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Demonstrating Leachate Treatment Report on a Full-Scale Operating Plant

DEMONSTRATING LEACHATE TREATMENT

REPORT ON A FULL-SCALE OPERATING PLANT

This report (SW-758) was written
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DEMONSTRATING LEACHATE TREATMENT
Report on a Full-Scale Operating Plant

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Summary and Conclusions

The results of 3 years of operation of a full-scale sanitary landfill leachate treatment plant are reported. The plant is designed to provide a variety of chemical/physical and biological treatment sequence options. The chemical/physical units include equalization, lime precipitation, sedimentation, air stripping, neutralization and nutrient supplementation. These treatment processes are designed to remove heavy metals, ammonia and organic materials, and to encourage subsequent biological treatment by reducing the pH and adding the nutrient phosphorus. The biological treatment process is activated sludge designed to provide both organic 5-day biochemical oxygen demand (BOD_5) degradation and nitrification. The demonstration leachate treatment plant is designed to provide operational flexibility in that the flow can be directed through the various unit processes and operations in any sequence.

The purpose of this project was to demonstrate the efficiency of a number of treatment sequences. Specifically, five modes of operation were defined and have been investigated. System 1 consists of chemical/physical treatment followed by activated sludge; System 2, chemical/

physical treatment only; System 3, biological treatment followed by chemical/physical; System 4, biological treatment only; and, System 5, bench-scale studies, including activated carbon adsorption treatment.

Data have been collected which can be used to characterize the quality of raw leachate generated in an operating sanitary landfill. These data show that the leachate from this sanitary landfill source is high in organic matter (average chemical oxygen demand (COD)/liter of 18,553 mg, average BOD_5/liter of 10,907 mg) and nitrogen (average NH_4^+-N/liter of 1,001 mg). At the end of the first 2 years of operation these figures were 11,210 and 17,562; 4,460 and 10,773; and 1,503 and 1,047, respectively. Thus, although influent nitrogen values have fallen, the increase in organic strength has been extremely large. The raw leachate heavy metal concentrations are somewhat lower than expected, possibly reflecting the relatively high pH of the leachate. (Note that all data have been collected with nonfiltered samples.)

High concentrations of ammonia in the raw leachate exceed the plant's effluent criterion and are sufficient to inhibit the growth of the activated sludge microorganisms. For this reason the original plant design was augmented with an ammonia stripping lagoon.

System 5 studies have been conducted for a number of purposes. Bench-scale tests have provided optimal operating data for chemical/physical units. In particular, System 5 has provided data for the development of lime, sulfuric acid, and phosphoric acid dosages.

Activated carbon adsorption has been evaluated as a treatment method for raw leachate. For raw leachate, carbon adsorption did not prove to be an effective treatment procedure. The inability to use

carbon adsorption is the result of high suspended solids loading causing pore plugging and the wide range of flow variability.

Pilot scale data have been collected for System 5, carbon adsorption of System 1 effluent. In this mode, the carbon column would serve as a tertiary, or advanced waste, treatment process. The results indicate that the carbon can remove much of the remaining COD and heavy metals. The results have been analyzed in terms of Langmuir adsorption isotherms and carbon breakthrough curves. This way of handling the data provides preliminary full-scale design information.

Systems 3 and 4, those in which raw leachate is influent to the biological units, have received considerable operating attention. The results indicate that the raw leachate is not directly treatable by biological means. Systems 3 and 4 yield an effluent which is high in organic matter. The mean effluent BOD from System 3 was 763 mg per liter. The performance of Systems 3 and 4 has not been satisfactory for the treatment of this leachate.

Systems 1 and 2 are those in which the raw leachate is treated first by chemical and physical means. The results of these systems are most promising. During the third year, these systems were preceded by equalization. Lime precipitation followed by sedimentation has been successful in removing the heavy metals and a portion of the organic matter. Specifically, this sequence (System 2) has removed about one-quarter of the nitrogen; one-third of the dissolved solids; one-half of the organic matter; three-quarters of the suspended solids; and ninety percent of the phosphates. The sequence has been successful in

removing the heavy metals including one-half of the cadmium and mercury; two-thirds of the lead, chromium, and nickel; three-quarters of the copper; over ninety percent of the iron and zinc.

The performance of System 2 has been studied carefully in order to determine the treatment unit's response to a number of operational parameters. It was found that temperature and pH both exert an effect on the concentration of heavy metals in the lime treatment effluent. However, the response is not identical for all heavy metals. It may be possible to use the differences in these responses in an operational control strategy to achieve optimal removal efficiences of selected contaminants.

An ammonia stripping lagoon is included in the chemical/physical treatment sequence because of the excessive ammonia levels in the raw leachate. During the lime precipitation/clarification/ammonia stripping mode of operation, the following removal efficiencies have been achieved: 66 and 50 percent of the BOD and COD, respectively; approximately 60 percent of the ammonia-N and total Kjeldahl-N; approximately 75 percent of the suspended solids; 25 percent of copper; 50 to 60 percent of cadmium and nickel; 64 to 68 percent of lead; approximately 96 percent of zinc; 98 percent of iron.

The ammonia lagoon has a detention time of 1.74 days, thereby providing an equalizing effect. That is, the effect of the lagoon is to dampen the peaks and to minimize shock loadings on subsequent treatment units. For example, during the period in which the lagoon was included in the treatment sequence, the mean ammonia concentration

in the raw leachate was 1001 mg per liter with a standard deviation slightly larger, indicating tremendous variability. During the same period, the ± 1 standard deviation interval for the ammonia lagoon effluent was 203 to 641 mg per liter. Thus, the equalization effect is significantly beneficial in terms of lessening shock loadings.

During the third year, an equalization pond was used to further dampen the fluctuations in leachate quality and quantity. This was done to provide a more even flow to the lime treatment unit. The effect of the equalization was to reduce influent variability for many parameters, as measured by the coefficient of variation; and to enable more uniform dosing of raw leachate with lime.

System 1 provided the best degree of treatment. This sequence consists of equalization, lime precipitation/clarification/ammonia stripping/neutralization/phosphorus addition/activated sludge. In this operational configuration, excellent removal efficiencies have been observed, following the adaptation of the activated sludge to the waste (Table 1). Except for NH_4-N, BOD_5, and lead, the effluent concentrations comply with the criteria developed by the Pennsylvania Department of Environmental Resources and the Delaware River Basin Commission for discharge to the Delaware River. The standards for these parameters were not met because of the unusually severe temperatures of the winter of 1976-77, and secondarily because of the great increase in raw leachate strength which began during the second year of this project. (The treatment performance of System 1 met all standards during periods with relatively warm weather. During the period up to January 1977

TABLE 1

SUMMARY OF SYSTEM 1 OPERATION DATA

	8/1/76 to 5/1/77 and 4/1/78 to 8/31/78			
Parameter	Raw Leachate mg/liter	Final Effluent mg/liter	Percent Removal	Discharge Standard mg/liter
Ammonia-N	758	75	90.1	35
BOD_5	11886	153	98.7	100
Cadmium	0.08	0.017	78.2	0.02
Chromium	0.26	0.07	73.1	0.1
COD	18490	945	94.9	*
Copper	0.40	0.11	72.5	0.2
Iron	333	2.7	99.2	7.0
Lead	0.74	0.12	83.8	0.1
Mercury	0.006	0.004	27.4	0.01
Nickel	1.76	0.75	57.4	*
Zinc	19.5	0.53	97.3	0.6

*No discharge standard for this parameter.

System 1 consistently met the effluent criteria. Likewise, during the third project year, the summertime performance of System 1 was excellent.)

The System 1 operating data have been examined closely in order to characterize the ammonia removal mechanisms. In the lagoon this occurs as the result of volatilization of the free ammonia predominant at high pH levels. In the activated sludge units, the principal mechanism for ammonia removal is biological nitrification to nitrate. The rate of nitrification, expressed as the specific oxidation rate, is a function of temperature which follows the van't-Hoff Arrhenius relationship. The results show that the activation energy is approximately 12350 cal. per mole, and the Arrhenius frequency factor is 2.18×10^{9} day $^{-1}$ The data indicate that substrate inhibition due to ammonium ion concentration occurs in this system. This relationship has been fitted to the Haldane inhibition model. The maximum specific oxidation rate is 3.5 g N oxidized per g biomass/day. The saturation constant is 4 mg per liter, and the inhibition constant is 36 mg per liter.

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R.L. Steiner, J.D. Keenan, and A.A. Fungaroli

I. INTRODUCTION

The potential for water pollution from sanitary landfill sites has become recognized in recent years. A number of studies have documented the great pollutional strength of landfill leachates.[1-15] The quality of this material varies with landfill age, nature and moisture content of the wastes disposed at the site, and hydrologic and soil factors. In spite of this variability, it can be stated that, especially for young landfills, the values of the critical sanitary parameters of leachate are at least an order of magnitude greater than for domestic sewage. The deleterious consequences following contamination of ground and/or surface waters by leachate may be severe, and it is for this reason that leachate treatment is receiving attention.

Solid waste consists of matter which can be decomposed by bacterial or microbial action, as well as of materials which are inert to microbiological activity. Some of the compounds, cellulose in particular, are resistant to biological breakdown, but with sufficient time decomposition will occur. Because of this resistivity and necessity to acclimate the biological system, the chemical characteristics of leachate are time-dependent. To complicate treatment, as the paper

decomposes, some of the inorganic ions which are bound to the organic matrix are released and can be removed by water percolating through the landfill. The actual mechanism of removal varies with the component but includes solution as well as colloidal transport.

The generation of leachate in landfills is complicated and cannot be generalized simply as surface water percolating through the sanitary landfill. When refuse is placed in the landfill, decomposition begins to occur. Some decomposition products may be water soluble whereas the parent products might not have been. This is especially true of cellulose. In addition, the inorganic constituents also must be considered since they vary with the state of decomposition. The amount of water percolating through a sanitary landfill is the primary control of leachate quality, but the chemical characteristics of the leachate are dependent on other parameters, including temperature, water composition, moisture content, time, mode of decomposition (aerobic, etc.) and the amount of infiltration of rainfall at the landfill.

Recent studies have shown that leachate is produced in a sanitary landfill when the precipitation exceeds the net evapotranspiration of the region. Remson, Fungaroli and Lawrence developed a model for predicting the movement of leachate through a sanitary landfill.[16] Further results using this model have substantiated the validity of the approach and prediction of leachate generation patterns is reasonably accurate. Dass et al. have also used a water budget method for predicting leachate generation.[17]

Ground and surface waters can be protected if the landfill is underlain with an impervious membrane. With proper design, leachate

is then directed toward collection points. A waste such as this, which is properly considered an industrial waste, must be treated prior to surface discharge. The leachate treatment state-of-the-art is still embryonic, although a few small scale studies have been conducted. These have demonstrated that neither conventional chemical treatment nor biological treatment can achieve the high degree of treatment efficiency expected today. Consequently, although we know that the pollution potential of sanitary landfill leachate can be avoided by interception using impervious liners, we are not yet able to define the optimum sequence of unit operations and processes required for adequate wastewater renovation.

The U.S. Environmental Protection Agency, Office of Solid Waste, awarded a demonstration grant (S-803926) to investigate the effectiveness of alternative treatment sequences as employed at the full-scale facility in Falls Township, Pennsylvania. A 380 liter per minute (0.144 mgpd) plant had been constructed to treat leachate from the GROWS (Geological Reclamation Operations and Waste Systems, Inc.) landfill. This project had as its primary goal the evaluation of the technical feasibility, operational efficiency, and cost effectiveness of four alternative treatment sequences. These are: (1) chemical/physical followed by biological; (2) chemical/physical alone; (3) biological followed by chemical/physical; and (4) biological alone. The chemical/physical processing includes precipitation of heavy metals by lime addition, sedimentation, air stripping of ammonia, and neutralization using sulfuric and/or phosphoric acids. Equalization

of raw leachate was initiated during the third year of the project. Biological treatment consists of conventional activated sludge. Additional objectives of the study were the bench-scale evaluation of carbon adsorption on both raw leachate and unit process effluents; and bench-scale testing to determine chemical dosage, sludge return rates, aeration rates, and other plant operation criteria (System 5). The purpose of this document is to present and discuss the results of the 3 years of operation of this facility.

II. OVERVIEW OF LEACHATE TREATMENT OPTIONS

The purpose of this chapter is to review the literature regarding the composition of sanitary landfill leachates and their treatment. In brief, the character and variability of the leachate dictates the types of treatment systems which will be effective. The contaminants of greatest concern fall into several groups. The first group is the organic chamicals, important primarily because they exert an oxygen demand on receiving waters which may result in a depletion of dissolved oxygen deleterious to aquatic life. The second major group of contaminants found in sanitary landfill leachates is comprised of the heavy metals. As a group, these elements are of concern because they are toxic at sufficiently high concentrations. It is conventional practice to chemically characterize wastewaters such as leachate in terms of a number of other parameters. These are used for a variety of purposes including design, operation control, and evaluation of pollution potential.

Leachate Composition

In 1932, one of the first studies indicating that the disposal of solid waste could cause environmental pollution was reported by Calvert who investigated the liquid waste from a garbage reduction plant in Indianapolis.[2] In this process the garbage was cooked and the grease removed to produce fertilizer and animal feed, and the liquid waste was discharged into an impounding pit or lagoon. An analysis of this liquid is presented in Table 2, Column 1. Calvert analyzed the groundwater from existing wells surrounding the lagoon and found that wells up to

TABLE 2

THE STRENGTH OF RAW LEACHATES[24,25]*

Parameter	(1)	(2)	(3)	(4)	(5)	Average Age of Fill Material: 0.5 yr (6)	6 yr (7)	17 yr. (8)	(9)	(10)	Range 1 (11)	Range 2 (12)	Range 3 (13)
Acidity, as $CaCO_3$	3,000-3,300	100-9,450	-	-	-	-	-	-	-	-	-	-	-
Alkalinity, as $CaCO_3$	-	25-4,000	730-9,500	-	-	3,255	4,159	1,001	-	2,600-23,000	0-20,850	142-3,520	560
Aluminum Oxide	874	-	-	-	-	-	-	-	-	-	-	-	-
Ammonia-N	-	-	0.2-480	54	700	-	-	-	177	-	0-1,106	1.4-1,028	155
Arsenic	-	-	-	-	-	4.31	0.1	4.6	-	-	-	-	-
Barium	-	-	-	-	-	8.5	0.8	0.3	-	-	-	-	-
BOD-5	-	6-7,330	-	975	7,745	-	-	-	-	41,000-180,000	81-33,360	3.9-57,000	6,300
BOD-20	-	-	21,700-30,300	-	-	54,610	14,080	275	-	-	-	-	-
Cadmium	-	-	-	-	-	-	-	-	-	-	0.03-17	-	-
Calcium	66.3	-	240-2,330	-	-	-	-	-	-	-	60-7,200	76-3,900	550
Carbon, Total Organic	-	-	-	-	-	-	-	-	-	-	256-28,000	70-27,700	3,600
Chloride	2,950	280-12,300	96-2,350	128	2,000	1,697	1,330	135	2,340	-	4.7-2,467	60.2-2,467	470
COD	-	-	-	-	-	39,680	8,000	40	50,715	-	40-89,520	31.1-71,680	8,000
Copper	-	-	-	-	-	0.05	0.05	0.05	5.0	-	0-9.9	-	-
Cyanide	-	-	-	-	-	0.024	0.005	0.02	-	-	-	-	-
Dissolved Oxygen	-	0-5.6	-	-	-	-	-	-	-	-	-	-	-
Fluoride	-	-	-	-	-	-	2	0.31	-	-	-	-	-
Hardness, as $CaCO_3$	-	-	890-7,600	523	-	7,830	2,200	540	5,500	-	0-22,800	-	-
Iron	246	-	7-220	-	-	5,500	6.3	0.6	1,640	-	0-2,820	0.5-2,200	440
Lead	-	-	-	-	-	-	-	-	-	-	<0.1-2.0	-	-
Magnesium	182	-	64-410	-	-	-	-	-	-	-	17-15,600	35-1,140	210
Manganese	-	-	-	-	-	1.66	0.06	0.06	-	-	0.09-125	-	-
Nickel	-	-	-	-	-	-	-	-	0.8	-	-	-	-
Nitrate-N	-	-	-	-	-	1.70	0.70	1.60	-	-	-	-	-
Nitrite-N + Nitrate-N	-	-	-	-	-	-	-	-	-	-	0.2-10.29	0.4-10.29	1.5
Nitrogen, Total	-	-	-	-	-	-	-	-	-	2,000-10,000	-	-	-
Organic-N	-	-	2-465	7	200	-	-	-	482	-	-	-	-
pH	-	5.7-8.4	6.0-6.5	-	-	-	6.3	7.0	-	-	3.7-8.5	5.09-7.25	5.98
Phosphates, P	-	-	0.1-10	-	-	2	0.4	3.0	43	-	6.5-85	0.25-85	3.2
Phosphorus, Total, P	-	-	-	-	-	-	-	-	-	-	0-130	0.5-98	9
Potassium	-	-	28-1,700	-	-	-	-	-	-	-	28-3,770	35-2,300	380
Sodium	-	-	85-1,700	-	-	900	810	74	3,800	-	0-7,700	44-1,580	280
Specific Conductance	-	-	-	-	-	-	-	-	-	-	2,810-16,800	978-16,800	4,970
Sulfate	-	-	84-730	3	1,950	680	2	2	375	-	1-1,558	7.4-1,558	90
Sulfide	-	-	-	10	-	-	-	-	-	-	-	-	-
Suspended Solids	1,000-2,500	-	-	-	-	-	-	-	26,500	-	10-700	8.9-923	197
Total Dissolved Solids	-	-	-	-	-	19,144	6,794	1,198	-	-	584-44,900	-	-
Total Solids	-	-	-	-	-	-	-	-	43,000	-	0-59,200	911-55,348	6,080
Zinc	-	-	-	-	-	-	0.13	0.10	129	-	0-370	-	-
Reference No.	2	3	4	5	6		9		10	11		16	

*All units are mg per liter except pH (pH units) and specific conductance (μmho/cm).

500 feet downstream of the site showed a marked increase in magnesium, calcium, total dissolved solids and carbon dioxide.

Carpenter and Setter, working at New York University in 1940, conducted one of the earliest studies concerned with landfill leachate.[19] Auger holes were drilled through an existing landfill of undetermined age into the subsoil. Twenty-eight samples of leachate which were collected in the bore holes were analyzed chemically. The range of concentrations is presented in Table 2, Column 2. These results showed a wide variation of concentration over the site, thus indicating the difference of filled materials at various locations, or the differences in the age of the refuse at different points. Analysis of groundwater in the area was not performed; therefore, the effect on the subsurface environment was undefined.

The first comprehensive research study of sanitary landfills under controlled conditions was conducted at the University of Southern California.[20] Test bins, simulating landfill conditions, were constructed. Water was added to simulate the infiltration of 1.12 m and leachate was collected and analyzed. Table 2 gives the minimum and maximum (Column 3) values of the initial (first 45.9 liters of leachate per cu m of compacted refuse) leachate. The most rapid removal (the highest concentrations) occurred with the first 232 liters per cu m of refuse. Thus, it was postulated that removal would continue for many years but at a very slow rate, and it was considered unlikely that all the constituents would ever be removed.

The same study also examined a field site consisting of 2.4 m of refuse and 0.61 m of cover material. The refuse was in intermittent contact with the groundwater, analysis of which showed increases in all organic ions and a maximum biochemical oxygen demand of 125 mg/liter. One conclusion of the study was that the dissolved inorganic ions entering the groundwater through intermittent contact would decrease in concentration as a result of dilution and adsorption and travel in the direction of the groundwater movement.

The other conclusions reached in this study are summarized as follows: (1) A landfill, if located so that it is in intermittent or continuous contact with ground water, will cause the ground water in the immediate vicinity of the landfill to become grossly polluted and unfit for domestic or irrigational use; (2) dissolved mineral matter, entering ground water as a result of intermittent and partial contact of a landfill with the underlying ground water will have its greatest travel in the direction of flow, undergo a vertical diffusion to a limited extent, and be subject to dilution, the result of which will be a minimizing of the effect of the entering pollutant ions; (3) a landfill, if located so that no portion of it intercepts the ground water, will not cause impairment of the ground water for either domestic or irrigational use; (4) rainfall alone (in the area of this study) will not penetrate a 2.3 m thick landfill sufficiently to cause entry of leachate into the underlying ground water.

Longwell stated in 1957 that an appreciable proportion of refuse could be extracted by water to produce a leachate rich in organic

matter, inorganic salts (ions), and bacteria.[21] The analysis of a surface leachate obtained from an unnamed landfill is given in Table 2 (Column 4).

In 1961 the British Ministry of Housing and Local Government conducted extensive research on the placement of landfills above the groundwater table (which they called "dry tipping"), and the placement of landfills below the groundwater table (which they called "wet tipping").[22] In the "wet tipped" experiment the refuse was completely submerged and the horizontal groundwater flow rate was equivalent to 138 liters per sq m per day. The leachate quality is included in Table 2 (Column 5). Analyses of the groundwater before and after contact with the refuse are given in Table 3. These results show the considerable extent of groundwater quality degradation due to pollution by leachate.

In 1965, Qasim studied the seepage waters from simulated landfills at the University of West Virginia.[23] Three concrete cylinders 0.9 m in diameter and 1.2, 2.4 and 3.7 m in height were filled with municipal refuse. Approximately 102 cm of precipitation were artificially added to the cylinders over a period of 6 months and leachate samples were collected. The maximum concentrations of certain organic and inorganic components in the leachate from the three cylinders are presented in Table 4. Table 4 also presents the total weight removed per cubic meter from each depth of fill by 102 cm of simulated infiltration.

A summary of results presented by Qasim demonstrates the effect of depth on leachates generated by landfills. Concentrations of various pollutants were higher in leachates obtained from deeper fills. Concentrations of various pollutants per unit depth of fill decrease

TABLE 3

EFFECT OF SOLID WASTE DISPOSAL ON GROUNDWATER QUALITY. GROUNDWATER QUALITY BEFORE AND AFTER INTRODUCTION OF "WET TIPPED" LANDFILL - 1961[26]

Measured Quantity	Concentration (mg/liter) Upstream of Landfill	Concentration (mg/liter) Downstream of Landfill
Total Solids (Residue)	450	5,000
Chloride	30	500
Alkalinity, as $CaCO_3$	180	800
Sulfate	120	1,300
Biochemical Oxygen Demand (BOD_5)	0	2,500
Organic Nitrogen	0	70

Table 4

EFFECT OF LANDFILL DEPTH ON LEACHATE COMPOSITION AND POLLUTANT REMOVAL AT THE UNIVERSITY OF WEST VIRGINIA - 1965[29]

Parameter	Concentration (mg/liter)			Pollutant Removal (kg per cu m)		
	0.76 m Fill	1.98 m Fill	3.1 m Fill	0.76 m Fill	1.98 m Fill	3.1 m Fill
Alkalinity, as $CaCO_3$	10,630	16,200	20,850	--	--	--
Bicarbonate	--	--	--	9.4	7.1	5.9
BOD_5	14,760	26,200	33,360	12.7	10.6	9.0
Chloride	951	2,000	2,310	0.8	0.6	0.6
Hardness, as $CaCO_3$	7,600	13,100	10,950	2.8	1.8	1.1
Nitrogen, Total	613	1,389	2,508	0.6	0.6	0.6
Sodium and Potassium	1,634	3,963	5,109	22.0	16.6	14.4
Solids, Total	21,140	49,800	59,000	--	--	--
Sulfate	--	--	--	0.5	0.3	0.2

with increasing depths of refuse. For an equal amount of influent, shallower fills showed greater extraction rate per unit volume of fill than deeper fills. The bulk of the pollution was attributed to initial leaching.

Anderson and Dornbush conducted an extensive investigation of the groundwater leaving a landfill in Brookings, South Dakota in 1967.[27] An abandoned gravel pit of 160 acres with its base well below the water table was filled with municipal solid waste. The purpose of the investigation was to determine which chemical parameters were the most reliable indicators of the influence of landfills on the groundwater. Groundwater samples from 22 wells located over the site were analyzed for chloride, total hardness, alkalinity, sodium, pH, potassium, iron, nitrate, and specific conductance. A considerable increase in all constituents measured was observed in three wells immediately downstream of the fill area. Although the authors did not evaluate the potential pollution of municipal refuse, they did report an increase of up to 50 times the chloride content of native waters in the groundwater affected by the leachate. The major conclusion of this investigation was that two of the most important indicators of pollution from landfills are chlorides and specific conductance or total dissolved solids. Chloride ions are easily detectable, not readily absorbed by soils, not affected by biological processes, and apparently an abundant product of leachates.

Disposal sites in northern Illinois were investigated in 1970 by Hughes et al.[28] Leachate samples from three landfills of varying age

were obtained as near to the base of the refuse layer as possible. The results of these analyses are presented in Table 2 (Columns 6-8). Although no information is given in the study as to the composition of the solid waste in each fill, and the analyses were performed on only one sample, the results do show a decreasing trend with time. However, it was noted that refuse more than 15 years of age can still have a high total dissolved solids content--indicating that the stabilization of landfills is a long process.

The laboratory simulated landfill or lysimeter study conducted at Drexel University from 1967 to 1972 is the only study reported that was conducted under completely controlled laboratory conditions. It was also the only study reported in which the environmental conditions completely simulate the existing climatic conditions of a region, in this case, southeastern Pennsylvania. The refuse was placed at as received moisture content and allowed to reach field capacity naturally through the addition of amounts of distilled water equal to the precipitation of the area minus the evapotranspiration. This infiltration was added on a weekly basis and varied from a rate of 8.9 cm per month during the wet periods to zero during the dry or summer periods. Approximately one year was required for the refuse to reach field capacity, but small quantities of leachate were generated before field capacity was reached. The maximum concentrations obtained in the first year are given in Table 2, Column 9.[30]

It was concluded that this initial leachate production came from the following sources: (1) From the refuse. Most of the initially generated leachate is squeezed from the organic components of the refuse

by the compaction and placement procedure. (2) From channeling. Some of the water added at the top of the lysimeter may find a direct route through the refuse to the collection trough, due to any inhomogeneities in the refuse. (3) From an advanced wetting front. The wetting front in the refuse probably moves as a broad band rather than as a single line interface. As a result, substantial increases in leachate will occur before the entire system is at field capacity. (4) From the main wetting front. This is the leachate which is produced when the system reaches field capacity. At this time, the input water and the output leachate quantities become approximately equal.

Other studies have mentioned the leachate problem of refuse disposal in papers dealing with other aspects of the solid waste problem. Leo Weaver has stated that municipal refuse can generate leachates high in organic pollutants.[31] Data from this study are included in Table 2 (column 10).

Engineering Science in a study conducted in 1967 in southern California concluded that groundwater pollution, which may arise from refuse leachate reaching a water source, will be shown largely as an increase in total dissolved solids and specific conductance.[32]

Walker in 1969 found that a sand and gravel aquifer in Illinois was ineffective in removing dissolved chemical ions generated by a landfill.[33] He did report that travel of leachate through a short distance (3 to 5 m) of this aquifer will remove organic pollutants generated by landfills in Illinois and concluded by stating that inorganic pollutants constitute the greatest source of concern.

Roessler noted an increase in inorganic pollutants in an industrial water supply 2½ miles downstream from a refuse dump 10 years after the dump had started operation.[34]

Table 2 (columns 11 to 13) presents a summary of values of raw leachate composition as compiled by Chian and DeWalle.[35] The ranges represent leachates examined by a number of investigators (Range 1--Column 11) and a variety of leachates studied at the University of Illinois (Range 2--Column 12). These data are the results of a recently completed literature review. Another recent report summarizes the state-of-the-art with respect to ground water monitoring for leachate contamination.[36] This paper should be consulted before initiating a monitoring program.

The conclusion to be drawn from this review of landfill leachate quality (as summarized in Table 2) is that its composition is highly variable from site to site. In addition, the data show that even at a given landfill, considerable variation is encountered with respect to both space and age. That is, variability is a factor within a landfill and also over the history of the site. Consequently, it is concluded that landfill leachate quality cannot be predicted a priori; and that this quality is even variable at a given site.

Leachate Treatment

Leachate treatment systems have been evaluated on a laboratory scale at Drexel University. In one study, the purpose was to characterize the biodegradation of organic matter both with and without the supplementary addition of chemicals.[37] The system consisted of

five aerobic units which were treated in the following manner: (1) control-no treatment; (2) addition of sodium hydroxide to pH 9; (3) addition of sodium hydroxide to pH 11; (4) addition of lime; (5) addition of lime plus sodium carbonate. Otherwise, all units were handled in the same manner. This procedure included preparation of an activated sludge culture by aerating leachate. Each experimental unit was seeded with this culture and was aerated at a rate of 94 liters of air per gram chemical oxygen demand (COD) (1500 cu ft per lb COD). During the testing, all settled solids were recycled to the aeration tank with no sludge wastage. The aeration treatment systems were operated on a continuous basis with a hydraulic residence time of five days.

The COD values decrease quite rapidly during the first six days and thereafter approach a limit (Figure 1). The results indicate that there are components of leachate which are not amenable to treatment in an aerobic system. The time of adaptation of microorganisms for treatment of the organic fraction of leachate may be considerably longer than normal sewage. Volatile solids concentrations in these tests were low when compared to normal activated sludge systems. This may be one reason for the long time required for stabilization.

A high variation in the concentration of total dissolved solids in the treated effluent was noted (Figure 2). The cyclic variation of several systems is of interest, but not all of the systems show this phenomenon. Since the withdrawal and addition of leachate was constant, there was no reason for the cyclic effect. Only pretreatment with lime

FIGURE 1. REDUCTION IN COD DURING AEROBIC TREATMENT

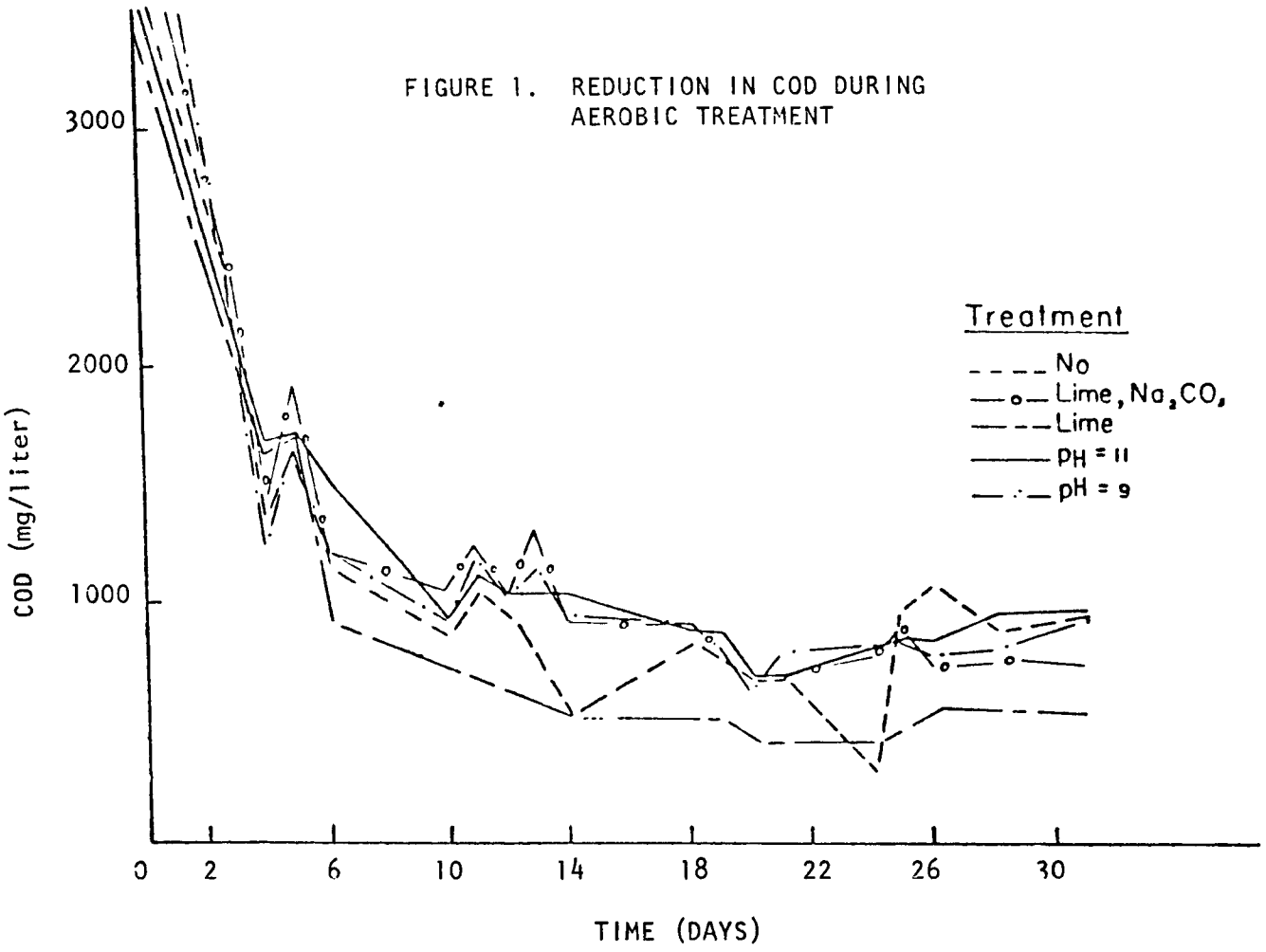
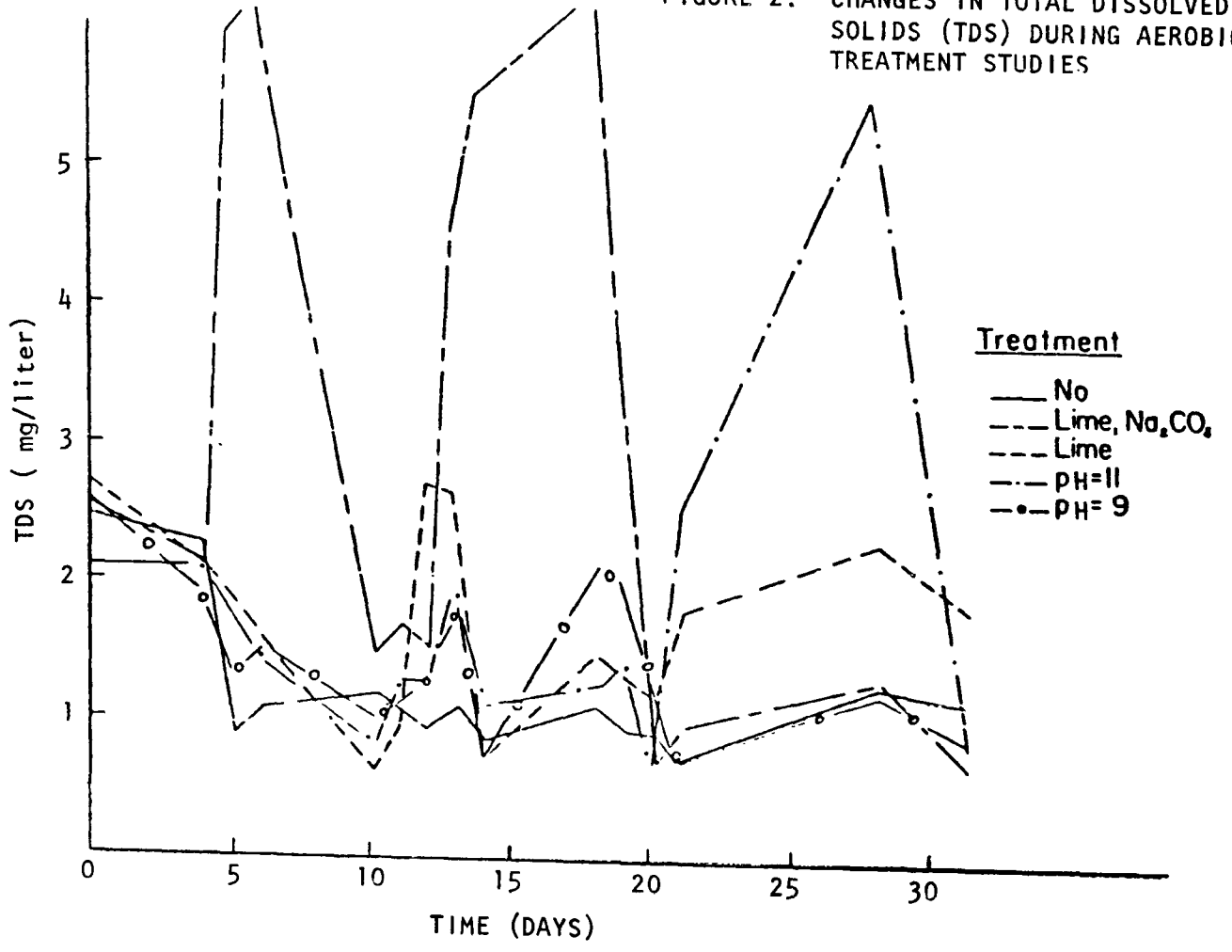


FIGURE 2. CHANGES IN TOTAL DISSOLVED SOLIDS (TDS) DURING AEROBIC TREATMENT STUDIES



gave any type of stability and COD reduction.

Thus, neither biological waste treatment nor chemical-physical treatment separately is able to reduce the biochemical oxygen demand (BOD) more than eighty percent. In fact, the efficiency of the chemical-physical process is considerably below this level. It is hypothesized that two reasons exist for the poor removal efficiency of each individual system: 1) the large percentage of high molecular weight organic materials, and 2) the biological inhibition caused by heavy metal presence. The physical-chemical treatment is needed to remove the metals and also to hydrolyze some of the organics, and biological treatment to stabilize the degradable organic matter.

In addition, biological treatment alone does not remove significant amounts of the heavy metals. In fact, biological units may be inhibited due to the toxic effects of the metals. Consequently, chemical and/or physical processing is needed for the removal of substantial amounts of these materials. Lime treatment is particularly effective in that it creates the alkaline conditions under which the metals become insoluble.

The removal of heavy metals during lime precipitation depends upon the formation of insoluble metal compounds, primarily hydroxides, at alkaline pH. The optimum set of conditions is not identical for all metals, and the result is that it is impossible to achieve the maximum theoretical removals for each metal within a single tank. In general, the optimum pH levels are in the range of 7-10.3 (Table 5).[38] Hexavalent chromium is not removed by lime addition unless it has previously been reduced to trivalent chromium.

TABLE 5

THEORETICAL REMOVAL OF HEAVY METALS DURING LIME PRECIPITATION[41]

	Optimum pH Range	Theoretical Effluent Concentration mg/liter
Cadmium	10	1.0
Hexavalent chromium	--	--
Trivalent chromium	8.5-9.5	<1
Copper	9.0-10.3	0.01
Soluble Iron	7	
Lead	--	<0.1
Nickel	10	0.01
Zinc	--.	<0.1

These studies demonstrated that the aerobic treatment of sanitary landfill leachate is feasible and that pretreatment may be required. Lime precipitation appears to be the most favorable pretreatment method. The organic fraction of leachate was found to contain substances not readily assimilated by the microorganisms, and it was hypothesized that chemical treatment is needed to remove these organics.

Chian and DeWalle have treated lysimeter leachate anaerobically.[39] They used a completely mixed anaerobic filter with recirculation of effluent. The unit responded well to shock loads, produced low sludge yields and operated without nutrient supplementation in spite of a COD: N:P ratio as high as 4360:112:1. Heavy metal toxicity was minimized by the addition of sodium sulfide.

Chian and DeWalle have recently completed an extensive review of leachate treatment techniques.[40] Their conclusion was that leachate collected from recently leaching landfills is best treated biologically. This is because the organic fraction of such leachate is composed predominantly of free volatile fatty acids which are readily biodegradable by either aerobic or anaerobic means. On the other hand, leachate from older landfills is more efficiently handled by chemical-physical processes, because these organics are more resistant to biodegradation. They also concluded that activated carbon and reverse osmosis were the most efficient chemical-physical methods in terms of the removal of organics.

A more recent study by Chian has been devoted to a detailed analysis of the constituents of the organic fraction of grossly polluted groundwater and of leachate collected from wells or underdrains near

solid waste disposal sites.[42] The techniques used for concentrating, separating, and characterizing the soluble organics were membrane ultrafiltration, gel permeation chromatography and analysis for functional groups and specific organics. The free volatile fatty acids constituted the largest fraction and this fraction became relatively smaller as the age of the landfill increased. Increasing stability with increasing landfill age was noted for other groups of organics. These results tend to confirm the concept that biological treatment is best suited for treating leachate from a young landfill, and that physical-chemical processes are more appropriate for older landfills.

The compilation of data presented by Chian and Dewalle indicate the following range of COD removal efficiencies for various treatment methods: 0 to 98 percent for aerobic biological; 87 to 99 percent for anaerobic biological; 17 to 40 percent for aerobic/anaerobic biological; 0 to 40 percent for chemical precipitation with alum, ferric chloride, ferrosulfate or lime; 34 to 94 percent for activated carbon and ion exchange; 0 to 48 percent for chemical oxidation; 56-98 percent for reverse osmosis.[43]

As a means to bring order to the wide disagreement found in the literature, Chian and DeWalle postulated that the age of the landfill affected the character of the leachate, and that this character is best measured in terms of the ratios of chemical oxygen demand to total organic carbon (COD/TOC) or of biochemical oxygen demand to chemical oxygen demand (BOD/COD) (Table 6).[44]

A recent laboratory scale study by Uloth and Mavinic is closely related to the present effort.[45] They studied aerobic biological

TABLE 6

LEACHATE TREATABILITY AS HYPOTHESIZED BY CHIAN AND DeWALLE[47]

Leachate Quality				Treatment Efficiency*						
COD/TOC	BOD/COD	Age of Fill	COD, mg/l	Biological	Chemical Precipitation	Chemical Oxidation	Ozonation	Reverse Osmosis	Activated Carbon	Ion Exchange
>2.8	>0.5	Young (<5 yr)	>10,000	G		P	P	F	P	P
2.0-2.8	0.1-0.5	Medium (5 yr-10 yr)	500-10,000	F	F	F	F	G	F	F
<2.0	<0.1	Old (>10 yr)	<500	P	P	F	F	G	G	F

*(G = good; F = fair; P = poor)

treatment of very strong leachates. They were able to develop kinetic constants fitting the Lawrence-McCarty model.[46] Successful operation was attained at mixed liquor volatile suspended solids concentrations of 8000 to 16000 ppm at sludge ages in excess of ten days.

Summary

The state-of-the-art concerning the composition and treatment of sanitary landfill leachates has been assessed. The most obvious characteristics of leachate are its strength and its variability. Leachate is generally of much greater strength than domestic sewage. This is especially true in terms of organic materials and the potentially toxic heavy metals. As important a characteristic as strength is the variability of leachate composition. Leachate quality not only fluctuates from landfill site to site, but also from time to time at one landfill. Changes over time result from differences in seasonal hydrology and microbiological activity. Rainy weather may dilute the leachate, but, at the same time, may flush out large quantities of pollutional material. The typical pattern observed over many years is that the pollution potential of leachate is greatest during the first five years or so after placement, but that leachate strength remains significant for as long as ten to twenty years. This sequence is encountered because the microbiological processes responsible for the decomposition of the solid wastes are relatively slow acting and are first directed at the most readily biodegradable components of the waste.

Considerable differences are encountered in leachate quality when comparing landfills. In addition to the seasonal, hydrologic and age

of landfill factors mentioned above, there are several other reasons for this observation. The chemical nature of the wastes accepted at the landfill has a marked effect on the composition of the leachate. The land disposal of industrial liquid and solid wastes is critical in this light.

The variability and the strength of leachate have important waste treatment implications. First, the sheer magnitude of the measures of pollution potential dictate the use of thorough waste treatment. Second, the changes encountered from landfill to landfill are such that waste treatment techniques applicable at one site are not necessarily directly transferable to other locations. That is, it may be mandatory that each instance be separately engineered to achieve adequate treatment. Third, the fluctuations in leachate quality which occur over both short and long term intervals must be accounted for in the treatment design. Not only must processes be designed to treat efficiently the waste flow from minute to minute, but the design must also reconcile the possibility that treatment techniques which work well for a young leachate may become wholly inadequate as landfill age increases.

It is apparent today that most landfill leachate cannot be treated adequately by just conventional chemical/physical treatment or conventional biological treatment. Rather, what is needed is a combination of the two approaches with perhaps a supplementary form of advanced wastewater treatment. The purpose of this project is to investigate, at both the full and bench-scale levels of operation, the efficiency of treatment afforded by these processes.

III. LEACHATE TREATMENT SYSTEM

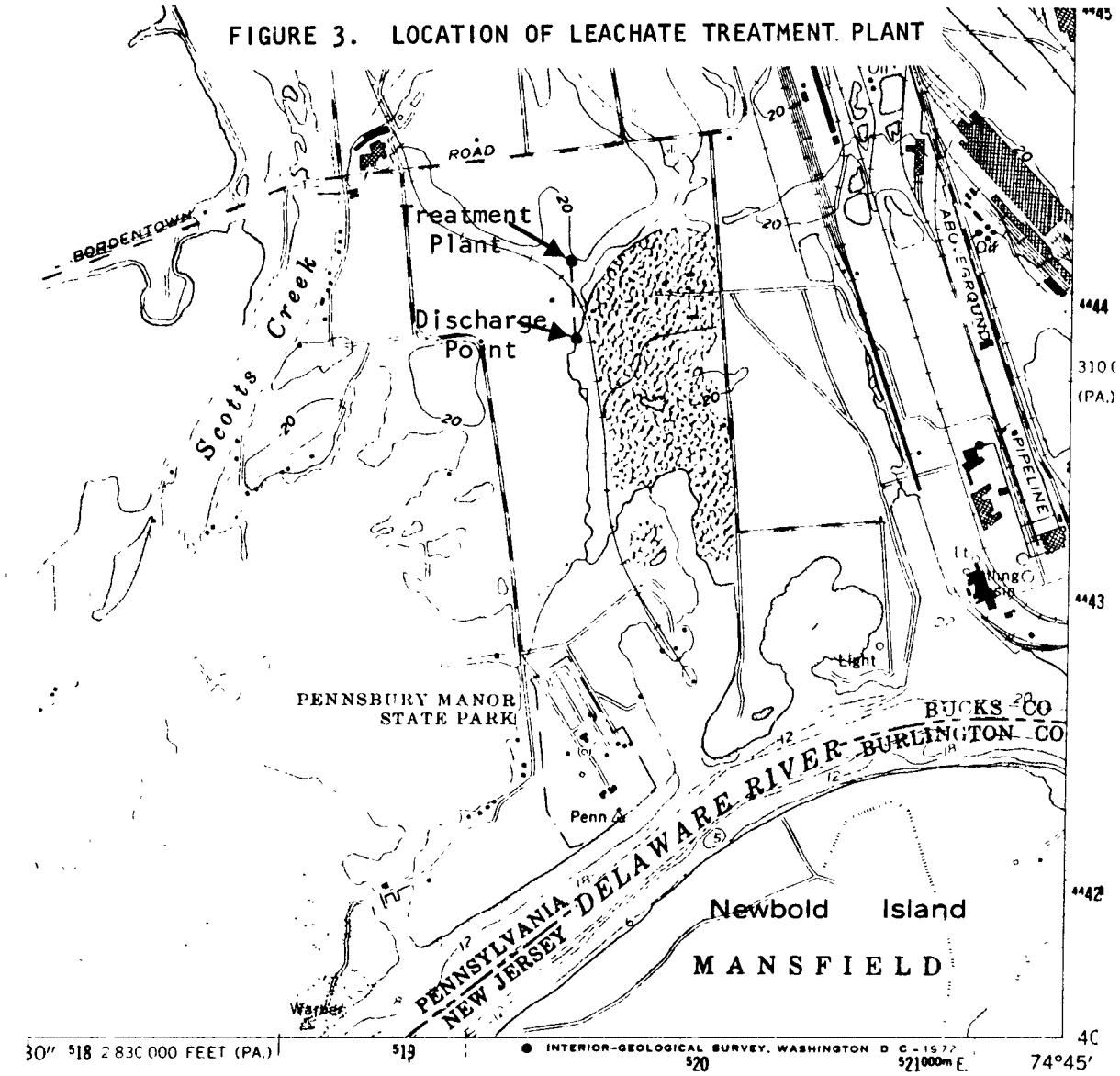
The leachate treatment facility used in this study is located at the GROWS landfill in Tullytown, Falls Township, Bucks County, Pennsylvania (see Figure 3). The plant is designed to provide maximum operational flexibility in order to permit full-scale testing of a variety of treatment sequences. Plant design and treatment modes are considered in subsequent paragraphs.

The sanitary landfill has a surface area of 50 acres. The landfill will be filled with about 1,400,000 cu m of refuse over the next several years. The time required to fill the landfill depends upon many unknown factors, but it is estimated that it will probably be between 5 and 10 years. The receipt of refuse is about 800 tons per day. Eighty-five percent of the refuse is from municipal sources. The remainder is industrial and commercial. The landfill is also permitted to accept sewage sludge and selected industrial liquid wastes.

The landfill is located in the semi-humid northeastern part of the United States. The thirty year monthly average precipitation and temperature data are given in Table 7. In this region there is a net positive infiltration of rainfall into the landfill. As long as there is a net positive infiltration, leachate will eventually begin to be produced by the landfill.

Because of these meteorological conditions and the site hydrologic situation, groundwater pollution potential existed. To alleviate this pollution potential the Pennsylvania Department of Environmental Resources required the landfill to be underlain by an impervious asphaltic membrane. This membrane system was designed to collect and transport the leachate

FIGURE 3. LOCATION OF LEACHATE TREATMENT PLANT

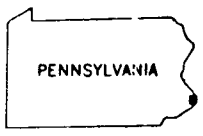


ROAD CLASSIFICATION

Heavy-duty ——— Light-duty ———

Medium-duty ——— Unimproved dirt - - - - - -

U S Route State Route Interstate Route



QUADRANGLE LOCATION

TRENTON WEST, PA.—N. J.

NE/4 BURLINGTON 15' QUADRANGLE

N4007.5—W7445/7.5

TABLE 7

PRECIPITATION AND AVERAGE MONTHLY TEMPERATURE DATA
TRENTON, NEW JERSEY[48]

Month	Rainfall		Temperature	
	cm	in.		
January	8.87	3.10	0.8 C	33.4 F
February	6.58	2.59	1.0	33.8
March	9.75	3.84	5.1	41.3
April	8.15	3.21	11.1	52.1
May	9.19	3.62	16.9	62.7
June	9.14	3.60	21.7	71.4
July	10.62	4.18	24.2	76.0
August	12.12	4.77	23.3	74.3
September	8.89	3.50	19.6	67.6
October	7.21	2.84	13.5	56.5
November	8.03	3.16	12.7	45.1
December	7.29	2.87	1.7	35.1
Total	104.85	41.28		

to the leachate treatment plant.

The treated effluent is discharged to the Delaware Estuary. The river zone is tidal and flow figures are not available. At the nearest gage (Trenton) the drainage area is 6700 square miles and the projected low flow is 33,000 liters per second. The discharge of treated effluent directly to the Delaware River occurs only during the months of December through April. During the remainder of the year, the effluent is returned to the landfill. During the latter portion of the third year, a program of land disposal was initiated. The landfill has ample storage capacity in the pore space so that storage for 6 months does not create any difficulties. The effluent is spread on the landfill using aeration nozzles.

The treatment plant operates under permits from the Commonwealth of Pennsylvania Department of Environmental Resources Water Quality Section and the Delaware River Basin Commission. The effluent criteria for the facility are summarized in Table 8.

Design Overview

The purpose of this section is to summarize briefly the design criteria and to discuss the design of the treatment facility. The effluent limits have been mentioned above and presented in Table 8. The following paragraphs are devoted to a discussion of the leachate quantity and quality as estimated for design purposes.

Design Flow. The source of liquid waste is the leachate which results from the degradation of refuse and percolation of rain water through the landfill. In addition, as the treated effluent is recycled to the landfill during the summer months, and to the Delaware River

TABLE 8

SUMMARY OF EFFLUENT CRITERIA[49] FOR
GROWS SANITARY LANDFILL LEACHATE TREATMENT FACILITY

Parameter	Maximum Concentration mg/liter
BOD_5	100.0
Ammonia-Nitrogen	35.0
Phosphate	20.0
Oil and grease	10.0
Iron	7.0
Zinc	0.6
Copper	0.2
Cadmium	0.02
Lead	0.1
Mercury	0.01
Chromium	0.1

during the winter, the raw leachate volume includes this recycled effluent. The quantity of waste which is generated is dependent upon many individual factors of the landfill. The maximum generation of waste (including the recycled volume) for design purposes was estimated to be about 20 liters per sq m-week at this site. However, the production of leachate is dependent upon the time cycle, both as to placement and to the season of the year. Leachate itself occurs as the result of the excess of infiltration over evapotranspiration and the soil moisture deficit. Thus, the actual generation of leachate depends upon precipitation patterns, landfill moisture and effluent recycling.

Since the generation of leachate is also a function of the age of the fill, not all the expected leachate will be produced simultaneously. There is an initial period of operation when the landfill comes to field capacity, followed by an extended period of leaching of contaminants, after which there exists a period when the leachate is no longer of a polluting nature. It is possible that some portions of the landfill will be in this latter state when the final parts of the landfill are being completed. Hence, the maximum flow of 20 liters per sq m-week is a value which may never be attained for extremely strong leachate. This maximum flow rate was determined using the site meteorological data presented in Table 7 and the procedure developed by Remson, Fungaroli and Lawrence.[50]

Design Leachate Characteristics. The leachate strength parameters used for design purposes are presented in Table 9. These were obtained through a modest sampling program conducted during the very early stages

TABLE 9

DESIGN LEACHATE CHARACTERISTICS

Constituents	Raw Leachate*
BOD_5	1500
Suspended Solids	1500
Total Solids	3000
Percent Volatile	55
pH, pH units	5.5
Chlorine	200
Iron, total	600
Zinc	10
Chloride	800
Organic Nitrogen	100
Nitrate	20
Sulfate	300
Copper	1
Hardness	800
Alkalinity	1100
Color, standard units	50
Flow, mgd	.144
Temperature, F	80

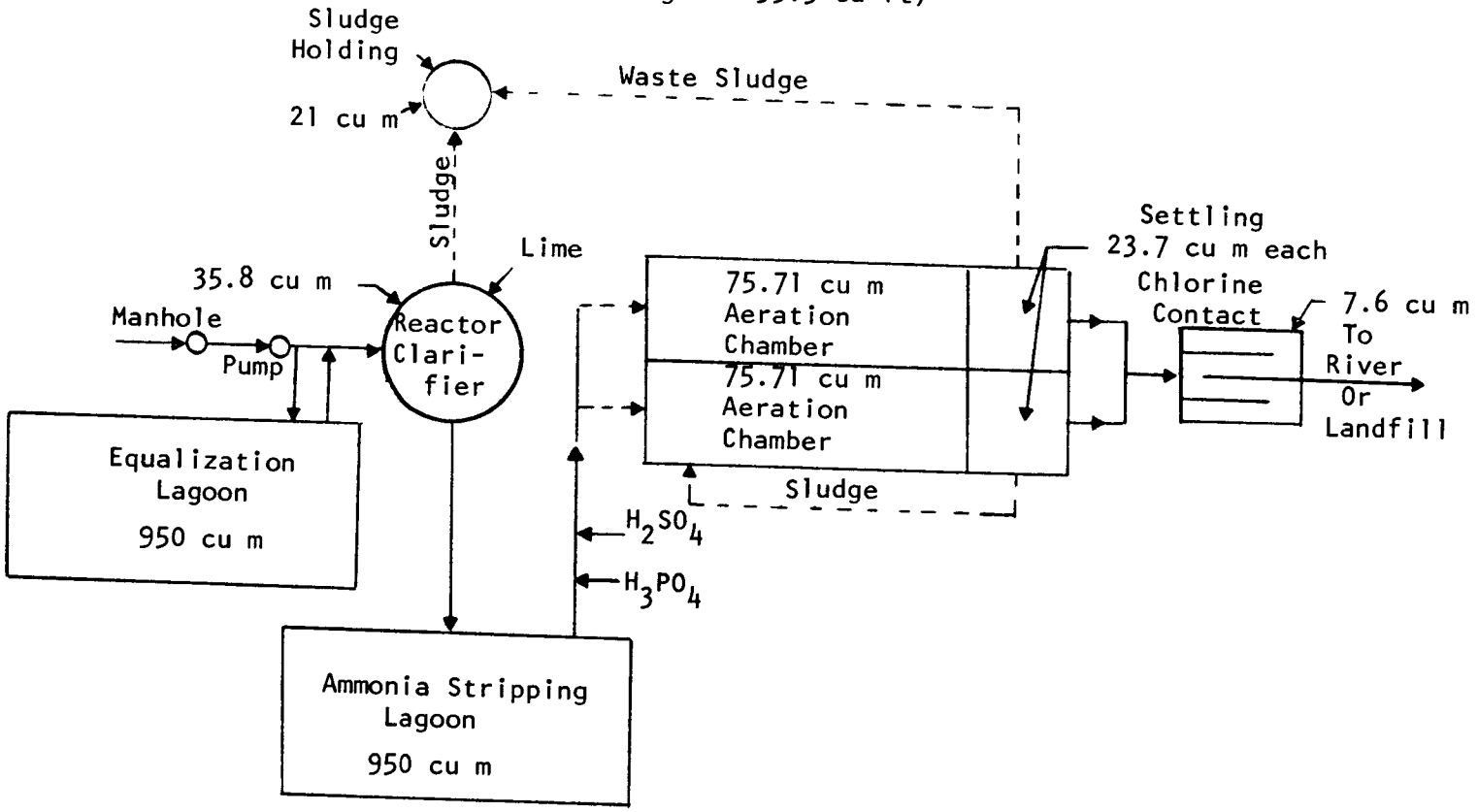
*All units are mg/liter except pH, color, flow, and temperature.

of the landfill. However, as discussed in Chapter II, the exact character of waste is difficult to predict for a number of reasons, including the fact that it is subject to dilution when the infiltration is high. In addition, because of the on-site variability, it is possible that single samples do not accurately reflect the character of the waste.

Design Concept. As discussed in Chapter II, a combination of chemical/physical treatment plus biological treatment is often required for leachate treatment. The principle is that the chemical/physical units can be used for the removal of refractory organics and for pretreatment prior to the biological process. In the latter case, the chemical/physical processes are used for the removal of potentially inhibitory materials such as heavy metals and ammonia-nitrogen. The function of the biological units is the stabilization of organic matter and the oxidation of ammonia nitrogen. As a result of the findings discussed in Chapter II and the design leachate quality, this treatment plant was designed to consist of lime treatment and sedimentation followed by activated sludge and chlorination. Equalization, air stripping of ammonia and nutrient addition have subsequently been added into the chemical/physical section. A schematic of the leachate treatment plant appears as Figure 4.

Leachate Collection System. The raw leachate is contained within the lined landfill which was designed to allow for the collection by gravity of leachate at three locations. These locations are outfitted with manholes from which the leachate is pumped and transported via pressure lines to the treatment facility. The leachate entered the plant

FIGURE 4. SCHEMATIC FLOW SYSTEM 1 WITH AMMONIA STRIPPING LAGOON
Unit volumes are shown in cubic meters (1 cu m = 1000 liters = 264.2 gal = 35.3 cu ft)



via a one thousand gallon holding tank in which little mixing occurred because the flow from the individual manholes is highly variable, and pumped sequentially. Following start-up of the equalization pond in the third year, the holding tank was by-passed.

Chemical/Physical Section

The chemical/physical portion of the plant consists of the following: equalization, chemical precipitation and coagulation, sedimentation of precipitate, air stripping at elevated pH for ammonia removal, neutralization and nutrient supplementation. Each of these are discussed in the following paragraphs.

An equalization pond was put on-line during the final project year. The volume is 950 cu m, and so the design detention time is 1.74 days. This pond is aerated to maintain aerobiosis and prevent solids deposition. A chlorinated polyethylene liner is used as the inner wall of the pond.

Chemical Precipitation. In the chemical treatment phase, the major design goal was the removal of inorganic materials. In particular, metals that may interfere with the subsequent biological treatment process are removed; also, the metals are removed to achieve discharge standards (Table 8). As part of the chemical treatment, the biochemical oxygen demand will also be reduced, and the design percentage of reduction was 30 to 50 percent, on the basis of the experience with municipal wastewater and with leachate as discussed in Chapter II.

The chemical treatment step consists of flash mixing followed by quiescent conditions favorable for coagulation as well as sedimentation of the chemical sludge. Lime has been the only chemical utilized in

this chemical precipitation step. However, additional feeders and points of injection have been provided for the use of other chemicals if necessary. Other chemicals which might be used include alum, ferric chloride, synthetic polymers, and powdered activated carbon.

This unit is an upflow solids contact reactor clarifier. Lime slurry is added to cause coagulation and precipitation of the waste materials. The lime is pumped at a rate commensurate with the rate of leachate production. The lime slurry is flash mixed with the incoming waste, and mixing, flocculation and upflow clarification occur within a single unit. Solids contact may be optimized by variable sludge recycle. The chemical treatment facility is a 3.66 m diameter, 3.66 m deep cylinder with a hydraulic retention time of 1.7 hours at 380 liter/min flow rate.

Sludge is drawn off the bottom of the reactor clarifier and placed in a common sludge holding tank with the waste activated sludge. Sludge return pumps are available to recirculate the sludge and mix it with the incoming waste water to reduce the amount of chemicals that are needed for precipitation. (However, the practice to date has been to use fresh lime and to not recirculate the sludge.). The amount of sludge that is produced in this step depends upon the composition of the leachate. The design projection was that approximately 5 percent of the flow will be produced as sludge at 1 percent solids concentration.

Air Stripping of Ammonia. As a means of controlling excessive levels of ammonia in the lime treated stream and in the final effluent, a lagoon incorporating air stripping of ammonia is included in the chemical/precipitation-clarification unit in order to take advantage of

the high pH of the upflow solids contact reactor clarifier effluent and to minimize the solids loading on the lagoon. On occasion, sodium hydroxide has been added to the lagoon to further elevate the pH and force off additional ammonia. This has been done during cold weather periods.

The volume of the ammonia lagoon is 950 cu m, thus providing a detention time of approximately 1.74 days at design flow. The primary function of the lagoon is to encourage air stripping of ammonia by an elevated influent pH of 10, aeration and high internal recycle. The lagoon is lined with chlorinated polyethylene. In addition to ammonia removal, the lagoon provides equalization in terms of both flow and sanitary parameters.

Neutralization and Nutrient Supplementation. Sulfuric and phosphoric acids are added to reduce the pH of the leachate prior to entering the biological waste treatment portion of the process. Phosphoric acid replenishes the supply of o-phosphate, a necessary biological nutrient, which is precipitated and removed following the addition of lime.

Biological Treatment Section

The biological treatment units consist of two aeration tanks and two secondary clarifiers. The units may be operated in series or parallel. The capacity of each tank is 75,710 liter, which corresponds to a 6.6 hour detention time at the maximum flow rate of 380 liter/min. The aeration chambers are provided with diffused aerators, each driven by a 14.2 cu m per min blower.

Depending on the actual hydraulic residence time in the aeration tanks, the activated sludge units were designed to operate in either the conventional or extended aeration modes. In order to achieve this, the mixed liquor volatile suspended solids (MLVSS) would be maintained in the range of 3000 to 8000 mg/liter. Because of the high organics loadings experienced during the last 2 years, the MLVSS was in the 8000 to 16,000 mg per liter range. This level is high relative to that normally maintained in units handling municipal wastewater. However, it is necessary because of the high BOD loading, and because of the requirement to remove about 90 percent of the BOD remaining after chemical/physical treatment. The MLVSS is maintained by return sludge pumps capable of delivering a return sludge flow equal to 200 percent of the influent flow.

The waste sludge from the activated sludge units and from the chemical treatment process is stored in the sludge holding tank. The capacity of this tank is 21 cu m, and sludge is removed as required and conveyed back to the landfill via tank truck.

Separation of treated wastewater from the MLVSS is achieved by gravity sedimentation in the secondary clarifiers. The total clarifier volume is 47,318 liters, in two parallel independently operable units. Sludge return is provided with air lifts installed in the final settling tanks. A skimming device is located in the settling basin in front of the scum baffle to remove floating material which is returned to the aeration compartment. The maximum surface overflow rate is 20.4 cu m per day per sq m (500 gpd/sq ft) based on the peak flow of 380 liter/min.

Final effluent is directed to the chlorine contact tank after secondary clarification. The chlorine contact tank provides a retention time of 20 minutes at the 380 liter/min flow rate. The effluent after chlorination is discharged to the Delaware River or to the land disposal site depending upon the season of the year. The effluent is not chlorinated when it is recycled to the landfill. The chlorine contact tank is a simple baffled tank to assure mixing of the chlorine which is provided by hypochlorination.

IV. MATERIALS AND METHODS

Experimental Systems

The leachate treatment plant, although designed for chemical/physical treatment followed by biological treatment, was equipped with sufficient flexibility to provide for operational evaluation of a variety of treatment sequences. These sequences are each defined in the following paragraphs with reference to Figure 4. Note that the final effluent is disinfected with sodium hypochlorite prior to discharge during the winter months. The periods of operation of each system is summarized in Table 10. The principal analysis was conducted during the first two years. Additional trials were conducted during the third year. The flow rate and raw leachate quality was sufficiently different in the third year to oftentimes prevent direct comparisons.

System 1 - Chemical/Physical followed by Biological Treatment. System 1 is the basic treatment sequence with lime treatment for metals removal followed by ammonia stripping and conventional activated sludge. System 1a refers to the use of System 1 when the air stripping was not used, whereas System 1b signifies that the lagoon was included in the flow sequence. System 1a was tested in the late winter of 1975-76, and System 1b in the summer of 1976, the winter of 1976-77, the early spring of 1977, and the spring and summer of 1978. During the 1978 test period, the raw leachate entered the plant via the equalization pond.

System 2 - Chemical/Physical Treatment. Two subsystems have been evaluated. These, Systems 2a and 2b, consist of lime treatment either without or with subsequent removal of ammonia by air stripping. The

TABLE 10

PERIODS OF OPERATION OF LEACHATE TREATMENT SYSTEMS

System	Period of Operation of Full-Scale Units
1a*	November 15, 1975 through January 12, 1976
1b+	June 14, 1976 through April 30, 1977
1b‡	January 1, 1978 through August 31, 1978
2a*	November 15, 1975 through January 12, 1976
2b+	June 14, 1976 through April 30, 1977
2b‡	January 1, 1978 through August 31, 1978
3*	January 12, 1976 through April 2, 1976
3+	May 1, 1977 through August 31, 1977
4*	January 12, 1976 through April 2, 1976
4+	May 1, 1977 through August 31, 1977

*Neither ammonia lagoon nor equalization pond used.

+Ammonia lagoon used.

‡Both ammonia lagoon and equalization pond used.

system without ammonia stripping (System 2a) was evaluated in the winter of 1975-1976; and System 2b in the summer of 1976, the winter of 1976-1977, early spring of 1977, and the spring and summer of 1978. The equalization pond was included in this treatment sequence during the most recent period.

System 3 - Biological followed by Chemical/Physical Treatment. This is the reversal of System 1. This system was studied during the winter of 1976. The results indicated poor treatment efficiency, most likely due to heavy metal and ammonia toxicity. However, it might have been argued that a sufficient amount of activated sludge had not developed. Therefore, System 3 was reevaluated in order to test this latter hypothesis. This took place during the late spring and early summer of 1977.

System 4 - Biological Treatment. This system has been tested, the results showing poor treatment efficiency. However, as indicated above, the performance might have improved if a previously acclimated activated sludge were available. Consequently, System 4 was operated and tested simultaneously with System 3 during the spring and early summer of 1977.

System 5 - Bench-Scale Testing. As a supplement to the full-scale treatment processing, some smaller scale work has been undertaken. This effort serves two purposes. First, it allows the operator to readily develop operational guidelines. For example, jar tests have been used to determine proper chemical dosages.

The second purpose is to provide an opportunity for evaluating additional treatment techniques. Specifically, bench-scale testing has been used to evaluate activated carbon treatment of raw leachate.

Granular activated carbon has been used in column studies to obtain performance characteristics. The results are discussed in Chapter IV.

Process Monitoring

An analytical laboratory was established in a trailer located immediately adjacent to the treatment plant. The trailer is outfitted with the apparatus to perform the analyses indicated below and is environmentally controlled with a heating/air conditioning system. The need for extensive bench-scale testing and the large number of analyses needed for process control and monitoring made the on-site laboratory mandatory. The laboratory is operated by the chemist-operator employed specifically for this project.

The chemical analyses performed routinely are presented in Table 11. These have been selected on the basis of four criteria: they represent the most common chemical parameters used in the literature to characterize landfill leachate; they provide sufficient data to completely evaluate the unit operations in terms of process and total system efficiency; they are needed for process control; and they are required to specifically define the leachate.

All analyses are performed in accordance with the 13th edition of Standard Methods, ASTM Standards pt-23, and the 1974 edition of EPA Methods.[51-54] The analyses are performed on total samples as opposed to filtrate samples. Some preparation of the raw leachate is required for heavy metals determinations.

Electrometric techniques are used in the determination of ammonia-N, dissolved oxygen (with periodic checks using the Azide Modification of

TABLE 11

ROUTINE LABORATORY CHEMICAL ANALYSIS

Item	Method	EPA Storet No.	Detection Limit
	Daily		
pH			
Chemical oxygen demand	Dichromate reflux	00349	--
Dissolved oxygen	Electrode	00299	--
Mixed liquor suspended solids	Gooch crucible	70300	--
Mixed liquor settleable solids	Imhoff cone	50086	--
Dissolved solids	Potentiometric	00536	--
Volatile suspended solids	Gooch crucible	00529	--
Total residue	Drying crucible	00520	--
	Weekly		
Alkalinity	Titrimetric (pH 4.5)	00410	--
Biochemical oxygen demand	Probe method	00310	--
Total hardness	Titrimetric	00900	--
Kjeldahl nitrogen	Titrimetric	00625	--
Ammonia nitrogen	Distillation & Potentiometric	00610	--
Phosphate	Persulfate digestion	00665	--
Sulfate	Gravimetric	00945	--
Chloride	Titrimetric	00940	--
Total iron	AA*	--	0.02
Chromium	AA	--	0.02
Copper	AA	--	0.01
Cadmium	AA	--	0.002
Lead	AA	--	0.05
Mercury	Mercury analyzer	--	0.0002
Zinc	AA	--	0.005
Nickel	AA	--	0.005
Calcium	AA	--	0.003
Magnesium	AA	--	0.005
Sodium	AA	--	0.002
Potassium	AA	--	0.005
	Aperiodic		
Oil & Grease	Freon extraction		

*Atomic Absorption Spectroscopy

the Winkler Iodometric procedure), pH, and dissolved solids. Atomic absorption spectroscopy is used for iron, chromium, copper, nickel, zinc, sodium, cadmium, lead, and potassium.

A number of sampling points are used in the analysis program. Routinely, samples are collected of (1) the raw leachate; (2) chemical/physical sedimentation tank effluent; (3) ammonia lagoon effluent; (4) final effluent. In addition, samples are collected on an irregular basis from the three landfill manholes and directly from the individual treatment units. In all cases, every effort is made to ensure that a representative sample is obtained.

A pilot-scale treatment plant was constructed in order to facilitate the smaller scale studies. This pilot plant was built during the spring of 1977. The basis of its design was to simulate System 1 operation as it was apparent that this was the most efficient treatment sequence for this leachate. Thus, the pilot plant would generate final effluent which could be used in the bench-scale experiments using granular activated carbon. A schematic of the pilot plant is presented in Figure 5.

Statistical Tests

The following notation is used throughout: n, number of data points; $\bar{x}$, arithmetic mean; and s, standard deviation. The mean is calculated as

$$\bar{x} = \frac{1}{n} \sum x_i$$

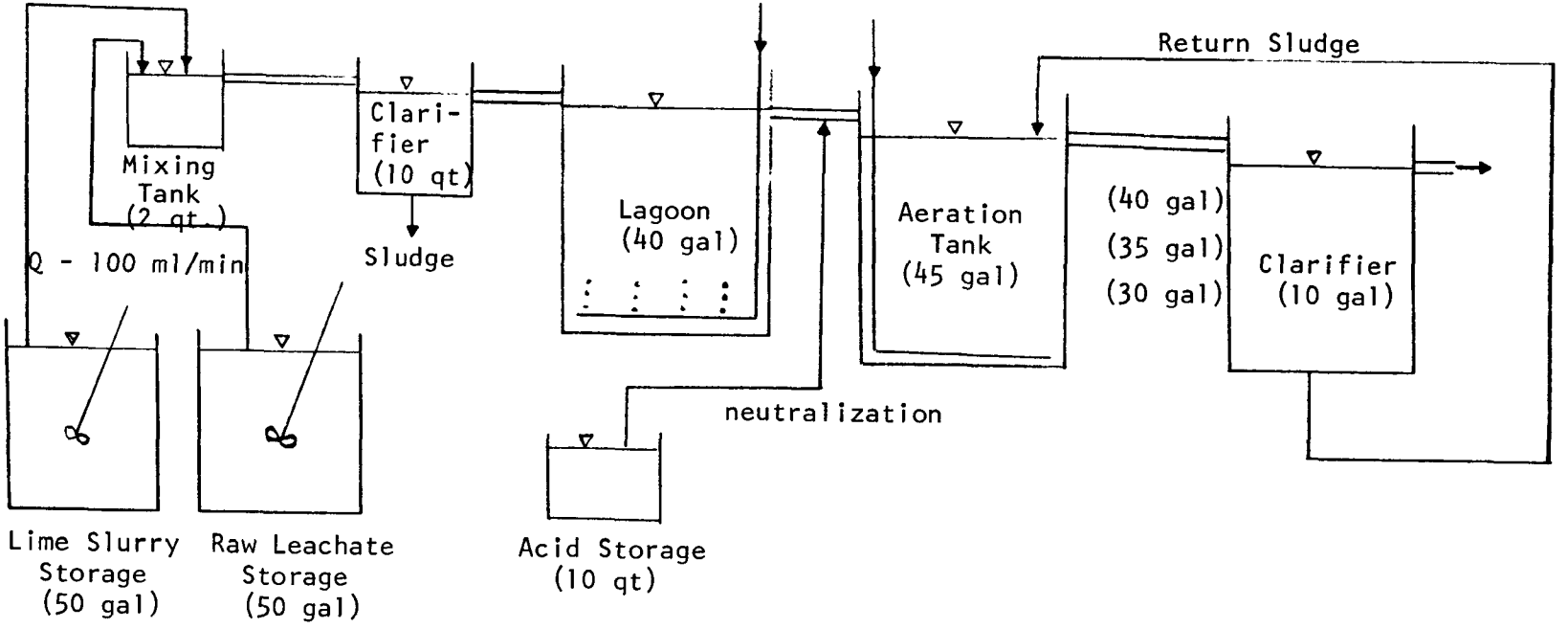
and the standard deviation as

$$s = \frac{\sum (\bar{x} - x_i)^2}{n-1}$$

where the x_i are the n data points,

and the coefficient of variation is

FIGURE 5. SCHEMATIC OF PILOT LEACHATE TREATMENT PLANT (SCALED VERSION OF SYSTEM 1)



$$cv = \frac{s}{\bar{x}}$$

The value of the coefficient of variation decreases with decreasing variability.

Presentation of Results

A note of caution is placed here for the reader. As would be expected in a three year study of this magnitude, a vast array of data has been collected. It is not appropriate to present the entire data set in this report. Consequently, many of the tables presented represent averages taken over certain specified time periods. Thus, values given in different tables are not necessarily comparable. This is especially true if the time periods are not identical. The reader is asked to pay particular attention to the time periods and to avoid making comparisons when these periods differ.

V. RESULTS AND DISCUSSION

Preliminary Results

Raw Leachate Quality. A summary of actual leachate quality is shown in Table 12. These data are a summary of the entire set of results. As is evident from a comparison of Tables 9 and 12, there are significant differences between the two. These changes toward increased leachate strength are seen mainly between the design and actual raw leachate organic matter, dissolved solids, pH and ammonia. The biodegradable organics concentration is three times the design level. Dissolved solids are an order of magnitude greater, caused by increased hardness, organic matter and chloride. The ammonia concentrations actually observed have been extremely high and have been a source of operating problems especially in the biological units. The factors influencing this difference between the projected and observed leachate quality have been discussed in Chapter II.

Considerable variability in the raw leachate quality has been noted on a day-to-day basis. The influent COD data are presented in Figure 6 to show this variability. (An additional indication is provided by the coefficient of variation data provided in Table 13, columns 1 and 2.) It was felt that the raw leachate variability had an adverse impact on the efficiency of the subsequent treatment units. This was because it was impossible to fine tune the operational controls as quickly as the influent quality changed. This was especially true for the lime dosage in the heavy metals removal step. For this reason, the equalization pond was constructed. The effect of the pond on dampening of the

FIGURE 6. RAW LEACHATE CHEMICAL OXYGEN DEMAND
(Note change in scale on ordinate)

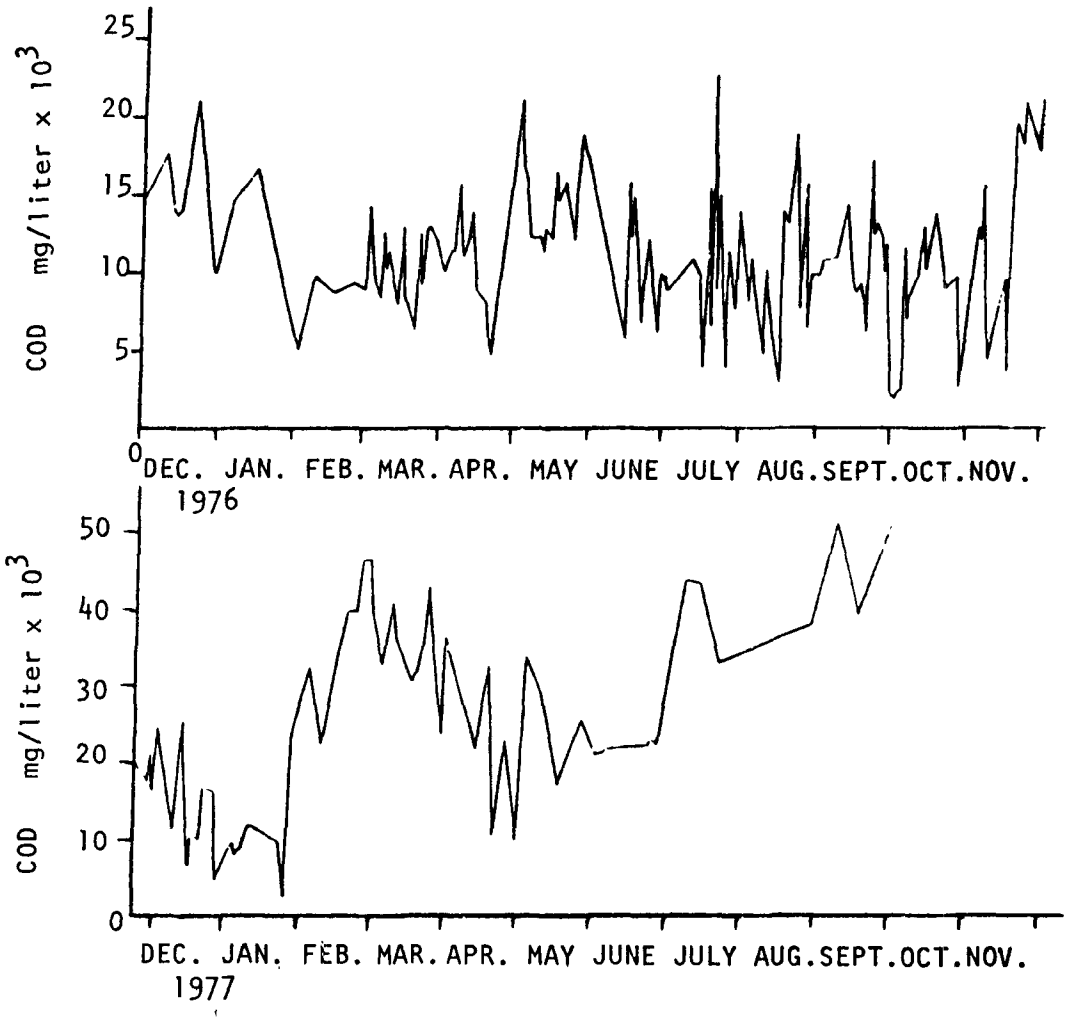


TABLE 12

LANDFILL LEACHATE CHARACTERISTICS*

Item	Concentration+ 11/15/75-9/1/76	9/1/76-9/1/77	9/1/77-8/31/78	11/15/75-8/31/78
Biochemical oxygen demand (5-day)	4,460	13,000	11,359	10,907
Chemical oxygen demand	11,210	20,032	21,836	18,553
Suspended solids	1,994	549	1,730	1,044
Dissolved solids	11,190	14,154	13,181	13,029
pH, pH units	7.06	6.61	7.31	6.85
Alkalinity, as $CaCO_3$	5,685	5,620	4,830	5,404
Hardness, as $CaCO_3$	5,116	4,986	3,135	4,652
Calcium	651	894	725	818
Magnesium	652	454	250	453
Phosphate	2.81	2.61	2.98	2.74
Ammonia-N	1,966	724	883	1,001
Kjeldahl-N	1,660	760	611	984
Sulfate	114	683	428	462
Chloride	4,816	4,395	3,101	4,240
Sodium	1,177	1,386	1,457	1,354
Potassium	969	950	968	961
Cadmium	0.043	0.09	0.10	0.086
Chromium	0.158	0.43	0.22	0.28
Copper	0.441	0.39	0.32	0.39
Iron	245	378	176	312
Nickel	.531	1.98	1.27	1.55
Lead	.524	0.81	0.45	0.67
Zinc	8.70	31	11.0	21
Mercury	.0074	.0051	0.012	0.007

*These values represent the arithmetic mean of raw leachate data collected during the indicated intervals.

+All units mg/liter except pH.

TABLE 13

EFFECT OF EQUALIZATION POND ON RAW LEACHATE VARIABILITY

	Coefficients of Variation		
	Unequalized Raw Leachate		Equalized Raw Leachate
	Project Year		
	First	Second	Third
Alkalinity, as $CaCO_3$	0.23	0.21	0.26
Ammonia-N	1.14	0.21	0.33
BOD	0.60	0.72	0.50
Cadmium	0.39	0.80	0.73
Calcium	0.31	0.57	0.57
Chloride	0.58	0.16	0.30
Chromium	0.56	0.32	0.49
COD	0.40	0.66	0.25
Copper	0.81	1.00	0.67
Dissolved Solids	0.24	0.58	0.16
Hardness, as $CaCO_3$	1.02	0.48	0.41
Iron	0.65	0.77	0.33
Kjeldahl-N	1.23	0.19	0.39
Lead	0.60	0.68	0.53
Magnesium	0.47	0.32	0.29
Mercury	0.90	1.04	1.73
Nickel	0.33	0.97	0.52
pH	0.64	2.33	--
Phosphates	0.63	0.74	0.84
Potassium	0.32	0.21	0.19
Sodium	0.32	0.31	0.16
Sulfate	0.90	2.10	0.71
Suspended Solids	0.65	1.32	0.64
Zinc	0.65	0.62	0.68

influent quality is impossible to ascertain because raw leachate samples were not collected after pond startup. Rather, the influent samples were taken from the pond. As an approximate indicator of the degree of attained equalization, Table 13 was constructed. This compares the coefficients of variation for each parameter during the three project years. As shown in Table 13, the variability decreased for one-half of the parameters and was approximately the same for several others. This is taken as indirect evidence of the efficiency of equalization.

Lime Dosage. Jar tests were carried out in the laboratory in order to determine proper dosages for the lime treatment unit. In the first series of tests, three types of lime were monitored for their ability to raise the pH of raw leachate to 10.0. The limes used were high magnesium lime, high calcium quick lime and high calcium hydrated lime. The results may be summarized as:

	Dosage	
	lb/1000 gal	kg/cu m
High Magnesium Lime	125	15
High Calcium Quick Lime	52	6.2
High Calcium Hydrated Lime	50	6.0

It is economically impractical to use the high magnesium because its properties are such that to raise the pH to 10.5 requires 30 kg per cu m (250 lb per 1000 gal).

Required dosages to obtain pH 10.0 are nearly identical for both types of high calcium lime. For pH greater than 10.0, the high calcium quick lime becomes more efficient and hence is desirable economically. However, the slaking characteristics of the quick lime have caused problems with pumping the resultant slurry so that this lime cannot be

used with the available lime feed system. On the other hand, the hydrated lime does not offer such problems, and consequently, the high calcium hydrated lime is being used.

Sulfuric Acid Dosage. The amount of sulfuric acid required to lower the clarifier effluent pH to 6.5 has been determined. To do this, approximately 0.6 ml of concentrated sulfuric acid per liter leachate (0.6 gal/1000 gal) is required. The actual dosages used are presented later in this chapter as part of treatment costs.

Phosphoric Acid Dosage. The need for a phosphoric acid supplement became apparent from three lines of evidence: (a) very low phosphate levels in the chemical/physical effluent; (b) unrealistically low values obtained in the biochemical oxygen demand test; and (c) poor biological treatment performance following the chemical/physical process. These points all indicated that the chemical/physical treatment effluent is phosphorus deficient, and that, if biological treatment is to follow, it must be supplemented with phosphorus. Additional evidence was collected by performing a series of BOD_5 tests in which a variable amount of phosphorus supplement was added to the bottles. It was observed that the BOD increased with the amount of phosphorus. In addition, bench scale tests indicated greater activated sludge production when o-phosphate was added. Thus, it has been concluded that orthophosphate, as phosphoric acid, should be added to form a nutrient supplement.

Additional experiments were performed to address the phosphate issue. These were conducted using the pilot scale unit shown in Figure 5. The unit was operated with and without an addition of phosphorus.

Raw leachate COD was 4528 mg per liter during the no addition run, and 4823 and 21406 mg per liter during the two runs receiving a phosphate supplement. The lime clarifier effluent COD values for these runs were 3926, 4062 and 18121, respectively, and the average fractions of COD removed during biological treatment were 0.711, 0.811, and 0.762, respectively. These results indicate that the removal efficiency of acclimated activated sludge can be improved by the addition of phosphorus, and that the removals were acceptable when the effluent phosphate concentration is 1 to 2 mg per liter as P.

The preliminary calculation of phosphoric acid dosage has been made on the basis of providing a ratio of BOD:N:P of 100:5:1. This is approximately 4-6 liter (1-1.5 gal) phosphoric acid per day. More recently, however, the criterion is to add phosphoric acid so that there is measurable o-phosphate in the bio-unit effluent. This amounts to about 3.8 liter (1 gal) of phosphoric acid per day.

System 1 - Physical/Chemical Plus Activated Sludge

System 1 consists of chemical/physical treatment followed by activated sludge. The early attempts (winter and spring 1976) to develop an activated sludge culture were not successful. As discussed in connection with Systems 3 and 4, phosphorus limitation and ammonia toxicity inhibited these efforts. These two difficulties were overcome by the addition of phosphoric acid as a neutralizing agent for the lime treatment effluent and by the use of air stripping of ammonia. System 1 was successful only after the implementation of these measures and, as a result, this discussion is limited to the time period after implementation.

The BOD, COD, and ammonia-N data showed a dramatic improvement in treatment efficiency during and after August, 1976. Approximately four weeks had been needed to develop the activated sludge microorganisms to the point where they were capable of rapid growth at the expense of the leachate substrate. A similar time sequence was observed in 1978 during a re-test of System 1. Table 14 shows the results following the successful adaptations of the activated sludge. The starting dates for analysis of these data were chosen at the points at which the activated sludge had become fully acclimated in terms of ammonia-N, BOD and COD removals. The time periods are August 1, 1976 to May 1, 1977 and July 1, 1978 to August 31, 1978.

The results presented in Table 14 demonstrate the high level of treatment efficiency attainable with System 1. This treatment system achieved removals during the 1976-77 trial of approximately eighty-nine percent or more for ammonia, BOD, COD, suspended solids, and iron; and greater than two-thirds for alkalinity, hardness, kjeldahl nitrogen, copper, chromium, magnesium, cadmium, lead, and zinc. Relatively poor removals of mercury were achieved with System #1. The fairly low removals of nickel may be related to the relatively low hydrogen ion concentrations. Based on theoretical considerations of the solubility of nickel hydroxide, the nickel concentration in the effluent should be on the order of 0.01 mg/l[35], as opposed to observed average of 0.75 mg/l. This observation is perhaps also due to the formation of nickel complexes with unknown chelating agents within the landfill. Thus, we are able to see removals as a function of clarifier pH, and this opens the possibility that the

TABLE 14

SYSTEM 1* TREATMENT PERFORMANCE AFTER ACCLIMATION OF ACTIVATED SLUDGE
(August 1, 1976 - May 1, 1977 and July 1, 1978 - August 31, 1978)

	August 1, 1976 - May 1, 1977			July 1, 1978 - August 31, 1978		
	Concentration			Concentration		
Parameter	Influent**	Effluent**	Percentage Removal	Influent**	Effluent**	Percentage Removal
Suspended solids	686	101	97.4	1655	478	71.1
Dissolved solids	13563	5693	58.0	13091	7244	44.7
COD	18488	939	94.9	18505	1008	94.6
BOD	12468	118	99.1	8143	464	94.3
Alkalinity	5479	685	87.5	5262	1496	71.6
Hardness	5331	1314	75.4	2504	1456	41.9
Magnesium	499	107	78.6	275	105	62.0
Calcium	929	347	62.6	653	113	82.7
Chloride	4264	2592	39.2	8578	2254	73.7
Sulfate	645	951	---	178	836	---
Phosphate	2.15	13.7	---	1.39	17.2	---
Ammonia-N	705	80	88.7	1076	6.3	99.4
Kjeldahl-N	748	102	86.4	---	---	---
Sodium	1310	821	37.3	1248	1145	8.3
Potassium	906	524	42.2	872	743	14.8
Cadmium	0.08	0.01	87.5	0.06	0.04	33.3
Chromium	0.28	0.07	75.0	0.16	0.04	75.0
Copper	0.44	0.10	77.3	0.20	0.16	25.0
Iron	376	3.0	99.2	9.7	0.71	99.3
Nickel	1.91	0.76	60.2	0.88	0.67	24.1
Lead	0.82	0.12	85.4	0.30	0.11	64.6
Zinc	22	0.57	97.4	3.38	0.16	95.3
Mercury	0.006	.004	28.9	0.003	0.002	33.3
Flow, gpd	21034			10,010		

*This system consists of lime addition, sedimentation, air stripping, neutralization, nutrient supplementation and activated sludge.
**mg/l

operator can control pH as a method of differentially affecting effluent heavy metals concentration.

The results observed with phosphates and sulfates should be noted. The concentration of phosphates and sulfates increase during the course of treatment because of the addition of sulfuric and phosphoric acids as neutralizing agents. Initially, both acids were used in excess in order to encourage the growth of the activated sludge microorganisms. That is, the goal was to provide a very favorable environment in terms of both pH and the nutrient phosphorus. However, following the successful acclimation of the activated sludge, the addition of sulfuric acid practically stopped while that of the phosphoric acid was drastically cut back. Neutralization was not needed because of the recarbonation effect of aeration in the lagoon. The final criterion for phosphoric acid addition was to provide just enough to satisfy the microorganisms' demand as indicated by an effluent concentration of about 1 mg/liter. That is, the criterion was to add enough H_3PO_4 so that there is residual phosphorus (1 mg/liter) in the effluent. This level is one to two orders of magnitude greater than the amount in the lime clarifier effluent.

The difficulties in obtaining a healthy culture of activated sludge were overcome. The operating experience indicated that the earlier problems were in fact due to ammonia toxicity and phosphorus limitation. The ammonia stripping lagoon maintained the concentration of this inhibitor below toxic levels. The mean and standard deviation of the lagoon effluent ammonia concentration were such that 95 percent of the

time, the feed to the activated sludge unit was less than 423 mg NH_3-N/liter. The corresponding raw leachate concentration was 1072 mg NH_3-N/liter. (Similar results were obtained during the other test period. Pooling all the data, the ± 1 standard deviation interval for the lagoon effluent was 203 to 641 mg per liter, whereas, for the raw leachate, the mean was 1,001 mg NH_3-N per liter and the standard deviation, 1049 mg per liter.) Thus, the lagoon functioned to minimize the shock loading effect of inhibitory ammonia concentrations. This in turn provided an opportunity for the development of microorganisms capable of extracting carbonaceous BOD. As this group became established, organic concentrations in the mixed liquor were reduced and this created conditions suitable for the development of nitrifying organisms. Growth of these groups of microorganisms has resulted in the low effluent concentrations of both BOD and ammonia.

As seen in Table 14, a considerable change in alkalinity occurs during biological treatment. There are two main mechanisms by which this occurs. First, the aeration causes some removal of gaseous carbon dioxide, resulting in a shift of the carbonate equilibria and a change in total bicarbonate alkalinity. It is probable, however, that in this case, nitrification has a more profound effect on alkalinity. As a result of nitrification, alkalinity is consumed and carbon dioxide is produced. Neglecting the effect of biomass synthesis, the theoretical value is 7.14 mg alkalinity as $CaCO_3$ destroyed per mg NH_4^+-N oxidized. In this study a ratio of 4.46 mg alkalinity per mg NH_4^+-N removed was observed after the development of the activated sludge culture. This is in excellent agreement with the theoretical value if

one considers that the observed value includes the effects of biomass growth and ammonia stripping in the bio-units as well as shifting chemical equilibria in addition to those of nitrification. These conclusions are drawn from the data presented in Tables 15 (Column 7) and 20 (Column 12) which represent activated sludge effluent and influent values, respectively.

System 1 was re-tested from January 1, 1978 through August 31, 1978, following completion of the equalization pond. Cold weather, the extreme strength of the process influent, and the high flows inhibited development of an activated sludge until April, 1978. The sludge did not become acclimated until July 1, 1978, following a process change from parallel to series deployment of the aeration tank-secondary clarifier system. A schematic is shown in Figure 7. The change was undertaken in an effort to gain greater use of the available aeration capacity. This was deemed necessary because of the tremendous process loadings observed in 1978 (Table 35).

The acclimated activated sludge performed well. The average flow into the biological units was 10,000 gpd, whereas, during the same period, the raw leachate flow was 50,000 gpd. The difference is due to the extreme strength of the leachate which inhibited the activated sludge so that only a portion of the flow could be treated biologically. (The entire flow was treated in the chemical/physical section of the plant during this period.)

The data for the re-test of System 1 are presented in Table 14, and a summary of both tests appears in Table 15. The results indicate

FIGURE 7. FLOW CHART FOR ACTIVATED SLUDGE IN SERIES

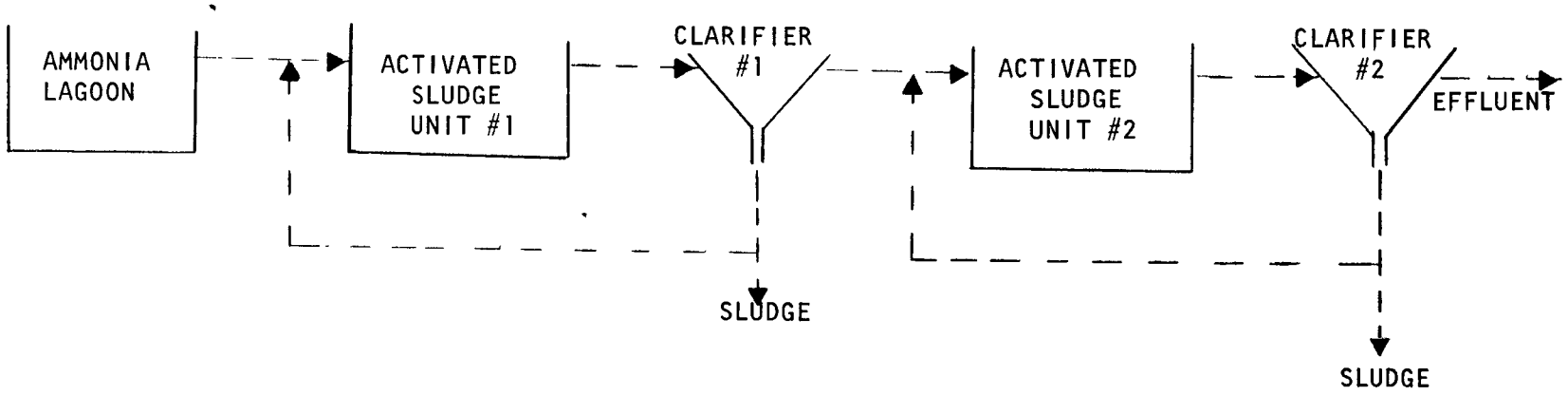


TABLE 15

SUMMARY OF SYSTEM 1 OPERATION

(8/1/76 to 4/30/77 and 4/1/78 to 8/31/78)

	Raw			Lagoon			Effluent			Percent
	$\bar{x}$*	cv	n	$\bar{x}$	cv	n	$\bar{x}$	cv	n	Removal
Alkalinity, as $CaCO_3$	5450	0.26	53	1878	0.43	44	803	1.02	48	85.2
Ammonia-N	758	0.32	56	350	0.05	53	75	1.01	74	90.1
BOD	11886	0.78	52	3930	0.63	46	153	1.75	69	98.7
Cadmium	0.078	0.91	54	0.025	1.37	45	0.017	1.64	55	78.2
Calcium	888	0.57	54	293	0.61	44	314	0.52	57	64.6
Chloride	4161	0.23	53	2616	0.08	43	2544	0.33	57	38.9
Chromium	0.26	0.77	54	0.07	1.19	44	0.07	0.59	66	73.1
COD	18490	0.71	172	6892	0.57	165	945	0.80	223	94.9
Copper	0.40	1.06	53	0.31	1.33	48	0.11	0.44	56	72.5
Dissolved Solids	13516	0.63	171	5995	0.30	175	5824	0.25	213	56.9
Hardness, as $CaCO_3$	5054	0.49	51	1211	0.54	38	1327	0.55	54	73.7
Iron	333	0.85	52	3.24	1.00	42	2.71	1.04	70	99.2
Kjeldahl-N	748	0.25	44	294	0.24	35	102	1.46	49	86.4
Lead	0.74	0.80	54	0.17	0.74	44	0.12	0.65	69	83.8
Magnesium	465	0.34	54	107	0.45	43	107	0.36	57	72.0
Mercury (ppb)	5.52	1.15	48	3.95	1.29	38	4.01	2.70	61	27.4
Nickel	1.76	1.13	55	0.61	1.18	43	0.75	0.78	56	57.4
pH	6.74	1.32	197	8.60	1.09	181	7.61	--	237	--
Phosphate	2.05	0.63	53	0.12	3.89	43	14.1	0.50	66	--
Potassium	903	0.20	47	514	0.22	38	535	0.15	50	40.8
Sodium	1301	0.29	53	785	0.38	43	862	0.39	56	33.7
Sulfate	577	2.77	48	363	0.68	41	937	0.76	55	--
Suspended Solids	555	1.46	167	193	1.13	165	133	1.42	209	76.0
Zinc	19.5	1.14	52	0.63	1.69	44	0.53	1.15	70	97.3

*$\bar{x}$ = mean, mg per liter
cv = coefficient of variation
n = number of data points

that System 1 is able to handle large loading rates, and to achieve high removal efficiencies. Data collected during the warm weather months (August 1, 1976 to December 1, 1976 and July 1, 1978 to August 31, 1978) have been analyzed separately. These data show that System 1 can produce an effluent of sufficient quality to meet the final effluent criteria (Table 16).

Approximately equivalent results are obtained using the biological reactors in either the parallel (1976-77) or the series (1978) mode (Table 17). In terms of percent removal efficiency, the series and parallel operations provided approximately equal performance with respect to BOD and COD. Removals of ammonia-N were much greater with the series operation. This is due to the localization of NH_4^+-N removal in the second tank following BOD oxidation in the first. (Note that the average flow during the series test was 10010 gpd, whereas during the parallel test, the flow was 21034 gpd (Table 14).

Operational Comments. Operating problems were encountered in the biological treatment unit. The most serious of these was a tendency of solids to float in the secondary clarifier. The result of this has been a decreased ability to achieve the expected level of solids separation. The presence of the floating sludge has been investigated and is characterized as being the result of three separate and distinct causes: flotation, turbulence and denitrification. It was apparent that there was some carryover of floating materials to the clarifier from the aeration tank. The leachate contains considerable amounts of surface active materials capable of flotation, and this contributes significantly

TABLE 16

WARM WEATHER OPERATION OF SYSTEM 1

Parameter	Effluent Concentration+	Permit Standard+
Ammonia-N	8.7	35.0
BOD	75.8	100.0
Cadmium	0.02	0.02
Chromium	0.06	0.10
Copper	0.10	0.20
Iron	1.22	7.0
Lead	0.11	0.10
Mercury	0.0045	0.01
Zinc	0.37	0.60

*Time periods included are 8/1/76 to 12/1/76 and 7/1/78 to 8/31/76.

+All units are mg per liter.

TABLE 17

COMPARISON OF SERIES AND PARALLEL OPERATION OF ACTIVATED SLUDGE UNITS

Parameter	Parallel Operation (8/1/76 - 5/1/77) Influent*	Effluent*	Removal Efficiency	Series Operation (7/1/78 - 8/31/78) Influent*	Effluent*	Removal Efficiency
Alkalinity, as $CaCO_3$	1604	685	57.3	3127	1496	52.2
Ammonia-N	286	80	72.0	738	6.3	99.1
BOD-5	3564	118	96.7	5966	464	92.2
Cadmium	0.021	0.01	52.4	0.04	0.04	0.0
Calcium	308	347	-12.7	227	113	50.2
Chloride	2508	2592	-3.3	2933	2254	23.2
Chromium	0.08	0.07	12.5	0.06	0.04	33.3
COD	6481	939	85.5	9873	1088	89.0
Copper	0.34	0.1	70.6	0.16	0.16	0.0
Dissolved solids	5710	5697	0.3	8635	7244	16.1
Hardness, as $CaCO_3$	1242	1314	-5.8	1007	1456	-44.6
Iron	3.6	3.0	16.7	1.85	0.71	61.6
Kjeldahl-N	294	102	65.3	---	---	--
Lead	0.18	0.12	33.3	0.12	0.11	8.3
Magnesium	105	107	-1.9	116	105	8.7
Mercury	0.004	0.004	0.0	0.003	0.002	33.3
Nickel	0.61	0.76	-24.6	0.62	0.67	-8.1
Phosphates	0.041	13.7	--	0.53	17.2	--
Potassium	487	524	-7.6	743	743	0.0
Sodium	712	821	-15.3	1160	1145	1.3
Sulfate	384	951	--	258	836	--
Suspended solids	147	101	31.3	663	478	27.9
Zinc	0.72	0.57	20.8	0.24	0.16	33.3

*mg/liter

to the carryover phenomenon. The original scum control device was not capable of handling the unexpectedly large amount of these materials. At the same time, an excessive amount of turbulence existed in the secondary clarifier.

The reduction of solids separation efficiency was compounded by a propensity of the activated sludge to become anaerobic and to rise in the clarifier due to denitrification. This is seen clearly when one follows closely the settleable solids test. At first, the sludge settles properly with a dense sludge layer overlain by a clear supernatant containing little turbidity, so that at the end of 30 to 45 minutes the settleable solids are about 300 mg/liter. If the test is continued for another hour, the sludge comes to the surface in typical rising sludge fashion. This is not a case of filamentous bulking as indicated by microscopic examination, the clear supernatant observed in the settleable solids test, and the sludge volume index of approximately 80 ml/g. Another indication of anaerobic denitrification as the cause of the floating sludge is the repeated observation of very low DO levels in the clarifier. This problem was accentuated when a portion of the plant aeration capacity was diverted to the ammonia-stripping lagoon.

These problems were resolved by minor design and operational changes. The installation of a more efficient scum removal system has ameliorated the floating sludge problem. Additional baffles were used to control the turbulence in the clarifier. Extra aeration capacity was installed to maintain appropriate concentrations of dissolved oxygen.

Cost Data. Costs incurred during the operation of the biological units are indicated in Table 18. The operation and maintenance costs

TABLE 18

OPERATION AND MAINTENANCE COSTS INCURRED DURING THE OPERATION OF SYSTEM 1
FOLLOWING ACCLIMATION OF ACTIVATED SLUDGE
(8/1/76 to 5/1/77 and 7/1/78 to 8/31/78)

Characteristics	Operational Period		
	8/1/76- 5/1/77	7/1/78 - 8/31/78	Total
Total Flow, gal	5332635	620620*	5953255
cu m	20186	2368	22554
Lime, lb	132600	84300	216900
lb/1000 gal	24.9	27.2	25.7
kg/ cu m	3.0	3.3	3.1
Sulfuric acid, gal	407	380	787
gal/1000 gal	0.076	0.122	0.093
liter/cu m	0.076	0.122	0.093
Phosphoric acid, gal	80.25	35	115.25
gal/1000 gal	0.015	0.011	0.014
NaOH, gal	733	0	733
gal/1000 gal	0.137	0	0.123
liter/cu m	0.137	0	0.123
NaOCl, gal	571.5	330	901.5
gal/1000 gal	0.107	0.532	0.151
liter/cu m	0.107	0.532	0.151
Costs, $/1000 gal			
Power	1.92	1.92	1.92
Lime	0.75	0.82	0.77
H_2SO_4	0.06	0.10	0.07
H_3PO_4	0.04	0.03	0.04
NaOH	0.09	0	0.08
NaCl	0.08	0.40	0.11
Total	2.94	3.27	2.99

*During this time period, the average flow through the chemical/physical section of the plant was 50,000 gpd, whereas that through the biological units was 10,010 gpd. The dosages in this table reflect these different flows.

are shown for the operational periods following acclimation: August 1, 1976 to May 1, 1977 and July 1, 1978 to August 31, 1978. The costs include those for NaOH, added to the ammonia lagoon to enhance ammonia stripping, and NaOCl, added to the final effluent to provide disinfection prior to discharge and to provide ammonia oxidation during the cold months.

The data indicate a cost of $2.99 per thousand gallons treated. The high power costs reflect the demand for electricity for leachate pumping, effluent pumping, and maintenance of the laboratory in addition to the requirements for actual treatment.

The costs during the re-test of System 1 warrant discussion. During this period, the flow through the System 2 section of the plant was approximately 50,000 gpd, while the flow through the activated sludge units was 10,010 gpd. The dosages of chemicals and the costs of treatment shown in Table 18 take account of these differences. Thus the dosage for lime is based on 50,000 gpd, whereas that for NaOCl is based on 10,010 gpd. The costs during the re-test are somewhat higher than anticipated. This results from two causes. First, the final effluent was chlorinated during the entire 1978 test period prior to land disposal. The effluent was chlorinated for a relatively small portion of the time during the earlier test. The second reason is that lime and sulfuric acid dosages were greater during the re-test. This was because more lime was added to enhance ammonia removals in the ammonia lagoon, and, as a consequence, sulfuric acid dosages were also high. The labor requirement is approximately 20 man-hours per week.

Nitrification

Nitrification is becoming a standard and widely used wastewater treatment process. It is the aerobic microbiological conversion of ammonia nitrogen to nitrate nitrogen. As such, nitrification is applied in situations where the pollution potential of ammonia is severe, especially in comparison with nitrate nitrogen. The adverse impacts associated with high concentrations of ammonia are promotion of eutrophication; toxicity, especially as a function of pH, to aquatic organisms; interference with chlorination due to reactions leading to the formation of chloramines; and, depletion of dissolved oxygen in receiving streams concomitant with the oxidation of ammonia to nitrate. As a result of considerations such as these, effluent ammonia standards are often established by regulatory agencies.

The nitrifying bacteria, typified by Nitrosomanas and Nitrobacter, oxidize ammonia to nitrite and nitrite to nitrate, respectively. These microorganisms are chemoautotrophs, and the nitrogen oxidation reactions provide the bacteria with a source of energy. A stoichiometric relationship can be written for the overall synthesis of biomass and oxidation of ammonia and nitrite as follows:[56]

$$NH_4^+ + 1.83\ O_2 + 1.98\ HCO_3^- = 0.020\ C_5H_7NO_2 + 1.041\ H_2O + 0.98\ NO_3^- + 1.88\ H_2CO_3 \quad (1)$$

Nitrifying bacterial biomass is represented as $C_5H_7NO_2$. Eqn (1) indicates that the theoretical cellular yield is 0.16 g biomass per g NH_4^+-N completely oxidized. (Also evident from Eqn (1) is the destruction of 7.1 g alkalinity per g NH_4^+-N oxidized, as discussed previously.)

Much of the literature concerned with waste treatment applications of nitrification has been devoted to municipal sewage. A recently published design manual has summarized this literature.[57] The ammonia content of municipal sewage is characteristically on the order of twenty to forty mg per liter. Occasionally, however, industrial wastes with much higher concentrations are encountered.[58-61] In this section of the report, data are presented and discussed showing that nitrification is inhibited at high substrate concentrations. Substrate inhibition such as described herein must be considered during both the design and operation of biological treatment plants intended for nitrification.

Boon and Laudelot have investigated the nitrite oxidizing bacterium, Nitrobacter winogradskyi.[62] They have shown that the rate of nitrite oxidation, which is inhibited by nitrite, is a function of the nitrite concentration which can be expressed as

$$\mu = \frac{\hat{\mu}}{1 + \frac{K_s}{S} + \frac{S}{K_I}} \qquad (2)$$

where μ is the specific growth rate, $time^{-1}$; $\hat{\mu}$, the maximum specific growth rate in the absence of inhibition, $time^{-1}$; S, the limiting substrate concentration, mass per unit volume; K_s, saturation constant, numerically equal to the lowest concentration of substrate at which μ is one-half of $\hat{\mu}$, mass per unit volume; K_I, inhibition constant, numerically equal to the highest concentration of substrate at which μ is one-half of $\hat{\mu}$, mass per unit volume.

The assumption of neglecting substrate inhibition is not particularly misleading at low substrate concentrations. This is because the third

term in the denominator of Eqn (2) becomes much less than the second term. As a result, as the value of S is reduced, Eqn (2) approaches the more conventional Monod expression

$$\mu = \frac{\hat{\mu} S}{S + K_s} \tag{3}$$

This equation is a reasonable description of nitrification at low values of S, as are encountered in municipal sewage treatment applications. Equation (2) becomes increasingly invalid as S increases, as in the treatment of leachate. The purpose of this section is to consider nitrification at high ammonia concentrations, and to discuss the results in terms of designing and operating nitrification and leachate treatment facilities.

The data were collected during the period August 1, 1976 to May 1, 1977. The fraction of nitrifying bacteria in the biomass has been calculated directly from the amounts of BOD and NH_4^+-N oxidized, and from the estimated yields of the two groups of oxidizers. The assumed yield values are 0.15 g biomass per g nitrogen oxidized-day, and 0.55 g biomass per g BOD oxidized-day.[63]

More detailed results of the removal of ammonia in the bio-units are given in Table 19. The concentration of NH_4^+-N is calculated from the equation,

$$NH_3 + H_3O \rightleftarrows NH_4^+ + H_2O \tag{4}$$

using the observed temperature to determine the equilibrium constant, the observed pH and the analytical results of the sum of NH_4^+-N plus NH_3-N (denoted as N_T in Table 19). Three removals are given in Table 19.

TABLE 19

AMMONIA REMOVAL IN ACTIVATED SLUDGE UNITS*

Date	Influent Data				Bio-Reactor Data					Removals		
	N_T	BOD	COD	Temp.	N_T	NH_4^+-N	pH	BOD	COD	R_1	R_3	R_4
5/27/76	549	2020	4863	24.6	736	---	8.04	2980	9725	0		
6/10	241	---	---	25.0	---	---	---	---	---	---		
6/14	277	2970	4961	25.2	496	---	7.59	2325	4186	0		
6/22	283	3550	4047	26.0	392	---	7.37	2200	1556	0		
6/30	325	3670	4351	25.0	330	---	7.80	3710	4656	0		
7/15	308	2499	3984	26.3	367	---	7.36	1152	717	0		
7/21	350	2049	3915	26.5	302	---	7.57	180	775	.14		
7/27	290	2555	3960	27.1	261	---	7.34	1181	3280	.10		
8/3	322	1763	3672	24.5	297	---	7.74	111	664	.08		
8/10	255	1949	3621	26.5	161	---	7.42	30	621	.37		
8/20	305	2760	4843	24.5	36	35	7.45	48	768	.88	.61	.026
8/23	364	---	5078	28.8	15	---	7.43	12	406	.96		
8/24	364	---	5175	27.5	10	---	7.31	36	420	.96		
8/25	364	3780	5080	24.4	14	14	7.35	27	384	.96	.63	.012
8/26	360	---	5039	26.5	17	---	7.42	24	526	.95		
8/27	356	---	3347	26.5	6	---	7.22	14	474	.98		
8/28	---	---	5118	28.2	1.2	---	7.82	35	299	---		
8/29	---	---	---	27.3	1.5	---	---	25	396	---		
8/30	---	---	5381	24.5	1.5	---	7.59	35	565	---		
9/3	369	---	4220	21.3	1.9	1.9	7.3	43	546	.99	.53	.015
9/10	302	---	5061	20.8	2.7	2.6	7.7	310	1053	.99		
9/13	364	---	6370	23.7	8.8	---	7.5	---	710	.98		
9/15	364	2905	5118	22.0	3.6	3.5	7.6	37	599	.99	.50	.022
9/23	322	2637	4264	24.5	6.0	5.8	7.7	123	620	.98	.92	.036

*N_T refers to the analytically determined value of NH_4^+-N plus NH_3, whereas NH_4^+-N is the calculated ammonia concentration. R_1 is the removal of N_T based on influent and effluent concentrations, R_2 is the fraction of N_T oxidized, and R_3 is the specific oxidation rate, g N_T oxidized/g biomass-day. Units are mg per liter unless otherwise noted.

TABLE 19 (Cont.)

Date	Influent Data				Bio-Reactor Data					Removals		
	N_T	BOD	COD	Temp.	N_T	NH_4^+-N	pH	BOD	COD	R_1	R_3	R_4
9/29/76	367	2660	4360	22.7	1.5	1.5	7.6	83	581	.99	.52	.013
10/7	255	1788	3068	23.2	13.2	12.9	7.5	31	299	.95		
10/13	218	1590	2791	18.9	5.2	5.2	7.0	52	271	.98	.57	.019
10/19	240	1850	3310	15.5	5.8	5.7	7.4	46	295	.98	.43	.014
10/28	227	---	3170	12.5	1.0	1.0	7.6	--	268	.99	.27	.007
11/3	235	1750	3454	14.7	3.4	3.4	7.6	53	321	.99	.65	.022
11/13	275	1830	3262	11.2	3.2	3.2	7.4	39	286	.99	.48	.011
11/18	296	1880	3461	12.2	110	109	7.6	29	296	.63	.35	.010
11/23	319	2730	5910	10.2	63	58	8.6	97	400	.80	.52	.015
11/24	---	---	6423	12.9	65	---	8.5	---	382	---		
12/2	319	3020	6902	6.9	74	71	8.4	78	392	.77	.50	.015
12/4	---	---	8055	4.4	33	---	8.4	38	501	---		
12/6	400	---	8716	4.2	123	---	8.4	---	564	.69		
12/11	---	---	9154	11.0	95	---	7.9	---	518	---		
12/13	342	---	8550	8.0	30	---	7.9	---	398	.91		
12/14	353	6630	9077	3.2	15	10	7.8	19	410	.96		
12/22	361	4435	7116	4.1	83	83	7.2	100	645	.77	.70	.020
12/27	---	---	7871	3.0	185	---	8.0	---	864	---		
1/4/77	442	3885	6798	5.0	151	143	8.6	61	2830	.66	.34	.008
1/10	308	---	3152	4.0	161	---	8.4	---	730	.48		
1/12	251	---	3178	3.0	---	---	8.5	---	---	---	---	
1/14	233	1630	2675	0.0	145	139	8.6	25	582	.38	.38	.006
1/24	232	---	---	0	---	---	---	---	---	---		
1/25	231	1620	---	0	146	140	8.6	37	560	.37	.17	.001
2/1	230	1725	2936	1.0	151	145	8.6	43	550	.34	.09	.001
2/9	176	1570	2761	3.0	144	140	8.4	47	538	.18	0	0
2/17	162	1490	2526	6.6	156	151	8.3	86	586	.04	0	0
2/23	164	1906	2557	9.0	153	149	8.1	84	565	.07	0	0
3/2	244	---	---	11.3	165	162	7.8	---	---	.32	---	---
3/3	283	5360	8635	12.3	174	170	7.9	94	917	.39	.15	0.15
3/10	160	9870	15271	15.5	140	135	8.0	666	1559	.13	.05	0.08
3/17	289	8990	16351	12.6	195	183	8.3	587	2321	.33	.12	0.45
3/24	316	9750	15683	5.8	---	---	7.9	834	3842	---	---	---
3/30	296	9440	15895	11.0	196	188	8.2	478	1713	.34	.33	0.98
4/6	255	2560	3881	15.0	202	197	7.9	983	2560	.21	.14	0.08
4/14	247	4090	6853	15.0	187	184	7.7	364	1820	.24	.19	.68
4/21	246	5010	8651	20.9	164	154	8.1	686	1787	.33	.28	.68

The first, R_1, is the percent removal efficiency based on influent and effluent concentrations; the second, R_2, is the fraction of N_T which is oxidized in the aeration tank; and R_3, is the specific oxidation rate. The units of R_3 are g nitrogen oxidized per g biomass-day, and it is calculated as the daily mass of nitrogen oxidized divided by the biomass. R_3 is determined using the fraction of nitrifiers in the biological solids, expressed as volatile suspended solids.

As indicated in Table 19 the overall removal of ammonia in the activated sludge units was considerable. Although this is primarily due to the microbial process of nitrification, the physical stripping of ammonia caused by aeration accounts for some or the removal. It is the purpose of this discussion to consider the factors affecting the ammonia converted by nitrification. It is apparent from Table 19 that a profound inhibitory effect was placed on the specific oxidation rate. as a result of extreme winter temperatures. Since the result was to decimate the nitrifying population, the following discussion is limited to the data obtained up to 25 January 1977. Data are not included from the third year of operation because of changes in flow rates and loading rates.

No simple pattern could be perceived which related nitrification measured as the specific oxidation rate (R_3, Table 19) with the concentration of organic matter. Nitrification did not occur when the reactor BOD_5 exceeded one gram per liter and when the COD exceeded three grams per liter. However, subsequent to the formation of a culture of acclimated activated sludge, capable of nitrification and organics oxidation, there was no consistent relationship between the specific

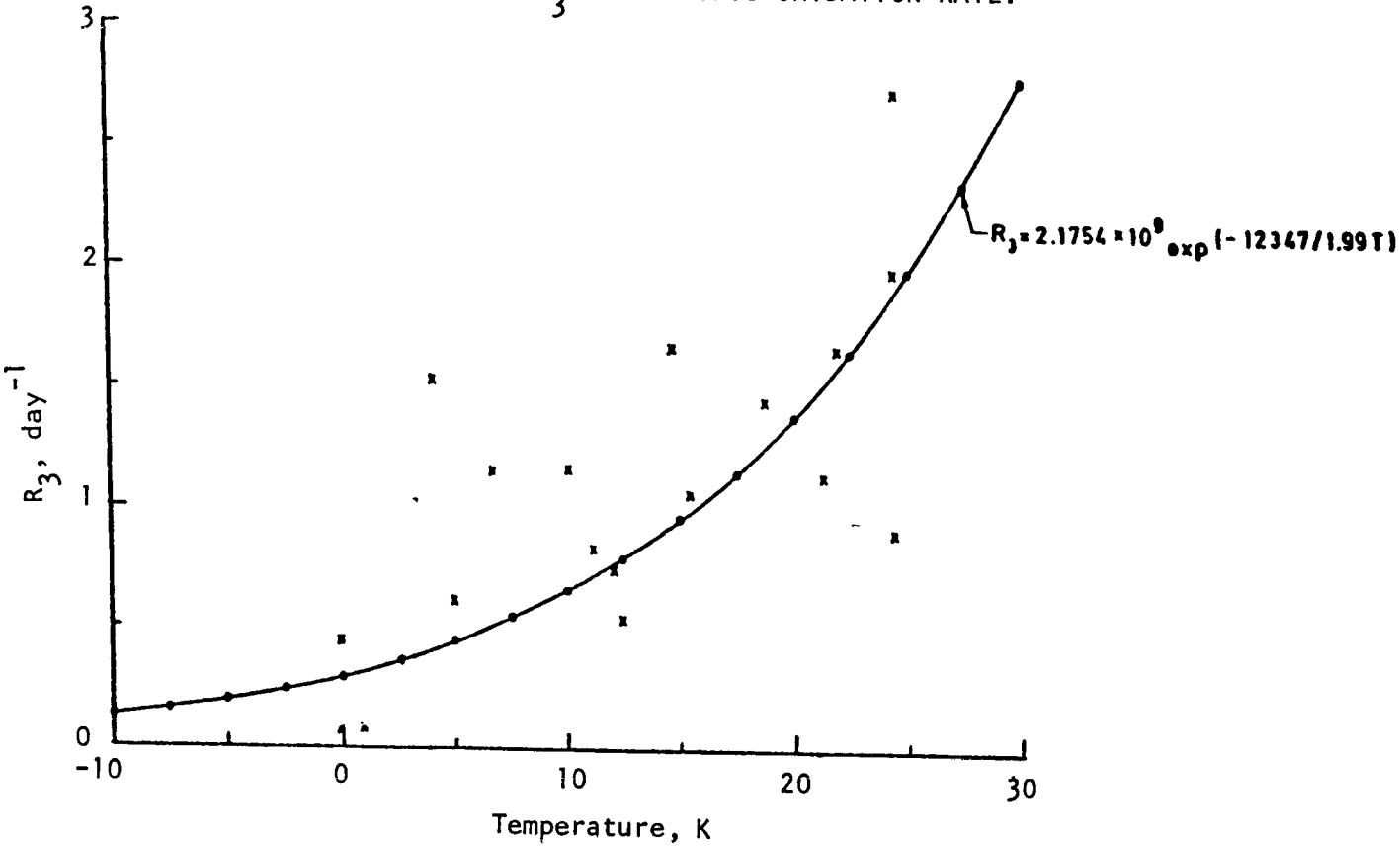
oxidation rate and the concentration of organic matter in the reactor. Nitrification proceeded even though the activated sludge influent concentration of BOD_5 and COD averaged 3564 and 6481 mg per liter, respectively. This was true when the ammonia content of the bio-unit influent did not exceed 300 mg per liter. At higher ammonia levels, the toxicity of ammonia predominated and very little oxidation of either organics or ammonia occurred.

It is reasonable to expect some inhibition due to the elevated levels of BOD_5 and COD recorded in Table 19. The nitrifers, such as Nitrosomonas and Nitrobacter, are chemollthotrophs, i.e., they are autotrophs, and their carbon source is inorganic. These bacteria are especially sensitive to organics in pure culture. Certain heterotrophic bacteria, fungi, and actinomycetes are capable of performing nitrification,[64,65] although it is generally believed that the rate of heterotrophic nitrification is much less than that of the autotrophic nitrifiers.[66] The sensitivity of these organisms to organics is presumably much less than it is for the autotrophs. Wild et al. observed no effect of BOD, in the range of 5-110 mg per liter, on the rate of nitrification in activated sludge processes.[67]

The effect of temperature on the specific oxidation rate is shown in Figure 8. This curve agrees well with curves developed and presented recently by the Environmental Protection Agency.[68] The curve has been fitted in the least squares sense and the equation of the line is

$$R_3 = Xe^{-E/RT} \qquad (5)$$

FIGURE 8. EFFECT OF TEMPERATURE ON SPECIFIC OXIDATION RATE. THE LEAST SQUARES LINE OF BEST FIT SHOWN. THE NOTATION 1 REFERS TO TEMPERATURE, K; AND R_3 IS SPECIFIC OXIDATION RATE.



where, R_3 = specific oxidation rate, day^{-1}

X = 2.175×10^9 day^{-1} = Arrhenius frequency factor

E = activation energy = 12347 cal/mole

R = gas constant = 1.99 cal/mole-K

T = temperature, K

The curve of Figure 8 is somewhat lower than the theoretical one developed by the EPA,[69] and this is most likely due to an inhibitory effect of some wastewater fraction such as heavy metals, organics, and substrate.

A number of values for E have been reported in the literature. Wong-Chong and Loehr presented data showing the variation of E with pH.[70] Their results indicated that for the ammonia oxidation, the value of E ranges from 16 to 21.6 K cal per g mole. Sutton *et al.* state that E is a function of the treatment mode, and in particular of the staging of the biological units, and the solids retention time.[71] For single stage units, such as this one (August 1, 1976 - May 1, 1977), they report that the values of E are 25.1, 21.25, and 11.9 k cal/g mole for solids retention times (SRT) of 4, 7, and 10 days, respectively. The figures refer to the overall nitrification process. The last number is of particular importance since an SRT of ten days is considered to be the minimum needed for thorough nitrification[72] (although Hutton and LaRocca[73] considered thirty days to be more reasonable, and others[74] consider three to four days as the minimum needed to ensure successful nitrification). The value of 12350 cal per g mole obtained here is in good agreement with that of Sutton *et al.*[75]

A number of factors were investigated for potential inhibition of nitrification. As discussed above, there is no consistent observed effect of organic matter, measured as BOD_5 and COD, on nitrification. However, based on the literature,[76] it is probable that some of the inhibition noted above results from the relatively high BOD and COD concentrations in the aeration tank. The heavy metals are another likely source of inhibition, although an obvious relationship was not observed. Average heavy metals concentrations in the aeration tank are listed in Tables 14 and 15 as effluent values.

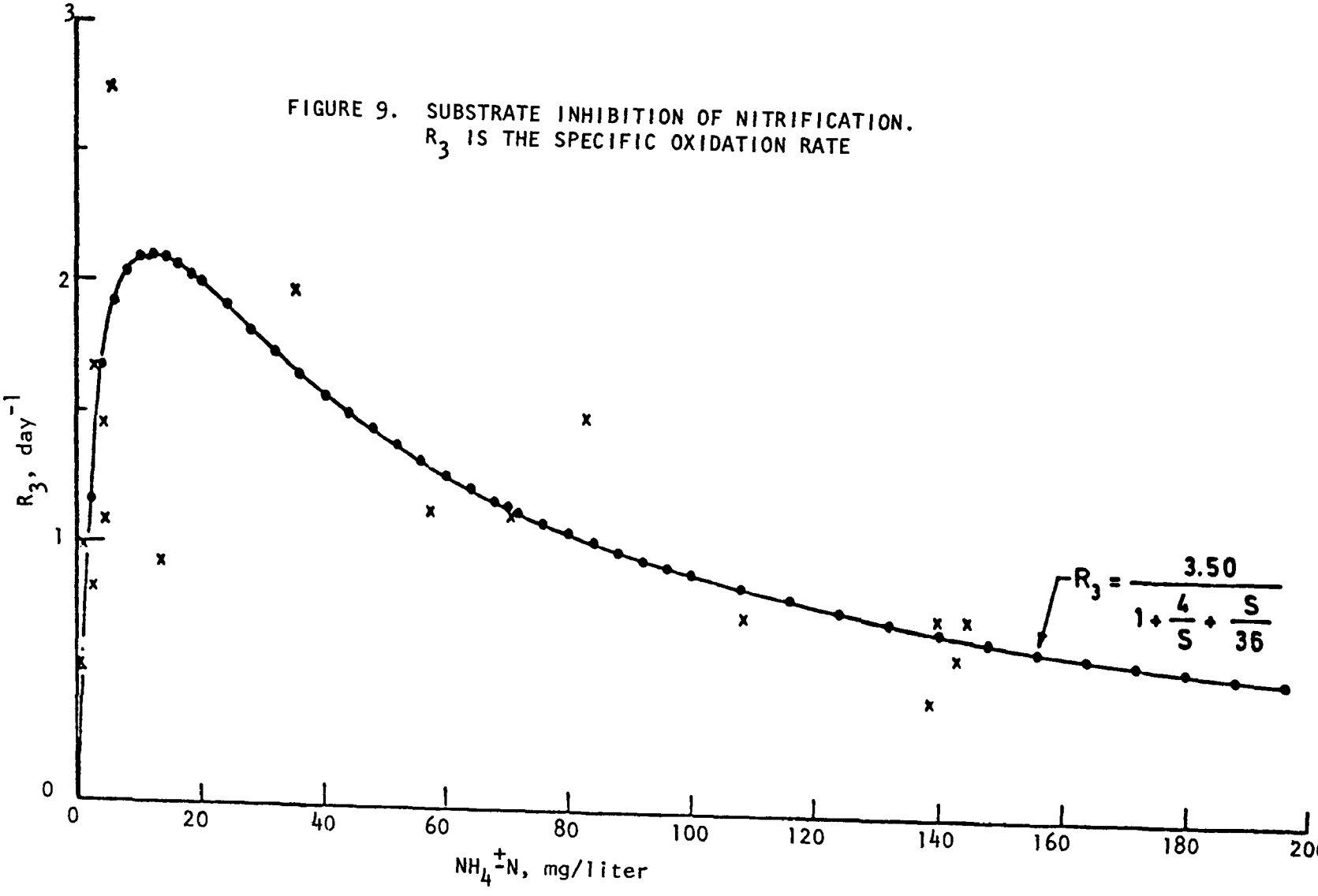
The clearest reason for the observed inhibition is that increasing concentrations of substrate are the cause. This is shown in Figure 9, where the data show a reasonable fit to the classic substrate inhibition model. The model is based on the Haldane[77] mechanism for the substrate inhibition of enzymes, and is expressed here as

$$R_3 = \frac{\hat{R}_3}{1 + \frac{K_s}{S} + \frac{S}{K_1}} \qquad (6)$$

where R_3 is the specific oxidation rate, day^{-1}; $\hat{R}_3$ is the maximum specific oxidation rate which would be obtained in the absence of substrate inhibition, day^{-1}; K_s is the saturation constant; and, K_1 is the inhibition constant. K_s and K_1 are numerically equal to the higher and lower substrate concentrations, respectively, at which R_3 equals one-half of $\hat{R}_3$.

The curve in Figure 9 has been developed using a quasi-least squares procedure and Lineweaver-Burke plots to evaluate the kinetic constants.

FIGURE 9. SUBSTRATE INHIBITION OF NITRIFICATION. R_3 IS THE SPECIFIC OXIDATION RATE



The equation used to generate the line is

$$R_3 = \frac{3.50}{1 + \frac{4}{S} + \frac{S}{36}} \qquad (7)$$

indicating that the value of $\hat{R}_3$ is 3.5 day^{-1}, K_s is 4.0 mg per liter, and K_1 is 36 mg per liter.

Figure 10 shows a Michaelis-Menton plot of the data obtained at the lower concentrations. These values correspond to the situation encountered in the treatment of domestic sewage, and this figure therefore resembles the type curve usually presented.[78] In the treatment of industrial wastes where the influent ammonia-N may be much higher, it will be necessary to consider the substrate inhibition of nitrification. It should be mentioned that the nature of the situation, i.e., a full scale plant treating a variable influent, with differences in pH, temperature, and other operating variables, contributes to the scatter of the data observed in Figures 9 and 10.

In the excellent review prepared by Focht and Chang, much of the literature regarding nitrification has been summarized.[79] They report that the saturation constant for the Michaelis-Menton model is in the range of one to ten mg N per liter for ammonium oxidation, and five to nine mg N per liter for the conversion of nitrite. Poduska and Andrews state that the saturation constants for Nitrosomonas and Nitrobacter are approximately one mg per liter for full scale activated sludge systems.[80] The value of four mg N per liter reported here is consistent with these data.

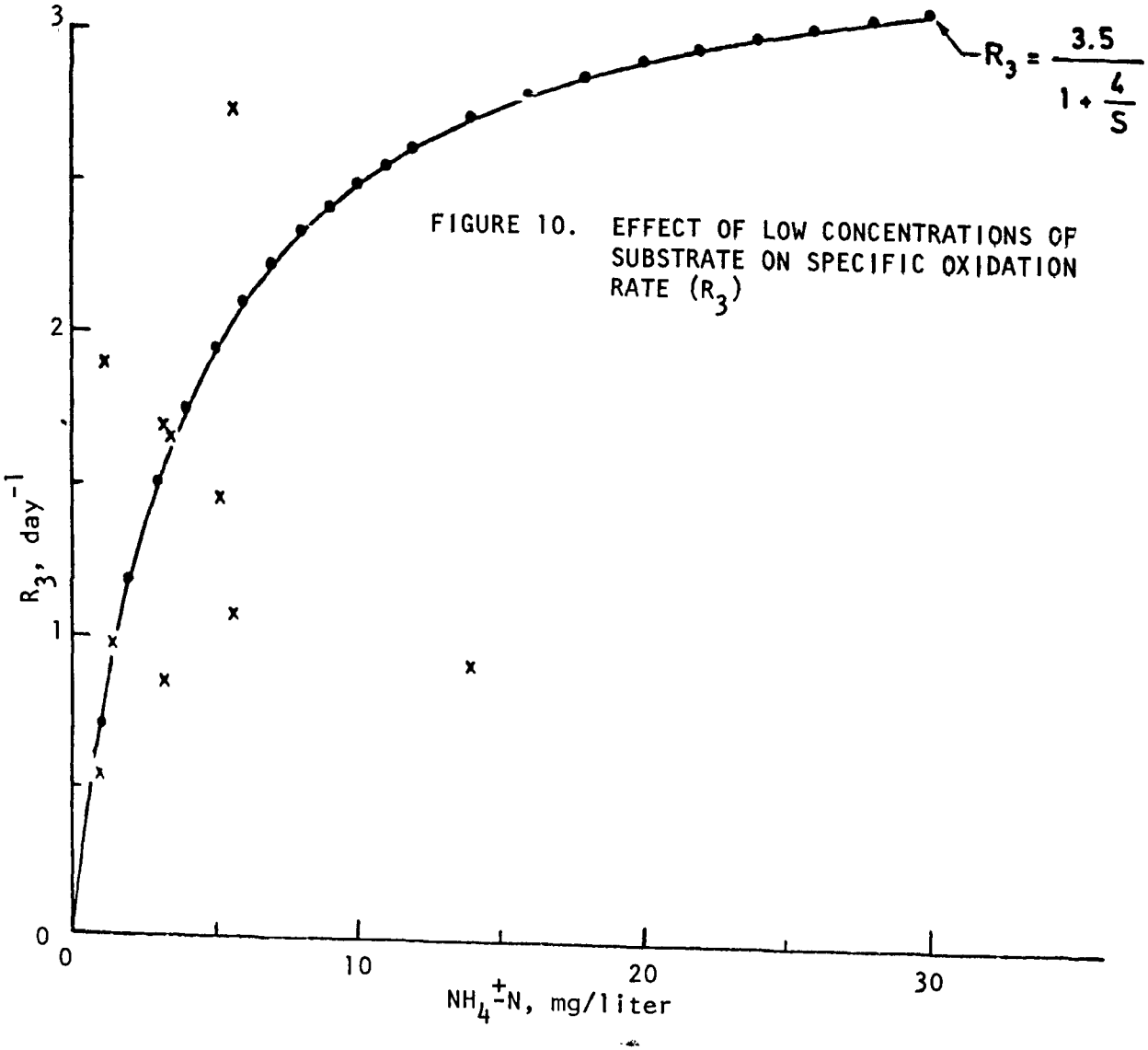


FIGURE 10. EFFECT OF LOW CONCENTRATIONS OF SUBSTRATE ON SPECIFIC OXIDATION RATE (R_3)

Focht and Chang also state that the first observation of substrate inhibition in nitrification was made in tne early studies of Meyerhof who showed that Nitrosomonas and Nitrobacter are inhibited at concentrations of NH_4^+-N and NO_2^--N exceeding 60 and 350 mg per liter, respectively.[81] Wild et al. found no evidence for inhibition due to ammonia in the range of six to sixty mg per liter.[82] Focht and Chang also point out that end product inhibition has been demonstrated with both Nitrosomonas and Nitrobacter.[83] This refers to the situation in which accumulated nitrate or nitrite inhibits further nitrification.

A number of investigators have reported that inhibition of nitrification is due to ammonia-N and to unionized nitrous acid.[84-88] Verstraete et al. recommend that startup of nitrification units treating highly nitrogenous wastes must consist of a gradual increase in the nitrogen loading in order to avoid the deleterious effects of these undissociated species of nitrogen.[89] The data shown in Table 19 have been examined in this light in order to assess nitrification inhibition which could be attributed to the free ammonia concentration. When this is done, however, it is observed that there is no relationship between the specific oxidation rate and the concentration of free ammonia. In this respect, the results of this study are in conflict with those cited above, and the question merits further study.

Kholdebarin and Oertli have reported recently their studies of batch growth nitrification.[90] They observed that the ionized NH_4^+-N has a stimulating effect on nitrite oxidation. In the present study, NH_4^+-N was observed to exert an inhibitory effect. As shown in Figure 9,

the effect is not profound until the concentration exceeds ten to twenty mg NH_4^+-N per liter. The ammonium ion levels used by Kholdebarin and Oertli were 2.8 mg N per liter, and in one experiement, 28 mg N per liter.[91] Thus, assuming that NH_4^+-N inhibits nitrification, the experiments of Kholdebarin and Oertli must be performed at higher concentrations in order to be comparable with the results presented here.

The approach which has been followed here has been to attempt to simplify an exceedingly complex microbial process. The conversion of ammonia has been considered the rate limiting step, and has received primary attention. The maximum growth rate of Nitrobacter is larger than that of Nitrosomonas and the value of the saturation constants is approximately the same. Thus, nitrite is oxidized more quickly than is the ammonia, and this forms the basis of the above assumption. Certain aspects of the inhibition of nitrification have not been considered. Examples are product inhibition due to nitrite and nitrate, and the non-competitive inhibitory effect of nitrous acid. A third area of simplification is that the environmental factors are quite variable at the leachate treatment plant, due to influent quality and quantity changes.

It is contended that this approach is justified because of the complexity of full-scale operation. The value is that nitrification is viewed from the overall perspective, and it is seen that substrate inhibition is a phenomenon operating in this system. This knowledge can serve as a guide in both the design and operation of nitrification systems, and can ultimately be incorporated within steady-state[92] and dynamic[93] models of the process.

Summary. The rate of nitrification, as expressed as the specific oxidation rate, follows the van't-Hoff Arrhenius relationship which indicates that the activation energy is approximately 12350 cal per mole, and that the Arrhenius frequency factor is 2.18×10^9 day^{-1}. The data indicate that substrate inhibition due to ammonium ion concentration occurs in this system. This relationship has been expressed as a Haldane inhibition model in which the maximum specific oxidation rate is 3.5 g N oxidized per g biomass day, K_s is 4 mg per liter, and K_I is 36 mg per liter.

System 2. Chemical/Physical Treatment

This discussion is presented in two parts. The first consists of the results associated only with lime treatment, and the second includes the ammonia stripping lagoon. Full-scale data were collected for System 2a without the lagoon during the periods November 15, 1975 to January 12, 1976 and June 14, 1976 to April 30, 1977, all dates inclusive. The results of this phase of the treatment plant operation are summarized in Table 20, columns 1-7. The distinction between the two periods permits an assessment of the performance of the ammonia lagoon.

Table 20 summarizes the changes in each parameter attributable to the lime treatment. In very approximate terms, the lime precipitation/clarification sequence, System 2a, removed (see Column 7, Table 20) one-quarter of the nitrogen; one-third of the dissolved solids; one-half of the organic matter, hardness and alkalinity; three-quarters of the suspended solids; and ninety percent of the phosphates. The removal of heavy metals was over one-half of the mercury and cadmium; two-thirds

TABLE 20

SUMMARY OF SYSTEM 2 RESULTS. EACH SYSTEM CONSISTS OF LIME TREATMENT AND CLARIFICATION SYSTEM 2a and 2b ARE WITHOUT AND WITH AIR STRIPPING OF AMMONIA, RESPECTIVELY.*

Parameter	System 2a							System 2b						
	Influent			Effluent				Influent			Effluent			
	n	x̄	cv	n	x̄	cv	R	n	x̄	cv	n	x̄	cv	R
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(14)	
Alkalinity, as $CaCO_3$	65	5668	0.23	43	3052	0.30	46.2	79	5316	0.78	70	2374	0.28	55.3
Ammonia-N	66	1167	1.25	48	890	1.26	23.7	88	785	0.31	86	412	0.52	47.5
BOD-5	65	10356	0.86	46	5265	1.03	49.2	77	11668	0.71	71	3600	0.84	69.1
Cadmium	62	0.07	0.87	41	0.03	0.49	57.1	80	0.086	0.82	71	0.035	1.09	59.3
Calcium, as $CaCO_3$	63	863	0.54	43	696	0.57	19.4	80	841	0.57	70	424	0.70	49.6
Chloride	75	4590	0.43	45	3516	0.74	23.4	78	3927	1.49	68	2669	0.15	32.0
Chromium	63	0.25	0.75	43	0.09	0.58	64.0	80	0.25	0.71	70	0.08	0.94	68.0
COD	212	16618	0.74	151	7188	0.67	56.7	261	18566	0.62	254	8793	0.63	52.6
Copper	62	0.46	0.93	52	0.10	0.47	78.3	79	0.43	0.94	73	0.27	1.27	37.8
Dissolved Solids	274	12652	0.56	218	7972	0.32	37.0	232	10456	1.04	236	4650	1.09	55.5
Hardness, as $CaCO_3$	76	5257	0.41	49	2461	0.50	53.2	76	4645	0.49	64	1587	0.53	65.8
Iron	61	350	0.74	43	3.8	3.05	98.9	74	300	0.82	68	5.61	1.28	98.1
Kjeldahl-N	72	1157	1.28	50	867	1.39	25.1	61	739	0.27	52	349	0.41	52.7
Lead	60	0.75	0.73	43	0.24	0.85	68.0	80	0.68	0.76	67	0.23	1.31	65.6
Magnesium, as $CaCO_3$	70	562	0.42	43	209	.90	62.8	80	421	0.42	69	117	0.62	72.1
Mercury	66	5.69	1.30	40	2.85	1.22	49.9	74	0.021	2.43	63	0.010	1.96	52.4
Nickel	63	1.58	1.21	43	.57	1.44	63.9	81	1.60	1.06	67	0.73	0.93	54.3
pH	300	6.80	1.28	242	8.46	8.04	--	394	6.93	1.56	383	866	1.79	--
Phosphates	63	2.40	0.63	42	.26	.83	89.2	84	2.52	0.75	74	0.27	2.07	89.3
Potassium	75	941	0.27	46	613	.36	34.9	61	944	0.21	52	572	0.25	39.4
Sodium	78	1284	0.35	48	830	.45	35.4	78	1366	0.30	66	956	0.40	30.0
Sulfate	72	409	3.23	46	426	.89	-4.2	79	512	2.46	70	525	0.67	-2.6
Suspended Solids	224	843	1.14	183	239	1.15	71.6	255	967	1.11	253	288	0.93	70.2
Zinc	61	19	1.06	43	0.61	1.35	96.8	86	15.9	1.15	70	0.85	1.39	94.6

*x̄ = mean, mg/liter. R stands for percent removal. System 2a effluent is the lagoon influent.

of the chromium, nickel, and lead; three-quarters of the copper and over ninety percent of the iron and zinc. The increase in sulfate is due primarily to contaminants in the chemicals, although oxidation of sulfides may contribute somewhat. In other words, this section of the system performed as expected in pre-treating the leachate prior to biological treatment.

The results of the overall chemical/physical section including the ammonia lagoon (System 2b) are listed in Table 20 (Columns 8-14) which shows the basic statistical relationships. Treatment performance in terms of percent removal efficiency of the lagoon alone and in conjunction with lime treatment are also seen in Table 20. The primary goal of the lagoon was achieved as the concentration of ammonia-N was reduced to a level which was found to be tolerable for purposes of biological waste treatment. A splash plate, which was installed to promote air/water contact, did not produce an appreciable effect on lagoon ammonia removals, and was therefore removed.

Many parameters other than ammonia were altered while in the lagoon (see Table 21). There was some stabilization of organic matter as shown by the reductions in BOD, COD and dissolved solids. This was mediated by biochemical processes and the increase in suspended solids is related to the growth of microorganisms. The reduction in alkalinity is due to aeration effects although nitrification reactions may partially contribute to the observation. The reduction of hardness, calcium and magnesium are related and may be explained by the formation of calcium and magnesium carbonates. In this form, these would not be detected by the usual tests. Most of the other changes noted in the lagoon effluent vs. lagoon

TABLE 21

SUMMARY OF EFFECTS OF CHEMICAL/PHYSICAL TREATMENT*

	Influent+	Lime Treatment Effluent+	Ammonia Lagoon Effluent+
Suspended Solids	1044	239	288
Dissolved Solids	13029	7972	4650
COD	18553	7188	8793
BOD_5	10907	5265	3600
Alkalinity	5404	3052	2374
Hardness	4652	2461	1587
Magnesium	453	209	117
Calcium	818	696	424
Chloride	4240	3516	2669
Sulfate	462	426	525
Phosphate	2.74	0.26	0.27
Ammonia-N	1001	890	412
Kjeldahl-N	984	867	349
Sodium	1354	830	956
Potassium	961	613	572
Cadmium	0.086	0.03	0.04
Chromium	0.28	0.09	0.08
Copper	0.39	0.10	0.27
Iron	312	3.8	5.6
Nickel	1.55	0.57	0.73
Lead	0.67	0.24	0.23
Zinc	21	0.61	0.85
Mercury	0.007	0.003	0.010
pH	6.85	8.46	8.66

*The influent data are those collected during the entire operational period, whereas the effluent figures refer to those periods when the specific units were operating.

+All units are mg/liter except pH which is expressed in pH units.

influent comparison are due to the limitations of the experimental techniques or to the radically variable nature of the raw leachate.

The overall treatment efficiency of the complete chemical/physical section is summarized in Table 20. These data do not include the effect of neutralization. The values in the last column (Column 14) represent removal efficiencies for the lime precipitation/sedimentation/ammonia stripping sequence. In terms of organic matter, 69.1 and 52.6 percent of the BOD and COD are removed, respectively. Approximately fifty to sixty percent of the ammonia-N, total nitrogen, suspended solids, alkalinity and hardness are removed. The removal of metals was as follows: 38-54 percent of copper, nickel and mercury; 59-68 percent of chromium, cadmium, and lead; 95 percent of zinc; and 98 percent of iron.

Chian and Dewalle have formed an hypothesis, which is summarized in Table 6, concerning the treatability of raw leachate.[94] The BOD/COD ratio observed in this study (Column 2 of Table 20) of the leachate was 0.62 and the average COD was 16618 mg/liter. This is also shown in Column 9 of Table 20, in which it is seen that the ratio is 0.63, and the average COD, 18566 mg/liter. Thus, according to Chian and DeWalle, the leachate treatment efficiency obtainable with lime should be fair. In this study (Column 7, Table 20) the lime treatment efficiency for BOD and COD has been about fifty percent. Hence, in terms of the removal of organics, the Chian and DeWalle hypothesis is supported.[95] However, it must be mentioned that their hypothesis did not include the removal of heavy metals, and that the lime treated heavy metal removals have been good to excellent at this facility.

An additional effect of the ammonia stripping lagoon is the equalizing effect which, as noted by LaGrega and Keenan, can be measured in terms of both flow variability and quality fluctuations.[96] The presence of the lagoon has allowed the operator to control the flow leaving the lagoon by control of the pump settings. This has provided additional flow equalization to the biological units.

Operational Comments. The primary operational factor has been the chemicals required for precipitation and neutralization. A summary of these is presented in Table 22. The rows labeled "average applied dose" have been calculated by omitting those days on which chemicals could not be added because of equipment malfunctions.

Cost Data. The cost of materials and electricity is a part of Table 22. The units are given in terms of dollars per one thousand gallons of leachate treated. The data indicate that the cost of System 2 with, and without, operation of the lagoon has been $2.37 and $2.35 per thousand gallons treated, respectively. The total cost figures have been obtained as the ratio of total costs to total volume of liquid treated. The power costs are quite high, reflecting energy consumption not only for chemical treatment, but also for leachate pumping, air compressors and the laboratory. Manpower costs for operation and maintenance are approximately twenty hours per week.

Factors Influencing Lime Treatment Performance

The principal operating characteristics of the lime treatment system are presented in Table 23 for data collected during the period June 14, 1976 to April 21, 1977. These data only are included as this was the

TABLE 22

SUMMARY OF OPERATION AND MAINTENANCE COSTS DURING EVALUATION OF SYSTEM 2
(11/15/75-5/1/77 and 11/1/77-8/31/78)

	During Operation Without Lagoon 11/15/75-5/1/77	During Operation with Lagoon (Ammonia) 6/14/76-5/1/77 & 11/1/77-8/31/78		
		Total	6/14/76-8/1/77	1/1/77-8/31/78
Flow, average gpd	22,805	38,618	21,394	17,224
lpd	86,326	146,170	80,987	65,183
total gal	8,004,483	16,798,842	5,348,622	11,450,220
total cu m	30,300	63,584	20,247	42,337
Lime, average dose,				
lb/1000 gal	29.7	19.40	36.6	11.39
kg/cu m	3.57	2.33	4.39	1.37
total lb	238,055	326,050	195,650	130,400
kg	108,077	147,894	88,825	59,069
NaOH, average dose,				
gal/1000 gal	0	0.044	0.137	0
l/cu m	0	0.044	0.137	0
total gal	0	733	733	0
total liter	0	2,926	2,926	0
NaOCl, average dose,				
gal/1000 gal	0	0.054	0.107	0.03
l cu/m	0	0.054	0.107	0.03
total gal	0	901.5	571.5	330
total liter	0	3,413	2,163	1,250
Costs, $/1000 gal				
Power	1.48	1.70	1.70	1.70
Lime	.89	0.58	1.10	0.34
NaOH	0	.03	0.09	0
NaOCl	0	.04	0.08	0.02
Total	2.37	2.35	2.97	2.06

TABLE 23

SUMMARY OF OPERATIONAL DATA FOR LIME TREATMENT AND CLARIFICATION*

Date	Cadmium C	Cadmium R	Chromium C	Chromium R	Copper C	Copper R	Iron C	Iron R	Lead C	Lead R	Magnesium C	Magnesium R	Mercury C	Mercury R
6/14	.020	.231	.04	.50	.08	.771	.48	.994	--	--	312	.448	1.17	.957
6/22	.028	.282	.04	.60	.10	.895	2.72	.982	--	--	312	.525	1.06	.960
6/30	.01	.700	.06	.25	.09	.763	2.54	.983	--	--	323	.441	6.5	.606
7/15	.025	.50	.06	.684	.12	.90	2.22	.964	.07	.873	87	.858	2.96	.80
7/21	.018	.617	.06	.739	.26	.807	1.52	.996	.05	.889	43	.936	1.72	.204
7/27	.020	.615	.08	.714	.2	.796	2.89	.995	.07	.879	36	.860	8.5	.444
8/3	.025	.667	.04	--	.01	.808	.1	.997	.02	.80	22	.900	3.1	.852
8/10	.02	.091	.03	.25	.18	--	.92	.997	.03	.864	123	.836	3.4	--
8/20	.05	.444	.09	.571	.078	.926	.68	.997	.11	.929	257	.471	3.5	.364
8/25	.05	.286	.10	.286	.064	.559	.58	.997	.04	.871	250	.520	3.	.857
9/3	.05	.375	.09	.625	.10	.545	.85	.997	.48	.392	225	.595	5.5	.633
9/15	.019	.525	.07	.632	.1	.919	1.09	.997	.22	.728	45	.912	2.1	.781
9/23	.015	.400	.06	.625	.11	.931	1.15	.996	.35	.646	25	.947	3.9	--
9/29	.017	.452	.09	.654	.13	.859	.42	.999	.1	.815	54	.894	7.5	.074
10/7	.015	.50	.05	.500	.05	.643	1.74	.983	.1	.667	71	.862	1.8	--
10/19	.021	.222	.08	.529	.08	.75	2.59	.994	.4	.20	92	.793	1.78	.282
11/13	.009	.710	.03	.625	.02	.90	1.98	.966	.1	.875	212	.668	.09	.930
11/18	.012	.707	.03	.667	.03	.786	2.13	.981	.1	.981	136	.809	.21	.756
11/23	.03	.333	.11	.500	.01	.909	2.43	.995	.1	.787	115	.818	.15	.865
12/14	.009	.95	.07	.854	.04	.934	2.99	.997	--	--	97	.883	.22	.808
12/22	.01	.90	.08	.333	.06	.455	1.78	.996	.2	.333	101	.789	.15	.934

*For each chemical species, the effluent concentration (C) is given in mg/liter except mercury (µg/liter), pH (pH units), lime dosage (lb), Temp. (C), and flow (gpd), and R represents the fraction of material removed by this treatment section.

TABLE 23 (cont.)

Nickel		Phosphates		Suspended Solids		Zinc		pH	Lime Added	Flow	Temp.
C	R	C	R	C	R	C	R				
.31	.38	,025	.987	800	.444	.24	.933	10.30	900	35,500	25.2
.4	.394	.085	.965	600	.618	.47	.955	10.08	1000	32,500	26.
.21	.667	.05	.974	280	.800	.3	.969	9.78	1000	37,000	25.0
.26	.509	.09	.952	260	.783	.24	.933	10.00	700	14,500	26.3
.23	.733	.05	.992	840	.786	.25	.974	10.78	1000	13,450	26.5
.19	.740	.026	.992	260	.913	.2	.977	9.82	800	13,445	27.1
.02	0	.02	.977	70	--	.16	.927	12.20	900	5,870	24.5
.29	.700	.074	.979	80	.931	.12	.948	11.21	950	11,960	26.5
.22	.511	.05	.962	220	.593	.98	.897	8.90	800	13,200	24.5
.31	.510	.05	.933	112	.762	.19	.931	11.30	1000	8,140	24.4
.2	.706	.09	.942	44	.915	.69	.922	11.02	1000	11,100	21.3
.32	.733	.09	.925	25	.952	.30	.947	10.5	1000	15,500	22.0
.32	.68	.026	.989	88	.955	.08	.977	11.7	950	11,500	24.5
.11	.872	.06	.933	29	.896	.10	.985	11.1	950	11,200	22.7
.23	.465	.03	.917	50	.737	.07	.952	10.4	950	16,150	23.2
.22	.569	.09	.931	200	.394	.76	.797	9.4	800	15,670	15.5
.38	.191	.04	.982	230	--	.21	.953	9.3	800	14,630	11.2
.41	.523	.07	.960	120	.564	.31	.965	10.1	800	18,450	12.2
.96	.329	.06	.977	180	.481	.23	.990	11.1	1100	14,160	10.2
.68	.534	.07	.952	63	.991	.76	.979	10.4	1000	15,410	3.2
.45	.55	.06	.946	33	.931	.62	.977	11.7	800	40,000	4.1

period of primary analysis, and also because of the change in the leachate which occurred during the third year.

The function of the lime treatment/clarification section of the plant is to pre-treat the leachate prior to biological treatment, i.e., to remove a portion of the organic matter and toxic substances. The latter include ammonia as well as the heavy metals. The lime precipitation process has consistently produced an effluent which meets the standards except for cadmium and lead. (It should be noted that the final effluent met these standards up to the onset of cold weather, and that the probable mechanism for the additional removal is adsorption onto the surface of the biological floc.) It is apparent that, considering the variability of the incoming waste, equalization would improve process efficiency and effluent quality. The influent changes occur so rapidly that the lime feed mechanism cannot maintain a constant dose, with the result that there are occasions when the lime dosage is inefficient and/or inadequate. As a result of this consideration, the raw leachate equalization lagoon was constructed.

A desirable goal is to be able to operate the lime treatment process selectively to improve the quality of the effluent with respect to one or more of the heavy metals. As the solubilities of the metals vary as different functions of pH[18], it is not possible to optimize the removal of all metals at a given pH, and the pH becomes an operational indicator the operator can use to achieve differential removals. Thus, one can fine tune the operation to provide an effluent of suitable characteristics. With this goal in mind, the data of Table 23 were examined to discover a

relationship between pH, temperature, and the concentration of heavy metals in the clarifier effluent.

In order to develop a relationship, which could be used as an operational tool, between pH and the removal of heavy metals, the effluent concentrations were examined as possible functions of pH. Figures 11 and 12 show the relationship between pH and nickel and mercury effluent concentrations, respectively. In these figures, the circled data points were collected when leachate temperatures were less than 16 C, whereas the others represent higher tempratures (see Figure 13).

The effects of pH and temperature on the nickel content of the clarifier effluent are shown in Figure 11. Process efficiency is not a strong function of pH over the range of 8.9 to 11.7, and it does not matter whether one measures nickel in the effluent or the fraction removed. Effluent concentrations of nickel centered about 0.20-0.30 mg/l over the entire pH range, except at low temperatures. For liquid temperatures less than 16 C, the effluent nickel level increased substantially. This is shown in Figure 13.

Iron concentration decreased with increasing pH with the lowest concentrations resulting at pH 10.3-12.2. The effect of low temperatures (<16 C) was to increase the amount of iron in the clarifier effluent. In terms of the iron removal efficiency, the fraction of iron removed was independent of pH and temperature, as it was always greater than 0.98.

The response of chromium, lead and phosphate to pH was more or less flat with no apparent relationship. In each case, temperature did not influence the effluent concentrations. There was a tendency for lower effluent chromium concentrations in the pH 9-10.5 range, and for better

FIGURE 11 EFFECT OF pH ON CLARIFIER EFFLUENT NICKEL CONCENTRATION. THE CIRCLED VALUES REPRESENT WASTEWATER TEMPERATURES OF LESS THAN 16°C.

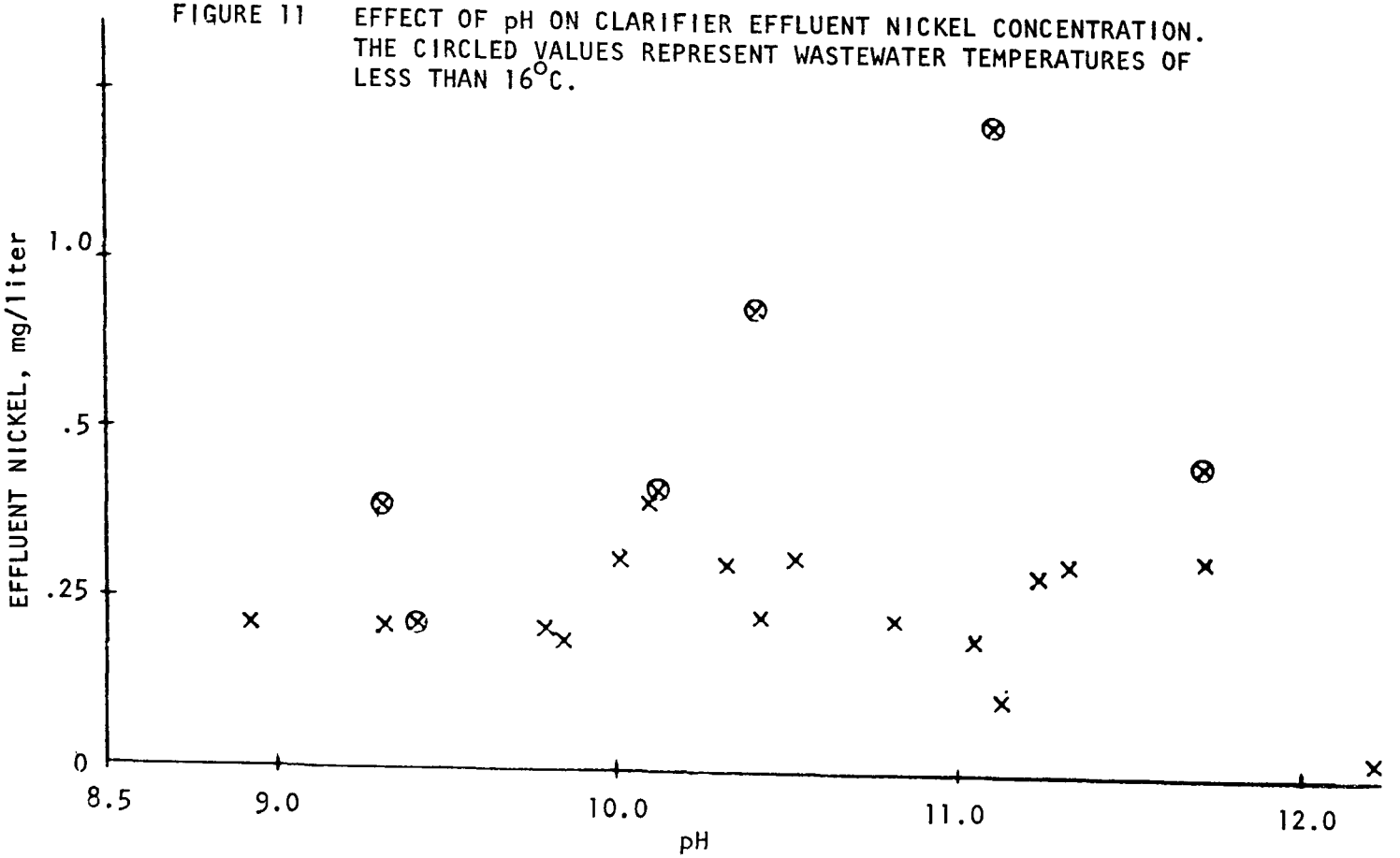


FIGURE 12. EFFECT OF pH ON CLARIFIER EFFLUENT MERCURY CONCENTRATION. THE CIRCLED VALUES REPRESENT WASTEWATER TEMPERATURES OF LESS THAN 16°C.

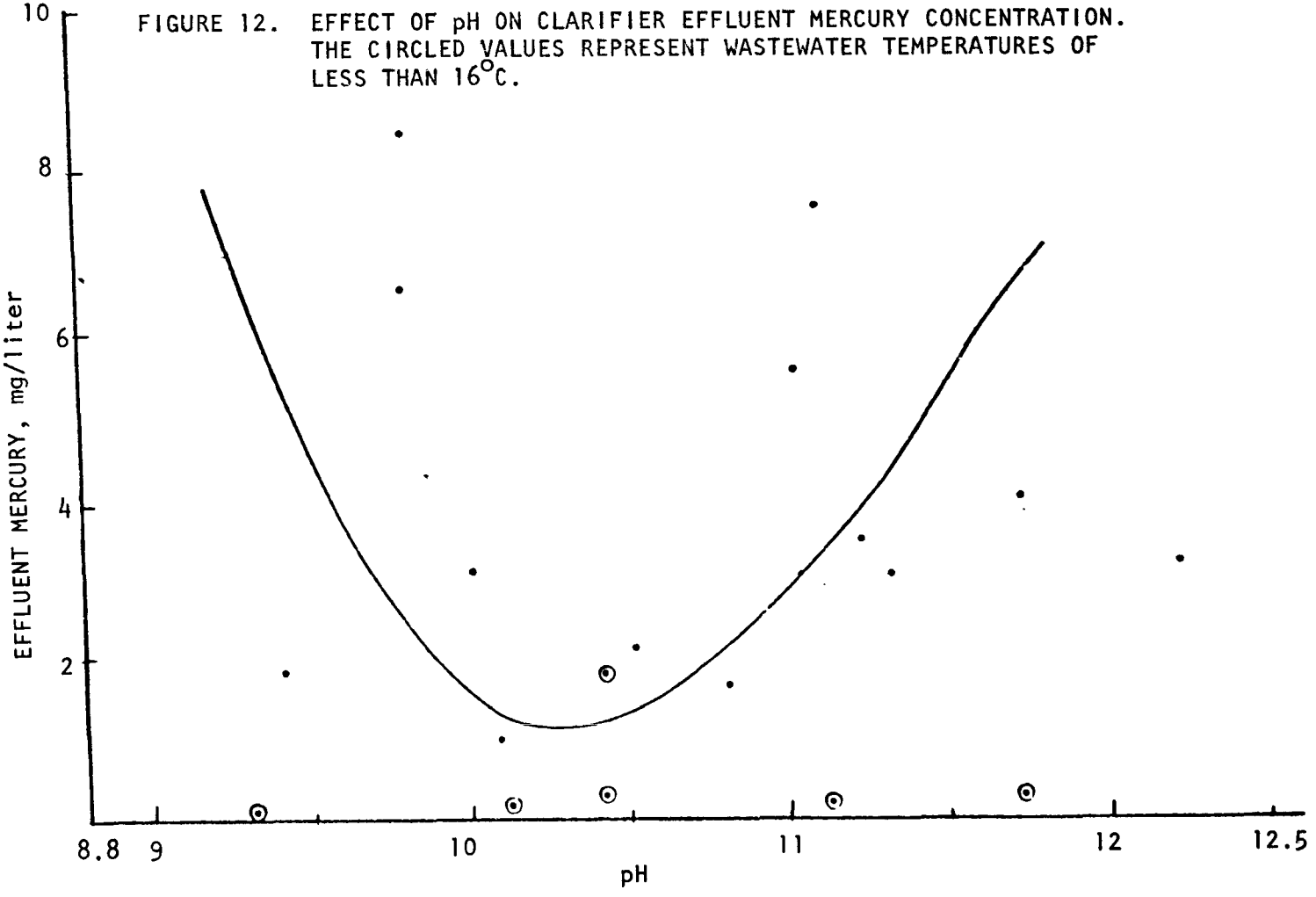
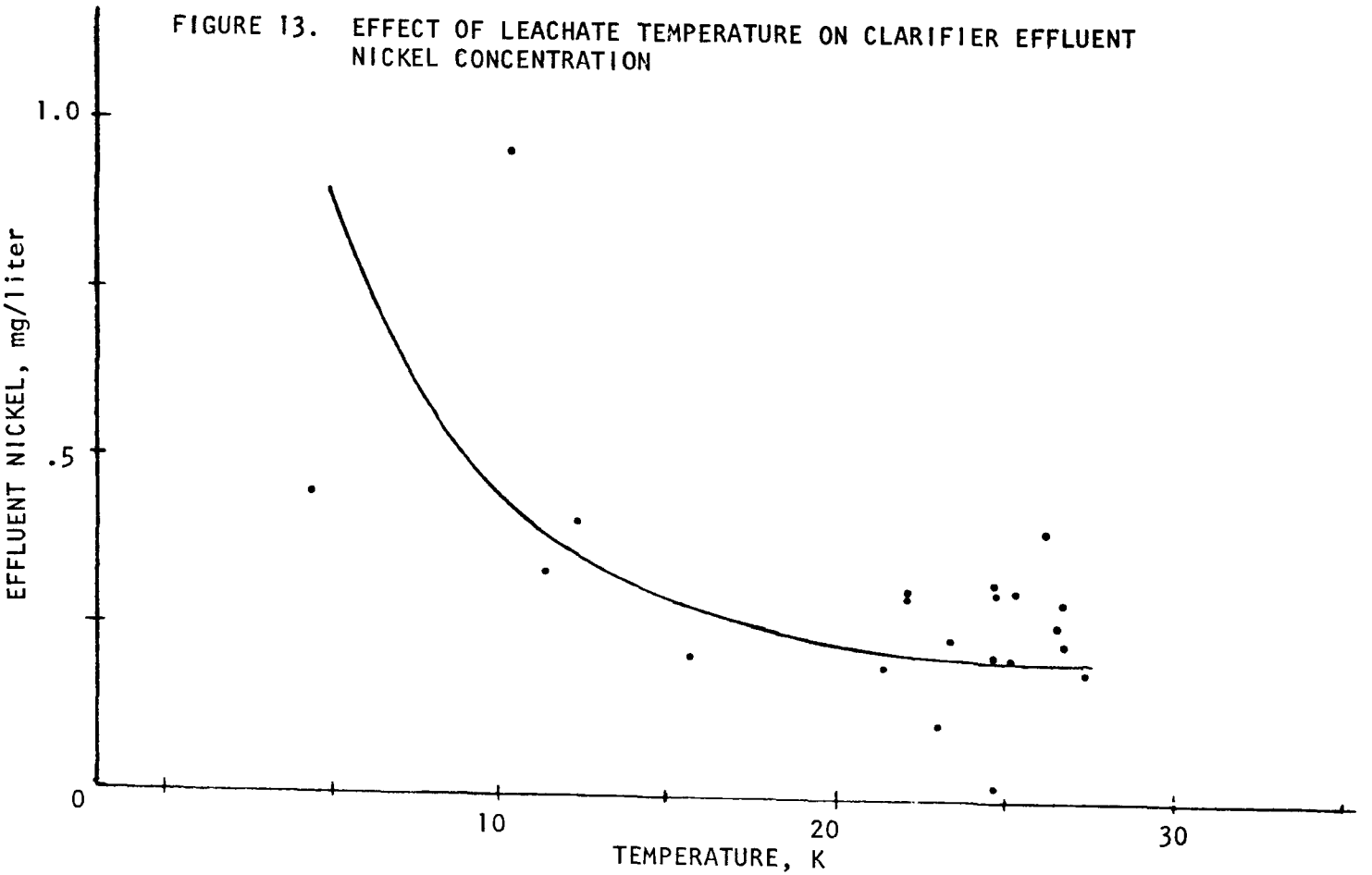


FIGURE 13. EFFECT OF LEACHATE TEMPERATURE ON CLARIFIER EFFLUENT NICKEL CONCENTRATION



removals of lead at pH levels below 10.1. However, these effects are certainly not dramatic.

The concentration of zinc in the clarifier effluent decreased with increasing pH. Minimum concentrations occurred at pH 10.4 to 12.2. The effect of low temperatures was to increase the zinc content of the effluent.

Chromium, copper and mercury concentrations show a tendency toward a U-shaped response to pH. The curve for mercury best illustrates this relationship and is presented in Figure 12. For each of these metals, the effect of low temperatures is to reduce effluent concentrations. The best pH values for chromium, copper and mercury removal are 10.2-11.2, 10-11, and 9.8-10.8, respectively.

Systems 3 and 4 - Biological Treatment of Raw Leachate

These treatment sequences were tested in full-scale during the late winter and early spring of 1976. Severe problems were encountered in achieving successful treatment. The primary reason underlying these problems was the inability to develop a healthy activated sludge. Approximately eight weeks were allocated to attempts to adapt a sewage activated sludge culture to the law leachate. After this did not succeed, an investigation revealed that growth of activated sludge was not possible because of ammonia inhibition and phosphorus limitation. The problems were demonstrated by the observations that the average concentrations in the biological units during this time were 940 mg/liter of ammonia-N and less than one of phosphorus. The data thus indicated that in the aeration tanks, the ratio of BOD:N:P was 6620:760:1 which is in marked contrast to the usual recommendations which are in the range of 90-150:5:1.

The phosphorus limitation was investigated in two ways. First, replicate BOD tests were set up with varying additions of phosphate buffer. It was found that the BOD_5 increased with the phosphorus addition up to an upper level, indicating that, within this range, phosphorus was limiting. As a result of this finding, the BOD procedure was modified by the addition of sufficient phosphorus to overcome the limitation.

Second, a bench test was initiated to evaluate the hypothesis that phosphorus limitation was the reason for the poor development of activated sludge (see Table 24). The tests consisted of once daily batch draw-and-fill experiments in which the increase in settleable solids was used to monitor the growth of activated sludge. The control reactor received raw leachate only, whereas the sample reactor received raw leachate plus seven ml of BOD phosphate buffer per liter of raw leachate. Thus, in the sample reactor, the BOD:N:P ratio was about 118:13.5:1. The results are summarized in Table 24. It is seen that over the short-term, there was an apparent positive impact upon the production of activated sludge and the utilization of COD. However, when the tests were continued for several weeks, it became obvious that there was no effect of phosphorus addition on either the development of activated sludge or the removal of organics.

The results of these experiments have been interpreted in the following manner. First, the biochemical oxygen demand tests, and the chemical analyses showed that the leachate was severely phosphorus limited. This problem became more serious when biological treatment

TABLE 24

RESULTS OF BATCH DRAW-AND-FILL ACTIVATED SLUDGE EXPERIMENTS TO DETERMINE THE EXTENT OF PHOSPHORUS LIMITATION. RESULTS SHOW GROWTH OF ACTIVATED SLUDGE AS ML SETTLEABLE SOLIDS PER LITER, AND COD AS MG/LITER.

BOD:N:P / time, days	Control 6620:760:1			Sample 118:13.5:1		
	influent	effluent		influent	effluent	
	COD	COD	SS	COD	COD	SS
0	12813			12813		
1	7704			7704		
2	9339			9339		
3	--			--		
4	8388		26	8388		40
5	12868	10698	20	12868	7597	40
6	10193		15	10193		35
7	11603			11603		
8	NR			--		
9	9912			9912		
10	--			--		
11	5963			5963		
12	9012	7115		9012	7115	
13	13174			13174		
14	8606			8606		
15	8221			8221		
16	NR					
17	--			--		
18	6349			6349		
19	--	5625		--	5469	

followed lime addition because of the precipitation of calcium phosphate salts in that unit. Secondly, the batch draw-and-fill experiments showed that alleviation of the phosphorus limitation alone is not enough to encourage the growth of activated sludge microorganisms. It was concluded it would be necessary to reduce ammonia concentrations to a non-inhibitory level before successful biological treatment could be achieved. Consequently, the ammonia-stripping lagoon was started up prior to evaluating System 1.

Systems 3 and 4 were re-evaluated during the spring and summer of 1977. The change-over from System 1 occurred on May 1, 1977, and data were collected until August 31, 1977. Summaries of the operating results for Systems 3 and 4 are presented in Tables 25 and 26, respectively. System 4 did not operate well enough to recommend its further use.

System 3, biological treatment followed by chemical/physical treatment, achieved very good removal efficiencies, as shown in Table 25: approximately three-quarters or more of nitrogen, all the heavy metals, and suspended solids; and, ninety percent or more of the organic matter. However, as shown in Table 27, the effluent quality does not approach the standards placed on it, in terms of ammonia-N and organic matter. In addition, the standard for lead has not been met with System 3. In sharp contrast, System 1 met all standards during the warmer months of late summer and early Fall, 1976 (see Table 16).

System 5 - Laboratory Studies

Activated Carbon. The preliminary evaluation of this system (System 5) has been carried out for raw leachate treatment. These data

TABLE 25

SYSTEM 3 OPERATION*

	influent			effluent			Percent
	n	$\bar{x}$	cv	n	$\bar{x}$	cv	Removal
Alkalinity, as $CaCO_3$	12	5087	0.20	8	1178	0.83	76.8
Ammonia-N	12	649	0.17	8	153	0.85	76.4
BOD_5	13	12649	0.22	9	763	1.42	94.0
Cadmium	13	0.11	0.52	10	0.02	1.15	81.8
Calcium	13	937	0.17	10	287	0.51	69.4
Chloride	13	4178	0.19	9	1496	0.73	64.2
Chromium	13	0.48	0.33	10	0.08	0.36	83.3
COD	38	21152	0.21	32	2257	1.06	89.3
Copper	13	0.27	0.38	10	.07	0.60	74.1
Dissolved Solids	39	14742	0.20	33	5353	0.42	63.7
Hardness, as $CaCO_3$	13	4463	0.21	10	924	0.43	79.3
Iron	13	348	0.39	10	1.02	1.15	99.7
Kjeldahl-N	12	708	0.16	8	180	0.76	74.6
Lead	13	0.76	0.28	10	0.15	0.75	80.3
Magnesium	13	350	0.22	10	48	0.58	86.3
Mercury	13	0.007	0.51	10	.002	1.08	71.4
Nickel	13	2.0	0.50	10	0.27	0.78	86.5
pH	39	7.6	0.56	32	10.20	4.38	--
Phosphates	12	2.3	0.57	8	0.56	1.26	75.7
Potassium	13	1076	0.13	10	476	0.56	55.8
Sodium	13	1536	0.09	10	719	0.68	53.2
Sulfate	14	658	0.23	9	513	0.87	22.0
Suspended Solids	39	1136	0.47	32	180	1.38	84.2
Zinc	13	40	0.42	10	0.51	0.51	98.7

*Data collected from May 1, 1977 through August 31, 1977. System 3 is biological treatment followed by chemical/physical treatment. ($\bar{x}$ = mean, mg/liter)

TABLE 26

SYSTEM 4 OPERATION*

	influent			effluent			Percent
	n	$\bar{x}$	cv	n	$\bar{x}$	cv	Removal
Alkalinity, as $CaCO_3$	12	5087	0.20	11	2788	0.13	45.2
Ammonia-N	12	649	0.17	11	312	0.35	51.9
BOD_5	13	12649	0.22	12	2150	0.72	83.0
Cadmium	13	0.11	0.52	11	0.08	0.46	27.3
Calcium	13	937	0.17	11	573	0.66	38.8
Chloride	13	4178	0.19	11	3778	0.23	9.6
Chromium	13	0.48	0.33	11	0.37	0.39	22.9
COD	38	21152	0.21	37	4680	0.77	77.9
Copper	13	0.27	0.38	11	0.22	0.22	18.5
Dissolved Solids	39	14742	0.20	39	10081	0.20	31.6
Hardness, as $CaCO_3$	13	4463	0.21	11	2805	0.48	37.1
Iron	13	348	0.39	11	195	0.79	44.0
Lead	13	0.76	0.28	11	0.50	0.52	34.2
Magnesium	13	350	0.22	11	242	0.46	30.9
Mercury	13	0.007	0.51	11	.007	0.47	0
Nickel	13	2.0	0.50	11	1.29	0.37	35.5
pH	39	7.6	0.56	38	8.55	0.78	--
Phosphates	12	2.3	0.57	10	4.6	0.84	--
Potassium	13	1076	0.13	11	996	0.14	7.4
Sodium	13	1536	0.09	11	1412	0.09	8.1
Sulfate	14	658	0.23	12	853	0.44	--
Suspended Solids	39	1136	0.47	36	1322	0.68	--
Zinc	13	40	0.42	11	19	0.65	52.5
Kjeldahl-N	12	708	0.16	16	347	0.38	51.0

*Data collected from May 1, 1977 through August 31, 1977. System 4 is biological treatment only. ($\bar{x}$ = mean; mg/liter)

TABLE 27

SUMMARY OF SYSTEM 3 OPERATION DATA
(5/1/77-8/31/77)

Parameter	Raw Leachate mg/l	Final Effluent mg/l	Percent Removal	Discharge Standard mg/l
Ammonia-N	649	153	76.4	35
BOD_5	12649	763	94.0	100
Cadmium	0.11	0.02	81.8	0.02
Chromium	0.48	0.08	83.3	0.1
COD	21152	2257	89.3	*
Copper	0.27	0.07	74.1	0.2
Iron	348	1.02	99.7	7.0
Lead	0.76	0.15	80.3	0.1
Mercury	0.007	0.002	71.4	0.01
Nickel	2.0	0.27	86.5	*
Zinc	40	0.51	98.7	0.6

*No discharge standard for this parameter.

are presented in Table 28. These tests have been performed with an upflow column of depth 0.3 m and diameter 0.46 m, containing 15.9 kg of granular activated carbon. The influent flow was 38 liter/min, thus providing a hydraulic loading rate of 232 liter/min-sq m. As shown in Table 28, no appreciable treatment can be attributed to the carbon treatment. It should be noted that excessive suspended solids loading and influent variability contributed to this finding. The effect of the solids is to cause blockages and hence reduce process efficiency. The influent was not constant during any of the tests because it was drawn from the actual plant influent. Therefore it is impossible to calculate removal efficiency. However, it is evident from Table 28 that no renovation is occurring in the carbon columns. Hence, it is concluded that carbon adsorption is not appropriate when applied to raw leachate, although, as mentioned below, it may be suitable for final effluent polishing.

System 5 has also been assessed as an advanced waste treatment technique. This has been done using the effluent from the pilot facility shown in Figure 5. A summary of the data is given in Tables 29 and 30. The data in Table 28 have been developed using small carbon columns and a flow rate of 10 ml per min. In each case, a 25 ml sample was collected at each sampling interval. Although batch data are more amenable to such mathematical treatment, a preliminary analysis has been conducted to describe the results of Table 29 in terms of a Langmuir adsorption isotherm. The Langmuir isotherm results from assuming reversible adsorption and an adsorbed monolayer:

TABLE 28

SUMMARY OF RESULTS OF CARBON ADSORPTION TREATMENT OF RAW LEACHATE*

Parameter	Experiment Number								
	1			2			3		
Gallons Treated	0	50	250	0	50	320	0	100	370
pH	8.31	7.90	8.11	---	---	---	---	---	---
Suspended Solids	2880	2280	3060	980	640	20	820	540	430
Dissolved Solids	10570	10490	9130	10600	10450	11150	11100	11000	10970
Total Volatile Solids	4240	4040	---	5120	3950	4230	5220	4930	5000
Chemical Oxygen Demand	4450	3840	5760	8645	7217	9864	9530	9440	9841
	Experiment Number								
	4			5			6		
Gallons Treated	0	60		0	20	260	0	60	300
pH	---	---		---	---	---	---	---	---
Suspended Solids	520	420		770	500	740	1120	1020	1040
Dissolved Solids	10060	10690		10460	10130	11040	10040	9400	10230
Total Volatile Solids	4530	5330		5010	4360	5020	6440	6170	6180
Chemical Oxygen Demand	9840	10784		10013	9170	10040	8833	9723	9960

*All units are mg/liter except pH and gallons treated.

TABLE 29

TREATMENT OF FINAL EFFLUENT WITH BENCH-SCALE ACTIVATED CARBON COLUMNS*

Sample	Carbon Volume, cm^3	Weight of Carbon, g	Flow ml	COD	Cu	Fe	Zn	Cr	Ni	Ca	Mg
			0	2088	0.015	5.10	0.99	0.30	1.46	174	142
1	270	100	100-125	354	0	2.58	.30	.15	.08	0.74	0.89
2	270	100	225-250	657	0	3.98	.58	.20	.15	1.72	2.00
3	270	100	350-375	830	.015	4.80	.53	.16	.26	2.29	2.59
4	270	100	475-500	748	.30	5.50	.56	.15	.22	2.05	3.47
5	270	100	600-625	827	.68	1.60	.61	.19	.26	5.86	8.6
6	270	100	725-750	869	.12	2.30	.55	.18	.25	>10	>10
1	14.5	5	250-275	1858							
2	14.5	5	500-525	1818							
3	26.2	10	250-275	1660							
4	26.2	10	500-525	1760							
5	40.7	15	250-275	1620							
6	40.7	15	500-525	1660							
7	52.5	20	250-275	1500							
8	52.5	20	500-525	1620							
9	77.8	30	250-275	1386							
10	77.8	30	500-525	1500							

*All units are mg per liter, unless otherwise stated.

TABLE 30

PILOT-SCALE CARBON TREATMENT OF FINAL EFFLUENT

Volume of Carbon Treated Final Effluent, liter	Sorbate Concentration Following Carbon Treatment, mg COD/liter
0	1900
95	25
189	35
289	395
379	1312
416	1539
454	1695
492	1773
530	1828
568	1859
606	1875
662	1852
719	1891
795	1883
871	1848

$$\frac{x}{m} = \frac{b(x/m)^{o}C_e}{1+b\ C_e}$$

$(\frac{x}{m})^{o}$ = value of $\frac{x}{m}$ when monolayer has been completed

x = moles of sorbate adsorbed

m = weight of carbon

C_e = equilibrium molar concentration of sorbate

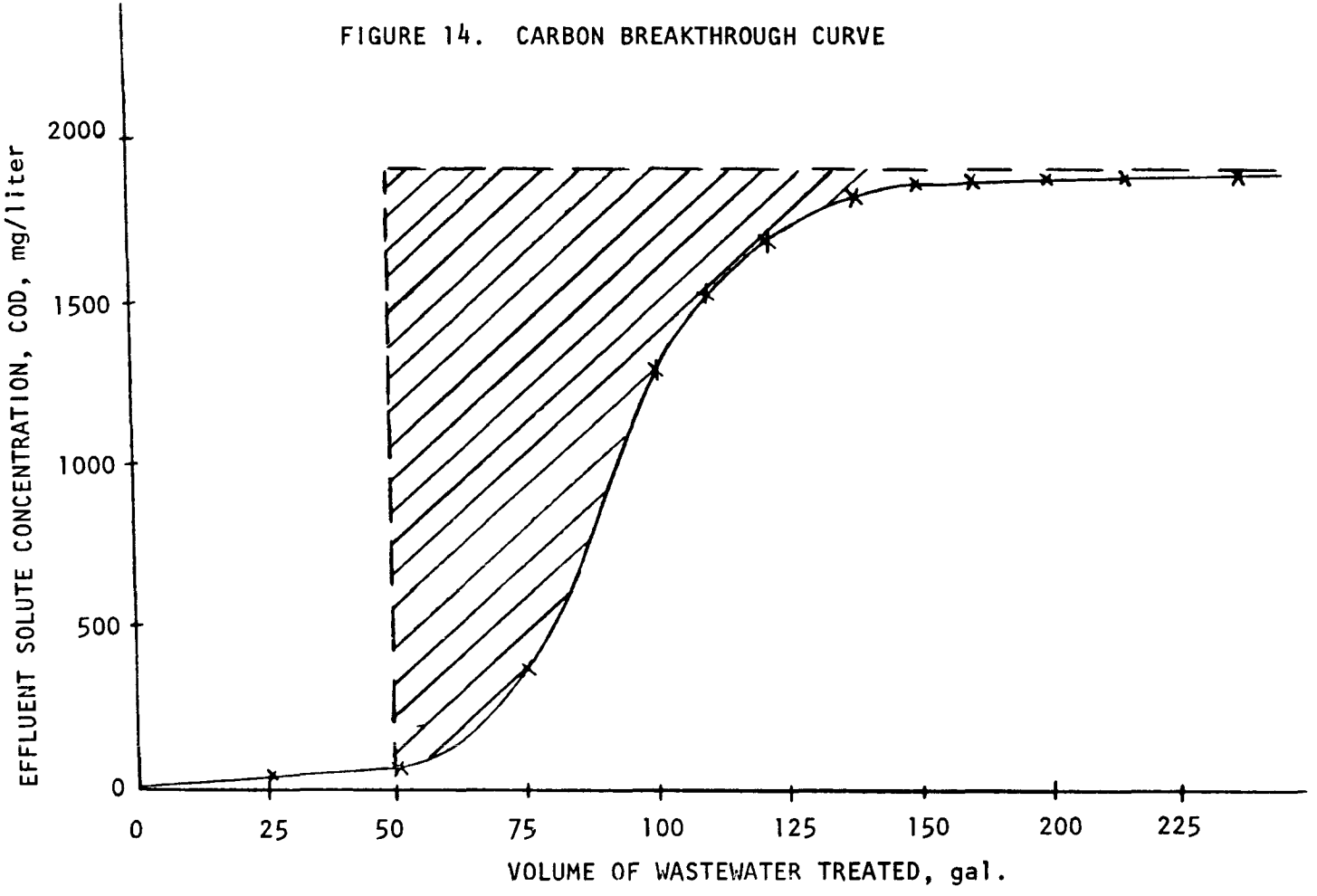
b = adsorption coefficient

The analysis indicated that $(\frac{x}{m})^{o}$ is 9.709 mg per mg, and that b is 5.79 liters per mg.

The data shown in Table 30 have been collected from a larger column charged with 120 lb of carbon at a flow rate of 4 gal per min. These results have been plotted as a carbon breakthrough curve in Figure 14. The cross-hatched area of Figure 14 can be used to determine the fractional capacity, f, of the adsorption zone. The value of f is estimated at 0.31. From this, it is estimated that the depth of the adsorption zone is 8.99 ft. These values can be used as the basis of the design of a full-scale unit.

Additional Laboratory-Scale Studies. A number of smaller scale studies were undertaken during the third year. These were designed to evaluate a number of possible technologies which might be applied to more efficiently treat the leachate. In addition to the activated carbon treatment discussed above, the following were also assessed: alkaline chlorination, effluent filtration, and effluent breakpoint chlorination. In addition, the use of additives in the lime treatment process was investigated as a means of increasing the compaction of the lime sludge. Each of these topics is discussed in subsequent paragraphs.

FIGURE 14. CARBON BREAKTHROUGH CURVE



Alkaline Chlorination. During a part of the third year, difficulties were encountered in the efficiency of the lime treatment process. It was believed that the problems were possibly due to excessive hydraulic loadings. In this light, the use of compacting agents as discussed below was studied, and minor design changes were instituted. One other explanation for the difficulties encountered in the removal of heavy metal is that the metals may have formed complexes with organic matter or with cyanides. In this chemical form, the metals resist removal by lime treatment. It might have been possible to improve the efficiency of lime precipitation of heavy metals by adding chlorine during this step. Alkaline chlorination has the effect of disrupting heavy metal complexes, particularly those involving cyanides. In this manner, the metals are freed from the complexing agents, after which they precipitate under the alkaline pH conditions.

Preliminary evaluations of alkaline chlorination were conducted. The results were negative as shown in Table 31. The samples of raw leachate were supplemented with the chemicals indicated in Table 31, mixed for 5 min with a magnetic stirrer, and then allowed to settle for 30 min. The volume of sludge produced was recorded, and analyses for heavy metals were performed on the clarified supernatant. The addition of NaOCl had no significant effect on sludge volume, nor on the concentration of copper and cadmium, may have been associated with reduced concentrations of zinc, nickel and lead, and was definitely associated with reduced concentrations of iron and chromium. The results were deemed negative, because the addition of small amounts of chlorine

TABLE 31

RESULTS OF ALKALINE CHLORINATION STUDIES

Sample #	Lime Addition*	NaOCl Addition*	pH	Sludge Volume*	Fe^+	Cu^+	Cr^+	Pb^+	Ni^+	Cd^+	Zn^+
1	0	0	--	--	7.5	0.25	0.175	0.25	1.095	0.076	10.6
2	19	0	11.3	100	2.28	0.213	0.153	0.3	0.831	0.071	0.09
3	19	5	11.2	120	0.3	0.275	0.141	0.25	0.769	0.061	2.08
4	25	10	11.1	150	0.263	0.216	0.134	0.24	0.691	0.073	1.27
5	30	15	11.3	120	0.275	0.293	0.138	0.24	0.668	0.056	1.95
6	19	10	10.5	>90	0.313	0.21	0.104	0.15	0.69	0.04	0.09
7	19	15	10.0	>90	0.425	0.209	0.099	0.18	0.668	0.059	0.05

*milliliters

+milligrams per liter

did not significantly affect the abillty of the process to meet effluent standards. Very high concentrations of NaOCl may be helpful in attaining the chromium standard (see Table 1).

Compaction of Lime Sludge. The second possible cause of poor lime treatment performance to be investigated was that of inferior settleability of the sludge. A number of jar tests have been conducted in an effort to evaluate the effect of additives on the efficiency of heavy metal precipitation and on the compaction of the resultant lime sludge. These tests have been performed to evaluate the performance of lime, a commercial aluminate preparation, and sodium hydroxide. The results are presented in Tables 32 and 33. The first of these tables shows the experimental protocol which was, in brief, to treat each flask with lime to give a final pH of 11.7. Aluminate was added at the rate of 300 mg/l as recommended by the manufacturer's representative. Sodium hydroxide was added at the rate of 125 ppm in accordance with the observation of the leachate treatment plant operator who noted a decided improvement in process efficiency at this dosage of caustic. It should be noted that the use of aluminate did not result in an especially clear supernatant and that it did result in a relatively large volume of sludge. On the other hand, the addition of NaOH provided a very clear supernatant, at least equal to that obtained with lime alone, and a relatively small sludge volume. The results, in terms of the removal of heavy metals, are presented in Table 33. None of the additives were an improvement over lime alone, in terms of meeting the standards (see Table 1). In absolute terms, neither additive, alone or in combination, provided improved treatment across the board. In fact, in several cases,

TABLE 32

EXPERIMENTAL PROTOCOL AND PRELIMINARY RESULTS
IN EVALUATION OF LIME TREATMENT ADDITIVES*

Flask Number	Experimental Protocol Additives			Preliminary Results	
	Lime, ml	Aluminate, ml	NaOH, ml	Supernatant Clarity‡	Sludge Volume, ml
1	0	0	0	--	0
2	18	0	0	++	110
3	18	10	0	-	120
4	12	0	0.1	++	80
5	15	10	0.1	+	120

*The experimental flasks each contained raw leachate plus the additives as indicated.

‡The clarity of the supernatant was evaluated qualitatively as follows: --, very turbid; -, turbid; +, clear; ++, very clear. Also the volume of sludge (in ml) produced was noted.

TABLE 33

RESULTS OF ADDITIVE EVALUATION*

Paramater Analyzed	Experimental Protocol				
	Raw Leachate Control	Lime Only	Lime + Aluminate	Lime + NaOH	Lime + NaOH + Aluminate
Iron	52.0	0.45	1.21	0.77	1.71
Copper	0.24	0.14	0.16	0.14	0.24
Cadmium	0.04	0.06	0.04	0.07	0.03
Chromium	0.15	0.09	0.07	0.08	0.09
Lead	0.19	0.16	0.19	0.16	0.15
Zinc	6.40	0.03	0.12	0.10	0.08
Nickel	0.71	0.56	0.52	0.58	0.53
Mercury	0.002	0.002	0.002	0.001	0.002

*All units are mg per liter in the supernatant following indicated protocol.

the removal decreased due to the additives. The conclusion is that neither NaOH nor aluminate, when added to lime and leachate at a final pH of 11.7, results in improved removal of heavy metals. However, the addition of 125 ppm NaOH provides a significant reduction in sludge volume, a fact which would improve the efficiency of the lime clarifier operation. Sludge handling and disposal will also be rendered more efficient. Therefore, the addition of NaOH was recommended.

An added benefit is a higher pH in the ammonia lagoon which increases the ammonia stripping capacity of the lagoon. This is illustrated by the observation that the supernatant pH where NaOH was added had fallen to only 11.5, whereas, in the flasks not receiving NaOH, the supernatant pH had dropped to less than 11. This is a demonstration of the strong buffering properties attributable to the addition of NaOH.

An additional recommendation was made which improved the efficiency of the lime clarifier. This was that the depth of the sludge blanket be kept minimal. This prevented solids carryover which occurred on occasion in the past. Sludge blanket depth may be minimized by semi-continuous withdrawal of settled sludge. An automatic timing mechanism was installed to ensure sludge removal semi-continuously on a 24 hr basis.

Effluent Filtration. The physical process of filtration has several potential applications in leachate treatment. Filtration of activated sludge effluent would be needed before activated carbon or ion exchange treatment, if these operations are necessary. This is

required to reduce the solids loadings on these units, and hence, to minimize problems due to clogging.

A second application of filtration would be to use it between the ammonia stripping lagoon and the activated sludge process. The purpose of doing this is to remove residual heavy metal precipitates as well as calcium carbonate which may form during lagooning or which may escape the lime clarifier unit. The benefits which would accrue include lower heavy metals loadings and solids loadings on the biological treatment units.

The first step in evaluating the efficacy of filtration is a number of small scale units. The purpose of these would be to provide a preliminary evaluation of the removal of heavy metals and particulates from the ammonia lagoon effluent, and to determine the compatability of a filtered effluent from the activated sludge process with granular activated carbon.

The principal design parameters which must be considered are filter configuration; method of flow control; terminal headloss (ft of water); filtration rate (gal/min-sq ft); filter media, sizes and depths; and, backwashing requirements. The basic filter configurations are upflow filtration through a relatively deep, coarse filter medium; using a filtered water collection device within the filter medium and bringing water in from both the bottom and the top; dual or mixed media with conventional downflow; and single medium downflow filtration.

Preliminary testing of filtration has been conducted using filter paper (Whatman No. 40). The results are presented in Table 34, and they show that additional removals of most of the heavy metals are

TABLE 34

PRELIMINARY FILTRATION RESULTS*

Metal	Raw Leachate		Ammonia Lagoon Effluent		Final Effluent	
	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered	Filtered
Iron	256.	194.	32.	18.	10.	5.6
Copper	0.48	0.40	0.13	0.20	0.26	0.25
Cadmium	0.13	0.08	0.06	0.08	0.05	0.04
Chromium	0.36	0.36	0.18	0.15	0.12	0.09
Lead	0.47	0.35	0.23	0.19	0.12	0.10
Nickel	1.46	1.29	1.22	1.08	1.06	0.88
Mercury	0.003	0.004	0.003	0.0025	0.004	0.0025
Zinc	23.4	17.2	4.63	3.36	1.28	1.70

*All units are mg per liter.

achieved by filtration at any intermediate step of the treatment sequences.

Effluent Breakpoint Chlorination. Although nitrification is an extremely efficient process for the removal of ammonia-N, it is a biological treatment method. As a result, nitrification can be temperamental and prone to upset. As noted earlier, the nitrifying organisms are very sensitive to temperature. Also, the ammonia stripping process is less effective during the winter. Consequently, the effluent in the colder months is very high in ammonia-N. The removal of residual ammonia in the final effluent may be accomplished by breakpoint chlorination. This procedure oxidizes the NH_4^+-N to gaseous end-products including N_2. Breakpoint chlorination has been practiced at the GROWS treatment facility and is a proven technology for meeting the effluent criterion for ammonia (see Table 1).

The chlorine demand, and therefore chlorination operating costs, are expected to decrease as the degree of organics removal increases, and this savings can affect some portion of the carbon costs. An economic tradeoff can be made here vis-a-vis the costs of activated carbon treatment of the final effluent.

Leachate Treatment Plant Startup. The results of this study have indicated clearly that Systems 1 and 2 are very effective in the treatment of leachate. The best results were obtained with a process train consisting of raw leachate equalization, lime precipitation and clarification, ammonia stripping lagoon, activated sludge providing for carbonaceous and nitrogenous oxidation, sedimentation, and

effluent chlorination. As noted in Tables 14, 15, 20 and 21, the removal efficiencies observed with Systems 1 and 2 are extremely high, and provide the best opportunity for meeting the effluent criteria.

Nevertheless, in spite of the success of Systems 1 and 2, some problems were encountered during startups. Some of these have been discussed elsewhere. These include the nutrient deficiency due to phosphate precipitation in the lime treatment unit; and substrate inhibition resulting from excessive ammonia-N concentrations.

Excessive loadings have been received by the plant in terms of ammonia, metals, and organics. For the past year, raw leachate flows have been in the 50,000 to 80,000 gpd range, which when coupled with the extremely high influent concentrations yields process loadings in excess of those which had been experienced during the initial operational phase of the plant. The combination of excessive concentrations and loadings is the primary factor inhibiting rapid successful process startup.

There are a number of secondary reasons for the poor startup performance. The first of these is that the third year operational effort was initiated in mid to late winter. As a result, the development of a healthy activated sludge culture was inhibited due to low temperatures, as well as to the presence of high concentrations of metals and organics. These high concentrations resulted not only because of the leachate strength, but also because of operational problems. Examples of these problems include instances where raw leachate has by-passed the chemical/physical section, and insufficient air has been provided to the bio units.

Other secondary factors underlying the startup problems include those relating to plant operation and the behavior of the sedimentation tanks. Frequent problems were encountered which affected adversely the performance of both the chemical/physical and the secondary clarifiers. Eddy currents were occasionally noted in the secondary clarifier and these resulted in carry-over of biological solids. The high rate of internal recycle in the activated sludge undoubtedly contributed to this condition. In the case of the chemical/physical sedimentation tank, some reduction in clarification efficiency was observed as a result of excessive sludge volumes. Lime sludge production had increased as the acidity and the rate of generation of leachate increased.

Many of the problems mentioned above are essentially different aspects of plant reliability. Each section of the plant needs a high level of reliability. This is especially true of the lime treatment section. It is recommended that, in the future, as these plants become more sophisticated, greater consideration be given to automatic process control techniques. As an example consider the lime slurry system. At the present time, if this system malfunctions such that the lime feed stops, then raw leachate passes to the ammonia lagoon and thence to the bio units where pronounced inhibitory effects are observed. These problems could be avoided by an automatic valving system which would recycle the lime clarifier effluent to the equalization pond whenever the effluent pH dropped below some set point such as pH 10 or pH 10.5. Process reliability is important at plants such as this because they normally operate at very close to inhibitory concentrations of

materials such as ammonia, metals, and organics. Thus, small perturbations can result in process upset followed by an extensive period during which the discharge standards are contravened.

Most of the startup problems, however, are related directly to the increased leachate flow and strength. Higher flows have not diluted the leachate, but have been associated with increased concentrations of pollutants. This, in turn, is partially a result of the introduction of industrial liquid wastes.

An indication of the extremely high loadings is provided in Table 35. The data show process loadings applied to System 2 (lime treatment/ ammonia lagoon) and to System 1 (activated sludge). These data are for the period April 1, 1978 through June 30, 1978. This represents the startup period for the most recent evaluation of Systems 1 and 2. For comparison, the original design loadings, derived from Table 9, are included. It can be seen that the more recent loadings are very high (except for the metals and suspended solids). When this is coupled with the high concentrations of inhibitory substances, the basis for the poor startup performance becomes clear.

The role of high concentrations relates to a previous discussion. As noted in Figure 9, the phenomenon of substrate inhibition must be considered. Even substrates such as ammonia-N or BOD which are vital requirements at low concentrations become inhibitory at higher concentrations. The significance for leachate treatment is that the system operates at influent concentrations high enough to be inhibitory. Slight perturbations result in process instability and/or poor startup.

TABLE 35

PROCESS LOADING RATES AND CONCENTRATIONS OBSERVED
DURING THE PERIOD APRIL 1, 1978 THROUGH JUNE 30, 1978.

	Concentration of Raw Leachate mg/liter		Process Loading Rates lb per day			
			Raw Leachate		Applied to Lime Treatment Section	Applied to Activated Sludge System
	Observed	Design	Observed	Design		
Alkalinity, as $CaCO_3$	4915	1100	2710	1320	1730	210
Ammonia-N	990	--	546	--	350	40
BOD	13695	1500	7550	1800	4830	560
Cadmium	0.09	--	0.05	--	0.03	0.003
Calcium	895	--	493	--	315	40
Chloride	2965	800	1634	960	1045	155
Chromium	0.24	--	0.13	--	0.08	0.007
COD	19864	--	10950	--	7000	880
Copper	0.24	1	0.13	1.20	0.08	0.009
Dissolved Solids	13225	--	7290	--	4660	605
Hardness, as $CaCO_3$	3750	800	2065	960	1320	135
Iron	165	600	90	720	60	0.42
Kjeldahl-N	860	--	475	--	305	45
Lead	0.37	--	0.20	--	0.13	0.02
Magnesium	275	--	150	--	95	7.8
Mercury	0.253	--	0.14	--	0.09	0.01
Nickel	1.45	--	0.80	--	0.51	0.07
Organic-N	≈0	100				
Phosphates	1.98	--	1.09	--	0.80	0.02
Potassium	1000	--	550	--	350	55
Sodium	1455	--	800	--	515	80
Sulfate	515	300	285	360	180	55
Suspended Solids	1510	1500	830	1800	530	20
Total Solids	14735	3000				
Zinc	11.44	10	6.31	12	4.03	0.06

Thus, the principal source of process startup problems are the combination of excessive loadings and concentrations near the upset threshhold.

The activated sludge system has been operated most successfully at a mixed liquor volatile suspended solids (MLVSS) concentration of 6000-12,000 mg per liter, depending upon the influent BOD concentration. During periods of satisfactory operation the food to microorganism ratio has been in the 0.12 to 0.32 day^{-1} range, as calculated by

$$L = \frac{Q\ C_o}{V\ X_a}$$

where

L = F:M, lb BOD per lb MLVSS-day

Q = Process hydraulic loading, gpd

C_o = Process influent BOD, mg per liter

V = Aeration tank volume, gal

X_a = MLVSS, mg per liter

The operation of the activated sludge units in series (see Figure 7) was accomplished by maintaining 12,000 mg MLVSS per liter and 6000 mg MLVSS per liter, in the first and second stages, respectively.

The following recommendations are made in an effort to reduce future startup problems:

1. Raw leachate equalization is a valuable aid in dampening peak concentrations of materials which are inhibitory to subsequent biological processes; and, in controlling chemical dosages in the lime precipitation units.

2. Ammonia removal by stripping via aeration reduces concentrations to a level below the point of inhibition.
3. Nutrient supplementation may be necessary. This is especially true for the case of a high carbon waste with biological treatment units preceded by lime precipitation.
4. Excessive loadings may necessitate treatment of only a portion of the total waste flow during startup. At these times, the balance of the flow should be recycled to the landfill.
5. With a waste containing very high levels of ammonia-N, startup should occur during warm weather months. Otherwise, nitrification will be inhibited, and the resulting ammonia concentrations will not permit biological activity.

VI. CONCLUSIONS

1. The GROWS landfill leachate is characterized by high organic strength and by large day-to-day variations. Much of the variability can be dampened by raw leachate equalization.
2. Considerable experience has been gained in the operation of activated sludge units on raw leachate and on leachate which has received chemical/physical treatment. It has been concluded that this raw leachate must be pre-treated in order to render it amenable to activated sludge processing. The results indicate that the raw leachate inhibits the growth of the activated sludge microorganisms. System 3 (biological treatment of raw leachate) has yielded an average effluent BOD_5 of 763 mg per liter, a concentration which is clearly not acceptable.
3. The operation of the chemical/physical units (System 2) has continued for some time to gain experience under a wide variety of operating conditions and sufficient data have been collected to provide an evaluation of this method of treating raw leachate. Lime treatment alone (System 2a) provides removal efficiencies of approximately 50 percent of the organic matter, 75 percent of suspended solids, one-half of mercury and cadmium, and at least two-thirds of the other heavy metals.
4. The complete chemical/physical treatment sequence consisting of lime precipitation/sedimentation/ammonia stripping (System 2b) achieved the following removals of efficiency: 48 to 69 percent of the organic matter, ammonia-N and total kjeldahl-N; 70 percent of the suspended solids, and 50 percent or better of the heavy

metals except copper, for which the removal efficiency was 37.8 percent. In the final year of the project, System 2b was augmented with an initial raw leachate equalization step.

5. Temperature and pH have an effect on the concentration of heavy metals in the lime treatment effluent. However, the response is not identical for all heavy metals. If the differences were more thoroughly characterized, it might be possible to use them in an operational control procedure.

6. Activated sludge treatment of the effluent from the chemical/physical units has been extremely successful (System 1). It is apparent that the reduction in ammonia-N afforded by the ammonia stripping lagoon provides conditions suitable for the growth of activated sludge microorganisms. The ammonia lagoon, in conjunction with the balance of System 2, provides ammonia removals of approximately 50 percent resulting in activated sludge influent concentrations of 149-423 mg NH_4^+-N/liter (95 percent confidence interval). During the final year of the project, these concentrations increased somewhat due to the maintenance of a lower pH in the lagoon. Under this condition, the activated sludge quickly adapted to the leachate with the result that effluent BOD_5 concentrations were consistently low except during cold weather. Nitrifying organisms developed and produced a nitrified effluent with very low concentrations of ammonia. Cold winter weather inhibited the biochemical oxidation of organics and ammonia.

7. Activated sludge treatment has been effective in both the series (Figure 7) and parallel (Figure 4) modes of operation. That is, the

plant configuration has had the aeration tanks in either parallel or series, with approximately equal results.

8. Overall, the treatment sequence consisting of chemical/physical (lime precipitation, sedimentation, ammonia stripping, and neutralization) followed by activated sludge (System 1) has produced an excellent final effluent with the following characteristics:

    a. Organic matter has been reduced to 153 mg BOD_5/liter. This is a 99 percent removal. The corresponding COD removal efficiency is 95 percent. The effluent BOD to COD ratio is 0.16.

    b. The effluent ammonia concentration is 75 mg/liter, representing 90 percent removal.

    c. Heavy metals are found in the effluent at the following levels (percent removals are shown in parenthesis): 0.017 mg cadmium/liter (78.2 percent); 0.07 mg chromium/liter (73.1 percent); 0.11 mg copper/liter (72.5 percent); 2.7 mg iron/liter (99.2 percent); 0.12 mg lead/liter (83.8 percent); 0.004 mg mercury/liter (27.4 percent); 0.75 mg nickel/liter (57.4 percent); 0.53 mg zinc/liter (97.3 percent).

9. The kinetics of nitrification have been followed during System 1b operation. The rate of nitrification, expressed as the specific oxidation rate, follows the van't-Hoff Arrhenius relationship. The data indicate that the activation energy is approximately

12350 cal per mole, and that the Arrhenius frequency factor is 2.18×10^{9} day^{-1}.

10. The data show that substrate inhibition due to ammonium ion concentration occurs in System 1b nitrification. This relationship has been expressed as a Haldane inhibition model in which the maximum specific oxidation rate is 3.5 g N oxidized per g biomass day, K_s is 4 mg per liter, and K_1 is 36 mg per liter.
11. Pilot scale operation of System 5 shows that activated carbon treatment of System 1 effluent is an effective way of removing much of the remaining organic matter. In addition, considerable removals of heavy metals occur in the carbon columns.
12. A bench-scale evaluation of alkaline chlorination as a means of improving heavy metals removal indicated that the technique is not appropriate.
13. Studies of lime sludge compaction and supernatant clarity reveal that the addition of sodium hydroxide (125 mg per liter) improves both factors. The addition of a commercial aluminate preparation (300 mg per liter) had an adverse impact on compaction and clarity.
14. Preliminary testing of filtration shows that additional removals of most heavy metals can be achieved.
15. Full-scale studies of breakpoint chlorination have shown that this method can be used to attain the ammonia effluent criterion.

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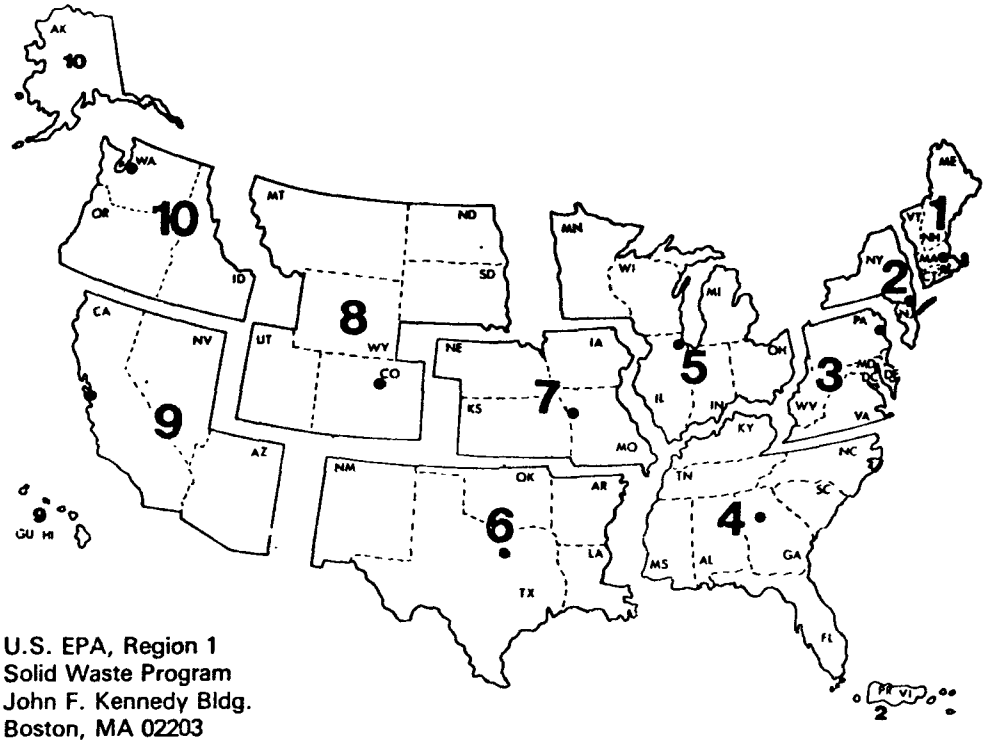

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