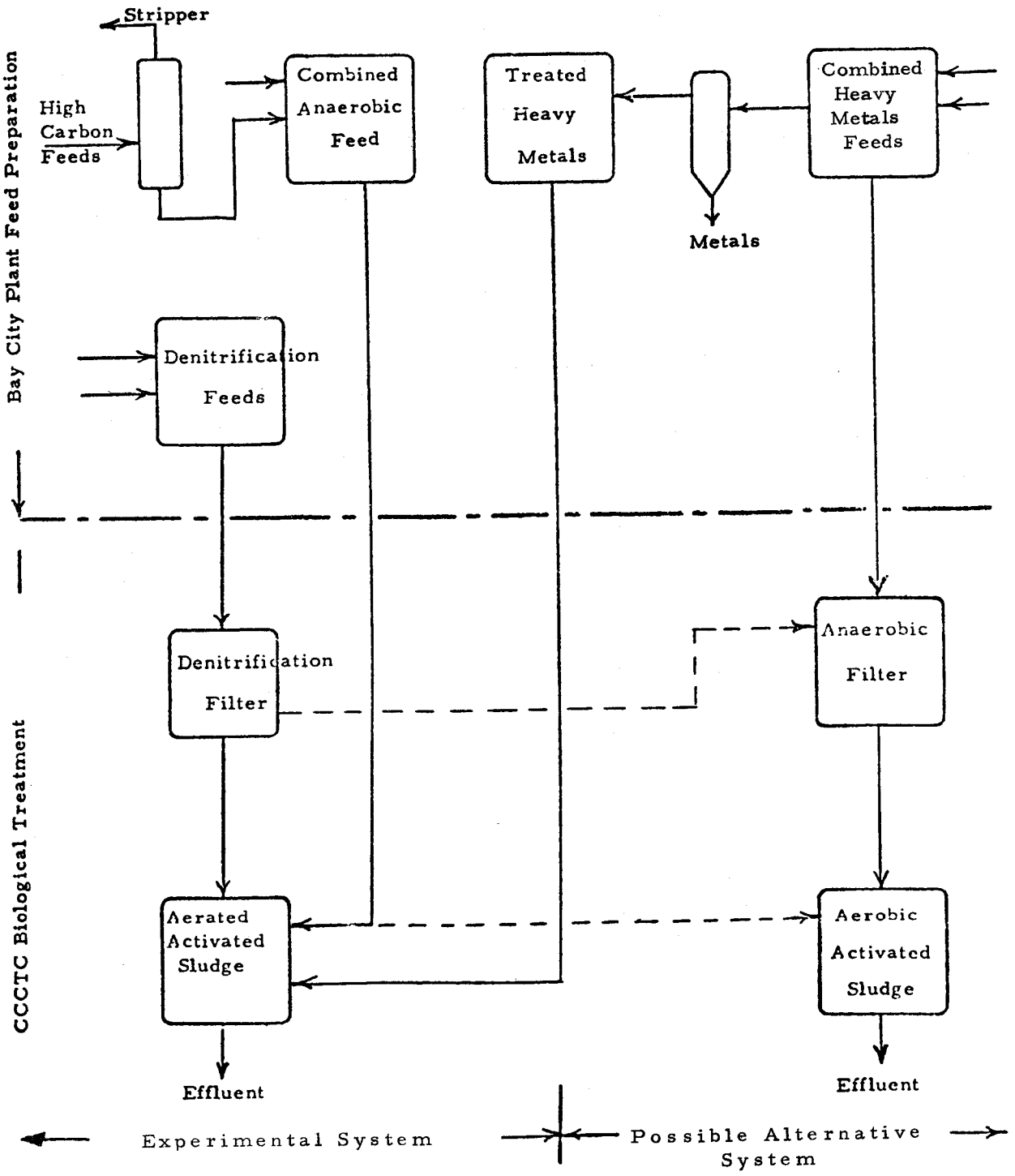


Figure 7. Feed compositing - pretreatment and biological treatment.

B. PILOT PLANT

The pilot plant constructed at Bay City originally was designed to treat the entire combined process wastewater stream by anaerobic methanogenic filters followed by high purity oxygen activated sludge system. Feed equalization and parallel reactor systems were included in the original design with considerable flexibility designed into the system for later modifications. The pilot plant phase of the project overlapped the laboratory bench scale studies. Modifications in the mode of operation of the pilot plant resulted as additional information became available. The evolution of the pilot plant work is summarized below.

1. Stage I

Parallel two-stage treatment of the combined feed by anaerobic methanogenic filters followed by high purity oxygen activated sludge system was initiated. Difficulties in maintaining acceptable performance of the biological units led to Stage II operation.

2. Stage II

Streams containing nitrates, amines, and chlorinated organics were pumped into an anaerobic denitrification filter. The denitrified effluent was fed into the oxygenated activated sludge system. The remaining streams were passed through an anaerobic methanogenic filter and the effluent from this unit could be fed either into the oxygenated activated sludge unit or discharged from the pilot plant. These operations were characterized by difficulties in maintaining stable operation and acceptable performance of the biological processes.

3. Stage III

The pilot plant was operated with segregated streams in a three-stage sequence consisting of denitrification followed by anaerobic methanogenesis with the final stage being oxygenated activated sludge system. The high nitrate streams were directed to the denitrification unit. The feed to the anaerobic methanogenic filter included the effluent of the denitrification unit plus those streams which were free of nitrates and chlorinated organics. The effluent of the anaerobic system was mixed with the third stream which contained chlorinated organics plus other organic containing streams and fed into the oxygenated activated sludge system. At this time 13 individual waste streams were delivered via seven pipes to the pilot plant. Difficulties were encountered with heavy metals from the high nitrate stream and from the activated sludge feed stream. The ion exchange guard beds performed quite well; however, periodic excursions in pH caused acid conditions and high

concentrations of heavy metals were released from the ion exchange resins into the biological reactors resulting in loss of the biological population.

A schematic diagram of the pilot plant in its final Stage III configuration is shown in Figures 8 and 9. Thirteen streams were segregated and diverted from the general plant area via seven pipes to the pilot plant feed equalization constant volume head tank. Head tank timer controls were periodically adjusted to achieve feed blends representative of the plant wastewater.

High nitrate streams were fed to equalization tank. These streams were pumped at rates up to 0.56 gpm to denitrification filter which was equipped with a 20 gpm recirculation pump. The denitrified effluent was fed to the anaerobic methanogenic packed bed filter along with those streams which are free of nitrates and chlorinated organics.

Effluent from the anaerobic reactor was pumped into the aerobic reactors along with raw aerobic feed. Oxygen was introduced via a downflow bubble contact aerator in the activated sludge unit. The reactor was equipped with a pump to recycle the mixed liquor through a CO_2 stripper and the downflow bubble contact aerator. After clarification, a portion of the settled sludge was recycled to the aerobic reactor. Periodic sludge blowdown was done manually.

The pilot plant also was equipped with on-line instrumentation to monitor TOC, dissolved O_2, and copper concentration. In addition to the variability of hydraulic and organic loading, this system was also plagued with mechanical problems and difficulties with keeping the on-line instrumentation in working order. The gear type metering pumps initially installed in the pilot plant could not be operated for more than 48 hours at any time without extensive maintenance and repair. These pumps were eventually replaced with peristaltic pumps which performed well. Extensive foaming in the downflow bubble contact aeration unit resulted in carryover of volatile suspended solids and reduced the efficiency of this process. Modifications in the design were ineffective in remedying this problem.

Two types of dissolved oxygen probes were used in an attempt to monitor the dissolved oxygen level in the aerobic system. At the time of the pilot plant evaluation, there was no commercially available dissolved oxygen (DO) analyzer which could provide adequate service for continued oxygen measurement or control in the aerobic system. The on-line DO monitoring system was one of the first installations in the U.S. Attempts to make the system operable required a great deal of time and effort. Many of the problems were attributed to the high mixed liquid volatile suspended

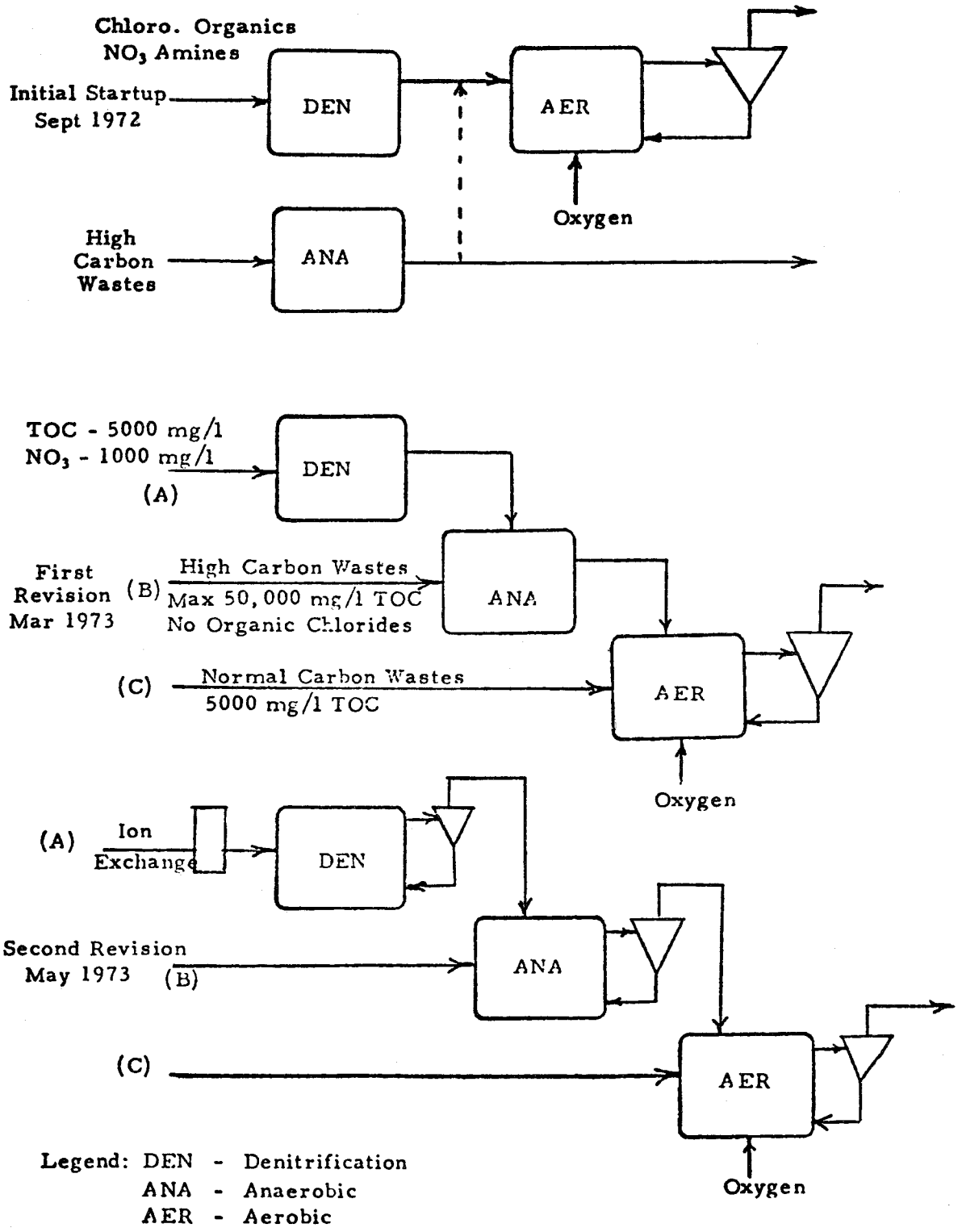


Figure 8. Pilot plant configurations.

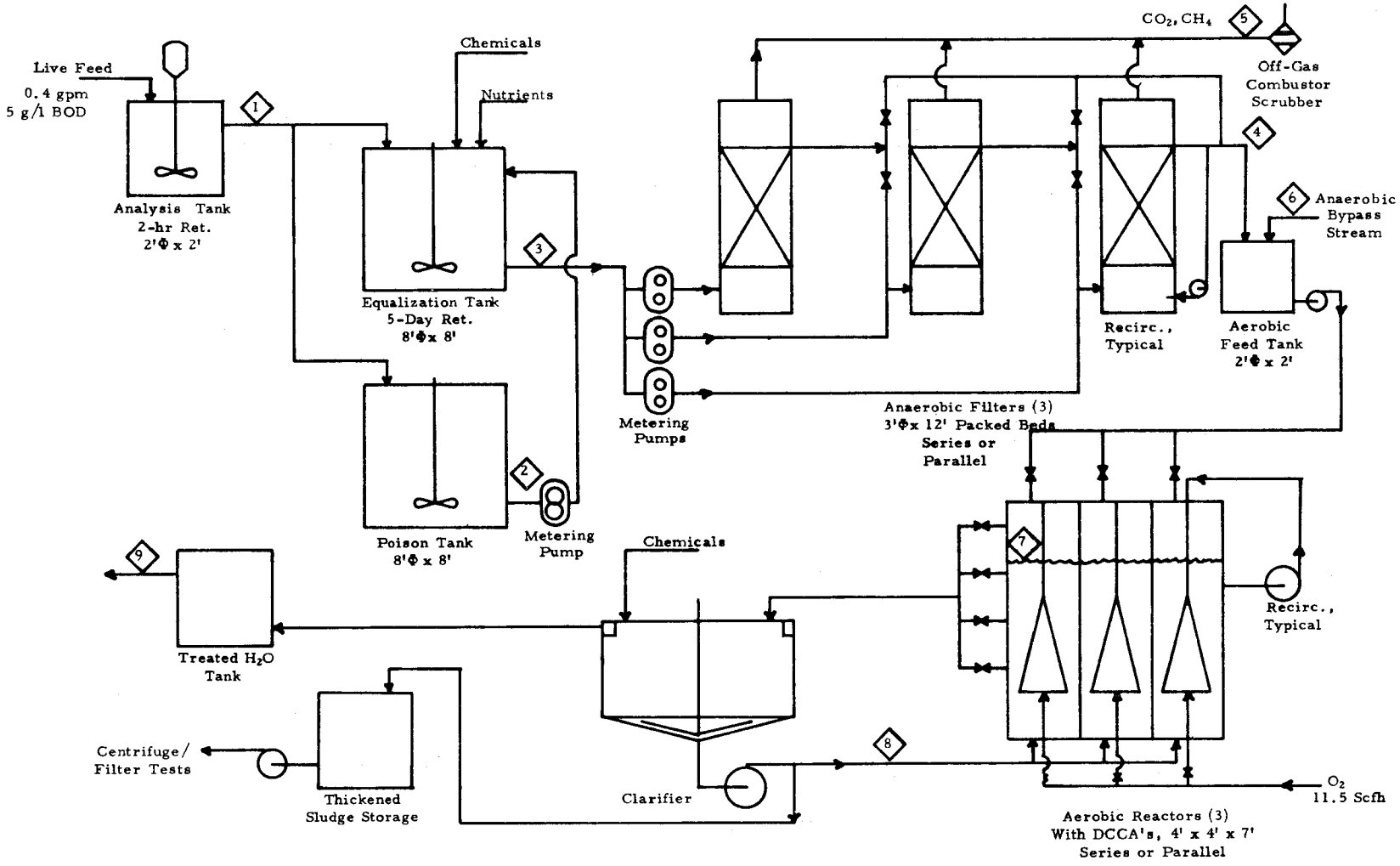


Figure 9. Pilot plant schematic.

solids concentration (5000 mg/l) as well as grit particles which passed by the probe. The membrane type DO probe was abandoned in favor of the thallium probe. Fouling of the membrane was a major drawback of the membrane type probe and erosion of the thallium limited the applicability of that probe at high velocities. The system was modified to reduce the velocity at the face of the thallium probe. This was done to minimize the problems with erosion but reliable operation was never obtained in the pilot plant.

The continuous total organic carbon analyzer initially installed could not be used in monitoring the pilot plant. Once again a great deal of time and effort went into the development of this system and eventually the system was modified by the manufacturer so that the continuous analysis of total organic carbon was possible. The heavy metal analytical system to continuously monitor the copper concentration in the effluent stream suffered from similar problems to those mentioned above. No successful operation was obtained.

Continuous operation of the pilot plant required the attention of an operator and instrument mechanic to maintain the instrumentation around the clock. These experiences indicated that sophisticated and reliable on-line analyzers were required for the control of the complex biological system. Unfortunately, these systems were not available during the pilot plant studies.

C. ANALYTICAL METHODS

The characteristics of the feed material to the various biological systems are expressed in terms of biochemical oxygen demand, chemical oxygen demand, total organic carbon, nitrates, pH, suspended solids, and metals. The analytical procedures used during these studies are described in detail in EPA Manual of Wastewater Analyses with the exception of COD which for the most part was determined by instrumental analysis rather than the standard two-hour dichromate reflux method. The instrumental COD for the wastewaters used in this study was approximately 20% greater than the reflux COD values.

SECTION 5

RESULTS AND DISCUSSION OF GLASSWARE AND PILOT PLANT STUDIES

A. BENCH SCALE STUDIES

Laboratory scale glassware studies of the treatability of the combined process wastewater and of various blends of the components of the combined process wastewater were carried out at both the Celanese Chemical Company Technical Center at Corpus Christi, Texas and the Bay City plant at Bay City, Texas. Every effort was made to obtain representative samples of each of the waste streams. A portion of the composite samples were used in the Bay City glassware studies and a portion was shipped to the Technical Center.

The laboratory glassware studies at the Bay City plant were terminated shortly after the startup of the pilot plant; however, the glassware studies at the Technical Center continued throughout the duration of the project. Samples for the glassware studies were prepared at the Bay City plant by collecting samples of the individual streams. The combined wastewater or any blends which were anticipated as a result of the waste reduction program were prepared at the Bay City plant and shipped to Corpus Christi at regular intervals.

B. BAY CITY PILOT PLANT STUDIES

Individual wastewater components of the entire process stream were fed to the pilot plant during approximately a one-year period. Operating difficulties led to modifications to the piping, pump replacement, installation of clarifiers, changes in the size of downflow bubble contact aerator, and CO_2 stripping system.

The pilot plant was seeded with a combination of domestic activated sludge and acclimated biomass. Acclimation to the process wastewater was a slow process. Throughout the entire pilot plant operation, one-half of the system was operated on the plant wastewater while the other parallel system was fed a synthetic blend of wastewater components to maintain an available acclimated biological population.

The various modifications of the pilot plant system were discussed previously and the normal configuration of the pilot plant is presented in Figure 9. Mechanical and instrumentation problems during startup in the initial phases of the pilot plant study made it almost impossible to evaluate the performance of any of the biological processes.

All nitrate containing streams were channeled directly to the denitrification unit, the high carbon streams went directly to the anaerobic methanogenic treatment unit, and the remainder of the waste stream containing the chlorinated organics was fed into the aerobic unit. The final treatment scheme included a series of units employing denitrifying, methanogenic and finally aerobic bacteria.

In addition to the mechanical difficulties which were experienced during the startup of the pilot plant, other problems were experienced by the denitrification unit; namely, a) excessive lime neutralization requirements; b) poor gas production and/or accountability; c) plant power failure; d) excessive instrument maintenance requirements; e) poor performance of ion exchange resin in removing soluble copper; and f) intermittent feed supply with widely varying composition.

The variable flow of the wastewater to the pilot plant coupled with varying concentration in the feed made manual control of changes in the pH by adjustment of feed rates almost impossible. The changes in nitric acid concentration resulted in widely varying pH between the feed with pH = 1 to pH = 3 and the bioreactor which had a pH = 6 to pH = 9. At low values of pH, copper and heavy metals removed by an exchange were released into the biological system. The ion exchange system was subsequently replaced by precipitation of the heavy metals with sulfide.

1. Denitrification

The activity of the denitrifying ecosystem was evaluated by the addition of massive doses of methanol and nitric acid. The hydraulic loading also was temporarily increased to 2200 gallons per day resulting in a hydraulic detention time of about 19 hours. These operating conditions resulted in a) loss of biomass; b) lowering of the reactor pH to pH = 5.5; c) marked reduction in gas production; and d) increase in the methane content in the off-gas to 20% by volume. Therefore, increasing the nitrogen load to the denitrification unit by increasing the hydraulic loading at same nitrate concentrations did not provide a solution to the problem.

The organic carbon content of the feed was continuously analyzed with an on-line TOC analyzer for a single week. During the test period, the TOC varied in diurnal cycles between 2000 and 2100 mg/l. None

of the large upsets experienced in previous operations were seen during this single test period. Operating data for the denitrification unit are presented in Table 4. The data reported during the early phases of the pilot plant operation are somewhat erratic; however, only average values are reported for the first six-month period. The bulk of the data in Table 4 represents biweekly averages of daily analyses.

During the last three-month period of operation of the pilot plant, the denitrification unit operated at a mean hydraulic detention time of about five days and the average nitrogen removal efficiency was 67.7%. The feed to the denitrification unit contained an average TOC of 10,400 mg/l and BOD 16,200 mg/l and nitrate concentration of 600 mg/l. The TOC to NO_3 ratio in the feed averaged 9.1. The average loading was 0.15 lb of organic carbon per cu ft per day and the removal efficiencies were relatively low in the order of 32.2% for TOC and 19.2% for BOD.

The denitrification process required particular attention to alkalinity and TOC to NO_3 ratio control. Excess nitrates in the reactor effluent usually was correctable by the addition of methanol.

The biweekly averages of the carbon concentrations varied as much as 80 to 90%. This variability accented by equally variable heavy metal concentrations in the feed contributed to the reduced nitrogen removal efficiency during the latter part of the pilot plant operation. The data observed in the early phases of the pilot plant operation indicated that nitrate removal efficiencies in excess of 90% were readily obtainable. The chemical unbalance reduced the operating capability of the unit.

Towards the end of the pilot plant operation, the hydraulic loading to the denitrification unit was increased to 1,100 gallons per day which resulted in deactivation of the unit. The BOD loading during this time was increased to 0.5 lb/cu ft/day which is more than three times the previously identified stable range of operation.

2. Methanogenic Unit

The operation of the methanogenic unit was the most difficult. Overall growth rate of the methane bacteria was extremely low and the amount of organic conversion was almost negligible. In the early stages of the pilot plant operation, low rate of activity in the methanogenic unit was attributed to the solids washout. In the first quarter of operation, the methanogenic filter was treating waste with a TOC of 1000 mg/l. Shortly thereafter, the TOC concentration was increased to 2000 mg/l and progressively to 8000 mg/l. Within four days the gas production was completely stopped. A period of 30-60 days was required to regain activity in the methanogenic unit.

TABLE 4. SUMMARY OF PILOT PLANT DATA

GPD	TOC Feed	TOC Product	BOD Feed	BOD Product	NO_3-N Feed	NO_3-N Product	TOC Loading	REMOVAL, % * TOC	REMOVAL, % * BOD	REMOVAL, % * NO_3-N	TOC/ NO_3-N
DENITRIFICATION											
290	5,837	2,625	11,520	6,181	609	106.2	15.9	55.0	46.3	82.6	9.58
381	11,387	6,593	21,625	10,683	474	148.5	46.4	42.1	50.0	68.7	2.40
315	16,443	13,180	23,889	29,306	575	410.0	55.0	19.8	-22.7	28.7	2.86
335	11,661	7,145	13,242	11,103	891	70.3	37.0	38.7	16.2	92.1	13.09
217	8,340	6,219	12,312	10,232	726	214.0	14.5	25.4	16.9	70.5	11.48
575	8,898	7,738	14,800	13,600	590	214.0	43.4	13.0	8.6	63.7	15.08
METHANOGENIC											
11.5	15,461	142		1,170			1.3	99.1			
138	2,895	622	7,269	2,065			3.3	78.6	71.7		
220	2,843	1,346	6,001	2,543			5.1	52.7	57.6		
291	2,732	1,544	4,198	2,491			6.5	43.5	40.7		
327	3,703	2,206	6,223	2,645			9.8	40.4	57.5		
AEROBIC											
132	3,803	2,082	7,748	2,250			6.3	45.3	71.0		
61	6,722	1,843	10,822	2,682			3.6	72.6	75.2		
173	5,710	1,302	9,029	2,376			7.7	77.2	73.7		
61	3,947	789	8,613	484			0.9	80.0	94.4		
375	2,102	134	3,194	61			7.4	93.6	98.1		
398	3,743	1,239	5,861	1,120			12.1	66.9	80.9		

*Based on Concentrations.

A synthetic blend of sodium acetate, methanol and nutrients was used during the reacclimation period to develop a healthy methanogenic bacterial population. At that time the Bay City plant waste was introduced as feed to the anaerobic unit.

Key to the operation of the methanogenic unit was frequent attention to: a) pH of the reactor; b) the cationic concentrations; c) off-gas analysis; and d) organic loading rates. The mean hydraulic detention time was nine days and the methanogenic unit was fed a blend containing 5500 mg/l of TOC and a BOD of 5900 mg/l. This loading is equivalent to 0.03 lb organic carbon/cu ft/day resulting in removals of 50-60% of the TOC and 72.6% of the BOD. The gas production rate was 68.5 cu ft/day of which 60-80% was methane. At a detention time of less than ten days the loading to the reactor markedly affects the removal efficiency of the methanogenic unit. The organic carbon loading was generally less than 10 lb/day.

Operating the methanogenic unit at a hydraulic detention time of six days resulted in relatively stable operating conditions. The off-gas contained approximately 70% methane with less than 2% oxygen. Approximately 6.8 lb of organic carbon were converted into methane and biomass per day.

The biomass production rate is equivalent to 500 mg/l or 0.16 mg per mg BOD removed. Periodic inspection indicated that the biomass concentration in the effluent was 400-500 mg/l under normal hydraulic rates. As the hydraulic rate reached 500 gal/day with a detention time of 3.5 days, the volatile suspended solids concentration increased to 2500-5000 mg/l. This high washout rate contributed significantly to the rapid deterioration of the process as the hydraulic loading was increased. Within a 24-hour period at the higher hydraulic loading rates, gas production was decreased by 90%. However, by reducing the hydraulic loading to 392 gal/day, gas production began to return to normal after seven days of operation. Therefore, the system was not completely inactivated since only a portion of the active biomass was lost at the higher hydraulic loading rates.

3. Activated Sludge Unit

Operation of the activated sludge plant was extremely vulnerable to malfunctions in the dissolved oxygen controller and to the influx of heavy metals in the feed blends to the system. Each of these problems caused at least one major reactor deactivation during the pilot plant operation. In one case, a complete replacement of the biomass was required.

The mean hydraulic detention time was 5.5 days and the average TOC loading of 0.4 lb/cu ft/day. The average TOC removal was 72.6% with a BOD removal of 82.2%. The characteristics of the feed to the activated sludge system also are shown in Table 4. The average BOD was 7500 mg/l and the average TOC was 4300 mg/l during the last quarter of operation. The plant operated on the feed blend which varied in composition sufficiently to change the biweekly feed concentration averages by 80-90%. The feed to biomass ratio (F/M) ranged from 0.2 to 1.3 lb of BOD/lb of MLSS. The best operating efficiency was obtained at F/M equal to 0.2 to 0.6 lb of BOD/lb of MLSS. The BOD to TOC ratio in the feed to the activated sludge plant varied from 1.5 to 2.2 which provided for 32% change in the oxygen demand within a change in the total organic carbon content.

C. TREATABILITY STUDIES

Extensive laboratory treatability studies were conducted at the Technical Center to define in more detail the effectiveness and limitations of the anaerobic and aerobic processes in treating the complex petrochemical wastewater. Composited pretreated samples of wastewater were collected at the Bay City plant and shipped to the Technical Center (Phase III). Synthetic blends of typical components were prepared for some of these studies. The results of the aerobic studies are presented in Appendix D, Table D-1 through D-3.

1. Aerobic Treatment

Two stage oxygen activated sludge systems were operated at detention times of four days per stage. At feed concentrations of 13.5 gm/l of TOC and 30 gm/l of BOD overall removals of 85% for TOC and 95% for BOD were observed. The effluent after clarification contained dispersed growth (1000 mg/l suspended solids) and was turbid. High concentrations of amine by-products from the nylon unit was toxic to the system.

Pretreatment and distillation eliminated the toxic amines, and the TOC of the resulting wastewater was approximately 4000 mg/l. This stream could be treated in the two-stage oxygen system at efficiencies of 90% for TOC removal and 98% for BOD removal at detention times of one to three days per stage. The system was unstable and easily upset at the one day detention time. In all cases, however, the effluent was turbid because of poor settling of dispersed biomass and was yellow in color.

Percolation of the effluent through a granular activated carbon bed (Filtrasorb 300 Calgon) did remove the color. However, additional information which defines effective carbon life, regeneration capabilities, etc., are not available. Ozone and hydrogen peroxide also removed some of the color but the cost of these oxidants is economically prohibitive.

2. Anaerobic System

The high oxygen requirements (approximately 40 tons/day) for commercial scale aerobic treatment of the combined Bay City plant process wastewater led to the consideration of anaerobic treatment.

The results observed in the initial anaerobic studies led to the segregation of the process plant wastewater into the following three composites: a) a composite containing all the organic chlorides; b) nitrate containing waste streams; and c) normally biodegradable hydrocarbon waste which is free of organic chlorides and nitrates (Figure 10). Composite A was treated aerobically and the results are discussed above. Composite B containing the nitrates was fed to an anaerobic backmixed filter for denitrification. The characteristics of composites B and C are presented in Tables 5 and 6, respectively. The relatively high TOC concentrations of composite B is caused by a high carbon containing stream which was not used in the composites fed to the aerobic units.

a. Denitrification

The startup of the denitrification anaerobic filter was almost immediate as indicated by the data presented in Appendix E, Figures E-1 through E-2. The operation of the system was relatively stable. Nitrate-nitrogen is almost completely removed from the feed containing 2.6 grams/liter and the effluent contained a concentration less than 5 mg/l of nitrate-nitrogen (analytical detectability). The removal of 2.6 g/l of nitrate-nitrogen results in the removal of approximately 2.5 g/l of TOC. The organic carbon content in composite B is too low to reduce all the available nitrate; therefore, approximately 10% by volume of composite C was added to the denitrification feed in order to provide additional TOC. A more detailed evaluation of the performance of the denitrification filter in terms of influent flow gas production, nitrogen production, detention time, BOD removed per liter of feed, volume ratio of gas produced feed, mole fractions of nitrogen, methane and N_2O as well as pH is presented in Figures E-1 through E-2.

These data indicate that during stable operations the pH was between pH = 7.0 and 7.5 and constant. The ratio of gas produced per unit of feed was constant, gas composition was also constant and the effluent was completely

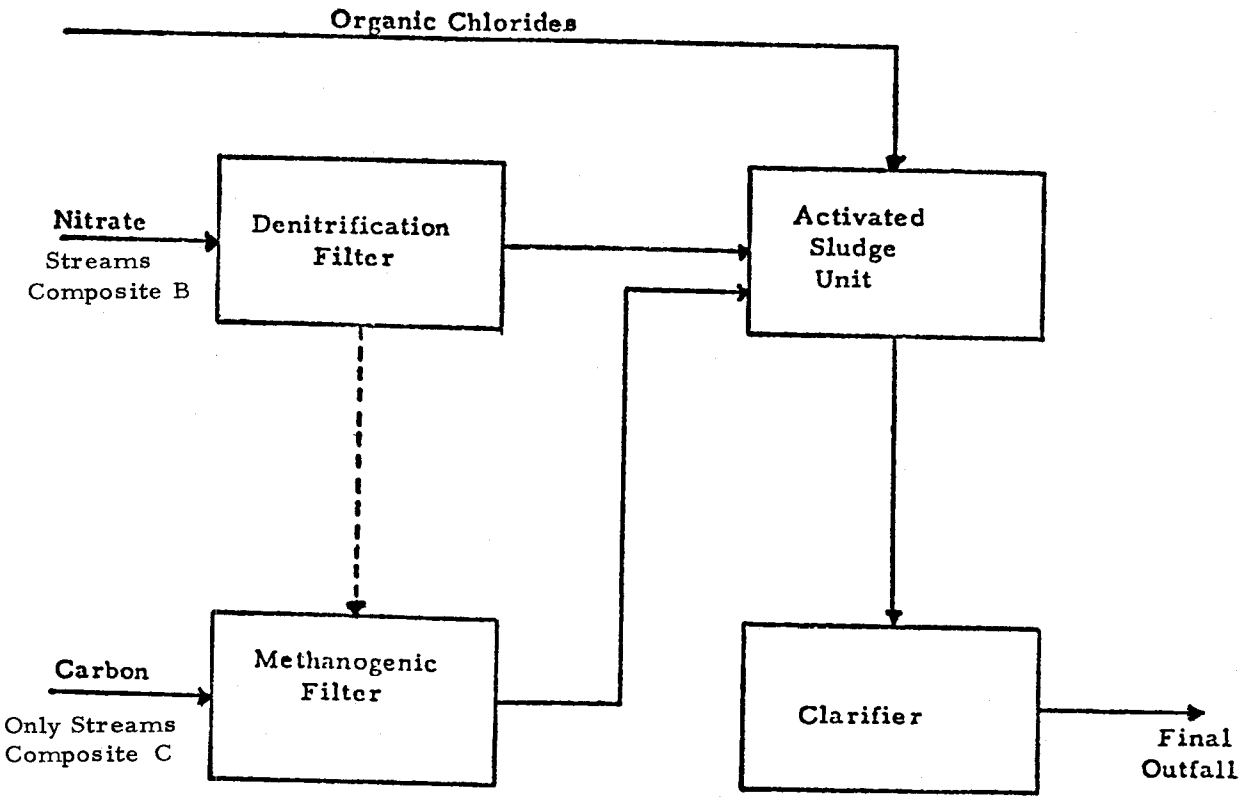


Figure 10. Denitrification - anaerobic - aerobic treatment of Bay City effluent.

TABLE 5. COMPOSITE OF NITRATE-CONTAINING BAY CITY WASTES "COMPOSITE B"

Identification	28-1	28-2	13-1	13-2
Appearance	Clear, Yellow	Clear, Yellow	Clear, Yellow	Clear, Yellow
pH	0.9	0.8	1.4	< 1.0
TC, mg/l	2660	2050	3700	3130
IC, mg/l	200	200	380	
TOC, mg/l	2460	1850	3320	3130
COD, mg/l	6900	8000	10500	8300
Total Chlorides, mg/l	< 20	< 20	< 100	< 100
Total Nitrogen, mg/l	2500	2900		
Sodium, mg/l	2900	2500	1.0	7.0
Phosphorus, mg/l	< 20	< 20	< 10	< 10
Copper, mg/l	10.1	10.2	30	0.2

TABLE 6. BAY CITY COMPOSITE, CARBON-ONLY WASTES "COMPOSITE C"

Identification	26-1	26-2	14-1	14-2
Appearance	Brown	Brown	Amber	Amber
pH	3.1	3.4	2.9	3.3
TC, mg/l	8000	28000	56500	67000
IC, mg/l	3	10	93	93
TOC, mg/l	38000	28000	56500	67000
COD, mg/l	80400	60600	184000	208000
Total Chlorides, mg/l	35	20	< 100	< 100
Sodium, mg/l	400	410	4000	4500
Total Nitrogen, mg/l	1200	1400		
Nitrate Nitrogen, mg/l	< 10	<10		
P as $PO_4^{=}$, mg/l	3200	36000	1200	2400
Copper, mg/l	4.6	2.4	22	22

devoid of nitrate nitrogen. Under upset conditions there was a drop in pH, an appreciable amount of nitrate-nitrogen appeared in the effluent, and the composition of the gas produced changed markedly with a reduction in the mole fraction of nitrogen accompanied by a corresponding increase of N_2O in the off-gas. Recovery of the system after upset apparently could be quite rapid. The upsets are a result of a high TOC to nitrate ratio in the absence of sufficient buffering capacity. Under these conditions, a considerable amount of the residual organic carbon is not oxidized by the nitrate, and since the influent is quite acid, the pH drops. At the lower pH, the denitrification reaction proceeds to N_2O rather than to nitrogen gas. Therefore, the amount of oxygen available for destruction of the TOC is reduced and additional lowering of pH occurs. As the pH drops further, the denitrification to nitrogen gas practically stops and reaction results in the generation of NO which leads to an additional decrease in the pH. Therefore, once the environment is such that denitrification to nitrogen gas is inhibited or ceases, the situation in the reactor rapidly deteriorates. Under the low pH conditions, copper present in the feed may dissolve and add to the toxic effects.

Composite B which contains adipic acid as the main source of carbon was blended with known amounts of nitrate, TOC and alkalinity in order to better define the parameter affecting denitrification. Sodium bicarbonate was added to provide buffering capacity and copper also was added at a constant concentration of 20 mg/l to simulate the major heavy metal present in the waste. The stoichiometry involved in the oxidation of adipic acid via biological denitrification is expressed below:

$$2\ HNO_3 \rightarrow H_2O + N_2 + 50$$

MW = 126

$$HOOC(CH_2)_4COOH + 13\,O \rightarrow 6\,CO_2 + 5\,H_2O$$

MW = 146

$$26\,HNO_3 + 5\,HOOC(CH_2)_4COOH \rightarrow 38\,H_2O + 30\,CO_2 + 13\,N_2$$

Approximately two grams of adipic acid were required per gram of nitrate-nitrogen. The feed blend contained a constant one gram per liter of nitrate-nitrogen and 4.5 g/l of sodium bicarbonate (54 millimoles of sodium per liter) providing buffering. The sodium bicarbonate was sufficient to neutralize the adipic acid which was not biologically degraded during the denitrification process. In addition to the nitrate and buffer capacity, various amounts of adipic acid were added to the feed, namely, 2, 2.5, and 3, and 3.5 g/l. The hydraulic detention time in the unit was

one day based on the void volume. The response of the reactor to increasing amounts of adipic acid from 2 to 3.5 g/l were as follows: the residual TOC increased from 150 mg/l up to 750 mg/l while the COD increased from 100 mg/l to 1200 mg/l. No copper was detectable in the effluent and the nitrate-nitrogen concentration in the effluent was less than 5 mg/l (detectable limit) throughout the study except when the feed adipic acid concentration was 2 gm/l. At that time, the nitrate nitrogen concentration decreased with simultaneous appearance of between 10 and 15% of N_2O in the product gas. The appearance of the N_2O and the breakthrough of the nitrates resulted from an insufficient amount of organic carbon in the feed.

Methane was present in the produced gas at all feed rates in small amounts; namely, from 0.5 to 10% by volume. The volume fraction of methane in the product gas increased as the concentration of adipic acid in the feed increased.

Denitrification occurred by complete oxidation of adipic acid to CO_2 and water rather than by stepwise oxidation, since no intermediate degradation products of the adipic acid were present in the effluent.

b. Treatment of Composite C to Methanogenesis

Acclimation of the anaerobic unit to Composite C containing a high concentration of carbon but a very low concentration of nitrates required a considerable amount of time. Gas production was satisfactory when the feed was diluted to half strength; however, the system failed when full strength waste was fed. After failure of the system, the reactor was once again acclimated to a feed containing equal volumes of composite C and the effluent of the denitrification unit treating composite B. The volume ratio of the two streams was estimated to be similar to the actual ratio of the streams at the Bay City plant. It should be pointed out at this time that the effluent of anaerobic reactor treating the composite C is decolorized from an extrapolated APHA color of greater than 10,000 to APHA color of 150. This color removal represents a marked improvement of the effluent since the color remained unchanged after the various aerobic treatment systems.

Approximately 65% of the feed to the anaerobic methanogenic unit consisted of denitrified effluent and the full strength composite C made up approximately 35%. Variations in the performance of the methanogenic units are presented in Figures F-1 through F-2. The activity in the unit remained relatively poor until the amine streams were removed from the composite C. At that time, the operation of the anaerobic methanogenic units improved considerably in spite of mechanical troubles.

The anaerobic methanogenic unit operated quite well until day 142 when the volume percent of the composite C in the feed to the unit was increased to 25%. At that time the gas production decreased steadily and the system did not get back to normal performance until the feed strength was cut in half to 12.5% by volume.

The final phase of the anaerobic methanogenic treatment of composite C used a feed which contained 30% strength composite C diluted with water to determine the minimum hydraulic detention time for the anaerobic methanogenic unit. Performance of the anaerobic filter was relatively marginal at a detention time of two days and the TOC removal decreased to 60% compared to the 75 to 80% removal of TOC observed at a four-day detention time. The detention times mentioned in this discussion are based on the original void volume of the filters and the actual detention time is considerably less since the void volume was decreased by growth of biomass in the units.

c. Process Limitations and Design Criteria for Denitrification

Process wastewaters from the Bay City plant contain several streams which have relatively high concentrations of nitrates. The nitrates inhibit methanogenesis but can be converted to nitrogen gas (N_2) quite effectively anaerobically. Off-gas from the denitrification filters consists essentially of N_2 and CO_2 with only trace amounts of methane, less than 1% by volume. The denitrification process is affected by the ratio of organics to the nitrates in the influent. At high concentrations of organics in comparison to nitrates the system is characterized by a sharp decrease in the effluent pH and the appearance of N_2O in the off-gas. If the system continued to operate at the relatively high organic to nitrate ratio the N_2 in the off-gas would drop to zero and NO would be detectable in the off-gas. However, the biomass in the system could be regenerated after being upset by high organic to nitrate ratio by flushing the system with dilute bicarbonate of soda followed by the addition of the substrate which contained more alkalinity and/or more nitrates in comparison to the organic substrate. In the presence of sufficient substrate and residual alkalinity, the bacterial denitrification reaction goes to N_2:

$$2\ HNO_3 \rightarrow H_2O + N_2 + 5\ (O) \qquad \text{Reaction I}$$

In this reaction one part of nitrate N is reduced by 2.857 parts of substrate COD. At low pH values, the denitrification reaction is not complete and the N_2O appears as an end product:

$$2\ HNO_3 \rightarrow H_2O + N_2O + 4\ (O) \qquad \text{Reaction II}$$

In this case, one part of nitrate N corresponds to only 2.286 parts of substrate COD. If the appearance of N_2O was caused by an acidic organic substrate with limited alkalinity the residual substrate concentration would be higher and result in a further decrease in the pH and a larger proportion of N_2O in the effluent. As the pH continues to drop, the denitrification becomes less efficient:

$$2\ HNO_3 \rightarrow H_2O + 2\ NO + 3\ (O) \qquad \text{Reaction III}$$

Therefore, one part of nitrate N now corresponds to only 1.714 parts of substrate COD. Analytically NO is difficult to measure, but its presence was evident by NO_2 fumes which were generated when the off-gas contacted the atmosphere. The denitrification of the effluent to N_2O via Reaction II can represent a stable mode of operation, for example, when there is insufficient substrate. Results of laboratory experimentation indicate that rather than leave residual nitrate in the effluent, the denitrifying organisms will produce enough N_2O in the off-gas to balance the substrate COD against the oxygen from denitrification.

The process wastewaters from the Bay City plant commonly contain relatively high concentrations of organics relative to the nitrate. Therefore, a bench scale evaluation was undertaken to determine if a stable operation could be maintained in the pH range of 4.6 as the carboxylic acid. If this scheme were possible, denitrification could take place without the addition of large amounts of alkalinity.

A synthetic substrate was used in the bench scale studies, and the composition is presented in Table 7. Operating data for the anaerobic denitrification filter are presented in Figures G-1 through G-5 in the Appendix. The various parameters used to describe the performance of the anaerobic denitrification process are presented graphically.

The synthetic substrate was designed so that denitrification according to Reaction I would remove 0.05 ml/l of acetic acid and leave a buffer containing 0.05 ml/l of acetic acid and 0.05 ml/l acetate. Under these conditions, the denitrification reaction would be forced to proceed at the pH of the carboxylic acid-carboxylate buffer and would approach the conditions of a COD rich denitrification feed similar to that from the Bay City plant except the process waste would contain C_5 to C_6 dibasic acid instead of acetic acid.

After initial startup problems a low feed rate was maintained until the performance of the system resembled steady state conditions, approximately 50 days based on washout kinetics for a well mixed reactor.

TABLE 7. COMPOSITION OF SYNTHETIC DENITRIFICATION EFFLUENT

CH_3COOH = 6.0 g/l ≡ 0.1 mole/l ≡ 6.4 g COD/l

CH_3COON_a = 4.1 g/l ≡ 0.05 mole/l ≡ 3.2 g COD/l

HNO_3 = 1.12 g nitrate N/l ≡ 4.57 g COD/l ≡ 0.071 moles acetic acid/l via denitrification to NH_3

≡ 3.2 g COD/l ≡ 0.05 mole acetic acid/l via denitrification to N_2

≡ 2.56 g COD/l ≡ 0.04 mole acetic acid/l via denitrification to N_2O

Alkalinity from CH_3COONa = 0.05 equivalent/l

Alkalinity from NH_3 generated via denitrification = 0.08 g/l

P:COD of nitrate N = 1:100

P added as H_3PO_4

CO^{++} = 2 mg/l

Fe^{++} = 2 mg/l

5 = 20 mg added as Na_2SO_4

Under the low loading conditions, the pH continued to drop to the pH= 5.76, and then began to increase gradually to about pH = 7 when the calculated washout was achieved. At the same time, the amount of N_2 in the off-gas began to drop and after approximately 25-30 days the N_2 accounted for only approximately 15% of the nitrate N in the feed. The data indicate that the denitrification was complete at all times. Analysis of the effluent of the reactor indicated that the total Kjehdahl nitrogen was relatively high. It was possible that at these low loading feeds denitrification was resulting in ammonia as an end product.

$$HNO_3 + H_2O \rightarrow NH_3 + 4\,(O) \qquad \text{Reaction IV}$$

Denitrification to ammonia represents 4.57 g COD per part of nitrate N in the feed, and therefore, a considerably greater quantity of substrate would be consumed in denitrification to ammonia than would be consumed by conventional denitrification to N_2 gas. The denitrification reaction resulting in ammonia also produces an appreciable amount of alkalinity which aids in buffering the unoxidized fraction of the acidic substrate. In this case, the nitrate N in the feed would be denitrified entirely to ammonia, consuming 0.08 moles per liter acetic acid. This compares with 0.05 moles per liter of acetic acid if the denitrification proceeded to N_2 gas. At the same time, the ammonia would result in 0.08 equivalent of buffer which could be used to neutralize any acetic acid substrate. Denitrification via ammonia was confirmed by calculating the amount of ammoniacal N accumulated in the reactor by assuming all the nitrogen not accounted for as off-gas is converted to ammonia. A nitrogen balance maintained during these studies verified the various nitrogen products in the offgas at various carbon loadings.

Under conditions of increased pH in the reactor (pH greater than 6) an increasing amount of methane was observed in the off-gas. Contribution of this methane to COD removal is quite significant and by day 40 was comparable in magnitude to the amount removed by denitrification. At about the same time, the amount of N_2 gas in the off-gas, also began to increase. It may be possible that methanogenesis can compete successfully with the relatively feeble energetics of the reaction of N_2-NH_3. The system approaches steady state at a relative low loading of COD between 0.5-0.6 gm/l/day and a hydraulic detention time of approximately 15 days. This resulted in about 70% of the nitrate-N accounted for in the off-gas. Also, the effluent pH was practically neutral. Under these conditions the N and methane in the off-gas accounted for approximately 90% of the 9.6 gm/l of the COD in the feed to the unit and was initially in agreement with the removals calculated based on effluent analysis.

The feed rate to the unit was increased gradually in an attempt to develop conditions in the anaerobic filter where methanogenesis would be overwhelmed by the increased load of nitrates. However, only a small decrease in methanogenesis was observed under these high nitrate loadings. The COD load was increased to about 8 gm/l/day (approximately 500 lb/1000 cu ft/day). More than 95% of the nitrogen in the feed was accountable as N_2 gas in the off-gas, and the effluent is completely denitrified in the system. The denitrification reaction under these conditions proceeds entirely to N_2 gas; the COD removal is greater than 95% based on the analysis of the off-gas in terms of methane and nitrogen. A substantial fraction of the substrate COD is converted to biomass which is lost from the system. The various denitrification reactions induced by changing the feed composition and organic loading are represented by the bar diagrams in Figure 11.

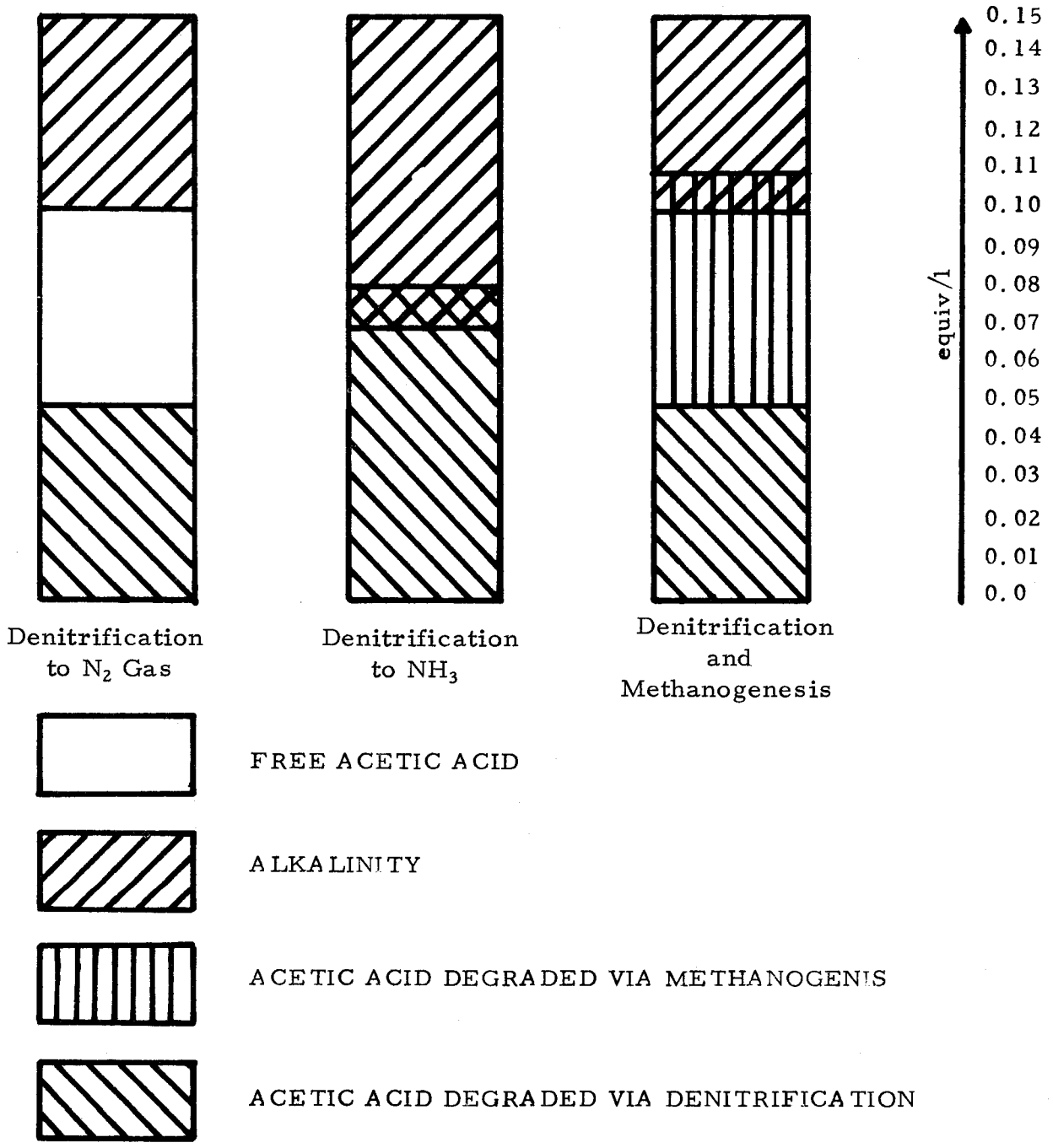


Figure 11. Acid-base relationships in the synthetic substrate used for denitrification studies.

SECTION 6

CAPABILITIES OF PROPOSED TREATMENT SEQUENCE

The two biological treatment sequences which were evaluated are illustrated schematically in Figures 12 and 13. Scheme I involves denitrification and a concurrent heavy metal removal process. The denitrified effluent plus other composites were then treated by the activated sludge process. Scheme II also involved denitrification to remove nitrates and the denitrified effluent was mixed with the aerobic composite and the heavy metal composite which was not pretreated for metal removal. These three streams were fed to an anaerobic process for the removal of most of the BOD and all of the residual heavy metals. The effluent of the anaerobic system was fed to an activated sludge unit in order to provide final polishing and removal of residual organics.

A. CHARACTERISTICS OF THE COMPOSITES

1. Denitrification Composite

The characteristics of the grab samples used for the startup of the packed bed anaerobic denitrification unit and of the composites used during the demonstration run showed the variation expected by this sampling procedure.

Several analytical discrepancies and limitations were evident from analysis of the data. The nitrate N reported by the Technical Center differed appreciably from those reported by the Bay City plant laboratory. A comparison of these data with the "kinetic" nitrate N removal as N_2 indicates that the data reported by the CCCTC more closely approximated the actual concentration, but in most cases the nitrate concentration reported is still too low. The total nitrogen concentration determined by microcoulometry performed at the Tech Center most nearly approximated the actual data observed in the units more closely. The nitrate N data reported by the Technical Center were much lower than those reported by the Bay City laboratory. The data reflect the destruction of nitrite under acidic conditions in these effluents by the several days of sample storage between analysis of the Bay City laboratory and the Technical Center. The average nitrate N calculated from the Technical Center data observed for the

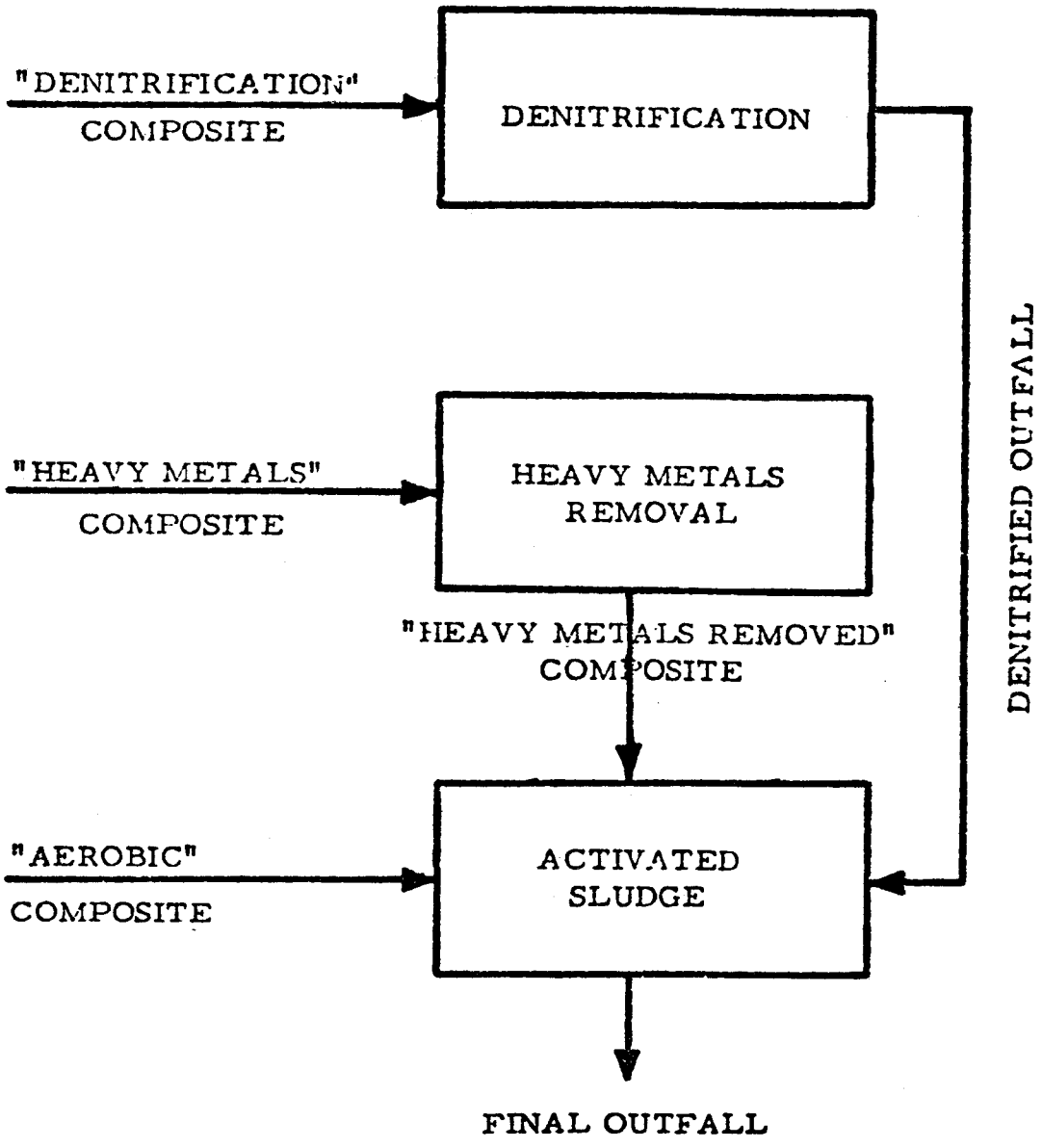


Figure 12. Treatment sequence of Bay City plant effluents.

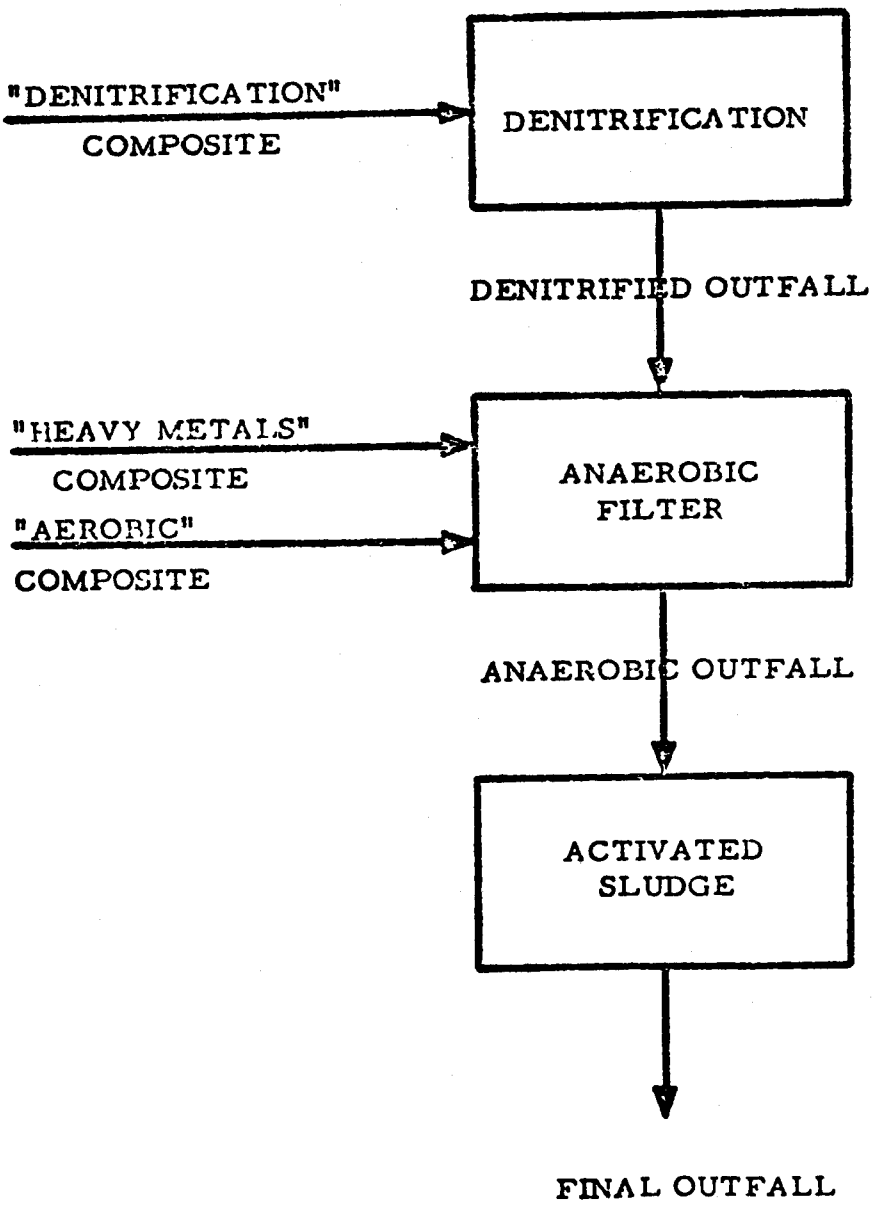


Figure 13. Alternative treatment sequence of Bay City plant effluents.

denitrification composites was 1.334 ± 0.625 g/l which corresponds to 3.811 ± 1.786 g/l of oxygen equivalent or COD of the sample.

Analyses of the data also indicate that the instrumental (Aquarator) COD results were markedly affected by the nitrate concentration in the sample. Attempts were made to correct the observed COD values by incorporating a "nitrate factor". However, it was not possible to develop any correlation of the effects of the nitrates on the instrumental COD by analyzing samples containing known concentrations of COD and nitrates. Therefore, analyses of these nitrate-rich samples must be performed by the classical reflux technique. In the few cases when the reflux COD data were available from both the Technical Center and the Bay City laboratory, the agreement was quite good as was that of the TOC's.

The TOC concentration of the denitrification composite was 3.179 ± 2.994 g/l which indicates a very strong organic waste. These composite samples were also quite acidic and contained a relatively high but fairly constant concentration of copper (about 45 mg/l).

The variability in the organic and nitrate N concentration in these composites at times resulted in insufficient organic material for the reduction of the nitrates. Therefore, the feed to the unit was supplemented with additional "organics" COD from the aerobic composite.

2. Heavy Metal Composite

The characteristics of these two composites should be essentially identical with the exception that the heavy metals have been removed from one of the composites. The COD concentration of these composites is relatively high and extremely variable with an average of 11.126 ± 9.282 g/l of COD for the heavy metal composites and 9.280 ± 6.905 g/l of COD for the composite with heavy metals removed. The ratios of the COD to TOC were 3.069 ± 0.638 and 3.759 ± 0.662, respectively, for the heavy metal sample and the composite with the heavy metals removed. These ratios indicate a relatively low oxidation level for the organic matter in the two composites.

3. Aerobic Composite

A complete analysis of all the aerobic composites was made to represent all the streams at the Bay City plant which are free of nitrates, heavy metals and chloraldehydes. The COD content of these samples is approximately twice the COD of the heavy metals composites; however, the variability is less than these samples. The average COD concentration

is 21.235 ± 7.958 g/l. The ratio of the COD to TOC is 3.379 ± 0.511 which indicates a more oxidized substrate at oxidation state approximating that of acetaldehyde. Sodium content in the aerobic composites also is relatively high and relatively constant. The average sodium concentration is 4.022 ± 1.435 g/l.

B. TREATMENT PERFORMANCE

1. Denitrification

The anaerobic denitrification was carried out in two different modes; namely, a packed column with recirculation and a fluidized bed biological reactor with recirculation of the reactor contents. The denitrification process in both systems resulted in effluent nitrate N concentrations of less than 10 mg/l. Consistently low nitrate concentration in the effluent is somewhat remarkable in view of the fact that denitrification composites were not balanced in composition of COD to nitrate N required for the denitrification reaction to go from nitrates to N_2 gas. In general, the COD at 5-10 g/l exceeded the oxygen available from the nitrate N at concentration of 1 - 2 g/l. In two cases, the oxidative power of the nitrate exceeded the COD and required the addition of a calculated amount of the heavy metal composite to the feed.

a. Packed Bed Unit

The conventional anaerobic denitrification filter was operated at a hydraulic detention time of about 1.2 days with a corresponding loading of approximately 300 lb of COD (nitrate O)/100 cu ft/day for a feed nitrate N concentration of 2 g/l. The operating data observed for the packed bed anaerobic filter are presented in Figure E-1 through E-2 in the Appendix.

Relatively poor nitrate analyses coupled with poor instrumental results of the COD analyses caused by the presence of high nitrate concentration samples resulted in difficulty in controlling the ratio of COD to nitrates N entering the denitrification unit. These difficulties were particularly significant at the beginning of the demonstration run when the nitrate O exceeded the COD in the denitrification composite resulting in the appearance of significant amounts of N_2O in the off-gas.

When the ratio of COD to nitrate O in the effluent to the denitrification unit was approximately balanced (COD only slightly greater than nitrate O) the off-gas contained primarily nitrogen with very small concentrations, less than 0.5% by volume, of methane. Under these conditions, the high nitrate concentration inhibits methanogenesis. The effluent of the reactor also contains very little ammonia nitrogen as indicated by the relatively low

concentration of total nitrogen as measured by the microcoulometric technique. However, when the feed contains a much greater concentration of COD to nitrate O, for example, greater than 1 g/l of COD over and above the nitrate concentration, significant amounts (approximately 5 to 15% by volume) of methane are found in the off-gas. The effluent also contains between 100 and 200 mg/l of ammonia nitrogen. These data indicate that a significant concentration of methanogenic organisms are able to survive in the packing of the reactors in spite of the presence of inhibitory nitrate concentrations. During these time periods, significant amounts of methane were found in the off-gas, although the major constituent of the off-gas was nitrogen.

The amount of ammonia nitrogen in the effluent during these same time periods also is significant indicating that reduction of some of the nitrate O to ammonia also takes place as well as the conventional pathway of converting the nitrate N to N_2 gas. At the end of the run, the packed bed was dismantled and a considerable accumulation of biomass was observed in the packing. However, this biomass was in a relatively loose form which should not lead to channeling and was relatively easily removed from the packing.

b. Fluidized Bed Reactor

The circulated fluidized bed unit was evaluated in view of the success with denitrification observed in the packed bed system because of the obvious freedom from channeling and easy removal of the excess biomass in the fluidized bed system. The data observed during this demonstration run are presented in Table G-1 through G-5 in Appendix G.

The fluidized bed denitrification unit was run for only a relatively short period of time and the data are somewhat erratic; however, the potential capability of the fluidized bed denitrification unit are clearly indicated by the data. In fact, during the course of the demonstration run, the entire contents of the unit was lost and the system was restarted with relatively few difficulties. The loading to the fluidized bed unit was approximately 1.5 lb of COD (or nitrate O) per cu ft per day without evidence of overloading. The hydraulic detention time with these loading conditions is less than 0.2 days. The only significant difference observed in the fluidized bed system compared to the packed bed system was the absence of methanogenic acitivity in the fluidized system when the feed COD concentration exceeded the available nitrate O.

The off-gas in the fluidized system never contained more than 0.1% by volume of methane, even under the same feed conditions that resulted in a generation of about 10% by volume of methane in the off-gas of the

packed bed unit. The lack of any significant methanogenic activity in the fluidized bed system may be attributed to the more violent hydraulics of the system which tends to wash out the slower growing and more loosely attached methane organisms while the denitrifying organisms adhered to the fluidized media.

At the end of the denitrification run with the fluidized bed reactor, a portion of the fluidized bed material (liquor plus biomass coated activated carbon) was removed and analyzed. The volatile suspended solids concentration was relatively high and account for the capability of the system in the fluidized bed reactor to handle high loadings. The data also indicate that the copper which was trapped in the system as insoluble copper sulfide was uniformly distributed between the biomass and the activated carbon.

The major problem in the control of the denitrification system was a need for relatively slow reflux COD analysis since the nitrates interfere with the much more rapid instrumental analysis of COD.

2. Methanogenesis

Performance of the anaerobic system was very poor for reasons which are not very clear. In view of the poor performance, the system was shut down after a relatively short period of operation. However, an anaerobic filter which had been treating effluents from another plant with COD removal of greater than 90% became available, and the Bay City plant composite consisting of the aerobic feed, denitrified effluent, and heavy metals composites were fed to the unit. The COD removals were only in the order of 30 to 40% which was insufficient to justify an anaerobic treatment system, and this procedure was discontinued for the final study.

3. Aerobic Treatment

a. Activated Sludge Treatment

The activated sludge treatment of the aerobic composites from Bay City plant was started much sooner than this final demonstration run. The operating data are presented in Appendix D. In the early parts of the activated sludge treatment studies, the feed to the units was aerobic grab samples. During the later stages, the unit began receiving the demonstration run composites made up of the denitrified effluent, the aerobic composite, and the heavy metals removed composite. The components were blended each week in a ratio which corresponded to the rate of generation of these wast streams at Bay City. Mechanical operation of the bench scale activated sludge system posed no problems; however the effluent COD concentration was greater than 1000 mg/l. The addition of an extended

aeration system following the activated sludge system did not result in any marked reduction in the effluent COD. The cause of the high COD was attributed to either (a) presence of major non-biodegradable components in the feed to the system which passed through the aerobic biological treatment into the effluent, or (b) the generation in the bioreactor of refractory secondary metabolites.

The first alternative was evaluated by measuring the biodegradability of all the major contributors of COD in the Bay City effluent. The results of this study indicate that all of the major components are readily biodegradable.

The second alternative was evaluated by starting a second activated sludge unit in another area of the laboratory, in order to develop new sludge flora. The results were inconclusive because the second unit initially produced an effluent COD concentration which was relatively low but the effluent COD increased to more than 1000 mg/l while the first unit improved and the effluent COD began to decrease. However, the overall performance of the activated sludge system throughout the demonstration was relatively uniform. COD removals were as follows: March -- 83.40 ± 1.45%; April -- 81.62 ± 2.51%; May -- 86.47 ± 1.60%; June -- 87.63 ± 2.96%. The effluent BOD analyses were performed by an independent laboratory, and the BOD concentrations ranged between 24 and 50 mg/l during this time period.

Nitrification did not occur to any substantial extent, and the effluent nitrate N concentration was less than 10 mg/l during most of the time period. The outfall color and suspended solids, however, were relatively high. Variations in the mixed liquor volatile suspended solids concentration (MLVSS) over a wide range of about 2000 up to 9000 mg/l did not markedly affect the quality of the effluent.

A portion of the effluent of the activated sludge unit was processed by distillation to concentrate and segregate the organic constituents in order to simplify identification. Distillation was performed in a stainless steel packed column. Three volatile fractions and the residue were collected , and each sample was analyzed for COD and carbon. The analyses presented in Table 8 indicate that approximately 31% of the COD in the raw sample contained volatile components, while 43% of the COD was non-volatile. The remaining 26% was unaccounted for and was assumed to be entrapped in the distillation apparatus. Therefore, the volatile fraction would contain 57% of the original COD. Organic carbon accountability was poor; however, some useful information can be extracted. The major portion of the organic carbon was in the residue. The ratio of the COD to TOC ratio was 11.81 which is relatively high and indicated that the volatile COD is primarily made up of non-carbon components such as amino nitrogen containing compounds. Additional distillation was performed on the first

TABLE 8. FRACTIONAL DISTILLATION OF FINAL BAY CITY PLANT EFFLUENT

Sample	NH_3-N (mg)	Total Carbon (mg)	Inorganic Carbon (mg)	Organic Carbon (mg)	COD * (mg)
Raw Sample	450	1874	1436	438	1450
Fraction-1	281	306	273	36	425
Fraction-2		45	34	11	13
Fraction-3		20	14	6	13
Residue-1		1138	600	538	625
Total (2-5)		1509	921	591	1076
% Accountable		81%	64%	135%	74%

* COD Analyzed in the Aquarator.

fraction in order to determine the nature of the volatile COD. The fraction was acidified with phosphoric acid to prevent distillation of any amines. These data are presented in Table 9. The fractions collected (1-A) would contain any volatile acids or neutral compounds. The COD in this fraction was 29 mg. The residue remaining was made alkaline with sodium hydroxide and redistilled. Under these conditions the amines would be distilled over. The distillate (1-B) was collected in dilute hydrochloric acid to prevent loss of volatile amines. The COD of this final fraction was 22% of the raw sample; however, the TOC was only 8 mg. The inorganic carbon remained in distillation flash as insoluble carbonates. The data do not provide any conclusive data to substantiate the proposition of the accumulation of secondary metabolites in the aerobic reactors.

b. Extended Aeration of Effluent from Activated Sludge Treatment

In view of the high residual COD and turbidity in the effluent of the activated sludge system, extended aeration lagoon was added to the system to provide eight day retention. The mechanical operation of this unit was satisfactory and the clarity of the lagoon outflow was distinctly improved; however, the yellow color remained unchanged and the effluent COD was only marginally improved. The amino nitrogen compounds interfere with the instrumental analysis (Aquarator) of COD and result in COD values which are higher than those observed using the classical COD reflux method. This phenomenon may explain the reason for higher instrumental COD values presented in Table 10 which includes analysis of the Bay City plant extended aeration effluent.

This final series of laboratory demonstration runs was an effort to combine the most probable sequence of biological treatment that had been attempted during the entire study. Segregation of the various types of compatible feed to biological systems after pretreatment to remove known toxic compounds or excessive carbon loading provided considerable improvement in final effluent. However, even after the extended aeration, this system did not obtain satisfactory outfall except for a single value of 7 mg/l BOD_5. The other parameters of color, TOC and COD are excessive for discharge to surface water.

These results shown in Table 10 are the best results obtained under ideal operating periods. The final outfall from the Bay City plant to the Colorado River must meet a maximum concentration of 90 mg/l TSS, 25 mg/l as BOD and 50 mg/l as TOC.

TABLE 9. DISTILLATION OF FRACTION-1

	Total Organic (mg)	Inorganic Carbon (mg)	Organic Carbon (mg)	NH_3-N (mg)	COD** (mg)
Fraction-1	306	273	36	281	425
Fraction-1-A (H_3PO_4)	35	23	12	-	29
Fraction-1-B (NaOH)	8	< 1	8	187	320
Total (2-3)	43	< 24	20	187	349
% Accountable *	14%	9%	56%	67%	82%

* Loss in carbon accountability primarily due to formation of carbonates after caustic addition.

** COD Analyzed with an Aquarator.

TABLE 10. ANALYSIS OF BAY CITY PLANT EXTENDED AERATED EFFLUENT

(Values as mg/l.)

Sample Number*	T.C.	T.I.C.	T.O.C.	Inst. COD**	4 Hr COD***	BOD_5	BOD_{20}
1	1874	1436	438	1450	-	-	-
2	1639	1384	255	1320	851	7	30
3	1387	1233	154	625	609	-	-

* CCCTC Code Numbers are as follows:

1 - 22882-4

2 - 22905-23-11, 12, 13, and 14 22918 11-15 and 16

3 - 22918-48 23, 26, 28, 30, 2

** Inst. COD = Aquarator COD

*** 4 hr. COD = 4 hr. reflux dichromate method.

APPENDIX A

STREAM SEGREGATION

Aerobic biodegradability of the individual compounds was evaluated and these data are presented in Table A-1. The results of tests using Petri cultures treated with each of the wastewater components and published information were used to select the individual wastewater streams to be included in the final feed blend for each of the three unit treatment processes. The biodegradability of individual streams under anaerobic and aerobic conditions also was evaluated. These data are presented in Table A-2 for fifteen of the individual wastewater streams which are included in the combined process wastewater stream. Anaerobic pretreatment of a wastewater stream would not always promote improved efficiency of wastewater stabilization. All of the streams with the exception of stream number 15 which contains aldehydes and alcohol were anaerobically biodegradable. However, a number of the streams which contain amines, ammonia, organic acids, some chlorinated organic compounds, phosphoric acid, aldol products, aldehydes and alcohols and one caustic stream were not aerobically biodegradable in spite of the anaerobic pretreatment.

The form of nitrogen and relative nitrogen requirements for the anaerobic and aerobic processes also were briefly investigated. Data presented in Table A-3 indicate that the mixed culture in the anaerobic reactors favored nitrate nitrogen while ammonia or amines was preferred in the activated sludge process.

The combined process wastewater can be classified in the three basic categories; namely, (a) streams containing high organic carbon, (b) streams containing high nitrogen concentrations, and (c) a third component which generally originates from sumps throughout the plant which contained high concentrations of heavy metals.

The elimination of one low volume wastewater stream which contained about half of the total organic carbon in the combined process wastewater markedly improved the degradability of the composite wastewater stream in the anaerobic/aerobic system. The composition of the modified process wastewater blend is presented in Table A-4.

TABLE A-1. RELATIVE AEROBIC BIODEGRADATION RATES FOR SPECIFIC COMPOUNDS IN THE PROCESS WASTEWATER

Compounds	ppm-TOC Removal/Day
Acetaldehyde	745
Crotonaldehyde	305
Cyclohexanone	25
Acetic Acid	92
Propionic Acid	180
Butyric Acid	49
Adipic Acid	27*
Methanol	250
n-Butanol	280
Cyclohexanol	152
2-Ethylhexanol	76
Vinyl Acetate	168
Hexamethylenediamine	276
1,6-Hexanediol	235
Nylon Salt	273

*Aerobic studies with adipic acid indicated that the adipic molecule was consumed entirely as opposed to partial degradation.

TABLE A-2. STREAM BIODEGRADABILITY TESTS

Stream No.	Major Component	Aerobic Biodegradable	Anaerobic Biodegradable
1	Kerosene	yes	yes
2	Amines	no	yes
3	Nitric, organic acids	yes	yes
4	Caustic	no	yes
5	Phosphoric acid, aldol products	no	yes
6	Amines	yes	yes
7	Organic acids	no	yes
8	Alcohol	yes	yes
9	Chlorinated organics	yes	yes
10	Chlorinated organics	no	yes
11	Chlorinated organics	yes	yes
12	Organic acids, aldol products	yes	yes
13	Esters	yes	yes
14	Amines, ammonia	no	yes
15	Aldehydes, alcohols	no	no

TABLE A-3. SOLUBLE NITROGEN REQUIREMENTS FOR WASTE TREATMENT

Form of Nitrogen	Anaerobic Filter mg/l Nitrogen Utilized/ mg/l BOD Removed	Activated Sludge mg/l Nitrogen Utilized/ mg/l BOD Removed
Ammonia-Nitrogen NH_3-N	0.11	0.07
Nitrite-Nitrogen NO_2-N	< 0.01	< 0.01
Nitrate-Nitrogen NO_3-N	2.10	< 0.01

TABLE A-4. COMPOSITION OF COMBINED PROCESS WASTEWATER AT BAY CITY PLANT AFTER ELIMINATION OF LOW VOLUME HIGH CARBON STREAM

	Concentration mg/l
Total Organic Carbon	5,000
Biochemical Oxygen Demand	4,500
Chemical Oxygen Demand	21,000
Nitrate-Nitrogen	780
Nitrite Nitrogen	27
Ammonia-Nitrogen	770
Phosphate-Phosphorus	130
Chloroaldehydes	2,085
Inorganic Chlorides	35-400
Sodium	20
Copper	2-100
Iron	0.06
Chromium	0.02
Manganese	<0.2
Palladium	<0.2
Nickel	<0.4
Cobalt	<0.02
pH	1.5-3.1 (a)
Color, APHA	7,500-10,000 (b)

(a) pH units

(b) color units

The results of the batch anaerobic/aerobic treatability test based on the removal of soluble TOC indicate that all of the individual process wastewater streams containing organics with one exception can be treated anaerobically. One stream also was anaerobically treatable following neutralization. Approximately 75% (volume) of the high strength wastewater streams was treatable aerobically and with neutralization this volume was increased to 80%. Anaerobic pretreatment increased the aerobic treatability of four of the individual wastewater streams, but anaerobic pretreatment reduced the aerobic treatability of three other wastewater streams.

The performance of the three stage anaerobic/aerobic biological treatment system is markedly affected by variations in the composition and flow of wastewaters to the system. Therefore, the variability in the carbon concentration and the concentration of specific components of 62 streams were evaluated. These data were analyzed in an attempt to develop the best technical treatment or disposal scheme for each individual wastewater stream. Streams were classified according to the process which would best reduce the pollution potential; namely, (a) incineration, (b) conventional biological treatment; (c) physical/chemical pretreatment; (d) specialized high strength biological treatment; and (e) reuse within the plant. Categorization of the wastewater streams was based on the following criteria: (a) carbon concentration; (b) presence of components potentially toxic to biodegradation; (c) for potential reclaiming product; and (d) the variability coefficient of the components in the wastewater stream.

Wastewater streams containing a soluble carbon concentration with a variability coefficient of more than 50% were considered to require additional process control prior to being acceptable as feed to a biological treatment. Toxic streams would either be detoxified, incinerated or pretreated with the physical/chemical process. Results of this analysis indicated that nine or ten of the streams considered as feed to the high strength biological treatment process have carbon variabilities in excess of 50% of the mean carbon concentration for the individual wastewater stream. High variability in the carbon concentration coupled with varied flow rates indicated that the control of the quality of the biological feed blend was almost impossible. The greatest degree of variability in the concentration of the components as well as flow was observed in those streams generated from batch operations or cyclic work schedules. The wastewater from tank car washings, maintenance repair areas, and chemical sumps exhibited the most variability in carbon concentration, component concentration, and flow volume.

APPENDIX B

WASTE REDUCTION

1. CHLORINATED ORGANICS

The toxicity to biological systems of these compounds at concentrations normally found in the process wastewater indicates that this type of waste must be handled by some physical/chemical system. Incineration is considered as the best alternative. Process modifications to minimize water utilization result in increasing the carbon concentration in the wastewater stream to approximately 10% by weight prior to incineration. The possibility of by-product recovery of HCl adds incentive for employing incineration.

2. HIGH CARBON CONCENTRATION WASTEWATER

Most of the process wastewater streams can be classified into two categories based on TOC. Most wastewater streams with a TOC concentration in excess of 60,000 mg/l will be considered for incineration while those wastewater streams with a TOC concentration less than 60,000 mg/l will be treated biologically. It is anticipated that the recovery of heat will reduce the minimum supplemental fuel required to maintain the temperatures necessary for complete combustion. However, most of the plant wastes which have high carbon concentrations typically contain large amounts of ash or nitrogen containing compounds. In-process modification can reduce sources of ash; however, a NOx abatement system will be required to remove the nitrogenous combustion products.

3. VOLATILE LIGHT ENDS

Water phases from decanters contain soluble volatile organics and insoluble oil resulting from incomplete phase separation. The results of laboratory studies indicate that the installation of strippers can alleviate this problem. The strippers provide additional product recovery, are effective in smoothing carbon variations, and can be effective in reducing the carbon load of wastewater streams although partially offset by energy required. Wastewater streams containing small amounts of vinyl acetate, cyclohexane, cyclohexanol and cyclohexanone are suitable for stripping.

4. HEAVY METALS

The main sources of heavy metals in the process wastewater are the process unit sumps. This problem is common to all plant operating areas. Therefore, all continuous discharges to unit sumps will be eliminated by transporting these discharges directly to the ultimate destination. Some type of centralized physical/chemical treatment scheme will be necessary to handle intermittent sump discharges. The exact physical/chemical treatment scheme has not been developed, but will more than likely include one or more of the following processes: pH adjustment, sulfide addition, coagulation, sedimentation, filtration, and ion exchange. Discharge from the physical/chemical treatment will be amenable to biological treatment. Heavy metal residuals will be suitable for disposal in a registered sanitary landfill.

5. AMINES

Amines are typically toxic and/or inhibitory to biological systems and may be present at high enough concentrations to exceed the nutrient requirement of the biological system resulting in unacceptable concentrations of nitrogen in the final treated effluent. Incineration is currently considered as a means of handling the amine containing streams with the possible exception of sump discharges. NOx abatement systems to treat the combustion products will be necessary.

6. NITRATES

Nitrates are one of the most common constituents in the wastewater from the adipic acid unit; however, spills or leaks in other plant units are also a source of nitrates. The concentration of nitrates usually is in excess of nutrient demand of biological systems; therefore, anaerobic denitrification of the nitrate containing streams offers a possible solution. The waste reduction and stream segregation programs led to three categories of process wastewaters, and the evaluation of these streams by a series of anaerobic denitrification, anaerobic methanogenic and aerobic activated sludge processes.

APPENDIX C

DESCRIPTION OF BENCH SCALE REACTORS

1. AEROBIC BIOLOGICAL TREATMENT (OXYGEN)

The two-stage oxygenated activated sludge system consisted of duplicate aeration tanks and clarifiers operated in series. The first stage of the two-stage system is illustrated in Figure C-1. The combined process wastewater blend with nutrients added at a ratio of COD:N:P equal 100:5:1 was stored in a 20-liter reservoir constructed of a six-inch diameter, four-ft section of Pyrex glass pipe flanged at the bottom and calibrated to facilitate accurate measurement of the wastewater feed to the aeration unit. A peristaltic pump (Cole-Parmer Masterflex) fed the wastewater from the reservoir to the aeration tank. The wastewater feed was intermittent and controlled by timer (Tork Timer 60-minute repeater timer). A burette was located immediately upstream of the pump and provided a means of quickly estimating pumping rate at any pump speed by feeding from burette over a controlled time period.

The aeration tank was constructed of a Plexiglas tube which was 8-inch in diameter and 4-ft long with 1/8" wall thickness. The Plexiglas tube was held between upper and bottom machined stainless steel plates. Oxygen was introduced near the bottom of the aeration tank through three fritted glass spargers which were connected by means of Swagelok fittings to a 1/4" diameter stainless steel tubing manifold. The oxygen was presaturated with moisture in a wash bottle and the flow measured by means of a rotameter. A pressure gauge was installed in the oxygen line to measure increases in the pressure drops across spargers as biomass accumulated on the spargers. Agitation was provided by three shipscrew shaped impellers mounted on a vertical shaft extending the full length of the aeration tank axis. These impellers were driven by a Fisher Dyna-Mix variable speed stirrer. An opening in the top plate provided access for sampling of the biomass and offgas for introduction of the dissolved oxygen probe and for the returned sludge line.

Mixed liquor from the aeration tank overflowed through a tube to a clarifier which also was constructed of 4-inch Plexiglas tubing and fitted with a conical bottom. The overflow tube was so located that the volume

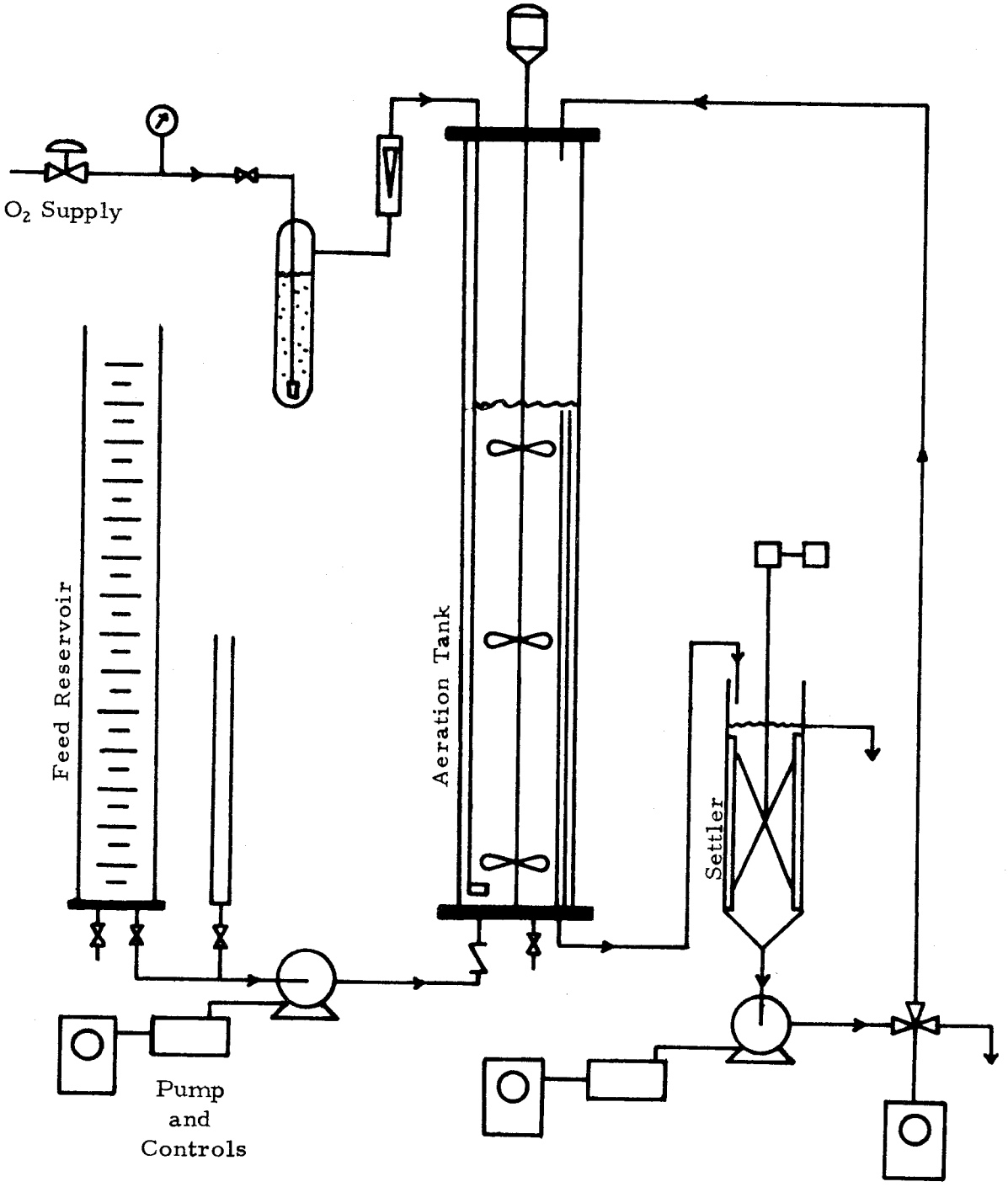


Figure C-1. First stage of two-stage bench-scale oxygen-aerated activated sludge unit.

of the mixed liquor in the aeration tank was 15 liters. Sludge which collected at the bottom of the clarifier was recirculated to the aeration tank by means of a peristaltic pump operated by a timer. A three-way solenoid valve activated by a timer was installed in the sludge return line. This device permitted for wasting of the sludge, but during operation the valve tended to plug and become inoperative. Therefore, sludge wasting was done manually. A device consisting of three windshield wiper blades mounted on a slowly revolving shaft (4 rph) also was installed in the clarifier to prevent bridging of the sludge in the clarifier. Clarified effluent from the first stage was pumped into the second stage or discharged to waste from the second stage.

This unit was started with a domestic activated sludge which was initially fed a wastewater consisting of easily degradable organics; namely, two grams per liter each of malt extract, lactose, dextrose, peptone, and yeast extract. The combined process wastewater from the Bay City plant was added to this initial feed material in increasing amounts until feed consisted of 100% of the process wastewater. This unit also was operated with a number of other individual process wastewater components.

The aerated activated sludge systems operated at the Bay City plant and the CCCTC consisted of a reactor similar to the unit illustrated in Figure C-2. A peristaltic pump was used to transfer the process wastewater blend with nutrients added to the aeration chamber. Air was introduced to the aeration chamber through a diffuser stone located at the bottom of the unit. The flow of air was controlled by a needle valve. An adjustable baffle separated the aeration chamber from the clarification section. The volume of the mixed liquor in the aeration chamber was approximately seven liters and the volume of the clarification zone was three liters. The clarified effluent was discharged through an adjustable overflow tube.

2. ANAEROBIC METHANOGENIC TREATMENT

The initial attempts at evaluating the anaerobic treatability of the combined process wastewater were performed at Bay City in an anaerobic mixed liquor contact system. A 12-liter round bottom flask was the reactor. The flask was fitted with a heating mantle and an agitator. Provisions were made for measuring offgas, withdrawal of effluent and addition of fresh feed. The unit was operated in a batchwise fashion with daily withdrawal of mixed liquor and daily addition of combined process wastewater blend. Neutralization of the feed was required to maintain a pH in the range of pH = 6.7 to pH = 7.3 necessary for methanogenesis. The cost of neutralization resulted in the abandoning of the anaerobic mixed liquor contact system.

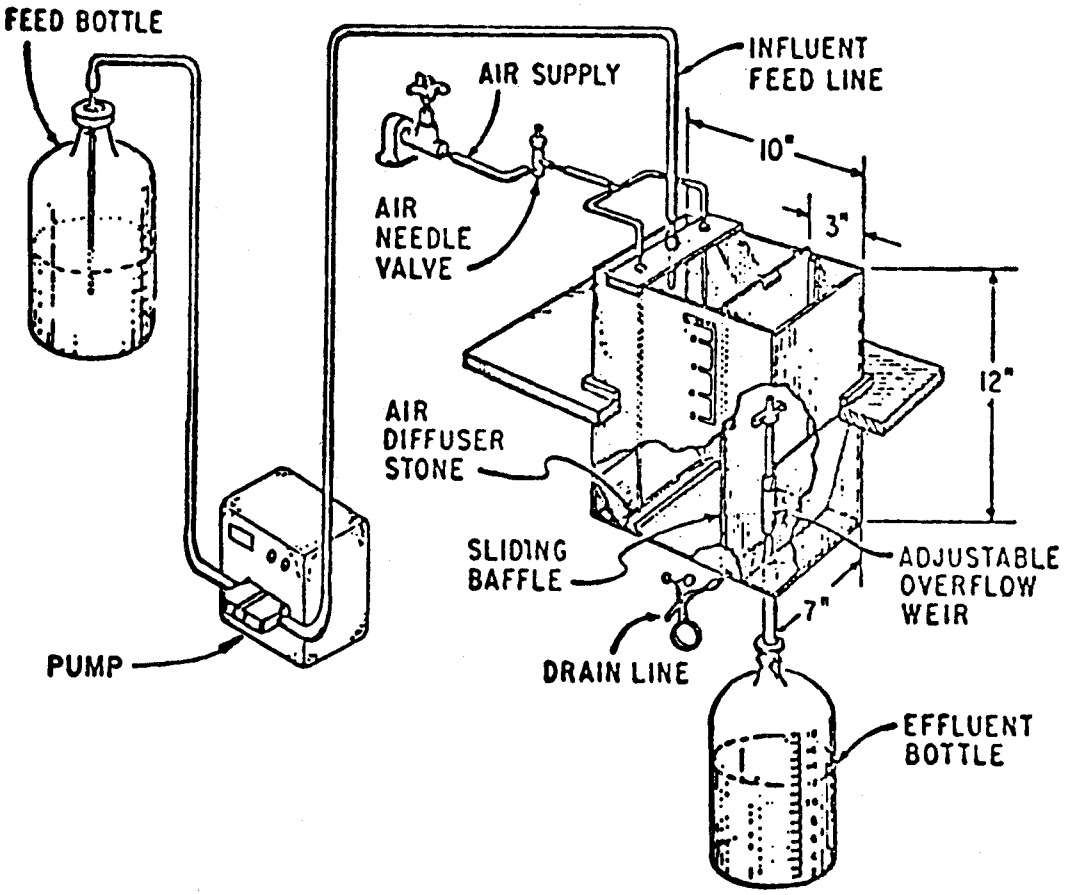


Figure C-2. Continuous Simulation Reactors.

Additional anaerobic studies were continued at CCCTC using an anaerobic packed bed. A schematic diagram of the initial design of the anaerobic filter is illustrated in Figure C-3. The reactor consisted of a 4-ft long section of 6-inch diameter Pyrex industrial glass pipe flanged at both ends. The pipe was filled with procelain Berl saddles as packing material. The pipe was wrapped with heating tape and the temperature controlled by a powerstat. Temperature in the anaerobic filter was monitored with a thermocouple. A gas separation bulb was located at the top of the filter and permitted separation of gas from the effluent. The gas passed through a gas sampling ampoule and the volume of gas produced was recorded on a wet test meter. The effluent passed through a flow splitter which diverted a portion of the effluent to a surge vessel which consisted of a 12-liter round bottom flask. The purpose of the surge vessel was to provide some neutralization of the process wastewater feed. The logic behind this concept involved the fact that under steady state conditions the organic material in the process wastewater would be converted to methane and carbon dioxide. Therefore, the liquor in the filter would consist of a solution of bicarbonates which are capable of neutralizing the incoming acid. The surge vessel also contained a supply of solids from an anaerobic digester which slowly wash into the filter. Combined process wastewater blend with some caustic added was pumped into the surge vessel. This mixture of process wastewater, caustic, recycled filtered effluent, and digested solids was pumped through the reactor. During startup operations, the anaerobic filter was seeded with digested sludge from the municipal wastewater treatment plant and fed a synthetic substrate consisting primarily of sugars and methanol as indicated in Table C-1. The system was considered acclimated when several liters of gas were produced per liter of feed and the methane to carbon dioxide CH_4:CO_2 was approximately 3:1. At this point the combined process wastewater blend from the Bay City plant was introduced in increasing amounts. The gas production dropped off drastically when the combined process wastewater blend reached about 30% by volume of the total feed.

The inability of aerobic or anaerobic processes to satisfactorily treat the combined process wastewater blend resulted in the segregation of the combined process wastewater stream into three composites; namely, a) composite A which included the nitrate containing streams but was free of amines and organic chlorides; b) composite B containing streams which were free from nitrates, organic chlorides, and amines; and c) composite C which included streams which contained ammonia, amines, and organic chlorides. Composite B was considered to be amenable to anaerobic methanogenesis without pretreatment. Composite A also was considered to be suitable for anaerobic treatment but only after pretreatment by anaerobic denitrification. The last composite blend, composite C, can be treated by aerobic activated sludge. These components were made into a

TABLE C-1. SYNTHETIC STARTER FEED FOR ANAEROBIC FILTERS

Solution A:	200 g MeOH in 22 liters tap water	
Solution B:	malt extract	5 g
	yeast extract	5 g
	peptone	5 g
	urea	9.5 g
	H_3PO_4 (85%)	4.8 g
	Na acetate, anhydrous	33.8 g
	$MgSO_4 \cdot 7\ H_2O$	1.7 g

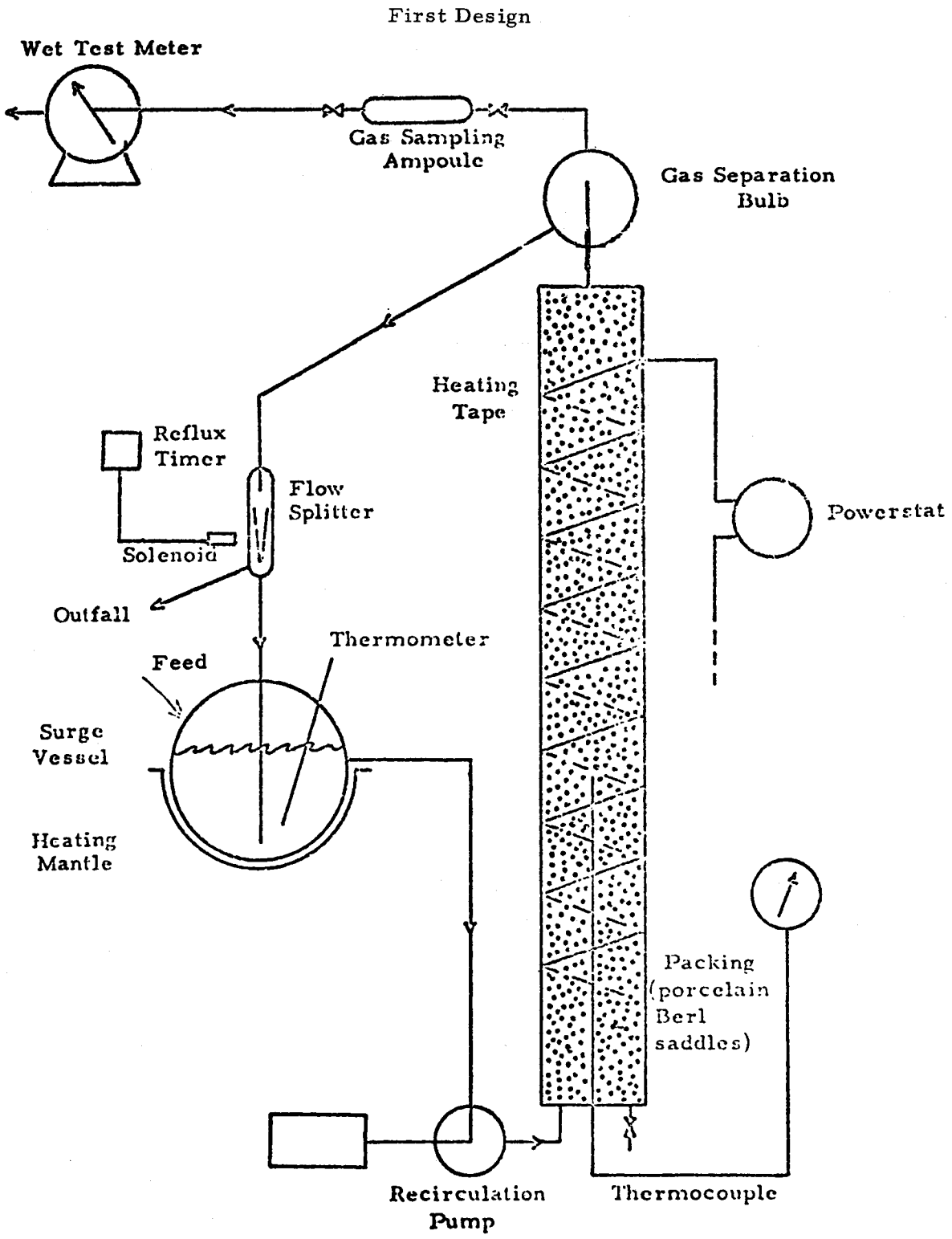


Figure C-3. Anaerobic packed bed.

volume of 165 ml with water and mixed with solution A at the rate of 7.5 ml per liter. Preparation of a concentrated solution B gives it shelf life and largely prevents the spontaneous fermentation of the starter.

A much less complex starter solution was evolved using methanol and acetic acids as the only organics, and with COD:N:P = 1000:5:1. The nutrients were supplied as urea for N, phosphoric acid for P and used sodium sulfate for the sulfur required to form insoluble sulfide.

The segregation program led to reevaluation of the capability of anaerobic and aerobic processes for treating individual components. A revised backmixed anaerobic filter was constructed and is described schematically in Figure C-4. This concept of backmixed anaerobic filter had been designed and operated successfully using wastewater from a Celanese Chemical Company plant in Pampa, Texas. The filter proper consisted of a 4-ft section of 6" diameter Pyrex industrial glass pipe flanged at both ends. The gross volume of the pipe was 20 liters but the void volume was reduced to 15 liters after filling the pipe with 1-inch ceramic Raschig rings. The detention time and volumetric loadings were calculated on the basis of this void volume although in the course of a run the accumulation of biomass in the filter reduced the void volume. Heating tapes connected to a powerstat were used to heat the filter. The entire pipe covered with glass wool pipe insulation to reduce heat losses as well as to exclude light which would lead to the appearance of photosynthetic organisms, and the oxygen produced would be inhibitory to the anaerobic organisms. Temperature in the filter was measured by a single thermocouple which was considered sufficient since the system was backmixed.

The combined process wastewater effluent with nutrients and reserve alkalinity added was stored in a 20-liter plastic feed tank. A peristaltic pump actuated by a timer pumped the feed blend into the recirculation loop. The fluid in this loop was pumped continuously into the bottom of the filter by a recirculation pump at a rate of about 150 liters per day which corresponds to approximately 10 void volumes per day. A check valve was installed on the recirculation loop immediately before the fluid entered the filter in order to prevent loss of mixed liquor from the filter in the event of a leak in the recirculation loop. The filter effluent and gas generated in the filter passed through a gas separation bulb. The gas passed through a sampling ampoule and the volume of the gas produced was recorded on a wet test meter. The effluent of the system overflowed from the gas separation bulb through a liquid seal. The sampling port was installed in the liquid seal to permit sampling of effluent for pH measurements. If the effluent was allowed to remain in contact with the air for even a few minutes dissolved CO_2 was lost and the pH rose between 0.5 and 1.0 pH units. The majority of the liquid leaving the filter reentered the recirculation loop

Final Design

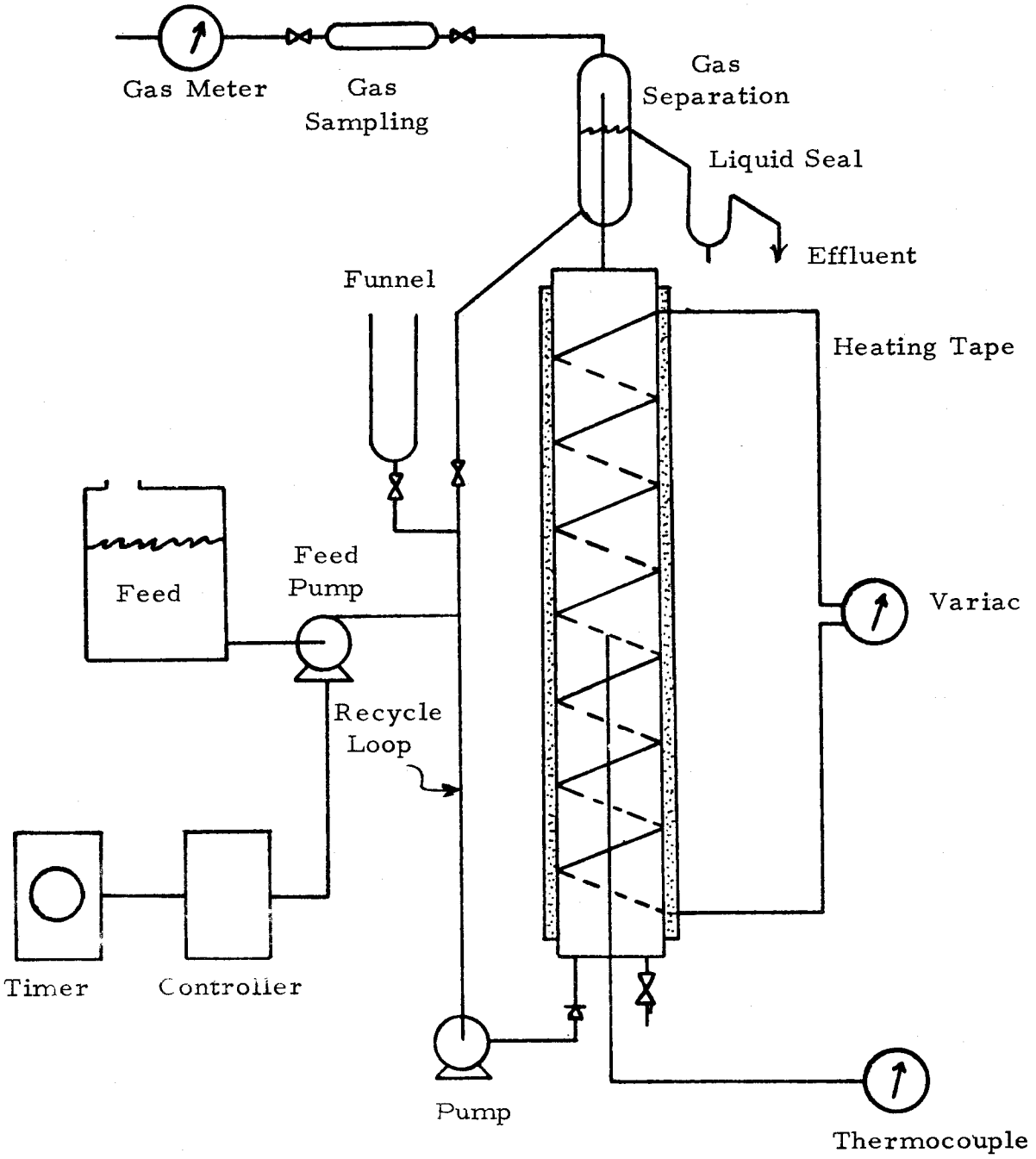


Figure C-4. Backmixed anaerobic filter.

from the gas separation bulb. A funnel and two pinch clamps were installed in the recirculation loop to permit the introduction of sludge seed, nutrients, and other liquids to the system bypassing the feed reservoir. The performance of the anaerobic filter was evaluated in terms of gas production and changes in the concentration of total carbon, inorganic carbon, total organic carbon, and chemical oxygen demand. The gas produced was analyzed for CO_2 and CH_4 by mass spectrometer. Heavy metal and calcium concentrations in the effluent also were monitored. Calcium carbonate was added to the feed reservoir to provide buffering. A significant portion of the calcium carbonate precipitated in the filter.

Startup of the anaerobic methanogenic packed bed involved seeding with anaerobically digested sludge and feeding a synthetic substrate, the composition of which is listed in Table C-1. An acclimated anaerobic population developed as indicated by production of several liters of gas per liter of feed and a CH_4:CO_2 ratio of 3:1 was achieved. A composite B blend was introduced to the system in increasing amounts until the feed was made up only of composite B. The anaerobic methanogenic filter also was fed a blend of composite B and the denitrified composite A.

3. ANAEROBIC DENITRIFICATION

The bench scale anaerobic denitrification studies were conducted in backmixed filter illustrated in Figure C-4 and described above. The startup procedure was essentially the same as that described for the anaerobic methanogenic system with the exception that the synthetic substrate contained 5 grams per liter of sodium nitrate (0.82 grams per liter of nitrate-N). Composite A blend was then incorporated in the feed in increasing proportions until the feed was essentially 100% composite A. The feed also was enriched with composite B to the extent of about 10% by volume since the degree of the biodegradability of the organics in composite A was unknown and the concentration of nitrates in composite A was relatively high. This procedure insured the presence of excess COD relative to the corresponding oxidizing capacity of the nitrates. This approach was satisfactory for some time but some unexplainable upsets occurred. The fact that the denitrification unit survived these upsets and was able to recover, usually in a matter of days, was a good indication of potential application of this process in the prototype system.

The anaerobic denitrification system had been modified and the packing material was replaced initially with sand, and finally with granular activated carbon and operated in a fluidized bed fashion. A schematic flow diagram of the fluidized bed anaerobic is illustrated in Figure C-5. The main reactor of the system consisted of a cylindrical section about 7 cm in diameter with a volume of about 1.64 liters. Cylindrical section was

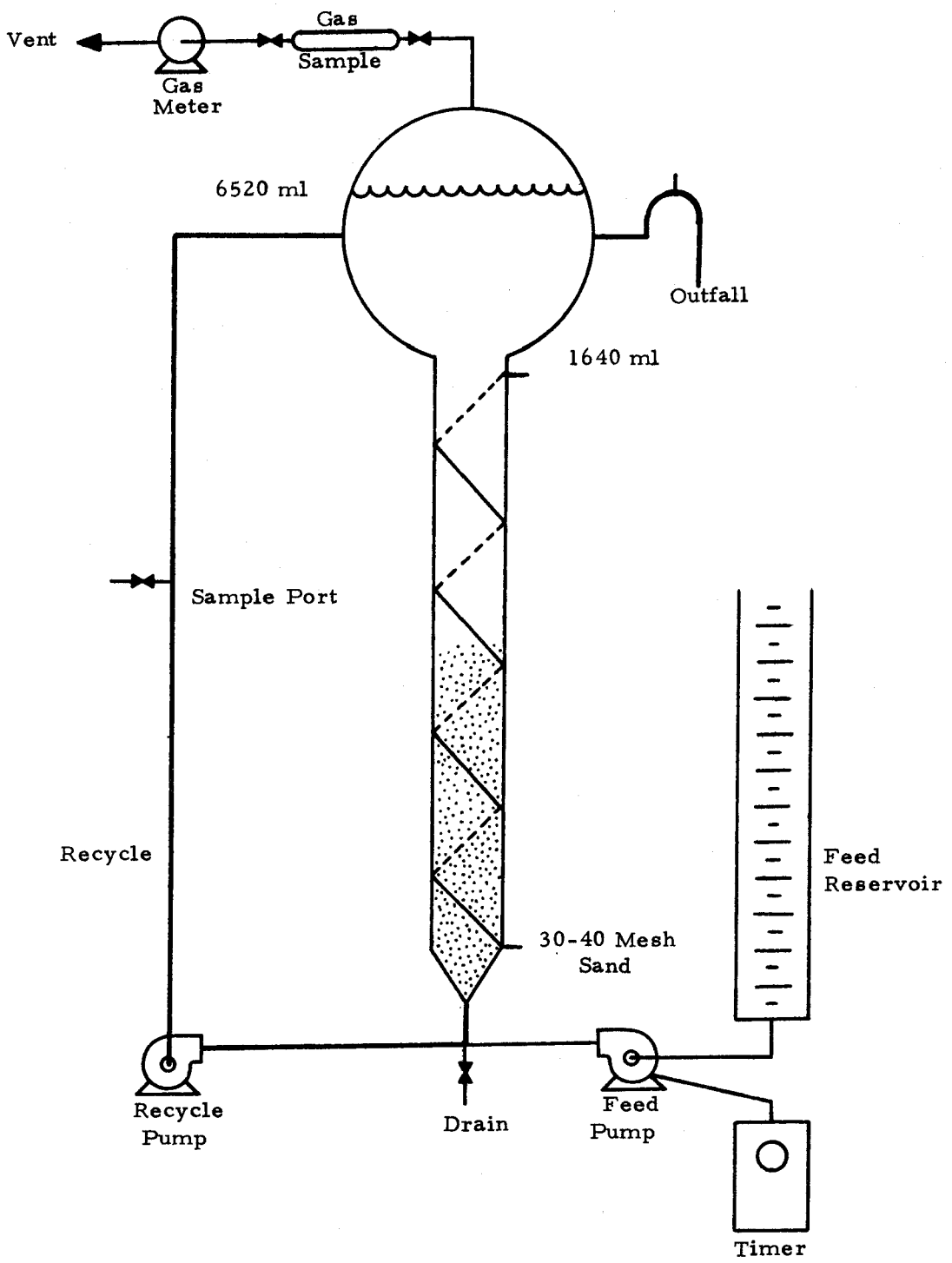


Figure C-5. Fluidized bed denitrification anaerobic filter.

wrapped with a heating tape and the temperature controlled by means of a thermocouple. The upper end of the fluidized bed section expands into a bulb made of a 5-liter round bottom flash. An effluent overflow port and a gas outlet were installed in the overhead section. The gas passed through a gas sampling ampoule, and the volume was recorded on a wet test meter. The effluent was recirculated from the overhead section to the bottom of the fluidized bed by peristaltic pump. A sampling port also was installed in the recirculation loop. The wastewater feed was stored in a calibrated reservoir and pumped to the bottom of the reactor by a time actuated peristaltic pump. The fluidized bed consisted of 20 to 40 mesh Ottawa sand which filled two-thirds of the volume of the reactor. Fluidization caused the bed to expand two inches. Sand particles became wedged in the lower portion of the fluidized bed section and were difficult to dislodge. This wedging became more pronounced with time and eventually forced the shutdown of the unit. The unit was rebuilt and granular activated carbon was used as a fluidized bed.

This fluidized bed system for denitrification was a modification of a process described by Dr. J. S. Jeris (*). His system was operated as a single pass system with fluidized sand bed. The process developed in this study uses high recycle flow through a granulated carbon bed which provides dilution of high strength waste to provide high rate denitrification. This modification may be considered for patent application under the grant study.

4. PRETREATMENT

The composition of the process wastewaters to be treated as a result of the waste reduction and segregation programs made it necessary to operate a laboratory scale stripping column and heavy metals removal system to simulate the wastewaters which would be treated in anaerobic or aerobic biological systems. A laboratory scale stripping column was constructed with a 30-tray 2" Oldershaw column with feed injected on Tray 20. The column overhead was equipped with a decanter allowing the overhead water phase to be totally refluxed. The overhead oil phase was collected but not refluxed. The primary purpose of the stripper was to reduce the carbon content in the composite C blend. The input to this column contained the relatively low carbon stream and the sodium containing streams from the cyclohexane oxidation and cyclohexanone units. These streams constituted approximately 55% of the total flow of the composite C blend. The column feed was composited according to the average flow rates of the stream.

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* Jeris, J.S., and R. G. Owens, "Pilot Scale High Rate Biological Denitrification at Nassau County, N.Y.". Presented at the New York Pollution Control Association, Winter Meeting, January 21-23, 1974.

Heavy metal removal was accomplished by precipitating the metals as the metal sulfide and decanting the liquid for further treatment. The streams requiring heavy metal removal contained relatively low concentrations of nitrates and carbon. However, the heavy metals posed a toxicity problem for the aerobic biological treatment units. The streams requiring heavy metal removal have a highly variable flow and include intermittent contributors such as rainfall, runoff, wash-downs and sump discharges.

Composite samples of the effluents of the stripper column and the heavy metal removal system were fed to the activated sludge system. The composite sample of the heavy metal containing streams also was fed without metal removal to the anaerobic filters with the addition of sufficient sulfates to encourage the formation of insoluble heavy metal sulfides under anaerobic conditions.

APPENDIX D

AEROBIC TREATABILITY PERFORMANCE DATA

TABLE D-1. COMPOSITION OF BAY CITY "AEROBIC" COMPOSITE (FREE OF NITRATE- AND ORGANOCHLORINE-CONTAINING WASTES

	Drum No. 1 20673-23-1	Drum No. 2 20673-23-2	Drum No. 3 20673-23-3	Drum No. 4 20673-23-4
pH	4.5	4.5	4.3	4.3
TC (mg/l)	7200	8000	10 080	9750
IC (mg/l)	<10	<10	10	5
TOC (mg/l)	7200	8000	10 070	9780
COD (mg/l)	21 400	20 200	18 200	17 200
Total N (Kjehldahl) (mg/l)	185	155	150	155
Nitrate N (mg/l)	50	60	45	48
Ammonia N (mg/l)	89	86	105	100
Sodium (mg/l)	710	730	800	760

TABLE D-2. ACTIVATED SLUDGE TREATMENT OF BAY CITY EFFLUENT

(First Stage)

Date	Feed COD, ml/l	Feed, ml/day	Detention, day	Loading, lb/cu ft/day	Outfall, COD	% COD Removal
20 Mar		3383	1.5	1.08		
21		4034			1500	83.2
22	8950	3790				
23		4006				
24		3881			1600	82.1
25		4085	1.5	0.38		
26		3954	1.5	0.37	1460	83.7
27	8750	3756	1.6	0.35		
28		3807	1.6	0.34	1500	82.9
29		3750	1.6	0.35		
30		3920	1.5	0.36		
31		3881			1700	80.6
1 Apr		3722				
2		3443	1.7	0.32	1600	81.7
3	9500	3699	1.7	0.33		
4		3545	1.7	0.36	2000	78.9
5		3443	1.7	0.36		
6		3523	1.8	0.34		
7		3454	1.8	0.34	1850	80.5
8		3352	1.8	0.33		
9	6450	3334	1.8	0.33	1700	82.1
10		3352	1.8	0.23		
11		3295			1400	78.3
12		3290				
13		3210				
14		3188			1350	79.1
15		3193	1.9	0.22		
16	6400	3045	1.9	0.21	1300	79.8
17		3057	2.0	0.20		
18		3073	2.0	0.20	1050	83.7
19		2955	1.9	0.21		
20		3335	1.9	0.21		

(continued)

TABLE D-2. (CONTINUED)

Date	Feed COD, ml/l	Feed, ml/day	Detention, day	Loading, lb/cu ft/day	Outfall, COD	% COD Removal
21 Apr		2989	2.0	0.20	1050	83.7
22		4216	1.4	0.28		
23	5600	4199			1100	8.29
24		4079				
25		4210	1.4	0.24	1100	80.4
26		4142	1.4	0.24		
27		4619	1.4	0.24		
28		3846	1.4	0.24	973	82.6
29	8750	4131	1.4	0.24		
30		4170	1.4	0.38	1100	87.4
1 May		4244	1.4	0.38		
2		4188	1.4	0.38	1350	85.7
3		2875	2.1	0.15		
4		4278				
5	8750	4250			1150	86.9
6		4267	1.4	0.38		
7		4244	1.4	0.39	1150	86.9
8		4295	1.4	0.39		
9		4290	1.4	0.39	1100	87.4
10	7750	4239	1.4	0.39		
11		4358	1.4	0.35		
12		4329	1.4	0.34	860	88.9
13	6050	4148	1.4	0.34		
14		4227	1.4	0.26	732	87.9
15		4250	1.4	0.26		
16	4750	4199	1.4	0.27	738	87.8
17		4273	1.4	0.21		
18		4159	1.4	0.21		
19	3700	4170	1.5	0.20	660	86.1
20		4040	1.5	0.16		
21		4136	1.5	0.16	670	85.9
22		4045	1.5	0.16		
23	4400	4119	1.4	0.16	595	87.5
24		4057	1.5	0.19		
25		4307	1.5	0.19		
26	3600	4051	1.5	0.19	600	86.4
27		4148	1.4	0.15		
28		4114	1.5	0.15	670	84.8

(continued)

TABLE D-2. (CONTINUED)

Date	Feed COD, ml/l	Feed, ml/day	Detention, day	Loading, lb/cu ft/day	Outfall, COD	% COD Removal
29 May	3450	4096	1.5	0.15		
30		4221	1.5	0.15	623	81.9
31		4040	1.4	0.15		
1 Jun		4250	1.4	0.15		
2	4600	4381			695	79.9
3		4131				
4		4108	1.5	0.20	550	88.0
5	6300	4330	1.5	0.20		
6		3710	1.5	0.23	673	89.3
7		4244	1.5	0.27		
8		3960	1.5	0.27		
9	6250	4119	1.5	0.26	683	89.2
10		4063	1.5	0.27		
11		4023	1.5	0.27	685	89.0

TABLE D-3. ACTIVATED SLUDGE TREATMENT OF BAY CITY EFFLUENT

(Second Stage)

Date	Feed COD, ml/l	Feed, ml/day	Detention, day	Loading, lb/cu ft/day	Outfall, COD	% COD Removal
9 May	7.75					
10		398	12.4	0.04		
11		460	13.1	0.04		
12		714	8.6	0.06	170	
13		665	8.8	0.05		
14		869	7.0	0.07	125	
15		767	7.9	0.06		
16		1085	5.5	0.09	50	
17	4.75	1106	5.3	0.09		
18		1170				
19		1190			< 50	
20		1108				
21	3.70	1364			10	
22		693	8.5	0.03		
23		1659	3.6	0.06		
24		1687	3.4	0.07		
25	4.40	1761	3.5	0.07		
26		1722	3.5	0.08		
27		1744	3.4	0.08		
28		1733	3.5	0.08	50	
29	3.45	1721	3.5	0.08		
30		1807	3.4	0.08	< 50	
31		1943	3.0	0.09		
1 Jun	4.60	2045	2.9	0.09		
2		2433	2.5	0.11	< 50	
3		2352	2.5	0.11		
4		2960	2.0	0.14	< 50	
5	6.30	3181	2.0	0.14		
6		2682	2.1	0.19	< 50	
7		3273	1.9	0.21		
8	6.30	2966	1.9	0.20		
9		3307	1.8	0.21	245	96.1

(continued)

TABLE D-3. (CONTINUED)

Date	Feed COD, ml/l	Feed, ml/day	Detention, day	Loading, lb/cu ft/day	Outfall, COD	% COD Removal
10 Jun	6.70	?				
11		3455	1.8	0.23	350	94.8
12		3216	1.9	0.22		
13		3256	1.8	0.23	485	92.8
14		3239	1.8	0.23		
15		3324	1.9	0.23		
16	7.15	3188	1.8	0.23	1700	74.6
17		3506	1.7	0.26		
18		3455	1.8	0.25	2600	61.2
19		3148	1.9	0.24		
20		3381	1.8	0.25	3750	47.6
21		3426	1.8	0.25		
22		3244	1.9	0.24		
23	6.75	2915	1.9	0.23	2600	63.6
24		2830	1.8	0.24		
25		3244	1.8	0.23		
26		3449	1.7	0.24		
27		3347	1.8	0.24	1035	84.7
28		3511	1.8	0.24		
29		3358	1.8	0.24		
30		3369	1.8	0.24	970	85.6
1 Jul		3278	1.8	0.23		
2		3403	1.8	0.24	1200	82.2

APPENDIX E

DENITRIFICATION IN PACKED BEDS

TABLE E-1. COMPOSITION OF BAY CITY NITRATE-CONTAINING EFFLUENT COMPOSITE (Analytical Summary)

	20673-6-1	20673-6-2	20673-46-1	20673-46-2	22754-8-1
pH	1.1	1.1	1.45	1.45	1.1
TC (mg/l)	1470	1520	1640	1690	1810
IC ;mg/l)	200	200	240	210	260
TOC (mg/l)	1270	1320	1400	1480	1550
COD (mg/l)	3100[a]	3900[a]	4980[a]	4980[a]	6000[a]
Total N (Kjehldahl) (mg/l)	2650	2800	2040	1790	1550
Nitrate N (mg/l)	2400	2600	2650	1600	1500
Nitrate N (mg/l)	180	220	6	52	4
Copper (mg/l)	33	35	26	29	20

(a) Wet chemical analysis (dichromate oxidation).

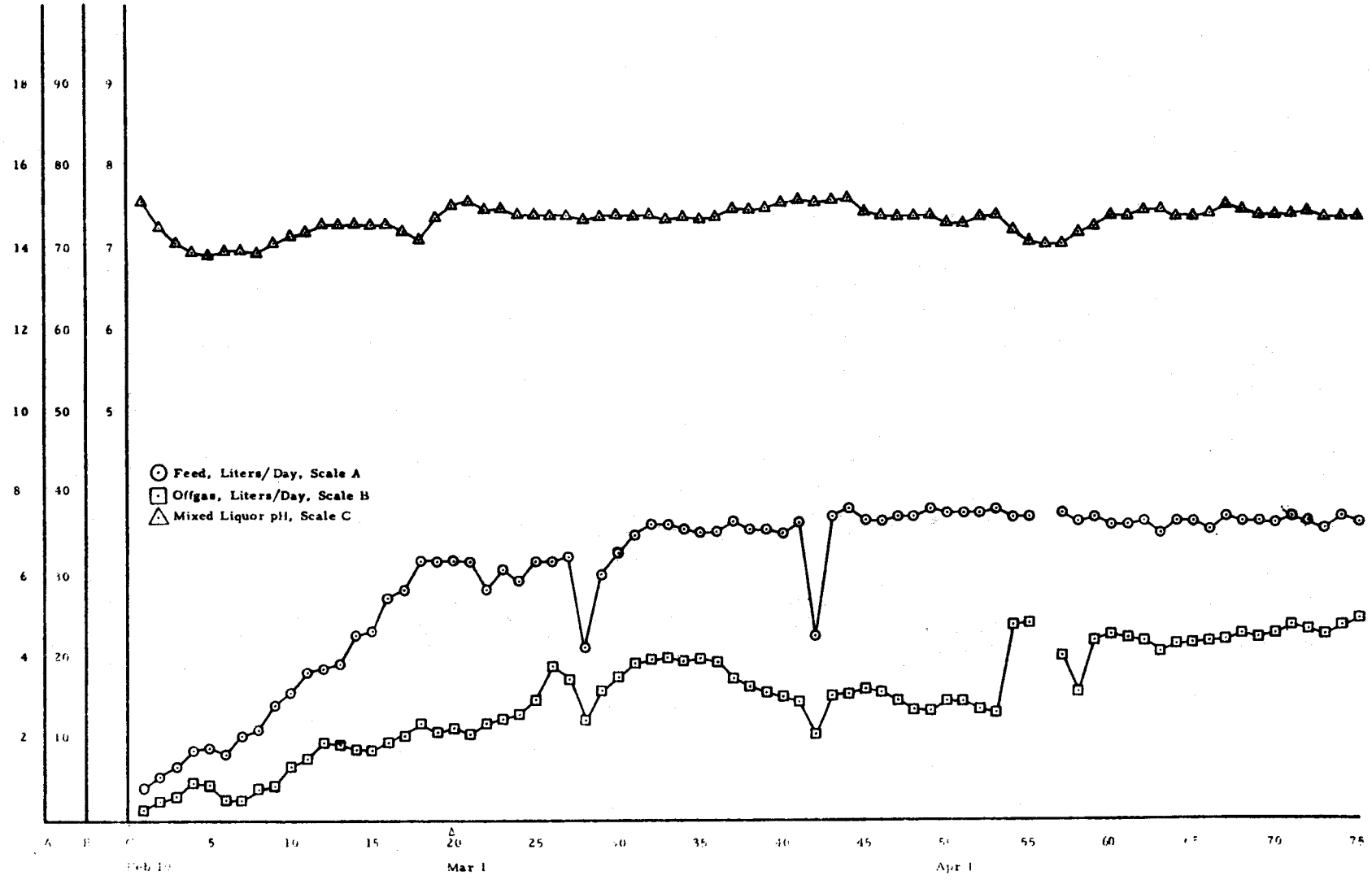

Figure E-1. Packed bed denitrification unit.

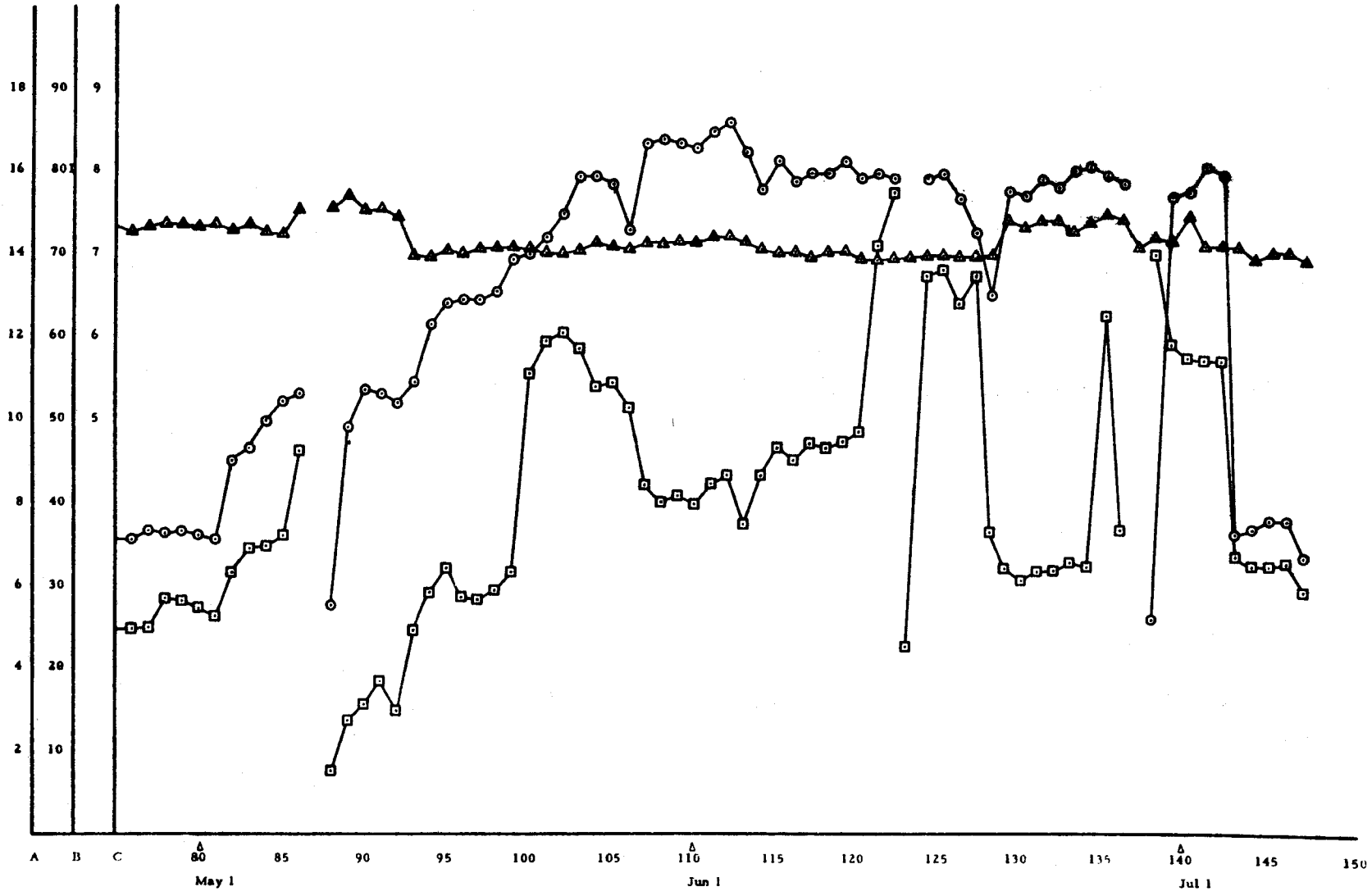

Figure E-1. (Continued)

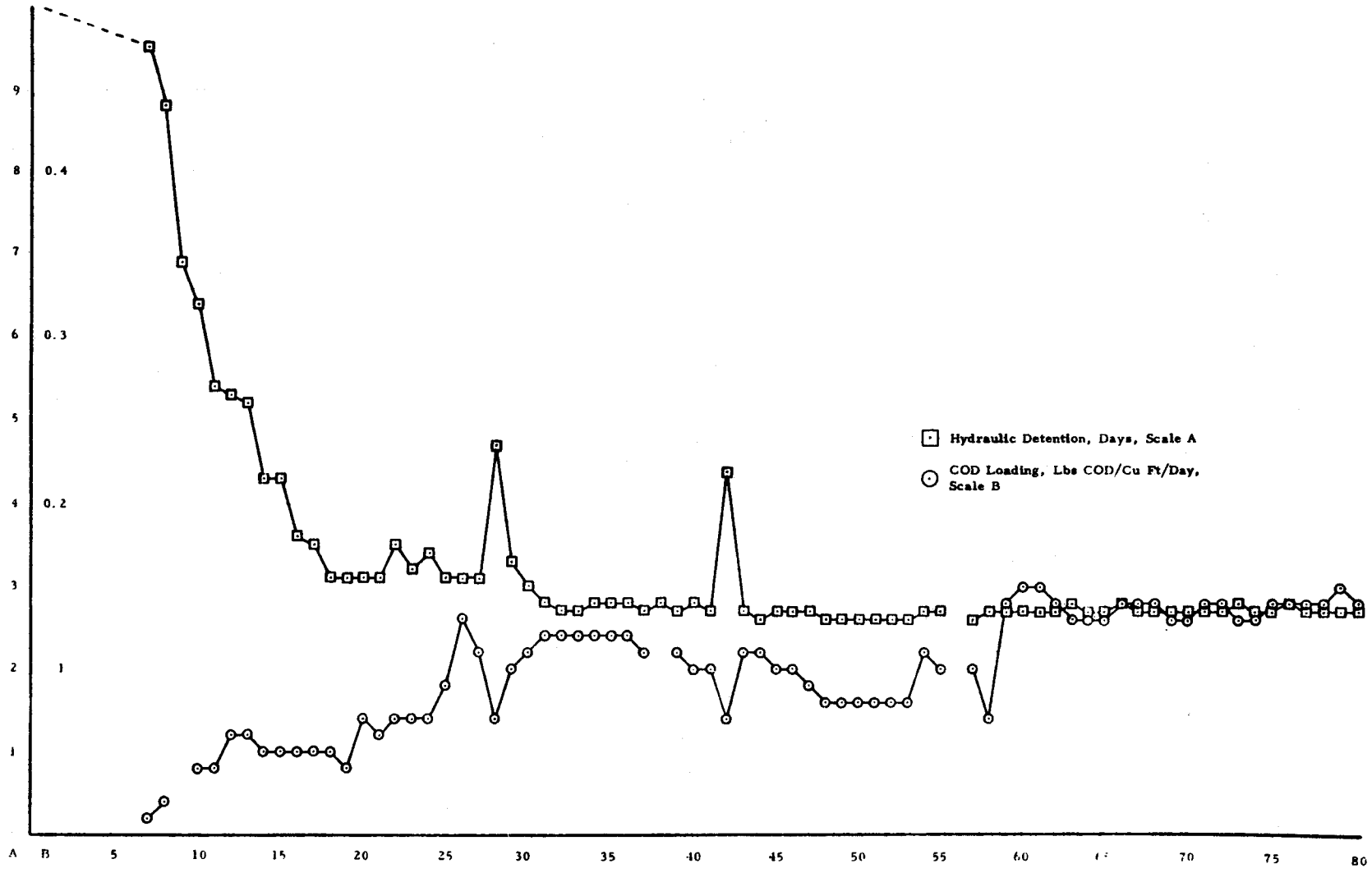

Figure E-2. Packed bed denitrification unit.

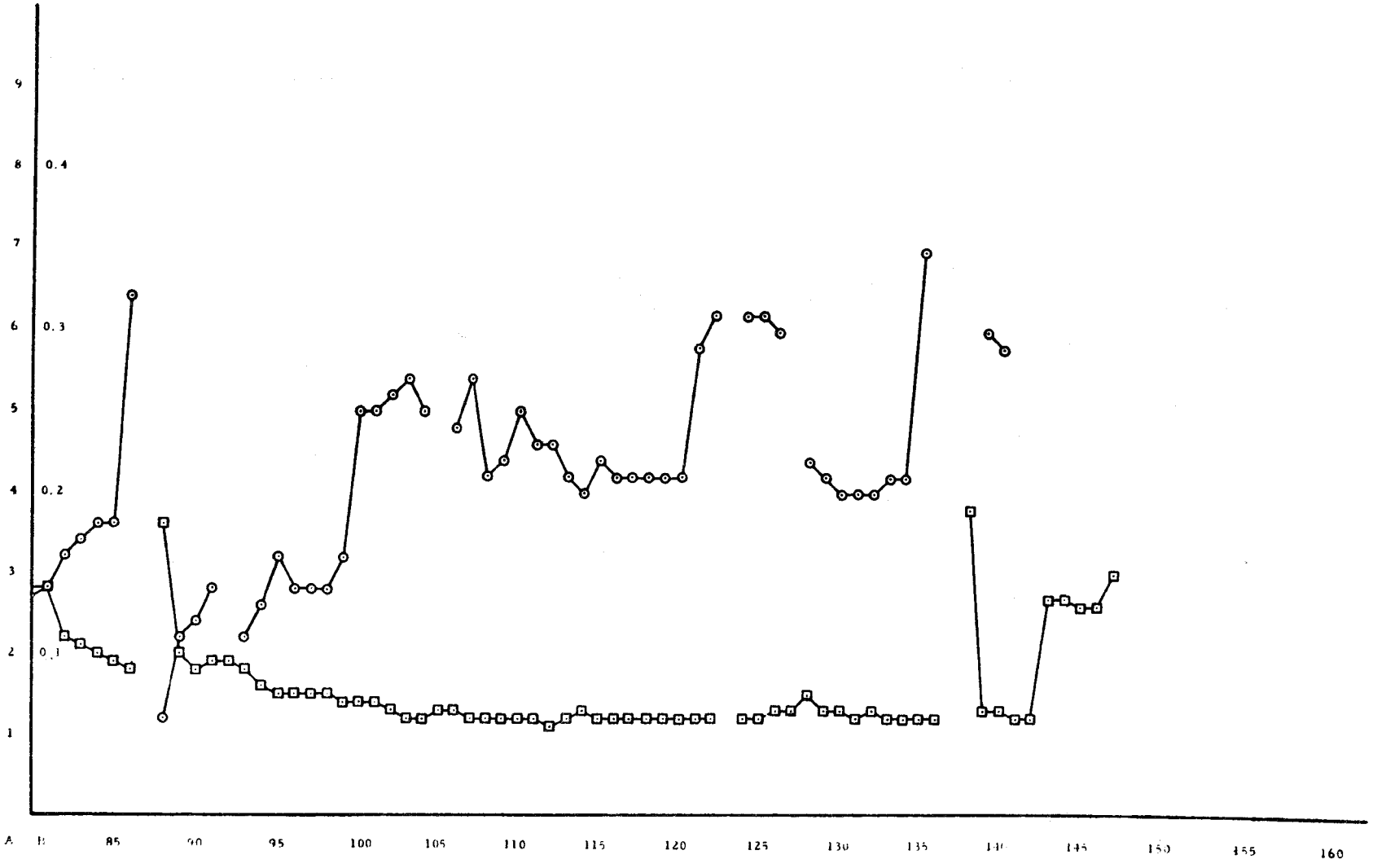

Figure E-2. (Continued)

APPENDIX F

ANAEROBIC METHANOGENIC TREATMENT

(13.6 Liter Initial Void Volume, Operating Temperature = 37°C, pH, Hydraulic Detentions, Specific Gas Yield)

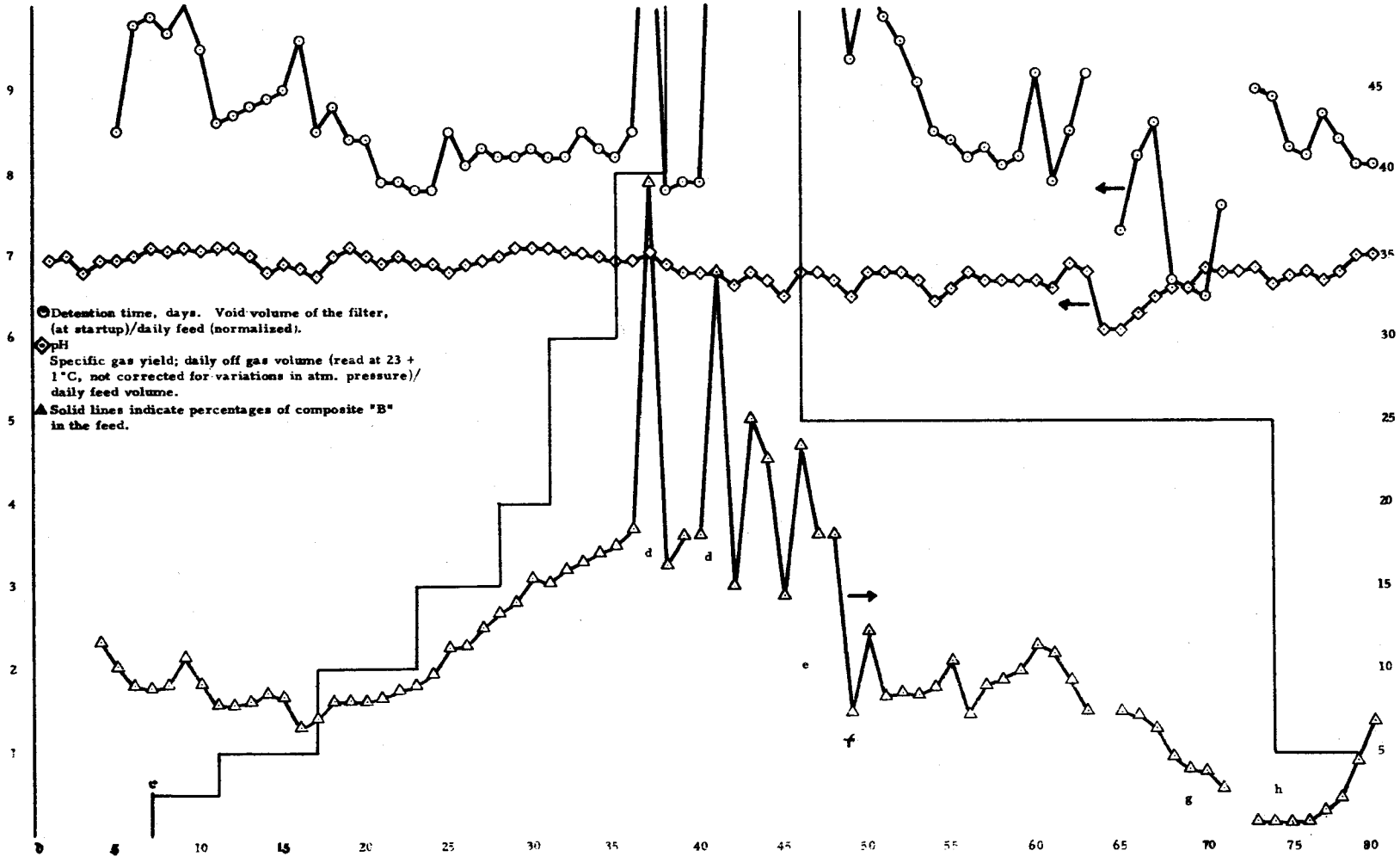

Figure F-1. Operating parameters for backmixed anaerobic filter.

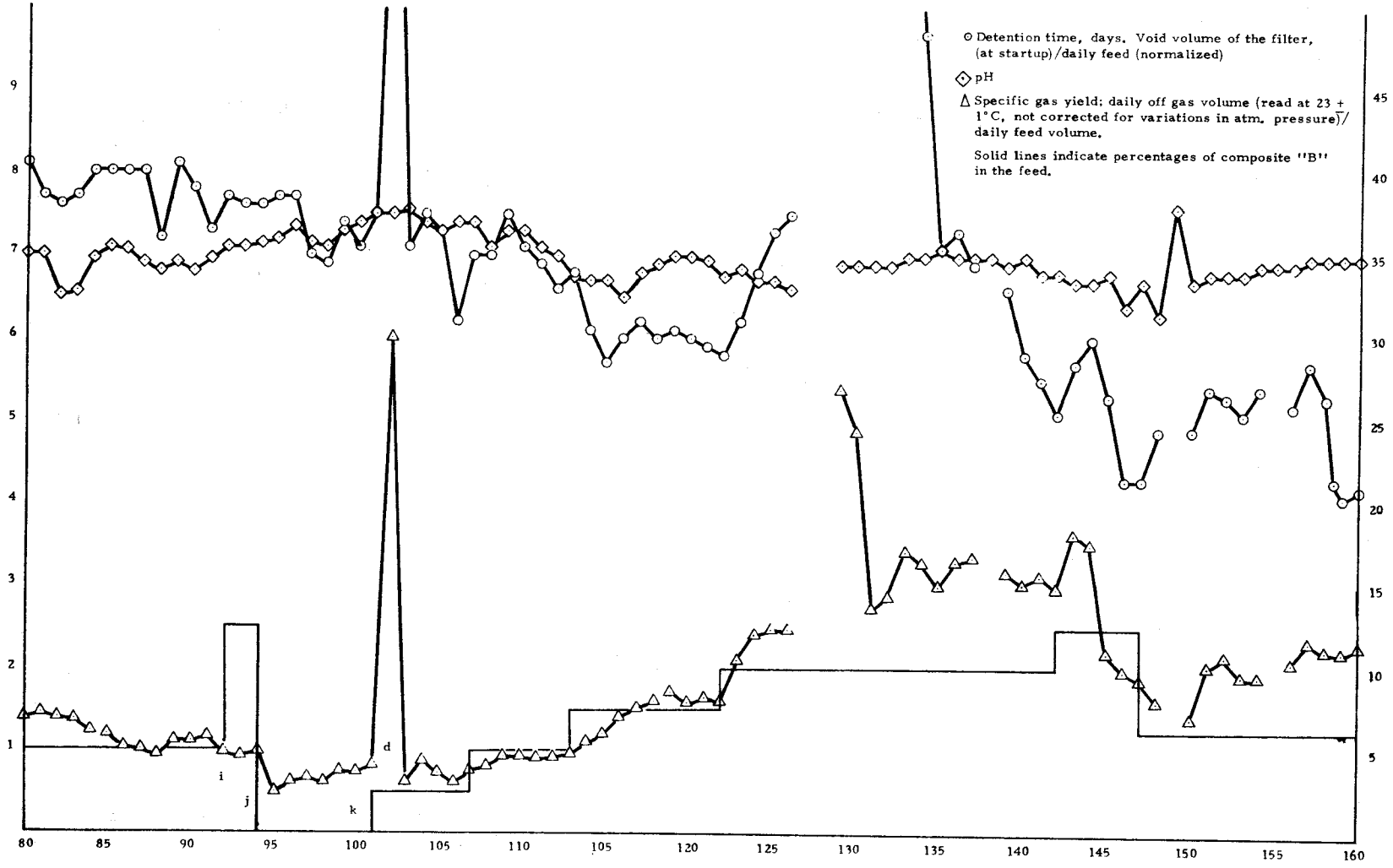

Figure F-1. (Continued)

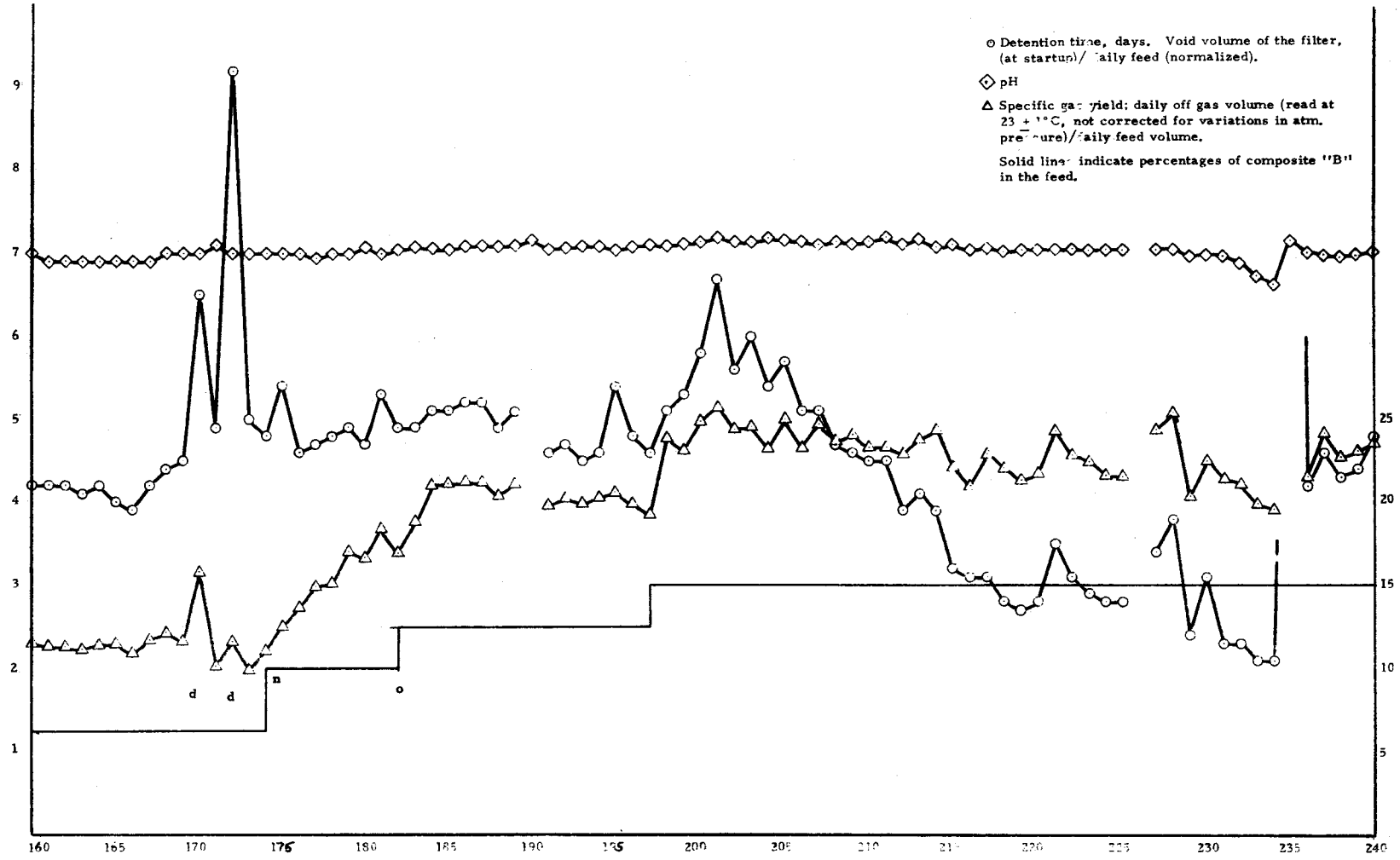

Figure F-1. (Continued)

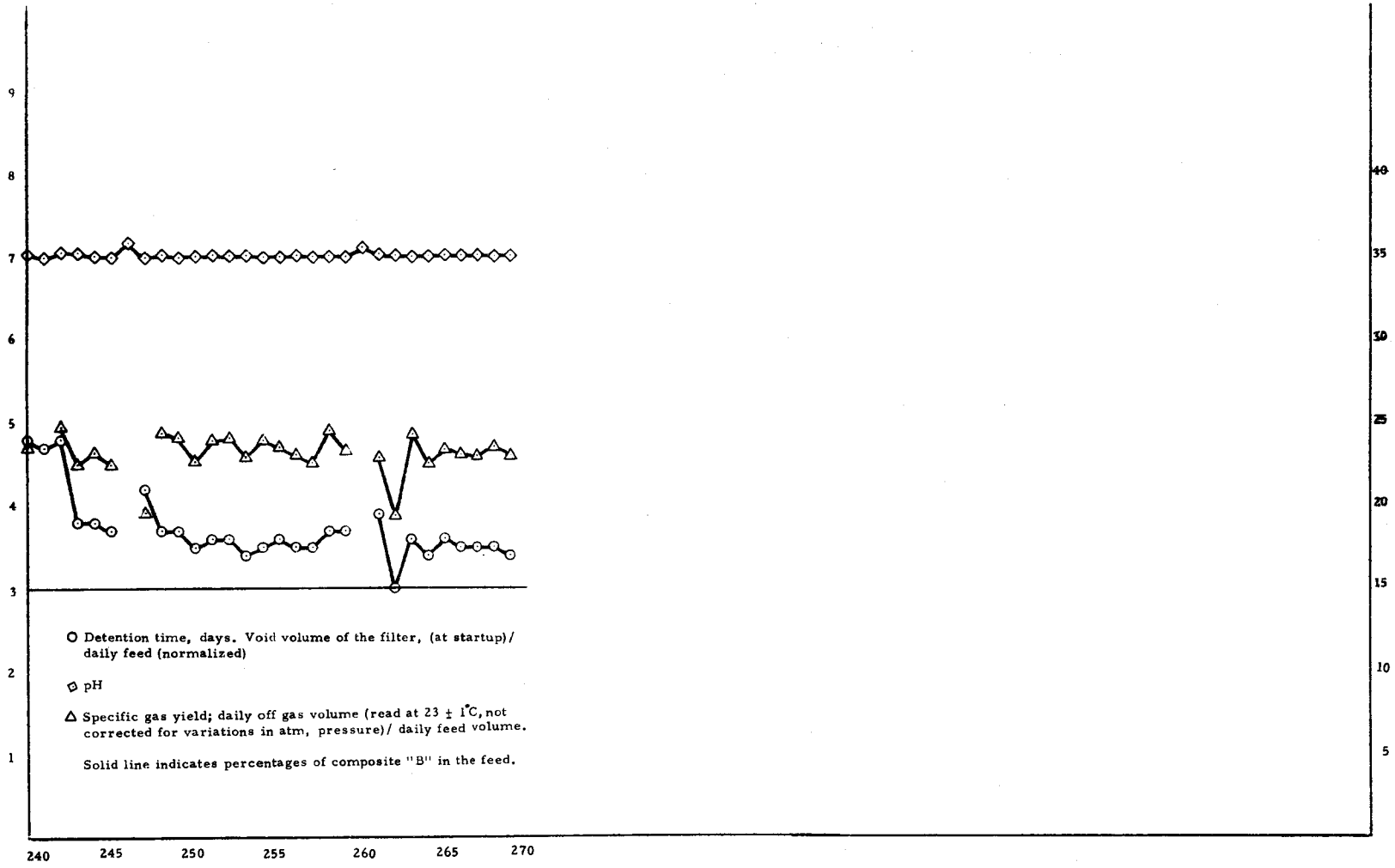

Figure F-1. (Continued)

(13.6 Liter Initial Void Volume, Operating Temperature = 37°C, Off-Gas Composition, TOC and COD Removal)

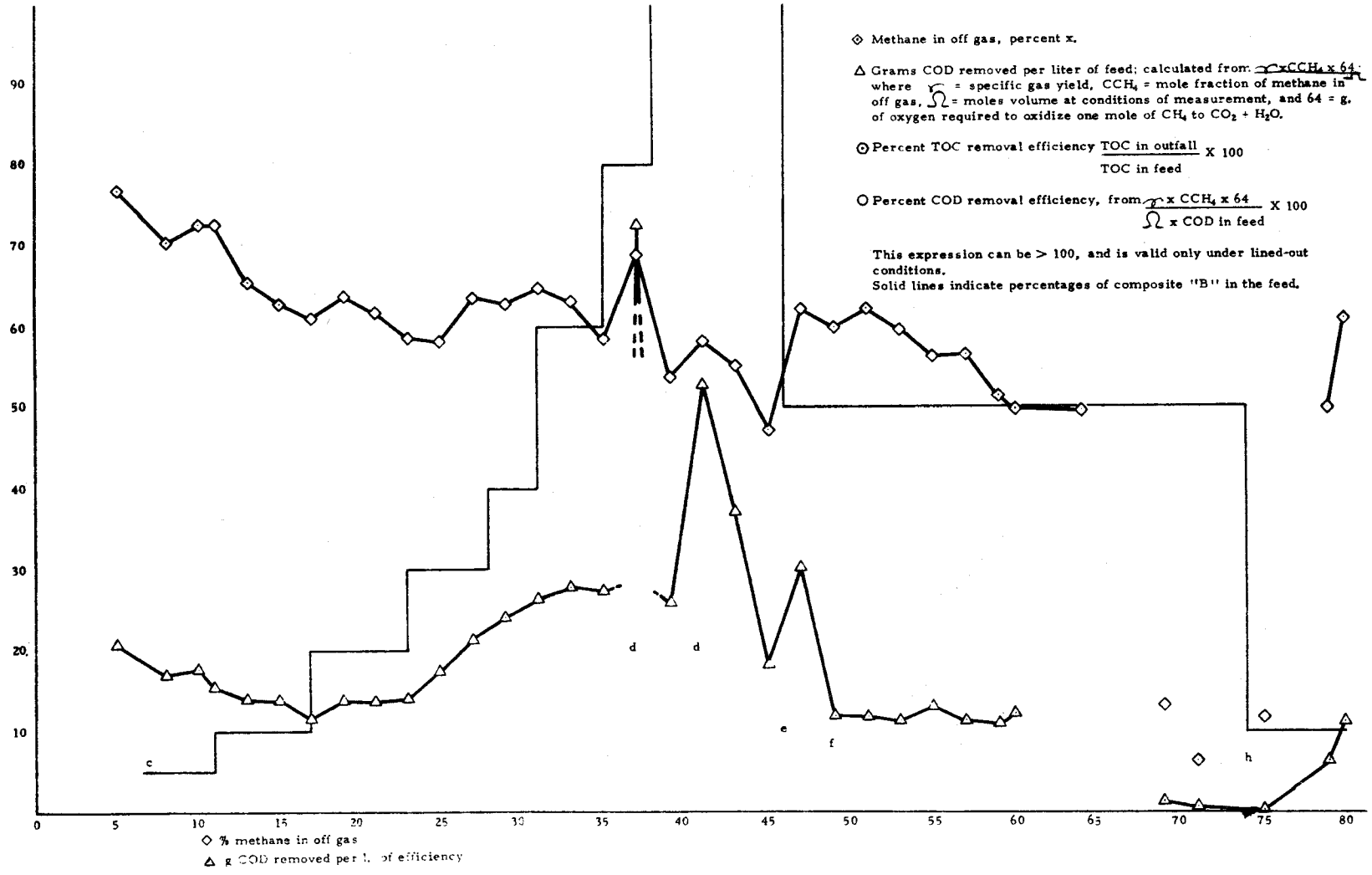

Figure F-2. Operating parameters for backmixed anaerobic filter.

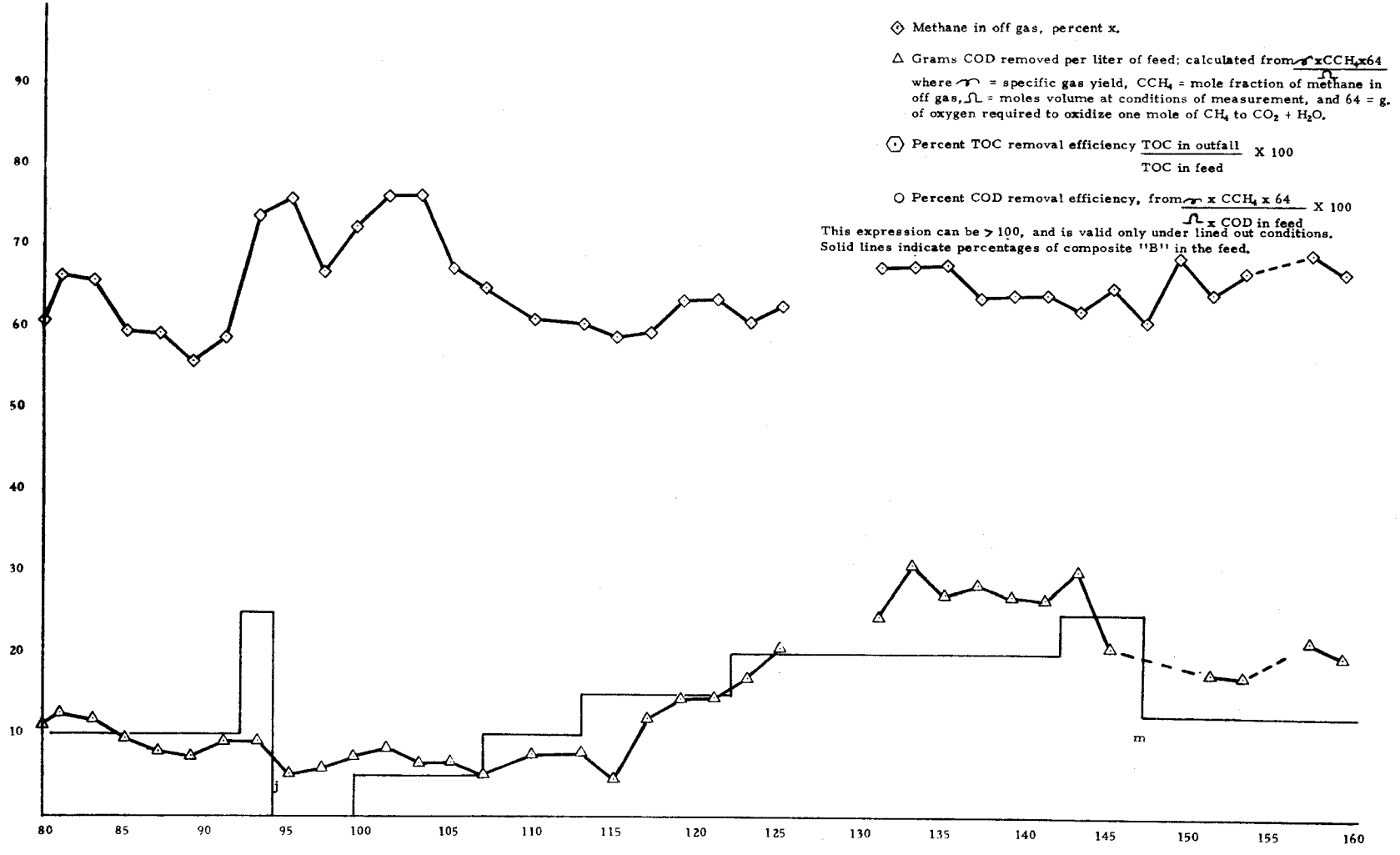

Figure F-2. (Continued)

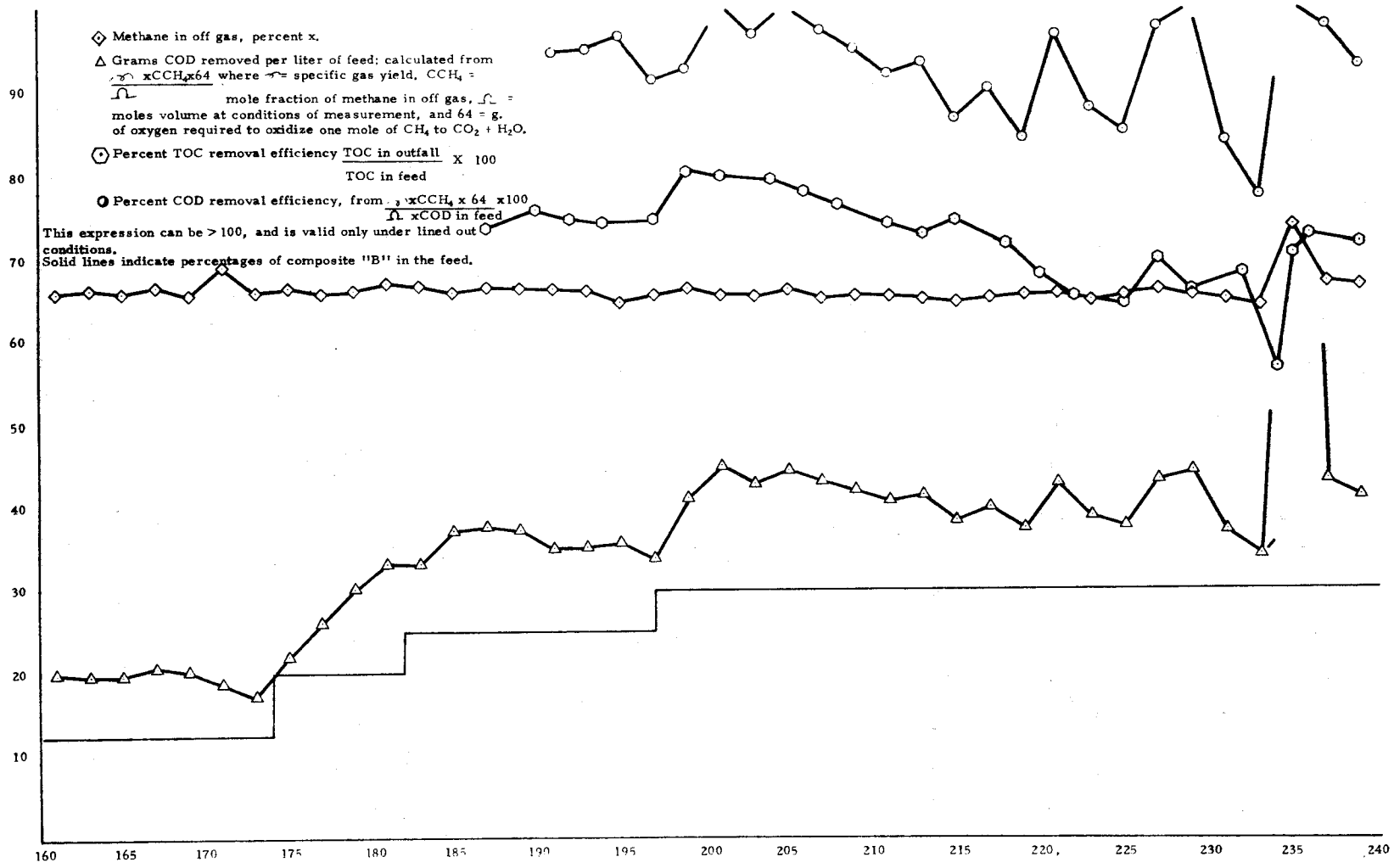

Figure F-2. (Continued)

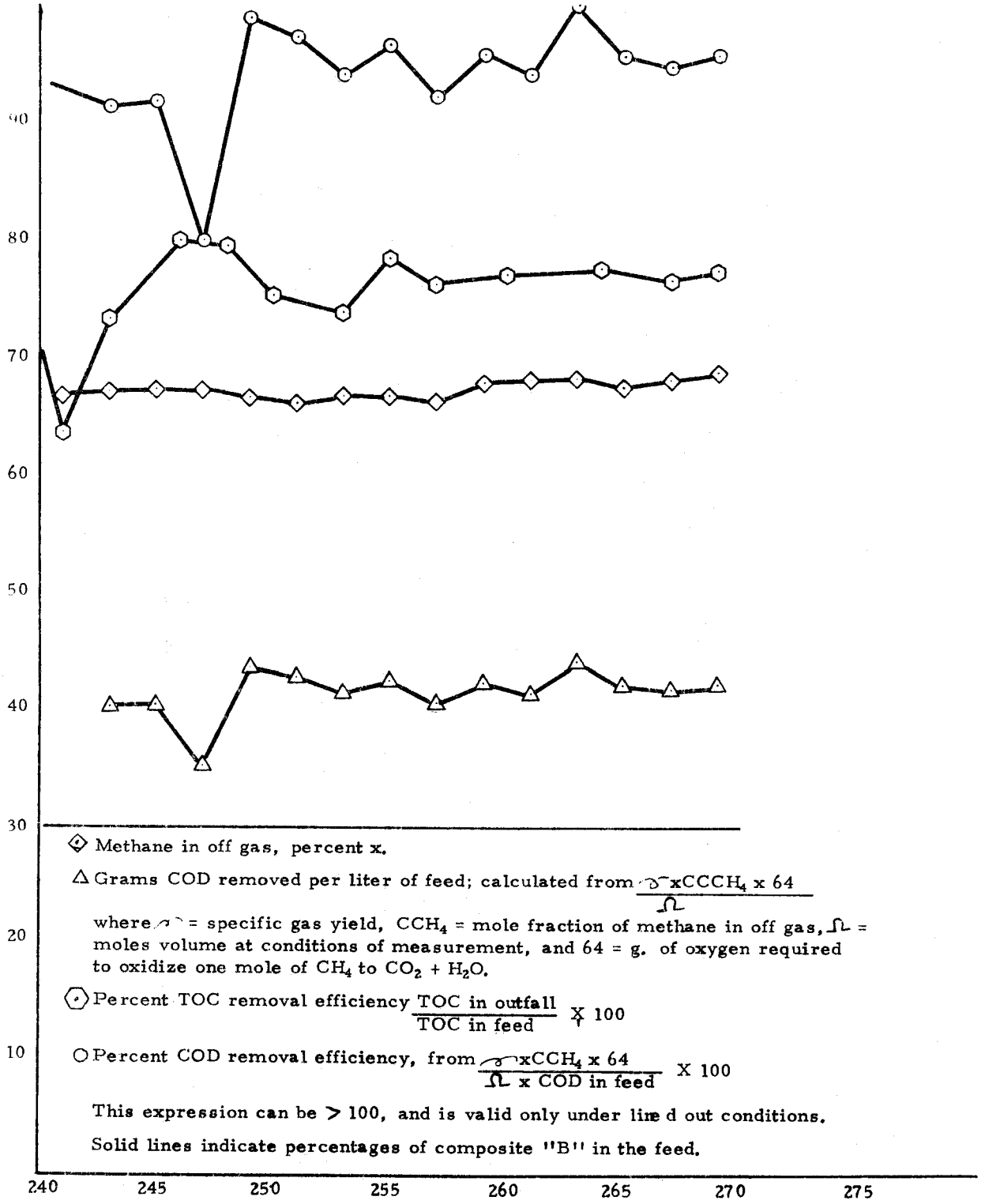

Figure F-2. (Continued)

APPENDIX G

ANAEROBIC DENITRIFICATION FLUIDIZED BED

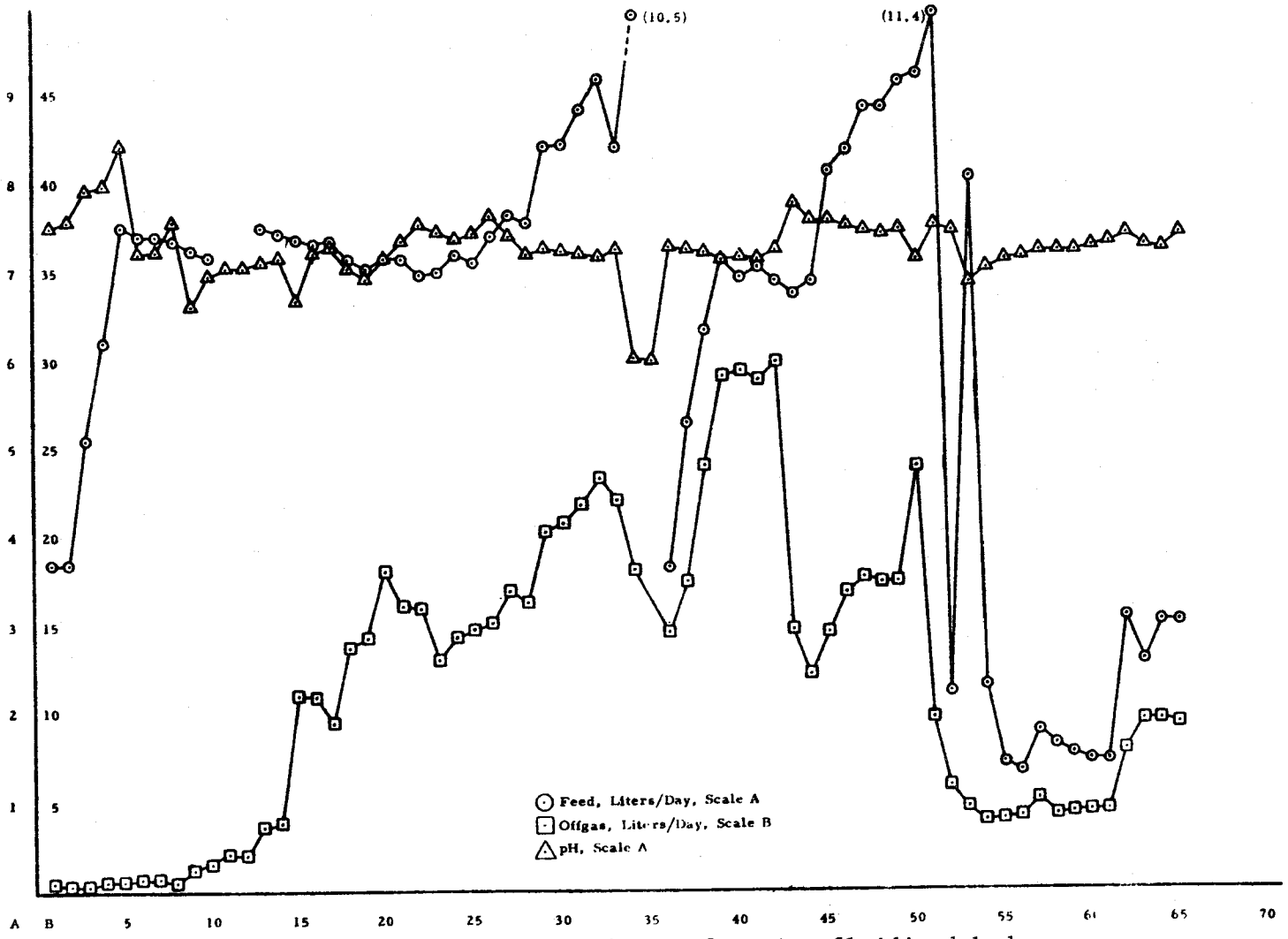

Figure G-1. Anaerobic denitrification fluidized bed.

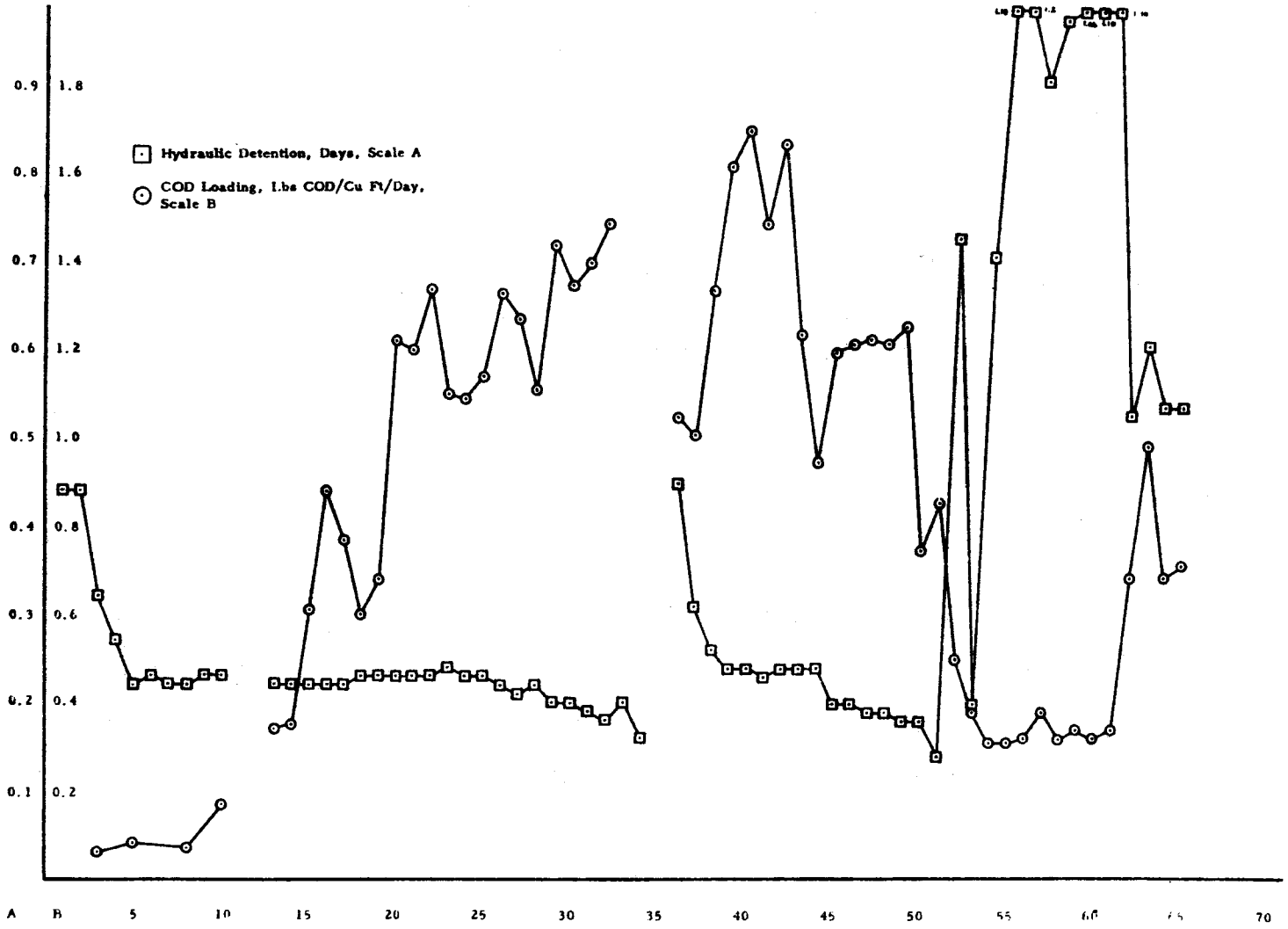

Figure G-2. Anaerobic denitrification fluidized bed.

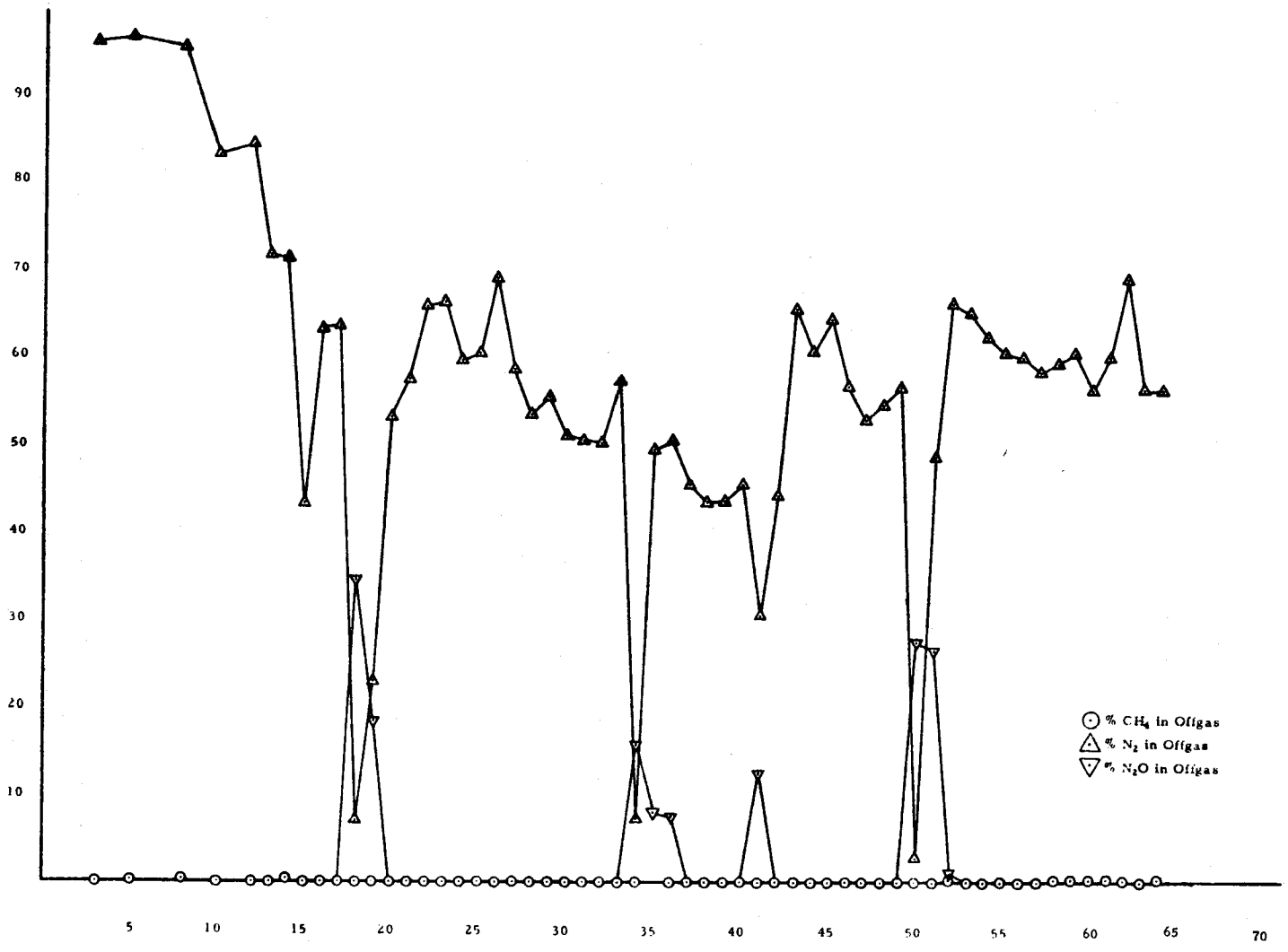

Figure G-3. Anaerobic denitrification fluidized bed.

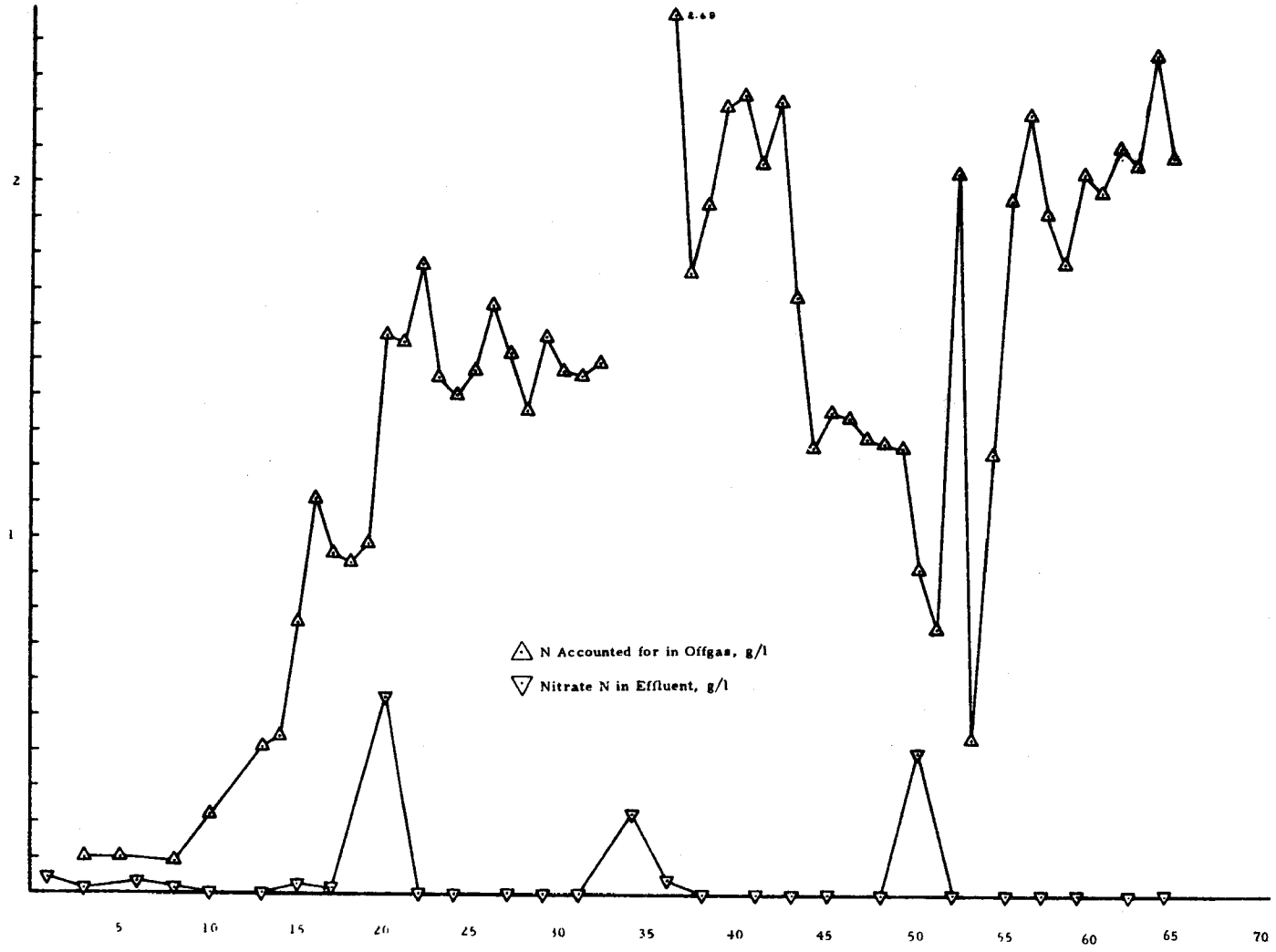

Figure G-4. Anaerobic denitrification fluidized bed.

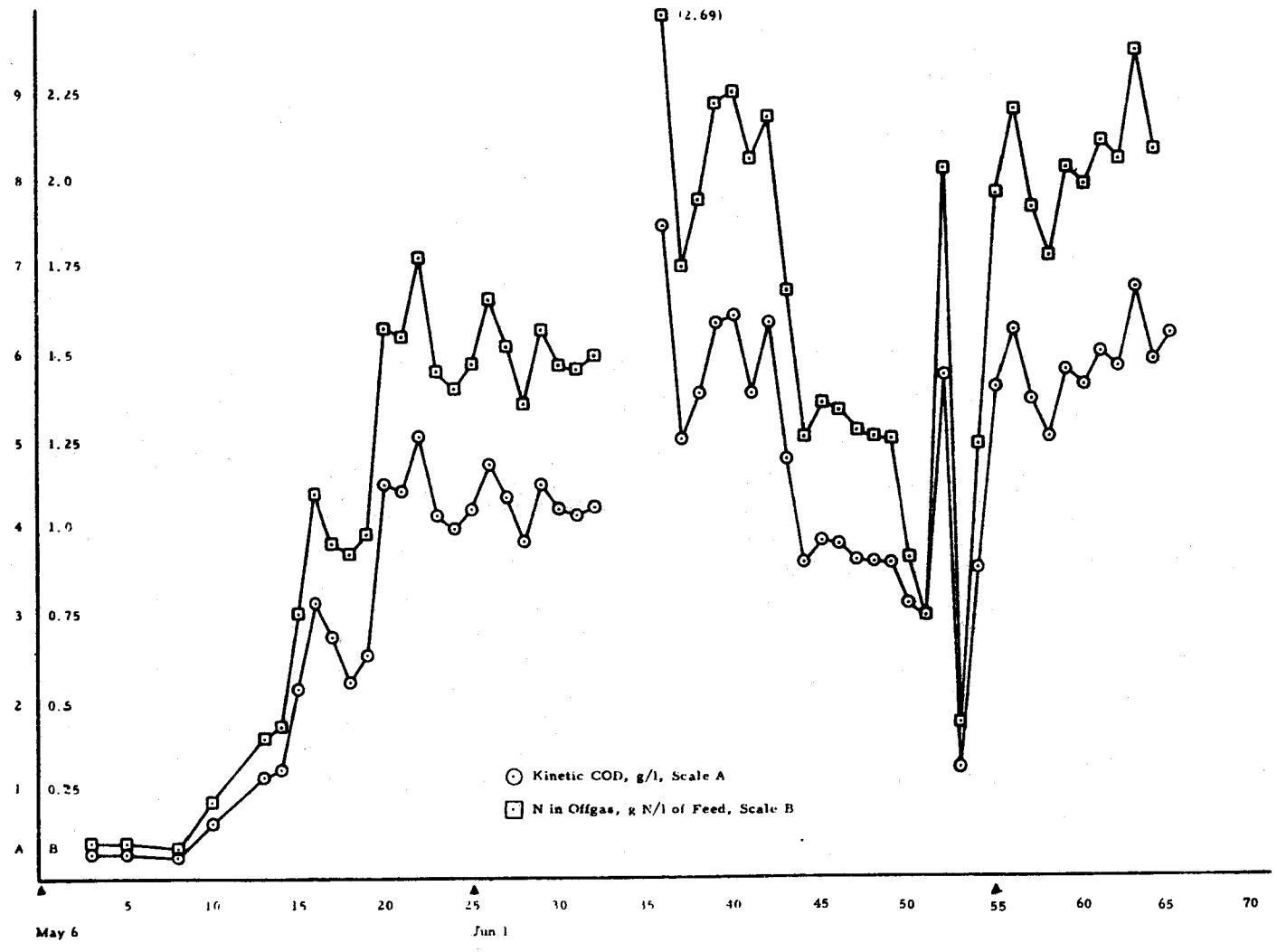

Figure G-5. Anaerobic denitrification fluidized bed.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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7. AUTHOR(S) William J. Humphrey and Enrique R. Witt		8. PERFORMING ORGANIZATION REPORT NO.
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15. SUPPLEMENTARY NOTES

16. ABSTRACT

The biological treatment of a complex petrochemical wastewater containing high concentrations of organic chlorides, nitrates, and amines was initially studied using a sequence of anaerobic methanogenesis and oxygen activated sludge. Bench-scale and pilot-plant treatability studies were conducted using various composite samples and process wastewater blends. The results of preliminary studies indicated the need for stream segregation and waste reduction programs at the petrochemical plant. Segregation of components of the combined plant waste stream was required to eliminate nonbiodegradable materials and pretreatment minimized the concentration of substances which were toxic or inhibitory to biological treatment. Nitrates inhibited methanogenesis in the anaerobic system but quantitative removal of nitrates was accomplished. Only partial removal of chemical oxygen demand (COD) was achieved during anaerobic denitrification because of the relatively low nitrate/COD ratio. Anerobic methanogenic treatment also was unsuccessful in reducing the COD concentration to any great extent, even after pretreatment by anaerobic denitrification. The activated sludge system was effective in removing the biodegradable portion expressed as biochemical oxygen demand (BOD) of the pretreated combined wastewater stream; but the yellow color of the effluent was unacceptably dark. The activated sludge system performed equally well when high purity oxygen, or air was used for aeration.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Activated Sludge Process Anaerobic Processes Industrial Waste Treatment Pilot Plants	Denitrification Petrochemicals Industry Organic Chlorides Bench-scale Plants Oxygen Activated Sludge	68D

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