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Anaerobic treatment of metal plating wastewater the treatment of industrial wastewater at varying hydraulic retention times.

Raymond E. Lappan
University of Windsor

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Anaerobic Treatment of Metal Plating Wastewater

The Treatment of Industrial Wastewater
at Varying Hydraulic Retention Times

A Thesis Submitted to the
Faculty of Graduate Studies and Research
Through the Department of Chemical Engineering
in Partial Fulfillment of the Requirements for the
Degree of Master of Applied Science
at the University of Windsor

by

Raymond E. Lappan

Windsor, Ontario, Canada
September 1987

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ABSTRACT

Anaerobic reactors dominated by sulfate reducing bacteria (SRB) are capable of precipitating and separating heavy metals from plating wastewater. The use of such a reactor requires the supplementation of the wastewater with organic matter and sulfates. The SRB bacteria within the reactor consume the organics and reduce the sulfates to produce sulfides which precipitate the heavy metals. A wastewater treatability experiment has shown that soluble copper, nickel and zinc could be precipitated at efficiencies of 99.0, 80.1 and 91.6%, respectively. Effluent from the reactor contained soluble metal concentrations which were always less than 1 mg/L. Total metal separation, except for zinc, was high enough to maintain an effluent which satisfied the suggested discharge limit of 1 mg/L.

Further study of the operation of the reactor at various hydraulic retention times (HRT) between 6.5 and 59.5 hours demonstrated that BOD and COD removal, sulfate consumption and reduced soluble sulfur production and heavy metal separation are all functionally dependent on the HRT. As expected, soluble metal precipitation efficiencies were not dependent on the HRT when excess sulfides are present. Effluent quality was comparable with the treatability study results. Effluent redox potential was found to correlate with the reduced soluble sulfur concentrations.

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Professors J.K. Bewtra, C.C. St. Pierre and L.Wong for their guidance and encouragement throughout this project.

I am thankful to Mr. G. Ryan for the construction of the reactors and Mrs. L. Breschuk for her assistance in the preparation of this manuscript. I am indebted to Greg Kuhun and Bill Henderson for their help throughout the experimental part of this investigation. I must also thank Mr. Gerry Tuck of Universal Fasteners Ltd. for his help in the acquisition of the wastewater.

This research was financed by grants from the Natural Sciences and Engineering Research Council of Canada.

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I. INTRODUCTION

The environmental effects of metals in water and wastewater range from beneficial through troublesome to dangerously toxic. Some metals are essential, others may adversely affect water consumers, wastewater treatment systems, and receiving waters. Some metals may be either beneficial or toxic, depending on their concentration [1].

In Canada, effluent discharge regulations have been implemented to protect the environment from the impact of metals. Discharges of metal contaminated wastewater into local sewage systems are being controlled by individual municipalities. For example, the City of Windsor, Ontario has passed by-law 8319 enforcing strict sewage quality discharge into sewers. Provincial and federal regulations have been written for controlling the effluent discharge into the environment. The Ontario Ministry of the Environment [37] has requirements under the Ontario Water Resources Act which limits the maximum levels of wastewater constituents which are allowed for direct discharge, while the Department of Fisheries and the Environment regulates provinces and territories which do not have their own regulations. Table 1.1 lists the permissible limits for

metals in wastewaters.

Studies have shown that the untreated discharges originating from metal plating processes exceed regulation limits [3]. Table 1.2 lists the constituents typically found in such wastewaters. Most of the constituents are the heavy metal ions which originate from three main sources: the dumping of plating solution, the spillage and leaks of plating solution and product rinsing [20].

Compliance has required the implementation of one or more treatment techniques. These treatments are categorized into: recovery and solids removal. Recovery techniques are treatment methods used for the purpose of recovering or regenerating process constituents which would otherwise be lost in the wastewater. Included in this group are evaporation, ion exchange, electrolytic recovery, electrodialysis and reverse osmosis. Solid removal techniques are employed to remove metals and other pollutants from process wastewater to make the waters suitable for reuse or discharge. These methods include hydroxide and sulfide precipitation, sedimentation, diatomaceous earth filtration, membrane filtration, granular bed filtration, peat adsorption, insoluble starch xanthate treatment and floatation [10].

An alternative to these methods would be the metal precipitation implemented in a reactor developed by Wong et al [53]. This process removes heavy metals from sludge

Table 1.1: Effluent Metal Limits Set by the City of Windsor,
Ontario Ministry of the Environment and
Environment Canada [19,37,55]

Metals (mg/L)	City of Windsor *		Province of Ontario †	Environ- ment Canada †
	I	II		
Cadmium	2.0	0.5	0.0001	1.5
Chromium	5.0	1.0	1.0	1.0
Copper	5.0	1.0	1.0	1.0
Lead	5.0	1.0	1.0	1.0
Mercury	0.1	0.03	0.001	-
Nickel	5.0	1.0	1.0	2.0
Tin	5.0	1.0	1.0	-
Zinc	5.0	1.0	1.0--	2.0
I - less than 500 000 litres per day usage II - greater than 500 000 litres per day usage				

* - For discharge into sanitary sewers

† - For discharge into receiving water bodies

Table 1.2: Principal Constituents Typically Found in Plating Wastewater [17]

Constituent	Plating on Steel	Plating on Zinc Casting	Plating on Brass	Plating on Plastic	Anodising	Concentrations
						mg/L
Fe^{+2}	x					1-10
Cu^{+2}	x (1)	x	x	x		5-50
Ni^{+2}	x	x	x	x	x	2-15
Cr^{+6}	x	x	x	x	x	10-120
Cr^{+3}	x	x	x	x	x	0.1-1.0
Zn^{+2}	x (2)	x				10-50
Cd^{+2}	x (3)					10-50
Sn^{+2}	x (4)			x		0.1-20
CN^{-1}	x (5)	x	x			1-50
SO_4^{-2}	x	x	x	x	x	15-25
Cl^{-1}	x	x	x			1-250
CO_3^{-2}	x	x	x	x		10-50
Si_3^{-2}	x	x	x	x		30-50
PO_4^{-3}	x	x	x		x	20-50
Organics	x	x	x	x		0.1-1.0

Note 1) When copper plating is used.

2) When zinc or brass plating is used.

3) When cadmium plating is used.

4) When tin plating is used.


5) When copper, zinc, brass or cadmium plating are used.

slurry by first solubilizing the heavy metal solids, separating the metal concentrate supernatant from the slurry and then precipitating the heavy metal by means of an anaerobic reactor. Further work encompassing only the anaerobic reactor found it capable of separating up to 50 mg/L of a combined concentration of cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) from a synthetic wastewater. Effluent quality in terms of metal content was found to be in the ~~parts per billion~~ (ppb) range. Recommendations from this study suggested experimental verification of the system capability in treating industrial wastewater for regulatory compliance and the determination of the operational parameters which influence the treatment of the wastewater.

The objective of this study was to prove experimentally that the process would effectively treat industrial wastewater to comply with regulations. Also, the effects of hydraulic retention time, a major operational parameter in sizing the reactor, on metals separation efficiencies was determined. The scope of this study was to:

- (i) characterize the wastewater from a local plating plant, Univeral Fasteners, and determine whether nutrient supplements were needed for anaerobic treatment of the wastewater;

- (ii) determine whether the process could treat the wastewater and comply with regulations by conducting a treatability study, and to estimate the nutritional requirements of the process;
- (iii) prove the existence of sulfate reducing bacteria within the anaerobic reactor and that the wastewater feed supported their growth only;
- (iv) determine the rates of organics and sulfates consumption and sulfides production for different hydraulic retention times;
- (v) determine the soluble metal precipitation efficiencies, along with total metal retention as a function of the reactors hydraulic retention time; and
- (vi) determine whether the redox potential of the effluent is a parameter which defines the activity of the reactor in separating heavy metals.



II. LITERATURE REVIEW

Investigations regarding the toxic effects of heavy metals on anaerobic digestors are dated as far back as the 1920's [23]. Lawrence and McCarty [26] found biogas production by anaerobic digestors under high heavy metal loadings was dependent on the presence of sulfate, the precursor used by sulfate reducing bacteria (SRB) for sulfide production. Sulfides precipitated the toxic heavy metal ions which were present in the influent wastewater.

Hayes and Theis [23] studied the distribution of heavy metals in an anaerobic sludge stabilization digester. Their experiments confirmed Lawrence and McCarty's observations of metal influence on biogas production. In addition, it was demonstrated that high metal loadings caused a drop in the percentage of methane in the biogas and subsequent accumulation of intermediate organic acids substrates within the reactor. This accumulation was less at shock loadings because of rapid toxification of all active bacterial forms in the digester. Further testing gave results which allowed the ranking of the metals in order of toxicity on a molar basis. Nickel (Ni) was the most toxic, while copper (Cu), lead (Pb), chromium (Cr), zinc (Zn) and cadmium (Cd)

followed in order of toxicity. Heavy metal behaviour was found to be controlled by the solubilities of inorganic precipitates and sorption onto and subsequent incorporation of metals into the digester biomass. A suggested method for the control and minimization of the impact of heavy metals was the addition of more precipitate ligands such as sulfides.

DeWalle et al. [13] studied the heavy metal removal efficiency of a completely mixed anaerobic filter. Their study used a feed which consisted of a high chemical oxygen demand (COD) and a low sulfate feed. Metal precipitates formed within the reactor were found as sulfides, carbonates and hydroxides that deposited at the bottom of the reactor as a slurry. A decrease in the removal efficiency and an increase in the slurry metal content was also observed when the reactor hydraulic retention time (HRT) was decreased. Additional experiments by Chian and DeWalle [12] proved that the process could separate heavy metals from a fatty acid wastewater stream which contained high levels of heavy metals.

Rivera [45] found the Freundlich-type equation useful in modelling the separation of heavy metals in an upflow anaerobic fixed film reactor (UAFFR). High cell sorption and the precipitation of metals as sulfides and carbonates were concluded as being the mechanisms for metal separation. Overall, the process was described as operating like an ion

exchange column. The reactor was fed with a wastewater containing nutrient broth and glucose having 2000 mg O_2/L of COD, 75 mg SO_4/L of sulfate and dissolved zinc chloride at levels up to 1000 mg Zn/L.

Maree and Strydom [30] employed an UAFFR for the treatment of mine water with high sulfate but low metal levels. The optimum operating retention time was 11 hr when a stone packing was used. Speciation of effluent sulfur compounds indicated that sulfides were the prime metabolic endproducts existing at levels seldom exceeding 100 mg/L as S^{2-} while sulfites were typically less than 4.2 mg/L as SO_3 .

Wong [54] confirmed that an UAFFR reactor was able to treat a solution containing up to 50 mg/L of each of Cd, Cu, Ni, Pb, and Zn. The synthetic wastewater used consisted of a high COD and a high sulfate feed supplemented with macro and micro nutrients. Digested metals were added to the feed as the metal source.

A. Sulfide Precipitation

Studies using sulfide salts have demonstrated why sulfide precipitation of heavy metals is advantageous over other precipitation methods. The advantages given by McAnnaly [31] and Cherry [10] are as follows:

1. Sulfide has the ability to remove chromates and dichromates without requiring the reduction of chromium to its trivalent state;
2. sulfide will precipitate metals with most complexing agents;

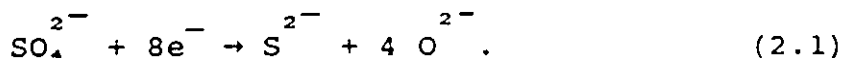
3. sulfide precipitates exhibit less of an amphoteric nature than hydroxide precipitates and have less tendency to resolubilize; and,
4. lower sludge volumes are associated with sulfide precipitates when compared to hydroxide precipitate sludge.

Table 2.1 lists the solubility products for Cu, Ni, Pb and Zn sulfides, carbonates and hydroxides.

Cherry [10] summarized the current treatment methods developed by the U.S. Environmental Protection Agency (EPA) during full scale pilot plant studies. To date there has been a limited use of sulfide precipitation techniques because of their relative high chemical cost. [10] Most recently, McAnally [31], Aldrich [2] and Eisenberg [15] have attempted to make the process more economical by combining sulfide salts with carbonates, lime and hydroxides.

B. Sulfate Reducing Bacteria for Sulfide Production

Sulfate reducing bacteria are responsible for the production of sulfide in anaerobic reactors. [26] The name "dissimilating sulfate-reducing bacteria" is conventionally reserved for the class of microbes which use sulfate (SO_4^{2-}) as their terminal electron acceptor. [7] The respiratorial reaction which all SRB follow is:



This reaction only represents the overall metabolism of sulfate. A pathway postulated by Postgate [42] is presented in Figure 2.1.

Table 2.1: Molar Solubility Products, K_s , of Copper, Nickel, Lead and Zinc between 18 and 25 °C [33,49]

Hydroxides	K_s
$\text{Cu}(\text{OH})_2$	1×10^{-19}
$\text{Ni}(\text{OH})_2$	6.5×10^{-18}
$\text{Pb}(\text{OH})_2$	3×10^{-16}
$\text{Zn}(\text{OH})_2$	1.2×10^{-17}
Carbonates	K_s
CuCO_3	1×10^{-10}
NiCO_3	6.6×10^{-9}
PbCO_3	3.3×10^{-14}
ZnCO_3	1.4×10^{-11}
Sulfides	K_s
Cu_2S	3×10^{-48}
CuS	6×10^{-36}
$\alpha\text{-NiS}$	3×10^{-19}
$\beta\text{-NiS}$	1×10^{-24}
$\gamma\text{-NiS}$	2×10^{-26}
PbS	1×10^{-28}
$\alpha\text{-ZnS}$	2×10^{-24}
$\beta\text{-ZnS}$	3×10^{-22}

A possible cyclic pathway for dissimilatory sulphate reduction. The sulphate ion, outside the cell, is accumulated by a process which selenate inhibits competitively. Once inside it reacts with ATP to form adenosine phosphosulphate (APS) plus pyrophosphate (PP), a reaction which only proceeds to the right because the pyrophosphate is removed as inorganic phosphate (P). APS is reduced to sulphite + AMP. Sulphite dehydrates to metabisulphite which is reduced via intermediates (the dithionite ion, $S_2O_4^{2-}$, is wholly speculative) to give trithionate ($S_3O_6^{2-}$). This is reductively split to give thiosulphate and to regenerate some sulphite; the thiosulphate is reduced to give sulphide and more sulphite. Enzyme preparations capable of forming the unbracketed components from the unbracketed precursors have been isolated from *Desulfovibrio* species and some from *Desulfotomaculum*.

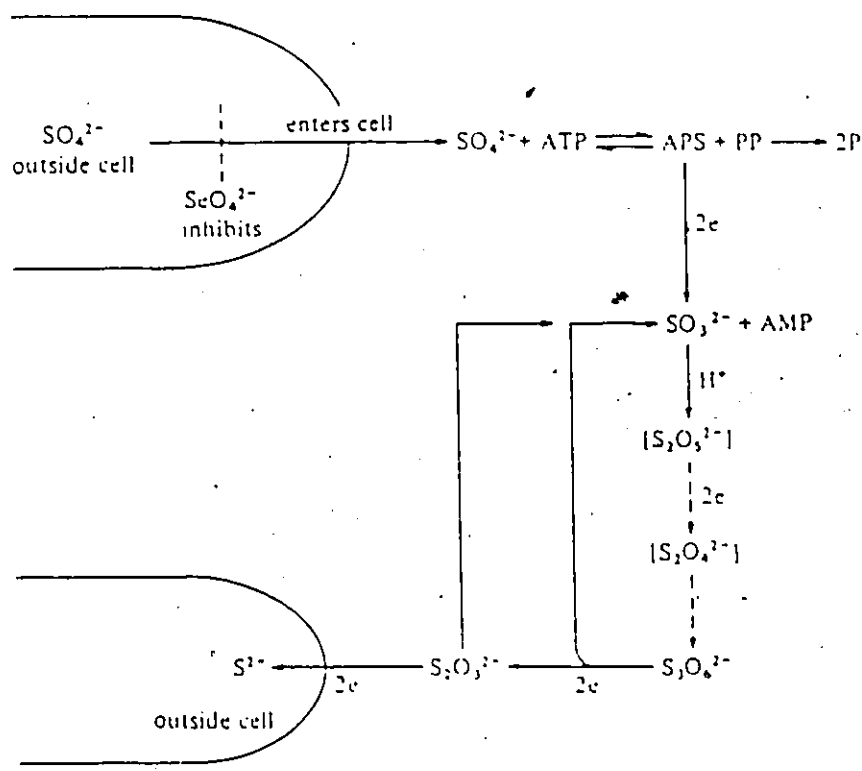


Figure 2.1: A Possible Cyclic Pathway for Dissimilatory Sulfate Reduction [42]

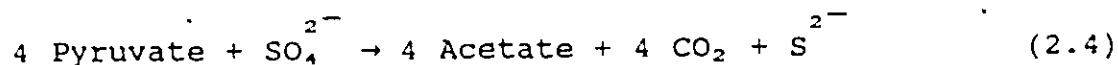
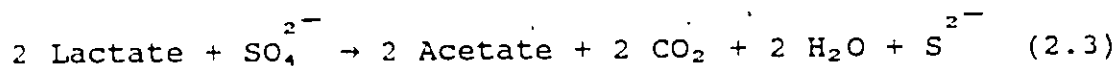
The sulfide ion, S^{2-} , produced would be available to react with any available metal present in the feed to form a stable metal precipitates, as expressed by the following reaction:




where M^{2+} is any divalent metal ion. [45]

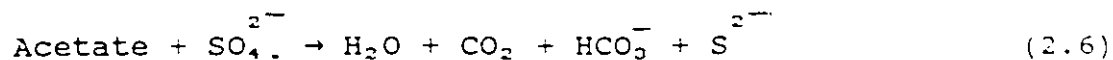
1. Metabolism

Currently, there are eight genera of dissimilating sulfate-reducing bacteria recognized and they are categorized into two broad physiological subgroups. The first subgroup is the Desulfovibrio genera. This family is capable of utilizing lactate, pyruvate, ethanol or certain fatty acids as carbon and energy sources. The second genera, Desulfotomaculum specialize in the oxidation of fatty acids, particularly acetates, while reducing sulfates to sulfide [7]. Reactions 2.3, 2.4 and 2.5 represent the overall metabolic reactions used by the Desulfovibrio subgroup [42].



The Desulfotomaculum subgroup can only dissimilate acetates as shown in Equation 2.6.





From these sets of metabolic reactions, it can be noted that a symbiotic relation exists between the Desulfotomaculum and the Desulfovibrio subgroups for the utilization of organics.

All of the above metabolic reactions are influenced by the environmental conditions. SRB are anaerobes, requiring anoxic condition for growth; the redox potential of their environment must be within E_h of -150 to -200 mV [42]. SRB are either mesophilic or thermophilic and are limited to a pH range of 5 to 9.5 [42].

A variety of minerals are also required for bacterial growth. These minerals can be separated into two groups, macronutrients and micronutrients. They are used primarily for the formation of cell membranes, enzymes, phospholipids, and nucleic acids. [7] Table 2.2 lists the essential nutrients and categorizes them into two groups.

Table 2.2: Lists of Essential Macro and Micro Nutrients [7]

Macronutrients	Micronutrients
Phosphorous (P)	Zinc (Zn)
Potassium (K)	Copper (Cu)
Magnesium (Mg)	Cobalt (Co)
Calcium (Ca)	Manganese (Mn)
Sodium (Na)	Molybdenum (Mo)
Iron (Fe)	

2. Inhibitors

Most bacteria are inhibited by heavy metals such as Hg, Cu, Ni, and Zn. However, SRB exhibit extraordinary resistance to high concentrations of these metals [7]. Postgate [42] has stated that sulfate reducing bacteria survive by stabilizing the metals as sulfide precipitates. Also, the high concentration of H_2S , an intrinsic toxin to all living systems, will inhibit or even stop growth unless metal ions, namely ferrous ions, are present for sulfide precipitation [42]. Thus, for successful microbial growth, metals must be present to control sulfide levels.

A third inhibitor to SRB is oxygen (O_2). Sulfate reducing bacteria are strict anaerobes, unable to grow on or use O_2 , and often they are even killed by O_2 . [7] Cyanide, commonly used by the plating industry has been classified by Brock et al. [7] as being another bacterial inhibitor, but it is not specifically stated whether cyanides inhibit SRB. Postgate described the effects of a number of inhibitors on SRB but did not mention the effects of cyanide on SRB [42].

C. Filter Design

Recently, research has focused on designing anaerobic reactors, mostly for the reduction of COD and to enhance the production of methane. Downflow anaerobic fixed film reactors (DAFFR) were developed by Samson, van den Berg and Kennedy [47,48,52] while Guiot and van den Berg [22] used a combined upflow anaerobic fixed film reactor-upflow

anaerobic sludge blanket reactor (UAFFR-UASBR) for sugar waste treatment. Riera et al. [44] studied the use of upflow anaerobic sludge blanket (UASBR) for the treatment of stillage from sugar cane molasses.

Fiebig and Dellweg [15] compared the operation of an UASBR to a combined UAFFR-UASBR and found that the latter design was able to treat an acetic acid waste with a higher efficiency at a lower HRT. Dohanyos et al. [14], in their comparative study of the UAFFR, DAFFR and the UASRB, concluded that the UAFFR was less sensitive to inhibitors, lower temperatures and fluctuations in load. These observations were based primarily on the reactor's ability to retain biomass by allowing it to fix and accumulate on the packing material within the reactor.

III. OPERATIONAL PARAMETERS AFFECTING HEAVY METAL SEPARATION IN ANAEROBIC REACTORS

Biological reactors operate by favouring the environment for a specific bacteriological group and create conditions to allow for the domination of one particular bacterial species over others. Wong [54] studied the effectiveness of SRB to separate heavy metals in an UAFFR. This configuration [54] effectively retained biomass on packing material. Scale-up, however, requires knowledge of the operational parameters which effect the retention of biomass and produce sulfides from sulfates.

A. Reactor Configuration and Volumetric Flow Rate

The geometric configuration and volumetric flow rate are important factors in evaluating the reactor's ability to retain biomass. The cross sectional area, the volumetric flow rate and packing porosity are the parameters which determine the superficial velocity. An increase in superficial velocity has a positive influence on mass transfer between the wastewater and the biomass. However a negative effect on biofilm thickness results since an increase in the rate of biofilm sloughing occurs [5,25].

The reactor packing also influences performance by

affecting the reactor's ability to retain biomass. Biomass requires a surface for adhesion. An increase in reactor total internal surface area will increase biomass accumulation [48]. Adhesion of biomass to the surface produces a biofilm which covers the packing material. The thickness of this biofilm has been found to be a function of the superficial velocity, packing configuration, size and the type of material used for packing fabrication. Increased plugging can occur with an increase in packing surface area [5,25,48].

B. Hydraulic Retention Time

Hydraulic retention time is the expected time required for a particle of fluid to travel through the reactor or the total contact time the wastewater has with the biomass. By assuming plug flow, HRT is calculated by dividing the reactor void volume by the volumetric flow rate. Hydraulic retention time affects efficiency because both mass transfer and metabolic kinetics, the two mechanisms governing the production of sulfide, are time dependent.

C. Operational Temperature

All processes of growth are dependent on chemical reactions, and the rates of these reactions are influenced by temperature. Thus the rate of microbial growth as well as the total amount of growth can be affected by temperature as shown in Figure 3.1. Mesophiles are characterized as having an optimum growth temperature of approximately 37 °C

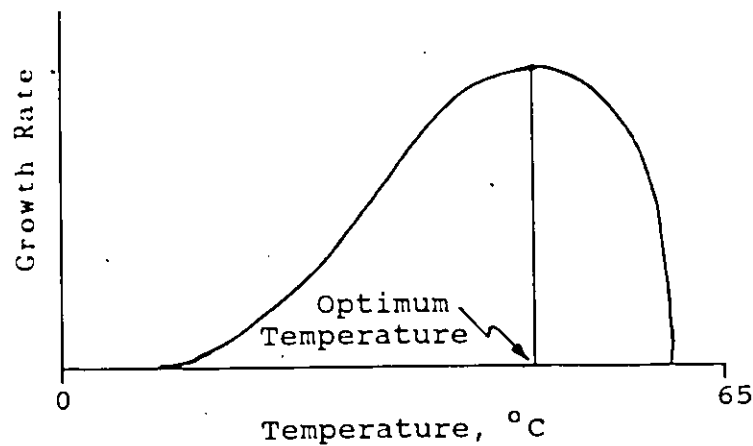


Figure 3.1: Typical Effect of Temperature on Microbial Growth Rate

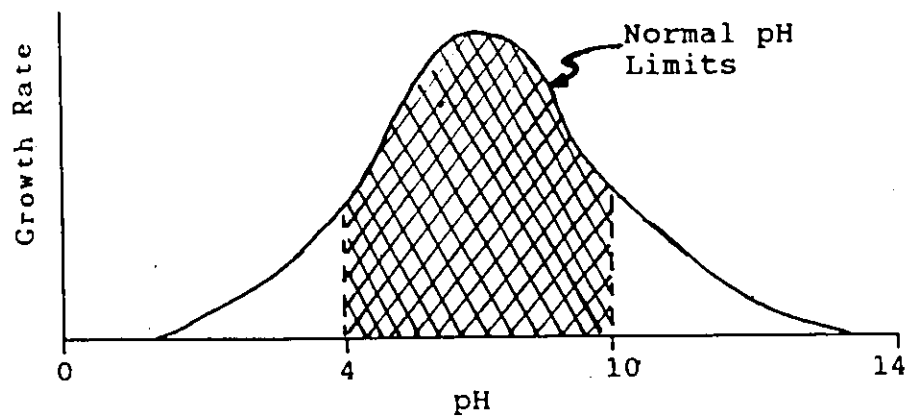


Figure 3.2: Typical Effect of pH on Microbial Growth Rate

while thermophiles have an optimum growth at approximately 67 °C [4].

D. Optimal pH

For most bacteria and thus for most wastewater treatment processes, the extremes of the pH range for growth fall somewhere between 4 to 9. The optimum pH for growth generally lies between 6.5 and 7.5. Figure 3.2 illustrates the effects of pH on the growth rate [7].

E. Operational Redox Potential

The maintenance of SRB in a culture requires not only the exclusion of air but also a redox potential (ORP) of E_h equal to -100 mV or less. The presence of a redox-poisoning agent is necessary; sodium and potassium sulfide are two possible agents. For a large inocula, the production of hydrogen sulfide by the SRB is sufficient to maintain a low reactor ORP [42].

F. Light Effects

Light is not required by SRB for growth but is required by phototrophs. Phototrophs produce oxygen, a bacterial inhibitor, which forces SRB into a dormant phase [42]. Thus, the overall performance of the reactor would be affected by the presence and growth of phototrophs.

G. Wastewater Characteristics

The concentrations of substrate, inhibitors and metals affect the ability of the SRB to separate heavy metals. Table 3.1 lists the constituents monitored by Wong [54] for

the study on reactor performance when using a synthetic wastewater. Organics, sulfate and micro and macro nutrient content will influence sulfide production by limiting the bacterial growth rate.

Inhibitors, like cyanide might also effect sulfide production. As reported in the literature review, cyanide has not been classified as an inhibitor by Brock [7] or Postgate [42]. Metal loading affects the treatment process. Metal loading rates which exceed the capacity of the reactor by consuming all of the sulfide would decrease the reactors resistance to dissolved oxygen and force the addition of a redox poison to maintain an E_h of less than the recommended -100 mV [42].

Table 3.1: List of Constituents Monitored by Wong During Synthetic Wastewater Study [54]

Chemical Oxygen Demand	COD
pH	
Total Sulfides	S^{2-}
Sulfates	SO_4^{2-}
Cadmium	Cd
Copper	Cu
Lead	Pb
Nickel	Ni
Zinc	Zn

IV. EXPERIMENTATION

Experimentation proceeded in three phases:

- the preliminary study to characterize the wastewater,
- the treatability tests, and
- the hydraulic retention time study.

A. Wastewater Characterization

Characterization encompassed a series of analytical tests for evaluating the suitability of wastewater as a feed for SRB. Chemical oxygen demand and biological oxygen demand were used to estimate organic loadings. Sulfate was determined since it is needed for SRB respiration. Inhibitors such as cyanides and dissolved oxygen were identified and quantified to determine the need for wastewater pretreatment. Total and dissolved metal analyses facilitated estimation of the expected metal loading rates into the SRB reactor.

B. Treatability Study

The treatability phase used an UAFFR in order to evaluate separation of heavy metals. This reactor was one of the two used by Wong [54] for a theoretical study of the

system using synthetic wastewater. The feed consisted of metal plating wastewater which had been supplemented with nutrients. Influent and effluent sulfates and organic loading, and effluent acid-soluble sulfides and macronutrients were monitored to determine production and consumption rates throughout the test. Effluent redox potential (ORP) was monitored to check for a correlation with other parameters such as sulfide production.

The operational parameters: reactor temperature, pH, redox potential and dissolved oxygen were not controlled strictly since the prime objective of this phase was to demonstrate an ability to treat the wastewater. The hydraulic retention time was maintained at approximately 48 hr. Light energy was prevented from reaching the reactor to prevent the growth of phototrophs.

C. Hydraulic Retention Time Study

During the third experimental phase, the effects of HRT on the heavy metal separation efficiencies were studied. Hydraulic retention time was selected because it is a major economic factor in process implementation [6,54]. The retention times ranged from 59.5 to 6.5 hours to include the 48 hour retention time used by Wong et al. [54] and the 11 hour value reported by Maree and Strydom [30]. Table 4.1 summarizes the experimental HRTs used for reactor performance evaluation. Note that the tests reported for reactors identified as A1 and A2, B1 and B2 and C1 and C2

were conducted on the same reactors, respectively.

Table 4.1: Selected Hydraulic Retention Times used for Reactor Evaluation

Hydraulic Retention Time (hours)			
Reactor Designation	Test 1	Reactor Designation	Test 2
A1	27.8	A2	6.5
B1	38.2	B2	12.0
C1	59.5	C2	24.4

The reactor pH, dissolved oxygen content and ORP were neither monitored nor controlled because excessive sulfide in the effluent indicated whether the process was operating within the specified ranges. Reactor temperature and feed pH were maintained within 25 ± 1 °C and 6.5 to 7.5 respectively. Light effects were eliminated by using grey PVC tubing.

Although metal separation was the main parameter under consideration, soluble sulfide (along with other reduced sulfur compounds), sulfates, COD and biological oxygen demand (BOD) were also monitored in the effluent to determine their production or consumption rates. Effluent ORP was monitored to check for a correlation with reactor performance.

D. Apparatus Used for Wastewater Collection and Treatment

The characterization phase required a composite

wastewater sample representative of the wastewater produced by a typical plant. The large sample volumes required as feed for treatability and HRT studies necessitated the construction of a sampler which would deliver the wastewater to a storage drum in approximately 30 minutes.

The treatability study employed one UAFFR while the HRT study employed three UAFFRs which were similar in design to the UAFFR used during the treatability phase. Corrosion from sulfide was a major concern when selecting construction materials. All reactors and supporting equipment were constructed from plastic or rubber [42].

1. Characterization Wastewater Sampler

A composite sample was needed for wastewater characterization. Figure 4.1 illustrates the collection system for a composite sample. The sampler consisted of Tygon tubing, a peristaltic pump with a flow capacity of 0 to 363 mL/min and a 25 L carboy. The peristaltic pump was calibrated to provide a flow rate of 167 mL/min in order to collect approximately 22.5 L over a 2.5 hr sampling period. The pump was calibrated employing the time required to collect 150 to 200 mL of water in a 250 mL graduated cylinder. Figure 4.2 indicates the location of the sampling point in the Universal Fasteners plant. This location was selected because all waste streams converge there before entering the wastewater treatment unit.

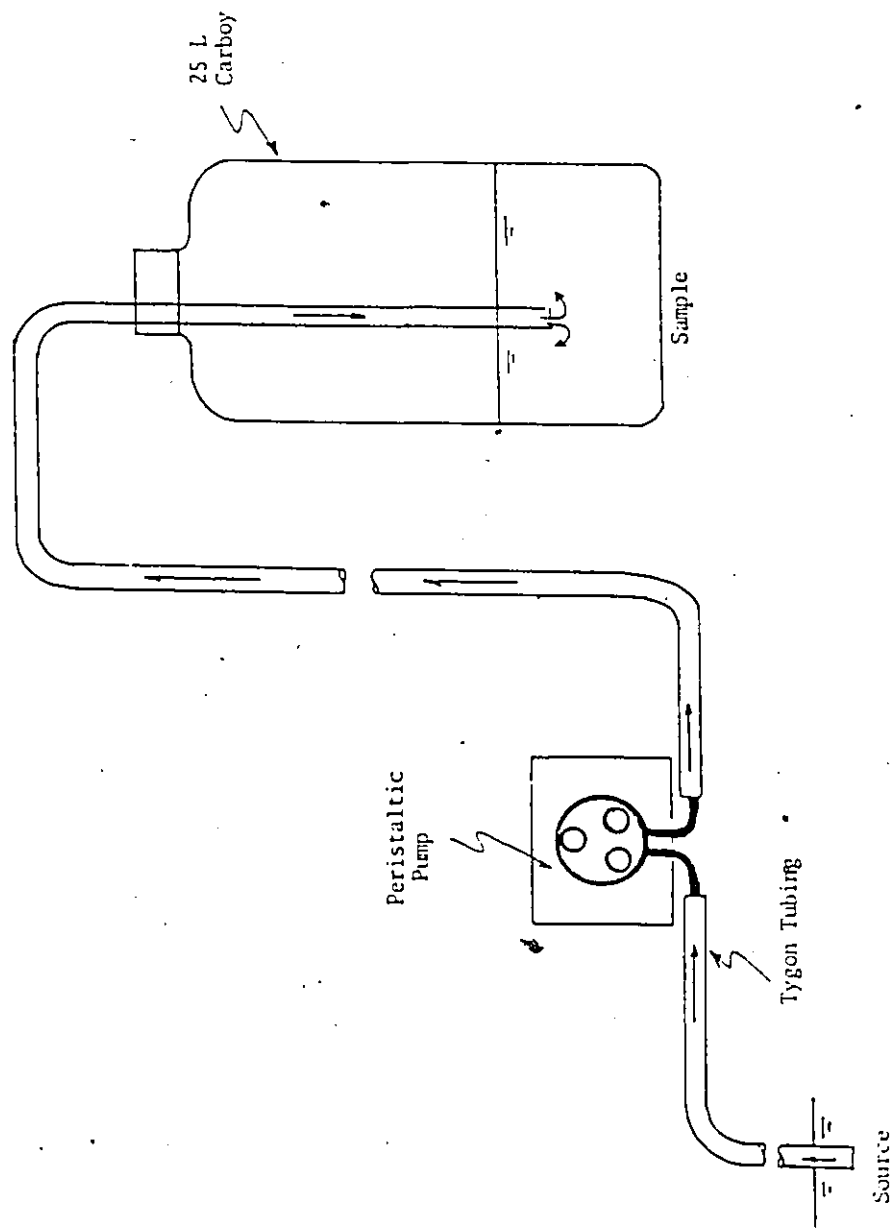


Figure 4.1: Wastewater Sampler used for Composite Sample Collection

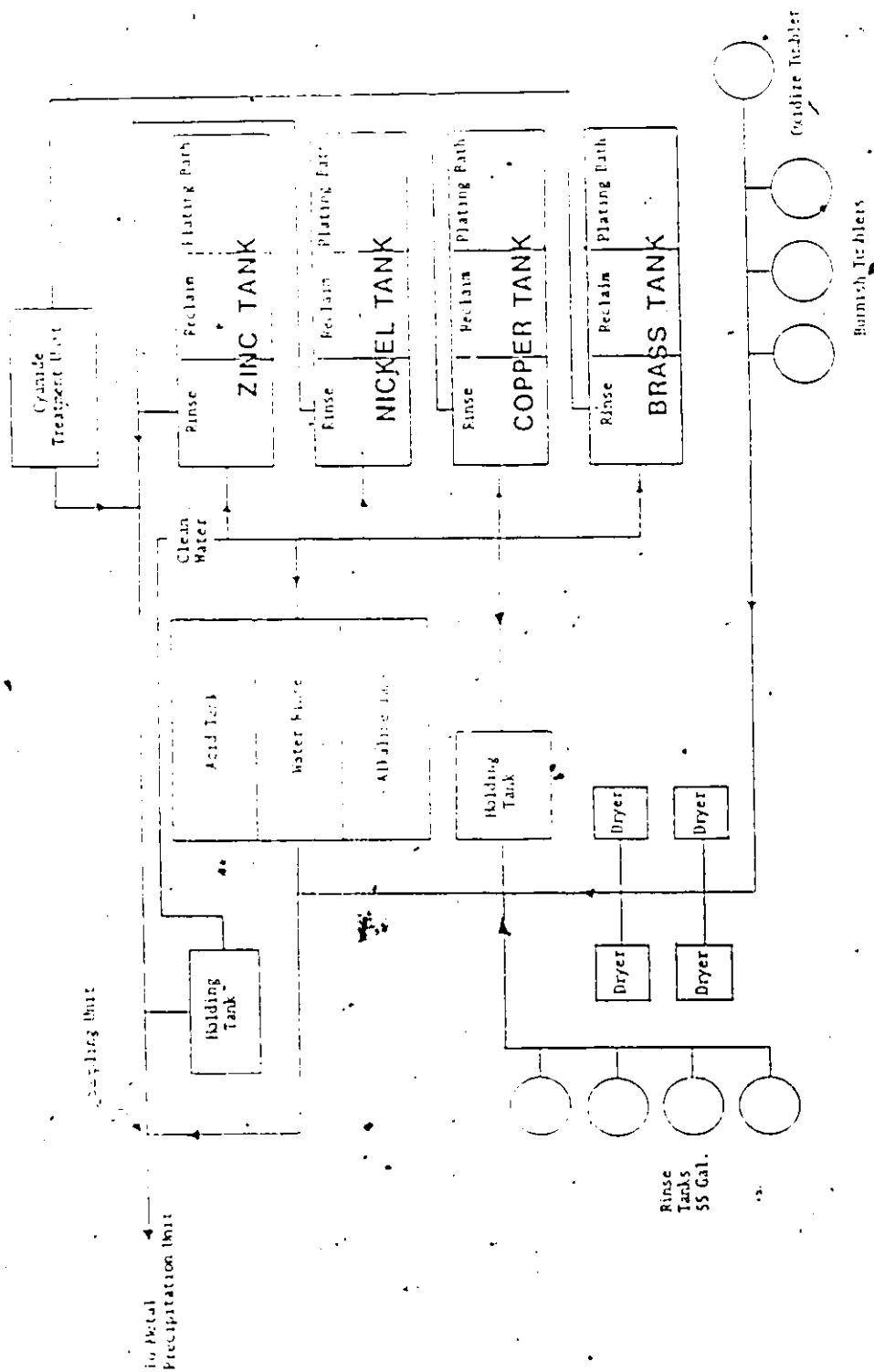


Figure 4.2: Layout of Wastewater Collection System at Universal Fasteners

2. Feed Water Sampler

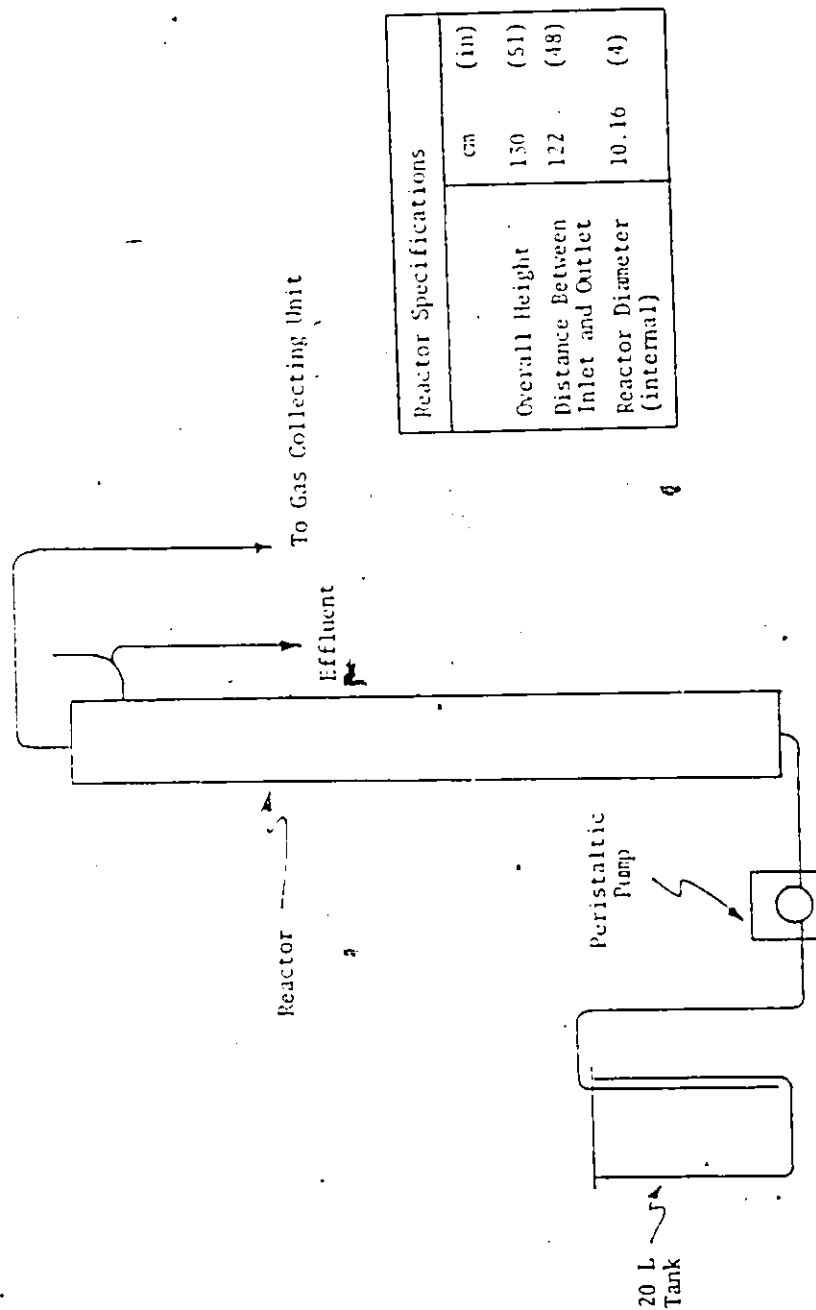
Wastewater for the treatability and the HRT study was collected at the same location used for the wastewater characterization. However, the collection apparatus shown in Figure 4.1 was modified to provide the larger sample volumes needed. The treatability and HRT samples were collected with a flexible impeller pump using neoprene tubing to provide a calibrated sampling rate of 18 L/min. The samples for the treatability study samples were collected once a week in four 25 L carboys. The samples for the HRT study were collected weekly in one or two 200 L plastic drums.

The feed samples were stored immediately in a cool room at 4 °C. [1] Transportation of the samples was conducted with permission from the Ministry of the Environment as required under Regulation 309 [36,38].

3. Treatability Reactor and Supporting Equipment

As illustrated in Figure 4.3, the wastewater was pumped from the 20 L glass tank to the inlet of the reactor by means of a variable speed peristaltic pump. This pump was calibrated on the first day of the experiment and checked on the 14th day for a flow rate of 2.97 mL/min that provided the reactor with a retention time of 48 hr.

Calibration of the pumping system was conducted by measuring the time required for the collection of 3 to 4 mL of reactor effluent in a 5 mL graduated cylinder.



Reactor Specifications	
Overall Height	130 (in)
Distance Between Inlet and Outlet	122 (in)
Reactor Diameter (internal)	10.16 (in)

Figure 4:3: Treatability Study Reactor and Supporting Apparatus

Figure 4.3 shows the dimensions of the reactor used in the treatability study. The reactor was constructed with an acrylic body and filled with 15.9 mm (5/8 inch) plastic Pall rings. The exterior of the reactor was covered with aluminum foil to prevent light penetration.

Figure 4.4 depicts the gas collection system used to capture sulfide and methane gases typically evolved in anaerobic reactors [52]. The unit consisted of a one litre beaker containing an acidic solution ($\text{pH} < 2$) and an inverted 100 mL graduated glass cylinder. A "J" shaped glass tube connected to the top of the reactor with a 6.4 mm (1/4 inch) rubber tubing allowed the evolved gases to enter the inverted cylinder. A liquid seal, shown in Figure 4.3, prevented any gases from escaping with the effluent.

4. Hydraulic Retention Time Study Apparatus and Supporting Equipment

The HRT study tested the UAFFR at different volumetric flow rates. Two experimental runs were conducted on each of the three reactors. The specifications of the three reactors were identical to those of the treatability reactor. Polyvinyl chloride (PVC) pipe of 102 mm (4 inch) diameter was packed with 15.9 mm polypropylene Pall rings. The porosities of the packing in the reactors before seeding are presented in Appendix I. Appendix I also provides the residence time distribution (RTD) parameters determined by a series of tracer experiments for a reactor which was similar

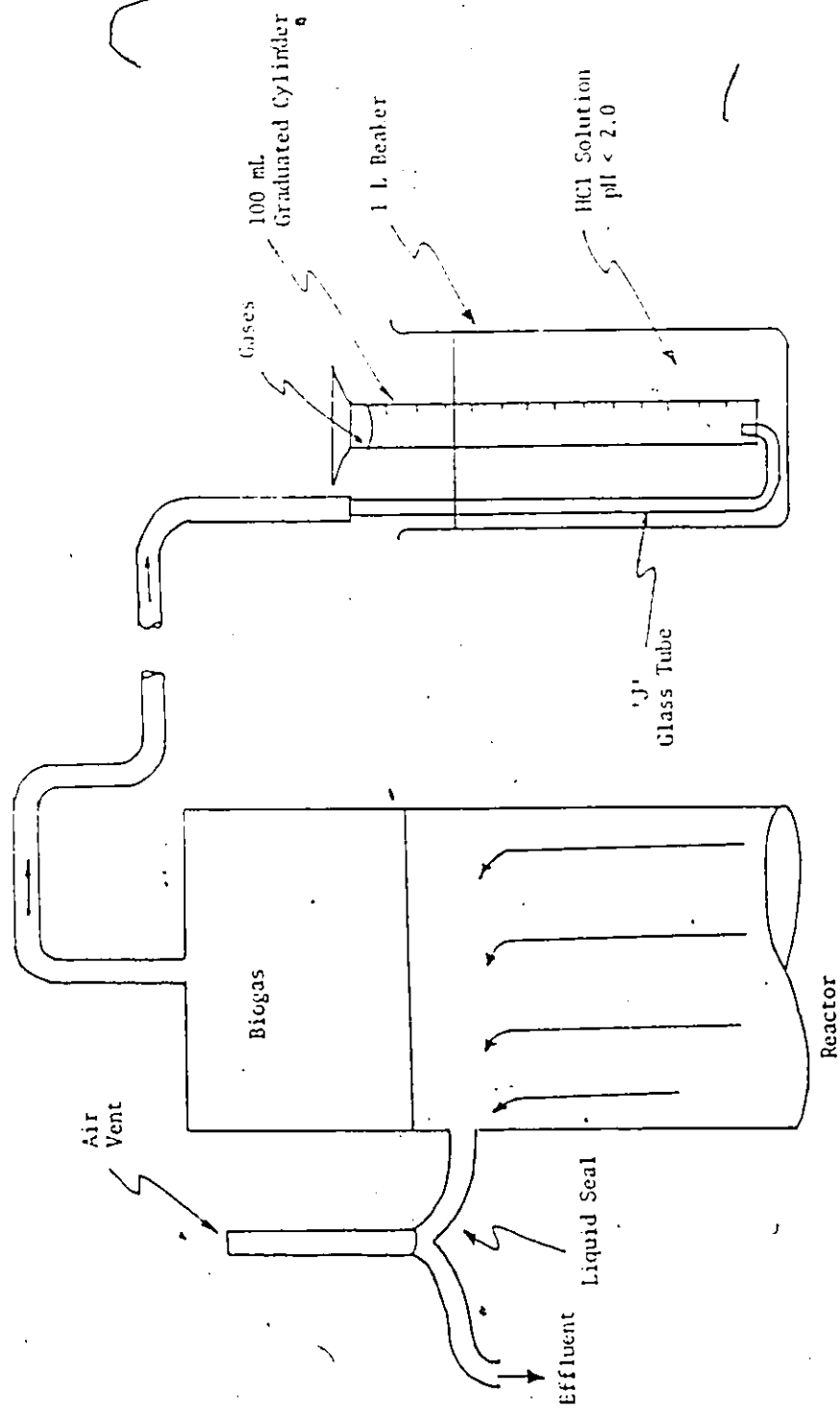


Figure 4.4: Gas Collecting Apparatus

in construction to the reactors used during the HRT study.

The reactors were seeded with anaerobic sludge consisting of a mixture of 24% (by volume) sludge taken from a SRB reactor previously used by Wong and 76% of anaerobic sludge from the Chatham Sewage Treatment Plant. The redox potential of this sludge was reduced to the range of -150 to -200 mV as specified by Postgate [42] by adding potassium sulfide.

The temperatures of the reactors were maintained at 25 ± 1 °C by placing them into a 322 L constant temperature bath to eliminate temperature effects on reactor efficiency while studying the effects of hydraulic retention time.

Two changes were made to the supporting apparatus. The gas collection unit was eliminated because no gases evolved during the treatability study. Sampling units were used to collect the liquid effluent at any time. Figure 4.5 illustrates the flow path through the liquid sampler. The actual retention time for the samplers ranged from 16 to 190 minutes. In view of the high dispersion in the sampler each sample was representative of the reactor's output for the sampling period. Since the HRTs were much larger than the sampling period, it was assumed that each sample was representative of the reactors output for that day. Appendix II presents the effluent retention times for the sampler when subjected to the HRT study's highest and lowest

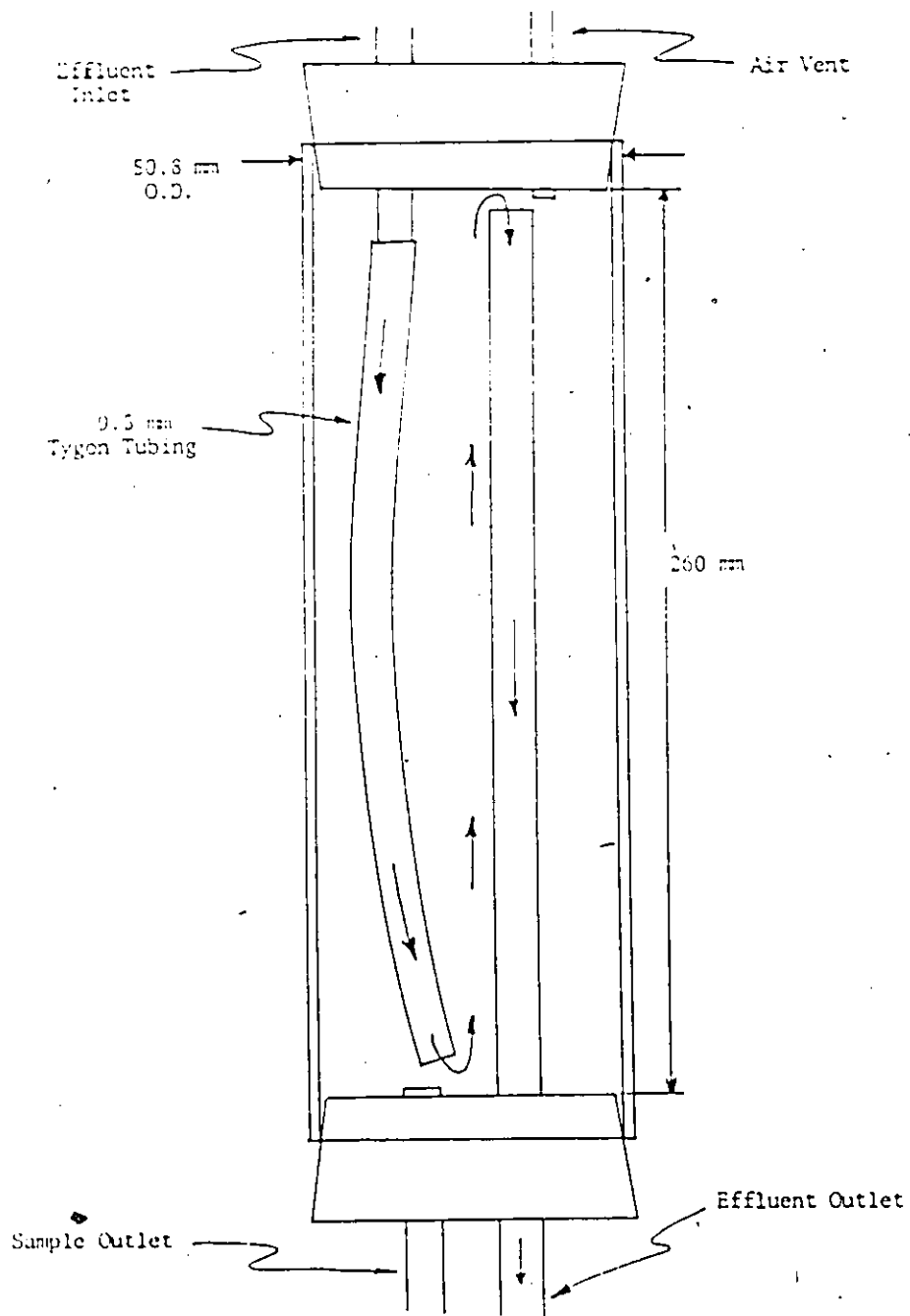


Figure 4.5: Effluent Collecting Apparatus

volumetric flow rates. Collection of a sample for analysis was accomplished by opening the air vent on the top of the sampler and draining the treated wastewater sample from the bottom of the sampler unit. The air vent was then closed after the removal of the sample in order to prevent any losses of volatile sulfide.

E. Method of Analysis

The initial characterization of the wastewater and the reactor performance evaluation for heavy metal removal required the analyses summarized in Table 4.2. The testing frequency, aliquot size and number of analyses conducted throughout the three phases are noted also. All tests conformed to "Standard Methods" (STMD) [1] except for the ORP and acid-soluble sulfide measurements. All reagents used were ACS quality unless otherwise specified.

Samples for the treatability study were taken by collecting the needed aliquot in a beaker just before the test was to be performed. The HRT samples were withdrawn from the sampler as they were needed.

1. Chemical Oxygen Demand

The chemical oxygen demand (COD) test is used to determine the total oxygen demand of wastewaters. This measurement of organic content is determined by having a strong oxidizing agent convert all organics into carbon dioxide and water. Interferences occur when inorganics such as sulfides and ferrous ion and nitrites are present and are

Table 4.2: List of Constituents used for Wastewater Characterization and Reactor Performance Evaluation

Chemical Constituents	Method of Analysis	Characterization Phase		Treatability Phase		Hydraulic Retention Time Phase		
		Sample Volume (ml)	Frequency of Sample Analysis	Sample Volume (ml)	Frequency of Sample Analysis	Frequency of Testing per week	Sample Volume (ml)	Frequency of Sample Analysis
Alkalinity	403	50.0	3	-	-	-	-	-
Ammonium	417 A, D	50.0	1	50.0	3	1	(25-40)/1000	1
BOD	507	(1-20)/100	3	(0.1-5)/100	-	2	-	-
Chloride	(electrode)	A	-	-	-	-	50.0	2
CO ₂	508 A	50.0	5	50.0	3	2	-	-
Dissolved Oxygen	421 B, F	A	-	A	1	1	-	-
Nitrate	418 b	A	1	A	1	1	-	-
Kjeldahl Nitrogen	420 A, 417 A, D	-	-	50.0	3	1	-	-
pH	423	A	1	A	1	1	-	-
Phosphate Soluble	(electrode)	-	-	A	1	3	A	1
Redox	427 A, D	10.0	1	-	-	-	25.0	3
Sulfide Soluble	Smittenberg	10.0	1	10.0	1	3	-	-
Total								
Metals (s - soluble, t - total method 102E)								
Calcium (s)	Plasma	A	-	A	3	3	-	1-5
Copper (s, t)	Plasma	A	-	A	3	3	A	1-5
Lead (s, t)	Plasma	A	-	A	3	3	-	-
Magnesium (s)	Plasma	A	-	A	3	3	-	1-5
Nickel (s, t)	Plasma	A	-	A	3	3	-	-
Potassium (s)	Plasma	A	-	A	3	3	-	-
Zinc (s, t)	Plasma	A	-	A	3	3	A	1-5
Solids (t - total and s - suspended)								
Fixed Solids	209 D	A	6	-	-	-	-	-
Total Solids	209 A	A	6	-	-	-	-	-
Volatile Solids	209 D	A	6	-	-	-	-	-
A - Analyzed								
s - Smittenberg Method For Monosulfidic Sulfide [50]								

oxidized with the organics. The open reflux method, STDM 508 A [1] was employed for COD measurements. B

Influent and effluent COD measurements provide a measure of the reactor's overall organic consumption rate. In this study measurement of influent and effluent lactate content would have been a more accurate measure because it is the organic supplement added to the wastewater. However, for future studies involving the mixing of organic wastewater, as a second wastewater stream, with the metal plating wastewater as feed for the reactor, the organic content of this second wastewater stream would be quantified by measuring its COD and biological oxygen demand rather than measuring the individual concentrations of organic species which may be present. For this reason COD measurements were deemed to be in appropriate in this study.

2. Biological Oxygen Demand

The BOD test is used as an indicator similar to the COD test. Biological oxygen demand measures the amount of oxygen required by bacteria while stabilizing decomposable organic matter under aerobic conditions. This analysis differs in that only biologically degradable organics are measured. Biological oxygen demand was conducted according to STDM 507 [1]. The seed used in the dilution water originated from the Chatham Sewage Treatment Plant.

The BOD results are only considered to be an

✓

estimate of the total organic content of the wastewater because biological degradation of organics follows first-order reaction kinetics. A five day incubation period has been found to allow for the consumption of only 70 to 80 percent of total organics [49].

3. Sulfates

Sulfates, SO_4^{2-} , are used by the SRB for respiration as shown in Equation 2.1. Analyses were conducted by turbidimetric method described by STDM 426 [1].

4. Sulfides

Sulfides are the metabolic products of SRB respiration. The Smittenburg *et al.* method for acid-soluble sulfide analysis [50], as recommended by Wong [54], was employed during the wastewater characterization phase and during the treatability study. This method required the digestion of the sample with 1:1 (volume ratio) hydrochloric acid which caused the decomposition of monosulfidic sulfur compounds [50].

It was decided after the treatability study that soluble sulfides would give a better indication of the reactor's capacity for separating heavy metals since acid-soluble sulfide analysis would overestimate this capacity by including sulfides which are already bound to metals. The Iodometric Method, STMD 427 D [1] for soluble sulfide analysis required pretreatment of the sample. The STMD 427 A [1] pretreats the sample by flocculating and

removing any suspended solids. The iodometric method has the inherent problem with interference from sulfite and thiosulfates which may be present in the wastewater [1]. As indicated in the Literature Review, this interference is expected to be minimal as was found by Maree and Strydom [30]. Figure 2.1 gives the postulated sulfate reduction pathway and shows that thiosulfates and sulfite are metabolic intermediates. Maree and Strydom found sulfite at low concentrations relative to sulfide levels. Because of this interference the sulfide results are reported as reduced soluble sulfur.

5. Metals

Total and soluble metals were the main parameters studied during the three experimental phases. Table 1.2 lists the most common metals used by the metal plating industry. However, only copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) were used by Universal Fasteners and were found in the rinse water. The samples for total metal analysis were first digested as per STMD 302 E , Nitric Acid-Sulfuric Acid Digestion [1] and then analyzed on a Beckman Spectraspan V Plasma Spectrophotometer.

Instrumental detection limits were determined each time the plasma arc spectrophotometer was used. See Appendix IV for details. Hence, each run produced different limits of detection (LOD). The method used for calculation of the limits of detection is detailed in Appendix IV.

6. Redox Potential

The measurement of effluent redox potential (ORP) indicates whether the reactor is operating within the specified ORP range. Measurements were conducted in a sealed vessel in which the solution completed the circuit between the platinum and calomel electrodes as shown in Figure 4.6. The empty vessel was first purged with nitrogen gas to prevent any interference by oxygen [41,42]. A single point verification of the electrode response was conducted using a pH buffer solution saturated with quinhydrone.

In the treatability study, ORP readings were recorded after 5 to 10 minutes to allow the system to reach equilibrium. However, the instability of the instrumental response signified that the recorded results were inaccurate. It was discovered that the electrode required over one hour to reach equilibrium. To ensure consistency all measurements were conducted after ten minutes. This time period ensured an ORP measurement of at least 95% relative equilibrium response. The effluent was introduced into the nitrogen purged ORP measuring vessel. After filling the vessel to the level shown in Figure 4.6, the sample was stirred for one minute only. Stirring homogenized the sample, but was limited to one minute to prevent excessive losses of dissolved gases which would change the actual ORP value of the effluent [41]. A reading was taken after nine additional minutes. Appendix III

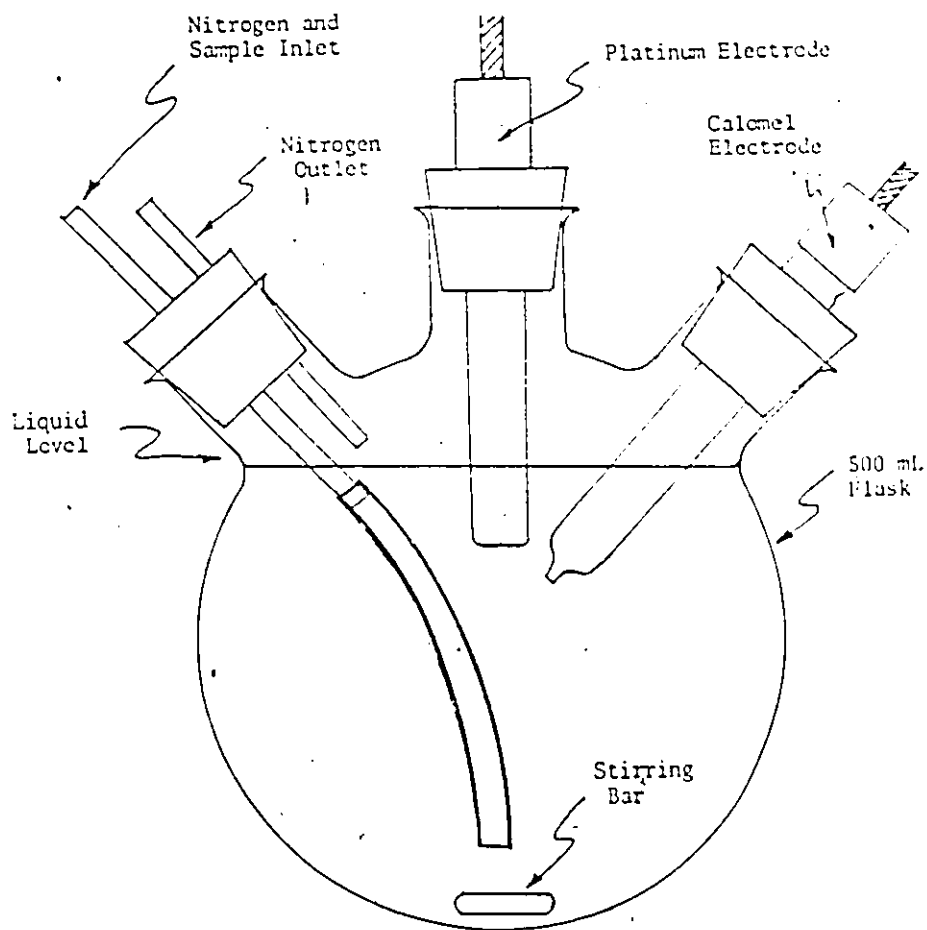


Figure 4.6: Redox Potential Measuring Apparatus

presents further details.

7. Mineral Nutrients

The tests for the macronutrients listed in Table 4.3 were conducted several times during the treatability study. These tests confirmed that an excess of macronutrients existed and that the nutrients would not repress microbial growth by becoming the limiting growth factor.

8. Inhibitors

Table 1.2 lists the major constituents found in metal plating wastewater. Of these only the cyanides were suspected as a possible inhibitor. Results of the cyanide analyses during the characterization phase indicated no further testing was necessary. Total cyanides were tested by first distilling the sample according to STMD 412 B and then titrating it with silver nitrate as described by STMD 412.C, Titrimetric Methods [1].

Dissolved oxygen was also tested during the characterization phase and the first few weeks of the treatability study. Since the reactor showed no signs of failure from dissolved oxygen, no further testing was conducted. Measurements were performed by using a calibrated dissolved oxygen electrode as per STMD 421 F, Membrane Electrode Method, [1]. Calibration of this electrode was performed before the characterization phase, and at the beginning of the treatability study, Test 1 and 2

of the HRT phase using the STMD 421 B, Azide Modification [1]. This probe was also used for dissolved oxygen analysis during BOD determination.

9. Alkalinity, Acidity and pH

The intensity of the acid or alkaline condition of the wastewater is expressed by its pH [49]. This pH is an important growth parameter for bacteria. Alkalinity and acidity measurements indicate the amount of acid or base required to neutralize the solution to insure a proper microbial environment. Throughout the treatability test pH was measured according to STDM 423 [1] for wastewater characterization. The alkalinity test, STMD 402 [1], was employed only during the wastewater characterization phase. Acidity analysis was never conducted because the wastewater always had a pH value greater than 7.

F. Wastewater Nutrient Supplements

Table 4.3 lists the organic and mineral nutrients added to the wastewater. The characterization study indicated that some nutrients were insufficient or lacking to sustain SRB growth. For this reason, supplemental nutrients were added to the wastewater. The recipe used was a slight modification of that given by Postgate; and accommodated the needs of both *Desulfovibrio* and *Desulfotomaculum* subgroup bacteria. Calcium was eliminated from the treatability recipe because of the difficulties in dissolving it in the presence of high phosphates in the feed. Phosphates were

added as a mixture of mono- and di-basic phosphate to buffer the solution to a pH of 7 [1].

Table 4.3: List of Nutrients used to Supplement Wastewater

Constituents [g/L]	Synthetic	Treatability	HRT
Sodium Lactate	3.5	3.5	0.5
Na_2SO_4	1.5	1.5	1.5
$(\text{NH}_4)_2\text{SO}_4$	1.5	1.5	1.5
$\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$	2.0	2.0	2.0
KH_2PO_4	0.084	0.084	0.084
K_2HPO_4	0.2072	0.2072	0.2072 / 0.3959†
$\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$	0.4045	0.4045	0.4045 / 0.0
$\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$	-	-	0.1324
† - increased to compensate for a decrease in sodium phosphate			

Observations from the treatability study allowed for some modifications to the recipe. They included an addition of calcium and a reduction of organic supplement. The organics were always in excess during the treatability study and for this reason the amount was lowered to approximately 10 times the stoichiometric amount needed for the precipitation of the four metals. Other nutrients such as sulfates, were also present in excess but they were maintained at that level because of the possible

difficulties which would occur in the analysis of the reactor data if a failure occurred. Too many changes would not have allowed for the determination of the factor causing failure. For this reason, calcium was added even though the treatability study showed no operational problems due to its absence. Addition was possible by first making phosphate buffer and calcium concentrates and then adding them to the feed supply.

Feed for the treatability and the HRT studies was produced by taking one or two day's supply of wastewater and mixing in the required nutrients. The supplemental chemicals were of technical grade or better.

A synthetic feed was used for a 12 day period for bacterial activation before starting the treatability experiments. The synthetic feed was produced according to the specifications given in Table 4.3 and supplied to the reactor at a rate of 3 mL/min. The first HRT reactor run was activated in a similar manner for 7 days prior to the start of the experiment. The second run was activated by feeding the reactor supplemented wastewater at the same volumetric flow rates as the first run for a period of 14 days.

At the end of the HRT experimental runs, spikes of 50 mg/L of each of Cu, Ni, Pb, and Zn were added to a two day batch of feed water. These spikes were used to determine the response of the reactor to sudden high loading

rates of heavy metals. Spiking simulated a spillage of plating waste solution which may occur during plant operation.

V. RESULTS AND DISCUSSION

The characterization phase indicated that the wastewater would have to be neutralized and supplemented with nutrients before treatment. The types and amounts of nutrients added were based on Wong *et al.* [54] studies. The treatability study showed an excess of all nutrients and excessive production of sulfides, which indicated that these were not the limiting factors for process control. The HRT study was subjected to the same feeding recipe except for a reduction in organic supplementation to determine an optimum operation retention time for effective wastewater treatment.

A. Characterization Results

The wastewater characterization results are presented in Table 5.1. These results are comparable with the Environment Canada averages [17] provided previously in Table 1.1.

The industrial wastewater was found to have low organic content, a BOD of 13.4 mg O₂ /L and a COD of 68.0 mg O₂/L. The COD to BOD ratio was 5 to 1 which is much higher than the typical 2:1 [6]. This difference is postulated to result from interferences with respect to COD and BOD measurements. Reduced inorganics will cause an

Table 5.1: Wastewater Characterization Results

Constituent	Concentration	Concentration after 7 days *		
Temperature (°C)	21	-		
pH	10.83	10.62		
ORP (mV)	199.4	192.4		
Conductivity (mmho/cm)	1.68	1.72		
Alkalinity (mg CaCO ₃ /L) as carbonate	538	-		
as bicarbonate	21	-		
Ammonium (mg N/L)	4.11	1.62		
BOD (mg O ₂ /L)	13.4	6.68		
Cyanide (mg CN/L)	0.0	-		
COD (mg O ₂ /L)	64.8	41.7		
Chloride (mg/L)	86	-		
Dissolved Oxygen (mg O ₂ /L)	6.95	-		
Nitrate (mg NO ₃ /L)	14.2	24.9		
Sulfate (mg SO ₄ /L)	64.8	-		
Acid-Soluble Sulfide (mg S/L)	0.0	0.0		
Solids (mg/L)				
Total Suspended	110	145		
Volatile Suspended	61	134.5		
Fixed Suspended	49	10.5		
Total Dissolved	1233	-		
Metals (mg/L)				
	Sol.	Tot.	Sol.	Tot.
Copper	0.568	7.26	-	-
Lead	<LOD	<LOD	-	-
Nickel	0.393	1.30	-	-
Zinc	0.74	14.28	-	-

* - Sample stored for seven days at 7°C

overestimation of COD content (in terms of organics) while high metal and sulfate concentrations will inhibit the biological oxidation of organics during the BOD testing.

Sulfates at a concentration of 68 mg SO_4/L were three times higher than the expected norm, although not high enough to produce sufficient sulfides for wastewater treatment. According to the loading values for the four metals, a minimum of 34.1 mg SO_4/L and 17.1 mg O_2/L as COD are needed for their separation as sulfide precipitates, based on the experimental COD value of 578.3 mg O_2/L per gram of 71 % sodium lactate. However, these levels did not meet the growth needs specified by Postgate [42] so supplemental nutrients (Table 4.4) were added according to the recipe given by Wong *et al.* [54].

The high pH of 10.8 for the wastewater was attributed to the cyanide wastewater pretreatment illustrated in Figure 4.2. The high pH was responsible for the low levels of soluble metal ions summarized in Table 5.1. This pH level was too high to support SRB growth according to Postgate [42]. Hence, the pH was lowered to the optimum range of 7 to 8, by adding either sulfuric acid or hydrochloric acid.

Since the wastewater feed had to be stored in a cooler at 4° C until needed, tests were conducted to determine its stability over a one week period under similar conditions. The characterization sample was stored at 7° C and the results obtained from the analysis are reported in Table 5.1

Significant decreases in BOD, COD and ammonium content were found with appreciable increases in the nitrate and volatile suspended solid contents. The bacteria content within the wastewater increased and were of the nitrifying type.

Nitrifying bacteria are psychrophile which can survive high pH environments [7,8]. These results show that the sample is unstable at 7° C which is only 3° C higher than the accepted storage temperature at which no bacterial growth occurs [6].

B. Treatability Study Results

The treatability study demonstrated the domination of SRB in the reactor. Effluent ORP measurements indicated that the reactor was in a reduced state. Although, effluent ORP levels were slightly underestimated, as discussed in Appendix III, their magnitude provides an estimate of the actual levels. No dissolved oxygen was found in the effluent. The ORP and dissolved oxygen levels, shown in Table 5.2, indicate that the growth of anaerobic bacteria within the reactor altered the wastewater characteristics to suit their growth needs.

Table 5.2: Redox Potential, Dissolved Oxygen Content and pH of the Effluent throughout the Treatability Study

Parameter	Day of Test	Range
ORP	3,7,9,14,18	-155.6 mV to -193.6 mV
Dissolved Oxygen	2,8,14	< 0.5 ppm O ₂ *
pH	2,8,14	7.10 to 7.74

* - limit of detection

No methane gas evolved during the study. Methogens, when present within a culture, produce methane [7], but the lack of captured gases throughout the 18 day study period indicates their absence. This absence of methogens is an unique observation since other studies reported in the literature survey had methogens co-habiting with the SRB. This phenomenon can be attributed to two documented facts; SRB have been found to dominate over methogens when both are subjected to an anaerobic environment [7,42], and the wastewater high metal loading can inhibit methogenic growth [42].

The sulfide production concurrently with organic and sulfate consumption, as shown in Table 5.3, is a trait indicating SRB growth. The absence of hydrogen sulfide gas is attributed to the high buffering capacity of the phosphate nutrient supplement. The pH of the effluent was always within the range 7.0 to 8.0. The plot of basic hydrogen sulfide dissociation versus pH, as presented in Figure 5.1, indicate that less than 50% of all soluble sulfide radicals exists as H_2S .

Visual inspection of the packing material revealed the presence of a slime layer on the surface indicating that the SRB were adhering to the packing material surface.

1. Nutrient Consumption and Sulfide Production

The influent and effluent sulfate concentrations

Table 5.3: Averaged Influent and Effluent Sulfates, COD, BOD and Acid-Soluble Sulfide Concentrations

Constituent	Average Concentration †		Average Percentage Consumption (%)
	Influent mg/L	Effluent mg/L	
BOD	803.5	575.3	28.4
COD	1832.7	1408.7	23.1
SO ₄ ²⁻	5692.4	4686.5	17.7
S		132.1	

† - Integral Averages from Day 7 to Day 18, see Appendix IV

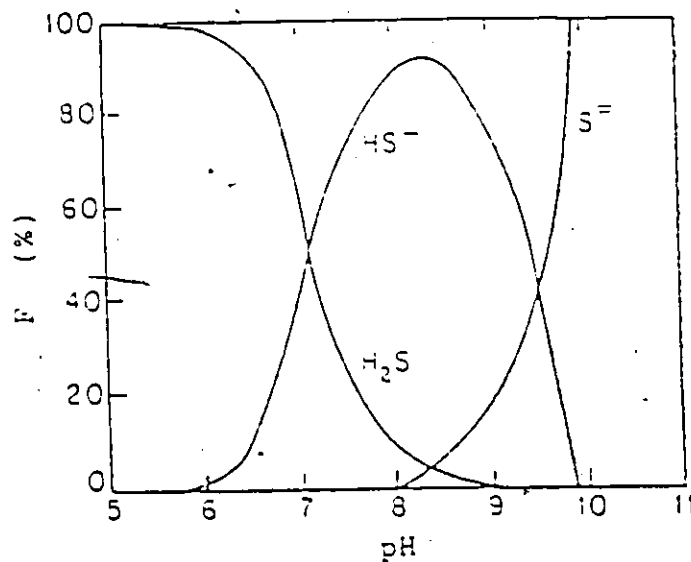


Figure 5.1: Hydrogen Sulfide Dissociation Fraction, F, as a Function of pH [49]

are illustrated in Figure 5.2 for the 18 day study period. All treatability constituent plots, including the sulfate plot, presents the influent as step inputs because each plotted step represents the concentration of that particular feed batch. The average sulfate consumption for day 7 to Day 18 of the study period was 1006 mg SO_4/L for an average conversion of 17.7% (See Table 5.3). Appendix IV details the method used to calculate the constituents averages. The changes in the influent sulfate concentrations over this period were due to the addition of sulfuric acid for wastewater neutralization. The alkalinity of the wastewater changed which affected the amount of sulfuric acid needed. The similarity between the two curves indicates that the influent sulfate content had little effect on the amount of sulfate consumed and sulfates were not limiting the bacterial growth. The lag between the effluent and the influent curves was attributed to the residence time of the reactor.

The BOD and COD removals were low, averaging of 28.4 and 23.1%, respectively. These low removal efficiencies indicate an excess of organics in the influent. Influent and effluent BOD and COD results are presented in Figure 5.3 and 5.4, respectively.

Effluent acid-soluble sulfide concentration is illustrated in Figure 5.5. The acid-soluble sulfide production increased throughout the 18 day study period.

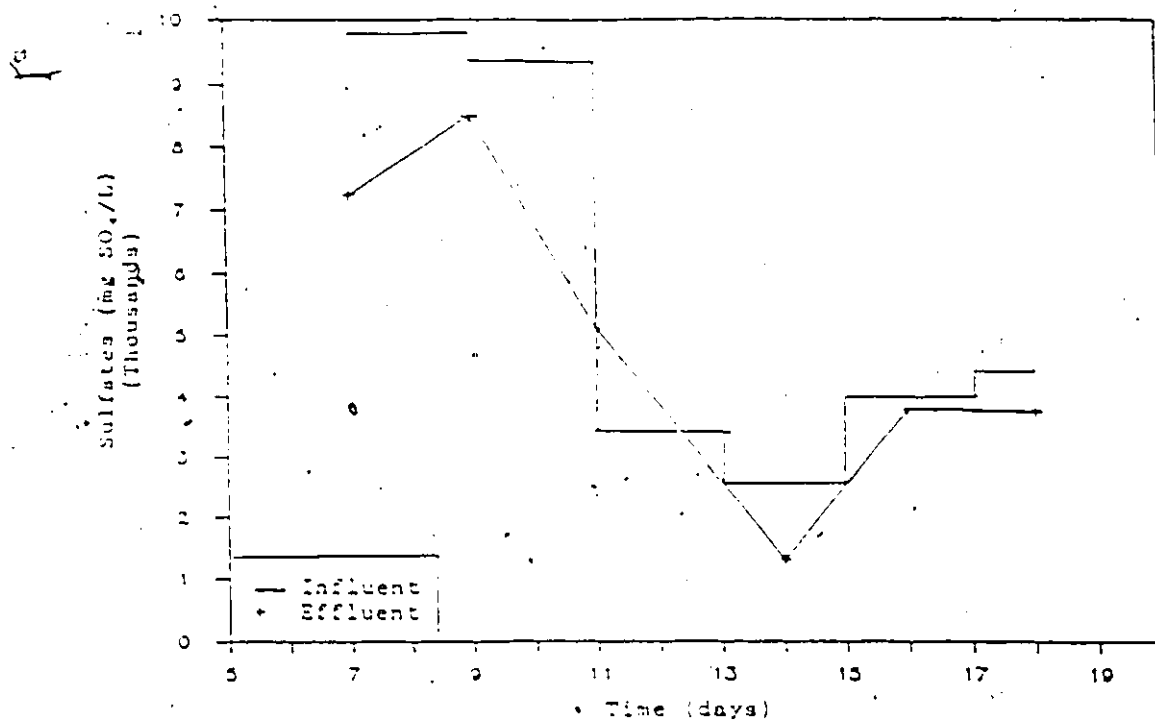


Figure 5.2: Influent and Effluent Sulfate Content versus Time

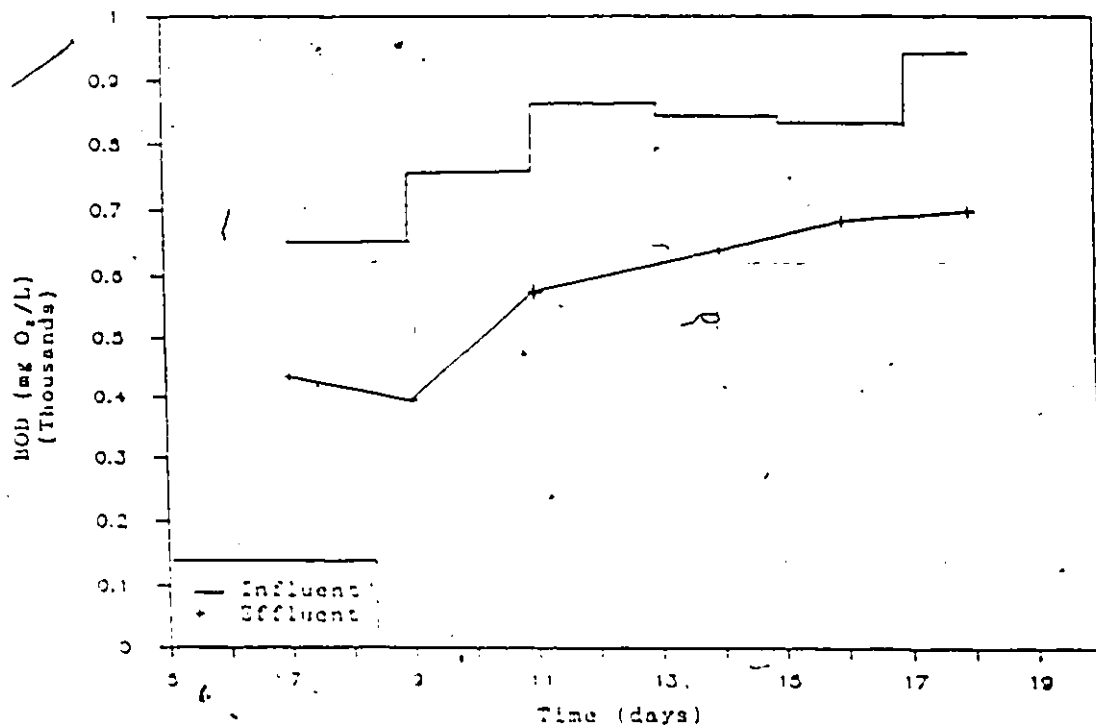


Figure 5.3: Influent and Effluent BOD Content versus Time

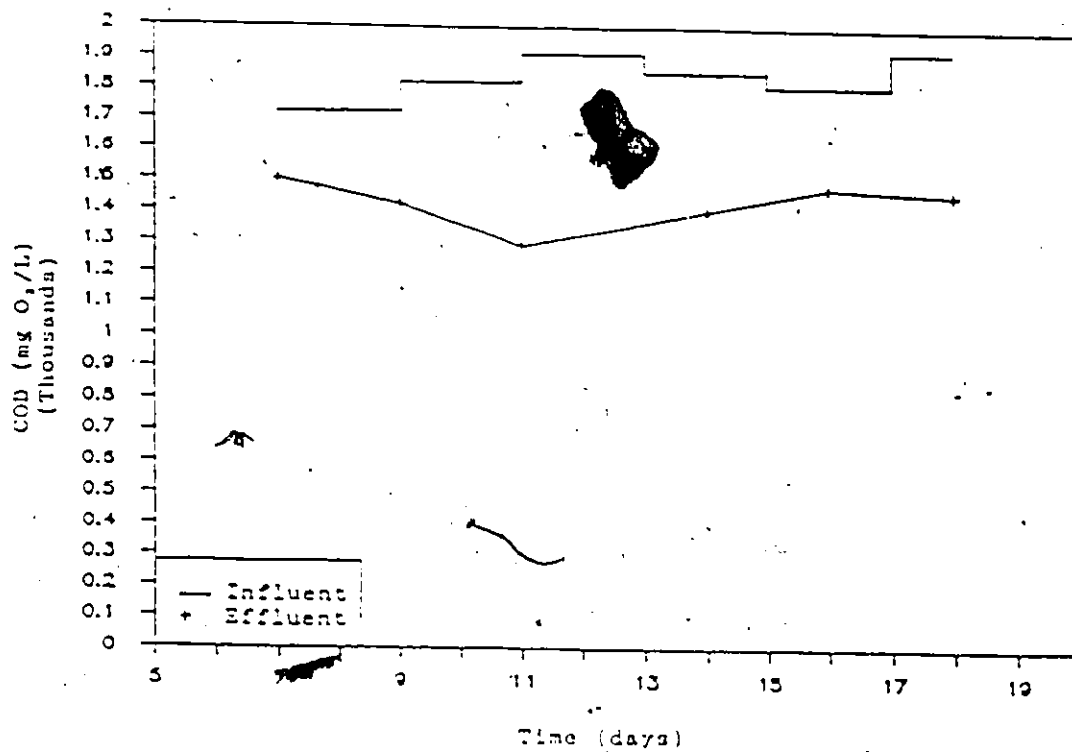


Figure 5.4: Influent and Effluent COD Content versus Time

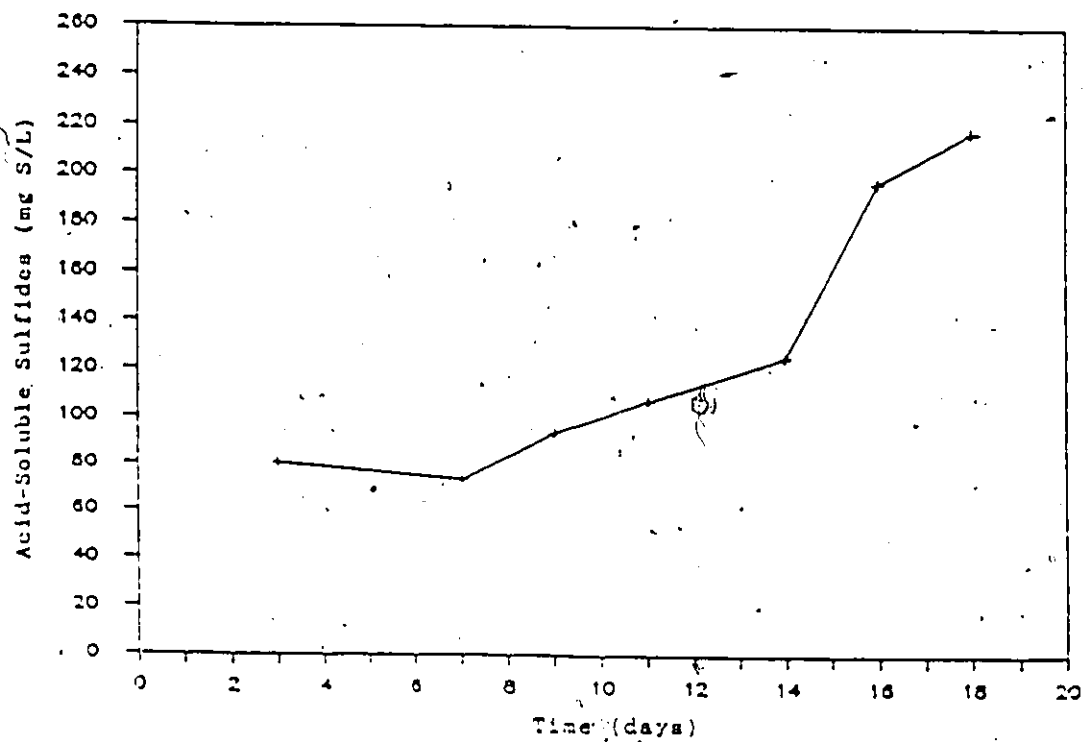


Figure 5.5: Effluent Acid Soluble Sulfide Content versus Time

3 This trend shows that the bacteria were slowly acclimatizing to the environment and the process had not reached a pseudo-steady state. Pseudo-steady state operation occurs when the reactor production of total sulfide reaches a steady value for the biomass content. Excess acid-soluble sulfide throughout the study period also indicates that the reactor had the capacity to treat a higher metal loading while still maintaining enough sulfide to compensate for dissolved oxygen and competing metals ions, such as iron.

The presence of excess effluent sulfide poses an effluent disposal problem because of the regulatory effluent limits. For example, the City of Windsor has set the limits for sanitary sewers at 2.0 mg $\text{H}_2\text{S}/\text{L}$ for less than 0.5 ML/day wastewater flow rate and 1.0 mg $\text{H}_2\text{S}/\text{L}$ for greater than 0.5 ML/day flow rate [55]. Compliance can be accomplished by bypassing some of the raw wastewater and mixing it with the effluent of the reactor in order to precipitate the sulfides.

The macronutrients were monitored in the effluent to determine whether excess amounts were present. The parameters tested were the soluble calcium, magnesium, potassium, ammonium and phosphates. The results are summarized in Table 5.4. Micronutrients were not monitored because the tap water used in the plant contained sufficient amounts of these micronutrients [34].

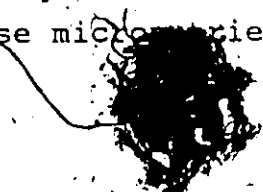


Table 5.4: Treatability Study Effluent Macronutrient Concentration Ranges for Soluble Calcium, Magnesium, Potassium and Phosphates.

Nutrient		Day of Test	Concentration Range (mg/L)
Calcium	as (Ca)	3, 7, 14, 18	6.0 - 9.7
Magnesium	as (Mg)	3, 7, 14, 18	72.8 - 102.6
Phosphorous	as (PO ₄)	10	138.4
Ammonium	as (NH ₄)	2, 7, 14, 17	243 - 340
Potassium	as (K)	3, 7, 14, 18	60.6 - 72.6

2. Metal Separation Results

Figures 5.6 to 5.9, show the variation with time for total and soluble metal concentrations in the influent and effluent streams. Table 5.5 lists the average influent and effluent metal loadings along with the average percentage of separation for the study period. The total to soluble metal ratios for the influent and effluent are presented in Table 5.6. The characterization study indicated that most of the metals were insoluble. The influent ratios presented in Table 5.6 showed that the reduction of the pH to neutrality had liberated a large percentage of the total metals. Lead was the only metal not found as a soluble ion. This was due to the presence of sulfates which were added as soluble salts to the wastewater. Lead has a low solubility with respect to sulfates. The solubility product (K_s) of 1.6×10^{-8} [33]

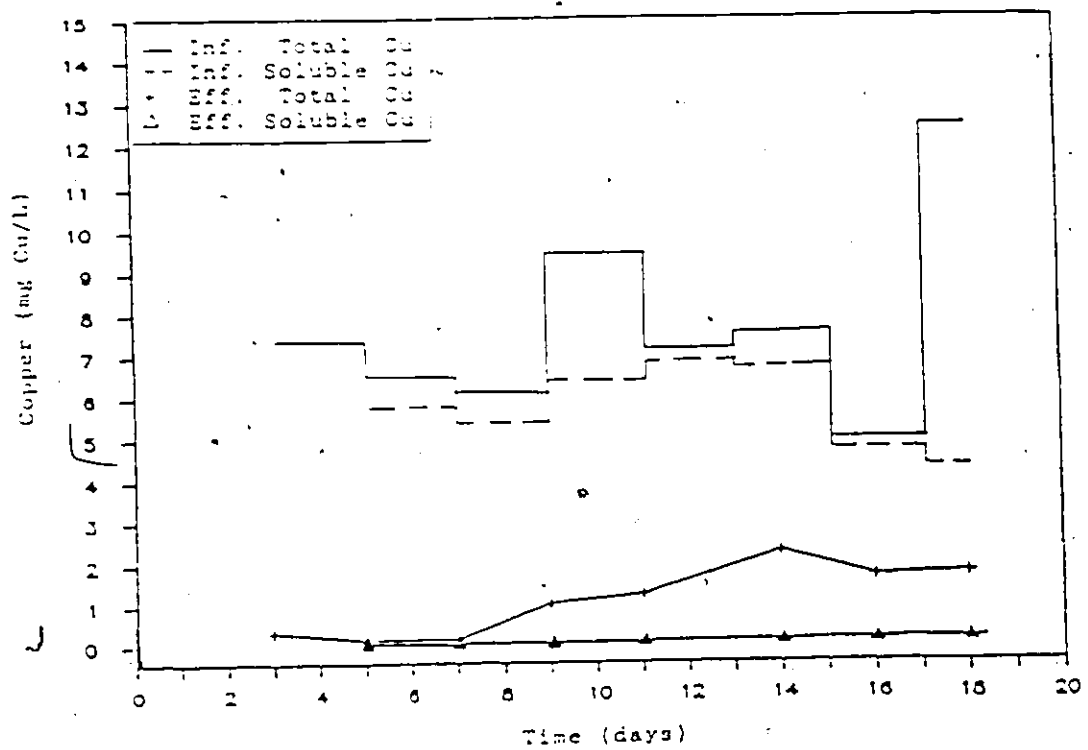


Figure 5.6: Influent and Effluent Soluble and Total Copper Content versus Time

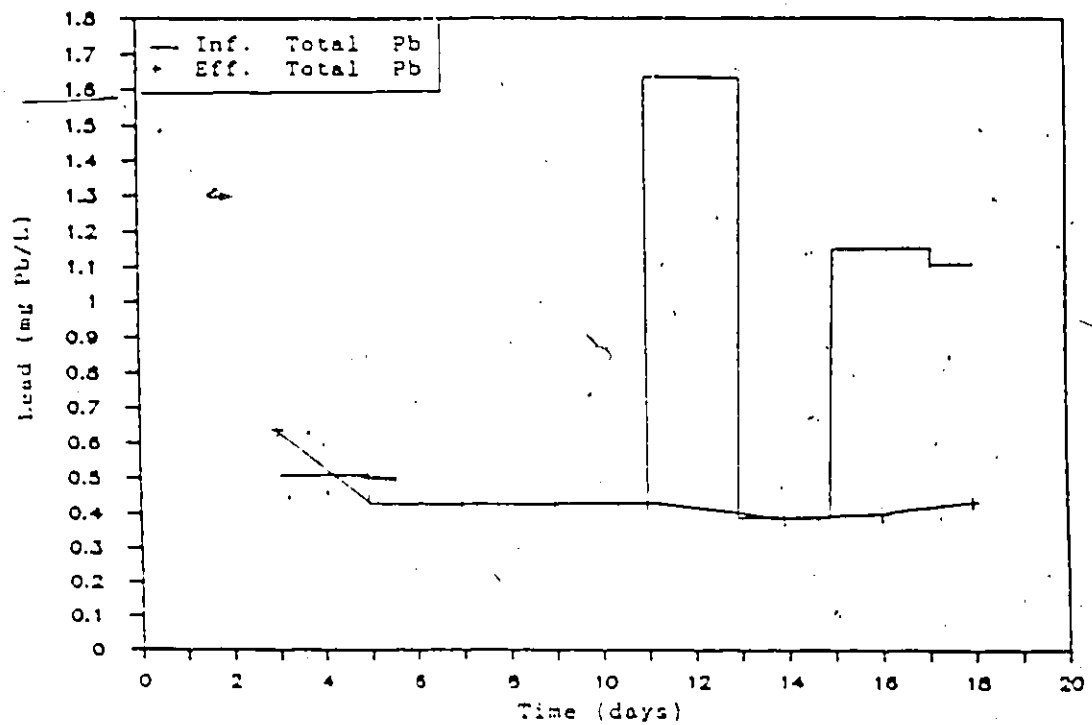


Figure 5.7: Influent and Effluent Total Lead Content versus Time

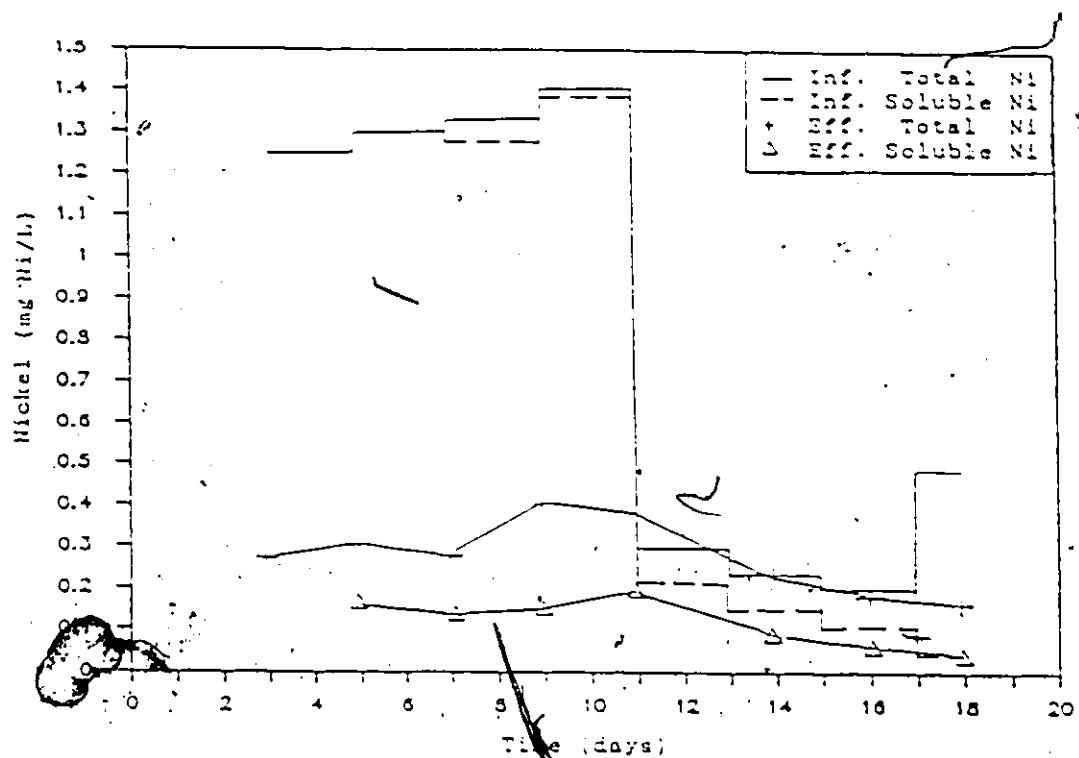


Figure 5.8: Influent and Effluent Soluble and Total Nickel Content versus Time

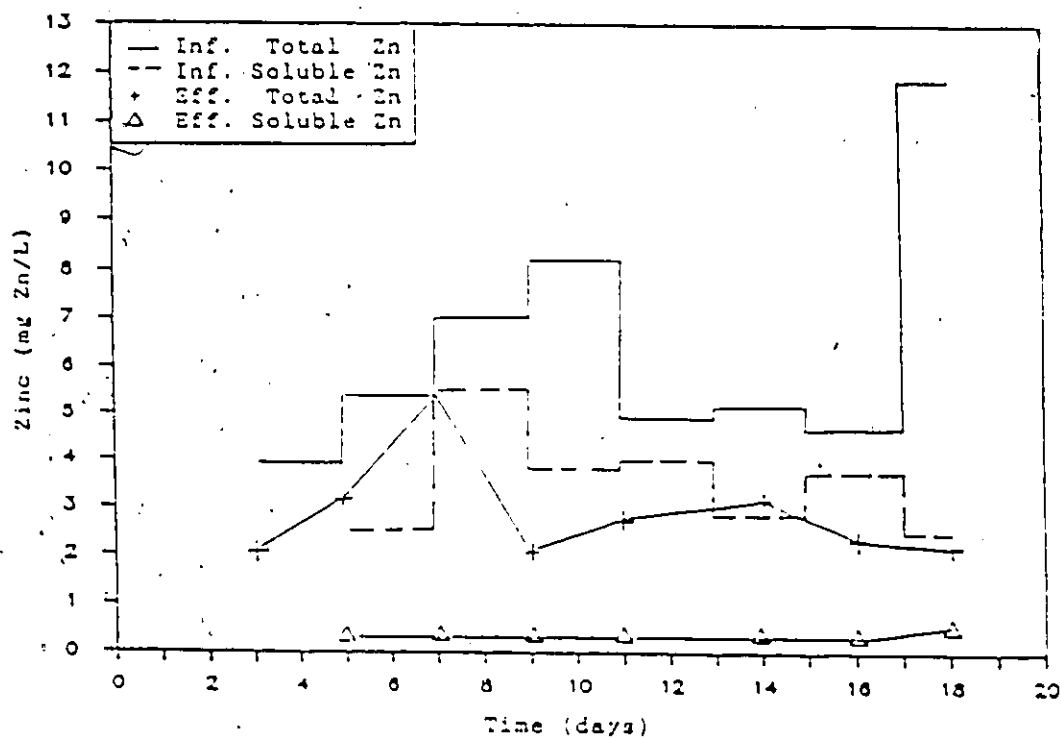


Figure 5.9: Influent and Effluent Soluble and Total Zinc Content versus Time

Table 5.5: Averaged Influent and Effluent Copper, Lead, Nickel and Zinc Concentrations

Metal	Average Concentration (mg/L)			Average Separation Percentage
	Influent	Effluent	Separation	
Total †				
Copper	7.37	1.004	6.36	86.4
Lead	0.728	0.429	0.299	41.1
Nickel	0.830	0.284	0.546	65.8
Zinc	5.97	2.88	3.10	51.8
Soluble ‡				
Copper	5.84	< LOD *	>5.83	99.9
Lead	< LOD *	< LOD *	-	-
Nickel	0.683	0.121	0.562	82.3
Zinc	3.58	0.298	3.29	91.7

† - Integral Averages from Day 3 to Day 18
‡ - Integral Averages from Day 5 to Day 18
LOD * - Limit of Detection a) Copper 0.008 mg/L
b) Lead 0.094 mg/L
c) Nickel 0.011 mg/L
d) Zinc 0.282 mg/L

Table 5.6: Soluble to Total Metal Ratios for the Influent and Effluent.

Metal	Percentage in Influent		Percentage in Effluent	
	Range	Average	Range	Average
Copper	34.8 - 97.1	82.0	0.4 - 8.4	2.6
Lead	-	-	-	-
Nickel	8.5 - 100.0	73.2	26.7 - 53.5	42.2
Zinc	19.9 - 80.3	61.1	5.3 - 23.3	12.2

indicates that most of the lead would be complexed as lead sulfate.

Metal precipitation as metal sulfides separated over 80% of the soluble Ni, 92% of the soluble Zn and over 99% of the soluble Cu. These precipitation efficiencies confirm the results obtained by Wong et al., during their study with synthetic wastewater. Precipitation reduced the soluble metal concentrations in the effluent to very low levels. The ratios of soluble to total metals in the effluent provide additional proof that most of the soluble metals had been precipitated as metal sulfide. Total metal concentrations in the effluent (Table 5.5) indicate that most of the precipitated metals were retained by the reactor. The only metal which exceeded 1 mg/L of total metal in the effluent was zinc, averaging 2.83 mg Zn/L. This value exceeds the permitted limits for sanitary sewers, as summarized in Table 1.1. A settling chamber or alternate particulate separation unit would be required after the reactor to meet this limit. Sizing of this unit would require the particle size distribution for each of the four metals when complexed as sulfides.

In summary, the treatability reactor for metal separation was dominated by SRB. Sufficient sulfide are produced to precipitate soluble metals from the wastewater and separate them as metal sulfides. All metals, except zinc, were effectively separated in the reactor to produce

an effluent that was within the limits established by regulatory agencies (Table 1.1). The effluent analysis showed that the organics, sulfates and macronutrients were not the limiting factors under these operating conditions. The high degree of metal separation and high acid-soluble sulfide production suggests that the reactor HRT can be reduced. Acid-soluble sulfide production was steadily increasing during the study period, indicating that the reactor had not reached a pseudo-steady state. The excess acid-soluble sulfide produced in the reactor can be used to precipitate additional amounts of the metals by bypassing a part of the influent and mixing it with the effluent.

C. Hydraulic Retention Time

The average nutrient consumption, reduced sulfur production and metal separation efficiencies for each reactor were plotted against the reactor's HRT to determine any correlations. The HRT results for Test 1 and Test 2 are not compared because Test 2 preceeded Test 1. The 74 days during Test 1 and the interval between Test 1 and Test 2 allowed the bacteria to multiply and acclimatize themselves to the metal wastewater. In addition, the wastewater characteristics changed between Test 1 and Test 2 because of the daily variations in production at the plant. To overcome these problems, Reactor C2 of Test 2 was operated at a HRT of 24.5 hours, which is close to the 27.8 hour HRT used for Reactor A1 during Test 1. These similar HRTs

provided a continuity between the results produced by Test 1 and Test 2.

The influent and effluent compositions for Test 1 and 2 when plotted against time are connected with straight lines rather than step inputs because constituent concentrations were not measured for every feed batch. The conclusions drawn from the data are believed to be acceptable because the three or four feed batches used during each week originated from the same 7-day wastewater sample. The nutrient supplementations were held constant according to the recipe given in Table 4.4

1. Nutrient Consumption and Reduced Sulfur Production

The average influent and effluent sulfate, BOD and COD concentrations along with percentage removal and average reduced sulfur production rate, before spiking, are presented in Table 5.7, for Tests 1 and 2. All results are tabulated in Appendix IV.

a. BOD and COD Consumption

The COD and BOD concentrations in the influent feed and effluent (Reactor A1, B1 and C1 or as Reactor A2, B2 and C2) are plotted as a function of time in Figures 5.10 through 5.13. The average BOD and COD percentage removal before spiking, are plotted against the HRT in Figure 5.14. These data indicate that the percentage of organic conversion was dependent on the reactor's HRT. The average consumption rate of organic matter decreased as

Table 5.7: Influent and Effluent Averaged Reduced Sulfur, Sulfates, COD and BOD Concentrations

Reactor	Reduced Sulfur (mg S/L)	Sulfates (mg/L)	Consumption (%)	COD (mg/L)	Consumption (%)	BOD (mg/L)	Consumption (%)
Test 1							
Influent		3075		331.1		179.4	
A1	62.3	2853	7.2	216.3	34.7	105.5	41.2
B1	62.1	2843	7.5	200.9	39.3	86.9	51.5
C1	77.3	2751	10.5	192.2	41.9	85.4	52.4
Test 2							
Influent		2499		314.4		191.7	
A2	82.2	2151	13.9	301.1	4.2	140.4	26.8
B2	102.2	2099	16.0	238.9	24.0	128.7	32.9
C2	105.5	2030	18.8	224.1	28.7	127.3	33.6

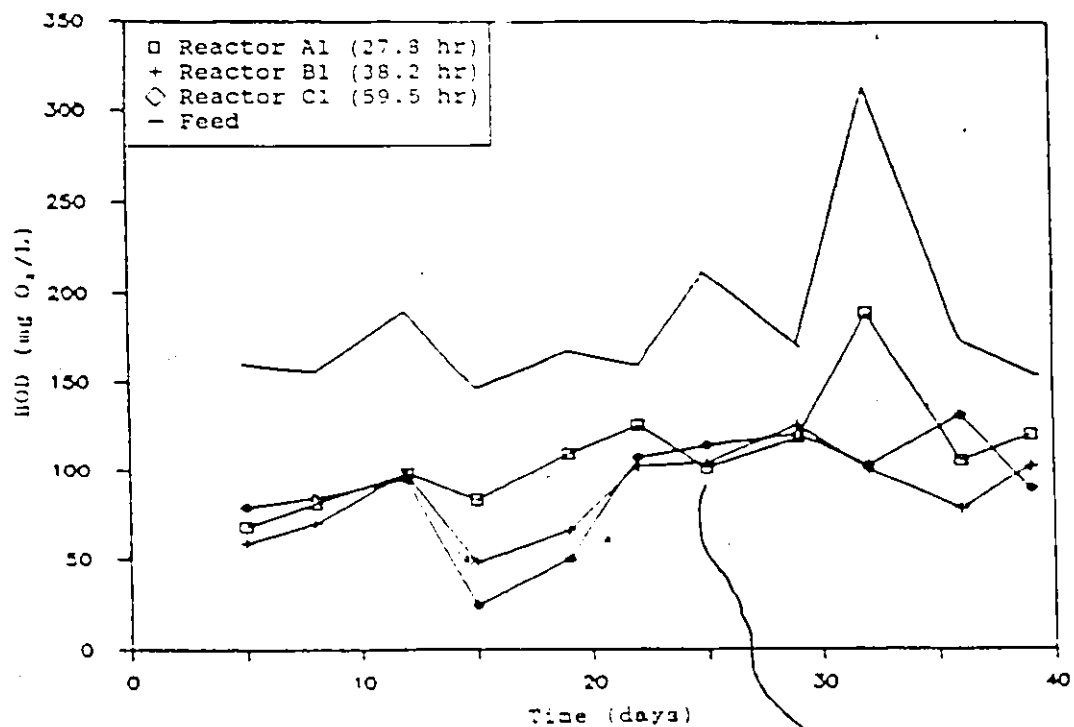


Figure 5.10: Influent and Effluent BOD versus Time for Test 1

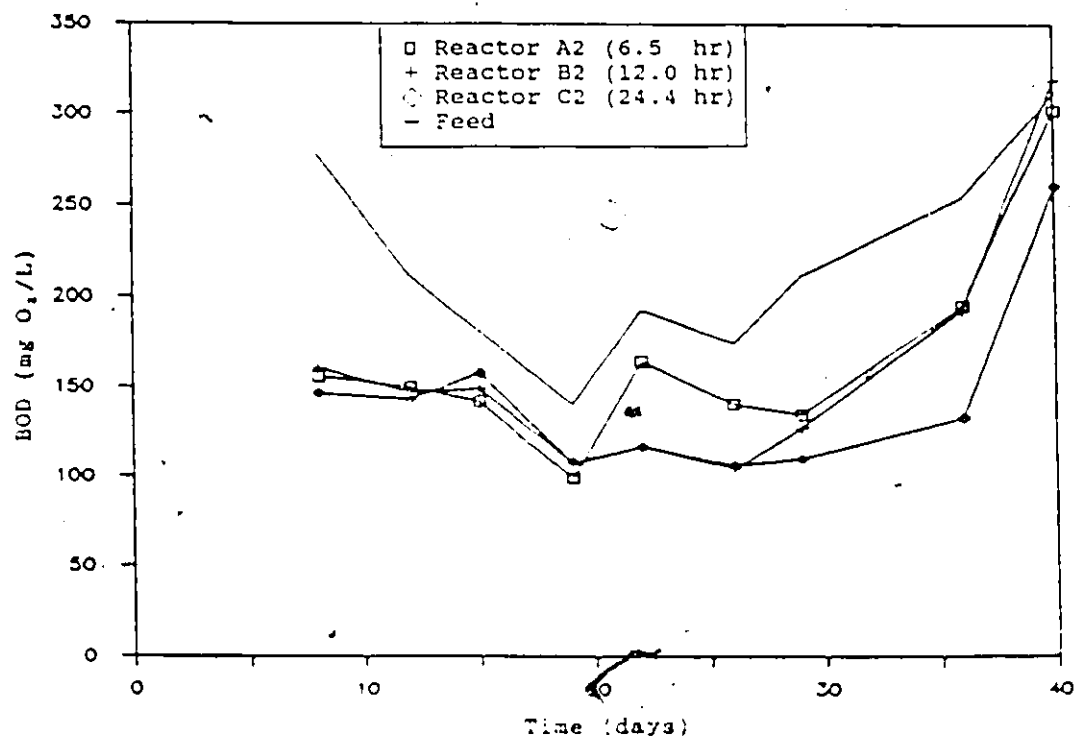


Figure 5.11: Influent and Effluent BOD versus Time for Test 2

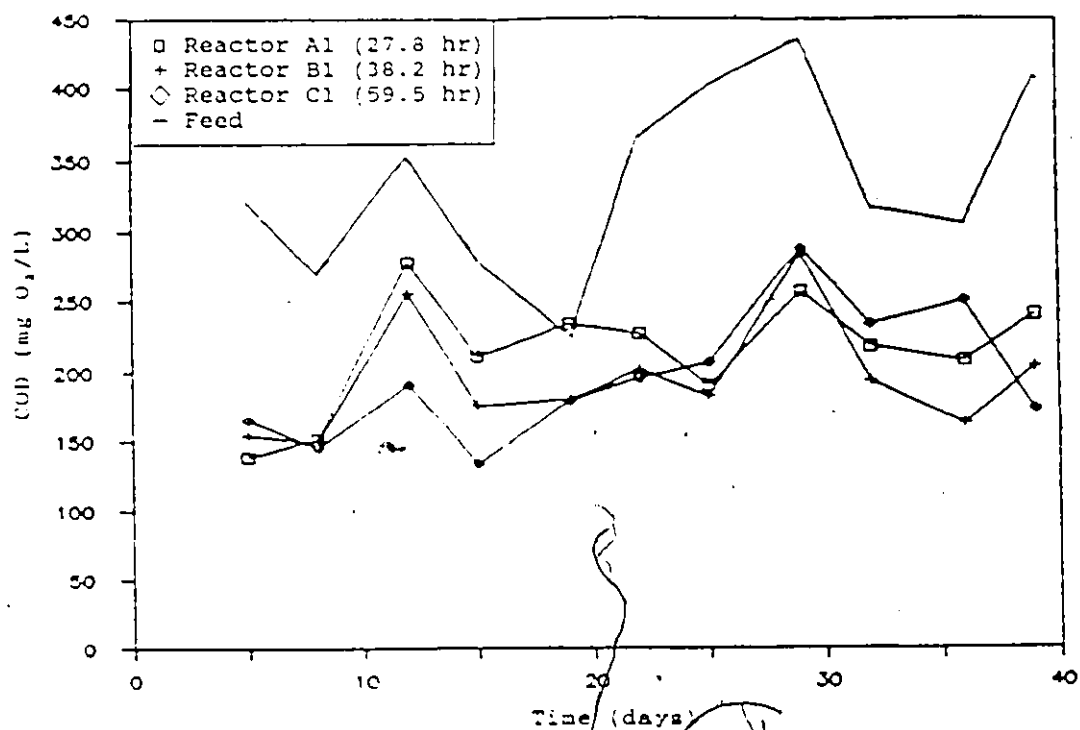


Figure 5.12: Influent and Effluent COD versus Time for Test 1

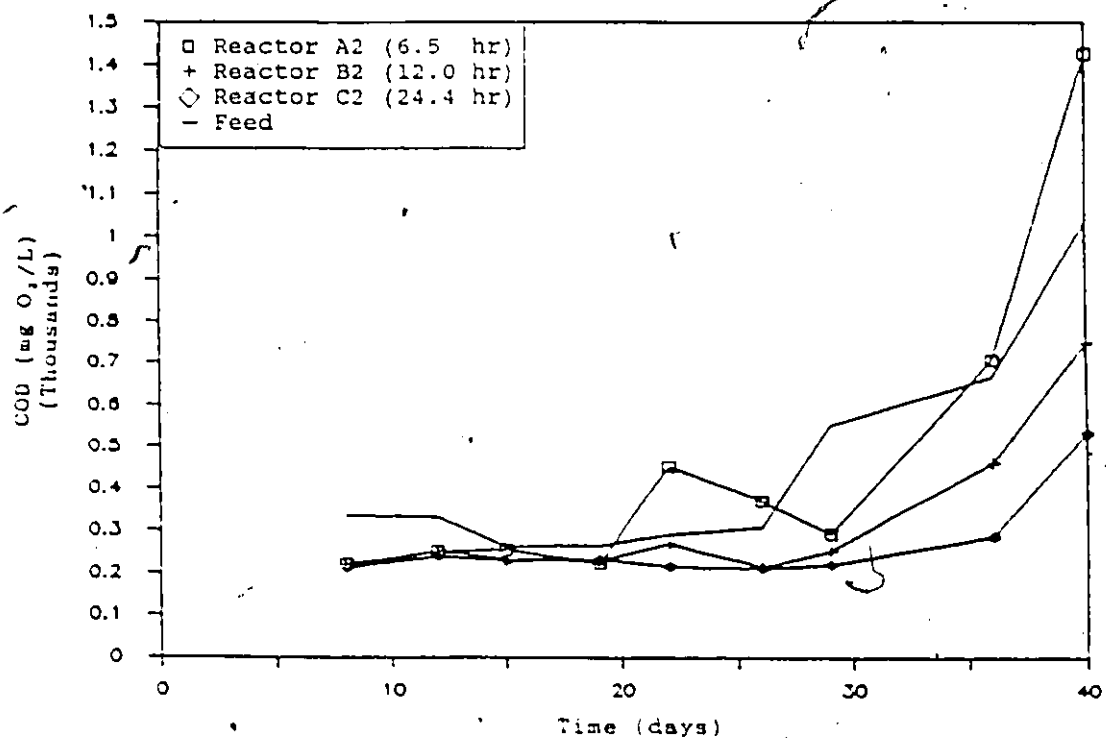


Figure 5.13: Influent and Effluent COD versus Time for Test 2

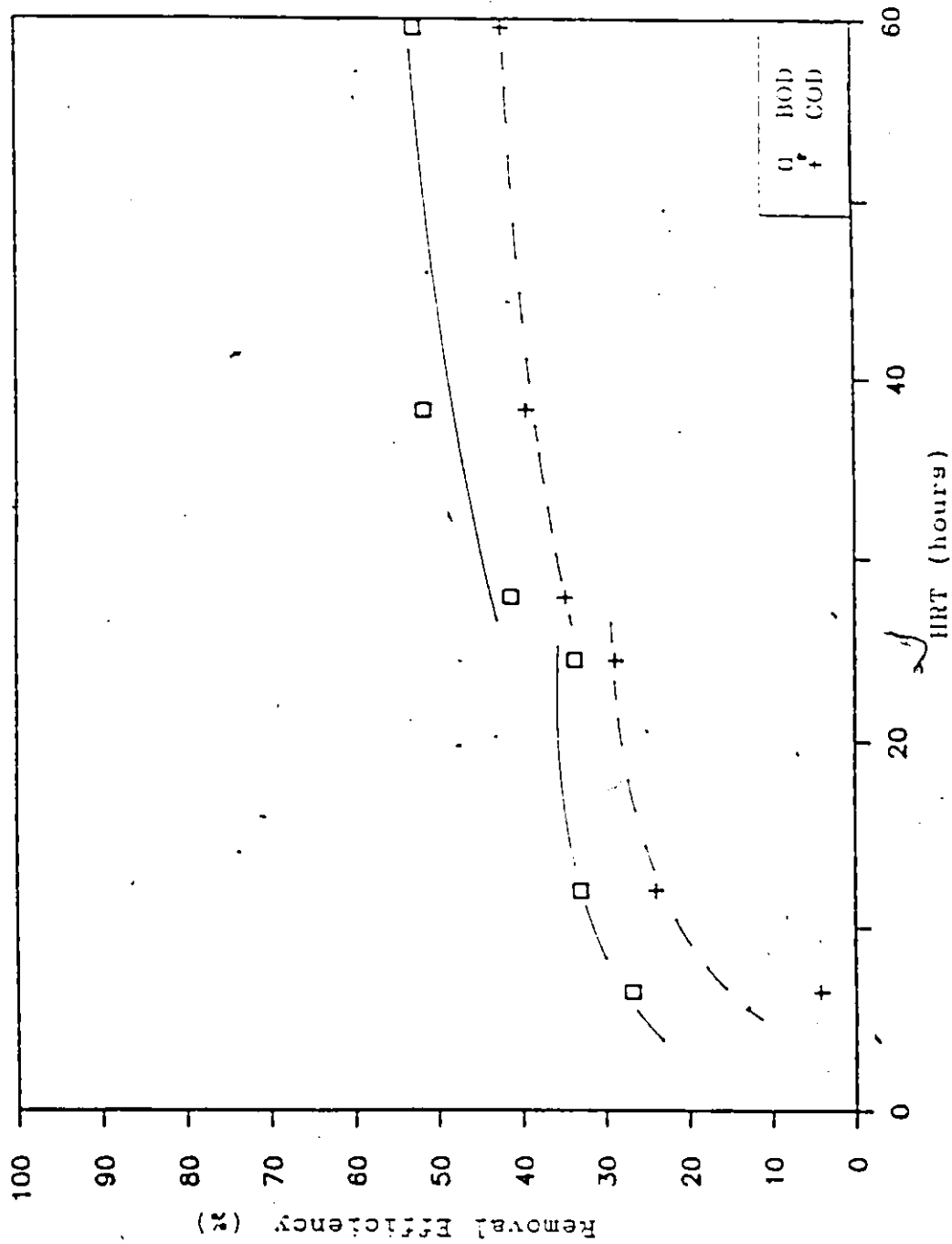


Figure 5.14: Averaged BOD and COD Removal Efficiency versus Hydraulic Retention Time

the HRT decreased, which is expected because consumption of organic matter is dependent on its contact time with biomass [5].

Chemical oxygen demand analyses were interfered with by soluble and complexed sulfides especially after wastewater spiking during Test 2. The effluent COD concentrations exceeded the influent concentrations. This observation is consistent with effluent total metal concentrations which increased in all cases after wastewater spiking.

The presence of reduced sulfide in the effluent caused an over-estimation of the wastewater's organic content. Thus using COD measurements to estimate the organic content of the wastewater would be incorrect. Measuring BOD removal would not be useful either because the BOD value has a large error associated with its measurement (approximately 10% [6]). Also it only provides a partial measurement of total organic content. A more reliable method of estimating the effluent organic content is needed. Total organic carbon (TOC) may be used in conjunction with BOD and COD measurements to provide results which accurately reflect organic content. Biological oxygen demand and COD analyses are necessary because they are regulated parameters while TOC is not.

The effects of wastewater spiking on BOD and COD consumption cannot be interpreted because these parameters

were not monitored daily. Wastewater spiking was done on Day 33 through Day 35 for both Test 1 and 2, while BOD and COD testing was performed for Days 36 and 39 for Test 1 and Days 36 and 40 for Test 2.

b. Sulfate Consumption

The time variation of influent and effluent sulfates concentrations are plotted in Figures 5.15 and 5.16. For Test 1, the influent and effluent sulfate levels increased to the range 4000 to 5500 mg SO_4/L on Days 11 and 13. These elevated concentrations resulted from the use of sulfuric acid as the wastewater neutralizing agent. After Day 17 hydrochloric acid was substituted as the neutralizing agent to produce a feed which had a consistent sulfate content. The average sulfate consumption was dependent upon the HRT of the reactor as shown in Figure 5.17. This behaviour is similar to that for the conversion of organics. The influent and effluent sulfate concentrations show that wastewater spiking did not significantly effect the sulfate consumption.

c. Reduced Sulfur Production

Soluble reduced sulfur effluent concentrations as a function of time for Tests 1 and 2 are presented in Figures 5.18 and 5.19. In Test 1 there was an initial drop of soluble reduced sulfur at the beginning of the test and steady increase in production thereafter. This can be attributed to a change in the feed. A synthetic feed

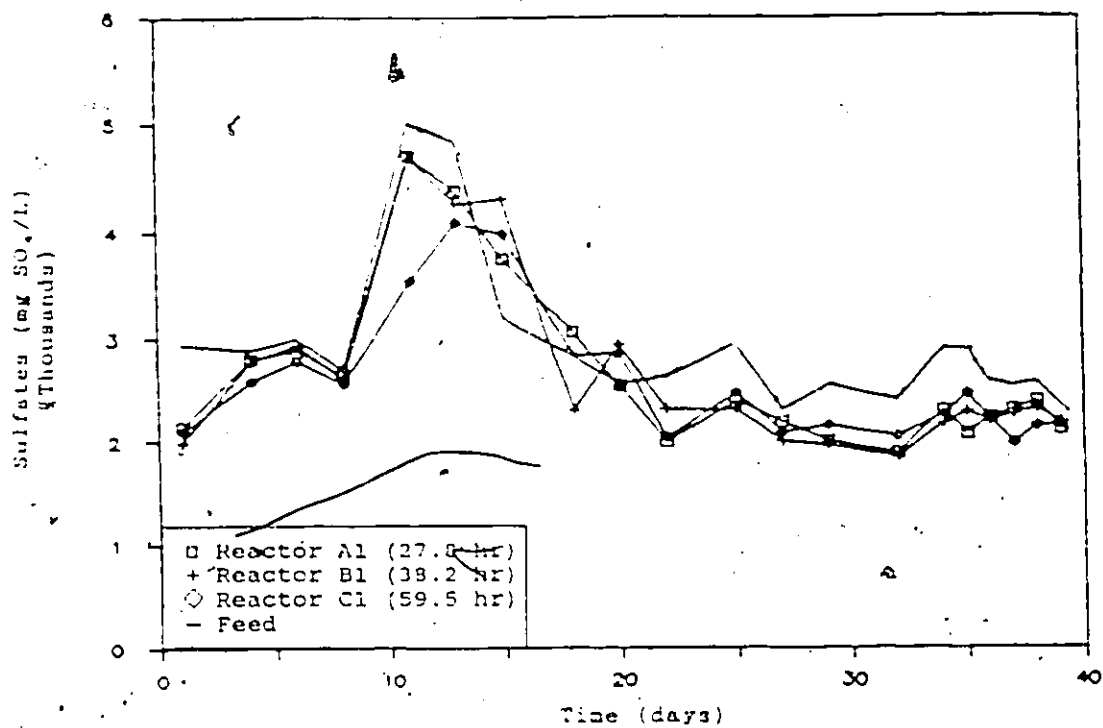


Figure 5.15: Influent and Effluent Sulfate versus Time for Test 1

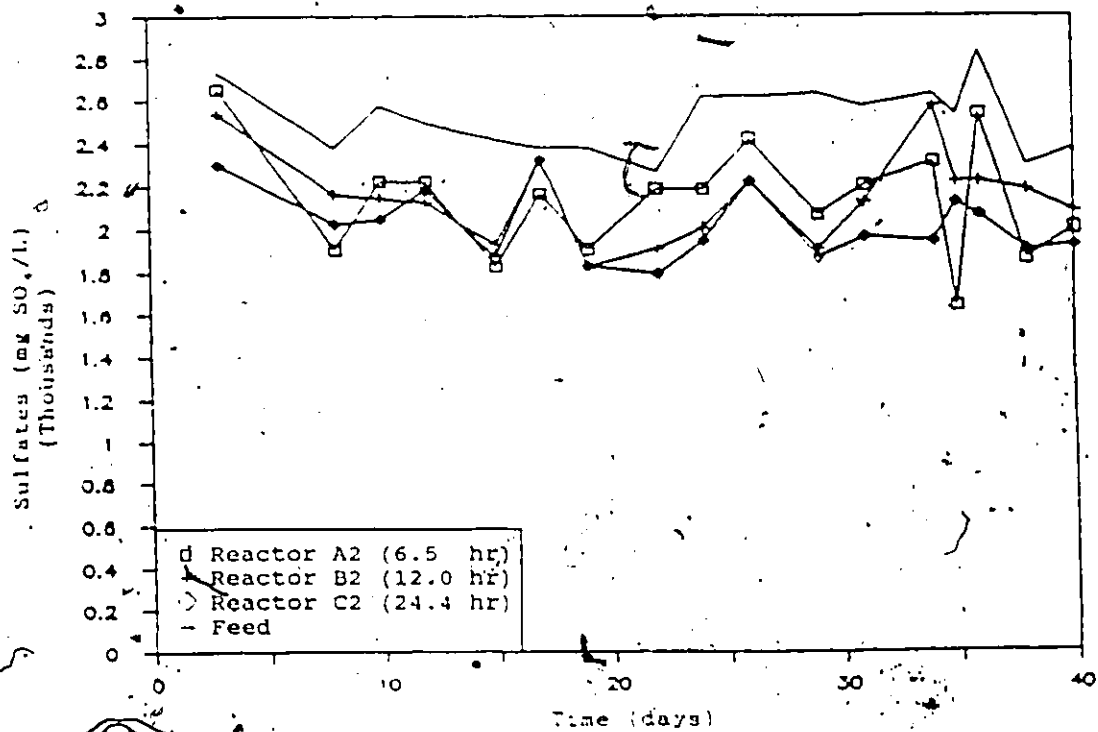


Figure 5.16: Influent and Effluent Sulfate versus Time for Test 2

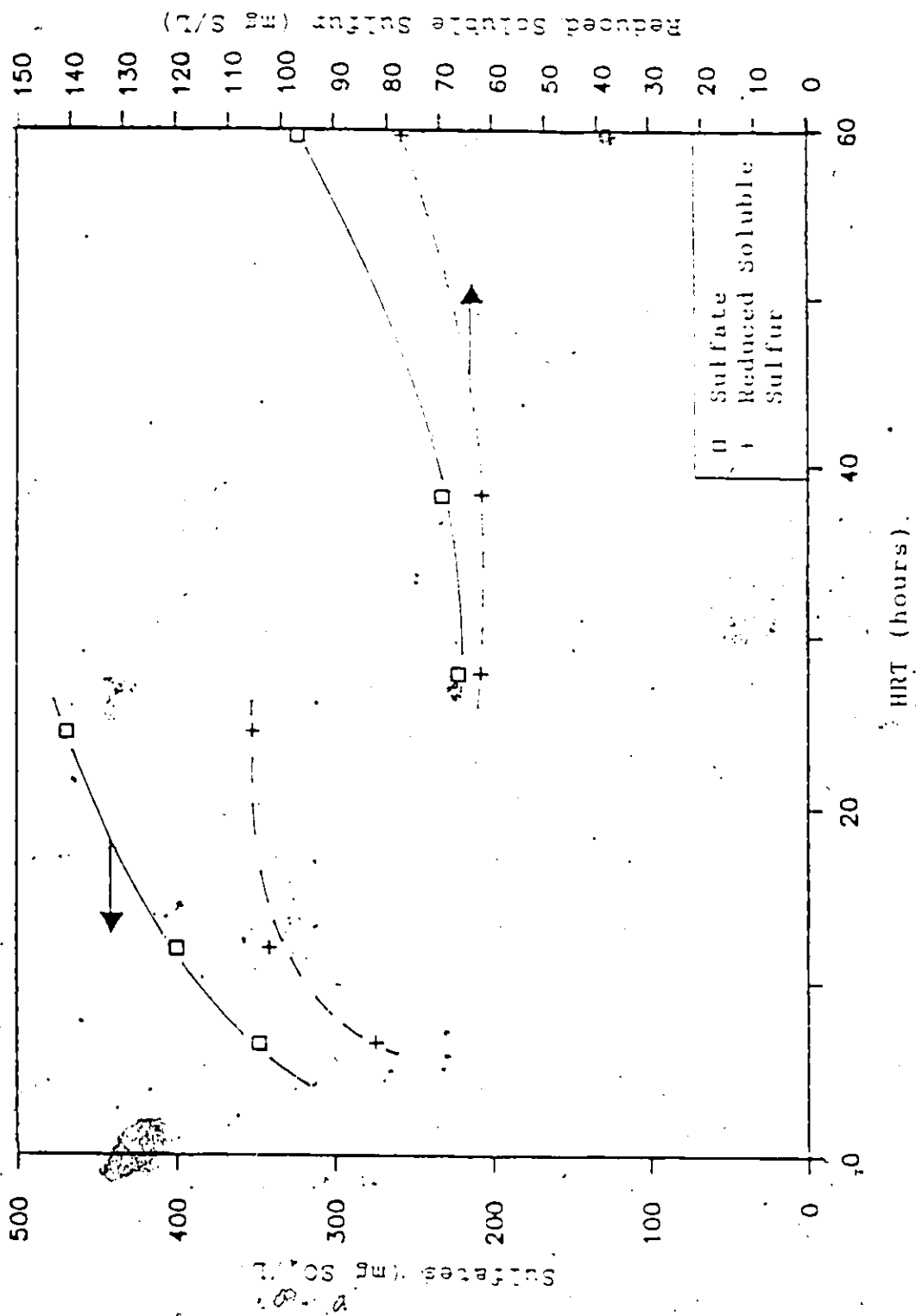


Figure 5.17: Average Sulfate Consumption and Soluble Reduced Sulfur Production versus Reactor Hydraulic Retention Time.

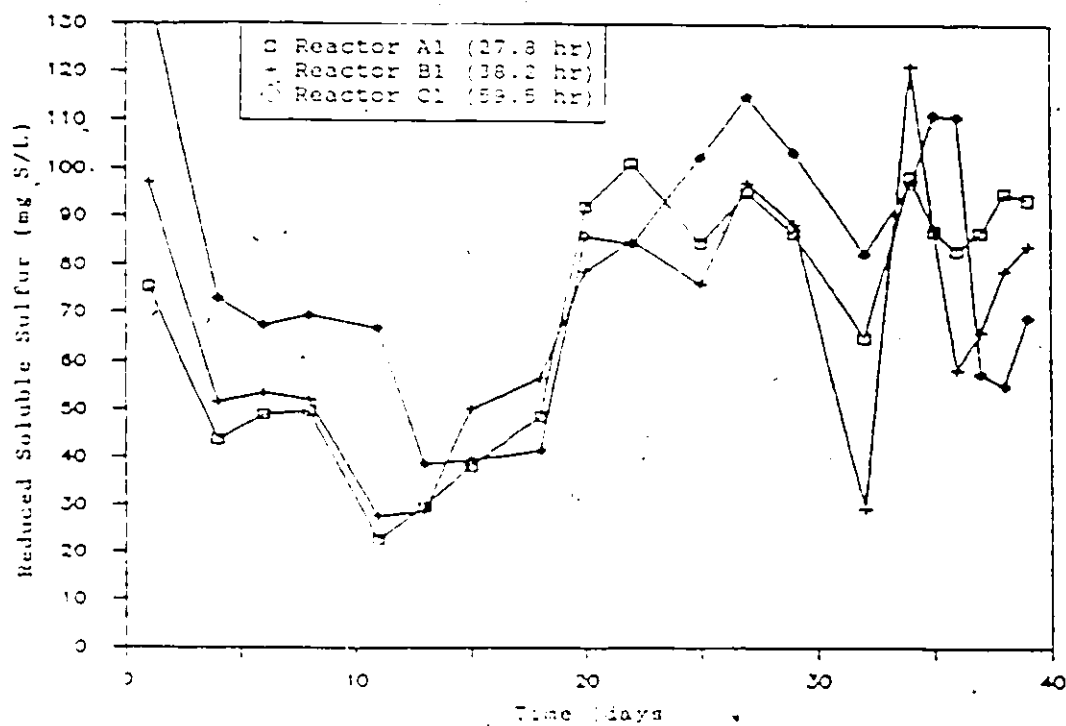


Figure 5.18: Effluent Reduced Soluble Sulfur versus Time for Test 1

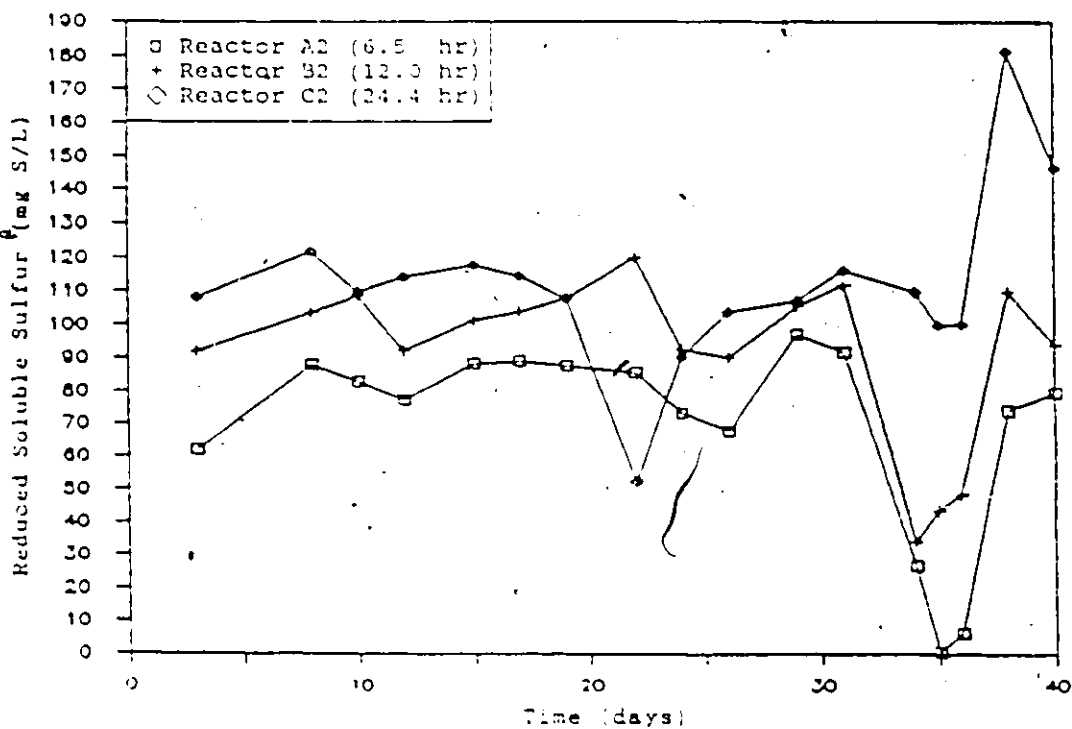


Figure 5.19: Effluent Reduced Soluble Sulfur versus Time for Test 2

was introduced into the reactor until day "zero" when the industrial wastewater replaced the synthetic feed. Since the bacteria were not acclimatized to the new feed the production of reduced sulfur dropped. However, as the bacteria acclimatized they started producing a more consistent level of reduced sulfur.

The excess of reduced sulfur throughout Test 1 and Test 2 indicates that the reactor had the capacity to treat higher metal loading rates than the levels present in the wastewater. Figure 5.17 shows the average effluent levels of excess reduced soluble sulfur as a function of the reactor's HRT. This plot demonstrates how reduced soluble sulfur production increased as the reactor's HRT increased.

During wastewater spiking, the reduced sulfur levels fell drastically with the reduced sulfur concentration in Reactor A2, operating at a 6.5 hour HRT, dropping to near zero. This drop indicates that Reactor A2 was operating at full capacity and that further reduction in HRT under these high loading conditions would consume all the sulfides produced and thus eventually cause the reactor to fail. Failure would occur because excessive sulfide levels are needed for both bacterial growth and metal precipitation.

2. Metal Separation Efficiencies

The average soluble and total metal loading rates are summarized in Tables 5.8 and 5.9. These values are

Table 5.8: Averaged Influent and Effluent Soluble and Total Copper and Lead Concentrations

Reactor	Copper			Lead		
	Soluble (mg/L)	Removal (%)	Total (mg/L)	Removal (%)	Soluble (mg/L)	Removal (%)
Test 1						
Influent	13.06		16.75		<LOD†	
A1	0.040	99.7	0.176	98.9	<LOD†	26.1
B1	0.036	99.7	0.190	98.9	<LOD†	13.2
C1	0.041	99.7	0.158	99.1	<LOD†	9.3
Test 2						
Influent	1.880		10.43		<LOD	
A2	0.043	97.7	1.030	90.1	<LOD	13.1
B2	0.030	98.4	0.336	96.8	<LOD	20.5
C2	0.028	98.5	0.415	96.0	<LOD	24.6

† Weighted Average LOD

Table 5.9: Averaged Influent and Effluent Soluble and Total Nickel and Zinc Concentrations

Reactor	Nickel			Zinc		
	Soluble (mg/L)	Removal (%)	Total (mg/L)	Removal (%)	Soluble (mg/L)	Removal (%)
Test 1						
Influent	1.314		1.763		5.217	10.52
A1	0.072	94.5	0.371	78.9	<LOD†	>88.4
B1	<LOD†	>96.8	0.401	77.2	<LOD†	>88.4
C1	<LOD†	>96.8	0.398	77.4	<LOD†	>88.4
Test 2						
Influent	0.303		0.656		0.591	20.63
A2	<LOD	>74.3	0.303	43.8	<LOD	>48.6
B2	<LOD	>74.3	0.233	64.5	<LOD	>48.6
C2	<LOD	>74.3	0.215	67.2	<LOD	>48.6

† Weighted Average LOD

average influent and effluent concentrations before wastewater spiking. Figures 5.20 and 5.21, respectively, show the soluble and total metal precipitation and separation efficiencies for the four metals. The overall soluble metal precipitation efficiencies were not dependent on the reactor's HRT. Soluble metal precipitation efficiency depends on the sulfide concentration and it was always in excess. Actual curves for nickel and zinc could not be generated because effluent metal concentration were usually less than the LOD. The curves plotted for these metals are the minimum efficiency curves because the LOD is used for the determination of the precipitation efficiencies. Total lead, nickel and zinc separation efficiencies were dependent on the reactor's HRT. Total metals, as noted by DeWalle et al. [13], are related to the suspended solids leaving the anaerobic filter [13]. Thus, total metal separation efficiencies are dependent on the retention of suspended solids.

Effluent metal concentrations were compared to suggested discharge limits for Ontario of 1 mg/L because these limits are more stringent or comparable to the limits proposed by the City of Windsor and Environment Canada.

a. Copper Separation

Soluble copper had a precipitation efficiency ranging from 98.5 to 99.7% for both tests. Copper had the highest precipitation efficiencies when compared to the

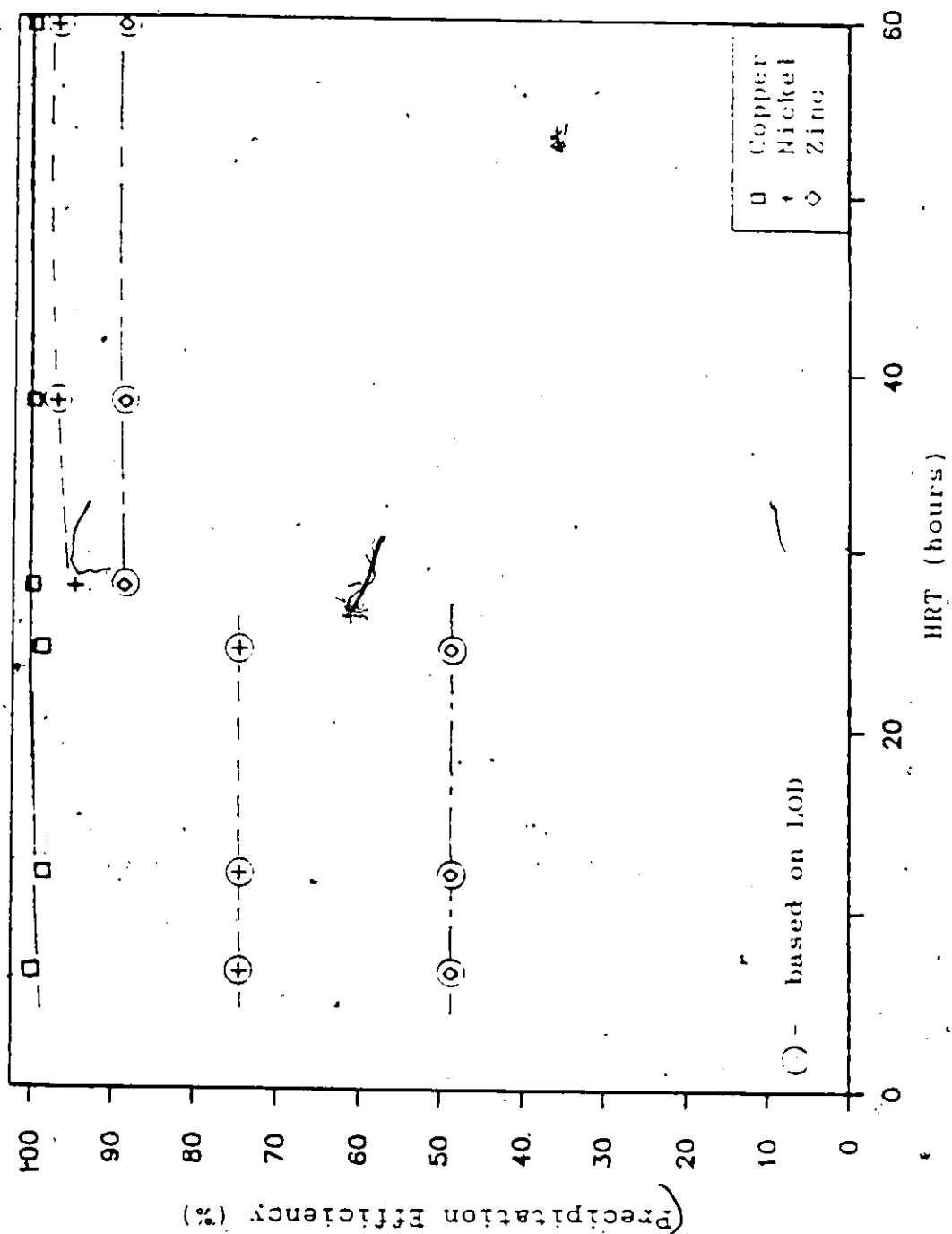


Figure 5.20: Averaged Soluble Metal Precipitation Efficiency of Copper, Nickel and Zinc versus Hydraulic Retention Time

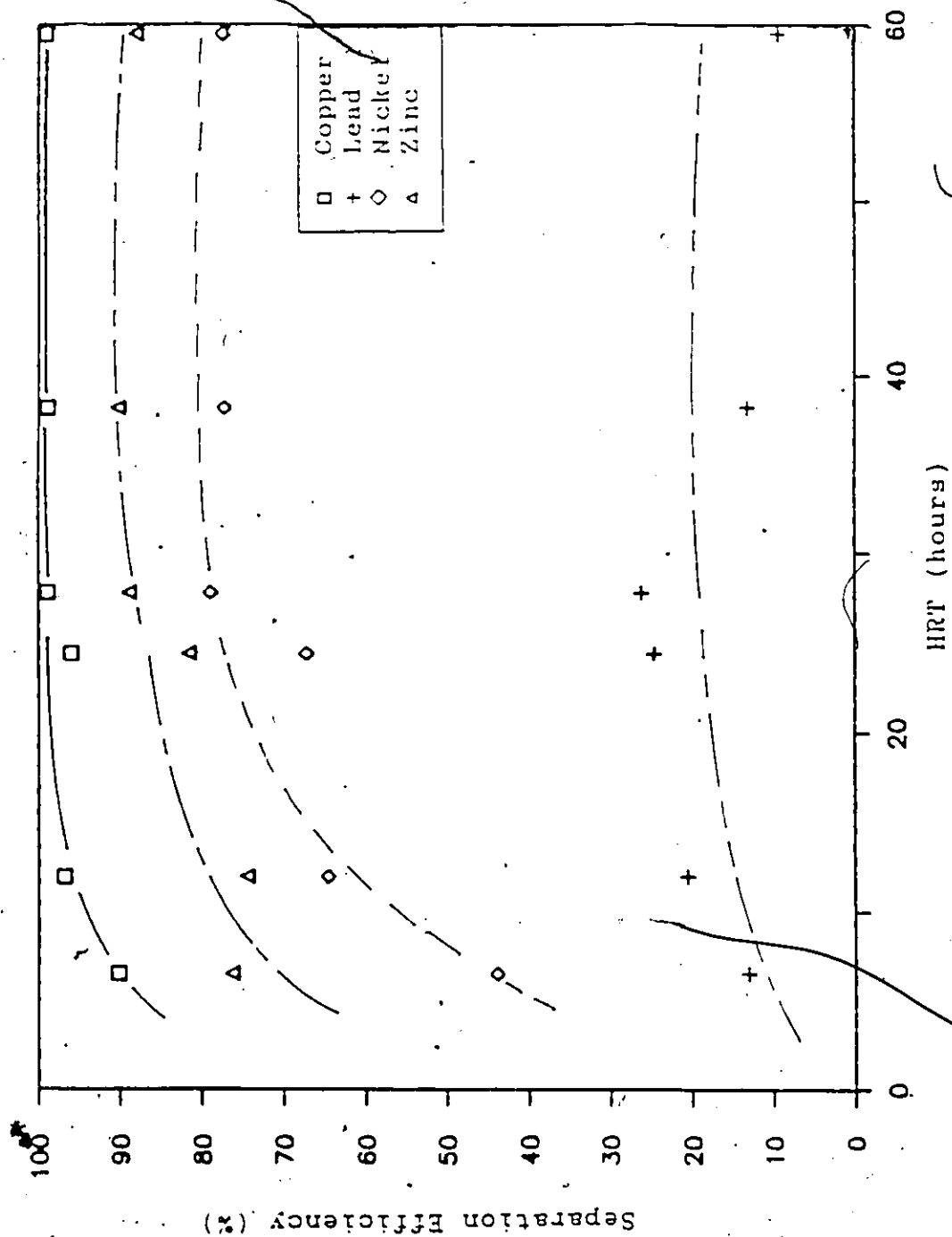


Figure 5.21: Averaged Total Metal Separation Efficiency of Copper, Lead, Nickel and Zinc versus Hydraulic Retention Time

other metals. This observation can be attributed to the low solubility of copper sulfide, Table 2.1. Figures 5.22 and 5.23 present influent and effluent soluble copper concentrations for Tests 1 and 2, respectively. Soluble copper effluent concentrations were low throughout the study periods. This was expected because excess reduced sulfur was always present throughout the normal operation periods. For both tests, effluent soluble copper levels were below 1 mg/L.

The reactor was also effective in separating the total copper from the wastewater. As noted in Table 5.8, metal separation efficiencies ranged from 90.1 to 98.9% for both tests. This high degree of total copper separation was observed by DeWalle et al. [13] who found that copper was associated with the largest particles within an anaerobic reactor [13]. Larger particles means faster settling rates within the reactor and better retention of these particles. The concentrations-time curves for total copper in Tests 1 and 2 are shown in Figures 5.24 and 5.25. Except for Reactor A2 of Test 2, average total copper levels were below 1 mg/L.

Figures 5.22 and 5.23 show that the spiking of the wastewater caused no drastic changes in effluent soluble copper content. Test 2 exhibited increases in effluent concentration for Reactors A2 and B2 of Test 2, but these increased concentrations were still below the 1 mg/L limit.

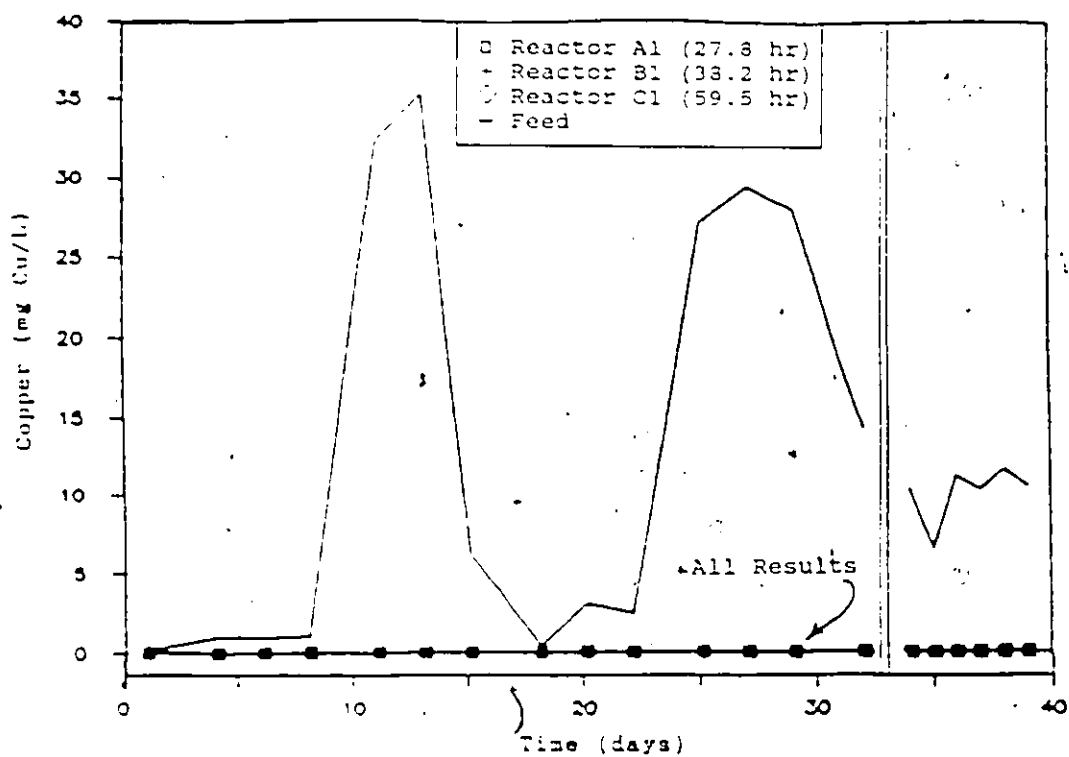


Figure 5.22: Influent and Effluent Soluble Copper versus Time for Test 1

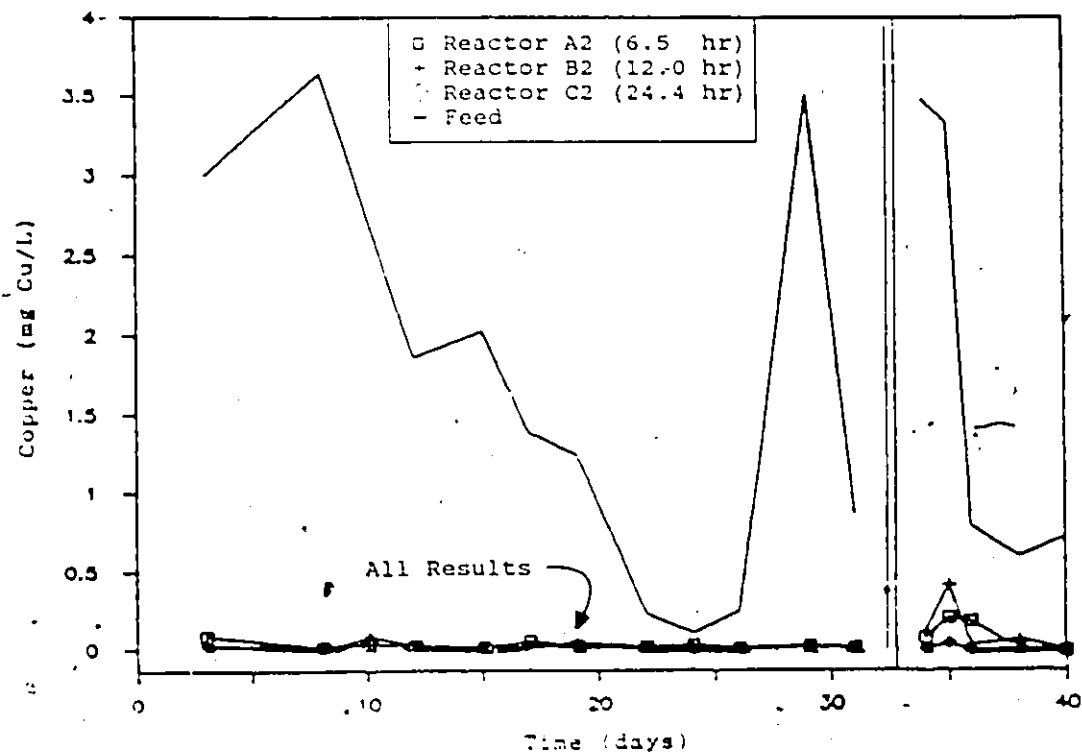


Figure 5.23: Influent and Effluent Soluble Copper versus Time for Test 2

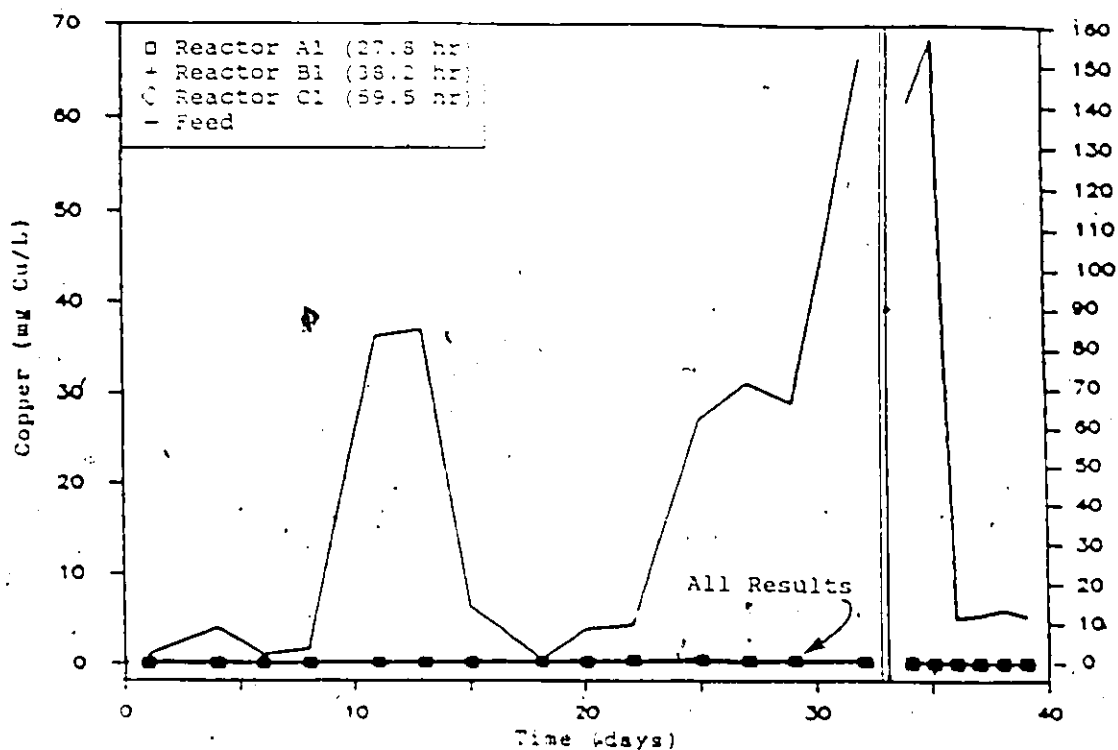


Figure 5.24: Influent and Effluent Total Copper, versus Time for Test 1

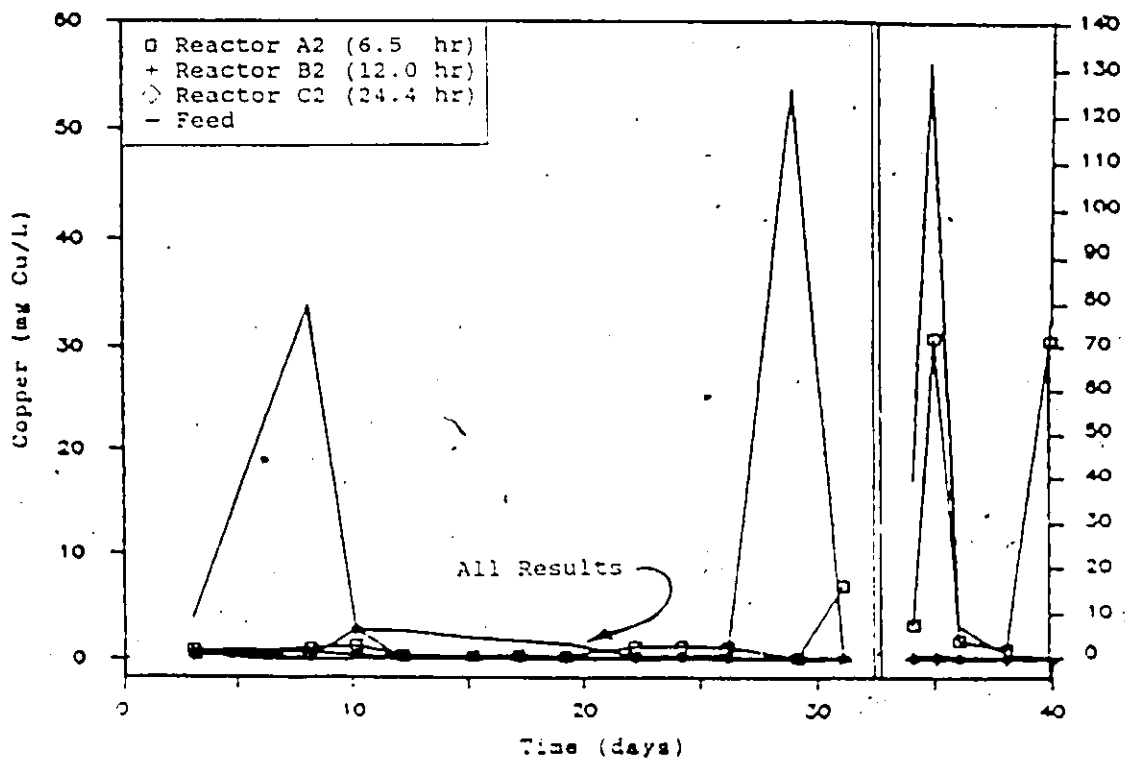


Figure 5.25: Influent and Effluent Total Copper versus Time for Test 2

Five out of the six HRT reactors showed no changes in total copper output when subjected to the spike. Reactor A2 of Test 2, operating at the lowest HRT of 6.5 hours, showed an increase in total metal effluent content from an average of 43 $\mu\text{g/L}$ to over 71 mg/L .

b. Lead Separation

Soluble lead was rarely detected in the influent and effluent throughout the test period and is attributed to the high levels of sulfates in the feed. Total lead influent and effluent concentrations for Test 1 and Test 2 are presented in Figures 5.26 and 5.27, respectively. In Table 5.8 the average effluent total lead concentration is found to be approximately equal to or greater than 1 mg/L . Also, the separation efficiencies for lead ranged from 9.3 to 26.1%. Figure 5.21 graphs the separation efficiencies as a function of the reactor's HRT. These efficiencies indicate poor retention of total lead by the reactor.

Subjecting the reactors to the spiked wastewater caused the effluent levels of total lead to increase as shown in Figures 5.26 and 5.27. Results from Test 2 Reactor A2 show a poor retention for total lead, similar to ~~the~~ for total copper.

c. Nickel Separation

Soluble and total nickel/precipitation efficiencies are summarized in Table 5.9. Figures 5.28

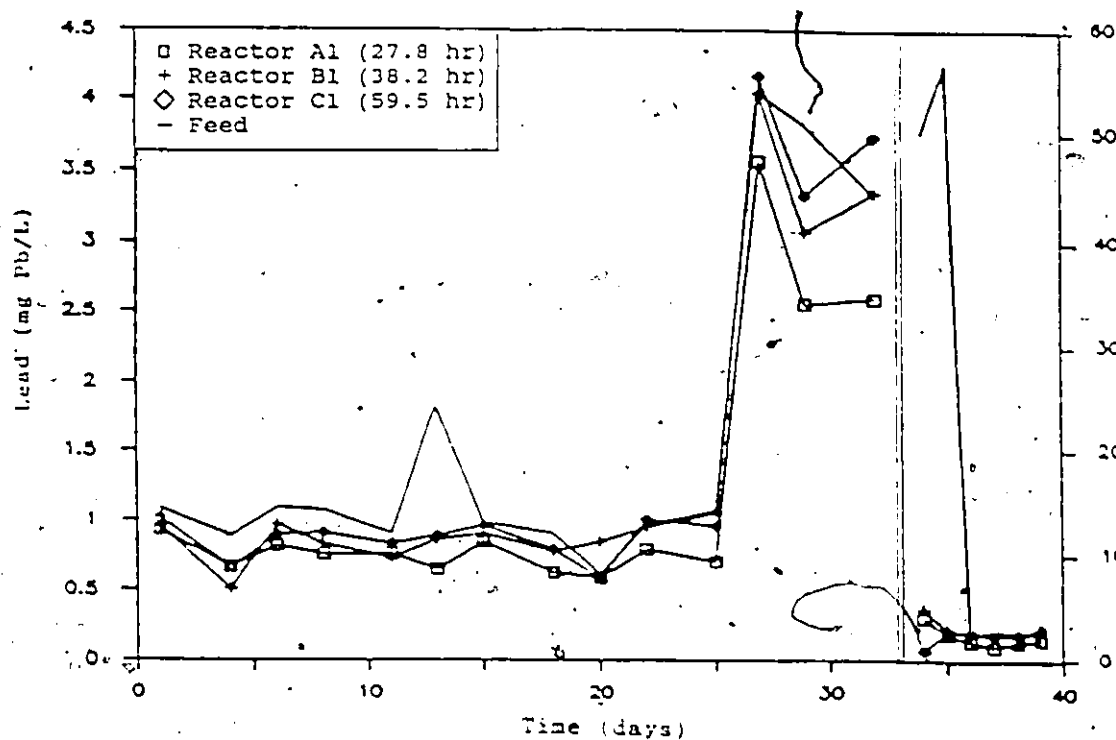


Figure 5.26: Influent and Effluent Total Lead versus Time for Test 1

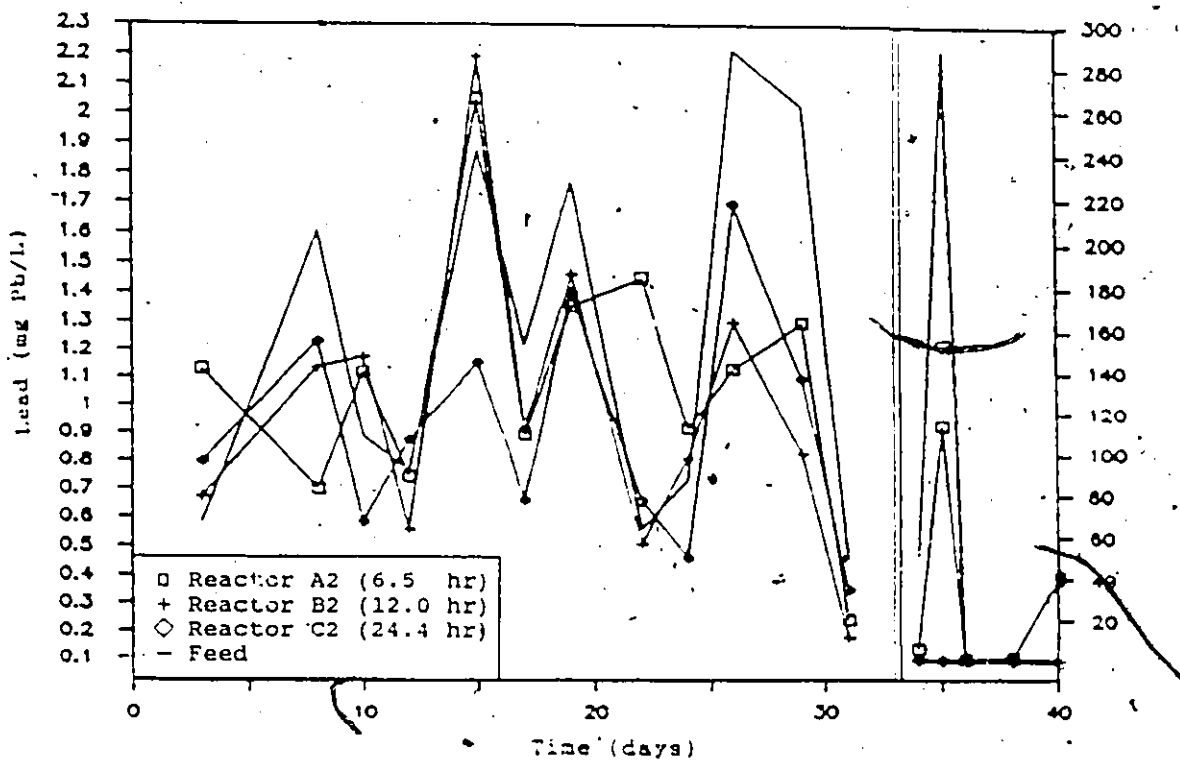


Figure 5.27: Influent and Effluent Total Lead versus Time for Test 2

through 5.31 show the nickel concentrations observed in the influent and the effluent. Typical effluent levels for both soluble and total nickel were below 1 mg/L. Spiking produced results similar to that for copper, i.e. the reactor effectively separated soluble nickel to a concentration below 1 mg/L, except for the Reactor A2 of Test 2 in which the effluent concentration peaked at 3.94 mg/L. Reactors A2 and B2 of Test 2 exceeded the 1 mg/L total nickel level when subjected to the spiked metal loading. Effluent concentrations for Reactors A2 and B2 peaked at 33.1 and 1.52 mg/L respectively.

d. Zinc Separation

Figures 5.32 through 5.35 show the time variation of the influent and effluent zinc concentrations. Table 5.9 summarizes the averaged values. Soluble zinc was effectively treated during Test 1 with precipitation efficiencies exceeding 88.4%. Test 2 produced a soluble zinc precipitation efficiency greater than 48.6%. These efficiencies are minimum values because they were based on the instrumental limit of detection, LOD, concentration.

The total zinc separation efficiencies ranged from 74.4 to 90.2%, but these performances were still not high enough to remove total zinc to concentrations below 1 mg/L. All reactors exceeded the 1 mg/L limit, mimicking the treatability study observations.

The data generated from the wastewater

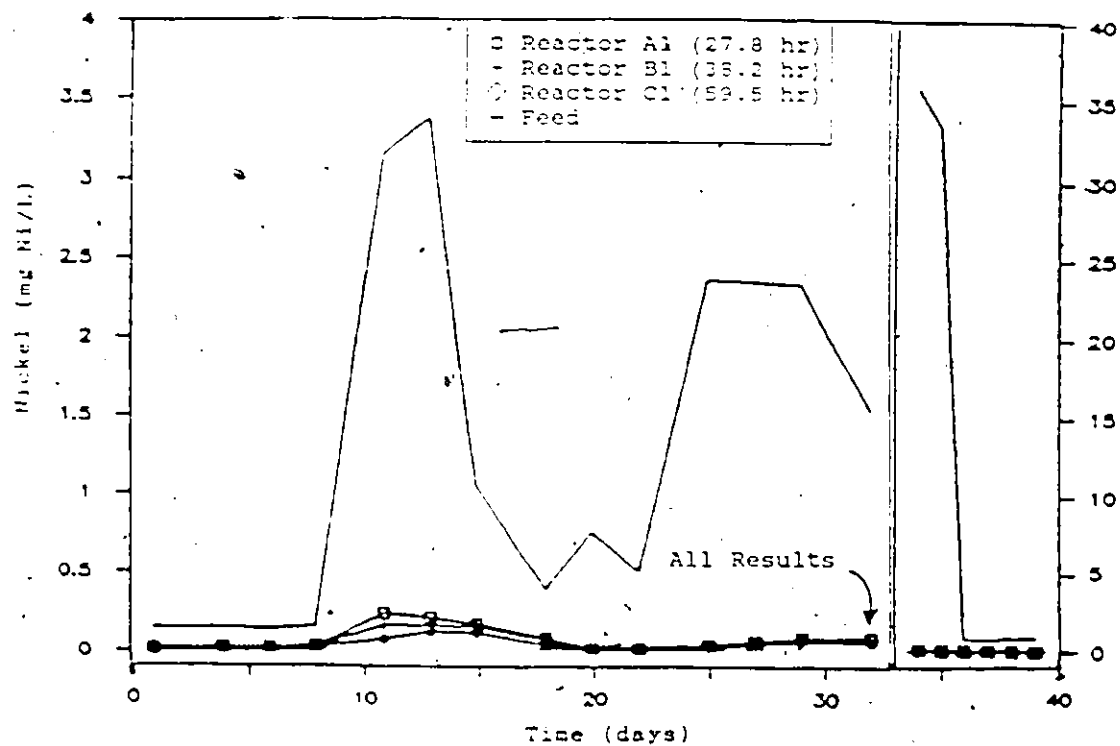


Figure 5.28: Influent and Effluent Soluble Nickel versus Time for Test 1

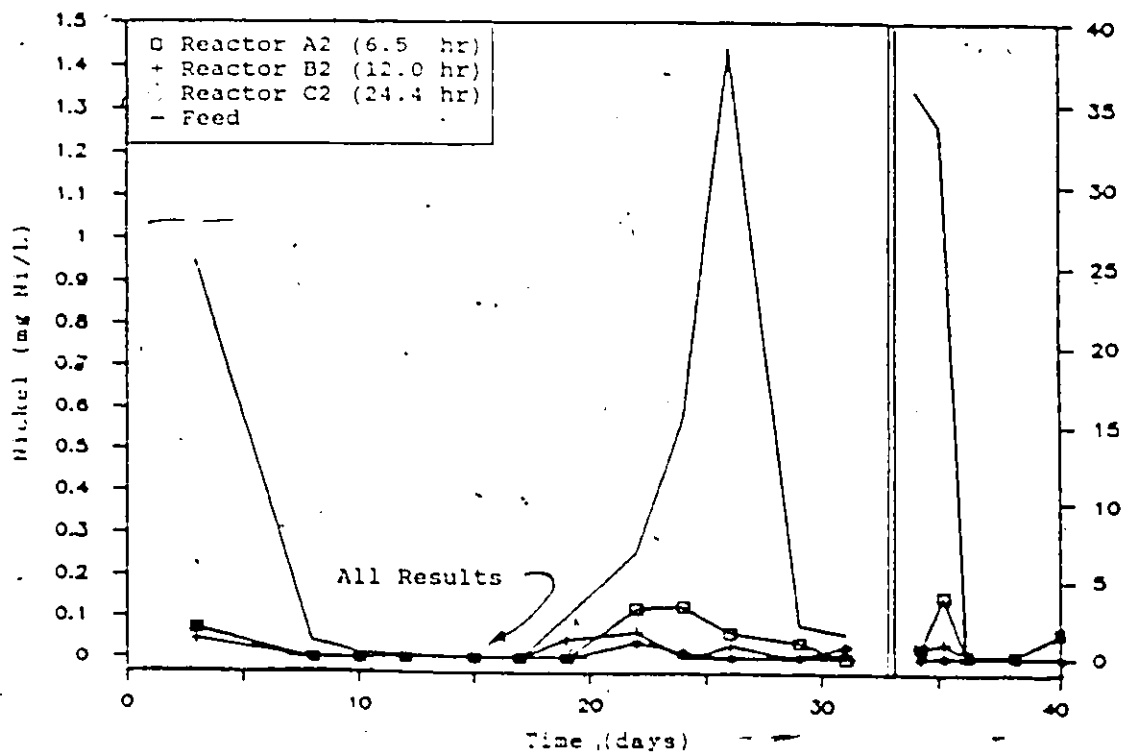


Figure 5.29: Influent and Effluent Soluble Nickel versus Time for Test 2

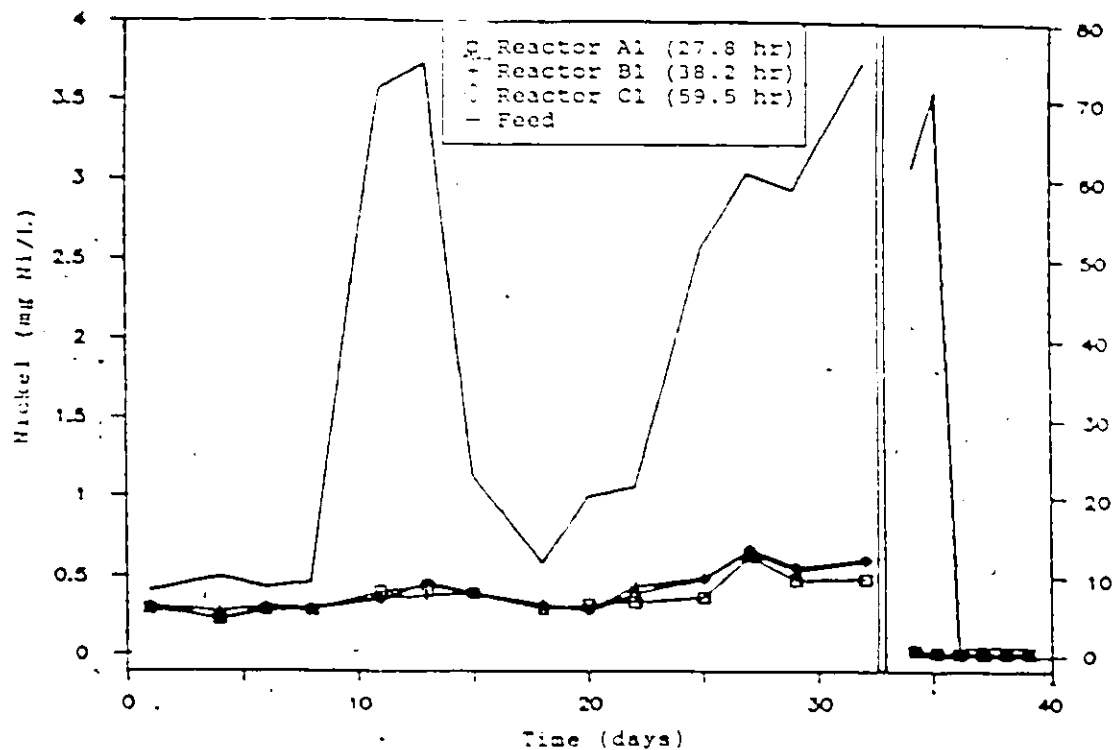


Figure 5.30: Influent and Effluent Total Nickel versus Time for Test 1

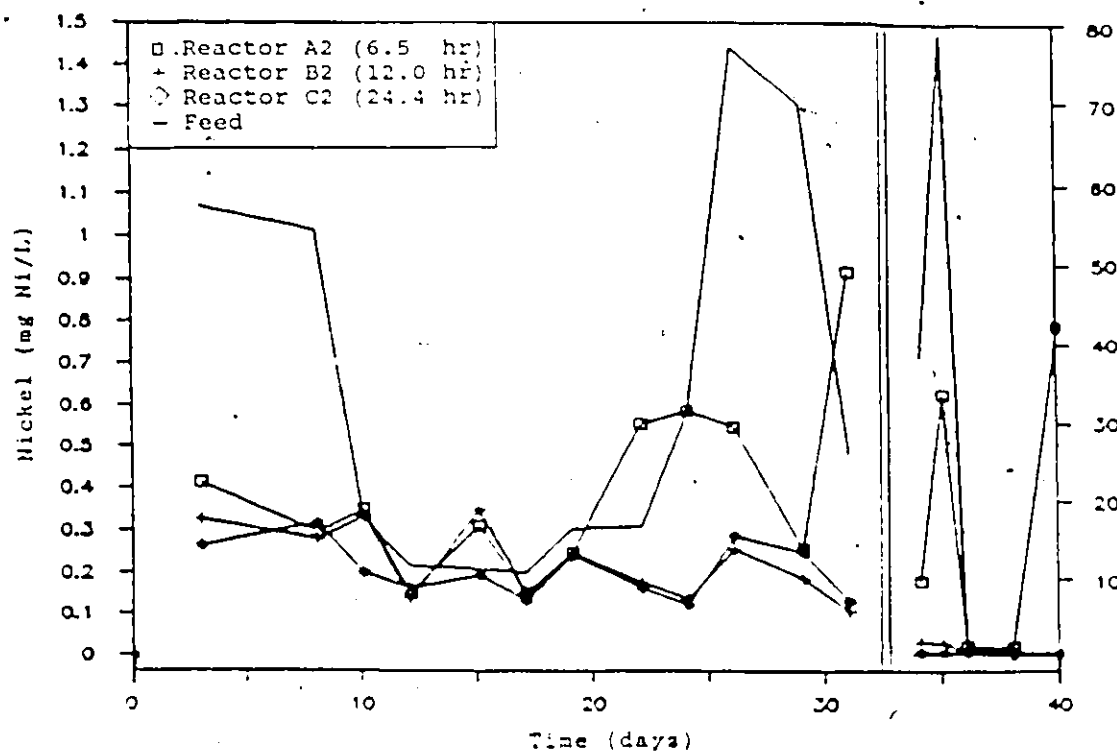


Figure 5.31: Influent and Effluent Total Nickel versus Time for Test 2

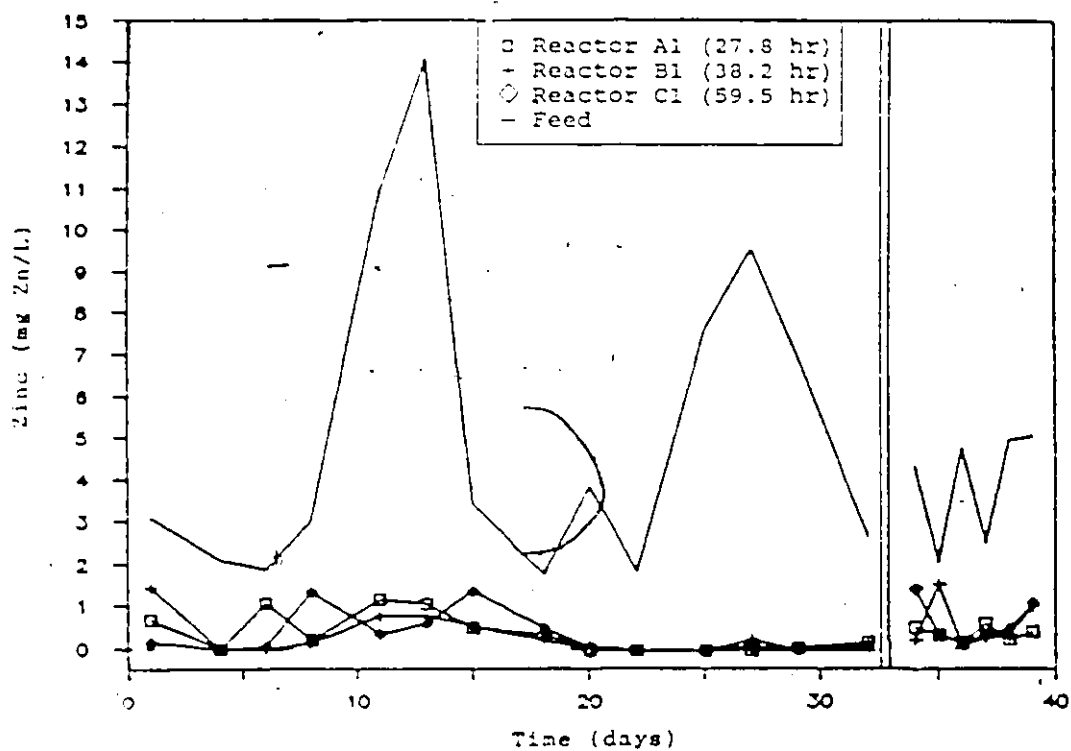


Figure 5.32: Influent and Effluent Soluble Zinc versus Time for Test 1

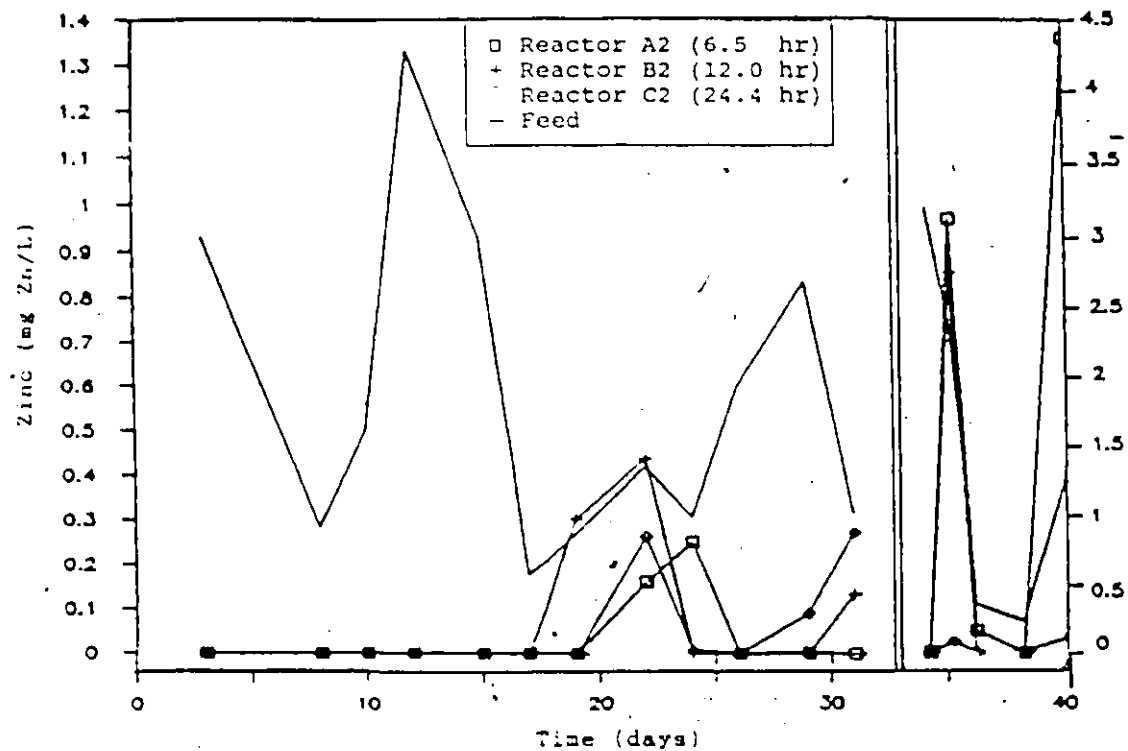


Figure 5.33: Influent and Effluent Soluble Zinc versus Time for Test 2

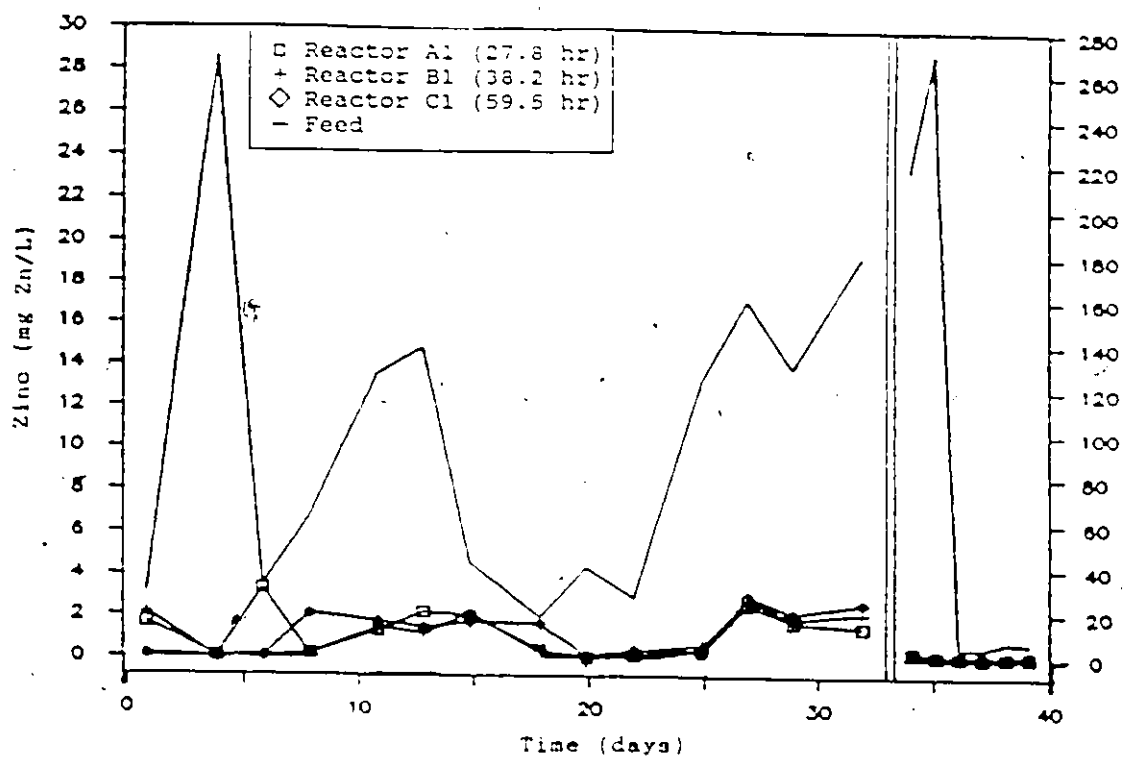


Figure 5.34: Influent and Effluent Total Zinc versus Time for Test 1

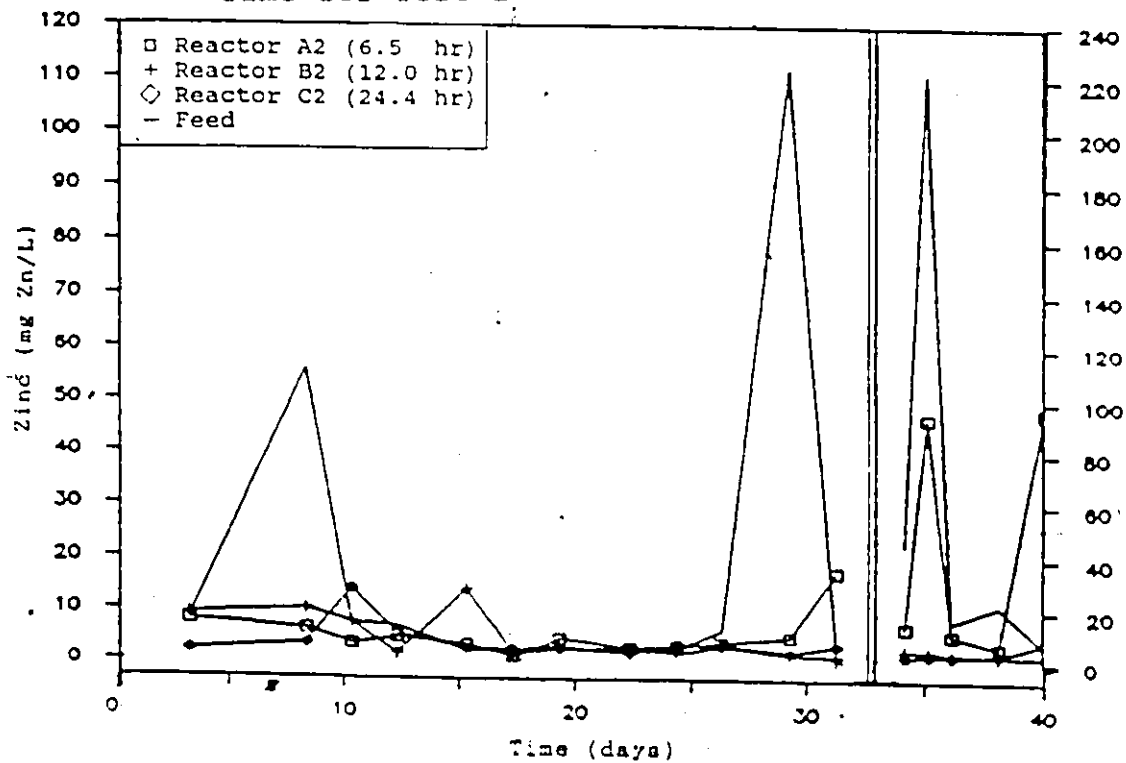
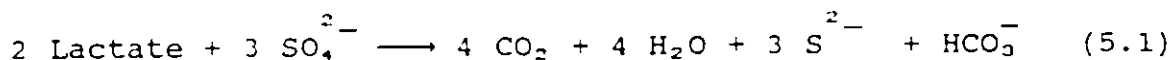


Figure 5.35: Influent and Effluent Total Zinc versus Time for Test 2

spiking indicate that soluble zinc was treated effectively with the exception of Reactor A2, in which the effluent concentration peaked at 3.1 mg/L. The results obtained with wastewater spiking confirm the previous observation on treating just wastewater, that the effluent does not comply with the 1 mg/L limit.

3. Stoichiometric Analysis

Combining Equation 2.3 with Eq. 2.6 produces the overall theoretical metabolic equation:



Using the averaged results from the treatability and HRT studies the BOD/COD ratios can be calculated and the sulfur balanced. The sulfur balance involves:

- calculation of the theoretical sulfide production from sulfates;
- comparison of the theoretical sulfide production to the effluent sulfide concentration (assuming all of the reduced soluble sulfur is sulfide);
- calculation of the differences as complexed sulfur; and,
- determination of the theoretical sulfide concentrations needed for the treatment of the four metals in the wastewater.

Tables 5.10 and 5.11 summarize these results.

The BOD/COD ratio ranged between 64 to 83%, excluding the results from Reactor A2, operating at a HRT of 6.5 hr. because of sulfide interferences. This range is

Table 5.10: Organic and Sulfate Ratios

HRT hr	Removed Sulfates mg SO ₄ /L	Removed COD mg O ₂ /L	Removed BOD mg O ₂ /L	BOD/COD	SO ₄ /BOD
HRT Study Test 2					
6.5	348	13.3	51.3	3.86	6.78
12	400	75.5	63.0	0.834	6.35
24.4	469	90.3	64.4	0.713	7.28
HRT Study Test 1					
27.8	222	114.0	73.9	0.644	3.00
38.2	232	130.2	92.5	0.710	2.51
59.5	324	138.9	94.0	0.677	3.45

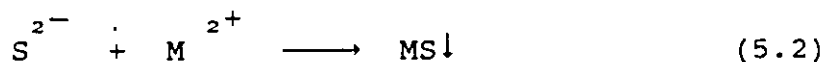
Table 5.11: Sulfur Balance

HRT hr	Removed Sulfates mg SO ₄ /L	Theoretical Sulfides mg S/L	Effluent Sulfides mg S/L	Theoretical Complexed Sulfide mg S/L	Metal Sulfide mg S/L
HRT Study Test 2					
6.5	348	116.0	82.2	33.8	15.9
12	400	133.3	102.2	31.1	15.9
24.4	469	156.3	105.5	50.8	15.9
HRT Study Test 1					
27.8	222	74.0	62.3	11.7	14.8
38.2	232	77.3	62.1	15.2	14.8
59.5	324	108.0	77.3	90.7	14.8

within the 70-80% range typically found for wastewater containing short-chain organics [49]. The treatability and HRT BOD/COD results differ from the 20% found in the characterization study. This is believed to be due to the relatively higher organic content of the supplemented wastewater. Inhibitors for the BOD test and reduced inorganics for the COD test are still present but organic content is much higher, hence their effects are relatively lower.

A sulfur balance indicates that sulfides had been used by the reactor to remove metals, and that the theoretical amount of sulfide used to precipitate metals is higher than the calculated amount needed for the four metals. The exception to this generalization was Reactor A1. The high levels of sulfide removal are attributed to:

- the presence of other metals which were not monitored but form metal sulfides. viz. iron (Fe) and chromium (Cr)
- Oversimplification of the metal sulfide reaction:



which assumed a 1:1 sulfide/metal ratio.

The theoretical complex sulfide concentration for Reactor A1, operating at an HRT of 27.8 hr is lower than the amount assumed to be needed for the precipitation of the four metals. This indicates that not all of the metals may

have been complexed as sulfides. Some metals could also be complexed as carbonates since Eq. 5.1 shows that carbonates are produced during sulfate reduction. A speciation of the sludge is recommended to determine the fraction of metals which are complexed as sulfides and carbonates.

The differences between the sulfate/BOD ratios for Tests 1 and 2 indicate that sulfates were more effectively removed with time (Test 2 followed Test 1). This is believed to be due to the simplicity of Eq. 5.1. Over time, due to acclimatization, the SRB may have found better metabolic pathways to reduce sulfates more effectively, thus organic requirements decrease with time.

4. Redox Potential

Effluent redox measurements are plotted in Figures 5.36 and 5.37. Reduced soluble sulfur is the only parameter which correlates to the effluent redox potential. This is expected because redox potential is a measure of the solutions oxidation/reduction strength. Figure 5.38 plots the effluent ORP readings versus the corresponding reduced soluble sulfur (RSS) concentrations. A semi-log correlation of the following form was used to determine the best fit between the two parameters:

$$\text{ORP} = m * \ln [\text{RSS}] + b \quad (5.3)$$

where ORP = redox potential (mV),

m = constant (mV),

RSS = activity of reduced sulfur (mg S/L)

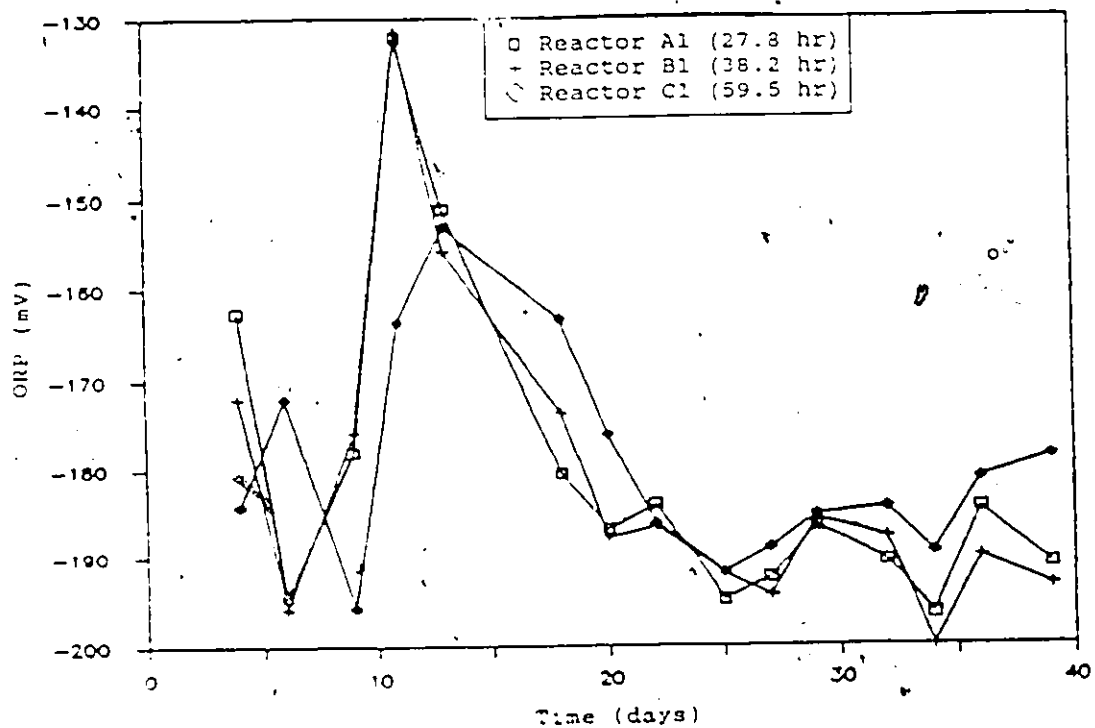


Figure 5.36: Effluent ORP versus Time for Test 1

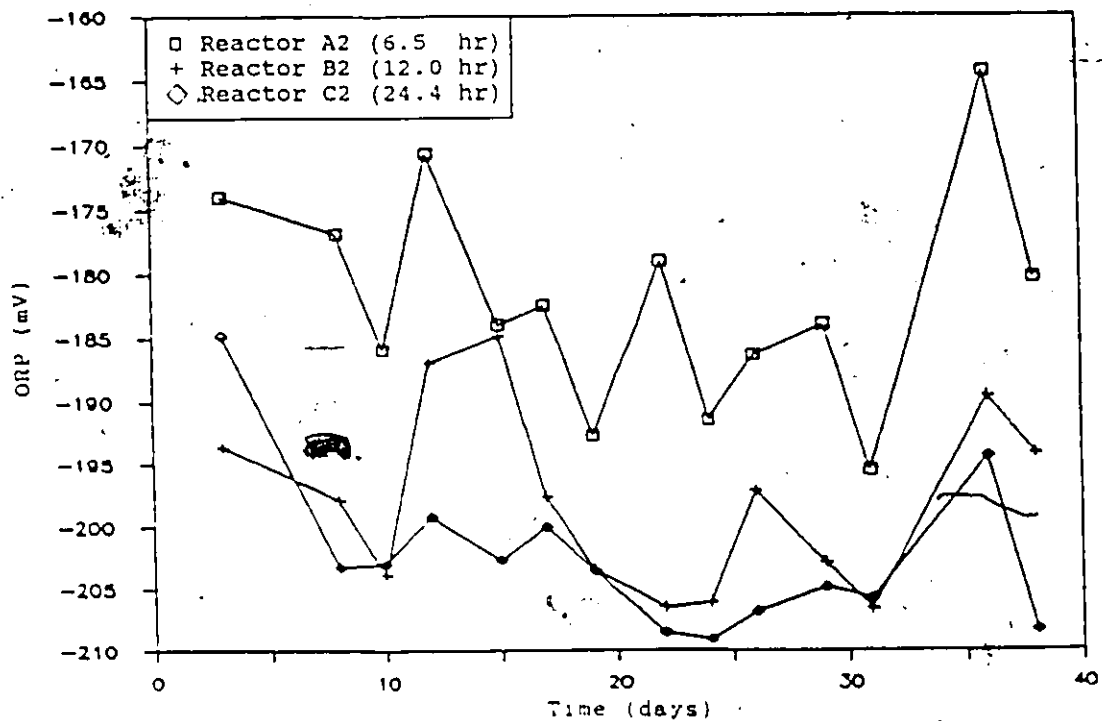


Figure 5.37: Effluent ORP versus Time for Test 2

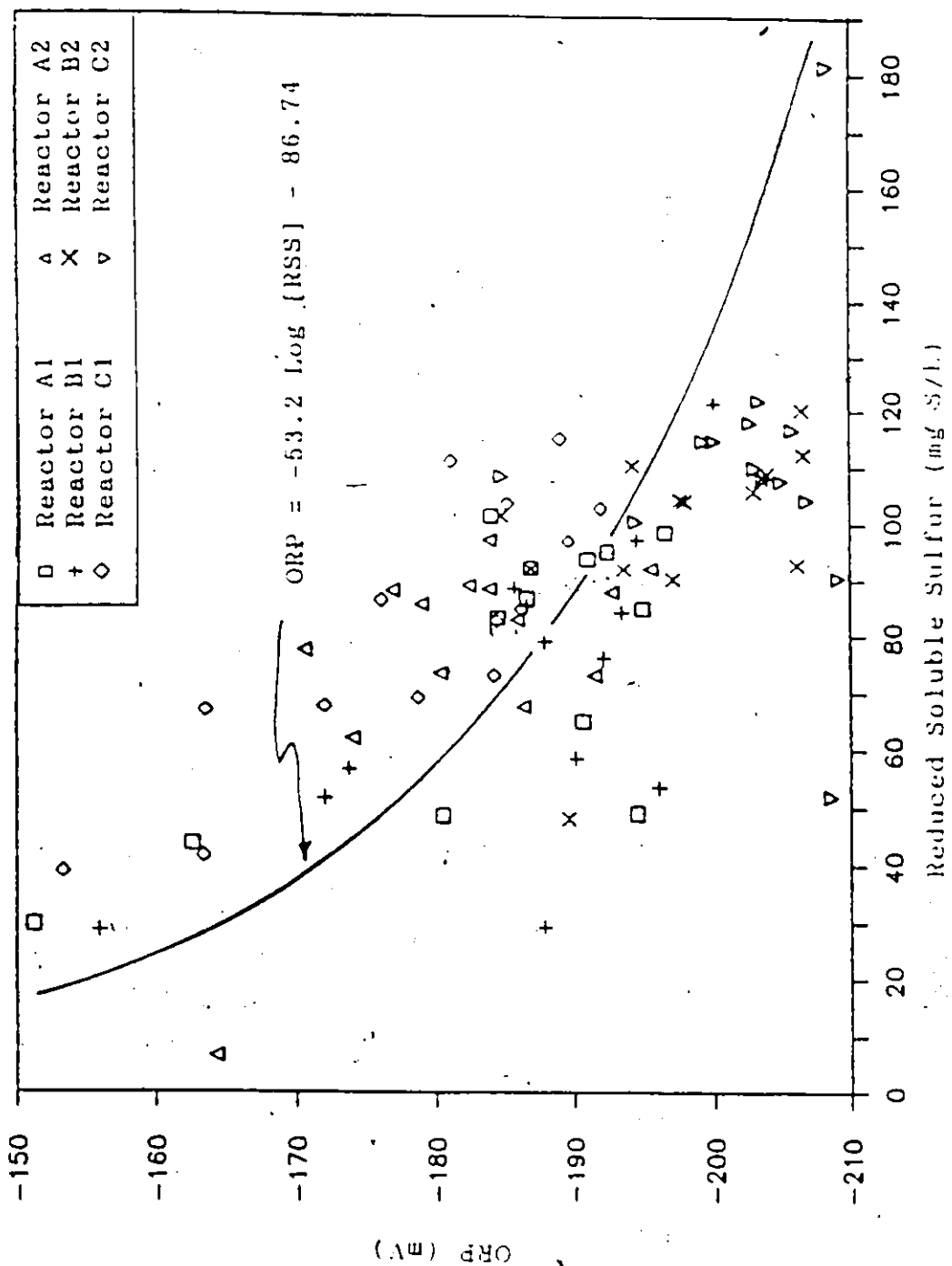


Figure 5.38: ORP versus Soluble Reduced Sulfur

b = constant (mV).

Fitting Equation 5.1 to the data in this form is justified by electrochemical theory presented in Appendix III. Comparing this form of correlation equation to the Nernst equation gives the following theoretical definitions for the two constants in Equation 5.1:

$$m = \frac{R T}{F} \quad (5.4)$$

and
$$b = E^0 + \frac{R T}{F} \ln (\text{oxid}), \quad (5.5)$$

where E^0 = constant,

R = ideal gas constant,

T = temperature of the effluent,

F = Faradays constant, and

Oxid = activity of constituents in a reduced state

Equation 5.2 predicts that the theoretical slope of Equation 5.1 should be -59.1 mV, when \log_{10} is substituted for \ln in Equation 5.1. Curve fitting the results with a least squares technique produced Equation 5.4 with $r = 0.701$

$$\text{ORP} = -53.2 * \log_{10} [\text{RSS}] - 86.74 \quad (5.6)$$

Comparison of the theoretical slope to the actual slope indicates that the redox potential of the effluent is dependent on the concentration of reduced soluble sulfur. Deviation in the slope from theoretical value was less than 10%. The spread of the data in Figure 5.38 indicates that other parameters also influenced the redox potential of the effluent. These factors include:

- the difference between soluble reduced sulfur concentration and the activity of these species [41].
- the presence of other constituents which are in a reduced state, thus contributing to the redox potential of the solution. Organics are a good example of reduced constituents which were present in the effluent [41].
- the error associated with the actual ORP measurements. (Appendix III explains this observation):
- the presence of constituents in an oxidized state whose concentration varied, thus causing the constant b of Equation 5.4 to vary.

It can be concluded that redox measurement can be used to indicate the quantity of reduced soluble sulfur in the effluent. The redox value determines whether excess reduced sulfur is being produced and indicates whether the reactor is treating the wastewater. It may also be used to monitor the treatability capacity of the reactor in terms of its ability to precipitate a given concentration of metals.

VI. CONCLUSIONS AND RECOMMENDATIONS

The conclusions of this study will be drawn in terms of the characterization, treatability and the HRT phases, respectively.

A. Characterization Study

In the characterization phase the metal plating wastewater obtained from Universal Fasteners Ltd. was found to contain Cu, Ni and Zn at concentrations exceeding Ontario's suggested discharge limits of 1 mg/L. Lead was not present in a measurable concentration. The pH of the wastewater was high and resulted in low soluble metal concentrations. The organic and sulfate contents of the wastewater were low. Storage of this wastewater at 7° C for a 7 day period showed instability due to nitrification bacterial growth.

B. Treatability Study

The lack of evolved gases, production of reduced sulfur, consumption of sulfates and organics, removal of dissolved oxygen and the decrease in the wastewaters redox potential indicate that SRB were the dominant bacterial species in the reactor.

Influent and effluent monitoring has shown that the

supplemented wastewater contained an excess of:

- sulfates
- organics, and
- macronutrients.

This indicates that the recipe used for wastewater supplementation can be modified in future studies.

Acid-soluble sulfides steadily increased throughout the 18 day study period indicating continuous bacterial growth within the reactor. This excessive sulfide production poses a potential environmental problem which may be resolved by bypassing part of the influent and mixing it with reactor effluent in a ratio which would precipitate all of the soluble sulfides and soluble metals. Further work is needed to determine how such a process could be implemented.

Effluent soluble metal concentrations were always less than 1 mg/L for each of the four metals. Copper had the highest metal precipitation efficiency with zinc and nickel following in order. Total metal separation efficiencies, except for zinc, were high enough to meet the 1 mg/L effluent limit. The order of separation efficiency for the four metals was $Cu > Ni > Zn > Pb$ (note: lead was found in the wastewater samples collected for the treatability phase). Separation of the complexed zinc to levels within the suggested limit can be accomplished by employing a solids separation unit. A particle size distribution of the effluent suspended solids would be required in the

implementation of this separation process.

C. Hydraulic Retention Time Study

The HRT study demonstrated that BOD and COD removal were a function of the reactor's HRT. The interference of sulfide with the COD test was apparent in the analyses during reactor operation at a 6.5 hr HRT. For this reason, the COD is a dubious measure of effluent organic content. Total organic carbon (TOC) can be substituted for COD and BOD measurements since it is a more accurate measure of the organic content. However, correlations relating TOC with BOD and COD would be needed since they are the regulated discharge parameters.

Sulfate consumption and reduced soluble sulfur production were also dependent on the reactor's HRT. Sulfate levels during the HRT study, which were comparable to the concentrations used during the treatability study, were in excess showing that the amount provided could be reduced in future studies. Reduced soluble sulfur is a measure of sulfides, sulfites and thiosulfates. Further work regarding the separation of reduced soluble sulfur into these three sulfur compounds may produce further information regarding the activity of the bacteria within the reactor. A ratio of intermediate (sulfites and thiosulfates) to sulfides may be correlated with the reactor's capacity to treat heavy metals and with the growth of the bacterial population within the reactor.

Soluble metal effluent concentrations were less than 1 mg/L and were not a function of the reactor's HRT when excess sulfide is present, whereas total metal separation efficiencies depended on the reactor's HRT. The order of total metal removal in terms of separation efficiency was $\text{Cu} > \text{Zn} > \text{Ni} > \text{Pb}$. High metal precipitation efficiencies at the lowest HRT, 6.5 hr. means that the HRT could be reduced further. Total metal separation efficiencies would be expected to drop at a lower HRT, but so long as the metals were complexed with sulfides, these complexed metals could be removed by a solids collection unit as recommended in the treatability phase.

The fluctuations in the influent metal loadings caused by the two day feed batches created difficulties in the analysis of the data. The reactors were always under transit response. Making larger feed batches would reduce the fluctuation of the feed. This feed would have to be stored at 4 °C to prevent bacterial degradation and constantly mixed to ensure homogeneity.

The spiking of the wastewater did not affect reactor performance except for Reactor A2 operating at an HRT of 6.5 hr. Reduced soluble sulfur levels in the effluent dropped to zero as a result of the spiking. This indicates that the reactor was operating at or exceeding its capacity. Total metal effluent concentrations during spiking had increased and surpassed the 1 mg/L limit for the Reactors A2

and B2 operating at HRT's of 6.5 and 12 hrs respectively.

Effluent redox potential was found to correlate with the effluent reduced soluble sulfur concentration. Redox potential measurements would indicate the amount of excess reduced soluble sulfide produced by the reactor. It could be employed to monitor the capacity of the reactor in terms of ability to precipitate metals.

The long response time of the ORP electrodes indicates that further research is needed in developing a standard method for ORP measurement. the use of a polished platinum electrode, calomel electrode and pH meter for ORP measurement may not produce accurate results. The polished platinum electrode may be quickly polarized and/or coated by metals which were initially in the dissolved state. Future studies would require the use of a null meter and a porous platinum electrode. These changes would reduce polarization effects.

D. Future Application

Actual employment of the anaerobic reactor by industry would require further research into finding a suitable wastewater which could be mixed with the metal plating wastewater. This would eliminate the need for adding expensive chemical salts for wastewater supplementation. A possible source of nutrient at the plant is sewage water. Experiments using sewage wastewater and plating wastewater as feed for the reactor would have to be conducted. These experiments would start with the characterization of the

sewage water and then determining a proper plating wastewater to sewage water mixing ratio.

Reactor sludge production is another parameter which must be considered when implementing such a unit. Sludge accumulates within anaerobic reactors and must be periodically removed and disposed. Disposal of this sludge is usually difficult and expensive. In this study, the HRT reactors were operated for 100 days without any sludge removal. Calculation of the amount of metals accumulated within the reactor using the average metal loading rates and using an assumed solids content of 15.64 g/L [53] (value found for a different filter system) produces concentrations of 162 g Cu/kg filter solids for copper, 3 g Pb/kg, 8 g Ni/kg and 224 g Zn/kg. Summing these concentrations gives a metal content of 39.7% which is very high when compared to ores typically used for metal refining. Hence, reclamation is a viable alternative to disposal. The metal concentrations within the sludge are only rough estimates because of the assumed solids content within the reactor. Further research is needed to determine the actual metal concentrations within the sludge.

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APPENDIX I
RESIDENCE TIME DISTRIBUTION STUDY FOR
AN UNSEEDED HRT REACTOR

In a reactor the production of sulfide ions and precipitation of metals depend on hydraulic behavior. Ideally it would be desirable to know the fluid velocity at any point within the reactor or to know how an individual fluid particle travels through the reactor. However, this study was limited only to the overall performance of the reactor. Microscopic phenomena were not investigated. Residence time distribution (RTD) can characterize the overall hydraulic behaviour of the reactor and describe performance at a particular volumetric flow rate.

A. Volume and Porosity

The total volume and void volume of the reactor are important parameters for the RTD experiments. Table I.1 summarizes these data for the treatability reactor, the HRT reactors and the tracer study reactor. The total volume for the treatability reactor was given by Wong et al. [54], All others were found experimentally. The total and void volumes were determined by first filling the reactors with water and then measuring the fluid drained from the reactor. For total volume, this method was acceptable. However, when measuring the void volume a small error was introduced due to surface tension effects [46]. The void volumes were corrected by measuring the difference between the volume of water used to fill the tracer reactor and subtracting the volume collected when the reactor was drained. This volume

was found to be 110 mL which led to an underestimation of the void volume by 1.3%. The void volumes given in Table I.1 are the corrected values. The porosity, ϵ , was calculated by dividing the void volume by the total volume.

Table I.1: Volume and Porosity Values for the Reactors used during the Treatability, HRT and Tracer Studies

Reactor	Total Volume (L)	Void Volume (L)	Porosity ϵ
Treatability Reactor *	9.5	8.5	0.895
A	10.10	9.21 [†]	0.912
B	10.08	9.14 [†]	0.907
C	10.05	9.14 [†]	0.910
Tracer Column	9.67	8.67	0.897
* - determined by Wong <i>et al.</i> [54] † - corrected using Tracer Reactor results			

B. Residence Time Distribution

Elements of fluid taking different routes through the reactor will require different periods of time to pass through the vessel. The distribution of these times for the stream of fluid leaving the vessel is called the exit age distribution, or residence time distribution of the fluid. [27,28] A residence time distribution (RTD) curve is the response curve generated when a reactor is subjected to a stimulus.

Experimental determination of the RTD for a reactor begins with the injection of a tracer of known concentration into the inlet of the reactor. Tracer injection can be in any one of the following input forms:

- random,
- step,
- cyclic, or
- pulse.

Of these forms, the pulse input and the step input are favoured because of their simplicity [27,28]. The effluent tracer concentration, C , is monitored and the resulting concentration profile used to determine the overall flow condition of the reactor.

Figure I.1 illustrates a number of different responses which may occur when a step input of tracer is introduced. The dimensionless group, D/uL is called the reactor dispersion number and characterizes the intensity of dispersion. From the curve, a number of tracer parameters can be calculated. The following parameters are fundamentally defined and reduced to a usable form when a step input of tracer is utilized. The text Chemical Reaction Engineering by Levenspeil [27] presents additional information concerning the other forms of tracer input along with the resulting RTD parameter equations.

1. Mean Residence Time

The mean time, \bar{t} , is the average time a fluid

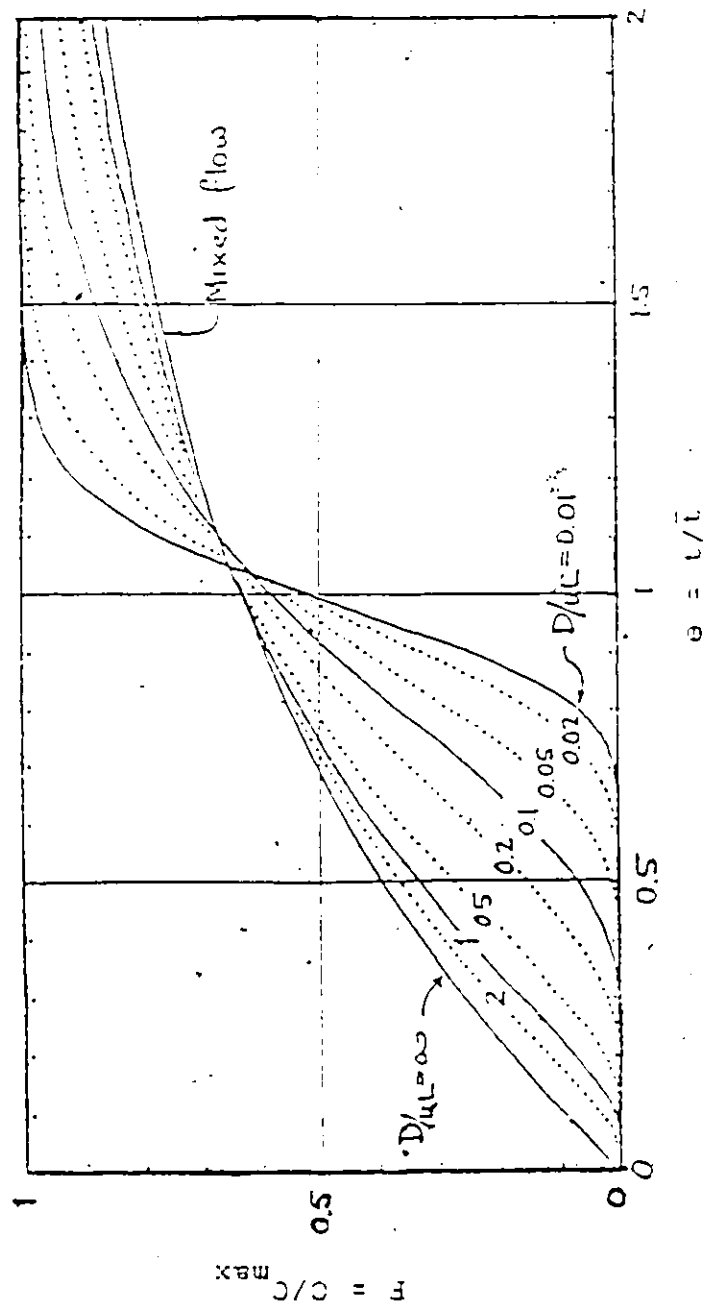


Figure 1.1 Closed Vessel Response (Curves With Large Dispersion [28])

particle is retained by a reactor. The basic definition of the mean time is given by:

$$\bar{t} = \frac{\int_0^{\infty} t C \, dt}{\int_0^{\infty} C \, dt}, \quad (I.1)$$

where:

t = time, and
C = concentration of the tracer in the effluent.

When a step input is employed, Eq. (I.1) is reduced to:

$$\bar{t} = \int_0^1 t \, dF, \quad (I.2)$$

where F is the instantaneous concentration divided by the maximum concentration, (C/C_{\max}) .

2. Variance

The variance, σ^2 , represents the square of the spread of the distribution curve as given by Eq. (I.3):

$$\sigma^2 = \frac{\int_0^{\infty} t^2 C \, dt}{\int_0^{\infty} C \, dt} - \bar{t}^2. \quad (I.3)$$

This equation reduces to

$$\sigma^2 = \int_0^1 t^2 \, dF - \bar{t}^2 \quad (I.4)$$

for a step input.

3. Dispersion Number

The mean and variance are used to calculate the reactor dispersion number, d. Calculation of d is dependent on the experimental method employed to generate the RTD

curve. For these experiments, the closed vessel equation, Eq. I.5, was employed for calculating dispersion number:

$$\sigma_n^2 = \frac{\sigma^2}{\bar{t}^2} = 2d - 2d^2 \cdot \left[1 - e^{-(1/d)} \right] \quad (I.5)$$

where;

σ_n^2 = the normalized variance,

$d = \left[\frac{D}{uL} \right]$ = is the dimensionless dispersion number.

The dispersion number indicates whether the reactor is behaving as a plug flow or as a continuously stirred tank reactor (CSTR). When $d = 0$, the reactor is considered to operate as a plug flow reactor with no dispersion. When $d < 0.01$, low dispersion occurs; when d is between 0.01 and 0.1 moderate dispersion occurs; and when $d > 0.1$, high dispersion occurs. Finally when $d = \infty$ the reactor is considered to behave like a CSTR.

4. Time Indexes

Two other indexes commonly used to describe the behaviour of the reactor are:

\bar{t}/T = the ratio of the actual mean residence time to the theoretical, and

t_i/T = the ratio of the time of the inflection point of the RTD curve to the theoretical residence time.

The theoretical time, T , is calculated from Equation I.6

$$T = \frac{\text{Void Volume } (V_v)}{\text{Flow Rate } (Q)} \quad (I.6)$$

C. RTD Reactor Experiments

Two RTD experiments were conducted to determine the mean residence time and flow conditions for the reactor configuration used during the HRT study. The highest and lowest volumetric flow rates used during the HRT study were employed for the two experiments. These flow rates provided results which could be used to predict reactor behaviour under the operating conditions used for the HRT study.

The reactor used for these experiments was smaller than the reactor used during the HRT study. The void volume was 8.76 L as compared to the average of 9.2 L capacity of the unseeded HRT reactors. Thus, the values generated by these experiments are not the actual values for the HRT. In active reactors, the actual RTD values would change with time because of the continuous growth of bacteria within the reactors and the retention of metal precipitates. However, it is assumed that the RTD parameters found by these tests are fair indications of the actual HRT reactor parameters. Samson et al. [48], in their study on the mixing characteristics of a downflow anaerobic fixed film reactor had found that the dead space to void volume ratio within the reactor had increased from 11% at the start up to 30% after 90 days of operation. This increase of dead space was

the result of bacterial growth and floc separation.

Initially, sodium chloride (NaCl) was selected as the tracer in the form of a pulse input, but it was found to be unsuitable. Further investigations with sodium fluorescein as the tracer produced better results. Sodium fluorescein was superior to NaCl because its density was closer to that of water. See Table I.2. Also, the diffusion coefficient for sodium fluorescein is smaller when compared to NaCl tracer. Changing from a pulse input to a step input of the sodium fluorescein tracer minimized the effect of the limit of instrumental detection. Previous work using pulse inputs produced results which did not yield a correct mass balance.

Table I.2: Properties of Dilute Solutions of Sodium Chloride and Sodium Fluorescein at 26 °C

Tracer	Density (g/cm ³)	Diffusion † Coefficient (cm ² /s)
Sodium Fluorescein (1000 mg/L)	0.9974	1.48×10^{-5}
NaCl (8000 mg/L)	1.0064	5.03×10^{-6}
Distilled Water	0.9974	

† - calculated from state correlations [43]

The apparatus used for the three experiments is illustrated in Figure I.2. A 1000 mg/L sodium fluorescein stock solution was used as the primary standard for the

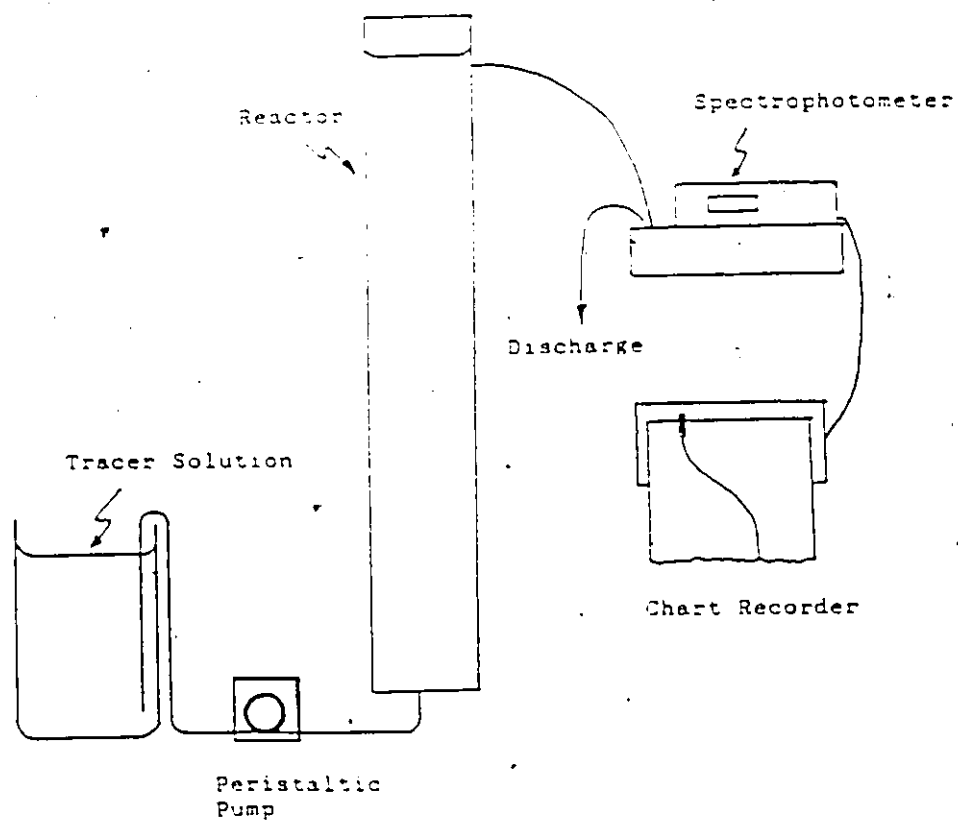


Figure I.2: Tracer Experiment Apparatus

preparation of calibration standards for the spectrophotometer and as the concentrate to produce the tracer solution. The calibration curve for the spectrophotometer was linear between the range of 0 to 7.5 mg/L when measuring absorbance at 493 μm [39]. It should be mentioned that for spectrophotometric analysis, the pH of the fluorescein solution must be greater than 8 [39].

Each step input solution had a tracer concentration which was within the instrumental calibration range. The size of these batches was approximately 100 L. The tracer solution was pumped into the bottom of the reactor by means of a precalibrated peristaltic pump. This pump was calibrated twice, once at the beginning and once at the end of the experiment by measuring the amount of water collected in a graduated cylinder over time. After entry, the tracer travelled through the packing to the top, exited through the side port and then into the flow-through cell in the spectrophotometer. The effluent absorbtion was measured and recorded on a strip chart recorder.

The small diameter inlet and outlet tubing along with the slow flow rate allow for the assumption of plug flow through the tubing [28]. These inlet and outlet conditions dictated why a closed vessel dispersion model was used to determine the dispersion number.

Two "S" shaped curves resulted from these experiments. They are illustrated in Figures I.3 and I.4 and results are summarized in Table I.3.

Table I.3: Residence Time Distribution Data for the Two Hydraulic Retention Times

TEST	HRT (hr)	\bar{t} (hr)	σ^2 (hr ²)	d	\bar{t}/T	t_i/T
1	5.39	4.909	2.639	0.05814	0.910	0.852
2	65.09	47.28	1486	0.7291	0.726	0.813

The lower retention time experiment indicated a dispersion number which varied between 0.01 and 0.1. This reactor behaved like a plug flow reactor with moderate dispersion. The reactor, which was subjected to the higher retention time, had a dispersion number of 0.73. Thus it operated as a plug flow reactor with high dispersion. Therefore, the HRT reactors operated as plug flow reactors with moderate to high dispersion.

The Reynolds number for the lower retention time tracer study was 0.7 which is within the laminar flow range for a packed bed reactor. Hence, both tracer reactors were operating under laminar flow conditions. These flow conditions explain why the higher retention time reactor had a higher dispersion number. The dispersion number, d , under laminar flow conditions is influenced by the bulk fluid motion and molecular diffusion [28]. The reactor operating

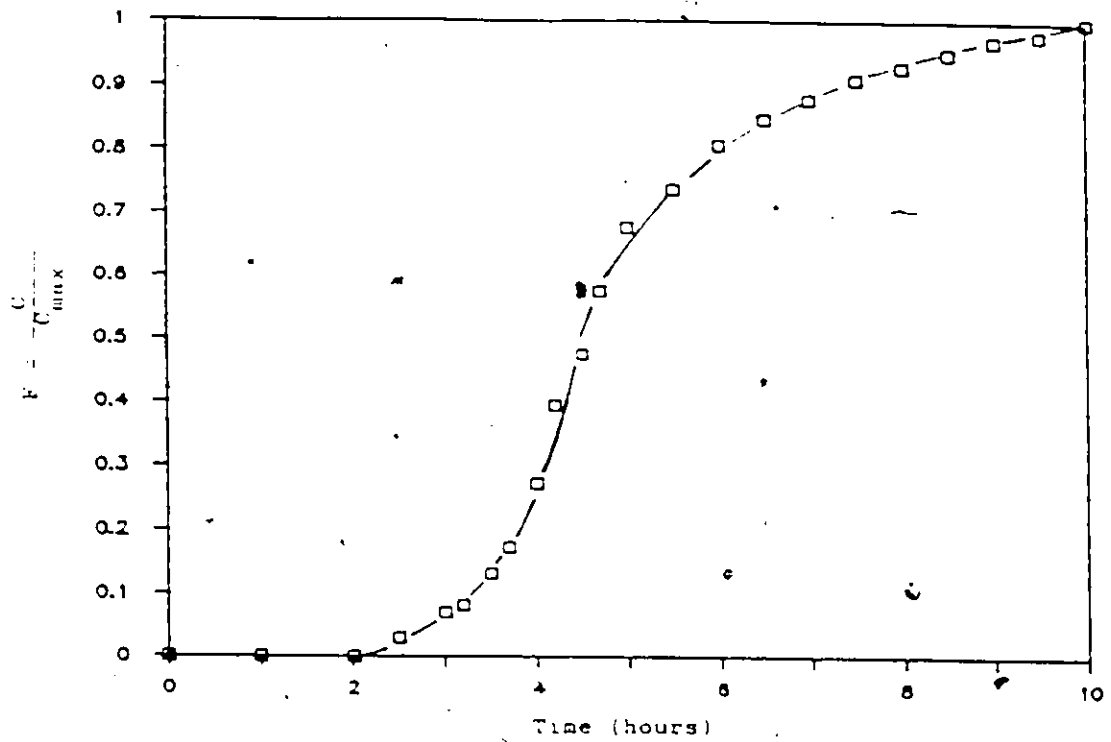


Figure I.3: Tracer Response Curve for Maximum Volumetric Flow Rate

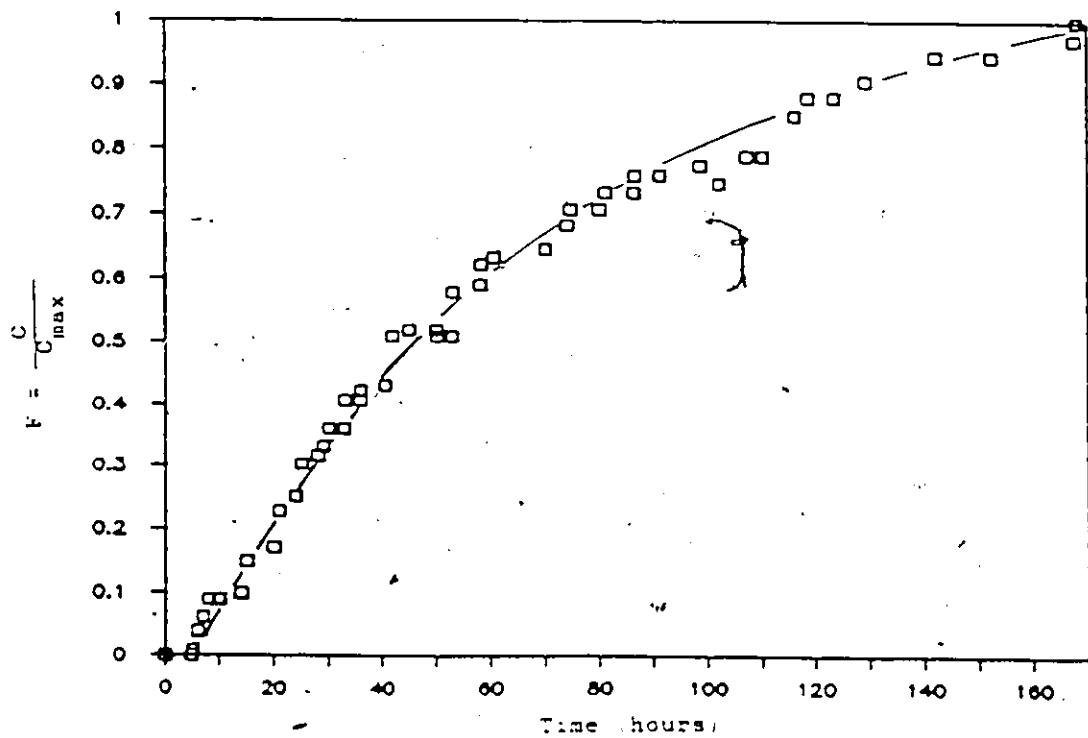


Figure I.4: Tracer Response Curve for Minimum Volumetric Flow Rate

at a higher retention time allowed the tracer to diffuse to a higher degree than the lower retention time reactor. This caused an increase in the dispersion number. This observation can be verified by rearranging Eq. I.7, which is the basic definition of the dispersion number,

$$d = \left[\frac{D}{u L} \right], \quad (\text{I.7})$$

where D is the axial dispersion coefficient,

u is the velocity of the fluid, and

L is the length of the reactor

to give Equation I.8:

$$\frac{d_2}{d_1} = \frac{T_2}{T_1}, \quad (\text{I.8})$$

where the subscripts denote the tracer test number.

Substituting the results tabulated in Table I.2 into the left hand side of Eq. I.8 gives a value of 12.1, while the right hand side gives a value of 12.5. This good agreement indicates that under laminar flow conditions the retention time affects the dispersion number.

Both experiments had mean residence times which were less than the theoretical residence times. This and the inflection to theoretical time ratio indicate that short circuiting or channelling had occurred and this short circuiting is attributed to dead space within the reactor [27,28,48] .

Visual inspection of the tracer entering the reactor confirmed the short circuiting results. The tracer

entered the bottom of the reactor as a stream and travelled up the sides of the reactor rather than spreading evenly across the cross sectional flow area. To decrease channelling, the reactor inlets must be redesigned to provide an even distribution of the influent across the cross sectional area.

APPENDIX II
RESIDENCE TIME DISTRIBUTION STUDY FOR
THE EFFLUENT HRT SAMPLER

Two tracer experiments were conducted covering the extreme ends of the HRT study volumetric flow rate range to verify the sampler's performance in collecting representative output samples. The testing procedure was similar to that employed in the tracer experiments as detailed in Appendix I. Table II.1 summarizes the results of the two tests. The low volumetric flow rate had a residence time of 3.6 hours, while the highest flow rate had a residence time of 13.4 minutes. Both tests proved that the sampler was collecting representative effluent and did not retain any of the effluent longer than the expected theoretical time as shown by the mean to theoretical ratios given in Table II.1. Figures II.1 and II.2 are the two tracer response curves for the sampler from which the RTD parameters were calculated. The high dispersion numbers indicate that the effluent collected in this sampler was highly mixed. Essentially they performed as a CSTR sampler, not a plug flow sampler.

Table II.1: The Mean Residence Times for the Sampler at the Two Extreme Volumetric Flow Rates

Flow Rate (mL/min)	Mean Time (hr)	Variance σ^2 (hr ²)	Dispersion Number d	Mean to Theoretical Time Ratio
26.77	0.2243	0.3323	> 10	0.7748
2.162	3.569	23.234	> 10	0.9957

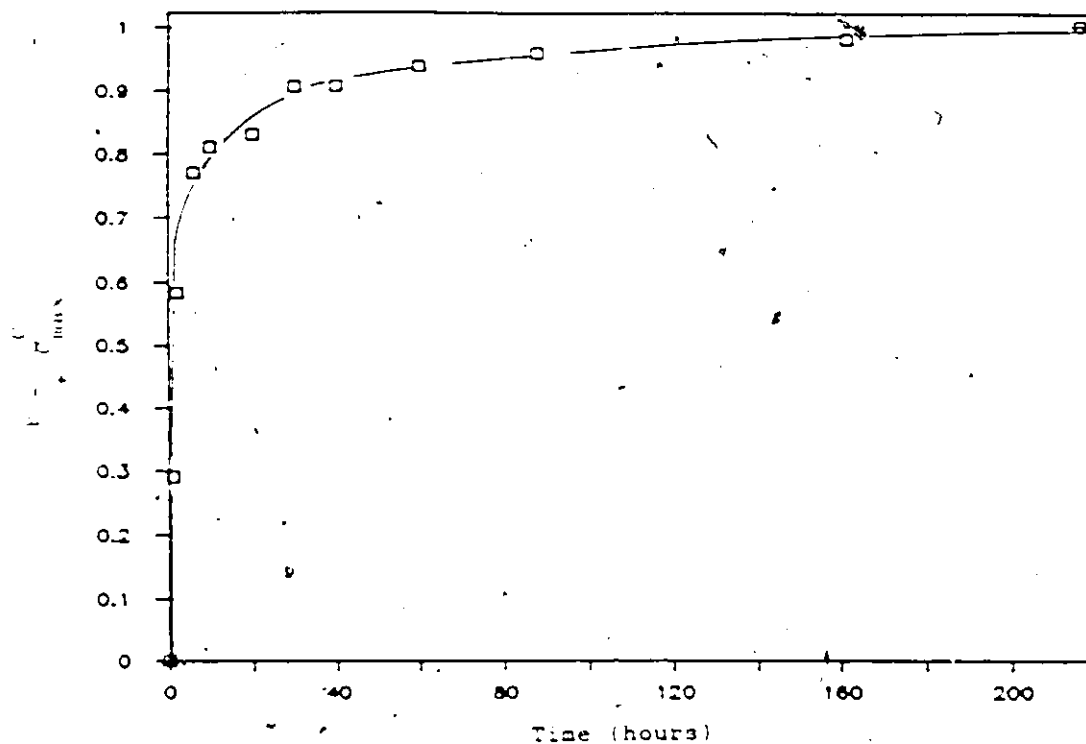


Figure II.1: Tracer Response Curve for Maximum Volumetric Flow Rate

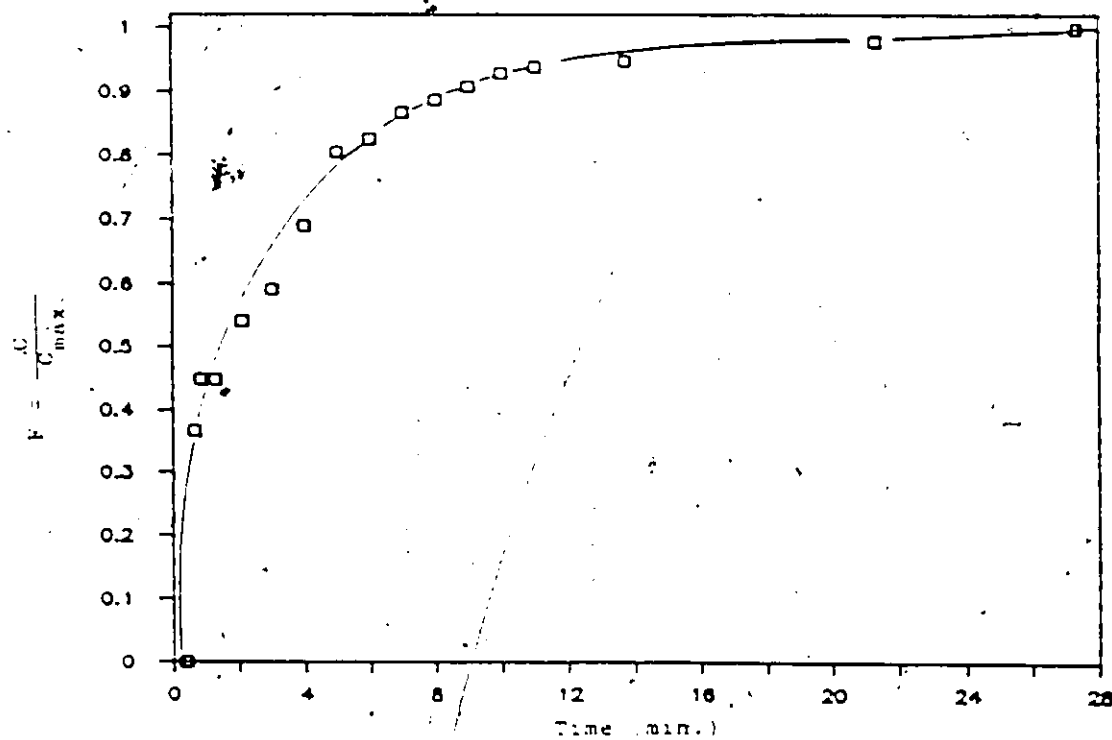


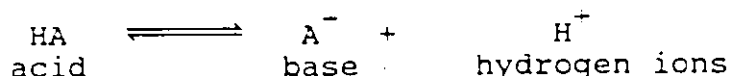
Figure II.2: Tracer Response Curve for Minimum Volumetric Flow Rate

APPENDIX III

REDOX POTENTIAL MEASUREMENT

Redox potential measurement is understood as being a measure of the reduction-oxidation potential of a solution. Its determination is similar to that for pH and can be explained using an acid-base theory analogy.

A strong acid is defined as a substance that is capable of liberating hydrogen ions:



Accordingly, a base is a substance that is capable of absorbing hydrogen ions. Thus every acid has its complementary base. The pH measurement, which is a measurement of hydrogen ion activity, gives an indication of the acid/base status of a solution.

It is possible to define the redox system in a form analogous to that of acid-base definition. An agent in the reduced state (Red) is capable of liberating an electron:



Hence, an agent in the oxidized state (Ox) is capable of accepting an electron. The redox potential measurement, which is actually a measurement of electron activity, serves to indicate the reduction/oxidation status of the solution [41].

Measurement of the redox potential is accomplished by immersing a platinum and a reference electrode into the solution. The resulting potential which develops between the two electrodes can be predicted theoretically by adding

the electrode half cell potential equations. Each half cell equation represents the potential obtained from the exchange of electrons at the individual electrodes. The half cell potential developed at the platinum electrode (E_{plat}) is modelled by the Nernst equation:

$$E_{\text{plat}} = k_1 + \frac{-R T}{F} \ln \frac{a_{\text{ox}}}{a_{\text{red}}}, \quad (\text{III.2})$$

where k_1 is a temperature dependent constant,
 R is the gas constant,
 T is the absolute temperature,
 F is the Faraday constant,
 a_{ox} is the activity of the Ox agent, and
 a_{red} is the activity of the Red agent.

The reference electrode, by definition, produces a half cell potential which follows the Nernst equation and ideally is independent of the solution matrix. Hence its potential (E_{calomel}) is only governed by temperature according to the following equation:

$$E_{\text{calomel}} = k_2, \quad (\text{III.3})$$

where k_2 is the temperature dependent constant.

Combining Equations III.2 and III.3 gives the following redox potential equation for the solution:

$$E_h = E_{\text{plat}} + E_{\text{calomel}} = E^{\circ}_{\text{ox-red}} + \frac{R T}{F} \ln \frac{a_{\text{ox}}}{a_{\text{red}}}, \quad (\text{III.4})$$

where, E_h is the redox potential of the solution relative to the standard hydrogen electrode, and

$E^{\circ}_{\text{ox-red}}$ is the temperature dependent constant which equals to the sum of k_1 and k_2 .

The E_h of the solution is found experimentally by placing the electrodes into the solution and then correcting the reading according to:

$$E_h = IR + K_{\text{calomel}} \quad (\text{III.5})$$

where IR is the instrumental reading at 25 °C using a platinum and a calomel electrode, and

K_{calomel} is the potential difference between the calomel and the hydrogen electrode at 25 °C and has the value of 244.4 mV [43].

Equation III.4 predicts that the redox potential of the solution will decrease as the activity of the Red increases. Since activity increases with concentration, the redox potential would decrease as the concentration of the Red increases. Sulfide influences the potential of the solution since it is a strong Red.

The treatability results were erratic as a stable measurement was not obtained 5 minutes after the connection of the electrodes to the ion specific meter. Further investigation showed that the response time allocated for the instrument was insufficient for the establishment of an equilibrium measurement.

Biological fluids with negative redox potential have been found to produce slow and erratic redox measurements [41]. This phenomena is attributed to organics

which exchange electrons slowly with the platinum electrode [41,54]. Petersen [41] suggested the use of a redox mediator to reduce the time required for the instrument to reach equilibrium. A mediator is a redox system capable of making both rapid and simple exchanges of electrons with a platinum electrode. In order that such a mediator can function satisfactorily, the activity occurring in its oxidized form should be equal to that occurring in its reduced form. However, Wong *et al.* [54] observed no differences in instrumental response rates when employing the mediators suggested by Petersen [41] in his analysis of effluent derived from the sludge decontamination apparatus.

For this reason, a consistent method was adopted for redox measurements during the HRT study. Measurements were recorded 10 minutes after the placement of the sample into the ORP vessel and connection of the electrodes to the potentiometric meter. In order to determine the 10 minute relative responses and the time required for the establishment of instrumental equilibrium, five experiments were conducted. Each of these five tests was carried out with effluent samples obtained from HRT study Test 2. Table III.1 lists the different samples and the 10 minute relative response percentages. Figure III.1 illustrates the relative response curves for the five experiments. These graphs show that the instrument reached at least 95% of the equilibrium reading within 10 minutes. Hence, all ORP measurements

(before correction for difference in calomel and hydrogen electrode potential) are underestimated by an average of $1.94 \pm 1.96\%$ with a confidence interval of 0.95, as calculated from a Students-t distribution [35].

Table III.1: Ten Minute Relative Response for Five Effluent Samples

Effluent From HRT Test 2			Relative Response (percent)
Test	Reactor	Day	
1	C	20	97.40
2	C	23	95.83
3	A	38	98.12
4	B	38	98.98
5	C	38	99.98
Average Relative Response			98.06
Sample Standard Deviation			1.58

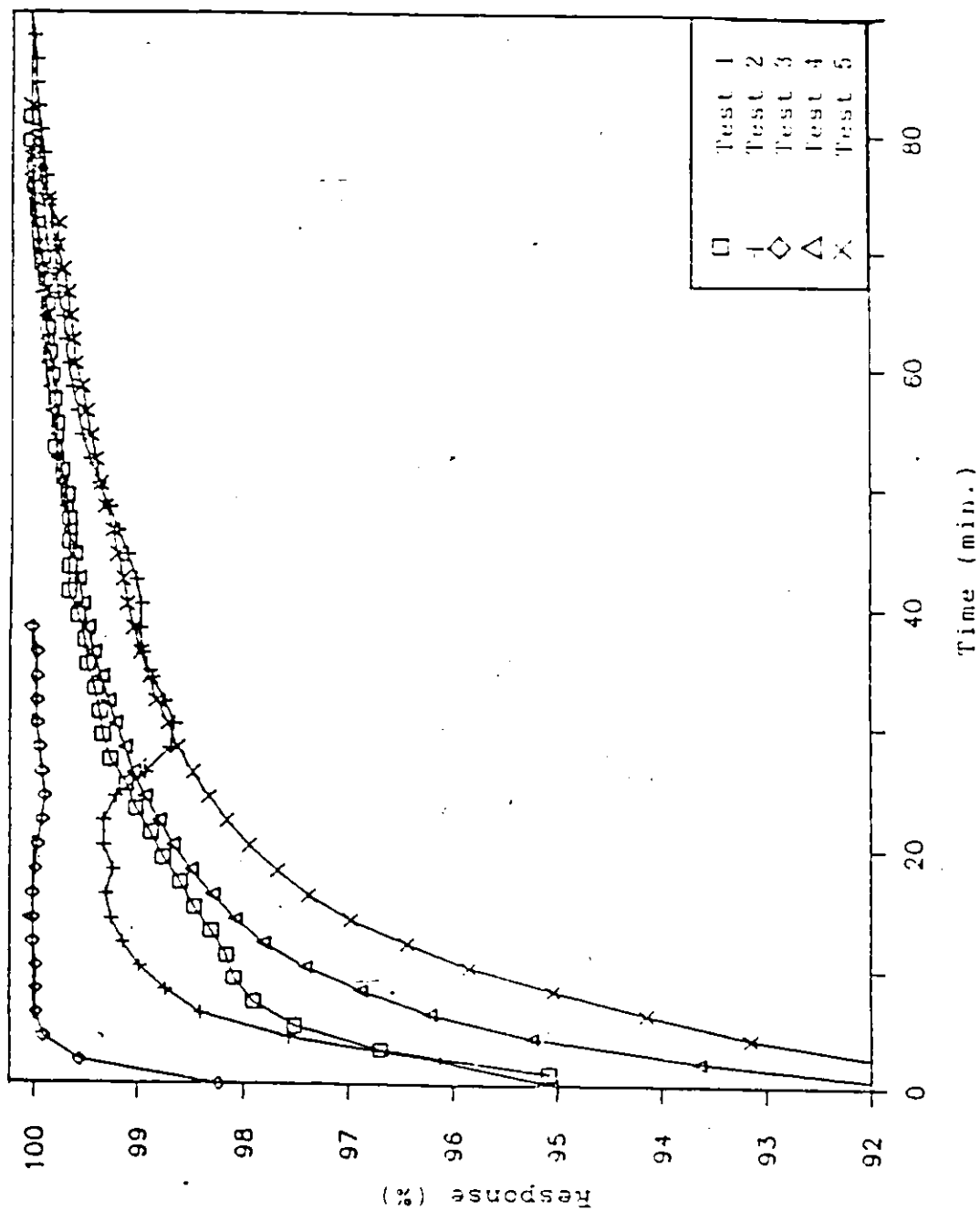


Figure III.1: Relative Response Curves for Five Effluent Samples

APPENDIX IV
TREATABILITY AND HYDRAULIC RETENTION TIME
RESULTS

A. Determination of Constituent Averages

The influent and effluent average constituent concentrations were calculated using an time integral average:

$$C_{\text{int. avg.}} = \frac{\int_{t_i}^{t_f} C \, dT}{t_f - t_i}, \quad (\text{IV.1})$$

where C is the constituent concentration,
 t_i is the time of the first constituent data point, and
 t_f is the time of the last constituent data point before the spiking.

The integral in Equation IV.1, represents the area under the constituent concentration versus time curve as shown in the plots presented in Chapter 5. Influent concentrations for the treatability study were plotted as step inputs because the feed for the treatability study was produced in one or two day feed batches and each batch was tested for the respective constituent. The treatability effluent concentration curves were plotted and connected linearly. Both influent and effluent concentrations in the HRT study are linearly connected because influent constituent concentrations were not determined for each feed batch. Evaluation of the integral was accomplished by employing the trapezoidal rule.

For the metal concentration plots, the metal

concentration values were plotted as calculated without any correction for the limit of detection.

All the raw data for this study are summarized in Tables IV.1 to IV.18. Table IV.10 provides the LODs for concentrations reported in Table IV.11 to IV.18

B. Calibration Procedure and LOD Calculation for Metals

All metal concentrations were determined using a Plasma Arc Spectrophotometer. Hence, there is a lower analytical limit or limit of detection (LOD) for which the results can be expressed. The LOD is defined as the lowest concentration level that can be statistically different from the blank [24,29]. The LOD values for HRT study Test 2, Table IV.10, were calculated by the following procedure.

- (1) A set of calibration standards, blank, 0.01, 0.1, 1, 10, 50 and 100 mg/L standard, were prepared according to the Standard Methods [1]. These standards were analyzed just before the analysis of the unknowns on the Spectrospan V Plasma Spectrophotometer. Five intensity readings were experimentally found for each calibration standard and the unknown.
- (2) The average intensity for each calibration standard was plotted and curve fitted using the least square linear curve fitting technique. All calibration curves had a correlation of 0.999 or greater.
- (3) The blank intensity readings and standard deviations were then calculated and used to calculate the LOD intensity values, as follows:

$$I_{\text{LOD}} = I_{\text{blank}} + 3 \cdot S_{\text{blank}} \quad (\text{IV.2})$$

where I_{LOD} is the intensity value for the LOD,

I_{blank} is the average intensity value for the blank, and

S is the intensity standard deviation for the blank.

The intensity standard deviation of the blank was multiplied by three to give a 99.86% confidence level in determining the presence of the metal [29]. The calculated I_{LOD} value was then used in the intensity - concentration calibration equation to determine LOD concentration.

For the wastewater characterization phase, the treatability study and Test 1 of the HRT phase, the concentration versus intensity calibration curves were determined using only a blank and a high concentration standard, usually 10 or 50 mg/L, according to the instruction given by the Spectrospan V Plasma Arc operations manual [51]. However, three intensity readings for each standard were determined after every fourth unknown analysis to compensate for the use of only 2 calibration points.

Table IV.1: Acid-Soluble Sulfide, Sulfate, COD and BOD Results
Obtained During the Treatability Study

Reduced Sulfur mg S/L		Sulfate mg SO ₄ /L			COD mg O ₂ /L			BOD mg O ₂ /L		
day	Eff.	day	Inf.	Eff.	day	Inf.	Eff.	Day	Inf.	Eff.
3	80.4	2	-	7870	3	-	1569	4	-	494
7	73.4	7	9774	7232	7	1723	1503	7	652	434
9	93.6	9	9350	8503	9	1819	1421	9	758	395
11	107	11	9420	5110	11	1915	1291	11	863	576
14	125	14	2570	1300	14	1851	1403	14	844	640
16	197	16	3988	3777	16	1809	1477	16	832	683
18	218	18	4412	3734	18	1926	1462	18	941	698

Table IV.2: Soluble and Total Metal Results Obtained During the Treatability Study

day	Copper mg Cu/L		Lead mg Pb/L		Nickel mg Ni/L		Zinc mg Zn/L	
	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.
Total								
3	7.36	0.295	0.497	0.635	1.25	0.266	3.86	1.97
5	6.47	0.10	0.415	0.427	1.30	0.303	5.31	3.10
7	6.13	0.115	0.423	0.419	1.33	0.274	6.98	5.34
9	9.46	0.903	0.419	0.419	1.40	0.408	8.17	2.04
11	7.15	1.09	1.64	0.418	0.291	0.382	4.87	2.67
14	7.54	2.11	0.376	0.394	0.223	0.226	5.06	3.02
16	4.89	1.47	1.14	0.385	0.192	0.183	4.59	2.24
18	12.5	1.53	1.10	0.415	0.485	0.161	11.9	2.08
Soluble								
5	5.72	< LOD	0.101	< LOD	1.30	0.162	2.49	< LOD
7	5.35	< LOD	< LOD	< LOD	1.28	0.133	5.49	< LOD
9	6.40	< LOD	< LOD	< LOD	1.39	0.142	3.80	< LOD
11	6.86	< LOD	< LOD	< LOD	0.209	0.194	3.91	< LOD
14	6.73	< LOD	< LOD	< LOD	0.144	0.089	2.78	< LOD
16	4.75	< LOD	< LOD	< LOD	0.099	0.061	3.64	< LOD
18	4.35	< LOD	< LOD	< LOD	0.041	0.043	2.37	< LOD
LOD - Limit of Detection								
			Cu - 0.008		mg Cu/L			
			Pb - 0.093		mg Pb/L			
			Ni - 0.011		mg Ni/L			
			Zn - 0.282		mg Zn/L			

Table IV.3 The Hydraulic Loading Rates for the
Two HRT Study Tests

day	Test 1 (mL/min)			day	Test 2 (mL/min)		
	A	B	C		A	B	C
0	6.373	4.215	2.703	3	22.67	-	5.201
11	5.767	4.192	2.863	8	21.03	12.52	7.812
23	4.921	3.637	2.265	10	21.99	11.46	7.270
27	5.442	4.204	2.516	12	22.52	12.20	5.956
29	5.207	4.062	2.476	15	22.01	12.88	6.025
32	5.812	4.095	2.517	17	22.03	11.72	5.596
34	5.146	3.804	2.208	19	25.66	14.81	5.930
36	4.896	3.273	2.245	22	25.48	13.24	6.463
39	5.745	4.096	2.646	24	25.47	13.28	6.404
				26	24.56	12.19	5.835
				29	24.72	13.48	6.312
				31	24.19	12.04	5.816
				36	24.30	12.61	6.237
Avg.	5.532	3.985	2.563	Avg.	23.55	12.72	6.247

Table IV.4: Reduced Sulfur and Sulfate Results for HRT Study
Test 1

day	Reduced Sulfur (mg S/L)			Sulfate (mg SO ₄ /L)			
	A	B	C	A	B	C	Feed
1	75.4	97.1	137.2	2150	1990	2100	2940
4	43.6	51.6	73.0	2810	2780	2600	2890
6	49.0	53.5	67.5	2890	2950	2790	3000
8	49.8	52.2	69.6	2660	2600	2570	2710
11	22.8	27.6	66.7	4700	4680	3540	5020
13	29.7	28.7	38.8	4370	4250	4080	4840
15	38.3	50.1	39.4	3740	4290	3970	3180
18	48.7	56.6	41.5	3060	2310	2830	2830
20	92.1	78.8	86.2	2550	2940	2870	2570
22	101.4	85.2	84.7	1996	2312	2040	2630
25	84.7	75.9	102.7	2390	2310	2470	2940
27	95.0	97.1	114.9	2190	2000	2080	2310
29	86.5	88.4	103.5	2000	1960	2150	2550
32	65.0	29.3	82.5	1880	1840	2040	2390
34	98.5	121.3	96.9	2290	2160	2250	2890
35	87.3	87.8	111.2	2065	2280	2460	2895
36	83.1	58.4	110.9	2223	2184	2204	2579
37	86.8	66.1	57.6	2300	2260	1970	2540
38	95.0	78.9	55.0	2380	2302	2140	2580
39	93.6	84.1	69.1	2107	2184	2144	2342

Table IV.5: Reduced Sulfur and Sulfate Results for HRT Study
Test 2

day	Reduced Sulfur (mg S/L)			Sulfate (mg SO ₄ /L)			
	A	B	C	A	B	C	Feed
3	61.9	91.7	108.2	2658	2540	2302	2737
8	87.9	103.9	121.9	1907	2164	2026	2381
10	82.8	108.8	109.9	2223	2144	2045	2579
12	77.2	92.0	114.5	2223	2124	2184	2500
15	88.2	101.4	117.9	1828	1928	1867	2421
17	88.9	104.2	114.6	2164	2322	2322	2381
19	87.7	108.0	108.0	1907	1828	1828	2381
22	85.5	120.3	52.0	2184	1907	1788	2262
24	73	92.8	90.4	2184	2006	1947	2619
26	67.5	90.1	104.2	2421	2223	2223	2619
29	97.1	105.8	107.5	2065	1907	1867	2638
31	91.9	112.3	116.6	2204	2124	1966	2579
34	26.6	34.0	110.1	2312	2579	1947	2633
35	0.8	43.2	100	1645	2223	2124	2534
36	6.5	48.1	100.3	2541	2223	2067	2831
38	73.4	110.1	181.4	1867	2184	1907	2302
40	78.8	93.7	146.8	2006	2085	1927	2381

Table IV.6: Chemical Oxygen Demand and Biological Oxygen Demand Results for HRT Study Test 1

day	COD (mg O ₂ /L)				BOD (mg O ₂ /L)			
	A	B	C	Feed	A	B	C	Feed
5	139.0	155.0	166.0	321.0	67.6	59.5	79.7	160.4
8	151.6	149.1	145.0	270.3	80.9	70.0	83.9	156.3
11	-	-	-	-	98.4	97.6	93.8	190.8
12	277.0	255.4	191.5	354.4	-	-	-	-
15	211.2	176.9	133.6	278.7	83.8	48.7	23.5	146.1
19	233.7	180.6	179.6	225.5	108.9	65.6	50.3	168.4
22	226.5	202.7	195.5	366.2	125.3	102.1	107.1	159.4
25	190.5	183.3	206.9	401.5	101.3	104.0	114.8	211.5
29	256.4	282.8	286.8	435.8	117.8	124.7	119.7	170.8
32	217.5	194.4	233.4	317.8	189.0	100.4	101.6	314.3
36	207.6	162.7	249.5	305.4	105.0	78.3	131.7	174.3
39	239.7	204.3	173.7	406.7	120.8	102.3	89.1	155.5

Table IV.7: Chemical Oxygen Demand and Biological Oxygen Demand Results for HRT Study Test 2

day	COD (mg O ₂ /L)				BOD (mg O ₂ /L)			
	A	B	C	Feed	A	B	C	Feed
8	223.6	213.8	210.1	336.2	156.0	160.9	146.9	278.5
12	252.6	254.4	238.1	330.9	150.2	147.2	143.3	211.7
15	255.1	232.7	229.6	262.2	142.0	149.2	158.0	-
19	222.3	232.1	233.6	264.5	99.0	107.8	108.2	840.4
22	453.7	268.2	216.3	291.5	163.8	116.9	116.9	192.9
26	370.4	215.6	212.5	308.9	140.4	104.4	106.3	174.3
29	291.5	252.2	219.9	550.8	134.6	127.5	110.4	211.3
36	703.3	460.9	285.1	664.3	195.0	192.9	132.7	254.0
40	1426.0	743.0	530.0	1032.0	302.0	319.2	260.7	311.2

Table IV.8: Effluent Redox Potential Values for HRT
Study Test 1

day	Redox Potential (mV)		
	A	B	C
4	-162.6	-172.0	-184.2
6	-194.5	-196.0	-172.0
9	-178.1	-175.8	-195.8
11	-132.3	-131.5	-163.6
13	-151.2	-155.9	-153.3
18	-180.5	-173.7	-163.4
20	-186.9	-187.9	-176.1
22	-184.0	-186.6	-186.2
25	-194.9	-192.1	-191.9
27	-192.4	-194.5	-189.0
29	-186.6	-185.7	-185.2
32	-190.6	-187.9	-184.4
34	-196.5	-200.0	-189.6
36	-184.5	-190.1	-181.1
39	-191.0	-193.4	-178.7

Table IV.9: Effluent Redox Potential Values for HRT
Study Test 2

day	Redox Potential (mV)		
	A	B	C
3	-174.0	-193.6	-184.8
8	-176.9	-197.9	-203.3
10	-185.9	-203.9	-203.0
12	-170.6	-186.9	-199.2
15	-183.9	-184.8	-202.7
17	-182.4	-197.6	-200.0
19	-192.7	-203.5	-203.6
22	-179.0	-206.5	-208.5
24	-191.4	-206.1	-209.1
26	-186.3	-197.1	-206.8
29	-183.9	-202.9	-204.9
31	-195.5	-206.6	-205.8
36	-164.3	-189.6	-194.4
38	-180.3	-194.2	-208.3

Table IV.10: The Detection Limits of Copper, Lead, Nickel and Zinc as found Experimentally During the HRT Study

Limit of Detection	Copper	Lead	Nickel	Zinc
Soluble (mg/L)				
LOD ₁	0.035	0.224	0.050	0.519
LOD ₂	0.015	0.335	0.033	0.738
LOD ₃	0.013	0.187	0.078	0.487
Total (mg/L)				
LOD ₄	0.019	0.463	0.067	0.304
LOD ₅	0.021	0.645	0.089	0.533
LOD ₆	0.012	0.159	0.110	0.289

NOTE: All LODs reported in Tables IV.11 to IV.18 are referenced to the above values.

Table IV.11: Soluble and Total Copper Results for HRT Study Test 1

Day	Soluble Copper (mg Cu/L)				Total Copper (mg Cu/L)			
	A	B	C	Feed	A	B	C	Feed
1	< LOD ₁	< LOD ₁	0.118	0.212	0.157	0.197	0.140	1.073
4	< LOD ₁	< LOD ₁	< LOD ₁	1.023	0.109	0.239	0.087	3.996
6	< LOD ₁	< LOD ₁	< LOD ₁	0.961	0.133	0.080	0.087	1.100
8	0.036	0.037	0.041	1.091	0.106	0.090	0.058	1.689
11	0.042	< LOD ₁	0.046	32.29	0.136	0.083	0.080	36.3
13	< LOD ₁	0.062	< LOD ₁	35.3	0.111	0.107	0.090	36.96
15	< LOD ₁	0.039	0.046	6.183	0.151	0.114	0.202	6.328
18	0.051	0.045	< LOD ₁	0.373	0.106	0.120	0.159	0.419
20	0.060	0.052	0.057	3.026	0.154	0.201	0.120	3.740
22	0.049	0.047	0.044	2.407	0.340	0.337	0.258	4.211
25	0.071	0.063	0.055	24.51	0.360	0.535	0.398	27.1
27	0.044	0.027	0.038	29.4	0.192	0.162	0.138	31.12
29	0.040	0.029	0.030	27.9	0.229	0.140	0.147	28.82
32	0.047	0.038	0.040	14.29	0.123	0.225	0.229	66.4
34	0.033	0.024	0.079	10.35	0.157	0.173	0.579	141.2
35	0.028	0.017	0.055	6.522	0.120	0.264	0.098	156.7
36	0.028	0.015	0.035	11.18	0.102	0.087	0.136	11.25
37	0.042	0.016	0.044	10.31	0.075	0.069	0.083	12.11
38	0.037	0.026	0.024	11.64	0.106	0.026	0.069	13.38
39	0.044	0.044	0.038	10.52	0.080	0.090	0.103	11.80

Table IV.12: Soluble and Total Copper Results for HRT Study Test 2

day	Soluble Copper (mg Cu/L)				Total Copper (mg Cu/L)			
	A	B	C	Feed	A	B	C	Feed
3	0.083	0.028	0.028	3.000	0.933	0.696	0.402	3.874
8	0.024	0.018	< LOD ₃	3.650	1.105	0.658	0.295	34.0
10	0.044	< LOD ₃	0.089	2.744	1.398	0.449	2.869	2.869
12	0.034	0.018	0.041	1.866	0.407	0.253	0.170	2.715
15	0.031	0.024	< LOD ₃	2.035	0.370	0.263	0.211	2.045
17	0.066	0.031	0.028	1.394	0.388	0.174	0.160	1.799
19	0.037	0.063	0.031	1.261	0.332	0.198	0.156	1.505
22	0.041	0.034	0.031	0.248	1.268	0.202	0.174	0.370
24	0.050	0.028	< LOD ₃	0.125	1.301	0.202	0.188	0.351
26	0.031	0.034	0.021	0.267	1.203	0.207	0.188	0.495
29	0.047	0.047	0.037	3.510	0.207	0.253	0.244	53.80
31	0.034	0.021	0.024	0.882	6.988	0.272	0.277	1.086
34	0.096	0.128	0.024	3.479	7.714	0.584	0.319	39.09
35	0.225	0.430	0.063	3.327	71.54	1.021	0.351	131.2
36	0.202	0.053	< LOD ₃	0.805	4.186	0.453	0.207	7.398
38	0.021	0.083	0.028	0.614	2.120	0.323	0.165	0.770
40	0.015	0.024	0.018	0.737	70.94	0.388	0.216	0.784

Table IV.13: Soluble and Total Lead Results for HRT Study Test 1

day	Soluble Lead (mg Pb/L)				Total Lead (mg Pb/L)			
	A	B	C	Feed	A	B	C	Feed
1	< LOD ₁	< LOD ₁	< LOD ₁	< LOD ₁	0.930	0.954	1.017	1.087
4	< LOD ₁	< LOD ₁	< LOD ₁	< LOD ₁	0.664	0.502	0.661	0.885
6	< LOD ₁	< LOD ₁	< LOD ₁	< LOD ₁	0.818	0.973	0.901	1.096
8	< LOD ₁	< LOD ₁	< LOD ₁	< LOD ₁	0.755	0.832	0.912	1.074
11	< LOD ₁	< LOD ₁	< LOD ₁	< LOD ₁	0.753	0.732	0.834	0.905
13	< LOD ₁	< LOD ₁	< LOD ₁	< LOD ₁	0.647	0.863	0.894	1.823
15	< LOD ₁	< LOD ₁	< LOD ₁	< LOD ₁	0.841	0.904	0.962	0.986
18	0.469	0.252	< LOD ₁	0.237	0.623	0.776	0.793	0.908
20	< LOD ₂	< LOD ₂	< LOD ₂	< LOD ₂	0.585	0.848	0.579	0.619
22	< LOD ₂	< LOD ₂	< LOD ₂	< LOD ₂	0.797	0.958	1.012	0.970
25	< LOD ₂	< LOD ₂	< LOD ₂	< LOD ₂	0.701	1.058	0.963	1.081
27	< LOD ₂	< LOD ₂	< LOD ₂	< LOD ₂	3.571	4.050	4.169	4.046
29	< LOD ₂	< LOD ₂	< LOD ₂	< LOD ₂	2.555	3.069	3.334	3.829
32	< LOD ₂	< LOD ₂	< LOD ₂	< LOD ₂	2.594	3.352	3.745	3.336
34	< LOD ₂	< LOD ₂	< LOD ₂	< LOD ₂	4.183	5.162	< LOD ₄	50.38
35	< LOD ₂	< LOD ₂	< LOD ₂	< LOD ₂	2.592	3.142	2.925	56.74
36	< LOD ₂	< LOD ₂	< LOD ₂	< LOD ₂	1.939	2.743	2.907	2.562
37	< LOD ₂	< LOD ₂	< LOD ₂	< LOD ₂	1.473	2.576	2.507	3.035
38	< LOD ₂	< LOD ₂	< LOD ₂	< LOD ₂	1.889	2.560	2.717	2.795
39	< LOD ₂	< LOD ₂	< LOD ₂	< LOD ₂	2.144	2.836	3.270	2.882

Table IV.14: Soluble and Total Lead Results for HRT Study Test 2

day	Soluble Lead (mg Pb/L)				Total Lead (mg Pb/L)			
	A	B	C	Feed	A	B	C	Feed
3	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	1.134	0.675	0.801	0.585
8	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	0.702	1.143	1.232	1.610
10	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	1.125	1.179	0.585	0.891
12	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	0.747	0.558	0.882	0.765
15	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	2.050	2.194	1.161	1.880
17	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	0.900	0.927	0.666	1.223
19	< LOD ₃	0.253	< LOD ₃	< LOD ₃	1.358	1.466	1.403	1.772
22	0.204	0.473	< LOD ₃	< LOD ₃	1.457	0.514	0.666	0.567
24	0.190	< LOD ₃	< LOD ₃	< LOD ₃	0.927	0.819	0.469	0.738
26	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	1.143	1.304	1.700	2.220
29	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	1.304	0.837	1.107	2.030
31	< LOD ₃	< LOD ₃	0.204	< LOD ₃	< LOD ₆	< LOD ₆	0.361	0.469
34	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	6.570	0.594	1.134	51.35
35	< LOD ₃	0.361	< LOD ₃	< LOD ₃	113.9	1.134	0.846	289.4
36	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	1.403	1.250	1.457	1.502
38	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	2.113	1.116	0.397	0.370
40	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	41.14	1.107	0.594	0.343

Table IV.15: Soluble and Total Nickel Results for HRT Study Test 1

day	Soluble Nickel (mg Ni/L)				Total Nickel (mg Ni/L)			
	A	B	C	Feed	A	B	C	Feed
1	< LOD ₁	< LOD ₁	< LOD ₁	0.141	0.293	0.316	0.306	0.406
4	< LOD ₁	< LOD ₁	< LOD ₁	0.142	0.232	0.277	0.224	0.500
6	< LOD ₁	< LOD ₁	< LOD ₁	0.133	0.289	0.314	0.283	0.430
8	< LOD ₁	< LOD ₁	< LOD ₁	0.146	0.285	0.302	0.295	0.463
11	0.222	0.151	0.070	3.15	0.404	0.365	0.353	3.569
13	0.196	0.149	0.113	3.38	0.436	0.375	0.457	3.737
15	0.156	0.144	0.101	1.04	0.394	0.391	0.394	1.127
18	0.075	0.063	< LOD ₁	0.378	0.293	0.318	0.328	0.579
20	< LOD ₂	< LOD ₂	< LOD ₂	0.744	0.324	0.291	0.283	0.998
22	< LOD ₂	< LOD ₂	< LOD ₂	0.489	0.334	0.436	0.391	1.060
25	< LOD ₂	< LOD ₂	< LOD ₂	2.355	0.371	0.492	0.485	2.578
27	0.049	0.035	0.039	2.339	0.633	0.659	0.679	3.038
29	0.075	0.049	0.044	2.322	0.475	0.533	0.560	2.932
32	0.076	0.044	0.044	1.527	0.487	0.603	0.608	3.742
34	0.059	0.047	0.051	35.7	0.707	0.808	0.750	61.68
35	0.065	0.058	0.089	33.3	0.475	0.500	0.474	71.41
36	0.091	< LOD ₂	0.079	0.773	0.393	0.499	0.479	1.083
37	0.059	0.073	0.069	0.733	0.288	0.454	0.439	1.248
38	0.039	0.056	0.059	0.816	0.356	0.416	0.442	1.224
39	0.035	0.040	< LOD ₂	0.853	0.371	0.441	0.495	1.172

Table IV.16: Soluble and Total Nickel Results for HRT Study Test 2

day	Soluble Nickel (mg Ni/L)				Total Nickel (mg Ni/L)			
	A	B	C	Feed	A	B	C	Feed
3	< LOD ₃	< LOD ₃	< LOD ₃	0.946	0.413	0.326	0.263	1.068
8	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	0.295	0.279	0.318	1.013
10	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	0.350	0.334	< LOD ₆	0.326
12	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₆	< LOD ₆	< LOD ₆	< LOD ₆
15	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	0.311	0.350	< LOD ₆	< LOD ₆
17	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₆	< LOD ₆	< LOD ₆	< LOD ₆
19	< LOD ₃	< LOD ₃	< LOD ₃	0.102	0.247	0.247	0.239	0.303
22	0.121	< LOD ₃	< LOD ₃	0.255	0.555	< LOD ₆	< LOD ₆	0.311
24	0.125	< LOD ₃	< LOD ₃	0.580	0.587	< LOD ₆	< LOD ₆	0.580
26	< LOD ₃	< LOD ₃	< LOD ₃	1.440	0.547	0.255	0.287	1.440
29	< LOD ₃	< LOD ₃	< LOD ₃	0.082	0.255	< LOD ₆	0.247	1.305
31	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	0.918	< LOD ₆	< LOD ₆	0.484
34	0.608	0.647	< LOD ₃	35.86	9.386	1.518	0.279	37.77
35	3.941	0.997	0.098	33.67	33.09	1.329	0.247	78.70
36	0.149	< LOD ₃	< LOD ₃	0.243	0.973	0.389	0.271	0.997
38	0.105	< LOD ₃	< LOD ₃	< LOD ₃	0.973	0.287	< LOD ₆	< LOD ₆
40	1.625	< LOD ₃	< LOD ₃	0.082	41.88	0.279	0.224	0.16

Test

day	Soluble Zinc (mg Zn/L)				Total Zinc (mg Zn/L)			
	A	B	C	Feed	A	B	C	Feed
1	0.685	1.435	< LOD ₁	3.075	1.688	2.149	< LOD ₄	3.126
4	< LOD ₁	< LOD ₁	< LOD ₁	2.096	< LOD ₄	< LOD ₄	< LOD ₄	28.58
6	1.073	< LOD ₁	< LOD ₁	1.891	3.296	< LOD ₄	< LOD ₄	3.506
8	< LOD ₁	< LOD ₁	1.340	3.034	< LOD ₄	< LOD ₄	2.131	6.695
11	1.190	0.794	< LOD ₁	10.93	1.324	1.480	1.767	13.52
13	1.100	0.796	0.634	14.07	2.173	1.202	1.489	14.80
15	0.520	0.563	1.382	3.468	2.045	2.145	1.702	4.541
18	< LOD ₁	< LOD ₁	0.534	1.783	< LOD ₄	< LOD ₄	1.635	1.939
20	< LOD ₂	< LOD ₂	< LOD ₂	3.852	< LOD ₄	< LOD ₄	< LOD ₄	4.331
22	< LOD ₂	< LOD ₂	< LOD ₂	1.848	< LOD ₄	< LOD ₄	< LOD ₄	2.862
25	< LOD ₂	< LOD ₂	< LOD ₂	7.577	< LOD ₄	0.620	< LOD ₄	13.24
27	< LOD ₂	< LOD ₂	< LOD ₂	9.540	2.532	2.792	2.961	17.12
29	< LOD ₂	< LOD ₂	< LOD ₂	7.015	1.671	1.846	2.137	13.80
32	< LOD ₂	< LOD ₂	< LOD ₂	2.686	1.489	2.150	2.618	19.3
34	< LOD ₂	< LOD ₂	1.438	4.351	2.771	3.569	2.376	218.2
35	< LOD ₂	1.562	< LOD ₂	2.087	1.445	1.661	1.671	269.8
36	< LOD ₂	< LOD ₂	< LOD ₂	4.794	< LOD ₅	1.463	1.752	4.849
37	< LOD ₂	< LOD ₂	< LOD ₂	2.534	< LOD ₅	1.357	1.401	4.934
38	< LOD ₂	< LOD ₂	< LOD ₂	4.990	< LOD ₅	1.414	1.437	7.493
39	< LOD ₂	1.054	1.140	5.067	1.068	1.528	1.887	6.601

Table IV.18: Soluble and Total Zinc Results for HRT Study Test 2

day	Soluble Zinc (mg Zn/L)				Total Zinc (mg Zn/L)			
	A	B	C	Feed	A	B	C	Feed
3	< LOD ₃	< LOD ₃	< LOD ₃	0.932	8.036	9.484	2.139	8.373
8	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	6.397	10.30	3.570	56.07
10	< LOD ₃	< LOD ₃	< LOD ₃	0.502	3.497	7.835	14.14	7.553
12	< LOD ₃	< LOD ₃	< LOD ₃	1.334	4.718	1.629	5.520	7.124
15	< LOD ₃	< LOD ₃	< LOD ₃	0.932	3.379	14.13	2.613	2.012
17	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	0.946	1.720	2.477	2.622
19	< LOD ₃	0.301	< LOD ₃	0.268	4.609	2.422	2.659	2.868
22	< LOD ₃	0.437	0.263	0.418	2.914	2.960	1.693	2.003
24	0.249	< LOD ₃	< LOD ₃	0.305	3.297	1.757	3.525	2.622
26	< LOD ₃	< LOD ₃	< LOD ₃	0.596	3.889	3.206	3.397	6.368
29	< LOD ₃	< LOD ₃	< LOD ₃	0.835	5.056	1.456	2.057	111.9
31	< LOD ₃	< LOD ₃	0.273	0.315	17.53	1.210	3.424	3.998
34	< LOD ₃	< LOD ₃	< LOD ₃	3.177	13.90	4.992	2.732	45.23
35	3.096	2.732	< LOD ₃	2.329	93.34	4.873	3.288	221.9
36	< LOD ₃	< LOD ₃	< LOD ₃	0.348	11.02	3.734	3.051	16.31
38	< LOD ₃	< LOD ₃	< LOD ₃	< LOD ₃	6.550	3.224	3.789	22.45
40	4.372	< LOD ₃	< LOD ₃	1.298	95.86	3.269	8.865	6.450

VITA AUCTORIS

- 1962 Born in Tecumseh, Ontario, Canada, on August 11.
- 1980 Awarded a High School Graduation Diploma from St. Anne's High School, Tecumseh, Ontario, Canada.
- 1981 Awarded a High School Honour Graduation Diploma from St. Anne's High School, Tecumseh, Ontario, Canada.
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