# BIOLOGICAL-CHEMICAL TREATMENT OF LANDFILL LEACHATE

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#### ABSTRACT

Leachate is an effluent generated via the percolation of surface and groundwater through sanitary landfills. Depending on local conditions, large volumes of high strength and potentially toxic leachate can be produced resulting in significant deterioration of receiving water quality. Leachate collection and treatment systems are currently being developed. The purpose of this study was to determine the treatability of high-strength leachate using a series biological-chemical treatment system; that is, aerobic biological degradation in a fill and draw reactor followed by lime precipitation in a separate vessel.

The system proved to be highly efficient in treating high-strength leachates both in terms of organics and heavy metals removal. Using a series of treatment combinations on a leachate with a COD of greater than 19,000 mg/l and high metal concentrations, all the British Columbia "AA" Level pollution control guidelines could be met with the exception of pH and manganese. Assessed on operating stability and treatment efficiency, the two most favourable treatment configurations were; an aerobic biological unit of 12 day mean cell residence time (MCRT), with an addition of 800 mg/l Ca (OH) 2 for polishing, and a biological unit of 15 days MCRT, with an addition of 450 mg/l Ca (OH) 3.

The biotreatment system was very effective in the removal of organics. Soluble COD removals ranged from 97.2% to 98.6% over a temperature range of 5° to 24°C and mean cell residence times of 9 days to 25 days. Soluble BOD<sub>5</sub> removals ranged from 99.5% to 99.9%. Trace metals were also removed effectively. Metal removals were greater than 96% for Fe, Mn, and Zn, better than 80% for Ca, better than 70% for Pb, between 70 and 80% for Cr and Ni, and 40% for Magnesium.

Temperature reductions did not significantly influence the biotreatment removal efficiencies; however, some stress was noted in the biological systems at 5°C. Decreasing settleability and excess foaming was prevalent especially in the lower MCRT units. Unit failure was observed in the 6 day MCRT digester when the temperature was reduced from 9° to 5°C. Further tests on the cold temperature operation of biological units indicated that ambient temperature acclimatization may be required, prior to cold temperature operation.

Lime precipitation performed well on most effluents over the range of dosages tested. Unfortunately, the dosages required were quite high, principly because of the very high sample alkalinities. For a lime dosage of 900 mg/l Ca(OH)2, at 25% reduction in COD was obtained on a sample with an initial COD of 551 mg/l and suspended solids less than 25 mg/l. Metal removals were substantially more impressive. At a pH of 11.5 (900 mg/l Ca(OH)2), typical reductions were >99% for Fe, 91% for Zn, 83% for Mn, 91% for Mg, and 73% for Ca. Other metals were initially at very low concentrations and as a result, were not monitored during the lime precipitation studies.

The principle removal mechanisms for organic materials were adsorption and entrapment. A reasonable correlation was developed between initial COD and alkalinity, and the quantity of Ca(OH)<sub>2</sub> required to achieve a prescribed treatment level. Metals were removed by chemical precipitation, and to a small extent, adsorption and entrapment. The removal of metals was extremely dependent upon the solubilization pH of the respective metal hydroxides.

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#### CHAPTER 1

#### INTRODUCTION

The continuing use of sanitary landfills for disposing of solid wastes and the subsequent percolation of precipitation and groundwater through these fills generates an effluent known as leachate. Under certain environmental conditions, large volumes of high strength, and sometimes toxic, leachates can be produced. As a result of the potential for serious deterioration of receiving water quality, landfill leachates are now being given considerable attention.

The magnitude of the problems associated with the leachates generated is dependent on a number of factors. These include the amount and composition of the refuse, the site hydrology, the infiltration rates, the season, the climate, and the dilution available in the receiving waters. A range of typical leachate characteristics is presented in TABLE 1.

The age of the landfill is also significant due to the changes in the physical and chemical structure of the landfill over time. The gradual degradation of the accumulated solid waste is a slow and highly complex process. Initially, aerobic conditions are prevalent; this results in the production of CO<sub>2</sub> gas and low molecular weight volatile acids. As a result, the pH of the active waters drops and its extraction capabilities increase (1). With the enhanced extractive capability, the "leachate" leaches out compounds from the decaying wastes resulting in a liquid waste as varied as the refuse itself.

The decomposition of the solid waste is an extremely slow process.

This factor is essentially what makes the landfill leachate problem so significant. Leachate generation is continuous and independent of the operation of the landfill itself. Leachates will continue to be

## TABLE 1 RANGE OF COMPOSITION OF LEACHATES (2,3)

Parameter

Range of Values or Concentrations\*
(Landfills or Test Lysimeters)

BOD <sub>5</sub>	9-55,000
COD	0-89,520
TOC	256-28,000
μ	3.7-8.5
Total Solids Total Suspended Solids Total Dissolved Solids	0-59,200 10- 1,450 600-45,000
Acidity Alkalinity	0- 9,560 0-20,900
Aluminum Arsenic Barium Calcium Cadmium Chloride Chromium Copper Iron Lead Magnesium Manganese Mercury Nitrogen - total - NH <sub>3</sub>	0-122 0-11.6 0- 5.4 5- 7,200 0-17.0 4.7- 2,800 0-33.4 0-10 0- 5,500 0- 5.0 17-15,600 0.06- 1,400 0-0.064 0- 2,406 0- 1,106
Nickel Phosphorus - total Potassium Sodium Sulphates Zinc	0.01-0.80 0- 154 28- 3,770 0- 7,700 1- 1,826 0- 1,000

<sup>\*</sup>all values except for pH are in  $mg/\ell$ 

generated 20 to 30 years after the landfill operation has been terminated. More and more cases have been documented where leachates have been an ongoing problem, thus, causing serious health and environmental consequences (3,4,5,6).

There are a number of design precautions which can be performed to control or minimize the generation of leachate at the landfill. They include diverting surface water away from the site, lining the landfill to prevent contact between the refuse and groundwater, and generally more careful initial site selection. In arid and semi-arid climates, where precipitation is minimal, sealing and sloping the surface of the landfill, to reduce precipitation infiltration, has been used very effectively. Unfortunately, most of these precautions can only be used on newly designed landfill sites. There are many old landfills, still generating leachates which must be handled and neutralized. The problem of handling leachates generated from old landfills is a topic of much current research; however, very few adequate solutions have been devised.

This thesis deals with treatment of the landfill leachates generated. There have been numerous, previous studies on leachate treatment, but there are still unanswered questions. The purpose of this study, therefore, was to attempt to answer some of these questions and to suggest and evaluate an effective means (in terms of practicality and performance) of treating high strength, sanitary landfill leachates.

#### CHAPTER 2

#### BACKGROUND

## 2.1 Introduction

The purpose of this research work was to develop an effective method of treating high-strength sanitary landfill leachates under varying operating conditions. Before this could be done, a complete survey of relevant literature had to be undertaken to determine the most appropriate methods to examine.

Leachate treatment has been a major concern over the last ten years.

Many investigations have already been undertaken, yet none has produced a treatment method considered to be totally satisfactory. Methods such as biological treatment, physical-chemical treatment, and leachate recycle have shown promise but each method has its own limitations and related problems. Because of this, it was concluded that some combination of the above methods might be the most effective method of treatment, both in terms of applicability and treatment efficiency.

Prior to the study, certain treatment goals were established. The British Columbia Pollution Control Board 'AA' level guidelines (PCB) were adopted as the treatment criteria (7). Although criteria listed in the guidelines is not rigidly applied, it is a good measure of treatment effectiveness.

## 2.2 Literature Review of Previous Treatment Efforts

(a) <u>Biological Treatment</u> - Aerobic biological treatment systems have been used very successfully in treating high strength landfill leachates.

Numerous laboratory studies including those done by Boyle and Ham (8), Chian and DeWalle (2,9), Cook and Force (10), Lee (1), and Uloth and Mavinic (11)

have reported COD removals of greater than 90%, at detention times from 5 to 20 days, for leachates ranging from 1,700 to 57,900 mg/L COD. Unfortunately, few attempts have been made at treating leachates by aerobic systems in the field. Steiner et al. (12) unsuccessfully tried to operate a lagoon system in 1977. They attributed the failure to ammonia toxicity; however, it seems more likely that the problems were related to the cold temperature acclimatization conditions. In the literature, there is very little said about the effects of temperature on the operation of aerobic biological leachate treatment systems.

The fate of heavy metals in aerobic biological systems has been examined in a number of studies (1,9,10,11). At moderate metal levels, kinetic parameters have indicated some metal inhibition to biological growth. In general, however, trace metal concentrations have shown little significant adverse effects on the overall operation of aerobic biological treatment systems.

Metal reductions have ranged from very good to very poor. Uloth and Mavinic (11) indicated that for a detention time of 20 days and initial metal concentrations as high as 1,260 mg/l (Fe), removals of greater than 96.8% could be achieved for Al, Cd, Ca, Cu, Fe, Mn, and Zn. Pb, Ni, and Mg achieved reductions between 68.5% and 83.6%. Potassium (K) concentrations were not significantly reduced by biological treatment.

Similarly, Chian and DeWalle (9), with initial metal concentrations as high as 2,125 mg/ & (Fe) and a 30 day detention time, achieved Fe, Ca, and Zn removals of 99.4% or greater. They also achieved 81.9% Mg removal; however, they found the removal of Na and K to be negligible.

Other research has indicated that the optimum nutrient requirements for an aerated lagoon, treating leachates, is  $100:3:1 \; (BOD_5:N:P)$ , rather

than the conventional ratio 100:5:1 (13).

There have been many studies performed on the anerobic treatment of landfill leachates (3,8,9,14). COD removals of between 92% and 97% have been achieved, using detention times from 7 to 27 days, for leachates ranging from 5,000 mg/l to 62,000 mg/l COD. Poorman and Cameron (14) found no adverse effects on the anaerobic degradation process as a result of high heavy metal concentrations. Boyle and Ham (8) found that anaerobic treatment produced greater than 90% BOD removal, providing that the temperature was between 23°C and 30°C. Treatment was significantly inhibited by temperatures lower than 23°C, when the detention time was 30 days. Failure occurred at detention times less than 20 days.

(b) <u>Chemical Treatment</u> - The principal chemical treatment methods include precipitation, coagulation, and oxidation. All three mechanisms have been only marginally successful in leachate treatment in previous studies.

The two most common chemicals used as precipitants are lime and sodium sulphide. Ho et al. (15) found that better results were obtained with lime, although neither method performed well enough by itself to be considered an effective treatment method. Bjorkman and Mavinic (16) showed that Fe, suspended solids, and colour were reduced very effectively by lime precipitation. P, Zn, Cd, K, and Ca also showed some reductions; however, organics removals were poor, with a COD reduction of only 0% to 26% being achieved with lime dosages as high as 2,760 mg/& Ca(OH) (16). Sludge production rates were found to be very high (1, 15, 16).

The common chemical coagulents are alum, ferric chloride, ferrous sulphate, and certain polymers. Results achieved with these chemicals were similar to those obtained with lime and sodium sulphide (15,16). Fe, colour, and suspended solids were removed effectively, while the removal of other

metals and organics was minimal. Chemical dosage rates and the sludge volumes produced were prohibitively high.

Chemical oxidation can be performed using chlorine, calcium hypochlorite, potassium permanganate, and ozone. The most impressive results were obtained using ozone. COD removals ranging from 22% to 48% were achieved under variable ozone contact times (2). Bjorkman and Mavinic (16) showed the Fe and colour were also effectively removed; however, ozone dosages were found to be high (130 mg/l ozone). Lime and ozone together, provided some improvements in effluent metal concentrations; however, for the best value (lowest achieved) effluents, lime dosages were greater than 2,000 mg/l Ca(OH) and ozone dosages were greater than 97 mg/l ozone.

(c) Physical Treatment - The principal physical treatment methods include activated carbon adsorption, reverse osmosis and ion exchange.

Activated carbon adsorption, with batch and column systems, have achieved anywhere from 34% to 85% COD removals, with dosages between 10,000 mg/l and 160,000 mg/l carbon (2). The removals of metals are not well documented.

Because of high organic loadings, low adsorptive capacities, and the presence of suspended solids in the raw leachates, regular fouling of the carbon columns have been observed (9). Indications are that the activated carbon process is currently uneconomical for raw leachate treatment.

Reverse osmosis of raw leachates was quite successful in treating organics. Chian and DeWalle (2) found COD reductions of between 56% and 89%, for a high strength leachate of 53,300 mg/l COD. Removal of total solids was up to 99% when influent prefiltration was performed. Organic removals were greatly improved when the pH of the raw leachate was increased. Like activated carbon, reverse osmosis units were subject to membrane fouling,

when the suspended solids levels were higher. There is no documentation of the metal removal effectiveness of reverse osmosis units.

The use of ion exchange processes for raw leachate treatment was considered only for the removal of ammonia in low strength leachates (9). It was found to be a very ineffective means of ammonia removal, due to the presence of interfering substances which compete for bonding sites. Organic removal was not examined but was believed to be very low.

(d) <u>Combined Treatment</u> - From the foregoing it can be assumed that no single system can completely satisfy all treatment requirements. Combined treatment is therefore considered necessary for achieving effective leachate treatment.

Chian and DeWalle (2,9) present a survey of treatment combinations that have been tried. The combinations can be separated into three catagories; aerobic biological treatment with polishing, anaerobic biological with polishing, and activated carbon adsorption, with some sort of pretreatment.

Activated carbon, ion exchange, ozonation, and reverse osmosis have been employed as aerobic treatment polishing steps. In terms of organic removal, reverse osmosis was the most effective (85% to 97% COD removal).

Because of membrane - solids fouling, sand filtration or chemical precipitation was required prior to the reverse osmosis unit. Reverse osmosis was followed in effectiveness by activated carbon (86% COD removal), ion exchange using strong base ion exchange resins (82% to 85% COD removal), and ozonation (37% to 48% COD removal) (9).

The removal of trace metals by the polishing steps is not well documented. With activated carbon, Lee (I) indicated that 99% removal of Fe was possible; however, boron levels showed no sign of improvement. There

was no metal removal information available on the other treatment methods.

Anaerobic biological treatment has been combined with activated carbon, reverse osmosis, and lime precipitation. As with aerobic bio-treated effluents, reverse osmosis provided the best organics removal (98% removal with an initial COD of 900 mg/%). Activated carbon provided a 50% COD removal from an effluent with a COD of 932 mg/% (2). Ho et al. (15) achieved only a 7.7% COD removal, using lime polishing; however, they did achieve complete Fe and colour removal, and good suspended solids removal. They concluded that the combination of lime polishing and biological treatment was promising.

Lime addition and alum addition have been used as preliminary steps to activated carbon adsorption. For an initial COD of 3,290 mg/l, activated carbon, with lime pretreatment, achieved 81% COD removal (10). Van Fleet et al. (17) found that for an initial COD of 2,000 mg/l, activated carbon column treatment of alum-pretreated leachate achieved a 94% COD removal. Both methods achieved effective suspended solids and colour removals; however, trace metals were not mentioned.

### 2.3 General Conclusions

TABLE 2 presents a summary of the major potential treatment methods. After an evaluation of previous work performed at U.B.C. and elsewhere, it was decided that two particular systems were quite promising: a two-stage biological system and a two-stage aerobic biological-lime precipitation system.

When considering sanitary landfill leachates highly variable nature, the most flexible system would probably be the most effective. The chemical precipitation system would appear to be the more operationally flexible. It is also well suited to being combined with aerobic biological treatment.

TABLE 2

A SUMMARY OF THE POTENTIAL TREATMENT METHODS

Method	Organics Removal	Metals Removal	Comments
Aerobic Biological	Very Good	Good to Very Good	-If organics are bio- degradable, organics removal is excellent -Not good on refractory organicsSettling and sludge dis- disposal are serious problem areas.
Anaerobic Biological	Good to Very Good	Good to Very Good	-Same as above except required tighter opera- ting controlPossibility of energy production from gases produced.
Activated Carbon Adsorption	Good	Not well known for Leachates	-Most effective on refractory organics removalCarbon fouling can be a problem. Activated carbon adsorption is very expensive.
Lime Precipitation	Poor	Good to Very Good	-Not effective at removal of organics, although removal is better on refractory organics than biodegradable organics. Metals and suspended solids removal is very goodLime is readily available and inexpensive if dosages can be minimized -High sludge production and subsequent disposal might be a problem.

Aerobic biological treatment would effectively reduce the organics and most metals; the lime treatment would then remove the residual metals, some refractory organics, and excess suspended solids and colour from the biological effluents. Because this treatment combination has not been previously examined in detail under low operating temperatures, this study was instigated to evaluate this treatment combination.

## 2.4 Experimental Format and Goals

The operating variables that were controlled in the aerobic biological units included temperature, aeration rate, solids detention time and nutrient levels. In the precipitation units, the chemical dosage rate was controlled. Lime was chosen as the chemical for polishing because of its relatively low cost, its availability, and its effectiveness in previously tested treatment systems.

The key parameters in the system were temperature, solids detention time, and lime dosage rate. For each temperature selected, the biological systems were operated at a series of solids detention times. Lime dosage rates were varied according to the physical characteristics of the first stage effluents, so as to optimize the system removal efficiencies.

Characteristics evaluated included BOD<sub>5</sub>, COD, suspended solids and selected metal concentrations.

Although it is recognized that this optimization procedure would only be of value for the leachate used in this study, it does give some idea of the detention times and the lime dosages required for a leachate of comparable strength. It also indicates whether this type of system can operate over a wide range of temperatures and how temperature affects such important parameters as settling, system stability, and sludge morphology.

The study was carried out in three phases. The "temperature reduction

phase" (or TRP) was designed to acclimatize the microbial population to landfill leachates at room temperature, and then to reduce the temperature downward, step by step, to a minimum temperature of 5°C. At each temperature step, full effluent characterization was carried out.

The "cold temperature phase" (or CTP) was designed to observe more completely the operation of the bio-system under the coldest practical temperature conditions. Throughout the TRP and the CTP, settled and filtered effluents were stored for use in the lime-precipitation unit.

The "lime-precipitation phase" (or LPP) was initiated to observe and evaluate the effectiveness and dosage requirements of lime-polishing as a means of treating aerobic biological effluents. The level of testing in the LPP was determined by the quality of the incoming first-stage effluents (7).

## 2.5 Temperature Effects on Biological Growth

The effect of temperature on bio-synthesis has been of great concern ever since biological waste treatment methods were first attempted; however, only recently has any real progress been made on the subject. Previously, the Streeter-Phelps empirical modification of the Arrhenius law was used to define the effect of temperature on the reaction rate constants involved in biological treatment. Recent work by Novak (18) and Friedman and Schroeder (19) has shown that the Streeter-Phelps modification is really of limited value when predicting such temperature effects.

The modified Arrhenius equation can be written as follows (20):

$$k_{T} = k_{20}^{20} \theta^{(T-20)}$$
 (1)

where  $k_{\mathrm{T}}^{}$  = the unknown rate constant of temperature T °C.  $k_{\mathrm{20}}^{}$  = the known rate constant at 20°C

6 = the temperature activity coefficient.

The limitations lie in the fact that the temperature activity coefficient,  $\theta$ , is dependent upon many factors and therefore, cannot be assumed to be constant. It has been found that  $\theta$  varies with the temperature range, the substrate concentration, the food to micro-organism ratio, the number of test temperatures employed, the type of substrate, and the method of chemical analysis (18). As a result, to give a true representation of the temperature-substrate effects,  $\theta$  must be a multi-variable function. Novak suggested that the growth rate k, for a given organism and substrate, should follow a general equation of the form

$$k = f$$
 (composition) .  $f$  (temperature) (2)

Proper evaluation of the two functions would then produce an equation that truly reflects the interrelationship of temperature and substrate. Another limitation of the Arrhenius modification is that it only accounts for temperature effects on the growth rate. The temperature effects on the other constant,  $k_s$ , is not accounted for at all. Since  $k_s$  modifies the specific utilization rate as defined below,

$$U = \frac{kS}{k_s + S} \tag{3}$$

where U =the specific utilization rate,  $M/L^3T$ 

k =the growth rate,  $T^{-1}$ 

S =the substrate concentration,  $M/L^3$ 

 $k_s$  = the substrate concentration when the rate of substrate uptake = 1/2 k, M/L<sup>3</sup>

it would be significant if k, along with k, was found to vary with temperature. For aerobic biosynthesis, Novak (18) found that, as temperature was

increased, both k and  $k_{_{\rm S}}$  increased logarithmically. Based on the Novak results it would appear that a comparable temperature function for  $k_{_{\rm S}}$ , similar to Equation (1), may be appropriate; however, more specific research to verify this is required.

Because leachates are highly variable, both in terms of strength and composition, the interdependence of substrate and temperature is critically important when considering the possible effects of temperature on the biodegradation of landfill leachates. Although there is insufficient data from this study to fully evaluate both k and  $k_s$ , a subsequent manuscript with Zapf-Gilje (21), in conjunction with this research, should provide a more complete evaluation of the temperature kinetics and leachate bio-synthesis.

A short summary of the specific effects of cold temperatures on biodegradation is presented in Appendix I.

#### CHAPTER 3

#### EXPERIMENTAL METHODS AND MATERIALS

## 3.1 Design of the Treatment System

(a) The Biological Digesters - Since this research was an extension of on-going work at U.B.C., the treatment system design was derived from those previously used by the Environmental Engineering Group. The first-stage biological units were four, 10-litre capacity glass bottles. The bottom of each bottle was removed and the necks were fitted with large rubber stoppers secured in place by heavy stainless steel wires. Holes were bored through the stoppers and porous glass, coarse bubble air diffusers were fitted in the bottom of each unit. Oil-free air was supplied by the laboratory compressed air system at a rate controlled by adjustable clamps placed on the air line to each unit.

Though the diffusing air bubbles created some turbulence, mechanical surface mixers were also employed to ensure complete mixing. The air flow rates and the mechanical stirring speeds were adjusted to maintain aerobic conditions throughout the digesters, while minimizing foaming. Only 5 litres of mixed liquor were maintained (as another precaution against foaming), thus allowing approximately 7 inches (18 cm) of freeboard in each unit. A schematic diagram of a typical digester is presented in FIGURE 1.

(b) <u>Temperature Control</u> - The system was initially installed in the main section of the laboratory, where there are no temperature controls.

As a result, the start-up was performed at room temperature (between 22°C and 25°C).

When it was time to reduce the system temperature, the units were transferred to a temperature controlled room. All testing at 16°C, 9°C, and 5°C was performed therein.

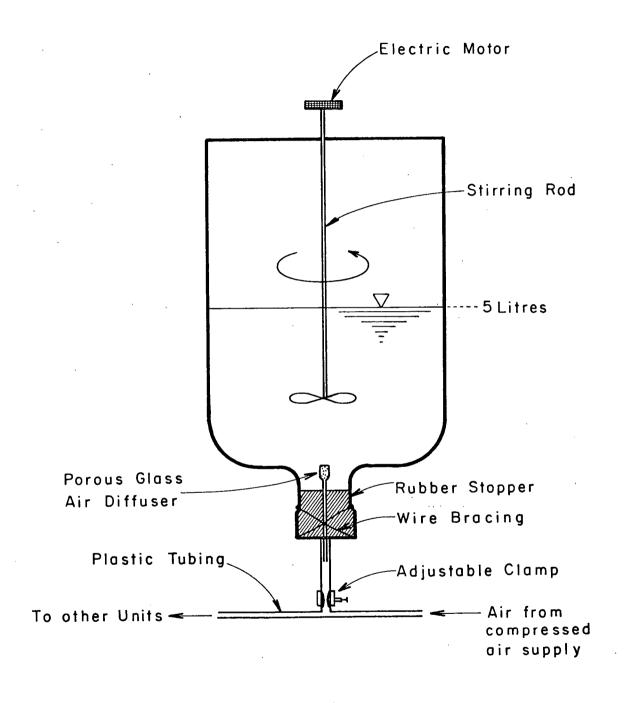


FIGURE 1: Biological Treatment Unit (11)

- effluents were collected, identified and labelled in accordance with temperature, sludge age, and degree of settling, and stored at 4°C for second-stage treatment. To maintain a uniform first-stage effluent sample, no second-stage tests were performed until there was sufficient sample to do a complete set of lime-precipitation experiments.
- (d) <u>Lime-Precipitation Testing Procedure</u> Although there are a number of chemical combinations commonly referred to as lime, for the purpose of this paper, lime was defined as Ca(OH)<sub>2</sub>. The lime-precipitation unit processes were performed on two standard six-paddle jar testing units (as manufactured by Phipps and Bird). Since the stored first-stage effluent volumes were in short supply (due to the limited quantities of raw leachate available), 600 ml. beakers were chosen as the jar test containers. The lime was added as a slurry at concentrations calculated to ensure that the final volumes in the jar test beakers were approximately constant.

### 3.2 Leachate Source and Characteristics

The leachate produced by four lysimeters located at the University of British Columbia, was used as the first-stage influent for the systems. The characteristics of the lysimeters are found in TABLE 3.

The typical percentage garbage composition in the lysimeters were:

Food Waste - 11.8

Garden Waste - 9.8

Paper Products - 47.6

Cardboard - 5.4

Textiles - 3.6

Wood - 4.7

TABLE 3

PHYSICAL CHARACTERISTICS OF LABORATORY LYSIMETERS

Lysimeter Code Number	Dimensions	Cover Material	Total Wt. of Garbage (lbs)	Depth of Garbage (ft)	Wt. Density Before Final Cover (lb/yd <sup>3</sup> )	Rainfall (in/yr)	Moisture Content (%)
T	14 ft. deep, 4 ft. in diameter	Hog Fuel	3,420	8	884	15	34.7
х	Same	Hog Fuel	3,506	8	874	15	35.1
Н	Same	Soil	3,556	8	876	15	39.9
W	Same	Soil	3,556	8	879	15	37.0

Metals - 8.7

Glass & Ceramics - 7.0

Ash, Rock, and Dirt - 1.4

TOTAL 100.0%

Leachate from the lysimeters was collected and stored (at 4°C) in plastic containers for two months, prior to the system start-up. Before the activation of the biological units, the stored samples were combined, mixed, and re-stored at 4°C to ensure as homogeneous an influent as possible. Approximately 250 litres of leachate was made available for this and another parallel study being performed in the lab (Zapf-Gilje (21)).

The leachate composition during the temperature reduction phase (TRP) is shown in TABLE 4. Tests were performed throughout the duration of the TRP and little variation in the characteristics of the leachate was observed.

As the TRP continued, it became apparent that there was going to be insufficient leachate sample for the cold temperature phase (CTP). To offset this for the month prior to the CTP, more leachate was collected from the lysimeters and stored separately at 4°C. The characteristics of the CTP composite sample are also shown in TABLE 4. The CTP leachate constituent concentrations, particularly for the metals, are slightly lower than those found in the TRP leachate. However, this is characteristic of landfill leachates, as the landfill ages. Other parameters differed only marginally.

## 3.3 Operating Variables in the Biological Units

(a) <u>pH</u> and <u>Dissolved Oxygen</u> - No form of pH control was employed, since previous experiments indicated that the pH of the bacterial culture would naturally adjust itself to a preferred operating level (10,11).

TABLE 4

COMPOSITION OF LEACHATE FEED USED DURING THIS STUDY

Parameter	Temperature Reduction Phase (mg/l)	Cold Temperature Phase (mg/l)
BOD <sub>5</sub>	13,640	12,920
COD	19,250	19,370
Total Carbon	6,170	<del>-</del>
Total Organic Carbon	6,115	we
Total Solids Total Volatile Solids	10,440 5,810	10,445 5,890
Total Suspended Solids	1,040	1,470
Total Volatile Suspended Solids	750	965
Acidity as CaCO <sub>3</sub> (pH=8.3)	3,100	2,930
Alkalinity as CaCO <sub>3</sub> (pH=3.7)	4,110	4,120
Aluminum	0.62	0.49
Calcium	775	638
Cadmium	0.04	0.035
Chromium	0.098	0.102
Iron	1,225	1,035
Lead	0.031	0.026
Magnesium	71.5	66.0
Manganese	14.0	12.2
Nitrogen - TKN	32.0	29.2
- NO <sub>3</sub> +NO <sub>2</sub>	<0.05	-
Nickel	0.33	0.10
Phosphorus	10.0	10.1
Zinc	39.2	22.8
pH*	5.2	5.2

<sup>\* -</sup> Not in mg/l

After 15 days of operation, the pH in all four units had stabilized above 8.1. The pH after this time remained relatively stable, varying only by ±0.2, depending upon the mixed liquor dissolved oxygen level. FIGURE 2 shows that as the mixed liquor dissolved oxygen increased, the mixed liquor pH also increased. The mixed liquor dissolved oxygen was maintained as high as the air supply system would permit.

A significant reduction in dissolved oxygen was noted immediately after feeding. Yet, only on a few occasions was the dissolved oxygen monitored below 2.0 mg/l. On two occasions, air lines were broken and for short periods of time, no air was being supplied to the system. The tanks temporarily went anaerobic and in each case, it took a few days for the system to stabilize once again. No tests were performed during these "down" periods.

- (b) Nutrients As the influent BOD $_5$ /N/P ratio was only 100/0.23/0.07, nutrient addition was necessary to achieve the recommended nutrient level of 100/5/1 (22). The additional nutrients were supplied by the daily addition of predetermined quantities of NH $_4$ NO $_3$  and NH $_4$ H $_2$ PO $_4$ .
- (c) Organics and Metal Concentrations No modifications were made to the organic and metal concentrations in the influent.

## 3.4 The Temperature Reduction Phase

The purpose of this phase of the study was to acclimatize the bacteria to the leachate feed and then gradually reduce the system temperature.

Before start-up, it was necessary to decide upon "safe" mean cell retention times (MCRT). Uloth (11) indicated that the optimum MCRT for a very high-strength leachate (BOD<sub>5</sub> = 36,000 mg/ $\ell$ , COD = 48,000 mg/ $\ell$ ) was 20 days for a system operated at 23°C. Koers (23) found that, with aerobic digestion of domestic sludge, when the mixed liquor suspended solids (MLSS)

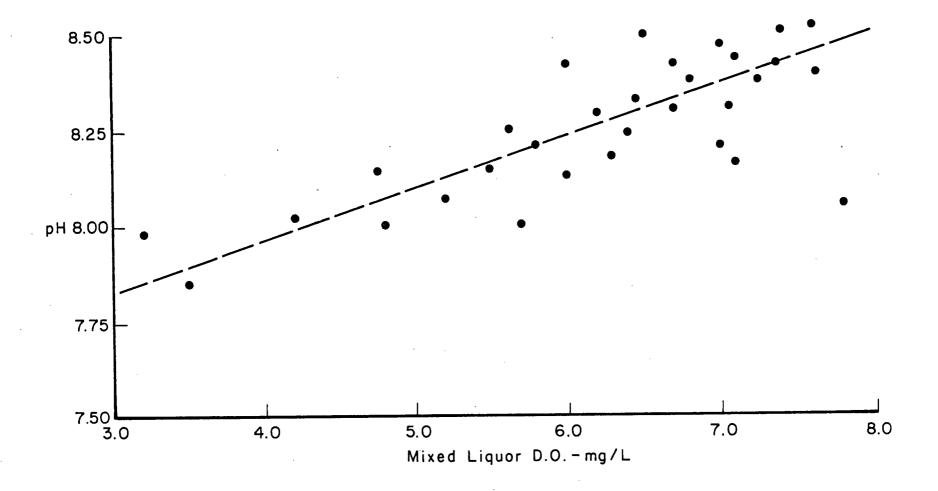


FIGURE 2: pH of Mixed Liquors vs. Mixed Liquor Dissolved Oxygen (24°C)

were very high, the optimum MCRT varied by a factor of four when operating at 5°C as compared to 20°C. As a result, even though this system's leachate sample was half as strong as the Uloth sample, it was decided that the MRCT's should be long enough (10, 15, and 20 days) to allow for variation as the temperature was reduced.

This study would operate two digesters at 10 days and two at 20 days, while a third set of three reactors would be operated by R. Zapf-Gilje at an MCRT of 15 days. The reactors are identified in TABLE 5. The reason for splitting the study in this manner was that both studies required as much homogeneous first-stage effluent as possible; therefore, multiple units were required at each MCRT. Because the systems were identical, it was agreed that biological kinetics would be examined at a later date using data from both studies.

TABLE 5
REACTOR IDENTIFICATION

рил стор	MEAN (	CELL RESIDENCE TIME -	days
REACTOR	AT START-UP	STEADY-STATE - TRP	STEADY-STATE - CTP
A 20		25	25
В	20	25	25
С	10	15	15
D	10	·15	12
E	· <b>–</b>	-	9
F	-	_	, 6*

<sup>\* -</sup> Unit failed at 5°C.

(a) Start-Up - The bacterial seed used for the digesters was obtained from the Mamquam extended aeration Sewage Treatment Plant in Squamish, B.C. The Mamquam activated sludge had been previously used successfully by the Environmental Group; therefore, it was also chosen for these systems. The MLVSS of the seed was between 3,600 mg/l and 4,000 mg/l; as a result no modifications were made to the sludge solid levels prior to use.

The study was initiated by filling reactors A and C with 5 litres of sludge feed. The air lines were then connected and adjusted and the mechanical stirrers were turned on. Stirring speeds were set approximately equal in each tank. The pH was recorded and the nutrients and initial leachate dosages were added.

The leachate dosage rates were calculated assuming that the system was complete mix - no recycle. With that assumption, the prescribed dosages rates were as shown in TABLE 6:

TABLE 6

LEACHATE DOSAGE RATES

MCRT - days	REACTOR VOLUME - litres	LEACHATE DOSAGE RATE - ml/day
25	5	200
20	5	200
15	5	330
12	5	420
10	5	500
9	4.5	500
6	4.5	750

Although the dosage rates were to be 250 ml/day for reactors A and B and 500 ml/day for reactors C and D, it was decided to initially feed the reactors with a combination of raw sewage and leachate at a somewhat lower rate. The initial dosage to both tanks was 100 ml leachate plus 100 ml domestic sewage. It was hoped that because the sludge was accustomed to degrading sewage, the acclimatization process might be hastened by sewage addition. However, within two days of start-up, the pH and the mixed liquor suspended solids concentrations in each reactor started to drop. Initially, it was believed that this was due to the addition of the low pH leachate feed and that it would adjust itself when the system became acclimatized. But by day 5, the solids were still dropping and it was decided to artificially adjust the pH up to 8.0. Within one hour of the pH adjustment, the pH was back down to 5.5 again and it was apparent that something might be wrong with the systems.

To determine what would happen, it was decided to eliminate the sewage addition. Within two days, the pH started to rise and the systems began to stabilize. It is still unclear what was wrong with the system while the sewage was being added; however when it was ceased the problems were resolved.

On day 8, reactors B and D were initiated, using one-third sludge from tanks A and C and two-thirds new activated sludge from the treatment plant. By day 11, the systems had stabilized and a regular operating procedure could be established.

- (b) Operation and Testing The initial operating schedule was designed to increase the MLSS concentrations as rapidly as possible. The daily procedure was as follows:
  - (1) Replace water lost through evaporation by the addition of

- distilled water up to the 5 litre mark.
- (2) Scrape tank walls in each digester to remove most of the adhering micro-organisms, thus returning them to the mixed liquor.
- (3) Check the pH, dissolved oxygen, and temperature.
- (4) Turn off air and stirrers to allow the biological solids to settle.
- (5) Settle until there is sufficient clean supernatant to withdraw 250 ml from digesters A and B and 500 ml from digesters C and D. The supernatant was wasted.
- (6) Turn on air and stirrers again.
- (7) Add volumes of leachate equal to those withdrawn from each digester.
- (8) Add nutrients.

Solids concentrations were monitored every 3 to 5 days through this period. No other tests were performed on a continuous basis.

On day 26, it was decided that sludge wasting could begin and the systems could be allowed to approach steady-state. The new operating schedule was the same as previously noted, except mixed liquor was wasted rather than supernatant.

On day 30, the sludge ages were changed from 10 to 20 days to 15 and 25 days, respectively, because it appeared at that time, that the predetermined sludge ages might be too low and problems might arise at the colder temperatures. The systems were operated for two and one-half weeks under the new conditions and by day 48, steady-state solids levels were achieved.

(c) <u>Steady-State Testing</u> - The major change in the steady-state operating procedure was that the withdrawn mixed liquor was settled (or

filtered), and then collected and stored for the second-stage tests. The testing schedule was also expanded significantly. TABLE 7 presents the characteristics which were monitored throughout the TRP. All tests were performed according to Standard Methods (24).

At the end of each temperature operating period, the temperatures were reduced, the the systems were allowed one week of acclimatization prior to the resumption of normal testing. This time period was somewhat short, but was a consequence of the limited quantity of feed available.

TABLE 7
THE TESTING SCHEDULE FOR THE TRP

SAMPLE	CHARACTERISTIC TESTED FOR	REGULARITY OF TESTING
Collected Effluents		- 5 to 7 days - 2 weeks
	Metals	- At the end of each temperature level.
Stored Effluents	COD, BOD <sub>5</sub> TSS, VSS, Metals, TS, Alkalinity Acidity	<ul><li>3 weeks</li><li>Immediately prior to second-stage testing</li></ul>
Mixed Liquors	COD, MLSS, MLVSS TS Metals	- 5 to 7 days - 2 weeks - At the end of each temperature level

## 3.5 The Cold Temperature Phase

The purpose of this phase of the study was to observe the effects of even colder temperatures on a biological treatment system (temperatures which might be encountered under Canadian field conditions). To this end,

two new reactors and a new leachate composite sample were employed.

The reactors were adopted from Zapf-Gilje (21) nine days prior to the CTP, and were already acclimatized to both colder temperatures and leachate feed. With the addition of the new reactors and the modification of reactor D to 12 days MCRT, a complete cross-section of MCRT units, ranging from 6 to 25 days, was available for the CTP. This would allow an expanded analysis, including biological kinetics at 5°C.

The intensity of testing during the CTP was greater than during the TRP. Characteristics such as sludge volume index, COD, suspended solids, and  $BOD_5$  were measured every three or four days. The operating schedule of the CTP, however, was identical to that of the TRP.

## 3.6 The Lime-Polishing Phase

The purpose of this phase of the study was to evaluate the effectiveness of lime precipitation as a means of polishing the aerobic biological
effluents. Throughout the TRP and CTP, first-stage effluents were
collected for the lime-polishing phase (LPP). No polishing was performed
until the biological units were "shut down"; as a result, some of the stored
samples were held for more than three months prior to their use. The long
storage period resulted in some minor alterations in the characteristics of
the stored effluents, especially in those with higher initial solids;
however, the changes were not so great that they would nullify the secondstage procedure.

(a) <u>Sample Selection</u> - The second-stage tests were only performed on those effluents which required further treatment by PCB standards (7). The first-stage filtered effluents from 24°C, 16°C, and 9°C were quite acceptable; consequently minimal testing was carried out on those samples.

Complete lime-polishing was performed on all the 5°C filtered effluents and all poorly settled effluents from higher temperature runs.

The characteristics monitored depended upon the initial characteristics of the sample. COD, pH, iron, calcium, manganese, zinc, and magnesium testing were performed on all samples. Other metals were tested where necessary; however, in many cases, the initial concentrations were very low. BOD<sub>5</sub> was not tested because there was insufficient sample to do a complete analysis. COD was employed as the measure to determine the quantity of organics removed by the lime treatment process.

- (b) The Test Procedure The lime-precipitation test procedure employed was similar to that used by MacLean (25). It was as follows:
  - (1) Fill 600 ml beakers with 400 ml of sample and turn on paddles.
  - (2) Add dosage of lime slurry at a concentration that would leave between 500 ml and 520 ml of solution in the beaker.
  - (3) Rapid mix (100 rpm) the solution for 1 minute to disperse and completely mix the lime and the sample.
  - (4) Slow mix (20-30 rpm) the solution for 5 minutes to enhance coagulation and flocculation.
  - (5) Turn off paddles and settle for 30 minutes. It was found that if settling was going to occur, only 15 minutes of settling time was required. For the purpose of the experiments however, 30 minutes was arbitrarily chosen as the settling time.
  - (6) Prepare the samples for testing.
- (c) Operational Problems Unfortunately, the lime-precipitation tests did not run smoothly. A significant problem arose during floc settling.

When the paddles were turned off, the floc was allowed to settle. The initial settling was usually good; however, after approximately 10 minutes, a scum layer would form on the surface of the solution and the supernatant would start to cloud up. It was evident that the fine flocs were being carried by a gas to the surface of the solution, but there was no immediate explanation as to where the gas was coming from.

Although no specific tests were performed on the gas, a hypothesis has been developed to explain what it was and possibly how it was formed. It is believed that the gas was  $N_2$  and that it was formed by denitrification during the extended storage period.

Most of the nitrogen in the biological effluents was  $\mathrm{NO_3}$ -N. During storage, the samples became anaerobic and the  $\mathrm{NO_3}$ -N was converted by denitrification to  $\mathrm{N_2}$  gas. This resulted in the stored (at 4°C) samples becoming supersaturated with  $\mathrm{N_2}$  gas. When the samples were exposed to room temperature air, the  $\mathrm{N_2}$  gas slowly bubbled out of solution. As the bubbles rose to the surface, they picked up particles of lime floc. Eventually the surface became so clogged with floc that the gas could not escape and the solution began to cloud up with fine, suspended floc particles.

To alleviate this problem, a simple procedure was developed. After the paddles were turned off, the samples were allowed to settle for 15 minutes. At that time, the quality of settling and the clarity of the supernatant were assessed. If it was evident that the settling was satisfactory, the settling was continued for the allotted 30 minutes. If after the 15 minutes, the floc was not forming well and the settling was poor, it was concluded that the dosage used was too low to permit good settling and sample/dosage was labelled "poor clarification".

The samples which were deemed "satisfactory" were filtered using

Whatman #4 filter paper and subsequently tested. This procedure was considered acceptable because previous studies have shown that filtration would produce similar effluent to lime-precipitation where there was good floc formation (25). No filtration was performed on samples that did not settle adequately.

#### CHAPTER 4

### RESULTS AND DISCUSSION

# 4.1 First-Stage Biological Treatment

(a) <u>Biological Environment</u> - Mixed liquor leachate acclimatization was complete after 26 days of operation. Sludge wasting was then started and three more weeks elapsed before the system achieved steady-state conditions. These conditions were maintained for one and a half months, during which time effluent collection and analysis was performed. The temperature was then reduced and similar procedures were followed at subsequent temperature levels.

A summary of the steady-state operating conditions is presented in TABLE 8. The mixed liquor volatile suspended solids (MLVSS) and the mixed liquor suspended solids (MLSS) concentrations are average values and derived from composite graphs of the digester solids (see Appendix II).

As the temperatures were reduced, the MLSS, the MLVSS, and MLVSS/MLSS ratio were all found to increase. There are a number of possible explanations for the observed effects. The traditional explanation states that the increased MLVSS is due to less endogenous respiration at low temperatures, which allows a greater net growth of bacteria at long solids retention times (22). This assumes that the bacterial species present are similar at the reduced temperatures as at the higher temperatures. However, when considering a gradual temperature drop from 20°C to 5°C, it is possible that there have been significant changes in the predominant bacterial species present. Theoretically, as the temperature drops, the predominant bacterial species will shift from the mesophilic range which predominates at the mid-range temperatures (15°C to 35°C), to the psychrophilic range, which predominates at

TABLE 8
BIOLOGICAL REACTOR OPERATING CONDITIONS

Operating Temperature	24°C		16°C		9°C		5°C				
MCRT (days)	15	25	15	25	15	25	9	12	15	25	
Kg COD/kg MLVSS-day	0.41	0.26	0.34	0.26	0.26	0.19	0.38	0.31	0.24	0.17	
Kg BOD <sub>5</sub> /kg MLVSS-day	0.29	0.18	0.24	0.18	0.18	0.13	0.25	0.21	0.16	0.11	
MLSS (mg/l)	6,590	6,685	6,820	5,500	8,110	6,845	9,030	8,320	8,310	7,495	
MLVSS (mg/l)	3,105	3,115	3,760	3,010	4,980	4,060	5,600	5,210	5,265	4,600	
MLVSS MLSS	0.471	0.466	0.551	0.547	0.614	0.593	0.620	0.626	0.634	0.614	
Mixed Liquor pH	8.2	8.3	8.1	8.2	8.1	8.2	7.9	8.1	8.0	8.2	

the lower temperatures (-5°C to 20°C). Because their active metabolic rates and motility are lower, the psychrophiles depend more on food storage than do mesophiles (26). Therefore, as more psychrophilic bacteria are present, the food required per bacteria is reduced (because each bacteria requires less food from the feed due to greater storage and less mobility) and a greater number of bacteria is required to degrade the same quantity of substrate. The MLVSS is shifted upward accordingly until a new steady-state MLVSS is established.

The non-volatile suspended solids level is dependent upon the inorganic solids in the feed, the formation of non-volatile end products through bio-activity, and the suspended solids formed by precipitation due to the high mixed liquor pH (8.2). With this waste, the increase in MLVSS with temperature was significantly greater than the increase in MLSS. As a result, the MLVSS/MLSS ratio also increased accordingly.

The sudden drop in solids in the 25 day MCRT reactors between 24°C and 16°C was unexpected. It is believed to have been caused by the unstable conditions encountered in the digesters after they were transferred from the open laboratory to the temperature controlled room. The 15 day MCRT units showed some initial instability due to the transition; however, they recovered quite rapidly. The subsequent temperature drops caused very little stability problems in the 15 and 25 day MCRT units.

When the 6, 9, and 12 day MCRT units were adopted for the CTP work, maintaining stability in these units was a problem. The 12 day MCRT unit, which was converted from a 15 day MCRT unit, showed some excess foaming due to the change in feed rate; however, the solids remained stable and no remedial measures were required.

The 9 day MCRT unit, however, had serious foaming problems throughout

the entire CTP. Foaming was so great that, to prevent foam from flowing over the walls of the reactor, the feed had to be added intermittently over an hourly period. Surprisingly, the solids levels in the 9 day units were quite stable, despite the foaming problems.

The 6 day MCRT unit failed when the temperature was dropped to 5°C. For the first few days after the temperature drop, the reactor appeared to be operating satisfactorily (other than some minor foaming problems); however, by day 5 of the CTP, the unit began to change colour from dark brown to grey brown, and smell like the leachate feed. The oxygen uptake was checked after feeding and was very close to zero. By day 8, it was apparent that the unit had failed.

The failure was initially believed to be due to a combination of the change of the leachate feed and the temperature drop. When looking at the CTP kinetics however (see APPENDICES III, IV, and V), it would appear that the failure would have occurred regardless of the change in the feed and was directly a result of the temperature drop. Calculations in APPENDIX V, show that the minimum operational MCRT at 5°C was approximately 7.6 days. This explains the failure of the 6 day MCRT unit and also shows why the 9 day MCRT unit experienced such instability problems.

After the 6 day MCRT unit failed, an effort was made to start-up a new 25 day MCRT unit at 5°C; however, within 10 days of operation, this unit also failed. The failure occurred in a similar way to that with the 6 day unit. Immediately after start-up, the reactor appeared to be operating as was hoped for. The mixed liquor pH was gradually increasing and foaming was at a minimum. But after 5 days, the mixed liquor solids started to drop and the colour of the mixed liquor changed to grey-brown. By day 10, the unit had failed.

This is a very interesting result, in so much as it indicates that, even though the systems can operate at cold temperatures, warmer temperature acclimatization appears to be necessary with a leachate feed as strong and as toxic as that used in this study.

Another aspect of the biological environment not previously mentioned, is the steady-state trace metal concentration in the mixed liquor, as presented in TABLE 9. From TABLE 9, it can be seen that under some circumstances, the mixed liquor metal concentrations were higher than those in the leachate feed. The major point to be drawn here is that the biological system was able to operate effectively, regardless of the high metal levels.

There was also no change in the mixed liquor metals concentrations as the temperatures were reduced. This implies that the mixed liquor metal concentrations were determined more by hydraulics and other factors, than by biological conditions. The actual metal state (solid, dissolved, complexed etc.) in the mixed liquor is related to the biological conditions and metal solubilities. This point will be considered later.

(b) <u>Filtered versus Settled Effluents</u> - Before examining treatment efficiencies, it might be helpful to present a brief description of the effluents. Both filtered and settled samples were taken at each temperature level, with the exception of 16°C, where only filtered samples were taken (due to the short operating period at that temperature).

Filtration was performed using Whatman #4 filter paper. The effluents were light brown in colour and possessed a "dusty" smell. Despite filtration, there was still fine colloidal solids in the samples.

Settling was performed in one litre graduated cylinders for a period of 2 hours. The colour and smell of the settled samples was the same as was found in the filtered samples. The quantity of solids present depended upon

TABLE 9
BIOLOGICAL REACTOR MIXED LIQUOR METAL CONCENTRATIONS

Operating Temperature	24°C			16°C		9°C		5°C					
MCRT (days)	TRP Leachate Feed	15	25	15	25	15	25	CTP Leachate Feed	9	12	15	25	
Aluminum (mg/l)	0.62	0.53	0.53	0.56	0.51	0.53	0.51	0.49	0.48	0.44	0.40	0.42	
Cadmium (mg/l)	0.04	0.049	0.033	0.041	0.035	0.039	0.035	0.035	0.038	0.036	0.035	0.036	
Calcium (mg/l)	775	129	153	124	127	199	221	638	241	167	149	131	
Chromium (mg/l)	0.098	0.109	0.094	0.090	0.112	0.095	0.091	0.102	0.102	0.080	0.103	0.105	
Iron (mg/l)	1,225	1,175	1,152	1,190	1,140	1,186	1,093	1,035	1,025	1,029	1,025	994	
Lead (mg/l)	0.031	0.023	0.056	0.020	0.033	0.019	0.032	0.026	0.027	0.033	0.020	0.023	
Magnesium (mg/l)	71.5	57.0	61.2	53.6	61.0	54.6	55.5	66.0	64.2	56.0	51.0	53.5	
Manganese (mg/l)	14.0	8.2	10.7	8.3	9.3	10.4	13.5	12.2	10.6	8.3	8.1	8.3	
Nickel (mg/l)	0.33	0.36	0.32	0.26	0′.31	0.42	0.29	0.10	0.12	0.10	0.13	0.07	
Zinc (mg/l)	39.2	28.5	26.3	31.2	26.1	32.1	24.2	22.8	21.2	18.9	18.7	17.6	

the quality of settling which was achieved.

There were two reasons for collecting both filtered and settled effluents. Firstly, filtered samples were collected to determine the idealized soluble organic and metal removal efficiencies, independent of the problems related to settling. Secondly, the filtered sample data was also used in the biological kinetics calculations presented in APPENDICES IV and V. The settled samples were collected to observe what effect the temperature drop would have on the quality of settling.

(c) <u>Settling</u> - TABLE 10 presents a summary of the settling encountered throughout the operating period. Before the data can be evaluated, a few qualifications must be made. Firstly, the COD values in the table are the stored sample COD's and as a result, are the average values from throughout the entire operating period. This explains some discrepancy between the effluent TSS and the effluent non-soluble COD. Secondly, the Sludge Volume Index (SVI) values cannot be compared directly to those achieved using other wastewaters, because of the very high suspended solids concentrations. The SVI's can, however, be compared to each other.

As can be seen, the quality of settling throughout the operating schedule was highly variable. However, there were some general trends observed. The following is a brief summary of the observations.

- (1) At colder temperatures, the settling rate was more erratic.
- (2) Effluent clarity was also worse at colder temperatures.
- (3) The rate and quality of settling was slightly better at higher MCRT's.

The principal conclusion is that, as the biological conditions become more extreme (higher feed rates, colder temperatures etc.), more problems are encountered in solids settling. This, combined with the well documented

TABLE 10
BIOLOGICAL REACTOR SETTLING CONDITIONS

Operating Temperature	24	l°C	9	°C	5°C					
MCRT (days)	15	25	15	25	9	12	15	25		
Kg COD/kg MLVSS-day Kg BOD <sub>5</sub> /kg MLVSS-day	0.41 0.29	0.26 0.18	0.26 0.18	0.19 0.13	0.38 0.25	0.31 0.21	0.24 0.16	0.17 0.11		
Soluble COD effluent	352	331	270	262	551	448	331	314		
(mg/l) Non-Soluble COD effluent	71	26	145	130	680	177	67	108		
(mg/l) Total COD effluent	423	357	415	392	1,231	625	398	422		
(mg/l) MLSS (mg/l)	6,590	6,685	8,110	6,845	9,030	8,320	8,310 140	7,495 120		
Total Suspended Solids Effluent (mg/l)	70 (30-140)*	60 (45-100)	275 (250-300)	230 (190-270)	705 (450-900)	250 (210-270)	(110-160)	(105 <b>-</b> 145)		
Typical Sludge Volume	75	62	55	44	33	27	33	25		
Index (ml/gm) Physical Description	(61-125)* -very slow	(51- 70)	(46- 63) -adequate	(38- 51) -good	(27- 42) -good to	(24- 29) -very good	(26-38) -very good	(18- 33) -very good		
of Settling	settling	settling	settling	settling	very good settling	settling	settling	settling		
	-clear to	-very	-very	-very	-very, very	-very	-cloudy	-cloudy		
	very	clear	cloudy	cloudy	cloudy	cloudy	super-	super-		
	clear	super-	super-	super-	super-	super-	natant	natant		
	super- natant	natant	natant	natant	natant	natant		·		

<sup>\* -</sup> Refers to the range of values encountered.

NOTE: - No settling tests were performed at 16°C.

problems associated with transient loading conditions and the fill-and-draw feeding procedure, resulted in the settling observed (21).

The main symptom of the extreme operating conditions was poor floc formation. It was especially evident at the colder temperatures. This was also observed by Selna and Schroeder under parallel treatment conditions (27,28). They attributed the problems to the sudden increases in organic loading, which resulted in greatly varying growth rates and less extracellular slime, thus inducing breakup and poor formation of floc. The fill-and-draw feeding procedure, by nature, continuously shock loads the biological sludge. The extremes in settling, therefore, were a result of general system instability. In a full-scale treatment system, this instability may not be a problem because the loading conditions are likely to be less severe.

Another possible cause of the erratic settling behaviour was micro-biological speciation. Although no detailed tests were performed to determine the composition of the biological population, it is well known that as temperature and feed rate change, the bacterial population can alter accordingly (26). The floc formation characteristics of one population can be significantly different than another and therefore can induce changes in settling conditions.

(d) <u>Biotreatment Removal Efficiencies</u> - Unless otherwise specified, this section deals primarily with filtered effluents. A summary of the typical organic removal efficiencies is presented in TABLE 11.

COD removal was found to range from 97.2% (5°C, 9 day MCRT) to 98.6% (9°C, 25 day MCRT). The range in  $BOD_5$  removals was from 99.5% (5°C, 9 day MCRT) to greater than 99.9% (24°C, 25 day MCRT). For MCRT greater than 12 days, the effluent  $BOD_5$  levels were superior to the B.C. Pollution Control Board standards under all temperature conditions (7), with all effluent

TABLE 11

EFFECT OF TEMPERATURE, SETTLING RATE AND MCRT ON THE REMOVAL OF ORGANIC MATERIAL

Operating Temperature	5°C	9°C	16°C	24°C
Mixed Liquor COD	A=8,080 (53.3)*			
(mg/l)	B=7,395 (61.8)	*		
	C=7,335 (62.1)	C=7,160 (62.8)*	C=6,020 (68.7)*	C=4,680 (75.7)*
	D=6,480 (66.5)	D=5,530 (71.3)	D=4,800 (75.1)	D=4,205 (78.2)
Settled Effluent COD mg/l)	A=1,231 (93.6)			
(2 hour settling period)	B= 625 (96.8)			
(=	C= 398 (97.9)	C= 415 (97.8)	_	c= 419 (97.8)
	D= 422 (97.8)	D= 392 (97.9)		D= 357 (98.1)
Filtered Effluent COD (mg/l)	A= 551 (97.2)			
(Whatman #4 filter)	B= 448 (97.7)			
(Wild Single III 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	C= 331 (98.3)	C= 270 (98.6)	C= 295 (98.5)	C= 352 (98.2)
	D= 314 (98.4)	D= 262 (98.6)	D= 315 (98.4)	D= 331 (98.3)
Settled Effluent BOD <sub>5</sub> (mg/l)	A= 176 (98.6)			
(2 hour settling period)	B= 98 (99.2)			
(1 110 m )	C= 29 (99.8)	C= 31 (99.8)	_	C= 21 (99.8)
	D= 41 (99.7)	D= 24 (99.8)		D= 12 (99.9)
Filtered Effluent BOD <sub>5</sub> (mg/l)	A= 70 (99.5)			
(Whatman #4 filter)	B= 29 (99.8)			
(	C= 15 (99.9)	C= 9 (99.9)	C= 16 (99.9)	C= 10 (99.9)
	D= 31 (99.8)	D= 6(>99.9)	D= 10 (99.9)	D= 4(>99.9)

Digester Description:

A = 9 day MCRT units

B = 12 day MCRT units

C = 15 day MCRT units

D = 25 day MCRT units

\*brackets refer to percent removal with respect to raw leachate values

 $BOD_5$ 's less than 31 mg/ $\ell$ . This indicates that raw leachate can be effectively treated through aerobic bio-treatment (assuming good solids removal is provided).

COD removal efficiency was found to be relatively independent of the organic loading rate and the temperature level for the 15 day and 25 day MCRT units. During the CTP however, in the lower MRCT units, the COD removal efficiency decreased as the food to micro-organism ratio (F/M) was increased. FIGURE 3 shows the COD removal efficiency as a function of the organic loading during the CTP.

FIGURE 3 also gives some indication of the operational changes which occurred as failure was approached in the biological unit. The removal efficiency of the system remained relatively constant up until the loading rate approached the loading rate at which failure occurred. At that time, the vital characteristics deteriorated very rapidly, with the unit failing suddenly. This point of failure was a result of several factors, including the system temperature, the system operational stability, and the developed organic and metal toxicity (resulting from higher feed concentrations). This was similarly observed at the warmer temperatures by Zapf-Gilje (21).

There is one inconsistency in the data presented. Unexpectedly, as the temperature was reduced from 24°C to 9°C, the filtered COD removal efficiency improved slightly. There was no corresponding change in the settled effluent COD removal efficiency. This discrepancy possibly resulted from the more stable operating conditions in the temperature controlled room, and as a result, was not necessarily related to the rate of bio-activity achieved at the different temperatures.

TABLE 12 and TABLE 13 present a summary of the metal removal efficiencies through biological treatment of the leachate. In general, the

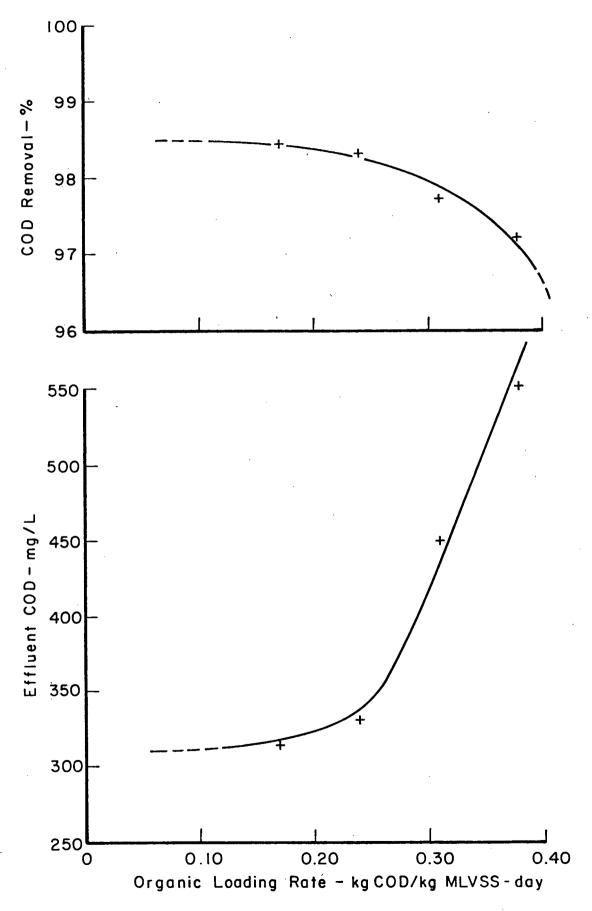


FIGURE 3: COD Removal vs. Organic Loading Rate During CTP

removal of metal contaminants was very good. Removals of greater than 96% were achieved for Fe, Mn, and Zn in the filtered samples. Ca (86.8% to 96.0%), Pb (greater than 70%), Cr (70.0% to 80.0%), and Ni (67.8% to 82.0%) were also effectively removed. Reduction of Mg (32% to 40%) was found to be substantially less. No figures are reported for Cu and Al because of contamination in the stored samples.

Biological systems can remove metals by three mechanisms; simple precipitation, micro-organism uptake by the sludge, and physical adsorption to or entrapment by the biological flocs. The primary removal mechanism for each metal depends upon the solubility products and the relative affinity for sludge uptake of the given metal. The factors affecting the uptake of metals by the sludge include pH, metal concentrations, MLVSS concentration, and metal form, either soluble or insoluble (29).

Because of the large increase in fixed suspended solids between the leachate feed (pH = 5.2) and the mixed liquor (pH > 8.0), it appears that metal precipitation was the major metal removal mechanism in this study. Most likely, sludge uptake also contributed to metal removal, particularly with metals such as Pb and Cr (30); however, with the pH increase and the very high metals concentrations, precipitation was probably much more prominent. Listed below is a brief evaluation of possible removal mechanisms for each metal:

- (1) Calcium Ca was primarily removed as CaCO<sub>3</sub> precipitate. The settling of CaCO<sub>3</sub> was aided by adsorption and entrapment onto the biological floc. Other mechanisms were not considered likely because of the magnitude of the removals achieved (3).
- (2) Iron Fe was probably removed by precipitation as  $\text{FePO}_4$  and  $\text{Fe}\left(\text{OH}\right)_3$ , and settled out with the aid of adsorption and

TABLE 12
SUMMARY OF METAL REMOVAL EFFICIENCIES DURING THE TRP

Operating Temperature			24°C			16	5°C	9°C				
MCRT - days F-Filtered, S-Settled	TRP Leachate Feed	15 F	15 S	25 F	25 S	15 F	25 F	15 F	15 S	25 F	25 S	
Calcium (mg/l)	775	39.7 (94.9) <sup>2</sup>	41.0	58.6 (92.4)	60.0 (92.3)	31.2 (96.0)	82.7 (89.3)	61.1 (92.1)	62.7 (91.9)	102.5 (86.8)	103.9 (86.6)	
Chromium (mg/l)	0.098	0.014 (85.7)			0.028 (71.4)	0.026 (73.5)					0.029 (70.4)	
Iron (mg/l)	1,225	1.1 (99.9)	8.7 (99.3)	1.4 (99.9)	12.1 (99.0)	1.4 (99.9)	1.5 (99.9)	4.1 (99.7)	33.2 (97.3)	1.1 (99.9)	31.0 (97.5)	
Lead (mg/l)	0.031	<0.01 (>68)	<0.01 (>68)	<0.01 (>68)	<0.01 (>68)	<0.01 (>68)	<0.01 (>68)	<0.01 (>68)	<0.01 (>68)	<0.01 (>68)	<0.01 (>68)	
Magnesium (mg/l)	71.5	48.2 (32.6)	49.2 (31.2)	46.3 (35.2)	47.0 (34.3)	46.0 (35.7)	45.9 (35.8)	44.2 (38.2)	46.0 (35.7)	45.2 (36.8)	45.6 (36.2)	
Manganese (mg/l)	14.0	0.05	0.15 (98.9)	0.02	0.14 (99.0)	0.17 (98.8)	0.02 (99.9)	0.08	0.25 (98.2)	0.17 (98.8)	0.33 (97.6)	
Nickel (mg/l)	0.33	0.11	0.11 (66.7)	0.07 (78.8)	0.07 (78.8)	0.06 (81.8)	0.06 (81.8)	0.06 (81.8)	0.06 (81.8)	0.06 (81.8)	0.06 (81.8)	
Zinc (mg/l)	39.2	0.20 (99.5)	0.51 (98.7)	0.20 (99.5)	0.57 (98.5)	0.16 (99.6)	0.19 (99.5)	0.86 (97.8)	2.02 (94.8)	0.16 (99.6)	1.41 (96.4)	

<sup>\* -</sup> Brackets refer to percent removal.

TABLE 13 SUMMARY OF METAL REMOVAL EFFICIENCIES DURING THE CTP

Operating Temperature					5°C				
MCRT - days	CTP	9	9	12	12	15	15	25	25
F-Filtered, S-Settled	Leachate Feed	F	S	F	S	F	S	F	S
Calcium (mg/l)	638	51.0	51.2	44.8	45.6	54.7	55.2	66.1	67.8
, , , , , , , , , , , , , , , , , , ,		(92.0)*	(92.0)	(93.0)	(92.9)	(91.4)	(91.3)	(89.6)	(89.4)
Chromium (mg/l)	0.102	0.30	0.39	0.024	0.039	0.025	0.050	0.024	0.047
(,		(70.6)	(61.8)	(76.5)	(61.8)	(75.5)	(51.0)	(76.5)	(53.9)
Iron (mg/l)	1,035	1.4	35.0	1.2	35.1	0.8	25.6	2.5	23.2
11011 (1119) 20 /	.,	(99.9)	(96.6)	(99.9)	(96.6)	(99.9)	(97.5)	(99.8)	(97.8)
Lead (mg/l)	0.026	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
nead (mg/ ~/	0.020	(>61.5)		1	(>61.5)	(>61.5)	(>61.5)	(>61.5)	(>61.5)
Magnesium (mg/l)	66.0	45.0	45.0	43.9	44.6	43.8	44.8	43.1	44.0
magnesium (mg/~)	00.0	(31.8)	(31.8)	(33.5)	(32.4)	(33.6)	(32.1)	(34.7)	(33.3)
(may / 0 )	12.2	0.46	0.71	0.29	0.64	0.20	0.53	0.22	0.55
Manganese (mg/l)	12.2	(96.2)	(94.2)	(97.6)	(94.8)	(98.4)	(95.7)	(98.2)	(95.5)
		0.40	0.40	0.07	0.08	0.07	0.09	0.07	0.09
†Nickel (mg/l)	0.10	0.10	0.10	(30.0)	(20.0)	(30.0)	(10.0)	(30.0)	(10.0)
					4 47	0.17	0.80	0.23	1.32
Zinc (mg/l)	22.8	0.27 (98.8)	1.16	0.21 (99.1)	1.47 (93.6)	0.17 (99.3)	(96.5)	(99.0)	(94.2)

\* - Brackets refer to percent removal† - Influent too low to provide significant results

- entrapment. The soluble iron concentration is highly pH dependent.
- (3) Zinc, Lead, and Chromium Zn, Pb, and Cr were removed by a combination of precipitation and biological uptake. Zn and Pb could have formed carbonate or phosphate precipitates, while Cr probably formed hydroxides. All these metals have been shown to have a high affinity for sludge uptake (30).
- (4) Manganese Mn was probably removed by carbonate precipitation.

  Biological uptake and adsorption may also have played a role
  in Mn removal (1).
- (5) Nickel Ni may have been precipitated out as a hydroxide or complexed with other compounds present. It is unlikely that biological uptake played a significant role in the removal of Ni, because of the very low micro biological requirements for Ni.
- (6) Magnesium Magnesium hydroxides will not precipitate out at a pH lower than 10.5; therefore Mg removal was poor. The removal achieved was probably a result of some precipitation, adsorption, and entrapment in the floc.

No significant change was noted in the effluent metals' concentrations as the detention time was reduced. Neufeld (30) and Cheng (29) showed previously, that much of the metal uptake and precipitation in the mixed liquor (95%) occurs very rapidly after feeding; therefore, detention time would not play a significant role in metal removal.

Although the metal-compounds are, in general, slightly more soluble at warmer temperatures, filtered effluent metal removals were not significantly affected by temperature reduction. However, some metal removals, particularly

at the colder temperature, were quite different in the settled effluents.

This was a result of the variable levels of settling noted and the chemical form which the metal was predominently in (solid, dissolved, complexed etc.).

Fe and Zn, and to a lesser extent Mn and Cr, showed increases in concentration in the poorly settled effluents. Apparently, these metals were tightly bound into the biological floc and this removal was highly dependent upon the quality of settling. The other metals, Pb, Mg, Ca, and Ni, were either dissolved in the mixed liquor or were in a form which could be settled more readily, than the flocs with higher Fe and Zn content. It would be interesting to examine the characteristics of poorly settled floc, as compared to well settled floc, to see whether there is a chemical difference.

## 4.2 Lime-Precipitation Polishing

(a) <u>Introduction</u> - Biological treatment was found to be effective in treating the raw leachate, both in terms of organic removal and metal removal, but because of the very high initial concentrations, further treatment was still required to reduce the effluent concentrations to below the PCB standards.

TABLES 12, 13, and 14 present the second-stage influent characteristics of the stored samples. Any discrepancies between TABLE 14 and those tables previously presented are a result of modifications which occurred during storage. Tests were performed on all of the samples identified. All data from the lime precipitation schedule are presented in APPENDIX VII.

(b) Clarification - The level of clarification was dependent upon the pH of the treated sample. The pH final at which adequate clarification took place (the clarification pH), ranged from 9.45 to 10.10 for samples with initial alkalinities and hardness between 396 mg/ $\ell$  and

TABLE 14
SECOND-STAGE INFLUENT CHARACTERISTICS

TEMPERATURE	MCRT-days F or S	Sample	рH	COD (mg/l)	BOD <sub>5</sub> (mg/l)	Total Solids (mg/l)	Total Suspended Solids	Alkalinity mg/l as CaCO3	Acidity mg/l as CaCO <sub>3</sub>	Dissolved
24	15 - S	1	7.4	419	21	1565	140	629	37	1425
24	25 - S	2	7.6	357	12	1720	120	528	11	1600
24	15 - F	3	7.9	352	10	1795	25	528	14	1770
24	25 - F	4	7.8	331	4	1855	25	523	12	1830
16	15 - F	5	8.2	295	16	1420	15	518	3	1405
16	25 - F	6	8.2	315	10	1700	25	427	2	1670
9	15 - S	7	7.7	415	31	1745	220	555	16	1525
9	25 - S	8	7.8	392	24	1920	380	466	13	1540
9	15 - F	9	8.1	270	9	1540	25	540	10	1515
9	25 - F	10	8.2	262	6	1685	5	424	6	1680
5	9 <b>-</b> s	11	7.6	1231	176	2275	450	851	21	1825
5	12 - S	12	7.8	625	98	2110	240	498	16	1870
5	15 - S	13	8.0	398	29	1795	145	631	10	1650
5	25 - S	14	8.0	422	41	1955	100	437	8	1355
5	9 <b>-</b> F	15	7.8	551	70	1920	20	732	16	1900
5	12 - F	16	8.1	448	29	1860	10	485	7	1850
5	15 - F	17	8.0	331	15	1645	5	570	6	1640
5	25 <b>-</b> F	18	8.2	314	31	1610	5	396	3	1605

851 mg/ $\ell$ , and 100 mg/ $\ell$  and 150 mg/ $\ell$  as CaCO $_3$  respectively. This is similar to results obtained with raw wastewater and secondary effluent, where for high alkalinity-hardness samples (greater than 350 mg/ $\ell$  of CaCO $_3$ ), a clarification pH of 9.5 was common (31). This pH roughly corresponds to the pH where insoluble CO $_3^{-2}$  alkalinity (which can readily form precipitates) becomes the predominent carbonate specie present rather than soluble HCO $_3^{-1}$  alkalinity (22).

The relationship between the lime dosage added and the  $pH_{\mbox{final}}$  of the solution is presented in FIGURE 4. This general curve will be used on the subsequent curves indicating organic and metal removals relative to lime dosage.

(c) Organic Removals - FIGURE 5 indicates the levels of COD reduction as related to the lime dosages applied (relative to the pH<sub>final</sub> after effluent settling). In a sample with an initial COD of between 262 mg/l and 551 mg/l and suspended solids equal or less than 25 mg/l, a dosage of 900 mg/l Ca(OH) was required to achieve a 25% reduction in COD. This removal rate is equal or better than that achieved using lime-precipitation on raw leachate (16,31). Lime-precipitation treatment is traditionally more effective on refractory organics (31). Since most of the organic material remaining after biological treatment is non-biodegradable, the improved removal rate was as expected.

The levels of suspended solids in the influent were an important factor in the removal of residual organics. An attempt was made to correlate the suspended solids level with organic removal but no statistically significant relationship could be developed. Generally, the higher the suspended solids, the greater the percent removal in COD was achieved (at a constant lime dosage). This occurred primarily because of the quantity of organic material which was initially present in the suspended solids of the samples.

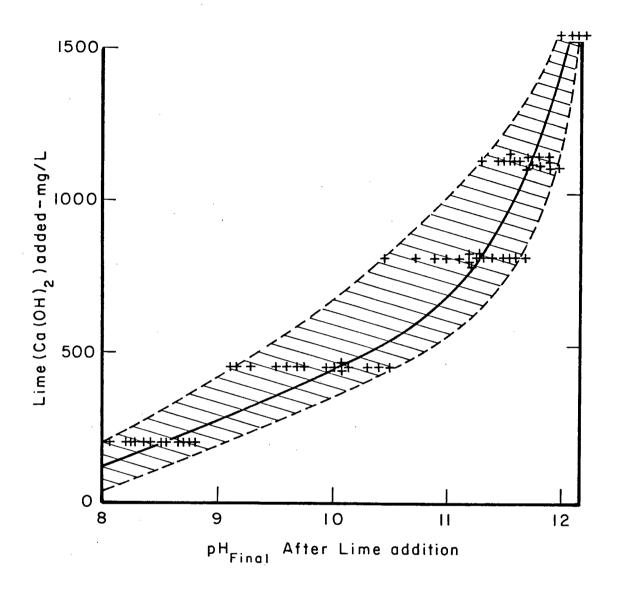
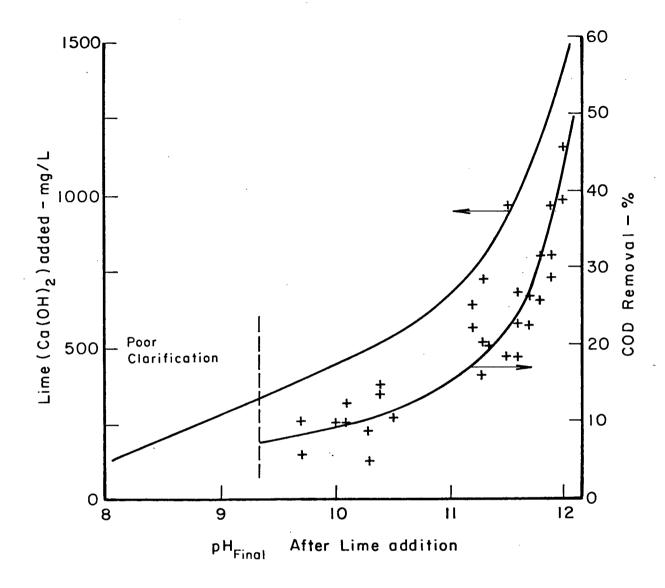


FIGURE 4 : Lime Additions\* vs. pH final After Lime Additions

\*NOTE For second stage lime addition.

All influent solids levels.



\*NOTE: For Second Stage Lime Addition, Where Total Suspended Solids is 25 mg/L or Less in the Influent. Percent removals are misleading in samples containing higher initial solids levels.

The addition of lime improved the settling of the biological solids and thus the apparent COD removal was greater.

In the higher suspended solids samples, the clarification pH appeared to be higher than the average. This was primarily a result of the slower settling rates (due to the very high solids levels in the test beakers). As expected, the higher initial suspended solids samples produced greater volumes of sludge.

The other factors affecting the clarification pH, and consequently, the lime dosage required to achieve further organic removals, were the influent COD and the alkalinity. FIGURES 6 and 7 show the quantity of lime required to achieve a further 20% COD removal at the corresponding COD and alkalinity levels. Both figures show reasonable correlation between the initial characteristic measured and the dosage required. An attempt was made to relate the alkalinity with the COD; however, no statistical correlation could be developed. Even though neither figure has quite enough points to be totally convincing, it is possible to reach general conclusions:

- (1) At lower suspended solids levels (≤25 mg/l), sample alkalinity and COD are both very important in determining the lime dose required. Alkalinity is probably more important than COD.
- (2) The higher the alkalinity and COD, the higher the lime dosage required to achieve a consistent percentage organic removal efficiency. This is roughly defined on FIGURES 6 and 7.
- (3) At high suspended solids levels (not shown), the COD is more significant relative to the percent removal efficiency (because of the presence of organics in the excess solids), although alkalinity is still important.
- (d) Metal Removals Fe, Zn, Mn, Mg, and Ca were all monitored after

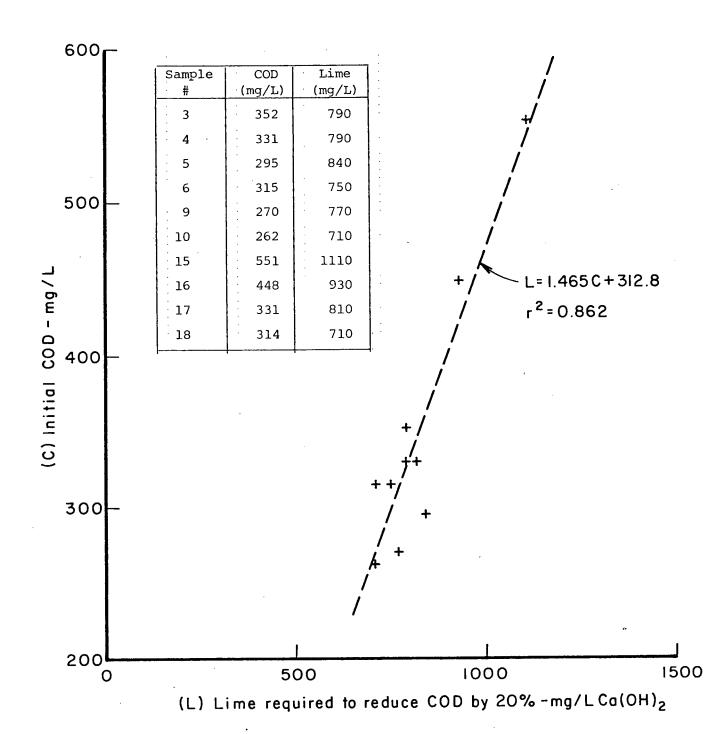


FIGURE 6: Lime Required to Reduce COD by 20%  $\underline{\text{vs}}$ . the Influent COD\*.

\*NOTE: For Second Stage Lime Addition, Where Suspended Solids is 25 mg/L or Less in the Influent.

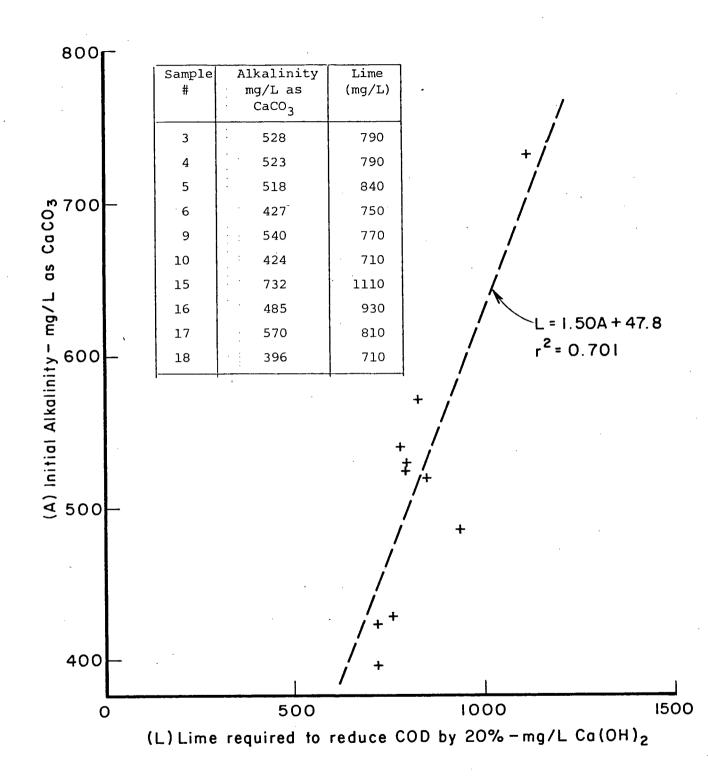


FIGURE 7: Lime Required to Reduce COD by 20% vs. the Influent Alkalinity\*

\*NOTE: For Second Stage Lime Addition, Where Suspended Solids is 25 mg/L or Less in the Influent.

the lime-precipitation tests, where possible. The other metal concentrations were below the PCB standards already (7). FIGURES 8 through 12 indicate the removals observed for the respective metals.

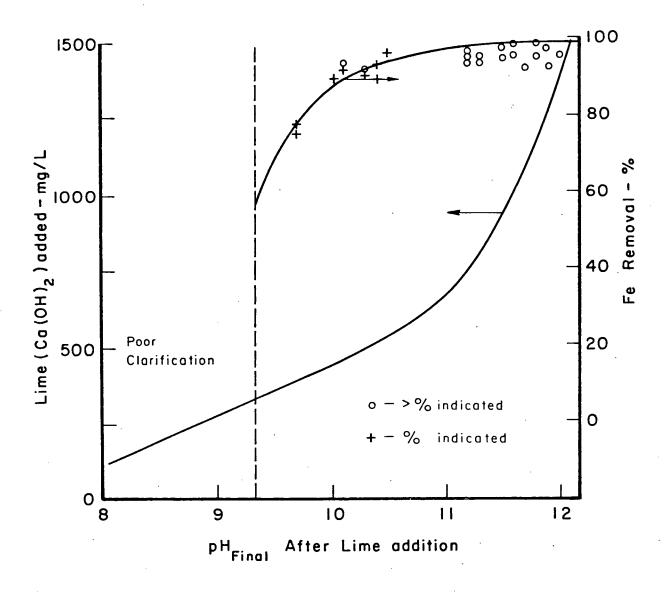
Fe, Zn, Mn, and Mg all followed essentially the same removal pattern. The higher the lime dosage (and pH<sub>final</sub>), the greater the metal removal. The pH at which "effective" metal removal occurred, varied from metal to metal. As pH was increased, Fe was removed first, then Zn, then Mg and finally Mn. This corresponds well with the hydroxide solubility products presented in APPENDIX VI. The level of suspended solids in the influent did not significantly affect the pH at which "effective" metal removal was achieved.

Calcium showed a slightly different removal pattern. At lime dosages between 300 mg/l and 700 mg/l Ca(OH) $_2$ , Ca removal was consistently around 79%; however, at dosages greater than 700 mg/l Ca(OH) $_2$ , Ca removal declined. At a dosage of 1,350 mg/l Ca(OH) $_2$ , the effluent Ca level was slightly greater than the influent Ca concentration and was increasing with higher dosages. Apparently, at a dosage of roughly 700 mg/l Ca(OH) $_2$ , the residual alkalinity in solution was used up, and the excess Ca added, accumulated in solution.

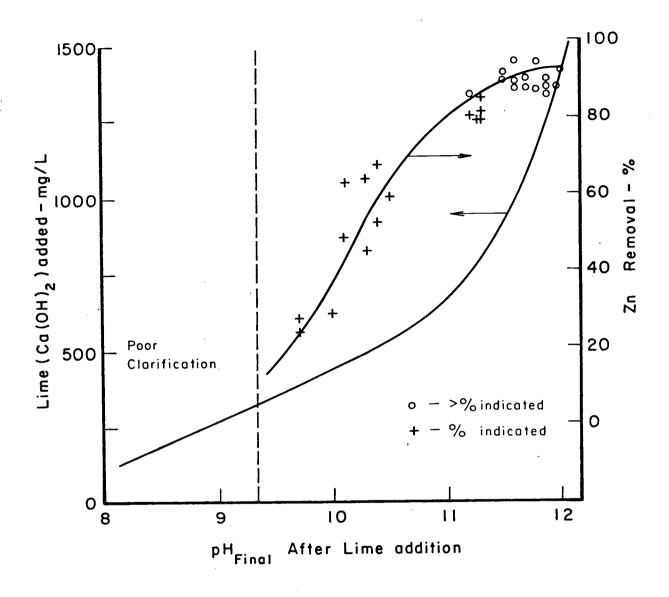
(e) Removal Mechanisms - Generally, the level of organic material removed directly corresponded to the visually observed quantity of floc developed and the subsequent quality of settling. As there was no specific transition pH at which the organic removal rate improved (as with the metals), it would appear that the organics were removed by a general increase in the floc formed. This implies that organic removals with lime precipitation are related to physical mechanisms such as adsorption and entrapment in con-

and the second second second second

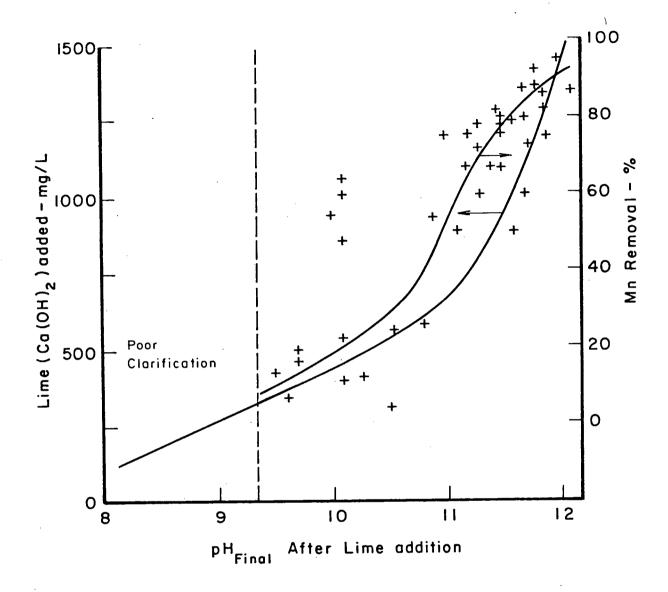
<sup>1&</sup>quot;effective as defined by PCB removal requirements (7).



\*NOTE: For Second Stage Lime Addition,
Where Total Suspended Solids is
25 mg/L or Less in the Influent.
In samples with TSS greater than
25 mg/L, percent removals are
misleading because of high initial
Fe in solids.



\*NOTE: For Second Stage Lime Addition,
Where Total Suspended Solids is
25 mg/L or Less in the Effluent.
In samples with TSS greater than
25 mg/L, percent removals are
misleading because of high initial
Zn in solids.



\*NOTE: For Second Stage Lime Addition.
All influent solids levels.

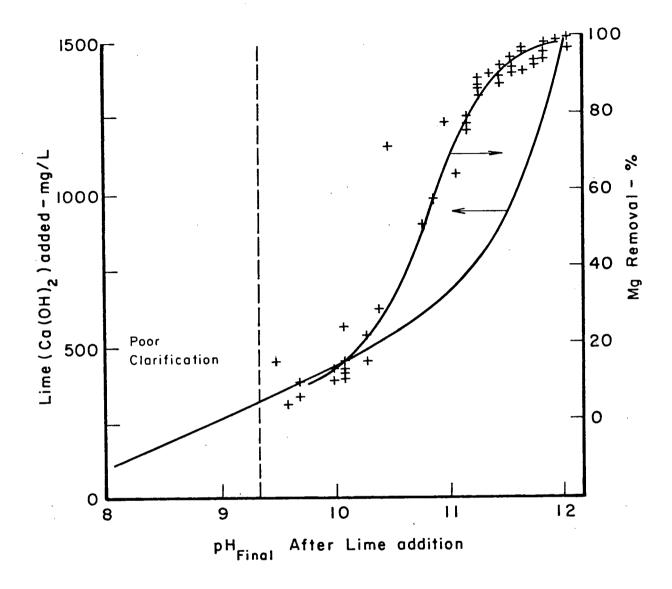
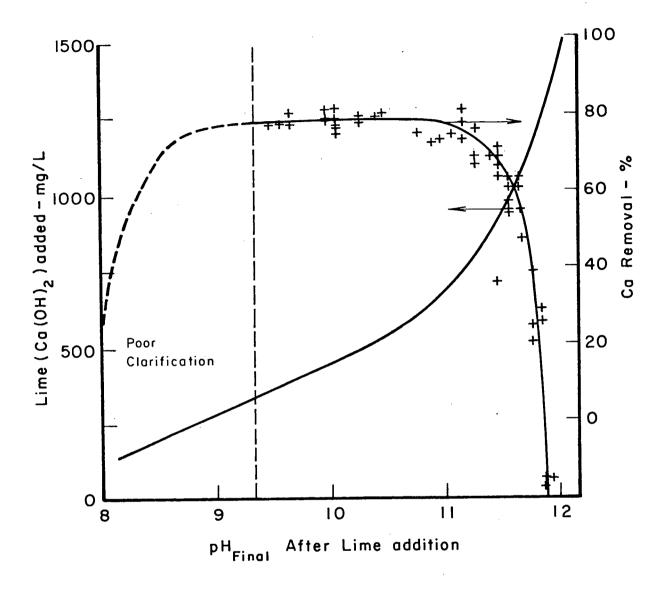


FIGURE 11: Lime Additions and Magnesium Removals\*

vs. pH final After Lime Additions.

\*NOTE: For Second Stage Lime Addition.
All influent solids levels.



\*NOTE: For Second Stage Lime Addition.
All influent solids levels.

junction with the metal precipitation. Apparently, as the metal hydroxides (and CaCO<sub>3</sub>) are formed, the organic materials, which are probably initially complexed with the metals, are carried out of solution with the settling hydroxides. There is also probably some physical entrapment of organic suspended solids during settling. The result is, that as the quantity of floc is increased (as the pH is increased), the level of organic removal is increased.

This was not necessarily the case with the removal of metals from solution. Although floc formation was important, the metal removals appear more directly related to the pH at which the corresponding metal hydroxides were formed. The observed sequential metal removals, as pH was increased, appears to verify this.

- (f) <u>Suspended Solids Removal</u> Indications are that the addition of lime reduced suspended solids most effectively. The lime dosage required to achieve acceptable suspended solids removal (based on visual observation), was approximately 450 mg/ $\ell$  Ca(OH)<sub>2</sub>.
- When considering a treatment system when pH adjustment is required, it is extremely important to evaluate the natural buffering capacity of the waste. The quantity of chemical required, in this case lime, can be very high if the system buffering capacity is high. Bjorkman and Mavinic (16) found that with an initial alkalinity of roughly 4,000 mg/l CaCO<sub>3</sub>, with raw leachate, 2,700 mg/l lime was required to increase the pH from 5.2 to between 10 and 11 where precipitation will occur. Although treatment using lime precipitation (with no biological pre-treatment), is unsatisfactory based on organic removals alone, the prohibitively high lime dosage makes it doubly unsuitable.

With an alkalinity removing step, like biological treatment, prior

to lime addition, the lime dosages can be reduced significantly. TABLE 14 indicates the reductions in alkalinity derived by bio-treatment in this study. With initial raw leachates alkalinities of roughly 4,120 mg/ $\ell$  CaCO $_3$ , the average first-stage effluent alkalinity was 540 mg/ $\ell$  CaCO $_3$ . This is a reduction of 85%.

The resulting reductions in lime required for lime precipitation after bio-treatment are dramatic. To achieve a similar pH of between 10 and 11 (as with Bjorkman), as average lime dosage of roughly 600 mg/l Ca(OH) was required. This is a reduction of lime required (as compared to Bjorkman) of greater than 75%. Although the lime dosages are still quite high, they are significantly less than if there was no pre-treatment.

## 4.3 Combined Biological-Chemical Treatment

The combination of aerobic biological treatment, followed by limepolishing, was shown to be a very effective means of treating moderate to
high strength sanitary landfill leachates. There are two possible ways of
operating the system, each being effective under different circumstances.

The first format would operate the biological unit at a low MCRT, thus relying upon the lime-polishing unit to a greater extent. This would be effective if the temperature variations were not expected to be too great.

A "safe" MCRT would be established, designed to achieve only "adequate" treatment and removal rates. Lime additions would be quite large but could be varied according to the first stage effluent quality. This study has shown that at lower MCRT levels (higher organic loading rates), settling can be a problem; however, with higher lime dosages, the inferior quality first-stage effluents would be clarified without much trouble. The major problem with this system would be the quantity of sludge being produced and subject to further treatment and disposal, as well as the cost of such large

quantities of lime. The advantage of this system would be, that the biological reactor would be relatively small and capital costs could be minimized.

The second operating format would have a longer MCRT in the biotreatment portion and employ substantially smaller lime dosages in the polishing unit. This would be effective if the temperatures were expected to be more variable. The system would depend almost entirely upon the biological unit for organic and metal removals. Lime treatment would only be employed if the settling was poor, or at very cold temperatures when the effluent quality was less consistent. The advantage of this system is that the lime dosages would be reduced substantially and the chemical costs would be reduced accordingly. This system would also be less prone to operational problems (because of the longer detention time), than the first system. The disadvantage is that, with a larger biological reactor, the capital costs would probably be higher.

Either of these formats would be improved significantly if the lime dosages could be reduced. The best means of reducing the lime requirement might be by the addition of magnesium. Lime-magnesium treatment has also been shown to improve metal removals from wastewater (25). This should be examined in a future study.

The best operating MCRT for leachates like those in this study, would be from 12 to 15 days. At 12 days, the removals were not quite as good as 15 days; however, the system was quite stable and with lime addition, good quality effluents were produced. If the 12 day MCRT unit was used, continuous lime addition would probably be required, since settling was a problem and the biological effluents did not quite meet the effluent standards at the cold temperatures. If the 15 day MCRT unit was used, little lime polishing would be required. Lime polishing would only be employed if

settling deteriorated or if other problems occurred at the colder temperatures. TABLE 15 presents the net removal efficiencies achieved using 12 and 15 day MCRT units, and the "optimum" lime dosages at 5°C. All PCB standards (7) were met, with the exception of pH and Mn.

TABLE 15 COMBINED TREATMENT REMOVAL EFFICIENCIES

Constituent	CTP Leachate (mg/l)	MCRT=12 d. Settled Sample (mg/l)	Lime Added =800 mg/l	Net Percent Removal	MCRT=15 d. Settled Sample (mg/l)	Lime Added =450 mg/l	Net Percent Removal	PCB Standard (mg/l)
pH <sup>1</sup> BOD <sub>5</sub> COD TS TSS Ca Cr	5.2 12,910 19,370 10,445 1,470 638 0.102	7.8 98 625 2,110 240 45.6 0.039 35.1	11.2 <29 <sup>2</sup> 383 1,550 <100 <sup>3</sup> 9.6 <0.01	- >99.8 98.0 85.2 >93.2 98.5 >91.2 >99.9	8.0 29 398 1,795 145 55.2 0.050 25.6	10.0 <15 <sup>2</sup> 358 1,430 <100 <sup>3</sup> 10.0 <0.01	- >99.9 98.2 86.3 >93.2 98.4 >91.2 >99.9	6.5-8.5 45 - 100 - 0.1 0.3
Fe Pb Mg Mn Ni Zn	1,035 0.026 66.0 12.2 0.10 22.8	35.1 <0.01 44.6 0.64 0.08 1.47	<0.07 <0.01 9.8 0.21 <0.08 0.11	>61.5 85.2 98.3 >20.0 99.5	<0.01 44.8 0.53 0.09 0.80	<0.01 40.2 0.24 <0.08 0.21	>61.5 39.1 98.0 >20.0 99.1	0.05 150 0.05 0.3 0.5

 $<sup>^{\</sup>rm 1}$  - Not in mg/l  $^{\rm 2}$  - From filtered samples or if suspended solids were removed by improved settling  $^{\rm 3}$  - Assumed from clarification data

#### CHAPTER 5

#### CONCLUSIONS AND RECOMMENDATIONS

The previous chapter presented the experimental results obtained from this study. The purpose of this chapter is to present a summary of the results and to make suggestions for future research projects.

#### 5.1 Conclusions

The experimental results led to the following conclusions:

- (1) Aerobic biological treatment is very effective in the treatment of high strength sanitary landfill leachates (BOD $_5$  = 13,300 mg/ $\ell$ , COD = 19,300 mg/ $\ell$ ). Soluble COD removals ranged from 97.2% (5°C, 9 day MCRT) to 98.6% (9°C, 25 day MCRT). Soluble BOD $_5$  removals ranged from 99.5% (5°C, 9 day MCRT) to greater than 99.9% (24°C, 25 day MCRT).
- (2) Within the operating range tested, the soluble COD removal efficiency was independent of the organic loading rate and temperature for units with an MCRT of 15 days or greater.

  At 5°C, for units with MCRT of less than 15 days, COD removal efficiency decreased as the organic loading rate was increased.
- (3) The kinetic parameters obtained at 5°C indicated that biological growth was influenced by temperature reduction. The predicted minimum MCRT was 7.6 days. Extreme instability was noted in the 9 day MCRT unit and the 6 day MCRT unit failed at 5°C.
- (4) As the temperatures were decreased, the mixed liquor volatile suspended solids concentrations increased, resulting in lower operating F/M ratios at the colder temperatures. The reduced

- F/M ratios seemed to counterbalance the lower bacterial metabolic rates and resulted in adequate treatment at the colder temperatures.
- (5) It was not possible to start-up a 25 day MCRT unit at 5°C.

  This indicates that, even though effective removals are

  possible at colder temperatures, warmer temperature acclimatization, followed by gradual temperature reduction, may be necessary to prepare the units for cold temperature operations.
- (6) Metals were removed by biological uptake/entrapment and/or chemical precipitation due to the high system pH. Metal removal efficiency, during aerobic biological treatment, was greater than 96% for Fe, Mn, and Zn, better than 80% for Ca, better than 70% for Pb, between 70 and 80% for Cr and Ni, and 40% for Mg. There was no significant change in metal removal efficiency as the temperatures were reduced or as the MCRT was increased.
- (7) The highly variable settling conditions were primarily a result of the "shock load" nature of the fill-and-draw feeding procedure. The deterioration in settling quality at colder temperatures was probably a result of biological speciation and higher MLVSS levels.
- (8) The poor settling at the colder temperatures resulted in a carryover of excess organics into the first-stage effluent. Some metals (Fe and Zn, and to a lesser extent, Mn and Cr) also showed significant increases in concentration in the poorly settled effluents.
- (9) The efficiency of clarification, due to lime addition, was

- dependent upon the pH  $_{\rm final}$  of the treated sample. The clarification pH ranged from 9.45 to 10.10 for samples with initial alkalinities and hardnesses between 396 mg/ $\ell$  and 851 mg/ $\ell$ , and 100 mg/ $\ell$  and 150 mg/ $\ell$  as CaCO $_{3}$ , respectively.
- (10) In a sample with an initial COD of between 262 mg/l and 551 mg/l and low suspended solids (≤25 mg/l), a dosage of 900 mg/l. Ca(OH) was required to achieve a further 25% reduction in COD. The samples with higher suspended solids concentrations had better percent removals of COD and produced a greater volume of sludge.
- (11) The influent COD and alkalinity were significant in determining the clarification pH and consequently the lime dosage required. When plotting the lime dosage required to reduce COD by 20%, versus COD and alkalinity, it was found that;
  - L (lime required) = 1.465 C (COD) + 312.8

    described the relationship between lime and initial COD

    (with 86% confidence) and;
  - L (lime required) = 1.50 A (alkalinity) + 47.8 described the relationship between lime and alkalinity (with 70% confidence). The similar slopes indicate that COD and alkalinity are equally significant in the range of values presented here.
- (12) Fe, Zn, Mg, and Mn followed essentially the same removal pattern. The higher the lime dosage, the greater the amount of metal removed. The pH at which each metal was effectively removed was roughly determined by the hydroxide solubility product of each metal.

- (13) The lime dosage required to achieve "adequate" suspended solids removal was approximately 450 mg/ $\ell$  Ca(OH)<sub>2</sub>, the point where clarification was concluded to be effective.
- (14) An aerobic biological unit of 12 days MCRT, with an addition of 800 mg/l Ca(OH)<sub>2</sub> for polishing, and a biological unit of 15 days MCRT, with an addition of 450 mg/l Ca(OH)<sub>2</sub> for polishing, were found equally effective at treating the raw leachate samples at 5°C. Both systems produced effluent which would meet most of the PCB standards (7).

#### 5.2 Recommendations for Future Studies

Much work has been done to the treatment of sanitary landfill leachates, but there is still some research that should be carried out. It should include:

- (1) An evaluation of methods which might be used in treating the metal-rich sludge which is produced by the biological system.
- (2) An examination of how the initial leachate strength affects the kinetic parameters. This could be performed by taking an initial leachate sample and making three or four dilutions, then testing the characteristically proportional samples under identical biological treatment conditions.
- (3) A pilot-scale biological study, using effluents from a new sanitary landfill, to observe the effects of the changes in the leachate characteristics on the biological system.
- (4) An investigation of other potential biological systems including Rotating Biological Contact Units (RBC), which

- would be capable of handling the variable flows involved with leaching systems.
- (5) An investigation of lime-magnesium treatment as a means of reducing the lime dosages required in the polishing unit.
- (6) An examination of the potential for lime regeneration and reuse from leachate-lime precipitation sludge. As indicated in this study, lime dosages can be high. It would be extremely valuable if lime regeneration from the sludge could be performed, thus effectively reducing the actual lime required for the treatment system.

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#### APPENDIX I

#### EFFECT OF COLD TEMPERATURE ON BIODEGRADATION

This is a brief summary of the possible effects of temperature reduction on aerobic biological treatment. The conclusions presented are derived from the treatment of domestic wastewaters between 4°C and 20°C and may vary slightly from that which occurred with the leachate feed (33):

- (1) The cell-synthesis yield coefficient (mixed liquor volatile solids produced/unit of substrate utilized) is independent of temperature at low influent soluble substrate concentrations; however, at higher influent substrate levels, temperature will effect the yield coefficient.
- (2) The micro-organism decay coefficient is independent of temperature, but can vary with the mean cell residence time.
- (3) Reducing the temperature will reduce the soluble substrate removal efficiency, especially at higher feed rates.
- (4) Dissolved oxygen uptake rate is reduced significantly as temperature is reduced.
- (5) Sludge settling, in terms of the sludge volume index (SVI), is satisfactory between 4°C and 20°C; however, nothing has been conclusively said about supernatent clarity in the settled effluents as the temperatures are reduced.
- (6) As the temperature is reduced, the mixed liquor volatile suspended solid concentrations (MLVSS) increase; the greater the system feed rate, the greater the MLVSS increase observed.

#### APPENDIX II

# BIOLOGICAL SOLIDS LEVELS THROUGHOUT THE OPERATING SCHEDULE

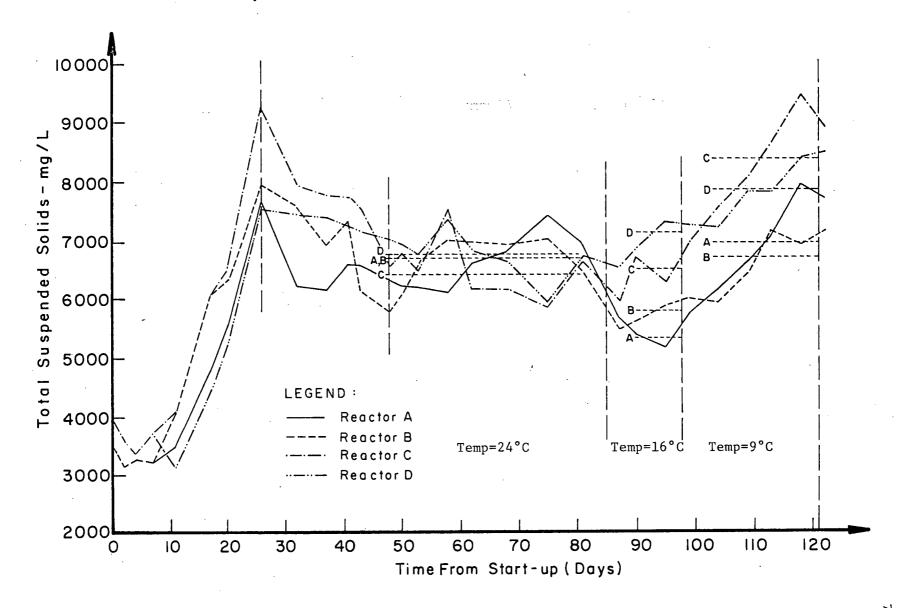


FIGURE A: TSS During The TRP

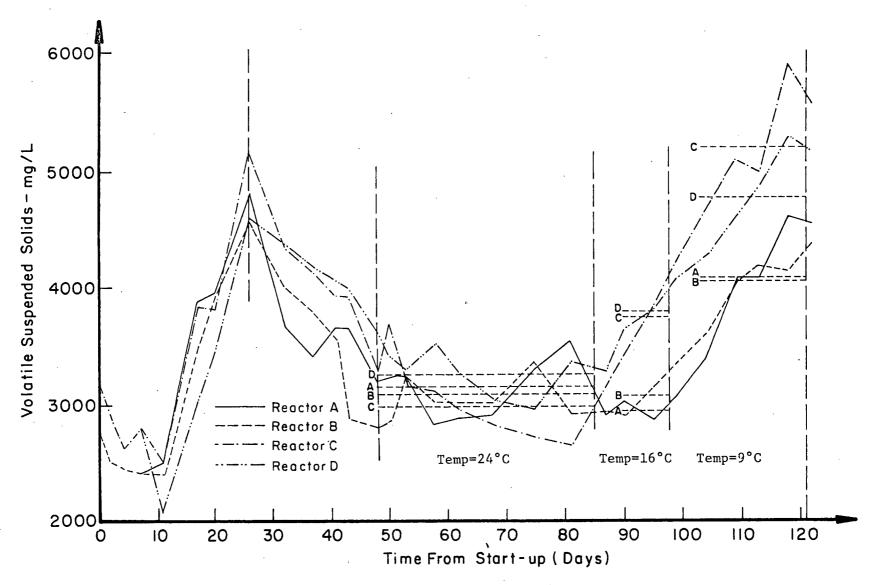


FIGURE B: VSS During the TRP

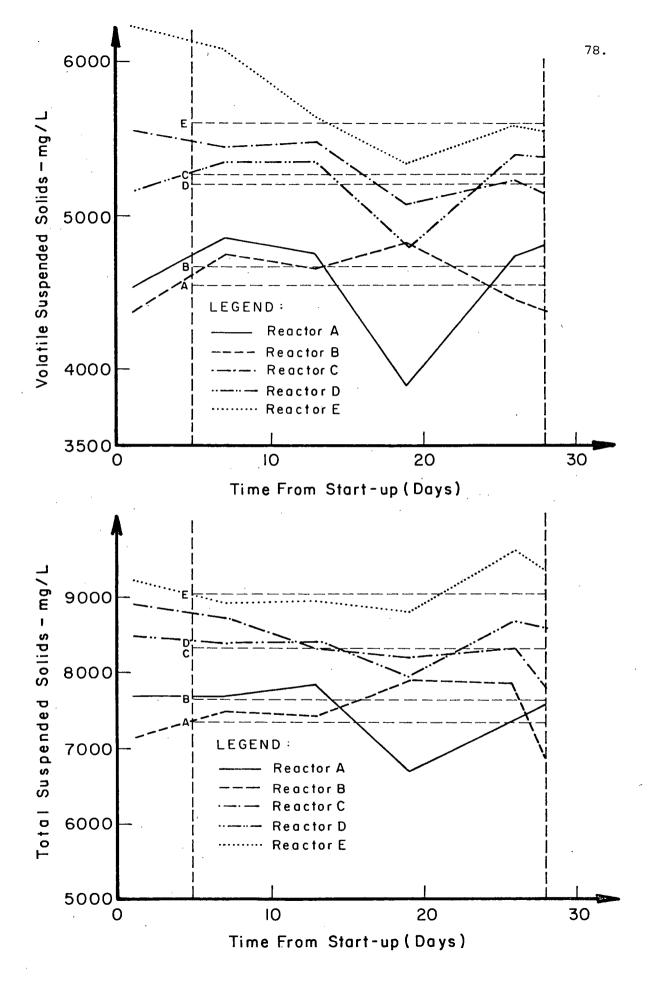


FIGURE C: Suspended Solids During the CTP (Temp=5°C)

#### APPENDIX III

#### BIOLOGICAL TREATMENT DESIGN EQUATIONS

The equations employed to define the biological operations and kinetics are presented in Metcalf and Eddy (22). These include:

$$\frac{dX/dt}{X} = Y \frac{ds/dt}{X} - b \dots (2)$$

where

$$\frac{dS}{dt}$$
 = rate of substrate utilization,  $\frac{mass}{volume-time}$ 

S = soluble substrate concentration, mass/volume

X = mixed liquor micro-organism concentration, mass/volume

 $\frac{dx}{dt}$  = net growth rate of micro-organism, mass/volume-time

$$K_{S}$$
 = substrate concentration when  $\frac{dS/dt}{X} = \frac{K}{2}$ 

Y = growth-yield coefficient, mass of micro-organisms/mass
 of substrate utilized

b = micro-organism decay coefficient, time<sup>-1</sup>

$$\theta_{C} = \frac{X}{dX/dt}$$
, time

For a complete-mix-no-recycle system, fixing the mean cell residence time  $\theta_{\text{C}}$  establishes the micro-organism concentration in the reactor.

Metcalf and Eddy showed that on a finite time basis, that the rate of food utilization could be defined as:

and in turn, the biological solids concentrations as

$$X = \frac{Y (S_o - S_e)}{1 + b\theta} \qquad (5)$$

where Q = influent waste flow rate, volume/time

V = volume of the reactor, volume

 $S_{O}$  = total influent waste concentration soluble, mass/volume

 $S_{e}$  = effluent waste concentration, mass/volume.

To determine the minimum solids detention time,  $\theta_{\text{c}}$  min's can be replaced by S in Equation (3). That is,

The minimum solids detention time is defined as "the residence time at which cells are washed out of the system more rapidly than they can reproduce".

#### APPENDIX IV

#### BIOLOGICAL KINETIC PARAMETERS

Although an analysis of kinetics over the entire temperature range is not possible due to insufficient data, biological kinetics can be determined for the cold temperature phase. A more complete evaluation of the kinetics will be presented in a future report, using data from both this work and that of Zapf-Gilje (19).

### (1) Determination of Y and b (BOD, Basis)

From Appendix II, Equation (2):

$$\frac{\Delta X/\Delta t}{X} = Y \frac{\Delta S/\Delta t}{X} - b$$

where 
$$\frac{\Delta S}{\Delta t} = \frac{S_0 - S_e}{\theta_C}$$

and 
$$\frac{\Delta X}{\Delta t} = \frac{X_e^{-X}}{\theta_c} = \frac{X_e}{\theta_c} \text{ (assume } X_o = 0)$$

and 
$$\frac{\Delta X/\Delta t}{X} = \frac{1}{\theta}$$

A plot of  $\frac{\Delta X/\Delta t}{X}$  vs.  $\frac{\Delta S/\Delta t}{X}$  should yield a straight line with Y being the slope and -b being the y-axis intercept.

TABLE 16

KINETIC PARAMETERS, Y AND b - BOD<sub>5</sub> BASIS

θ c days	X mg/l	S o mg/l	S e mg/l	ΔS/Δt mg/l/day	(ΔS/Δt)/X day -1	$(\Delta X/\Delta t)/X=1/\theta c$ day
9	5,600	12,920	70	1,428	0.255	0.111
12	5,210	12,920	29	1,074	0.206	0.083
15	5,265	12,920	15	860	0.163	0.067
25	4,600	12,920	31	515	0.112	0.040
	•					

The above data plotted in FIGURE D, with a least squares fit gives:

$$Y = 0.49 \text{ mg VSS/mg BOD}_5$$

and

$$b = 0.0148 \text{ day}^{-1}$$

The correlation coefficient is 0.99.

## (2) Determination of K and K (BOD Basis)

From Appendix II, Equation 1:

$$\frac{\Delta S}{\Delta t} = \frac{KXS_e}{K_s + S_e}$$

Rearranging this, we get

$$\frac{x}{\Delta S/\Delta t} = \frac{K_{s}}{K} (\frac{1}{S_{e}}) + \frac{1}{K}$$

Plotting  $\frac{X}{\Delta S/\Delta t}$  vs.  $\frac{1}{S_e}$  should yield a straight line with  $\frac{K}{S}$  as the slope

and  $\frac{1}{K}$  as the y-intercept.

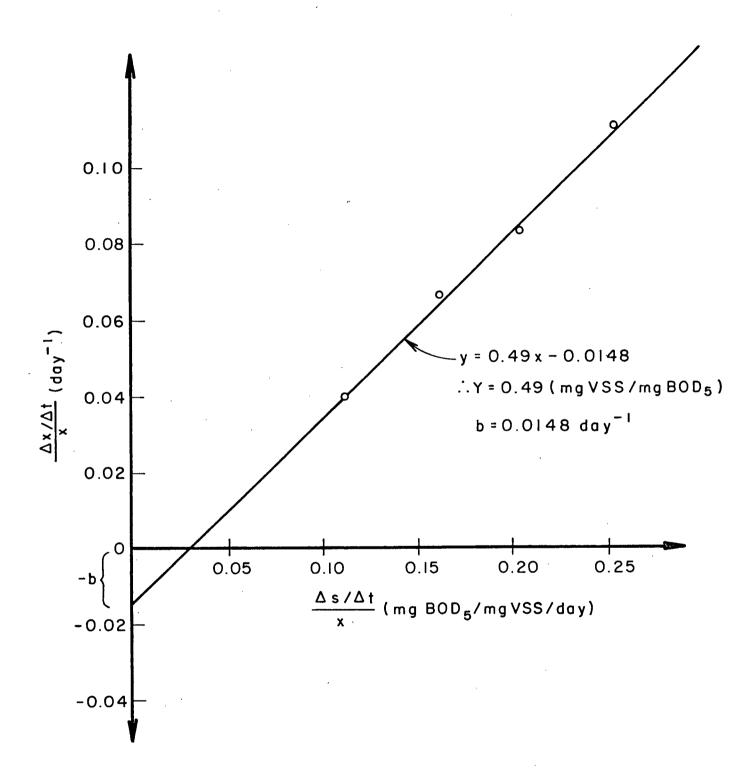


FIGURE D: Determination of Y and b Based on  $\mathrm{BOD}_5$  Data

TABLE 17 KINETIC PARAMETERS, K and K  $_{
m S}$  - BOD  $_{
m 5}$  BASIS

θ <sub>c</sub>	Х	S e	ΔS/Δt	1/S <sub>e</sub>	X/(ΔS/Δt)
days	mg/l	mg/l	mg/l/day	l/mg	day
9	5,600	70	1,428	0.014	3.92
12	5,210	29	1,074	0.034	4.85
15	5,265	. 15	860	0.067	6.13
25	4,600	31	515	0.032	8.93

The above data plotted in FIGURE E, with a least squares fit gives:

$$K = 0.29 \text{ mg BOD}_5/\text{mg VSS/day}$$

$$K_{S} = 20.2 \text{ mg/l}$$

The correlation coefficient is only 0.08. This is due to the erratic performance of the 25 day reactor at 5°C. If the 25 day reactor is not included, the correlation coefficient is 0.99 (the dotted line on FIGURE E). This line gives:

$$K = 0.30 \text{ mg BOD}_5/\text{mg VSS/day}$$

and 
$$K_{S} = 12.3 \text{ mg/l}$$

Thus, the resultant kinetic parameters are not significantly different even though the correlation coefficient is low; the K and  $K_{\mbox{\scriptsize S}}$  parameters would appear to be acceptable.

#### (3) Determination of Y and b (COD Basis)

Using similar procedures as developed in part (1),  $\frac{\Delta X/\Delta t}{X}$  vs.  $\frac{\Delta S/\Delta t}{X}$  can be plotted, yielding Y as the slope and -b as the y-intercept.

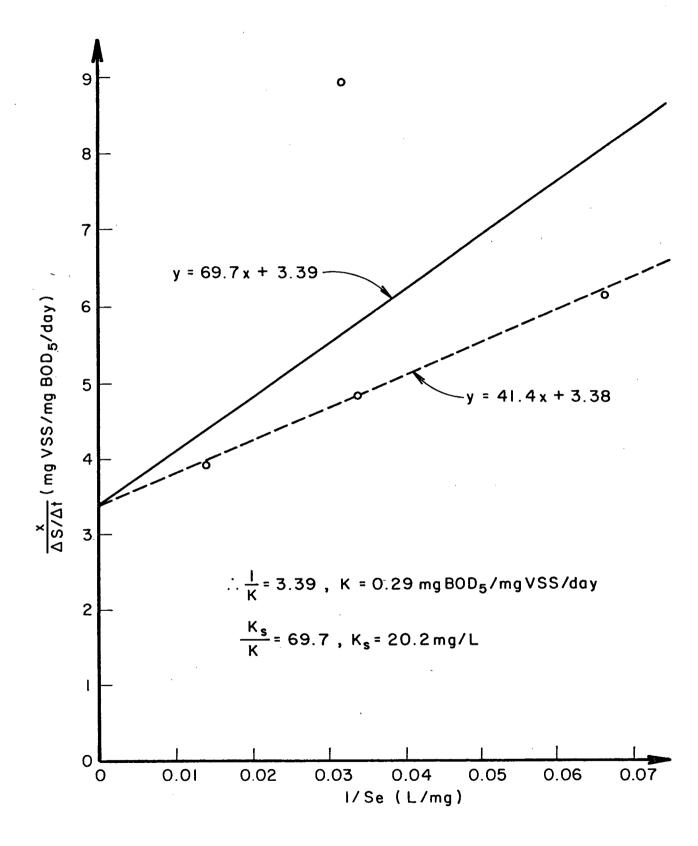


FIGURE E: Determination of K and K  $_{\mbox{\scriptsize S}}$  Based on  $\mbox{\scriptsize BOD}_{\mbox{\scriptsize 5}}$  Data

TABLE 18

KINETIC PARAMETERS - COD BASIS

θ c days	X mg/l	S. o. mg/l	S e mg/l	ΔS/Δt mg/l/day	(ΔS/Δt)/X day <sup>-1</sup>	$(\dot{\Delta}x/\dot{\Delta}t)/x=1/\theta_{C}$ day
9	5,600	19,370	551	2,091	0.373	0.111
12	5,210	19,370	448	1,577	0.303	0.083
15	5,265	19,370	331	1,269	0.241	0.067
25	4,600	19,370	314	762	0.166	0.040

The above data plotted in FIGURE F, with a least square fit gives:

Y = 0.34 mg VSS/mg COD

and

$$b = 0.0157 \, day^{-1}$$

The correlation coefficient is 0.99.

It was not possible to develop K and K on a COD basis because when  $\frac{X}{\Delta S/\Delta t} \quad \text{and} \quad \frac{1}{S} \quad \text{were plotted,} \quad \frac{1}{K} \quad \text{was found to be a negative value.} \quad \text{Apparently,}$ 

COD data occasionally cannot be used for kinetic parameters.

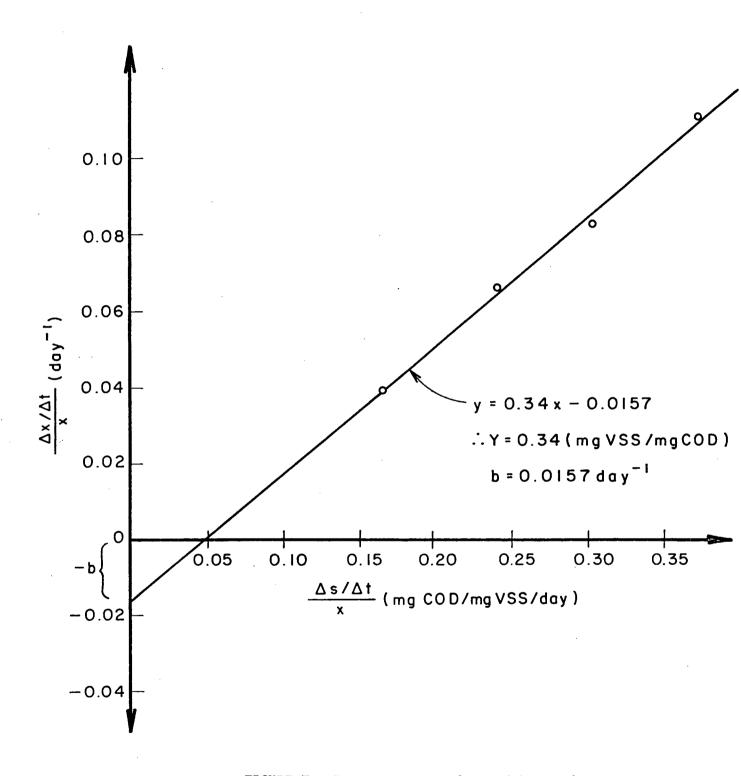


FIGURE F: Determination of Y and b Based on COD Data

#### APPENDIX V

#### THE MINIMUM CTP SOLIDS DETENTION TIME

From Appendix IV, on a  $BOD_5$  basis:

 $Y = 0.49 \text{ mg VSS/mg BOD}_{5}$ 

 $b = 0.0148 \text{ day}^{-1}$ 

 $K = 0.29 \text{ mg} BOD_5/\text{mg} VSS/\text{day}$ 

 $K_{s} = 20.2 \text{ mg/l}$ 

From Appendix III, the minimum solids detention is defined as

$$\frac{1}{\theta_{\text{c min}}} = \frac{\text{YKS}_{\text{o}}}{\text{K}_{\text{s}} + \text{S}_{\text{o}}} - \text{b}$$

With an influent waste concentration of 12,920 mg/l BOD,  $\theta_{\rm c}$  min can be calculated:

$$\frac{1}{\theta_{\text{c min}}} = \frac{(0.49) (0.30) (12,920)}{12.3 + 12,920} - 0.0148 = 0.132$$

Therefore, the minimum solids detention time,  $\theta_{\text{c}}$  min, would be 7.58 days at 5°C.

#### APPENDIX VI

# RELEVANT SOLUBILITY PRODUCTS OF CATIONIC HEAVY METAL OXIDES AND HYDROXIDES (32)

Compound	ksp (@25°C)
Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$1 \times 10^{-54}$
Fe (OH) <sub>3</sub>	$6 \times 10^{-38}$
Cr(OH) <sub>3</sub>	$1 \times 10^{-30}$
Cu(OH) <sub>2</sub>	$3 \times 10^{-19}$
Zn(OH) <sub>2</sub>	$4.5 \times 10^{-17}$
Ni(OH) <sub>2</sub>	1.6 x 10 <sup>-16</sup>
Fe(OH) <sub>2</sub>	1.8 x 10 <sup>-15</sup>
Pb <sub>2</sub> O(OH) <sub>2</sub>	1.6 x 10 <sup>-15</sup>
Pb <sub>3</sub> CO <sub>3</sub>	1.5 x 10 <sup>-15</sup>
Cd(OH) <sub>2</sub>	$2 \times 10^{-14}$
Mn(OH) <sub>2</sub>	$2 \times 10^{-13}$
Mg(OH) <sub>2</sub>	$8.0 \times 10^{-12}$
MnCO <sub>3</sub>	8.8 x 10 <sup>-11</sup>
ZnCO <sub>3</sub>	$2 \times 10^{-10}$
CaCO <sub>3</sub>	$4.7 \times 10^{-9}$
Ca(OH) <sub>2</sub>	1.3 x 10 <sup>-6</sup>

#### APPENDIX VII

#### LIME PRECIPITATION REMOVAL DATA

The following are notes on the tables presented below:

- 1) All units are  $mg/\ell$  unless otherwise indicated. pH is dimensionless.
- 2) "PC" indicates that "poor clarification" was obtained and no other tests were performed.
- 3) All metals were performed on a total basis.
  That data is presented in Section 5.3.
- 4) Samples 12 and 13 had tests for extra metals performed on them.
- 5)  $BOD_5$  is not presented because of sample contamination.

## APPENDIX VII Lime Precipitation Removal Data

Sample Description: T=24°C, MCRT=15 d., TSS=140 mg/ $\ell$  Alkalinity = 629 mg/ $\ell$  as CaCO

1

2

3

0	200	450	800	1100	1540
7.4	8.0	9.3	10.8	11.5	12.1 210
8.7	PC	PC	0.11	<0.07	<0.07
0.51 0.15	PC PC	PC PC	0.17 0.11	0.09 0.05	0.04 <0.02
49.2 41.0	PC PC	PC PC	24.2 9.8	4.61 26.0	0.78 78.0
	7.4 419 8.7 0.51 0.15 49.2	7.4 8.0 419 PC 8.7 PC 0.51 PC 0.15 PC 49.2 PC	7.4 8.0 9.3 419 PC PC 8.7 PC PC 0.51 PC PC 0.15 PC PC 49.2 PC PC	7.4 8.0 9.3 10.8 419 PC PC 275 8.7 PC PC 0.11 0.51 PC PC 0.17 0.15 PC PC 0.11 49.2 PC PC 24.2	7.4 8.0 9.3 10.8 11.5 419 PC PC 275 231 8.7 PC PC 0.11 <0.07 0.51 PC PC 0.17 0.09 0.15 PC PC 0.11 0.05 49.2 PC PC 24.2 4.61

Sample Description: T=24°C, MCRT=25 d., TSS=120 mg/ $\ell$  Alkalinity = 528 mg/ $\ell$  as CaCO

3

Lime Dosage	0	200	450	800	1100	1540
pH COD Fe Zn Mn Mg Ca	7.6 357 12.1 0.57 0.14 47.0 60.0	8.4 PC PC PC PC PC	9.6 262 0.19 0.36 0.13 44.9	11.1 245 <0.07 0.19 0.07 16.9	11.6 210 <0.07 <0.02 0.07 3.10 21.1	12.2 193 <0.07 <0.02 0.02 1.02 103.0

3 Sample Description: T=24°C, MCRT=15 d., TSS=24 mg/ $\ell$  Alkalinity = 528 mg/ $\ell$  as CaCO

3

Lime Dosage	0	200	450	800	1100	1540
рН	7.9	8.2	9.7	11.3	11.7	-
COD	352	PC	332	280	260	-
Fe	1.1	PC	0.24	<0.07	<0.07	_
Zn	0.20	PC	0.15	0.04	<0.02	-
Mn	0.05	PC	0.04	0.02	0.02	-
Mg	48.2	PC	45.1	5.95	2.50	_
Ca	39.7	PC	9.1	10.9	16.2	-

APPENDIX VII
Lime Precipitation Removal Data

Sample Description: T=24°C, MCRT=25 d., TSS=25 mg/ $\ell$  Alkalinity = 523 mg/ $\ell$  as CaCO<sub>3</sub>

Lime Dosage	0	200	450	800	1100	1540
рН	7.8	8.0	10.0	11.3	11.6	-
COD	331	PC	298	264	242	-
Fe	1.4	PC	0.16	<0.07	<0.07	· <del>-</del>
Zn	0.20	PC	0.14	0.04	<0.02	_
Mn	0.02	PC	0.02	0.03	<0.02	-
Mg	46.3	PC	40.1	6.90	2.91	-
	58.6	PC	12.3	15.0	21.0	-

Sample Description: T=16°C, MCRT=15 d., TSS=15 mg/ $\ell$ Alkalinity = 518 mg/ $\ell$  as  $CaCO_3$ 

5

Lime Dosage	0	200	450	800	1100	1540
pH	8.2	8.6	10.1	11.3	11.8	-
COD	295	PC	265	244	201	-
Fe	1.4	PC	0.13	<0.03	<0.02	-
Zn	0.16	PC	0.08	0.03	<0.02	-
Mn	0.17	PC	0.15	0.05	0.02	
Mg	46.0	PC	39.1	5.95	2.01	_
Ca	31.2	PC	7.9	10.1	23.2	-

Sample Description: T=16°C, MCRT=25d., TSS=25 mg/ $\ell$  Alkalinity = 427 mg/ $\ell$  as CACO<sub>3</sub>

Lime Dosage	0	200	450	800	1100	1540
pН	8.2	8.9	10.4	11.6	12.0	_
COD	315	PC	271	243	192	_
Fe	1.5	PC	0.16	<0.07	<0.07	-
Zn	0.19	PC	0.06	<0.02	<0.02	_
Mn	0.02	PC	0.02	<0.02	<0.02	-
Mg	45.9	PC	36.2	3.90	1.12	_
Ca	82.7	PC	17.2	24.1	110.0	_

APPENDIX VII
Lime Precipitation Removal Data

Sample Description: T=9°C, MCRT=15 d., TSS=220 mg/ $\ell$  Alkalinity = 555 mg/ $\ell$  as CaCO<sub>3</sub>

7

Lime Dosage	0	200	450	800	1100	1549
рН	7.7	8.7	10.1	11.5	11.8	_
COD	41.5	PC	210	193	176	-
Fe	33.2	PC	0.11	<0.07	<0.07	-
Zn	2.02	PC	0.51	0.11	<0.02	-
Mn	0.25	PC	0.13	0.07	<0.02	-
Mg	46.0	PC	39.7	5.12	2.96	-
Ca	62.7	PC	14.1	19.2	49.2	-

Sample Description: T=9°C, MCRT=25 d., TSS=380 mg/ $\ell$  Alkalinity = 466 mg/ $\ell$  as CaCO<sub>3</sub>

Lime Dosage	0	200	450	800	1100	1540
На	7.8	8.4	10.1	11.0	11.6	-
COD	392	PC	221	196	183	-
Fe	31.0	PC	<0.07	<0.07	<0.07	-
Zn	1.41	PC	0.19	0.06	<0.02	_
Mn	0.33	PC	0.13	0.08	0.06	-
Mg	45.6	PC	34.2	10.2	2.93	-
Ca	103.9	PC	21.1	27.1	45.6	-

9 Sample Description: T=9°C, MCRT=15 d., TSS=25 mg/ $\ell$  Alkalinity = 540 mg/ $\ell$  as CaCO<sub>3</sub>

Lime Dosage	0	200	450	800	1100	1540
рН	8.1	9.0	10.4	11.6	11.8	_
COD	270	PC	229	220	200	-
Fe	4.1	PC	0.29	<0.07	<0.07	-
. Zn	0.86	PC	0.39	<0.02	0.06	-
Mn	0.08	PC	0.06	<0.02	<0.02	-
Mg	44.2	PC	31.4	3.56	3.06	-
Ca	61.1	PC	12.3	24.1	37.2	_
1	1	1	1	1	1	1

APPENDIX VII
Lime Precipitation Removal

Sample Description: T=9°C, MCRT=15 d., TSS=25 mg/ $\ell$  Alkalinity = 540 mg/ $\ell$  as CaCO<sub>3</sub>

Lime Dosage	0	200	450	800	1100	1540
рН	8.2	8.5	10.1	11.2	11.9	_
COD	262	PC	229	204	179	i -
Fe	1.1	PC	<0.07	<0.07	<0.07	-
Zn	0.16	PC	0.06	<0.02	<0.02	-
Mn	0.17	PC	0.13	0.06	0.03	-
Mg	45.2	PC	37.6	10.2	1.46	-
	102.5	PC	19.0	18.1	76.2	-

Sample Description: T=5°C, MCRT=9 d., TSS=450 mg/ $\ell$  Alkalinity = 851 mg/ $\ell$  as CaCO<sub>3</sub>

Lime Dosage	0	200	450	800	1100	1540
рН	7.6	8.3	9.1	10.9	11.7	12.2
COD	1231	PC	PC	622	545	416
Fe	35.0	PC	PC	0.89	0.24	0.15
Zn	1.16	PC	PC	0.27	0.09	0.07
Mn	0.17	PC	PC	0.33	0.09	0.03
Mg	45.0	PC	PC	19.2	4.27	2.76
Ca	51.2	PC	PC	13.6	18.3	97.0

Sample Description: T=5°C, MCRT=12 d., TSS=240 mg/ $\ell$  Alkalinity = 498 mg/ $\ell$  as CaCO<sub>3</sub>

Lime Dosage	0	200	450	800	1100	1540
рН	7.8	8.2	9.5	11.2	11.5	_
COD	625	PC	518	383	342	_
Fe	35.1	PC	1.6	<0.07	<0.07	-
Zn	1.47	PC	1.21	0.11	0.10	-
Mn	0.64	PC	0.55	0.21	0.13	-
Mg	44.6	PC ·	37.2	9.8	3.96	_
Ca	45.6	PC	10.1	9.6	16.5	-
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APPENDIX VII
Lime Precipitation Removal Data

Sample Description: T=5°C, MCRT=15 d., TSS=145 mg/ $\ell$  Alkalinity = 631 mg/ $\ell$  as CaCO<sub>3</sub>

13

Lime Dosage	0	200	450	800	1100	1540
pH COD Fe Zn Mn Mg Ca	8.0 398 25.6 0.80 0.53 44.8 55.2	8.8 PC PC PC PC PC	10.0 358 0.13 0.21 0.24 40.2 10.0	11.6 254 <0.07 0.11 0.11 3.88 25.3	11.9 248 <0.07 0.09 0.13 0.65 63.1	12.3 176 <0.07 <0.02 0.02 0.41 128.0

Sample Description: T=5°C, MCRT=25 d., TSS=100 mg/ $\ell$  Alkalinity = 437 mg/ $\ell$  as CaCO<sub>3</sub>

Lime Dosage	0	200	450	800	1100	1540
pН	8.0	8.7	10.1	11.4	11.7	-
COD	422	PC	351	323	290	
Fe	23.2	PC	0.79	<0.07	<0.07	-
Zn	1.32	PC	0.30	0.10	0.06	-
Mn	0.55	PC	0.20	0.18	0.15	-
Mg	44.0	PC	39.1	4.4	1.30	_
Ca	67.8	PC	16.0	21.0	30.1	-

Sample Description: T=5°C, MCRT=9 d., TSS=20 mg/ $\ell$  Alkalinity = 732 mg/ $\ell$  as CaCO<sub>3</sub>

				9		
Lime Dosage	0	200	450	800	1100	1540
рн	7.8	8.0	9.1	10.3	11.3	12.0
COD	551	PC	PC	501	395	300
Fe	1.4	PC	PC	0.13	<0.07	<0.07
Zn	0.27	PC	PC	0.10	0.04	<0.02
Mn	0.46	PC	PC	0.40	0.10	0.02
Mg	45.0	PC	PC	34.3	5.01	0.44
Ca	51.0	PC	PC	11.5	15.8	107.6
1	ì	1	1	1	1	1

APPENDIX VII
Lime Precipitation Removal Data

Sample Description: T=5°C, MCRT=12 d., TSS=10 mg/ $\ell$  Alkalinity = 485 mg/ $\ell$  as CaCO<sub>3</sub>

Lime Dosage	0	200	450	800	1100	1540
рН	8.1	8.5	9.7	11.2	11.5	_
COD	448	PC	402	333	276	-
Fe	1.2	PC	0.30	<0.07	<0.07	_ ·
Zn	0.21	PC	0.15	0.04	<0.02	
Mn	0.29	PC	0.24	0.10	0.07	-
Mg	43.9	PC	39.1	8.9	4.01	-
	44.8	PC	9.9	12.1	15.0	-

Sample Description: T=5°C, MCRT=15 d., TSS=5 mg/l
Alkalinity = 570 mg/l as CaCO<sub>3</sub>

Lime Dosage	0	200	450	800	1100	1540
рН	8.0	9.0	10.3	11.7	11.9	_
COD	331	PC	314	257	236	-
Fe	0.8	PC	<0.07	<0.07	<0.07	_
Zn	0.17	PC	0.09	<0.02	<0.02	-
Mn	0.20	PC	0.15	0.04	<0.02	_
Mg	43.8	PC	36.8	1.45	0.96	-
Ca	54.7	PC	11.9	28.9	64.0	-

Sample Description: T=5°C, MCRT=25 d., TSS=5 mg/ $\ell$  Alkalinity = 396 mg/ $\ell$  as CaCO<sub>3</sub>

0	200	450	800	1100	1540
8.2	8.7	10.5	11.5	11.9	_
314	PC	282	256	195	_
2.5	PC	0.11	<0.07	<0.07	_
0.23	PC	0.09	<0.02	<0.02	-
0.22	PC	0.21	0.05	0.03	-
43.1	PC	12.1	4.50	2.01	-
66.1	PC	12.9	19.0	47.0	-
֡	8.2 314 2.5 0.23 0.22 43.1	8.2 8.7 314 PC 2.5 PC 0.23 PC 0.22 PC 43.1 PC	8.2 8.7 10.5 314 PC 282 2.5 PC 0.11 0.23 PC 0.09 0.22 PC 0.21 43.1 PC 12.1	8.2 8.7 10.5 11.5 314 PC 282 256 2.5 PC 0.11 <0.07 0.23 PC 0.09 <0.02 0.22 PC 0.21 0.05 43.1 PC 12.1 4.50	8.2 8.7 10.5 11.5 11.9 314 PC 282 256 195 2.5 PC 0.11 <0.07 <0.07 0.23 PC 0.09 <0.02 <0.02 0.22 PC 0.21 0.05 0.03 43.1 PC 12.1 4.50 2.01