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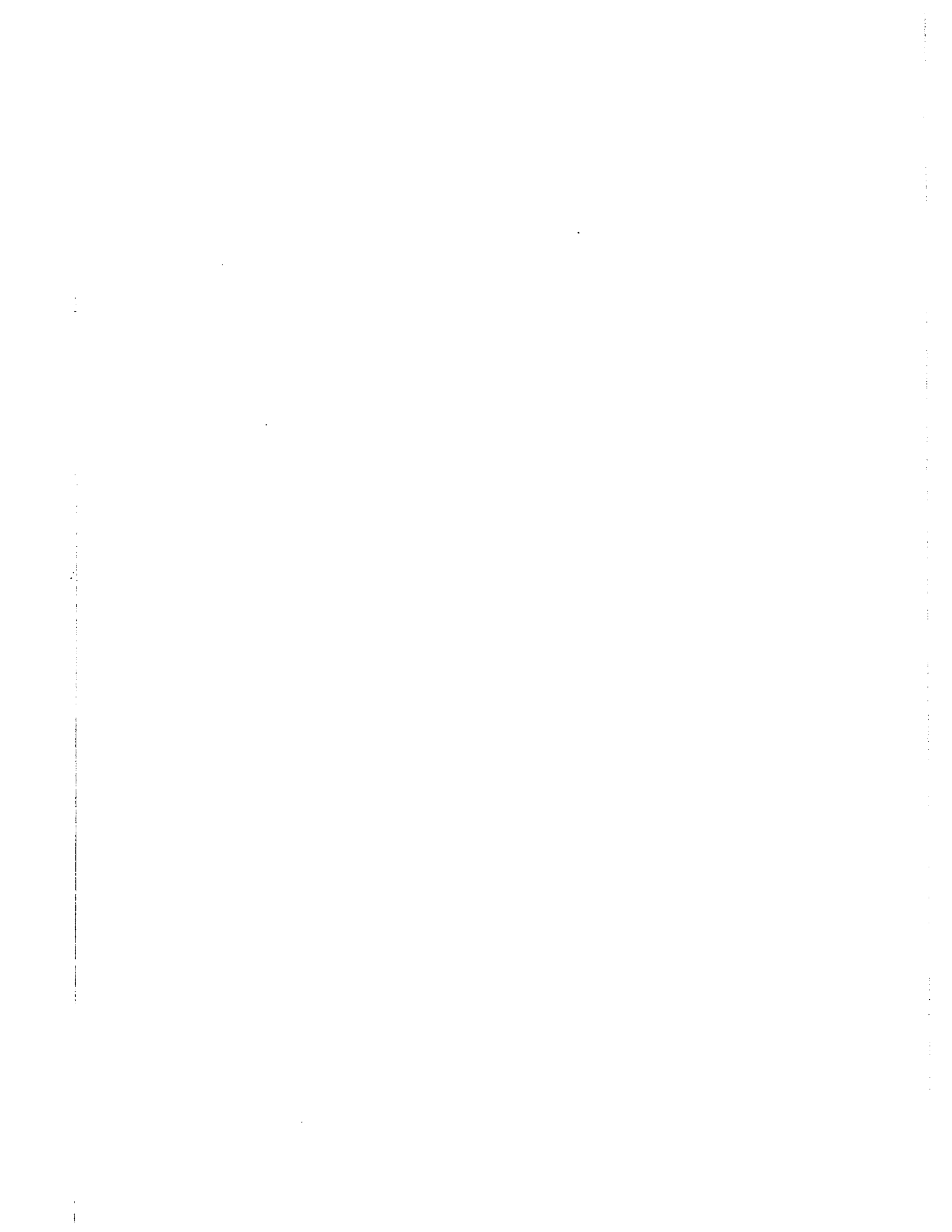
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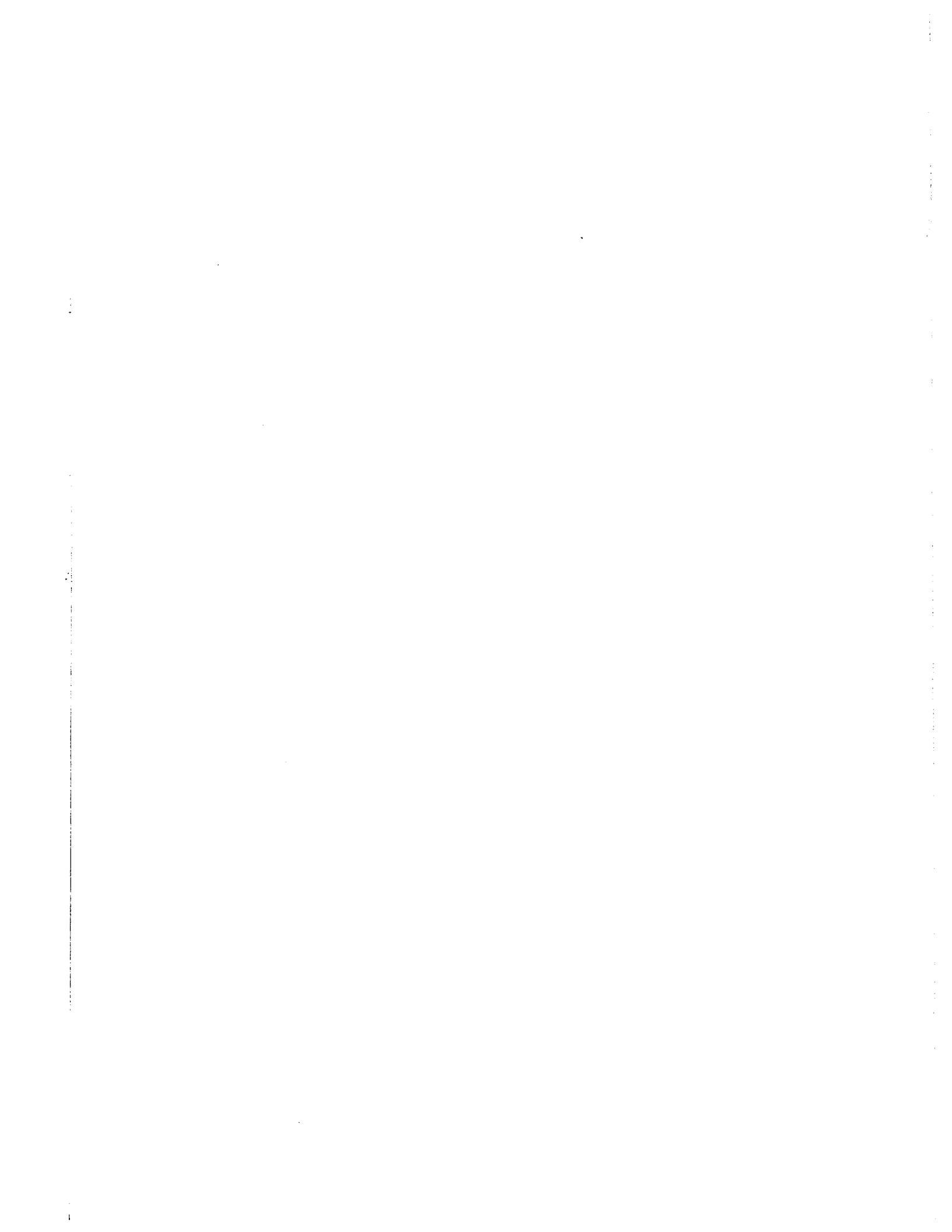
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METALS RECOVERY FROM INDUSTRIAL  
WASTEWATERS AND METALLIC HYDROXIDE  
SLUDGES THROUGH MICROBIAL SULPHATE-REDUCTION

BY

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Thesis submitted to the  
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ABSTRACT

This paper describes how metals originate in industrial wastewaters from the mining and metal finishing industries. Treatment of wastewaters containing dissolved metals produces a metallic hydroxide sludge which has to be disposed of in an environmentally acceptable way. It is estimated that the metal finishing industry annually disposes of 2,500,000 pounds and 49,000,000 pounds of non-ferrous metals in Canada and the United States respectively. These non-ferrous metals are either discharged to municipal sewers as untreated wastewater where they can interfere with the sewage treatment process and can also pose serious problems for sewage sludge disposal, or they can be disposed of as metallic hydroxide sludges in landfills, deepwells, or holding lagoons.

The value of the metals contained in these sludges has long been recognized, and technology has been developed for their recovery. This recovery technology is based on well known chemical unit processes such as leaching, selective precipitation, ion exchange, and electrowinning. These processes are capable of recovering metals in a pure form, however, this technology does not appear to be economical at this time due to high energy costs, high chemical cost, and undue competition of this pure product from virgin metals.

The paper describes a process whereby these non-ferrous metals can be recovered via microbial sulphate-reduction as metallic sulphides suitable as basemetal smelter feed. The bacterium Desulfovibrio desulfuricans is capable of reducing sulphate sulphur to sulphide sulphur while simultaneously oxidizing organic carbon to carbon dioxide. The hydrogen sulphide thus produced reacts with metal hydroxide sludge leachate to produce a high grade metallic sulphide concentrate suitable for basemetal smelter feed. The process described utilizes three industrial waste streams, namely: metallic hydroxide sludge, waste sulphuric acid, and biodegradable waste organics, as feedstocks for the reaction. Bench

scale experiments are described which produced concentrates containing in excess of 28 per cent copper and zinc as sulphides.

The paper includes a flow sheet and process design for a pilot plant recovering 1000 pounds per year of non-ferrous metal as metallic sulphides.

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INDEX

ABSTRACT	i
ACKNOWLEDGEMENTS	iii
INDEX	IV
LIST OF FIGURES	VII
LIST OF TABLES	X
1. INTRODUCTION	1
2. BACKGROUND	3
2.1 SOLUBLE METALS FROM PRIMARY INDUSTRIAL ACTIVITIES	3
2.1.1 MINING	5
2.1.1.1. CHEMICAL OXIDATION OF SULPHIDES	5
2.1.1.2. MICROBIOLOGICAL OXIDATION OF SULPHIDES	6
2.1.2. SMELTING AND REFINING	8
2.1.3. TREATMENT TECHNOLOGY FOR EFFLUENTS FROM PRIMARY INDUSTRIES	9
2.1.4. SLUDGE DISPOSAL FROM PRIMARY INDUSTRIAL ACTIVITIES	11
2.1.5. CASE STUDY - ACID MINE DRAINAGE	12
2.2.1. METAL FINISHING	13
2.2.1.1. DEGREASING	13
2.2.1.2. PICKLING	14
2.2.1.3. CHEMICAL STRIPPING OF METALLIC COATINGS	14
2.2.1.4. PHOSPHATING	14
2.2.1.5. CHROMATING	15
2.2.1.6. BRIGHT DIPPING	15
2.2.1.7. METAL COLOURING	15
2.2.1.8. ELECTROCLEANING	16

2.2.1.9.	ANODIZING	16
2.2.1.10.	ELECTRO AND ELECTROLESS PLATING	16
2.2.2.	METAL FINISHING PLANT EFFLUENT STREAMS	17
2.2.2.1.	EFFLUENT TREATMENT	18
2.2.2.2.	DIRECT DISCHARGE TO MUNICIPAL SEWERS	19
2.2.3.	DISPOSAL OF METAL CONTAINING SLUDGES	20
2.2.3.1.	MUNICIPAL SLUDGE DISPOSAL	20
2.2.3.2.	DISPOSAL OF METAL FINISHING SLUDGES	21
2.3.	METAL RECOVERY TECHNOLOGY REVIEW	22
2.3.1.	RECOVERY OF METALS FROM SEWAGE SLUDGE	23
2.3.2.	RECOVERY OF METALS FROM WASTE WATER TREATMENT HYDROXIDE SLUDGES	23
2.4.	HYDROGEN SULPHIDE GENERATION	26
2.4.1.	CHEMICAL SULPHIDE PRODUCTION	26
2.4.2.	MICROBIAL SULPHATE REDUCTION	26
3.	THEORETICAL CONSIDERATIONS	29
3.1.	SLUDGE LEACHING	29
3.2.	MICROBIAL SULPHATE REDUCTION	29
3.3.	METAL SULPHIDE PRECIPITATION	33
3.4.	SULPHIDE CONCENTRATE AS BASE METAL SMELTER FEED	40
4.	EXPERIMENTAL PROCEDURES	42
4.1.	GENERAL APPROACH	42
4.2.	ANALYTICAL PROCEDURES	44
5.	RESULTS AND DISCUSSION	49
5.1.	CULTURE ENRICHMENT	49

5.2	ZINC SULPHIDE PRODUCTION	51
5.3.	COPPER/ZINC SULPHIDE PRODUCTION	68
5.4.	UPGRADING OF THE REACTOR SLURRY INTO BASEMETAL SMELTER FEED	81
5.5.	GENERAL DISCUSSIONS	81
6.	ENGINEERING SIGNIFICANCE	85
6.1.	EFFECT ON PRESENT WASTE DISPOSAL PRACTICE	85
6.2.	EFFECT ON RESOURCE RECOVERY AND RECYCLE	86
6.3.	EFFECT ON ENERGY CONSERVATION	88
7.	CONCLUSIONS	90
8.	RECOMMENDATIONS	92
	REFERENCES	93
	APPENDIX I - PICTORIAL DISPLAY OF REACTOR SYSTEM AND PRODUCTS	96
	APPENDIX II - SOLUBLE EQUILIBRIUM ZINC CONCENTRATION IN THE ZINC SULPHIDE PRODUCTION REACTOR	99
	APPENDIX III - PILOT PLANT DESIGN FOR EXTENSIVE STUDIES OF THE SULPHATE REDUCTION/METAL RECOVERY PROCESS	101
	APPENDIX IV - EXPERIMENTS TO IMPROVE THE SULPHIDE ANALYTICAL DETERMINATION	108

LIST OF FIGURES

Figure		Page
1	THEORETICAL SOLUBILITIES OF METAL IONS AS A FUNCTION OF pH	10
2	IONIZATION CONSTANTS OF AQUEOUS HYDROGEN SULPHIDE AS A FUNCTION OF TEMPERATURE	36
3	SOLUBILITY PRODUCT OF SOME COMMON SULPHIDES AS A FUNCTION OF TEMPERATURE	39
4	SULPHATE-REDUCING REACTOR SYSTEM	43
5	CULTURE ENRICHMENT PHASE: TOTAL SULPHIDE CONCENTRA- TION AS A FUNCTION OF TIME	50
6	AUTOMATIC FEEDER FOR METAL SULPHATE SOLUTIONS	52
7	ZINC SULPHIDE PRODUCTION PHASE: ZINC ADDITION AS A FUNCTION OF TIME	53
8	ZINC SULPHIDE PRODUCTION PHASE: SOLUBLE SULPHIDE AS A FUNCTION OF TIME	55
9	ZINC SULPHIDE PRODUCTION PHASE: TOTAL SULPHIDE CONCENTRATION AS A FUNCTION OF TIME	56
10	ZINC SULPHIDE PRODUCTION PHASE: VOLATILE SOLIDS AS A FUNCTION OF TIME	57
11	ZINC SULPHIDE PRODUCTION PHASE: TOTAL SOLIDS AS A FUNCTION OF TIME	58
12	ZINC SULPHIDE PRODUCTION PHASE: COD ADDITION AS A FUNCTION OF TIME	60
13	ZINC SULPHIDE PRODUCTION PHASE: SOLUBLE COD AS A FUNCTION OF TIME	61

14	ZINC SULPHIDE PRODUCTION PHASE: pH AS A FUNCTION OF TIME	62
15	ZINC SULPHIDE PRODUCTION PHASE: ALKALINITY AS A FUNCTION OF TIME	63
16	ZINC SULPHIDE PRODUCTION PHASE: CALCULATED SULPHIDE PRODUCTION AS A FUNCTION OF TIME	67
17	COPPER/ZINC SULPHIDE PRODUCTION PHASE: TOTAL REACTOR SOLIDS AS A FUNCTION OF TIME	69
18	COPPER/ZINC SULPHIDE PRODUCTION PHASE: VOLATILE SOLIDS AS A FUNCTION OF TIME	70
19	COPPER/ZINC SULPHIDE PRODUCTION PHASE: COPPER/ZINC SULPHATE ADDITION TO THE REACTOR AS A FUNCTION OF TIME	71
20	COPPER/ZINC SULPHIDE PRODUCTION PHASE: SOLUBLE SULPHIDE CONCENTRATION AS A FUNCTION OF TIME	72
21	COPPER/ZINC SULPHIDE PRODUCTION PHASE: pH AS A FUNCTION OF TIME	74
22	COPPER/ZINC SULPHIDE PRODUCTION PHASE: REACTOR SOLUBLE ALKALINITY AS A FUNCTION OF TIME	75
23	COPPER/ZINC SULPHIDE PRODUCTION PHASE: COD ADDITION AS A FUNCTION OF TIME	76
24	COPPER/ZINC SULPHIDE PRODUCTION PHASE: SOLUBLE REACTOR COD AS A FUNCTION OF TIME	77
25	COPPER/ZINC SULPHIDE PRODUCTION PHASE: CALCULATED SULPHIDE PRODUCTION RATE AS A FUNCTION OF TIME	78
26	SETTLING OF ZINC SULPHIDE SLUDGE	82
27	PROCESS FLOW SHEET FOR PILOT SCALE METAL RECOVERY PLANT UTILIZING MICROBIAL SULPHATE REDUCTION	102

28

ZONE SETTLING VELOCITY AS A FUNCTION OF SOLIDS  
CONCENTRATION

105

LIST OF TABLES

I	METALS FOUND IN WASTEWATERS, THEIR SOURCES, ESTIMATED ANNUAL DISPOSAL, AND COMMERCIAL VALUE	4
II	STEADY STATE RELATIONSHIPS FOR MIXED BIOLOGICAL REACTOR WITHOUT SOLIDS RECYCLE	32
III	SOLUBILITY PRODUCTS OF SOME COMMON SULPHIDES AT 25 <sup>0</sup> C	38
IV	CALCULATED SULPHIDE PRODUCTION RATES FOR ZINC SULPHIDE PRODUCTION PHASE	65
V	SULPHIDE PRODUCTION DURING ZINC/COPPER SULPHIDE PHASE	80
VI	REACTOR SLUDGE ANALYSIS	83
VII	COMPARISON OF ANALYTICAL METHODS FOR THE DETER- MINATION OF SOLUBLE SULPHIDES	109

## CHAPTER ONE

### 1. INTRODUCTION

Non-ferrous metals are among the most useful commodities produced by man. Modern technology and a high standard of living are putting continuous strains on the supply of these vital raw materials. Because of their value and their potentially deleterious impact when disposed of in the environment, the recovery and recycle of non-ferrous metals from wastewaters is a necessity.

Water-soluble, non-ferrous heavy metals in wastewaters usually result from mans activities in mining of them, and producing or consuming products containing them. Initial removal of these metals from wastewaters is usually accomplished by pH adjustment and precipitation of metal hydroxides. The resulting thixotropic sludge is not suitable as smelter feed or amenable to other economical recovery technique. It has to be stored in expensive impoundment basins where the potential for redissolving exists.

Secondary industrial activities also release soluble non-ferrous heavy metals. Some of these metals find their way into municipal sewers, where they can interfere with traditional sewage sludge disposal methods, while others are disposed of as sludges in landfills and deepwells. Both of these disposal methods pose potentially serious threats to the environment.

Because of their commercial value and the difficulty of their safe disposal, non-ferrous heavy metals have long been identified as desirable for recycle.

Various schemes ranging from electrowinning to ion exchange have been investigated to accomplish the recovery of these metals from

wastewaters or waste water sludges. However, none of these processes appear to be economically viable because of their high chemical and energy costs. In addition, most of these processes produce a pure metal or metal salt which faces strong competition from virgin materials produced on a large scale. Thus, to seriously consider the recyclability of water-soluble non-ferrous heavy metals, a process is needed which is both technically sound economically feasible, and does not face undue competition from virgin metal producers.

Most non-ferrous heavy metals form a precipitate with hydrogen sulphide. This precipitate is suitable as non-ferrous smelter feed.

Under appropriate conditions hydrogen sulphide can be produced microbially by the action of sulphate-reducing bacteria utilizing sulphate in the presence of biodegradable organics.

Since both sulphate (waste sulphuric acid) and biodegradable organics are industrial wastes, the sulphate-reduction process can use wastes to treat wastes in order to produce a recyclable product. Thus, the objective of this research was to demonstrate that a microbial sulphate reduction process feeding on three waste streams, i.e., metal sludges, waste sulphuric acid and waste organics, can produce a commercially recyclable product, i.e., metal sulphides.

## CHAPTER TWO

### 2. BACKGROUND

Water-soluble non-ferrous heavy metals originate from primary industrial activities such as mining, smelting and refining of metals, and from secondary industrial activities such as electroplating (metal finishing), electronics, and etching, etc. All of these soluble heavy metals possess toxic effects towards aquatic life. High concentrations have lethal effects on all life and low concentrations have been shown to have sublethal effects on fishes. Waller and Cairns<sup>(1)</sup> in 1972 showed that zinc concentrations as low as 0.054 ppm in soft water had avoidance effects on young salmon.

Because of these toxic effects<sup>(2)</sup>, all metal containing effluents regardless of their origin should be treated prior to their discharge to the environment.

Since metals are a valuable non-renewable resource, efforts have been made in many industrial sectors to recover and revert the valuable materials into consumer products. Metal recovery from wastewater sludges has generally been neglected because of the lack of suitable recovering technology. Table I lists some of the metals found in wastewaters, their source, and their commercial market value.

#### 2.1. SOLUBLE METALS FROM PRIMARY INDUSTRIAL ACTIVITIES

Primary industrial activities which contribute non-ferrous heavy metals to the environment include mining and milling of ore, smelting of concentrates, and refining of impure metal in order to produce a raw material for secondary industries.

TABLE I

METALS FOUND IN WASTEWATERS, THEIR SOURCE, ESTIMATED ANNUAL DISPOSAL, AND THEIR COMMERCIAL VALUE \*

SOURCE	METAL	ESTIMATED DISPOSAL		\$/lb	COMMERCIAL VALUE	
		1b/YEAR			ANNUAL DISPOSAL \$/YEAR	
		CANADA	U.S.A.		CANADA	U.S.A.
MINING	Zn	-	-	0.38	-	-
"	Cu	-	-	0.65	-	-
"	Ni	-	-	2.20	-	-
METAL	Zn	300,000	6,000,000	0.38	114,000	2,280,000
FINISHING	Cu	245,000	4,900,000	0.65	159,000	3,185,000
	Ni	1,115,000	22,300,000	2.20	2,453,000	49,060,000
	Cd	23,000	460,000	3.00	69,000	1,384,000
		1,683,000	33,660,000		2,795,000	55,909,000
	Cr as	600,000	12,000,000	0.05	30,000	600,000
	Cr <sub>2</sub> O <sub>3</sub>					
TOTAL		2,283,000	45,660,000		2,825,000	56,509,000

\* Industrial Survey by Environment Canada and extrapolation of U.S. data from Canadian data.

### 2.1.1. MINING

Most of the non-ferrous metals mined in Canada are found as sulphide deposits, that is the metal of interest is tied up in the rock matrix as a sulphide. Ores rarely contain only the metal of interest, but are a mixture of various elements invariably iron sulphide. Once the mineral is exposed, the sulphide, especially the iron sulphide, can undergo oxidation. According to Hawley,<sup>(3)</sup> this oxidation may proceed either chemically or microbially.

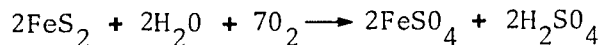
#### 2.1.1.1. CHEMICAL OXIDATION OF SULPHIDES

When the natural sulphuritic material in the form of a sulphide, (and usually in combination with iron), is exposed to the atmosphere (oxygen), it can theoretically oxidize in two ways with water (or water vapour) as a limiting condition:

a) Assuming the process takes place in a dry environment, an equal amount of sulphur dioxide will be generated along with the formation of water soluble ferrous sulphate:

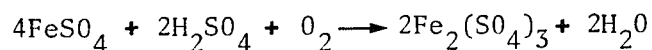


b) If, however, the oxidation proceeds in the presence of sufficient quantity of water, then the direct formation of sulphuric acid and ferrous sulphate in equal parts results:



In moist mining environments the above reaction is favoured.

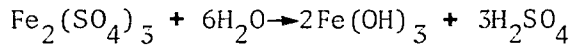
The ferrous sulphate in the presence of sulphuric acid and oxygen oxidizes to ferric sulphate:



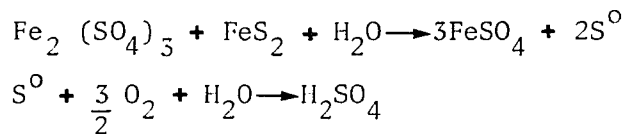
Here water is not limiting since it is not required for the reaction, but is rather a byproduct of the reaction. Most evidence seems to indicate a specific bacterium Thiobacillus ferrooxidans is responsible

for accelerating the oxidation of the ferrous iron to the ferric state.

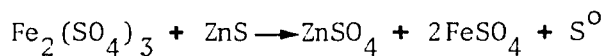
The ferric iron usually hydrolyzes or combines with hydroxyl (OH<sup>-</sup>) ions of water (HOD) to form ferric hydroxide. As the ferric hydroxide is formed it precipitates and forms sulphuric acid as a byproduct.



However, the ferric ion can also enter into an oxidation-reduction reaction with iron sulphide whereby the ferric ion "back-triggers" the oxidation of further amounts of sulphuritic materials to the sulphate form, thereby accelerating the acid forming process"



Thus, oxidation of iron sulphide generates the well known acid mine drainage problem. The leaching and backtrigger reaction may also react with other minerals, thus releasing non-ferrous metals which do not hydrolyze and precipitate in acid solutions



The presence of non-ferrous heavy metals in acid mine drainage enhances its toxicity during uncontrolled discharge to the receiving environment.

#### 2.1.1.2 MICROBIOLOGICAL OXIDATION OF SULPHIDES

The bacterium Thiobacillus ferrooxidans has adopted itself to live and grow in the strongly acidic environment (pH values of 1.5 to 3.0) which results from the oxidation of sulphides and in the presence

of many heavy metals which are released into solution from minerals during the oxidation process.

Thiobacillus ferrooxidans are rather unique bacteria. Their activity is rather independent of temperature and they use atmospheric carbon dioxide as their sole source of carbon necessary for the generation of cellular material. These bacteria obtain their energy solely by the oxidation of inorganic materials such as ferrous iron or sulphur in the form of elemental sulphur or as metallic sulphides. Thus, these bacteria are active leaching agents wherever a sulphide substrate, oxygen, carbon dioxide, water, and certain nutrients make up a suitable environment.

Thiobacillus ferrooxidans convert the sulphide to sulphate, and with the disruption of the solid matrix, the metal ions go into solution. The metals remain in solution as water soluble sulphates, although iron may subsequently precipitate as the hydroxide or basic sulphate. The hydrolysis of ferric sulphate produces sulphuric acid along with a precipitate (hydroxide or basic ferric sulphate). The pH tends to stabilize near 2 due to the resolution of the ferric precipitate.

This acid generation and metal solubilization do not only occur in mines, but also in tailings ponds, and thus, it poses a very real post abandonment problem for most mine properties.

Not all sulphide mineral mines have acid mine drainage problems. If the natural basicity of the rock is high enough to neutralize the generated acid, then the problem may be minimal or even non-existent. Duncan and Waldon<sup>(4)</sup> have designed a series of simple tests to assess the acid generation potential of a mineral deposit.

Ore beneficiation (or milling) to produce a sulphide concentrate also releases heavy metals by mechanical action on the ore and by milling reagents used to suppress or enhance the floatation characteristics of certain sulphides.

#### 2.1.2. SMELTING AND REFINING

The conversion of these ores or concentrates into their respective metals by smelting and refining produces considerable amounts of soluble metals (up to 6 pounds per ton of metal produced). Many of the concentrates contain hazardous trace elements which are liberated during the roasting operation (conversion of sulphide to oxide). These elements, such as mercury, cadmium, and selenium have a high vapour pressure, and they are released to the gas phase and subsequently scrubbed out during gas cleaning operations.

Most operators will either recycle the smelter and refinery effluent into the tailings pond, release the effluent directly, or precipitate the soluble metal salts in treatment plants prior to discharging the effluent. Many of the hazardous trace elements are not removed by the currently employed lime treatment technology.

Currently in 1976, the precipitate or sludge containing the heavy metals is being disposed of by landfilling, by impoundment in specially constructed basins, or by discharging into the tailings pond.

Most operators have recognized that future sludge disposal will be a serious problem because of the chemical and physical characteristics of the sludge. Most operators also have realized the value of the contained metal, and they are actively working on feasible means of recovery, even to the point of chemically separating the metals, preci-

precipitating them as sulphides and reverting these sulphides to the smelter<sup>(5)</sup>.

### 2.1.3. TREATMENT TECHNOLOGY FOR EFFLUENTS FROM PRIMARY INDUSTRIES

The effluent treatment technology employed for the mining, ore beneficiation, and metal producing industries is essentially the same, namely pH adjustment to promote neutralization and metal precipitation.

Each metal has a characteristic pH where the formed metal hydroxide has the lowest solubility. Figure 1 shows the solubilities of various metal hydroxides as a function of pH. Thus, to treat an effluent containing several metals for total metal removal is impractical and costly since it requires several pH adjustments and settling steps. Instead, a pH range is chosen where most metals precipitate to specified low levels to produce a non-toxic effluent. Most mine effluents usually contain iron in addition to non-ferrous heavy metals. Iron promotes coprecipitation of several elements, thus lowering metal content in the effluent below that expected from precipitation without the presence of iron.

Smelter and refinery effluents usually do not contain large amounts of iron, but do contain cadmium, mercury and selenium which respond poorly or not at all to hydroxide precipitation. It is quite evident that certain streams require a different treatment technology in order to produce an acceptable effluent. Many regulatory agencies and operating companies are currently addressing the problem of trace element removal from wastewater streams. Some processes which are under consideration are:

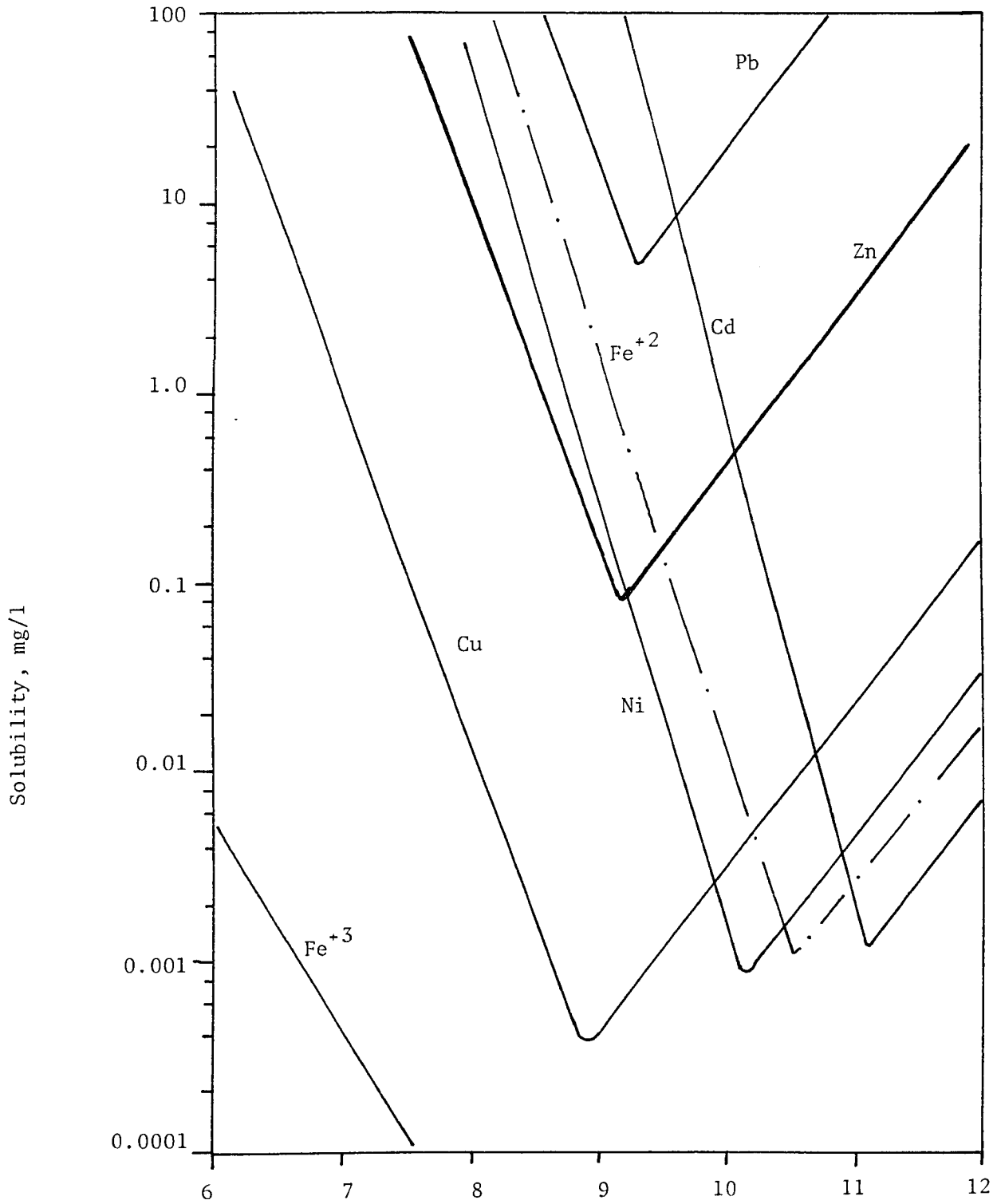


Figure 1. Theoretical solubilities of metal ions as a function of pH.

- sulphide precipitation
- ion exchange
- cementation
- electro dialysis
- reverse osmosis

Reagents usually considered for pH adjustment and hydrolysis are calcium carbonate, caustic soda, soda ash and lime.

Calcium Carbonate (limestone) is a desirable reagent from a cost point of view, but is sluggish for metal hydrolysis and pH adjustment due to the coating action of the precipitates on the limestone particles.

Reagent utilization is poor and hardly ever exceeds 31 per cent. The cost of limestone in bulk loads is about 0.5 cents per pound.

Caustic soda (sodium hydroxide) is desirable but uneconomical for large consumers. Caustic soda in bulk loads is about 6.5 cents per pound.

Soda Ash (sodium carbonate) like caustic soda is desirable but uneconomical for large consumers. It is highly reactive for pH adjustments and metals are precipitated as carbonates, which usually have a lower solubility than their hydroxides. In bulk loads soda ash costs about 4.0 cents per pound.

Lime (calcium hydroxide) is the most commonly used reagent because of its low cost and relatively high reactivity. It is seventy-five times more soluble than calcium limestone on a comparable basis. Lime solutions easily develop pH values as high as 11, whereas limestone may only attain a pH of 8 to 9. In bulk loads, lime costs about 1.75 cents per pound.

#### 2.1.4. SLUDGE DISPOSAL FROM PRIMARY INDUSTRIAL ACTIVITIES

The use of lime produces a sludge containing heavy metals as hydroxides, calcium sulphate and some unreacted lime. Storage or disposal of these sludges poses a serious problem. Some operators deposit

these precipitates into their tailings pond where they may redissolve if the tailings pond ever becomes acidic, which can happen during post abandonment of the mine property. Some sludges are landfilled, thus posing a solid waste and a leaching problem. Some companies successfully feed small amounts to the smelter where the basemetal content is recovered and unwanted calcium sulphate slagged off, while others store the sludge with the objective of eventually recovering the basemetal content. One company in Japan<sup>(5)</sup> is actually recovering the contained metal by leaching, followed by sulphide precipitation with sodium hydro-sulphide and recycling of the sulphide cake to a smelter.

Thus, it can be seen that metals can be recovered and recycled in the form of metallic sulphides. Such a process appears to be viable only if cheap hydrogen sulphide could be generated at the site where the soluble metals have to be removed.

#### 2.1.5. CASE STUDY - ACID MINE DRAINAGE

A lead-zinc mine in New Brunswick known as Brunswick No. 12 generates 250 imperial gallons per minute of mine drainage with the following analysis<sup>(6)</sup>.

Pb	-	3.9 mg/l
Zn	-	1158.0 mg/l
Cu	-	10.0 mg/l
Fe	-	1534 mg/l
Total Metals	-	2707 mg/l
Acidity	-	6511 mg/l as CaCO <sub>3</sub>
Sulphate	-	10100 mg/l
Suspended Solids	-	176 mg/l

Pilot treatment plant results indicated a lime demand of 70 lb/1000 Igal and a sludge production of 170 lb/1000 Igal.

Thus, this treatment system consumes 4600 tons of lime annually, and 760 tons of zinc are disposed of.

With an inexpensive source of sulphide, wastewater treatment in this case could be made a profitable operation by recovering the contained non-ferrous metal instead of disposing of it as a sludge.

## 2.2. SOLUBLE METALS FROM SECONDARY INDUSTRIAL ACTIVITIES

Many secondary industrial activities depend on metals and their related chemicals as raw materials. Many of these activities result in soluble metals being discharged to the environment. However, it is generally accepted<sup>(7)(8)</sup> that the largest release of non-ferrous heavy metal is from the metal finishing or electroplating industry.

### 2.2.1. METAL FINISHING

Metal finishing usually involves the application of a coating onto a metal or non-metal surface in order to give the workpiece the required physical, chemical or decorative characteristics.

Most of the unit operations in this industry are chemical in nature and include degreasing, pickling, chemical stripping of metallic coatings, phosphating, chromating, bright dipping, metal colouring, electrocleaning, anodizing, and electro and electroless plating.

#### 2.2.1.1. DEGREASING

Degreasing is a process used to remove soils and foreign matter

from the workpiece. Chemicals used include hydrocarbon solvents, emulsifiable solvents, detergents, alkaline and acid cleaners.

#### 2.2.1.2. PICKLING

Pickling is a process used primarily to remove scale, rust and other oxides, and solder from a variety of metals.

Pickling reagents are usually nitric, hydrofluoric, sulphuric, chromic, acetic and phosphoric acids.

#### 2.2.1.3. CHEMICAL STRIPPING OF METALLIC COATINGS

Stripping is an operation employed to salvage parts which have been rejected as a result of the faulty application of a finish.

Typical stripping baths in conjunction with reverse current include:

- Hydrochloric or sulphuric acid
- Sodium hydroxide or carbonate
- Phosphoric acid with triethanolamine
- Sodium cyanide and Sodium hydroxide
- Nitric acid
- Phosphoric acid and chromic acid
- Nitric acid and hydrofluoric acid

#### 2.2.1.4. PHOSPHATING

Phosphating is a process designed to change a relatively unstable metallic surface into a stable, absorptive non-metallic surface. The surface will also be non-conductive, an important factor in reducing corrosion.

The basic chemicals used are zinc and iron phosphates with phosphoric acid.

#### 2.2.1.5. CHROMATING

Chromating is used on certain metals to produce a coating that is corrosion resistant, a good base for painting or a decorative finish. The chromating bath is always acidic, containing hexavalent chromium compounds such as chromic acid plus organic or inorganic compounds which serve as activators or catalysts.

As the dissolved metal and trivalent chromium contamination increases it is periodically necessary under present technology to dispose of the bath.

#### 2.2.1.6. BRIGHT DIPPING

Bright dipping is a special application of pickling, performed on aluminum, cadmium, copper, steel, zinc and stainless steel. Because of the vigorous chemical action of pickling and bright dipping, a heavy metal load accumulates in the bath and periodic dumping is required.

#### 2.2.1.7. METAL COLOURING

Metal colouring is a special technique used to apply a variety of colouring effects on metals by dips, i.e., antiquing or blueing of gun barrels. Most of the antiquing effects are obtained from alkaline sulphide solutions or thiosulphates. Some colouring formulas contain

copper sulphate, ferric chloride, mercuric chloride, nitric acid and alcohol.

#### 2.2.1.8. ELECTROCLEANING

Electrocleaning is a process used as a final preparation of parts prior to application of the coating. The operation takes place in a heavy duty alkaline solution and the work may be anodic, cathodic or alternating between each condition.

#### 2.2.1.9. ANODIZING

Anodizing is an electrochemical process to produce an oxide on a metal in a controlled manner. The oxide layer acts as a corrosion resistant surface and as acceptor for other finishes. The most commonly used reagents are chromic and sulphuric acids.

#### 2.2.1.10. ELECTRO AND ELECTROLESS PLATING

Electroplating is the deposition of an adherent metallic coating upon an electrode (the workpiece) for the purpose of obtaining a surface with properties or dimensions different from those of the basic metal.

These properties may include improvement in appearance, corrosion protection and wear resistance.

The operation takes place in aqueous solutions containing the metal ion to be plated. The work piece is cathodic, and in most instances the metal ion is constantly replenished from an anode containing

the metal. A notable exception is chromium where the anode is insoluble and metal ions are replenished by addition of chromic acid.

Workpieces may receive single or multiple layers of electro-deposits. If multiple layers are applied then careful rinsing of the previous electrolyte is required to prevent plating bath contamination.

Removing of the electrolyte film results in the loss of soluble metal to the effluent. These losses are called drag out and are replenished by the addition of purchased metal salts to the plating baths. In addition, these baths become contaminated with use and some require periodic dumping to assure a consistently high quality coating.

Electroless plating is a process whereby the desired cation is auto-catalytically deposited onto any immersed surface. This process is widely used to apply a metallic coating onto plastics prior to electroplating. These baths usually contain strong chelating and reducing agents. Once the reducing agent is exhausted, these baths are considered "dead" and are dumped.

#### 2.2.2. METAL FINISHING PLANT EFFLUENT STREAMS

The metal finishing plant effluent streams thus contain heavy metals from both rinse operations and dumps. In addition, there are many highly acidic and alkaline streams contaminated with heavy metal which are discharged on an intermittent basis.

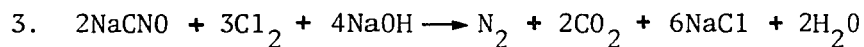
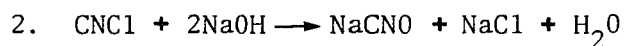
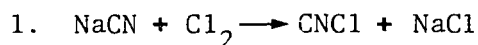
Many of these concentrated waste streams are collected and disposed of by contractors, while other, more dilute streams are either treated for heavy metal removal or are directly discharged to a municipal sewer system.

### 2.2.2.1. EFFLUENT TREATMENT

Simple pH adjustment of the metal finishing effluent does not always result in adequate metal removal because some effluents contain cyanides and hexavalent chromium.

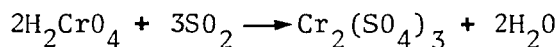
Many plating processes use alkaline metal cyanide baths. Thus the resulting rinse water contains cyanide as well as heavy metals. Since cyanide is a strong complexing agent, this chemical has to be destroyed by oxidation before the metals can be precipitated as hydroxides. The oxidation method most commonly employed is alkaline chlorination, whereby chlorine gas or sodium hypochlorite are added to a mix tank containing the cyanide effluent.

The reaction is believed<sup>(7)</sup> to take place in three steps:



Once the complex cyanides are destroyed, the metals are precipitated as hydroxides.

Effluents containing hexavalent chromium require chromium reduction to the trivalent state since Cr(VI) is alkaline soluble. A number of reducing agents are suitable for this reduction, however the chemicals most frequently used are sulphur dioxide and sodium metabisulphite. The Cr(VI) reduction reaction is believed to be as follows<sup>(7)</sup>:



Once the chromium has been reduced, it can be precipitated as a hydroxide by pH adjustment with an alkali.



Other metals will similarly precipitate as hydroxides, however, the extent of precipitation of course depends on the pH and the metal

precipitated since each metal hydroxide has its own pH range where the solubility is lowest, See Figure 1.

The value of the precipitated metals is forcing operators to consider ways of extracting and recycling metals and of course consider alternate treatment technology such as ion exchange, evaporation and reverse osmosis. However, most operations are much too small to even consider the large capital investment required for such recoveries and recycles.

Precipitation of metal hydroxides produces sludges which require careful disposal in order to minimize the environmental impact over long periods of time.

#### 2.2.2.2. DIRECT DISCHARGE TO MUNICIPAL SEWERS

Some municipalities are allowing metal finishing operations to discharge their effluents containing heavy metals directly into the sanitary sewer. It is generally accepted that some of these metals are adsorbed onto the organic sewage matter and thus become precipitated during the sewage treatment. The remainder are discharged along with the sewage plant effluent to the receiving waters. Abbott<sup>(9)</sup> reports that the experience of the Ministry of the Environment of Ontario is that with the exception of nickel, about 70-80 per cent of the heavy metals are removed during sewage treatment.

It is well known that heavy metals reduce or inhibit microbiological activities, thus, heavy metals can interfere with the aerobic and anaerobic biological treatment processes used in sewage treatment plants. Black<sup>(10)</sup> reports, that a model sewer use bylaw, prepared jointly by the Ministry of the Environment and the Municipal Engineers Association,

limits the concentration of most metals discharged to municipal sewer to 5 mg/l in order to minimize the inhibitory effects of heavy metals on biological activity at the treatment plant.

Thus, many of the heavy metals discharged to the sewer report to the solids or sludge phase. Traditionally, sewage sludge is considered to be a soil conditioner with good nutrient value. However, the application of heavy metal containing sewage sludge onto agricultural soil poses serious problems of heavy metal contamination of the soil and heavy metal poisoning of the food chain.

Although all our vegetation plants requires trace amounts of heavy metals as micro nutrients, higher concentrations derived from sludges can become toxic and result in reduced plant growth. Bates<sup>(11)</sup> reports on numerous heavy metal poisonings of soils experienced by various authors and countries.

Indications are that many heavy metals are taken up and concentrated by plants. Van Loon<sup>(12)</sup> shows that certain vegetation grown on sludge containing soils contain up to four times as much heavy metal than control samples.

Therefore, if metal finishing effluent is discharged directly to the sewer, the sewage sludge may not be acceptable for land application.

### 2.2.3. DISPOSAL OF METAL CONTAINING SLUDGES

#### 2.2.3.1. MUNICIPAL SLUDGE DISPOSAL

Many municipalities realize that disposal of metal containing

sewage sludge on agricultural land may soon not be acceptable.

A number of alternate disposal means exist, namely:

- a) Municipality owned sludge disposal sites. The municipality purchases land to be used purely as a disposal site for sewage sludges, as has been done for such cities as Chicago and Denver. In the case of Chicago the sludge is barged 120 miles and then piped an additional 40 miles to old strip mine areas. The sludge is used for land reclamation, however, the problem of heavy metal leaching, runoff and food chain poisoning still exist.
- b) Sanitary landfills. Disposal of sewage sludge into sanitary landfill is a very attractive alternative since almost every municipality has a landfill site. However, sludges are not always suitable for such disposal since they contain in excess of 90 per cent water and have the potential of seriously contaminating the surface and groundwaters near the site.
- c) Incineration. Incineration appears to be economically feasible for large cities. The resulting ash still contains the heavy metals and must be suitably disposed of.
- d) Reduction of heavy metals in sewage sludge. The most obvious alternative appears to be the reduction of heavy metals in the sludge by controlling the metals at the source, and applying the low metal sewage sludge to agricultural land as soil conditioner.

#### 2.2.3.2. DISPOSAL OF METAL FINISHING SLUDGES

Metal finishing sludges are a result of wastewater treatment by pH adjustment with an alkali to promote metal hydroxide precipitation.

Since these hydroxides can easily redissolve, careful disposal practice is necessary to minimize the impact on the environment. Alternatives are:

- a) Deepwell disposal. Many sludges and strong wastes in Ontario are collected by trucking contractors and disposed of by injection into deep wells. It is not certain whether these sludges will be confined to the injected area or if they will move with the groundwater to contaminate other areas.
- b) Landfill disposal. Landfill disposal of dewatered sludges is economically much more attractive than deepwell disposal. However, the hydroxides can easily redissolve in the landfill leachate and thus threaten the receiving environment.
- c) Lagooning. Because of the lack of proper disposal facilities lagoon storage of metal wastes is practiced by some companies. Thus EPA<sup>(13)</sup> reports that one metal finishing operation in Nassau County N.Y., stored metal finishing wastes in a lagoon from where it contaminated the groundwater.
- d) Metal recovery. If metals are removed from the sludge for the purpose recycling, then only the inert constituents of the sludge will have to be disposed of by landfilling. The metal itself is a vital and valuable raw material, and if removed from the sludge and recycled, it would not have a deleterious effect on the environment.

### 2.3. METAL RECOVERY TECHNOLOGY REVIEW

Because of the value and disposal problems of sludges containing metals, many private companies and government agencies are addressing the ultimate disposal alternative of recovery and recycle.

Many processes to facilitate such recovery have been and are being investigated. Some of the processes under consideration are as follows, and can be divided into two groups, namely those that recover metals from sewage sludge and those that recover metals from metallic hydroxide sludges.

### 2.3.1. RECOVERY OF METALS FROM SEWAGE SLUDGE

Considerable amount of work has been done to recover metals and phosphates from sewage sludges. Scott and Horling<sup>(14)</sup> developed an acid leach process to accomplish this recovery. This process uses a strong acid leach followed by differential hydroxide precipitation or solvent extraction if phosphates are to be recovered. The report does not recommend means to recover metal from the hydroxide sludge, nor does it address the economics of such a recovery. Oliver and Carey<sup>(15)</sup> attempted direct electroplating with fluidized electrodes from leached sludge. They report that a pH of 1.5 was required, and acid costs were on the order of \$41 to \$77 per ton of dry solids. The report concludes that metal recovery from sludge, or sludge incinerator ash is not economically viable. Diosady<sup>(16)</sup> also attempted metal and phosphate recovery from incinerator ash. He concludes that the heavy metals are present as refractory oxides and are difficult to process for recovery.

### 2.3.2. RECOVERY OF METALS FROM WASTE WATER TREATMENT HYDROXIDE SLUDGES

A variety of processes have been developed and evaluated to produce a recoverable metal or metal salt from heavy metal containing wastewater treatment sludges.

FMC's Fibers Division at Fort Royal, Va., had accumulated about

80 million pounds of zinc as zinc hydroxide/calcium sulphate sludge in a lagoon. Cosgrove, et al.<sup>(17)</sup> report that the company has successfully developed a leaching and impurity precipitation process to recover the valuable zinc as zinc sulphate solution to be re-used in the company's Rayon manufacturing process.

It has been reported<sup>(18)</sup> that the Osaka Prefectural Industrial Research Institute in Japan has developed a chemical treating process to separate and recover such valuable metals as chromium, copper, nickel, and zinc contained in mixed sludges discharging from plating factories. The treatment process is as follows: First, trivalent chromium and iron are dissolved and separated from bivalent metals (Cu, Ni, Zn) which become insoluble oxalate precipitates when the sludge is dissolved in oxalic acid. Then iron and chromium are separated as hydroxides by adjusting the pH. The bivalent oxalate precipitate is treated with caustic soda to extract copper, nickel and zinc as hydroxides. The article further suggests that the hydroxides be shipped to metal refineries for further purification. The economics of this process are not available. Reinhardt<sup>(19)</sup> reports that MX Processers AB in Sweden are making efforts to commercialize waste metal recovery based on solvent extraction technology. This process is reportedly applicable to all types of wastes including pickling acids and sludges containing metals. The process produces pure metal hydroxides which may be further converted into other salts or into metals by electro-winning. Reinhardt presents several flow schematics but does not discuss economics beyond the mention that a plant producing 500 tons of metals would probably break even if the sludge is delivered to the plant free of cost.

A detailed study on the reclamation of metals from sludges was done by Battelle Columbus Laboratories<sup>(20)</sup>. The study included an extensive literature survey to determine the state of the art regarding the

generation, disposal, and recovery treatment practice relevant to metal finishing sludges, and to identify metal recovery processes possibly applicable to those sludges.

The extraction of metal values from waste sludges by various leaching agents, and the recovery of metal values by techniques including electrowinning, cementation and liquid-liquid ion exchange were studied at bench scale during the program.

The report concludes that sludges are readily leachable, however, the metal recovery technology available and assessed does not make metal recovery economically viable.

Environment Canada is currently undertaking a similar study to investigate technology and economics of metal recovery from metal finishing sludges.

The Oshio Copper Mining and Smelting Company<sup>(5)</sup> in Japan had accumulated metal hydroxide/calcium sulphate sludge from its mine-drainage water treatment plant. Realizing the value of the contained metal (up to 4 per cent Cu), the company developed a process to leach the copper, precipitate it as a sulphide with sodium hydrosulphide and return the sulphide cake to the smelter for metal recovery.

A co-operative waste acceptance/treatment organization in West Germany known as Ruhrverband<sup>(21)</sup> will dispose of heavy metal sludges in separate disposal areas for eventual recovery. High metal content sludges and solutions are given away for free to recycle companies.

Although most of the above processes have been deemed as uneconomical, the following research work will develop and at bench scale demonstrate a process that will be both technically and economically feasible.

Metals are mined in Canada on a large scale from sulphide deposits. Smelters are set up to accept sulphide concentrate, therefore,

if metals from sludges can be recovered as a crude concentrate containing metallic sulphides, these metals could be reverted as smelter feed. The economics of such a process depend on a cheap source of hydrogen sulphide.

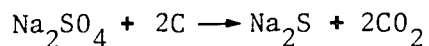
#### 2.4. HYDROGEN SULPHIDE GENERATION

Hydrogen sulphide and its associated sulphide compounds are of great industrial importance. Hydrogen sulphide is generally derived as a byproduct of fuel gas sweetening or petroleum desulphurization.

Sulphides can also be derived chemically or microbially by the reduction of inorganic or organic sulphur compounds.

##### 2.4.1. CHEMICAL SULPHIDE PRODUCTION

Various ways of producing sulphide compounds are available, for example, sour gas recovery from fuel as hydrogen sulphide or inorganic sulphides. High pressure pyrolytic reaction of sulphur and fuel produces hydrogen sulphide. Sodium sulphate (or other sulphates) can be reduced chemically with coal to produce sulphide.

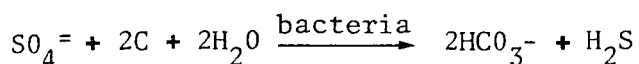


The reduction requires drastic conditions (850°C) and specially designed furnaces.

Because of the high cost of producing and distributing a highly toxic sulphide reagent, this chemical is often considered uneconomical for water treatment and metal recovery.

##### 2.4.2. MICROBIAL SULPHATE REDUCTION

The production of sulphides in sewers by biological activity is a well known fact. The major amount of sulphide results from the reduction of inorganic sulphur compounds, mainly sulphate. Microbial sulphate-reduction is a process in which bacteria of the species Desulfovibrio desulfuricans (also called Desulfatomaaculum desulfuricans) utilize sulphates as an electron acceptor in the oxidation of organic matter. Sulphate, in which sulphur is in the +6 oxidation state is reduced to sulphide, in which the sulphur is in the -2 oxidation state. Biodegradable organic compounds are simultaneously oxidized to carbon dioxide. The following reaction illustrates the process:



where C = biodegradable organic carbon.

Conditions which promote sulphate reduction in sewers were investigated by Pomeroy, et al.<sup>(22)</sup>, and were found to be sources of sulphate, biodegradable organics, and an anaerobic environment.

Lawrence and McCarty<sup>(23)</sup> in 1965 showed that microbially generated hydrogen sulphide could be used to prevent heavy metal toxicity in anaerobic digesters, instead of adding stoichiometric amounts of sulphide as suggested by Masselli, et al.<sup>(24)</sup>. Lawrence and McCarty operated a series of laboratory anaerobic digesters to which various amounts of metal sulphates were added. The daily gas production over a 60 day run was virtually the same as the control, indicating no heavy metal toxicity resulted from the heavy metal sulphates. However, when chloride was substituted for sulphate, gas production dropped almost instantly showing heavy metal toxicity to the anaerobic biomass.

King, et al.<sup>(25)</sup> conducted an intensive study into acid strip mine lake recovery. It was concluded that acid lakes recover because of the microbial action converting sulphate to sulphide and alkalinity.

The alkalinity is consumed to neutralize the acid while the sulphide reacts with heavy metals to form a metallic sulphide precipitate or it escapes to the atmosphere as  $H_2S$ .

Pugsley, et al.<sup>(26)</sup> studied ways and means to remove heavy metals from acid mine drainage in Colorado. They investigated hydroxide precipitation and sulphide precipitation both with chemical sulphide and bacteriologically produced  $H_2S$ . Pugsley concluded that if anaerobic conditions and sufficient retention time could be maintained, microbial sulphate reduction for metal removal from mine waters might be feasible.

Middelton and Lawrence<sup>(27)</sup> produced the first mathematical model of the sulphate reduction reaction. Determination of the kinetic coefficients was based on acetic acid as the source of organic carbon and organic carbon being the growth limiting substance.

Since microbially produced sulphide is of relatively low cost, it may lend itself to the economic recovery of metals from wastewater and wastewater sludges.

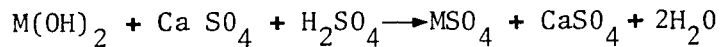
## CHAPTER THREE

### 3. THEORETICAL CONSIDERATIONS

The recovery of metals from metal finishing sludges involves a number of individual steps, namely, leaching of sludges; microbial sulphate-reduction; utilization of the produced sulphide to precipitate metals; and the recovery of metallic sulphide concentrate as base metal smelter feed.

#### 3.1. SLUDGE LEACHING

Metal finishing sludges are usually hydroxide sludges resulting from metal precipitation with alkali such as caustic soda or lime. These sludges are readily soluble in sulphuric acid, with the calcium sulphate remaining as an insoluble precipitate.

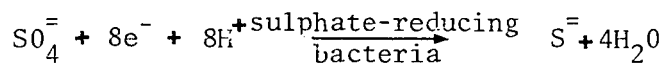


The rate of leaching is dependent on pH and on the soluble metal concentration. Undesirable impurities such as iron can be removed from the leach liquor by pH adjustment. Careful pH control in a fairly dilute liquor can produce a ferric hydroxide precipitate low in entrained heavy metal and suitable for disposal.

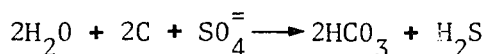
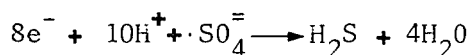
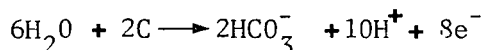
#### 3.2. MICROBIAL SULPHATE REDUCTION

The principle organism involved in sulphate reduction is the bacterium Desulfovibrio desulfuricans. This organism is a strict mesophilic anaerobe. It derives its energy for synthesis and cell maintenance from the metabolism of organic matter, and uses sulphate as its

terminal electron acceptor. The reduction of sulphates in this process may be expressed by the following equation:



or by the following oxidation-reduction reactions:



The reduction of one mole of sulphur (32g) by this process corresponds to the oxidation of eight equivalents of organic matter, or about 64 g on a COD or oxygen equivalent basis.

Since each bacterial cell can be viewed as a chemical reactor where this oxidation-reduction reaction takes place, the volumetric reaction rate is directly proportional to the bacteria concentration. The bacterial growth model used to study the kinetics <sup>(28)</sup> of this reaction was the Monod function which relates the organic carbon utilization and hence the sulphate reduction, and bacteria concentrations:

$$r_S = - \frac{kSX}{K_S + S}$$

where  $r_S$  = volumetric reaction rate of organic carbon,  $\text{M/L}^3\text{T}$ ;

$k$  = maximum specific rate of organic carbon utilization,  $\text{T}^{-1}$ ;

$S$  = soluble organic carbon concentration,  $\text{M/L}^3$ ;

$X$  = bacteria concentration,  $\text{M/L}^3$ ; and

$K_S$  = half velocity coefficient,  $\text{M/L}^3$ .

The bacteria growth rate can be related to carbon utilization by the following function:

$$r_X = - Yr_S - bX$$

where  $r_X$  = volumetric rate of bacterial cell growth,  $\text{M/L}^3\text{T}$ ;

$Y$  = yield coefficient,  $\text{M/M}$ ; and

$b$  = decay coefficient,  $\text{T}^{-1}$ .

The bacteria concentration can be controlled to give maximum sulphide production by controlling the solids retention time in mixed flow reactor. If there is no recycle of solids to the reactor, then the bacteria mass is controlled by the hydraulic retention time of the reactor.

Table II gives the steady-state equations of bacterial growth for a mixed flow reactor where organic carbon is considered to be the growth limiting substance.

TABLE II

STEADY STATE RELATIONSHIPS FOR MIXED BIOLOGICAL REACTOR WITHOUT SOLIDS RECYCLE.

---


$$\theta_c = \frac{1}{\mu} = \frac{X}{r_x}$$

$$\theta = \theta_c$$

$$S_1 = \frac{K_s (1 + b\theta_c)}{\theta_c (Yk - b) - 1}$$

$$X = \frac{Y(S_0 - S_1)}{1 + b\theta_c}$$

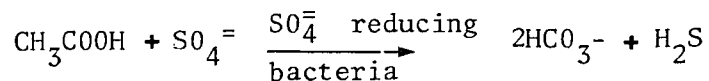
$$-r_s = \frac{S_0 - S_1}{\theta}$$


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where  $\theta_c$  = solids retention time, T;  
 $\theta$  = hydraulic retention time, T;  
 $\mu$  = net specific growth rate of bacteria, T<sup>-1</sup>;  
 $X$  = bacteria concentration, M/L<sup>3</sup>T;  
 $r_x$  = volumetric rate of bacterial cell growth, M/L<sup>3</sup>T;  
 $S_1$  = effluent soluble organic carbon concentration, M/L<sup>3</sup>;  
 $S_0$  = influent organic carbon concentration, M/L<sup>3</sup>;  
 $r_s$  = volumetric reaction rate of organic carbon, M/L<sup>3</sup>T;  
 $k$  = maximum specific reaction rate of organic carbon utilization, T<sup>-1</sup>;  
 $K_s$  = half velocity coefficient, M/L<sup>3</sup>;  
 $Y$  = yield coefficient, M/M; and  
 $b$  = decay coefficient, T<sup>-1</sup>.

In previous studies <sup>(28)</sup> the bacterial mass (X) has been estimated as equal to the experimentally measured volatile suspended solids concentration (VSS) <sup>29</sup>. In systems containing both organic and inorganic suspended solids the experimentally measured VSS can include some inorganic solids, however, most systems have proven the fact that bacterial mass increases with increases in VSS.

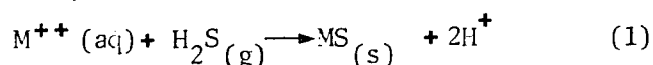
Desulfovibrio desulfuricans bacteria themselves can not utilize long chain biodegradable organic compounds for synthesis and cell maintenance. These bacteria depend on acid forming bacteria to decompose or digest long chain molecules into short chain organic acids (acetic and propionic acid) called volatile acids. These volatile acids in turn are consumed by the sulphate reducers:



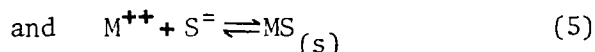
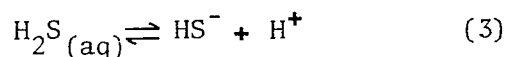
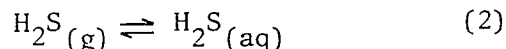
To maintain a production of sulphide, the acid forming and sulphate-reducing bacteria must be in a state of dynamic equilibrium. If the acid production exceeds its consumption, the pH may drop to the point where the sulphate reduction reaction is hindered. Thus, an adequate alkalinity is required as an absorbant for the unconsumed volatile acid.

### 3.3. METALLIC SULPHIDE PRECIPITATION

The effectiveness of H<sub>2</sub>S precipitation as applied to any particular metal is determined by the equilibrium solubility of the metal sulphide formed and the rate at which the equilibrium is approached. In the case of a divalent metal ion (M<sup>++</sup>) precipitation with gaseous H<sub>2</sub>S, the overall stoichiometry can be represented by:



This reaction actually involves four separate equilibria:



The extent to which each of the reactions (2) through (5) is able to proceed is determined by an equilibrium constant. For these reactions the constants are:

$$K_2 = \frac{\{\text{H}_2\text{S}_{(aq)}\}}{\left[ \text{H}_2\text{S}_{(g)} \right] \cdot \gamma \text{H}_2\text{S}} \quad (6)$$

$$K_3 = \frac{\{\text{HS}^-\} \cdot \{\text{H}^+\}}{\{\text{H}_2\text{S}_{(aq)}\}} \quad (7)$$

$$K_4 = \frac{\{\text{H}^+\} \{\text{S}^{=}\}}{\{\text{HS}^{=}\}} \quad (8)$$

$$K_5 = \frac{\{\text{MS}\}}{\{\text{M}^{++}\} \{\text{S}^{=}\}} \quad (9)$$

where  $\{\}$  = thermodynamic activity of the *i*th component in a reaction

$[ ]$  = molar concentration

*i* = activity coefficient of *i* th component in solution

$\gamma$  = mole fraction of gaseous component

$\pi$  = Total pressure in atmospheres

$\gamma$  = Activity coefficient of component in gas phase.

When any reaction (1) is carried out, the equilibrium relations (6) through (9) must be simultaneously satisfied, and through them the equilibrium concentration of the metal ion  $\text{M}^{++}$  may be calculated. In solutions where the concentration of the ion in question is low, no

appreciable error is introduced by substituting molarity for activity. This is valid for the metal ion and sulphide and bisulphide ions, but should be used only as a first order approximation for hydrogen ions, particularly at low pH where the hydrogen ion activity and molarity are appreciable. The activity of a solid phase, regardless of the quantity present in suspension is unity, hence equation (9) can be written:

$$K_5 = \frac{1}{[M^{++}][S^{=}]}$$

and  $K_5$  in this form is the inverse of the solubility product constant  $K_{s.p.}$ . Thus, the solubility product is basic for  $H_2S$  precipitation determination.

$K_3$  and  $K_4$  are the first and second ionization constants of  $H_2S$ .

$$K_3 = \frac{\{H^+\} [HS^-]}{[H_2S(aq)]} = 1.02 \times 10^{-7}$$

$$K_4 = \frac{\{H^+\} [S^{=}]}{[HS^-]} = 1.23 \times 10^{-13}$$

$$K_3 K_4 = \frac{\{H^+\}^2 [S^{=}]}{[H_2S(aq)]} = 1.26 \times 10^{-20}$$

These ionization constants are temperature dependant and their temperature dependancy as graphically demonstrated by Simons,<sup>(30)</sup> is shown in Figure 2.

The microbially generated hydrogen sulphide will achieve equilibrium in solution according to the above equations. According to Henry's law, the aqueous  $H_2S$  will achieve equilibrium with the gas phase resulting in a mass transfer from dissolved  $H_2S$  to gaseous  $H_2S$ . The distribution takes place according to the following equation (Henry's Law):

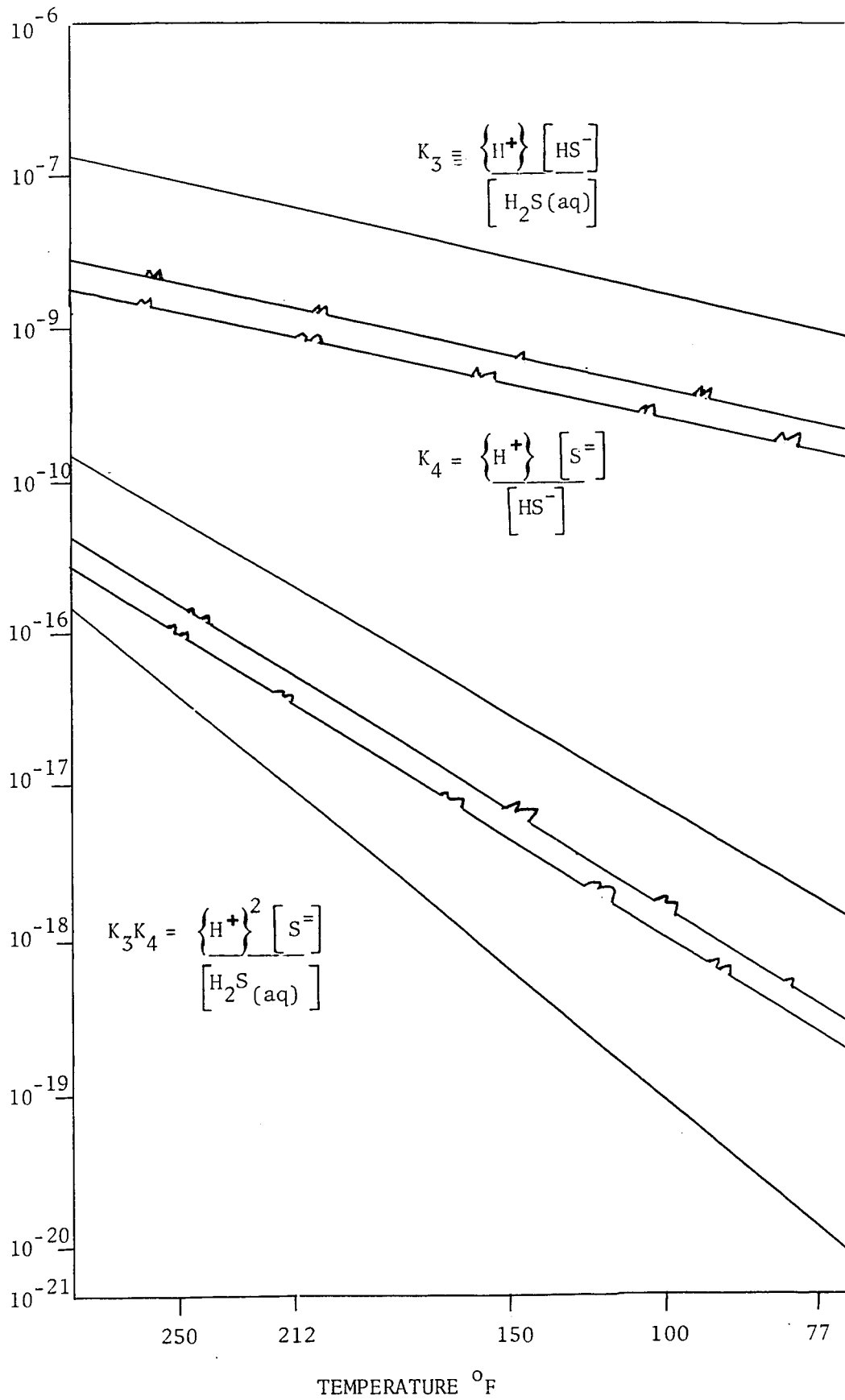


Figure 2

Ionization constants of aqueous Hydrogen Sulphide as a function of temperature

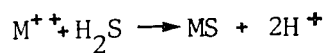
$$[\text{H}_2\text{S}(\text{aq})] = [\text{H}_2\text{S}(\text{g})] \frac{T}{273} \alpha$$

where  $\alpha$  is the absorption coefficient.

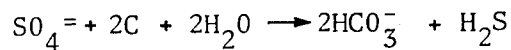
Distribution to the gas phase is of course pH dependant due to the equilibrium shift to or from the aqueous hydrogen sulphide species.

Metal ions introduced into the reactor will consume sulphide ( $\text{S}^-$ ) thus forcing the equilibrium for further hydrogen sulphide ionization and resulting in less release to the gas phase.

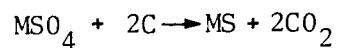
Since hydrogen sulphide is considered an acidic gas, metallic sulphide precipitation is accompanied by a drop in pH.



Thus for every mole of metal precipitated as sulphide, 2 equivalents of acidity are generated. However, during the sulphate reduction reaction two equivalents of alkalinity are generated for every mole of sulphide produced.



This alkalinity reacts with the acidity resulting from the metal sulphide precipitation, and hence, the overall reaction is self sufficient in alkalinity and the only raw materials required are two waste products, namely metal sulphate and biodegradable organic carbon. The overall reaction may be written as:



where C= biodegradable organic carbon.

Metallic sulphides are among the most insoluble metal salts known. Table III shows the solubility products of some common sulphides (30). The value of Ks.p. for some of the metal sulphides as a function of temperature are presented graphically in Figure 3.

TABLE III

SOLUBILITY PRODUCTS OF SOME COMMON SULPHIDES AT 25°C

Metal Sulphide	Log Ks.p.	Ks.p.	
		Components	Value
MnS	- 12.55	$[Mn^{++}] [S^{=}]$	$2.8 \times 10^{-13}$
FeS	- 17.31	$[Fe^{++}] [S^{=}]$	$4.9 \times 10^{-18}$
NiS	- 20.55	$[Ni^{++}] [S^{=}]$	$2.8 \times 10^{-21}$
CoS	- 21.64	$[Co^{++}] [S^{=}]$	$1.8 \times 10^{-22}$
Co <sub>2</sub> S <sub>3</sub>	-125.9	$[Co^{+++}]^2 [S^{=}]^3$	$1.2 \times 10^{-126}$
ZnS	- 24.05	$[Zn^{++}] [S^{=}]$	$8.9 \times 10^{-25}$
CdS	- 26.15	$[Cd^{++}] [S^{=}]$	$7.1 \times 10^{-27}$
PbS	- 27.03	$[Pb^{++}] [S^{=}]$	$9.3 \times 10^{-28}$
CuS	- 35.05	$[Cu^{++}] [S^{=}]$	$8.9 \times 10^{-36}$
Cu <sub>2</sub> S	- 47.70	$[Cu^+]^2 [S^{=}]$	$2.0 \times 10^{-48}$
Ag <sub>2</sub> S	- 49.10	$[Ag^+]^2 [S^{=}]$	$8.0 \times 10^{-50}$
HgS	- 51.89	$[Hg^{++}] [S^{=}]$	$1.4 \times 10^{-52}$

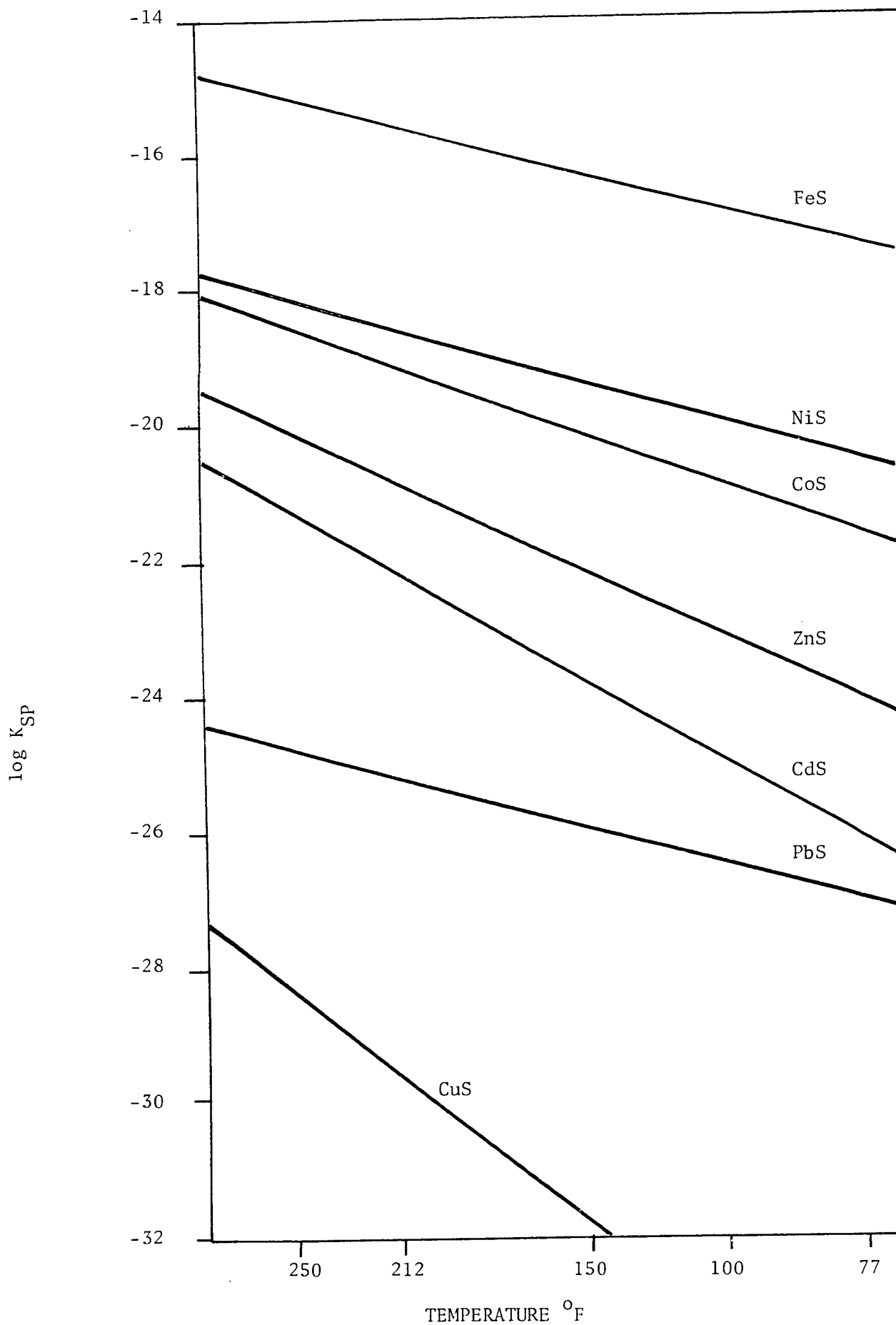
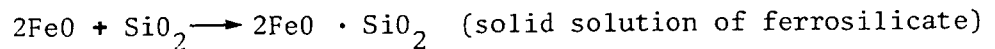


Figure 3  
Solubility product of some common sulphides as a function of temperature

### 3.4. SULPHIDE CONCENTRATE AS BASE METAL SMELTER FEED

Most base metal smelters operating today accept a metal sulphide containing a variety of metals, sulphur and gangue (residual rock). In the case of copper and nickel smelting<sup>(31)</sup>, the concentrate contains substantial amounts of copper, nickel, iron, and sulphur (a host of other elements are present in trace amounts). The concentrate is roasted to convert the iron sulphide to oxide. During smelting the roasted concentrate melts and silica added as flux reacts with iron oxide to form a slag.

The essential reactions are as follows:



The ferrosilicate along with the molton gangue and some undesirable trace elements are disposed of as slag, while the copper and nickel sulphides have settled to the bottom of the furnace bed to form a high grade metal sulphide concentrate known as "bessemer matte". This matte is further processed to produce high grade copper and nickel metals as well as other metal and non-metal byproducts.

A sulphate-reducing reactor producing metallic sulphides could be operated to produce sulphide concentrates containing groups of metal which are acceptable to a base metal smelter, i.e., Cu/Ni and Pb/Zn/Cd.

The slurry leaving the reactor contains metallic sulphides, inerts such as silicates and carbonates and organic solids. After settling, filtering and drying to remove excess water, the solids would be acceptable as smelter feed. The organic residue in the solids is combustible and could serve as a fuel supplement in roasting or flash smelting while the metallic sulphides are recovered in the matte. If the organic residue is undesirable to the smelter or as excess bulk for shipping, the organics can be oxidized to carbon dioxide by employing

high temperature drying of the reactor solids.

### 3.5. CHROMIUM CONTAINING SLUDGES

It is recognized that chromium is not precipitated as a sulphide. The processing and/or recovery of chromium from chromium containing sludges is outside the terms of reference for this research.

## CHAPTER FOUR

### 4. EXPERIMENTAL PROCEDURES

The experimental portion of this study was conducted to demonstrate that sulphate-reducing bacteria could indeed be used in a continuously stirred reactor feeding on primary municipal sewage sludge and heavy metal sulphate solution to produce a metallic sulphide concentrate suitable as smelter feed.

#### 4.1. GENERAL APPROACH

A 6 liter anaerobic reactor was constructed from a 9 liter glass jug, with appropriate apparatus for sampling, feeding and gas collection, as shown in Figure 4 and by pictorial display of the reactor in Appendix I. The reactor was agitated first with a diaphragm gas recirculation pump and later with a magnetic stirrer because the pump seal started to leak. The apparatus was housed inside a constant temperature box, which was controlled at 35°C.

The reactor was seeded with one gallon of digested sludge from Watts Creek Pollution Control Plant in Ottawa. In order to prevent clogging of the feed and sample points, the sludge seed and feed sludges, (primary sewage sludge), were screened through a No. 30 mesh sieve. A synthetic substrate consisting of glucose, sodium sulphate and sodium bicarbonate dissolved in tap water, was added daily till an enriched culture of sulphate-reducing bacteria had been obtained. Within four days the glucose was replaced by primary sewage sludge, while the reactor was operated at a solids retention time of 20 days.

After 10 days of enrichment, the reactor was changed to 15 days solids retention time, and metal sulphate was added daily according to

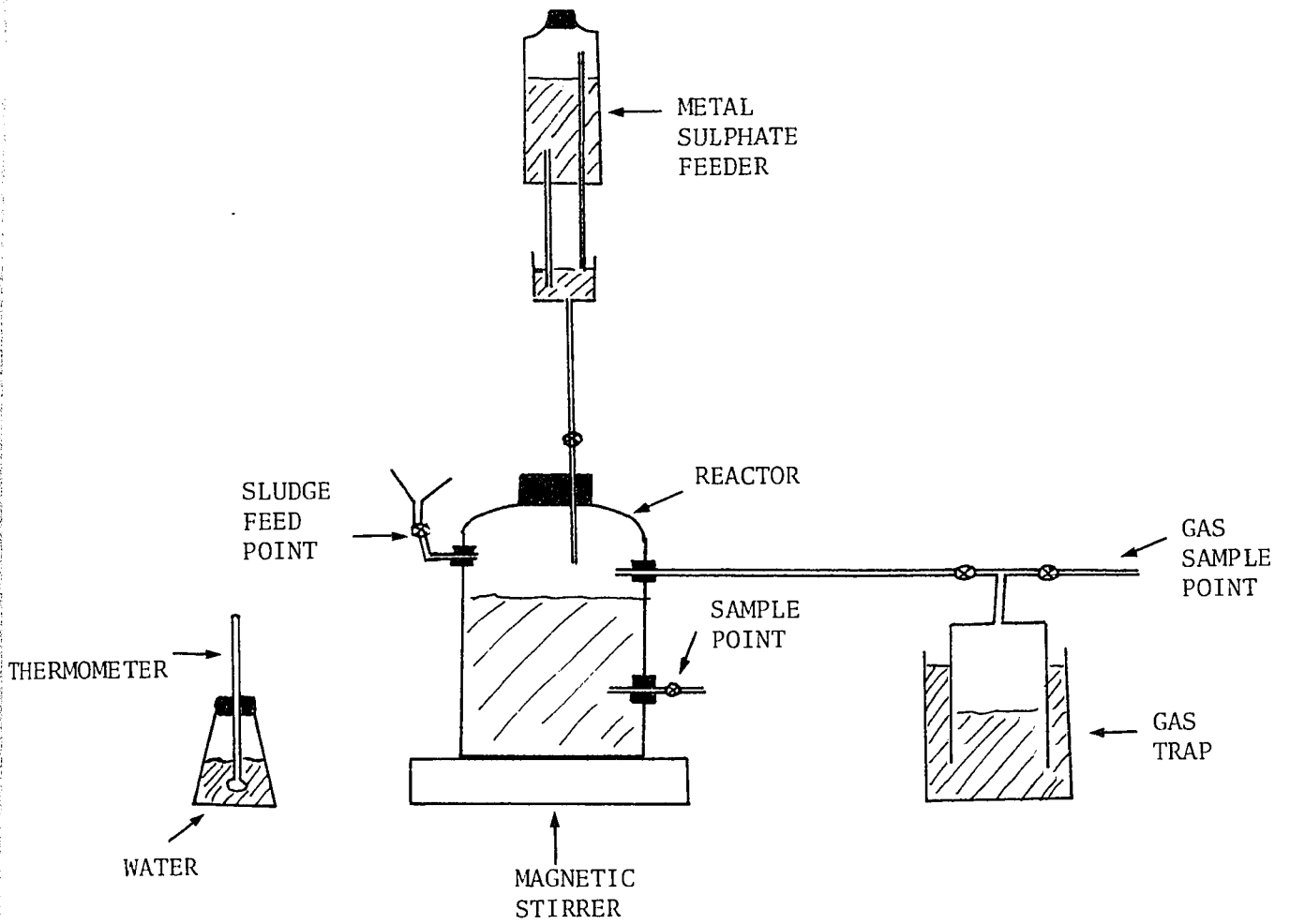


FIGURE 4  
SULPHATE-REDUCING REACTOR SYSTEM

demand. The demand was measured by the total and soluble sulphide in the reactor mixed liquor. The metal feed solution for the first 45 day run consisted of 8 gram per liter zinc as zinc sulphate with 3 grams per liter sodium sulphate. The excess sulphate in the feed was necessary to prevent sulphate depletion in the reactor due to the daily sample withdrawals and the conversion of sulphate to sulphide. The organic feed consisted of screened primary sewage sludge from Watts Creek Pollution Control Plant. After achieving apparent steady-state conditions during the 45 day zinc sulphate run, the metal feed solution was switched to 4 grams per liter copper and 4 grams per liter zinc, as sulphates. The copper feed solution was prepared by leaching previously precipitated copper hydroxide/calcium sulphate sludge with sulphuric acid. Because of the highly acidic feed solution (pH= 2.5), periodic reactor pH adjustment with calcium oxide was necessary.

The two types of reactor sludges were collected for settling rate determination.

#### 4.2. ANALYTICAL PROCEDURES

The following analytical tests were conducted daily to monitor the reactor performance, Standard Methods<sup>(28)</sup> was the analytical reference.

- a) Total reactor solids: Slurry withdrawn from the reactor was weighed into a tared evaporating dish. The water was evaporated on a steambath and the dish and residue dried in a constant temperature oven at 103°C. The dried dish and residue were cooled in a desiccator and then weighed. Total per cent solids was calculated as:

$$\frac{\text{Dry weight} - \text{tare weight}}{\text{Wet weight} - \text{tare weight}} \times 100$$

Standard Methods reports a precision of approximately  $\pm 0.5$

per cent for the total solids concentration used in this experiment.

- b) Reactor volatile solids: the sample from the total solids analysis was ignited at 550°C for 60 minutes, cooled in a desiccator and weighed.

The per cent volatile solids was calculated as:

$$\frac{\text{Dry weight} - \text{ignited weight}}{\text{Wet weight} - \text{tare weight}} \times 100$$

Standard Methods reports a precision of approximately  $\pm 0.5$  per cent for the range of volatile solids used in these experiments.

- c) pH: pH was measured with a pH meter standardized daily.
- d) Soluble reactor COD: A sample of reactor mixed liquor was withdrawn, and to a 50 ml sample, 2 ml of 2N ZnSO<sub>4</sub> solution was added to precipitate any soluble sulphide. The sample was centrifuged at 10,000 rpm for 15 minutes, and the filtered through Whatman GFC paper. A 5 ml sample was pipetted and refluxed for 2 hrs along with a blank in a solution of 10 ml of 0.25 N potassium dichromate, 30 ml sulphuric acid containing silver sulphate and 0.4 g mercuric sulphate. The sample and blank were cooled and the excess potassium dichromate was titrated in the presence of ferroin indicator with standard ferrous ammonium sulphate solution.

The soluble COD was calculated as:

$$\frac{(\text{Volume of FAS of blank} - \text{Volume of FAS of sample}) \times N \text{ FAS} \times 8,000}{\text{Volume of sample}}$$

where FAS= ferrous ammonium sulphate

Standard Methods reports a precision of  $\pm 6.5$  per cent

- e) Soluble reactor alkalinity: a sample of the reactor mixed liquor was withdrawn and 50 ml were measured, centrifuged at 10,000 rpm for 15 minutes and filtered through Whatman GFC paper. The filtrate was titrated with 1N H<sub>2</sub>SO<sub>4</sub> and the aid of pH meter to pH 4.2.

The soluble reactor alkalinity was calculated as:

$$\frac{\text{Volume of acid} \times \text{Normality of acid} \times 1000 \times 50 \text{ mg CaCO}_3}{\text{Volume of sample} \times \text{equivalent}}$$
$$= \text{alkalinity in } \frac{\text{mg CaCO}_3}{\text{l}}$$

Standards Methods reports a precision of about  $\pm 4$  per cent

- f) Total reactor sulphides - a 10 ml sample of reactor mixed liquor was pipetted and placed through a pinch clamped funnel into a stoppered reaction flask. The sample was acidified with 25 ml hydrochloric acid. The liberated hydrogen sulphide was stripped by bubbling carbon dioxide below the surface of the reaction flask. The hydrogen sulphide was absorbed by two in series absorbers, each containing water and 10 ml of 2N zinc acetate solution. After stripping for 1.5 hrs the absorbing solutions were transferred into a beaker and excess standard iodine solution was pipetted to consume to zinc sulphide precipitate. The sample was then acidified and the excess iodine titrated with standard thiosulphate solution in the presence of starch indicator.

The total sulphide concentration was calculated as follows:

Total S= in mg/l=

$$\left[ \text{ml of I}_2 \text{ added} - \text{ml of Na}_2\text{S}_2\text{O}_3 \times \left( \frac{\text{N of I}_2}{\text{N of Na}_2\text{S}_2\text{O}_3} \right) \right] \times \left( \frac{\text{N of I}_2 \times 16000}{\text{Vol. of sample}} \right)$$

Standard Methods does not report the precision of this analysis

- g) Soluble reactor sulphide - To a 30 ml sample of reactor mixed liquor, 5 ml of 6 N NaOH and 2 ml of 6N  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  were added and the sample was slightly agitated. The sodium hydroxide was added to absorb any undissociated hydrogen sulphide and the aluminum chloride to promote rapid settling. The sample was centrifuged at 10,000 rpm for 15 minutes and then filtered through Whatmans GFC paper. The filtrate was diluted and transferred to the gas stripping reaction flask and acidified with 50 ml of concentrated hydrochloric acid. The gas stripping and analytical technique was identical to the one used for total reactor sulphides.

Standard Methods does not report the precision of this analysis

- h) Sodium thiosulphate standardization - To 20 ml of 0.025 N  $\text{K}_2\text{Cr}_2\text{O}_7$ , 2 g KI were added and the solution was acidified with  $\text{H}_2\text{SO}_4$ . The liberated iodine was titrated with sodium thiosulphate in the presence of starch indicator.

$$N_{\text{Na}_2\text{S}_2\text{O}_3} = \frac{V_{\text{K}_2\text{Cr}_2\text{O}_7} \times N_{\text{K}_2\text{Cr}_2\text{O}_7}}{N_{\text{Na}_2\text{S}_2\text{O}_3}}$$

Standard Methods does not report on the precision of this standardization

- i) Iodine standardization - The iodine solution was standardized daily against freshly standardized sodium thiosulphate solution

$$N_{\text{I}_2} = \frac{V_{\text{Na}_2\text{S}_2\text{O}_3} \times N_{\text{Na}_2\text{S}_2\text{O}_3}}{V_{\text{I}_2}}$$

Standard Methods does not report on the precision of this standardization

- j) Ferrous Ammonium sulphate standardization - The ferrous ammonium sulphate solution was standardized daily with acidified standard potassium dichromate solution

$$N_{\text{FAS}} = \frac{V_{\text{K}_2\text{Cr}_2\text{O}_7} \times N_{\text{K}_2\text{Cr}_2\text{O}_7}}{V_{\text{FAS}}}$$

Standard Methods does not report on the precision of this standardization

- k) Standard potassium dichromate solution - 0.025 N  $\text{K}_2\text{Cr}_2\text{O}_7$  solution was prepared by dissolving 1.226 g of previously dried ( $103^\circ\text{C}$ )  $\text{K}_2\text{Cr}_2\text{O}_7$  in water and diluting up to 1,000 ml. Standard Methods does not report on the precision of the preparation of this solution.
- l)  $\text{H}_2\text{S}$  in gas phase - A known volume of gas from the gas trap was drawn through a solution of zinc acetate. The precipitated zinc sulphide was reacted with an excess standard iodine solution, and the excess iodine was backtitrated with standard thiosulphate solution in the presence of starch indicator. The sulphide concentration was calculated as in (f).
- m) Spot tests for metals in the reactor supernatant was carried out according to the spot test techniques described by Feigel<sup>(29)</sup>.

## CHAPTER FIVE

### 5. RESULTS AND DISCUSSION

The objective of this study was to demonstrate that sulphate-reducing bacteria could be used to precipitate metals as metallic sulphides in order to produce a sulphide concentrate suitable as base metal smelter feed. Appendix I shows a pictorial display of the reactor system and products.

The study can be divided into four separate phases, namely:

- culture enrichment
- zinc sulphide production
- copper/zinc sulphide production
- upgrading the reactor slurry into smelter feed

#### 5.1. CULTURE ENRICHMENT

The bacteria seed from the digested sewage sludge acclimated very well with the synthetic substrate of glucose, sodium sulphate and sodium bi-carbonate. Figure 5 shows a time series plot of reactor total sulphide during this phase. An immediate increase in sulphide is seen in this figure. Primary sewage sludge addition commenced on Day 3, and sulphide production decreased until the bacteria had been acclimatized to the new substrate. From Day 5 the sulphide increased and continued to increase even after the addition of zinc sulphate commenced. The lower value on Day 7 was judged an analytical error. Upon initial zinc addition there was a decrease in the rate of sulphide production. This decrease was again considered to be an acclimatization period for the bacteria. Around Day 13 the gas recirculation pump

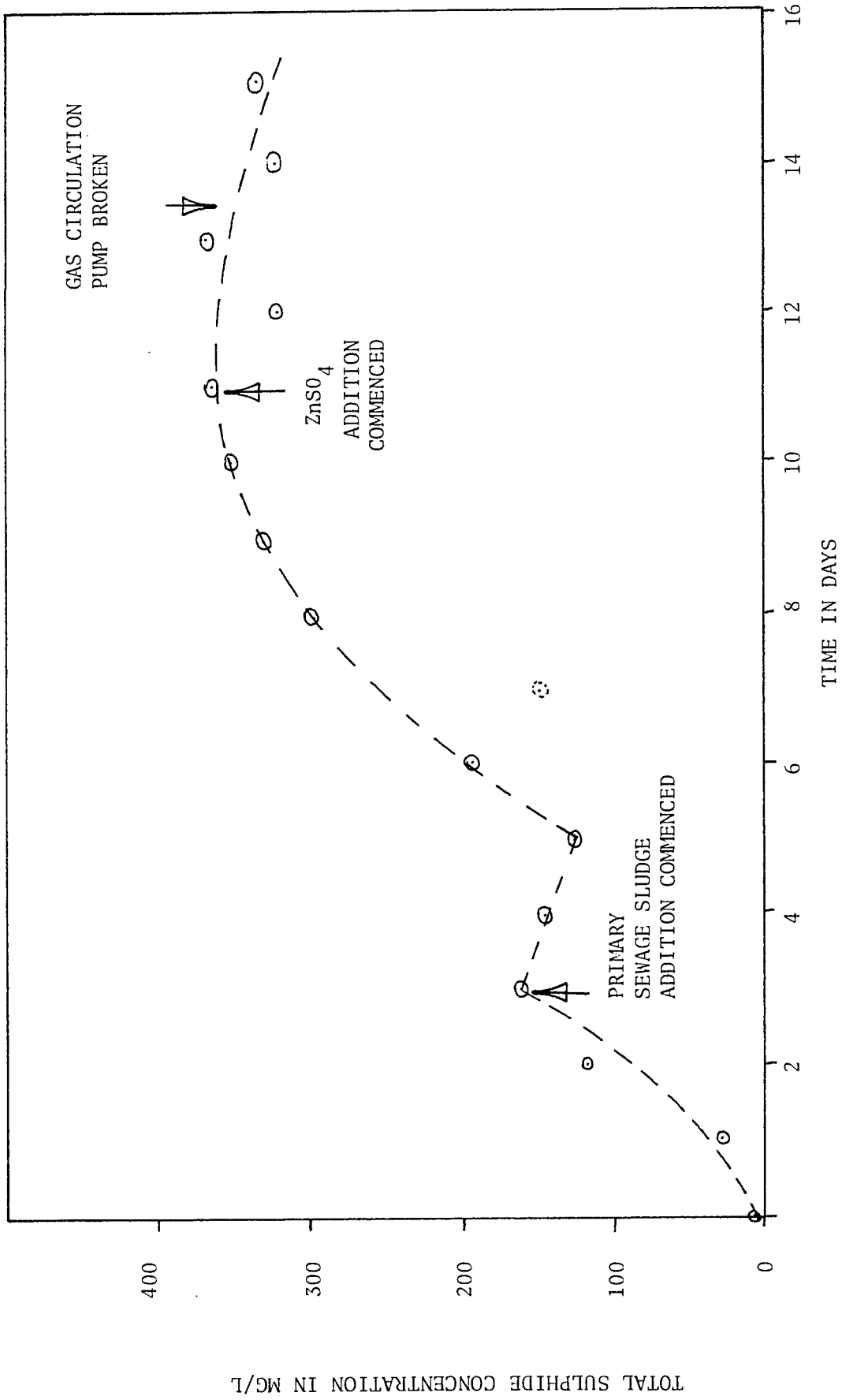


FIGURE 5  
CULTURE ENRICHMENT PHASE: TOTAL SULPHIDE CONCENTRATION AS A FUNCTION OF TIME

diaphragm started to leak and air entered the system. Thus, it is not absolutely certain if the continued sulphide decrease is attributable to acclimatization or temporary aerobic conditions in the reactor as a result of mechanical problems.

Zinc addition continued during the pump outage in order to allow proper bacteria acclimatization.

## 5.2. ZINC SULPHIDE PRODUCTION

Normal reactor operation continued at Day 23, when the gas recirculation pump had been successfully replaced by a heavy duty magnetic stirrer.

The total and soluble sulphides were measured daily and zinc sulphate solution was added according to the available soluble sulphide. On Day 38 an automatic metal sulphate feeder was installed to add a predetermined volume of metal containing feed solution over a 24 hour period. The continuous feed was thought desirable to avoid shock loading of the reactor and perhaps temporary, localized bacteria inhibition due to slug addition of heavy metal sulphate solution.

Figure 6 shows the feeding device which worked on the constant head principle. However, because of the low required flow rates, control was at times difficult. Figure 7 shows the zinc addition in mg Zinc per liter of reactor volume versus time. Over the 34 day period a total of 8600 mg of Zinc per liter of reactor volume was added. The resulting average zinc sulphide production was 253 mgZn/1-day.

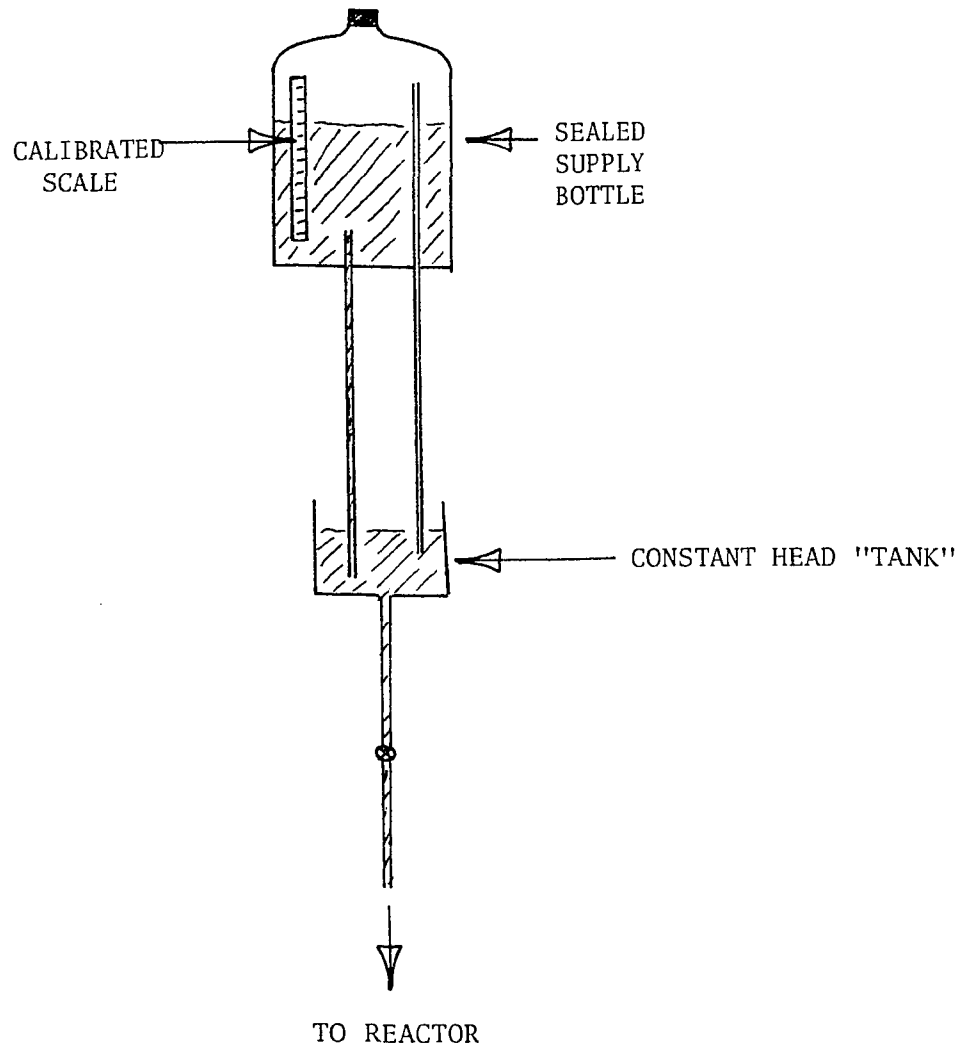


FIGURE 6  
AUTOMATIC FEEDER FOR METAL  
SULPHATE SOLUTIONS

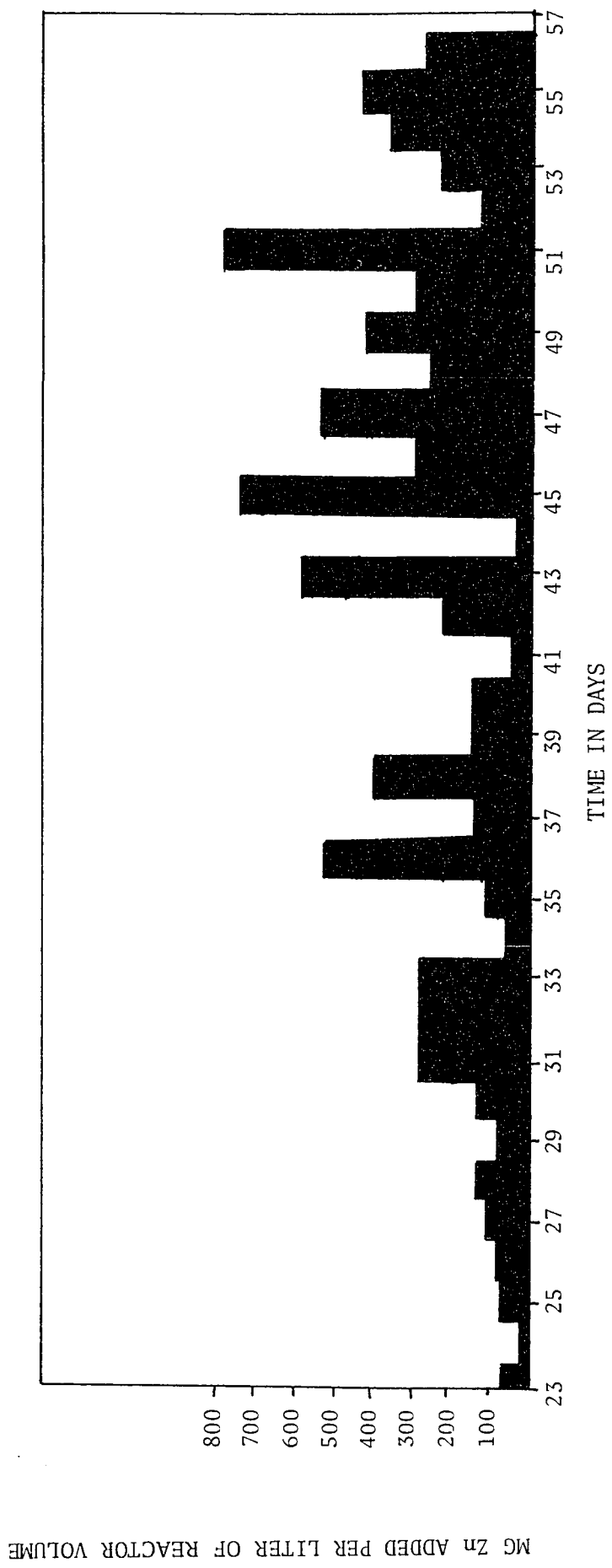


FIGURE 7

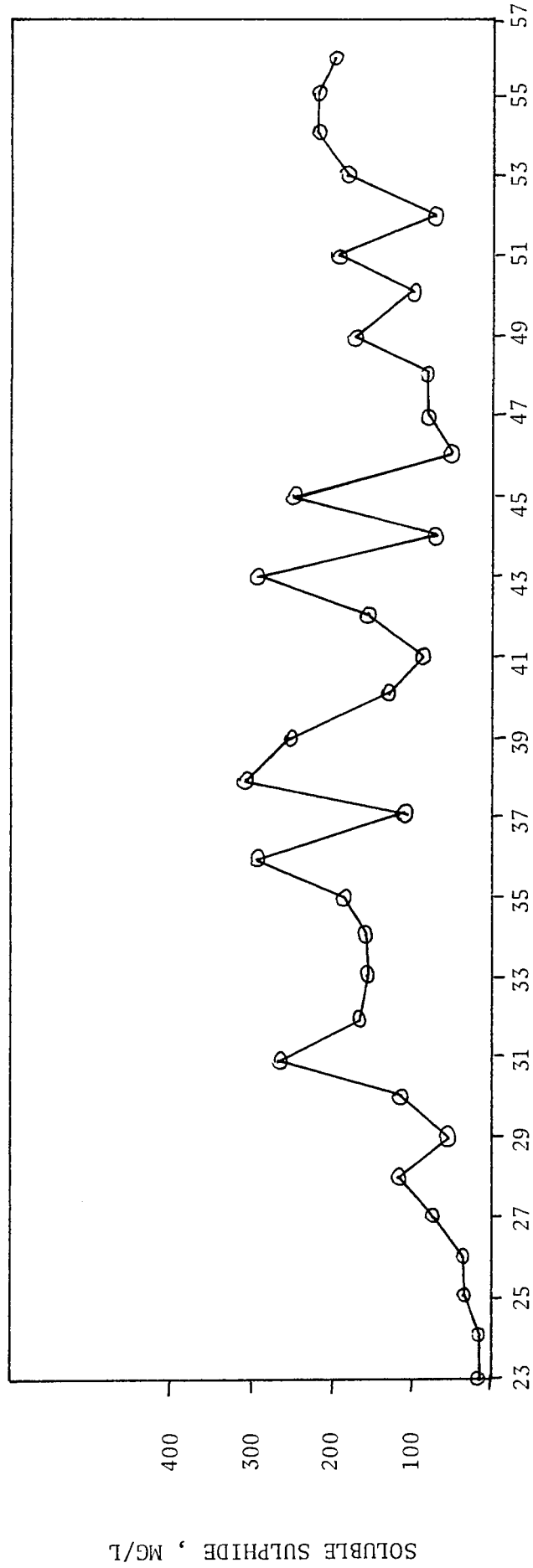
ZINC SULPHIDE PRODUCTION PHASE: ZINC ADDITION AS A FUNCTION OF TIME

An excess of soluble sulphide was maintained at all times to avoid heavy metal poisoning of the bacteria. Figure 8 shows the daily soluble sulphide concentrations. The figure shows that the average soluble sulphide concentration was maintained around 150 mg/l, dipping to a low of 11.8 mg/l at the beginning of the zinc sulphide run. Appendix II shows the calculation for the soluble zinc in the reactor effluent.

Figure 9 shows a time series of the total sulphide concentration during this phase. The total sulphide concentration increases from 450 mg/l up to 2300 mg/l during this phase. Some data are scattered, but this scatter was judged to be due to the precision of the sulphide test and other random process variables. Experiments were carried out to improve the sulphide test. These tests and their results are described in Appendix IV.

Figure 10 shows the per cent volatile solids as a function of time during this phase. The measurement of VS is only a rough indicator of the bacteria concentration for the two biological reactions, namely acid formation and sulphate-reduction. After two solids retention times had passed (30 days), the VS became relatively constant. At this time most of the original seed sludge was washed from the reactor, and the reactor was approaching its true steady state composition.

Figure 11 shows the reactor total solids concentration throughout the zinc sulphide production phase. It should be again noted that initially the total and volatile solid concentration were both high due to the reactor seeding with digested sludge.



TIME IN DAYS

FIGURE 8

ZINC SULPHIDE PRODUCTION PHASE: SOLUBLE SULPHIDE AS A FUNCTION OF TIME

SOLUBLE SULPHIDE, MG/L

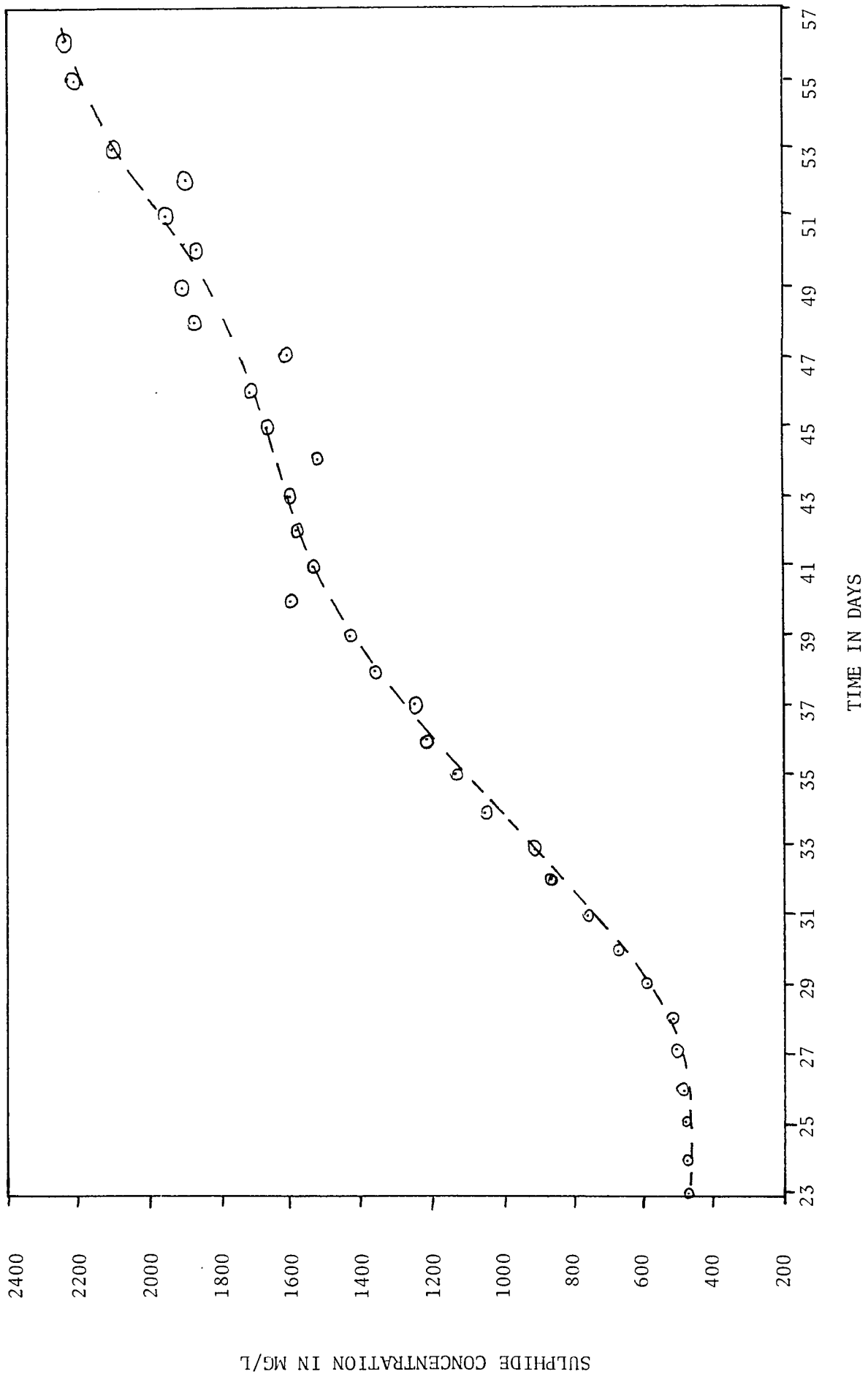
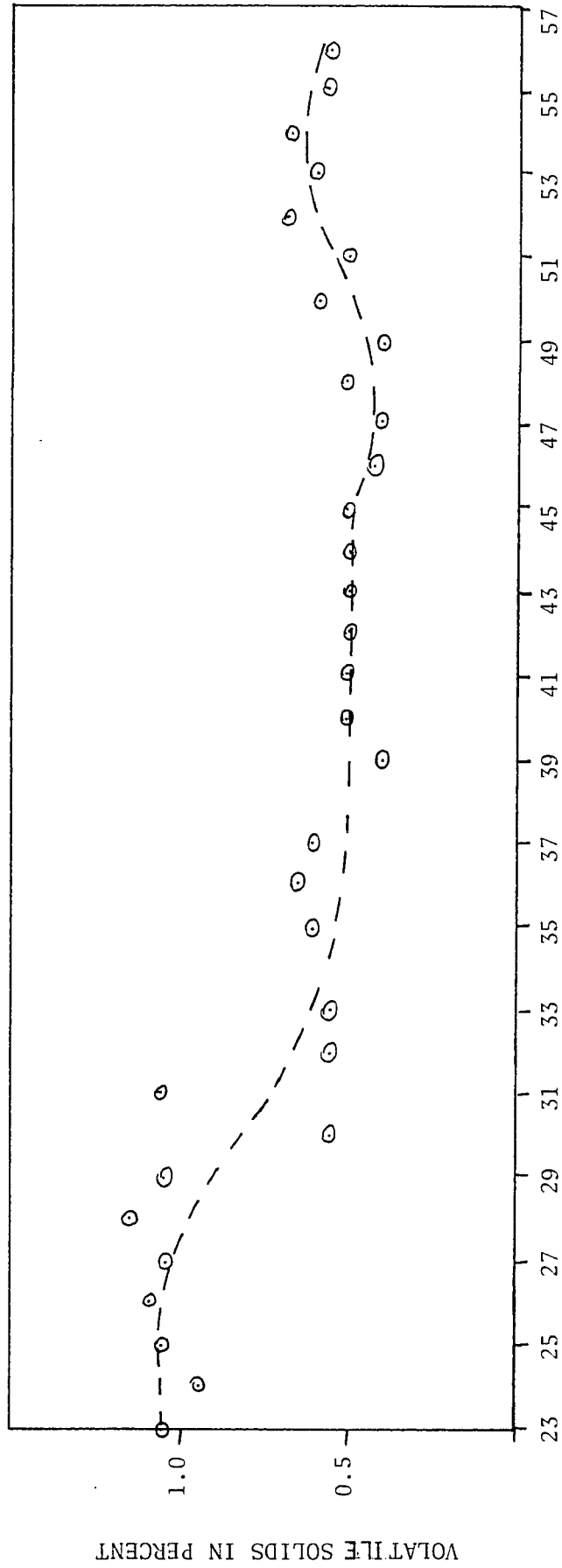


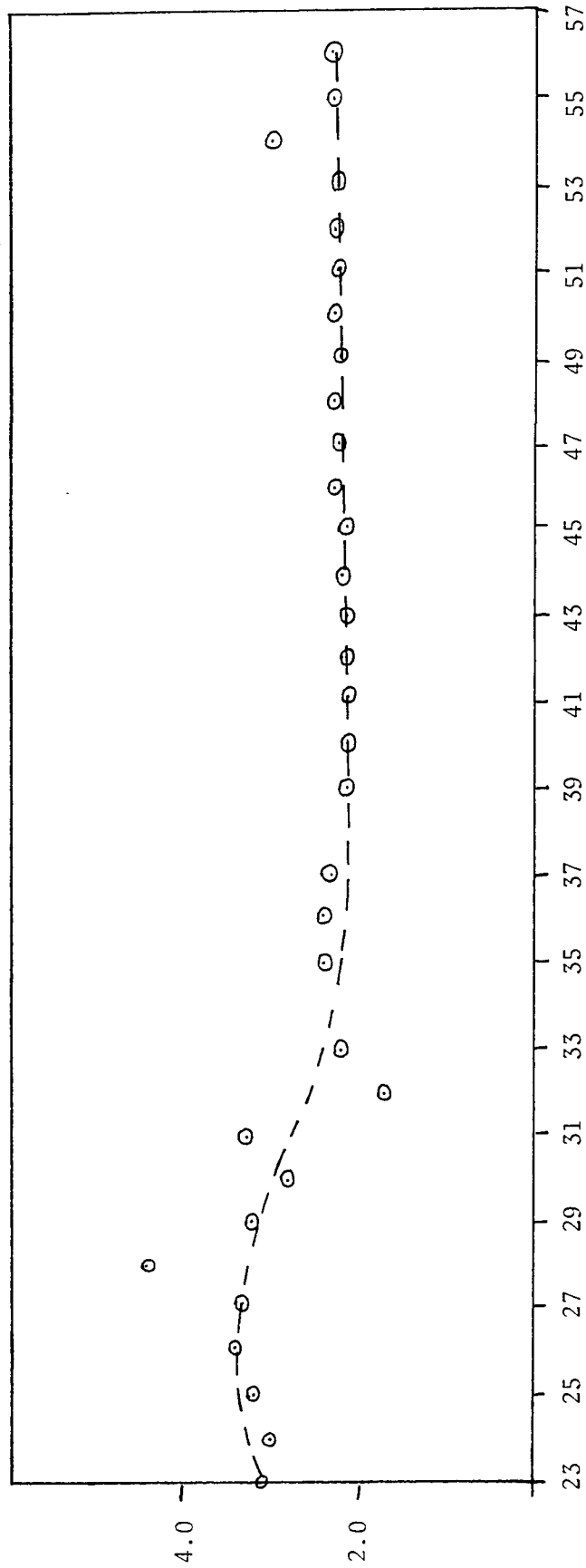
FIGURE 9  
ZINC SULPHIDE PRODUCTION PHASE: TOTAL SULPHIDE CONCENTRATION AS A FUNCTION OF TIME



TIME IN DAYS

FIGURE 10

ZINC SULPHIDE PRODUCTION PHASE: VOLATILE SOLIDS AS A FUNCTION OF TIME



TIME IN DAYS  
FIGURE 11  
ZINC SULPHIDE PRODUCTION PHASE: TOTAL SOLIDS AS A FUNCTION OF TIME

TOTAL SOLIDS IN PERCENT

Once these solids washed out, both the TS and VS concentration stabilized. Throughout the run there is a slight increase in total solids due to the increase in reactor total sulphide, being precipitated zinc sulphide.

Figure 12 shows the schedule of COD addition during this phase. During the 34 day period a total of 34000 mg of COD was added per liter of mixed liquor, resulting in an average addition rate of 1000 mg/l-day.

Figure 13 shows the soluble COD concentration throughout the zinc sulphide precipitation phase. The curve becomes relatively constant between days 48 and 53. This portion of the curve occurred during a period when the daily COD addition rates were high and uniform, suggesting that steady-state conditions might have been achieved.

Figure 14 shows the variation in pH throughout the zinc sulphide precipitation phase. The pH was not allowed to drop below 6.8, and the average pH was maintained around 6.95.

Figure 15 shows the supernatant alkalinity during the zinc sulphide experiment. An adequate alkalinity buffer for the acid forming microbial reaction and for the acidic zinc sulphate solution addition was necessary. This buffer range was arbitrarily chosen as between 2500 and 3750 mg/l  $\text{CaCO}_3$ . Thus, when the alkalinity dropped below pH 6.8, calcium oxide was added. The effect of the acidic zinc sulphate solution can be seen on Figures 7, 14 and 15. For instance between Days 43 and 44, when 720 mg Zn as  $\text{ZnSO}_4$  solution was added per liter of mixed liquor, the alkalinity dropped from 3120 mg/l to 2550 mg/l and the pH dropped from 7.05 to 6.8, making calcium oxide addition necessary.

MG COD ADDITION PER LITER OF MIXED LIQUOR

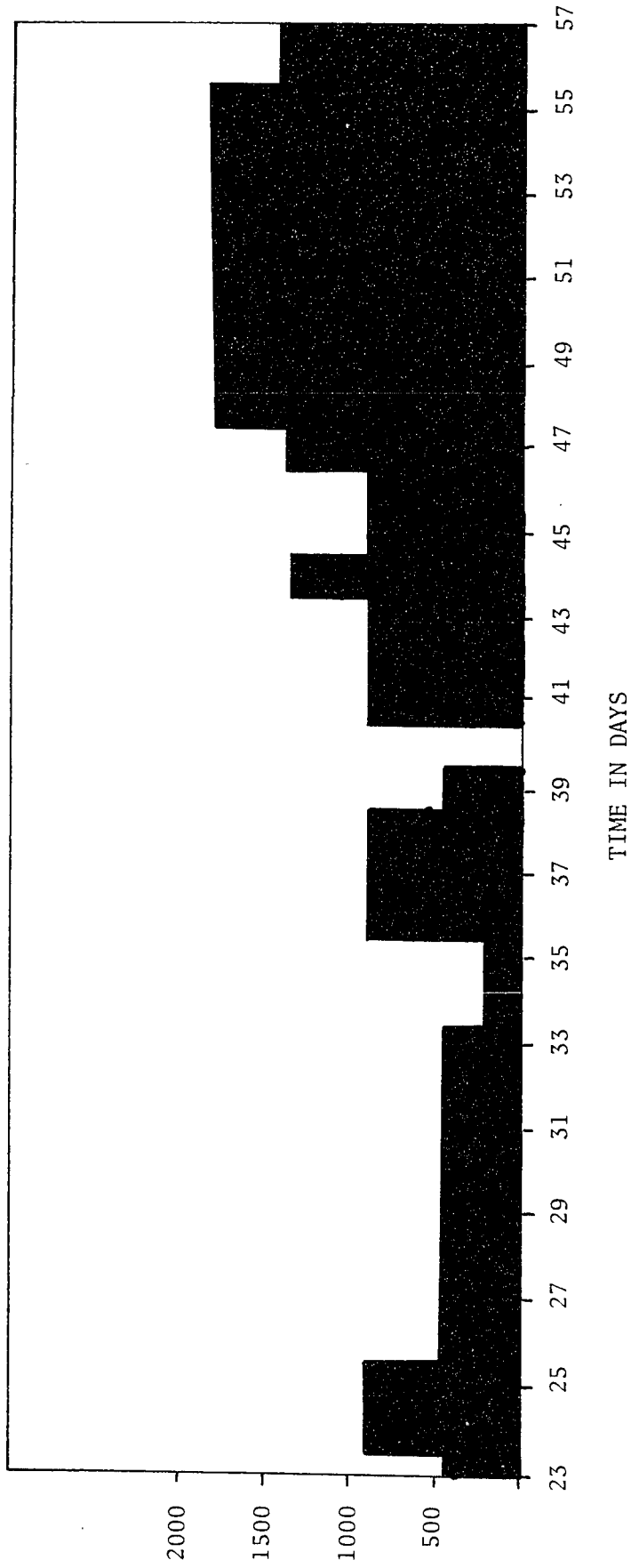
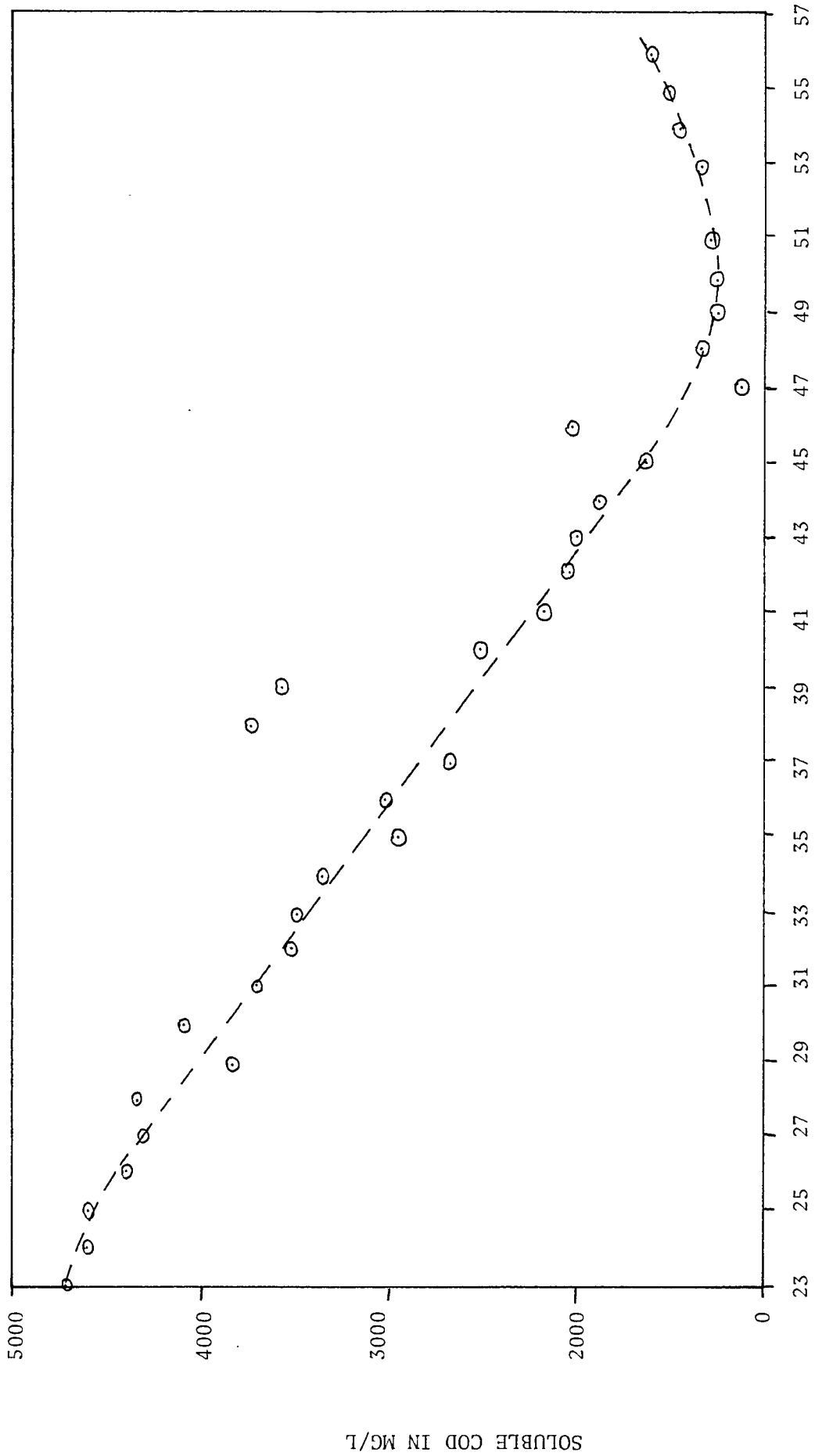


FIGURE 12

ZINC SULPHIDE PRODUCTION PHASE: COD ADDITION AS A FUNCTION OF TIME



TIME IN DAYS

FIGURE 13

ZINC SULPHIDE PRODUCTION PHASE: SOLUBLE COD AS A FUNCTION OF TIME

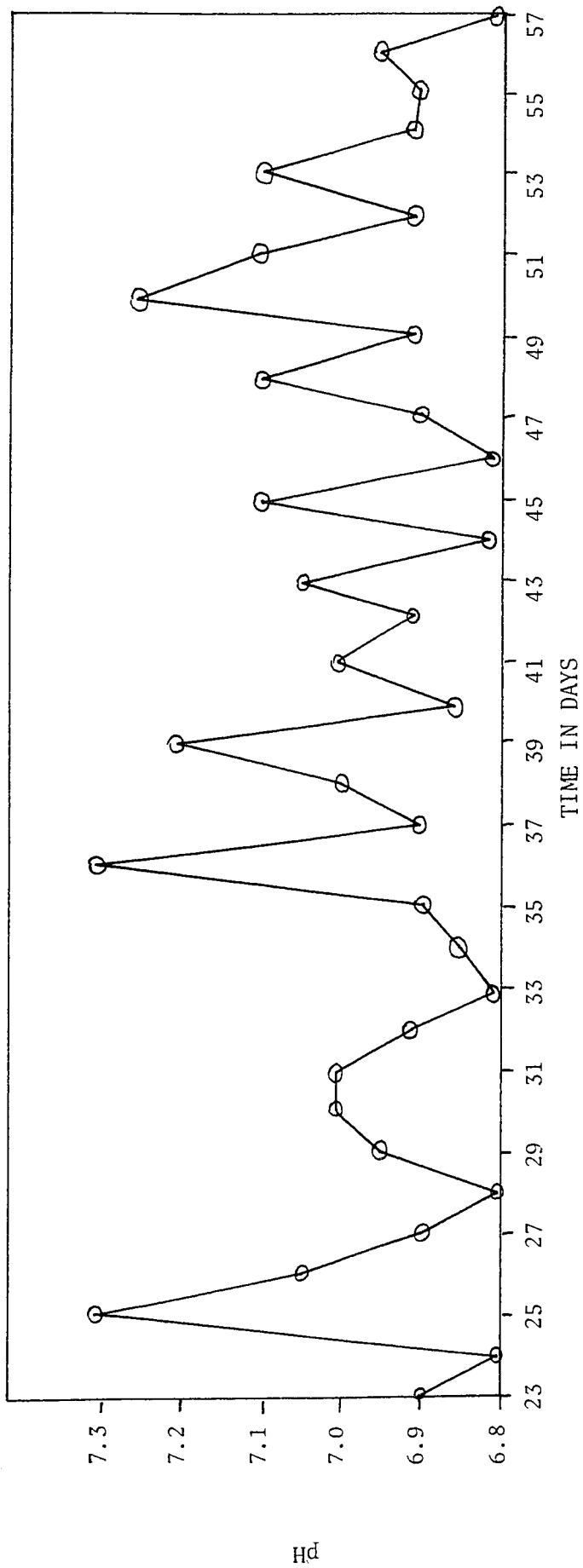


FIGURE 14  
ZINC SULPHIDE PRODUCTION PHASE: pH AS A FUNCTION OF TIME

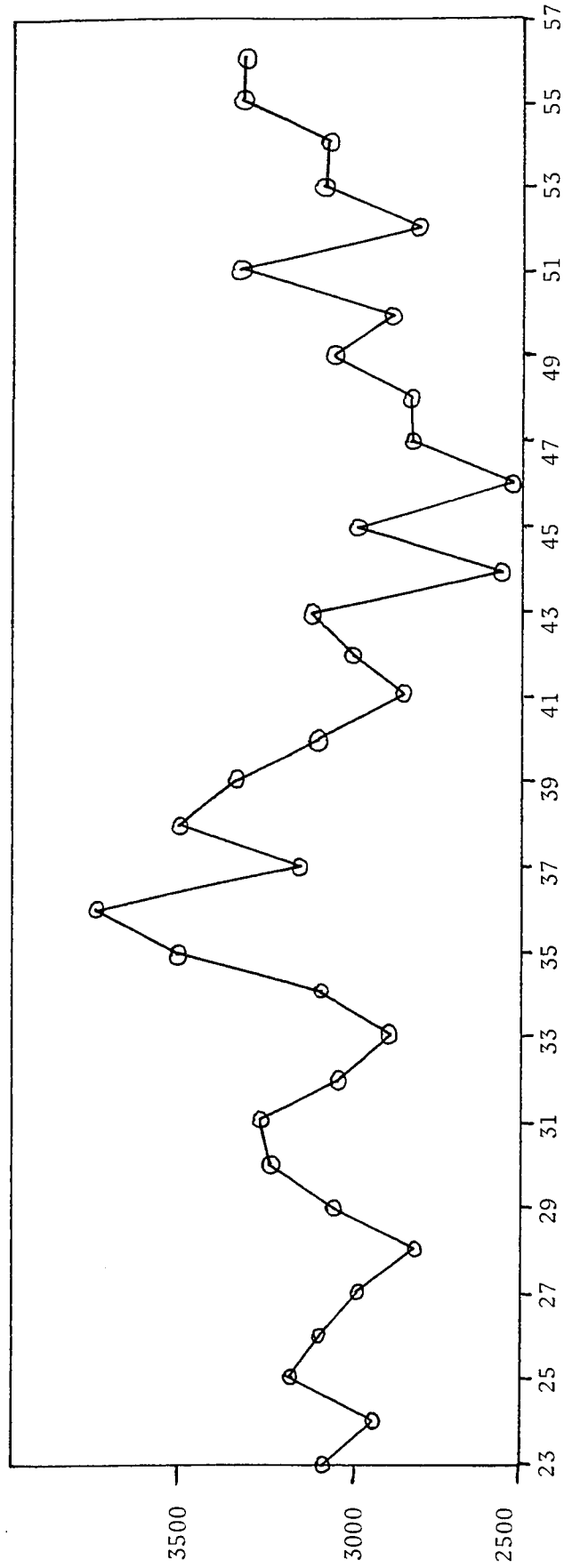


FIGURE 15

ZINC SULPHIDE PRODUCTION PHASE: ALKALINITY AS A FUNCTION OF TIME

ALKALINITY IN MG/L CaCO<sub>3</sub>

The daily sulphide production rate can be calculated from a reactor sulphide mass balances as follows:

$$\frac{S_{n+1} - S_n}{T} + \frac{S_n}{\theta} \quad \begin{array}{l} \text{daily sulphide production} \\ \text{rate in mg/l/day} \end{array}$$

where  $S_{n+1}$  = Sulphide concentration in mg/l on day  $n+1$

$S_n$  = Sulphide concentration in mg/l on day  $n$

$T$  = Time between assays in days

$\theta$  = hydraulic retention time of the reactor in days.

Table IV shows the calculated daily sulphide production rate. The data are considerably scattered, inhibition due to inconsistent feeding rates, and several instances bacteria inhibition by accidental high metal additions. These incidents resulted in unusually low production rates, until the biomass recovered from the shock. A better trend of the production data is obtained by averaging the production rate with the previous days rate. This data is also shown in Table IV and graphically represented in Figure 16. The average rate shown in Figure 16 is in mg/l-day. There is no doubt, that with sophisticated control equipment which would minimize the variations in the day to day operation, that much of the scatter in the rate data can be removed.

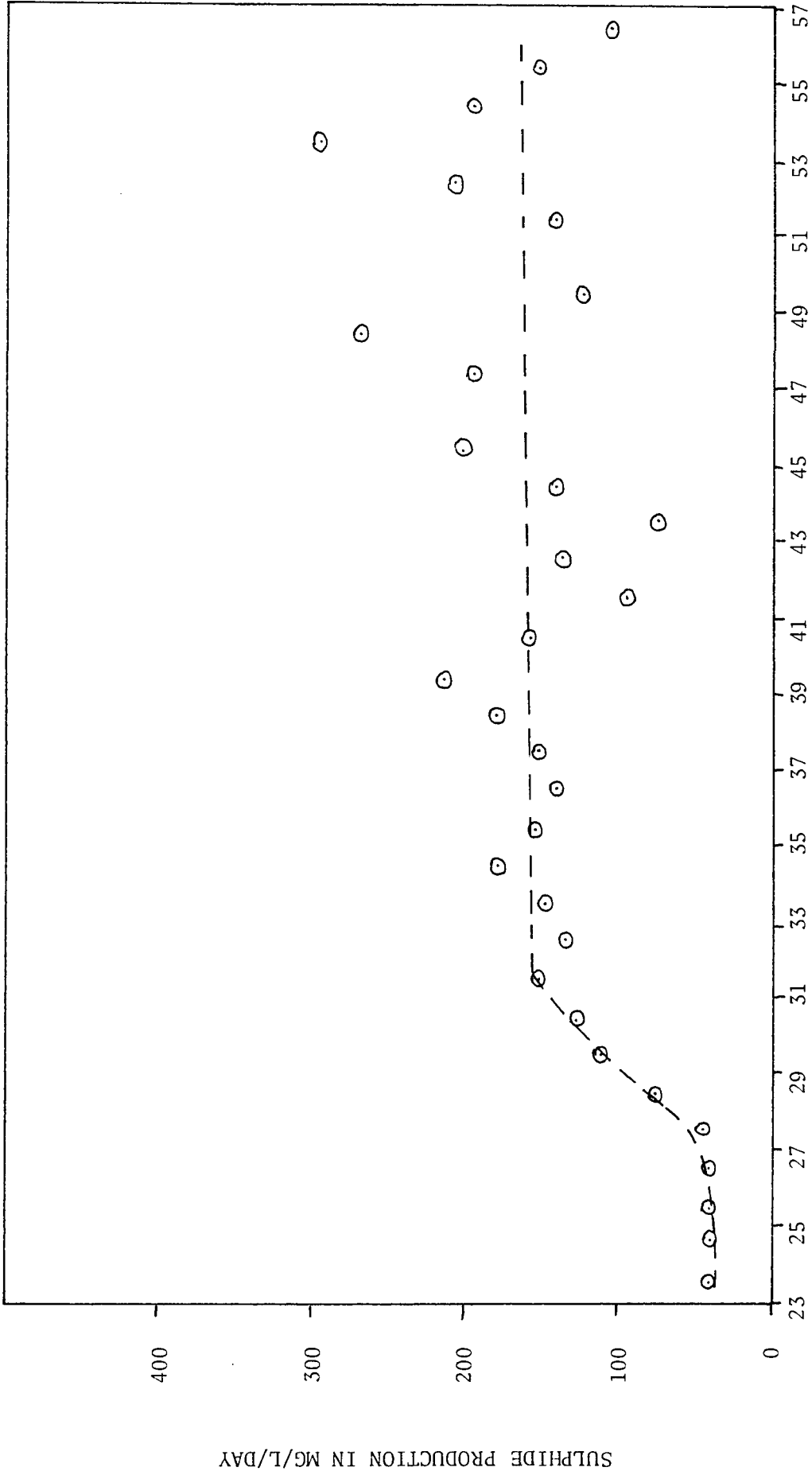
Although true steady-state conditions may not have been obtained, the above data confirms the belief that the sulphate-reduction process can indeed be used to recover zinc from metal waste leach solutions as zinc sulphide.

TABLE IV  
CALCULATED SULPHIDE PRODUCTION RATES

<u>Day No.</u>	$\frac{(S_{n+1} - S_n)}{T} + \frac{S_n}{\theta}$ mg/1/day	Moving Average Rate mg/1/day
23	44.7	39.7
24	34.7	38.9
25	43.0	42.1
26	41.3	40.0
27	38.8	44.3
28	49.8	77.4
29	104.9	113.6
30	122.3	128.7
31	135.0	151.5
32	168.0	131.4
33	94.7	146.6
34	198.6	177.1
35	155.6	156.0
36	156.4	141.1
37	116.8	153.0
38	189.3	177.8
39	166.3	214.0
40	261.7	147.9
41	34.0	93.2
42	152.4	138.3
43	124.2	

TABLE IV (continued)

<u>Day No.</u>	$\frac{(S_{n-1} - S_n) - \frac{S_n}{\theta}}{T}$ mg/l/day	<u>Moving Average Rate mg/l/day</u>
44	28.3	139.0
45	249.8	200.1
46	150.4	75.9
47	1.3	193.2
48	385.0	270.9
49	156.7	121.8
50	85.9	148.6
51	211.2	140.9
52	70.5	205.5
53	340.5	294.7
54	248.8	193.4
55	138.8	152.5
56	167.0	107.0
57	46.9	



ZINC SULPHIDE PRODUCTION PHASE: CALCULATED SULPHIDE PRODUCTION AS A FUNCTION OF TIME  
FIGURE 16

### 5.3 COPPER/ZINC SULPHIDE PRODUCTION

On day 57 the metal feed solution to the reactor was switched from 8 grams per liter zinc to 4 grams per liter zinc and 4 grams per liter copper as sulphates.

The copper sulphate solution was prepared by leaching a previous precipitated cupric hydroxide, calcium sulphate sludge. The leaching reaction was carried out at pH 2. Thus, the mixed solution of copper and zinc sulphate was highly acidic, having a pH of approximately 2.5.

The addition of copper was necessary to determine if the presence of a new metal would require bacteria acclimatization. If acclimatization was necessary, the sulphide production rate would initially decrease and again increase once the bacteria was used to the new metal salt.

Since copper sulphide is not acid labile, the total sulphide analysis was discontinued when the addition of copper sulphate commenced.

Figure 17 shows that the per cent total solids in the reactor during the copper/zinc sulphide phase remained constant as did the volatile solids shown in Figure 18.

Figure 19 shows the copper/zinc sulphate addition rate to the reactor. On Day 60, an accidental high addition of 953 mg of metal per liter of mixed liquor almost destroyed the bacteria population. In order to allow a buildup of soluble sulphide in the system, metal sulphate addition was discontinued on Days 61 and 62.

Figure 20 shows the soluble sulphide concentration of the mixed liquor. When the accidental high metal addition occurred on Day 60, the soluble sulphide dropped from 227.3 mg/l to 14.9 mg/l.

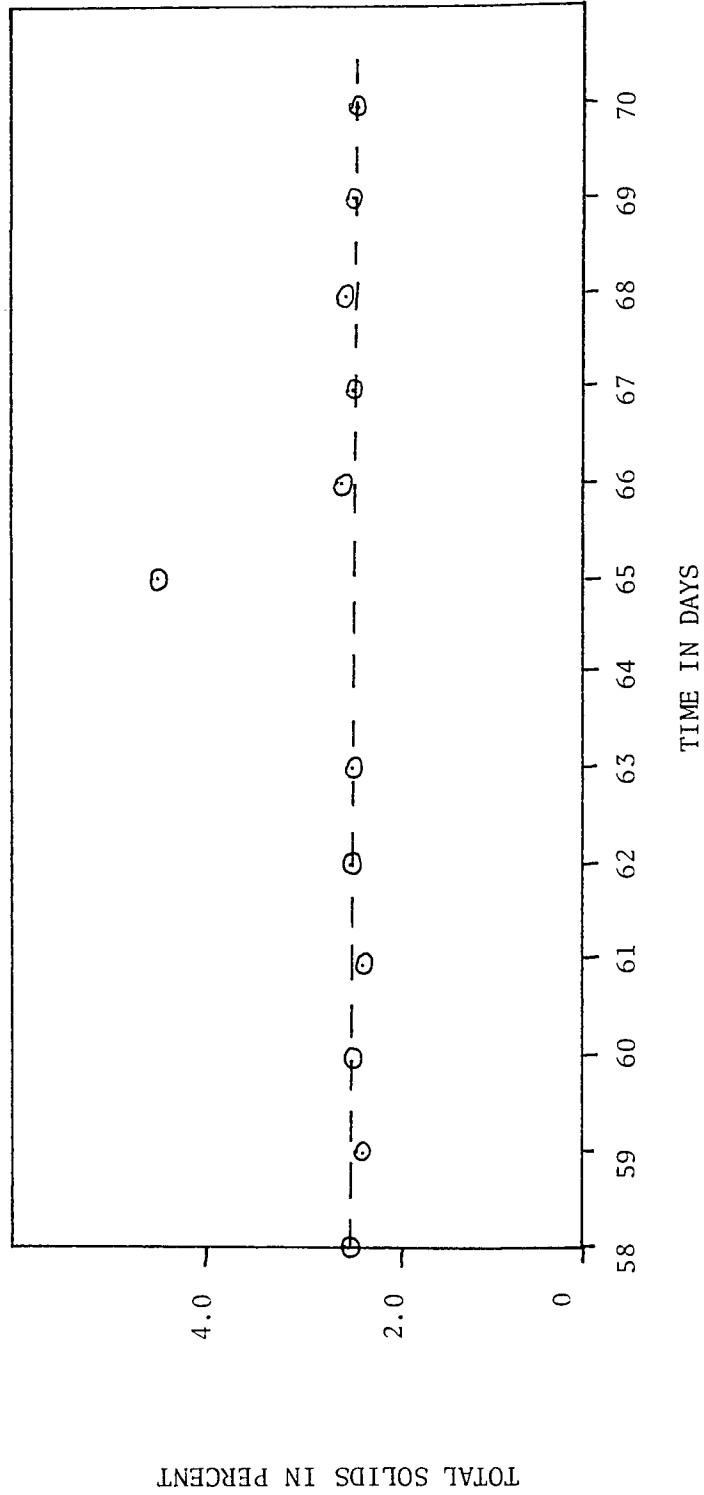


FIGURE 17

COPPER/ZINC SULPHIDE PRODUCTION PHASE: TOTAL REACTOR SOLIDS AS A FUNCTION OF TIME

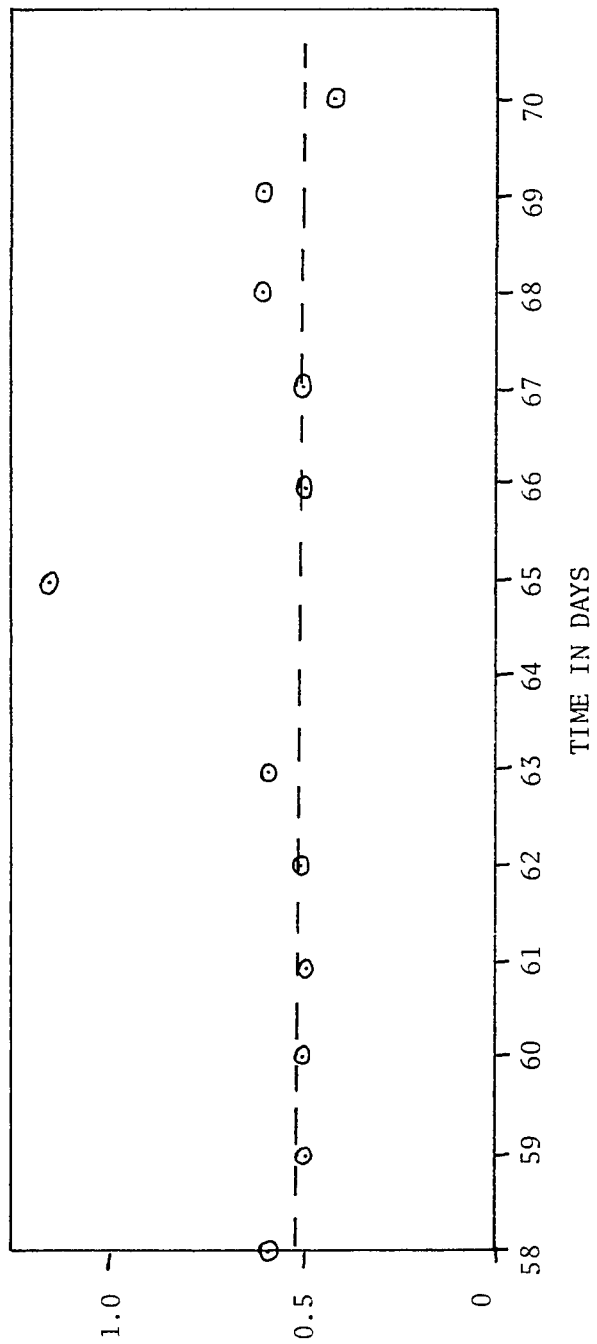
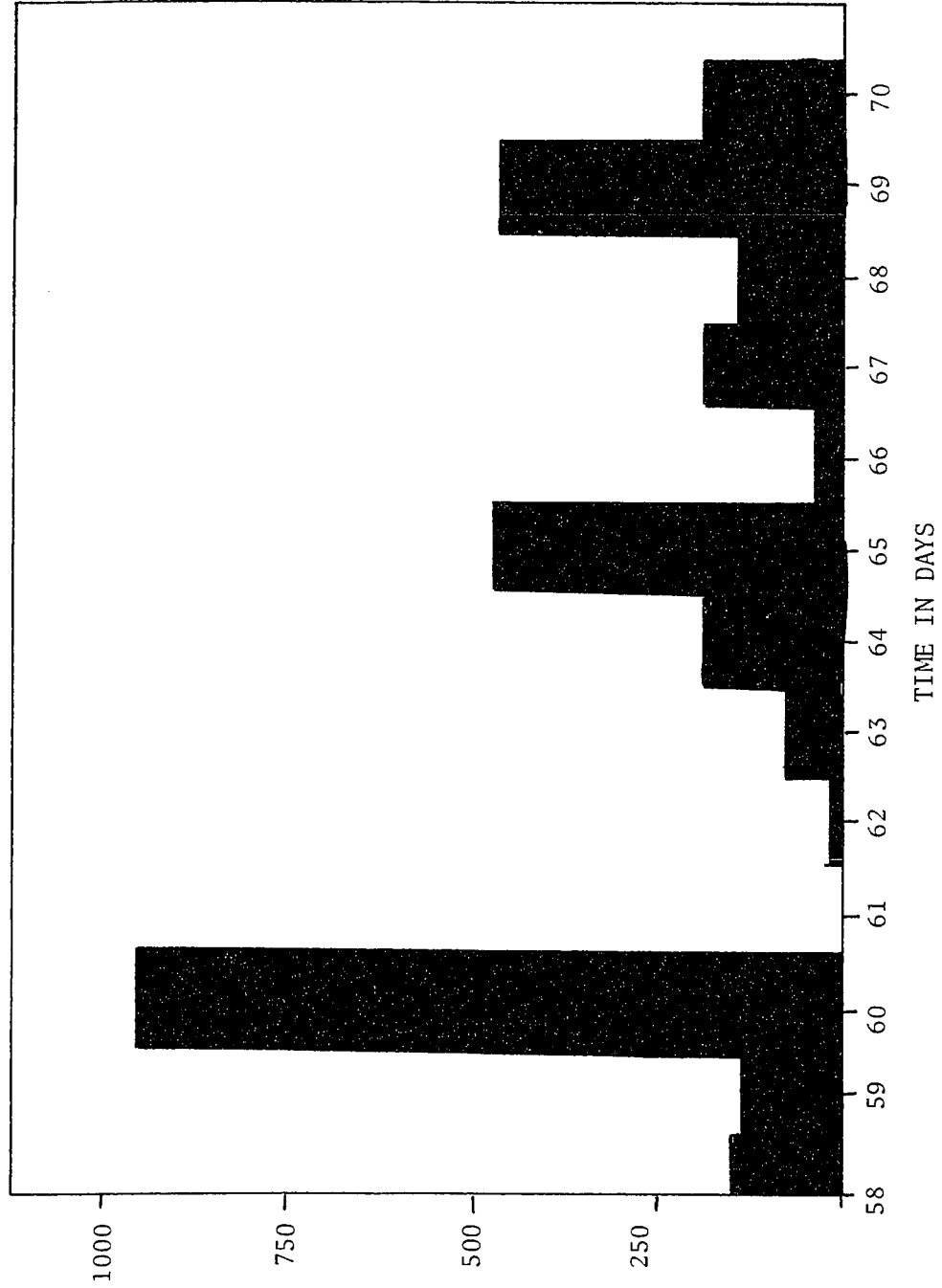


FIGURE 18

COPPER/ZINC SULPHIDE PRODUCTION PHASE: VOLATILE SOLIDS AS A FUNCTION OF TIME

VOLATILE SOLIDS IN PERCENT



COPPER/ZINC SULPHIDE PRODUCTION PHASE: COPPER/ZINC SULPHATE ADDITION TO THE REACTOR AS A FUNCTION OF TIME  
FIGURE 19

MG COPPER PLUS ZINC ADDITION PER LITER OF MIXED LIQUOR

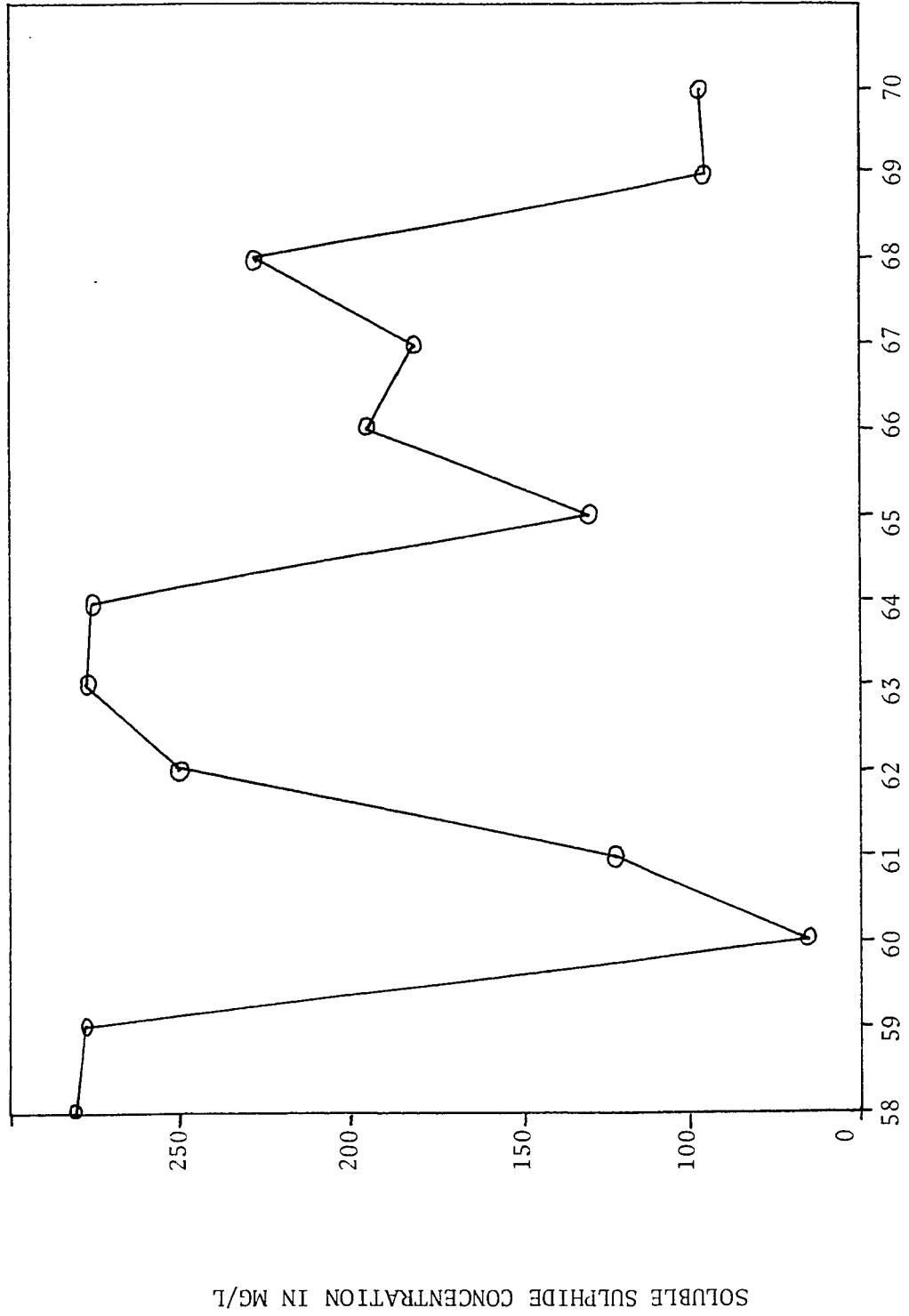


FIGURE 20

COPPER/ZINC SULPHIDE PRODUCTION PHASE: SOLUBLE SULPHIDE CONCENTRATION AS A FUNCTION OF TIME

Figure 21 shows the reactor pH as a function of time during this phase. The effect of high metal solution addition rates to the reactor can be seen in this figure. The addition of 953 mg metal per liter of mixed liquor dropped the pH from 6.9 to 6.6. The metal solution was highly acidic and the reactor required calcium oxide addition every other day in order to control the pH.

Figure 22 shows the soluble reactor alkalinity throughout the copper/zinc sulphide precipitation experiment. During periods of high metal addition, the alkalinity dropped sharply, indicating that the acid added with the metal solution consumed the alkalinity and liberating CO<sub>2</sub> gas.

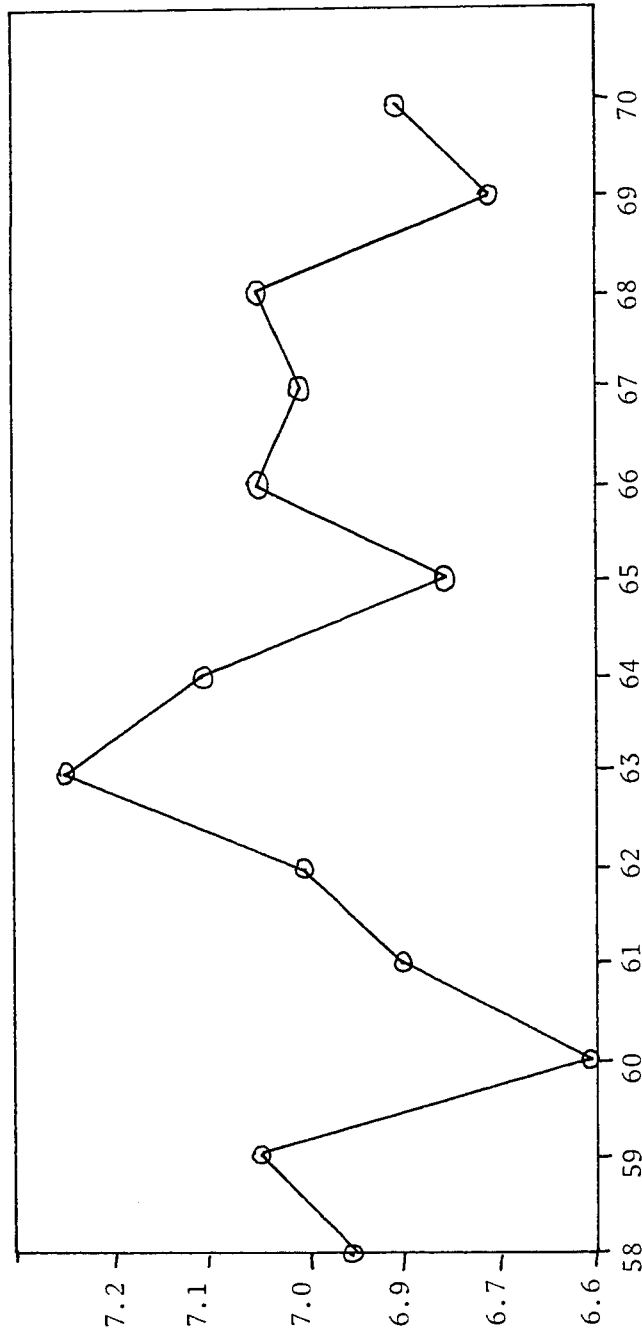
Figure 23 shows the COD addition rate from primary sewage sludge, and Figure 24 shows the soluble reactor COD as a function of time. The COD addition was attempted to be tailored to the soluble COD available in the reactor. Thus, as the soluble COD increased, the addition of sludge was reduced. This method of addition probably did not allow the bacteria to grow at their maximum rate. Also, since the biochemical oxygen demand was not known, the reaction might have been carbon limited.

The sulphide production rates can be calculated from the soluble sulphide mass balance and the known metal solution addition rate. Table V lists calculated sulphide production rates during this phase. The sulphide production rates were calculated as follows:

$$\frac{(S_{n+1} - S_n)}{T} + \frac{S_n}{\theta} + \frac{v \times C}{VT} \times \frac{32}{64.7} = \text{mg S}^{-2} / \text{l/day}$$

where:

$S_{n+1}$  = Soluble sulphide concentration on day n+1



TIME IN DAYS

FIGURE 21

COPPER/ZINC SULPHIDE PRODUCTION PHASE: pH AS A FUNCTION OF TIME

pH

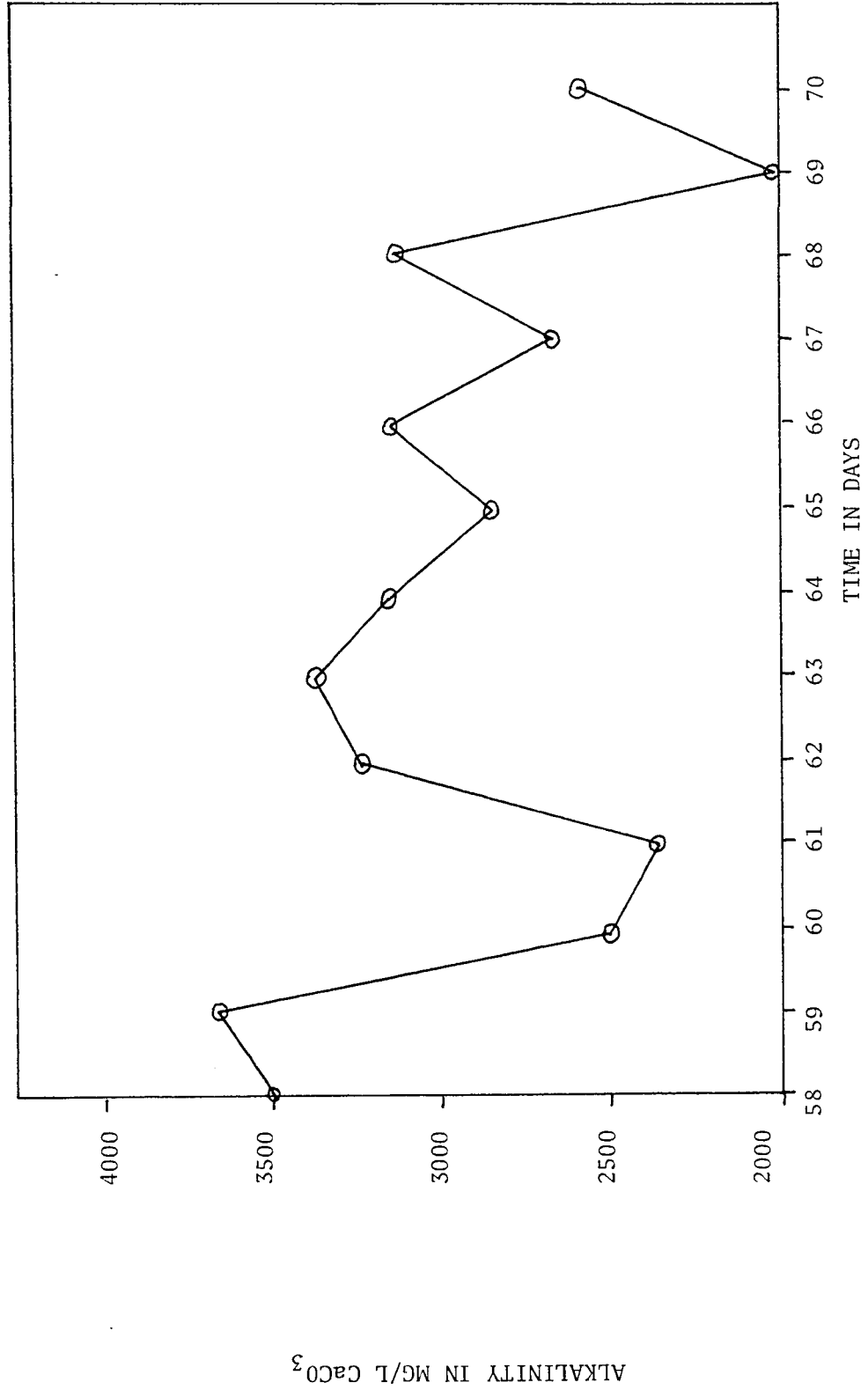


FIGURE 22

COPPER/ZINC SULPHIDE PRODUCTION PHASE: REACTOR SOLUBLE ALKALINITY AS A FUNCTION OF TIME

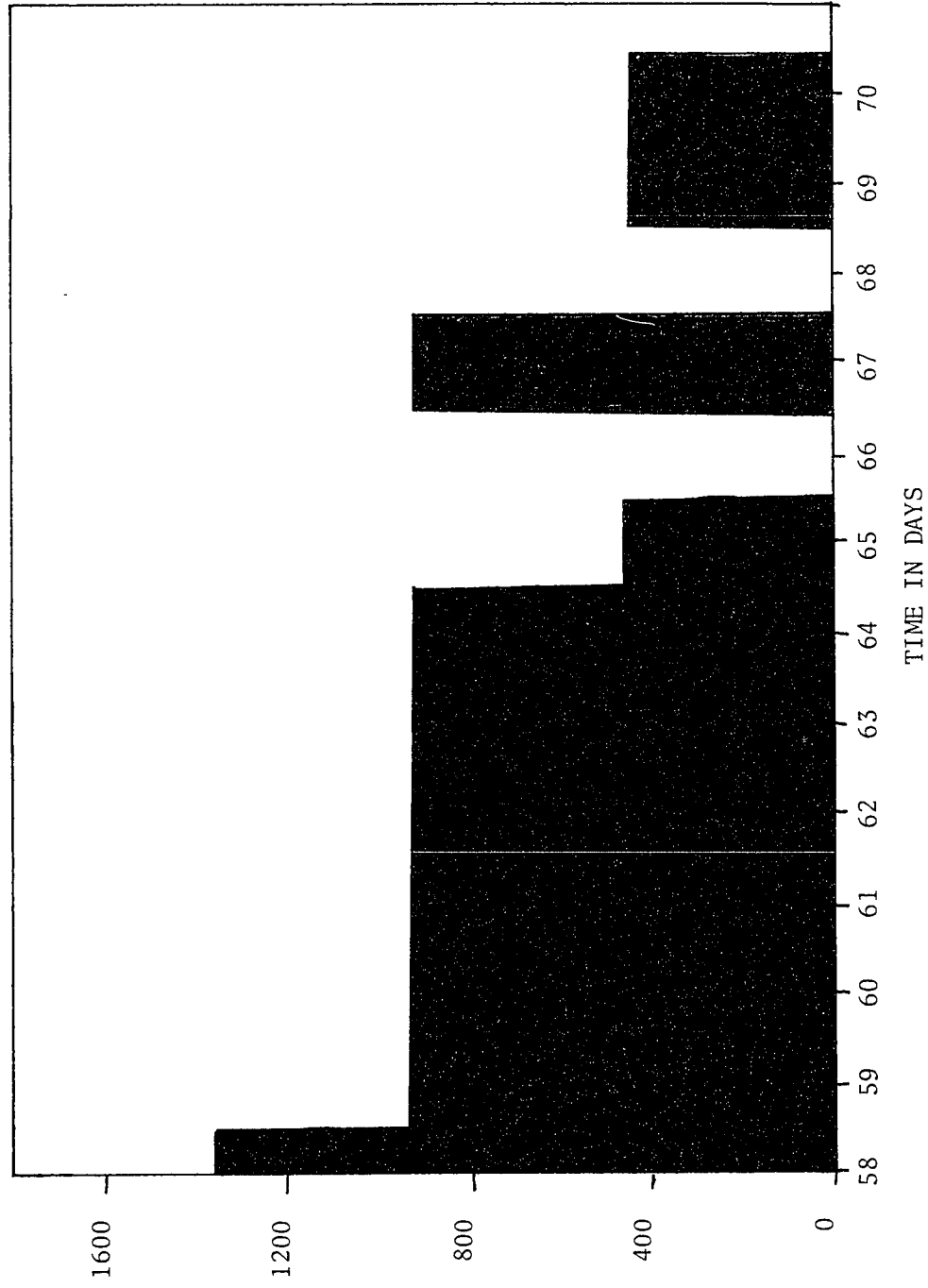
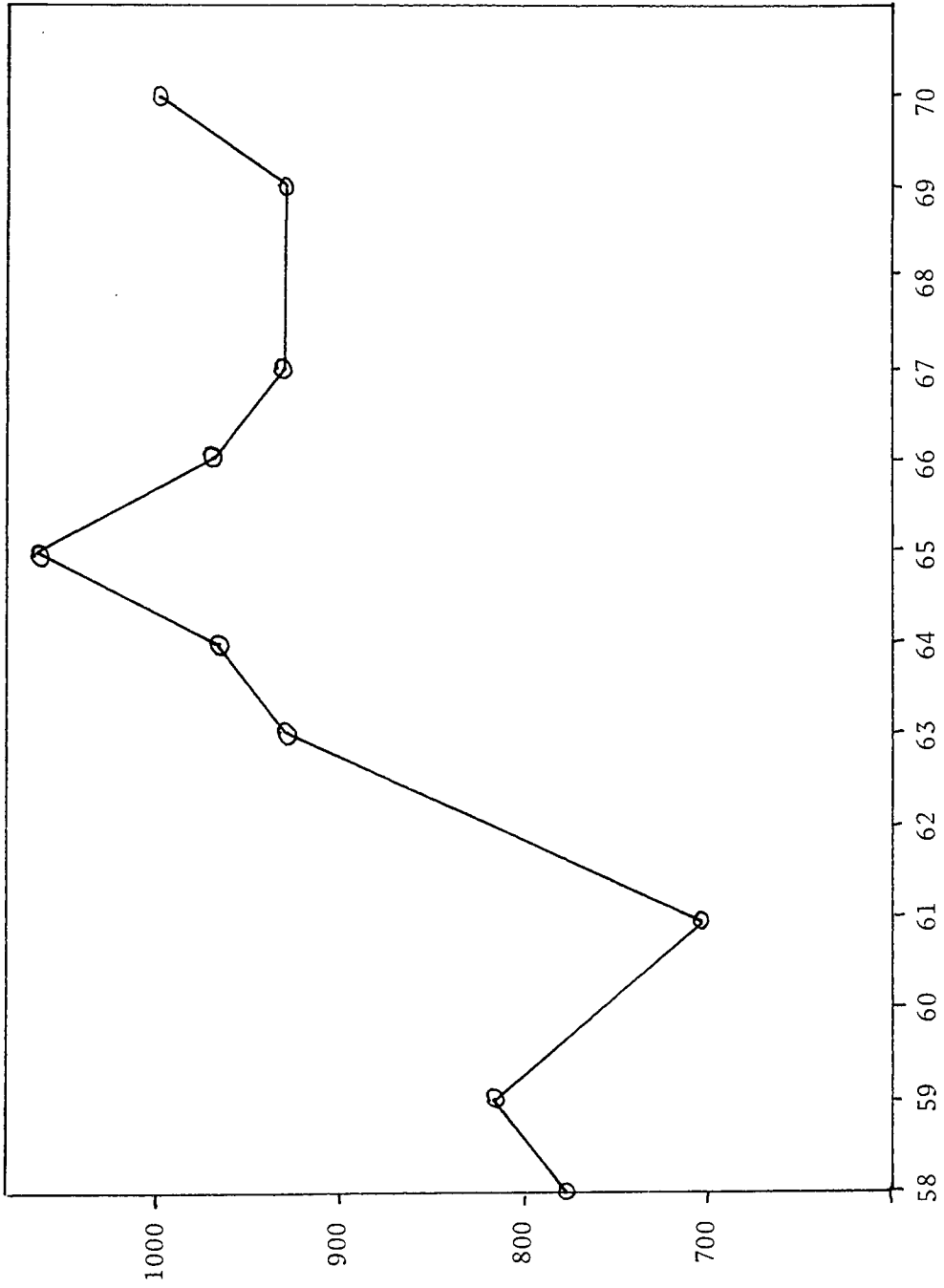


FIGURE 23

COPPER/ZINC SULPHIDE PRODUCTION PHASE: COD ADDITION AS A FUNCTION OF TIME

COD ADDITION IN MG/L



TIME IN DAYS

FIGURE 24

COPPER/ZINC SULPHIDE PRODUCTION PHASE: SOLUBLE REACTOR COD AS A FUNCTION OF TIME

SOLUBLE COD IN MG/L

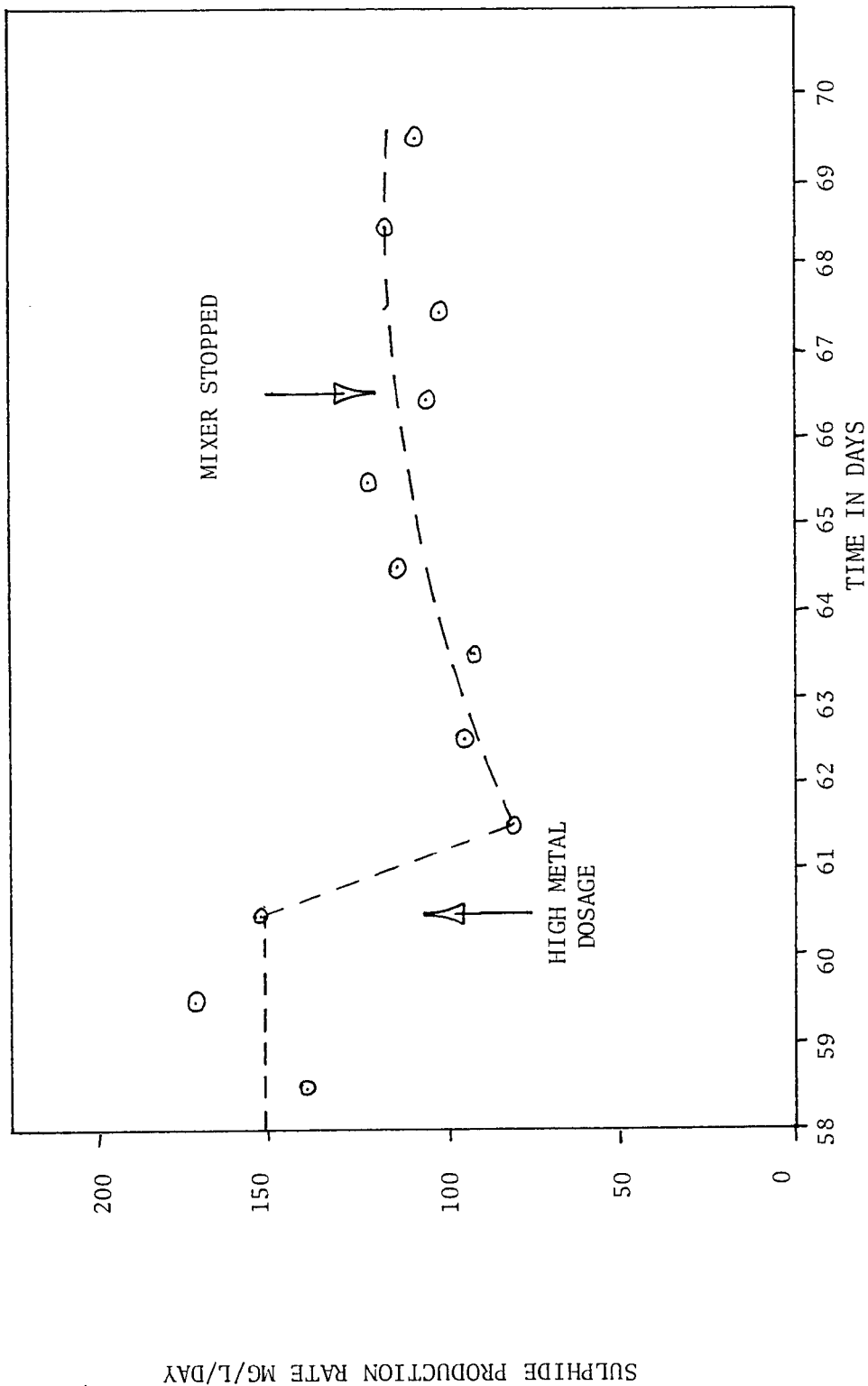


FIGURE 25

COPPER/ZINC SULPHIDE PRODUCTION PHASE: CALCULATED SULPHIDE PRODUCTION RATE AS A FUNCTION OF TIME

- Sn Soluble sulphide concentration on day n
- T time in days between sulphide analyses
- $\theta$  reactor hydraulic retention time in days.
- v volume of metal solution added
- C Concentration of metal in the metal feed solution
- V reactor volume
- 32 molecular weight of sulphur
- 64.7 average molecular weight of metals in solution

The data scatter in Table V can be dampened by averaging the production rate with the previous days production rate. Figure 25 shows these rates as a function of time, a definite trend of this data can be seen in this figure. After the high metal addition rate on day 60, there was a sharp decrease in the sulphide production rate from the rate of the previous day. For the following few days, the bacteria appeared to operate rather sluggishly, indicating that there was a definite effect due to the high metal addition rate. A definite increase occurred after allowing the bacteria to recover without metal addition for two days, this rapid recovery however appeared to be interrupted when the mixer stopped during the unattended period. Figure 25 shows that after day 60 there was a definite overall increase in the sulphide production rate, indicating that the bacteria are capable of recovering from heavy metal shock addition. The data also suggest that the bacteria need an adequate soluble sulphide buffer to avoid temporary reduced activity due to the presence of heavy metal.

Although the maximum sulphide production rate was not achieved due to mechanical problems, insufficient COD addition, and temporary bacteria deactivation with heavy metal ions, the data clearly show that sul-

TABLE V

SULPHIDE PRODUCTION RATES DURING ZINC/COPPER SULPHIDE PHASE

Day No.	Sulphide Production Rate mg/l/day	Moving Average $\frac{(n-1) + n}{2}$
58	181.4	128.1
59	74.8	172.3
60	269.7	156.7
61	43.6	80.3
62	117.0	96.4
63	75.8	93.5
64	111.2	114.5
65	117.7	119.0
66	120.3	104.6
67	88.8	100.4 (mixer stopped)
68	111.9	118.3
69	117.5	107.7
70	97.8	

phate-reducing bacteria can utilize copper sulphate, as well as zinc sulphate to produce valuable metallic sulphide precipitates.

#### 5.4 UPGRADING OF THE REACTOR SLURRY INTO BASEMENTAL SMELTER FEED

The residual of the daily reactor withdrawals was collected in order to assess the settling characteristics of the slurry.

The settling characteristics of the zinc sulphide slurry were assessed at three different solid densities, which were prepared by allowing the solids to settle and withdrawing some of the supernatant. Figure 26 shows the settling curves for the slurry at 2.25, 2.76 and 3.32 per cent solids. After 20 hours all three slurries settled to a solids density of 11.75 per cent.

The settled slurry was filtered to remove residual water. Filterability tests were not conducted due to the lack of suitable filtration equipment. The filter cake was dried and then calcined at 1000<sup>o</sup>F to remove excess organics. The dried and calcined residues from the zinc sulphide run and copper/zinc sulphide run were analyzed by an independent laboratory for base metal content, the analyses are shown in Table VI.

#### 5.5 GENERAL DISCUSSION

Although the reactor never really achieved true steady-state operating conditions, the data clearly show that a metal sulphide concentrate comparable to a mixed sulphide concentrate can be produced by

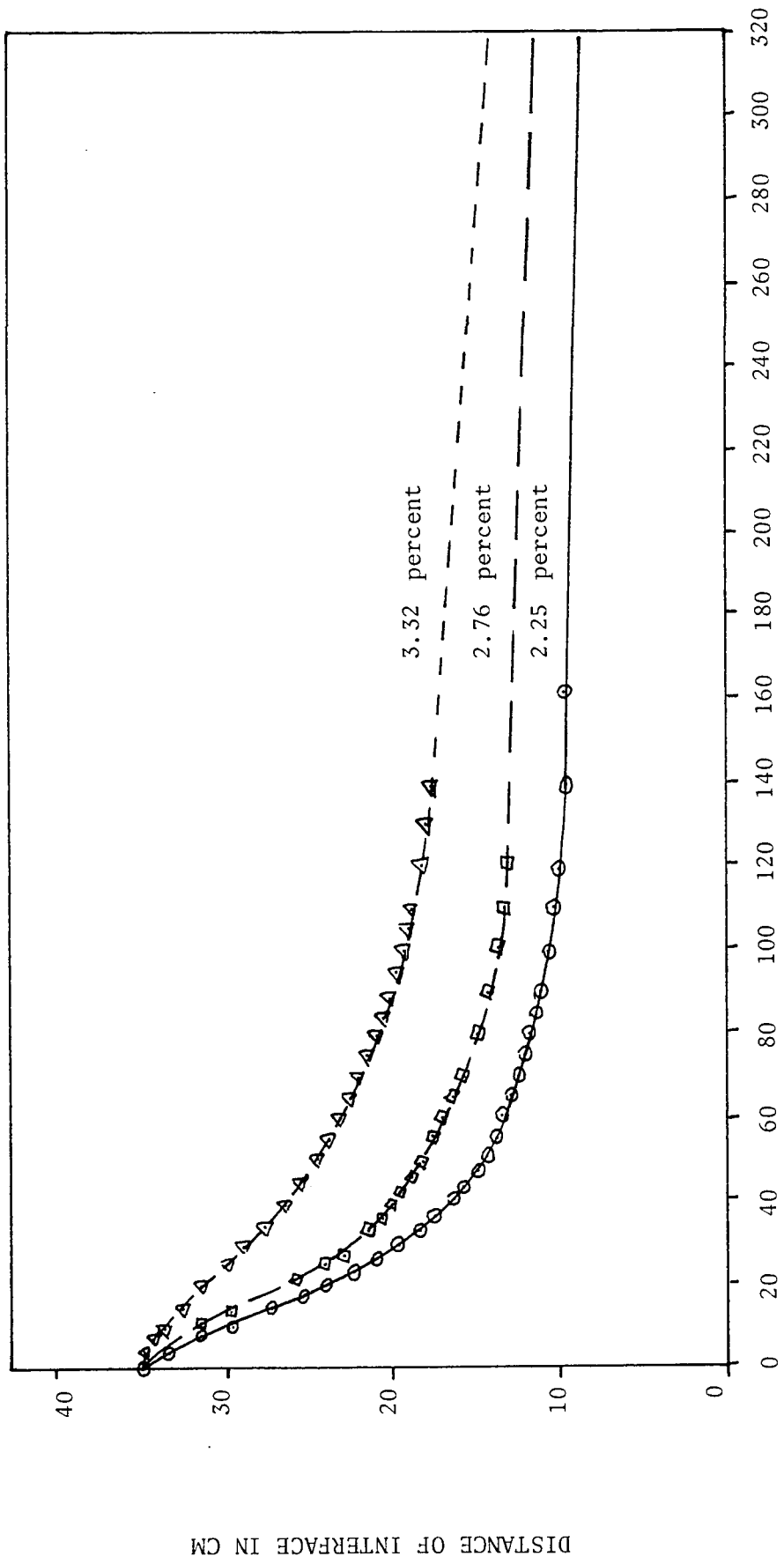


FIGURE 26  
SETTLING OF ZINC SULPHIDE SLUDGE

DISTANCE OF INTERFACE IN CM

TIME IN MINUTES

TABLE VI

REACTOR SLUDGE ANALYSIS

---

	Dried Sludge	Calcined Sludge
<hr/>		
<u>Zinc Sulphide Run</u>		
Zinc, percent	20.72	27.68
Iron, percent	1.67	1.99
<u>Copper/Zinc Sulphide Run</u>		
Zinc, percent	17.5	19.3
Copper, percent	7.3	8.6
Iron, percent	0.84	1.04

---

feeding the anaerobic sulphate-reducing reactor with metallic hydroxide leach liquor, waste biodegradable organic material and some alkalinity for pH control. The metal content in the reactor sulphide sludge is expected to depend on the operating conditions of the reactor and on the type of waste organic material used as feedstock.

The experiments also showed that the sulphate-reducing bacteria readily acclimatize to the presence of metallic sulphides. However, a soluble sulphide buffer is necessary to avoid heavy metal poisoning of the bacteria. It is expected that any metal capable of forming a sulphide precipitate could be fed to the reactor in order to produce a high grade sulphide precipitate acceptable as base metal smelter feed.

Appendix I shows a pictorial display of the reactor set up and the two separate production phases, namely the zinc sulphide phase and the copper/zinc sulphide phase. The pictures show the metal feed solutions, the settled sludge, the dry and calcined sludges.

## CHAPTER SIX

### 6. ENGINEERING SIGNIFICANCE

If the small laboratory scale process can be demonstrated on larger pilot plant scale to be technically and economically viable for commercial exploitation, then the significance of this development could be far reaching. The commercial exploitation of this process could have a direct impact on:

- present waste disposal practices
- resource recovery and recycle
- energy conservation

#### 6.1. EFFECT ON PRESENT WASTE DISPOSAL PRACTICE

As pointed out in Chapter 2, the disposal of metal finishing wastes poses certain environmental problems. Deepwell disposal has been identified as the best current disposal method, however, due to the lack of suitable deepwell locations, the Ministry of the Environment of Ontario is allowing these sludges to be disposed of in landfill sites. A sulphate-reduction reactor could accept these sludges and along with their acceptance remove the environmental hazards associated with their disposal.

The metal finishing industry also produces a considerable amount of high strength acid wastes highly contaminated with heavy metals. These wastes cannot be simply neutralized and released, but they require environmentally acceptable disposal. Like with most toxic wastes, deepwell disposal is currently the only acceptable means of disposal. Deepwelling is usually very expensive since the client has to pay for the transportation to the deepwell, as well as a dumping fee for the material to be disposed of. A sulphate-reducing reactor accepting metallic hydrox-

ide sludges can also accept these waste acids for sludge leaching, releasing only water and some inert salts like sodium sulphate and calcium sulphate to the environment.

The laboratory scale reactor demonstrated that primary municipal sludge could be used as an organic feedstock for the sulphate-reducing reaction. The precipitation of one ton of metal as metallic sulphide requires about 2140 lb BOD or about 8,000 imperial gallons of primary sewage sludge at 3 per cent solids. Consuming this sludge in the sulphate reduction process removes it from the costly anaerobic stabilization, dewatering and disposal processes.

Like primary sewage sludge, other high BOD waste streams from other industrial activities can be accepted for the reduction reaction.

Thus the employment of the sulphate-reduction process for metal recovery on a commercial basis can definitely influence the disposal practice of toxic or difficult to dispose of material. Instead of requiring a costly, no benefit disposal as is presently practiced, the use of these waste streams in a sulphate-reducing reactor can produce a useful material of considerable market value.

## 6.2. EFFECT ON RESOURCE RECOVERY AND RECYCLE

An increasing standard of living is putting continuous stress on the world's non-renewable resources. The increasing demand for non-ferrous metals can be seen from the fact that the world's output of these raw materials is increasing at an annual rate of 6 to 8 percent.

It is estimated that the free world annually disposes of 200 to 400 million pounds of non-ferrous metals from the metal finishing and associated industries. This disposal is equivalent to the production from several mines. It is recognized that all of these metals may not be economically recoverable, however the majority of these waste products are produced in large urban centres where centralized collection is possible. Thus, the use of the sulphate-reduction technology for metal recovery could significantly reduce the amount of metals being disposed, and could effectively recover these metals for their reuse, thereby directly influencing the rate of resource exploitation.

In a recent address (32), Dr. V.E. McKelvey, Director of the U.S. Geological Survey, Department of the Interior, pointed out that because of the rising demand and dwindling supply of low cost resources, the U.S. has to import 15 percent of the total non-fuel mineral supply. McKelvey warned that "aside from a relatively few cases, we shall face extensive shortages by the end of the century unless prompt and effective actions are taken to avoid them". McKelvey further said that aside from searching for and developing new ore bodies, conservation and recycle of used materials is necessary. The recycle of materials, and especially metals, not only saves energy but also reduces the amount of solid waste requiring disposal at the taxpayers expense.

It is estimated that the U.S. annually disposes of about 100 million pounds of non-ferrous metals from the metal finishing and associated industries, at an average value of about \$1 per pound of metal, this recovery could have effect of 100 million dollars on the balance of payment. In addition, the operation of the sulphate-reduction process and the processing of the resulting metallic sulphide would create urban employment so desperately needed in many areas of the U.S.

### 6.3. EFFECT ON ENERGY CONSERVATION

The mining, beneficiation, smelting and refining of non-ferrous metals are all high energy consuming operations. However, when high grade ore bodies are depleted, and lower grade ore has to be mined, the energy consumption for mining and beneficiation will increase in proportion to the decrease in the mineral concentration. It is generally accepted (33) that mining a 2 percent copper ore body requires 6000 kwh of energy for mining per ton of copper produced. Thus, if a 1 percent ore body is mined, 12,000 kwh of energy are consumed for the mining operation.

Recovering non-ferrous metals from metal finishing wastes, and returning it to the smelter does not require mining and thus offers a net energy incentive of 6,000 - 12,000 kwh per ton of metal.

The metal finishing waste acid neutralization and disposal at a suitable deepwell site requires energy in the form of chemicals, transportation and pumping and perhaps sludge fixation. Diversion of these wastes to the sulphate-reduction/metal recovery process avoids most of these energy related costs.

Stabilization and suitable disposal of organic wastes are also energy demanding operation which could be avoided by consuming these materials in the microbial sulphate reduction reaction.

Thus, it can be seen, that by commercially exploiting the sulphate reduction technology, the impact may be felt in:

- waste disposal practices
- resource recovery
- balance of payment
- urban employment
- energy conservation

CHAPTER SEVEN

7. CONCLUSIONS

Although the small laboratory reactor never achieved true steady-state operating conditions, its successful operation does make possible a number of conclusions:

1. The sulphate-reduction reaction in conjunction with soluble metal sulphate salts can produce a reactor sludge very high in metallic sulphides. The soluble metal sulphate can be a direct industrial waste or a leachate produced by treating industrial wastes.
2. Without achieving steady-state, the reactor sludge contained 28 percent by weight metals. The metal content is expected to rise to as high as 50 percent during steady-state operation.
3. The reactor sludge containing metallic sulphides is comparable in quality to a mine/mill concentrate, and would be suitable as base metal smelter feed.
4. The presence of heavy metal sulphides in the reactor proved not to be toxic to the acclimatized bacteria. A soluble sulphide buffer however appears to be necessary to avoid reduced microbial activity due to heavy metal poisoning.
5. An average sulphide production rate of 150 mg/l/day was demonstrated during the zinc sulphide experiment. However, rates as high as 385 mg/l/day were experienced during the same period.
6. Changing the metal feed solution from zinc to copper plus zinc did not have a drastic effect on the bacteria, however, some acclimatization appears to be necessary.
7. Primary municipal sewage sludge proved to be a suitable organic feed stock for the reduction reaction. However, any biodegradable organic

material is expected to equally as suitable as a reductant.

8. Any non-degradable organic residue remaining in the sludge can be removed by "calcining" of the dried reactor sludge, or it may serve as a fuel substitute during roasting and smelting of this sludge at a suitable base metal smelter.

9. The sulphate reduction process offers a viable, environmentally sound alternative to the present method of metal hydroxide sludge disposal.

10. The laboratory process demonstrated in this work offers an alternative to the purely chemical processes being considered for metal recovery from hydroxide sludges.

11. The demonstrated process is unique, for it uses only waste materials in order to produce a valuable, recyclable metallic sulphide precipitate.

CHAPTER EIGHT

8. RECOMMENDATIONS

The microbial sulphate-reduction process for metal recovery as metallic sulphides has been successfully demonstrated on a laboratory scale. In order to assess the commercial application of this new process technology, extensive pilot plant operations are necessary to demonstrate on a semi-commercial basis the technical and economic viability of such a process.

This type of process lends itself to be operated in conjunction with a waste acceptance terminal, where all the necessary feed stocks are either accepted on a fee basis, or are available free of charge.

If further studies on the sulphate-reduction/metal recovery process are performed, it is suggested that investigations be also directed towards the treatment of metal bearing mine waters.

Appendix III shows a flow sheet and the process design for a pilot plant capable of recovering 1000 pounds of non-ferrous metals per year.

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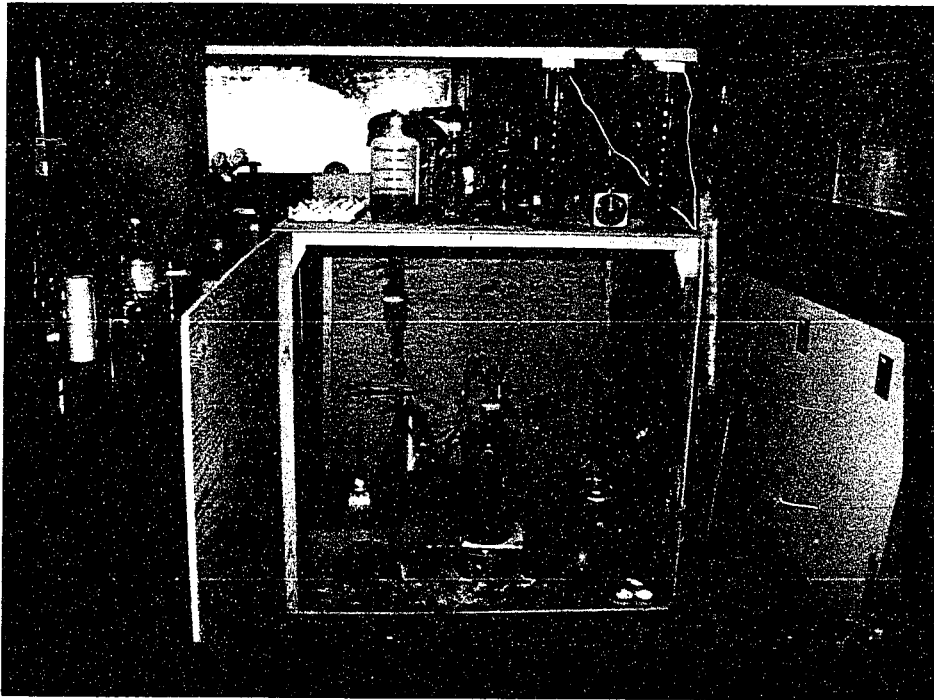
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APPENDIX I

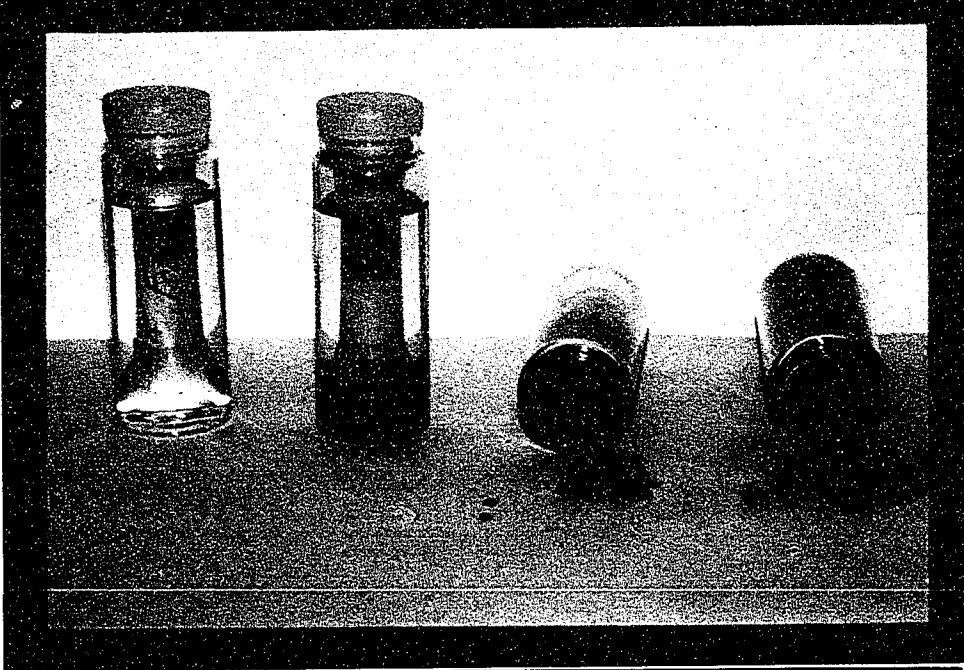
PICTORIAL DISPLAY OF REACTOR SYSTEM AND PRODUCTS



Sulphate reduction reactor feeding on copper/zinc sulphate and primary sewage sludge

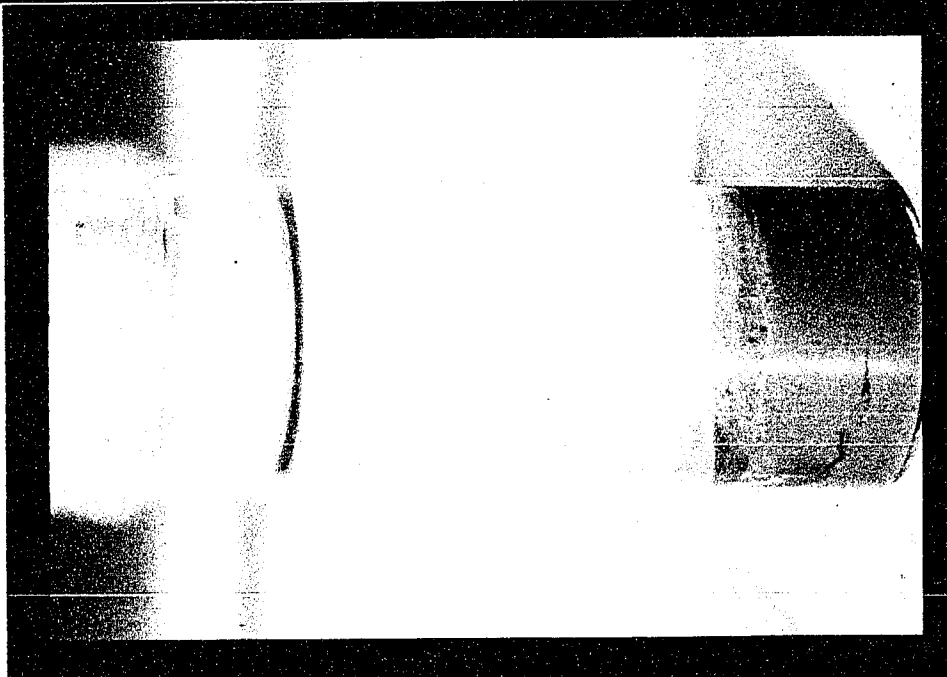


Close up of Reactor

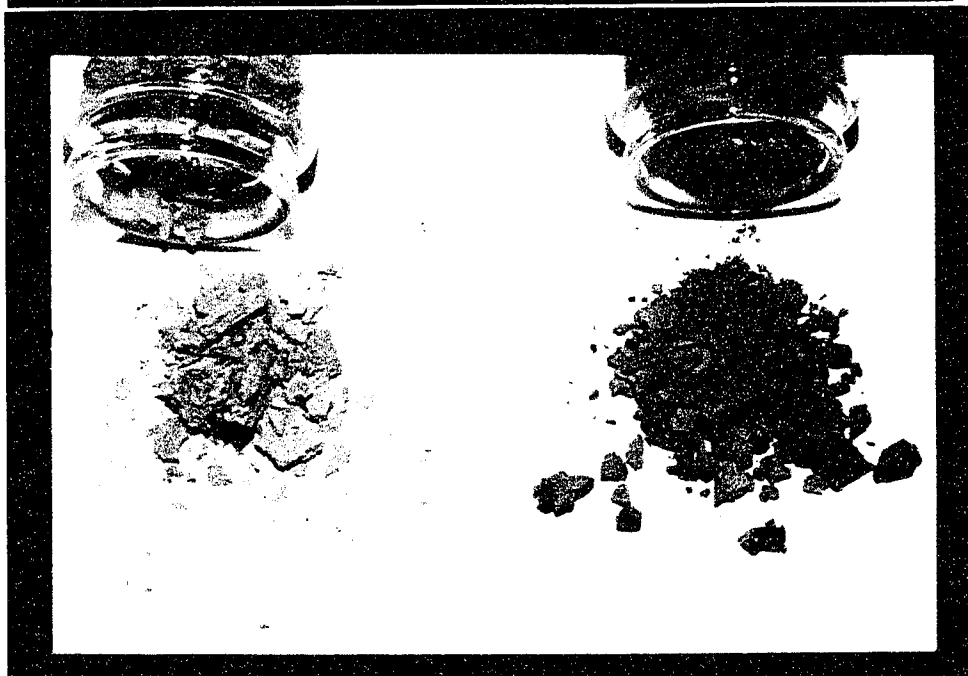


ZINC SULPHIDE EXPERIMENT

- Left to right
- 8 gpl Zn Feed
  - Settled reactor zinc sulphide sludge
  - Dry reactor zinc sulphide sludge
  - Calcined reactor zinc sulphide sludge

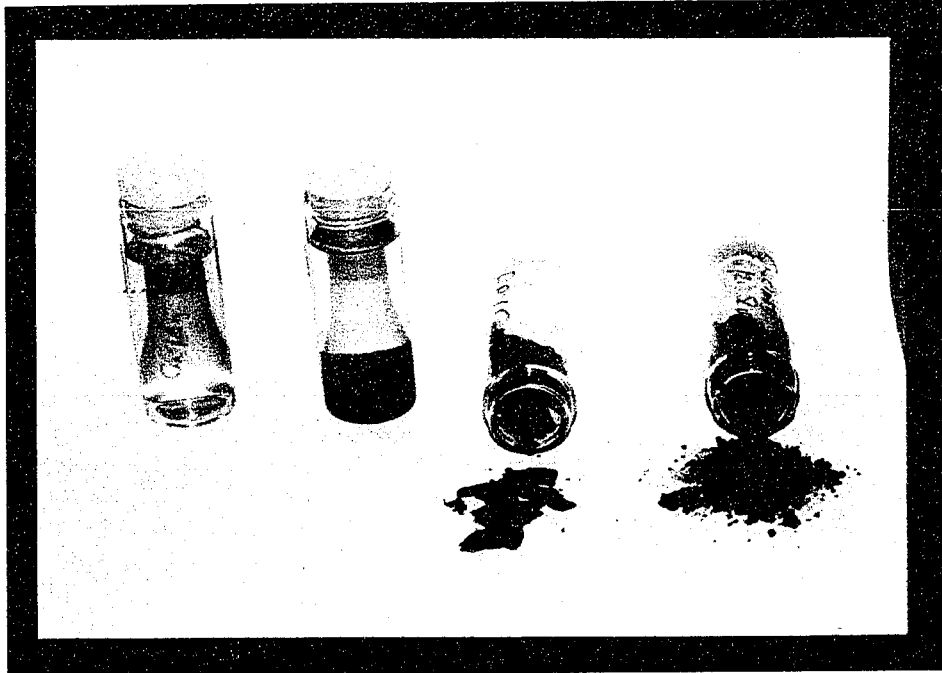


Close up of settled reactor zinc sulphide sludge



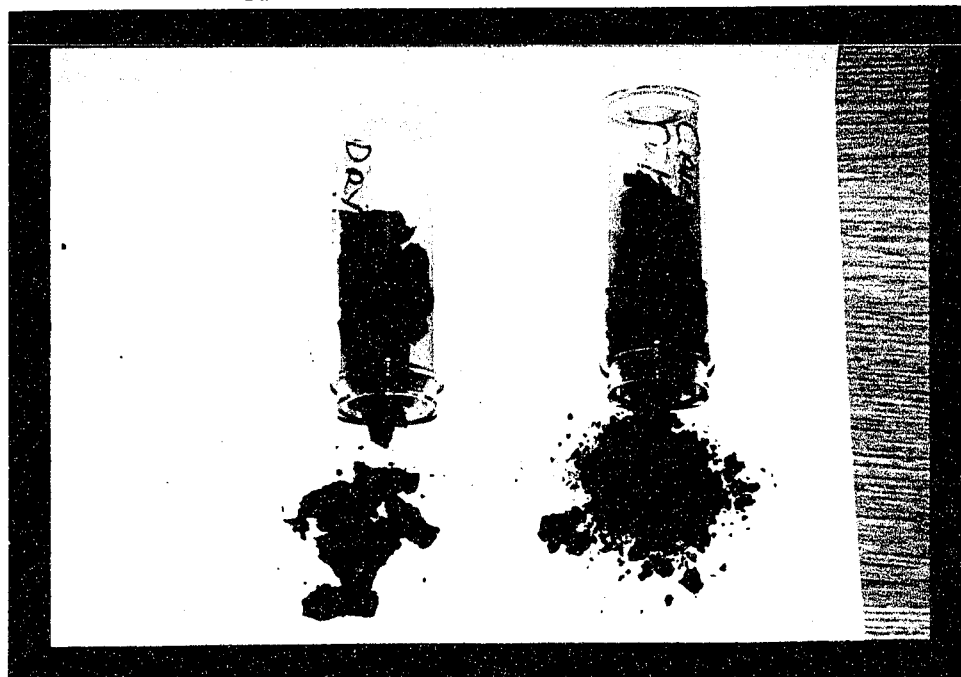
Close up of left to right  
- dry zinc sulphide sludge  
- calcined zinc sulphide sludge

COPPER/ZINC SULPHIDE EXPERIMENT



Left to right

- 1 gpl Cu plus 4 gpl Zn feed
- Settled copper/zinc sulphide reactor sludge
- Dry copper/zinc sulphide sludge
- Calcined copper/zinc sulphide sludge



Close up of: left to right

- Dry copper/zinc sulphide
- Calcined copper/zinc sulphide

APPENDIX II

SOLUBLE EQUILIBRIUM ZINC CONCENTRATION IN THE ZINC SULPHIDE PRODUCTION REACTOR

The minimum soluble sulphide encountered was 11.8 mg/l at a pH of 6.9 and a temperature of 30°C.

$$[\text{Zn}^{2+}] [\text{S}^{2-}] = K_{sp} = 10^{-24}$$

The ionized sulphide concentration is

$$[\text{S}^{2-}] = \frac{K_2 K_3 \cdot [\text{H}_2\text{S}]}{\{\text{H}^+\}^2} = \frac{1.26 \times 10^{-20} \times \frac{11.8 \times 10^{-3}}{32}}{(1.25 \times 10^{-7})^2} = 2.97 \times 10^{-10}$$

∴ The soluble zinc concentration is

$$[\text{Zn}^{2+}] = \frac{10^{-24}}{2.97 \times 10^{-10}} = 3.36 \times 10^{-13} \text{ Moles / l Zn} \\ = 2.15 \times 10^{-8} \text{ mg/l Zn}$$

This concentration is the maximum concentration occurring at the minimum soluble sulphide concentration, and is beyond the limit of detection.

The following spot test<sup>(29)</sup> was carried out to confirm the low zinc levels in solution:

Diphenylthiocarbazon (dithiazone) forms insoluble coloured inner complex salts with a number of heavy metals. These products are easily extracted by organic solvents. The purple-red zinc salt, formed in neutral, alkaline or acetic acid solutions, is soluble in carbon tetrachloride without change of colour.

To avoid interference from other metals, the test is best carried out in alkaline solutions, where zincates will produce the red organic extract.

Feigel reports the limit of alkaline zinc detection by this method

as  $10^{-6}$  grams.

The test was carried out by filtering reactor supernatant and adding 2 per cent by weight sodium hydroxide. One liter reactor supernatant was transferred to a 2 l. separatory funnel and 25 ml carbon tetrachloride containing 2.5 mg. dithiazone was used to perform the zinc extraction. After allowing careful phase separation the dithiazone solution remained green and did not show the characteristic red colour of the zinc-dithiazone complex.

Thus, the spot test confirmed that the zinc concentration was below 0.001 mg/l.

APPENDIX III

PILOT PLANT DESIGN FOR EXTENSIVE STUDIES OF THE SULPHATE REDUCTION/  
METAL RECOVERY PROCESS

Assume the pilot plant is to be capable of producing 1000 lb of metals as metallic sulphides in a 10 month period.

Figure 27 depicts a flow sheet for such a pilot process.

1. RAW MATERIALS AND STORAGE REQUIREMENT

a) Metal Hydroxide Sludge

Assume a hydroxide sludge at 15 percent total solids and dry solids contain 8 percent metal

∴ Sludge requirement is

= 8,333 lb sludge per month

= 700 Igal sludge per month

b) Waste Acid for Sludge Leaching

1 lb metal as sludge consumes about 3 lb of sulphuric acid

∴ the leaching process requires 300 lb sulphuric acid per month

Assume the waste acid is available at 10 percent  $H_2SO_4$ .

∴ The volume of waste acid required = 3000 lb/month = 300 I gal/month.

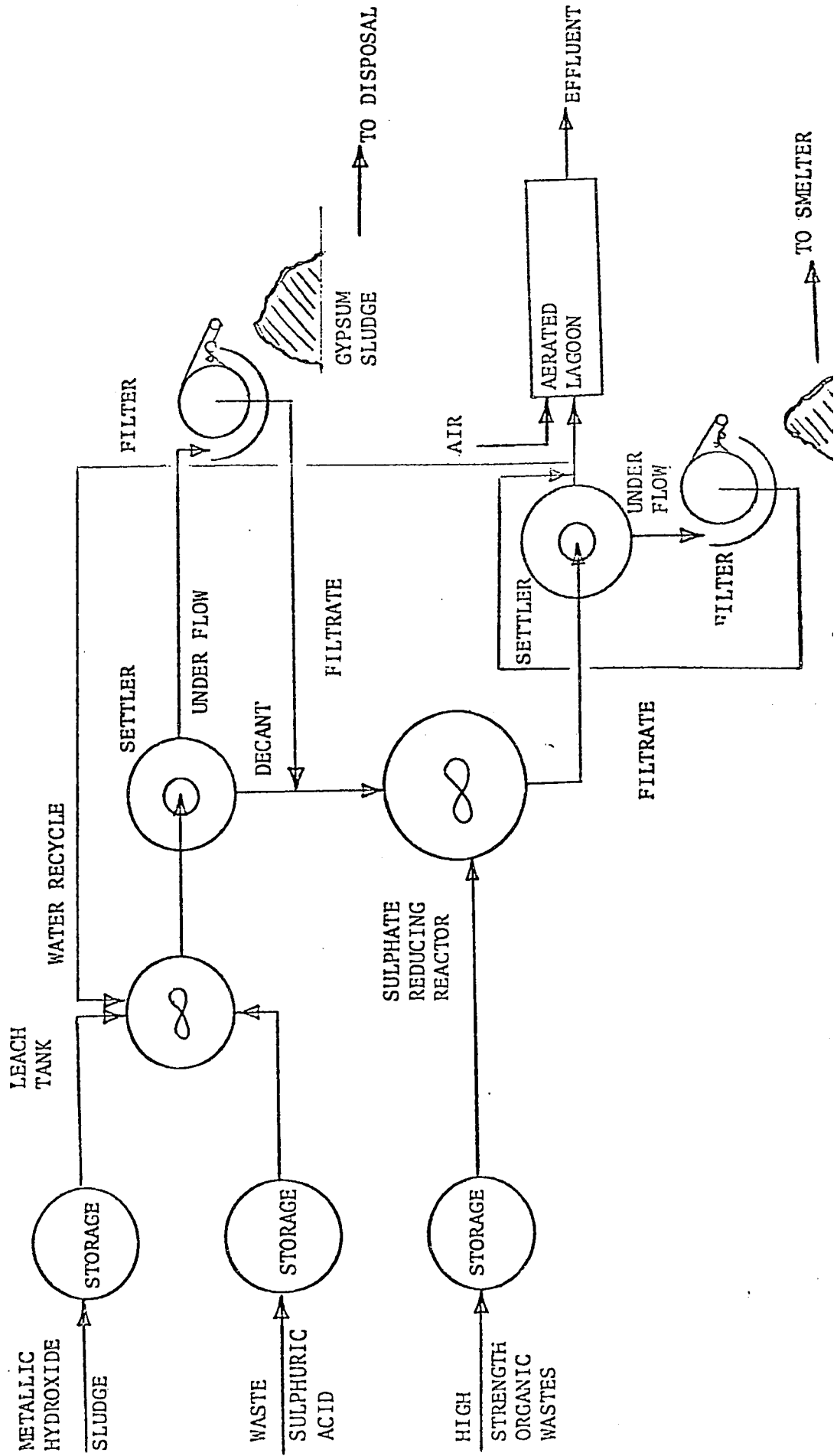
c) Organic Feed Stock

Assume the pilot like the laboratory reactor will utilize primary municipal sewage sludge as organic substrate for the reduction reaction.

1000 lb. metal requires about 1070 lb. of biodegradable organics for the reduction reaction.

FIGURE 27 . . . PROCESS FLOW SHEET FOR PILOT SCALE METAL RECOVERY PLANT UTILIZING

MICROBIAL SULPHATE REDUCTION



Assume primary sewage sludge at 3 percent solids with COD= 50,000  $\frac{\text{mg}}{\text{l}}$  and 50 percent biodegradable.

.∴ Volume of sewage sludge required= 428 I gal/month  
say  $\approx$  500 I gal/month

## 2. LEACH TANK

Feed materials to the leach tank are 700 I gal per month metal sludge and 300 I gal per month of waste sulphuric acid.

The leach reaction is quick, as long as adequate agitation is provided. The leach tank size is not critical, any make shift equipment can be used.

Assume that the water input for leaching is minimal to avoid undue dilution.

.∴ The volume of leachate generated is  $\approx$  1000 I gal per month at a concentration of 10 gpl metal.

## 3. LEACHATE SETTLER OR FILTER

Since the leach liquor is not expected to contain very many undissolved solids, either a settling tank or a filter press can be used for suspended solid removal.

Leachate production can be a batch operation and batch clarification of the liquor can be provided.

Settling characteristics of the leachate are not available.

## 4. SULPHATE REDUCING REACTOR

The laboratory reactor demonstrated an average non-steady-state sulphide production rate of 150 mg/l/day, with individual daily rates as high as 385 mg/l/day.

Reactor Volume at a production rate of 150 mg/l/day

= 5263 l

= 1159 I gal

Reactor volume at the 385 mg/l/day rate

= 452 I gal

∴ Assume a conservative steady state rate of 275 mg/l/day with the required reactor volume of 750 I gal.

The daily reactor throughput rate is about 50 I gal, thus the reactor would operate at a solids (and hydraulic) retention time of 15 days.

## 5. SETTLING TANK

a) Area required for zone settling

Figure 28 shows the relationship between sludge zone settling velocity and total solids concentration for the zinc sulphide sludge.

The following equation describes the relationship

$$ZSV = 5.4^{-0.066TS}$$

in which, ZSV= zone settling velocity, ft/hr.

and TS= total solids, g/l

Assume a settler underflow concentration  $C_u$  of 10 percent solids or 100 gpl (12 percent was demonstrated in the laboratory)

∴ Limiting solids concentration

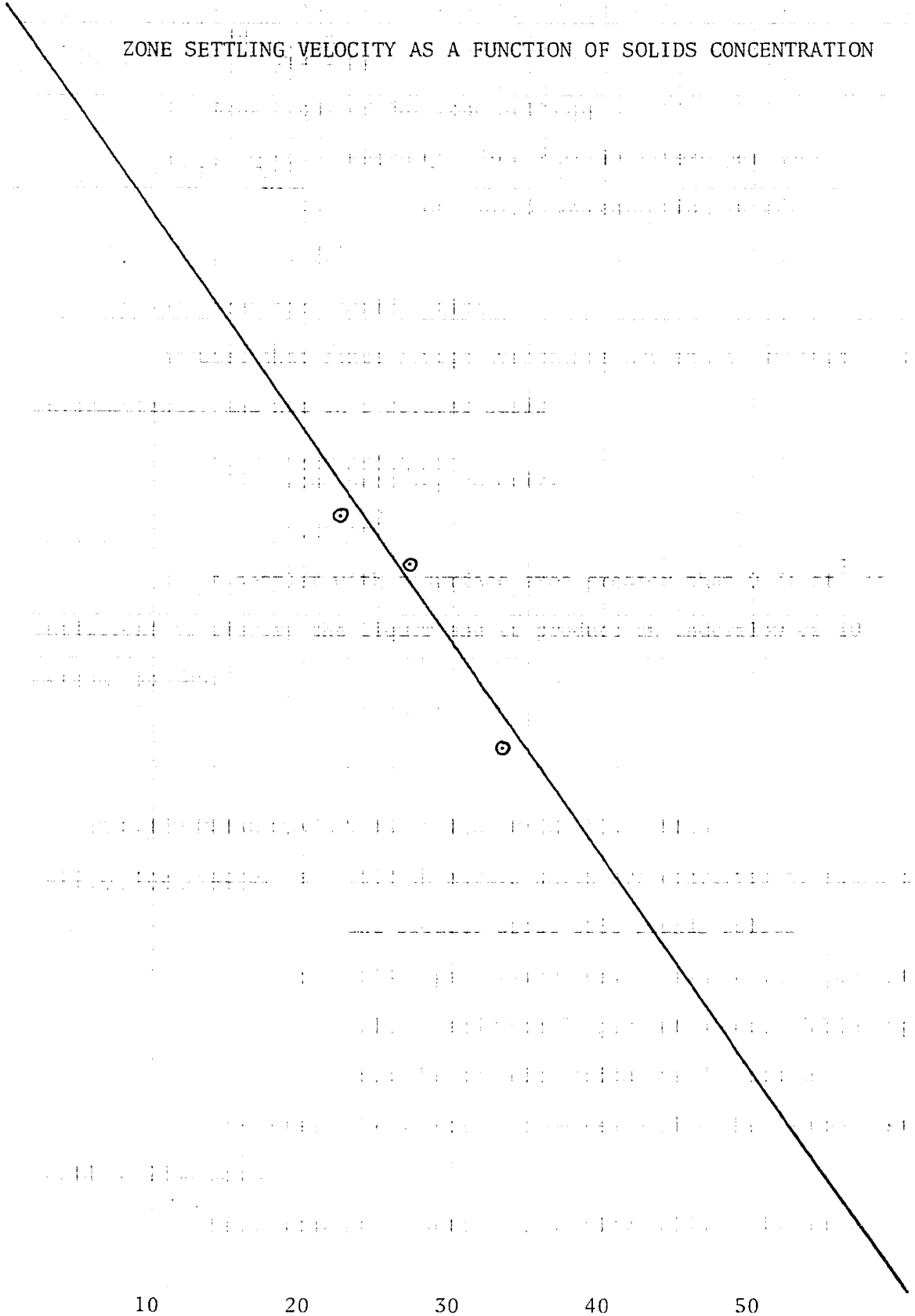
$$C_e = \frac{C_u + \sqrt{C_u^2 - \frac{4 C_u}{k}}}{2}$$

FIGURE 28

ZONE SETTLING VELOCITY AS A FUNCTION OF SOLIDS CONCENTRATION

CS-61

ZONE SETTLING VELOCITY FT PER HR



Thus,  $C_e = 81 \text{ g/l}$

∴ The limiting solids flux is given by

$$G_e = kC_1^2 ZSVe^{-kC_e}$$
$$= 307 \frac{\text{g}}{\text{ft}^2 - \text{hr}}$$

∴ Area required for zone settling

$$A_{ZSR} = \frac{Q C_o}{G_1} \quad \text{where } Q = \text{flow rate in liters per hour}$$

$C_o = \text{solid concentration in g/l}$

$$= 0.71 \text{ ft}^2$$

b) Area for clarification

Assume, that since sludge quantities are small, wastage is done intermittently and not on a regular basis

$$\therefore A_{cl} = \frac{\text{Overflow rate}}{\text{Zone settling velocity}}$$
$$= 0.28 \text{ ft}^2$$

∴ A settler with a surface area greater than  $0.71 \text{ ft}^2$  is sufficient to clarify the liquor and to produce an underflow of 10 percent solids.

#### 6. EXPECTED METAL CONTENT IN SETTLER UNDERFLOW SOLIDS

Feed to the reactor a) 1000 lb metals which are converted to sulphides and produce about 1530 pounds solids

b) 5000 I gal primary sewage sludge at 3 percent solids, and with 50 percent biodegradable organics.

Thus the organic residue is 750 pounds

∴ The total bulk of solids produced during the 10 month study would be 2280 pounds.

∴ Metal content in settler underflow solids = 44 percent

Calcining of dry settler solids.

During calcining, non degradable organics from the sewage sludge are thermally degraded.

According to laboratory tests, 60 percent of the primary sewage sludge is volatile.

Thus, with 50 percent of the solids consumed in the reactor, the other 10 percent are thermally degraded during calcination.

∴ The residual solids from the primary sewage sludge= 600 lb

∴ The metal content of the calcined product is expected to be 47 percent.

Thus it can be seen that if an organic feed material is used that has little or no residue after ignition, the metal content in the calcined solids could be as high as 65 percent.

APPENDIX IV

EXPERIMENTS TO IMPROVE THE SULPHIDE ANALYTICAL DETERMINATION

During the course of the experiment, it became apparent that the analytical technique employed for sulphide determination might have been producing low analytical results. The method employed was to digest a sample with acid, strip the resulting hydrogen sulphide gas with carbon dioxide gas and absorb the hydrogen sulphide gas with zinc acetate. The zinc sulphide was reacted with a known volume of standard iodine solution, and the excess iodine was titrated with standard thiosulphate solution. The soluble sulphide analysis was checked by taking three samples of reactor slurry, processing the fixed supernatant of one as previously described in order to determine the soluble sulphide. One of the other two samples was fixed with caustic soda to prevent  $H_2S$  flashing. To the third sample an excess of zinc sulphate was added to consume any soluble  $H_2S$ . After centrifuging and filtering, an excess amount of standard iodine was added to each sample. The samples were acidified and the unconsumed iodine was titrated with standard thiosulphate solution. Thus, the sample with the excess zinc sulphate added was used as a blank to determine the iodine consumption by the soluble organics. Another cross check was run by comparing the direct titration method with a gas stripping method where the stripping medium was nitrogen gas and the liberated hydrogen sulphide was absorbed in a strong sodium hydroxide solution. The sodium sulphide solution thus produced was analyzed as previously with iodine and thiosulphate. The results of the cross checks are shown in table VII.

Table VII suggests that the analytical sulphide data shown in this study may be low, and that the sulphide production rates are actually higher than indicated.

TABLE VII

COMPARISON OF ANALYTICAL METHODS FOR THE DETERMINATION OF SOLUBLE SULPHIDES

Analytical Method	Soluble Sulphide
Comparison 1	
Digestion of fixed filtrate, gas stripping and absorption of H <sub>2</sub> S into zinc acetate. Reaction of the zinc sulphide with excess iodine and backtitration of the excess iodine with thiosulphate	42.3 mg/l
Direct titration of the fixed filtrate and blank with iodine and thiosulphate as previously described	174.2 mg/l
Comparison 2	
Direct titration of fixed filtrate and blank with iodine and thio-sulphate as previously described	262.5 mg/l
Digestion of fixed filtrate, gas stripping with N <sub>2</sub> and absorption of the H <sub>2</sub> S with caustic soda. Reaction of the absorbed sulphide with excess iodine and back-titrating the excess iodine in the acidified solution	273.7 mg/l