The University of Texas CENTER FOR RESEARCH IN WATER RESOURCES Environmental Health Engineering Research Laboratory Department of Civil Engineering

THE EFFECT OF PROCESS VARIABLES ON SLUDGE FLOC FORMATION AND SETTLING CHARACTERISTICS

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PREFACE

There are many variables which affect the operation of the activated sludge treatment of municipal and industrial wastes. The objectives of this study were to evaluate the effects of some of these variables in a laboratory scale investigation and to correlate this information with field data where possible.

Six continuous flow units were operated in parallel, each unit being subjected to different organic loadings. Raw waste provided by the particular industry was shipped to the laboratory in 55-gallon drum containers, and then fed to the units at the appropriate flow rate by the use of sigma motor pumps. These wastewaters included a brewery waste from San Antonio, a petrochemical waste from the Houston area, and a domestic sewage from the municipal treatment plant.

Several analytical methods were used to evaluate the solids-liquid s eparation and the biological floc development resulting from the various operating conditions. The morphological characteristics of the organisms were studied by the use of optical and electron microscopy. The settling characteristics of the biological sludge were determined by using stirred settling columns. Dehydrogenase enzyme measurement, oxygen uptake rate, and BOD removal were used to determine the relative activity of the sludges. Temperature, pH, mixed liquor dissolved oxygen, and nutrient availability were constantly controlled and thereby eliminated as process variables. Acclimation procedures were employed and approximate steady-state conditions were established prior to making the evaluations.

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SYMBOLS AND ABBREVIATIONS

A	Activity, cpm
a	Synthesis fraction
a'	energy fraction
b	endogenous respiration factor
b'	endogenous respiration factor (oxygen basis)
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
С	Concentration, cpm/ml
cpm	counts per minute
DPN	Diphosphopyridine nucleotide
DO	Dissolved Oxygen, mg/l
FAD	Flavin Adlnine Dinucleotide
F/M	Food to Microorganism Ratio
Kr	Oxygen Uptake Rate / gm MLSS
Lo	Initial BOD
Le	Effluent BOD
L_{f}	Organic Loading Factor, lbs. BOD ₅ /day/lb MLSS
L _f '	Organic Loading Factor, lbs. COD/day/lb MLSS
MLSS	Mixed Liquor Suspended Solids
MLVSS	Mixed Liquor Volatile Suspended Solids

SYMBOLS AND ABBREVIATIONS (Cont'd.)

mµ	milli-microns
μM	micro-moles
Ν	Nitrogen
ORP	Oxidation Reduction Potential
Р	Phosphorus
Q	Flow Rate
hr	oxygen uptake rate
SVI	Sludge Volume Index
S	COD or BOD, mg/l
t	time
\mathbf{TF}	Triphenylformazan
TTC	Triphenyltetrazolium Chloride
TSS	Total Suspended Solids
TKN	Total Kjeldahl Nitrogen
V	Volume
Х	Volatile Suspended Solids, mg/l
Δ	Change
Φ	μ amp reading (oxygen analyzer)/Winkler D.O.

Chapter 1

INTRODUCTION

Successful biological treatment of the many wastewaters presently flowing from our industries and municipalities is achieved by combining a well-conceived plan with competent plant design and proper operation. The biological system is most responsive to the wastewater character and to the environment in which it must function. Many investigators have therefore oriented their research efforts toward design development based on biological laws and concepts. Unfortunately, there are many variables to be considered in a waste treatment plant and recognition of this fact is of primary importance in the development of design criteria.

The importance of these process variables is underscored when the problem of solid-liquid separation in the activated sludge process is considered. This treatment step is a prerequisite to successful treatment, and has been one of the more difficult operations in the process. Sludge settleability, or lack of it, is being investigated incorder to develop techniques for defining and quantifying these variables.

1-1 Objectives

The primary objectives of this research were (a) to develop the laboratory equipment and methodology necessary for properly analyzing the biological responses to various wastewaters, (b) to evaluate organic loading effects of a given waste using simultaneous, continuous-flow units,

(c) to predict the sludge settleability at defined organic loadings, (d) to observe microbial responses to different waste loadings and character situations by the use of microscopy, (e) to study possible methods of improving sludge settleability, and (f) to evaluate the applied organic loading effects on phosphorus and nitrogen removal, bound water content, and the sludge activity parameters.

1-2 Scope

Wastewaters of the same strength and character as that found in the field were used as a laboratory unit substrate source. The sampling, transport, and laboratory feeding procedures were therefore developed to achieve this objective. The laboratory analyses were formulated to estimate best the system variables for each condition. Laboratory and field data were compared in two instances. A favorable comparison of the data proved the validity of the approach herein developed. It is suggested that this approach could be applied to any organic soluble industrial wastewater. There are obviously many treatment systems today which cannot be classified by loading factor alone. Continual organic and hydraulic loading fluctuations, incomplete mixing, and changing environmental conditions create an overall situation which is difficult to predict in the laboratory. This approach, nevertheless, can be used as a basis for making engineering decisions. In many instances, treatment plants are subjected to relatively constant hydraulic and/or organic inputs by means of plant

processes or treatment facility design. When this is the case, we can more accurately develop design criteria and make biological predictions. This laboratory solution was therefore formulated, recognizing these applicability restrictions.

Chapter 2

LITERATURE REVIEW

The performance of a bio-oxidation system is characterized by the amalgamation of many related process variables, all functioning together to produce a given end result. Since the primary interest of the engineer is to obtain stability of operation with an effluent of desired quality, the importance of recognizing and comprehending the effects of these variables is underscored. Selective variable control in the laboratory with field correlation when possible can provide a good basis for predicting the effects of transient conditions.

2-1 General Considerations

There are an infinite number of factors which affect the operation of a bio-system. As a result, the steady state condition in the true sense of the word is rarely obtained in the prototype. The effect of many of these factors is minimal, emphasis thereby being placed on those of more significance. The significant factors include organic loading variations, temperature and pH changes, and nutrient availability. The latter three items were not varied in the laboratory phase of this study and will be only briefly mentioned.

Fluctuating organic loading in an activated sludge plant is of primary importance. Recently published figures by Montgomery and Lynn (1) indicate the BOD loading can vary from as low as 10 per cent to as high as 300 per cent of the mean value for municipal plants, regardless of size. Although

industrial waste treatment facilities are frequently subjected to less organic load fluctuations because of process control, the variations are nevertheless significant. These load variations result in changing food to microorganism ratios which in turn dictate the organic removal rates by the microorganisms. The flora and fauna of the system will respond in different ways to this changing environment. In the case of activated sludge, where gravity separation of the floc from the liquid is necessary for proper treatment, the physiological state of the floc-forming organisms is most important.

The hydrogen ion concentration is associated with the enzymatic processes in the bio-treatment system, and retards biological oxidation and synthesis outsideo of certain ranges. Conditioned activated sludge is little affected by pH changes within the range of pH 6 to pH 9 (2) but the optimum pH is 7.0 to 7.5 for activated sludge treatment of domestic wastewaters (3).

The nutritional requirements of the heterogeneous population comprising the activated sludge floc have been the subject of many investigations (4), (5), (6). Although domestic waste waters contain sufficient concentrations of nitrogen and phosphorus, it is often necessary to supplement particular industrial wastes with some of the required nutrients. A BOD: N: P ratio of 100: 5: 1 will generally enable the microbial population to grow and proliferate (5).

Temperature has a pronounced effect on all biological reactions. Mathematical formulations of temperature effects on biological reation rates have been expressed in various ways (5), (7), (8), (9). It can generally be

stated that a rise in temperature has a favorable effect on biochemical reactions. However, there are two important points to consider here. Low saturation values of oxygen at high temperatures will have a negating effect on activated sludge efficiency, and there is a limit in the higher temperature ranges above which most of the enzymes are inactivated.

2-2 Sludge Bulking

Bulking sludge is a significant phenomenon in biological treatment of wastes since sludge-liquid separation is the final and necessary step in the treatment scheme. Investigators have reported a variety of mechanisms in explaining the bulking phenomenon.

Philip Jones (10) and others have proposed that bulking sludge is a biophysical response to a change in the ecological balance of the environment. This results in the emergence of a dominant population of filamentous microorganisms growing as a diffuse floc. The filamentous organism most consistently reported as being dominant in bulking sludge has been identified as <u>Sphaerotilus natans</u>. This is a higher bacterium, induced by a substrate rich in carbohydrates, which displays many fungal properties. Pipes and Jones (11) proposed that a variety of filamentous microorganisms are more intimately associated with sludge bulking than are <u>Sphaerotilus</u>, but that because of the similarity of morphology and the lack of information concerning the physiological responses of <u>Sphaerotilus</u>, many of these organisms have been incorrectly identified. In following up

this work, Jones isolated and identified a microorganism associated with sludge bulking as an obligate aerobe, <u>Geotrichum candidum</u>. He observed, in fact, that <u>Geotrichum</u> was found more frequently and in larger numbers than Sphaerotilus.

Anderson (12) suggested that sludge flocs comprised of <u>Zoogloea</u> <u>ramigera</u> will not bulk under any condition. He tried to induce bulking by feeding glucose to a pure culture of <u>Zoogloea</u> growing in a synthetic sewage medium. The experiment was continued for ten days with continuous aeration, but bulking did not occur. Higher concentrations of glucose were added with the same result. He therefore concluded that bulking in activated sludge was caused by stimulation of the filamentous microorganisms to overgrow the natural Zoogloea organisms.

Richards and Sawyer (13) also studied the microorganisms and characteristics of the sludge floc. Counts of the bacterial and protozoan populations were made at various intervals and an inverse relationship between them was observed. High bacterial counts were associated with poor settling sludge, whereas a populous protozoan sludge correlated with rapid settling of the flocs.

Heukelekian and Weisberg (14) have made a comprehensive study of sludge bulking that established a relationship among bulking, bound water content, and the biochemical characteristics of activated sludge. Wilson (15) first called attention to the importance of the water relationships of activated sludge. He recognized two different kinds of water, namely, that water attached to the floc which maintains its inherent properties and that bound by the colloid micelles with entirely different properties. This "bound water" content in the floc is dependent upon the chemical, physical, and electrical properties of the system. Heukelekian took a zooleal type sludge and aerated it for twelve days, feeding only on the first day, with the following results:

Table 2-1

Food/Microorgani s m Ratio	Aeration Period	Bound Water	Sludge Volume Index
high	1 day	363	400
	6 d a ys	148	85
low	12 days	59	6 2

Effects of F/M Ratio on Bound Water and SVI

They offer the following explanation of sludge bulking and high bound water in the floc during periods of high food/microorganism ratios: When easily degradable substrates are available in excess amounts, the organisms produce products which have a great affinity for water. They further postulate that microorganisms in the log growth phase produce more capsular material which is polysaccharide in nature and highly hydrated. The increase in bound water produces a more perceptible change in the specific gravity of the sludge.

Heukelekian not only worked with the zoogleal type sludge but also studied one in which Sphaerotilus was dominant. The bound water content of the <u>Sphaerotilus</u> sludge remained relatively constant, indicating a fundamental physical difference between the two bulky sludges. Contrary to some investigators, he espoused two basic types of bulking: <u>Sphaerotilus</u> and <u>Zoogloea</u>. The <u>Sphaerotilus</u> bulking, once the organism is dominant, is not caused by bound water or available substrate, but rather by the physical bouyancy and frictional resistance of the filaments. The <u>Zoogleal</u> bulking, on the other hand, is a direct result of both bound water and high substrate concentrations. The presence of <u>Sphaerotilus</u> was not noted at any sludge volume index level when evaluating the <u>Zoogleal</u> sludge. The difference in the settling nature of this sludge was therefore due to a change in the biochemistry and not the gross biological characteristics of the process.

The literature offers several causes of sludge bulking, the investigators being in general agreement. The theory of bound water contribution to bulking appears to be valid, although its proportional contribution is unknown. There can be little doubt that the morphology of the dominating microbial population is most important. Other causative factors which have been proposed include the biochemistry of the system and the rigidity of the floc, reduced oxygen tension, and the nature and concentration of available substrate.

2-3 Anaerobiosis

It has been commonly held that the return of sludge from the secondary clarifier should be as rapid as possible because of the detrimental effects

of the anaerobic holding time. However, the possibility of system improvement using anaerobic tanks has been, and is being, explored.

The most common problem inherent with anaerobiosis is that of floating sludge in the clarifier. This rising sludge, caused by reduction of nitrates and organic carbon to gaseous nitrogen and carbon dioxide has caused the plant operator considerablettrouble. Witcher (16) and Tapelstay (17) stated that settled sludge should be returned to the aeration tank as soon as possible, as the stale sludge would exert a higher oxygen demand when returned, and sludge floating problems would persist.

Wurhmann (18) measured respiration rates of washed activated sludge before and after an anaerobic period of 4.5 hours. He noted no significant change in either the fed or unfed respiration rates. As he had previously shown the utilization of organic matter by microorganisms is related to the respiration rate, he concluded that defined periods of anaerobiosis had little effect on the purification capacity of the sludges.

Westgarth (19) substantiated Wurhmann's conclusions by conducting pilot plant studies and comparing the results. Two identical pilot plants were operated in parallel, one of which was kept aerobic at all times and the other had an unaerated holding tank incorporated within. Westgarth concluded that periods of anaerobiosis up to ten hours were not determental to the overall activated sludge operation. The respiration rates remained relatively unaffected and the organic removal efficiencies did not deteriorate. The oxygen demand in the aeration tank for low-rate and conventional

loadings was also unchanged. He explained this phenomenon as follows: At the low-rate loading, the microorganisms were in the endogenous phase and during anaerobic conditions, little or no breakdown of the organic material was taking place. Upon returning to aerobic conditions, they simply began to respire at the same endogenous rate. Some decomposition of the complex organic matter took place at the conventional loading, leading to certain hydrolysis and fermentation products. When aerobic conditions were restored, there was an excess accumulation of oxidizable fermentation products. This excess was in turn balanced by the loss of cellular activity. At high loading conditions, this excess of oxidizable material more than offset the reduced activity of the microorganisms and, in fact, resulted in a higher oxygen demand when returned to the aeration chamber.

Westgarth also observed that the high rate process in combination with an anaerobic sludge return period produced only about half as much sludge as that normally produced. He introduced the possibility of alleviating sludge disposal problems encountered in high rate treatment plants by using the indicated modification of partial anaerobic decomposition.

Clesceri (20) studied some of the factors involved in the selection of rapidly settling mixed cultures as employed in the activated sludge process. She concluded that either a periodic supply of a readily available substrate or a constant supply of a relatively unavailable substrate would select rapidly settling cultures that are free of filamentous organisms. She further hypothesized that at high oxygen levels, starvation for some nutrient (

(presumably carbon) was a necessary prerequisite for flocculent nonfilamentous growth. It was also observed that better floculation and settling occurred when a 2 to 4 hour period of anaerobiosis was incorporated into the continuous fermentation system of high oxygen tension. This would lead one to conclude that some of the more filamentous aerobes, i.e. <u>Geotrichum candidum as isolated by Jones (10) are inhibited during anaerobic</u> periods. Both Clesceri and Wurhmann observed, however, that most filamentous organisms have the capacity to maintain their viability during short periods of residence in a food and oxygen deficient environment. The fact that a readily available substrate produced filamentous forms both with and without anaerobic holding times led her to conclude that the formation of filaments is a nutritional effect rather than the effect of the oxygen level.

McClellan (21) noted several effects of anaerobiosis in the activated sludge process. Contrary to Westgarth, he determined that oxygen utilized by endogenously respiring sludge following anaerobic storage was significantly greater than that utilized by aerobically stored sludge. He found that this difference was minimized if the sludge was fed immediately following storage. He agreed with previous investigators that the subsequent removal of organic matter was independent of the type of storage (aerobic or anaerobic) and the length of storage up to six hours.

2-4 Sludge Activity

Sludge activity, the amount of bio-oxidation taking place, can be measured in a variety of ways. Oxygen utilization rates of a system are a

valid indicator. The volatile solids buildup and BOD removal is indicative of the magnitude of microbial respiration and systhesis. More recently, a measurement of dehydrogenase activities has been used to evaluate sludge activity.

The oxygen utilization rate may be defined as the weight of oxygen consumed by a given weight of sludge per unit of time. Oxygen uptake rates are measured by manometric techniques, off-gas analyses, polarographic methods, or by the more recently developed galvanic cell procedure. Mancy and Westgarth (22) developed the oxygen analyzer which employs a galvanic couple to measure oxygen activity. Wood (23) compared oxygen uptake rates using the analyzer and the Warburg respirometer (at 135 oscillations per minute) and found the results to be quite comparable. Specific oxygen uptake rates (mg $0_2/hr/gm$ sludge) have been reported as 1.5 to 9.8 for endogenous sludges and 10 to 76 for active sludges (5). Once the range of values is established for a given sludge, the relative activity for a given condition can be determined.

An increase in volatile sludge concentration accompanied by a decrease in BOD is also indicative of the sludge performance. There can be no cellular increase without BOD removal and the two are both dependent on the microorganisms' ability to utilize the existing substrate for synthesis and respiration.

In biochemical metabolic pathways, organic compounds are broken down through a series of dehydrogenations. The activity of the various

dehydrogenases is therefore a good measurement of microbial activity. These enzymes can easily be measured by using a tetrazolium salt (triphenyltetrazolium chloride, or T. T. C.) as the hydrogen acceptor. This couples the oxidation of the substrate to the reduction of the colorless salt and is illustrated as follows:

TTCH₂ (TF) (RED) +2H ORGANIC MATERIAL OXIDIZED ORGANI MATERIAL MICROORGANISMS DEHYDROGENASES TTC (COLORLESS)

Figure 2-1

Transfer Mechanism

The intensity of the red color, characteristic of the reduced form (triphenyl formazan, or T.F.) can then be taken as a measure of dehydrogenase activity. The dehydrogenase enzyme evaluation as a method for determining sludge activity was first introduced by Lenhard and Nourse (24) and Bucksteeg and Thiele (25). Using this preliminary work as a reference, Ford and Eckenfelder (26) modified and expanded the application of this approach on a laboratory and plant scale basis. By analyzing laboratory and field data, they concluded that an excellent correlation of oxygen uptake and dehydrogenase activity did exist, giving credibility to the dehydrogenase measurement as a true indicator of sludge activity. They further confirmed the cellular dehydrogenase activity association with the growth phase of the microbial population (27), and proposed correction factors for varying pH and temperature values.

2-5 Review of Wastewaters

(a) <u>Brewery Wastewater Treatment</u> Brewery wastes are most successfully treated by biological methods and such brewery waste treatment plants have been built in many locations. All soluble waste products can readily be assimilated biologically. The main problems associated with treatment are therefore nutritional and environmental in nature.

In the production of beer, an extract of a malt and malt adjunct mixture is boiled in the presence of hops. The resultant "wort" is then filtered to remove the spent hops and cooled. Brewers yeast is added and the "wort" fermented at controlled low temperatures. The freshly fermented product is aged, stabilized, filtered, and carbonated. The final processing step is packaging in cans and barrels, or in bottles cleaned and sterilized in hot caustic solutions. It has been estimated that the production of 1 bbl. of beer results in 13 bbls. of wastewater. The nature of this waste will depend to some extent on the quality of water used and the in-plant process of the particular brewery. The waste sources and approximate compositions have been estimated as follows (35):

Table 2-2

	Source	Composition	Relative Amt. (%)
1.	Fermentation tanks and finishing cellars	water with dead yeasts, coagulated protein	50
2.	Bottling Operation	rinse water, polyphosphate	es 35
3.	Sanitary and Misc.		8
4.	Coolers	water, NaOH, hop resins	5
5.	Hop Separator	spent hops, sugars	1
6.	Lauter Tanks	wash waters	1
	Total		100

Brewery Waste - Source and Composition

The characteristics of a typical brewery waste as compared with domestic sewage are given in the following table (36):

Table 2-3

Comparison of Brewery and Domestic Wastewater Characteristics

	Brewery Waste	Domestic Sewage
5 Day BOD (ppm)	2,170	292
Total Nitrogen (ppm).	29	32.4
Organic Nitrogen (ppm)	27.6	113.7
Total Phosphorus (ppm)	7.0	5.6
Soluble Phosphorus (ppm)	2.9	4.4
рН	varies with source	6 - 9
Ratio, BOD/N	75	9
Ratio, BOD/P	310	52

The BOD/N and BOD/P ratios exceed the recommended value of 20 and 100 respectively, indicating a nutritional deficiency. A readily available source of nitrogen and phosphorus is therefore required in most biological waste treatment systems, depending on the value of this ratio.

Brewing companies have successfully used the activated sludge and trickling filter forms of bio-treatment. Many of the solids - disposal problems have been minimized by the product - recovery policy of most breweries. These include the recovery of the spent grains and hops, spent yeasts, and precipitated proteinaceous materials. Successful plant operation is therefore dependent on control of the nutritional and environmental aspects in the biological treatment of the soluble fraction. (29) (b) <u>Petrochemical Wastewater Treatment</u> The petrochemical industry applies processes that use previously unreacted hydrocarbons from oil and gas by physical separation methods, equivalent hydrocarbons produced by chemical reactions, or their impurities to produce new chemicals (30). These chemicals are used in the produced form or they may be reacted further to make related chemicals. The wastewaters contain myriad hydrocarbon contaminants, the exact composition depending upon the plant processes. In addition to these, a significant portion of the wastewater is composed of non-hydrocarbon contaminants (31) such as:

Table 2-4

Non-hydrocarbon	Petrochemical	Wastewater	Contaminants

From Process	From Utilities
$ m Gases~(CO_2,~CO,~H_2S,~NH_3,~N_2,~H_2)$	Boiler blowdown - phosphates, ligins, etc.
Spent caustic (sulfides, mercaptans, etc.)	
Acids and acid sludges	Cooling system blowdown - (heat, chromates, phosphates, etc.)
Spent catalysts(containing iron, nickle, etc.)	
Filter aids	Water treatment blowdown - calcium, magnesium, chlorides
Solvents and absorbents (furfural, phenols,	
etc.)	Oil and grease
Spent lime	Sanitary and Misc.

Generally, wastes of the manufacturing process can be categorized into four pollutional groups: toxic, high level, medium, and low level. The characteristics are given in the following table:

Table 2-5

Manufacturing Process Wastewaters - Poll	lutional	Catagorie	÷s
--	----------	-----------	----

Quality	Toxic	High Level	Medium	Low Level
COD (ppm)	1,800,000 (theoretical)	12,000	1,500	700
BOD (ppm)	-	8	1,300	600
Total Organic N ₂ (ppm)	250,000 (theoretical)	3,500(-	89
pH	6.0	5.4	5.0	7.5
Oil	0	150	500	varies
Phenol	0	850	65	7
Sulfides	q	0	5	2
Total Alkalinity as CaCO3-ppm	0	2,000	æ	100
Sulfates (ppm)	0	1, 800	0	0
Color	clear	coffee brown	white	light t a n
Odor	cyanide	phenolic	aromatic	sweet, oily

Biological treatment of petrochemical wastes can be accomplished if appropriate in-plant control measures are taken to eliminate the excessive solids, neutralize the wastes, and stabilize the flow of the waste stream. Normally, only diffuse and selected microorganisms prevail, but they have a sufficient bio-oxidation capacity provided environmental conditions are favorable and acclimation procedures are employed. (c) <u>Domestic Wastewaters</u> Activated sludge treatment of domestic wastewaters has been the subject of many investigations and will be only briefly mentioned. here. The characters of such wastes are highly variable in composition and concentration with typical values given in Table 2-3. These wastes normally contain no toxic or inhibiting substances and nutrients are in abundant supply. Because of the very nature of the fluctuating waste load, municipal plants are generally more difficult to control than properly designed industrial treatment facilities.
Chapter 3

EQUIPMENT AND EXPERIMENTAL PROCEDURES

3-1 Sampling Procedures

A domestic sewage and two industrial wastewaters were brought into the laboratory and fed to the laboratory-scale continuous units. These wastewaters were transported in fifty-five gallon drums and were cooled to 4°C until used. COD values were determined at the sampling point and at the point of discharge into the continuous units. The difference indicated the amount of COD reduction caused by air stripping and/or biological oxidation during transport.

(a) <u>Brewery Waste</u> The brewery waste was pumped from a collection manhole at the plant site, transported 85 miles to the laboratory, and immediately cooled to 4^oC. The sampling point, as shown in the following diagram, was selected to minimize the sanitary sewage contribution.





The sampling was performed at the same time each selected day in order to maintain uniformity in waste composition. The average COD of the raw waste during a seven month sampling period was 650 mg/l with a standard deviation of 96 mg/l (Coefficient of Variation = 14.7%). The COD reduction during transport never exceeded 8% of the original value. The brewery waste sampling process is shown in Figure 3-2.



Figure 3-2

Brewery Waste Sampling Procedure

(b) <u>Petrochemical Waste</u> The petrochemical wastewater was shipped from the Houston, Texas, area to the Austin laboratories in 55 gallon drums. The petrochemical waste was being deposited into an existing aerated lagoon by three different feeder lines, as shown in Figure 3-3. Each of the three waste portions was put into an individual container and proportionately mixed in the laboratory. These waste constituents are listed as follows:

Table 3-1

Petrochemical Waste Constituents

Waste Portion	pH	COD	‰ o f Total Flow
Maleic Acid	1.4	30,000 - 36,000	2.4
	6.8	1,100	69.0
Scrubber Waste	6.5	5,500	<u>28.6</u> 100.0

Because of the plant processes and the feeder piping arrangement, there was little fluctuation in the raw waste composition. The average COD during a four month testing period was 2,970 mg/l with a standard deviation of 99 mg/l (Coefficient of Variation = 3.3%). Each of the separate wastes was biologically sterile, and only negligible stripping was noted during transport. The petrochemical plant and aerated lagoon are shown in Figure 3-4 with the petrochemical waste sampling procedure being shown in Figure 3-5.





Feeder Line Diagram to Existing Aerated Lagoon (Courtesy of Petro-Tex Chemical Corp.)



Figure 3-4

Petrochemical Plant and Aerated Lagoon





Petrochemical Waste Sampling Procedure

(c) <u>Domestic Waste</u> Samples of domestic sewage were collected each day at the Austin, Texas, Govalle Plant. The sewage was brought into the laboratory and immediately fed to the continuous units from a refrigerator. This procedure resulted in a fresh waste supply to each of the units. The average COD during the two week sampling period was 245 mg/l with a standard deviation of 49 mg/l (Coefficient of Variation = 20%).

3-2 Aeration Units - Design and Methodology

Plexiglass units were constructed and mounted on portable tables. Two different schemes for activated sludge units were employed in this study. The first provided a separate calibrated settling chamber with sludge being continuously recycled to the aeration unit (Figure 3-6).



Figure 3-6

Laboratory Activated Sludge Units - Separate Settling

The fixed overflow weir set the volume of the aeration tank (Figure 3-6, A) at 9.6 liters which required a feed rate of 10 to 40 liters per day to obtain conventional detention times. An independent sigma-pump was used to recycle settled sludge from the clarifier (Figure 3-6, B) and provided a versatile operation by allowing a wide recycle ratio operating range. This particular scheme was primarily applicable to conventional treatment studies at relatively low loadings.

The second type of continuous treatment model combines aeration and settling compartments in a single unit using a baffle separator. Six of these units were operated in parallel, each being subjected to different organic loadings (Figure 3-7). An adjustable overflow weir was employed, providing an aeration volume range of 3 to 8 liters.

The air supply came from a 14-psi wall source outlet, then was presaturated with water before going to the individual diffusers in order to minimize evaporation. The flow rates were measured by observing the effluent bottle levels (Figure 3-7, A) at various times. Evaporation losses were determined to be negligible. The operating temperature of the systems was maintained at 23°C and the pH was continuously monitored.

Three sigma-pumps were used to feed the raw waste, each pump serving two units. Different flow rates from one pump could be established by using different tube sizes or partially clamping one of the feed lines. The flow rates varied from 2 liters/day to 20 liters/day, depending on the desired loading factor. All suspended material was removed from each of the wastes prior to use. The substrate was pumped from a feed bottle stored in a refregerator (Figure 3-7,, B) if the waste was not sterile, or pumped from an unrefrigerated supply (Figure 3-7, C) when a sterile substrate was used. The complete flow diagram is shown in Figure 3-8)



Figure 3-7

Laboratory Activated Sludge Units - Combined Settling and Aeration



Figure 3-8

(a) Detention Time Determination by Radioisotope Methodology

The mean flowthrough time of the continuous units was determined by use of a 134 Cs tracer. 134 Cs is a high energy beta emitter with a radioactive half life of 2.3 years.

The unit overflow weir was set for an aeration volume of four liters and a settling volume of one liter. 4.7 liters of distilled water were added and then dosed with 0.3 liters of the ¹³⁴Cs solution. The strength of the solution was calculated to give approximately 40,000 counts per minute when diluted to 5 liters. Distilled water was pumped to the unit at a rate of 18.0 liters per day, giving a theoretical detention time of 5.35 hours. Using the Sharp Low Beta counter, the activities (cpm/ml) of the aeration tank contents and the final effluent were determined, using duplicate samples. The activity at various times following the initial ¹³⁴Cs addition is shown in Figure 3-9. As can be seen from the plot, the residence time in the settling compartment was about 30 minutes at 18 liters/day. The mean aeration residence time was taken as the centroid of the area under the decay curve and was determined as follows:

(a) Graphical Integration

The planimetered area under the curve was 204,000 cpm \cdot hours

$$T_d = \frac{204,000 \text{ cpm hr}}{36,000 \text{ cpm}} = \frac{5.66 \text{ hrs}}{5.66 \text{ hrs}}$$

(b) Mathmatical Integration

(1) $\frac{dA}{dA}$	=	-CQ		
dt				C = concentration cpm/ml
		Δ		Q = flow rate 1/day
С		$\frac{\Lambda}{V}$		A = activity counts/minute
7.6		v	DI	t = time V = volume
<u>dA</u>	=	+ V _		v - volume
dt			ατ	
- CO	=	v	dC	
- UQ		v	dt	

(2) Rearranging and integrating:

$$-t = \frac{V}{Q} \quad \ln C + K$$
$$-t = \frac{V}{Q} \quad \ln \frac{C}{C_0}$$
$$or C = A = e^{-Q/v(t)}$$

(first order relationship as shown in Figure 3-10)

(3) Average detention time: A

$$T_{d} = \frac{\sum \Delta \cdot At}{\sum \Delta \cdot A} = \frac{0 \int_{A_{o}}^{A_{o}} \frac{t(dA)}{dA}}{\int_{A_{o}}^{A_{o}} \frac{dA}{dA}} = \frac{0 \int_{A_{o}}^{A_{o}} \frac{t \cdot d(A_{o}e^{-Q/V(t)})}{\int_{A_{o}}^{A_{o}} \frac{dA}{dA}}$$

or
$$T_{d} = \frac{0 \int_{A_{o}}^{A_{o}} \frac{t^{O}}{(-Q/V(A_{o})(e^{-Q/V(t)})}}{\int_{A_{o}}^{A_{o}} \frac{dA}{dA}}$$
$$= \frac{-Q/V(A_{o}) \int_{A_{o}}^{A_{o}} \frac{t \cdot e^{-Q/V(t)}}{dt}}{\int_{A_{o}}^{A_{o}} \frac{dA}{dA}}$$

(4) Changing the limits of integration: $t = 0 \text{ at } A = A_0$ $t = \infty \text{ at } A = 0$

$$T_{d} = \frac{-Q/V(A_{o})}{A_{o}} \int_{t-e}^{0} \frac{-Q/V(t)}{dt}$$

and integrating: CRC Handbook Integral No. 353

$$T_{d} = -Q/V(A_{0}) \left[\frac{e^{-Q/V(t)}}{(Q/V)^{2}} (-Q/V(t) - 1) \right]_{0}^{\infty}$$

or $T_{d} = V/Q \left[e^{-Q/V(t)}(Q/v(t) + 1) \right]_{0}^{\infty}$
-Q/V = K where K is the slope of the line in Figure 3-10
Simplifying between the practical limits of t = 0 and t = 24

$$T_{d} = \frac{1}{K} \left[e^{-Kt}(Kt + 1) \right]_{0}^{24}$$

= 5.87(1.0 - e^{-4.1})
= 5.87(1.0 - .085) = 5.45 hours

This value was used to apply a slight correction factor to the theoretical detention times in computing the loading factors. The theoretical and calculated detention times were practically the same, indicating the system was essentially completely mixed.



Figure 3-9





Figure 3-10

Constant Determination

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3-3 Technicon Autoanalyzer Application

The Technicon Autoanalyzer was used to automate the chemical analyses of COD, dehydrogenase enzyme (T. T. C.), and nitrogen. The values obtained from the automated system were continually verified using manual chemical methods. When the correlation between the methods was poor, only the results obtained from the manual analysis were used. The Autoanalyzer is shown in Figure 3-11.



Figure 3-11

Technicon Autoanalyzer

Manifolds consisting of the proper reagent and mixing lines were constructed for each of the tests, using calibration techniques as recommended by the manufacturer. The manifold schematics for COD and nitrogen analyses are shown in the following figures.



Figure 3-12

Automated COD Manifold





Automated Nitrate - Nitrogen Manifold



Figure 3-14

Automated Kjeldahl Nitrogen Manifold

The dehydrogenase enzyme test was automated for application in the continuous monitoring of sludge activity. The color development (using the T. T. C. test procedure as discussed in Chapter 5) was measured and recorded, giving relative activity values. It was necessary to blank out the natural color by determining the per cent transmission of the sample with and without the color-forming reagents. This automated technique is not practical for measuring individual samples, and should only be used for monitoring purposes. A pictorial and diagrammatic representation of the proposed dehydrogenase enzyme manifold is shown in Figures 3-15 and 3-16.



Figure 3-15

Proposed Dehydrogenase Enzyme Manifold (T.T.C.)



Figure 3-16

Proposed T.T.C. Manifold for Continuous Monitoring

3-4 Sharp's LowBeta Counter

The Sharp's LowBeta Counter was used to measure beta radiation activity in the lab unit detention time experiment. The counter has two window (800 micro-grams/cm²) gas flow detectors which are incorporated in a single heavy shield essentially to eliminate background from environmental radiation. The resolving time of the counting circuits is electronically set at 300 microseconds. This limits the maximum counting rate to approximately 10^5 counts per minute. The sensitivity of the counter is greater than 99% for alpha and beta particles passing the window.

3-5 Beckman Model DB Spectrophotometer

Colorimetric determinations of dehydrogenase enzyme activity and phosphate concentration were made using the Model DB ultraviolet spectrophotometer. This model is a double-beam instrument measuring transmittance and absorbance in the 205 to 770 mµ wavelength range. The double-beam system allows direct differential transmission comparison between the sample and blank.

3-6 Beckman Zeromatic pH - ORP Meter

The Beckman Zeromatic II was used to determine system pH and ORP values. The instrument has a pH range of 0 to 14 pH and a millivolt range of 0 to \pm 1400 mv. The instrument was calibrated prior to use. The pH was set using a known buffer and checking reproducibility. The reliability of ORP values was established by noting any variation in the difference between observed and calculated millivolt readings.

3-7 Optical Microscopy

Slide preparations using the Gram stain were made of each of the wastes at the various loadings. Optical photomicrographs were taken on a Leitz "Ortholux" microscope and Leitz "Orthomat" microscopic 35 mm camera arrangement. The microscope had a built-in illuminating system with a low voltage filament bulb, blue filter, and ground glass screen for transmitted or incident light. Ektachrome film EX 135-20 with an ASA rating of 25 was used. The magnification of all photomicrographs taken with the optical camera was 1200 X.

3-8 Electron Microscopy

Electron photomicrographs were taken using an RCA E. M. U. 3-G Electron Microscope operating at 100 KV. The microbial population under study was prepared in the following manner:

- 1. 2-1/2% glutaraldehyde buffered at pH6 with veronal acetate buffer was added to the centrifuged cellular mass and allowed to stand for two hours at room temperature
- 2. The sample was rinsed in a buffer solution.
- 3. A 1% osmium solution was added and the resulting mixture allowed to stand for one hour at room temperature and four hours at 4° C.
- 4. The sample was rinsed in a buffer solution.
- 5. A 5% uranyl acetate solution was added and the sample was allowed to stand for 6 hours at 4°C.
- The sample was rinsed in distilled water and put through an alcohol series of 25%, 50%, 70%, 90%, 95%, and 100% alcohol (15 minutes each).

7. The sample was put through an alcohol-acetone series of:

33% Acetone	67% Alcohol	5 minutes
67% Acetone	33% Alcohol	5 minutes
100% Acetone	0% Alcohol	5 minutes

8. The sample was embedded by using an acetone-plastic series of:

33% plastic	67% Acetone	30 minutes
67% plastic	33% Acetone	30 minutes
100% plastic	0% Acetone	30 minutes

9. The embedded sample was put into a 60°C oven overnight.

. ,

- 10. The sample was sectioned on an M. T. -1 microtome and placed on 300-mesh grids.
- 11. The sections were stained for 2 minutes with Reynold's lead citrate.
- 12. The sections were ready for electron microscope examination.

Chapter 4

LABORATORY ANALYSES

- 4-1 Chemical Oxygen Demand

The chemical oxygen demand (COD) was used to measure the portion of organic matter in the sample susceptible to oxidation by potassium dichromate. The procedure used was that as outlined in <u>Standard Methods</u> (32). Mercuric sulfate was added to complex any chlorides that may have been present in order to eliminate the need for a chloride correction factor. Because of the testing simplicity and time involved, COD's were used extensively in evaluating raw waste and effluent quality. Chemical oxygen demand tests were made only on filtered samples because relative differences in soluble COD were desired.

4-2 Biochemical Oxygen Demand

The biochemical oxygen demand (BOD) of each waste used in this study was determined by the dilution technique in accordance with <u>Standard Methods</u> (32). This was considered necessary in order to determine exactly what portion of the COD was amenable to bio-oxidation. Acclimated microorganisms were used as seed in the BOD tests.

4-3 Solids Determinations

The mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were measured in each of the continuous units. This was done by stoppering the overflow weir, raising the baffle for complete tank mixing, and withdrawing the sample. The net sludge increase from synthesis was wasted as required in order to maintain a constant loading factor. Only settled wastes were fed to the units and the MLVSS/MLSS ratio was therefore relatively unchanged. The average ratios for the wastes under study are listed as follows:

Waste	MLVSS/MLSS Ratio
Domestic	. 78
Brewery	. 82
Petrochemical	. 90

4-4 Sludge Settling Characteristics

The settleability of the activated sludge mixed liquor under various loading conditions was evaluated by determining the zone settling velocity and the sludge volume index.(32). A graduated cylinder with a stirring mechanism rotating at 12 rph was used in the zone settling velocity studies. This apparatus is shown in Figure 4-1. 1,000 ml of mixed liquor was taken from the respective units once the system had stabilized and poured into the cylinder. The rotating mechanism was connected, and the sludge - liquid interface level was recorded at various time intervals. The solids level (MLSS) was adjusted to the same value in all cases in order to obtain a strict comparison of the sludge settleabilities for the different organic loadings.



Figure 4-1

Apparatus for Determining Sludge Settleability

Stirred sludges which have been allowed to settle for 30 minutes are shown in cylinders A and B. The bulky sludge in B was taken from an overloaded unit, while the sludge in A was from a low loading situation and settled rapidly. The sludge in cylinder C is the same as that in A but was unstirred and was used for sludge volume index (SVI) determinations. As can be seen in the above figure, the unstirred, 30-minute settled sludge occupied about 1.3 times the volume of the stirred sludge.

4-5 Oxygen Uptake

A Precision Galvanic Cell Oxygen Analyzer was used to determine oxygen uptake rates. The probe was calibrated daily using the Winkler Method to insure reliability. A BOD bottle was filled with mixed liquor from a particular unit. The probe was then inserted into the bottle as shown in Figure 4-2.



Figure 4-2

Oxygen Uptake Analysis Using the Galvanic Cell

The displaced liquid overflowed, preventing the accumulation of air bubbles inside the bottle. The contents were mixed using a magnetic stirring rod. The depletion of dissolved oxygen was plotted against time and the slope of the line was taken as the true oxygen uptake rate (mg oxygen/liter/minute). The probe was cleaned and the membrane replaced each week. Dissolved oxygen levels in all units never fell below 2 mg/l. The air flow was set to maintain an adequate dissolved oxygen level, but was never raised to a point where the floc was broken up as a result of overagitation.

4-6 Dehydrogenase Enzyme Activity Using T. T. C.

The bio-oxidative activity of the various sludges was measured by oxygen uptake rate evaluation and dehydrogenase enzyme activity. The dehydrogenase enzyme test using triphenyltertrazolium chloride (T. T. C.) as first proposed by Lenhard and Nourse (24) and modified by Ford and Eckenfelder (26) is as follows:

- A. REAGENTS
 - 1. Tri-HCl Buffer, .05M pH 8.4

Add 6.037 grams of tris-buffer and 20 ml 1.0 N HCl to one liter of distilled water.

2. T.T.C. -Glucose Reagent

Dissolve 0.2 grams T. T. C. and 1.50 grams of anhydrous glucose in 100 ml distilled water. Store the solution in the dark at 2°C and make up fresh weekly.

- 3. Absolute Ethyl Alcohol
- 4. Tri phenylformazan (T.F.) Standard

Dissolve 0.300 grams of triphenylformazan (molecular wt. = 300.4) in 500 ml of ethyl alcohol. 1, 2, 3, 4, and 5 ml samples of this solution are diluted to 50 ml with ethyl alcohol to give standard solutions containing 2.0, 4.0, 6.0, 8.0, and 10.0 micromoles (\measuredangle m) of T.F. per 50 ml. The standard curve using this method is given as follows: (the slope of the line may vary slightly with the spectrophotometer).



Figure 4-3

Standard Light Transmission Curve for Triphenylformazan Production

- B. PROCEDURE
 - 1. Add 5 ml of tris-buffer to each of four test tubes (50 ml capacity or greater) for each desired test sample.
 - 2. Add 5 ml of the test activated sludge mixed liquor of known volatile solids concentration to each of the four test tubes.
 - 3. Place in hot tap water bath and bring the temperature of the solution (buffer and mixed liquor) to 37°C, rapidly as possible.
 - 4. Add 1 ml of distilled water to the control test tube and 1.0 ml of T.T.C. reagent to each of the three remaining test tubes.
 - 5. Maintain the solution at 37°C in a water bath or in an incubator for exactly 15 minutes following T. T. C. innoculation.

- 6. At the end of the 15 minute incubation period, stop the reaction by adding ethyl alcohol to a final volume of 50 ml in each of the 4 test tubes.
- 7. Shake each tube, filter, and measure the filtrate % transmission at a wavelength of 490 m μ using the control solution as a blank and the average % transmission of the 3 samples as the true value.
- 8. Take the average % transmission, enter on the standard curve, and determine the \mathcal{U} -moles of triphenylformazan produced. This value indicates the relative dehydrogenase activity.

Several precautions concerning the test procedure should be mentioned. It is important to bring the test solution to exactly $37^{\circ}C$ (Step 3) before inoculating with T. T. C. as the reaction is temperature dependent. The reaction should be stopped exactly 15 minutes after incubation (Step 6) as any deviation from this incubation time will give erroneous results. The time lapse after a five-minute minimum between Step 6 and Step 7 is not important as tests have indicated that the per cent transmission does not change once the reaction has been stopped by alcohol addition. If the percent transmission readings are too low because of an inactive sludge, or a low MLSS concentration or both, a larger volume of test mixed liquor can be used as long as the same volume is used throughout the testing period (Step?2).

The pH of the test solution will be approximately 8.4 if the buffer is prepared in accordance with the aforementioned procedure. The approximate pH relationship within the pH 7-pH 9 range is $(\underline{T}, \underline{F}, \underline{produced})_1 = (\underline{pH})_1^{3.1}$ $\overline{T}, \overline{F}, \underline{produced}_2^{3.1}$

It is preferable to carry out the reaction as close to pH 8.4 as possible and mandatory to stay within the pH 7 - pH 9 limits.

The dehydrogenase activity and consequent T. T. C. reduction increases with increasing temperature up to $40^{\circ}C(24)$. If the test is carried out at 37°C, or all tests are carried out at the same temperature, no temperature correction is necessary. The testing should never be made outside the $20^{\circ}C - 40^{\circ}C$ range. The ratio of micromoles of T. F. produced at temperature, T, to micromoles of T. F. produced at 20°C as a function of temperature is shown in Figure 4-4. Based on this plot, the temperature correction factor within the 20°C - $40^{\circ}C$ limit is:



Temperature Effect on T.F. Production

Excess amounts of the T.T.C. salt and glucose were added to the reagent solution to insure that the substrate and the hydrogen acceptor were not the limiting factors. It is probable that the principle reaction being measured is the glucose dehydrogenase activity of the sludge, although endogenous substrates could make some contribution. The important thing is the fact that the amount of T.T.C. reduced is an indicator of relative activity and correlates with the microbial respiration rate.

If the dehydrogenase activity of the cell represents the true sludge activity, a direct relationship between the microbial respiration rate and the associated enzymatic activity should exist. This should be true irrespective of the substrate serving as the hydrogen donor in an aerobic system. As can be seen in Figure 4-5, the two agree quite well.



T.F. Production and Oxygen Uptake at Various Aeration Periods

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It was previously observed that the cellular dehydrogenase activity was directly associated with the cell growth phase (34). This association of the dehydrogenase activity with cellular growth for a young sludge and an older sludge is shown in Figure 4-6.



Growth Phase Relationship

The young sludge had a higher initial specific activity than the 24 hour sludge when contacted with a brewery waste, indicating a partial enzyme inactivation with overstabilization. Once contacted with the waste, the young sludge was able to respond to the substrate with the production of various dehydrogenase enzymes. This initial increase in specific activity seemed to indicate that the waste-induced dehydrogenase activity contributed significantly to the glucose dehydrogenase activity. Once the substrate was limiting, the MLVSS and the specific T.F. (T.T.C.H₂) were proportionately reduced.

4-7 Bound Water

Bound water is defined as that water in the activated sludge floc which is bound by the colloid micelles with different properties from those existing in the free liquid state (14). The dilatometric method was used for measuring bound water in the various flocs (35), (36), (37). This method is based on the theory that bound water does not freeze at temperatures below the free water freezing point. The total water was determined by drying a sample of activated sludge for 12 hours at 103°C and the free water was calculated by noting the expansion caused by freezing the sludge. Based on the aforementioned concept, the following relationship will hold:

Total Water - Free Water = Bound Water

A diagram of the dilatometer used in this experiment is shown in Figure 4-7.



Dilatometer For Bound Water Determination

The laboratory procedure used in this study is as follows:

- 1. A volume of mixed liquor was concentrated to approximately 2% solids and introduced into the bottom section of the dilatometer.
- 2. Petroleum was added up to the zero mark of the calibrated stem, recording the volume required.
- 3. The dilatometer and a "dummy" (a stoppered bottom section of a dilatometer filled with petroleum and containing a thermometer) were immersed in an ethanol solution.
- 4. Dry ice was added, and the glass stem readings at various temperatures were noted. The temperature range was +25°C to ~25°C.
- 5. A standard petroleum curve was plotted in order to determine the contraction expansion characteristics of the petroleum. This was done by filling the dilatometer with a known amount of petroleum and observing the stem level at various temperatures. The same procedure was used for the derivation of the standard petroleum-water curve, except 10 ml. of distilled water were added to the petroleum.

4-8 Acidity

The acidity of the petrochemical industrial waste was evaluated in order to determine the natural buffering capacity of the system. The pH of the raw waste was between 5 and 6, but the bicarbonate salts resulting from microbial respiration were sufficient for neutralization up to a particular acid loading. The acidity was reported as pH 8.3 acidity (mg/l as CaCO₃) in accordance with the <u>Standard Methods procedure</u>.

4-9 Phosphates

Total inorganic phosphate (polyphosphate and orthophosphate) was measured as prescribed in Standard Methods. The Stannous Chloride method was used in the petrochemical waste study, while the aminonaptholsulfonic method of determining inorganic phosphate was used for domestic waste. Organic phosphorus was determined by the dry combustion procedure (38).

4-10 Nitrogen

Ammonia-, organic-, nitrite-, and nitrate-nitrogen values were determined using the Standard Methods procedure and using the automated Autoanalyzer technique. (See Chapter 3, Section 3).

Chapter 5

EXPERIMENTAL RESULTS - BREWERY WASTE

5-1 Acclimation Procedure and Results

The oxygen uptake and COD removal were used to determine the acclimation time required for the brewery waste. Mixed liquor from the Austin Govalle Plant was used as the initial seed. The COD removal and specific oxygen uptake response to continuous brewery waste feeding are



The data (Appendix B) indicated that the acclimation time was approximately 2 days, and experiments were performed on this basis.

5-2 BOD/COD Relationship

Although the COD analysis was primarily used to evaluate the organic strength of the waste, periodic BOD analyses were considered necessary to indicate more accurately the amount of organics which were bio-degradable. A long-term BOD analysis was run, using an acclimated seed in a waste sample exerting a COD of 444 mg/l. As shown in Figure 5-2, the ultimate BOD was 300 mg/l and the average five day BOD was 270 mg/l.





The BOD/COD ratio of 0.6 indicated the presence of dichromate oxidizable materials which were non-biodegradable.

5-3 Anaerobic Study

The effect of anaerobiosis on the settling characteristics of the sludge and nature of the microbial population were studied. The related effects on oxygen uptake and COD removal efficiency were also considered. The entire contents of a continuous unit were put into a stirred, oxygen-free carboy. After various anaerobic holding times, one liter was withdrawn, transferred to a batch unit, and fed with 500 ml of brewery waste. The mixed contents were then aerated for a period of six hours. The results of this particular study follow:

(a) <u>Effect on Oxygen Uptake</u> - Oxygen uptake rates were determined after 15 minutes and again after 6 hours aeration following various anaerobic times. The results, as shown in Figure 5-3 indicate that on a batch basis, only prolonged periods of anaerobiosis (40 hours or longer) have a negatory effect on active uptake rates.

(b) <u>Effect on COD Removal Efficiency</u> - The COD removal for 6 hours of aeration did not change significantly, even with a sludge subjected to a 72-hour anaerobic period. This indicated that the population change in response to the anaerobic environment did not affect the overall assimilative capacity.


Figure 5-3

Effect of Anaerobiosis on Oxygen Uptake and COD Removal

(c) <u>Effect on Settling Characteristics</u> Settling characteristics of the various sludges were determined using the stirred columns as shown in Figure 4-1, Chapter 4. The settling curves of the sludge before and after six hours of aeration are plotted in Figure 5-4.



Figure 5-4



Zone Settling Velocities at Various Anaerobic Times

The zone settling velocities were calculated from the settling curves and plotted in Figure 5-5. It is observed that the aeration period serves to improve the sludge settleability. This can be attributed to (1) the breaking up of entangled decomposed filaments and (2) providing a more healthy environment for floc-forming bacteria.

(d) <u>Photomicrographs</u> A representative photomicrograph of a bulky sludge from an overloaded unit is shown in Figure 5-6(a). The same population following a 48-hour anaerobic period before and after six hours of aeration is shown in Figure 5-6(b) and (c), respectively.



Figure 5-6 (a)

Population before Anaerobiosis





Figure 5-6 (b) Population after 48 Hours Anaerobic Time

Figure 5-6 (c)

Population after 48 Hours Anaerobic Time and 6 Hours Aeration Time

The larger filamentous forms appeared to have been broken up as a result of the anaerobic environment, as indicated by the settling curves. The presence of certain filamentous forms are still noted in Figure 5-6 (c), however.

5-4 Variable Loading Analyses

Both types of Activated Sludge units (Figures 3-6 and 3-7, Chapter 3) were used in studying the effects of various loadings on the sludge characteristics. Daily checks on (a) flow rates, (b) solid levels, (c) oxygen uptake, (d) dehydrogenase enzyme activity, and (e) COD removals were made to provide a continuous evaluation and control of each loading system. An approximate steady-state condition could likewise be assumed when the fluctuation of these parameters was minimal. Once this condition was obtained, the loading run was terminated by additionally evaluating the settling characteristics and the general microbial morphology.

(a) <u>Loading Factor Control</u> The separate settling and recycle treatment scheme was used for the lower loadings and is diagrammatically illustrated as follows:



Separate Settling and Recycle Unit

This unit was in operation approximately one week at each of the loading levels. It was impractical to use this unit for a higher loading condition, so the type of unit combining aeration and settling compartments was used (Figure 3-7, Chapter 3). The loading factor (L_f) of each unit was held as constant as possible by wasting an equivalent amount of synthesized sludge daily, controlling the flow rate, and using consistent raw waste sampling techniques. The loading factor control data are itemized in Tables B-6 and B-7, Appendix B.

(b) Oxygen Uptake, Dehydrogenase Enzyme Activity, and Removal

<u>Response</u> The response of the aforementioned parameters to the various loadings is depicted in Figure 5-8. The average oxygen uptake increased with loading, while the dehydrogenase enzyme activity followed the same

general pattern. As noted, the enzyme activity and oxygen uptake correlation appears to be good, confirming the earlier work of Ford, Yang and Eckenfelder (26).

(c) <u>Settling Curves</u> The sludge settleability was evaluated at the end of each loading run by noting the sludge-liquid interface location at various times. Stirred columns were used in this study while unstirred columns were used to determine sludge volume index (SVI). The zone settling velocities were computed by extending a tangent to the time scale and taking the slope as the settling rate in ft/hr (Figure B-3, Appendix B).

The weekly averages of these parameters are summarized in the following table and plotted in Figure 5-9.

Table 5-1

Avg. Loading Factor L_{f}' Avg. (Oxygen)Avg. T.T.C.Avg. $\%$ COD RemovalZone Settling Velocity (ft/hr)SVIBeaker* Float Time \bigtriangleup ORP** 2 Hours0.3313.0.01888%17.1552 hrs.700.4114.5.0368713.768none600.6914.5.037858.5901 hr 34 min.650.8018.5.032817.6912 hrs. 42 min.1351.1522.0.036763.114012 hrs. 12 hrs.1201.5023.0.030770.2490none135	and the second	and the second					Contractory of the Linear Street States	(D-M10)
0.33 13.0 .018 88% 17.1 55 2 hrs. 70 0.41 14.5 .036 87 13.7 68 none 60 0.69 14.5 .037 85 8.5 90 1 hr 34 min. 65 0.80 18.5 .032 81 7.6 91 2 hrs. 42 min. 135 1.15 22.0 .036 76 3.1 140 12 hrs. 120 1.50 23.0 .030 77 0.2 490 none 135	Avg. Loading Factor L _f '	Avg. Uptake (Oxygen)	Avg. T.T.C.	Avg. % COD Removal	Zone Settling Velocity (ft/hr)	SVI	Beaker [*] Float Time	∆ORP** 2 Hours
0.41 14.5 .036 87 13.7 68 none 60 0.69 14.5 .037 85 8.5 90 1 hr 34 min. 65 0.80 18.5 .032 81 7.6 91 2 hrs. 42 min. 135 1.15 22.0 .036 76 3.1 140 12 hrs. 120 1.50 23.0 .030 77 0.2 490 none 135	0.33	13.0	.018	88%	17.1	55	2 hrs.	70
0.69 14.5 .037 85 8.5 90 1 hr 34 min. 65 0.80 18.5 .032 81 7.6 91 2 hrs. 42 min. 135 1.15 22.0 .036 76 3.1 140 12 hrs. 120 1.50 23.0 .030 77 0.2 490 none 135	0.41	14.5	.036	87	13.7	68	none	60
0.80 18.5 .032 81 7.6 91 2 hrs. 42 min. 135 1.15 22.0 .036 76 3.1 140 12 hrs. 120 1.50 23.0 .030 77 0.2 490 none 135	0,69	14.5	.037	85	8.5	90	1 hr 34 min.	65
1.1522.0.036763.114012 hrs. 1201.5023.0.030770.2490 none135	0.80	18.5	.032	81	7.6	91	2 hrs. 42 min.	135
1.50 23.0 .030 77 0.2 490 none 135	1.15	22.0	.036	76	3.1	140	12 hrs.	120
	1.50	23.0	.030	77	0.2	490	none	135

Average Parameter Values - Brewery Waste

* Indicates time required for 250 ml of the mixed liquor to settle and then float.

** Indicates the change in oxidation-reduction potential with time when 1 liter of the mixed liquor is turned anaerobic.



Figure 5-8

Daily Record of Sludge Activity and COD Removal Efficiency - Brewery Waste



Figure 5-9

Parameter Response to Organic Loading - Brewery Waste

5-5 Photomicrographs

Photomicrographs (1200X) of representative populations responding to the various loadings are shown below:



Figure 5-10 (a) L_f' = 0.11 SVI - 105



Figure 5-10 (b) $L_{f}' = 0.33$ SVI = 55



Figure 5-10 (c) L_f' = 0.80 SVI = 100



Figure 5-10 (d) $L_{f}' = 1.50$ SVI = 490

5-6 Summary

The brewery waste analyses are summarized as follows:

1. The BOD_{ult}/COD ratio of the brewery waste was 0.68, indicating the presence of certain soluble materials which exerted a COD but were non-biodegradable.

2. Prolonged periods of anaerobiosis (24 hours or longer) had a negatory effect on the filamentous microorganisms, although many appeared to have survived. The settleability of this sludge was improved only after prolonged batch anaerobic periods and this improvement was not considered significant. A continuous anaerobic holding tank would have been more realistic, however, in predicting the effect of anaerobiosis in a complete treatment system.

3. The oxygen uptake and COD removal capacity of the microorganisms were not appreciably reduced, even after being subjected to long anaerobic phase times.

4. Oxygen uptake can be correlated to dehydrogenase enzyme activity and the level of both will depend on the organic loading of the system.

5. There is a microbial population response to the level of organic loading. Few of the filamentous forms appeared at low or conventional loading conditions ($L_f = 0.1$ to 0.5), while they were prolific at high loadings.

6. Sludge settleability is reduced at both ends of the load spectrum, but this reduction is most significant at the higher organic loadings. The poor settleability at the very low loading levels is probably due to unoxidized fragments of the floc being broken up with a consequent reduction in specific gravity, while the very nature of the dominant filamentous microbial population is responsible for high load bulking. The best sludge settleability for the Brewery waste was obtained between BOD loadings of 0.2 to 0.7 lbs BOD/day/lb MLSS.

Chapter 6

EXPERIMENTAL RESULTS - PETROCHEMICAL WASTE

6-1 Sampling and Acclimation Procedure

The raw petrochemical wastewater was taken directly from the plant waste feeder lines and the three constituents transported to Austin in separate containers (Chapter 3, Sampling Procedures). Forty liters of mixed liquor were taken from the plant aerated lagoon (Figure 3-4) to use as the initial laboratory seed. The microorganisms were fully acclimated to the petrochemical waste, and the four-hour transport time had no inhibitory effects on the culture.

Because of the equalization tanks and piping arrangement at the Petro-Tex plant, the waste constituents as listed in Table 3-1, Chapter 3, remained relatively constant. It is noted that there was only a 3.3% variation in COD values of the raw waste over a four-month period.

6-2 Buffer Capacity

The pH range of the petrochemical waste was 5.0 to 6.5. At the treatment plant loading of 0.25 lbs BOD/day/lb sludge, no buffer additive was required as the end-product of carbon dioxide produced by microbial respiration is bicarbonate (HCO_3). This natural buffering mechanism was sufficient to maintain the aeration system near pH 8.0. Similarly, no pH problems were encountered in the laboratory at this loading. However, as a result of the higher loadings employed in several units, the natural buffering capacity of the system had to be evaluated. In the preliminary work, the raw waste was not buffered,

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and the mixed liquor pH would fall to waste pH where high hydraulic loadings were used. This drastically reduced the oxygen uptake and dehydrogenase enzyme activity in the unit, and experience showed that it was impractical to re-neutralize the system and obtain normal operation within a reasonable period of time. Thereafter, two separate feed carboys were used, the one serving the high load units being buffered with sodium bicarbonate. The exact buffering capacity of the system was evaluated as follows:

1. A different flow rate of the acid waste was applied to each of the six units.

2. The acidit loading (mg/day as CaCO3) to each unit was determined.

3. The pH and oxygen uptake of the aeration tank contents, and the

COD removal were monitored.

Table 6-1

Unit	Flow (1/day)	Waste Acidity (mg/l as CaCO3)	Acid Loading (mg/day as CaCO ₃)	Oxygen Uptake (mg O ₂ /day/gm)	%COD removal	pН
3	11.6		4,790	0	nil	4.8
4	6.3	412	2,600	6	6	4.8
6	5.3	412	2,180	6	12	7.3
8	1.2	412	495	24	85	7.5

Buffering Capacity Data



Figure 6-1

Buffering Capacity - Petrochemical Mixed Liquor

As can be seen from Figure 6-1, there is a rapid deterioration of COD removal and oxygen uptake below pH 7. This indicates a maximum acid loading of 400 mg/l acidity as $CaCO_3$ per liter aeration volume at 1,500 mg/ l MLSS, or 0.27 mg acidity/mg MLSS. Under these conditions, up to 4.9 liters/day of the unbuffered petrochemical waste could be fed to the 5-liter aeration tank (MLSS = 1,500 mg/l) without any expected drop in pH.

6-3 BOD/COD Relationship

(a) Loading Effect The BOD and COD of the raw waste and effluents of the six units were determined. The raw waste, long-term BOD data, as shown in Figure 6-2, show a BOD₅ of 1,150 mg/l and a BOD_{ult} of 1,450 mg/l. The BOD_{ult}/COD ratio of 1,450/2970 = 0.49 indicates that half of the raw waste COD is actually bio-degraded.



Figure 6-2



As taken from the data in Appendix C, the following average BOD_5/COD ratios of the different loading effluents are:

Table 6-2

BOD/COD Ratios at Various Loadings - Petrochemical Waste

Unit No.	L _f (lbs BOD/day/lb sludge)	Effluent BOD ₅ /COD (avg.)
3	1.60	0.34
4	0.96	0.26
6	0.58	0.07
7	0, 17	0.05
8	0.10	0.03

Practically all of the biodegradable materials were utilized when loadings of 0.5 or less were applied.

(b) <u>Air Stripping</u> It was necessary to determine the portions of BOD and COD which were air stripped from the units in order to check the significance of this removal mechanism. This was done by aerating the sludge-free waste and checking the COD level at various aeration times. As shown in Figure 6-3, 20% of the dichromate oxidizable materials were air stripped. This value was confirmed when the effluent of Unit 3 in the buffer study (no significant biological activity) showed approximately 80% of the raw waste COD.



COD Removed by Air Stripping

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A graphical representation of the COD and BOD5 disposition for the various loadings is shown in Figure 6-4. It is possible that a small portion of biologically removed BOD was actually due to air stripping, but this exact amount was not determined.

6-4 Process Materials Balance

Sufficient data were taken to formulate a process materials balance (5) during the petrochemical waste test series.

(a) Sludge Production The sludge production as a function of COD removal is plotted in Figure 6-5. From this plot, the sludge yield can be expressed as:

$$\frac{\Delta X}{X_{a}} = \frac{a(24\Delta S)}{X_{a}t} - b$$
or
$$\Delta X = \underline{a\Delta S}_{t} - bX_{a}$$

(wt. VSS produced/day = a(wt. COD removed/day) -b(wt. MLSS) or The "a" value of 0.20 appeared to be low, but it is possible that many of the substrate materials used for energy could not actually be assimilated into cellular material. Loss of COD through stripping action would also lower the value of "a".

(b) Oxygen Requirements Based on Figure 6-5, the oxygen requirement can be expressed as:

$$\frac{24 r_r}{X_a} = \frac{a' 24(S_o - S_e) + b'}{X_a t}$$
$$r_r = a' (\Delta S) + b'X_a$$

or

or

(wt. oxygen/day) = a'(wt. COD removed/day) + b'(wt MLSS) Generally, the synthesis fraction (a) plus the energy fraction (a') should be unity.

The sum in this case was 1.02, although (a) appeared lower and (a') appeared higher than the generally reported values (5).



Figure 6-4

Continuous Unit BOD and COD Removal

Petrochemical Waste



Figure 6-5

Oxygen and Sludge Materials Balance

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6-5 Phosphates

Total inorganic phosphates of the raw waste and of the effluents were measured to determine if the applied loadings had any significant effects on phosphate removal. The inorganic phosphate removal is normally accompanied by an equivalent organic phosphorus build-up in new cellular material. Organic phosphorus in each system was measured by combusting the sample to ash, where it is contained in the form of pyrophosphate. The ash was then hydrolyzed and measured as orthophosphate. No reproducible organic balance was obtained using this procedure, as the phosphorus deficit ranged from 15% to 50%. It is possible that at least part of this deficit was due to organic phosphorus being lost from the ash in the form of a gas, P_2O_5 . (4)

The removals of inorganic phosphorus (orthophosphates and polyphosphates) for several loadings are reported in Appendix C, Table C-3. The average values using the stannous chloride analytical technique are summarized below:

Table 6-3

Inorganic Phosphorus Removals

Raw Petrochemical Waste	mean (mg/1)	standard deviation (mg/l)	coefficient of variation
Total inorganic phosphorus	10.96	2.55	23%
Effluent			
Unit 3 (L _f =1.6) 56% Removal of inorganic – P	4.77	1.21	25%
Unit 4 (L _f =0.96) 56% R _e moval of inorganic – P	4.84	1.69	34%
Unit 6 (L _f =.58) 54% Removal of inorganic – P	्र 5 ु 01	1.72	34%
Unit 8 (L _f =.10) 60% Removal of inorganic - P	4.36	1.68	38%

It was observed that although slightly better removals were obtained at the lowest loading, the change was not significant, and no definite loading effect on phosphate removal could be concluded from this particular study.

6-6 Bound Water Analysis

Relative amounts of activated sludge floc "bound water" were evaluated for each unit to determine if this phenomenon did in fact contribute to sludge bulking. Using the procedure as outlined in Chapter 4, and assuming the theoretical basis to be valid, the standard petroleum curve and standard petroleumwater curve were experimentally obtained. This information is plotted in Figure 6-6, and the expansion value of free water is therein calculated. An expansion curve for 60 ml of petroleum and 10 ml of concentrated mixed liquor was then run for each unit. Based on these stem readings at -14°C and the free water expansion value, a bound water index for each loading was calculated in the following manner:

Unit 8 Bound Water at $L_f = .10$

(1) Mixed liquor concentrated to 6, 266 mg/l

Total Wt. = 9.93600 gms -.07435 gms dry solids 9.90165 gms total water

@ 14°C, stem reading = 0.700 (60 ml petroleum + 10 ml mixed liquor) petroleum alone = 60/70(1.87) = 1.60 ml petroleum + sample 0.70 ml free water expansion .90 ml

> <u>.90 ml</u> = 9.0 ml free water .10 ml/ml

(2) Total Water - Free Water = Bound Water

9.90165 ml - 9.0 ml = .90165 ml bound water

<u>.90 ml bound water</u> = 12.0 bound water index .07 gms dry solids

Units 3, 4, 6, and 7 were calculated in a similar manner with the results as summarized as follows:

Bound Water Data Summary

Unit	L_{f}	Gms. Total Water	Calculated ml free water	Calculated ml bound water	Gms dry solids	Bound water index
3	1.60	9.93734	8.0	1.93	.06266	30
4	.96	9.91130	7.8	2.11	,08870	24
6	.58	9.94415	9.2	0.74	.05585	13
7	.17	9,93860	9.0	1.04	.06140	15
8	.10	9.90165	9.0	0.90	.07435	12

The sludge bound water index with the corresponding settling velocities and SVI values are listed in Table 6-4.

Table 6-4

Loading Factor (L _f) <u>lbs BOD/day</u> <u>lb solids</u>	Zone Settling Velocity (ft./hr)	SVI	Bound Water Index
1.60	bulking	>1,000	30
0.96	0.3	480	24
0.58	13.0	110	13
0.17	14.5	96	15
θ.10	6.5	164	12

Loading Effects on Zone Settling Velocity, SVI, and Bound Water Index

Based on this data it can be deduced that bound water contributes to sludge bulking, the amount of bound water will increase with loading, and the SVI and zone settling velocity values will depend in part on the bound water content. This is somewhat contradictory to the results stated by Heukelekian and Weisberg (14) as they concluded that bound water contributed only to non-filamentous sludge bulking.

6-7 Variable Loading Analysis

The effects of various loadings on the sludge characteristics were evaluated using the same procedure as that employed for the brewery sludge analysis. The continuous units were operated simultaneously. This was done in order to eliminate any possible environmental differences between the individual systems during the testing period.

(a) <u>Oxygen Uptake</u>, <u>Dehydrogenase Enzyme Activity</u>, and <u>Removal</u> <u>Efficiency Response</u> The response of these parameters to various loading conditions is shown in Figure 6-7. The average oxygen uptake and dehydrogenase activity increased with organic loading. The COD removals ranged from 50% at the overload condition to approximately 75% at the low loads. The raw waste source for the L_{f} '=1.16 unit (Figure 6-7) was not buffered on day 13, and the mixed liquor of the system fell to the waste pH of 5.8 on day 14. The response of all three parameters to this pH drop is noted on days 14 and 15. (b) <u>Settling Curves</u> The sludge settleability of each loading was evaluated by measuring the zone settling velocity and the SVI. The zone settling velocities were computed from the settling curves as plotted in Figure C-1, Appendix C.





Bound Water Analysis

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Figure 6-7

Daily Record of Sludge Activity and COD Removal Efficiency - Petrochemical Waste 81



Figure 6-7 (con't.)



Figure 6-7 (con't.)



Figure 6-8

Parameter Response to Organic Loading - Petrochemical Waste

6-8 Plant Operating Data

The plant operating data were compared with laboratory information to check the compatibility of the two. Plant COD removals had been previously

reported and oxygen uptake and T. T. C. analyses were performed by the author at the plant site. The results were:

Treatment Plant Data:

- (a) Loading: 0.24 lbs BOD/day/lb sludge
- (b) MLSS: 1,363 mg/l
- (c) Oxygen Uptake (Corrected from 34°C to 23°C): approximately
 9 mg O₂/hr/gm
- (d) Lagoon Temperature: 34^oC
- (e) COD Removals at 34° C: 78% to 84%
- (f) Dehydrogenase Enzyme Activity (test temp. = 37^oC): .023µ
 moles/mg VSS
- (g) SVI: 130 to 150

Table 6-5

	SVI	L _f (1bs BOD/day 1bs sludge)	Oxygen Uptake (mgO ₂ /hr/gm sludge)	Dehydrogenase Enzyme (µ moles/mg VSS)	COD Removal (%)	Zone Settling Vel (ft/hr)
	164	0.10	5	. 021	73	6.5
	96	0.17	6	. 023	72	14.5
Plant	130-	0.24	(9) ₂₃ °	. 023	(78-84)340	-
Data	150					
	84	0.39	11	. 032	69	20.0
		0.40	13	. 038	68	
	110	0.58	24	. 025	60	13
		0.83	31	. 064	61	
	480	0.96	55	.035	52	. 30
	<u>-</u>	1.60	65	. 060	54	nil
	-	2.30	78	. 105	50	nil

Average Operational Values*

*Temperature = 23^oC

The plant data are inserted in the above table according to the indicated loading. The plant values appear to be generally consistent with those reported from the laboratory study.

6-9 Photomicrographs

(a) Optical photomicrographs (1200 X) of representative populations responding to the various loadings are shown below:



Figure 6-9 (a) L_f¹ = 0.10 SVI = 164



Figure 6-9 (b) L_f' = 0.40 SVI = 86



Figure 6-9 (c) L_f' = 1.60 SVI = bulking



Figure 6-9 (d) L_f' = 2.30 SVI = bulking The microbial response to the organic loading level is again noted. The filamentous organisms were predominant only at the higher loadings. Two types of filamentous forms appeared, as shown in Figure 6-9 (c) and (d). One gives the appearance of being lower protist in nature, Fig. 6-9 (d), while the other form resembles a true fungus, Figure 6-9 (c).

(b) Electron photomicrographs of these and other specimens are shown in Figure 6-10. Figure 6-10 (a) shows the general microbial population present in the laboratory aerated lagoon treating petrochemical waste. Very low loadings were applied and no filamentous forms were present. The microorganism shown in Figure 6-10 (b) is typical of the population. Figure 6-10 (c) shows a highly magnified view of the fungal like organisms which were observed in Figure 6-9 (c). The stems are septate and approximately 2.5 microns in diameter. They take the form of <u>Fungi imperfecti</u>, although differential analyses were not performed. These forms and the <u>Spaerotilus</u>-like organisms flourished under high loading conditions.



Figure 6-10 (a) General Microbial Population @ $L_{f}' = .5$ (10,000X)



Figure 6-10 (b)

Typical Microorganism $@ L_{f}' .5$



Figure 6-10 (c) Higher Forms in Aerated Lagoon System @ L_f' = 1.60 (7,000 X)

6-10 Nutrient Deficiency

It was previously determined that this particular petrochemical waste was deficient in nitrogen (39). Two units were operated in parallel, with the same organic load applied to each. The calculated concentration of nitrogen in the form of ammonium sulfate was added to one unit, while no nutrients were added to the other. The two units were operated on a continuous basis until the systems were adapted to the imposed nutritional conditions. The sludge settling curves of the two can be compared in Figure 6-11. There was no significant reduction in the BOD removal efficiency of the nutrient-free system, although the settling characteristics of the sludge were somewhat poorer than that where ample nitrogen and phosphorus were available.



Effect of Available Nitrogen on Sludge Settleability

6-11 Summary

The petrochemical waste analyses are summarized as follows:

1. The natural buffering capacity of this waste mixed liquor was established. Maintaining 1,500 mg/l MLSS in a 5-liter aeration chamber, up to 4.9 l/day of the petrochemical waste (pH 5-to pH 6.5) could be applied without any expected acid range pH.

2. The BOD_{ult}/COD ratio of .49 indicated that half of the waste COD was bio-degradable.

3. Twenty per cent of the waste COD was air stripped within a 24 hour aeration period. It was determined that 29% of the material stripped out exerted a BOD.

4. A materials balance of the process indicated the synthesis fraction (a) to be 0.20 and the energy fraction (a') to be .82.

5. No significant loading effect on inorganic phosphate removal was observed.

6. The bound water content of a bulking sludge was much higher than that of an endogenous sludge. The bound water phenomenon appears to contribute to the sludge settling characteristics in some measure.

7. Oxygen uptake and dehydrogenase enzyme activity function together as previously mentioned, and the magnitude of both depended on the applied petro-chemical waste load.

8. The sludge settleability for the petrochemical waste was best between BOD loadings of 0.2 and 0.6 lbs BOD/day/lb sludge.

9. The COD reduction, oxygen uptake, and dehydrogenase enzyme data taken at the plant was quite compatible with that taken from a laboratory continuous unit undergoing a similar loading.

10. Two different forms of filamentous microorganisms were prolific in the higher loaded units. The presence of these organisms were primarily responsible for the deterioriation in sludge settleability. One of the forms was a <u>Sphaerotilus</u>-like filament, while the other had true fungal properties.

Chapter 7

EXPERIMENTAL RESULTS - DOMESTIC WASTE

7-1 Sampling and Acclimation Procedure

Domestic wastewater was obtained daily from the Austin Govalle Plant. The sample was taken from a 30-minute detention primary settling tank and immediately cooled prior to use. Using this procedure, the food source for the laboratory units was kept fresh at all times. Mixed liquor from the treatment plant was used as the initial seed and no acclimation time was required. Each loading run was two weeks in duration allowing the system to equilibrate to its particular loading level.

Higher L_f values were difficult to obtain using domestic waste because of the low BOD concentration. Excessive hydraulic loadings resulted in a wash-out situation, limiting the maximum L_f that could be applied.

7-2 BOD/COD Relationship

The BOD₅ and COD of the raw waste were evaluated over a two week period. The BOD/COD ratio fluctuated between 0.55 and 0.70, with an average value of 0.61. The Govalle Plant range was reported to be from 0.40 to 0.60. The average BOD/COD ratios of the effluents with different loadings were:

Unit No.	L_{f} (lb BOD $_{5}$ /day/lb. sludge)	Effluent BOD/COD
3	0.88	0.30
5	0.56	0.18
4	0.43	Θ.18
6	0.27	0.10
7	0.15	0.10

Tak	10	7.	1
Tar	JTG	1-	Т

BOD/COD Values at Various Loadings - Domestic Waste

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A graphical representation of the BOD and COD removals for different loadings is shown in Figure 7-1.





7-3 Variable Loading Analysis

The daily fluctuations of dehydrogenase activity, oxygen uptake, and COD removal for each applied loading are shown in Figure 7-2. The fluctuations were more pronounced than those observed for the petrochemical and brewery wastes as a result of the daily changes in the domestic wastewater characteristics.

The sludge settleability was evaluated using the aforementioned procedures, and these parameters along with BOD and COD removal efficiences for each loading are plotted in Figure 7-3.

7-4 Nitrogen Analyses

The nitrogen data, as listed in Table D-3 were obtained in order to understand better the loading effects on the degree of nitrification in the activated sludge process. An attempt to obtain a nitrogen balance for the system was also made. Total Kjeldahl nitrogen (organic - N + ammonia - N) of the raw waste and the effluent was determined, as well as the effluent nitrite and nitrate concentrations. An indirect measure of nitrification is the total Kjeldahl nitrogen reduction through the system. This value and the total nitrite effluent concentration for each L_f are plotted in Figure 7-4.

7-5 Photomicrographs

Photomicrographs of the domestic waste activated sludge floc are shown in Figure 7-5 (a) and (b). As in the two previous studies, the filamentous forms were present under low organic loading conditions, but were predominant only in the higher range.



Figure 7-2

Daily Record of Sludge Activity and COD Removal Efficiency Domestic Waste



Figure 7-2 (con't.)



Figure 7-3 Parameter Response to Organic Loading -Domestic Waste



Figure 7-4 Organic Loading Effect on TKN Reduction and Nitrification



Figure 7-5 (a) L_f = .25 SVI = 85



Figure 7-5 (b) L_f = 1.00 SVI = 120

7-6 Summary

1. The average BOD/COD ratio of 0.6 is normal for domestic wastes, with the plant from which the waste was obtained reporting a ratio variation of 0.4 to 0.6?

2. There was good correlation of dehydrogenase enzyme activity and oxygen uptake, although the daily fluctuations of the two were more pronounced than those of the industrial wastes. This and the high coefficient of variation of the daily sample BOD values demonstrated the higher variable nature of the wastewater.

3. The sludge settleability for the domestic waste was best between BOD loadings of 0.1 and 0.6 lbs BOD/day/lb sludge.

4. The total Kjeldahl nitrogen reduction and subsequent nitrite and nitrate concentrations decreased significantly with increasing organic loading. An average of 10% of the input nitrogen was not accounted for in the nitrogen balance calculations.

5. Filamentous microorganisms were present under all loading conditions, but were predominant only at L_f values higher than 0.7.

Chapter 8 DISCUSSION

Sludge settling and adequate compaction are necessary for the successful operation of an activated sludge process. Sludge bulking and its related aspects have been the subject of many investigations, the researchers generally agreeing on the cause but not the cure.

A batch laboratory arrangement was used to study the effects of anaerobiosis as a bulking control device. It was apparent that such a change in environment had a definite inhibitory effect on the filamentous forms that were present, but the settling characteristics were not significantly improved and many of these microorganisms survived even the longer periods of anaerobiosis. A continuous aerobicanaerobic system would have provided more realistic data, however. The ability of most microbes developed in the aerobic environment to maintain their assimilative capacity following anaerobic contact periods was substantiated by this investigation. It is proposed, however, that the microbial population is capable of maintaining this capacity for longer anaerobic periods than mentioned by Wurhmann (18) and McClelland (21).

Bulking, regardless of the form it takes, can be related to organic loading. The primary cause appears to be the biological response to the environment brought about by a particular loading level. This was true for each of the three different wastewaters studied. Tests also indicated high bound water contents at the higher organic loadings, accompanied by sludge settling deterioration. Various investigators have reported different organic loading values at which bulking first appeared. These values range from 0.50 lbs BOD/day/lb MLSS to 2.00 lbs BOD/ day/lb MLSS. The results from this investigation indicated that bulking occurred above 0.70 lbs BOD/day/lb MLSS for each waste under consideration. These contraditions can best be explained by considering the reported values absolute and

comparable only when complete mixing prevails. Since the significant parameter is the concentration of food in contact with the organisms, the geometry of the system and the mode of introduction of the waste must be considered. A changing food-to-microorganism ratio within the tank will correspondingly induce an unpredictable biological response.

Oxygen uptake and dehydrogenase enzyme measurement appear to be excellent parameters of sludge activity. The response of each to organic loading and environmental changes was consistent throughout the testing period. This correlation was reported earlier by Ford, Yang, and Eckenfelder (26) and the relationship was valid for each test series of this study. The increase of oxygen uptake with organic loading using a domestic waste substrate followed the same relationship as set forth by Orford, Heukelekian, and Isenberg (40).

The effects of BOD loading on sludge volume index were approximately the same for the three wastes studied. Logan and Budd (41) evaluated these effects for a domestic waste using a completely mixed pilot plant and found the same trend, although good sludge settleability was restricted to a BOD loading range of 0.2 to 0.4.

The effects of organic loading on phosphate removals and nitrification were considered in two instances. A phosphorus balance was difficult to obtain; the problem of evaluating organic phosphorus accurately was most prevalent. No loading effect on inorganic phosphorus removal was observed. Reasonably accurate nitrogen balances were recorded, and the effect of organic loading on nitrification was significant.

Chapter 9

CONCLUSIONS

The results of this study of the three wastewaters can be summarized as follows:

(1) Prolonged periods of anaerobiosis (24 hours or longer) had an adverse effect on the filamentous microorganisms developed from the brewery waste, although many appeared to survive. The improvement in sludge settleability was not considered significant on a batch basis, although a continuous system analysis might have provided more realistic data. However, prolonged periods of anaerobiosis and the consequent microbial response had little effect on the assimilative capacity of the system.

(2) The sludge settleability as measured by zone settling velocity and SVI followed the same general pattern for all three wastes. The settleability was reduced at both ends of the loading spectrum, but the reduction was most significant at the higher organic loadings. The poor settleability at the low loadings was probably due to unoxidized fragments of the floc being broken up with a consequent reduction in specific gravity, while the very nature of the dominant filamentous microbial population was considered responsible for the high load bulking. The best sludge settleability for all wastes occurred in the L_f range of 0.2 to 0.7 lbs BOD₅/day/lb solids.

(3) The changing microbial population with organic loading responded in a similar manner to each of the wastewaters applied. Filamentous microorganisms were present under all loading conditions, but were predominant only at L_f values exceeding 0.7. Two different filamentous forms were observed. One was a Sphaerotilus-like filament, while the other had true fungal properties.

(4) Oxygen uptake, COD removal, and dehydrogenase enzyme were used to monitor system changes throughout the testing period. The daily fluctuations of

these parameters were most pronounced during the domestic wastewater test series because of the variable nature of the waste itself.

(5) There was an excellent correlation between the mixed liquor oxygen uptake and the dehydrogenase activity, and the magnitudes of both were dependent on the applied organic load. As seen in Figure 9-1, this was true for all three wastewaters.

(6) The bound water content of the petrochemical sludge increased with organic loading as shown in Figure 9-1. The indication here is that this phenomenon is at least partially responsible for sludge bulking at the higher organic loadings.

(7) The COD reduction, oxygen uptake, and dehydrogenase enzyme data of the petrochemical waste obtained under similar conditions at the treatment plant and from the laboratory units compared quite favorably.

(8) No significant loading effect on inorganic phosphate removal from the petrochemical waste was observed.

(9) Effluent nitrite and nitrate concentrations, as well as total Kjeldahl nitrogen reduction through the biological system, decreased with increasing domestic waste organic inputs. An average of ten perscent of the influent nitrogen was not accounted for in the nitrogen balance calculations.

10.0



Effect of Organic Loading on Oxygen Uptake, Dehydrogenase Enzyme, and Bound Water

e

APPENDIX A

TABLE A-1

Time	Cum. Time	Effluent Activity - cpm/ml	Aeration Tank Activity-cpm/ml
1456	0	0	36,000
1500	:04	21,100	-
1514	:18	29,055	-
1526	:30	31,330	32,050
1556	1:00	22,310	-
1700	2:04	21,390	21,110
1800	3:04	19,500	-
2020	5:24	11,936	11,150
22 30	7:34	10,036	10,545
0630	15:34	3,530	3,260
0900	18:04	3,008	2,420
1456	2 4:00	1,192	1,084

134 Cs Residence Time Determination

*8cpm background and natural decay neglected

.

APPENDIX B

•

TABLE B-1

			φ = .6	D.O. = <u>µ</u>	amps ∮
Date	Time	Reading µ amps	D.(Э.	Cum. Time
9-17-65		7 05	11	70	0
3:30	.15	6 75	11	20 20	0
	•15	6.40	10	20 70	.10
	•15	6.20	10	30	•45
	•15	6.10	10	10	1.00
	•15	6.00	10	00	1.00
	1.00	5.60		. 30	2.15
	1:00	5.20	8	. 70	3.15
	2:00	4,40	7	.35	5:15
	3:00	3.20	5	.35	8:15
	2:00	2.30	3	.84	10:15
9-17-65				10	
4:20	1 -	6.80	11	.40	0
	:15	6.70	11	. 10	:15
	:30	6.40	10	.65	:45
	:30	6.20	10:	30	1:15
	:30	5.90	9	.80	1:45
	1:00	5,40	9	.00	Z :45
	1:00	4.85	8	. 10	3:45
	2:00	3.75	6	.25	5:45
	2:00	2.60	4	. 35	7:45
9-18-65		F 00	0	70	
11:30	.20	5.20	8	. 70	20
	:30	5.00	8	. 30	:30
	:30	4.80	8	.00	1:00
	:30	4.60	7	۵0 «	1:30
	:30	4.45	/	.40	2:00
	:30	4.30	/:	15	2:30
	:30	4.20	7	.00	3:00
	2:00	3,40 2,60	5	24	5:00 7:00
	4:00	2.00	4	.34	/:00

Acclimation Oxygen Uptake Determinations - Oxygen Probe

Date	Time	Reading µamps	D.O.	Cum. Time
0 10 65				
9-19-02		5.00	8.35	
12:30 a.m	·• :15	4.75	7.92	:15
	:15	4.60	7.68	:30
	:45	4.30	7.15	1:15
	1:00	4.00	6.67	2:15
	1:00	3.70	6.18	3:15
	1:00	3.40	5.66	4:15
	1:00	3.00	5.00	5:15
9-19-65				
10:00 a.m	1.	4.60	7,68	
	:30	4.25	7.09	:30
	1:00	3.85	6.42	1:30
	1:00	3.40	5.67	2:30
	1:00	3.00	5.00	3:30
	1:00	2.60	4.34	4:30
9-19-65				
9:00 p.m.	,	5.90	9.83	
	:30	5.60	9.34	:30
	1:00	5.20	8.67	1:30
	1:00	4.85	8.09	2:30
	1:00	4.45	7.42	3:30
	1:00	4.10	6.83	4:30
	1:00	3.70	6.18	5:30
	1:00	3.30	5,50	6:30

TABLE B-1 (Cont'd.)



Figure B-1

Oxygen Uptake Rate Evaluation



Figure B-1



Figure B-1



Figure B-1



Figure B-1

TABLE B-2

Oxygen Uptake Summary

Time-hrs.	Time-days	r (mg/l/min)	r (mg/l/hr)	MLSS mg/l	^K r mgO ₂ /hr/gm
0	0	.61	36.8	2600	12.3
1.0	.04	.89	53 .2	2570	20.0
19.1	.80	<i>°</i> 60	36.0	2 300	15.5
32.1	1.30	.55	33.0	2200	15.0
41.6	1.70	.68	41.0	2 100	20.0
52.6	2.20	.70	42.0	1850	22.0

TABLE B-3

COD Removal Summary

Time-days	COD Removal (%)
0	-
1.10	76%
1.80	92%
2.05	93%

Settling Data

Date	Anaerobic Time (hrs)	Aeration Period (hrs)	Settling Time (min)	Interface level (ml)
10-22-65	0	2	0	1000
			20	805
			40	730
			60	560
			100	480
	1	2	0	1000
			20	760
			40	550
			60	360
			120	295
	5	2	0	1000
			11	870
			35	700
			46	560
			88	480
	10	2	0	1000
			10	800
			27	690
			40	560
	24	2	0	1000
			6	740
			10	660
			17	590
			24	555
5-13-66	0	6	0	1000
			1	1000
			14	990
			35	960
			60	900
	6	6	0	1000
			6	990
			12	980
			2 3	950
			48	850
	12	0	0	1000
			11	980
			35	900

Date	Anaerobic Time (hrs)	Aeration Period (hrs)	Settling Time (min)	Interface level (ml)
5-13-66	23	0	0 6 16 30 45 60	1000 990 980 950 860 750
	23	6	0 14 30 45 72	1000 980 890 600 240
	48	0	0 10 16 24 34 45 60	1000 980 960 910 790 650 500
	48	6	0 10 14 20 27 38 48 52 66	1000 950 910 790 650 480 400 370 280
	72	0	0 6 17 26 30 46 63	1000 980 920 840 800 600 440
	72	6	0 6 14 20 22 28	1000 980 870 700 640 520



Sludge Settling Curves following Various Anaerobic Periods

TABLE B-5

Data Summary - Anaerobic Study

(ft/hr) Aeration		20	20	25	15	40	.73
<u>I Curves</u> n After		0.	0	0.	1.	1,	1.
<u>Settling</u> Before Aeratio		0.20	0.20	0.25	0.35	1.10	1.00
% Removed		77	82	I	80	76	75
Effluent COD mg/l		105	64	I	, 72	06	95
Raw Waste COD mg/l		460	370	I	370	370	370
MLSS mg/l	•1	1110	750	I	720	730	720
tch Jptake Rate /gm sludge	Aer 6 hr. Aer	ı	12	I	21	18	15
Bat Oxygen U MgO2 /hr/	<u>15 min. </u>	1	96	ł	86	86	60
Anaerobic Time (hrs)		0	9	12	23	48	72

		.1	TOAUTIN Data D	Initia	IN LOI	o F hat o	DAY & BIITINA A REC	ACTE OTITI	
Date	$Q^{\left(\frac{1}{day}\right)}$	S _a (mg/l)	$t^{(\frac{9.6}{Q}.24)}$	ъ°	ы ^е	Ŋ	$L_{a} \left(\frac{L_{o} + aL_{e}}{1 + 2} \right)$	(COD Basis) Loading Factor 24 L _a / s _a · t	Comments
3-15	8.5	3200	27 hrs.	820	150	2.1	370	.103	
3-17	0°6	3090	24.2	920	130	2.0	393	.123	Avg. $L_f =$
3-18	0°6	3260	24.0	820	120	2.0	354	.110	0.11 Run#
3-20	11.5	3200	20.0	800	400	1.6	555	.21	
3-21	11.6	2800	19.7	800	450	l.6	585	.25	
3-22	11.9	3400	19,3	800	380	1 ,5	548	.20	Avg. L _f =
3-23	14.1	3050	16.8	740	220	1.4	442	.21	0.21
3-24	18.4	3620	12.5	800	60	1,1	412	.22	Run #2
3-25	13.0	2500	17.8		60	1.4			
3-26	19.0	2720							
3-27	15.1	2250	15.2	700	60	2.0	272	.19	Avg. $L_f =$
3-28	18.0	3240	12.8	800	110	2.0	340	.20	0.22
3-29	21.5	2700	10.8	800	60	2.0	303	.25	
3-30	16.0	2500	14.3	750	60	2.0	290	.19	
3-31	I	I	I	ı	ı	ı	I	I	Run #3

Loading Data Summary For Separate Settling & Recycle Unit

TABLE B-6

Unit No.	Date	Flow (1/daÿ)	MLSS	(COD Basis)* L _f '	Comments
				-	
5	4-19	-	2140	*2	
	4-20	5.4	1970	.37	
	4 - 21	5.8	2100	.36	
	4-22	8.0	2640	.43	Avg. L _f '= .41
	4-23	7.8	2230	.44	
	4 - 24	7.5	2020	.47	
	4-25	6.8	2060	. 43	
	4-26	6.7	2670	,35	Run 1
5	4-27	17.8	-	-	
	4 - 28	15.5	2000	0.95	
	4-29	14.4	3310	.70	
	4-30	17.0	2880	.85	Avg. $L_{f}' = .80$
	5-1	17.0	2880	.80	0 1
	5-2	14.5	2270	.80	
	5-3	-	œ	_	Run 2
5	5-4	5.4	2200	.35	
	5-5	6.2	2470	.29	
	5-6	8.2	2160	. 40	
	5-7	5,8	2020	.32	Avg. $L_{f}' = .33$
	5-8	5.4	2050	.31	
	5-9	6.1	2400	.31	
	5-10	6.0	2340	.31	Run 3

TABLE B-7

Loading Data Summary for Combined Aeration and Settling Unit

Unit No.	Date	Flow (1/day)	MLSS	(COD Basis)* ${ m L_{f}'}$	Comments
3	4-19		1710	-	
	4-20	10.1	1570	.87	
	4-21	13.3	1650	.92	
	4-22	14.8	3440	.70	Avg. $L_{f}' = .69$
	4-23	10.3	2500	.54	0
	4-24	11.0	2340	.61	
	4-25	10.1	2800	.51	
	4-26	9.0	3480	-	Run 1
3	4-27	25.0	6	1.25	
	4-28	23.2	3100	1.15	
	4-29	22.3	2760	1.25	
	4-30	22.8	2700	1.25	Avg. $L_{f}' = 1.15$
	5-1	20.0	3020	1.00	U
	5-2	19.2	2500	1.00	
	5-3	17.0	83	-	Run 2
3	5-4	23.0	2570	1.12	
	5-5	26.2	3600	0.95	
	5-6	26.7	2540	1.33	Avg. $L_{f}' = 1.50$
	5-7	27.8	2400	1.39	
	5 - 8	26.5	2710	1.20	
	5-9	26.0	1220	2.60	
	5-10	25.5	1950	1,50	Run 3

TABLE B-7 (Con't.)

Parameter Response

Date	(<u>lbs COD/day</u>) lb solids L _f '	mgO ₂ /gm O ₂ Uptake	<u>µmoles</u> mg VSS TTC	% COD Removal	
4	0.33	18.5	.029	_	
5		14.0	.023	81	
6		13.0	.017	85	
7		11.0	.015	90	
8		12.5	.013	88	
9		11.0	.006	89	
10		12.5	.021	91	
20	0.41	14.0	.052	87	
21		22.0	.039	82	
22		14.0	.033	84	
2 3		15.0	.039	87	
24		13.0	.030	90	
25		13.0	.034	88	
2 6		12.0	.025	-	
				51	
20	0.69	20.0	.052	85	
21		18.0	.055	82	
22		14.5	.033	84	
23		11.5	.034	84	
2 4		12.5	.033	87	
25		11.0	.028	86	
2 6		11.5	.024	85	
27	0.80	-	_	_	
28		2 1.5	.035	87	
29		17.0	.030	88	
30		18.5	.034	78	
1		17.5	.030	76	
2		18.5	.033	80	
3		18.5	.03 2	81	
27	1.15	-			
28		15.5	.021	85	
29		24.0	.040	79	
30		25.0	.042	74	
1		22.5	.038	70	
2		22.0	.036	72	
3		22.0	.036	76	
4	1.50	9.0	.011		
5		28.0	.022	72	
6		18.0	.019	82	
7		18.5	.024	77	
8		37.0	.032	77	
9		32.0	.042	79	
10		27.5	.049	80	



Figure B-3

Sludge Settling Curves for Various Organic Loadings



Ľf '	Time (min)	Cylind Leve (ml)	er 21	L _f '	Time	Cylinder Level (ml)	L _f '	Time	Cylinder Level (ml)
0.11	0	1000	1000	0.41	0	1000	1.50	0	1000
	3	940	920		1	900		1	1000
	4	920	880		2	700		2	1000
	7	760	620		3	400		3	1000
	10	570	500		4	320		5	1000
	12	480	440		5	270		7	1000
	19	330	290		6	240		9	1000
	21	290	2 80		8	200		16	985
	24	270	2 60		11	-		22	980
	29	230	-		16	180		38	940
	40	210	-		21	170	1.15	0	1000
					31	170		1	980
0.21	0	1000	1000	0 00	0	1000		2	960
	6	485	480	0.69	0	1000		3	940
	10	370	365		1	920		5	900
	12	330	330		2	620		7	8 2 0
	15	290	285		3	460		9	740
	20	245	240		4	400		12	520
	28	220	225		57	370		14	470
	35	210	210		15	320		20	380
0.00	0	1000	1000		10	220		25	320
0.22	0	700	740		20	200		30	300
	2	790 660	740 660		30	190		38	300
	3	570	500	0 00	0	1000			
	4 5	570	520	0.00	1	2000			
	5	170	320 470		2	620			
	7	470	470		2	500			
	2 2	415	430		5	400			
	10	350	350		7	365			
	18	240	240		ģ	-			
	27	220	220		12				
	30	215	210		14	230			
	40	210	210		20	200			
	10	210	410		25	200			
0.33	0	100	0		30	195			
0.00	1	750 480 280 200 180 160 120 120			00	100			
	2								
	3								
	5								
	7								
	9								
	16								
	22								
	38	11	0						

APPENDIX C
BOD and COD Data

Effluents

Date	Uni COD	t 3 BOD	Unit COD	:4 BOD	Unit COD	: 6 BOD	Uni COD	t 7 BOD	Unit COD	8 BOD
5-31					985		868		817	
6-1 6-2	1450	578	1390	178	1007	38	040	28	860	38
6-3 6-3	1410	284	1310	130	1025	97	0 1 7	27		27
6-4	1420		1685				1047		915	
6-5										
6-6										
6-8						44		75		19
6-9	1414		1680		1065					
6 - 10	1575	610	1510	570	1585					
6-11	1855		1320		1285					
6-13	1960		1530		1160					
6-14	1570		1435		1090					
6-15	1530	363	1620	425	1190	88		70		21
6 - 16	1165		1095		954		1025			
6-17	941	312	960	344	893	70			845	28
6 - 18	778		1130		674					
6 - 20	1215		1765		707				754	
6-21	1350		1260		1940					
6-22	1050		1655							

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Table C-l (cont'd)

BOD and BOD Data Petrochemical Waste

	Raw Waste		Air Stripped			
Date	COD	BOD	COD	BOD		
	2020					
5-31	2930	1100				
6-1		1100				
6-2	2800					
6-3	2705					
6-4	3070					
6-5	3180					
6-6	3170		3180			
6-8	3000	1260	2 450	990		
6-9	2870		2370			
6-10	2960	1148	2450			
6-11	2900		2520			
6-13	2880		2460			
6-14	2870		2435			
6-15	3030					
6-16	2870					
6-17	2940	1665				
6-18	3110					
6-20	3000					
6-21	3140					
6-22	3000					

Long Term BOD - Petrochemical Waste

Time (days) Sample 1		Sample 2	Average
1	30	30	30
2	60	60	60
3	780	800	790
4	1080	1000	1040
5	1110	1080	1095
7	-	1110	1110
10	1260	1160	1210
14	1140	1140	1140
20	1380	1440	1410

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	r						
	mg O ₂ /1	Xa	so	Se		t	ΔX
Unit No.	hr	mg/l	mg/l	mg/l	∆S mg∕l*	hrs	mg/l/day
3	114	1657	29 70	1370	1600	13.5	468
4	100	1676	2970	1400	1570	21.5	303
6	40	1540	2970	1060	1910	38.5	160
7	13	2100	2970	970	2 000	95.0	72
8	8	2000	2970	830	2140	168.0	66
Comp	putation:						
	$\frac{24 \Delta S}{X_a \cdot t}$			$\frac{24 r_r}{X_a}$		ΔX X_a	
3	<u>24(1600)</u> 1657 (13	$\frac{1}{3.5} = 1.7$	7	<u>24(114)</u> 1657	- = 1.65	$\frac{468}{1657} =$.28
4	<u>24(1570)</u> 1676 (21	= 1.0)5	<u>24(100)</u> 1676	= 1,43	$\frac{303}{1676} =$.18
6	<u>24(1910)</u> 1540(38	.5) = .7	7	<u>24(40)</u> 1540	= .64	$\frac{160}{1540} =$.10
7	<u>24(2000)</u> 2100(95.	$\frac{1}{0}$ = .2	4	<u>24(13)</u> 2100	= .15	$\frac{72}{2100} =$.03
8	<u>24(2140)</u> 2000(168	$\frac{1}{3}$ = .13	5	<u>24(8)</u> 2000	- = .10	$\frac{66}{2000} =$.03

*Values are taken from Fig.6-4, Biological Removed COD $\,$

	% Rem.			25	8 8	53	83	74	72	57	132	60%
	Unit 8 Conc. mg/l			7.4 7.0 0.4	6.1 5.7 0.4	6,4 6,4 -	2.0 1.8 0.2	3.1 3.0 0.1	3.5 2.6 0.9	4. 2 3.5 0.7	2.2 1.6 0.6	6.6
	it 6 % Rem.	48	64	2 3	51	66	75	83	54	21	43	54.0%
	Un: Conc. mg/1	5.2 5.0	ດ ຕ ຕ ເ ເ	7.6 7.4 0.2	4 °8 4 °5 33	4.6 3.7 0.9	2.9 2.6 0.3	2.0 1.8 0.2	5.8 5.3 0.5	7.7 5.8 1.9	5.6 4.9 0.7	5,95
	nit 4 % Rem.	19	47	26	62	66	77	78	73	27	66	56.0%
4	Ur Conc. mg/1	8.1 7.8 0.3	0.270	7.3 6.2 1.1	3。8 2。7 1,1	4。6 3。5 1 , 1	2°7 2.5 0,2	2.6 2.5 0.1	3.3 2.2 1.1	7.1 6.8 0.3	3.2 3.0 0.2	6.12
)	. 3 % Rem .	36	48	50	60	65	76	50	51	0 0	67	56.5%
	Unit Conc. mg/l	6.4 5.5 0	0 2 2 0 • 1 2 0 • 1 2 0	5.0 4.3 0.7	3°9 3,3	4.7 4.5 0.2	2°8 0.58 0.30	6,0 4,8 1 ,2	6.1 4.8 1.3	0 % °0 • 4 0	3.3 2.5 0.8	6,19
	Raw Waste (mg/l)	10.0 9.4 0.6	10°7 9.4 1.3	8° I I 6	8 . I I 6	13.6 13.1 0.5	11.9 11.8 0.1	11 °9 	12.5 11.4 1.1	9°7		10.96
	Form	total ortho polv	total ortho poly	total ortho poly	total ortho poly	total ortho poly	total ortho poly	total ortho poly	total ortho poly	total ortho poly	total ortho poly	ige.
	Date	13 June	14	15	16	17	18	20	21	22	23	Avera

Inorganic Phosphate Data

Parameter Response

	(lbs BOD/day)	(mg O ₂ /hr/gm)	(<u>(µ moles)</u>)	~ COD	
Date	lbs solids L. avg.	O ₂ Uptake	mg VSS TTC	% COD Removal	Comments
E 22	24(1450)	ى يې پېرې د يې پېرې د يې پېرې پېرې پېرې پېرې پېرې پېرې پېرې پ			
5-22	$\frac{24(1450)}{997(15-2)} =$				
5-25	997(13.2)				
5-24	2.30	16	022	50	
5-25		28	.022	30	
5-20		20 46	.038	50	
5-4/		79	125	50	
5-20		70 95	.135	10	
5-25		0J 05	.130	-	
5-30		00	144	51	
5-31		90	.144	10	
6-2		07	.007	49	
6-7	24(1450)		. 01	17	
6-8	$\frac{1657(13-5)}{1657(13-5)} =$.01	23	
6-9	1007(10.0)	54	036	51	
6-10	1 60	43	.000	47	
6-11	1.00	75	085	36	
6-12		, 5	.000	-	
6-12		70	040	32	
6 - 14		7 <i>3</i> 92	.040	15	
6-15		78	.001	50	
6-16		61	.070	50	
6-17		50	055	60	
610		56	.033	75	
6-10		50	.040	/5	
6-20		10	055	60	
6-20		4J 70	.055	57	
6-22		20	.000	65	
0-22		00	.005	05	
6-7	24(1450) _		.013	38	
6-8	1676(21.5)	10	.017	27	
6-9		24	.029	42	
6-10	.96	12		49	
6-11		32	.060	54	
6-12		-	-	-	
6-13		75	.022	47	
6-14		90	.028	50	
6-15		80	.035	47	
6-16		67		. .	
6-17		45	.046	67	
6-18		60	.038	64	
6-19		-	_	-	
6-20		51	and t	41	
6 -2 1		72	.035	60	
6-22		-	.022	45	

Data	(<u>lbs BOD/day</u>) lbs solids	mg O ₂ /hr/gm	$\left(\frac{\mu \text{ moles}}{\text{mg VSS}}\right)$	% COD	Commonte
Date	<u> </u>	<u>Oj Oplake</u>	110	Removar	Comments
5-22	24(1450)		_		
5-23	1270(33.4)	11		66	
5-24		24			
5-25	= .83	19	.067	67	
5-26		30	.060	64	
5-27		25	.080	64	
5-28		28	.058	-	
5-29		28	.065	56	
5-30		34	.051	_	
5-31		36	.070	57	
6-1 6-2		32	-	55	
0-2		0.5	000	60	
6-7		25	.028	62	
6-8	$\frac{24(1450)}{12(120)}$	35	.029	66	
6-9	1540(39)	22	.024	63	
6-10		19		46	
6-11	= <u>.58</u>	27	.041	56	
6-12		-	-	-	
6-13		20	.020	60	
6-14		24	.024	62	
6-15		22	.021	61	
6-16		27	576G	-	
6-17		24	.020	70	
6-18		25	.022	78	
6-19		-			
6-20		29	-	76 <	System pH
6 -2 1		0	0	38	dropped be-
6-22		0	0	0	low 6
5-22	24(1450)	6	-		
5-23	1715(50)	10	-	68 ·	
5-24		7		-	
5-25	= <u>.40</u>	12	.043	68	
5-26		12	.044	70	
5-27		12	.050	70	
5-28		20	.040		
5-29		12	.050	65	
5-30		12	.033	1965	
5-31		17	.0 2 5	67	
6-1		16	.040	67	
6-2		-		67	

Table C-4 (Cont'd.)

Date	(<u>lb BOD/day</u>) lb solids Le avg.	mg O ₂ /hr/gm O2 Uptake	(<u>µ moles</u>) mg VSS TTC	% COD Removal	Comments
	-1 -1 -1 -1				
5-22	24(1450)	6		- 4	
5-23	1680(52)	6		74	
5-24		7		-	
5-25	= .39	9	.028	69	
5-26		11	.034	73	
5-27		10	.038	71	
5-28		14	.034	-	
5-29		15	.037	67	
5-30		18	.034	-	
5-31		13	。0 2 8	67	
6-1		14	.028	-	
6-2		-			
5-22	24(1450)	5			
5-23	2100(95)	4		72	
5-24		6		-	
5-25	= .17	7	.022	71	
5-26		6	.027	73	
5-27		5	.024	73	
5-28		7	.020		
5-29		12	.037	68	
5-30		5	.019	-	
5-31		5	.020	71	
6-1		6	.016	-	
6-2		_	-	-	
E 22	24(1450)	5			
5-22	$\frac{24(1430)}{2000(168)}$	1		73	
5-23	2000(100)			75	
5-24	- 10	- <u>-</u>	0 2 3	72	
5-25	<u> </u>	5	.023	74	
5-20		3	.024	74	
5-2/ 5-20		4	.020	/4	
5-20		4	.030	70	
5-49		4	.044	/0	
5-30		с С	.010	- 72	
5-31		5	010.	/ 3	
0-1		5	.012	_	
0-2		_	-		

Table C-4 (Cont'd.)

L _f	Time (min)	Cylinder Level (ml)	L_{f}	Time (min)	Cylinder Level (ml)	L _f	Time	Cylinder (min) Level(ml)
0.10	0 1 2 4 6 10 15 22 30	1000 980 970 800 580 430 400 375 330	0.40	0 1 2 6 10 15 22 30	1000 750	0.96	0 1 2 4 .7 11 22 34	1000 990 980 970 950 935 910 840
0.17	0 1 2 4 6 10 15 22 26 30	1000 750 660 500 390 270 200 190 180 180	0.58	0 1 2 3 6 8 15 24 30	1000 830 590 420 290 250 160 140 135	1.60	0	1000 Bulking
0.39	0 1 2 4 6 10 15 22 26 30	1000 540 360 270 210 180 170 165 165				2.30	0	1000 Bulking

Table C-5 Settling Curve Data



Figure C-1



APPENDIX D

BOD and COD Data - Domestic \	waste
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					Effluent	ts			
Del	, Raw Wa	ste	Unit	3	Un	it 4	Unit	: 5	
Date	COD	BOD	COD	BOD	COD	BOD	COD	BOD	
7-11	452		95		95		85		
7-12	323		71		81		71		
7-13	470	260	70	20	90	11	80	24	
7-14	255		95		85		85		
7-15	255	135	85	35	75	7	65	7	
7-16	150		120		80		80		
7-17	190		100		80		100		
7-18	170		80		60		80		
7-19	242		116		66		111		
7-20	275	204	115	83	70	16	70	9	
7-22	260	173	125	31	115	34	100	18	
	IInit	6	TIN	+ 7	<u>. </u>	۲			
Date	COD	BOD	COD	BOD					
					<u></u>				
7-11	85								
7-12	-		71						
7-13	70	6		8					
7-14	-	-	80						
7-15	70	7	-	2					
7-16	-		75						
7-17	-		6 00/21						
7-18	60		80						
7-19	50		-						
7-20	-	10	90	39					
7-22	60	6	65	6					

Table D-2

Parameter Response

Date	lbs BOD/day/lb sludge L _f avg.	mg O ₂ /hr/gm O ₂ Uptake	(<u>µ moles</u>) mg VSS TTC	% COD Removal
6-11	24(170)			
6-12	1216(3.9)			
6-13		2 3	.043	
6-14	= 0.88	34	-	63
6-15		25	.046	63
6-16		-	.035	80
6-17		34	-	53
6-18		27	.038	47
6-19		36	.038	53
6-20		-	.049	5 9
6-21		45	.041	-
6 -2 2		36	.046	53
6-11 6-12	<u>24(170)</u> 1378(7)			
6-13		22		
6-14	= 0.43	20	.041	67
6-15		16	.038	68
6-16		18	.033	40
6-17		18		59
6-18		13	.011	65
6-19		17	.029	72
6-20		-	.035	75
6 -2 1		20	.025	-
6-22		14	.024	56
6-11 6-12	<u>24(170)</u> 1365 (5.4)			
6-13		15		
6-14	= 0.56	19	.043	67
6-15		17	.041	74
6-16		19	.034	40
6-17		-	-	
6-18		14	.026	53
6-19		24	.040	54
6 -2 0			.037	74
6-21		25	.048	-
6-22		14	.039	62

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Date	lbs BOD/day/lb sludge L _f avg.	mgO ₂ /hr/gm O ₂ Uptake	$\left(\frac{\mu \text{ moles}}{\text{mg VSS}}\right)$	% COD Removal
6-11	<u>24(170)</u>			
6-12	1170(1 2 .8)			
6-13		10		
6-14	= 0.27	6	.027	
6-15		6	.026	73
6-16		10	.010	_
6-17		-	_	-
6-18		8	.009	65
6-19		13	.028	79
6-20		-	_	_
6-21		15	.037	_
6-22		10	.013	77
			•	
6-11	24(170)			
6-12	1102(24.5)			
6-13				
6-14	= 0.15	5	.033	69
6-15		8	.027	
6-16		5	.009	
6-17		-	-	
6-18		8	005	
6-19		9	.000	
6-20		-	013	
6-21		5	007	75
6-22		8	.007	70
0-22		0		

Table D-2 (Cont'd.)

			Settling Curve Data*							
L _f	Time	Cylinder Level (ml)	Lf	Time	Cylinder Level (ml)	L _f	Time	Cylinder Level (ml)		
.88	0 2 3 6 8 10 12 16 30	1000 940 790 440 340 310 285 240 170	.56	0 2 3 6 8 10 12 16 30	1000 880 700 160 130 110 100 95 75	.43	0 1 2 4 6 8 18 30	1000 980 930 520 450 300 120 110		
.27	0 1 2 4 6 8 9 20 30	1000 910 760 330 240 190 120 110 110	.15	0 1 2 3 7 20 30	1000 700 540 190 100 90 90	0	0 2 3 6 7 20 30	1000 620 500 310 240 150 140		

able D-	3	
	`	2

* MLSS = 1,000 mg/1

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Figure D-1

Sludge Settling Curves for Various Organic Loadings

TABLE D-4

NITROGEN DATA

Unit 3	Date	Flow (l/day)	Influent TKN	TKN	Effluent NO ₂ , NO ₃	Total	MLSS wasted (gms as N)	Balance (%)
Lf=.88	11	30.6	34.0	15.0	8.8	23.8		
	12	26.6	37.0	17.4	8.5	25.9	.203	-19.0
	13	26.8	33.5	17.0	10.0	27.0		
	14	31.3	26.0	10.0	7.3	17.3	.545	+ 5.4
	15	25.1	31.0	14.8	6.8	21.6	.232	+ 0.6
	16	31.9	33.5	22.0	5.5	27.5	.154	- 3.5
	17,18	67.0	30.4	22.0	5.8	27.8	.125	- 2.8
	19	31.2	23.5	12.3	1.5	13.8	.230	- 9.6
	20	31.0	27.0	13.5	0.9	14.4	.232	
	21.	33.4	23.0	15.2	0.5	15.7	.293	+ 6.3
	22	32.7	29.8	23.0	0.2	23.2	.218	+ 0.3
<u>Unit 4</u>								
Lf=.56	11	19.1	34.0	6.0	15.4	21.4		
	12	17.0	37.0	8.5	16.8	25.3	.110	-26.0
	13	17.4	33.5	4.5	16.4	20.9		
	14	18.0	26.0	4.5	15.4	19.9	.375	+ 4.4
	15	17.1	31.0	6.8	13.9	20.7	.193	+ 3.2
	16	16.7	33.5	13.0	11.8	24.8		
	17,18	36.8	30.4	6.0	13.6	19.6	.202	-20.9
	19	16.8	23.5	2.5	12.8	15.3	.184	+11.6
	20	16.7	27.0	2.8	11.0	13.8	.188	- 7.2
	21	18.5	23.0	5.3	10.5	15.8	.220	+20.7
	22	17.5	29.8	19.0	2.2	21,2	.086	-12.5
<u>Unit 5</u>								
Lf = .43	11	6.9	34.0	4.3	16.8	21.1		
	12	15.1	37.0	6.5	16.0	22.5	.081	-28.8
	13	26.0	33,5	12.5	10.8	23.3		
	14	27.2	26.0	4.5	13.9	18.4	.546	+ 4.7
	15	14.8	31.0	5.0	15.1	20.1	.175	+ 3.3
	16	25.2	33.5	13.0	12.1	25.1	. 093	-13.9
	17.18	52.6	30.4	12.0	8.8	20.8	.312	- 3.6
	19	23.1	23.5	2.3	10.8	13.1	.262	+ 4.0
	20	21.7	27.0	2.2	10.8	13.8	.2.90	+ 0.7
	21	25.2	23.0	7.8	6.5	14.3	.113	-18.5
	22	18.1	29.8	19.0	1.2	20.2	.220	+ 8.3

TABLE D-4 (cont.)

		F		t1				1
<u>Unit 6</u>	Date	Flow ((/day)	Influent TKN	TKN	Effluent NO ₂ , NO ₃	Total	MLSS wasted (gms	Balance (%)
	1		L	<u> </u>			as N)	
Lf = .27	11	0.7	34.0	1.5	17.7	19.2		
	12	2.8	37.0	4.3	18.8	23.1	.072	+17.9
	13	5.3	33.5	5.6	17.7	23.3	.072	+10.7
	14	8.7	26.0	3.0	16.8	19.8	.022	-14.1
	15	4.7	31.0	5.0	14.6	19.6	.077	+15.0
	16	4.2	33.5	4.0	17.1	21.1		
	17,18	25.3	30.4	1.8	16.8	18,6	.089	-28.8
	19	13.5	23.5	2.2	12.9	15.1	.088	- 7.6
	20	10.9	27.0	1.7	11.5	13.2	.142	- 3.1
	21	13.3	23.0	1.8	11.3	13.1	.023	-35.6
	22	9.2	29.8	10.0	7.8	17.8	.104	- 2.2
<u>Unit 7</u>								
Lf = .15	11	2.3	34.0	2.3	16.0	18.3		
	12	3.2	37.0	4.3	17.7	22.0		
	13	5.0	33.5	3.6	17.7	21.3	.025	-33.0
	14	5.8	26.0	3.6	16.8	20.4	.046	+ 8.6
	15	4.7	31.0	3.6	15.4	19.0	.043	- 8.9
	16	5.0	33.5	3.5	16.8	20.3	.028	-17.0
	17,18	10.8	30.4	2.3	16.8	19.1	.021	-31.5
	19	5.3	23.5	1.7	16.4	17.1	.028	- 4.8
	20	4.3	27.0	4.8	9.8	14.6	.049	- 4.7
	21	5.3	23.0	1.7	12.1	13.8	.124	+ 6.1
	22	5.4	29.8	2.0	15.0	17.0		

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