Metals Removal from Acidic Drainage - Chemical Methods

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METALS REMOVAL FROM ACIDIC DRAINAGE - CHEMICAL METHODS

FOR MEND

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Part I: Resource Recovery From AMD: Sulphide Precipitation.
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Part II: Alternative Processes and Cost Analysis For Resource Recovery From AMD.
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EXECUTIVE SUMMARY

In collaboration with McGill University's Dept. of Mining and Metallurgical Engineering, Noranda Technology Centre (NTC) investigated the prospect of recovering valuable metals from acid mine drainage (AMD) while maintaining effluent quality and reducing the amount of sludge generated. Several chemical methods were evaluated to selectively precipitate and recover metal ions, leading to the development of a conceptual flowsheet for a three-step precipitation process (Figure 1). This flowsheet was further evaluated, along with the associated process economics. The research was funded by Noranda and carried out for the MEND program.

The original three-step precipitation process (Figure 1) was developed and investigated in detail at the laboratory scale (**Part I**) by McGill University. This process consisted of: a) Fe precipitation in the presence of surfactant (dodecylamine, *DDA*, which was expected to alter the surface properties of $Fe(OH)_3$, thus reducing co-precipitation of Zn); b) sulphide precipitation to obtain a Zn rich sulphide precipitate; and c) a final lime treatment to remove residual metals if, necessary to comply with water quality standards.

Several concerns were raised pertaining to this process. Solid/liquid (S/L) separation and materials handling appear difficult. Furthermore, residual DDA in the effluent may be detrimental to aquatic life. Ultimately, process control and cost are the key problems for sulphide precipitation. As a result, alternative processes were sought.

To this end, three alternatives processes were developed and evaluated by NTC (**Part II**). In one process, the first step consisted of Fe(III) precipitation with $CaCO_3$, followed by precipitation of metals with $NaOH/Na_2CO_3$. In another process, Cu was removed by cementation, using Fe powder. Iron (III) was subsequently precipitated as a phosphate, using H_3PO_4; and Zn was removed as a hydroxide, using $Ca(OH)_2$. These processes are depicted in Figure 2 and Figure 3, respectively. The use of Na_2S to obtain ZnS/CuS precipitates was further investigated in a reverse version of the three-step process (Figure 4). Following the removal of Zn and Cu as sulphides at pH 3.5 in the first step, lime neutralization in conjunction with aeration

at pH 9.5 was applied to simultaneously precipitate iron and the remaining metal ions, and to produce acceptable effluent quality together in one step.

The results obtained from both studies are:

Part I - McGill Study (Figure 1):

1. With the use of lime, the iron present in AMD can be completely removed as ferric hydroxide at pH 3.5, following oxidation with H_2O_2. The solid content of the settled sludge ranges from 6 to 8%.
2. The use of DDA in the first step to reduce co-precipitation of other metal ions onto ferric hydroxide sludge slightly improved the subsequent Zn recovery. However, settling of precipitates in all stages deteriorated and the content of the leachable metals in the iron sludge increased. As a result, the use of DDA is not recommended in the process.
3. The iron sludge required several washing cycles in order to remove leachable metals.
4. Zn and Cu can be selectively recovered by using either Na_2S, H_2S or NaHS in the second step. The Zn/Cu selectivity is closely dependent on pH (e.g. 3.5) and the alkaline reagent (e.g. NaOH) used for pH control. However, as the Zn/Cu recovery increases with increasing pH, the Zn/Cu grade of the sludge decreases.
5. More than 90% Zn recovery and greater than 50% Zn grade can be obtained at pH 4.5 when lime and Na_2S are used to set the pH and precipitate the Zn.
6. H_2O_2, O_3 and Trapzene (a CaO_2 mixture; patent pending FMC Corp.) were evaluated as Fe oxidants. O_3 was technically the most effective when it was used in stoichiometric quantities.
7. Lime treatment of the overflow from the second step to pH 9.5 resulted in an effluent quality similar to that from the conventional lime neutralization process.

Part II - NTC Study (Figure 2, Figure 3, Figure 4):

1. The McGill process was further examined in reverse order and as a two-step process. In this two-step process the removal of Zn/Cu as sulphides at pH 3.5 was performed first followed by the oxidation of iron with air and precipitation with lime at pH 9.5. This method required a large quantity of Na_2S (e.g. 3-4x stoichiometric requirement) and technical difficulties in the separation of the Zn-rich sludge were encountered.
2. Of the chemical processes examined, the two-step process yielded the least contaminated iron precipitate and the highest Zn recovery. In addition, this process did not produce sludge requiring special disposal. However, the Zn grade of the precipitate was about 30%.
3. Biological oxidation could oxidize iron, but the required retention time was 2-6 days. On a cost basis, biological oxidation seems to be at least one order of magnitude cheaper than chemical methods.

4. Although the use of $CaCO_3$ resulted in the least contaminated $Fe(OH)_3$ precipitate and its cost was one order of magnitude less than other chemicals tested, the iron still needed to be oxidized before precipitation.
5. Process economics for each process investigated and oxidizing reagent used were assessed. The cost for each process was compared to the cost of the lime neutralization treatment plant being operated at Les Mines Gallen, site of the AMD used in the tests. The most expensive method was the three-step ZnS precipitation, and the least expensive was the two-step $CaCO_3$/NaOH process.
6. Use of PO_4^{3-} to selectively remove ferric iron, following cementation of copper with iron, and precipitation of zinc with lime was also explored (based on initial Dahnke's master's thesis, 1985). The process was not technically or chemically feasible.
7. Requirements for dewatering of each precipitate, generated at each step along the processes were determined. ZnS precipitates required flocculation, clarifier settling and good filtering (e.g. via filter press).

The processes investigated suffer from high costs relative to conventional lime treatment. In particular, the costs of chemical sulphide reagents, and H_2O_2 are not economical. As a result, further research aimed at optimising the existing flowsheets is not recommended, unless new concepts which radically reduce costs or S/L separation steps are involved.

Some alternative options for developing a process flow sheet should be examined. Suggestions are listed below in order of priority:

I. Following the reduction of all iron in the AMD to ferrous iron with SO_2, precipitate $ZnCO_3$ in the first step; then oxidize iron with air and precipitate iron and other residual metal ions with lime.

II. Investigate the biological sulphate reduction process and/or a combined biological/chemical processes.

III. Selective leaching of Zn from lime sludges should also be explored as a potential alternative. Particularly, the sludge generated from the two-step NTC process should be looked at, due to its co-absorption property. Zn selectively leached out from the sludge can be subsequently precipitated with Na_2CO_3.

Any new process must consider the acceptability of end products from each process for recycling to a Zn roaster, Zn concentrator or lead circuit.

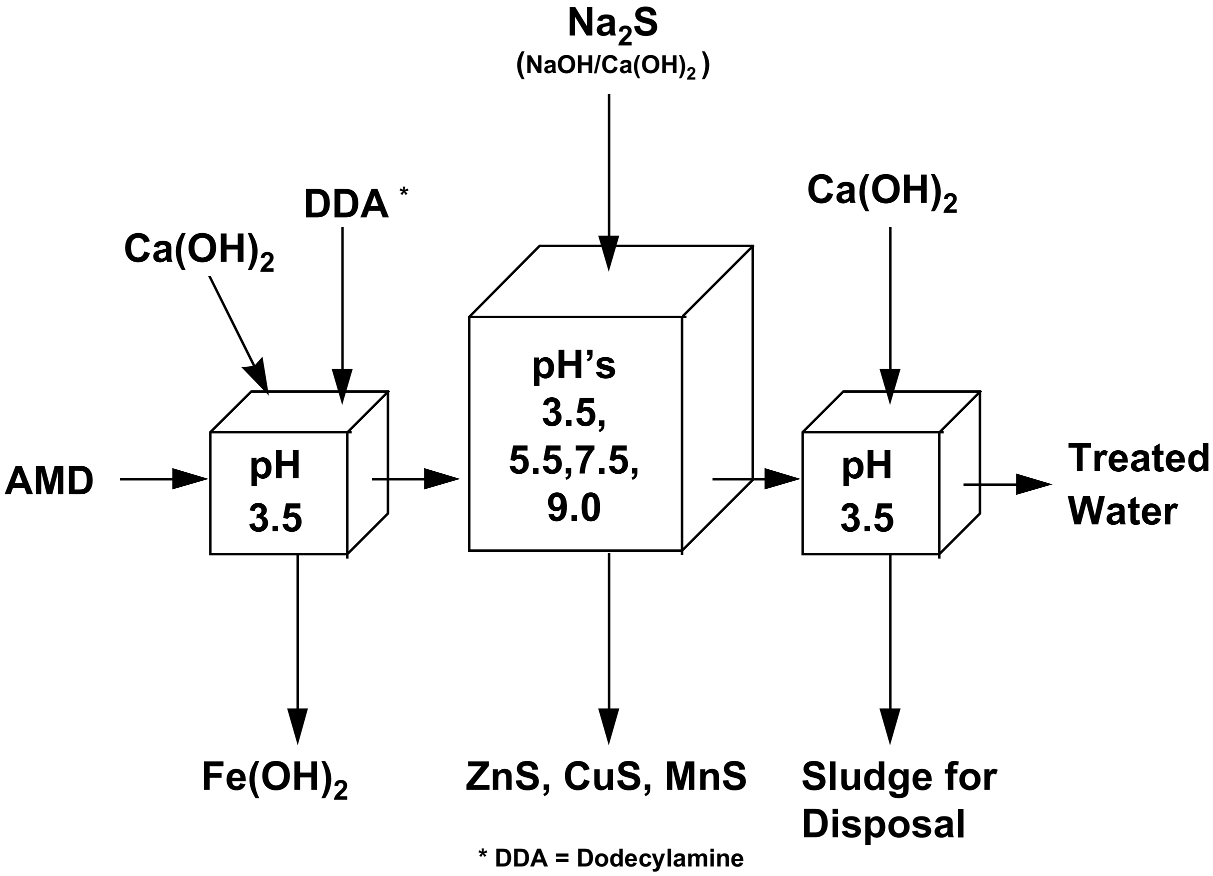


Figure 1. **Process flowsheet for three-step precipitation process evaluated by McGill-NTC**

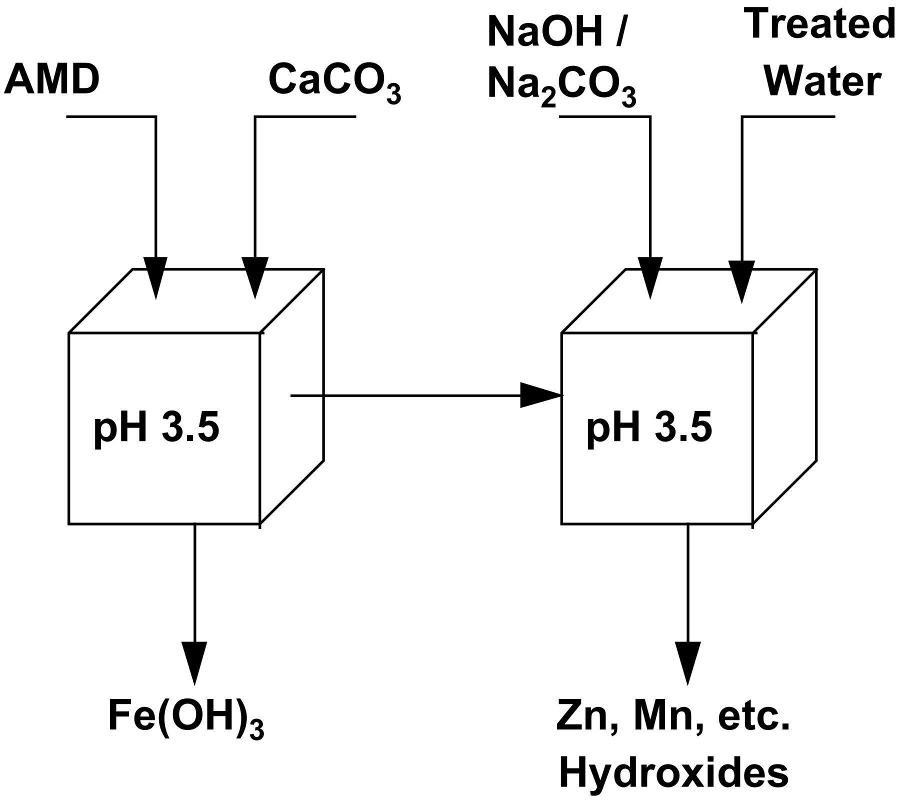


Figure 2. Process flowsheet for alternative-two-step precipitation process.

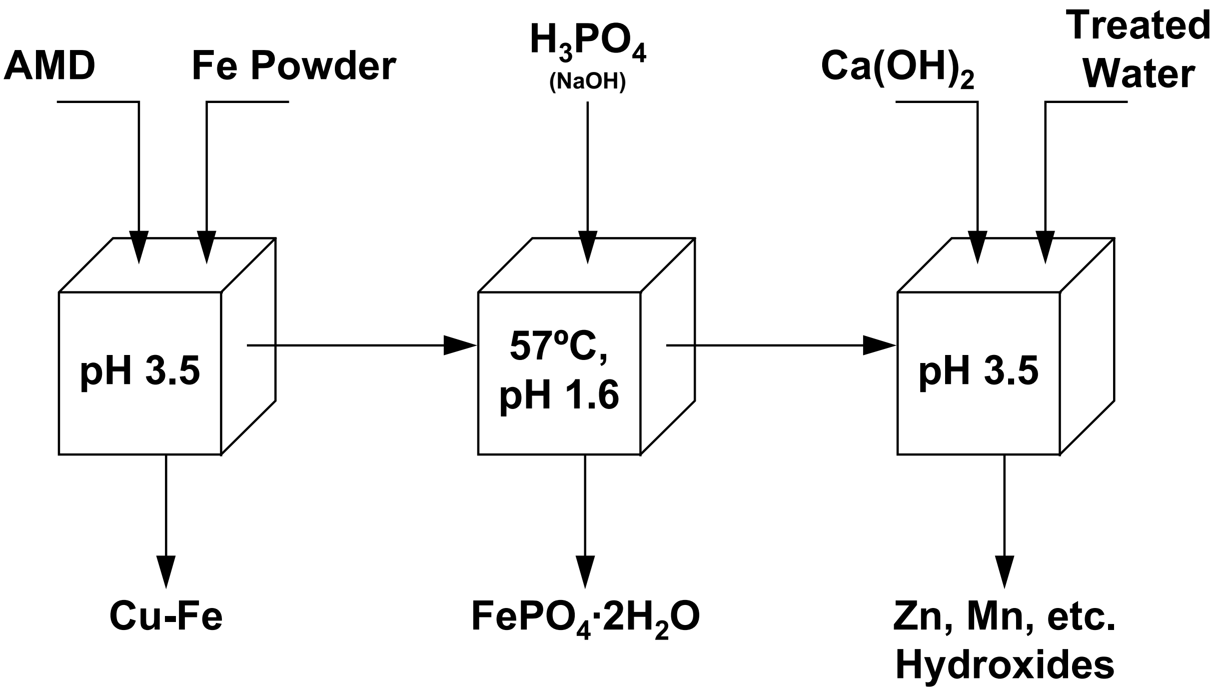


Figure 3. Process flowsheet for alternative three-step recovery process evaluated by NTC.

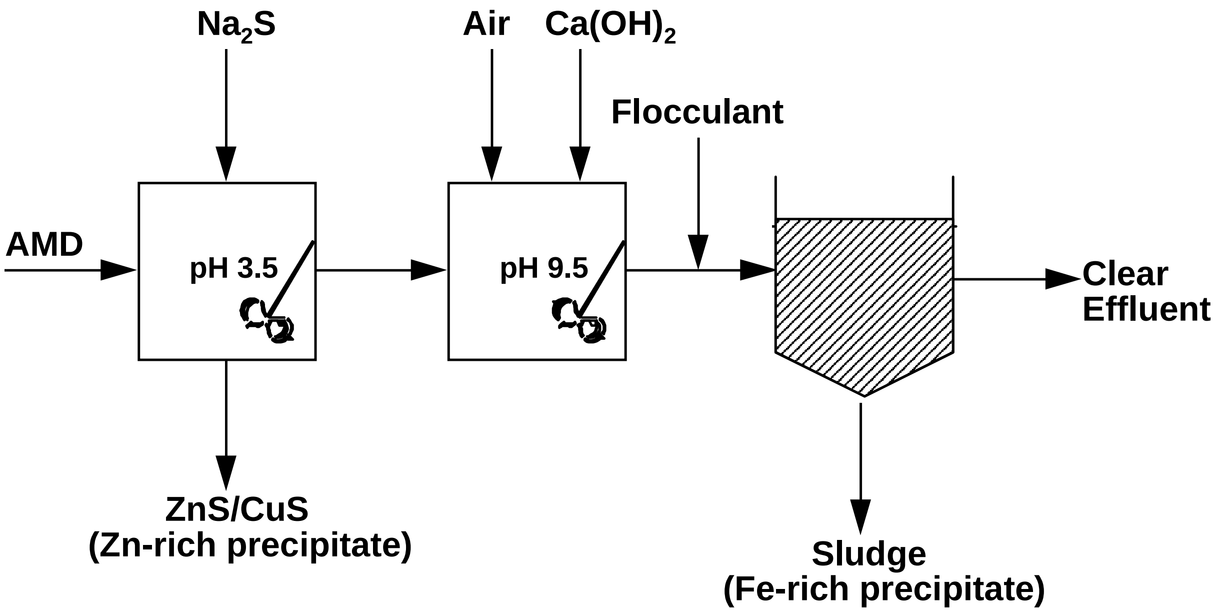


Figure 4. **Process flowsheet for reverse three-step precipitation process.**

RÉSUMÉ

De concert avec le département de génie minier et métallurgique de l'Université McGill, le Centre de technologie Noranda (CTN) a étudié la possibilité de récupérer des métaux de grande valeur à partir du DMA (drainage minier acide) tout en maintenant la qualité de l'effluent liquide et en réduisant la quantité de boues produites. Plusieurs méthodes chimiques ont été considérées pour précipiter les métaux de manière sélective et les récupérer avant d'élaborer le schéma simplifié de traitement d'un procédé de précipitation en trois étapes (Figure 1). Le schéma simplifié de traitement a été évalué par la suite, de même que ses aspects économiques.

Le procédé original de précipitation en trois étapes (Figure 1) a été mis au point et étudié de façon détaillée à l'échelle du laboratoire (**partie I**) par l'Université McGill. Ce procédé consistait à précipiter le Fe en présence d'un agent tensio-actif (DDA , ou dodécylamine) (ce qui devait modifier les propriétés en surface du $Fe(OH)_3$, réduisant ainsi la précipitation simultanée du Zn), à faire précipiter les sulfures en vue d'obtenir un précipité sulfuré riche en Zn et à effectuer un traitement final à la chaux visant à éliminer les métaux résiduels s'il y a lieu pour satisfaire aux exigences relatives à la qualité de l'eau.

Plusieurs problèmes techniques ont été soulevés pendant l'élaboration du procédé. La séparation solide/liquide et la manutention des matières se sont avérées difficiles. En outre, la DDA résiduelle dans l'effluent peut nuire à la vie aquatique. Finalement, la surveillance du procédé et les coûts qu'il engendre sont les principaux problèmes associés à la précipitation des sulfures. C'est pour cette raison que des procédés de remplacement ont été étudiés.

Trois procédés de remplacement ont été mis au point et évalués par le CTN (**partie II**). La première étape de l'un des procédés consiste à précipiter le Fe(III) en présence de $CaCO_3$, puis à précipiter des métaux en présence de NaOH et de Na_2CO_3. Dans un autre procédé, le Cu a été récupéré par cémentation, au moyen de poudre de Fe. Le fer-III a été par la suite précipité sous forme d'un phosphate, au moyen de H_3PO_4 et le Zn a été récupéré sous la forme d'un hydroxyde, au moyen de $Ca(OH)_2$. Ces procédés sont illustrés à la Figure 2 et à la Figure 3 respectivement. L'utilisation de Na_2S en vue d'obtenir les précipités ZnS et CuS a été étudiée en profondeur dans une version inverse du procédé en trois étapes (Figure 4). À la suite de la récupération du Zn et

du Cu sous forme de sulfures à un pH de 3,5 au cours de la première étape, on a procédé à la neutralisation par la chaux accompagnée d'aération à un pH de 9,5 qui a été effectuée simultanément pour précipiter le fer et les ions métalliques résiduels et pour produire un effluent de qualité acceptable en une seule étape.

Les résultats obtenus dans le cadre des ces études sont les suivants :

Partie I - Étude réalisée par McGill (Figure 1) :

1. En présence de chaux, le fer contenu dans le DMA peut être entièrement récupéré sous forme d'hydroxyde ferrique à un pH de 3,5 après oxydation au H_2O_2. La teneur en matières solides de la boue décantée se situe entre 6 et 8 %.
2. L'emploi de DDA au cours de la première étape en vue de réduire la précipitation simultanée d'autres ions métalliques dans la boue d'hydroxyde ferrique a quelque peu amélioré la récupération subséquente du Zn. Toutefois, la décantation des précipités à toutes les étapes s'est avérée moins fructueuse et la teneur en métaux pouvant faire l'objet de lixiviation dans la boue de fer a augmenté. Par conséquent, l'emploi de DDA n'est pas recommandé pour ce procédé.
3. La boue de fer a nécessité plusieurs cycles de lavage afin de récupérer les métaux pouvant faire l'objet de lixiviation.
4. La récupération sélective du Zn et du Cu a été réalisée au moyen de Na_2S, de H_2S ou de NaHS au cours de la deuxième étape. La sélectivité Zn/Cu dépend dans une large mesure du pH (p. ex. 3,5) et de l'agent réactif alcalin (p. ex. le NaOH) employé pour régulariser le pH. Ainsi, à mesure que la récupération du Zn et du Cu s'accroît avec l'augmentation du pH, la teneur en Zn et en Cu de la boue diminue.
5. On peut récupérer plus de 90 % du Zn et obtenir une teneur en Zn de plus de 50 % à un pH de 4,5 lorsqu'on utilise de la chaux et du Na_2S pour régulariser le pH et précipiter le Zn.
6. On a évalué le H_2O_2, le O_3 et le trapzène (mélange de CaO_2 et de CaO; le brevet est en cours d'obtention par la FMC Corp.) à titre d'agents oxydants du Fe. Le O_3 a été techniquement considéré comme le plus efficace de tous lorsqu'il a été utilisé en quantités stoechiométriques.
7. Le traitement à la chaux du déversement à partir de la deuxième étape à un pH de 9,5 a permis d'obtenir un effluent dont la qualité est semblable à celle obtenue par le procédé classique de neutralisation par la chaux.

Partie II - Étude du CTN (Figure 2, Figure 3, Figure 4)

1. Le procédé de McGill a été examiné de façon plus approfondie dans l'ordre inverse et comme un procédé en deux étapes. Dans le procédé en deux étapes, la récupération du Zn et du Cu sous forme de sulfures à un pH de 3,5 a été effectuée et suivie par l'oxydation du fer par l'air et la précipitation en présence de chaux à un pH de 9,5. Pour ce procédé, de grandes

quantités de Na_2S sont requises (p. ex. des exigences stoechiométriques de 3 à 4x) et des difficultés techniques sont survenues pendant la séparation de la boue riche en Zn.

2. De tous les procédés chimiques étudiés, le procédé en deux étapes a produit le précipité de fer le moins contaminé et a permis de récupérer la plus grande quantité de Zn. En outre, ce procédé n'a pas produit de boues nécessitant une évacuation particulière. Toutefois, la teneur en Zn du précipité était d'environ 30 %.
3. L'oxydation biologique pourrait ioniser le fer, mais la durée requise de rétention est seulement de deux à six jours. En matière de coûts, l'oxydation biologique semble être moins coûteuse d'au moins un ordre de grandeur comparativement aux méthodes chimiques.
4. Bien que l'utilisation de $CaCO_3$ ait produit le précipité de $Fe(OH)_3$ le moins contaminé et ce, à un coût moindre d'un ordre de grandeur par rapport aux autres produits chimiques mis à l'essai, il faut toujours oxyder le fer avant la précipitation.
5. Nous avons étudié l'aspect économique de chaque procédé et les agents oxydants employés. Le coût de chaque procédé a été comparé aux coûts des procédés suivis à l'usine de traitement de neutralisation par la chaux des Mines Gallen, site du DMA employé dans les essais. La méthode la plus coûteuse s'est avérée la précipitation en trois étapes du ZnS alors que la moins coûteuse est celle du procédé $CaCO_3$/NaOH en deux étapes.
6. Le recours à l'ion PO_4^{3-} pour éliminer de façon sélective le fer ferrique à la suite de la cémentation du cuivre et du fer et pour précipiter le zinc en présence de chaux a également été étudié. Nous avons constaté que le procédé n'est ni techniquement ni chimiquement réalisable.
7. Les exigences relatives à l'assèchement de chaque précipité produit à l'une ou l'autre des étapes des procédés ont été déterminées. Les précipités de ZnS ont nécessité une floculation, une décantation du clarificateur et un bon filtrage (p. ex. au moyen d'un filtre-presse).

Les procédés étudiés entraînent des coûts relativement élevés en comparaison du traitement classique à la chaux. En particulier, les coûts des agents réactifs chimiques aux sulfures et du H_2O_2 sont très élevés. Par conséquent, des recherches ultérieures visant à maximiser les schémas simplifiés de traitement ne sont pas recommandées, à moins qu'elles ne portent sur de nouvelles notions réduisant considérablement les coûts ou les étapes de la séparation solide/liquide.

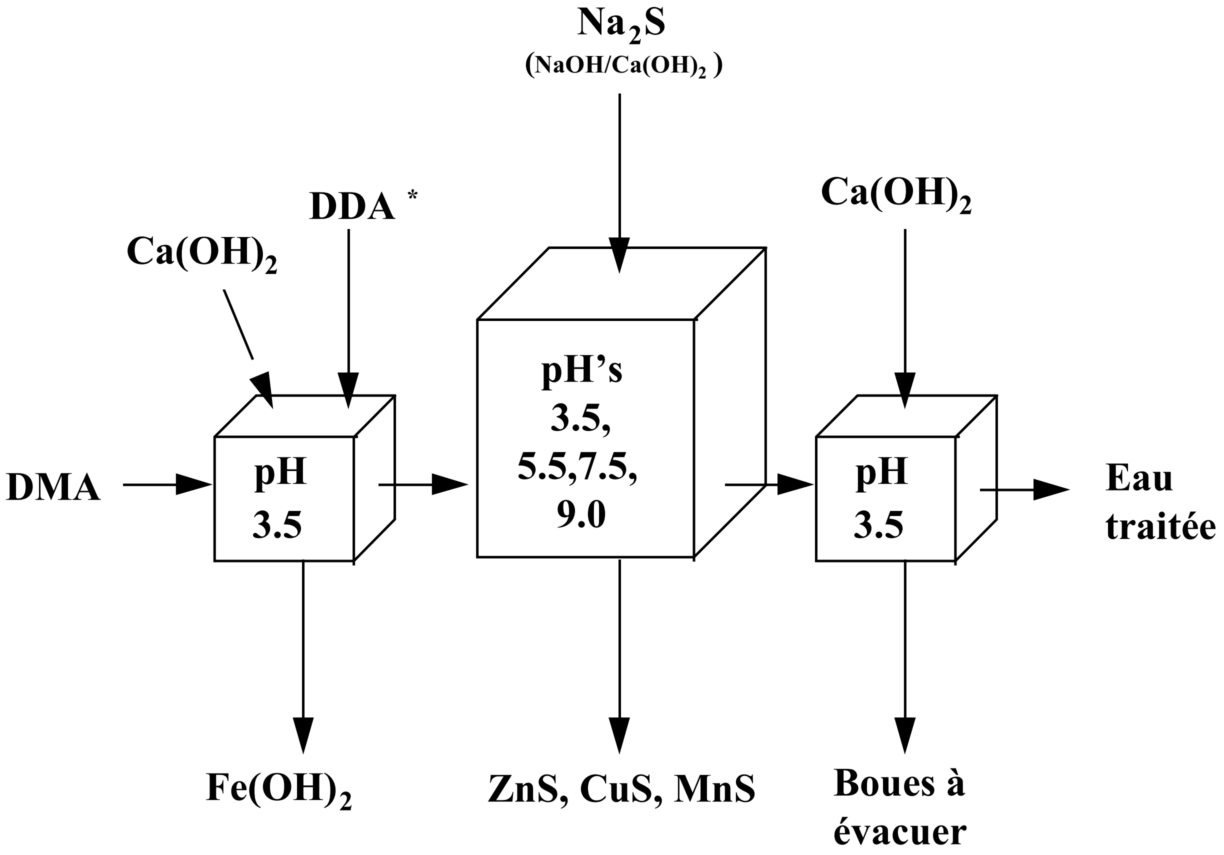
Quelques solutions de remplacement ont été proposées pour élaborer un schéma simplifié de traitement du procédé. Ces solutions devraient être étudiées de plus près. Voici les solutions proposées par ordre de priorité :

I. Après la réduction de tout le fer du DMA en fer ferreux en présence de SO_2, faire précipiter le $ZnCO_3$ au cours de la première étape, puis oxyder le fer en présence d'air et précipiter le fer et les autres ions métalliques résiduels en présence de chaux.

II. Étudier le procédé de la réduction biologique du sulfate ou une combinaison de procédés biologiques et chimiques.

III. Étudier la lixiviation sélective du Zn à partir de boues de chaux à titre de solution de remplacement possible. En particulier, la boue produite à partir du procédé en deux étapes du CTN devrait faire l'objet d'une étude, étant donné sa propriété d'absorption simultanée. Le Zn récupéré par lixiviation sélective à partir des boues peut précipiter ultérieurement avec du Na_2CO_3.

Il devrait être tenu compte, dans tout nouveau procédé, de l'obtention d'un produit final jugé acceptable et ce dernier devrait pouvoir être recyclé dans un four de grillage du Zn, dans un concentrateur de Zn ou dans le circuit Pb.



* DDA = Dodecylamine

Figure 1. Schéma simplifié de traitement pour le procédé de précipitation en trois étapes évalué par McGill et le CTN

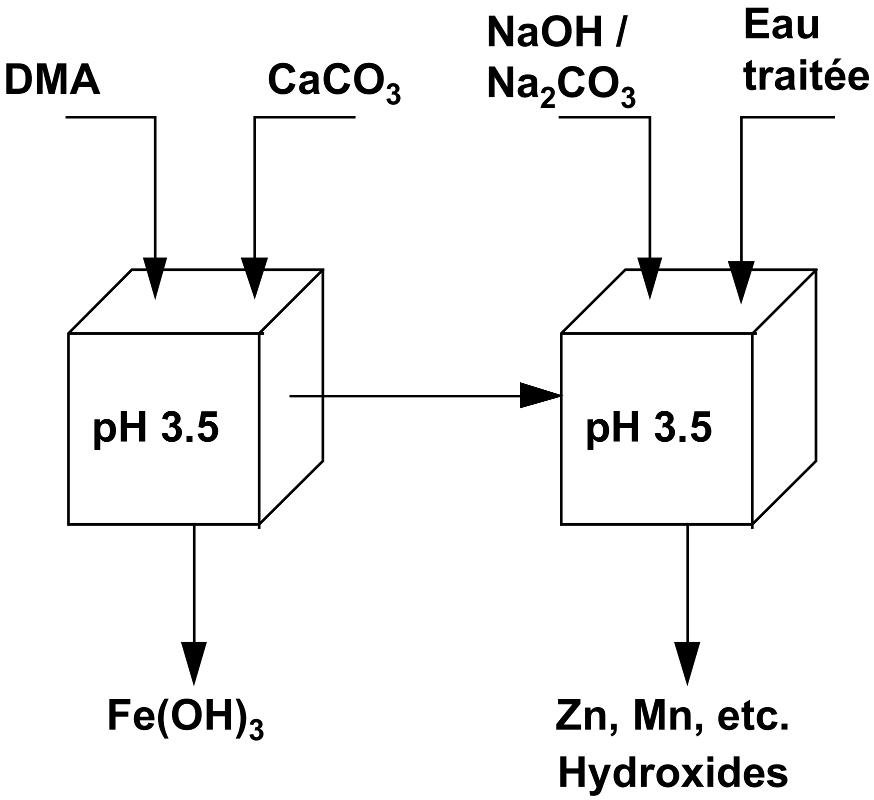


Figure 2. Schéma simplifié de traitement pour le procédé de remplacement de la précipitation en deux étapes

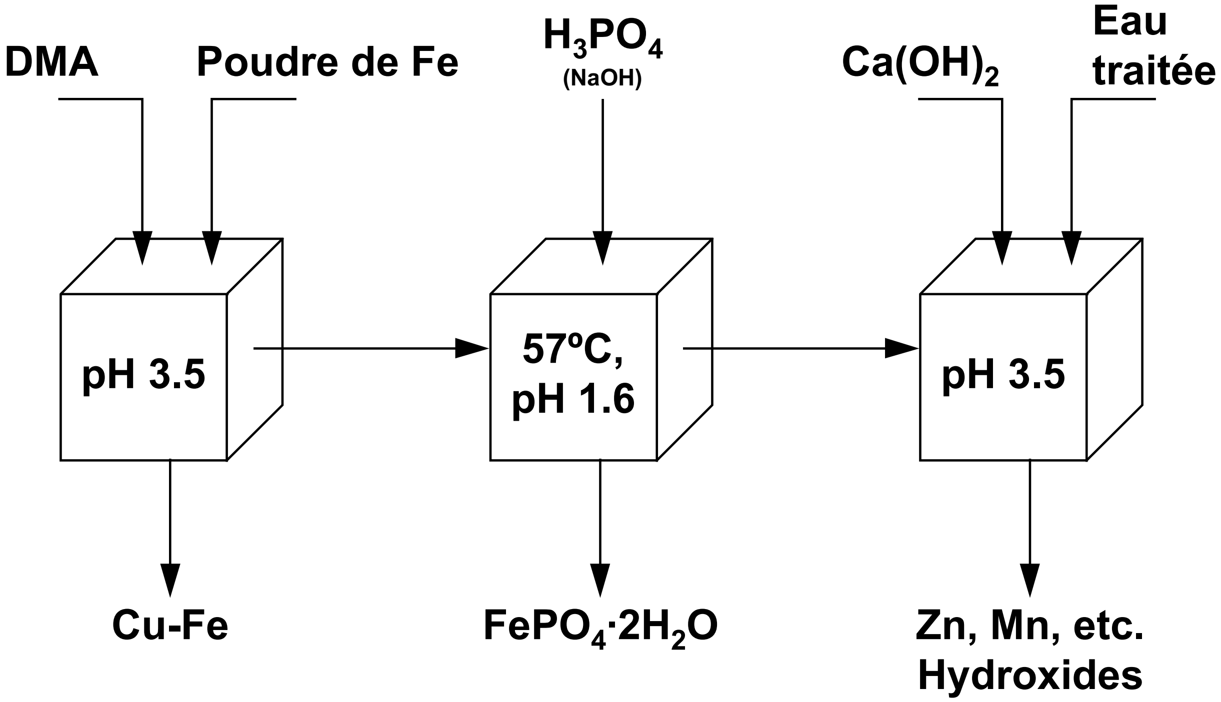


Figure 3. Schéma simplifié de traitement pour le procédé de récupération en trois étapes (solution de remplacement) évalué par le CTN

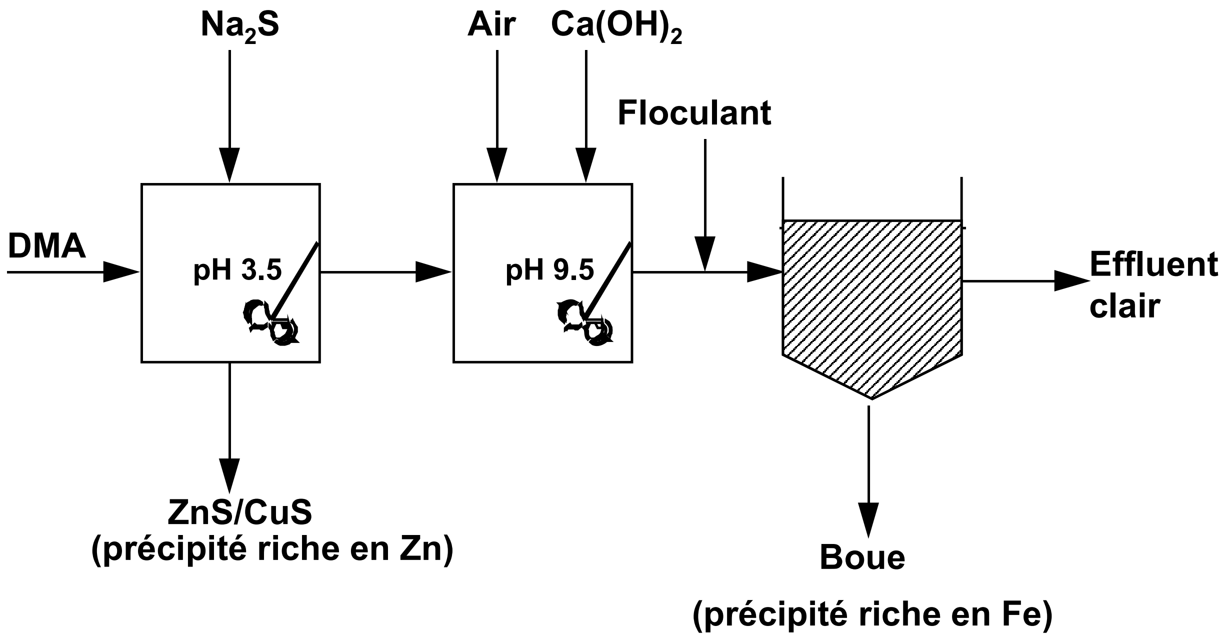


Figure 4. Schéma simplifié de traitement pour le procédé de précipitation inverse en trois étapes

RESOURCE RECOVERY FROM ACID MINE DRAINAGE

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PART I: McGill Work

RESOURCE RECOVERY FROM ACID MINE DRA1NAGE.

EXECUTIVE SUMMARY

Treatment of acid mine drainage (AMD) from les Mines Gallen has been investigated with the objective to recover zinc while maintaining a discharge effluent containing low (< 1 mg/L) toxic metal concentration and reducing amounts and toxicity of sludge for disposal.

The original material had 5.9 g/L Fe, 2.8 g/L Zn besides Cu (0.04 g/L), Mn (0.3 g/L), A1 (0.7 g/L), Mg (0.6 g/L) and Pb, As and Cd in smaller concentration.

The process was conducted in three steps:

Step 1: Removal of iron as the hydroxide. Iron was selectively precipitated by lime after oxidizing any Fe(II) to Fe(III) by hydrogen peroxide, ozone or trapzene^{TM}. A settled solids concentration of about 6-8% solids was achieved using Percol E-10. The use of dodecylamine (DDA) reduced the co-precipitation of Zn and other metals but the precipitate still failed the leachability test. (Ontario Regulatory).

Step 2: Recovery of zinc as the sulphide. After iron removal in *Step 1,* precipitation of zinc was investigated using Na_2S, NaHS and H_2S. The pH was controlled using NaOH or CaO (lime). When NaOH was used to set the pH to 3.5-3.9, recovery of zinc was only 65-75% but the product was high grade (60% Zn). Higher recovery was obtained at higher pH, but the grade was lower due to precipitation of Mn, Al and Mg.

When lime was used to set the pH recovery of zinc was higher (85-90%), apparently due to more complete dissociation of $ZnS0_4$, but the grade was lowered due to contamination by $CaS0_4$.

A promising combination was Na_2S and lime at pH 4.5; this gave more than 90% zinc recovery with a product grade of 50-55% Zn. Settling rate characteristics are superior to those found with sodium sulphide.

Step 3: Production of a final discharge effluent by lime treatment. After recovery of zinc the effluent was treated with lime to pH 9.5 to precipitate the remaining metals. The

discharge effluent achieved was similar in quality to that from conventional lime treatment (Fe, Cu. Zn, Mn, Al, < 1 mg/L).

Recommendations made include: continuous testing to evaluate *Step 1* precipitate settling and sludge characteristics with sludge recycle; evaluation of alternative sources of sulphide ion, namely calcium sulphide and sulphate reducing bacteria.

RESOURCE RECOVERY FROM ACID MINE DRAINAGE

1.0 INTRODUCTION

Acid mine drainage (AMD), generated wherever sulphide ores are processed, poses a serious environmental problem[**1**]. It contains a number of dissolved metal ion species, the most common and abundant being iron, Fe(II) or Fe(III), with Cu, Zn, Ni, Mn, As and Al in varying concentrations depending on the location.

Treatment of AMD by lime to precipitate the metals and disposal of the resulting sludge is the standard practice[**2**]. Among the objections to this process is the loss of metal. Metal recovery has the benefit of extending a natural resource and providing some revenue to offset the treatment/disposal costs while decreasing the sludge volume. The aim of the present project is to investigate methods for the treatment of AMD with the objective of recovering some of the base metals while maintaining a discharge effluent of acceptable quality. The general term adopted for this AMD treatment option is 'resource recovery'.

The work was initiated on AMD from Mattabi Mines Ltd. in 1990[**3**,**4**]. From a literature review, some form of selective metal precipitation was judged as the technology nearest to possible implementation, since it mainly required variations on current practice. Precipitation as the hydroxide, sulphide, and in the case of copper, by cementation were investigated. Two multi-step treatment options were demonstrated at the bench scale, however a simpler route was necessary to justify further evaluation, which is the basis of this report.

A common first step in the options was the need to remove iron. This was accomplished by precipitation as ferric hydroxide at about pH 3.5, with provision to oxidize any Fe(II) present. This product would still require disposal but if sufficiently clean could be classified as a non-toxic waste with less stringent (and costly) disposal restrictions. The possibility of it serving as a feed stock for production of a ferric sulphate coagulant was also considered[**5**]. Contamination of the iron hydroxide with Cu and Zn was found. By introducing dodecylamine, $C_{12}H_{25}NH_2$ (DDA), this was significantly reduced, which had the added benefit of increasing the Cu and Zn available for later recovery. DDA was tried because it is known to adsorb on iron hydroxides[**6**] and thus may act to "block" the adsorption sites for metal ions. The general term 'co-precipitation' was introduced to describe the inclusion of contaminants in the precipitate. Iron hydroxide precipitation was retained as the first step.

The Mattabi AMD contained both Cu and Zn. Their separation is desirable for subsequent metal extraction but proved difficult and led to the use of cementation. AMD from Les Mines Gallen, being essentially free of Cu relative to its high concentration of Zn, was considered a more promising candidate for process evaluation. Precipitation as the sulphide was selected because complete precipitation as the hydroxide required raising the pH to about 7 which caused contamination with Mn- and Ca-precipitates. Another factor which favours zinc sulphide is that it is the common feed material to a Zn extraction plant. The disadvantages are the cost and toxicity of the chemical sources of sulphide ion; in this regard, sulphate reducing bacteria may provide a low cost source of sulphide ion in the future[**7**].

A three step process (Figure 1) was consequently proposed which forms the basis of this report:

Step 1 - removal of iron as the hydroxide;

Step 2 - recovery of zinc as the sulphide; and

Step 3 - production of a final discharge effluent using lime treatment

2.0 EXPERIMENTAL

The majority of the experimental work was conducted at McGill with some complementary work at the Noranda Technology Centre (NTC).

2.1 Material Description

The AMD received from Les Mines Gallen was a seep water, pH < 1.8. It was diluted 5 times to correspond to more typical conditions and this is referred to as the "original" AMD. Two batches were taken for the test program and the metal content of each is given in Table 1.

Table 1. Composition of the Original AMD from Les Mines Gallen

Metal	*Fe Total*	*Fe(III)*	*Fe(II)*	*Cu*	*Zn*	*Mn*	*Al*	*Mg*	*Ca*	*Pb*	*Cd*	*As*
mg/L	5880	3295	2585	38	2760	29	704	558	1.0	0.4	9.1	10.0

2.2 Treatment Procedure for the Three Step Process

The basic experimental approach described before [**3,4**] was followed with some modifications.

Step 1: Removal of iron as the hydroxide.

Prior to-precipitation that portion of the iron in the ferrous Fe(II) state was oxidized to the Fe(III) state. (This decision was taken in part because the Fe(II) content slowly decreased with storage introducing an undesirable variation in the test samples.) Air oxidation was not successful at the low pH of the AMD. The following oxidants were used:

(i) Hydrogen peroxide, 15 mL of 30% H_2O_2 per L AMD. This was used in all experiments unless otherwise stated.

(ii) Trapzene^{TM} (20% CaO_2/80% CaO), supplied by FMC Corporation, Princeton, N.J. Details are given in Appendix 1.

(iii) Ozone, used in collaboration of Canadian Liquid Air. Details are given in Appendix 2.

After oxidation, dodecylamine (DDA) in concentrations up to 20 mg/L was added to the AMD. Following DDA addition, iron hydroxide was precipitated by adding lime until the pH reached 3.5-3.7. Experiments were conducted in a 1.5 L Agitair flotation cell with impeller speed at 800 r.p.m. The iron hydroxide was allowed to settle enhanced by adding Percol E-10 flocculant (0.05% solution) at an optimum dosage of 3.75 mg/L AMD; established by settling rate studies (see later). The precipitate was filtered to retrieve the effluent, which is Step 2 feed.

Step 2: Recovery of zinc as the sulphide.

Zinc was precipitated from the effluent of Step l using hydrogen sulphide (H_2S), sodium sulphide (Nags) and sodium hydrosulphide (Na_2HS). The pH was adjusted using principally lime (CaO) but also sodium hydroxide (NaOH); tests with NaOH were included to determine the quality of zinc sulphide product that can be formed without the simultaneous precipitation of calcium sulphate ($CaSO_4$). A calculated amount (stoichiometric to precipitate Zn) of Na_2S or NaHS was added from a 10% solution. For precipitation by H_2S the gas was bubbled through 1L of solution at a rate of 35 mL/min for 2 hours.

Treatment with Na_2S was studied at pH 3.9, 5.1 and 7.5. Treatment with H_2S was conducted at pH 3.5, 5.1 and 7.5.

The sulphide precipitate was allowed to settle and the solution clarified by filtration through 0.45 µm Millipore filter.

Additional experiments were (i) treatment with Na_2S followed by the required amount of lime to reach a pH of 4.5; and, (ii) Na_2S and lime as a mixture added to the AMD.

Step 3: Production of a final discharge effluent By lime treatment.

Each effluent from the various *Step 2* treatments was treated with lime to pH 10.

A test was conducted by raising the pH of the effluent of *Step 1* to 9.5 with lime in an attempt at combining Steps 2 and 3 to make a "two" step process.

Comparison was made with a base line test in which the pH of the original AMD was raised directly to 9.5 with lime as is done in the conventional AMD treatment process.

2.3 Settling Tests

In selected cases, the effluent and precipitate from an individual step were transferred into a 1000mL stoppered measuring cylinder. Percol E-10 flocculant was added from a 0.05% stock solution. The cylinder contents were mixed by tilting the cylinder end-over-end for 30 seconds. Readings corresponding to the settling interface were taken at 0.5, 1, 2, 5, 10, 15, 30, 45 and 60 minutes.

2.4 Leachability Tests

These were conducted on precipitates from Steps 1 and 3 according to the Ontario Regulatory Extraction Procedure[**8**]. Details are described in Appendix 4.

2.5 Analysis of DDA

A calorimetric method[**9**] was used to determine the concentration of residual DDA.

3 RESULTS

3.1 Step 1: Removal of Iron as the Hydroxide

3.1.1 Effect of Dodecylamine (DDA):

The results obtained with different quantities of DDA are shown in Table 2, which records the concentration of metal ions in the effluent (Table 2a) and the element composition of the iron hydroxide precipitates (Table 2b). The concentrations are the average of two trials with the range given for the key elements, Fe and Zn. The results show that the precipitation of iron was virtually complete at pH 3.5 (Table 2a) and that above 5-10 mg DDA/L, zinc contamination in the precipitate was reduced (Table 2b), with a corresponding increase in zinc concentration in the effluent (Table 2a) Repeat experiments at NTC confirmed this effect of DDA, although zinc levels were higher (Table 2c).

The mass balance check for iron and zinc (Table 2d) shows a satisfactory accounting with a maximum discrepancy between the measured and reconstituted feed of about 6.5%.

The DDA created a reddish-coloured froth which retained some solids: analysis showed they were mainly $CaS0_4$ with relatively little $Fe(OH)_3$ (despite the colour). This observation was pursued to determine if flotation holds any practical promise for selective recovery of precipitated calcium sulphate in this--or any other application where it is encountered: the results will be discussed elsewhere.

Table 2. Step 1- Precipitation of Ferric Hydroxide Using Lime: Effect of DDA
a) Effluent Composition

DDA	*concentration, mg/L*									
mg/L	*Fe*	*Cu*	*Zn*	*Mn*	*A1*	*Mg*	*Ca*	*Pb*	*Cd*	*As*
Original	5880	38	2840	29	704	562	1.0	0.4	9.1	10.0
0	10.3	34.3	2448	28	396	450	244	0.4	8.0	5.5
5	10.8	36.7	2752	29	426	554	248	0.4	8.1	5.5
10	12.0	37.1	2750	29	438	556	248	0.4	8.2	5.0
20	12.8	37.1	2746	29	445	556	248	0.4	8.2	5.0

Table 2b) Composition of Precipitates

DDA	% composition, dry wt. basis									
mg/L	*Fe*	*Cu*	*Zn*	*Mn*	*A1*	*Mg*	*Ca*	*Pb*	*Cd*	*As*
0	15.9	0.02	0.50	0.05	1.0	0.01	8.5	0.04	0.02	0.2
5	16.8	0.02	0.06	ND*	0.8	0.01	10.5	0.03	0.02	0.1
10	16.4	0.02	0.06	ND*	0.8	0.01	8.0	0.03	0 01	0.1
20	16.6	0.02	0.06	ND*	0.8	0.01	11.2	0.03	0.01	0.1

* not detected. Note: In all the following tables ND indicates that the metal was not detectable as concentration in solution was below the detectable limit mentioned in Appendix 3.

Table 2c) Composition of Precipitates Obtained in Repeat Experiment at NTC

DDA	*% composition, dry wt. basis*							
mg/L	*Fe*	*Cu*	*Zn*	*Mn*	*Al*	*Cd*	*Ca*	*S*
0	17.1	0.03	1.4	0.003	0.93	0.002	12.8	13.2
repeat	16.4	0.03	1.82	0.005	1.07	0.002	12.2	12.9
0	19.2	0.02	0.58	0.002	0.77	0.002	12.7	12.9
repeat	17.7	0.02	0.69	0.003	0.82	0.002	12.7	13

Table 2d) Mass Balance Calculated per AL Feed For Results in a) and b)

	Precipitate			*Mass Balance, grams (g)*							
DDA	*wt*	*Fe*	*Zn*	*Fe*				*Zn*			
mg/L	*%*	*%*	*%*	*ppt. (I)*	*eff. (II)*	*total I + II*	*feed*	*ppt (I)*	*eff. (II)*	*total I+II*	*feed*
0	35.3	15.9	0.5	5.6	0.01	5.61	5.88	0.18	2.45	2.63	2.84
5	32.9	16.8	0.06	5.52	0.01	5.53	5.88	0.02	2.75	2.77	2.84
10	33.4	16.4	0.06	5.48	0.01	5.49	5.88	0.02	2.75	2.77	2.84
20	32.8	16.6	0.06	5.45	0.01	5.46	5.88	0.02	2.75	2.77	2.84

3.1.2 Effect of Oxidants:

The results obtained using Trapzene^{TM} are shown in Table 3. The precipitation was virtually complete; however, there was a significantly greater level of zinc in the precipitate even in the presence of DDA. In this case, DDA has essentially no effect on reducing zinc contamination. Oxidation of the DDA (ultimately to carbon dioxide and water) by Trapzene^{TM} was thought to be responsible. Zinc losses to the precipitate were reduced by adding DDA after Trapzene^{TM} and before adding the additional quantity of lime required to raise the pH to 3.5 (Table 4). Details of the analysis are recorded in Appendix 1.

Table 3. Step 1 - Precipitation Using Trapzene^{TM}

Conditions: Trapzene (20%), 7 g/L
Additional $Ca(OH)_2$, 3 g/L

	effluent concentration, mg/L									
Description	*Fe*	*Cu*	*Zn*	*Mn*	*Al*	*Mg*	*Ca*	*Pb*	*Cd*	*As*
Original	5800	36	2790	28	695	552	1.0	0.4	8.8	9 0
Without	12.8	28	2242	28	312	540	142	0.2	7.1	5.8
With 10 mg DDA/L	8.5	32	2323	28	406	546	168	0.3	7.0	3.2

Table 4. Step 1 - Precipitation Using Trapzene: Effect of Adding DDA After Trapzene™

Conditions: Trapzene, 7 g/L
DDA added before $Ca(OH)_2$
Additional $Ca(OH)_2$, 3 g/L
pH when DDA was added, 2.6

	effluent concentration, mg/L									
Description	*Fe*	*Cu*	*Zn*	*Mn*	*Al*	*Mg*	*Ca*	*Pb*	*Cd*	*As*
Original	6103	37.5	2821	40.9	425	632.1	2.9	0.34	9.1	9.0
With 5 mg DDA/L	9.3	37.0	2788	40.7	206	609.3	180.3	0.4	7.7	3.6

The results of oxidation by ozone are recorded in Table 5. Complete oxidation of Fe(II) occurred with the stoichiometric amount of ozone. Details of the analysis are given in Appendix 2.

Table 5. Step 1 - Oxidation of Fe(Il) by Ozone

Conditions: 4L AMD, Concentration Fe(II) l.91g/L

Time of ozonization (min.)	*Quantity of 0^3 produced (g)*	*Stoichiometric ratio**	*Final pH*	*Concentration Fe(II) (g/L)*
0	0	0	2.1	1.73
8	1.6	0.5	2.3	1.31
13	2.4	0.8	2.2	0.34
18	3.3	1.0	2.2	0

*denotes ratio of quantity of ozone used to quantity required for complete oxidation calculated by stoichiometry

3.2 Step 2: Recovery of Zinc as the Sulphide

3.2.1 Comparison of Sulphide Reagents. pH Adjusted with NaOH:

The effluents from *step 2* show (Table 6a) that in stage 2 zinc was selectively precipitated below pH 4 relative to all components except copper. More complete precipitation was observed at higher pH, but the selectivity was reduced as manganese and aluminum were coprecipitated. Composition of the sulphide precipitates (Table 6b) showed the Zn grade was 55 to 60% at pH <4, decreasing to <50% at pH 7.4, with Al as the main contaminant.

A mass balance showed the Zn was correctly accounted for; the maximum discrepancy between calculated and measured feed was about 2% (Table 6c).

Table 6. Step 2 - Precipitation of Zinc Sulphide: Effect of Sulphide Reagents

Conditions: DDA (10 mg/L) used in Step 1
NaOH used for pH adjustment

a) Effluent Composition

		concentration, mg/L									
Description		*Fe*	*Cu*	*Zn*	*Zn*	*Al*	*Mg*	*Ca*	*Pb*	*Cd*	*As*
Original		5880	38	2840	29	704	562	1.0	0.4	9.1	10.0
Effluent After Step 1		10.8	36.7	2752	29	426	554	248	0.4	8.1	5.5
H_2S	pH 3.5	8.8	ND	965	28	329	554	246	ND	1.0	4.0
	5.1	1.0	ND	697	28	10	550	246	ND	ND	4.0
	7.4	1.0	ND	4.0	1.9	ND	535	246	ND	ND	3.5
Na_2S	pH3.9*	5.8	ND	542	28	316	556	250	ND	1.0	4.5
	5.1	2.1	ND	356	26	11	552	248	ND	ND	4.0
	7.4	1.0	ND	3.3	11	ND	517	246	ND	ND	3.5
NaHS	pH3.8*	3.9	0.1	1142	42.4	211	632	423	0.3	11	1.8
	3.8 (rpt)	2.5	1.2	1016	43.6	166	610	420	0.2	0.3	1.4

* natural pH

Table 6b). Composition of the Sulphide Precipitates

		% composition, dry wt. basis									
Description		*Fe*	*Cu*	*Zn*	*Mn*	*Al*	*Mg*	*Ca*	*Pb*	*Cd*	*As*
	pH 3.5	0.05	1.2	59.2	ND	3.0	0.05	0.05	0.1	0.1	0.1
H_2S	5.1	0.02	0.8	46.4	0.1	9.3	0.1	0.04	0.1	0.1	0.1
	7.4	0.02	0.6	49.4	0.5	7.6	0.4	0.04	0.1	0.1	0.1
	pH 3.9	0.05	1.0	60.0	ND	2.7	0.05	0.05	0.1	0.1	0.1
Na_2S	5.1	0.02	0.7	48.3	0.1	8.4	0.1	0.04	0.1	0.1	0.1
	7.4	0.02	0.6	49.2	0.3	7.5	0.5	0.04	0.1	0.1	0.1
NaHS	pH 3.8	0.3	0.6	57.6	ND	0.4	ND	0.1	0.1	0.2	0.2

Table 6c) Mass Balance Calculated per 1L Feed for Results in a) and b)

		precipitate		*mass balance on Zn, grams (g)*			
Description		*wt (g)*	*% Zn*	*ppt*	*eff*	*total*	*feed*
	pH3.5	2.97	59.2	1.758	0.965	2.723	2.752
H_2S	5.1	4.40	46.4	2.042	0.697	2.739	2.752
	7.4	5.55	49.4	2.692	0.004	2.696	2.752
	pH 3.9	3.67	60.0	$2._2O_2$	0.542	2.744	2.752
Na_2S	5.1	4.87	48.3	2.352	0.356	2.708	2.752
	7.4	5.59	49.2	2.686	0.003	2.683	2.752

3.2.2 Comparison of Lime and NaOH to Adjust pH:

Table 7shows the detailed composition of effluent (Table 7a) and precipitate (Table 7b) with lime for pH adjustment and either H_2S or Na_2S; Table 8 gives a summary comparison of the results using lime and NaOH for Zn only. The lime significantly increased recovery with Zn levels in the effluent being decreased to about 2 mg/L. In the case of H_2S the main contaminant in the precipitate was $CaSO_4$ (Ca ~ 15% at pH 5.1) but with Na_2S the Zn grade was maintained with Ca <2% (Table 7b).

Table 7. Step 2 - Precipitation of Zinc Sulphide: Use of Lime for pH Adjustment

Conditions: DDA (10 mg/L) used in Step 1
Lime used for pH adjustment a) Effluent Composition

Description		*Fe*	*Cu*	*Zn*	*Zn*	*Al*	*Mg*	*Ca*	*Pb*	*Cd*	*As*
		concentration, mg/L									
Original		5880	38	2840	29	704	562	1.0	0.4	9.1	10.0
Effluent After Step 1		10.8	36.7	2752	29	426	554	248	0.4	8.1	5.5
H_2S	pH 3.5	4.9	ND	306	28	333	554	296	0.1	ND	3.8
	5.1	ND	ND	2.0	2.0	2.5	156	353	ND	ND	1.6
	7.5	ND	ND	ND	ND	ND	30	386	ND	ND	0.9
Na_2S	pH 4.5*	2.0	0.03	1.1	20.7	56.1	478	524	ND	0.1	3.5
	4.5**	2.0	0.03	2.4	21.2	26.8	458	440	ND	0.1	2.9

* Na_2S added followed by lime
** Na_2S and lime added together

Table 7 cont.

b) Composition of the Sulphide Precipitates

Description		*Fe*	*Cu*	*Zn*	*Mn*	*Al*	*Mg*	*Ca*	*Pb*	*Cd*	*As*
		% composition, dry wt. basis									
H_2S	pH 3.5	0.3	0.7	43.8	ND	0.3	ND	8.6	0.03	0.3	0.2
	5.1	0.4	0.4	21.1	0.2	1.2	3.1	14.7	ND	0.05	0.2
	7.5	0.2	0.2	15.1	0.2	0.7	2.9	19.6	ND	0.02	0.2
Na_2S	pH 4.5	0.2	0.2	56.4	0.16	4.6	0.4	1.2	0.05	0.1	0.3
	4.5	4.5	0.2	54.8	0.06	5.2	0.1	1.6	0.05	1.0	0.3

Table 8. ***Step 2*** **- Comparison of Lime and NaOH (Data from Table 6 - Table 7)**

Description		*Zn in products*			
		effluent (mg/L)		*precipitate (%)*	
		NaOH	*lime*	*NaOH*	*lime*
	pH 3.5	965	306	59.2	43.8
H_2S	5.1	697	2	46.4	21.1
	5.1	356	-	48.3	-
Na_2S	4.5	-	1.1	-	56.4
	4.5	-	2.4	-	54.8

3.2.3 Effect of DDA Added in Step I:

Table 9 shows the Zn grade in the sulphide precipitate obtained with and without DDA in *Step 1* for (a) Na_2S at natural pH (conducted at NTC), and (b) H_2S and lime. The presence of DDA had no effect.

Table 9. **Step 2 - Effect of DDA Added in Step 1 on Sulphide Precipitate Composition.**

a) **Na_2S at natural pH**

DDA mg/L	*% Zn 1*	*2**
0.0	58.5	56.7
7.5	56.0	55.5

* repeat of 1

Table 9b) **H_2S and lime**

DDA mg/L	*% Zn* *pH 3.5*	*5.1*	*7.4*
0	43.8	21.1	15.1
10	42.5	20.5	14.87

3.2.4 Kinetics of Sulphide Precipitation:

Table 6a) showed that Na_2S at natural pH (3.9) left > 500 mg Zn/L in solution (representing a loss of about 20%).. Insufficient time allowed for reaction was considered. Table 10 shows, however, that zinc concentration in the effluent solution did not diminish with time up to 2 hrs.

Table 10. *Step 2* - Zn concentration in Effluent as a Function of Time.

Time	*Zn concentration, mg/L*			
(min)	*no DDA*	*no DDA (repeat)*	*7.5 mg DDA/L*	*7.5 mg DDA/L (repeat)*
15	-	891	995	744
30	787	691	1010	800
60	869	803	990	645
120	805	731	1010	799

3.3 *Step 3*: Production of a Final Effluent Discharge by Lime Treatment

3.3.1 Final Effluent for Various Step 2 Treatments:

The final discharge effluents obtained after treating the effluents from *Step 2* in general were low in heavy metals (Table 11) with about 1 mg Zn/L and 0.5 mg As/L as the principal toxic contaminants.

Table 11. Step 3 - Composition of Final Effluent for Various Step 2 Treatments

Conditions: NaOH used for pH adjustment in *Step 2*

Step 2	*pH*	*Fe*	*Cu*	*Zn*	*Mn*	*Al*	*Mg*	*Ca*	*Pb*	*Cd*	*As*
H_2S	3.5	ND	0.1	1.1	0.2	ND	119	84	ND	ND	0.5
	5.1	ND	0.1	0.9	0.1	ND	115	101	ND	ND	0.4
	7.4	ND	ND	0.7	0.1	ND	108	128	ND	ND	0.4
Na_2S	3.9	ND	0.1	0.9	0.2	ND	125	92	ND	ND	0.5
	5.1	ND	0.1	0.6	0.1	ND	120	109	ND	ND	0.4
	7.4	ND	0.1	0.5	0.1	ND	120	135	ND	ND	0.4

3.3.2 Two-Step Option:

Table 12 shows the concentration of the effluent obtained by raising the pH to 9.5 (in an attempt to combine *Steps 2* and *3*). The effluent contained only Ca and Mg in significant concentrations. The precipitate is mainly ZnS but it contains about 8% Al.

Table 12. Step 3 - Combination of Steps 2 and 3: Precipitation with NaOH to pH 9.5 of Effluent from Step 1

a) Effluent Composition

Description	*Fe*	*Cu*	*Zn*	*Mn*	*Al*	*Mg*	*Ca*	*Pb*	*Cd*	*As*
Before (mg/L)	20.9	39.2	2324	26.4	450	684	112	0.3	5	8.4
After (mg/L)	0.2	ND	0.1	0.4	ND	276	72	ND	0.1	0.05

Table 12b) Composition of the Precipitate

Metal	*Fe*	*Cu*	*Zn*	*Mn*	*Al*	*Mg*	*Ca*
Percent	0.02	0.5	45.5	0.5	8	1.5	0.1

3.3.3 Base Line Test:

The effluent from this simulation of the conventional lime treatment of AMD showed similar metal concentrations to those in the effluent of the three step process (Table 13); Zn levels were slightly better but As remained high.

Table 13. Base Line Test: Straight Lime Treatment of Original AMD to pH 9.5

Description	*Fe*	*Cu*	*Zn*	*Mn*	*Al*	*Mg*	*Ca*	*Pb*	*Cd*	*As*
Original (mg/L)	6020	38	2820	41	420	634	3.0	0.3	9.2	9.0
Effluent (mg/L)	0.1	ND	ND	ND	ND	3.2	423	ND	0.02	0.3

3.4 Leachability Tests

The results of leachability tests conducted on sludges from *step 1* and *step 3* are shown respectively in Table 14 parts a) and b).

The *step 1* (iron hydroxide) product failed the test with regard to Zn even after 10 washings in tap water. The *step 3* product passed the test only when *step 2* was conducted at pH 7.5.

Table 14. Leachability Tests

a) *Step 1* Precipitates

Conditions: 1 $Fe(OH)_3$ sludge, vacuum filtered
2 $Fe(OH)_3$ sludge, washed 4 times, 200 mL per 10 g each time
3 $Fe(OH)_3$ sludge, washed 10 times

Condition.	*solution compostition*, mg/L*									
	Fe	*Cu*	*Zn*	*Mn*	*Al*	*Mg*	*Ca*	*Pb*	*Cd*	*As*
1	15.6	8.5	443.0	4.0	102.0	106.0	144.0	ND	0.7	5.0
2	1.0	0.9	38.0	0.5	5.5	28.0	56.0	ND	0.2	2.5
3	0.2	0.1	8.6	ND	1.0	9.8	58.0	ND	ND	1.0

*Note: Regulatory limits for Cu and Zn are 5.0 mg/L; that for As, 2.5 mg/; for total metals (including As, Cd, Cr, Cu, Hg, Ni, Pb, Zn), 5.0 mg/L. (Gazette Officielle du Quebec, June 26, 1985, volume 117, no. 28).

Table 14 (cont).

b) *Step 3* Precipitates for Various Step 2 Treatments

Conditions: 1 H_2S, pH 3.5
2 H_2S, pH 5.1
3 H_2S, pH 7.5
pH control using lime

	solution composition, mg/L									
Condition.	*Fe*	*Cu*	*Zn*	*Mn*	*Al*	*Mg*	*Ca*	*Pb*	*Cd*	*As*
1	0.5	0.1	936	42	25	650	256	ND	1.5	2.0
2	ND	ND	58	38	14	420	386	ND	0.1	1.0
3	ND	ND	2.0	4.0	2.0	164	396	ND	ND	ND

3.5 Analysis of Residual Dodecylamine

Concentrations of DDA measured in various effluents are recorded in Table 15; they were consistently below 0.5 mg/L in the final effluent.

Table 15. Concentration of Residual DDA (mg/L) in Various Effluents.

Conditions: Initial DDA concentration 10 mg/L

Step 1	*Step 3 (Step 2 at pH 3.5)*	*Step 3 (Step 2 at pH 5.1)*	*Step 3 (Step 2 at pH 7.5)*
0.52	0.47	0.04	0.01

3.6 Settling Tests

3.6.1 Step 1:

Figure 5 shows the settling data for the *Step 1* precipitate (iron hydroxide) in the absence of Percol. The most obvious difference was the presence of froth with DDA which, by retaining water, caused the marked drop in starting height (time = 0) evident in the Figure. There is some evidence of a reduced settling rate with DDA which may be related to the small bubbles observed, which may have attached to particles and increased their buoyancy.

Figure 6 shows the effect of Percol dosage (in the absence of DDA) on the settling rate of the iron hydroxide precipitate. Over the range tested, 3.75mg Percol/L of solution gave (marginally) the best performance and was the dosage used in most cases.

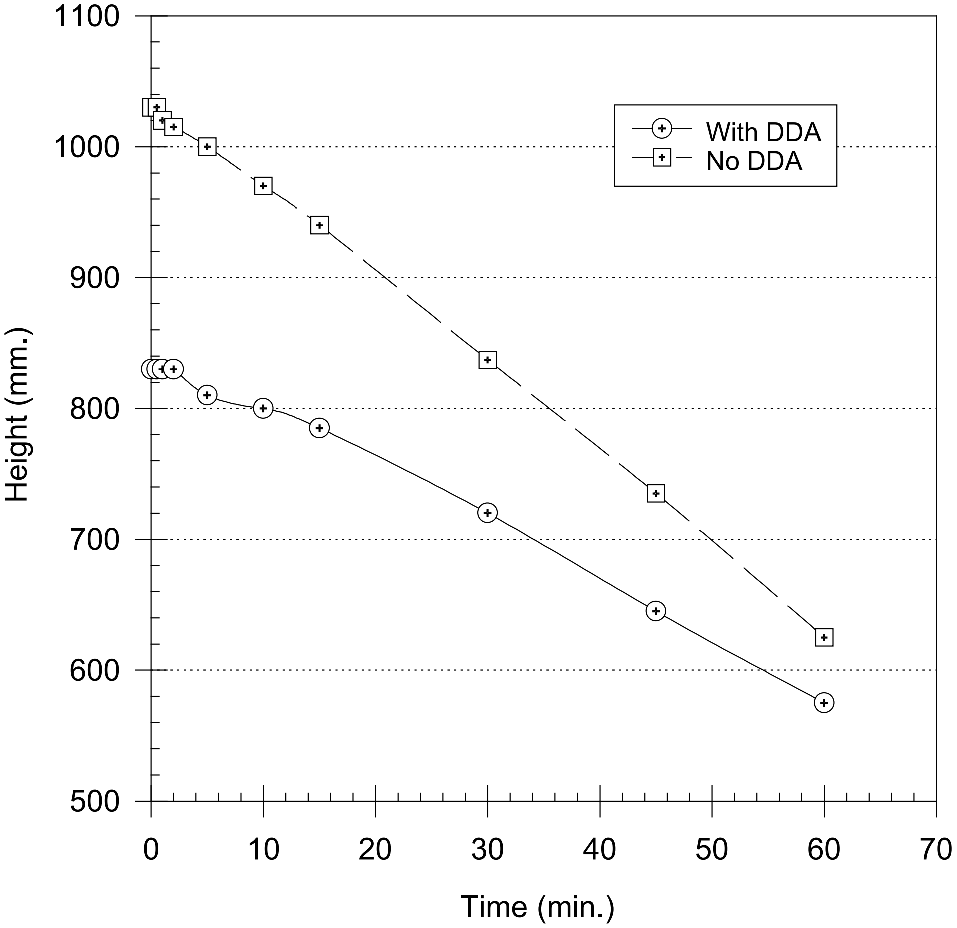

Figure 5. **Settling rate of ferric hydroxide: Effect of dodecylamine. (no Percol)**

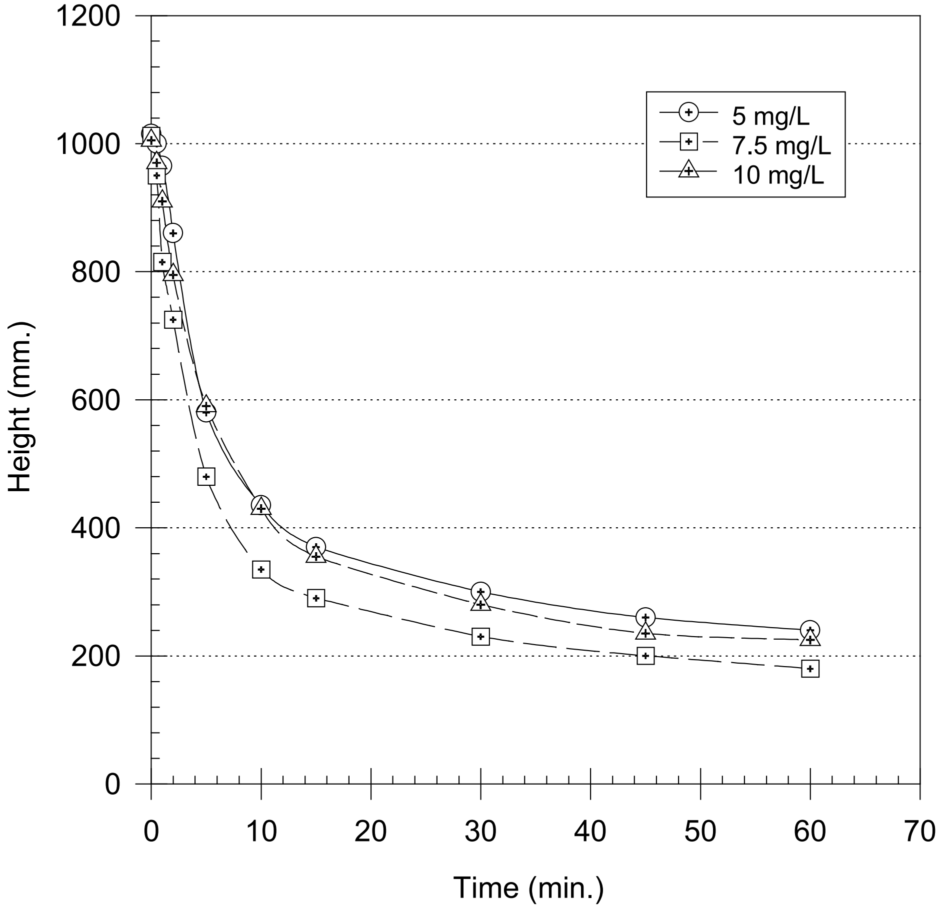

Figure 6. **Settling rate of ferric hydroxide: Effect of Percol concentration**

Some initial settling rates, final settled volumes and solids concentrations are recorded in Table 16. Typically, the settled material was about 7-8% solids (in the presence of Percol) and retained about 15-20% of the solution (effluent).

Table 16. Settling Data

a) *Step 1*

		final settled solids	
Description	*initial settling rate mm/min.*	*volume mL*	*% solids by wt (approx.)*
no DDA	2.47	630	3
10mg DDA/L	1.54	580	1.56
2.5mg Percol/L	4.76	238	6.7
3.75mg Percol/L	5.08	182	8.8
5.0mg Percol/L	4.75	230	6.7

Table 16 (cont.)

b) *Step 2*

			final settled solids	
Description		*initial settling rate mm/min.*	*volume, mL*	*% solids by wt (approx.)*
H_2S	pH 5.2	3.21	150	0.9
Na_2S	pH 3.8	3.03	170	0.9
	5.1	0.2	475	0.6
	7.5	0.32	465	0.6

3.6.2 Step 2:

Figure 7 shows settling rates of sulphide precipitates produced by treatment with Na_2S. The precipitate formed at pH 3.9 showed the fastest settling.

Figure 8 shows settling rate of the precipitate produced by H_2S at pH 5.2. The precipitates formed at pH 3.5 and 7.5 did not give a clear interface and no settling data could be collected. The absence of interface at pH 7.5 could be due to dispersion at the higher pH, but the reason for the absence of interface at pH 3.5 is not clear at present.

3.6.3 Step 3:

Figure 9 and Figure 10 show the settling rates of the hydroxide precipitates formed by lime treatment of the effluents from *Step 2*. Figure 10 shows an interesting phenomenon: hydrogen sulphide treated material at pH 5.2 flocculated and floated to the surface instead of settling. The 'buoyancy rate' was plotted since a clear interface, starting at the bottom of the cylinder and moving up, was clearly visible. The solution was noticeably frothy when treated with H_2S which is probably related to this 'buoyancy' phenomenon. The reason for this phenomenon is not clear. One possibility is inadvertent contamination caused by DDA from *step 1*.

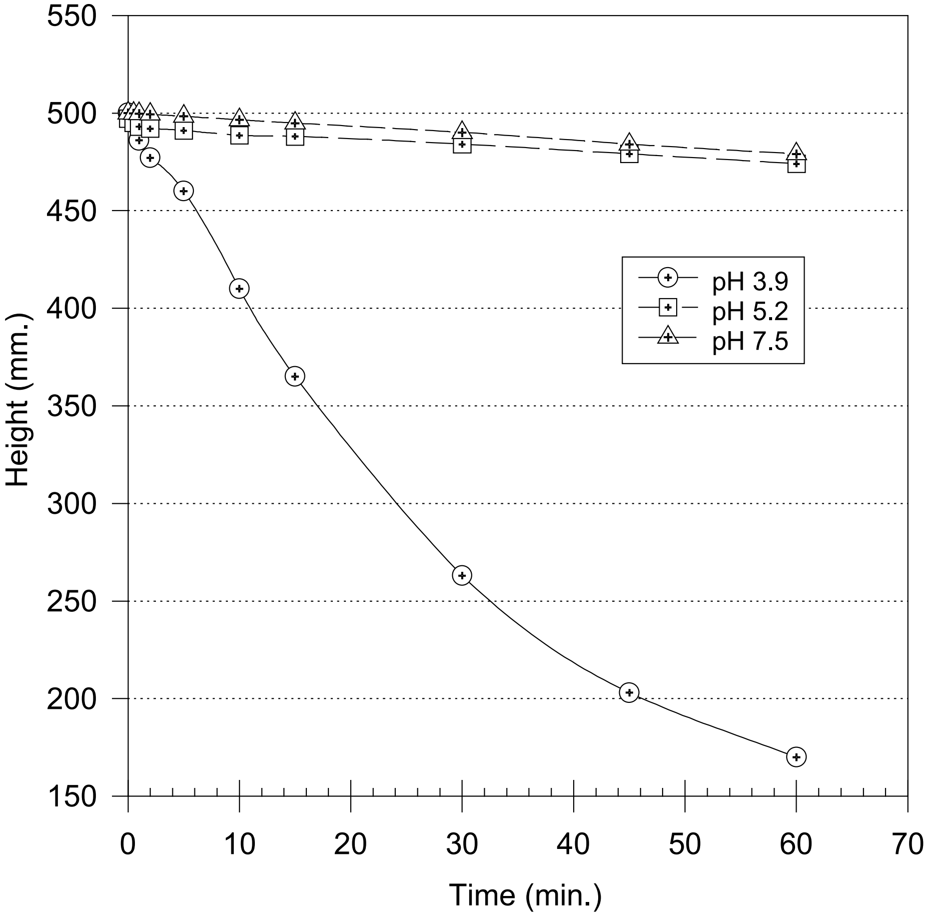

Figure 7. Settling rate of sulphides precipitated by Na_2S: Effect of pH.

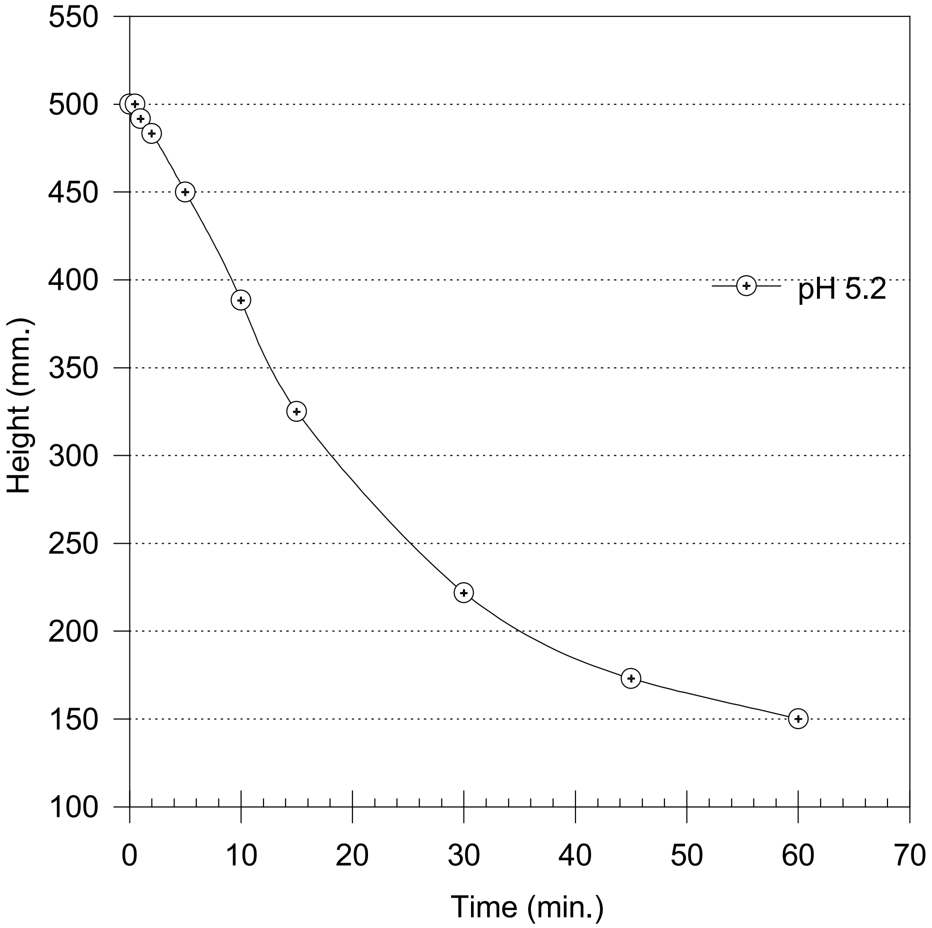

Figure 8. **Settling rate of sulphides precipitated by H_2S: Effect of pH.**

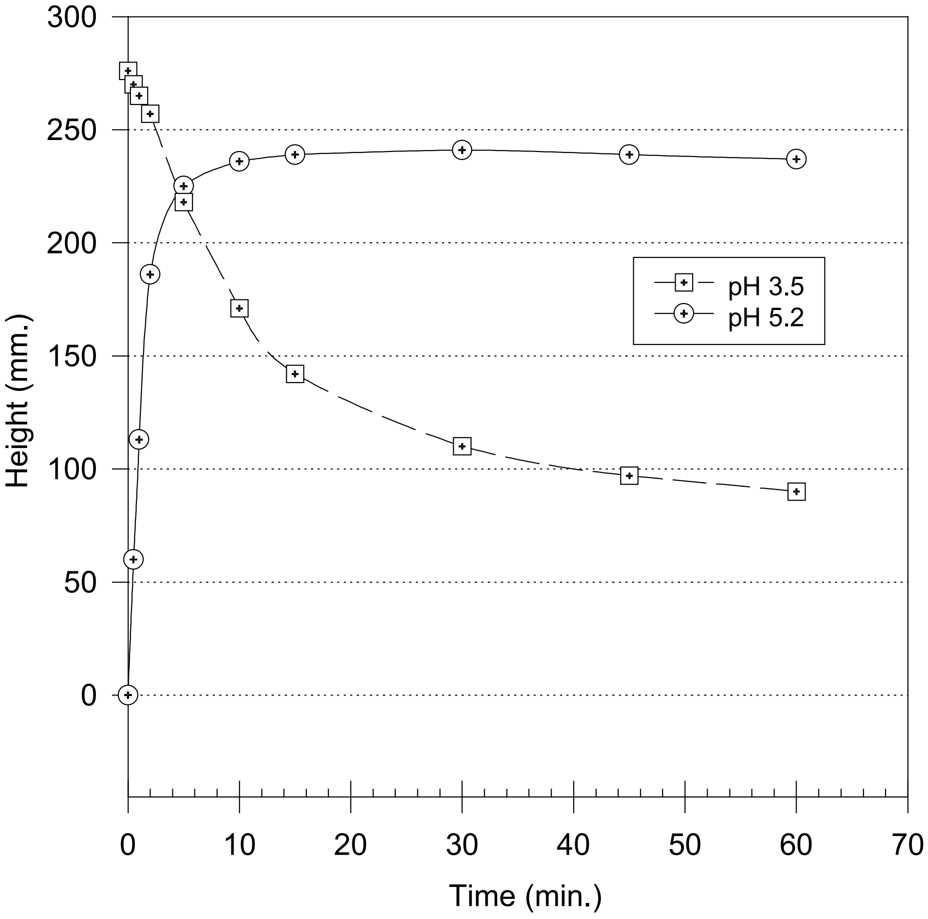

Figure 9. Settling rate of ***Step 3***: Metal hydroxides formed by lime treatment of effluent from ***Step 2*** (where Na_2S was used for precipitation).

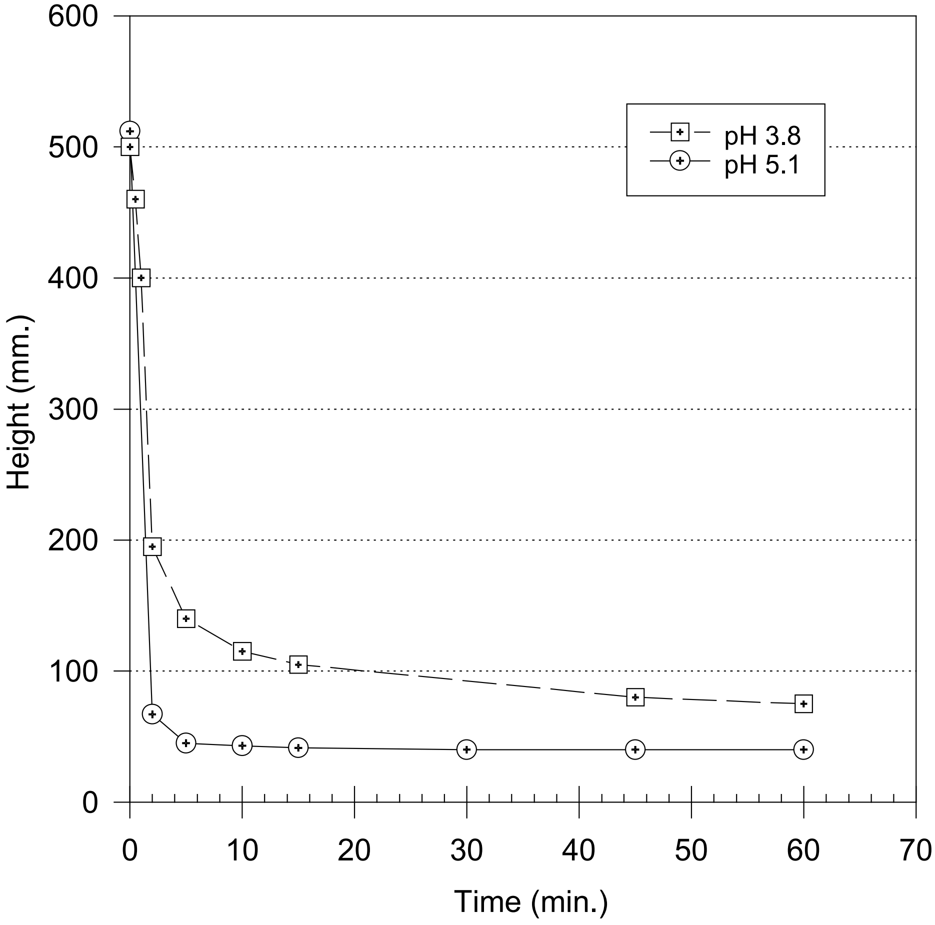

Figure 10. **Settling rate of *Step 3* metal hydroxides formed by lime treatment of effluent from *Step 2* (where H_2S was used for precipitation).**

3.7 Reagent Consumption

The reagent consumption is summarised in Table 17.

Table 17. Summary of Reagent Consumption

Step 1		*Step 2*		*Step 3*	
Reagent	*Consumption*	*Reagent*	*Consumption*	*Reagent*	*Consumption*
CaO	9.0 g/L	Na_2S	12 g/L	CaO	1.1 g/L
H_2O_2	15 mL 30%/L	H_2S	6000 cm^3/L		
Ozone	0.9 g/L	NaOH	1.2 g/L		
DDA	10.0 mg/L	CaO	2.0 g/L		

4.0 DISCUSSION

4.1 *Step 1.*

The two main chemical parameters in *Step 1* are the possible use of dodecylamine (DDA) and oxidation of Fe(II).

4.1.1 Effect of DDA

The results (Table 2) showed that the addition of more than 5 mg DDA/L AMD prior to the precipitation of iron hydroxide reduced co-precipitation of zinc (and copper). Table 2a) showed the effluent concentration increased by about 13% (from 2430 to 2760 mg Zn/L) when DDA was present, a significant increase given the replicate range in these experiments was about 4% (e.g. 2432 ± 16 mg Zn/L); this effect was reflected in the precipitate assay, the Zn grade decreasing from 0.52% to 0.06%. Testwork at NTC showed at least 7.5 mg/L was required which was apparently related to a higher iron concentration in that study (6917 vs. 5880 mg/L). The concentration of DDA required will depend on the iron levels and the ratio of DDA to iron may be the relevant parameter. Most testwork employed 10 mg DDA/L which was adequate for around 6000 mg Fe/L. Exploring the effect of the DDA/Fe ratio on co-precipitation was deemed to be outside the present scope of the work.

The mechanism of the action of DDA is not understood at present. Since DDA is known to adsorb on iron oxide/hydroxide minerals (and is used as a collector for these minerals) [**6**] it is suggested that by a similar mechanism it is adsorbed at the iron hydroxide precipitate surface and the adsorbed film reduces the co-precipitation of metals such as zinc. The concentration of the residual DDA (Table 15) showed that it was almost completely consumed. Oxidation of the DDA is not considered to be likely. In the time lapse between the start of the experiment and the spectrophotometric measurement, 3 to 4 hours, no measurable change in concentration was observed with DDA solution an water. Adsorption of DDA by ferric hydroxide is considered to be the likely cause of the concentration drop observed. Systematic basic studies are required to obtain a clear understanding; initial trials to measure the surface charge were not successful probably because of the high ionic strength of the AMD solutions.

The DDA did reduce co-precipitation, but the iron precipitate still failed the leachability test (although some concern was raised that the use of a mechanical shaker may have prejudiced these results). The potential benefit of additional Zn for recovery in *Step 2* only becomes significant if the iron precipitate is filtered, since about 15-20% of the effluent (and therefore 15-20% of the Zn) was retained in the settled sludge (Table 16) and this did not change materially with DDA being used. Also the froth produced was a disadvantage. Overall, the use of DDA, while its previously detected action [**4**] was confirmed, does not appear to yield a sufficient advantage to recommend its continued use.

4.1.2 Effect of Oxidants:

In the present flowsheet it is necessary to oxidize any Fe(II) present to the Fe(III) oxidation state in order to precipitate all the iron selectively at pH 3.5. If a significant quantity of iron occurs as Fe(II) and is not oxidized it will precipitate at a higher pH. The solubility product of FeS is $1.59*10^{-9}$ and of ZnS $2.93*10^{-25}$ [10]. In principle, therefore, at a controlled S^{2-} level FeS should not precipitate in *Step 2* along with ZnS and could be left unoxidized. This is worth studying as it would simplify *Step 1*. At the higher pH of *Step 2* there is the possibility of gradual oxidation of the residual Fe(II) to Fe(III) by atmospheric oxygen which would result in the precipitation of iron hydroxide thus contaminating the zinc sulphide precipitate.

4.1.3 Choice of Oxidant:

Hydrogen peroxide, the principal oxidant used in this work, is a commonly used oxidant. The quantity required in practice, however, frequently exceeds the stoichiometric value by up to 50% due to side reactions. In contrast, ozone, a stronger oxidant than H_2O_2, completely oxidized Fe(II) to Fe(III) with the stoichiometric amount.

Trapzene^{TM} performs the function of oxidation of Fe(II) and (partial) precipitation of the resultant Fe(III). Oxidation was complete. The use of Trapzene^{TM} had the disadvantage of reducing the effectiveness of DDA which was attributed to oxidation of the amine.

Of the three oxidants, ozone seems worthy of further evaluation as oxidation is achieved by the stoichiometric amount. In the natural environment, iron occurs in variable Fe(II) to Fe(III) ratios, perhaps reflecting seasonal effects. It would be worthwhile conducting field work to establish the factors controlling the natural oxidation and attempting to promote them to avoid addition of chemicals.

4.1.4 Composition of the Iron Hydroxide Precipitate:

A chemical analysis conducted on the iron hydroxide after removal of most of the $CaS0_4$ (by flotation, taking advantage of the selective flotation of calcium sulphate noted earlier) showed a yield of about 36% Fe. This is lower than the value of 52% Fe for stoichiometric $Fe(OH)_3$. It is believed that a sulphate group is included in the structure at these pH levels.

4.2 *Step 2*

4.2.1 Effect of Sulphide Reagent and pH:

The results obtained with Na_2S, H_2S and NaHS (Table 6 - Table 8) show the following features:

(i) When pH is set by NaOH at 3.5-3.9 effluent concentration was about 1000 mg Zn/L with H_2S and NaHS but about 500 mg Zn/L with Na_2S. The higher value with the former two is explained by a lower concentration of S^{2-} ions (and a proportionately higher concentration of HAS^- ions) than is the case with Na_2S.

(ii) The recovery of zinc is increased at higher pH as more of the sulphide is dissociated to S^{2-}. The grade of the product, however, is lowered as other metals (notably Al) partially precipitate with the zinc sulphide.

(iii) The recovery of zinc at pH 3.5 with H_2S is enhanced using lime rather than NaOH to set the pH. In addition to pH control, the calcium in the lime precipitates the sulphate ion in solution. This facilitates the dissociation of $ZnSO_4$ to free additional Zn^{2+} ions which are then precipitated [**11**]. The zinc sulphide product, however, contains about 8-9% Ca (present as $CaS0_4$), but remains free of other metals which confirms the high degree of selectivity in H_2S precipitation.

(iv) A possible route is to use Na_2S and lime. Experiments completed thus far setting the pH at 4.5 have shown this to be promising giving essentially 100% Zn recovery from the effluent of *Step 1* with high selectivity and a product much lower in Ca than that obtained with H_2S and lime. (The higher Ca levels with H_2S are because more lime is required to balance the acidity.) Various Na_2S - lime combinations should be evaluated. An added advantage of mixing lime with sodium sulphide before adding to AMD would be a reduced potential for hydrogen sulphide gas evolution. The results with Na_2S alone showed about a third of the zinc was unreacted, thus leaving residual Na_2S which at pH 3.5-4.0 would cause the formation of H_2S. The use of calcium sulphide as a precipitant for zinc has been described [**12**,**13**] and should be further explored.

4.2.2 Kinetics of Sulphide Precipitation:

While a detailed kinetic study was not undertaken, the results with sodium sulphide showed that the precipitation of zinc occurs within the first 15 minutes; there is no significant improvement even after 2 hours of reaction time. This is not surprising since zinc sulphide precipitation is essentially an ionic reaction.

4.3 *Step 3*

4.3.1 Comparison with Base Line Test:

The effluent composition after *Step 3* showed heavy metal ion concentration ≤ 1.0 mg/L. The effluent obtained in the base line test had a better quality with regard to Zn but, interestingly, a similar concentration of As.

4.3.2 The Two Step Option:

The results obtained by raising the pH of the effluent from *Step 1* to 9.5 with NaOH showed almost complete removal of zinc. The grade of the precipitate was comparable to that in *Step 2* with H_2S and Na_2S at pH 5.1. Effluent quality was between that from the three step process and the base line test for heavy metals but apparently better than either for As.

4.4 Leachability Tests:

The results of leachability tests showed that the iron hydroxide sludge failed the test even after filtering and repeated washing. The precipitates from *Step 3* did not pass the test unless zinc was fully recovered in *Step 2*.

5.0 Conclusions

A three step process was demonstrated at the laboratory scale showing zinc can be selectively recovered from Les Mines Gallen AMD with a final discharge effluent quality similar to that from conventional lime treatment.

Some specific conclusions on each step are:

Step 1.

- The iron present as Fe(III) in AMD was almost completely removed as iron hydroxide at pH 3.5-3.6
- Ozone was the most effective oxidant (Fe(II) to Fe(III))
- The use of dodecylamine before precipitation reduced co-precipitation of Zn.
- The settling rate of precipitates was enhanced by Percol E-10 and a sludge of about 6-8% solids by weight was obtained.
- The sludge failed the leachability test.

Step 2.

- The zinc can be selectively recovered by precipitating as a sulphide using sodium sulphide, hydrogen sulphide or sodium hydrosulphide.
- Maximum selectivity was obtained pH at 3.5-4.0 giving grades approaching 60% Zn but leaving about one-third of the Zn in the effluent, probably as undissociated $ZnSO_4$.
- A promising combination was Na_2S and lime to pH 4.5 which recovered > 90% Zn from effluent of Step 1 with a grade 50-55% Zn.

Step 3.

- Treatment with lime to pH 9.5 precipitated the remaining metals giving a final discharge effluent ≤ 1.0 mg/L in heavy metals.
- Effluent quality was similar to that from conventional lime treatment.

6.0 Recommendations

6.1 Continuous Testing to evaluate:

- density of settled sludge and the effect of sludge recycle, especially on *Step 1* precipitates: there is a reason to suspect that given the higher ionic conditions under which iron hydroxide is precipitated here, compared to those conditions prevailing in conventional lime treatment, that faster settling and higher sludge densities may be attainable due to the coagulating effect of high ionic strength solutions [**5**].
- Sludge filterability, especially from *Step 1* to determine potential zinc recovery from the starting AMD (as opposed to from the effluent of *Step 1* as determined here.

6.2 Evaluation of Alternative Sources of Sulphide Ion (Bench-Scale)

- Calcium sulphide: this reagent introduces the calcium necessary to dissociate residual zinc sulphate at pH’s 4 to 5 and increase zinc recovery.
- sulphate reducing bacteria: potentially the cheapest (and most environmentally friendly) source. (Work is now known to be ongoing on this area [**14**].)

6.3 Further Bench-Scale Studies on:

- impact of leaving Fe(II) unoxidized in *Step 1*.

- composition, structure, particle size distribution, morphology and stability (under simulated disposal conditions) of the precipitates.

Appendix 1. Treatment of Acid Mine Drainage with Trapzene™

Introduction:

Trapzene™ is a product of FMC Corporation, Princeton, New Jersey. It is essentially a mixture of calcium peroxide (CaO_2) and hydroxide ($Ca(OH)_2$). The peroxide oxidizes the Fe(II) ions of AMD while the hydroxide precipitates the metal ions. A product containing 20% CaO_2 was used for these studies.

Theoretical Considerations:

The oxidation of Fe(II) by CaO_2 is represented by the following equation:

$2\ Fe^{2+} + CaO_2 + H_2O\text{-}\ 2\ Fe^{3+} + CaO + 2OH^-$

Thus, 111.7 g Fe(II) theoretically requires 72 g CaO_2 for complete oxidation. As the AMD had 2.2g Fe(II) per litre it requires 1.4 g CaO_2 for oxidation or 7 g of 20% Trapzene.

Experimental:

Five litres of AMD was mixed with 35 g Trapzene in a flotation cell and mixed thoroughly. Further quantities of Ca(OH)2 were added until the pH was 3.5. The precipitated ferric hydroxide was flocculated with Percol and the effluent analysed.

In another experiment the AMD was mixed with 10 mg/L dodecylamine, then mixed with Trapzene as before.

Results and Discussion:

Analysis of the effluent is shown in Table 1. The precipitation of iron is virtually complete, which suggests that Trapzene has oxidized all Fe(II). However, there is a significantly greater loss of zinc even in presence of amine (DDA). One possible reason is that DDA is partially oxidized (amine converting to a nitro group) by the peroxide. An alternative procedure (which will be attempted) would be to add DDA after mixing Trapzene, but before adding the additional quantity of $Ca(OH)_2$ required to raise the pH to 3.5.

Appendix 2. Oxidation of Ferrous Ions in Acid Mine Drainage by Ozone

Introduction:

This set of measurements was conducted in order to explore the use of ozone as an oxidant to oxidize ferrous ions Fe(II) in acid mine drainage (AMD) prior to the precipitation and separation of all iron as ferric hydroxide at pH 3.5-3.6. As ozone is known to be one of the strongest oxidizing agents, second only to fluorine among common oxidants on the oxidation potential scale [1], it was thought that it could be well-suited to oxidize the ferrous ions in AMD. (The use of ozone as an industrial oxidant has been described [2]).

Ozone is generated in situ by an ozonator. Such an equipment (Griffin GTC model) has been installed at Université Laval, Dept. Mines et Metallurgie by Air Liquide. Access to this equipment was made available by Wavier Sara of Air Liquide, who conducted the ozonization run at Laval with help from Prof. H. Soto and Fabiola Nava (graduate student). The samples were analysed at McGill by one of us (S.R.R.).

Theoretical Considerations and Stoichiometry:

The following stoichiometric reactions were considered.

$$O_3 \rightarrow O_2 + O$$

$$O + 2e + H_2O \rightarrow 2OH^-$$

$$\frac{\left(Fe^{2+} \rightarrow Fe^{3+} + e\right)}{O_3 + 2Fe^{2+} + H_2O \rightarrow 2Fe^{3+} + 2OH^- + O_2}$$

In acid medium the OH- will be neutralized. As the AMD sample was strongly acidic (pH <2) the reaction would be

$$O_3 + 2\,Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + H_2 0 + O_2$$

The oxidation potential of ozone in acidic medium is 2.08 volt [1].

According to this stoichiometry 1 g mole ozone will oxidize 2 g atoms Fe(II); 48 g ozone will oxidize 111.7 g Fe(II).

Experimental:

AMD sample from les Mines Gallen (diluted 5 times [3]) was used for these studies. It had 1.91 g/litre Fe(II).

Four litres of the sample was pumped into a vertical column (diameter 5.5 cm) connected to the ozonator which was hooked to an oxygen cylinder. The ozonator was switched on with the oxygen flowing and set to produce ozone at a specific rate. The ozone bubbled through the AMD in the column. The oxygen formed (by the reduction of ozone) and the excess ozone were released through an exit port at the top of the column.

Samples were drawn from the column at specific time intervals, each corresponding to a specific quantity of ozone calculated on the basis of the rate of production of ozone. Each sample was analysed by standard dichromate titration to determine the concentration of Fe(II).

Results:

The concentrations of Fe(II) in the AMD samples treated with various quantities of ozone are recorded in Table A.2.1. (part of which is in Table 5 in the text).

During the experimental runs, after the stoichiometric ratio of 1.0 was reached excess ozone was observed (tested by KI) in the exit gas.

Discussion:

The results of these measurements clearly show ozone completely oxidizes the Fe(II) present in the AMD. The quantity required for complete oxidation follows stoichiometry of the reaction. The process is fast and clean (as the product of the ozone reduction is oxygen). Unlike hydrogen peroxide which has to be added in calculated amount as the excess causes problems in $Fe(OH)_3$ precipitation and sulphide precipitation any excess of ozone readily decomposes in the solution and is of no consequence.

In order to determine the feasibility of this method as a continuous operation further studies should be conducted with AMDs from different sources and on a pilot (continuous) scale.

Table A.2.1. Oxidation of Fe(II) by Ozone

Quantity of AMD taken 4 L. Concentration of Fe(II) l.91g/L. Total quantity of Fe(II) in the bath

Time of ozonization min-sec.	*Quantity of 0_3 produced (g)*	*Stoichiometric ratio**	*Final pH*	*Concentration of Fe(II) g/L*
0	0	0	2.1	1.73
8 - 33	1.6	O.5	2.3	1.31
12 - 54	2.4	0.8	2.2	0.34
18 - 22	3.3	1.0	2.2	0
27 - 08	5.0	1.5	2.1	0
36 - 08	6.6	2.1	2.1	0
55 - 06	10.0	3.0	2.1	0

Note * denotes the ratio of the quantity of ozone used to the quantity required for complete oxidation calculated by stoichiometry.

Acknowledgements:

The authors acknowledge with appreciation the interest and initiative of Javier Sara of Air Liquide for conducting this experimental run and travel to Quebec City. Permission of Air Liquide to conduct this study is also acknowledged. We also thank Prof. H. Soto and Fabiola Nava for their help and the hospitality extended to S.R.R. at Universite Laval.

References:

1. Handbook of Chemistry and Physics. 73rd Edition (1992-1993). David R. Lide, Editor-in-Chief. CRC Press. page 8-24.
2. *James W. Patterson*: Industrial Wastewater Treatment Technology, Second Edition. Butterworth Publishers (1985).
3. *S.R. Rao, M. Leroux, and J.A. Finch*: Report to Noranda Technology Centre, May 25, 1992.

Appendix 3. Determination of Metal Ion Concentrations

Atomic absorption spectroscopic technique was used for the determination of metal ion concentration instrument was model 357 of National Instruments: Standard solutions of definite concentrations of specific metal ions were prepared from the Fischer standard stock solutions (1000 mg/L) for each metal ions. The concentration range and the lower detection limit for the various metal ions are shown in the following table.

Metal Ion	*Concentration range of the standards (mg/L)*	*Detection limit (mg/L)*
Fe	2 - 6	0.5
Cu	2 - 6	0.5
Zn	0.5-2.0	0.25
Mn	1 - 3	0.25
Cd	0.5-2.0	0.25
As	5 - 15	1.0
Mg	0.1 - 0.4	0.1
Ca	1 - 4	0.25
Al	25 - 75	5.0

In most cases the solution to be analysed had metal concentrations far above the upper limit shown in the table. The solutions were diluted by a definite factor (10x, 100x, 1000x or 2000x) in standard volumetric flasks to bring the concentration within the instrument range.

Appendix 4. Leachability Test Procedure

Ontario Leachate Extraction Procedure was adopted, but the quantity of the sample and therefore the volume of the leachant solution were scaled down because of the limited quantities of the solid samples.

The moisture content of the dewatered sample was determined by drying a suitable liquid to constant weight at 60° C.

The equivalent of 25g dry weight of the dewatered undried iron hydroxide was placed in a one litre wide mouth bottle. 400 mL distilled, deionised water was added and the contents agitated in a mechanical shaker. As the pH was below 5.2 no acetic acid was required. After 6 hours the volume of the solution was adjusted to 500 mL. The solid component was separated. The amount of free liquid corresponding to 25 g of the dry solid material was added to the leachate. The combined solution was analysed.

Leachability tests for precipitates from Step 3 were conducted using 1 gram sample and 16 mL water (combined from 5-6 batches). Acetic acid (0.5 N) was added to maintain the pH at 5.0. Analysis was done as before.

Appendix 5. Determination of the Residual Dodecylamine (DDA)

A colorimetric method described in the literature was used [9]. It is based on the formation of a coloured compound when an amine is mixed with phenol red. Standard solutions of DDA in the concentration range 2-10 mg/L were prepared. 10 mL of solution was added to 5mL chloroform and was mixed with 0.5 mL of 0. 1% phenol red. The chloroform layer was separated in a separator funnel. Absorbance of the coloured compound in chloroform was measured at 447.6 mM in a spectrophotometer (Perkin Elmer). The lower detectable limit was 0.005 mg/L DDA.

PART II: NTC WORK

VALUE RECOVERY FROM ACID MINE DRAINAGE

Introduction

Noranda Technology Centre (NTC) conducted come laboratory experiments in parallel with McGill University tests. The purpose of this was (1) to reproduce the work done by McGill in order to improve the confidence level of the results, (2) to assess alternative reagents (e.g. oxidants), (3) to investigate different process flowsheets which could selectively separate recoverable metals from the AMD, and (4) to examine the technical and economical feasibility of the process.

1.0 Experimental Protocol

1.1 Description of MG AMD

Since the experimental program commenced in March 1992, it was only possible to obtain seep water from Mines Gallen (MG) and not pit water that is actually pumped to the treatment plant from June to October. The concentration of the original seep water was too concentrated: therefore, it was diluted 1/5 with tap water to simulate AMD that is fed to the treatment plant. For preliminary experiments involving biological oxidation of Fe(II), the seep water was diluted to a greater extent (1/23). The metal levels in original and diluted seep water are listed in Table 18

Table 18. Analyses of seep water (original and diluted) used in the experiments.

Description	*Concentration, mg/L*						
	Zn	*Fe**	*Cu*	*Mn*	*Al*	*Cd*	*As*
Original seep water (undiluted)	18,100	38,200	178.63	188.23	4140	53.3	64.17
Diluted 1/5 (theoretical)	3,620	7,640	35.73	37.65	828	10.7	12.8
Diluted 1/23 (theoretical)	787	1661	7.8	8.2	180	2.3	2.8

* ½ of the total iron was in the Fe(II) form

1.2 Fe oxidation

1.2.1 H_2O_2

The stoichiometric requirement of H_2O_2 for the oxidation of Fe(II) to Fe(III) is 1:2, as is expressed by the following equation:

$$H_2O_2 + 2Fe(II) + 2H^+ \rightarrow 2Fe(III) + 2H_2O$$

The stoichiometric quantity of H_2O_2 required to oxidize the Fe(II) present in the water, determined at the time that the experiment was conducted, was added as a 30 % solution (113 mL 30 % H_2O_2 in 20 L AMD). The mixture was stirred for 15 min and left for 12 h to allow for the dissipation of any residual H_2O_2 prior to the start of the experiments

1.2.2 Thiobacillus ferrooxidans (Tf bacteria)

As previously mentioned, the seep water was diluted 1/23 for this set of experiments. The rationale for this was to gradually acclimatise the bacteria to the metal levels. Subsequent experiments will utilise seep water diluted 1/5 as in all other experiments reported in this report.

The bacteria were enriched from waste rock at the Bell Mine site using 9 k medium (Payant, 1987). 1.5 L of AMD was inoculated with the isolated bacteria and the following nutrients were added: 1.605 g KNO_3 and 0.525 g K_2HPO_4.

The solution was agitated for 6 days with a magnetic stirrer, and samples were drawn for Fe(II) determination initially and after 1, 2, and 6 days.

Fe was precipitated using $Ca(OH)_2$ from a sample of 910 mL of biologically oxidized AMD. The settling rate and sludge qualities were compared to the case where H_2O_2 was used for oxidation (precipitation and settling rate methods are described in subsequent sections).

1.2.3 Ozone

Experiments involving the oxidation of Fe(II) in AMD with ozone were conducted at Laval University in conjunction with Air Liquide Inc. The experimental set-up is depicted in Figure 11. The diluted seep water (Table 18) containing 1661 mg/L Fe(II) was used. The theoretical amount of ozone required to oxidize Fe(II) is 1:2 on a molecular basis, as can be seen by the following equation:

$$2Fe(II) + O_3 + 4H^+ \Leftrightarrow 2Fe(III) + 2H_2O + \frac{1}{2} O_2$$

The vertical 5 cm diameter column shown in Figure 4 was filled with 4 L AMD. The ozone generator was used to bubble ozone through the AMD. At the top of the column, excess ozone and oxygen were sparged at an outlet port. The stoichiometric amount of ozone required for theoretical oxidation of Fe(II) was varied from 0 to 3.0. Samples were drawn for Fe(II) determination at time intervals equal to the amount of time required for a specific amount of ozone production

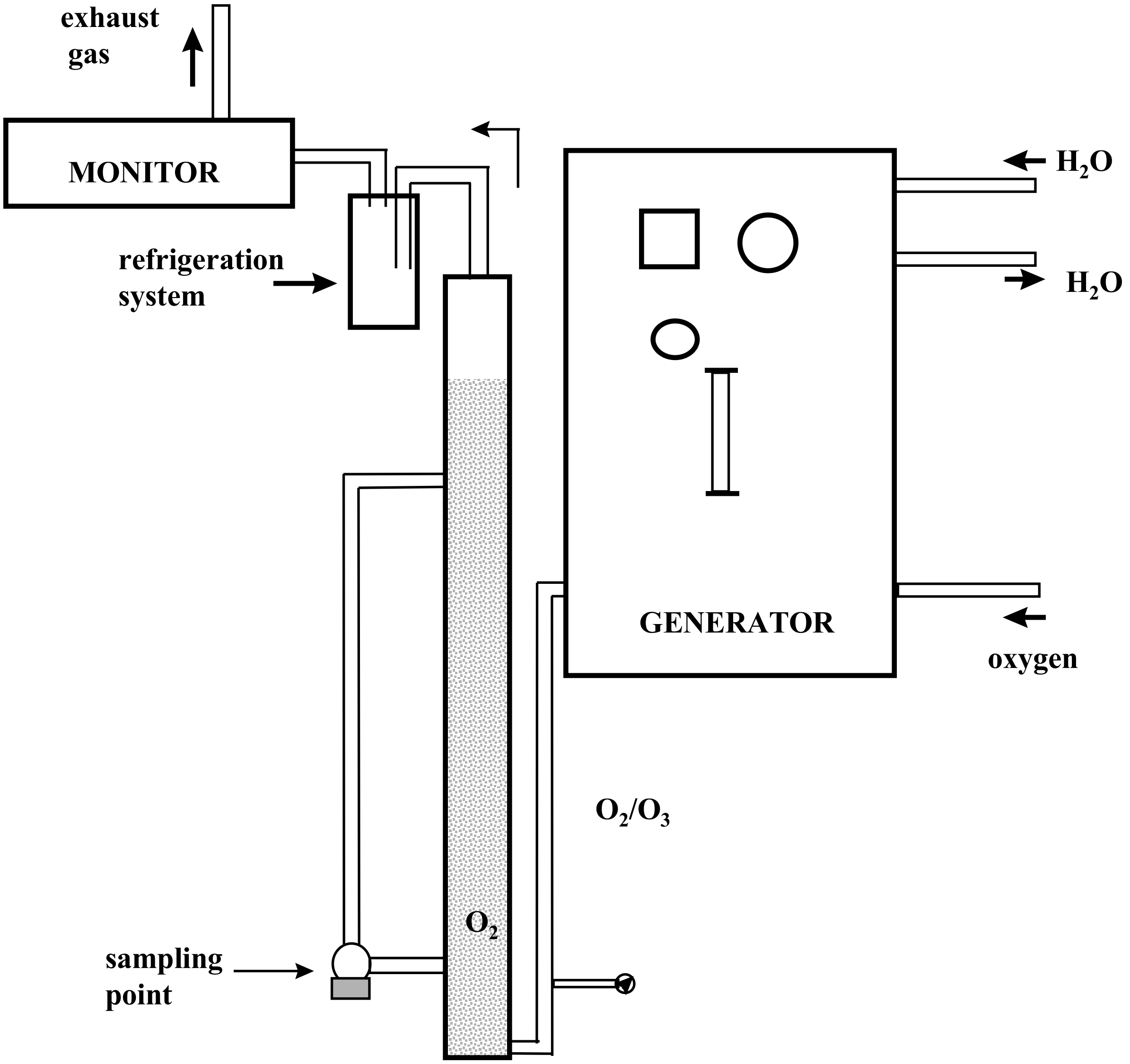

Figure 11. Apparatus for ozonation experiment

1.2.4 Trapzene

Trapzene, consisting of 20% CaO_2 and 80% $Ca(OH)_2$, was supplied by FMC Corporation. In this experiment, both oxidation of Fe(II) and precipitation of Fe(III) were accomplished in one step. Sufficient Trapzene was added to oxidize Fe(II) (i.e. 7 g of Trapzene was mixed with 1 L AMD). The pH increased to 2.6, and sufficient lime was added to further increase the pH to 3.5

1.3 Fe precipitation

For the removal of Fe described in this section, H_2O_2 was first used in stoichiometric ratio to oxidize Fe(II) to Fe(III)

1.3.1 $Ca(OH)_2$ precipitation

A sufficient amount of $Ca(OH)_2$ was added to increase the pH to 3.5. In the case of DDA, 7.5 mg/L DDA (from a 5 g/L stock solution) was first added to 2 L of AMD and the water was mixed for 15 min at 450 rpm.

1.3.2 $CaCO_3$ precipitation

After Fe(II) was converted to Fe(III) with H_2O_2, as described above Fe(III), 13.5 g $CaCO_3$ was required per L of AMD in order to increase the pH to 3.5. The slurry was mixed for an average of 80 min at 450 rpm.

1.3.3 Na_2CO_3 precipitation

Soda ash (Na_2CO_3) was also tested for the first step precipitation of Fe(III). Particularly, 15 g of Na_2CO_3 was required to increase the pH to 3.5, and the mixture was agitated for 45 min.

1.3.4 H_3PO_4 precipitation

The experimental procedure, as described by Dahnke (1985), for recovering metals from electroplating waste was simulated. 1.5 L of AMD was placed in the reaction vessel (Figure 5). An amount of concentrated H_3PO_4 (11.7 mL) containing enough PO_4^{3-}, equal to twice the molar equivalent of Al(III) and Fe(III), was added to the AMD. A sufficient amount of 2 N NaOH (160 mL over 73 h) was added to the reaction vessel from a burette connected to a control valve to maintain the pH at 1.6. The temperature was maintained at 57°C with a heating mantle, and the reactor was fitted with a condenser so as to avoid evaporation

1.4 Cu cementation

For Cu recovery from 1.5 L AMD, 33.4 g of Fe(II) powder was placed in the reaction vessel (Figure 12). The mixture was heated to 57°C as the mixture was stirred at 250 rpm for ½ h.

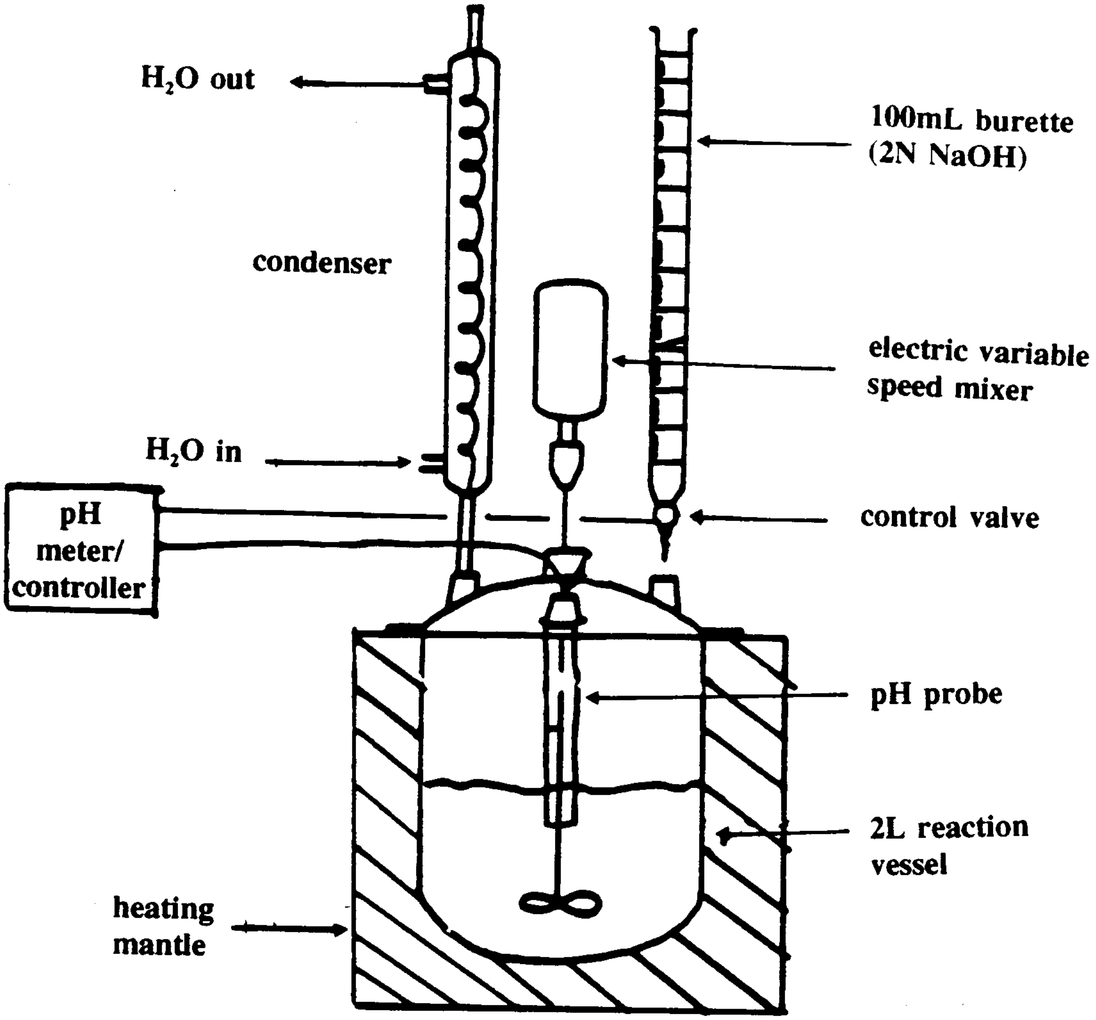

Figure 12. Reaction vessel for Cu cementation (Dahnke, 1985)

1.5 Zn precipitation

1.5.1 Sulphide Precipitation

$Ca(OH)_2$ and NaOH were individually tested to adjust the pH to 5.5, 7.5, and 9.5. The pH adjustment was not necessary for Na_2S precipitation at 3.5. A stoichiometric amount of 10 % Na_2S solution (68 mL) was added to the filtrate from step one whose pH was adjusted to precipitate Zn, Cu, and Mn. H_2S was also examined as a source of S^{2-} ions.

For precipitation at pH 3.5, the reactants were mixed at 450 rpm for 2 h, and 50 mL samples were taken at 15 min, 30 min, 1 h, and 2 h. The samples, filtered through 0.45 µm membrane filter paper, were analysed for metals to determine the reaction kinetics.

For all pH's, 5 mg/L Percol E-10 was added, and the mixture was stirred for 2 min at 250 rpm. Settling was recorded in the same manner as for step one Fe(III) precipitation.

1.5.2 NaOH precipitation

For NaOH precipitation of the filtrate from step one precipitation with $CaCO_3$ (Figure 2), pH 9 and 10 were tested. At pH 9, 70 mL of 4 N NaOH was used to increase the pH of the filtrate (1,670 mL). For pH 10, 82.6 mL of 4 N NaOH was required to increase the pH of the filtrate (1900 mL).

1.5.3 $Ca(OH)_2$ precipitation

Following Cu recovery by cementation and Fe recovery by phosphate precipitation, $Ca(OH)_2$ was used to precipitate Zn as $Zn(OH)_2$ (Figure 3). The pH was increased from 1.6 to 10 with 11.94 g $Ca(OH)_2$ per 730 mL solution.

1.5.4 Precipitation of Zn with Na_2S in the first step of the reversed three-step process (Figure 4)

The pH of the AMD was increased to 3.5 with NaOH. Then, Na_2S (as a 10% solution) was added in two different quantities; providing, in one test, S_{2-} in excess of the stoichiometric quantities of all the metals present and, in another test, stoichiometric quantities for Zn only.

1.6 Lime treatment

The filtrate from step two sulphide precipitation at pH's 3.5, 5.5, and 7.4 required further metal removal by lime treatment in order to render the effluent suitable for discharge. Filtrate from step 3 was combined with a sufficient amount of lime to increase the pH to 10. The slurry was stirred for 15 min at 450 rpm.

1.7 Preparation of suspensions for Zeta potential measurements

Suspensions of $CaSO_4$ and $Fe(OH)_3$ were prepared for zeta potential measurements. A suspension of 3 g/L $CaSO_4{\cdot}2H_2O$ was adjusted to pH 3.5 with 1 N HCl. The suspension was filtered and washed to remove residual Cl^- before being re-suspended at pH 3.8

1.8 Flocculation & settling

Following each precipitation step, 2 mg/L Percol E-10 (0.05 % solution) was added for flocculation, and the slurry was mixed for 2 min at 250 rpm. Settling was recorded at 30 s, 1 min, 2 min, 5 min, 10 min, 15 min, 30 min, and 1 h. The slurry was then filtered through # 40 Whatman paper, and the filtercake was dried overnight at 60°C for determination of the weight of dry solids. The volume of the filtrate was also measured

1.9 Reagents

Reagent grade $Ca(OH)_2$, $CaCO_3$, Na_2CO_3, Na_2S, and NaOH were supplied by Anachemia. DDA, a cationic flotation agent and Percol E-10, a polyacrylamide flocculant, were obtained from Amrack and Allied Colloids, respectively

1.10 Analytical Methods

Aqueous metal concentrations were measured by inductively coupled plasma (ICP) (Polyscan 61E Thermo Jarrell Ash) by Analytical Services at NTC. Ferrous iron was determined by the potassium dichromate volumetric method (Bassett et al, 1978). The surface charge and potential, defined as the zeta potential, were measured using a Zeta-Meter System 3.0 equipped with a Zeiss microscope. The metal grade of the precipitates was determined by measuring aqueous metals by ICP of acid digested solids. For acid digestion, 1 g of dried ground precipitates were combined with 10 mL concentrated HCl. After boiling for 5 min, the solution was cooled and diluted to 100 mL with distilled de-ionised water. Metals were analysed in the final 100 mL aliquot.

1.11 Solid/Liquid separation of sulphide precipitates

An attempt to measure the specific resistance to filtration of sulphide precipitates was made for the sulphide precipitates formed at pH 3.5 and 9.5. Precipitation at pH 3.5 was selected for the high grade of Zn (about 60%) that is achieved, and pH 9.5 was selected since step 3 precipitation would be eliminated.

Since sulphide precipitates are characteristically fine particles, they pose some difficulties in solid/liquid separation. Whang et al (1982) recommended the use of an anionic flocculant followed by gravity thickening and filtration with a frame type filter press. Similarly, at the

Boliden smelter, flocculation, gravity settling, and filtration were used for solid/liquid separation of sulphide precipitates (Bhattacharyya et al, 1981).

1.11.1 Polymer screening

In accordance with recommendations from the technical department of the Mineral Processing Department at Allied Colloids, the polymers described in Table 19 were tested for enhancing settling of sulphide precipitates.

Table 19. Polymers tested for S/L separation.

Polymer Name	*Charge Characteristic*
Percol 455	Cationic 5 %
Percol 155	Anionic 20 %
Percol 351	Non ionic
Percol E-10	Anionic 5 %
Percol 338	Anionic 8 %

An initial screening of the polymers was conducted where each type was tested for settling at a concentration of 3 mg/L in aliquots of 400 mL. For the case of sulphide precipitation at pH 9.5, it was necessary to increase the polymer dose to 9 mg/L for the initial screening to select the optimum polymer type. Settled volumes were recorded at 0, 30 sec, 2 min, 5 min, 10 min, and 15 min. The dosage of the polymer tested with the optimum settling characteristics was further optimised at less than 3 mg/L (i.e. 0.5, 1, and 2 mg/L were tested) for sulphide precipitation at pH 3.5, and at concentrations of 7, 8, and 9 mg/L for precipitation at pH 9.5.

From these data, the optimum polymer dosage and type were selected, and the settling characteristics of the sludge were established. Total metal concentrations at the optimum polymer type and dosage were analysed.

1.11.2 Specific resistance to filtration

In order to determine the relative filterability of the sulphide precipitates, an apparatus was constructed to measure the specific resistance of the sludge to filtration. As the specific resistance of a sludge increases, the more difficult it is to filter. Particularly, sulphide precipitates formed at pH 3.5 and 9.5 were tested with no polymer added and with the optimum polymer type and dosage applied. For comparison, the resistance to filtration of lime sludge was also measured. For all sludges tested, 0.45 μm membrane filter paper was used

The apparatus is depicted in Figure 13, and is described briefly here and in more detail by Cushnie (1984). Sludge is filtered and the rate of filtrate breakthrough in the graduated cylinder is recorded with time. The volume of filtrate is plotted against the time elapsed divided by the filtrate volume. The slope of the line, b, is then used to calculate the specific resistance according to the following equation:

$$r = 2PA^2b / \mu w$$

Equation 1

P= vacuum pressure, Pa
A=Area of Buchner filter, m^2
b=slope, sec/m^6
μ=viscosity, Pa·sec
w=volume filter cake/volume of filtrate, m^3/m^3
Once resistances are known, they may be used for filter selection

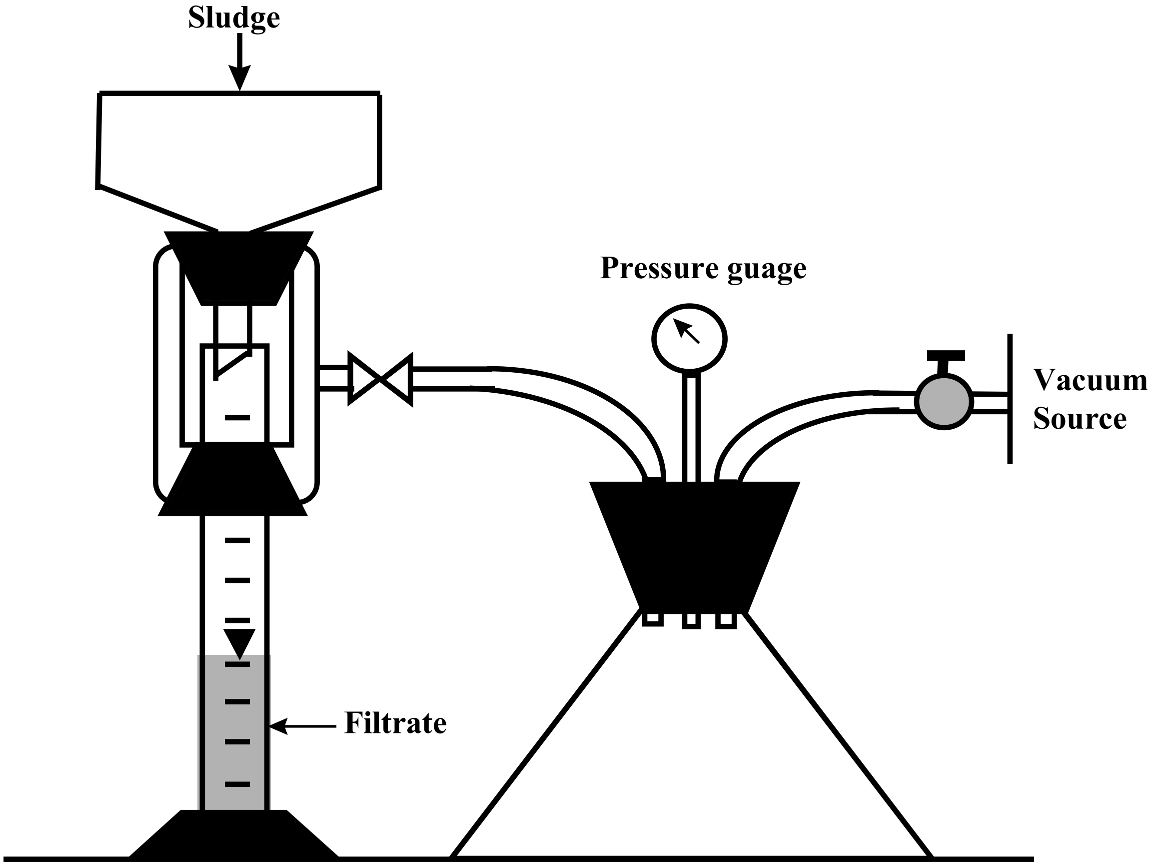

Figure 13. **Apparatus for specific resistance determination**

1.12 Ontario regulatory leaching test

To assess the toxicity of sludges produced for disposal, the regulatory leaching test was implemented (Ontario Regulation 309, 1990). The regulatory test includes procedures for a variety of solid waste types. It was not necessary to follow all of the procedures for the sludge. Therefore, only the relevant procedures were followed, and they are briefly described below in point form.

a) Percent solids of the original sample was determined.
b) A sufficient amount of sludge was vacuum filtered to make-up 60 g of dry solids. The volume and pH of the filtrate was recorded and set aside.
c) The % solids of a small portion of the vacuum filtered sludge was determined
d) A portion of the filtered material, equivalent to 50 g of dry material [determined from a) and c) above] was placed in a 1250 mL bottle
e) mL of distilled/de-ionised water minus the moisture content of vacuum filtered sludge [determined in c)] was added to the 1250 mL bottle
f) Slurry was mixed in an end-over-end shaker for 15 min and the pH was measured

g) Enough 0.5 N acetic acid, not exceeding 4 mL per g of dry solids for the entire procedure, was added to reduce the pH to 5.2.
h) Slurry was rotated for 24 h, with pH measurement/adjustment at 1, 3, and 6 h with 0.5 N acetic acid. The total amount of acid for pH adjustment should not exceed the amount specified in g). The amount of acid added should be recorded.
i) Enough distilled water was added to make the total volume of the liquid 1000 mL.
j) After 24 h, the material was filtered with 0.45 µm filter paper
k) The free liquid associated with 50 g of dry material (step b)) was calculated and mixed with the filtrate from i).
l) The composite leachate sample from j) was analysed for metals

2.0 Results

2.1 Selection of Flowsheet

The criteria for selection of the flowsheet were the following: a) production of an iron sludge that was low in co-precipitated metals such as Cu and Zn, and b) production of a Zn rich sludge suitable for recycle to the refinery/smelter. The quality of the two sludges produced under the various conditions described in the Experimental Protocol are detailed in this section.

2.1.1 Purity of $Fe(OH)_3$ sludge (step one precipitate)

The composition of sludge produced by various reagents are summarised in Table 20. It appears that sludge produced with $CaCO_3$ yielded the lowest levels of As, Cd, Mg, Mn, and Zn compared with the case of $Ca(OH)_2$ (with and without DDA) and Na_2CO_3. In terms of Zn losses to the $Fe(OH)_3$ precipitates, it would appear that $Ca(OH)_2$, even in the presence of DDA, resulted in the highest carry over of Zn (0.64 % with DDA). Sludge produced with H_3PO_4 also contained high levels of Zn (0.90 %) compared with that produced with $CaCO_3$ (0.03 %). Therefore, $CaCO_3$ is the most effective reagent for the production of a metal free $Fe(OH)_3$ sludge for disposal or possible re-use.

Table 20. **% composition of $Fe(OH)_3$ sludge formed in step one precipitation.**

Reagent	*% Composition (dry basis)*											
	Al	*As*	*Ca*	*Cd*	*Cu*	*Fe*	*Mg*	*Mn*	*Na*	*Pb*	*S*	*Zn*
$Ca(OH)_2$, no DDA	1.00	0.019	12.46	0.002	0.03	16.72	0.12	0.004	0.02	<0.0005	13.07	1.61
$Ca(OH)_2$, DDA	0.80	0.018	12.70	0.002	0.02	18.43	0.09	0.003	0.02	<0.0005	12.92	0.64
$CaCO_3$	1.10	0.016	14.27	0.0003	0.02	18.38	<0.001	<0.00001	0.02	<0.0005<0.0005	13.51	0.03
Na_2CO_3	0.98	0.027	0.01	0.0007	0.02	44.24	0.02	<0.00001	0.28	<0.0005<0.0005	6.60	0.20
H_3PO_4	0.32	-	-	-	0.02	23.7	-	0.001	-	-	-	0.90

2.1.2 Zn grade (step two precipitate)

2.1.2.1 Three-step precipitation process

For sulphide precipitation in step two, the Zn grade was affected by the pH and reagent type used to increase the pH. As the pH increased, the Zn grade decreased. Particularly, the Zn grade decreased from 53.30 % at pH 3.5 to 14.70 % at pH 9.5 when $Ca(OH)_2$ was used for pH control, and to 45.5 % when NaOH was used for pH control. Clearly, the highest grade of Zn was achieved when no neutralizing agent was used at pH 3.5 (53.30 % with no DDA and 55.10 % with 5 mg/L DDA).

According to the grade of ZnS precipitates, DDA seems to have had little effect on recovery. It was postulated that DDA would coat the $Fe(OH)_3$ precipitates thereby reducing the number of sites available for Zn adsorption. The zeta potential of a gypsum precipitate was determined as zero at pH 4.3, and that of $Fe(OH)_3$ as +18.62 mV at pH 3.8. Therefore, since DDA is cationic, it does not coat $Fe(OH)_3$ precipitates by virtue of electrostatic attraction.

Table 21. **% composition of Zn rich precipitates formed in step two sulphide precipitates.**

Element	*% composition (dry basis) of step two precipitates*						
	pH 3.5 (no $Ca(OH)_2$ /NaOH)	*pH (with $Ca(OH)_2$)*			*pH (with NaOH)*		
		5.1	*7.4*	*9.5*[1]	*5.1*	*7.4*	*9.5*[1]
Al	1.46[2] (0.09)[3]	1.0	0.6	2.54 (2.64)	(9.0)	(7.0)	8.0
As	<0.0005 (0.0010)	0.2	0.2	-	(0.1)	(0.1)	-
Ca	0.45 (0.19)	14.8	20.8	14.40 (14.00)	(0.04)	(0.04)	0.1
Cd	0.28 (0.27)	0.05	0.02	-	(0.1)	(0.1)	-
Cu	0.73 (0.72)	0.4	0.2	0.13 (0.12)	(0.4)	(0.2)	0.5
Fe	0.47 (0.17)	0.4	0.2	0.18 (0.33)	(0.04)	(0.02)	0.02
K	<0.01 (<0.01)	-	-	<0.01 (<0.01)	-	-	-
Mg	0.12 (0.093)	3.0	2.8	3.26 (3.35)	(0.1)	(0.2)	1.5
Mn	0.043 (0.053)	0.2	0.2	0.15 (0.16)	(0.2)	(0.5)	0.5
Na	0.36 (0.48)	-	-	0.34 (0.28)	-	-	-
Pb	<0.0005 (<0.0005)	<0.01	<0.01	<0.0005 (<0.0005)	(0.1)	(0.1)	-
Zn	53.30 (55.10)	20.5	14.8	14.70 (14.90)	(45.8)	(48.8)	45.5
S	24.90 (25.90)	-	-	17.30 (17.50)	-	-	-

[1] where the process becomes two-step

[2] no DDA

[3] 5 mg/L DDA

2.1.2.2 Two-Step precipitation process

When NaOH was used for step two precipitation according to the process flowsheet in Figure 2, the Zn grade ranged from 27.3% to 29.7% (Table 22). However, the main advantages of the Zn rich NaOH precipitates is that the step three lime treatment may be eliminated (thereby reducing sludge produced for disposal), and NaOH precipitation is more easily controlled compared to sulphide precipitation

Table 22. Zn grade of NaOH step two precipitates (Figure 2).

Element	*% composition (dry basis) of step two precipitates*	
	pH 9	*pH 10*
Al	4.07	3.74
As	0.03	0.02
Ca	0.97	1.16
Cd	0.08	0.09
Cu	0.20	0.20
Fe	0.39	0.24
K	<0.01	<0.01
Mg	3.89	5.57
Mn	0.27	0.29
Na	2.28	3.89
Pb	<0.005	<0.005
S	5.50	6.42
Se	<0.01	<0.01
Zn	27.33	29.66

When lime was used for Zn recovery according to the process flowsheet depicted in Figure 3, the Zn grade was only 11.2 % (Table 23)

Table 23. Zn grade of $Ca(OH)_2$ precipitates (Figure 3).

Element	*% Composition (dry basis)*
Al	0.008
Cu	0.0073
Fe	0.0341
Mn	0.0502
Zn	11.2

Although there is no sludge for disposal, the Zn grade is quite low.

2.1.2.3 Reversed three-step precipitation process

High Zn recovery (as much as 90%) was obtained from the test where S^{2-} ions were supplied in excess of the stoichiometric quantity of all metals present in the AMD. However, the Zn grade was 40% and solid/liquid separation was very difficult.

When S^{2-} was added in stoichiometric ratio to Zn, both Zn recovery and grade were very low. In addition, S/L separation was very difficult. The results are summarised in Table 24. The difficulties encountered during the S/L separation were due to the production of colloidal sulphur formed by the oxidation of sulphide by Fe(III). For the same reason, when S^{2-} was added tin stoichiometric ratio to Zn, the recovery was low since some of the sulphide was used by Fe(III).

Table 24. Results obtained from the use of Na_2S in the first step.

Element	*Sample*					
	S^{2-} in excess of all metals			*S^{2-} in proportion to Zn*		
	Original AMD (mg/L)	*Decant (mg/L)*	*Zn-rich precipitate (%)*	*Original AMD (mg/L)*	*Decant (mg/L)*	*Zn-rich precipitate (%)*
Al	758	497	0.0994	740	315	2.68
As	7.93	4.37	0.0153	7.23	2.50	0.0319
Ca	82.7	56.5	0.0120	79.2	67.5	0.0249
Cd	9.93	0.15	0.11	9.26	0.05	0.0649
Cu	34.3	< 0.02	0.42	33.2	< 0.02	0.25
Fe	6740	4090	5.49	6480	2320	30.0
K	< 5.00	< 5.00	< 0.01	< 5.00	< 5.00	< 0.01
Mg	613	396	0.071	600	497	0.15
Mn	31.5	18.7	0.0265	30.2	25.4	0.0030
Na	2.35	9600	1.60	20.1	1250	1.39
Pb	< 0.25	< 0.25	< 0.0007	< 0.25	< 0.25	< 0.0005
S	7800	10100	20.2	7710	6520	10.3
Se	1.16	< 0.50	< 0.00142	< 0.50	< 0.50	< 0.001
Zn	2960	8.89	40.01	2910	1700	9.34

2.1.3 Method of oxidation

Residence times required for chemical oxidation were significantly shorter than that required for biological oxidation (Table 25). Particularly, H_2O_2 required between 15 min and 2hr compared with 2-6 days for (Tf) bacteria.

Table 25. Residence times observed for various methods of oxidation.

Method/Reagent	*Residence Time*
Chemical/H_2O_2	15 min-2 hr
Chemical/Trapzene(20 % CaO_2-80 % $Ca(OH)_2$)	30 min
Chemical/Ozone	12 min
Biological (by T. Ferrooxidans)	2-6 days

[1] After 30 minutes, all of the Fe had precipitated; thus, implying complete oxidation.

In addition to residence time, the settling rate, purity of $Fe(OH)_3$ precipitate, and lime consumption were compared for the case of Fe precipitation with $Ca(OH)_2$ at pH 3.5 (Table 26)

Table 26. Comparison of $Fe(OH)_3$ sludge qualities for chemical (H_2O_2) and biological bacteria.

Parameter	*Method of Fe(II) Oxidation*	
	Chemical	*Biological*
Quality of $Fe(OH)_3$	1.09 % Zn 0.01 % Mn 0.02 % As 0.004 % Cd 0.04 % Cu 1.87 % Al	0.99 % Zn 0.02 % Mn 0.02 % As 0.003 % Cd 0.007 % Cu 1.67 % Al
Settling Velocity (initial 5 min)	0.39 cm/sec	0.23 cm/sec
Lime Consumption	2.4 g/L	2.7 g/L
Compacted Sludge Volume	111 mL/L	104 mL/L

Settling of sludge containing chemically oxidized Fe settled faster than sludge with biologically oxidized Fe (0.39 and 0.23 cm/sec, respectively). However, the compacted sludge volumes after 1 hr are similar (111 and 104 mL/L) and it is likely that the settling could be improved by optimisation of polymer type selection. There is also little difference in terms of the quality of sludges produced.

Therefore, since the sludge qualities are comparable, further experimental work is required to reducing the residence time for biological oxidation.

2.2 Sludge stability

$Fe(OH)_3$ sludge produced in step one by lime precipitation, with and without DDA, were examined for their chemical stability, in terms of metal leachability, using the Ontario regulatory test. Unfiltered $Fe(OH)_3$ sludge from step 1 (Table 27), contains Cu and Zn above the regulatory limit of 5 mg/L (Gazette Officiel Du Quebec, 1985). In filtered sludge, the level of leached Cu, in the presence and absence of DDA, is below the regulatory limit of 5 mg/L; however, Zn still does not meet the regulatory limit.

Leaching tests were not conducted for step one $Fe(OH)_3$ precipitate formed with $CaCO_3$, Na_2CO_3, of H_3PO_4. However, the results of the leaching tests on sludges from other tests indicate that filtration of the sludge reduces the degree that metals are leached from the sludge.

Table 27. Sludge stability of $Fe(OH)_3$ sludge.

Description of sludge	*Leachable metals, mg/L*					
	Zn	*Fe*	*Cu*	*Mn*	*Al*	*Mg*
Settled sludge						
a) no DDA	950	1.98	15.8	10.2	144	207
b) 5 mg/L DDA	1030	5.0	15	11.7	93.0	232
Filtered sludge						
a) no DDA	130	0.10	2.46	0.91	6.2	18.4
d) 5 mg/L DDA	280	0.18	4.8	2.1	10.3	38.7

2.3 Treated water quality

In this section, the overflow that is potentially suitable for discharge is presented. For the two step precipitation, overflow from sulphide precipitation at pH’s of 7.4 and 9.5 and for NaOH precipitation at pH’s of 9.0 and 10.0 are presented. For the three step precipitation process, step two consists of sulphide precipitation at pH’s of 3.5 and 5.5, followed by step three lime treatment

Table 28 contains treated water quality for the overflow from step two precipitation that would not require a step three lime treatment

Table 28. **Treated water quality for two and three step precipitation process.**

Description of Precipitation Process	*Total Metal Concentration, mg/L*							
	Al	*As*	*Cd*	*Cu*	*Fe*	*Mn*	*Pb*	*Zn*
1. pH 3.5/Ca(OH)2 2. pH 7.4/Na_2S+NaOH (with DDA)	nd[1]	0.9	ND	ND	ND	ND	ND	ND
1. pH 3.5/$Ca(OH)_2$ 2. pH 9.5/Na_2S+NaOH (with DDA)	ND	0.05	0.1	ND	0.2	0.4	ND	0.1
1. pH 3.5/$CaCO_3$ 2. pH 9/NaOH	1.69 (<0.25)	<0.25 (<0.25)	0.15 (0.13)	<0.02 (0.05)	<0.02 (0.05)	0.27 (0.17)	<0.25 (<0.25)	10.68 (0.05)
1. pH 3.5/$CaCO_3$ 2. pH 10/NaOH	1.56 (0.88)	<0.25 (<0.25)	0.04 (0.04)	0.05 (0.05)	0.05 (<0.02)	0.08 (0.05)	<0.25 (<0.25)	7.64 (4.11?)
1. pH 3.5/$Ca(OH)_2$ 2. pH 5.1/Na_2S+$Ca(OH)_2$ 3. pH 10/$Ca(OH)_2$ (with DDA)	ND	0.4	ND	0.1	ND	0.1	ND	0.6
1. pH 3.5/$Ca(OH)_2$ 2. pH 3.5/Na_2S 3. pH 10/$Ca(OH)_2$	23.24 (23.22)	<0.25 (<0.25)	<0.02 (<0.02)	0.03 (0.03)	0.03 (0.10)	0.01 (<0.005)	<0.25 (<0.25)	0.33 (<0.02)

[1] Numbers outside of parentheses denote total metal concentration; whereas, numbers in parentheses denote dissolved metal concentration

Dissolved metal concentration is sufficiently low following two step precipitation with $CaCO_3$/NaOH; however, the total concentration of Zn is high (7.64-10.68 mg/L). Therefore, solid/liquid separation possibly by optimisation of polymer type and dosage is required for NaOH precipitation. There also appears to be a problem with solid/liquid separation with sulphide precipitation at pH 3.5 (0.33 mg/L total and <0.02 mg/L dissolved Zn concentration). Sulphide precipitation at pH's 5.1 and 9.5 are also high in total Zn (0.6 and 0.1 mg/L, respectively). Dissolved metals were not tested in these last two cases

From the water quality data, it is evident that in each case where dissolved metals were measured, the water quality was sufficient for discharge. However, total metal levels were high (0.1-10.68 mg/L). Therefore, once the optimum process is selected, based on economics, the polymer type and dosage will have to be selected for solid/liquid separation.

2.4 Assessment of S/L separation requirements

As mentioned in the Experimental Protocol, the polymer type and dosage were selected for sulphide precipitates formed at pH 3.5 and 9.5. Following this, the specific resistance to filtration was measured for the optimised conditions, and compared to that involving no polymer and to the case of lime sludge

2.4.1 Polymer Optimisation For Sulphide Precipitates (pH 3.5)

Figure 14 shows settling rates for sulphide precipitates formed at pH 3.5 for a range of anionic/cationic/non-ionic polymer types (Table 28) at 3 mg/L. From settling curves, it is evident that low charge density anionic (E-10) and cationic (455) species are more effective than higher charged anionic (155 and 338) polymers

In fact, the non-ionic Percol 351 performed the best in terms of enhancement of settling. This would imply that bridging mechanism, rather than charge neutralization is the mechanism by which the sulphide particles agglomerate

Based on initial polymer screening, the dosage of Percol 351 was optimised. Concentrations of 0.5-3 mg/L were tested (Figure 19) and the optimum polymer dose was found to be 3 mg/L

2.4.2 Polymer Optimisation For Sulphide Precipitates (pH 9.5)

None of the polymers (anionic/cationic/non-ionic) enhanced the settling of sulphide precipitates formed at pH 9.5 at a concentration of 3 mg/L (Figure 18). Therefore, settling tests were conducted with Percol 338 (8 % anionic, Table 28) at concentrations ranging from 5 to 10 mg/L (Figure 17). Settling was most rapid with 10 mg/L of polymer. However, it was thought that this concentration of polymer was excessive; therefore, a concentration of 8 mg/L was selected for polymer dosage (Figure 18). The non-ionic Percol 351 enhanced settling to the greatest extent.

The dosage was further optimised (Figure 15), and it was found that there was little difference in settling at 7, 8, or 9 mg/L of polymer.

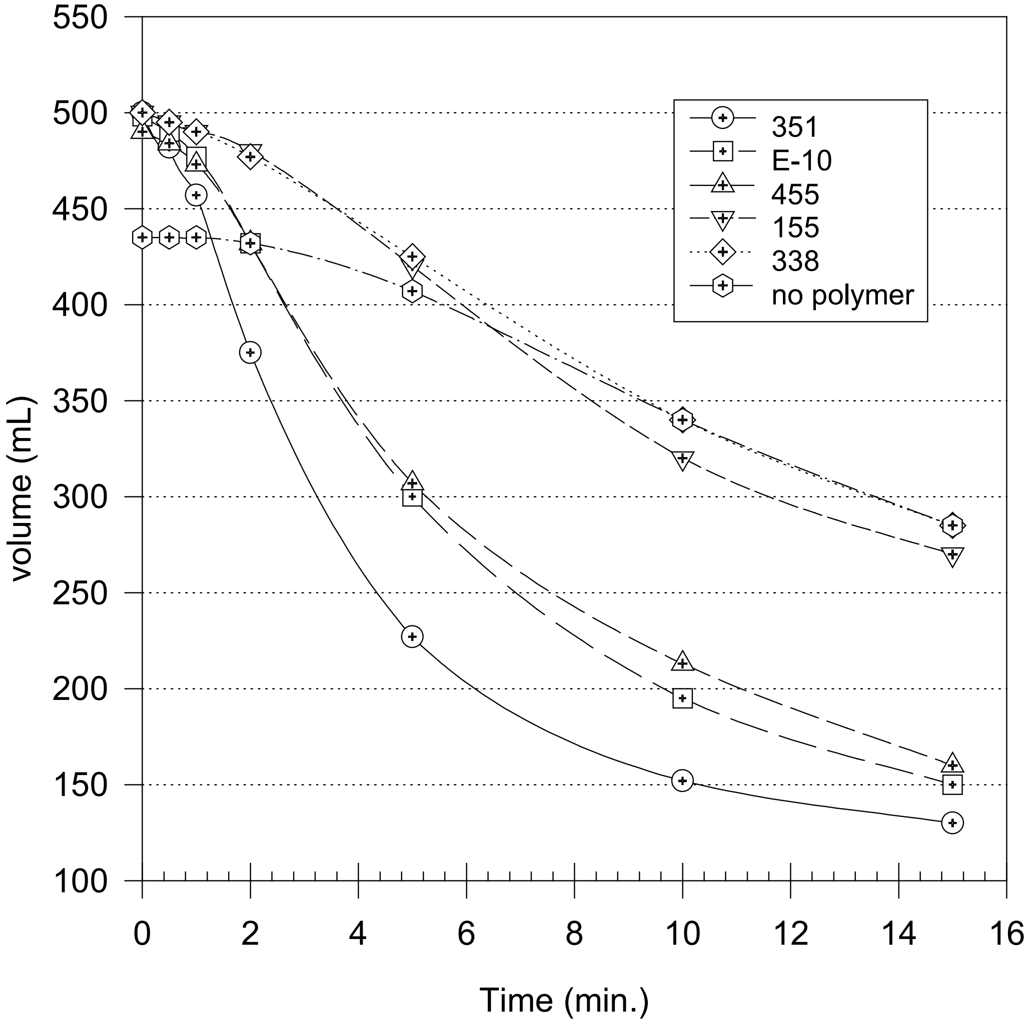

Figure 14. Polymer selection at 3 PPM for sulphide precipitates formed at pH 3.5.

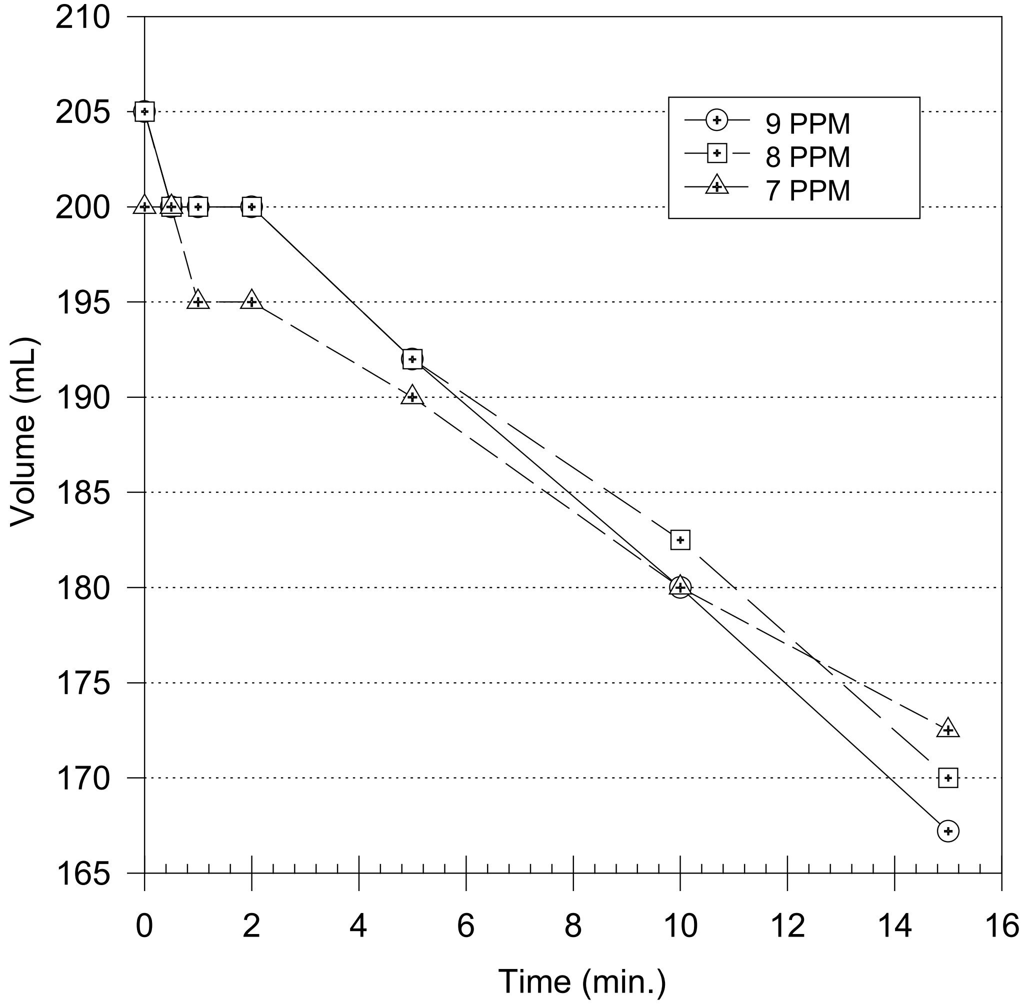

Figure 15. Polymer dose optimisation at pH 9.5 with Percol 351.

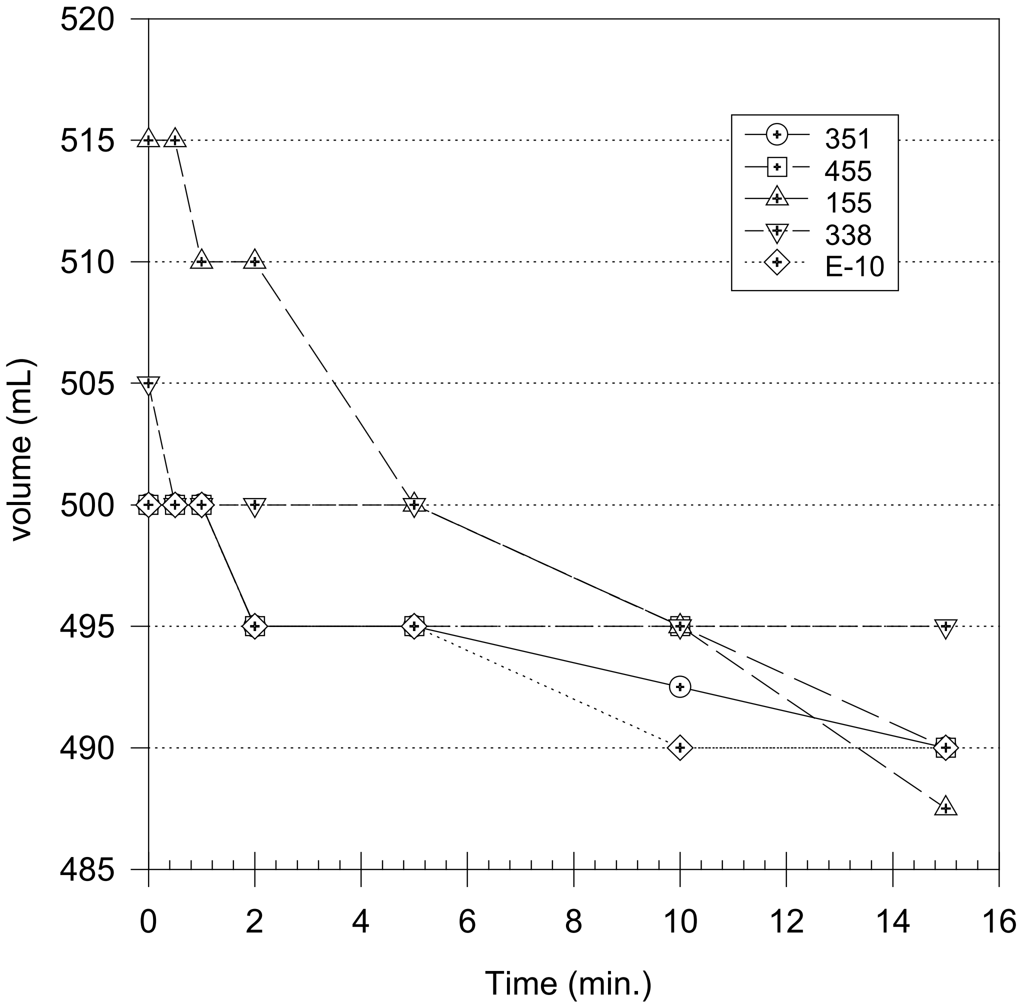

Figure 16. **Polymer Selection At 8 PPM For Precipitates Formed At pH 9.5.**

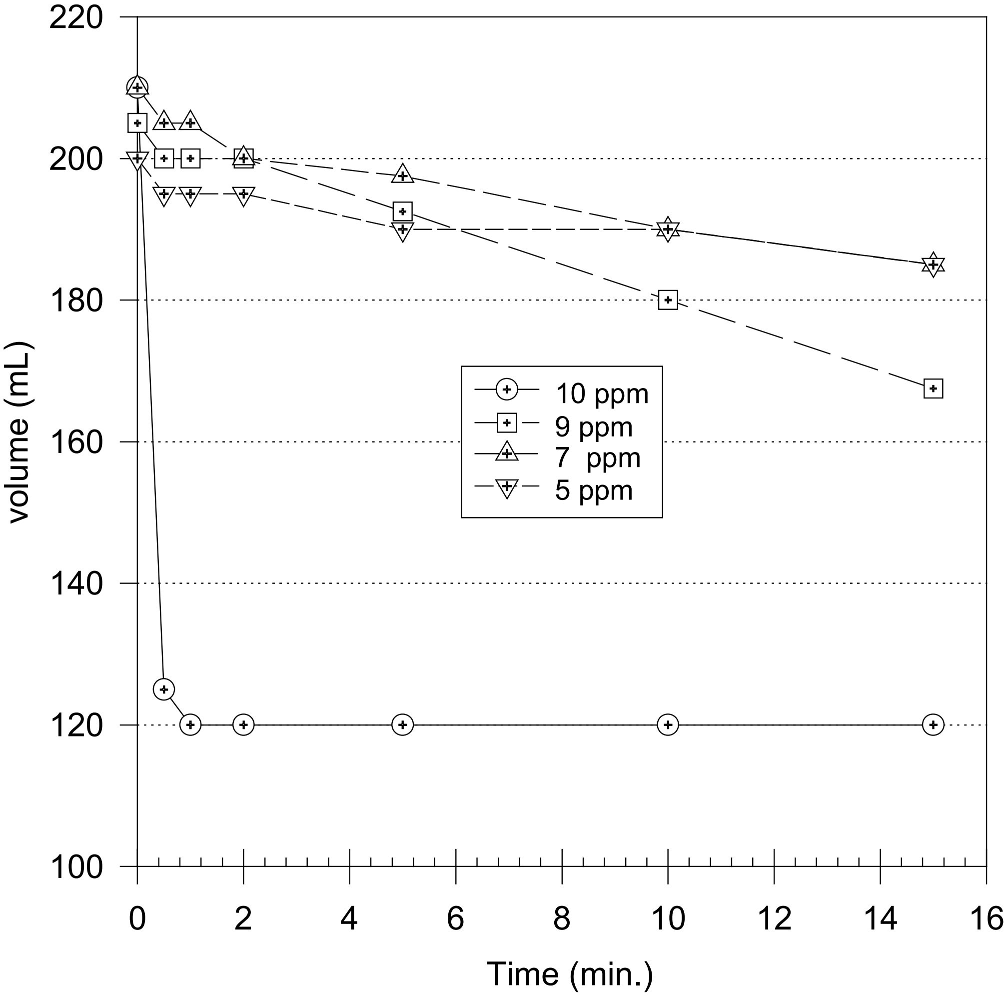

Figure 17. **Polymer Dose Determination For Sulphide Precipitates At pH 9.5 For Percol 338.**

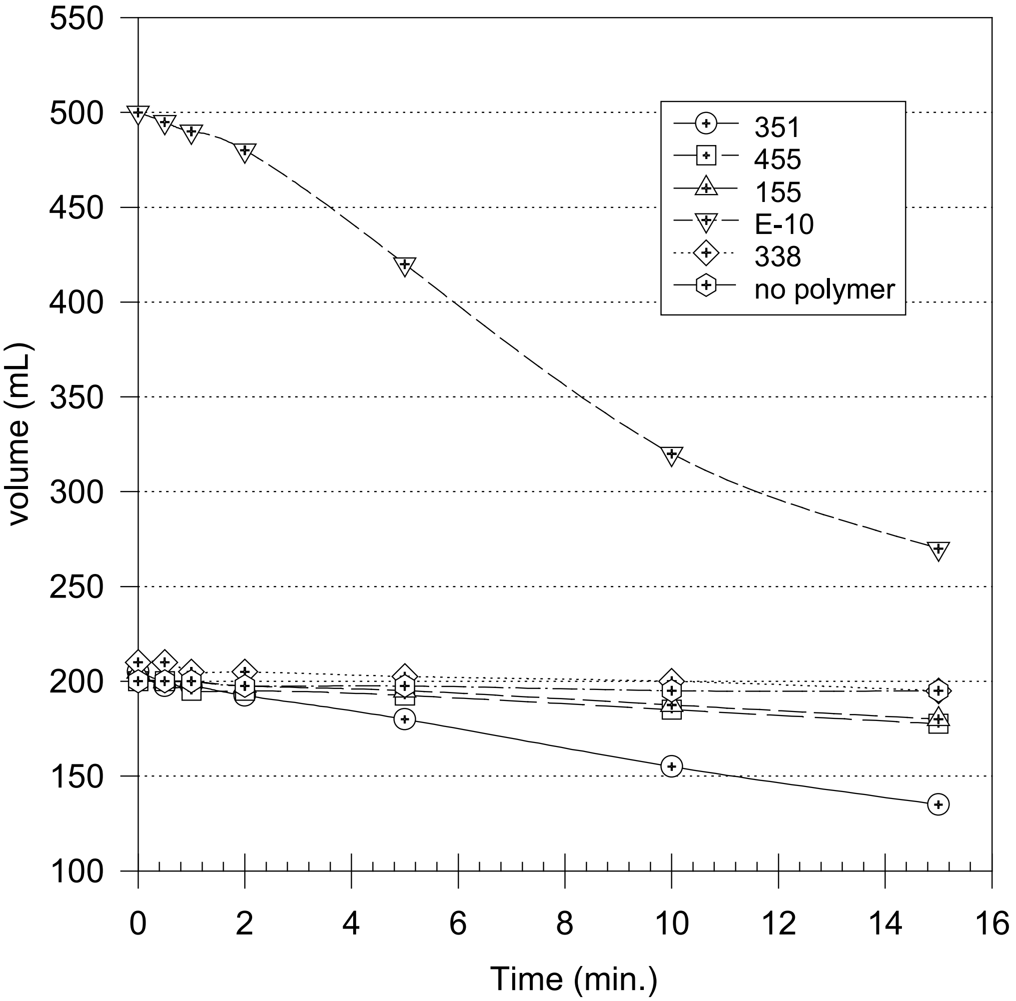

Figure 18. Polymer Selection at 3 PPM For Sulphides Formed at pH 9.5.

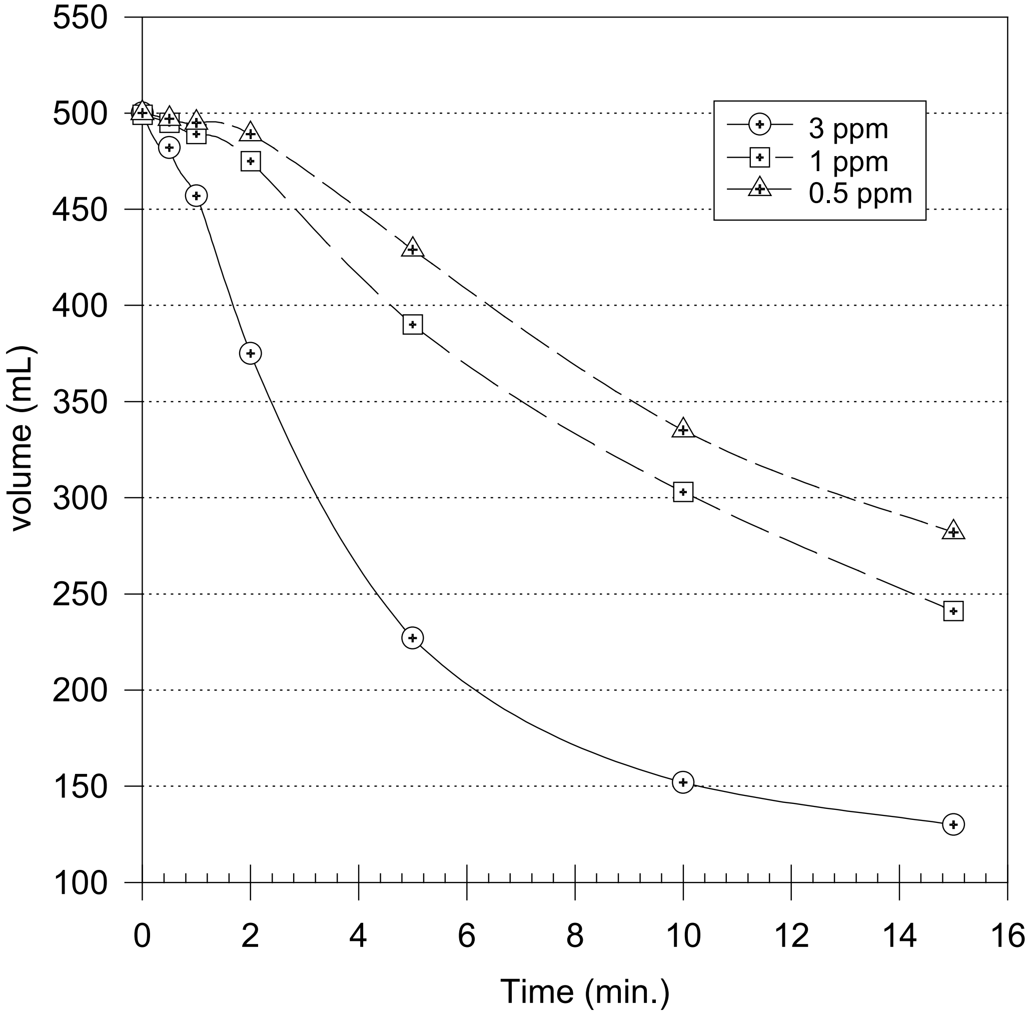

Figure 19. Polymer Dose Optimisation For Sulphide Precipitates Formed at pH 3.5.

2.5 Resistance To Filtration

The specific resistances of sulphide precipitates formed at pH 3.5 and 9.5, both with and without the optimum type and dose of polymer determined for settling, were measured using the apparatus described in the experimental protocol. As evidenced by lower resistance to filtration (Table 29), it is evident that for sulphide precipitates formed at pH 3.5, the polymer selected improves the filterability of sludge. For precipitates at pH 9.5, there is little difference in filterability (i.e. $1.6x10^{14}$ and $1.0x10^{14}$ m^{-2}). By comparison, lime sludge exhibits a resistance to filtration less than half the order of magnitude of that exhibited by sulphide precipitates (i.e. $3.8x10^{7}$ compared to $1.6x10^{14}$)

Table 29. Specific Resistance To Filtration.

Description	*Specific Resistance, m^{2-}*
Sulphide precipitates @ pH 3.5 no polymer	$6.4x10^{15}$
Sulphide precipitates @ pH 3.5 3 PPM Percol 351	$9.6x10^{14}$
Sulphide precipitates @ pH 9.5 no polymer	$1.0x10^{14}$
Sulphide precipitates @ pH 9.5 9 PPM Percol 351	$1.6x10^{14}$
Lime sludge @ pH 10 5 PPM Percol E-10	$3.8x10^{7}$

Filtration steps were not carried out for other $Zn(OH)_2$ sludges. However, since $Zn(OH)_2$ poses solid/liquid separation problems, similar tests could be performed so as to improve filtration.

2.6 Economics

A preliminary economic analysis was conducted to compare the various options in terms of available reagents for precipitation and methods for oxidation that are available.

2.6.1 Reagent Costs

The costs for various reagent combinations are summarised in Table 30. For step one precipitation of $Fe(OH)_3$, $CaCO_3$ is the least expensive and H_3PO_4 the most expensive neutralizing agents tested. For Zn precipitation and final water treatment, NaOH precipitation is the least expensive reagent.

Table 30. Reagent Costs For Various Precipitation Steps.

Precipitation step	*Reagent*	*Cost, (\$/m^3)*
Step 1 Fe precipitation	$CaCO_3$	0.16
	Na_2CO_3	2.40
	$Ca(OH)_2$	0.75
	CaO	0.65
	H_3PO_4	5.30[1]
Steps 2+3 in two steps	Na_2S (@ pH 3.5) $Ca(OH)_2$ (@ pH 10)	3.20 0.39
		3.59
Steps 2+3 in one step	NaOH (@ pH 10)	2.78
Steps 2+3 in one step	$Ca(OH)_2$ (@ pH 10)	-

[1] Excluding energy cost.

2.6.2 *Oxidation Costs*

The available costs for various oxidizing agents tested are summarised in Table 31.

Table 31. Costs Of Alternative Neutralizing Agents (100 % Efficiency).

Method/Reagent	*Cost[1] (\$/m^3)*
Chemical oxidation/H_2O_2	5.85
Chemical oxidation/Trapzene (20 % CaO_2)	9.49
Chemical oxidation/ozone	1.13
Biological oxidation/Thiobacillus ferrooxidans	0.32

[1] Not including capital cost

The least expensive oxidant was found to be the biological catalyst, *T.f.* However, as mentioned previously, the residence times observed for Fe(II) oxidation in preliminary tests was 2-6 days, and must therefore be optimised

2.6.3 Lime treatment vs. proposed flowsheet

Currently, the operating cost for the 1992 operating season at Les Mines Gallen treatment plant was $487,000. The itemised costs are summarised in Table 32.

Table 32. Operating Costs For AMD Treatment At Les Mines Gallen (Godbehere, 1992).

Item	*Cost ($1992)*
Operating Labour	110,000
Lime	150,000
Flocculant	7,000
Freight	2,000
Operating Materials	35,000
Repair & Maintenance Material	30,000
Contract Operating & Maintenance Labour	8,000
Contract Equipment Rental	15,000
Electricity	50,000
Sludge Handling	55,000
Communication & General Items	5,000
Analytical Costs	20,000
Total Costs	487,000

The costs associated with lime treatment and sludge handling would be eliminated by recycling all of the Zn and Fe. Therefore, in conducting a preliminary cost/benefit analysis, a credit for lime and sludge handling will be assumed.

The estimates of reagent costs, reported in Table 30, are based on the experimental results for the diluted seep water. However, due to stratification of the rock, the concentration of the pit water increases continuously throughout the operating season. Therefore, this must be taken into account in conducting an accurate cost/benefit analysis. Average monthly concentrations and loadings of Zn reported to the treatment plant in 1992 are summarised in Table 33.

Table 33. Average Monthly Concentrations And Loadings Of Zn To The Treatment Plant.

Month	*Average Zn Concentration, mg/L*	*Zn loading, kg*	*Operating time, days*
June	520	801	22
July	700	1519	31
August	1700	3689	31
September	1900	3990	30
October	2100	4557	31
November	2200	4620	30
December	2900	3045	15
Total	-	22,221	190

Based on the total Zn loading during, the operating season of the plant (22,221 kg), the Zn credit was calculated as $9,675 (assuming 50 % of the Zn value, $1046.92 per tonne ***American Metal Reporter*** Jan. 1993).

To estimate the feasibility of the project, possible benefits (i.e. credits) associated with replacing lime treatment with the costs (i.e. debits) of the Zn value recovery process are detailed in Table 34.

Table 34. Possible Credits And Debits Associated If Lime Treatment Is Replaced With Two Step Recovery Process With $CaCO_3$-Na_2S.

Description	*credit*	*debit*
Zn credit (22,221 kg Zn)	$9,675	-
Lime	$150,000	-
Sludge handling	$55,000	-
Fe credit from $Fe_2(SO_4)_3$ from weak acid plant	$120,000	-
Total credits	$334,675	-
$CaCO_3$/NaOH for Fe and Zn precipitation from AMD.	-	-$21,477

The cost of chemicals used for Fe and Zn precipitation are based on laboratory scale experiments. However, in full scale operation, due to lower efficiency, the costs of reagents will be higher. Also, the cost of solid/liquid separation is not taken into account. Therefore, since the credits outweigh the debits, the feasibility of the proposed value recovery project will be dependent on the costs associated with solid/liquid separation.

3.0 Discussion

In comparing chemical versus biological oxidation for conversion of Fe(II) to Fe(III), it was found that although residence time was excessive (2-6 days), the cost of biological oxidation is 72-97 % cheaper than that of comparable chemical oxidation. The calculated costs are based on the nutrients required by the bacteria. To improve the efficiency of biological oxidation, process parameters such as temperature, rate of aeration, and innoculum ratio should be examined.

As mentioned previously, one of the objectives in process development was to obtain a Zn free $Fe(OH)_3$ precipitate, so as to increase Zn yield in the second step, while rendering the $Fe(OH)_3$ precipitate as chemically stable as possible. Of the chemical precipitants tested ($CaCO_3$, $Ca(OH)_2$, H_3PO_4, and Na_2CO_3), $CaCO_3$ yielded the least contaminated $Fe(OH)_3$ precipitate. Additionally, the estimated cost of $CaCO_3$ is 4-22 times less per m^3 than the alternatives. Results also indicate that DDA was not effective at 5 mg/L in reducing the amount of Zn adsorption. The surface charge, or zeta potential, of $Fe(OH)_3$ and gypsum precipitates were measured to determine whether increasing the DDA dosage would hinder Zn adsorption. Since $Fe(OH)_3$ was found to have a net positive charge, and gypsum no charge at all, it was concluded that DDA is incapable of reducing Zn adsorption. Experimental results also indicate that filtration of the sludge would increase stability.

Sulphide precipitation carried out at pH 3.5 yielded the highest grade of Zn in the Zn precipitate (53.3-55.1 %). However, the overflow from this precipitation process did not contain suitably low metal levels, therefore requiring treatment with lime to precipitate metals and neutralize pH. Furthermore, the fine nature of sulphide precipitates was a concern in terms of recycling to the refinery/smelter, though Kidd Creek indicated that these sulphides may not pose a problem since the quantity is small, and they can be mixed with the primary feed.

Hydroxide precipitation using NaOH/$Ca(OH)_2$ was also examined. Precipitation of Fe free supernatant from step one with NaOH at pH 10 yielded a sludge of almost 30 % Zn with dissolved metals in the overflow that were sufficiently low for discharge. Use of $Ca(OH)_2$ to precipitate Zn as a hydroxide or to control pH for sulphide precipitation resulted in extremely low Zn grade (11.2-20.5 %) owing to gypsum precipitation.

The ZnS precipitate formed at pH 3.5 and $Zn(OH)_2$ formed at pH 10 each have certain advantages. In the latter case, although there is no sludge for disposal, there are concerns over high moisture content and elevated levels of Al and Mg (3.74 and 5.57 %, respectively) (J. Mouland, 1992). However, since there was only 22 tonnes of Zn treated at Les Mines Gallen's treatment plant in 1992, the impact of moisture content and impurities may be acceptable. To determine this, further communication with Kidd Creek is necessary

Although the fine nature of sulphide precipitates may result in the carry over of material from the roaster, the precipitates would be suitable for pressure leaching (Mouland, 1992). As described in the literature, a sedimentation-flocculation-filtration scheme may be possible for solid/liquid separation of the sulphide precipitates (Whang, 1982). Percol 351 (a non-ionic) polymer was found to enhance the filterability of precipitates

On an economic basis, the feasibility of the process involving $CaCO_3$ for Fe precipitation at pH 3.5 and NaOH for Zn precipitation at pH 10, depends on the costs associated with solid/liquid separation.

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