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TWO-STAGE TREATMENT OF A LANDFILL LEACHATE:
AEROBIC BIOSTABILIZATION WITH LIME-MAGNESIUM POLISHING

by

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ABSTRACT

Leachate is produced when water percolates through landfills, extracting suspendable and soluble organic and inorganic constituents from the refuse beds. This may lead to serious surface and/or ground water pollution. Recently, the control and treatment of leachate has been the subject of a great deal of research, particularly at the University of British Columbia.

This study was initiated as a follow-up to several of those previous studies. Investigated were the treatability of a medium strength ($BOD_5 = 8090$ mg/L) leachate by aerobic biostabilization, at a nutrient loading of $BOD_5:N:P$ of 100:3.2:1.1, and then polishing of the first stage effluents by lime-magnesium coagulation. In the biological treatment stage, the ranges of ambient air temperature and sludge age studied were 5° to $25^{\circ}C$ and 5 to 20 days, respectively.

In the biostabilization phase, a $BOD_5:N:P$ loading of 100:3.2:1.1 was found to be "adequate" for treatment, while the standard nutrient loading of 100:5:1 was found to be "excessive". This was evident by the much higher nitrite-nitrate concentration in the effluent of the $BOD_5:N:P = 100:5:1$ reactor. Organic removal by the first stage units was excellent. BOD_5 and COD removals of at least 99.4 and 96.4 percent, respectively, were achieved under all conditions investigated, except for the two units close to washout conditions (the 5-day sludge age units at 10° and $5^{\circ}C$). Temperature and sludge age also had minimal effects on the removal of metals, except

under the two conditions mentioned above; removals were greater than 90 percent, for most of the metals monitored. The reactors only reduced magnesium concentrations by 32.5 to 52.7 percent, mainly because the mixed liquor pH's (about 8.5) were not high enough for magnesium precipitation as magnesium hydroxide.

For the lime-magnesium polishing step, samples were dosed with lime to pH levels of 10.0, 10.7, and 11.4. Magnesium doses of 0, 10, 20, 35 and 50 mg/L were then added to the samples at each pH level. In general, removals of impurities were not enhanced significantly by these magnesium additions. This was due, in part, to the initial low concentrations of contaminants; in addition, there already existed greater than 20 mg/L of magnesium in the samples.

Aerobic biostabilization, at a sludge age greater than 15 days, at $\text{BOD}_5:\text{N}:\text{P} = 100:3.2:1.1$, and liquid temperatures of at least 3°C , followed by lime precipitation (to pH greater than or equal to 10.0), is capable of reducing most contaminants of a medium strength leachate ($\text{BOD}_5 = 8090 \text{ mg/L}$) to levels below local (Province of British Columbia) pollution control objectives.

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CHAPTER 1

INTRODUCTION

Sanitary landfills and their modifications have long been accepted as a "satisfactory" method of solid waste disposal. Although other techniques such as composting and resource recovery are more environmentally desirable, the simplicity and low cost of landfills have led to their popularity. Also, it is the only "final" solid waste disposal method currently in use; unlike composting, incineration, pyrolysis, and resource recovery, landfilling does not yield a residue which requires further disposal.

Most problems associated with municipal solid waste landfills have been overcome. Continuous compaction and daily cover have minimized vector problems, lessened airborne litter, and reduced odour problems. However, the generation of leachate is a problem of growing concern.

Leachate is produced when water percolates through landfills, extracting suspendable and soluble organic and inorganic constituents from the refuse beds. Although the leachate usually undergo some degree of self purification bacteriologically and chemically, the large amounts of extracted material can lead to a grossly polluted liquid. The quantity and quality of leachate produced is dependent on a number of physical variables - some of these are: the amount, composition, particle size, and moisture content of the refuse, the degree of compaction of the refuse, the depth of the refuse beds, the

hydrogeology of the site, and the climate of the region.

Table 1 (6) illustrates the wide range of composition of typical leachates.

Since leachate may be a serious source of surface and/or ground water pollution, environmental agencies are not allowing leachate generation and movement to go unchecked. There are three alternatives available for the elimination or minimization of the leachate problem; these are the reduction of leachate production, leachate recirculation, and the collection and treatment of leachate before discharge.

Eliminating or minimizing leachate production involves good site selection and design, with proper construction and operation. Measures employed may include milling and baling of refuse, surface water control, ground water control, and/or chemical immobilization. However, with some of the above measures, long term maintenance may be required and the potential for leachate production remains (mainly because of the reduced rate of waste stabilization due to the absence of water). Also, in areas of high precipitation, these methods may be ineffective or the costs of employing such methods may be prohibitively high.

A promising new technique for accelerating the rate of waste stabilization is leachate recirculation. The volume of leachate is reduced during the stabilization period and after this short period, leachate strength is greatly reduced. However, after waste stabilization, the recirculated leachate

TABLE 1 (6)
COMPOSITION OF TYPICAL LEACHATES

Parameter	Range of Values or Concentrations* (Landfills and Test Lysimeters)
BOD ₅	9 - 55 000
COD	0 - 90 000
Total Carbon	715 - 22 350
Total Organic Carbon	715 - 22 350
Total Solids	1 000 - 45 000
Total Volatile Solids	1 000 - 23 157
Total Dissolved Solids	0 - 42 300
Acidity	0 - 9 560
Alkalinity	0 - 20 900
Aluminum	0 - 122
Arsenic	0 - 11.6
Barium	0 - 5.4
Beryllium	0 - 0.3
Calcium	5 - 4 000
Cadmium	0 - 0.19
Chloride	34 - 2 800
Chromium	0 - 33.4
Copper	0 - 10
Iron	0.2 - 5 500
Lead	0 - 5.0
Magnesium	165 - 15 600
Manganese	0.06 - 1 400
Mercury	0 - 0.064
Molybdenum	0 - 0.52
Nitrogen - total	0 - 2 406
- NH ₃	0 - 1 106
Nickel	0.01 - 0.80
Phosphorus - total	0 - 154
Potassium	2.8 - 3 770
Sodium	0 - 7 700
Sulphates	1 - 1 826
Sulphides	0 - 0.13
Titanium	0 - 5.0
Vanadium	0 - 1.4
Zinc	0 - 1 000
pH	3.7 - 8.5
Tannin-like compounds	78 - 1 278
Colour (chloroplatinate)	0 - 12 000
Odour	not detectable to terrible

* All values except those for pH, colour and odour are in mg/L.

should be collected for ultimate treatment and disposal.

However, this method has obvious shortcomings under continuing fill operation and/or high precipitation areas.

The last alternative is the collection and treatment of the leachate generated. It is to this end that this study and many other research projects at the University of British Columbia have been carried out. This investigation is a follow-up to several of those previous studies.

The purpose of this study was to evaluate the treatability of a leachate by aerobic biostabilization at a nutrient loading of $BOD_5:N:P$ of 100:3.2.:1.1 and then polishing the effluents from the aerobic treatment process by physical-chemical treatment (through lime-magnesium coagulation). In the biological treatment stage, the ranges of ambient air temperature and sludge age (or mean cell residence time) investigated were 5° to $25^{\circ}C$ and 5 to 20 days respectively.

Temoin (31), in a previous study, found 100:3.19:1.11 to be the optimum nutrient loading. Several investigators (19, 20, 27) have found lime-magnesium coagulation to be an effective method in the treatment of wastewaters.

CHAPTER 2

BACKGROUND

2 - 1 Aerobic Biostabilization

2 - 1.1 Description of the Activated Sludge Process

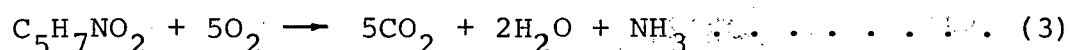
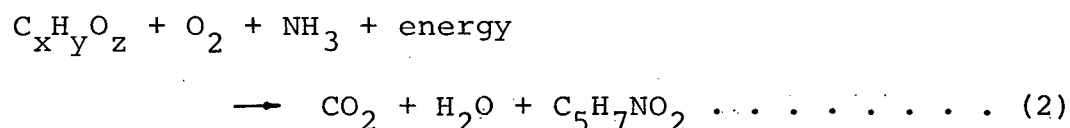
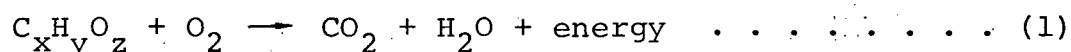
Activated sludge is an aerobic suspended-growth treatment process. The biological flocs, kept in suspension by aeration and perhaps mechanical mixing, are primarily responsible for the removal of organics in the wastewater.

Under normal operating conditions, bacteria are the dominant primary feeders in the activated sludge process. The species of the bacteria is dependent on the nature of the organic waste and the environmental conditions in the aeration tanks. The primary bacteria are maintained in the declining or endogenous growth phases, causing them to die, lyse, and thereby release their cell contents to solution. In this process, raw organic matter is converted to energy or synthesized and resynthesized by various groups of bacteria.

Also common in activated sludge are protozoans, the secondary feeders. The bacteria synthesize the organic matter, and the protozoans consume the bacteria. Other species of organisms present in the "zooglear mass" may include yeasts, molds, worms, algae, rotifiers, nematodes, and insect larvae.

In addition to organic removal, some degree of metal removal is obtained. The mechanism by which metal removal is achieved in activated sludge is a combination of flocculation and settling (5).

The average composition of the cell tissue in the zoogeal mass is taken as $C_5H_7NO_2$. An elemental analysis of bacterial cells, that includes the phosphorus requirement, is, however, $C_{60}H_{87}O_{23}N_{12}P$ (29). Oxidation, synthesis, and endogenous respiration are the metabolic reactions that occur. The chemical stoichiometric equations for these respective reactions are as follows:



In the presence of enzymes, about one-third of the organic matter removed is oxidized to CO_2 and H_2O in order to provide energy for the synthesis of the remaining two-thirds of the organic matter that is converted to cell material.

For efficient biological wastewater treatment, it is generally accepted that a nutrient loading level ($BOD_5:N:P$) of approximately 100:5:1 must be maintained (11). If insufficient nutrients are available, filamentous bacteria can predominate, resulting in sludge bulking and incomplete conversion of organics to end products (8, 29). Normally,

this is not a problem when treating domestic sewage since nutrients are present in sufficient quantity. Industrial wastewaters, however, often are deficient and require nitrogen and phosphorus supplements.

The quantity of nutrients added is of concern. Insufficient nutrients lead to problems as described previously, but excess nutrient additions can also lead to difficulties. Some of these are:

- (i) rising sludge (denitrification of excess nitrogen in the reactor, where NO_2^- and NO_3^- are converted to N_2 gas which becomes trapped in the sludge mass, causing poor settling in the clarifier),
- (ii) high levels of nitrogen and phosphorus in the final effluent, which are in excess of local pollution control standards and will fertilize receiving waters, and
- (iii) higher costs than necessary (both capital costs for storage and chemical feeding equipment and operating costs for the purchase of chemicals).

Temperature is another factor that affects the efficiency of the activated sludge process. Biological metabolic activity generally decreases with decreasing temperature. The temperature effect on the reaction rate is usually described by the modified Arrhenius equation (22):

$$K_T = K_{20} \theta^{(T-20)} \quad \dots \dots \dots (4)$$

where K_T = reaction constant at temperature T

K_{20} = reaction constant at 20°C

θ = temperature sensitivity coefficient

= 1.056 for a temperature between 20° and 30°C

= 1.135 for a temperature between 4° and 20°C

Other factors affecting activated sludge performance are sludge age, pH, and dissolved oxygen. pH should be maintained within a range of 6.5 to 9.0 (11). The dissolved oxygen level should be above 1.5 to 2.0 mg/L, for aerobic conditions to exist. Generally, as sludge age decreases, effluent quality worsens.

In investigating treatability systems involving the activated sludge process, three operational procedures are commonly used: continuous flow, fill-and-draw, and batch. The continuous flow system is favoured, since it more closely simulates the full-scale process, as well as providing more comprehensive data. However, bench-scale, continuous flow reactors are prone to operating difficulties such as clogged tubing and breakdown of pumps. The fill-and-draw method, on the other hand, requires far less mechanical equipment and is therefore a much simpler and troublefree system to operate. Also, the kinetics of a fill-and-draw system are similar to that of a plug-flow, full-scale system. Batch reactors are only useful for determining trends and approximating design values.

It is for the above reasons, plus the importance of tying into previous leachate treatability work performed under the fill-and-draw system, that the fill-and-draw method has been used for this investigation.

2 - 1.2 Previous Research

The earliest known aerobic "biostabilization of leachate" study was carried out by Boyle and Ham (4). Their 5-day sludge age units achieved 90, 93, and 80 percent BOD_5 removals for BOD_5 loadings of 0.019, 0.036, and 0.087 lb BOD_5 /day/ft³ (0.30, 0.58, and 1.39 kg BOD_5 /day/m³), respectively. Their 1-day sludge age unit never performed effectively during one month of operation. Sludge bulking problems predominated, resulting in poor quality effluent. This was attributed to an excessively high volumetric loading of 0.330 lb BOD_5 /day/ft³ (5.29 kg BOD_5 /day/m³) and a food-to-microorganism (F/M) ratio exceeding 1.5 kg BOD_5 /day/kg MLVSS. The units were operated on a fill-and-draw basis. Although the aerobic treatment studies were encouraging, several disadvantages of the process, including high power requirements and foaming problems, caused Boyle and Ham to direct the major thrust of their project toward anaerobic treatment.

Cook and Foree (9) evaluated the treatment of leachate by aerobic biostabilization under various organic loadings, nutrient additions, and pH conditions. The leachate used in this study was of "medium" strength. Some characteristics of the raw leachate were:

COD = 15,800 mg/L

BOD₅ = 7,100 mg/L

pH = 5.4

BOD₅:N:P = 100:2.5:0.18

Six bench-scale aerobic units were used to evaluate the biological stabilization of the leachate. Four units were daily fill-and-draw systems operating with various lime and nutrient additions and a 10-day sludge age (0.044 lb BOD₅/day/ft³ or 0.70 kg BOD₅/day/m³). An additional fill-and-draw unit was run at a 5-day sludge age and the last unit was a continuous feed system, with a 2-day sludge age. Both of these units failed, as predicted by the operational and kinetic characteristics determined. The theoretical detention time for failure was calculated to be 5.3 days.

The 10-day units all performed well. COD removals were from 97.6 percent for the unit fed leachate only, to 98.1 percent for the unit with lime and nutrients added. The BOD₅ of the effluents were all below 26 mg/L, corresponding to removal efficiencies of at least 99.7 percent. The settling properties of the mixed liquor were very good. The range of sludge volume indices (SVI) was from 39 to 55, with the lime supplemented units having the lowest SVI's. The range for total suspended solids (TSS) and volatile suspended solids (VSS) in the effluent were 39 to 77 mg/L and 24 to 57 mg/L, respectively.

The removal of three metals was examined. Iron concentrations were reduced from 240 mg/L to less than 10 mg/L, in all of the 10-day reactors. Cook and Foree attributed the high removals mainly to chemical precipitation at the high pH's. Calcium removals were much higher in the two units with a pH of 8.4. This was due to the precipitation of the calcium as calcium carbonate at this high pH. The magnesium concentrations were not reduced significantly. The pH was not high enough to cause precipitation of the magnesium as magnesium hydroxide. The removal that did occur was due to settling out of insoluble magnesium.

Most of the total Kjeldahl nitrogen (TKN) was removed in the 10-day units and $\text{NO}_3\text{-N}$ was produced in the nutrient supplemented units. The mixed liquor concentrations of TKN were lower than the concentrations for the leachate, with and without added $\text{NH}_3\text{-N}$, indicating that some ammonia stripping had taken place. Almost all of the phosphorus was found to be tied up in the microbial masses and settled sludge.

The nutrient additions that were made were in the form of ammonia nitrogen and orthophosphate. The results of Cook and Foree's study showed that nutrient additions were not needed for successful treatment of the leachate.

Palit and Qasim (24) studied the biological treatment kinetics of landfill leachate. Their study was conducted with dilute landfill leachate (diluted COD = 365 mg/L), using a bench-scale continuous flow activated sludge unit.

They concluded that leachate can be biologically treated in an activated sludge plant. Poor solids-liquid separation was encountered several times during the experiment. It was suggested that the addition of nutrients would enhance removal efficiencies.

There have also been several leachate treatability (by aerobic stabilization) studies done at the University of British Columbia. The first investigator was Uloth (33). He attempted to treat high strength leachate ($\text{BOD}_5 = 35000$ mg/L) using very high mixed liquor volatile suspended solids concentrations (8000 to 16000 mg/L). Provided that F/M ratios were kept below $0.22 \text{ kg BOD}_5/\text{day/kg MLVSS}$, stable reactor operations were maintained at solids detention times as short as 10 days. COD removals increased from 96.7 to 99.1 percent for sludge ages from 10 to 60 days. Greater than 99.6 percent BOD_5 removals were possible for solids detention times over 10 days. Metal removals were also high. Uloth attributed this to the high pH's (greater than 8.5) and VSS concentrations of the mixed liquors. $\text{BOD}_5:\text{N}:\text{P}$ ratios of 100:5:1 or lower were used. Analysis of the effluents indicated that the nitrogen and phosphorus additions were excessive and therefore, might be substantially reduced without impairing treatment efficiency. The biological reactors of this, and all subsequent studies at the University of British Columbia, were operated on a fill-and-draw basis. Settling was complete after 2 hours for this study.

An investigation by Temoin (31) was a follow-up to the work of Uloth. Temoin was concerned with the nitrogen and phosphorus requirements for the successful treatment of high strength leachate through aerobic biostabilization. With an "optimal" sludge age of 20 days and operating at room temperature, the nutrient loading ($BOD_5:N:P$) was varied from 100:3.19:0.12 to 100:5:1.1. The most effective treatment was achieved with a loading of 100:3.19:1.11. A partial summary (21) of Temoin's results are shown in Table 2.

Two main types of bacteria were found in the mixed liquors. One was a zooglear form common to domestic sewage treatment plants. The second was actinomycete *Geodermatophilus*. This bacteria had never before been isolated in a sewage treatment plant. The reactors with the high phosphorus loadings (271 mg/L) all had 90% *Geodermatophilus* and 10% zooglear floc. As the phosphorus loading decreased, the zooglear form started to predominate. When nutrient loading were sufficiently reduced, sludge bulking occurred. For this study, settling for effluents was given 2½ hours.

The two most recent leachate treatment studies at the University of British Columbia were carried out by Zapf-Gilje (34) and Graham (14). These studies were done concurrently. They treated a medium strength leachate ($COD = 19000$ mg/L) by aerobic biostabilization with sludge ages ranging from 6 to 25 days and temperatures ranging from 5° to 25°C. Nutrient loadings were slightly in excess of $BOD_5:N:P = 100:5:1$.

TABLE 2 (31)

PARTIAL DATA SUMMARY OF NUTRIENT
REQUIREMENT STUDY BY TEMOIN

NUTRIENT LOADING OF REACTOR BOD ₅ :N:P	EFFLUENT CONCENTRATIONS					
	BOD ₅ (mg/L)	TSS (mg/L)	Cr (mg/L)	Fe (mg/L)	Pb (mg/L)	Zn (mg/L)
Leachate Feed	19330	990	0.365	960	0.167	49.5
100:5.03:1.11	82	380	0.050	25.2	0.011	1.31
100:3.98:1.11	55	133	0.033	9.72	0.006	0.630
100:3.19:1.11	36	47	0.035	4.27	0.003	0.295
100:3.98:0.32	300	1805	0.103	27.3	0.023	2.10
100:3.98:0.12	1430	245	0.040	13.5	0.005	0.726
100:3.19:0.12	560	160	0.033	6.73	0.015	0.543

Zapf-Gilje then also employed aerobic biostabilization as a polishing step for his first stage biostabilized effluents. Graham's second stage polishing of his effluents was by lime precipitation.

Removal of organic material in the first stage was exceptionally good, with better than 99% BOD₅ and 95% COD removals. Metal removals were better than 90% for most of the metals monitored. For the temperature and sludge age ranges studied, the differences in performance of the reactors were not very significant. The exception to this was at the lowest temperature, particularly at the lower sludge ages, where reactor instability was observed. The settling characteristics of all the mixed liquors were highly variable. Hence, Zapf-Gilje filtered the samples in order to obtain a consistent effluent, whereas Graham collected both 2-hour settled and filtered effluents. Whatman No. 4 filter paper was used.

Zapf-Gilje found biological polishing of the first stage effluents not feasible at high temperatures, due to the low residual concentration of biodegradable organics. It was only marginal at the lowest temperature investigated (9°C), where 45 percent BOD₅ and 80 percent COD removal, plus a reduction of some metal concentrations was achieved. Graham found lime polishing to be effective; however, the lime dosages required were often very high.

2 - 2 Physical-Chemical Treatment

2 - 2.1 Chemical Precipitation and Coagulation

Chemical precipitation involves the addition of chemicals to alter the state of dissolved and suspended matter and facilitate their removal by sedimentation. In some cases the change is slight, and removal is effected by entrapment within a precipitate consisting primarily of the coagulant itself (22).

Several investigators have conducted chemical treatment of leachate experiments. Ho et al. (16) used lime, sodium sulfide, alum, and ferric chloride as their precipitation and coagulation chemicals. The best results were obtained with lime. However, metal and colour removals were possible only at high chemical doses. No significant organic removals were obtained and a large amount of sludge was produced. The results indicated that a combination of biological treatment to reduce organic levels, followed by lime precipitation was promising.

Various chemicals using various combinations of pH and dosage were tried by Cook and Foree (9). The chemicals used were: hydrated lime, alum, ferric chloride, ferric sulfate, polyelectrolyte, and sodium hydroxide. From the studies performed, Cook and Foree concluded that suspended solids and colour could be effectively reduced, but because of the high concentration of soluble organics, the total organic strength could not be significantly reduced.

Thornton and Blanc (32) examined the treatment of leachate by chemical coagulation and precipitation with regard to removals of biochemical oxygen demand, iron, calcium, magnesium, suspended solids, and colour. Initial tests on a low strength leachate (COD = 5033 mg/L) involved the use of alum and lime, with removal of colour and suspended solids as a measure of chemical effectiveness. At doses of 300 mg/L, suspended solids removals were approximately 50% for alum and 75% for lime. Due to the superior performance of lime over alum, all further tests were conducted with lime.

A higher strength leachate (COD = 12923 mg/L) was also used in order to determine the effects of increased leachate strength on lime requirements. For this leachate, a 900 mg/L lime dose was only effective for a 60% removal of suspended solids. From their studies, Thornton and Blanc concluded that substantial reductions in colour, suspended solids, and multivalent cations can be achieved by lime precipitation. These reductions were a function of the alkalinity of the sample and the ability of lime to raise the pH for the precipitation of calcium carbonate and metal hydroxides. However, significant removals of other dissolved solids and soluble organics, which constitute the major portion of BOD, were not achieved by the lime treatment.

Bjorkman (3), at the University of British Columbia, conducted a comprehensive study on the physical-chemical

treatment and disinfection of leachate. The chemicals studied were: lime, alum, ferric chloride, ferric sulfate, powdered activated carbon, and ozone. Supplemental to the chemicals, three high molecular weight synthetic polymers were tested as coagulation and settling enhancers. The COD of the leachate studied was 14000 mg/L.

Bjorkman achieved the best overall treatment using 110 mg/L ozone, followed by 2350 mg/L of lime. This resulted in disinfection and the following removals: 97.9% of pretreatment turbidity, 90% of colour, 20% of COD, 26% of Cu, 99.98% of Fe, 0% of K, 99.8% of Mn, 0% of Na, 98.5% of P, 39% of Pb, and 99.9% of Zn.

From the above investigations, it is apparent that physical-chemical treatment of leachate by itself does not appear to be feasible. It can only be cost effective if coupled with other pretreatment processes, that would substantially reduce oxygen demanding material first. In addition, lime, which appears to be the most favourable chemical, is required in such massive dosages that the costs and sludge generated would make the chemical treatment of raw leachate a poor alternative.

Ho et al. (16) added lime in sufficient doses to raise the pH to 9.0 and 11.0, for leachate pretreated anaerobically for 10 days, as well as other samples treated anaerobically for 10 days and then aerobically for 5 additional days. For the anaerobically treated leachate, a lime dose of

2700 mg/L was required to raise the pH to 11.0. At this dose, essentially complete iron removal and about 10 percent COD removal were achieved. For the anaerobically-aerobically treated leachate, a high lime dose of 1400 mg/L removed essentially all of the iron and 30 percent of the COD. Before lime precipitation, the concentrations were COD = 558 and 366 mg/L and Fe = 20.0 and 15.0 mg/L, for the anaerobic and anaerobic-aerobic effluents, respectively.

Graham (14) also investigated the polishing of a biologically stabilized leachate by lime precipitation. He found that the dosage of lime required to achieve adequate organic removals was dependent upon the influent COD, alkalinity, and the total suspended solids of the sample. To effectively reduce residual organics and metals in the bio-treated effluents, high lime dosages were often required.

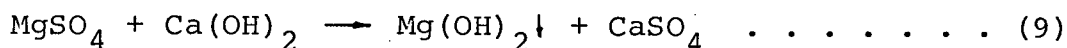
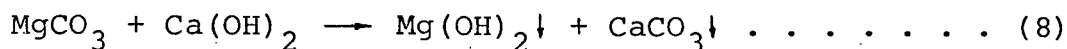
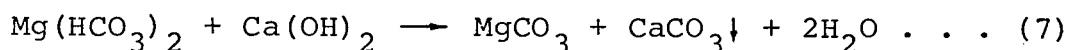
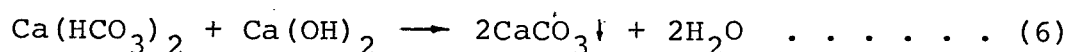
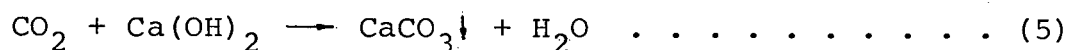
2 - 2.2 Lime-Magnesium Process

Chemical precipitation and coagulation by the lime-magnesium process involves precipitation, adsorption, complexation, chelation, flocculation and entrapment in the removal of dissolved, colloidal, and suspended matter from waters and wastewaters. For the removal of heavy metals, the primary mechanism is direct precipitation of insoluble metal hydroxides. Adsorption, flocculation and entrapment are the important mechanisms in the removal of organics. This removal is partly due to the in-situ precipitation of magnesium hydroxide, a gelatinous floc, which aids solids

removal as it settles. In this way, the lime-magnesium process offers better treatment than lime treatment alone (19, 27).

The magnesium addition is in the form of a magnesium salt, preferably magnesium carbonate. This is so that both magnesium hydroxide and calcium carbonate will precipitate out.

The chemistry of the lime-magnesium process is very similar to that of water softening. The following equations summarize the process (27):



Equations (5) and (6) show the necessary conversion of all the CO_2 and HCO_3^- to $\text{CO}_3^{=}$ and H_2O before the OH^- concentration (or pH) can increase. The conversion of magnesium bicarbonate (if any present) and calcium hydroxide to precipitated magnesium hydroxide and calcium carbonate is illustrated in Equations (7) and (8). A reaction such as Equation (9) occurs when magnesium is not added in the form of magnesium carbonate or if noncarbonate magnesium hardness is present. It should be noted that when magnesium carbonate is the coagulant, there is no increase in dissolved solids.

Another strong feature of this process is that magnesium carbonate trihydrate ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) and lime can be recovered from the sludge and recycled. Black et al. recently developed a relatively simple and inexpensive method for the recovery of magnesium (27). The method involves: the selective removal of $\text{Mg}(\text{OH})_2$ (to soluble $\text{Mg}(\text{HCO}_3)_2$) from the primary sludge by carbonation, the clarification of the $\text{Mg}(\text{HCO}_3)_2$ solution (usually by filtration), followed by heating to 35° to 40°C and then aeration, at which time $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ precipitates out. The precipitate can then be vacuum filtered and dried. The sludge can then be recalcined to recover lime. Recovery and recycle of magnesium and lime is an important economic factor, affecting both chemical and sludge handling costs. If recovery is not practised, sludge dewatering could be difficult because of the gelatinous nature of the $\text{Mg}(\text{OH})_2$ floc.

Most early applications of the lime-magnesium process have been in water treatment. Magnesium compounds as coagulants have not been used extensively because of their high costs. However, the advent of mandatory water-softening sludge elimination in many areas and the magnesium recovery innovation by Black et al. means a new, low-cost source of magnesium.

Rush (27) reports that a number of investigations in pulp and paper mill wastewater clarification have been conducted. They found that magnesium hydroxide formed in-situ

allowed much lower doses of lime to be used than if lime were used alone in the removal of COD, suspended solids, and colour. Rush also found that better decolourization of Kraft-mill effluents could be achieved using low magnesium and lime concentrations, as opposed to three to five times as much lime alone.

Rush (27) reports DuBose's pilot plant treatment studies of raw municipal wastes showed that much greater reductions in phosphate, suspended solids, and colour, and ten to thirty percent more COD could be removed with recycled magnesium bicarbonate and lime, rather than lime alone. He also found that the superiority of the lime-magnesium process over lime alone was even more pronounced with increasing wastewater strength.

MacLean (20) applied lime-magnesium coagulation to remove heavy metals from municipal wastewaters. He found that the effect of magnesium was most significant when used in conjunction with low lime treatment ($\text{pH} = 10.0$). Leung (19) studied the removal of trace organics from municipal wastewaters by the lime-magnesium process. His results indicated that enhanced removal, due to the presence of magnesium, was minimal.

2 - 3 Other Treatment Processes and Methods

While aerobic biostabilization and the lime-magnesium precipitation and coagulation are the only treatment processes examined in this investigation, it is important to recognize

that there are a number of other treatment alternatives available. The following is a brief synopsis of previous investigations of these alternative leachate treatment processes.

Boyle and Ham (4) and Poorman (25) studied anaerobic treatment of raw leachate. Although reasonably good treatment efficiencies were obtained, high residual BOD_5 values (165 to 3000 mg/L) indicated further effluent treatment was necessary to meet appropriate discharge levels.

Physical-chemical treatment schemes have already been discussed in the previous section. These do not appear to be a viable alternative for treating raw leachate, because of poor oxygen demanding matter removal. Although soluble organics can be removed by activated carbon absorption (9, 16, 18), cost effectiveness would probably rule this process out.

Boyle and Ham (4) and Temoin (31) looked at combined treatment of leachate with domestic sewage. Boyle and Ham found that leachate additions of at least 5 percent by volume (leachate COD = 10000 mg/L) could be added to an extended aeration plant, without seriously impairing effluent quality. Temoin combined leachate (BOD_5 = 19330 mg/L) with domestic sewage in proportions varying from 0 to 20 percent of total volume of leachate plus sewage. Very effective treatment of all the combined wastewaters was found.

CHAPTER 3

EXPERIMENTAL SYSTEM AND METHODS

3 - 1 Leachate Source and Characteristics

The leachate used in this study was generated from five of sixteen simulated landfills or "lysimeters" at the University of British Columbia. These lysimeters are part of a long-term research program to investigate the production and composition of leachate with time, precipitation, cover material, recycling of leachate and other parameters. This program was initiated in 1971 by Dr. R.D. Cameron of the Department of Civil Engineering. At the end of January 1979, watering of the lysimeter tanks was discontinued.

The five tanks (tanks H, R, T, W, and X) producing the highest strength leachates were watered for 2½ weeks in June of 1979 to generate enough leachate for this investigation. The watering rate of 5.65 Imperial gallons (25.7 litres) twice a week was equivalent to 90 inches (230 mm) of precipitation per year. Leachate was collected twice a week and stored in 20 litre polyethylene containers at 4°C to retard biological activity. When 450 litres of leachate were collected, all of the leachate was combined, well mixed and re-stored at 4°C in order to have a consistent wastewater to use throughout the study period. The characteristics of this leachate are shown in Table 3.

TABLE 3
LEACHATE CHARACTERISTICS

PARAMETER	CONCENTRATION*
pH	5.4
BOD ₅	8090
COD	13000
TSS	460
TVSS	280
TS	6910
TVS	3680
Acidity as CaCO ₃ (pH = 8.3)	2060
Alkalinity as CaCO ₃ (pH = 3.7)	3160
Carbon - TC	3820
- TOC	3800
Nitrogen as N - TKN	172
- NH ₃	130
- NO ₂ -NO ₃	<0.05
Phosphorus - total	5.3
Cadmium	0.22
Calcium	495
Chromium	0.08
Iron	955
Lead	0.03
Magnesium	39.2
Manganese	9.46
Nickel	0.083
Zinc	27.0

* All units in mg/L, except pH.

3 - 2 Biological Treatment System

3 - 2.1 The Biological Reactors

Bench-scale, daily fill-and-draw (or semi-continuous) reactors were used in the first stage treatment of the leachate. These reactors were employed to simulate a full-scale, plug-flow, activated sludge process.

The reasons for using this type of system are many. Some of these factors are:

- (i) there are fewer operational problems with a fill-and-draw system than with a continuous flow system. For example, pumps and timers can malfunction and fluid lines can clog up,
- (ii) the apparatus was available since previous leachate research had been carried out at the University of British Columbia using this equipment, and
- (iii) using this system allows for the tying in of this investigation to previous research performed at the University of British Columbia.

3 - 2.2 The Experimental Apparatus

Nine, 10 litre glass jars with their bottoms removed, were used as reactors. Rubber stoppers, with coarse bubble glass diffuser stones fitted through them, were placed in the necks of the jars. Oil-free air was supplied to the reactors by the laboratory compressed air system. A constant air flow was maintained with an air regulator on the air supply line. Since one air supply line served four or five

reactors, a uniform rate of air to each reactor was ensured by adjustable screw clamps on the air line to each individual unit. Mechanical, surface, cone-drive stirrers produced complete mixing and uniform distribution of food and micro-organisms within the reactors and helped to reduce foaming. A schematic diagram of a typical reactor is shown in Figure 1.

3 - 2.3 Operation of the Reactors

(a) Operational Parameters

The control parameters in this investigation were mean cell retention time (MCRT) or sludge age (θ_c) and temperature (T). The sludge ages investigated were 20, 15, 10 and 5 days. This study of sludge ages was done at ambient air temperatures of 19° to 24° (room temperature), 15°, 10°, and 5°C. These reactors had a nutrient loading rate of BOD₅:N:P of 100:3.2:1.1. In addition to these units, a control unit at room temperature with a sludge age of 20 days and the conventional BOD₅:N:P loading rate of 100:5:1 was operated. The parameters monitored included: pH, COD, TSS, TVSS, TS, and TVS of the mixed liquor; pH, BOD₅, COD, TSS, TVSS, TS, TVS, acidity, alkalinity, carbon (TC and TOC), nitrogen (TKN, NH₃, and NO₂-NO₃), total phosphorus, and a number of metals (Cd, Ca, Cr, Fe, Pb, Mg, Mn, Ni, and Zn) in effluents filtered through Whatman No. 4 filter paper.

Initially SVI's were also monitored. This was abandoned since the results were not meaningful. They ranged from 25 to

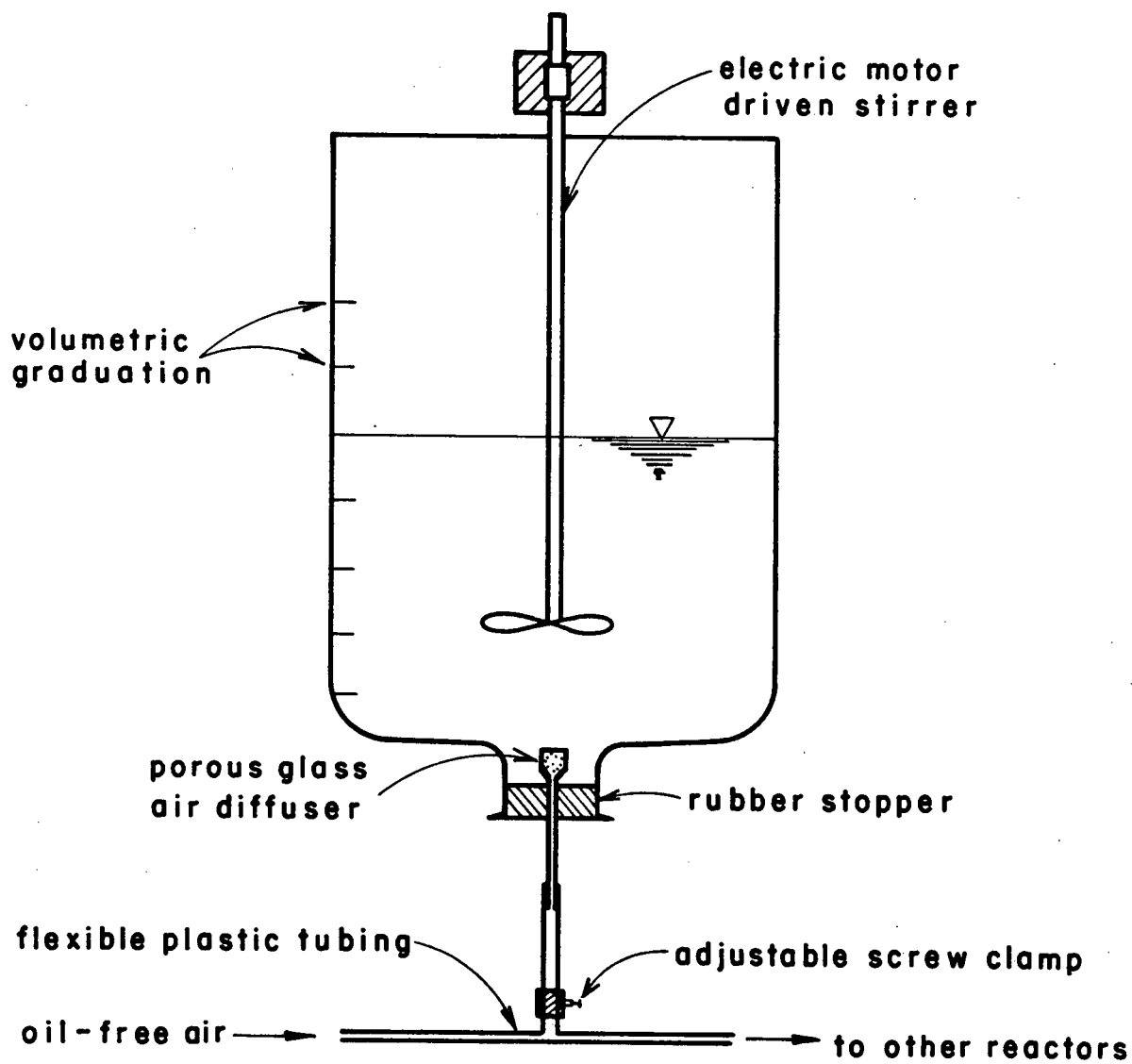


FIGURE I
TYPICAL LABORATORY REACTOR

55; the lowest SVI's corresponded to the worst settling sludges. These values were low since much of the suspended solids remained suspended.

BOD₅ testing on the mixed liquors was not done. Previous research (14, 33, 34) had shown that apparent biological inhibition (probably due to high metal concentrations) resulted in highly variable mixed liquor BOD₅ test values. (The BOD₅ tests of their effluents showed no sign of inhibition over a wide range of dilutions.)

All tests were performed according to Standard Methods (1). The Wet Ash digestion procedure for metals analysis was taken from Methods for Chemical Analysis of Water and Wastes (13). The laboratory instruments used for analysis were:

- i) Fisher Accumet Model 210 pH Meter for pH determinations,
- ii) Yellow Springs Instrument Co., Inc., YSI Model 54 Oxygen Meter for BOD₅ determinations,
- iii) Sartorius Model 2442 balance for solids determinations,
- iv) Technicon Auto Analyzer II for NO₂-NO₃ determinations,
- v) Bausch and Lomb Spectronic 88 for total phosphorus determinations,
- vi) Perkin-Elmer 703 Atomic Absorption Spectrophotometer for metals analysis, and
- vii) Jarrell Ash 810 Atomic Absorption Spectrophotometer for metal analysis when high sensitivity was required.

(b) Acclimation

The bacterial seed used in this investigation was activated sludge from the Mamquam sewage treatment plant in Squamish, B.C. This had also been the source of seed for several previous studies.

The MLVSS of the seed was approximately 13000 mg/L, much higher than the expected MLVSS of the experimental reactors. It was felt that by diluting the seed, the reactors would acclimate and reach steady state conditions faster. Therefore, the reactors were started up with about 2.5 litres of seed and 2.5 litres of distilled water. The reactors were then aerated and stirred overnight. Over the next five days, the amount of leachate feed was gradually increased daily (with the equivalent volume of mixed liquor withdrawn just before feeding) until the volume added corresponded to the sludge age of each unit.

A regular operating procedure (described in the next section) was then followed for 24 days before testing was started. This was to allow the microorganisms to become acclimated and the MLVSS to stabilize.

Initially, nine reactor units were started up; five at room temperature and four at 15°C (as described in 3 - 3.1 (a)). When testing at these temperatures was complete, the room temperature units were shut down and the cold room temperature gradually dropped to 10°C over three days. The units were then acclimated to the temperature for 10 days.

By the end of this period, steady state conditions were reached.

COD and TVSS of the mixed liquors and effluents were continually monitored. "Stabilized" COD and TVSS values were used as an indicator of steady state conditions.

When operation at 10°C was complete, the same procedure was used for the 5°C run.

(c) Daily Operating Procedure

After the initial 5-day start up period, a regular daily operating procedure was followed. This procedure consisted of:

- i) Take leachate out of the 4°C cold room and leave at room temperature for up to an hour before feeding the reactors. (The time interval depended on what temperature the reactors were at. This was so that the microorganisms in the mixed liquor would not receive a temperature shock.)
- ii) Scrape reactor wall and stirring bar to prevent significant loss of solids from the mixed liquor.
- iii) Turn off mixers and air supply. Top reactors off to 5.0 L with distilled water to replace evaporation loss. Turn mixers and air back on.
- iv) Withdraw the appropriate volume of mixed liquor from each unit. Allow to settle for about half an hour and then filter through Whatman No. 4 filter paper.
- v) Pipet appropriate volume of nutrient feed (diluted $(\text{NH}_4)_2\text{HPO}_4$ and NH_4Cl) to each unit.

- vi) Add the appropriate amount of leachate to each reactor (250, 333, 500 and 1000 ml to the 20, 15, 10, and 5-day sludge age units, respectively).

When testing was required, some of the mixed liquor from step (iv) was used. Any filtered effluent not used in testing was stored at 4°C for the lime-magnesium polishing phase.

The frequency of testing was approximately twice a week for pH, BOD₅, COD, TSS, TVSS, TS, and TVS. The analysis for the other monitored parameters was done at the end of operation of the reactors at each temperature.

3 - 3 Lime-Magnesium Treatment System

The testing procedure followed was largely adopted from the methods developed by MacLean (20). He used Rush's (27) research as a basis and investigated the time and mixing speed required for pH stabilization, rapid mixing, flocculation and settling. Also examined were the methods and dosages of magnesium and lime addition.

The volumes of effluent collected from the biological reactors were limited. It was felt that rather than attempt to polish each effluent, a much more comprehensive study could be done by combining several effluents. Hence, the filtered effluents from all the 20, 15 and 10-day reactors were combined to form SAMPLE 1 (low strength) and all the 5-day reactor effluents formed SAMPLE 2 (high strength). All jar testing was done at room temperature on a Phipps and Bird Laboratory Stirrer.

Lime ($\text{Ca}(\text{OH})_2$) was added in the powdered form. This procedure was adopted because MacLean (20) found that dry reagent grade $\text{Ca}(\text{OH})_2$ gave better reproducibility than a lime slurry. Presumably, this is due to slurry settling. The lime dosages used were such as to raise the sample pH to 10.0, 10.7, and 11.4.

Magnesium was added as a 10^3 mg/L Mg^{++} solution, prepared by dissolving 1.01 grams of reagent grade $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 ml of distilled water. MacLean (20) found better removal was obtained when coagulation was performed using Mg^{++} than $\text{Mg}(\text{OH})_2$. This follows the generally accepted theory that the magnesium must be added in the ionic form so that it precipitates "in-situ", for optimum removal. The Mg^{++} dosages used were 0, 10, 20, 35, and 50 mg/L.

The lime-magnesium coagulation test sequence used consisted of the following procedure:

- i) For each run, a set of 6, 1.0 litre samples were measured into 1 litre beakers, using a 1 litre graduated cylinder. One of the samples was used to calculate the $\text{Ca}(\text{OH})_2$ dosage. The sample was mixed at 100 rpm and the pH was constantly monitored to a pH of 10.0, 10.7, or 11.4. The lime requirement was calculated and five such doses were measured out.
- ii) 0.0, 1.0, 2.0, 3.5, and 5.0 ml of the Mg^{++} solution were pipetted into the remaining five samples. These additions corresponded to 0, 10, 20, 35 and 50 mg/L Mg^{++} , respectively. The samples were stirred for 1

minute at 100 rpm to disperse the Mg^{++} ions.

- iii) The lime additions were made and the samples were given a 15 minute rapid mix at 100 rpm for pH stabilization.
- iv) The samples were given a 10 minute flocculation period at 15 to 20 rpm.
- v) The samples were given a 30 minute settling period at 0 rpm.

After settling, the following analyses were done on the supernatants: pH, BOD_5 , COD, TSS, TVSS, total phosphorus, and a number of metals (Cd, Ca, Cr, Fe, Mg, Mn, Ni, and Zn). The analytical procedures for these analyses are as described previously. Lead (Pb) was not included since the Pb concentrations of all the first stage effluents were already below the minimum detection level.

Due to the nature of the jar test procedure, less than 1 litre of each supernatant was available for testing. This limited the number of analyses which could be performed. Hence, only the parameters which were considered essential were determined. Lack of sample prohibited determinations of alkalinity, TS, TVS, carbon and nitrogen (which were performed in the aerobic biological phase).

CHAPTER 4

RESULTS AND DISCUSSION

4 - 1 Activated Sludge Treatment Phase4 - 1.1 Mixed Liquor Characteristics and Kinetics

The kinetic coefficients k , K_s , Y , and b , as defined in Appendix A, are fixed for a specified waste biological community, and a particular set of environmental conditions. The determinations of the kinetic coefficients and minimum sludge ages are shown in Appendix A. For comparison, coefficients from previous investigations are included with the values from this study in Table 4. The calculated minimum sludge ages (the mean cell residence time at which reactor failure occurs, due to the biomass being removed faster than it can reproduce) were 1.8, 1.8, 4.0, and 5.4 for room temperature, 15° , 10° , and 5°C , respectively.

The above temperatures are ambient air temperatures. Room temperatures ranged from 19° to 25°C . The mixed liquor temperatures were from 2° to 5°C lower than the ambient air temperatures. The higher temperatures had the greatest differences between the liquid and air temperatures. The reason for this temperature difference is the compressed air used to provide oxygen to the reactors. The air was cold and it cooled the mixed liquors, thus more than compensating for the heat of respiration.

TABLE 4

KINETIC COEFFICIENTS OF THIS AND PREVIOUS INVESTIGATIONS

INVESTIGATIVE AUTHORS	LEACHATE COD (mg/L)	BASIS FOR KINETIC COEFFICIENTS	KINETIC COEFFICIENTS			
			k (days ⁻¹)	K _s (mg/L)	Y	b (days ⁻¹)
Typical Activated Sludge Process (22)		BOD ₅	5.0	60	0.6	0.06
Cook and Foree (9)	15800	COD	0.60	175	0.4	0.05
Palit and Qasim (24)	365	COD	1.8	182	0.59	0.115
Uloth (33)	48000	BOD ₅	0.75	21375	0.332	0.0025
Zapf-Gilje (34)	19250	soluble BOD ₅	0.74	19.6	0.374	0.015
This Investigation at Room Temp.	13000	soluble BOD ₅	1.16	81.8	0.49	0.009
This Investigation at 15°C	13000	soluble BOD ₅	1.12	63.8	0.51	0.018
This Investigation at 10°C	13000	soluble BOD ₅	0.51	34.6	0.51	0.006
This Investigation at 5°C	13000	soluble BOD ₅	0.35	17.0	0.55	0.002

Note: all temperatures are room temperature unless stated otherwise.

The values for maximum rate of substrate utilization per unit weight of microorganisms, k , are lower than that in a typical activated sludge process. This is probably due, in part, to high metal concentrations causing biological inhibition. The value of k also decreased with decreasing temperature. This was expected, since biological reaction rates slow down as temperature is lowered.

The substrate concentration when the rate of substrate utilization per unit weight of cells is one-half the maximum, K_s , also decreased with decreasing temperature. This is due to k decreasing with temperature.

The growth yield coefficient, Y , increased with decreasing temperature. This is because at lower temperatures, higher MLVSS's were maintained (with no solids recycle) and less substrate was utilized. This could be due, in part, to psychrophilic organisms becoming more dominant as temperature decreased. Table 4 also indicates Y is dependent on the strength of the leachate feed.

The endogenous decay coefficients, b , are quite low. This is the case for most high strength leachates since almost all of the cells are in the log-growth phase (due to the large amount of organics available). Thus, there is no need for auto-oxidation to occur.

Mixed liquor pH, COD, and solids were monitored about twice a week throughout the investigation. The results are presented in Table 5. No mixed liquor BOD_5 analyses were

TABLE 5

MIXED LIQUOR CHARACTERISTICS

REACTOR DESCRIPTION		pH	COD (mg/L)	TSS (mg/L)	TVSS (mg/L)	TS (mg/L)	TVS (mg/L)	F/M (days ⁻¹)
T (°C)	θ_c (days)							
Room Temp.	20*	8.3	4700	5940	3630	7050	3620	0.111
	20	8.6	4480	5980	3490	6660	3400	0.116
	15	8.6	4730	5820	3470	6560	3390	0.155
	10	8.6	5030	6240	3650	6960	3600	0.222
	5	8.5	5810	6540	4000	7420	3930	0.405
15	20	8.5	4900	6050	3690	6610	3640	0.110
	15	8.5	5000	5750	3430	6710	3550	0.157
	10	8.5	5200	5940	3520	6990	3840	0.230
	5	8.4	6200	6250	3790	7560	4190	0.427
	20	8.6	5380	6070	3810	7010	4040	0.106
10	15	8.7	6050	6530	3860	7360	4100	0.140
	10	8.7	6540	6960	4220	8300	4800	0.192
	5	8.5	6880	6300	4040	7050	4450	0.400
	20	8.5	6310	6580	4070	7420	4300	0.099
	15	8.4	6590	6820	4350	7670	4490	0.124
5	10	8.4	10460	7300	4790	7970	4770	0.169
	5	8.3	6710	6240	4320	7710	4910	0.375

* reactor nutrient loading BOD₅:N:P = 100:5:1, all others are 100:3.2:1

Note: the figures presented are mean values obtained from 2 to 4 analyses. As a typical example of the ranges obtained, the ranges of the 10-day, 15°C reactor were: pH = 8.4 to 8.5, COD = 4840 to 5470 mg/L, TSS = 5710 to 6270 mg/L, TVSS = 3200 to 3770 mg/L, TS = 6740 to 7310 mg/L, and TVS = 3390 to 3940 mg/L.

performed since previous investigations (14, 33, 34) have shown that biological inhibition made accurate determination of mixed liquor BOD_5 impossible.

In general, all solids levels increased with decreasing sludge age and/or temperature. The TVSS/TSS ratio increased from 0.59 to 0.65 as the temperature decreased from room temperature to $5^{\circ}C$. The mixed liquor volatile suspended solids (MLVSS) are plotted in Figure 2. As can be seen in Figure 2, at the lowest sludge age and lower temperatures, the solids levels started to drop. The most dramatic change was at 5 days and $5^{\circ}C$. This is explained by the fact that the reactor was on the verge of "washout" conditions. As previously stated, the minimum sludge age at $5^{\circ}C$ was calculated to be 5.4 days.

Cultural acclimation of the sewage sludge took about 4 weeks. For the first 2 weeks, severe foaming problems of all the mixed liquors were encountered. After this time, for the duration of this study, foaming problems persisted only in the 5-day sludge age reactors.

Temperature acclimation, as measured by mixed liquor COD and MLVSS, was complete within two weeks. This confirms the findings of Graham (14), Zapf-Gilje (34), and Benedict and Carlson (2). Benedict and Carlson used endogenous respiration rate per gram of biomass solids as the indicator of steady state conditions.

The settleability of the mixed liquors was poor. Settling problems also occurred in the investigations by Graham (14) and Zapf-Gilje (34). Zapf-Gilje used documentation from

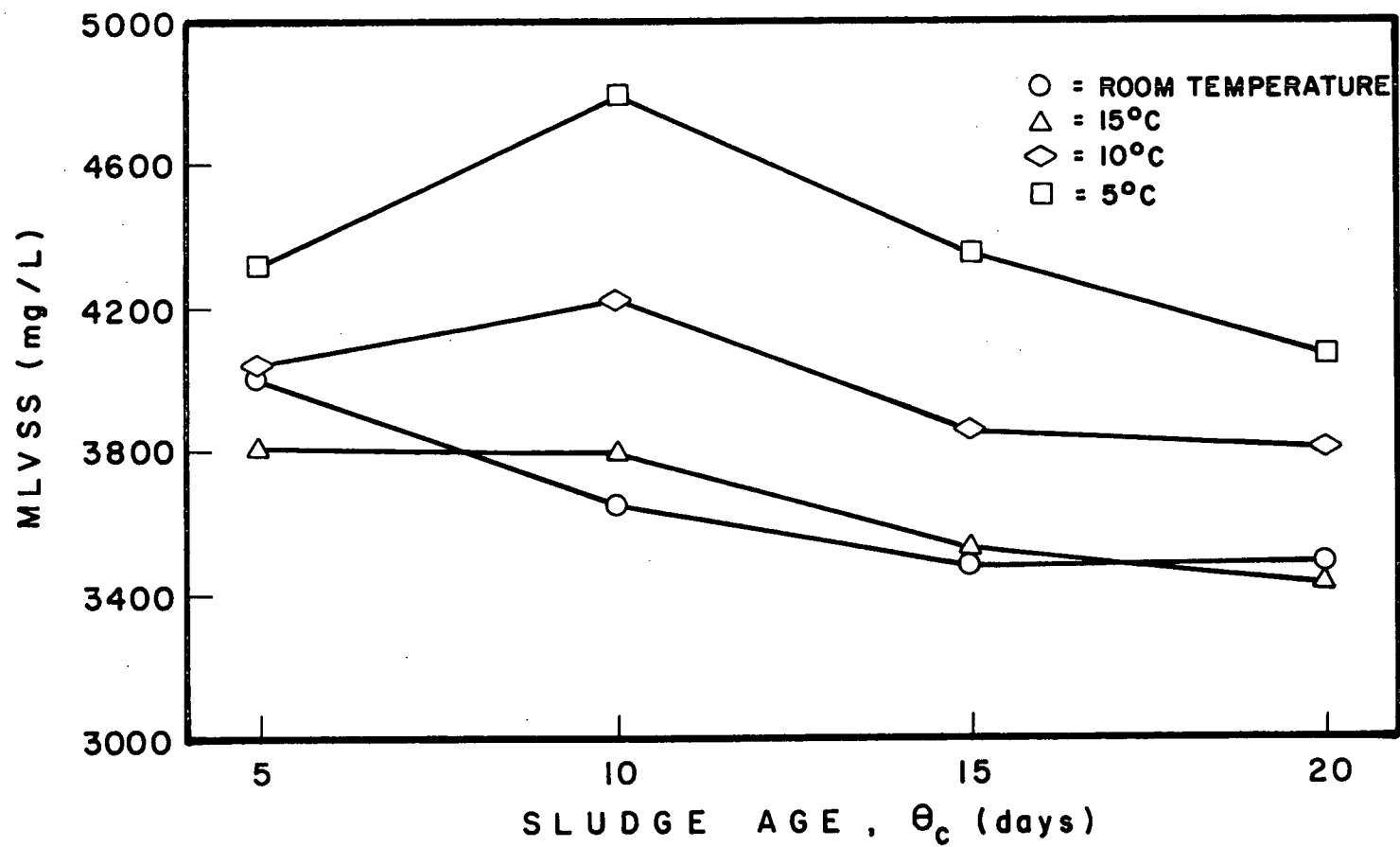


FIGURE 2
MLVSS VERSUS SLUDGE AGE

literature to argue that the sludge bulking is an effect of the fill-and-draw process. Hence, in order to obtain an effluent comparable to that of a continuous flow reactor, Graham and Zapf-Gilje used gravity filtration through Whatman No. 4 filter paper. This author followed the same procedure. The Whatman No. 4 filter paper has a high filter speed and retains coarse and gelatinous precipitates.

4 - 1.2 Removal and Organic Material and Solids

Table 6 shows the removal efficiencies of BOD_5 , COD, and solid material from this study.

All reactors reduced BOD_5 levels by at least 99.4 percent, except the $\theta_c = 5$ -day reactors at 5° and 10°C . Although their BOD_5 's were considerably higher, the minimum percentage removal was still 97.7 percent.

COD removal rates ranged from 98.9 to 93.2 percent. As with the BOD_5 levels, the COD levels of the $\theta_c = 5$ days reactors were significantly higher than the rest.

Of the solids, much higher removal rates of suspended solids, rather than total solids, occurred. This was probably largely due to suspended solids being filtered out by the Whatman No. 4 filter paper. Once again, the 5-day sludge age reactors, at the two lowest temperatures, exhibited substantially lower removal rates.

As expected, the general trend was decreasing removal rates of organics and solids with decreasing sludge age and/or temperature. However, of the conditions investigated (sludge

TABLE 6
ORGANIC MATERIAL (IN TERMS OF BOD₅ AND COD) AND SOLID MATERIAL
CONCENTRATION (IN EFFLUENTS) AND REMOVALS

REACTOR DESCRIPTION		BOD ₅		COD		TSS		TVSS		TS		TVS	
T (°C)	θ _c (days)	mg/L	% REMOVAL	mg/L	% REMOVAL	mg/L	% REMOVAL	mg/L	% REMOVAL	mg/L	% REMOVAL	mg/L	% REMOVAL
Leachate Feed		8090		13000		460		280		6910		3680	
RT	20*	7	>99.9	148	98.9	4	99.1	4	98.6	1660	76.0	420	88.6
	20	9	99.9	173	98.7	8	98.3	5	98.2	1080	84.4	280	92.4
	15	11	99.9	200	98.5	10	97.8	6	97.9	1060	84.7	290	92.1
	10	25	99.7	209	98.4	11	97.6	6	97.9	1040	84.9	290	92.1
	5	44	99.5	365	97.2	22	95.2	11	96.1	1340	80.6	490	86.7
15	20	7	>99.9	216	98.3	7	98.5	7	97.5	1050	84.8	290	92.1
	15	9	99.9	252	98.1	16	96.5	9	96.8	1150	83.4	320	91.3
	10	20	99.8	271	97.9	18	96.1	8	97.1	1230	82.2	330	91.0
	5	51	99.4	462	96.4	23	95.0	14	95.0	1340	80.6	480	87.0
	20	9	99.9	201	98.5	9	98.0	6	97.9	1080	84.4	300	91.8
10	15	16	99.8	215	98.3	6	98.7	5	98.5	1080	84.4	310	91.6
	10	17	99.8	308	97.6	8	98.3	5	98.5	1100	84.1	350	90.5
	5	112	98.6	633	95.1	55	88.0	36	87.1	1480	78.6	660	82.1
	20	14	99.8	270	97.9	14	97.0	8	97.1	1140	83.5	400	89.1
	15	20	99.8	317	97.6	8	98.3	5	98.5	1150	83.4	420	88.6
5	10	42	99.5	425	96.7	23	95.0	10	96.4	1240	82.1	500	86.4
	5	188	97.7	888	93.2	148	67.8	72	74.3	1780	74.2	840	77.2

* reactor nutrient loading BOD₅:N:P = 100:5:1, all others are 100:3.2:1.1

Note: the concentration figures presented are the mean concentrations obtained from 2 to 4 analyses. As a typical example of the ranges obtained, the ranges of the 10-day, 15°C reactor were: BOD₅ = 15 to 24 mg/L, COD = 245 to 310 mg/L, TSS = 13 to 22 mg/L, TVSS = 4 to 10 mg/L, TS = 1090 to 1440 mg/L, and TVS = 286 to 362 mg/L.

ages from 5 to 20 days and temperatures of 5°C to room temperature) the overall removal rates were very similar; the exceptions occurred for the lowest sludge age reactors at 5°C and 10°C. Even though these two reactors were approaching washout conditions, they performed surprisingly well. They still had an average BOD₅ removal of 98 percent, COD removal of 94 percent, and solids removal of about 75 percent.

The most stringent of the British Columbia pollution control objectives (10) (Level AA, receiving waters are streams, rivers, and estuaries with dilution ratios from 20 to 200:1) allows effluent BOD₅ = 30 mg/L and SS = 40 mg/L. All effluents, except from the two reactors near washout, met or were close to these guidelines.

The Whatman No. 4 filter paper used to gravity filter effluents retains coarse and gelatinous precipitates. As sludge builds up on the filter paper, more and more solids would be filtered out due to straining, impingement on sludge particles, and flocculation. Some of these solids filtered out would probably not settle out in a clarifier under field conditions in a continuous flow activated sludge system. Therefore, in order to obtain effluent of a quality as comparable as possible to that which would be obtained under field conditions, the filter paper was changed frequently. The only other alternative for this poor settling mixed liquor was to allow several hours of settling time. This was not feasible due to time constraints and the possible development of anaerobic conditions.

As a check to ascertain that filtration was not responsible for the high removal rates obtained, COD tests were run on filtered effluents and effluents obtained by allowing the mixed liquors to settle for 2 hours. These effluents were collected at the same time from the reactors at 5°C. The results are tabulated in Table 7. Generally, the differences in removal rates were within 0.5 percent. The exception was for the 5-day reactor, which had a discrepancy of 2.3 percent. Temoin (31) and Graham (14) found settled effluent BOD₅'s to be 2 to 4 times higher than filtered effluent BOD₅ (for the reactors which performed effectively). The differences in removal rates of these filtered and settled BOD₅'s were within 0.2 percent. In view of these minor differences, it is felt that the filtering procedure used is quite acceptable in the context of this study.

In order to determine the effects of the nutrient loading level, a suitable basis of comparison to other studies must be used. Since the characteristics and strength of the leachates and the MLVSS levels in the previous leachate treatment studies varied greatly, the most relevant parameter is the food-to-microorganism (F/M) ratio. Table 8 presents a comparison of oxygen demanding material removal of a number of aerobic biostabilization studies, with various nutrient loadings and F/M ratios (at room temperature).

From Table 8, it is difficult to draw conclusions of the effect on the removal of organic matter by the nutrient loading level. From the limited data available, it appears that nutrient loading has little, if any, effect on the organic

TABLE 7

COMPARISON OF COD VALUES OF FILTERED
EFFLUENTS AND TWO-HOUR SETTLED EFFLUENTS
FROM THE REACTORS AT 5°C

SLUDGE AGE, days	COD OF EFFLUENTS			
	FILTERED		SETTLED FOR 2 HOURS	
	mg/L	% REMOVAL	mg/L	% REMOVAL
20	294	97.7	338	97.4
15	342	97.4	398	96.9
10	465	96.4	521	96.0
5	914	93.0	1212	90.7

TABLE 8

COMPARISON OF OXYGEN DEMANDING MATERIAL REMOVALS
UNDER VARIOUS NUTRIENT LOADINGS AND F/M RATIOS

INVESTIGATIVE AUTHORS	NUTRIENT LOADING, BOD ₅ :N:P	F/M, kg BOD ₅ /day kg MLVSS	SLUDGE AGE, days	EFFLUENT BOD ₅		EFFLUENT COD	
				mg/L	% REMOVAL	mg/L	% REMOVAL
Cook and Foree (9)	100:3.9:0.18	0.161	10	26	99.6	360	97.6
	100:11:1.6	0.141	10	10	99.9	310	98.0
Uloth (33)	100:5:1.3	0.119	20	32	99.9	594	98.8
Temoir (31)	100:3.19:0.12	0.148	20	56	99.7	569	98.1
	100:3.98:0.12	0.137	20	85	99.6	1162	96.2
	100:3.98:0.32	0.124	20	28	99.9	585	98.1
	100:3.19:1.11	0.117	20	14	>99.9	476	98.4
	100:3.98:1.11	0.123	20	26	99.9	335	98.9
	100:5.03:1.11	0.119	20	44	99.8	273	99.1
	100:5:1	0.174	20	6	>99.9	300	98.4
	100:5:1	0.345	9	20	99.9	470	97.6
Zapf-Gilje (34)	100:5:1	0.487	6	26	99.8	580	97.0
	100:5:1	0.175	25	4	>99.9	331	98.3
Graham (14)	100:5:1	0.293	15	10	99.9	352	98.2
	100:5:1	0.111	20	7	>99.9	148	98.9
This Inves- tigation	100:3.2:1.1	0.116	20	9	99.9	173	98.7
	100:3.2:1.1	0.155	15	11	99.9	200	98.5
	100:3.2:1.1	0.222	10	25	99.7	209	98.4
	100:3.2:1.1	0.405	5	44	99.5	365	97.2

Note: Cook and Foree's and Uloth's effluents are settled effluents.
All others are filtered effluents.

All reactors were at room temperature.

removal efficiency of the process, except at very low phosphorus levels. A much more comprehensive study, covering a wider range of loadings, and with emphasis on the lower nutrient loading levels is required before more definitive conclusions can be made. This would include the effects of nutrient loading and the minimum loading level before process efficiency is impaired. Also, a series of these tests should be conducted at various organic loading levels or sludge ages to determine if the effect of nutrient loading changes as F/M changes. Sherrard and Shroeder (29) and Sikes and Nieminen (30) have found that the nutrient requirements of a food-processing wastewater and a Kraft-mill effluent were a function of the sludge age.

4 - 1.3 Removal of Metals

Many different factors affect the removal of metals in the activated sludge process. These may be divided into plant operating parameters, physical or chemical factors, and biological factors. Operating parameters which have been shown to affect metal removal are SVI, sludge age, suspended solids removal, dissolved oxygen concentration, and settling time. Physical and chemical factors affecting metal removal are temperature, pH, metal ion concentration, metal solubility, metal valency, concentration of complexing agents, and particle size. The main biological factor is the concentration of bacterial extracellular polymers (5).

The metal removal efficiencies of the biological reactors are presented in Table 9. In general, temperature and MCRT, in the ranges studied, had minimal effect on the removal of metals. However, similar to the organic removal discussed

TABLE 9

METAL REMOVAL EFFICIENCIES OF THE BIOLOGICAL REACTORS

REACTOR DESCRIPTION		PERCENT REMOVAL OF THE METAL								
T(°C)	θ_c (days)	Cd	Ca	Cr	Fe	Pb	Mg	Mn	Ni	Zn
R.T.	20*	>98.2	66.3	91.3	>99.9	>80.0	35.8	97.3	71.1	99.7
	20	>98.2	88.2	87.5	99.8	>80.0	48.6	99.0	69.9	99.7
	15	>98.2	91.3	86.3	>99.9	>80.0	52.7	99.4	66.3	99.7
	10	>98.2	92.0	82.5	>99.9	>80.0	47.3	98.8	59.0	99.6
	5	>98.2	93.0	81.3	99.3	>80.0	47.1	98.0	51.8	98.8
15	20	>98.2	87.7	87.5	>99.9	>80.0	50.6	98.5	65.1	99.7
	15	>98.2	89.2	86.3	>99.9	>80.0	49.4	98.3	38.6	99.2
	10	>98.2	89.9	81.3	>99.9	>80.0	42.7	97.7	56.6	99.4
	5	>98.2	90.9	62.5	99.4	>80.0	41.7	96.2	51.8	98.8
	20	>98.2	89.6	82.5	>99.9	>80.0	41.4	98.5	53.0	99.4
10	15	>98.2	91.1	82.5	>99.9	>80.0	45.5	98.7	48.2	99.5
	10	>98.2	90.6	81.3	>99.9	>80.0	41.7	98.4	54.2	99.4
	5	73.6	88.4	77.5	97.7	>80.0	35.3	94.9	47.0	96.1
	20	95.6	89.9	81.3	>99.9	>80.0	43.5	98.1	51.8	99.5
	15	95.6	90.8	77.5	>99.9	>80.0	43.5	98.4	53.0	99.7
5	10	95.6	89.1	78.8	99.6	>80.0	36.6	97.9	42.2	99.3
	5	73.6	88.3	72.5	97.2	>80.0	32.5	93.1	27.7	96.0

* reactor nutrient loading BOD₅:N:P = 100:5:1, all others are 100:3.2:1.1

earlier, several metal removals were significantly lower for the 5-day sludge age reactors at 10° and 5°C . These included cadmium, iron, manganese, and zinc. Chromium and nickel concentrations appear dependent on sludge age and temperature. The percent removals ranged from 87.5 and 69.9 at $\theta_c = 20$ days and $T = \text{room temperature}$ to 72.5 and 27.7 at $\theta_c = 5$ days and $T = 5^{\circ}\text{C}$ for chromium and nickel, respectively.

The excellent removal of most metals is presumed to be largely due to two mechanisms. As found by other researchers (5, 7, 9, 34), high molecular weight extracellular polymers of the biofloc provided many functional groupings that acted as binding sites for the metals. This resulted in metal uptake by the sludge, with subsequent removal by sludge settling. Also, because of high pH levels in the mixed liquor, metal hydroxide and metal carbonate precipitation probably occurred. Of the metals analyzed, magnesium had the lowest percentage removal. The reason for this was that the pH was not high enough to cause chemical precipitation of magnesium hydroxide.

Table 10 presents the residual metal concentrations of the effluents and the strictest objectives of the local pollution control board (10). If the two reactors close to washout are not included, then nearly all of the objectives are met under nearly all operating conditions. Only iron and magnesium concentrations greatly exceed the objectives; and even then, this usually occurred under the low sludge age and/or temperature conditions. Although most iron removals exceeded 99.9 percent, the very high iron concentration (955 mg/L) in

TABLE 10

METAL CONCENTRATIONS OF THE AEROBICALLY BIOSTABILIZED EFFLUENTS

REACTOR DESCRIPTION		METAL CONCENTRATION (mg/L)								
T(°C)	θ_c (days)	Cd	Ca	Cr	Fe	Pb	Mg	Mn	Ni	Zn
Leachate Feed R.T.	20*	0.22	495	0.08	955	0.03	39.2	9.46	0.083	27.0
	20	<0.004	167	0.007	0.21	<0.006	25.1	0.253	0.024	0.07
15	20	<0.004	58.2	0.010	1.70	<0.006	20.1	0.096	0.025	0.09
	15	<0.004	43.0	0.011	0.75	<0.006	18.5	0.061	0.028	0.09
	10	<0.004	39.8	0.014	0.85	<0.006	20.6	0.114	0.034	0.11
	5	<0.004	34.8	0.015	7.10	<0.006	20.7	0.187	0.040	0.33
	20	<0.004	60.7	0.010	0.47	<0.006	19.3	0.140	0.029	0.09
	15	<0.004	53.3	0.011	0.57	<0.006	19.8	0.157	0.051	0.22
10	10	<0.004	49.9	0.015	0.87	<0.006	22.4	0.215	0.036	0.15
	5	<0.004	45.2	0.030	6.07	<0.006	22.8	0.364	0.040	0.32
	20	<0.004	51.4	0.014	2.08***	<0.006	22.9	0.140	0.039	0.16
	15	<0.004	44.3	0.014	0.24	<0.006	21.3	0.126	0.043	0.13
	10	<0.004	46.5	0.015	0.78	<0.006	22.8	0.154	0.038	0.15
	5	0.058	57.6	0.018	21.7	<0.006	25.3	0.487	0.044	1.04
5	20	0.009	49.9	0.015	0.73	<0.006	22.1	0.178	0.040	0.13
	15	0.009	45.3	0.018	0.67	<0.006	22.1	0.153	0.039	0.09
	10	0.009	54.0	0.017	3.80	<0.006	24.8	0.202	0.048	0.20
	5	0.058	57.9	0.022	26.8	<0.006	26.4	0.654	0.060	1.09
PCB**		0.005		0.1	0.3	0.05		0.05	0.3	0.5

* reactor nutrient loading BOD₅:N:P = 100:5:1, all others are 100:3.2:1.1

** British Columbia Pollution Control Objectives (10), Level AA Objectives

*** sample contaminated.

the leachate probably resulted in the high effluent concentrations.

From the limited data, it appears that the nutrient loadings used made little difference in metal removal efficiencies.

4 - 1.4 Removal of Nutrients

The removals of the basic nutrients, nitrogen and phosphorus, are presented in Table 11. Since the greatest concern is the nutrient concentration of the influent leachate feed and of the final effluent, the nutrient supplements added (to bring the nutrient loading to the proper level) are not incorporated in the calculation of the percentage removals. This method of calculation is also more conservative (in terms of percentage removals) than if the nutrient additions were included.

Total Kjeldahl nitrogen (TKN) removals were excellent. Except for the 5°C, 5-day sludge age reactor, removals were all greater than 94.8 percent, corresponding to a residual of 8.9 mg/L. Ammonia nitrogen (NH₃) removals were also high. Residual concentrations were all below 1.0 mg/L (the minimum detection level for the sample size used) except for the 5°C, 5-day reactor. The percent removals of TKN and NH₃ for the low temperature, low sludge age reactor were 78.8 and 82.3 percent, respectively.

The major difference between the control-reactor (BOD₅:N:P = 100:5:1) and the other reactors (BOD₅:N:P = 100:3.2:1.1) was the effluent nitrite-nitrate nitrogen

TABLE 11

NITROGEN (TKN, NH_3 , AND $\text{NO}_2^- - \text{NO}_3^-$) AND PHOSPHORUS (TOTAL) CONCENTRATIONS
(IN EFFLUENTS) AND REMOVALS BY THE BIOLOGICAL REACTORS

REACTOR DESCRIPTION		TKN		NH_3		$\text{NO}_2^- - \text{NO}_3^-$		TOTAL PHOSPHORUS	
T (°C)	θ_c (days)	mg/L	% ** REMOVAL	mg/L	% ** REMOVAL	mg/L	% ** REMOVAL	mg/L	% ** REMOVAL
Leachate Feed		172		130		< 0.05		5.3	
R.T.	20*	5.4	96.9	< 1	> 99.2	43	< 0	0.07	98.7
	20	4.9	97.2	< 1	> 99.2	0.17	< 0	0.28	94.7
	15	5.3	96.9	< 1	> 99.2	0.12	< 0	0.15	97.2
	10	5.8	96.6	< 1	> 99.2	0.07	< 0	0.13	97.5
	5	6.7	96.1	< 1	> 99.2	< 0.05		0.68	87.2
15	20	6.0	96.5	< 1	> 99.2	0.16	< 0	0.29	94.5
	15	6.5	96.2	< 1	> 99.2	0.18	< 0	0.24	95.5
	10	7.0	95.9	< 1	> 99.2	0.06	< 0	0.15	97.2
	5	7.4	95.7	< 1	> 99.2	< 0.05		0.61	88.5
10	20	5.9	96.6	< 1	> 99.2	0.11	< 0	0.19	96.4
	15	6.2	96.4	< 1	> 99.2	0.12	< 0	0.14	97.4
	10	8.1	95.3	< 1	> 99.2	0.12	< 0	0.19	96.4
	5	8.1	95.3	< 1	> 99.2	0.16	< 0	1.66	68.7
5	20	7.3	95.8	< 1	> 99.2	0.12	< 0	0.15	97.2
	15	8.1	95.3	< 1	> 99.2	0.06	< 0	0.19	96.4
	10	8.9	94.8	< 1	> 99.2	0.09	< 0	0.36	93.2
	5	36.4	78.8	23	82.3	0.19	< 0	2.52	52.5

* reactor nutrient loading $\text{BOD}_5:\text{N}:\text{P} = 100:5:1$, all others are 100:3.2:1.1

** Note: the nutrient additions are not included in the % removals,
(i.e. % REMOVAL = $\frac{[\text{LEACHATE FEED}] - [\text{EFFLUENT}]}{[\text{LEACHATE FEED}]} \times 100\%$)

(NO_2^- - NO_3^-) concentrations. The control-reactor effluent concentration was 43 mg/L, whereas the concentrations of all other effluents were below 0.2 mg/L. This indicates that nitrification occurred in the control-reactor and not enough excess nitrogen was present in the $\text{BOD}_5:\text{N}:\text{P} = 100:3.2:1.1$ loaded reactors for nitrification to occur.

This result is significant. It is evidence that a $\text{BOD}_5:\text{N}$ ratio of 20:1 is low. With this nitrogen loading level, in addition to unnecessary chemical costs, problems could arise with rising sludge in the settling tank. This occurs when nitrites and nitrates are converted to nitrogen gas, which then becomes trapped in the sludge mass. The sludge then becomes buoyant, leading to poor solids-liquid separation in the clarifier.

The nitrogen additions were in the form of NH_4^+ (as diammonium hydrogen phosphate and ammonium chloride). Eckenfelder and O'Connor (12) state that when a nutritional supplement is required for biological processes, ammonia nitrogen should be used, since it is readily assimilable. Hattingh (15) reports that several investigators have found that all inorganic nitrogen and only a portion of organic nitrogen is available for sludge growth. The portion of organic nitrogen available varied widely, depending on the waste. Uloth (33) suggested that, during his investigation, much of the ammonia in his leachate feed may have been stripped out of the high pH mixed liquor by the vigorous aeration. Cook and Foree (9) also encountered some ammonia stripping during their studies.

Therefore, it appears that although a nitrogen loading of $\text{BOD}_5:\text{N} = 100:3.2$ was applied to the reactors in this investigation, not all of the nitrogen was available for microbial assimilation if any ammonia stripping did occur. This leads to the question of "similarity" of the nutrient loadings of this investigation and that of Temoin's (31) optimum of $\text{BOD}_5:\text{N}:\text{P} = 100:3.19:1.11$. Temoin reports that his leachate TKN = 616 mg/L, but does not record what portion of this is NH_3 nitrogen. Thus, although the available nitrogen loadings were probably similar, the similarity cannot be fully verified.

The removal of phosphorus was good. Excluding the 5-day sludge age reactors, all removals were greater than 93.2 percent. The 5-day reactor removals ranged from 87.2 to 52.5 percent - progressively worse as the temperature decreased. As expected, the control reactor, which had the least phosphorus added, demonstrated the best removal. Not including the two reactors near washout, all residual phosphorus levels met the local pollution control "AA" level objective (10) of 1.5 mg/L.

A possible explanation as to why the low $\text{BOD}_5:\text{N}:\text{P}$ loading of $100:3.2:1.1$ was so effective in the treatment of the leachate could be the presence of the actinomycete *Geodermatophilus* bacteria, mentioned previously. As reported, during Temoin's (31) investigation, at the higher phosphorus loading of $\text{BOD}:\text{P} = 100:1.11$, 90 percent of the biological floc consisted of *Geodermatophilus*, which had never been

isolated in a sewage treatment system before (to this author's knowledge). Although the Geodermatophilus cell tissue composition is probably similar to that of bacteria common to activated sludge plants, the metabolism of the Geodermatophilus could be sufficiently different to account for this difference in nutrient requirements (26).

Unfortunately, no microscopic examination of the mixed liquor was done in this study to confirm the presence of the Geodermatophilus. This verification was not done because this author did not learn of the Geodermatophilus until after the completion of the laboratory portion of this study.

4 - 2 Lime-Magnesium Coagulation Phase

The initial pH, acidity, alkalinity and lime dosages required for the samples that underwent the lime-magnesium process are shown in Table 12. The lime dosages shown were determined by adding lime until the pH stabilized at the desired level. As the Mg^{++} dose increased, the final pH dropped. The drop in pH was about 0.1 pH units at the low lime (pH = 10.0), low magnesium (0 mg/L) dose, up to 1.0 pH units at the high lime (pH = 11.4), high magnesium (50 mg/L) dose. This indicates that $Mg(OH)_2$, and probably other metal hydroxide precipitates, formed.

The results of organic material, suspended solids, and phosphorus concentrations and removals appear in Table 13. Although the percent removals of BOD_5 from the lower strength sample (SAMPLE 1) are fairly high (particularly at the high lime

TABLE 12

pH, ACIDITY, ALKALINITY, AND LIME
DOSAGES REQUIRED OF THE SAMPLES
USED FOR LIME-MAGNESIUM COAGULATION

PARAMETER	SAMPLE 1	SAMPLE 2
pH	7.7	7.2
Acidity to pH = 8.3 as CaCO_3 (mg/L)	16	37
Alkalinity to pH = 3.7 as CaCO_3 (mg/L)	384	414
Ca(OH)_2 Dosage (mg/L) for pH 10.0	228	329
Ca(OH)_2 Dosage (mg/L) for pH 10.7	307	408
Ca(OH)_2 Dosage (mg/L) for pH 11.4	433	549

TABLE 13

EFFLUENT ORGANIC MATERIAL (IN TERMS OF BOD₅ AND COD), SUSPENDED SOLIDS,
AND TOTAL PHOSPHORUS CONCENTRATIONS AND REMOVALS BY COAGULATION

SAMPLE DESCRIPTION			BOD ₅		COD		TSS		TVSS		TOTAL P	
SAMPLE NUMBER	pH	Mg ⁺⁺ DOSE (mg/L)	mg/L	% REMOVAL	mg/L	% REMOVAL	mg/L	% REMOVAL	mg/L	% REMOVAL	mg/L	% REMOVAL
1	7.7	Not Polished	7.5		204		6		3		0.19	
	10.0	0	3.5	53	194	5	48	<0	3	0	0.08	58
		10	3.5	53	196	4	47	<0	2	33	0.08	58
		20	3.0	60	192	6	77	<0	3	0	0.06	68
		35	3.3	56	188	8	54	<0	3	0	0.08	58
		50	2.9	61	192	6	63	<0	4	<0	0.10	47
	10.7	0	3.3	56	192	6	33	<0	3	0	0.09	53
		10	2.0	73	192	6	24	<0	2	33	0.09	53
		20	2.0	73	194	5	24	<0	4	<0	0.09	53
		35	2.0	73	190	7	42	<0	5	<0	0.09	53
		50	2.1	72	190	7	29	<0	2	33	0.07	63
	11.4	0	2.0	73	192	6	36	<0	4	<0	0.10	47
		10	1.7	77	190	7	58	<0	7	<0	0.06	68
		20	1.6	79	190	7	74	<0	10	<0	0.09	53
		35	1.3	83	186	9	105	<0	12	<0	0.10	47
		50	1.5	80	186	9	105	<0	13	<0	0.09	53
2	7.2	Not Polished	52		462		100		58		1.14	
	10.0	0	45	13	421	9	92	8	15	74	0.51	55
		10	36	31	433	6	109	<0	19	67	0.64	44
		20	41	21	425	8	83	17	13	78	0.44	61
		35	36	31	421	9	82	18	17	71	0.45	61
		50	37	39	437	5	102	<0	20	66	0.51	55
	10.7	0	27	48	433	6	98	2	18	69	0.63	45
		10	27	48	449	3	101	<0	17	71	0.63	45
		20	29	44	433	6	102	<0	18	69	0.65	43
		35	28	46	431	7	96	4	16	72	0.72	37
		50	30	42	429	7	98	2	24	59	0.58	49
	11.4	0	50	4	421	9	71	29	24	59	0.52	54
		10	41	21	413	11	54	46	21	64	0.36	68
		20	40	23	401	13	48	52	19	67	0.29	75
		35	41	21	397	14	42	58	15	74	0.28	75
		50	36	31	423	8	51	49	22	64	0.26	77

dosage), the absolute removals were very low. A BOD_5 removal of just 6 mg/L resulted in a 80 percent removal. For the higher strength sample (SAMPLE 2 BOD_5 = 52 mg/L), almost 50 percent BOD_5 removal was achieved at the medium lime dose (pH = 10.7). The maximum COD removal obtained for either sample was 14 percent. This indicates that the lime-magnesium process was much more effective in removing biologically degradable organic matter, than biologically resistant organic matter. The reason for this is not apparent. However, it is not an item of extreme importance since the primary concern is BOD_5 - this is an indication of the oxygen demand by the effluent on receiving waters.

For SAMPLE 1, the suspended solids levels were increased (<0 percent removal) up to about seventeen-fold by the coagulation process. This was due to the initial low suspended solids levels and the fact that some of the chemicals added remained suspended. The removal of total suspended solids was generally poor for SAMPLE 2. At the high lime dosage, however, "reasonable" removals of up to 58 percent were achieved.

The removal of total phosphorus did not follow a trend with the varying lime and magnesium dosages; but, the highest three percentage removals did occur at the high lime and highest three magnesium dosages for SAMPLE 1. The range of total phosphorus removal was from 37 to 77 percent. The highest phosphorus residual remaining was 0.72 mg/L, well below the local "AA" level (10) of 1.5 mg/L.

The results of the metal concentrations and removals are presented in Tables 14 and 15. In general, the removals did not increase markedly with increasing lime and/or magnesium dosages. This was probably due, in part, to the very low initial concentrations of the metals. From Table 15, the relative order of metal removal efficiencies were: Cd, Mn, Fe, Zn, Cr, Ni, Ca, and Mg. As expected, Ca and Mg had the lowest removals since these metals were added to the samples for the coagulation process. From Table 14, only iron concentrations of effluents from SAMPLE 2 substantially exceeded the local level "AA" objectives (10). Also, several of the effluents from SAMPLE 2 exceeded the allowable Mn concentration of 0.05 mg/L. The level "AA" objectives are met for all the parameters measured for the effluents of SAMPLE 1.

In general, removals were not enhanced significantly by the magnesium additions. Greater than 20 mg/L of Mg^{++} was already present in both samples, before any magnesium addition; hence, magnesium hydroxide precipitation occurred even in the samples without magnesium additions.

Table 14 shows a gain in concentrations of Ca and Mg for some of the effluents. This indicates that some of the Ca and Mg added remained in solution and did not precipitate out as $CaCO_3$ and $Mg(OH)_2$. Therefore, two means of improving removals by the lime-coagulation process are apparent. The first would be to increase the lime dosage to a pH level of, say, 12.0. This would lead to greater precipitation of $Mg(OH)_2$ and the other metallic hydroxides. The precipitation

TABLE 14

METAL CONCENTRATIONS OF THE FINAL EFFLUENTS
POLISHED BY THE LIME-MAGNESIUM PROCESS

SAMPLE DESCRIPTION			METAL CONCENTRATION (mg/L)							
SAMPLE NUMBER	pH	Mg ⁺⁺ DOSE (mg/L)	Cd	Ca	Cr	Fe	Mg	Mn	Ni	Zn
1	10.0	Not Polished	<0.001	40	0.011	0.66	20.1	0.10	0.039	0.16
		0	<0.001	20	0.007	0.21	17.4	0.01	0.035	0.08
		10	<0.001	32	0.007	0.17	29.0	0.01	0.034	0.09
		20	<0.001	33	0.010	0.18	39.3	0.01	0.039	0.09
		35	<0.001	42	0.005	0.22	54.0	0.02	0.038	0.16
	10.7	50	<0.001	45	0.006	0.13	65.4	0.01	0.037	0.07
		0	<0.001	22	0.006	0.14	16.1	0.02	0.033	0.10
		10	<0.001	26	0.006	0.14	25.5	0.02	0.031	0.09
		20	<0.001	38	0.006	0.17	35.3	0.02	0.030	0.23
		35	<0.001	45	0.007	0.15	50.6	0.02	0.031	0.14
	11.4	50	<0.001	44	0.007	0.13	63.5	0.02	0.030	0.42
		0	<0.001	31	0.007	0.19	14.1	0.03	0.030	0.11
		10	<0.001	38	0.007	0.18	20.0	0.03	0.030	0.14
		20	<0.001	45	0.008	0.17	26.0	0.03	0.028	0.11
		35	<0.001	59	0.007	0.14	35.5	0.02	0.028	0.43
2	10.0	Not Polished	<0.001	68	0.007	0.28	52.9	0.02	0.028	0.19
		0	0.004	44	0.016	20.4	23.2	0.38	0.041	0.79
		10	0.001	36	0.011	6.8	19.9	0.10	0.038	0.22
		20	0.001	39	0.010	10.8	30.3	0.09	0.039	0.19
		35	0.002	40	0.010	6.7	39.5	0.08	0.037	0.23
	10.7	50	0.002	38	0.009	6.7	54.3	0.08	0.037	0.23
		0	0.002	43	0.008	6.5	65.1	0.08	0.035	0.30
		10	0.001	34	0.010	9.9	17.2	0.19	0.034	0.20
		20	0.001	37	0.013	10.7	28.6	0.14	0.032	0.34
		35	0.001	39	0.010	10.3	38.7	0.13	0.033	0.29
	11.4	50	<0.001	40	0.009	9.7	51.7	0.12	0.033	0.32
		0	<0.001	38	0.013	8.5	61.5	0.10	0.031	0.25
		10	<0.001	23	0.011	7.8	10.7	0.17	0.029	0.18
		20	<0.001	21	0.011	4.2	11.8	0.10	0.025	0.15
		35	<0.001	25	0.007	3.4	16.3	0.08	0.025	0.09
P.C.B. Objectives*		50	<0.001	26	0.008	2.0	23.6	0.05	0.016	0.17
			<0.001	34	0.009	3.2	52.5	0.06	0.027	0.28
			0.005		0.1	0.3		0.05	0.3	0.5

* British Columbia Pollution Control Objectives (10),
Level AA Objectives

TABLE 15

METAL REMOVALS BY LIME-MAGNESIUM COAGULATION

SAMPLE DESCRIPTION			PERCENT REMOVAL OF THE METAL							
SAMPLE NUMBER	pH	Mg ⁺⁺ DOSE (mg/L)	Cd	Ca	Cr	Fe	Mg	Mn	Ni	Zn
1	10.0	0		50	36	68	13	90	10	50
		10		20	36	74	<0	90	13	44
		20		18	9	73	<0	90	0	44
		35		<0	55	67	<0	80	3	<0
		50		<0	45	80	<0	90	5	56
	10.7	0		45	45	79	20	80	15	38
		10		35	45	79	<0	80	21	44
		20		5	45	74	<0	80	23	0
		35		<0	36	77	<0	80	21	13
		50		<0	36	80	<0	80	23	0
	11.4	0		23	36	71	30	70	23	32
		10		5	36	73	1	70	23	13
		20		<0	27	74	<0	70	26	32
		35		<0	36	79	<0	80	26	<0
		50		<0	27	58	<0	80	26	<0
2	10.0	0	66	18	31	67	14	74	7	72
		10	62	11	38	47	<0	76	5	76
		20	58	9	38	67	<0	79	10	71
		35	61	14	44	67	<0	79	10	71
		50	61	2	50	68	<0	79	15	62
	10.7	0	67	23	38	51	26	50	17	75
		10	69	16	19	48	<0	63	22	57
		20	73	11	38	50	<0	66	20	63
		35	89	9	44	52	<0	68	20	59
		50	89	14	19	58	<0	74	24	68
	11.4	0	>90	48	31	62	54	55	29	77
		10	>90	53	31	79	50	74	39	81
		20	>90	43	56	83	30	79	39	89
		35	>90	41	50	90	<0	87	61	78
		50	>90	23	44	84	<0	84	34	65

of $\text{Mg}(\text{OH})_2$ would also aid in the removal of organics and suspended solids (as discussed in Section 2 - 2.2).

Secondly, if the alkalinities of the samples were raised by adding carbonate, all (as much as practically possible) of the Ca^{++} would precipitate out as CaCO_3 . Calcium carbonate is soluble to the extent of about 17 mg/L (28), whereas Ca^{++} concentrations were as high as 68 mg/L (= 170 mg/L as CaCO_3) in the effluents, thus indicating a carbonate deficiency. The best method of increasing the carbonate concentration would be through the use of recycled magnesium, in the form of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$. In some cases though, this carbonate may not be sufficient and more may have to be added. Although the alkalinity of SAMPLES 1 and 2 were around 400 mg/L, it appears that much of it was not due to the carbonate system.

It should be noted that the results from the lime-magnesium phase are very preliminary. The lack of sample volume limited the jar testing to just one run. A more detailed study is required before more definitive conclusions can be drawn.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5 - 1 Conclusions

- 1) Aerobic biostabilization is an effective means of removing contaminants from a medium strength leachate ($BOD_5 = 8090 \text{ mg/L}$).
- 2) In the ranges of temperature (ambient air temperatures from 25° to 5°C and corresponding liquid temperatures from 18° to 3°C) and sludge ages (from 20 to 5 days) investigated, the removals of contaminants were only nominally dependent on temperature and sludge age. The exceptions were when the sludge ages were close to or lower than the "minimum" sludge age as predicted by the kinetic parameters at a given temperature. This occurred for the 5-day sludge age reactors at 10° and 5°C .
- 3) The treatment performance of the reactors was excellent. Excluding the two reactors close to washout conditions, filtered effluents (using Whatman No. 4 filter paper) met the most stringent local pollution control objectives (10) for nearly all of the parameters monitored, under nearly all operational conditions. Only iron and magnesium concentrations greatly exceeded the objectives, and even then, this usually only occurred under adverse conditions (low sludge age and/or temperature).
- 4) For the leachate treated, a $BOD_5:N:P$ loading of 100:3.2:1.1 was "adequate". The efficiencies of the reactors under this loading were comparable to the control-reactor, which

had a standard loading of 100:5:1. The conventional $\text{BOD}_5:\text{N} = 20:1$ loading was found to be low. In the control reactor, the surplus nitrogen, not assimilated by the microorganisms, resulted in nitrification. This was evident by the nitrite-nitrate concentration of 43 mg/L in the control reactor effluent. The nitrite-nitrate concentrations of all the other reactors were below 0.2 mg/L.

- 5) The additions of magnesium in the lime-magnesium process did not enhance removal efficiencies significantly. This was due, in part, to the initial low concentrations of contaminants and also because there already existed greater than 20 mg/L of magnesium in the samples. Better performance of the lime-magnesium process could be accomplished by increasing the lime dosage (to $\text{pH} = 12$ for better magnesium hydroxide precipitation) and/or raising the alkalinity by adding carbonate (for better calcium carbonate precipitation).
- 6) Aerobic biostabilization at a sludge age greater than 15 days and liquid temperature of at least 3°C , followed by lime precipitation (to pH greater than or equal to 10.0) is capable of reducing contaminants of a medium strength leachate ($\text{BOD}_5 = 8090 \text{ mg/L}$), to levels below the local (Province of British Columbia) pollution control objectives.

5 - 2 Recommendations

- 1) Although a low $\text{BOD}_5\text{:N:P}$ loading of 100:3.2:1.1 has been shown to be effective, an even lower nutrient loading may be just as effective. Although Temoin (31) did attempt to optimize the nutrient loading level, a more comprehensive study is required. In particular, $\text{BOD}_5\text{:N}$ loadings of less than 100:3.19 and $\text{BOD}_5\text{:P}$ loadings between 100:0.32 and 100:1.11 should be more thoroughly investigated. The effect of sludge age (or F/M ratio) on nutrient requirements also warrants further research.
- 2) In conjunction with the above recommendation, a study of the stoichiometry of the leachate treatment process should be conducted. As previously discussed, the *Geodermatophilus* organism may have a different metabolism, and thus, possibly, different nutritional requirements than the population of microorganisms normally found in a domestic activated sludge plant. By following a procedure as outlined (with minor modifications) in Experiment XVIII - 1 of "Environmental Engineering Unit Operations and Unit Processes Laboratory Manual" (23), the stoichiometry of the processes can be determined. This will not only confirm or deny different metabolisms as a reason for the low nutrient requirements, but will also lead to a better understanding of the process. In addition, an assay of the *Geodermatophilus* should be done to confirm that the carbon-hydrogen-nitrogen-oxygen content is similar to that of the microorganisms normally present in an activated sludge plant ($\text{C}_5\text{H}_7\text{NO}_2$).

- 3) The problem of poor solids-liquid separation should be addressed in more detail. Settling problems have been encountered in a number of "aerobic biostabilization of leachate" studies. Good sludge settleability is extremely crucial in the operation of the process. Zapf-Gilje (34) and Graham (14) attribute the settling problems mainly to the repeated shock loadings of the fill-and-draw procedure, rather than to biomass reaction to the feed. Although this is likely to be an important reason, it is questionable whether this is the major cause. Palit and Qasim (24) ran a continuous flow system and sludge bulking occurred several times. Cook and Foree (9), Uloth (33), and Temoin (31) all used the fill-and-draw procedure without any serious settling problems.

Eckenfelder and Ford (11) list excessive organic loading as a possible cause of sludge bulking. The F/M ratios were less than $0.17 \frac{\text{kg BOD}_5/\text{day}}{\text{kg MLVSS}}$ for the three troublefree studies mentioned above. The systems of Palit and Qasim (24), Zapf-Gilje (34) and Graham (14) all had F/M ratios greater than $0.17 \frac{\text{kg BOD}_5/\text{day}}{\text{kg MLVSS}}$. In this investigation, the lower sludge age (5 and 10 days) reactors experienced settling problems. These reactors all had F/M ratios close to or exceeding 0.17. The higher sludge age (15 and 20 days) reactors all had F/M ratios less than 0.16.

The above evidence seems to indicate that F/M loading might be more important than the mode of operation (continuous flow or fill-and-draw).

Another possible factor may be temperature. The three studies in which no settling problems were encountered were operated at room temperature. The studies of Zapf-Gilje, Graham and this investigation were operated at temperatures ranging from 5° to 25°C. As temperature decreased, sludge settleability grew worse. Thus, the effect of temperature and/or the effect of different organism species (ie. mesophiles versus psychrophiles) should be investigated further.

- 4) The lime-magnesium process should be investigated more comprehensively. Two additional aspects that should be included are a lime dosage to raise the pH level to 12.0, and adding carbonate to the samples, to improve the removals of Ca^{++} and Mg^{++} as CaCO_3 and $\text{Mg}(\text{OH})_2$.
- 5) The quality and quantity of leachate generated is highly variable from season to season. The strength of the leachate also decreases as the age of a landfill increases. Therefore, rather than having a separate leachate treatment facility, it seems reasonable that a savings in treatment costs might be realized if leachate could be treated, along with domestic wastewater, in existing activated sludge plants. To date, only rudimentary studies (4, 31) have been conducted on combined treatment. A much more rigorous investigation is warranted.

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APPENDICES

APPENDIX A

Determination of Biological Treatment Kinetic Coefficients

The relationship between biological growth and substrate utilization is formulated in two basic equations by Lawrence and McCarty (17).

The first equation, developed empirically from waste treatment studies, describes the relationship between net rate of growth and rate of substrate utilization:

$$\frac{dX}{dt} = Y \frac{dF}{dt} - bX \quad (A.1)$$

where $\frac{dX}{dt}$ = net growth rate of microorganisms per unit volume of reactor (mass per volume-time)

Y = growth yield coefficient (mass of microorganisms per mass of substrate utilized)

$\frac{dF}{dt}$ = rate of microbial substrate utilization per unit volume (mass per volume-time)

b = microorganism decay coefficient (time^{-1})

X = microbial mass concentration (mass per volume)

The second equation relates the rate of microbial substrate utilization to the concentration of microorganisms and the concentration of substrate surrounding the microorganisms:

$$\frac{dF}{dt} = \frac{kXS}{K_s + S} \quad (A.2)$$

where k = maximum rate of substrate utilization per unit weight of microorganisms (time^{-1})

S = concentration of substrate surrounding the microorganisms (mass per volume)

K_s = half velocity coefficient, equal to the substrate concentration when $dF/dt = (\frac{1}{2})k$ (mass per volume)

Using the two basic equations, the kinetic coefficients Y , b , k , and K_s can be graphically determined from laboratory data (22).

Dividing both sides of Equation A.1 by X gives:

$$\frac{dX/dt}{X} = Y \frac{dF/dt}{X} - b \quad \dots \dots \dots (A.3)$$

Substituting $\frac{dX/dt}{X} = \frac{1}{\theta_c}$ and $\frac{dF}{dt} = \frac{S_o - S}{\theta_c}$

(where S_o = concentration of substrate in influent) into Equation A.3 gives:

$$\frac{1}{\theta_c} = Y \frac{(S_o - S)}{X\theta_c} - b \quad \dots \dots \dots (A.4)$$

Therefore, from a plot of $\frac{1}{\theta_c}$ versus $\frac{S_o - S}{X\theta_c}$, the y-intercept = $-b$ and the slope = Y

Rearranging Equation A.2 and substituting $\frac{dF}{dt} = \frac{S_o - S}{\theta_c}$ gives:

$$\frac{X\theta_c}{S_o - S} = \frac{K_s}{k} \frac{1}{S} + \frac{1}{k} \quad \dots \dots \dots (A.5)$$

Therefore, from a plot of $\frac{X\theta_c}{S_o - S}$ versus $\frac{1}{S}$, the y-intercept = $\frac{1}{k}$ and the slope = $\frac{K_s}{k}$

After the kinetic coefficients have been determined, the theoretical minimum mean cell retention time, θ_c^M , at which process failure occurs, can be calculated.

A materials balance for a reactor is written as

(17):

$$\left(\text{Net Rate of Change} \right) \left(\text{of Microbial Mass} \right) = (\text{Growth Rate}) - (\text{Washout Rate})$$

$$V \left(\frac{dX}{dt} \right)_n = \left(Y \frac{dF}{dt} - bX \right) V - QX \quad \dots \dots \dots (A.6)$$

where V = reactor volume (volume)

Q = flow rate (volume per time)

When steady state conditions exist, $\left(\frac{dX}{dt} \right)_n = 0$,

$$\text{then } \frac{1}{\theta_c} = Y \frac{dF/dt}{X} - b \quad \dots \dots \dots (A.7)$$

since $Q/V = \theta_c$ when there is no recycle.

Substituting Equation A.2 into Equation A.7 gives:

$$\frac{1}{\theta_c} = \frac{YkS}{k_s + S} - b \quad \dots \dots \dots (A.8)$$

When $\theta_c = \theta_c^M$ (the mean cell residence time at which the microorganisms are washed out of the system faster than they can reproduce), the effluent waste concentration, S , is equal to the influent waste concentration, S_o . Hence,

$$\frac{1}{\theta_c^M} = \frac{YkS_o}{k_s + S_o} - b \quad \dots \dots \dots (A.9)$$

The laboratory data used to determine the kinetic coefficients is shown in Table 16. The graphical determination of the coefficients is shown in Figures 3 to 10. The kinetic coefficient results and the calculated θ_c^M 's are tabulated in Table 17.

TABLE 16

COMPUTATION TABLE FOR THE GRAPHICAL DETERMINATION
OF KINETIC COEFFICIENTS

REACTOR DESCRIPTION		S_o (mg/L)	S (mg/L)	X (mg/L)	$\frac{1}{\theta_c}$ (days ⁻¹)	$\frac{1}{\bar{S}}$ (L/mg)	$\frac{S_o - S}{X\theta_c}$ (days ⁻¹)	$\frac{X\theta_c}{S_o - S}$ (days)
T (°C)	θ_c (days)							
R.T.	20	8090	9	3490	0.050	0.111	0.116	8.64
	15	8090	11	3470	0.067	0.091	0.155	6.44
	10	8090	25	3650	0.100	0.040	0.221	4.53
	5	8090	44	4000	0.200	0.023	0.402	2.49
15	20	8090	7	3690	0.050	0.143	0.110	9.13
	15	8090	9	3430	0.067	0.111	0.157	6.37
	10	8090	20	3520	0.100	0.050	0.229	4.36
	5	8090	51	3790	0.200	0.020	0.424	2.36
10	20	8090	9	3810	0.050	0.111	0.106	9.43
	15	8090	16	3860	0.067	0.063	0.139	7.17
	10	8090	17	4220	0.100	0.059	0.191	5.23
	5	8090	112	4040	0.200	0.009	0.395	2.53
5	20	8090	14	4070	0.050	0.071	0.099	10.08
	15	8090	20	4350	0.067	0.050	0.124	8.09
	10	8090	42	4790	0.100	0.024	0.168	5.95
	5	8090	188	4320	0.200	0.005	0.366	2.73

Note: S_o and S are soluble BOD₅ concentrations

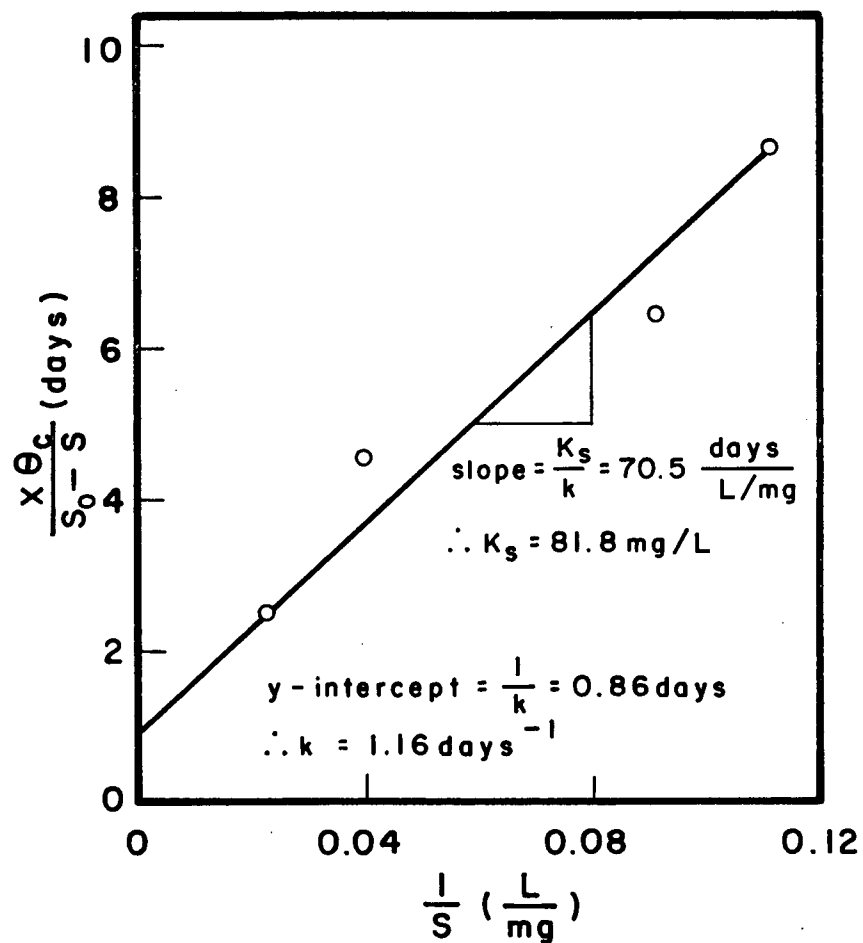


FIGURE 3

DETERMINATION OF k AND K_s
AT ROOM TEMPERATURE

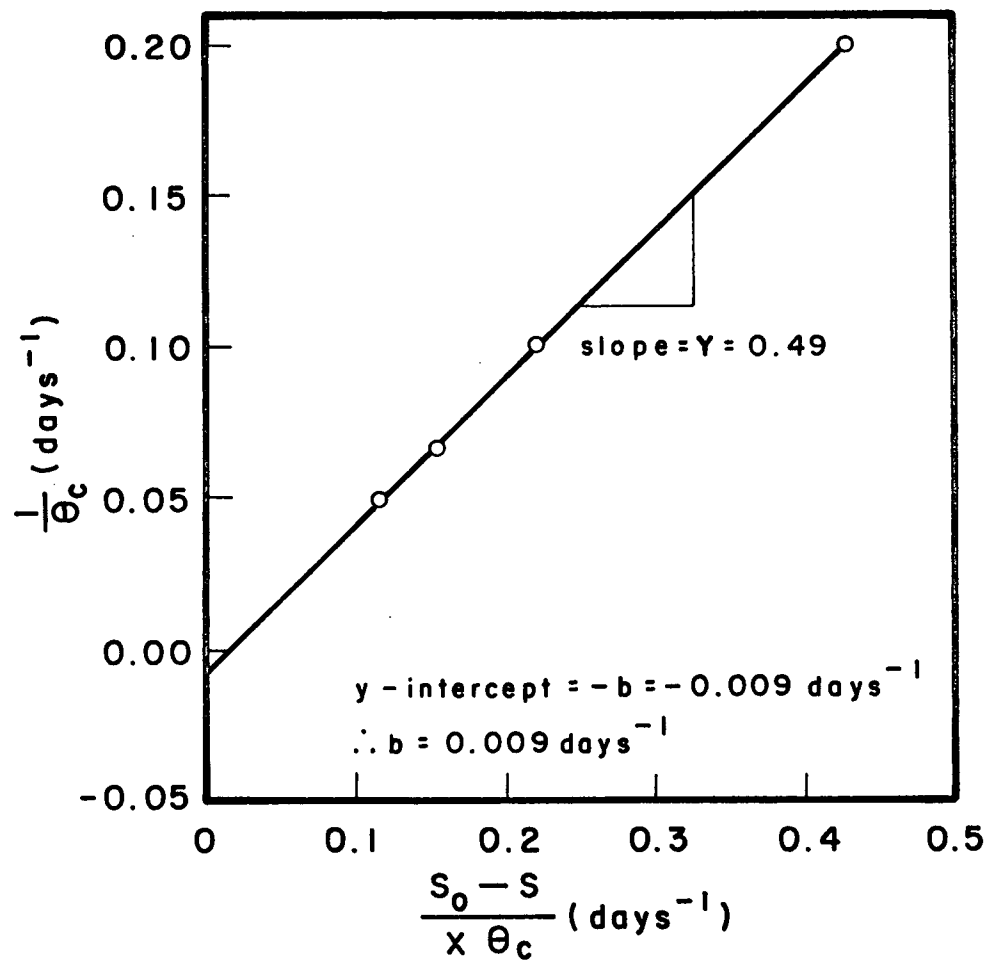


FIGURE 4

DETERMINATION OF Y AND b AT
ROOM TEMPERATURE

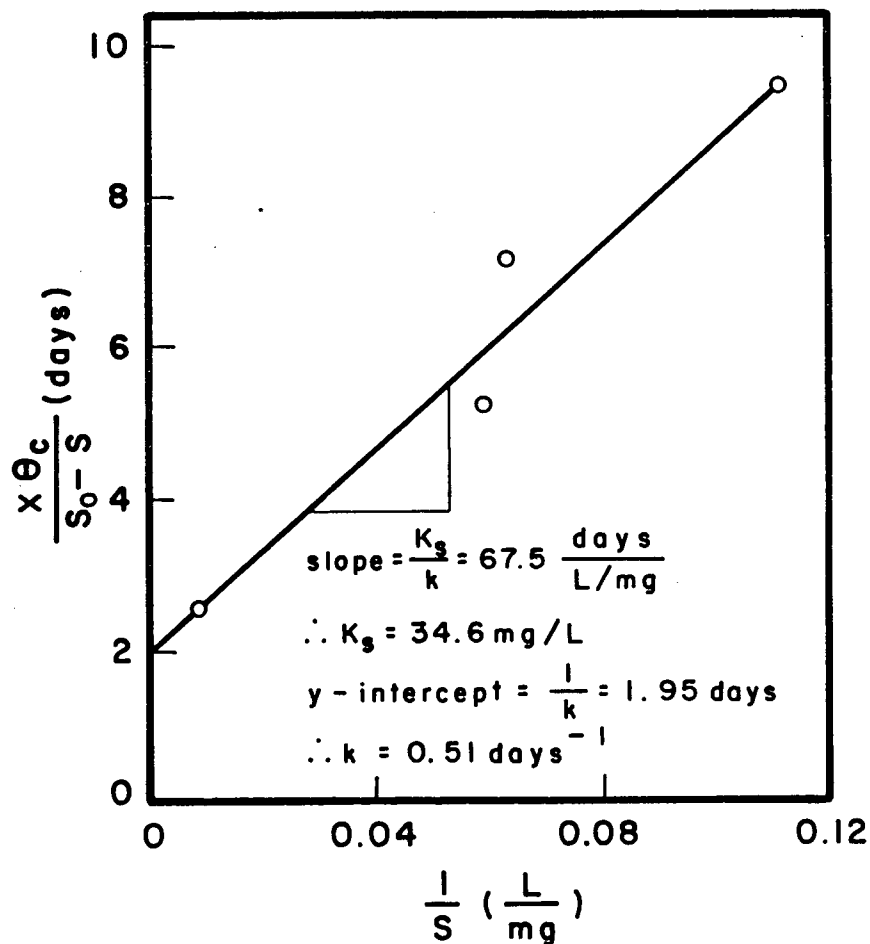


FIGURE 7

DETERMINATION OF k AND K_s
AT 10°C

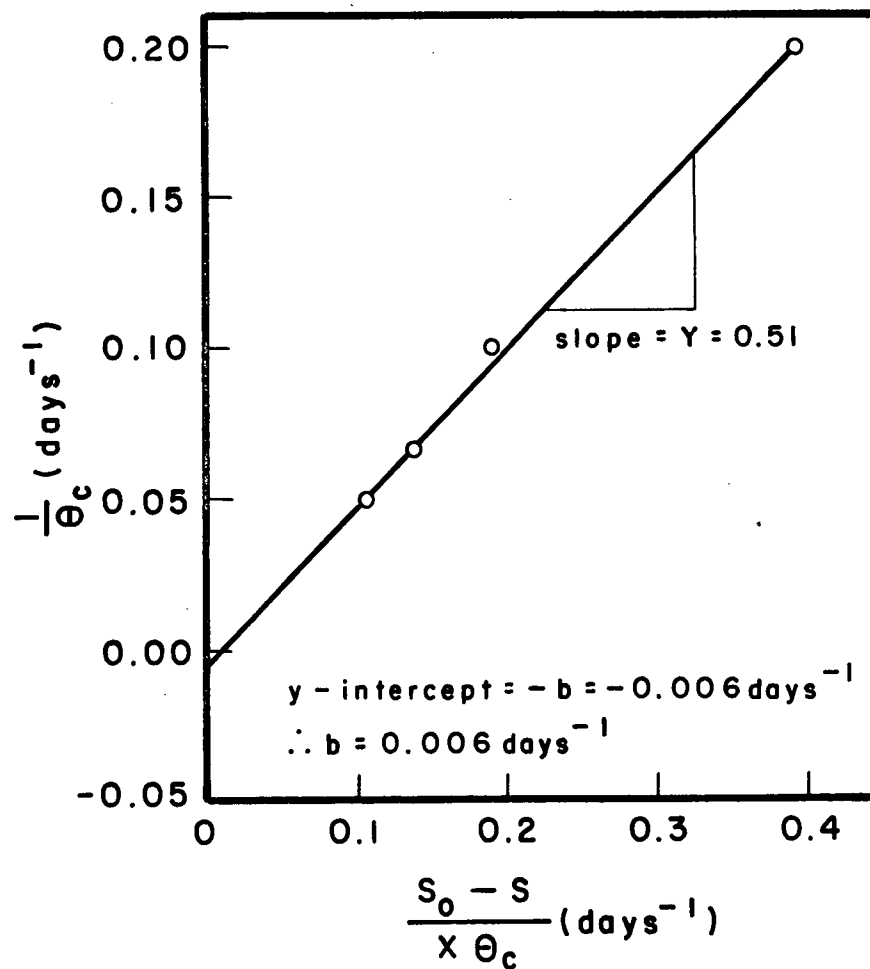


FIGURE 8

DETERMINATION OF Y AND b
AT 10°C

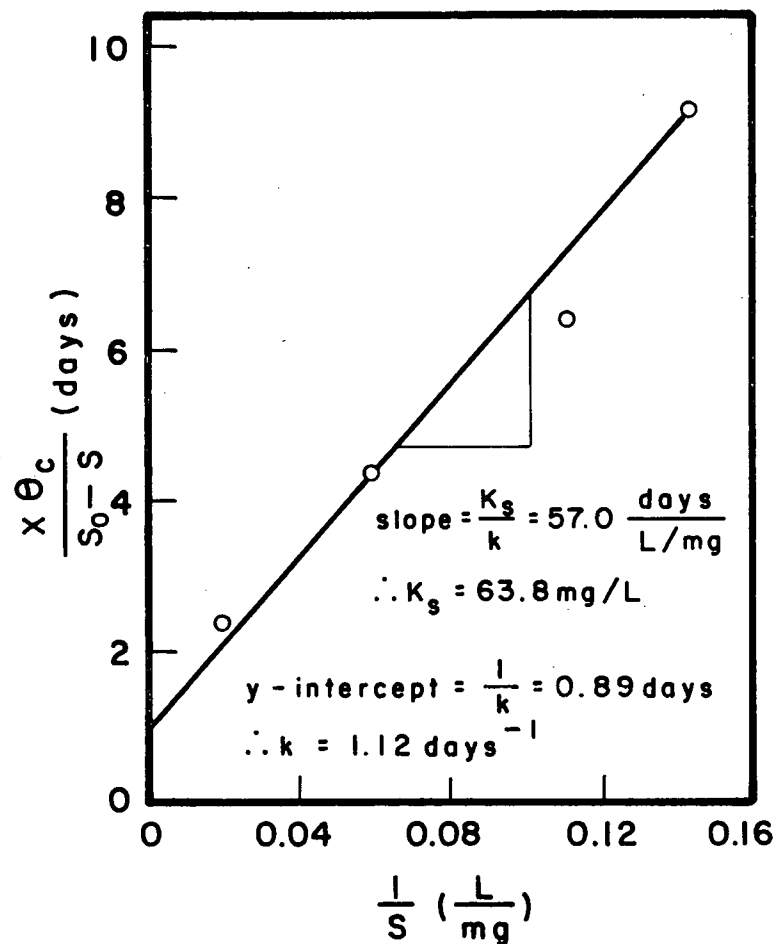


FIGURE 5

DETERMINATION OF k AND K_s
AT 15°C

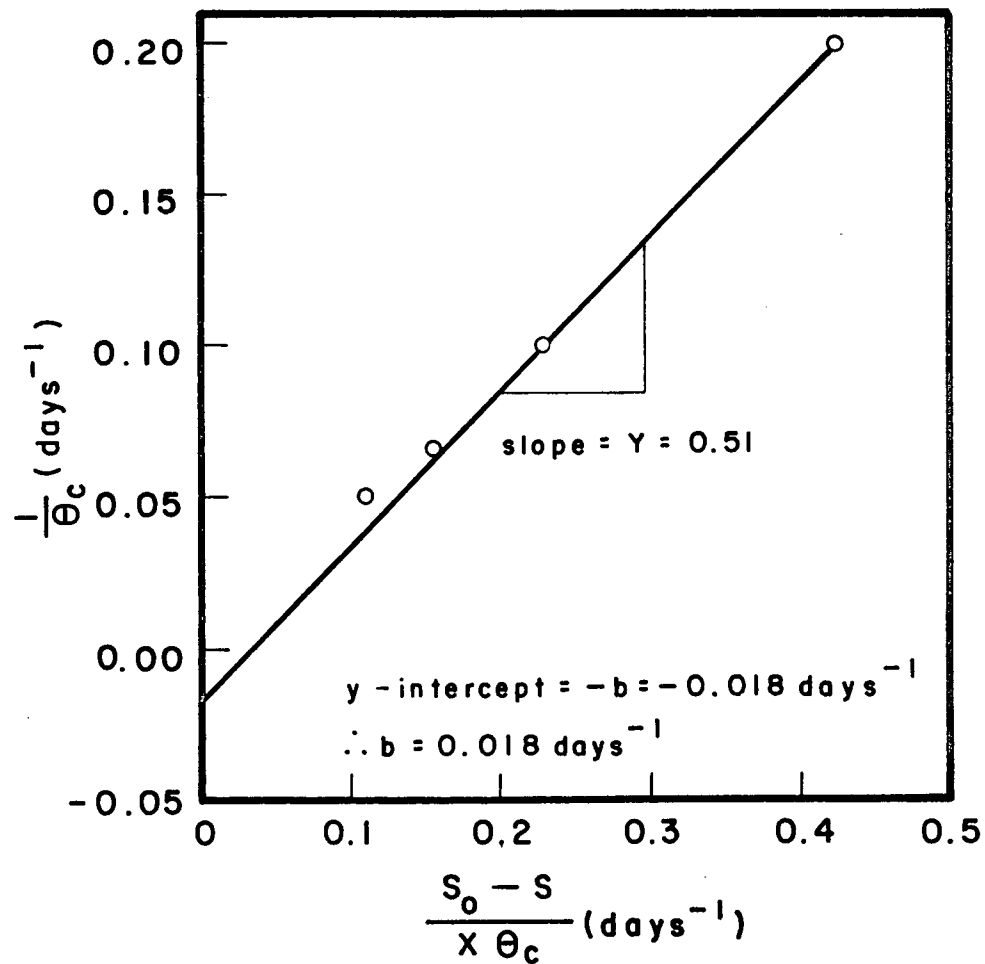


FIGURE 6

DETERMINATION OF Y AND b
AT 15°C

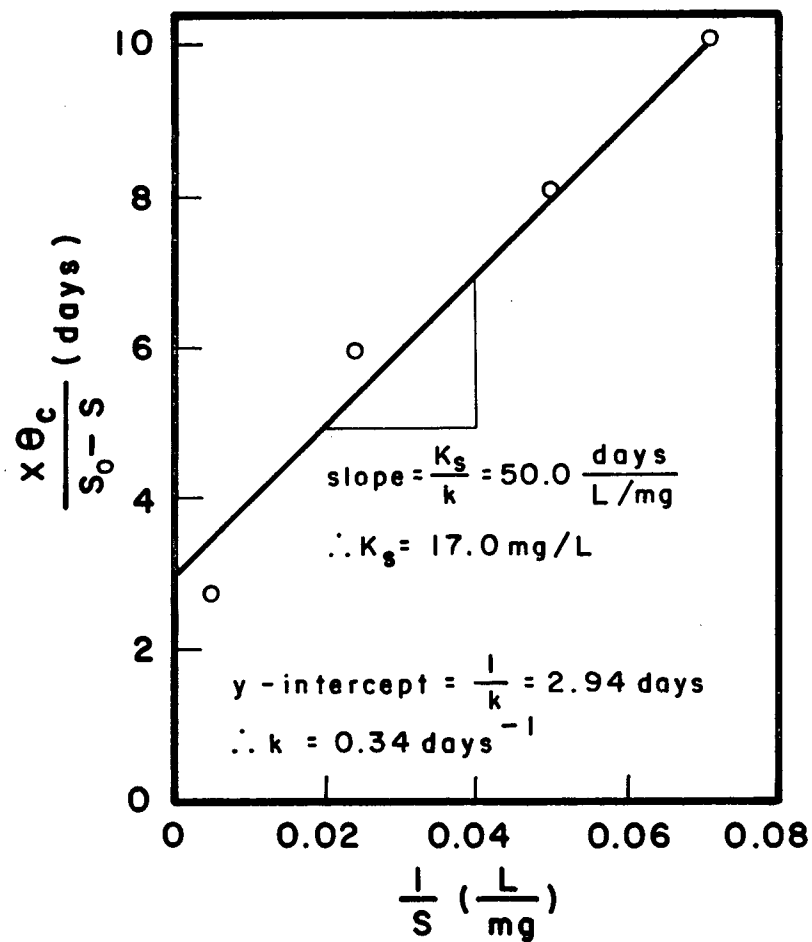


FIGURE 9

DETERMINATION OF k AND K_s
AT 5°C

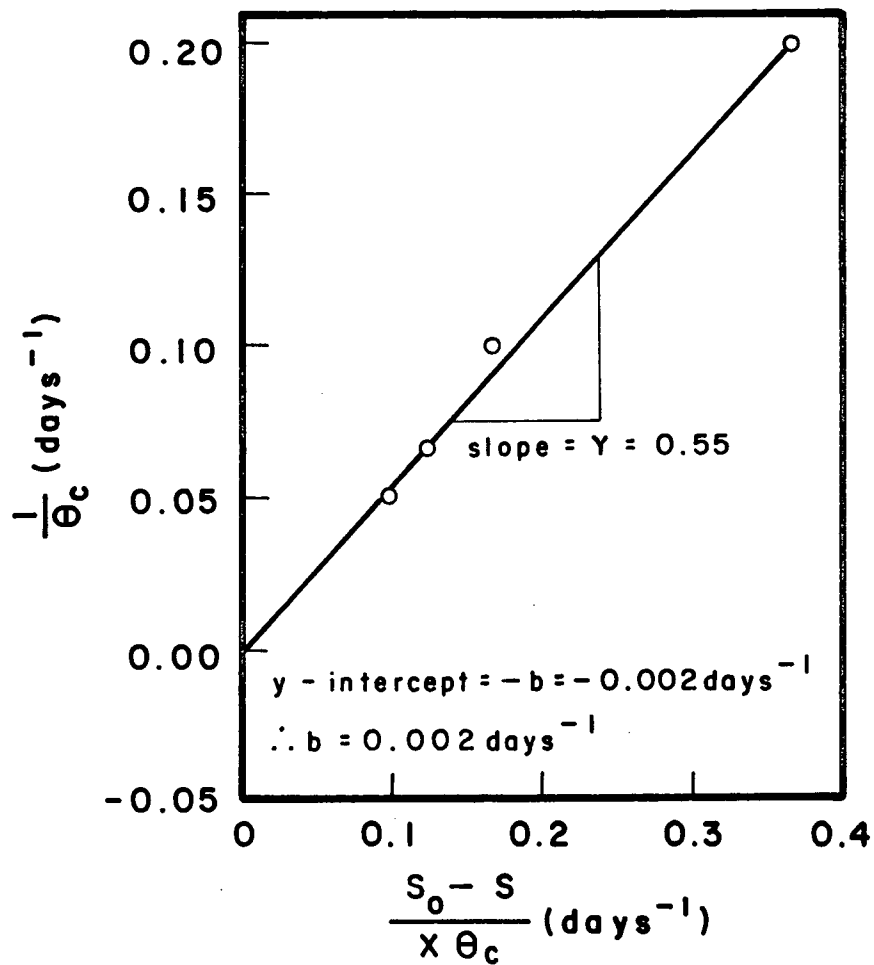


FIGURE 10

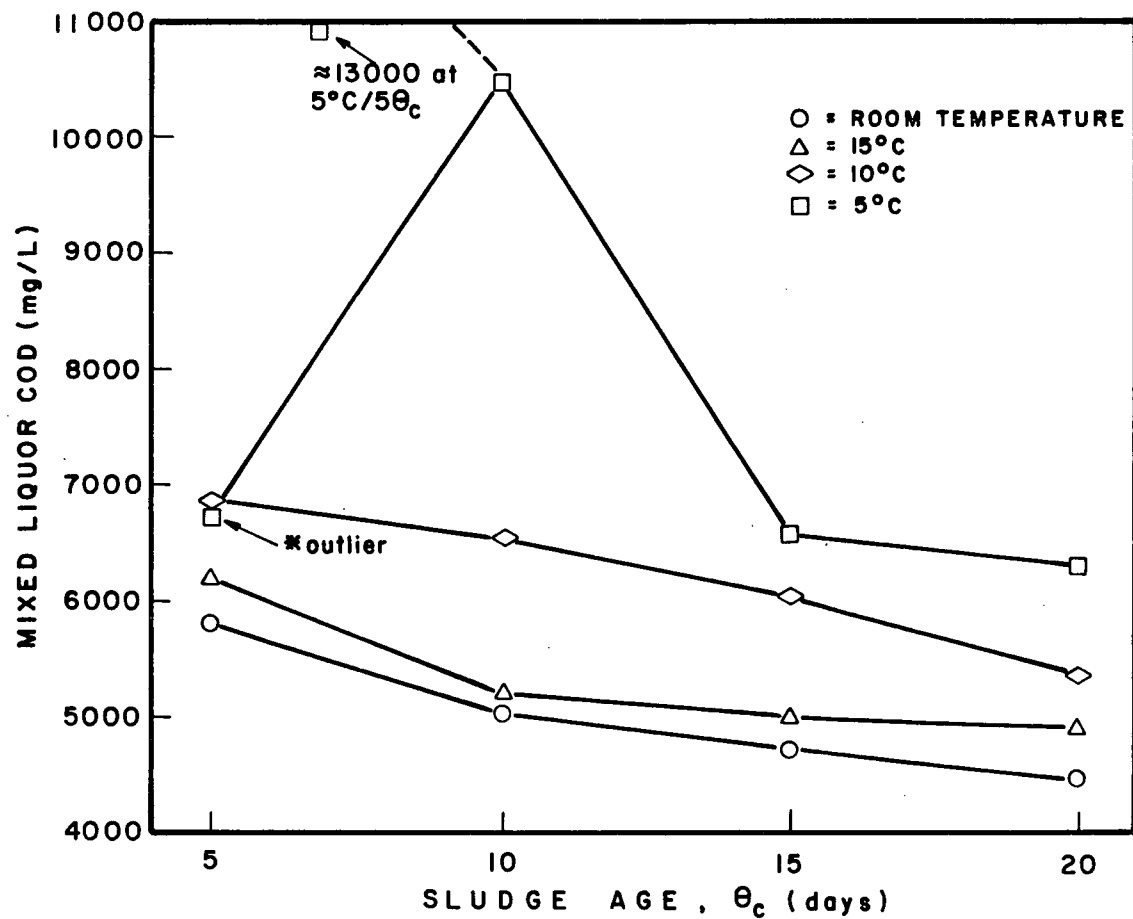
DETERMINATION OF Y AND b
AT 5°C

TABLE 17

KINETIC COEFFICIENTS AND MINIMUM MEAN CELL
RETENTION TIMES

TEMPERATURE (°C)	k (days ⁻¹)	K _S (mg/L)	Y	b (days ⁻¹)	θ _C ^M (days)
R.T.	1.16	81.8	0.49	0.009	1.8
15	1.12	63.8	0.51	0.018	1.8
10	0.51	34.6	0.51	0.006	4.0
5	0.34	17.0	0.55	0.002	5.4

Appendix B
Supplementary Results



* comment - three replicate samples were analyzed

FIGURE II
MIXED LIQUOR COD VERSUS SLUDGE AGE

TABLE 18

ACIDITY, ALKALINITY, TC, AND TOC CONCENTRATIONS
AND REMOVALS BY THE BIOLOGICAL REACTORS

REACTOR DESCRIPTION		ACIDITY		ALKALINITY		TC		TOC	
T (°C)	θ_c (days)	mg/L as CaCO_3 (pH = 8.3)	% REMOVAL	mg/L as CaCO_3 (pH = 3.7)	% REMOVAL	mg/L	% REMOVAL	mg/L	% REMOVAL
Leachate Feed		2060		3160		3820		3800	
R.T.	20*	0	100	148	95.3	101	97.4	55	98.6
	20	0	100	335	89.4	142	96.3	67	98.2
	15	0	100	350	88.9	149	96.1	67	98.2
	10	0	100	363	88.5	175	95.4	89	97.7
	5	0	100	338	89.3	226	94.1	142	96.3
15	20	0	100	345	89.1	162	95.8	81	97.9
	15	0	100	373	88.2	177	95.4	86	97.7
	10	0	100	387	87.8	190	95.0	92	97.6
	5	0	100	393	87.6	271	92.9	180	95.3
10	20	0	100	415	86.9	170	95.5	74	98.1
	15	0	100	390	87.7	182	95.2	88	97.7
	10	0	100	388	87.7	223	94.2	129	96.6
	5	0	100	393	87.6	371	90.3	281	92.6
5	20	0	100	411	87.0	217	94.3	117	96.9
	15	0	100	390	87.7	232	93.9	135	96.4
	10	0	100	412	87.0	278	92.7	177	95.3
	5	0	100	493	84.4	473	87.6	366	90.4

*reactor nutrient loading $\text{BOD}_5:\text{N}:\text{P} = 100:5:1$, all others are $100:3.2:1.1$