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UMI®
Electrowinning of Metal – DETA Complexes

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements of the degree of Master of Engineering

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Abstract

Sludges formed by lime treatment of acidic mine effluents are a widespread environmental hazard. One treatment option is to recover the toxic and potentially valuable contained metals. A method has been reported to selectively recover the metals by leaching with a complexing agent, diethylenetriamine (DETA). In this thesis a novel method has been developed to recover metals from the metal – DETA complexes by direct electrowinning. Copper was studied initially as a test system due to the relative ease with which it is recovered in conventional sulphate electrowinning. The main industrial interest, and hence the main focus of the work, is in the nickel – DETA system. For both metals, initially batch tests were run to determine acceptable electrowinning conditions. These were followed by recycle tests to simulate a potential process flowsheet. In the nickel – DETA system the effects of pH, nickel concentration, temperature, and DETA to nickel ratio on current efficiency were determined.

Recycle tests for copper showed that a steady DETA concentration was achieved after ca. six hours. In the case of nickel, the system seemed to continually deteriorate. A pH range of 4.6 to 4.8 maximized the current efficiency, due to a competition between hydrogen formation at low pH and increased complex stability at high pH. Both increasing Ni concentration and temperature increased the current efficiency, while increasing the DETA to nickel ratio lowered it.
Résumé

Les boues produites par le traitement des effluents acides miniers constituent un risque environnemental commun. Une des solutions au problème serait d’en récupérer les métaux toxiques, dont certains sont... Une des méthodes proposées est une lixiviation par agent complexant, la diéthylénetriamine (DETA). Dans ce mémoire, nous présentons une nouvelle méthode de récupération des métaux des complexes métal-DETA formés par ladite lixiviation. Nous avons d’abord étudié le système cuivre-DETA, à cause de la facilité relative avec laquelle on peut récupérer le cuivre par extraction par électrolyse (electrowinning). Toutefois, la technique est encore plus intéressante pour le nickel, et c’est surtout au système nickel-DETA que nous nous sommes intéressés. Pour le cuivre comme pour le nickel, nous avons faits des essais d’électrolyse en discontinu pour déterminer quelles en seraient des variables opératoires acceptables. Nous avons par la suite fait des essais avec recyclage pour simuler un schéma possible d’opération. Dans le système nickel-DETA, nous avons déterminé l’impact du pH, de la concentration en nickel, de la température et du rapport de concentration nickel/DETA.

Les essais avec recyclage dans le système cuivre-DETA ont produit une concentration de DETA stable après 6 heures d’opération. Dans le système nickel-DETA, l’équilibre n’a pas pu être atteint. Une fourchette de pH de 4.6 à 4.8 maximise l’efficacité d’utilisation du courant, à cause de l’équilibre entre la formation d’hydrogène à bas pH et la stabilité du complexe à pH plus élevé. Une augmentation de la concentration en nickel ou de la température fait augmenter l’efficacité d’utilisation du courant, tandis qu’une augmentation du rapport de concentration DETA:nickel la fait baisser.
Acknowledgements

I would like to thank the following people for their contributions to the preparation of this thesis.

- Professor Jim Finch for his vision, guidance, ideas, and insights without which none of this would have been possible. As well as the funding provided.
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Chapter 1: Introduction

1.1 Introduction

Mining provides commodities essential to modern life and has become a vital industry in many countries including Canada. For a mining company to be successful, it is required to implement low cost methods, while at the same time meeting ever stricter environmental standards. Not only must lower discharge limits be met, but accumulated problematic wastes from earlier operations must be treated.

One important source of pollution arising from mining is the generation of acidic effluents, known as acid mine drainage (AMD). AMD is a highly acidic solution containing up to thousands of parts per million of dissolved metals (Gazea et al. 1996, Demopoulos et al. 1995). This solution can be toxic and must be treated prior to discharge. Any time sulphide minerals are exposed to air AMD can be produced. This can include exposed mine surfaces, ore stockpiles, or tailings areas. The sulphide containing minerals oxidize when exposed to air and react with water to generate sulphuric acid, which in turn solubilizes metals from the oxidized mineral surface. This process occurs naturally, although to a much lesser degree prior to mining since very little of the sulphide surfaces are exposed. AMD is generally treated by neutralization, where typically lime is used to raise the pH of the solution to the point where the dissolved metals precipitate as metal hydroxides. The resulting metal hydroxide "sludge" is generally stored on site as a waste product. The sludge presents problems of its own since the metals can be easily resolubilized if the pH of the storage area drops sufficiently, and because of the large storage areas required. Additionally, the sludge represents lost metal values. Recovery of these metals is one of the foci of the mineral processing group at McGill.

It is possible to selectively recover valuable metals such as nickel, zinc, and copper from AMD sludges by leaching with diethylenetriamine (DETA) [Rao et al. 1995]. The subsequent solid residues consist mainly of iron hydroxides and calcium sulphate (gypsum), which are much less environmentally hazardous. The leach solutions
can have quite high metal concentrations (40-60 g/l), but to date no economically viable process has been developed for recovering the metals from these solutions.

This thesis will examine the possibility of using electrowinning to recover nickel and copper from their respective complexes with DETA. Copper-DETA solutions were used initially as a test system, since normal industrial electrowinning of copper is much easier than for nickel. Following that the commercially more interesting case of the nickel-DETA system is studied.

1.2 Thesis Outline

Chapter one introduces the topic of AMD, the associated problems and treatment options, as well as the rationale for the present investigation.

The second chapter deals with the theory behind the topics covered in the thesis, as well as a review of the literature. These topics include AMD formation, methods of treatment, electrochemistry, and electrowinning from metal–amine solutions.

The experimental set-up and procedure are described in the third chapter. Included are experimental program, solution chemistries, and details about the equipment and layout.

Test results and discussion are presented in the fourth chapter.

Lastly, chapter five summarizes the conclusions of the thesis as well as outlining potential future work.
Chapter 2: Literature Review and Background Theory

2.1 Acid Mine Drainage

Mining by its very nature is intrusive upon the environment. Whether open pit, strip, or deep shaft mining, local ecosystems invariably become disturbed. One seemingly unimportant result of the mining process is the generation of new exposed rock surfaces. Ironically this leads to the greatest environmental problem facing the mining industry today: Acid Mine Drainage (AMD) [Filion and Ferguson 1990, Filion et al. 1990]. In fact the United States have identified mining activities as the second greatest source of nonpoint pollution to surface waters [Drabowski 1993]. Not only is AMD generated from exposed mine surfaces, but anywhere sulphide minerals are exposed. This includes tailing areas, waste rock piles, and most often overlooked; abandoned mine sites. The economic impact of this is that treatment plants may have to be run by mining companies for hundreds of years [Filion and Ferguson 1990].

2.1.1 Formation of Acid Mine Drainage

When freshly exposed sulphide minerals, such as pyrite, become exposed to water and air, they begin to oxidize. This reaction is greatly enhanced (20 to 100 times [Filion et al. 1990]) when in the presence of oxidizing bacteria, such as Thiobacillus Ferrooxidans. This results in the production of sulphuric acid and an oxidized metal surface, as seen from the example of pyrite [Hawley and Shikaze 1971]:

\[
\text{FeS}_2 + \frac{7}{2}\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{FeO} + 2\text{H}_2\text{SO}_4
\]

The acid generated in this first step reacts with the oxidized metal surface to produce solubilized metal ions:

\[
\text{FeO} + \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{H}_2\text{O}
\]

The iron ions appear in the ferrous form. When in the presence of a sufficient quantity of sulphuric acid and residual oxygen the ferrous may then oxidize to ferric:

\[
2\text{FeSO}_4 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}
\]

This ferric iron can also act as an oxidant, thereby increasing the rate of AMD production.
Fe₂(SO₄)₃ + FeS₂ + 3H₂O + 5/2O₂ → 2FeSO₄ + 3H₂SO₄

Any free ferric ions that do not react with pyrite will precipitate as ferric hydroxide, which is largely insoluble, above a pH of ca. 3.5.

Other sulphide minerals such as chalcopyrite, sphalerite and galena react in a similar fashion [Hawley and Shikaze 1971].

Some typical AMD compositions are given in Table 2.1.

Table 2.1: Typical AMD Compositions and Environmental Limits [Gazea et al. 1996, Demopolous et al. 1995, Metal Mining Liquid Effluent Regulations 1999]

<table>
<thead>
<tr>
<th>Composition</th>
<th>Mixed Sulphide Mines</th>
<th>Coal Mines</th>
<th>B.C. Environmental Limits*</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>2.0 – 7.9</td>
<td>2.6 – 6.3</td>
<td>6.5 - 8.5</td>
</tr>
<tr>
<td>Fe (II)</td>
<td>8.5 – 2400</td>
<td>1.0 – 473</td>
<td>0.3 – 1</td>
</tr>
<tr>
<td>SO₄</td>
<td>10 – 16,000</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.04 – 1600</td>
<td>NA</td>
<td>0.2 – 1</td>
</tr>
<tr>
<td>Al</td>
<td>1.0 – 1300</td>
<td>1.0 – 58</td>
<td>0.5 – 1</td>
</tr>
<tr>
<td>Cu</td>
<td>0.005 – 76</td>
<td>NA</td>
<td>0.05 – 0.3</td>
</tr>
<tr>
<td>Mn</td>
<td>0.4</td>
<td>1.0 – 130</td>
<td>0.1 – 1</td>
</tr>
<tr>
<td>Pb</td>
<td>0.02 – 90</td>
<td>NA</td>
<td>0.05 – 0.2</td>
</tr>
</tbody>
</table>

* lower limits for new mills, higher limits for old mills

2.1.2 Scope and Effects of Acid Mine Drainage

Between 1984 and 1987, industry sponsored projects to examine the scope of the problem of base metal mine wastes capable of generating AMD in Canada. All provinces and territories with the exception of Alberta, Nova Scotia, and PEI were identified as having operating and/or abandoned base metal mining operations capable of generating AMD. The total area of the sites amounted to 37 000 acres [Filion and Ferguson 1990]. These figures do not include gold, uranium, or coal mines, so the problem becomes that much more extensive. These wastes to a large extent represent the effects of base metal mining since World War II. Due to the combined effects of mining lower grade ores and at higher tonnages, it is expected that the affected area will double in twenty years [Filion and Ferguson 1990]. Considering how much of an effect AMD has once it enters the local water system, the affected area can be easily ten times the size of the AMD.
generating area. In Ontario 20 abandoned mine sites were identified as being potentially AMD generating, containing 60,000,000 tons of reactive sulphide tailings covering 2030 acres. In Quebec 21 sites were identified covering 11 110 acres. Two main groups looking into the problem of AMD are the Canadian Mine Environmental Neutral Drainage (MEND) research program and the British Columbia Acid Mine Drainage (BC AMD) task force.

Any heavy metal in concentrations greater than 1ppm should be regarded as a potential source of trouble [Hawley and Shikaze 1971]. Even if no one heavy metal exceeds 1ppm, if the total exceeds this limit there is still cause for concern as synergistic effects can (and probably do [Hawley and Shikaze 1971]) occur. Effects of AMD pollution can affect people, plants, and animals. A municipality in Manitoba had to find a new water supply after it was discovered that the entire lake had become contaminated from an upstream AMD generating site. In the River Avoca, located in South-East Ireland, the abandoned copper-zinc mine at Avoca polluted the entire downstream 15km section of the river to the sea. The impact was severe, resulting in a wildlife species deficit of greater than 87% [Gray 1998]. All fish were eliminated with the exception of juvenile eels close to the estuary. The river had acted as a spawning area for salmon but had become unable to support these activities. A chart showing a simplified list of the effects of AMD on surface waters is given in Figure 2.1. Obviously AMD cannot be discharged to the environment and must be either prevented or treated.

![Diagram of AMD effects](image)

**Figure 2.1:** The major effects of AMD on non-stagnant water systems [Gray 1997]
2.1.3 Treatment of AMD

For the past several decades the typical AMD treatment has been through the addition of a base (usually lime), raising the pH of the solution and precipitating the heavy metals as a mix of metal hydroxides or a "hydroxide sludge". This process worked well to remove the dissolved metals and was simple and inexpensive to operate [Demopolous et al. 1995]. There are however several problems associated with this process. Firstly, this results in the loss of metal values to the sludge, which if recovered, could partially offset the cost of neutralization [Leppinen et al. 1997]. The sludge itself is very difficult to handle because the solids density is typically below 3%, and remains uncompacted, even after long times [Demopoulos et al. 1995]. Finally, the sludge is amorphous and consequently the heavy metals will dissolve in the course of natural weathering. This is unacceptable for final storage and several attempts have been made to prevent the production of these types of sludges.

Recently the High Density Sludge Process (HDS) was one solution. In this process, a portion of the sludge is recycled to the neutralization stage to act as a seed material for subsequent metal removal. The neutralization is also carried out in more than one stage in order to control the super-saturation of the solution. The combined effects are to produce a more crystalline sludge with a higher solids density. With this process solids densities of 70% were obtained [Demopoulos et al. 1995]. Although the sludge can now be handled, normal weathering can still leach metal ions.

![Diagram of the High Density Sludge (HDS) Process](image)
Another potential method is to selectively precipitate specific metals in stages for separate recovery. Rao et al. [1994] investigated this possibility. A mixed metal solution (Table 2.2) was treated in stages to primarily recover zinc. In one option, iron was removed by oxidizing all the ferrous to ferric, raising the pH to 3.5, and precipitating as ferric hydroxide. The second stage consisted of zinc, copper, and manganese precipitation as a sulphide. The final stage was to remove all remaining metals as hydroxides by raising the pH to 10 with the addition of lime. The results showed that 100% of the iron was removed in the first stage and greater than 90% zinc recovery was achieved in the second stage at a zinc grade of greater than 50%. The final effluent had less than 1 ppm heavy metals.

Table 2.2: Composition of solution treated by stages for selective metal recovery [Rao et al. 1994]

<table>
<thead>
<tr>
<th>Metal</th>
<th>pH</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Mn</th>
<th>Al</th>
<th>Mg</th>
<th>Pb</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc (ppm)</td>
<td>2.5</td>
<td>5960</td>
<td>38</td>
<td>2760</td>
<td>29</td>
<td>704</td>
<td>558</td>
<td>0.36</td>
<td>9</td>
</tr>
</tbody>
</table>

Research has also been performed with neutralization agents other than lime. Maree and du Plessis [1994] conducted tests using limestone (CaCO$_3$) to neutralize AMD solutions. Results showed that underground mine water can be neutralized effectively with limestone [Maree et al. 1996], with savings in chemical costs of 56% and overall cost reductions of 44% compared to using lime. In addition, over and under dosage of neutralization agent is avoided due to low limestone solubility at high pHs [Maree and du Plessis 1994].

A further reduction in operating cost can be realized by the use of passive systems for the treatment of AMD. Passive treatments use naturally occurring geochemical and biological processes to improve the quality of effluent waters with minimal operation and maintenance costs. In the past decade passive systems have gone from the laboratory size to full scale field applications. They have been used mainly to treat acidic waters with low metal contents. In the Appalachia region alone more than 200 wetlands are operating for the treatment of coal mine drainage [Gazea et al. 1996]. After several attempts, a wetland design evolved which was tolerant to AMD and could significantly reduce the levels of dissolved metals. Most of these treatment systems consist of a series of small wetlands vegetated with *Typha latifolia* (cattails), occasionally with the addition
of an organic substrate in which the cattails root [Gazea et al. 1996]. Metals such as iron and manganese become oxidized and precipitate as hydroxides, while other metals like copper and zinc can precipitate as hydroxides or sulphides. While not always suitable for final discharge, passive treatment schemes can be effective in achieving a great deal of AMD treatment, greatly reducing treatment costs. One problem with these systems is that they do not address what will be done with the wetlands upon completion of their task: the wetland itself becomes a potential environmental hazard. A table showing the application of passive treatment systems to drainage from some sulphide mining areas is given below.

Table 2.3: Application of passive treatment systems on sulphide mine drainage [Gazea et al. 1996]

<table>
<thead>
<tr>
<th>Site, Constructed year</th>
<th>Design</th>
<th>Substrate</th>
<th>Flow rate m³/day</th>
<th>pH</th>
<th>Fe ppm</th>
<th>Zn ppm</th>
<th>Cu ppm</th>
<th>Other components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leviathan mine, California, USA, 1993</td>
<td>3 cells: ALD, aerobic, anaerobic</td>
<td>Horse manure</td>
<td>5.5</td>
<td>4.7</td>
<td>6.5</td>
<td>310</td>
<td>31</td>
<td>Al: 48 As: 0.4 Ni: 1.8 Mn: &lt;BDL</td>
</tr>
<tr>
<td>Seeps, Gold mine, Nevada, USA, 1993</td>
<td>14 chambered aerobic system with algae</td>
<td>River rock with algae</td>
<td>5.5</td>
<td>6-8</td>
<td>6-9</td>
<td>0.05</td>
<td>0.03</td>
<td>1.6</td>
</tr>
<tr>
<td>ARD, Gold mine, Nevada, USA, 1993</td>
<td>3 cells: aerobic pond, anaerobic, rock filter</td>
<td>Cow manure, Sandy soil</td>
<td>3.3</td>
<td>3.2</td>
<td>6.5-7.1</td>
<td>216</td>
<td>0.9</td>
<td>1.8</td>
</tr>
<tr>
<td>Pit Cell, Brewer Gold mine, South California, USA, 1993</td>
<td>1 aerobic cell</td>
<td>Turkey litter, Sawdust Cow manure, Limestone</td>
<td>5.5</td>
<td>2.3</td>
<td>5.5</td>
<td>735</td>
<td>215</td>
<td>76</td>
</tr>
<tr>
<td>Heap Leach Pad Cell, Brewer Gold mine, South California, USA, 1993</td>
<td>1 aerobic cell</td>
<td>Turkey litter, Sawdust Cow manure, Limestone</td>
<td>4.2</td>
<td>2-4-7</td>
<td>6.2</td>
<td>25-380</td>
<td>44</td>
<td>2-30</td>
</tr>
<tr>
<td>Burleigh Tunnel, Colorado, USA, 1993</td>
<td>2 anaerobic cells: 1 Upflow &amp; 1 Downflow</td>
<td>Composted manure, Hay</td>
<td>5.5</td>
<td>6.8</td>
<td>5</td>
<td>&lt;BDL</td>
<td>40 Upf: 0.5</td>
<td>Downf: 10</td>
</tr>
<tr>
<td>Lasko West Fork Mine, Lead mine, Missouri, USA, 1994</td>
<td>1 anaerobic cell</td>
<td>Cow manure, Sawdust, Hay, Inorganic tailings Coarse mine waste</td>
<td>2.67</td>
<td>7.8</td>
<td>7.0</td>
<td>0</td>
<td>0.18</td>
<td>&lt;BDL</td>
</tr>
</tbody>
</table>

A simple way to help alleviate the AMD problem is to make the most of the available water resources to reduce the amount of AMD produced. Total or partial water recirculation in the mine and the mill can help lower the volumes of AMD which are treated. In addition, "under no circumstances should fresh water be permitted to gain access to a sulphide-bearing tailings area" [Hawley and Shikaze 1971]. Obviously rainwater will fall into the tailings area, but no run-off water or streams should be allowed to enter the tailings area.
Newer treatment schemes attack the cause and try to prevent the formation of AMD rather than treat the problem. This involves “(1) preventing sulphide oxidation; or (2) slowing down the oxidation process so that the resultant very low rate of acid production is of no significance” [Orava and Swider 1996]. This can happen by preventing either water or oxygen from contacting the tailings.

Leppinen et al [1997] examined the possibility of performing flotation on tailings in order to recover all sulphide minerals, including iron minerals, as a separate concentrate in order to reduce the reactive fraction. The experimental work was carried out on the plant tailings from the Pyhasalmi mine in Finland. Results showed that between 92 and 96% sulphides could be recovered generating a waste which was not AMD producing, with a sulphide content between 0.4 to 0.6%. The grades for the flotation concentrate are given in Table 2.4. Several treatment schemes for the recovery of these metals were presented. Of concern is the high reagent consumption, up to 150g/t of xanthate.

Table 2.4: Composition of bulk sulphide concentrate [Leppinen et al. 1997]

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>S</th>
<th>Cu</th>
<th>Zn</th>
<th>Au</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>33%</td>
<td>33%</td>
<td>0.7%</td>
<td>1.0%</td>
<td>2.8g/t</td>
<td>40g/t</td>
</tr>
</tbody>
</table>

Amaratunga and Hmidi [1998] studied the stability of cold-bonded pyrrhotite tailings agglomerates towards AMD when used as aggregates for disposal in underground paste backfill. The pellets consisted of pyrrhotite tailings, Portland cement and fly ash as binders, with various additives such as neutralizers, sealants and bactericides. The pellets were tested for strength and AMD generating potential by using humidity cells. The results showed that pellets using both Portland cement and fly ash as binders had sufficient strength and resistance to AMD production (“Enviroseal” appeared to be the most effective additive at preventing AMD), and that sodium silicate showed some promise as an alternative to “Enviroseal”.

Research was carried out by Fytas and Evangelou [1998] to determine if pyrite particles could be coated by iron phosphate in order to prevent contact between pyrite and oxygen. The particles were treated with a dilute H2O2 solution in order to slightly oxidize
the pyrite surface. When phosphate ions are present such that the solution is supersaturated with respect to iron phosphate, the following reaction takes place:

\[
\text{FeS}_2 + \frac{15}{2}\text{H}_2\text{O}_2 + \text{H}_3\text{PO}_4^- \rightarrow \text{FePO}_4 + 2\text{SO}_4^{2-} + 3\text{H}^+ + 7\text{H}_2\text{O}
\]

When the supersaturation is relatively high the iron phosphate will precipitate as a coating on the pyrite surfaces. After the surfaces were coated they were stabilized with a Ca(OH)\textsubscript{2} solution (800mg/l) in order to increase the phosphate coating resistance. The coated particles were leached with a 0.01M H\textsubscript{2}O\textsubscript{2} solution corresponding to an accelerated natural weathering cycle. The results were favorable (Figure 2.3) but careful optimization of test reagents must be maintained, and the process seems quite intricate.

![Figure 2.3: Results of leaching experiments: pH variation with time [Fytas and Evangelou 1998]](image)

Other types of oxygen blocking systems include wet covers such as vegetative and water covers, and dry covers such as clay, polymeric, and cemented sulphide tailings. Very successful vegetative methods were developed, and many sites were vegetated, but after several years the drainage quality had not improved [Filion and Ferguson 1990].

Perhaps the most effective method proposed is the water cover. Ironically, the greatest hurdle to overcome with this technology is not an engineering problem, but convincing the public that it is the safest route to go [Finch 1998]. This method works by
submerging the tailing under water, and relying on the low oxygen solubility in water to prevent oxygen from reaching the sulphide minerals in the tailings. Shallow water covers are very complex systems comprised of both physical and chemical processes occurring simultaneously and interdependently. These complex systems are site-specific and therefore it is hard to draw conclusions which apply to all shallow water cover situations. Figure 2.4 depicts the various processes affecting subaqueous oxidation of sulphides and water cover quality.

![Figure 2.4: Processes affecting subaqueous sulphide oxidation and water quality (Li et al. 1997)](image)

Several water covers for reactive sulphide tailings have been constructed and have shown very favorable results. The Solbec tailings pond is a good example. Over 2.5M cubic meters of sulphide waste was deposited between 1962 and 1977 [Amyot and Vezina 1997]. Flooding began in November 1994, the tailings were completely covered by September 1995, and in February 1996 the first overflow occurred. There was an immediate effect on the quality of the covering water as seen in Table 2.5. The pore water (water between settled particles) showed an initial increase in metal concentrations followed by a decrease, showing the effectiveness of the water cover. The initial increase was due to sulphates from prior oxidation of the sulphide particles. Although the surface
water values are encouraging, the pore water concentrations are still well above

Table 2.5: Covering water quality at the Solbec tailings pond

<table>
<thead>
<tr>
<th>Period</th>
<th>1987</th>
<th>Fall 94</th>
<th>Spring 95</th>
<th>Summer 95</th>
<th>Fall 95</th>
<th>Spring 96</th>
<th>Summer 96</th>
<th>Fall 96</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.0-3.5</td>
<td>5.0</td>
<td>10.7</td>
<td>6.7</td>
<td>7.6</td>
<td>7.8</td>
<td>7.2</td>
<td>7.3</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>10</td>
<td>142</td>
<td>2.9</td>
<td>1.8</td>
<td>0.35</td>
<td>0.29</td>
<td>0.17</td>
<td>0.3</td>
</tr>
<tr>
<td>Zn (ppm)</td>
<td>3</td>
<td>0.83</td>
<td>0.11</td>
<td>0.02</td>
<td>0.04</td>
<td>0.01</td>
<td>0.02</td>
<td>0.19</td>
</tr>
<tr>
<td>Cu (ppm)</td>
<td>1</td>
<td>0.49</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>0.03</td>
</tr>
</tbody>
</table>

environmental limits (Fall 96: [Fe] = 150ppm, [Zn] = 9.3ppm) and can be attributed to the already oxidized portion of the tails. Additionally an increase in sulphate reducing bacteria was seen as well as a decrease in sulphate oxidizing bacteria.

Excellent results were achieved at the Quirke mine, located near the town of Elliot Lake, which began flooding in 1992. Selected data for both surface and pore water is given in Table 2.6. The water quality has shown continuous improvements, as all water

Table 2.6: Selected water quality measurements of Quirke Mine flooded tailings pond [Kam et al. 1997]

<table>
<thead>
<tr>
<th>Year</th>
<th>Surface Water</th>
<th>Pore Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>Ra 226 (mBq/l)</td>
</tr>
<tr>
<td>1992</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>1993</td>
<td>7.1</td>
<td>325</td>
</tr>
<tr>
<td>1994</td>
<td>7</td>
<td>220</td>
</tr>
<tr>
<td>1995</td>
<td>6.7</td>
<td>165</td>
</tr>
<tr>
<td>1996</td>
<td>6.8</td>
<td>144</td>
</tr>
</tbody>
</table>

quality parameters monitored have shown a declining trend. The surface water now, for the most part, meets environmental standards and supports a variety of wildlife including birds, fish, and benthic organisms.

As more data accumulate it appears that AMD generation from waste rock and tailings can be controlled using water cover technologies. Although these innovations in
the prevention of AMD are proving effective, there still exist vast piles of reactive sulphide waste material and hydroxide sludges around Canada and the rest of the world. These environmental liabilities need to be treated, and while water covers can treat sulphide materials, there exists no method for the treatment of hydroxide sludges.

2.2 Treatment of Hydroxide Sludges

As explained in section 2.1.3, the most common method used to treat AMD has been by lime neutralization, resulting in a mixed metal hydroxide sludge. This results in a loss of resources and revenues, as well as the generation of a potentially hazardous substance if the toxic metals become resolubilized. Ideally, this hydroxide sludge should be treated to economically recover the valuable metals, while at the same time not generating any new hazardous waste.

2.2.1 Recovery Options

There are two basic leach options to recover metals from a sludge. The first would be to acidify the sludge thereby solubilizing all metals, selectively recovering the metals of interest, then re-neutralizing the solution to precipitate the “gangue” metals as new sludge. The second way would be to selectively leach and recover the valuable metals while rejecting the others. The second way has the advantages of having fewer

![Figure 2.5: Conceptual Process Options for Selective and Bulk Leaching Schemes for Metal Recovery from Hydroxide Sludge-](image-url)
steps and lower reagent costs if the selective extractant can be recycled. Figure 2.5 gives a conceptual idea of the two treatment options.

2.2.2 Selective Leaching

Although little research has been done on the selective leaching of hydroxide sludges, there has been much research on the selective leaching of minerals. The common factor to both has been the use of amines as the leachant, particularly ethylenediaminetetraacetate (EDTA) [Karagolge et al. 1992]. Amines are organic compounds containing nitrogen. The most important amine compound used in these applications are chelate ring compounds, which are formed only by ligands which have more than one point of attachment to the metal, as seen in Figure 2.6. The name is derived from the Greek word chela, which means lobster or crab claw, and refers to the "unusual stability of chelate ring compounds" [Bailar, 1956]. Examples of chelate ring stability constants with copper and nickel are given in Table 2.7. It should be noted that different degrees of complexation will occur, dependent on pH, as can be seen for the

![Chelate Ring Diagram](image)

Figure 2.6: Examples of Metal – Ligand Interactions [Bailar 1956]

<table>
<thead>
<tr>
<th>Chelating Agent</th>
<th>-log K\text{Ni}</th>
<th>-log K\text{Cu}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylenediamine (EDA)</td>
<td>18.38</td>
<td>10</td>
</tr>
<tr>
<td>Diethylenetriamine (DETA)</td>
<td>18.58</td>
<td>16</td>
</tr>
<tr>
<td>Triethylenetetramine (TETA)</td>
<td>13.77</td>
<td>20</td>
</tr>
<tr>
<td>Tetraethylenepentamine (TEPA)</td>
<td>17.44</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.7: Selected Nickel and Copper Chelate Ring Stability Constants [http, Eresen and Kammel 1981]
example of nickel complexation with EDA, in Table 2.8. Table 2.9 lists the formation constants of several metal-EDTA complexes, and shows its lack of selectivity. Chelate rings are employed in many chemical and biological processes. For example, hemin is an iron chelate and chlorophyll is a magnesium ring compound. Chelating agents are also used in the mineral industry; for example DETA is used as a depressant for pyrrhotite in pentlandite flotation [Yoon et al. 1995 and Kelebek et al. 1996]. At INCO's Clarabelle concentrator in Sudbury, pyrrhotite reports to the concentrate due to "inadvertent activation of the mineral by heavy metal ions such as Ni^{2+}, Cu^{2+}, and Ag^{+}" [Yoon et al. 1995]. The pyrrhotite is deactivated when DETA forms complexes with the ions from the pyrrhotite surface.

Mena and Olsen [1985] reported on the selective leaching capabilities of ammonia-ammonium carbonate solutions to recover copper from chrysocolla, a hydrous copper silicate: CuO•SiO_2•2H_2O. Technology exists to recover copper from chrysocolla through sulphuric acid leaching, but the presence of carbonates can increase acid consumption. Ammonia is a more attractive reagent because it is more selective, has a lower inventory cost, and is amenable to regeneration. It was reported that ammonia leaching was more complex than acid leaching but that good results could be obtained as seen in Figure 2.7.

<table>
<thead>
<tr>
<th>pH</th>
<th>Predominant Complex Stage (20 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5 - 5.8</td>
<td>[Ni(EDA)]^{2+}</td>
</tr>
<tr>
<td>5.9 - 6.6</td>
<td>[Ni(EDA)_2]^{3+}</td>
</tr>
<tr>
<td>&gt;7</td>
<td>[Ni(EDA)_3]^{4+}</td>
</tr>
</tbody>
</table>

Table 2.8: Predominant Complex Stage and Stability Constant vs pH [Eresen and Kammel 1981]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Log K_M</td>
<td>8.7</td>
<td>10.7</td>
<td>8.6</td>
<td>7.8</td>
<td>13.8</td>
<td>16.3</td>
<td>18.6</td>
<td>18.8</td>
<td>16.5</td>
<td>16.5</td>
<td>25.5</td>
</tr>
</tbody>
</table>

Table 2.9: Metal Chelate Compound Formation Constants of EDTA [Awakura et al. 1991]
Ammonia can also be used to leach copper from chalcopyrite as reported by Reilly and Scott [1984]. Although the goal of the tests performed was to recover elemental sulphur produced when the copper was leached, excellent copper recoveries were obtained in the copper leaching stage.

Figure 2.7: Typical Leaching Curves for Chrysocolla in Ammonia Solutions [Mena and Olsen 1985]

Figure 2.8: Leaching Curve of Copper from Chalcopyrite [Reilly and Scott 1984]
As previously stated, EDTA has been used as a metal extractant for several minerals because it is a strong chelating agent, even under mild operating conditions, and can be recovered for reuse [Karagolge et al. 1992]. Equilibrium experiments on the extraction of tungsten from synthetic scheelite (CaWO$_4$) with EDTA were carried out by Payne on a simulated low grade ore (2% CaWO$_4$) [Konishi et al. 1987]. The results showed that tungsten could be selectively extracted at atmospheric pressure and 373K, and that EDTA could be recovered for reuse. Marshall performed similar experiments on even lower grade ores (0.2 to 1.32% CaWO$_4$), achieving similar results [Konishi et al. 1987]. The proposed reactions for the process are:

\[
\begin{align*}
\text{CaWO}_4 & \rightarrow \text{Ca}^{2+} (\text{aq}) + \text{WO}_4^{2-} (\text{aq}) \quad (1) \\
\text{Ca}^{2+} + \text{Y}^{4+} & \rightarrow \text{CaY}^{2-} \quad (2)
\end{align*}
\]

where Y represents the EDTA anion. Reaction 1 describes the dissolution of scheelite in water. Scheelite is largely insoluble, but since the reaction constant of reaction 2 is $3.89 \times 10^7$ m$^3$/mol and the rate constant is in the order $10^6$ m$^3$/mol$\cdot$s, all tungsten solubilized is immediately complexed with EDTA.

Karagolge et al. [1992] investigated the leaching kinetics of colemanite (2CaO•3B$_2$O$_3$•5H$_2$O) by aqueous EDTA solutions:

\[
2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O} + 2\text{H}_2\text{Y}^{2-} + 2\text{H}_2\text{O} \rightarrow 2\text{CaY}^{2-} + 6\text{H}_3\text{BO}_3
\]

Even base metals such as copper can be effectively extracted from certain minerals by using chelate compounds. Awakura et al. [1991] studied the leaching of copper from malachite (Cu$_2$CO$_3$(OH)$_2$) using EDTA. Bauer and Lidstrom [Awakura et al. [1991] proposed a method in which EDTA would be used to selectively extract oxidized copper minerals from other carbonate minerals. Awakura et al. showed the overall leaching reaction to be:

\[
\text{Cu}_2\text{CO}_3(\text{OH})_2 + 2\text{H}_2\text{Y}^{2-} \rightarrow 2\text{CuY}^{2-} + \text{H}_2\text{CO}_3 + 2\text{H}_2\text{O}
\]

Using a selective extractant for this type of ore is beneficial since oxidized carbonaceous ores are not easily treated by flotation, and if treated by acid leaching, consume excessive amounts of acid.

Konishi et al. [1991] studied the leaching of copper from natural chalcocite (Cu$_2$S) in EDTA solutions. It was determined to be a two step process, firstly an intermediate product, covellite (CuS) was formed. The copper from the covellite then
leached into solution and was immediately complexed by the EDTA. The overall reaction was given as:

$$\text{Cu}_2\text{S} + 2\text{Y}^{4-} + 5/2\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{Cu(OH)}\text{Y}^3\text{-} + \text{SO}_4^{2-}$$

Two sets of leaching curves are given in Figure 2.9. The first shows the effect of EDTA concentration on the fraction of copper leached versus time, while the second shows the effect of pH. Since the species in the reaction is $\text{Y}^{4-}$, one would expect a high pH to be beneficial, since that is where the highest concentration of $\text{Y}^{4-}$ is found. This can be seen in Figure 2.10.

Figure 2.9: The Effect of a) EDTA Concentration and b) pH on the Fraction of Copper Extracted Versus Time [Konishi et al. 1991]

Figure 2.10: Distribution of EDTA Species Versus pH [Awakura et al. 1991]
Although EDTA is a powerful chelating agent, a drawback is that it is not selective, in particular with respect to iron. On the other hand, polyamines are very selective with respect to iron. This is because polyamines form only weak complexes with iron, and iron in solution will precipitate as Fe(OH)₃. Eresen and Kammel [1981] described a method to extract nickel from limonite type laterite ores by pressure leaching with aqueous polyamine solutions. EDA was the main polyamine tested, but experiments with DETA, TETA, and TEPA were also conducted. Results of this work showed that the greater the concentration of protonated EDA molecules, the greater the nickel extraction. The protonation of the EDA molecules was done through the addition of hydrochloric acid, which also lowers the pH. There is a two-step leaching process in which the first step is the solubilization of nickel ions, in which rate and concentration are dependent on pH. This would explain why more and faster leaching occurs at lower pHs. The subsequent reaction would be nickel ion complexation with EDA. Results also showed that increased extractions were achieved with successively larger chelate rings, i.e. TEPA had the highest extractions while EDA had the lowest. Table 2.10 shows the results of experiments performed with different polyamines and at different concentrations.

Table 2.10: Ni Extractions from Laterite Ore by Leaching with Various Polyamines [Eresen and Kammel 1981]

<table>
<thead>
<tr>
<th>Polyamine</th>
<th>Concentration (g/l)</th>
<th>Ni Extraction (%)</th>
<th>Ni Concentration (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDA</td>
<td>45</td>
<td>75</td>
<td>2.13</td>
</tr>
<tr>
<td>DETA</td>
<td>45</td>
<td>83</td>
<td>2.36</td>
</tr>
<tr>
<td>TETA</td>
<td>45</td>
<td>88</td>
<td>2.5</td>
</tr>
<tr>
<td>TEPA</td>
<td>45</td>
<td>85</td>
<td>2.42</td>
</tr>
<tr>
<td>EDA</td>
<td>15</td>
<td>16</td>
<td>0.45</td>
</tr>
<tr>
<td>DETA</td>
<td>15</td>
<td>75</td>
<td>2.13</td>
</tr>
<tr>
<td>TETA</td>
<td>15</td>
<td>69</td>
<td>1.96</td>
</tr>
<tr>
<td>TEPA</td>
<td>15</td>
<td>80</td>
<td>2.23</td>
</tr>
</tbody>
</table>

Conditions: 300 g/l ore, Temperature 220°C, 3hr Retention Time

Forward et al. [1960] developed a process for the production of high purity lead by amine leaching. This process generated solutions containing 650 g/l of lead, as well
as other metals such as copper, zinc, nickel, cobalt and cadmium. The lead can be selectively recovered from solution with a purity of 99.99+%. The flowsheet is given in Figure 2.11. The process comprises several interesting steps. Firstly the PbS is converted to PbSO$_4$ by acid pressure oxidation in aqueous solution. Next the PbSO$_4$ is leached by aqueous alkaline amines (EDA) at room temperature to form soluble lead-amine complexes.

\[
PbS + H_2SO_4 + \frac{1}{2}O_2 \rightarrow PbSO_4 + H_2O + S^0
\]

\[
PbSO_4 + 2EDA \rightarrow [Pb(EDA)_2]SO_4
\]

The lead is recovered from solution by the addition of CO$_2$ to form insoluble PbCO$_3$.

\[
2Pb(EDA)_2^{2+} + 3CO_2 + 5H_2O \rightarrow PbCO_3\cdot Pb(OH)\_2 + 2EDAH_2^{2-}
\]

The final step is to reduce the lead carbonate, which can be done with C, CH$_4$, CO or any other reducing gas. The reaction for carbon is:

\[
C + PbCO_3\cdot Pb(OH)\_2 \rightarrow 2Pb + 2CO_2 + H_2O
\]

The amines can be regenerated as seen from the following equation:

\[
EDAH_2^{2+} + Ca(OH)\_2 \rightarrow EDA + 2H_2O + Ca^{2+}
\]
Figure 2.12 shows the solubility of lead for several amines. Again it is the larger polyamines which seem to work better. The lead complex with DETA showed a very strong correlation between N atoms in the DETA and lead solubility in the ratio Pb/N:1/4.

Rao et al. [1995] performed work in the selective leaching abilities of amines in an attempt to extract Zn, Cu, and Ni from their hydroxides formed in the treatment of AMD. The leachant (DETA) is selective to these metals over Fe, Ca, and Al, which can be major constituents of AMD sludges. In this way the valuable metals can be selectively extracted.
leached and recovered. Extraction curves for Cu, Ni, Zn, and Fe are shown in Figure 2.13. These curves show that the base metals can indeed be selectively leached over iron. Leaching tests were carried out to determine the maximum concentrations of metal-DETA complexes in solution, which would help determine possible recovery options for the metals. These concentrations were found to be 38.5, 46.4, and 52.6 g/L for Zn, Cu, and Ni, respectively. These values give rise to the possibility of using electrowinning as a recovery method for the metals.

2.3 Electrowinning

Electrowinning is the process of recovering (“winning”) metals from a solution of metal ions (electrolyte) by applying a voltage across the solution. The voltage required for electrowinning depends on several factors. As an example the anodic and cathodic half-reactions for the electrowinning of copper are:

\[
\begin{align*}
\text{Cu}^+ + 2e^- & \rightarrow \text{Cu} & e^o = 0.34\text{V} & \text{cathode} \\
\text{H}_2\text{O} & \rightarrow 2\text{H}^+ + \frac{1}{2} \text{O}_2 + 2e^- & e^o = -1.229\text{V} & \text{anode} \\
\text{Cu}^+ + \text{H}_2\text{O} & \rightarrow \text{Cu} + 2\text{H}^+ + \frac{1}{2} \text{O}_2 & e^o = -0.889\text{V} & \text{overall}
\end{align*}
\]

The term \( e^o \) refers to the voltage required for the given reaction at standard state. The overall reaction theoretically requires 0.889V to proceed, but industrially requires about 2.1V. One contributor to this difference is the resistance of the electrolyte used, which can be adjusted through electrolyte chemistry and temperature. In the case of copper electrowinning, this value is typically 0.55V [Davenport and Biswas 1976]. The largest contributors to the difference between the actual and theoretical voltages are the overpotentials. There are two types of overpotentials, concentration overpotential and activation overpotential. The latter is analogous to activation energy, in that it is the energy needed above the equilibrium value to cause the reaction to proceed. Concentration overpotential is related to the mass transport properties of the solution. At high current densities, metals plate faster, and are therefore depleted faster at the electrode interface. It is for this reason that concentration overpotentials are more dominant at higher current densities. In copper electrowinning the overpotentials at the anode and cathode are 0.6V and 0.05V, respectively [Davenport and Biswas 1976]. The high value at the anode is because gas bubbles (oxygen) must nucleate and grow on the
anode surface. Certain processes such as electroplating attempt to increase the overpotential of metal plating reactions. When complexing agents like cyanide or DETA are added to electroplating solutions, the required voltage is higher because the complexed copper ions are harder to recover from solution. Complexing agents are added because the higher voltages cause the copper deposit to be smoother and shinier, which is important, as electroplating is generally a final cosmetic step. The voltage for copper electrowinning can be calculated as:

\[ V_{\text{operating}} = V_{\text{reaction}} + V_{\text{resistance}} = 0.889 + 0.55 + 0.05 + 0.6 = 2.09V \]

2.3.1 Electrowinning of Metal – Amine Solutions

Although no literature could be found concerning the electrowinning (EW) of metal-amine complexes, several papers were found which discuss the electroplating (EP) of metal-amine complexes. The first is a series of papers published by Brockman et al. in 1936, dealing with “alkaline plating baths containing ethanolamines”.

The first paper discusses “copper plating from triethanolamine (TEA) solutions [Brockman and Brewer 1936]. One reason to attempt the plating of copper from TEA instead of cyanide is that copper will undergo ion exchange with an iron or steel surface in cyanide solutions, resulting in a poor surface for EP. Another reason is to eliminate the use of cyanide, (a highly toxic chemical) in EP baths. With TEA solutions no copper deposited by displacement and the resulting copper plates had high current efficiencies (CE), although some of the deposits tended to peel. Additionally, the EP solution was non-poisonous and had higher CE than any of the previously existing copper EP baths.

The next paper in the series: “a study of baths containing TEA for the direct nickel plating of zinc” [Brockman and Nowler 1936] showed that solutions of several different nickel salts produced excellent nickel plates on strip zinc. Drawbacks of this process include a very intricate cathode cleaning procedure and low cathode efficiency, generally between 20 and 50%.

Cobalt plating from TEA solutions [Brockman and Nowler 1936] was also investigated. Cobalt was successfully plated on copper, zinc, steel, and nickel. The best
cathode efficiency of 98% was obtained at a CD of 100 A/m². These values dropped rapidly to ca. 65% when the CD was increased.

The next paper was titled “the deposition of nickel cobalt alloys from solutions containing TEA” [Brockman and Nowler 1936]. Results showed that a wide range of alloys could be deposited (25 to 80% cobalt) at CDs ranging from 340 to 1550 A/m². The alloys deposited have the advantage of higher corrosion resistance than either of the metals alone.

The fifth paper was titled “copper plating from diethanolamine (DEA) solutions” [Brockman and Whitley 1937]. The copper deposits from these tests were satisfactory only upon the addition of sodium oxalate (Na₂C₂O₄), when the weight ratio was 3:1 CuSO₄·5H₂O to Na₂C₂O₄. Under these conditions the cathode CEs were all between 95 and 101%.

The final paper in the series discussed “copper plating from monoethanolamine (MEA) solutions” [Brockman and Tebeau 1938]. The results for these experiments were worse than for the tests with DEA, although again with the addition of sodium oxalate acceptable deposits were achieved. As the size of the amines decreased (TEA→DEA→MEA) the deposit quality worsened. No reason for this continual degradation was offered.

A second set of two papers was published by Brockman et al. in 1937 regarding the EP of copper from diethylenetriamine (DETA) [Brockman 1937] and ethylenediamine (EDA) [Brockman and Mote 1938]. These chemicals were chosen in an attempt to find complexing agents which could be used at higher concentrations and CDs and lower degrees of decomposition than the ethanolamines studied in the first set of papers. DETA was the first reagent tested, and good deposits were obtained from copper sulphate and DETA solutions. There appeared to be no decomposition of the DETA during the tests. It was also seen that if there was an excess of amine present the efficiency of deposition would decrease and the voltage would increase in order to maintain a constant CD. The CEs for these tests ran between 75 and 122% (cuprous ions depositing), while the CDs were between 46 to 410 A/m².
The second paper, on the same topic, substituted EDA for DETA [Brockman and Mote 1938]. As with the DETA solutions good deposits were obtained with CDs of 40 to 320 A/m², and CE between 88 and 117%.

Although the deposits described above were bright, had high CDs, were stable and had cathode efficiencies approaching 100%, they were invariably brittle and were therefore useless from a commercial EP standpoint. A paper by Greenspan titled “electrodeposition of bright copper” [Greenspan 1940] addressed this problem. It was found that with the appropriate addition of ammonium sulphate to the copper sulphate and DETA EP baths, the brittleness was eliminated. It is probable that in industrial operation ammonia would evaporate, and therefore ammonium sulphate additions would have to be periodically made. The paper postulated that the brittleness might be due to nitrogen in the copper deposit, possibly derived from the DETA or ammonium ions.
Chapter 3: Experimental

3.1 Copper – DETA System

3.1.1 Reagents

The reagents used, the source and the grades are given in Table 3.1.

Table 3.1: Reagents, Source and Grades for Copper Experiments

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Source</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>DETA</td>
<td>Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>CuSO₄·5H₂O</td>
<td>Aldrich</td>
<td>98+%</td>
</tr>
<tr>
<td>NaOH</td>
<td>Fisher</td>
<td>98.1%</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Fisher</td>
<td>95 – 98%</td>
</tr>
<tr>
<td>NaCl</td>
<td>Anachemia</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>BDH</td>
<td>99.4%</td>
</tr>
<tr>
<td>KNO₃</td>
<td>Fisher</td>
<td>99.5%</td>
</tr>
</tbody>
</table>

3.1.2 Equipment

The electrolytic cell consisted of a 1L beaker, with a magnetic stirring bar to increase electrolyte circulation. Test cathodes included aluminum, copper, and stainless steel (347), with stainless steel ultimately being chosen. Stainless steel was also chosen for the anode after trials with aluminum and lead proved unsuccessful. The cathode surface area was limited to 4000mm², by using an epoxy resin coating to render sections of the cathode inert. The surface of the cathode was roughened using sandpaper to aid metal adhesion, while the surface of the anode was roughened in an attempt to reduce the overpotential. The distance between the anode and cathode was 4.5cm.

The voltage and current were measured with two Escort model EDM-1105A multi-meters, and recorded manually during the course of the test. Time weighted averages were calculated for both parameters. The average current was used to calculate a theoretical weight of deposit according to Faraday’s law. This weight was compared to
the actual weight deposited to give the current efficiency. The current density was calculated by dividing the average current by the cathode surface area. This method was verified by comparison with a coulometer. The power was supplied by a Protek model 3000B DC power supply.

3.1.3 Electrolyte Solution

Batch Tests

This exploratory work consisted mainly of trial and error testing in the search for suitable electrowinning conditions. The electrolyte solution which produced acceptable results consisted of ca. 8 g/L copper (from copper sulphate pentahydrate), 32.5 g/L DETA (1:2 Cu:DETA molar ratio), and 5.8 g/L sodium chloride added to increase electrolyte conductivity. The difference in a 1L flask was made up from distilled water. Sodium hydroxide pellets were added to raise the pH above 12, again to increase the conductivity of the electrolyte. Other additions tested to increase conductivity, but not used ultimately, included sulphuric acid, sodium sulphate, and potassium nitrate.

Recycle Tests

These tests were carried out to study the response of copper-DETA complexes to recycling, i.e. simulating the real process. The final solution from a batch test was used as the feed for the subsequent test. The electrolyte solution was maintained at 10 g/L copper (from copper hydroxide), 32.5 g/L DETA, 5.8 g/L sodium chloride and the balance of a 1L flask made up from distilled water. Sodium hydroxide was occasionally added to reduce the applied voltage. Solution losses occurred because samples were taken during each test. The loss of solution was made up with fresh feed solution at the start of each cycle. The actual weight of copper won during the previous test was used to determine the amount of fresh copper hydroxide to add at the start of the next cycle.
3.1.4 Procedure
The cathode and anode were cleaned by immersion in nitric acid for several minutes to ensure the surfaces were free of residual copper from previous tests, oxidation products, or oils and grease. Then they were washed with tap water, dried, and weighed. This initial weight of the cathode was compared to the weight after electrowinning to determine the weight of the deposit. The initial and final weights of the anode were used to check if the anode was dissolving during the EW test. Fresh EW solutions were prepared the same day as the test was to be carried out, in accordance with section 3.1.3. The power supply, ammeter (in series), and voltmeter (in parallel) were connected to the cathode and anode as seen in Figure 3.1. The voltage was increased until the ammeter read 0.8A, or 200 A/m². The voltage would be adjusted many times during the test to insure a steady current flow, and the test would run for several hours. At the conclusion of the test, the voltage was turned off, and the electrodes removed from the solution. They were washed with distilled water and placed on a table to air-dry. Once dry they were weighed to determine the EW parameters. The EW solution was discarded at the end of the test (unless it was a recycle test).

3.1.5 Apparatus

![Experimental Set-Up](image)

- Dashed line: current flow (in series)
- Solid line: voltage measurement (in parallel)

Figure 3.1: Experimental Set-Up
3.2 Nickel – DETA System

3.2.1 Reagents

The reagents used, the source and the grades are given in Table 3.2.

Table 3.2: Reagents, Source and Grades for Nickel Experiments

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Source</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>DETA</td>
<td>Aldrich</td>
<td>99 %</td>
</tr>
<tr>
<td>NiSO₄·6H₂O</td>
<td>Aldrich</td>
<td>98+ %</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>Aldrich</td>
<td>99+ %</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Fisher</td>
<td>98 %</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>Aldrich</td>
<td>99+ %</td>
</tr>
</tbody>
</table>

3.2.2 Equipment

The electrolytic cell for the nickel testwork was the same as that used for the copper tests. The voltage was measured with an Escort model EDM-1105A multi-meter. The current was measured with a Keithley model 177 DMM multi-meter. Both were recorded manually during the course of the test, and time weighted averages were calculated for the two parameters. The current density and current efficiency were both calculated the same way as for the copper tests. The power was supplied by a model 620C-ELIT ATR rectifier, while the voltage was regulated with a type 3PN1010V Staco Energy Products Company voltage adjuster.

3.2.3 Electrolyte Solution

Batch Tests

The stability constants of nickel (k=18.5) and copper (k=16) with DETA are similar, so it was hoped that similar EW results would be obtained by substituting nickel for copper in the electrolyte. Unfortunately initial tests conducted with nickel concentrations of 10 g/L yielded very poor results (i.e. little to no nickel deposited). A new series of EW tests were performed using an electrolyte similar to industrial nickel EW, and gave very good results. This electrolyte contained 60 g/L nickel, 12 g/L sodium sulphate added to
increase conductivity, and 12 g/L boric acid which acted as a pH buffer. To determine the effect of nickel – DETA interactions during EW, the electrolyte was modified by adding 105.3 g/L DETA (1:1 Ni:DETA molar ratio). Undiluted sulphuric acid was added to adjust the pH.

Recycle Tests

These tests were carried out to study the response of nickel-DETA complexes to recycling. The final solution from a batch test was used as the feed for the subsequent test. The electrolyte solution was the same as that used for the batch tests. Solution losses due to sampling were made up with fresh feed solution at the start of each cycle. The actual weight of nickel won during the previous test was used to determine the amount of nickel sulphate to be added at the start of the next cycle.

3.2.4 Procedure

The procedure for the nickel-DETA EW tests was the same as the copper-DETA EW tests with the following exceptions:

- Solutions for each test were prepared the day before, because the large volumes of acid added, raised the temperature of the solution (~60°C)
- A lower current (0.6 A) and current density were used (145 A/m²)
- Test length was one hour for batch tests and four hours for recycle tests

3.3 DETA Analysis

Analysis for the concentration of DETA in solution was done by forming copper-DETA-sulphite complexes, adapting the procedure described by Gass et al. [1998]. These complexes show a UV absorption peak at 242 nm which varied linearly with the concentration of DETA throughout the 0-30 mg/L DETA range.

Similar analysis was performed for nickel-DETA solutions, where the peak was observed at approximately 285 nm.
Chapter 4: Results and Discussion

4.1 DETA Stability

Initially the stability of DETA in an electrowinning environment was assessed. This was checked by exposing a 46.9 g/L DETA solution in the electrowinning cell to a voltage. The voltage was set to 2 V for 20 minutes, after which a sample was taken for DETA concentration analysis. Bubbles were seen to form on both the cathode and anode, presumably hydrogen and oxygen gas, respectively. This procedure was repeated in 1 V intervals up to a voltage of 8 V, and a total time of 140 minutes. The results in Figure 4.1 indicate that DETA does not decompose even up to 8 V.

![Figure 4.1: Solution Concentration of DETA versus Applied Voltage](image)

4.2 Copper - DETA System

4.2.1 Choice of Electrodes

An aluminum anode and cathode were selected at first. High voltages (≈4) and low currents led to the conclusion that the solution resistance was too high. Sodium
chloride, sodium sulphate, and potassium nitrate, all at 1M, were used to reduce solution resistance. All three resulted in high current densities (514, 99, and 345 A/m², respectively), non-adherent copper deposits, and dissolution of the anode. The anode from the test where sodium chloride was added is shown in Figure 4.2. The reason for the corrosion was the high pH and current density, probably resulting in the formation of Al(OH)₄⁻. A lead anode was used in conjunction with 0.1M potassium nitrate in an attempt to overcome the anode dissolution problem, but with no success. Finally, stainless steel was used for both anode and cathode along with 0.1M sodium chloride, a combination that worked well, with good reproducibility. Sodium chloride was chosen because it gave the highest current density per mole of salt.

Figure 4.2: Corroded Al Anode
(1M NaCl, Current Density = 514 A/m²)

4.2.2 Batch Tests

Targets for the electrolysis conditions were 200 A/m² current density, 85% current efficiency, and 2.6 volts. The 2.6 V was based on the 2.1 V normally used for sulphate copper electrowinning plus an unknown for the voltage required to break the copper-DETA complex. After many tests, the electrolyte described in 3.1.3 gave results of 100.6% current efficiency, a current density of 194 A/m² (using an estimated deposit area), at an applied voltage of 2.52V. The pH was adjusted to approximately 12.2 by adding sodium hydroxide pellets. A test with twice the copper-DETA complex
concentration (ca. 16 g/L Cu) gave virtually the same values of voltage and current density. The copper deposit was adherent, but seemed to flake a little at the edges. It is assumed that with the addition of leveling agents to the electrolyte, a smooth deposit can be obtained, although the objective is environmental and not deposit quality. The copper itself was brittle, which prompted the analysis of the deposit for sulphur, carbon, nitrogen, and oxygen. The results of the analysis are given in Table 4.1.

Table 4.1: Analysis of Copper Deposited During Batch Tests

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>O (%)</th>
<th>N (%)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.35</td>
<td>0.513</td>
<td>0.244</td>
<td>0.002</td>
</tr>
<tr>
<td>2</td>
<td>0.45</td>
<td>0.480</td>
<td>0.315</td>
<td>0.002</td>
</tr>
</tbody>
</table>

The presence of carbon, nitrogen, and oxygen suggests that the DETA is not completely stable. The same problem was reported by Greenspan (1940) for the electroplating of copper from a copper-DETA complex. This problem was solved through the addition of ammonia to the electrolyte, which "completely eliminated the brittleness in these deposits". While not tried here, it is anticipated that ammonia additions will have the same effect.

4.2.3 Recycle Tests

For this process to be viable, the leachant (DETA) must be recyclable. A possible process flowsheet is given in Figure 4.3. To test for the stability of DETA a batch electrowinning test was performed and the resulting solution was used as the feed for a second cycle. It was assumed that the DETA would not decompose in these tests and that only copper would have to be replaced. At the end of a test, the weight of copper electrowon from solution was calculated. This weight was used to calculate the amount of copper hydroxide needed for the next leach/electrowin cycle. This copper hydroxide was added, along with any fresh solution needed to make up the 1 L volume of the cell and the next cycle run.
The solution was recycled three times resulting in four tests. The first test was run at a current density of 195.7 A/m² and a voltage of 2.48 V. The current densities for the three subsequent tests were decreased to an average of 155.4 A/m² for an average voltage of 2.47 V. The average current efficiency for the tests was 100%. The pH was not controlled since the addition of copper hydroxide instead of copper sulphate was sufficient to raise the pH of the solution above 12.2.

The deposit for the first test was adherent but appeared "shredded", suggesting the current density was too high for the solution conditions. The copper deposit pulled away from the cathode in strips near the edges of the cathode. The reason for this was probably because the copper was added as copper hydroxide for the recycle tests as opposed to copper sulphate for the batch tests, resulting in a lower solution conductivity. Consequently, the current density was reduced to 160 A/m² for the three subsequent cycles. There was an immediate improvement in the deposit, which was quite rough but firmly adhered to the cathode. As the tests progressed, the deposit quality did decrease, becoming rougher and darker. This may also be due to a reduction in the conductivity of the solution.

Samples were taken during the tests and assayed for DETA to determine if the extractant was being recycled. The results are given in Figure 4.4, which shows the concentration decreased to a steady state value of approximately 21 g/L. This most likely reflects a build-up of decomposition products in the electrolyte. Possibly the addition of ammonia to the electrolyte suggested to eliminate cathode deposit brittleness could also
act to reduce the decrease in DETA concentration. It may also be that the equilibrium concentration of DETA with these electrochemical conditions is roughly 21 g/L. This will be more thoroughly examined in future investigations. In any event, it is evident that a steady state is reached, indicating that DETA can be recycled.

The decrease in DETA concentration corresponds to a decrease in copper-DETA complex concentration. The effects of this would be to lower the solution conductivity and cause a rougher surface deposit. This is what occurred with the deposits in the recycle tests.

![DETA Concentration vs Time](image)

**Figure 4.4: DETA Concentration for the Four Recycle Tests Versus Time**

Note: the dashed lines indicate start / stop of each cycle

### 4.2.4 Power Comparison

Although the voltage required for the EW of copper from DETA complexes is higher than in industrial copper sulphate EW, the CE is also higher. If the power required to produce 1kg of copper from two processes are compared using Faraday's equation

\[
Power = \frac{Voltage \times zF \times 1kg}{CE \times MM}
\]

where: 
- \( z \) = the charge of the ion being deposited
- \( F \) = Faraday's constant = 96500
- \( MM \) = the molecular mass of the ion being deposited
it is seen that the power requirements are the same.

<table>
<thead>
<tr>
<th></th>
<th>Sulphate EW</th>
<th>Batch DETA EW</th>
<th>Recycle DETA EW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current Density</td>
<td>200</td>
<td>200</td>
<td>160</td>
</tr>
<tr>
<td>Applied Voltage</td>
<td>2.1</td>
<td>2.52</td>
<td>2.47</td>
</tr>
<tr>
<td>Power (kWh / kg Cu)</td>
<td>2.08</td>
<td>2.13</td>
<td>2.08</td>
</tr>
</tbody>
</table>

4.3 Nickel – DETA System

4.3.1 Choice of Electrodes

Stainless steel was used for both the anode and cathode, since they had proved effective in the case of copper electrowinning.

4.3.2 Batch Tests

By examination of complex stability constants discussed in chapter 2, for copper (k=16) and nickel – DETA (k=18.5), it was assumed that simply substituting nickel ions for copper ions in solution would allow nickel to be electrowon under similar conditions. Unfortunately, such tests were unsuccessful. In an attempt to better understand the system, the reaction necessary for the electrowinning of nickel was considered:

\[
\text{DETA-Ni}^{2+} + H^+ \rightarrow \text{DETA-H}^+ + \text{Ni}^{2+}
\]

Essentially the nickel – DETA complex undergoes ion transfer between nickel and hydrogen. Therefore, the pH of the solution is an important factor in the EW behavior of the solutions.

4.3.2.1 pH

As the pH of the solution is increased, the DETA molecule will undergo a series of complexation stages, as seen in Figure 4.5.

Since the initial tests were run at pH's of 12, it is expected that the nickel ions were strongly complexed with DETA molecules. This would require substantial energy to liberate the nickel ions for subsequent EW. Tests were done to determine the pH at which the “first degree of complexation” occurs, i.e. equation 4.1.
Figure 4.5: Examples of Changing DETA Complexation with Increasing pH

The total nickel concentration was varied and the pH of first degree of complexation was determined visually. There is a transition from a very dark murky green colour to a clear light green colour during the transition of Ni – DETA to H – DETA. The results for that series of tests are presented in Figure 4.6. The trend shows a decreasing pH as the nickel concentration increases, which is expected from equation 4.1

Figure 4.6: pH for First Degree of Complexation versus Nickel Concentration

In an attempt to increase the possibility of EW from a nickel – DETA solution, conditions similar to industrial nickel sulphate EW were chosen, namely 12 g/l boric acid, 12 g/l sodium sulphate, and 60 g/l nickel sulphate [Kuzeci et al.]. By extrapolation of the plot
in Figure 4.6, the pH where the first degree of complexation occurs for a solution containing 60 g/l nickel (=1 mol/l) is approximately 3. Therefore the ideal pH for the EW of the nickel – DETA solutions would be just above a pH of 3, since the nickel would still be complexed with DETA, but be ready to undergo exchange with hydrogen ions. The complication is that there also exists a competition for reduction at the surface of the cathode between nickel and hydrogen. Figure 4.7 shows the position of the reduction potential lines for nickel, copper, and hydrogen. The higher along the y-axis, the more likely the reaction is to occur. Clearly, the deposition of copper is favored at all pH’s, while nickel deposition is favored only at pH’s above 3.9. The optimum pH will therefore be a

![Graph showing reduction potential lines for Cu, Ni, and H versus pH](image)

Figure 4.7: Reduction Potential Lines for Cu, Ni, and H versus pH

balance between two competing needs - to increase the pH to inhibit hydrogen gas evolution at the cathode, and to keep the pH below 5.1, which corresponds to the second degree of complexation of the nickel ion (DETA-Ni → DETA₂-Ni, [Ni]_{total} = 60g/L).

A series of tests was performed to determine the EW efficiency in the pH range of 4 to 5.5. These tests showed it was possible to recover nickel from complexes with DETA, and the results of this testwork are given in Figure 4.8. It is evident that there is a
pH range of 4.6 to 4.8 where the current efficiency (CE) is maximized. This range was chosen as the baseline for subsequent experiments. The average EW parameters for this range were a current of 0.59A, an applied voltage of 2.96V, a current efficiency 44.6%, and a current density of 145 A/m$^2$.

### 4.3.2.2 Nickel Concentration

Equation 4.1 shows the importance of both nickel and hydrogen ion concentration during EW. Since the initial testwork performed on the leaching of metal hydroxides showed a maximum nickel concentration of 52.6 g/l, experiments varying nickel concentration were performed. Figure 4.9 shows the results of varying the nickel concentration from 20 to 60 g/l. The concentration of sodium sulphate in solution was varied to keep the sulphate ion concentration constant, in an attempt to keep the solution conductivity constant. The results show that as the nickel concentration drops, so does the current efficiency. This is a well known effect in electrowinning and is due to a lower nickel ion concentration gradient from the surface of the cathode to the bulk solution.
Since the gradient is lower, more power is required to drive nickel ions from the bulk solution to the surface of the cathode. At the same time, the hydrogen ion concentration is constant, and combined with the higher voltage needed (tests run at constant current density) the proportion of hydrogen gas evolved at the cathode is higher. Ideally, the concentration of nickel in solution should be as high as possible.

4.3.2.3 Temperature

Temperature is an important variable in controlling the solution conductivity, and to a lesser extent, the reaction potentials, as seen from the following equation:

\[ e = e^o - \frac{RT}{zF} \ln \left( \frac{a_{\text{products}}}{a_{\text{reactants}}} \right) \]

Both of these effects can lower the applied voltage of the cell.

Tests were done with the temperature ranging from 25 to 65°C, and the results are shown in Figure 4.10. There is a large improvement in current efficiency as the
Figure 4.10: Variation of Current Efficiency and Voltage with Temperature

As the temperature is increased, and appears to be approaching 100% as the temperature approaches 70°C. The reason for this increase in current efficiency stems from the decrease in applied voltage seen in Figure 4.10. For all other batch tests, the voltage was constant, ranging from 2.95 to 3.05. Upon a drop in voltage, there is less drive for hydrogen gas evolution from the cathode, and therefore its production decreases. Since evolution of hydrogen gas consumes current from the cathode, this reduction results in more current being available for nickel production. Hence, the current efficiency increases. Ideally, the temperature of the solution should be high to minimize cell voltage. Unfortunately heating the solution is costly, and therefore a balance must be struck. As the goal is to clean up an environmental problem, more interest will likely be paid to the lower temperature region.
4.3.2.4 DETA Concentration

Initial testwork performed on the leaching of metal hydroxides with DETA was done with a DETA to metal ratio of 2:1. Since the baseline nickel EW tests were performed with a ratio of 1:1, the effect of electrowinning with a ratio of 2:1 was of interest. As can be seen from Figure 4.11, there is a large decrease in the current efficiency, from 45 to 24%. This is because the excess DETA molecules cause the stability of the nickel – DETA complexes to increase. This could be from either increased stability of the complexes or new complexes being formed. Additionally, the pH of the first and second degrees of complexation will be shifted. Therefore, a new series of current versus pH would have to be run in order to determine where the ideal pH to EW with a 2:1 ratio is located.

4.2.3 Recycle Tests

As with the copper – DETA system, the effect of recycling the EW solution was examined. Four cycles were performed, each four hours long. Although the values of the
voltage and current were virtually constant throughout, the current efficiency dropped from test to test, as shown in Figure 4.12.

Figure 4.12: Variation of Current Efficiency versus Recycle Test Number

The initial value was lower than expected based on the previous batch tests, 33% versus 45% (possibly due to a new batch of DETA being used), and declined to 15% by cycle number four. The trend does not appear to be reaching any asymptotic value, and the EW solution used is probably not suitable for recycling.

The quality of the deposit for each test appeared to be constant, only with less weight deposited from test to test.

Samples were drawn every hour during each test. A change in colour (progressively darker shades of clear green) occurred over the first one and a half cycles, but was constant from then on. The samples were left sealed in the lab for two weeks after the final test, and turned a very dark murky green. What this is due to is not known, possibly the DETA decomposed and nickel hydroxide was formed. Analysis of these samples showed DETA concentrations had decreased from ca. 100 g/l in the feed solution to ca. 10 g/l.
This problem can probably be overcome. Since the concentration of DETA reached a steady value in the copper EW system, it is stable in an EW environment. Therefore DETA should be stable in a nickel EW system, under the right conditions. The origin of the problem is more likely chemical in nature, and with the right additives, a recycle process should be feasible.
Chapter 5: Conclusions and Recommendations

5.1 Conclusions

DETA Stability

A batch test showed that DETA was stable for a wide range of applied voltages. Copper – DETA recycle tests showed that the concentration of DETA decreased to a stable value, while nickel – DETA tests were inconclusive.

Copper – DETA Batch Tests

Brittle high grade (~99%) copper was deposited on a stainless steel cathode from a 10 g/l copper solution at 100% CE, 194 A/m² CD, 2.52 V, and a pH of 12.2.

The brittleness in the deposited copper was due to the presence of carbon (0.4%), oxygen (0.5%), and nitrogen (0.28%).

Copper – DETA Recycle Tests

After approximately six hours, the concentration of DETA in solution fell to a stable value of ca. 21 g/l from an initial value of ca. 32 g/l.

The copper deposit quality was similar to the batch tests. The electrowinning conditions were 100% CE, 155 A/m² CD, 2.47 V, and a pH of at least 12.2.

Power Comparison

Power consumption for the copper – DETA solutions (2.13 for batch, 2.08 kWh / kg Cu for recycle) were comparable to the power used to electrowin copper from industrial copper sulphate solutions (2.08 kWh / kg Cu).

Nickel – DETA Batch Tests

Brittle nickel deposits were obtained on a stainless steel cathode from a 60 g/l nickel solution at 44.6% CE, 145 A/m² CD, 2.96 volts, in a pH range of 4.6 – 4.8.
The pH range of 4.6 – 4.8 had the maximum CE for the conditions tested due to a competition between hydrogen formation at lower pH and higher degrees of complexation and increased complex stability at higher pH.

Decreasing the nickel concentration lowered the CE.
Increasing the temperature improved the CE to near 100% at 65°C.
Increasing the nickel to DETA ratio from 1:1 to 1:2 decreased the CE from ca. 45% to ca. 24%.

**Nickel – DETA Recycle Tests**

A brittle deposit was obtained from a 60 g/l nickel solution at 148 A/m² CD, 3.02 V, and a pH of ca. 4.7. The CE continually dropped from an initial value of 33% to 15% and did not appear to achieve a steady value.

Samples of the electrowinning solution drawn during the tests degraded, preventing an accurate determination of DETA concentration.

**5.2 Recommendations**

**Copper – DETA System**

Excellent results were obtained for this system. The main item that needs to be addressed is the decomposition of the DETA. It is anticipated that the addition of ammonia to the electrowinning solution will prevent the decomposition of DETA. If this proves successful, the remaining obstacle for an industrial process may be the solid–liquid separation step. Since the initial feed is very fine and amorphous, it is difficult to settle. After leaching, the resulting solids would likely be more difficult to settle and filter. Another difficulty is that residual DETA solution would be carried with the solids, so washing the filtered solids would be mandatory. This would cause an increase in the volume of the recirculating solution. Possible solutions are to:

- Combine the DETA complexes with a collector (xanthate) and perform ion flotation, which would greatly decrease the volume of the solution which is being recycled. This would unfortunately add additional chemicals of unknown effect on the electrowinning performance.
Increase the temperature of the solution such that the rate of evaporation of water was equal to the rate of wash water addition. This would reduce voltage and power requirements of the process, but energy would need to be supplied to heat the EW solution.

Tests with higher concentrations of copper – DETA complexes should be considered since the maximum concentration obtainable from literature was 46.4 g/L, and only 10 g/L was tested. This higher concentration would reduce the voltage and power requirements for electrowinning, as it did for the nickel batch tests.

It might also be beneficial to investigate copper electrowinning at lower pH’s, where the copper ions may not be as strongly complexed, as was the case for nickel electrowinning.

**Nickel – DETA System**

Some type of additive is required to promote the stability of DETA in this system. Since DETA reached a stable concentration in the copper system, there is good reason to believe that it should in the nickel system as well. With the proper solution chemistry this problem should be solved.

The same water balance issues brought up in the copper system apply to the nickel system.

**Additional**

The nickel system is inherently more complex than the copper system, but the work presented has shown that the objectives of the research have been met. Namely, to recover copper or nickel from their respective complexes with DETA.

An interesting series of tests would be to see what happens when complexes of both copper and nickel are present in the electrowinning solution. Copper should plate first and at a lower voltage. Using this fact it may be possible to first recover a high grade copper deposit at a low voltage, and then an alloy of the two metals at a voltage where nickel would plate.

Since zinc is frequently found in AMD sludges, the ability to electrowin from zinc – DETA complexes should be examined.
The tests performed on leaching of AMD sludges reported in the literature involved artificially produced sludges. If the previously discussed problems can be solved a lab scale or pilot plant should be constructed, using real AMD sludge and long-term recirculation of the EW solution.

Other chelating agents that have lower stability constants with nickel could be used, such as TETA.
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