

EFFECTS OF OPERATING VARIABLES
OF SULPHIDE PRECIPITATION

EFFECTS OF OPERATING VARIABLES
OF SULPHIDE PRECIPITATION

by

Michael J. Whalley

A Project Report
Submitted to the Faculty of Graduate Studies
in Partial Fulfillment of the Requirements
for the Degree
Master of Engineering

McMaster University

July 1977

MASTER OF ENGINEERING (1977)
(Chemical Engineering)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: Effects of Operating Variables of Sulphide
 Precipitation

AUTHOR: MICHAEL JOHN WHALLEY, B.Sc. (Queen's)

SUPERVISOR: Dr. D.R. Woods

NUMBER OF PAGES: xi, 78

ABSTRACT

The effects of engineering operating variables in the sulphide precipitation of Cu^{+2} , Cd^{+2} and Zn^{+2} have been examined with a statistical experimental design. The independent (operating) variables studied were 1) the level of sulphide added, 2) the level of Fe^{+2} added as scavenger for excess HS^- ion and 3) the pH level. The dependent variables were the concentrations of dissolved, suspended and total metals in the supernatant after treatment and the zone settling velocities of the suspensions.

The major effect of the operating variables was to yield a precipitate which was either a stable colloid or a suspension which coagulated and settled. Stable colloid formation was associated with an excess of HS^- ion. For those conditions which produced coagulant suspensions, 1) ten of the thirteen correlations between dependent and independent variables were not statistically significant at the 95% confidence level, 2) for practical purposes, variations in engineering operating variables did not alter the levels of dissolved and suspended Cu^{+2} , Cd^{+2} and Zn^{+2} .

When the precipitates coagulated and settled, concentrations of approximately 100 mg/l of each of Cu^{+2} , Cd^{+2} and Zn^{+2} were reduced to mean values of 0.41, 0.33 and 0.62 mg/l total metals and 0.03, 0.01 and 0.37 mg/l dissolved metals respectively.

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to Dr. D.R. Woods for his invaluable guidance and encouragement during this work.

I would also like to thank others who helped:

Mr. Henry Behmann for interesting and useful discussions on sulphide precipitation and for advice and instruction during the chemical analysis;

Dr. W.J. Snodgrass for generous assistance in the preparation of the report;

Mrs. Debbie McCreath, whose excellent typing was very much appreciated;

The National Research Council for providing financial support for the research and McMaster University for awarding the teaching fellowship.

DEDICATION

To the members of the E.R. Hall Society whose lively weekly meetings dedicated to the higher pursuits provided the type of intellectual stimulation necessary to sustain good research.

TABLE OF CONTENTS

	<u>Page</u>
CHAPTER 1 - INTRODUCTION	1
CHAPTER 2 - REVIEW OF THEORY AND PRACTICE	5
2.1 Theoretical background	5
2.1.1 Solution chemistry	5
2.1.2 Precipitation	6
2.1.3 Adsorption	8
2.1.4 Coagulation	9
2.1.5 Flocculation	10
2.1.6 Settling velocity	10
2.2 Practical and experimental experience	11
2.3 Summary of experience	14
CHAPTER 3 - OBJECTIVES OF THE STUDY	16
CHAPTER 4 - EXPERIMENTAL	18
4.1 Choice of constants for the system	18
4.2 Independent variables and their levels	19
4.3 Design of experiments	21
4.4 Apparatus	21
4.5 Reagents	23
4.6 Experimental procedures	25
4.7 Analytical procedures	27
CHAPTER 5 - RESULTS AND DISCUSSION	29
5.1 Statistically designed experiments	29

	<u>Page</u>
5.1.1 General discussion of the statistical analysis	29
5.1.2 Regressions of the total metal data	35
5.1.3 Regressions of the suspended metal data	36
5.1.4 Regressions of the dissolved metal data	36
5.1.5 Regressions of settling velocities	38
5.1.6 Sulphide residuals	38
5.1.7 The role of iron	39
5.2 Additional experiments	
5.2.1 A comparison of continuous and batch precipitations	41
5.2.2 Adsorption of sulphide on preformed sludge before precipitation	44
5.2.3 Effects of pH	44
CHAPTER 6 - CONCLUSIONS	49
6.1 Effect of operating variables	49
6.1.1 General	49
6.1.2 Effect of ferrous iron	49
6.1.3 Level of sulphide addition	50
6.1.4 Level of pH	50
6.1.5 Comparison of continuous and batch precipitations	50
6.2 Mechanisms of the process	51
6.3 Overall effectiveness of the process	51
6.4 Recommendations for further work	52
6.4.1 Mechanistic studies	52
6.4.2 Practical application	52
REFERENCES	53

	<u>Page</u>
APPENDIX A - EXPERIMENTAL CONDITIONS AND PROCEDURES	55
A.1 Additional experimental procedures	56
A.1.1 Tests showing effect of iron on settling	56
A.1.2 Tests showing effect of adsorbing sulphide on preformed sludge	56
A.2 Experimental details for the continuous run	57
APPENDIX B - EXPERIMENTAL DATA	59
APPENDIX C - CALCULATIONS AND DISCUSSIONS	70
C.1 Sample calculation of equilibrium concen- trations	70
C.2 Calculation of mean velocity gradient	72
C.3 Discussion of analysis of transformations	72
C.4 Estimation of model parameters and related statistical tests	75
C.4.1 Parameter estimates	75
C.4.2 Analysis of variance	76
C.4.3 Statistical tests	76
C.5 Experimental error	78

LIST OF TABLES

	<u>Page</u>
1. Comparison of sulphide and hydroxide solubility products	3
2. Variable levels and their coded equivalents	20
3. Experimental design matrix	22
4. Summary of statistical tests of the regressions	33
5. Means and standard deviations of dependent variables for the experimental design runs, not including stable colloid results	34
6. Effect of Fe on settling by removing excess sulphur species	40
7. Effect of adsorbing HS^- on preformed sludge before precipitation	45
8. Effect of pH adjustment before and after precipitation	45
A1. Concentrations of stock solutions	55
A2. Concentrations of the feeds to the continuous reactor	58
B1. Concentrations of total metals after 40 minutes settling	59
B2. Concentrations of dissolved metals after 40 minutes settling	60
B3. Concentrations of suspended metals after 40 minutes settling	61
B4. Parameter estimates from least squares fit of data to empirical model	62
B5. Zone settling velocities of flocculant suspensions	64
B6. Combined residual concentrations of S^{-2} , HS^- and H_2S in the supernatant	65
B7. Metals concentration data for the effluent from the continuous precipitation vessel	66
B8. Composition of residual floc from experimental design runs	67

	<u>Page</u>
B9. Composition of residual floc from the continuous run	68
B10. Effect of adjusted pH on settling velocity of aged metal sulphide sludge	69
C1. Results of the analysis of transformations of the concentrations of total Fe	74
C2. Results of the analysis of transformations of the concentrations of total Cd	75
C3. Standard deviations of data from replicate runs	78

LIST OF FIGURES

	<u>Page</u>
1. The Busch Biological Reactor used in the continuous precipitation experiment	24
2. Interface settling velocity as a function of pH for aged metal sulphide precipitate	48

CHAPTER 1

INTRODUCTION

Economic and efficient processes must be available to remove metal ions from industrial waste waters. Even in small concentrations many heavy metals are toxic to humans and other organisms. As accessible mineral resources are depleted it becomes more important to recover metals solubilized during processing and discharged into waste streams. Recovery processes are especially required in the metal plating and mining industries.

Methods of metal ion removal currently used include reverse osmosis, ion exchange, cementation, electrodeposition, sulphide precipitation and hydroxide precipitation. Each of these is briefly discussed by Dean, Bosqui and Lanouette (1972). By far the most widely used technique involves neutralization and hydroxide precipitation, yet there are many problems associated with this process. Metal hydroxide slurries are very difficult to settle and to thicken. The solubilities of metal hydroxides combined with the difficulty in settling make metals removal incomplete to a considerable degree. The problems are compounded by the fact that the solubilities of the metals are lowest at different values of pH and some metals tend to redissolve under alkaline conditions, Rouse (1976).

The subject of this report is sulphide precipitation. Unlike hydroxide precipitation it has not been widely used in industry. Nevertheless, Rouse (1976) reports that (1) it is a primary technique for

mercury removal in chlor-alkali plants, (2) it is used for the removal of arsenic in the manufacture of phosphoric acid and (3) it has recently been applied in Japan to removal and recovery of cadmium. Because of the lack of operating experience and of data on effluent quality there is a need for study of the process to assess its operational advantages and disadvantages.

The solubility products of heavy metal sulphides in general are very low and smaller than the solubility products of the corresponding hydroxides. Therefore, precipitation with sulphide should provide better removal from solution of a given metal than hydroxide precipitation. A comparison of the solubility products of metal sulphides and hydroxides is given in Table 1. The range in solubility products of different metals also permits a sequential precipitation which has potential as a preliminary separation procedure. The main problem with metal sulphide precipitates is that they very often form as colloidal suspensions. If the separation of the precipitate from the liquid phase is difficult or incomplete the benefit of obtaining very low concentrations of dissolved metals is obviated.

There are several possible ways of introducing sulphide ions into the metals solution. The simplest is to bubble through hydrogen sulphide gas, but this compound is extremely toxic, obnoxious and difficult to handle. In quantitative chemical analysis thioacetamide is used as a source of sulphide ions. Under appropriate conditions thioacetamide very slowly hydrolyzes releasing sulphide at a rate which allows growth of large, dense crystals, Swift (1960). Despite this advantage, thioacetamide

TABLE 1

Comparison of Sulphide and Hydroxide
Solubility Products

Temperature 18°C; values from Weast (1974)

Metal Ion	K_{sp} (Sulphide)	K_{sp} (Hydroxide)
Cu^{+2}	8.5×10^{-45}	— a
Cd^{+2}	3.6×10^{-29}	— a
Zn^{+2}	1.2×10^{-23}	1.8×10^{-14}
Fe^{+2}	3.7×10^{-19}	1.6×10^{-14}

^a Values not available; formation of complexes dominant.

is prohibitively expensive for use on an industrial scale. In anaerobic digestion of sewage sludge metals removal from solution can be accomplished by adding sulphate ions. These are converted by sulphur reducing bacteria into sulphide ions, Lawrence (1965). Simple addition of a solution of sodium sulphide is a direct method which has been used in chlor-alkali plants, Perry (1974). Because sulphide ion is itself toxic, fairly sophisticated control equipment must be used to govern its introduction into the waste water. Residual sulphide in the effluent after precipitation is quite undesirable.

CHAPTER 2

REVIEW OF THEORY AND PRACTICE

2.1 Theoretical background

A discussion of the theory which may be applied to the sulphide precipitation process can be divided into six major areas: 1) solution chemistry, 2) precipitation, 3) adsorption, 4) coagulation, 5) flocculation, and 6) settling behaviour.

2.1.1 Solution chemistry

A theoretical analysis of the process may begin with an examination of the equilibrium solution chemistry involved. Ideally all species in solution and in the solid phase could be identified a priori and equations set up to describe the reactions between them. If equilibrium constants were available and if a solution to the set of equations were obtained it would predict the activities of all species at equilibrium after precipitation. A very simple example of such a calculation is provided in Sec. C.1.

However, such calculations can provide only a first approximation to the residual activities or concentrations of metals and sulphur species. There are two main reasons why the calculated values cannot be expected to accurately predict the real ones.

- (1) The liquid phase may not have achieved equilibrium with the

precipitates. Therefore the use of thermodynamic equilibrium constants may give inaccurate results.

(2) Conditions of the precipitation process give rise to homogeneous nucleation with the production of huge numbers of very small crystal nuclei and a large solid-liquid interfacial area. It can be expected that adsorption reactions play an important role, Salutsky (1959, p. 755) and that significant quantities of ions are removed from solution by adsorption. This will have an effect on the solid-solution reactions which presently cannot be quantified.

Three side reactions of importance in the sulphide precipitation system are: 1) complex formation of Cu^{+2} and Cd^{+2} with HS^- and S^{2-} which leaves both the sulphur and metal in solution, Stumm and Morgan (1970, p. 260), 2) oxidation of sulphide by dissolved oxygen and ferric iron, Chen et al. (1972), 3) complex formation of metals with chelating agents. The latter are commonly used in metal plating baths, Manahan and Smith (1973). When a metal is complexed it is no longer a free metal ion and cannot be precipitated, yet it is still soluble. Because of the difficulties referred to in the previous paragraph and because "the nature of metal sulphide complexes in solution seems remarkably unknown", Chen et al. (1972), experimental measurements are required to obtain reliable values of dissolved metal concentrations after precipitation.

2.1.2 Precipitation

According to Pohl (1954) the mechanism of metal sulphide formation

predominantly involves attack of the HS^- ion on a metal ion to form an intermediate reactive complex. This decomposes into a metal sulphide molecule. By random density fluctuations, the molecules may group into loosely structured embryos. If these assume the ordered geometric configuration of a nucleus, then crystal growth can proceed. The most important factor bearing on crystal formation is the ratio of the activity in solution to the root of the thermodynamic solubility product. This is called the saturation ratio. Because metal sulphide solubilities are so low, saturation ratios brought about by direct mixing of reactants are usually very high unless the solutions are extremely dilute.

During precipitation metal sulphide molecules can either join onto a previously formed crystal or combine with a small number of other molecules in the process of nucleus formation. When the saturation ratio is very high the nucleation process greatly predominates at the expense of crystal growth, Walton (1967, p. 155), resulting in the formation of huge numbers of minute particles with disordered lattices. Measurements of the solubility of such "active" forms of precipitate give solubility products which are higher than those for larger, ordered crystals, Stumm and Morgan (1970, p. 166). Apparently the only feasible way of reducing the saturation ratio is to use the techniques of precipitation from homogeneous solution, Gordon, Salutsky and Willard (1959), but these are too expensive for industrial use.

When one considers precipitation from a solution of several metals as opposed to a solution of a single metal the following questions arise. To what degree is there formation of true mixed crystals in which more than

one type of metal is accommodated into the crystal lattice without causing serious deformation? How would variations in crystal composition affect surface properties? The kinetics of nucleation are a strong function of the saturation ratio, Nielsen (1965), which in general will be different for different metals. Do the kinetics of the nucleation of the different metal sulphides play a significant role in the behaviour of mixed precipitates? Although these questions are pertinent to the problem investigated their examination must await future studies.

2.1.3 Adsorption

Adsorption effects can play a dominant role in the behaviour of precipitates formed by homogeneous nucleation. Such precipitates have a very high surface to volume ratio and a disordered lattice with numerous surface imperfections, Stumm and Morgan (1970, p. 166). Ions at the surface are incompletely co-ordinated and therefore free to attract ions of opposite charge from the solution. Surface defects such as steps or corners provide groups of adjacent ions which can hold an adsorbed ion more strongly than a flat surface.

Which ions in solution will be adsorbed and to what extent will adsorption occur? Salutsky (1959) states: 1) ions common to those within the precipitate are strongly attracted, 2) ions whose compounds with the oppositely charged constituent of the lattice are slightly soluble will be well adsorbed and 3) in general, adsorption increases with decreasing solubility of the impurity compound. According to these guidelines HS^- should be strongly adsorbed and OH^- less strongly adsorbed to heavy metal

sulphide precipitates.

Reviewing the evidence available before 1967, Walton (1967, p. 140) concluded that no existing unifying theory could describe the adsorption of ions on precipitates. However, Salutsky (1959, p. 755) held that the Freundlich isotherm was of considerable applicability. The form of the Freundlich equation is $\log Q = \log K + (\log C)/n$ where Q is the degree of adsorption, C the concentration of ions in solution and K and n are constants. Nevertheless, it can be generally stated that the degree of adsorption of an ion will increase with higher concentrations of that ion remaining in solution after precipitation.

2.1.4 Coagulation

The solids formed during precipitation from a highly oversaturated solution are too small to permit their separation from the liquid phase by sedimentation. Before sedimentation can occur the small particles must agglomerate into larger bodies. These will have a lower surface to mass ratio and can attain higher settling velocities before drag forces counter balance the net body force.

Coagulation is the process of reducing the coulombic barrier between particles so that when brought into close contact they may adhere. This may be accomplished by changing the surface properties of the particles to reduce repulsive forces, by altering the ionic strength of the solution to compress the double layer or by introducing a bridging agent that may attach two or more particles.

Altering the surface charge by adsorption of potential determining ions is perhaps the most important factor in the coagulation of metal sulphides precipitated by direct mixing of reactants. If HS^- is added in excess of the metal ions present in order to obtain high removal it will be adsorbed onto the precipitate surfaces. This will increase the surface charge which is inherently negative, Bituminous Coal Research Inc. (1969, p. 36), and make coagulation more difficult. The effect could be compounded if precipitation occurs at high pH and adsorption of hydroxyl ion becomes important.

2.1.5 Flocculation

Particles must be brought into close contact to have the opportunity to adhere or flocculate. If the overall force between two particles is attractive it usually comes into effect only at very small separations. Particles of sub micron size are subject to random Brownian motion and experience collisions even in liquid which has no macroscopic motion. Larger particles are much less subject to Brownian motion and can be made to collide only if turbulence and velocity gradients are imparted to the fluid by stirring. The average velocity gradient used for flocculation must be large enough to cause frequent interparticle contacts but not so large that agglomerates are torn apart by shear forces. Typical velocity gradients applied in water and waste water treatment are in the range 10 to 100 sec^{-1} , Weber (1972, p. 94).

2.1.6 Settling velocity

The type of settling behaviour which is often exhibited by coagulated

or flocculated suspensions is called zone settling. In a batch settling test, if the suspension is initially introduced at a uniform concentration, an interface forms near the top of the liquid dividing the zones of clarified supernatant and sludge. Initially, the interface travels downward at a constant velocity which provides an estimate of the clarification capacity of the system. In an ideal clarifier the overflow rate must be less than this settling velocity.

Because of the considerable difficulty of predicting the settling velocity of a suspension, measurements must be made to obtain it. Factors which influence settling velocity are concentration of solids in the suspension, density of the solid phase, average floc size and fluid viscosity.

2.2 Practical and experimental experience

Practical experience with the sulphide precipitation process is very limited to date. A report by Perry (1974) provides detailed information on sulphide precipitation as applied in a chlor-alkali plant for mercury removal. The process combined pH adjustment, addition of sodium sulphide and filtration on a precoated filter. It was chosen as "most consistently effective and practical" from several alternate treatment methods. The removal of mercury achieved was 87 -99.2% from solutions containing 0.3 to 6 ppm mercury with an average effluent concentration of 50 ppb. Capital costs for the 380 ℓ /min, 100 gpm system were \$144,000 and operating costs for the sulphide system were 13¢/1000 ℓ or 50¢/1000 gal.

A report by the Bituminous Coal Research Inc. (1969), provides results of a study using a lime, hydrogen sulphide process for the treatment

of acid mine drainage. The conclusion of the report was that the process was less attractive technically and economically than other methods of acid mine drainage treatment, but several interesting results were obtained. The freshly formed FeS sludge was found to be a stoichiometric compound corresponding to the formula FeS yet X-ray diffraction patterns indicated that it was "amorphous, structurally disordered and (presumably) hydrated". Its surface charge was negative and cationic flocculating aids were effective in promoting coagulation and more rapid settling. The recommendations of the report reflect the lack of understanding of the fate of sulphur species in solution and consequently the need to determine the optimum dosage of applied sulphur species. A report by Larsen, Shou and Ross (1973) also concerns treatment of acid mine drainage using lime neutralization followed by sulphide precipitation with H_2S . They claim that field trials of the technique were successful and that the metal removals obtained closely matched those predicted by calculations based on equilibrium data.

A problem not addressed by the two previously mentioned reports is that of residual sulphide or hydrosulphide ion (HS^-) in the effluent stream. A method for eliminating this problem was the basis of a U.S. Patent by Anderson and Weiss (1973). The process simply involves dissolving in the solution of the heavy metal pollutants a soluble salt of a heavy metal having a higher equilibrium sulphide ion concentration. When sulphide ion is added the heavy metal acts as a scavenger for excess sulphide remaining after precipitation of the less soluble metals. The number of moles of sulphide added must be greater than the number of moles of

pollutant ions in a suggested ratio of from 2:1 up to 10:1 but total sulphide must be less than the total of the pollutant metal plus added metal. The features of the process listed in the patent were: 1) avoidance of the use of H_2S , 2) avoidance of the formation of soluble complex ions such as HgS_2^{-2} , AgS^- etc., 3) formation of mixed metal sulphide precipitates, 4) more effective removal than hydroxide precipitation alone.

Preliminary investigations of the sulphide precipitation process have been made at McMaster University, Behmann and Norman (1972), Behmann, Netzer and Norman (1972), Behmann (unpublished report, 1973). They reduced the concentration of nine different heavy metals from concentrations of 100 mg/l to less than 1 mg/l. In all cases suspensions were filtered after precipitation and no measurement of settling ability of the precipitates was made. Attention was brought to the fact that the precipitates were of submicron size and did not settle or filter well. In an attempt to determine an optimum sulphide to metal ratio it was found that metals removal from solution increases with increased sulphide dosages, but further study was recommended. The idea outlined in the previously mentioned patent was employed. Fe^{+2} was used as the scavenging species in the removal of Ni^{+2} . It was suggested that the use of Fe^{+2} as a scavenger might also improve settling since under alkaline conditions excess Fe^{+2} would precipitate as the hydroxide. The short lived, charged hydroxo complexes which are formed as kinetic intermediates to ferrous hydroxide could be effective as coagulating agents, Weber (1970, p. 101). Behmann also suggested that recycling the precipitate might improve settling and lessen the phase separation problem by forming a denser precipitate.

Significant increases in the solids concentration of zinc hydroxide slurries obtained with the use of a precipitate recycle system were reported by the American Enka Company (1971). The influent metals solution was contacted with a dense slurry of previously precipitated zinc hydroxide. The authors of the report claimed that the zinc in solution adsorbed onto the solid phase and implied that when alkali was added the zinc precipitated on the surface of the old precipitate. Scanning electron microscope photographs graphically demonstrated the morphological differences between the laboratory formed precipitate and the recycled sludge. Even after 10 repeated precipitations the laboratory samples appeared as very loose leaflets of about 2μ in diameter whereas the recycled sludge appeared as solid rounded particles of average diameter 4 to 8μ .

2.3 Summary of experience

(1) The use of a scavenger metal as suggested by Anderson and Weiss (1973) holds promise for eliminating residual sulphur species.

(2) The use of hydrogen sulphide gas can be eliminated by using a solution of sulphide ion as the precipitant.

(3) Liquid phase concentrations of many heavy metals can be reduced to well under $1 \text{ mg}/\ell$ with sulphide precipitation. However, it appears that side reactions, in particular complexations, keep metals in solution at a greater concentration than would be calculated using equilibrium data. In industrial waste waters this situation would probably be aggravated by the presence of complexing agents and other impurities.

(4) A major problem is to effect phase separation of the fine, difficult to settle precipitates which are normally produced by direct mixing of reagents. Plant and pilot plant experience indicate that pressure filtration with the use of diatomaceous earth as a filter aid⁽¹⁾ or the use of cationic flocculant aids⁽²⁾ can overcome this problem. However, there has been little work done to discover how the conditions of precipitation affect coagulation and phase separation.

(5) Optimum operating conditions have not been defined and more important, the underlying mechanisms of the chemical and physical processes involved are not clearly identified.

(1) Perry (1974)

(2) Bituminous Coal Research Inc. (1969)

CHAPTER 3
OBJECTIVES OF THE STUDY

(1) The first objective was to choose an experimental system which would be representative of an industrial process without containing interferences which would obscure the behaviour common to all metal sulphide precipitation processes.

(2) The second objective was to examine the effect of the three independent variables on the dependent variables using a factorial experimental design. The independent variables to be studied were amount of sulphide added as precipitant, the amount of iron added as scavenger and the level to which the pH was adjusted just after precipitation. The range of each independent variable was kept within limits which could practically be reproduced in an industrial process. The dependent variables examined were concentration of dissolved metals in the effluent, concentration of suspended metals after forty minutes settling, concentration of total metals (dissolved plus suspended), residual levels of sulphur species and zone settling velocities of the suspensions after precipitation and flocculation.

(3) The third objective was to determine if contacting the sulphide solution with a preformed precipitate before precipitation would produce a suspension with improved settling characteristics. Tests were to be performed in a batch system and also in a continuous system similar in principle to the zinc hydroxide "Densator" reactor of the American Enka

Company report (1971).

(4) The data obtained were to be used to elucidate the important mechanisms involved in the precipitation, adsorption, coagulation and settling processes of metal sulphide precipitation.

CHAPTER 4

EXPERIMENTAL

4.1 Choice of constants for the system

By using pure synthetic solutions rather than a real industrial metals waste, complications arising from impurities in solution were avoided. The use of chelating agents in the plating industry is widespread and will have an important effect on sulphide precipitation since a complexed or chelated metal ion cannot be precipitated. However, the complicated cases can be dealt with only after a good understanding of the simplest cases is attained.

A solution containing more than one dissolved metal was thought to be more representative of a real system than a solution of a single metal. The metals copper, cadmium and zinc were chosen because they are very commonly used metals and because their solubility products cover a wide range, cf. Table 1. Each metal was introduced as the chloride salt. The concentrations of the metals used were the same for each experiment and approximately equal to 100 mg/l as the metal. The exact values for the stock solutions are given in Table A1. These concentrations are typical of rinse streams in plating plants.

4.2 Independent variables and their levels

Adding the precipitant in the form of a solution of sodium sulphide was chosen as the most practical method and one which had been successfully tested in an industrial process, Perry (1974). The lower level of sulphide addition was chosen as 1.25 times the total number of moles of pollutant metal ions. The excess was provided to ensure that a stoichiometric equivalent of sulphide ions would remain even after losses due to complexation, oxidation, etc. The higher level of addition was twice the lower.

The low level of ferrous iron addition was chosen as 0.4 times the total number of moles of pollutant metal ions. This level made the total moles of metals greater than the moles of sulphide provided by the low level addition. The high level of iron addition was 1.8 times the total moles of pollutant metal ions, so that the level of total metals would be greater than the high level of sulphide. The levels actually applied, Table 2, were slightly different from those originally intended, due to practical difficulties.

It was thought prior to the experiments that pH adjustment would play a major part in the coagulation process since the hydroxyl ion could be potential determining. Therefore this variable was examined at five levels. The cost of neutralizing solutions before discharge would make it impractical to operate the process at the extreme ranges of the pH scale. On that basis the upper and lower limits investigated were 10.5 and 5.5

TABLE 2
Variable Levels and their Coded Equivalents

Variable	Uncoded Level	Coded Level
Sulphide	5.25 m mole/l	-1
	7.95	0
	10.58	+1
Fe ⁺²	1.43 m mole/l	-1
	3.96	0
	6.47	+1
pH	5.5	-1.68
	6.5	-1
	8.0	0
	9.5	+1
	10.5	+1.68

4.3 Design of experiments

The experimental design was a two level three variable factorial design with four replicates of the centre point and eight star points for a more detailed investigation of the effect of pH. For star points in a 2^3 design the value of α is $1.68^{(1)}$. In Table 2 the level of the variables are related to the coded levels and the design matrix is presented in Table 3. The data were fitted to a linear model of the form:

$$\hat{Y} = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_1x_2 + b_5x_2x_3 + b_6x_1x_3 + b_7x_1x_2x_3 + b_8x_3^2$$

where \hat{Y} is the predicted response of the dependent variable, x_1 , x_2 , x_3 are the coded levels of sulphide addition, iron addition and pH respectively and the b_i terms are the parameters estimated by the regression. The use of a statistical experimental design was considered to be the most efficient way to conduct a set of preliminary, screening experiments. The merits of this approach and a list of references to the principle works in the field of experimental design are given by Murphy (1977) and Box and Hunter (1961).

4.4 Apparatus

The precipitation experiments were conducted in 1.6 l square glass jars which were part of the standard Phipps and Bird jar test apparatus. Rapid mixing and flocculation were achieved with a rectangular stainless steel impeller (7.6 x 2.5 cm).

For the continuous flow experiment a 6 l Busch Biological Reactor,

(1) Refer to Davies (1956, p. 532) for details on star points.

TABLE 3

Experimental Design Matrix

Run	S ⁻²	Fe ⁺²	pH
1	-	-	-
2	+	-	-
3	-	+	-
4	+	+	-
5	-	-	+
6	+	-	+
7	-	+	+
8	+	+	+
9	0	0	0
10	0	0	0
11	0	0	0
12	0	0	0
13	0	0	α
14	0	0	$-\alpha$
15	+	+	α
16	+	+	0
17	+	+	$-\alpha$
18	-	-	α
19	-	-	0
20	-	-	$-\alpha$

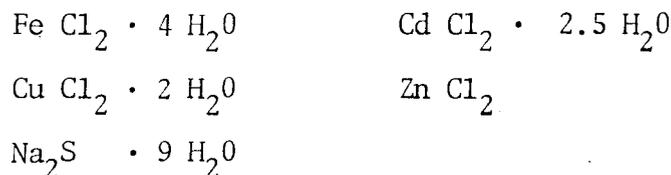
Figure 1, was employed. The sulphide and metals solutions were pumped with an LKB perpeX and a Masterflex peristaltic pump respectively.

Sartorius 0.45 micron cellulose acetate filters and Falcon Plastics disposable 150 ml filter units #7103 were used for phase separation.

Analytical instruments used were: a Varian Atomic Absorption Spectrometer Model AA-6, a Fisher Accumet pH/ionmeter model 230, and Orion Instruments Silver/Sulphide specific ion electrode model 94-16 and double junction reference electrode model 90-02.

4.5 Reagents

All solutions were made up with distilled de-ionized water. The following reagent grade salts were used in preparing the stock solutions:



The pH of the stock metals solutions was adjusted to about 2.5 to prevent hydroxide precipitation.

In all cases adjustment of the pH was effected with either reagent grade HCl or NaOH in a solution of an appropriate concentration.

All other reagents used in analyses were either reagent or analytical grade.

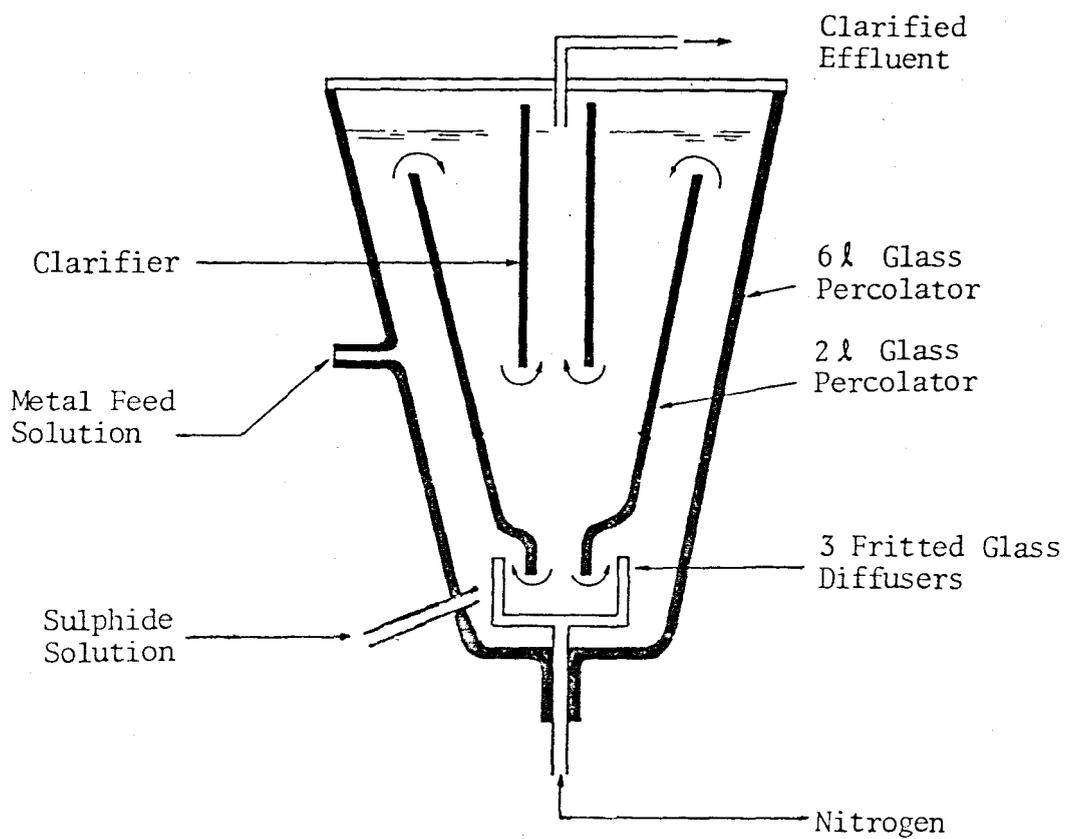


Fig. 1: The Busch Biological Reactor used in the continuous precipitation experiment.

4.6 Experimental procedures

The order of the 20 runs of the experimental design was randomized and the procedure used was the following:

(1) The jar was filled with the volume of distilled de-ionized water required so that after all solutions had been added the volume would be 1.00 l.

(2) 30.0 ml of the combined Cu, Cd, Zn stock solution were added and mixed into the water.

(3) The appropriate volumes of sulphide and ferrous iron stock solutions were measured into separate beakers.

(4) The temperature of the water although not controlled was measured and for all experiments fell between 21.5 and 23.8°C. Between these temperatures viscosity of water ranges from 1.00 to 0.97 cp.

(5) The impeller speed was set to 100 rpm which corresponds for this system to a mean velocity gradient of 55 sec^{-1} , see Sec. C.2, and the sulphide and iron solutions were added simultaneously. Solutions of HCl or NaOH were added until a steady reading of the desired pH value was obtained.

(6) Five minutes after the addition of the sulphide and iron solutions the impeller speed was reduced to 20 min^{-1} for a 15 minute period of flocculation. The mean velocity gradient at this speed was calculated to be 5 sec^{-1} , Sec C.2.

(7) Immediately after the flocculation period 250 ml of the slurry were poured into a 250 graduated cylinder and the position of the zone interface was measured for approximately 10 minutes.

(8) After 30 minutes of quiescent settling 25.0 ml of supernatant were transferred by pipette into a beaker and mixed with 25.0 ml of 2.0 N NaOH. The sulphide concentration in the resulting mixture was measured with the silver/sulphide electrode.

(9) After 40 minutes of quiescent settling 100 ml of supernatant were filtered through a 0.45 micron filter, the filtrate was acidified and stored for later analysis. An unfiltered, 50.0 ml sample of supernatant was mixed with 50.0 ml of a 50/50 by volume mixture of concentrated HNO_3 and HCl and stored for analysis. The final pH of the supernatant was recorded.

Concentrations of the stock solutions are given in Table A1.

For the continuous experiment the Busch Biological Reactor was initially filled with a slurry made of the reagents in the same ratio as they were to be fed in during the run. After the pumps had been calibrated they were set to deliver the desired flow of sulphide solution and metals solution, (containing Fe as well as Cu, Cd, Zn) and to withdraw the clarified effluent. Nitrogen was bubbled through the diffusers to provide a gentle, rolling, mixing action. Samples of the effluent were taken at hourly intervals and in the same manner as described in step (9) above they were prepared for analysis of dissolved metals and total (dissolved plus suspended) metals. The run was continued for 10 hours. Details of flow rates and concentration are presented in Sec. A.2.

The sludge from the continuous run was stored in the absence of air. It was used later in settling tests and experiments involving contact of reagent solutions with preformed sludge prior to precipitation. The

settling tests, done with constant sludge concentration, comprised 1) a rapid mix period of 5 minutes during which the pH was adjusted to the desired value ranging from 3 to 11.5, 2) a 10 minute period of slow mixing to allow flocculation and 3) a period of quiescent settling during which the settling velocity of the zone interface was measured.

Procedures used in other tests which varied slightly from those given for the experimental design runs are presented in Sec. A.1.

4.7 Analytical procedures

(1) Atomic absorption spectroscopy: Standard solutions of metals supplied by Canlab Ltd. were used to calibrate the instrument before each set of samples was analyzed. Dilutions with de-ionized distilled water using an automatic dilutor supplied by Labindustries Ltd. were made to bring sample concentrations into the optimum working range for a specific metal.

(2) pH measurements: The meter was calibrated using buffer solutions of both pH 4.0 and pH 10.0 supplied by J.T. Baker Chemical Co. Adjustments for temperature were made directly on the meter.

(3) Sulphide concentration measurements: Before each set of experiments the concentration of the stock sulphide solution was measured. This precaution was taken because sulphide ion is prone to oxidation, especially in bright light, although for fairly concentrated solutions as were being used the problem is not great. The method of sulphide analysis used was the precipitation method detailed in Hanson (1973, p. 460). Cadmium sulphide is precipitated by the addition of the sample to a solution

of cadmium acetate. The precipitate is separated and acidified in the presence of excess standard iodine solution. Hydrogen sulphide is liberated and is oxidized by the iodine, the amount of iodine consumed being determined by titration with sodium thiosulphate solution.

The analysis of residual sulphur species in the supernatant was done with the silver/sulphide electrode. By diluting the sample 50/50 with 2N NaOH practically all H_2S and HS^- were converted to S^{-2} and the ionic strength of each mixture was made essentially 1.0. A calibration curve of electrode potential vs. sulphide ion concentration was prepared. The sulphide solutions used for the calibration were standardized by potentiometric titration with standard silver solutions. Further details are available in the operation manual for the Orion silver/sulphide electrode.

CHAPTER 5

RESULTS AND DISCUSSION

This chapter is divided into two sections: the first section (Sec. 5.1) analyzes the experiments of the statistical design and the second section (Sec. 5.2) analyzes additional experiments not included in the statistical design. There are seven subsections in Sec. 5.1. In the first subsection the statistical treatment of the data is described and general conclusions are drawn from the nature of the correlations of dependent variables to independent variables. In the following 6 subsections the discussion is more specific. The individual correlations are examined and an attempt is made to interpret the significance of the parameter estimates. The results of the additional experiments are discussed in the final section of the chapter.

5.1 Statistically designed experiments

5.1.1 General discussion of the statistical analysis

The full set of metal concentration data collected in the experimental design runs is given in Tables B1, B2, and B3. Before the data were fitted to the empirical model they were transformed with the natural logarithm function. The use of this particular transformation was based on the following grounds: 1) Equations of mass action in solution are of the general form $y = A^a B^b \dots F^f$. If such an equation could describe

the metal concentrations obtained then its form after linearization with a log transform, $\log y = a \log A + b \log B + \dots + f \log F$, could be well represented by the empirical model used; 2) One of the assumptions on which the statistical tests in the analysis of variance are based is that there be a constant variance in the error terms associated with the data. The metal concentrations varied over several orders of magnitude and if they were higher than the optimum range for the spectrometer they were diluted into that range. This procedure tended to give a constant percentage error to the measurements. If the data were log transformed the constant percentage error would transform into a constant absolute term and the constant variance assumption would be validated; 3) The analysis of transformations of Box and Cox (1964) was used to give quantitative justification to the transformation. A brief description of this method is provided in Sec. C.3. For the total Fe and total Cd concentration data the results of the analysis of transformations, Tables C1 and C2, show that at the 95% confidence level the log transform is justified. These data were considered to be representative of the other metals with respect to which transform was most appropriate.

The preceding arguments hold only for the metal concentration data. The settling velocity data were treated both with and without the log transformation.

For each dependent variable (except residual sulphide) a linear least squares regression of the observed values against the independent variables was used to estimate the parameters of the empirical model. In each case the regression was examined with the following: 1) a lack of fit

test, 2) an extra sum of squares test on all parameters after the constant term, 3) an analysis of variance and 4) a plot of residuals versus predicted response. For each parameter estimate the limits of the individual 95% confidence region were calculated.

The lack of fit test compares the ratio $F = \text{mean square lack of fit} / \text{mean square pure error}$ with the $100(1-\alpha)\%$ point of an F distribution with the degrees of freedom of the lack of fit and pure error. If the computed ratio is less than the point from the F distribution "there appears to be no reason to doubt the adequacy of the model", Draper and Smith (1966, p. 30). Test (2) tests the hypothesis $H_0: b_1 = b_2 = \dots = b_8 = 0$ against $H_1: \text{not all } b_i \text{ are zero}$. If H_1 can be accepted at the 95% confidence level then a "statistically significant" regression has been obtained. The analysis of variance calculations are fully described in Draper and Smith (1966). Additional discussion of the statistical calculations is provided in Sec. C.4.

The correlations for total, dissolved and suspended metals were made using data from 18 of the 20 runs. In runs 2 and 6 a stable colloid was formed and nearly all of the metals remained in suspension. These runs were excluded from the regressions because they exhibited behaviour quite distinct from that of all the other runs. When they were included in a regression it was obvious from the pattern of residuals that the linear model was inadequate to describe the situation. Instead of falling in a broad band of constant width about the abscissa the residuals formed a perfectly straight line crossing the abscissa at the origin. Draper and Smith (1966, ch. 3) may be consulted for a discussion on the examination

of residuals.

A summary of the statistical tests of the regressions is presented in Table 4. In eleven of the thirteen regressions the model appeared to be adequate on the basis of the lack of fit test. However, because there were only four replicate measurements the value of F (d.f. lack of fit, d.f. pure error) was large and the test was not highly discriminating. The estimate of the error variance obtained from only four repeat experiments has a relatively large 95% confidence region.

On the whole, the correlations between the dependent variables and the independent variables were poor. Only three of the thirteen regressions were found to be statistically significant. For the other ten regressions the proportion of variation in the data which was accounted for by the equation was no greater than would be expected by chance in 95% of similar sets of data from repeated sets of experiments. One could describe the data as being insensitive to the changes in independent variables and subject to random deviations from constant values. The mean values and standard deviations for the thirteen sets of data are presented in Table 5. Those cases which were exceptions to this general statement are discussed below.

There are several possible explanations for the lack of significance of the regressions. The functional relationships between dependent and independent variables may not be adequately approximated by a simple linear model⁽¹⁾. The combined sources of error may have been large enough to overshadow the actual behaviour of the system. Perhaps the most obvious explanation is that the mechanisms operating in the metals removal process

(1) However, the patterns of residuals did not indicate model inadequacy.

TABLE 4

Summary of statistical tests of the regressions

Dependent Variable	Test of Model Fit ^a	Test of Regression ^b	R ²
1. Total Metals			
ln Fe	6.90	3.32	0.75
ln Cu	1.47	0.55	0.33
ln Cd	1.88	0.40	0.26
ln Zn	3.03	1.96	0.64
2. Dissolved Metals			
ln Fe	6.96	2.50	0.69
ln Cu	--	2.30	0.67
ln Cd	0.13	3.04	0.73
ln Zn	9.36	3.47	0.76
3. Suspended Metals			
ln Fe	0.98	5.60	0.83
ln Cu	1.71	0.51	0.31
ln Cd	2.21	0.45	0.29
ln Zn	1.62	0.72	0.39
4. Settling Velocity			
ln settling velocity	12.94	1.09	0.64
Settling velocity	11.01	0.93	0.60

^a The test of model fit should be less than 8.94 for metals regressions and 9.55 for settling velocity regressions for significance at the 95% confidence level.

^b For significance at the 95% confidence level the value of the test of regression should be greater than 3.23 for metals regressions and 4.82 for settling velocity regressions.

TABLE 5

Means and standard deviations of dependent variables for the experimental design runs, not including stable colloid results

Dependent Variable	Mean value	Standard Deviation
1. Dissolved Metals		
Cu	0.03 mg/l	0.03 mg/l
Cd	0.01	0.01
Zn	0.37	1.22
2. Suspended Metals		
Cu	0.39 mg/l	0.18 mg/l
Cd	0.32	0.21
Zn	0.25	0.15
3. Total Metals		
Cu	0.41 mg/l	0.18 mg/l
Cd	0.33	0.21
Zn	0.62	1.20
4. Settling Velocity		
	51.7 mm/min	12.82 mm/min

simply were not markedly affected by the changes made in the independent variables. Regardless of which explanation is correct, the conclusions in the following sections derived from an examination of the fitted parameters must be accepted as tentative in view of the poor statistical correlations which were obtained.

5.1.2 Regressions of the total metal data

The word total is used to designate dissolved plus suspended metals measured in the supernatant 40 minutes after the beginning of quiescent settling. Table B4 gives the estimates of the parameters of the model as fitted to \log_e [total metal concentration, mg/l]. Unbracketed entries are considered significant at the 95% confidence level. Bracketed entries are possibly significant, but contain zero near the boundaries of the 95% confidence limits of the parameter estimation. Where no entry is made, zero is central in the 95% confidence region.

The only significant parameter for the correlation of total iron is the one associated with the pH level. That the parameter value is negative implies that by increasing the pH after precipitation the total amount of iron decreases. This is probably explained by the fact that the residual iron after sulphide precipitation is removed by hydroxide precipitation at higher pH values.

For the other three metals only the parameters associated with the constant terms are significant.

5.1.3 Regressions of the suspended metal data

The parameter estimates for the regressions of the suspended metals after 40 minutes settling are given in Table B4. The behaviour of iron is different from that of copper, cadmium and zinc. The data of the suspended iron data was statistically significant and the model showed no lack of fit, (See Table 4). For this regression four parameters appear to be significant: they are the parameters associated with the constant term, the amount of iron added, the pH level and the third order interaction between iron added, pH level and sulphide added. The effect of pH is the same as it was in the case of total iron; the effect of adding a higher amount of iron seems to be to leave a higher amount in suspension; it is difficult to interpret the significance of the interaction term.

The only significant parameters for the regressions of suspended copper, cadmium and zinc are those associated with the constant terms. Interestingly, the values of these parameters indicate that on average the suspended metals occur in mass concentrations $Cu > Cd > Zn$. The order is just the reverse of the order of the solubility products of the metal sulphides. This matter is discussed in Sec. 5.2.1.

5.1.4 Regressions of the dissolved metal data

Zn was the only metal for which the regression of the dissolved metal concentrations provided a statistically significant regression. Zn forms the most soluble metal sulphide among the sulphides of Cu, Cd and Zn. It is therefore in the highest concentration in the supernatant and

could most accurately be measured. This may support the argument that for the measurement of very low metal concentrations the contributions of experimental error become dominant and cause the lack of significance of the regressions. Refer to Table C3.

The tests of overall regression for dissolved Fe, Cu and Cd, Table 4, indicate that at the 95% confidence level $b_1 = b_2 = \dots = b_8 = 0$. These regressions were not statistically significant. However, the 95% confidence limits on the individual parameter estimates suggest that not all the parameters are insignificant, Table B4. A similar pattern in the parameters emerges for the three metals Fe, Cd, and Zn. Because the concentration measurements were made independently the recurrence of this pattern supports the idea that the value of the parameters is non-zero.

The parameters in question are b_5 and b_6 , associated with the iron-pH interaction and the sulphide-pH interaction respectively. For Fe, Cd and Zn, b_5 is large and negative and b_6 is large and positive. The following hypotheses are consistent with these results and bear further testing: 1) When pH and iron levels are both high, significant amounts of ferrous hydroxide and related hydroxo complexes are formed and adsorb soluble metal ions before settling, 2) when sulphide and pH levels are both high the formation of metal sulphide complexes is favoured and higher levels of metal ions stay in solution. It is conceivable that if the sensitivity of the copper analysis had been greater the same pattern would have applied to that metal. In only 5 of the 18 runs were dissolved copper concentrations detectable with the flame spectrometer. For the purposes of taking log transforms of the data the undetected concentrations were set at 0.01 mg/l.

5.1.5. Regressions of settling velocities

The settling behaviour of the suspensions permitted the measurement of an interface velocity in 14 of the 20 experiments. In the other experiments the interface was either non-existent or too ill-defined to be located. The results are presented in Table B5. The tests of the regressions of the settling velocities, log transformed and untransformed, Table 4, show that there is no simple correlation between the measured settling velocities and the independent variables.

The variations in settling velocity of the non stable suspensions were not large, Table 5. If conditions which produce stable colloids are avoided it appears that small changes in the operating variables have minimal effects on the settling behaviour of sulphide precipitates. This information may be of some value in the design of a continuous clarification system.

5.1.6 Sulphide residuals

Table B6 shows the total concentrations of H_2S , HS^- and S^{-2} which were in solution after 30 minutes of quiescent settling. The method of analysis is described in Sec. 4.7. The stable colloidal suspensions, runs 2 and 6, contained the highest residuals: 6.3×10^{-5} and 4×10^{-5} mole/l respectively. If all metals in these runs were precipitated as sulphides the amount of sulphur species remaining would be about 5×10^{-3} mole. One can conclude that almost all the residual HS^- was complexed with the metal sulphides, adsorbed irreversibly, converted to stable polysulphides or in some other way removed from solution.

The residuals in the remaining runs were all considerably lower, in fact only 4 can be considered at all important. Each of these 4 runs was at a pH of either 6.5 or 5.5. All other sulphide concentrations were negligibly small.

A disadvantage of the method of analysis was that it did not account for the concentrations of polysulphides. These species are relatively stable and would not be converted to sulphide ion in the alkaline solution. As a result it is not known to what degree they are present in the effluents.

5.1.7 The role of iron

In the patent of Anderson and Weiss (1973), it was claimed that the addition of iron or other suitable metal would be beneficial for scavenging excess sulphur species. What was not discussed was the effect that this would have on the settling characteristics of the system. In Table 6 are results that indicate that, by scavenging excess sulphur species, ferrous iron improves the settling of sulphide precipitates. When the degree of excess sulphide is high, as it was in runs 2 and 6, a stable colloid is formed. (The "stable" suspensions eventually settled after about 40 days.) The results are consistent with the hypothesis that HS^- ion is strongly adsorbed onto the surfaces of metal sulphide precipitates and increases the negative surface charge. By removing HS^- ion from solution, ferrous iron controls the degree of HS^- adsorption the magnitude of the negative surface charge and ultimately the ease of coagulation and settling.

TABLE 6

Effect of Fe on settling by removing excess sulphur species

Run	Sulphide level	Iron level	pH level	Estimated S^{-2} excess mole/l	Nature of colloid
2	+	-	-	5.2×10^{-3}	stable; no settling
4	+	+	-	0.4×10^{-3}	flocculant
6	+	-	+	5.2×10^{-3}	stable; no settling
8	+	+	+	0.4×10^{-3}	flocculant
Test A	see sec. A.1 for details	0	~ 6	0.7×10^{-3}	flocculant
Test B		9×10^{-4} mole	~ 6	0	flocculant, settled twice as fast as in Test A

Note: S^{-2} excess designates moles S^{-2} added in excess of moles of Cu + Cd + Zn + Fe

A problem left to be resolved after this work concerns the fate of the Fe^{+2} ions introduced with the sulphide ions. Due to their simultaneous addition and subsequent pH adjustment it remains to be determined to what extent and how rapidly the different possible metal hydroxides, sulphides and intermediates are formed. How the presence of these compounds affects the processes of precipitation, crystal growth and settling must also be determined.

Behmann (unpub. report 1973) suggested that an additional benefit of the use of iron would be its action as a coagulating agent. In alkaline conditions, excess iron would precipitate as the hydroxide and the charged hydroxo complexes which form as kinetic intermediates to the hydroxide could act as coagulants. Unfortunately the experiments were not designed to test whether coagulation occurs by this mechanism in the sulphide precipitation system.

5.2 Additional Experiments

5.2.1 A comparison of continuous and batch precipitations

A continuous precipitation process was compared with the batch precipitation experiments to give additional insight into the physical and chemical mechanisms of metal removal. The experiments also tested the feasibility of continuous clarification of metal sulphide slurries. The basis for comparison was that the influent metal concentrations to the continuous reactor were approximately the same as the starting concentrations in the batch experiments. In both modes of precipitation Fe^{+2} was used as a scavenging agent for excess HS^- ion.

The concentrations of dissolved metals which can be obtained in the continuous operation do not appear to be very different from those obtained under similar conditions for batch tests. The average concentrations of dissolved Cu, Cd and Zn in the continuous reactor effluent were <0.1, approximately 0.5 and 1.6 mg/l respectively, Table B7. The Cu and Cd values are similar to the typical values obtained in the batch experiments, but the average Zn concentration is about four times higher than it was for

the batch runs. This is perhaps partly due to the relatively low pH value at which the continuous experiment was run. The pH ranged from a value of 5.6 to 5.9.

The effluent concentrations of suspended metals for the continuous reactor were considerably higher than for the batch experiments. The results in Table B7 may be compared with those in Table 5. A total of from 5 to 8 mg/l of Cu, Cd and Zn remained suspended in the continuous reactor effluent. Unless a subsequent separation process is used the carryover of pin floc considerably reduces the effective metal removal of the system.

There is some evidence, however, that a carefully controlled sludge blanket in an upflow clarifier may help to remove pin floc. Over the initial 6 hour period of operation there was a steady decline in the amount of floc which passed through the clarifier, Table B7. This was possibly due to the thickening of the sludge blanket in the clarifier and consequently its improved effectiveness as a filter. The upset which occurred at 7.5 hours into operation might have been caused by the filling and overflowing of the clarifier.

The precipitates formed in the continuous reactor appeared to have the same settling properties as those formed in the batch tests. Because the experiment was run for only 10 hours it is not possible to compare the results with those of the $Zn(OH)_2$ precipitation system of the American Enka Company (1972) which was operated for over a year. If the metal sulphide precipitates were recycled for a long period of time and repeatedly contacted with fresh metal and sulphide solutions such a comparison would be possible.

The composition of the suspended metals was different for the continuous system than it was for the batch tests. The floc compositions of all samples from the two systems are presented in Tables B8 and B9. The compositions of the floc from each sample are given as mass ratios of each metal with respect to copper. The trend $Cu > Cd > Zn$ in the batch test floc is just the reverse for the floc from the continuous run. The mean compositions of residual floc are:

<u>Mode of precipitation</u>	Cu/Cu (g/g)	Cd/Cu (g/g)	Zn/Cu (g/g)
Batch	1.0	0.76 (0.23) ^a	0.62 (0.15)
Continuous	1.0	1.36 (0.13)	1.47 (0.31)

^a bracketed values are standard deviations.

There are several differences between the batch and continuous systems which may be responsible for the differences in floc compositions. Among these are: 1) precipitation conditions, 2) mixing conditions after precipitation, 3) age of floc at the time of sampling and 4) history of floc before sampling. To determine how these differences would affect the floc composition requires an examination of theory which goes beyond the scope of this report. Topics relevant to such an examination are the kinetics of precipitation, the distribution laws of coprecipitation, the kinetics of the aging of precipitates and the effect of turbulence on aging of precipitates.

5.2.2 Adsorption of sulphide on preformed sludge before precipitation

A set of screening experiments was performed to test whether crystal growth and the formation of dense precipitates could be encouraged without using precipitation from homogeneous solution. The detailed procedures are outlined in Sec. A.1 and a summary of the results is given in Table 7. The metals solution was added into a mixture of preformed metal sulphide precipitate which had been contacted with the required amount of sulphide solution. The HS^- ion would readily adsorb onto the metal sulphide surface and it was hypothesized that when metal ions were introduced they would diffuse into the double layer and precipitate with the HS^- group directly onto the surface of the crystal.

The results shown in Table 7 indicate that better settling precipitates were not formed. Neither did the limited results from the continuous experiment show evidence of better settling precipitates. The procedure followed appears not to increase crystal growth to an appreciable extent. Adsorbed HS^- ion may not be available for precipitation because of the effects of adsorption and may have to be desorbed before it can precipitate with a metal ion.

5.2.3 Effects of pH

Two additional sets of experiments were performed to investigate specific pH effects. The first set involved contacting preformed metal sulphide sludge with the sulphide solution before addition of the metal ions. The purpose of the experiments was to determine the effects of adjusting the pH to different values before precipitation and of adjusting

TABLE 7

Effect of adsorbing HS^- on preformed sludge before precipitation

Run	Vol. of preformed sludge used	pH during slow mix	Nature of settling
C	750	7	slow; heavy residual
E(b)	250	6	interface poorly defined; heavy residual
D	0	6.2	large flocs; very fast settling

TABLE 8

Effect of pH adjustment before and after precipitation

Volume of sludge used was 250 ml.

Run	pH before precipitation	pH after precipitation	settling	(Fe) ^a (mg/l)	(Zn) ^a (mg/l)
E(a)	11.4	10	stable colloid	— ^b	— ^b
F	5	6.2	poor settling; high residual	29.0	0.64
G	5	10	worse than F	0.00	<0.01

^a Concentration of dissolved metal in filtered supernatant. The corresponding values for Cu and Cd were the same for both runs at <0.1 and <0.05 mg/l respectively.

^b Not measured.

the pH after precipitation but before coagulation. The procedures followed are outlined in Sec. A.1 and the results are summarized in Table 8.

The results support the hypothesis that adsorption of HS^- ion and OH^- ion plays an important role in determining the settling behaviour of the precipitates, but are too limited for more specific conclusions. In run E the pH before precipitation (unadjusted) was 11.4. Adjusting the pH to 10 during slow mix caused formation of a stable colloidal suspension, run E(a). Later readjustment to a pH of 6 destabilized the suspension possibly by causing desorption of hydroxyl ions, run E(b). In run G the pH before precipitation was adjusted to 5 and after precipitation was adjusted to 10. However, in run G the suspension was not stabilized as it had been in run E. A comparison of runs F and G illustrates that adjusting the pH to a high value after precipitation may enhance removal from solution of Fe and Zn by hydroxide precipitation. The runs were the same except that after precipitation the pH in run F was adjusted to 6.2 and in run G to 10. The concentrations of dissolved Fe and Zn in the final supernatant of run G were undetectable with the flame spectrometer.

The second set of experiments was designed to investigate the effect of changing the pH on the settling properties of a preformed precipitate. The precipitate from the continuous experiment, which had been stored for about one day in the absence of air, was used for these settling tests. The procedures are outlined in Sec. 4.6. The interface settling velocities decreased with increase in pH up to a pH of 11.5 at which the suspension stabilized. The data are listed in Table B10 and plotted in

Figure 2.

The data are consistent with the hypothesis that changing the pH of the suspension alters the surface charge of the precipitates. As the hydroxyl ion concentration in solution is increased the degree of adsorption of that ion should also increase. Consequently the surface charge should become more highly negative and coagulation and settling more difficult.

The results of this experiment and the results of the experimental design runs appear to be in some conflict, but are not strictly comparable. The sludge used in these experiments had been aged in the absence of air for one day. The process of aging, through agglomeration, Ostwald ripening and surface rearrangement generally lowers the surface areas of precipitates and thus alters their adsorption characteristics, Walton (1967). Another consideration is that for these tests the concentration of HS^- ion was probably very small in comparison to what it initially was for the precipitation experiments. According to the theory of soft and hard metal spheres, Stumm and Morgan (1970), Zn and Cd (and to a lesser degree Cu) have a greater affinity for the compounds of sulphur than for those of oxygen. This implies that HS^- would be more strongly adsorbed than OH^- . During precipitation, when HS^- is present in considerably concentrations, the greater degree of HS^- adsorption may obscure the effects of OH^- adsorption. The effect of pH on settling velocity appeared to be strongest below a pH of 5.5. This was below the levels of pH investigated in the experimental design runs.

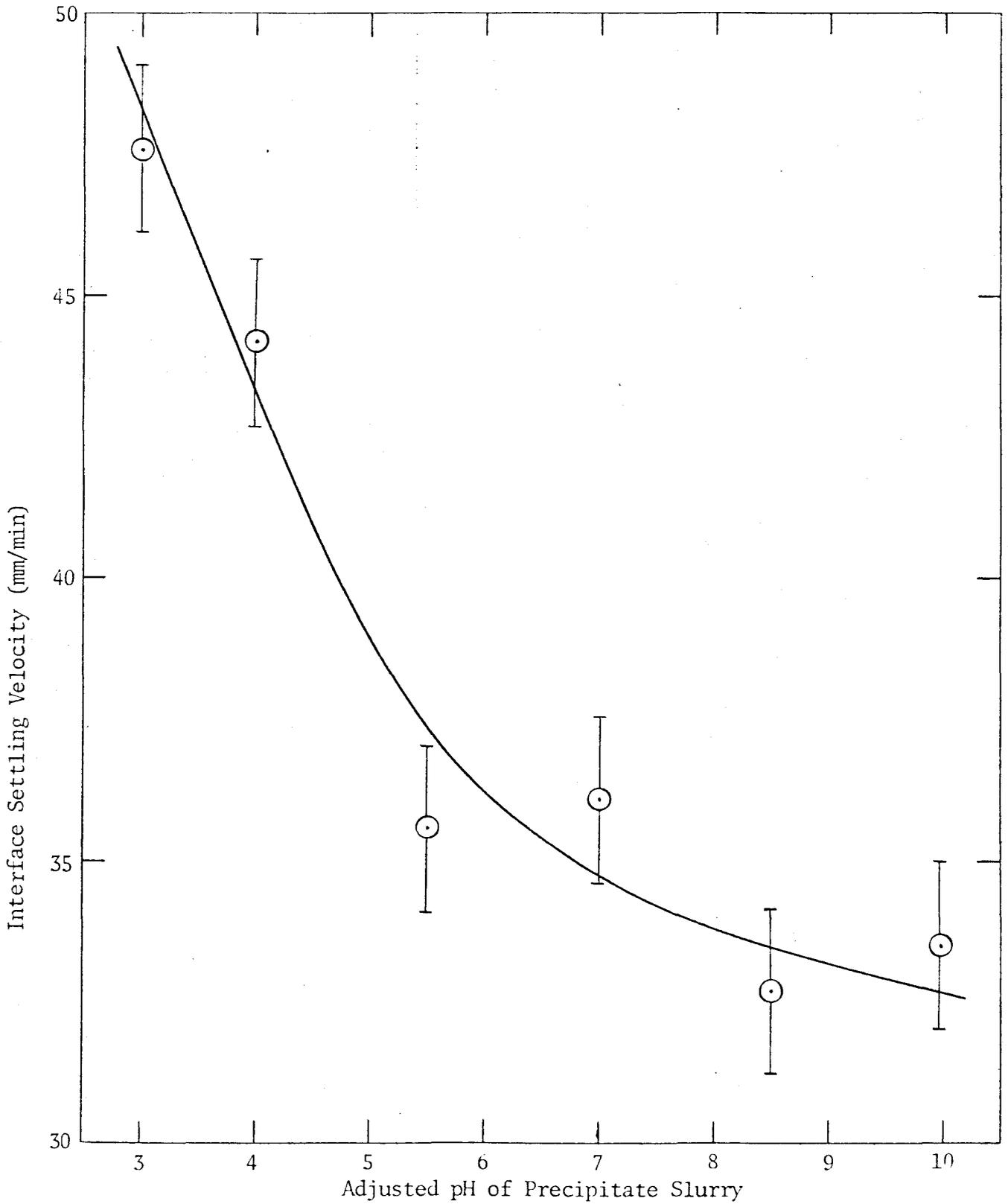


Fig. 2: Interface settling velocity as a function of pH for aged metal sulphide precipitate. Estimated 95% confidence limits are shown.

CHAPTER 6

CONCLUSIONS

6.1 Effect of operating variables

6.1.1 General

In batch studies the major effect of the operating variables was to yield a precipitate which was either a stable colloid or a suspension which coagulated and settled. For those conditions which produced coagulant suspensions (1) the correlations between dependent and independent variables were not statistically significant at the 95% confidence level, (2) for practical purposes variations in operating variables did not alter the levels of dissolved or suspended pollutant metal ions.

6.1.2 Effect of Ferrous Iron

The addition of ferrous iron to the metal solution before precipitation has the effect of scavenging the sulphur species which are in stoichiometric excess of the pollutant metal ions present. This is beneficial for two reasons: (1) the species H_2S , HS^- , S^{-2} in the effluent are reduced to very low levels, (2) since adsorption of HS^- ion is decreased, the negative surface charge of the particles decreases and facilitates coagulation. If the pH of the system is above 8 the excess iron will be partially removed from solution as a hydroxide precipitate.

6.1.3 Level of sulphide addition

Because side reactions such as adsorption and polysulphide formation consume available HS^- ion during precipitation, the amount of sulphide added should be in excess of the stoichiometric amount required for all pollutant metal ions. For the conditions investigated, 1.25 times the stoichiometric requirement gave good removal. If the amount added is greater than the equivalent of the total of the pollutant metal ions plus the ferrous iron, adsorption of excess HS^- ions can cause stabilization of the colloidal precipitates.

6.1.4 Level of pH

Within the range of pH investigated, this variable had a significant effect (at the 95% confidence level) on only one dependent variable - dissolved iron. When the pH was above 8 most dissolved iron was removed from solution, probably as ferrous hydroxide. This fact and several minor effects suggest that the optimum operating pH range is from 8 to 9.5.

6.1.5 Comparison of continuous and batch precipitations

Under conditions comparable to those of batch tests, continuous precipitation provided similar degrees of removal of dissolved metals, but higher levels of suspended metals. Over a period of ten hours continuous precipitation of the metal sulphides in the presence of a recycled sludge made no noticeable improvement in the settleability of the floc.

6.2 Mechanisms of the Process

(1) When the precipitant is added by direct mixing, homogeneous nucleation occurs. As a result the precipitates are extremely fine and the solid phase has a large surface to volume ratio. For such a system surface effects play a dominant role.

(2) The ease of coagulation is very dependent on surface charge which in turn is dependent on adsorption of potential determining ions. Strong indirect evidence indicates that HS^- ion is an important potential determining ion in this system. The hydroxyl ion may also be influential. When these ions are adsorbed to a large degree the colloidal precipitates are stabilized.

6.3 Overall effectiveness of the process

Concentrations of dissolved copper, cadmium and zinc lower than 0.4 mg/l can be obtained with sulphide precipitation. However, the concentrations of the total metals in the effluent are several times higher because of the pin floc which remains after sedimentation. Because the concentrations of pin floc are not significantly affected by variations in the practical operating variables, an additional unit operation such as pressure filtration is required. With nearly complete separation of the solid phase the full potential of sulphide precipitation as a metal removal process could be achieved.

The mean levels of dissolved metals obtained in these experiments were comparable to those obtained after hydroxide precipitation of an acid mine drainage, Montreal Engineering Co. Ltd. (1972). Effluent concentrations of 0.02 mg/l Cu and 0.4 mg/l Zn were routinely obtained in that system.

6.4 Recommendations for further work

6.4.1 Mechanistic studies

Further insight into the chemical and physical processes involved in sulphide precipitation is required. Subjects which need further study are: 1) the kinetics and nature of adsorption on fresh metal sulphide precipitates, 2) identification of all possible potential determining ions and their relative importance, 3) the fate of non-precipitated sulphur species, 4) the size distribution and morphology of the precipitates and 5) the effectiveness of ferrous hydroxo complexes as coagulants of metal sulphide precipitates.

6.4.2 Practical application

Areas for further work in the practical implementation of the process include the following: 1) design of continuous mixing, flocculation and sedimentation units, 2) design of a system to monitor influent metal concentrations and to control sulphide addition, 3) investigation of techniques for removal of pin floc. These could include pressure filtration, flocculation with polymers or filtration through a sludge blanket.

REFERENCES

1. American Enka Company (1971), "Zinc Precipitation and Recovery from Viscose Rayon Waste Water", U.S. EPA Project No. 12090 ESG.
2. Anderson, J.R., and Weiss, C.O. (1973), "Method for Precipitation of Heavy Metal Sulphides", U.S. Patent No. 3,740,331.
3. Behmann, H., Netzer, A., Norman, J.D. (1972), Tech. Rpt. 72-304-1, McMaster University, Hamilton, Canada.
4. Behmann, H., and Norman, J.D. (1972), Tech. Rpt. 72-303-1, McMaster University, Hamilton, Canada.
5. Behmann, H. (1973), Unpublished Rpt., McMaster University, Hamilton, Ontario.
6. Bituminous Coal Research Inc. (1969), "Sulphide Treatment of Acid Mine Drainage", Federal Water Pollution Control Association, (U.S.), FWPCA Grant No. 14010 DLC.
7. Box, G.E.P. and Cox, D.R. (1964), J. Roy Stat. Soc., B26, 211.
8. Camp, T.R. (1955), Trans. ASCE, 120, 1.
9. Chen, K.Y. and Morris, J.C. (1972), Proc ASCE, J. San. Eng. Div., 98, 215.
10. Dean, J.G., Bosqui, F.L., Lanouette, K.H. (1972), Envir. Sc. Technol., 6, 518.
11. Draper, N.R. and Smith, H. (1966), Applied Regression Analysis, Wiley Interscience.
12. Gordon, L., Salutsky, M.L., Willard, H.H. (1959), Precipitation from Homogeneous Solution, Wiley.
13. Hanson, N.W., ed. (1973), Official, Standardized and Recommended Methods of Analysis, The Society for Analytical Chemistry, London.
14. Larsen, P.H., Shou, J.K.P., Ross, L.W. (1973), JWPCF, 45, 1682.
15. Lawrence, A.W. and McCarty, P.L. (1965), JWPCF, 37, 392.
16. Manahan, S.E. and Smith, M.J. (1973), Water and Sewage Works, 120, 102.

17. Murphy, T.D. (1977), Chem. Eng., 84, 168.
18. Nielsen, A.E. (1964), "Kinetics of Precipitation", Pergamon.
19. Perry, R. (1974), "Mercury Recovery from Contaminated Waste Water and Sludges", U.S. EPA Rpt. No. EPA-660/2-74-086.
20. Pohl, H.A. (1954), J. Amer. Chem. Soc., 76, 2182.
21. Rouse, J.V. (1976), JASCE, Env. Eng. Div., 102, EES, 929.
22. Salutsky, M.L. (1959), "Precipitates: Their Formation, Properties and Purity" in Treatise on Analytical Chemistry, Part I, Vol. 1, Ch. 18, p.733, Interscience.
23. Stumm, W. and Morgan, J.J. (1970), Aquatic Chemistry, Wiley-Interscience.
24. Swift, E.H. and Anson, F.C. (1960), "The Analytical Chemistry of Thioacetamide", in Advances in Analytical Chemistry and Instrumentation, Vol. 1, p.293, Reilly C.N. ed., Interscience.
25. Walton, A.G. (1967), The Formation and Properties of Precipitates, Interscience.
26. Weast, R.C., ed., (1974), Handbook of Chemistry and Physics, 55th Edition, CRC Press.
27. Weber, W.J. (1972), Physicochemical Processes for Water Quality Control, Wiley-Interscience.
28. Box, G.E.P. and Hunter, J.S. (1961), Technometrics, 3, 333 and 449.
29. Davies, O.L., ed., (1956), The Design and Analysis of Industrial Experiments, Oliver and Boyd.
30. Montreal Engineering Co. Ltd. (1972), "Northeastern New Brunswick Mine Water Quality Program", Fredericton, Canada.

APPENDIX A
EXPERIMENTAL CONDITIONS AND PROCEDURES

TABLE A1
Concentrations of Stock Solutions

Solution	Ion/Element of interest	mg/ ℓ	mMole/ ℓ Concentration
Sulphide	S ⁻²	4950	154
Ferrous Iron	Fe	9110	163
Mixed Metals Stock	Cu	3520	55.4
	Cd	3730	33.2
	Zn	2950	45.1
	Fe	0.67	0.012
Stock Diluted (33.3 times) for Experiments	Cu	105.6	1.66
	Cd	111.9	0.996
	Zn	88.5	1.35

APPENDIX A

A.1 Additional Experimental Procedures

A.1.1 Tests showing effect of Fe on settling

Test A:

- (1) Stock metals solutions and appropriate volumes of de-ionized distilled water were added to the jars as described in Sec. 4.6.
- (2) Rapid mixing was initiated and sulphide added so that the excess was about 7×10^{-4} mole.
- (3) The slurry was mixed rapidly for 5 minutes and then slowly for 15 minutes. The settling velocity was measured.

Test B:

- (1) This test was identical to Test A except that step (2) included addition of 9×10^{-4} moles Fe^{+2} simultaneous with the sulphide.

A.1.2 Tests showing the effects of adsorbing sulphide on preformed sludge before precipitation and of adjustment of pH before and after precipitation

General Procedure:

- (1) The appropriate volume of preformed sludge was added to the jar.
- (2) Sulphide solution (40 ml, 4.25 g/l, 132.5 mM/l) was added to the sludge and stirred for several minutes.

- (3) The appropriate volume of water was added so that after all additions the volume was 1.0 ℓ . The pH was measured and in some cases adjusted.
- (4) The mixture was stirred rapidly and the stock metals solution added. This addition included 5 $\text{m}\ell$ of Fe stock (10 g/ℓ , 180 mM/ℓ) as well as the usual Cu, Cd, and Zn. The pH was adjusted to the desired value during the 5 minute period of rapid mix.
- (5) The slurry was slow mixed for 15 minutes. A 250 $\text{m}\ell$ sample was then poured into a 250 $\text{m}\ell$ graduate and the settling velocity was measured. The remainder of the slurry was allowed to settle for 40 minutes in the jar. Samples of the supernatant were then taken and filtered for analysis as described in Sec. 4.6.

A.2 Experimental details for the continuous run

Flow rate of the metals solution	- 2.00 ℓ/hr
Flow rate of the sulphide solution	- 63 $\text{m}\ell/\text{hr}$
Total flow rate	2.06 ℓ/hr or 10.9 igal/day
Cross-sectional area of the clarifier	- 15.2 $\text{cm}^2 = 0.0164 \text{ ft.}^2$
Upflow velocity in clarifier	- 22.7 mm/min
Mean settling velocity of suspensions	- 52 mm/min
	cf. Table 5
Overflow rate of clarifier	- 660 igal/day ft.^2
	or 800 gal/day ft.^2

TABLE A2

Concentrations of the feeds

Solution	Ion	Concentration (mg/l)	Concentration (m mole/l)	Feedrate (m mole/hr)
Metals	Cu	90	1.416	2.83
	Cd	115	1.023	2.05
	Zn	106	1.621	3.24
	Fe	50	0.895	1.79
Sulphide	S	4649	145.	9.14

Note: Feedrate of total pollutant metal ions = 8.12 m mole/hr

Feedrate of pollutant metals plus iron = 9.91 m mole/hr

APPENDIX B
EXPERIMENTAL DATA

TABLE B1

Concentrations of total (dissolved plus suspended) metals after
40 minutes settling.

Run	Fe (mg/l)	Cu (mg/l)	Cd (mg/l)	Zn (mg/l)
1	47.0	0.40	0.388	0.976
2	82.0	106.8	120.6	95.0
3	294.0	0.48	0.316	5.34
4	97.4	0.4	0.296	0.222
5	0.62	0.15	0.064	0.120
6	86.0	104.6	123.2	94.4
7	3.3	0.4	0.298	0.326
8	2.94	0.62	0.478	0.460
9	3.26	0.24	0.114	0.154
10	1.86	0.58	0.542	0.460
11	1.06	0.26	0.224	0.216
12	5.16	0.24	0.146	0.170
13	0.4	0.40	0.286	0.260
14	100.6	0.84	0.878	0.083
15	1.74	0.34	0.234	0.236
16	2.00	0.30	0.246	0.220
17	117.0	0.68	0.654	0.442
18	0.34	0.34	0.254	0.216
19	1.16	0.50	0.448	0.424
20	0.34	0.24	0.058	0.110

TABLE B2

Concentrations of dissolved metals after 40 minutes settling. Samples from Runs 2 and 6 could not be filtered

Run	Fe (mg/l)	Cu (mg/l)	Cd (mg/l)	Zn (mg/l)
1	44.7	0.06	0.005	0.735
2	-	-	-	-
3	275.0	a	0.013	5.23
4	91.0	0.08	b	0.068
5	0.02	a	0.002	0.015
6	-	-	-	-
7	0.02	a	b	0.021
8	0.00	0.06	b	0.015
9	0.75	a	b	0.018
10	0.20	a	0.019	0.045
11	0.04	a	0.005	0.034
12	0.43	a	b	0.023
13	0.10	a	0.050	0.058
14	91.5	a	0.011	0.136
15	0.04	0.06	b	0.021
16	0.04	a	b	0.015
17	115.0	a	0.002	0.108
18	0.01	a	0.008	0.018
19	0.20	a	0.002	0.119
20	0.01	0.06	0.017	0.038

Note: "a" and "b" denote undetectable levels of Cu and Cd respectively, which for purposes of calculation were taken as 0.01 mg/l and 0.001 mg/l.

TABLE B3

Concentrations of suspended metals after 40 minutes of settling

Run	Fe (mg/l)	Cu (mg/l)	Cd (mg/l)	Zn (mg/l)
1	2.3	0.34	0.383	0.241
2	-	-	-	-
3	19.0	0.48	0.303	0.110
4	6.4	0.32	0.296	0.154
5	0.6	0.15	0.062	0.105
6	-	-	-	-
7	3.28	0.40	0.298	0.305
8	2.94	0.56	0.478	0.445
9	2.51	0.24	0.114	0.136
10	1.66	0.58	0.523	0.415
11	1.02	0.26	0.219	0.182
12	4.73	0.25	0.146	0.147
13	0.30	0.40	0.236	0.202
14	9.10	0.84	0.867	0.694
15	1.70	0.28	0.234	0.215
16	1.96	0.30	0.246	0.205
17	2.0	0.68	0.652	0.334
18	0.33	0.34	0.236	0.198
19	0.96	0.50	0.446	0.305
20	0.33	0.18	0.041	0.072

TABLE B4

Parameter estimates from least squares fit of data to empirical model.

Variable (mg/l) or (mm/min)	b_0 (1)	b_1 (S)	b_2 (Fe)	b_3 (pH)	b_4 (S.Fe)	b_5 (Fe.pH)	b_6 (S.pH)	b_7 (S.Fe.pH)	b_8 (pH ²)
1. Total Metals									
Fe	(1.13)	(-0.633)	(1.66)	-1.64				(0.670)	(0.104)
Cu	-1.07			(-0.221)				(0.147)	
Cd	-1.335			(-0.333)			(-0.363)	(0.296)	
Zn	-1.283		(0.768)	(-0.345)		(-0.375)	(0.417)	(0.261)	
2. Dissolved Metals									
Fe	(-0.922)		(0.769)	(-2.03)		(-1.83)	(0.859)		0.544
Cu	-4.673		(0.543)		0.883				
Cd	-5.605	(0.555)	-1.28	(0.450)	-1.27	-1.167	1.23	(-0.669)	
Zn	-3.295		0.878			-1.41	1.46	(-0.361)	
3. Suspended Metals									
Fe	0.867	(-0.241)	0.918	-1.01	(-0.253)	(0.507)	(-0.488)	0.858	(-0.213)
Cu	-1.06			(-0.221)	(-0.184)		(-0.191)	(0.176)	
Cd	-1.35			(-0.387)			(-0.461)	(0.383)	
Zn	-1.45	(0.366)		(-0.367)	(-0.220)	(0.643)	(-0.679)	(0.445)	
4. Settling Velocity									
ln transformed 3.92 untransformed 51.0				(-0.151) (-7.13)		(-0.113) (-5.59)			

FOOTNOTES FOR TABLE B4:

1. The units of the predicted responses are mg/l for the metals concentrations and mm/min for settling velocities. All metals concentrations were transformed with the natural logarithm before they were fitted to the model.
2. Where no entry is made 0 was central in the 95% confidence region. Where an entry is bracketed, 0 was included near a boundary of the 95% confidence region.

TABLE B5

Zone settling velocities of flocculent suspensions

Run	Settling velocity (mm/min)
3	69.8
4	69.0
5	54.3
7	27.8
8	39.3
9	58.3
10	46.5
11	53.4
12	59.3
13	36.2
14	60.2
15	60.0
16	35.6
18	54.1

TABLE B6

Combined residual concentrations of S^{-2} , HS^{-} and H_2S in the supernatant. For the 14 runs not listed concentrations were less than 10^{-15} mole/l.

Run	mole/l	Concentration mg/l
2	6×10^{-5}	2.0
3	5×10^{-8}	2×10^{-3}
4	2×10^{-6}	5×10^{-2}
6	4×10^{-5}	1.3
14	3×10^{-12}	1×10^{-7}
17	5×10^{-7}	1.6×10^{-2}

TABLE B7

Metals concentration data for the effluent
from the continuous precipitation vessel

Time from start (hr.)	Fe (mg/l)	Cu (mg/l)	Cd (mg/l)	Zn (mg/l)
1. Dissolved Metals				
1.25	23.0	<0.1	0.06	1.47
2.5	21.5	<0.1	<0.05	1.64
3.5	19.0	<0.1	0.06	1.70
4.5	19.5	<0.1	<0.05	1.83
5.5	18.0	<0.1	<0.05	1.34
6.5	14.5	<0.1	<0.05	0.91
8.0	12.0	<0.1	<0.05	1.61
9.0	16.0	<0.1	<0.05	2.30
10.0	13.5	<0.1	<0.05	1.52
2. Suspended Metals				
1.25	10.0	3.9	5.19	5.88
2.5	6.7	1.9	2.51	3.88
3.5	--	1.28	1.92	2.3
4.5	--	1.20	1.75	1.79
5.5	--	0.06	0.81	0.86
6.5	0.6	1.3	1.87	1.79
8.0	7.6	21.9	24.55	28.19
9.0	24.0	82.9	102.0	81.7
10.0	1.8	3.4	5.15	4.28
3. Total Metals				
1.25	33.0	4.0	5.25	7.35
2.5	28.2	2.0	2.56	5.52
3.5	18.5	1.28	1.98	4.0
4.5	18.5	1.20	1.89	3.62
5.5	16.8	0.70	0.86	2.20
6.5	15.1	1.40	1.92	2.70
8.0	19.6	22.0	24.6	29.8
9.0	40.0	83.0	102.0	84.0
10.0	15.3	3.5	5.2	5.8

TABLE B8

Composition of residual floc from experimental design runs

Run	Cd/Cu (g/g)	Zn/Cu (g/g)
1	1.13	0.709
2	--	--
3	0.631	0.229
4	0.925	0.481
5	0.413	0.700
6	--	--
7	0.745	0.763
8	0.854	0.795
9	0.475	0.567
10	0.902	0.716
11	0.842	0.700
12	0.608	0.612
13	0.590	0.505
14	1.032	0.826
15	0.836	0.768
16	0.820	0.683
17	0.959	0.491
18	0.724	0.582
19	0.892	0.610
20	0.228	0.400
mean	0.76	0.62
std. dev.	0.23	0.15

TABLE B9

Composition of the residual floc from the continuous run

Time from start (hr.)	Cd/Cu (g/g)	Zn/Cu (g/g)
1.25	1.33	1.51
2.5	1.32	2.04
3.5	1.50	1.80
4.5	1.46	1.49
5.5	1.35	1.43
6.5	1.44	1.38
8.0	1.12	1.29
9.0	1.23	0.99
10.0	1.51	1.26
mean	1.36	1.47
std.dev.	0.13	0.31

TABLE B10

Effect of adjusted pH on settling velocity of aged
metal sulphide sludge

Adjusted pH	Settling velocity mm/min
3.0	47.6
4.0	44.2
5.5	35.6
7.0	36.1
8.5	32.7
10.0	33.5
11.5	precipitate restablized

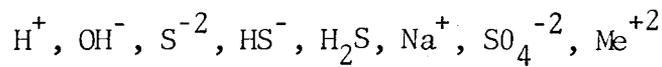
APPENDIX C

CALCULATIONS AND DISCUSSIONS

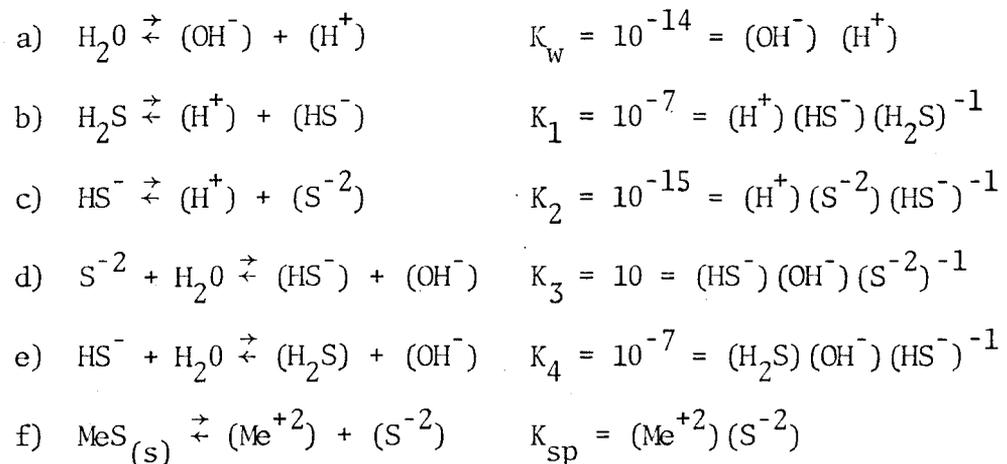
C.1 Sample calculation of equilibrium concentrations after precipitation

A dilute solution containing M_T moles of $Me SO_4$, where Me represents any divalent heavy metal, is precipitated with S_T moles of Na_2S . If the final volume of the mixture is V l the residual metal concentration can be calculated as follows. It is assumed that the dilution is small enough that concentrations closely approximate activities.

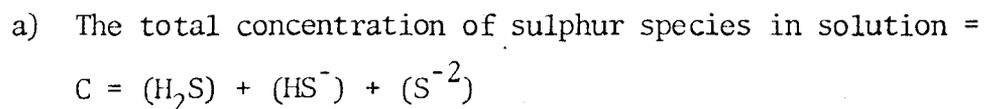
(1) Identification of Species in Solution:

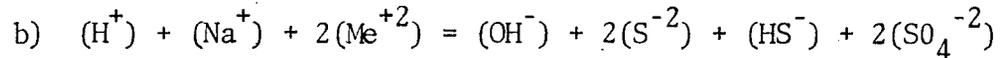


(2) Equilibria in Solution:



(3) Conditions Imposed by Mass and Electroneutrality Balances:





(4) Substitution and Rearrangement of Equations:

a) From hydrolysis constants:

$$(HS^-) = 10(S^{-2})(OH^-)^{-1}$$

$$(H_2S) = 10^{-6}(S^{-2})(OH^-)^{-2}$$

Therefore 3(a) becomes

$$C = (S^{-2})(1 + 10(OH^-)^{-1} + 10^{-6}(OH^-)^{-2})$$

$$\text{and } (S^{-2}) = (C)/(1 + 10(OH^-)^{-1} + 10^{-6}(OH^-)^{-2}) \quad (4a)$$

b) Assuming that all moles of sulphur removed from solution are precipitated as MeS, moles precipitated = $S_T - CV$

$$\text{Therefore } (Me) = (M_T - S_T + CV)/V \quad (4b)$$

$$\text{Therefore } K_{sp} = \left(\frac{M_T - S_T + CV}{V} \right) \left(\frac{C}{1 + 10(OH^-)^{-1} + 10^{-6}(OH^-)^{-2}} \right) \quad (4c)$$

This equation contains 2 unknowns (OH^-) and C and cannot be solved without another equation. The electroneutrality balance 3(b) will suffice, after a few substitutions and rearrangement:

$$(Na^+) - 2(SO_4^{-2}) + 10^{-14}(OH^-)^{-1} + 2\left(\frac{M_T - S_T + CV}{V}\right) =$$

$$OH^- + \frac{C}{1 + 10(OH^-)^{-1} + 10^{-6}(OH^-)^{-2}} (2 + 10(OH^-)^{-1}) \quad (4d)$$

Since (Na^+) and (SO_4^{-2}) are known equations (4c) and (4d) may be solved simultaneously, although the solution is untidy.

C.2 Calculation of mean velocity gradient

The expression derived by Camp (1955) for the dissipation function W was used to calculate $G_m = (W/\mu)^{1/2}$.

$$W = \frac{239 C_D (1-K)^3 N^3 \Sigma A(r_b)^3}{V}$$

C_D = drag coefficient , 1.2 for flat plates

K = 0.32 from discussion by Camp

N = frequency of shaft rotation

V = volume of liquid

A = paddle area

r_b = paddle to shaft distance, centre to centre.

$$A = 0.02045 \text{ ft.}^2 \quad r_b^3 = 0.00024 \text{ ft.}^3$$

$$\text{For slow mix with } N = 0.33 \text{ sec}^{-1} \quad G_m = 5 \text{ sec}^{-1}$$

$$\text{For fast mix with } N = 1.67 \text{ sec}^{-1} \quad G_m = 55 \text{ sec}^{-1}$$

C.3 Discussion of analysis of transformations

The method of Box and Cox (1964) for the analysis of transformations can be used as a quantitative guide to finding the most suitable transformation of the dependent variable. Transforming data is performed to make the analysis of empirical models simpler and easier to interpret.

For example, it may be possible to fit the data with a polynomial of low degree in the transformed variable rather than a polynomial of higher degree in the original variable. Further reasons for transforming data are to satisfy the assumption of constant variance and of normality of the error distribution on which the statistical tests of the least squares regression analysis are based. The Box and Cox method should be used only as a guide along with other considerations such as simplicity, ease of interpretation and physical meaning.

A summary of the method follows:

- (1) Let y stand for a dependent variable and let q be the index of a transformation of y . Let $y' = (y_1, y_2 \dots y_n)^{1/n}$. Consider the family of transformations

$$z^{(q)} = \frac{y^q - 1}{q y^{q-1}} \quad \text{where if } q = 0 \quad z^{(q)} = (\ln y) y'$$

Assume a range of values for q : $(-2, -1, -0.5, 0, 0.5, 1, 2)$.

- (2) For each q perform the transformation of the data to $z^{(q)}$.
- (3) Perform a regression on $z^{(q)}$ for each q and examine the residual sum of squares: $SS(q, z^{(q)})$.
- (4) For each q calculate $L_{\max}(q, z) = -0.5 n \ln \left\{ \frac{SS(q, z^{(q)})}{n} \right\}$
- (5) Plot $L_{\max}(q, z)$ versus q and find the maximum value of L_{\max} .
- (6) Calculate a confidence interval on q as

$$L_{\max}(\text{predicted}) - L_{\max}(\text{real})$$

is less than one half the value of the chi squared distribution function for one degree of freedom at the level of confidence desired, say 95%.

- (7) Choose a convenient value of q falling within the confidence interval which seems realistic on physical or theoretical grounds.

TABLE C1

Results of the analysis of transformations
of the concentrations of total Fe

q	$SS(q, z^q)$	L_{\max}
-2.0	87,750	-76.4
-1.0	1,904	-42.0
-0.5	570	-31.1
0.0	425	-28.4
0.5	906	-35.3
1.0	4,320	-49.3
2.0	355,430	-89.0

$$L_{\max}(\hat{q}) = 28.2 \quad -0.45 < q < 0.20$$

TABLE C2

Results of the analysis of transformations
of the concentrations of total Cd

q	SS(q, z ^q)	L _{max}
-2.0	693	-32.9
-1.0	126	-17.5
-0.5	69	-12.1
0.0	47	- 8.64
0.5	40	- 7.3
1.0	43	- 7.9
2.0	81	-13.6

$$L_{\max}(\hat{q}) = -7.2 \quad -0.1 < q < 1.4$$

C.4 Estimation of model parameters and related statistical tests

C.4.1 Parameter estimates

The method of linear least squares was used to estimate the parameters of the empirical model. The model may be expressed in matrix form as:

$$\underline{Y} = \underline{X} \underline{B} + \underline{E}$$

where \underline{Y} is the vector of observations, \underline{X} the matrix of the independent variables, \underline{B} the vector of parameters to be estimated and \underline{E} the vector of errors. A vector of parameter estimates \underline{b} was obtained by solving the

equation $\underline{b} = (\underline{X}' \underline{X})^{-1} \underline{X}' \underline{Y}$. The vector of predicted responses is then $\hat{\underline{Y}} = \underline{X} \underline{b}$ and the vector of residuals $\underline{e} = \underline{Y} - \hat{\underline{Y}}$. These equations were solved using the computer subroutine UWHAUS: a routine developed for non-linear parameter estimation, but adaptable to linear models.

C.4.2 Analysis of variance

The analysis of variance calculations were based on the discussion by Draper and Smith (1966, p. 61 ff). A computer subroutine was written to calculate all values and was used in conjunction with UWHAUS.

C.4.3 Statistical tests

Although parameter estimation by least squares techniques requires no assumptions about the error structure, certain statistical tests of the regression are based on the following assumptions:

- (1) the errors are random variables with mean 0 and constant variance,
- (2) the individual errors are uncorrelated,
- (3) the errors are normally distributed.

By transforming the data using the Box and Cox method the transform for which the above assumptions most nearly hold was chosen. This was accepted as partial justification for calculations of the lack of fit test, the overall test of regression and the calculations of 95% confidence intervals of the parameters done in UWHAUS.

The lack of fit test consisted of comparing

$$\left[\frac{SS(\text{lack of fit})/(n-p-n_e)}{SS(\text{pure error})/n_e} \right] \quad \text{with}$$

$$F[n-p-n_e, n_e, 1-\alpha]$$

The test of the overall regression was a test of the hypothesis $H_0 : B_1 = B_2 = \dots = B_{p-1} = 0$ against $H_1 : \text{not all } B_i = 0$. The ratio

$$\left[SS(R/b_0)/(p-1) \right] / s^2$$

was treated as an $F(p-1, n-p)$ variate.

Draper and Smith (1966) should be consulted for full details of the form of the calculations.

C.5 Experimental Error

The standard deviations of the data obtained for the four replicate runs of the experimental design are presented in Table C3. The standard deviations shown can be used as estimates of the standard deviation of the cumulative error of all steps in the experimental procedure.

TABLE C3

Standard deviations of data from replicate runs

Dependent Variable	Mean (mg/ℓ)	Standard Deviation
Total Fe	2.84	1.80
Total Cu	0.33	0.167
Total Cd	0.257	0.196
Total Zn	0.25	0.142
Suspended Fe	2.48	1.62
Suspended Cu	0.33	0.167
Suspended Cd	0.25	0.187
Suspended Zn	0.22	0.131
Dissolved Fe	0.355	0.308
Dissolved Cu	--	--
Dissolved Cd	0.012	0.010
Dissolved Zn	0.03	0.012
Settling Velocity	54.4 mm/min	5.84 mm/min