STUDY ON METALS RECOVERY/RECYCLING FROM ACID MINE DRAINAGE
PHASE IA: LITERATURE SURVEY

For: MEND Treatment Committee

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EXECUTIVE SUMMARY

Removal and recycling of metal contaminants and other by-products from acid mine drainage is the subject of this MEND project. Critical literature surveys and investigations in several selected research alternatives such as chemical treatment (that is modifications to lime neutralization), solvent extraction, ion exchange, bioadsorption and electrowinning, are aimed at the development of a viable treatment process. The technical and economic feasibility of the techniques will be evaluated, in search of a process that produces a high quality effluent, secures a satisfactory revenue and minimizes/eliminates hazardous sludge production.

A literature review was carried out by CANMET scientists from four different disciplines in the field of metals and/or by-products recovery from acidic mineral effluents. Existing expertise from the application of these technologies in related fields in mineral processing, as well as preliminary results from investigations with acidic mineral effluents have been utilized to evaluate selected publications and to determine the most promising process approaches. A preliminary compilation of data in acidic mineral effluents in Canada has been made, with particular interest in high metal concentrations.

Discussion provided in this report supports the opinion that the recovery of metals and/or by-products from acid mine drainage is a promising treatment approach from a technical, economical and environmental point of view. Detailed laboratory investigations should follow to study the recovery of various by-products, to develop a treatment process flowsheet and to evaluate the economical and environmental benefits. Samples from two milling operations should be selected to carry out the tests.

Keywords: acid mine drainage, treatment, metal contaminants, removal, recycling, biosorption, chemical treatment, electrowinning, ion exchange, solvent extraction

SOMMAIRE

Ce projet du Programme de neutralisation des eaux de drainage dans l'environnement minier (MEND) a pour objectif d'éliminer des eaux de mine acides les contaminants métalliques et autres sous-produits, et de les recycler. Les examens critiques de la documentation scientifique et les recherches relatives à plusieurs autres thèmes sélectionnés d'études, tels que les traitements chimiques (à savoir les modifications de la neutralisation par la chaux), l'extraction par des solvants, l'échange ionique, la bioadsorption et l'extraction électrolytique, ont pour but la mise au point d'un procédé de traitement valable. On cherchera à évaluer la faisabilité technique et économique de ces procédés, pour trouver une méthode qui permette d'obtenir un effluent de haute qualité, assure des revenus satisfaisants et permette de minimiser ou d'éliminer la production de boues résiduaires dangereuses

Des chercheurs de CANMET, spécialistes de quatre différentes disciplines dans le domaine de la récupération des métaux ou des sous-produits de la récupération, ou des deux à la fois, à partir des effluents minéraux acides, ont passé en revue la documentation scientifique à ce sujet. On a utilisé les compétences existantes, acquises lors de l'application de ces technologies à des domaines connexes du traitement des minéraux, ainsi que les résultats préliminaires fournis par les recherches sur des effluents minéraux acides, pour évaluer les publications sélectionnées et pour déterminer les méthodes les plus prometteuses. On a réalisé une compilation préliminaire des données sur les effluents minéraux du Canada, surtout dans le cas des concentrations métalliques élevées.

L'étude contenue dans ce rapport confirme l'opinion selon laquelle la récupération des métaux ou des sous-produits, ou des deux, dans les eaux de mine acides, serait un procédé de traitement prometteur des points de vue technique, commercial et écologique. Il faudrait ensuite entreprendre des recherches détaillées en laboratoire pour étudier la récupération de divers sous-produits, pour mettre au point un schéma de principe du procédé de traitement et pour évaluer les avantages économiques et écologiques du procédé. On doit également sélectionner des échantillons provenant de deux opérations de broyage du minerai pour exécuter les essais.

Mots-clés: eaux de mine acides, traitement, contaminants métalliques, élimination, recyclage, biosorption, traitement chimique, extraction électrolytique, échange ionique, extraction par solvants.

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INTRODUCTION

Waste disposal sites that contain billions of tonnes of acid generating sulphide tailings are found throughout Canada (1-4). At active (and some inactive) mine sites comprehensive systems to collect and treat effluents and seepage from all sources are operated. These facilities, under favourable conditions are sufficient to prevent downstream environmental impact. Since acid generation may persist for hundreds of years following mine closure, disasters may occur unexpectedly when maintenance is neglected.

The cost of stabilizing reactive wastes is highly site specific, and thus will vary from site to site. The estimated costs of stabilizing some sites with existing but unproven technologies are as high as $410,000 per hectare, while an average cost is $125,000 per hectare. A rough estimation of reclamation costs for existing and future accumulation of acid generating waste at non-ferrous metal mine sites reaches an astounding $3 billion over the next twenty years. To this amount, about $1 billion should be added for abandoned sites (1). These expenses add to the overall mining costs and pose a long term liability to mill operation.

It is well established that the formation of acidic conditions is due to the oxidation of iron sulphide minerals contained in sulphide tailings. These minerals, principally pyrite (FeS_2) and pyrrhotite ($Fe_{1-x}S$), are associated with base metals, uranium and precious metals extraction operations. Acid formation requires exposure of the minerals to oxygen (air) and moisture, and is enhanced by the presence of certain microorganisms (2).

Acidic drainage may contain very high concentrations of sulphate and ferrous ions. High concentrations of base metals such as copper, nickel, zinc, aluminum, or cadmium, are encountered at pH values significantly below 7. If acidic drainage is left uncollected and untreated, the drainage could contaminate groundwater and local watercourses, damaging the health of plants, wildlife, and fish (1). Attempts to prevent AMD generation have proven to be extremely difficult despite years of research and costly reclamation measures.

1.1 Conventional Treatment Technology

Acidic mineral effluents are treated to meet federal and provincial threshold values by removing suspended solids, neutralizing free acidity and removing iron and other metals, particularly arsenic, copper, lead, nickel, cadmium and zinc. In Table 1 the regulations for two provinces of Canada as well as federal regulations in Canada and the U.S. (3) are listed. Provincial requirements are stricter in certain cases, while scientific knowledge and public pressure continue to demand further reductions of acceptable metal concentrations and inclusion of new substances in the regulations list.

Table 1. Comparative Mining Effluent Regulations* (3)

Parameter	Canada					USEPA
	Federal, Total Metals, mg/L	Ontario, Total Metals, mg/L	British Columbia, Dissolved Metals, mg/L			Total Metals, mg/L
			A	B	C	
Arsenic	0.50	Not to exceed 1 individually or together				
Copper	0.30		0.05	0.30	1.00	0.05
Lead	0.20		0.05	0.10	0.50	0.20
Nickel	0.50		0.30	0.50	1.00	
Zinc	0.50		0.50	5.00	10.00	*mill* 0.20 *mine* 0.50
Suspended solids	25.0	15.0	50.0	150		20
^{226}Ra (pCi/L)	10.0	3.0				3.0
pH	6.0 or higher	5.5 to 10.6	6.5 to 8.5	6.5 to 9.5	6.0 to 10.0	6.0 to 9.0

*Figures given are monthly averages and represent total, (not dissolved) values, except for British Columbia and ^{226}Ra. A = objectives for new mines, B = upgraded objectives for new mines, C = objectives for existing mines, to attain immediately.

The Canadian industry, at present, is trying to meet these regulations by utilizing lime neutralization technology, which is considered the "Best Available Technology Economically Achievable". This technology involves:

- neutralization of the effluent with hydrated lime ($Ca(OH)_2$)
- oxidation of ferrous iron under alkaline conditions by aeration
- precipitation of ferric iron and base metals at pH of 9 to 10, and
- clarification following coagulant/flocculant addition.

Lime neutralization is used at both active and abandoned mining operations throughout Canada, producing a voluminous sludge that contains the metal contaminants mainly as metal hydroxides.

The precipitation of heavy metal hydroxides can be predicted by using standard solubility relationships. Figure 1 shows the expected metal concentrations at various solution pHs (5). Many heavy metal hydroxides exhibit minimum solubility at a distinct pH level that can be determined from the solubility product and chemical equilibrium relationships of the appropriate chemical species. The possibility of theoretically deriving precise values for dissolved metal ions is limited (6), due to the extremely broad range of soluble species for most of the metallic salts and the unknown activity coefficients at various temperatures and at high ionic strength of the effluents.

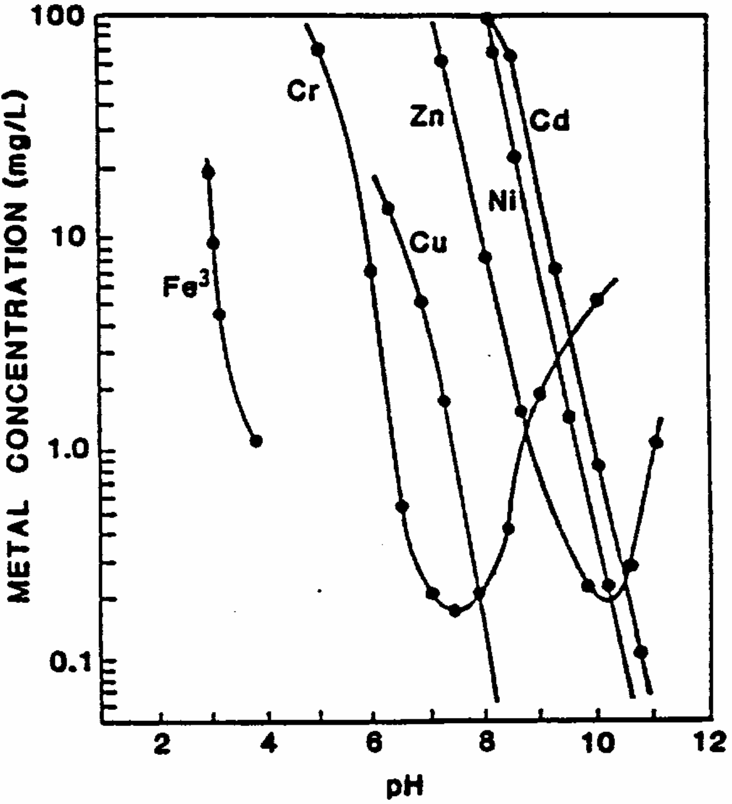


Figure 1. Precipitation of Heavy Metals as Hydroxides (5).

The annual volume of sludge generated by Canadian mineral industry treatment facilities exceeds 150,000 dry tonnes/year and is mainly produced by the base metal industry. In work performed for CANMET (7) it was found that sludge densities varied from 0.5% to 79% total solids, depending on whether or not sludge recycling was practised. Studies using a variety of leaching media were carried out to evaluate contaminant release from mineral industry effluent treatment sludges. A comparison of leach solution concentrations to the Quebec regulatory levels for hazardous wastes indicated that Zn, Ni, Cd, Cu and Pb exceeded the requirements in up to 50% of the sludge samples tested (7,8).

The low cost of lime and the precipitation of many species are the main advantages of lime neutralization (9). However, the high maintenance requirements, the instability of the large volume of sludge produced, and the introduction of stricter environmental standards dictate the need for an alternative approach to effluent treatment. Moreover, the long-term costs of AMD treatment justify a comprehensive investigation of metals and by-products recovery for revenue generation. This research approach does not minimize the importance of research on other unit processes, such as solids/liquid separation, gas contacting, agitation, settling, and reagent addition.

Numerous technologies for treating acid mine drainage and wastewaters have been proposed and detailed descriptions are presented elsewhere (3, 6, 8-25).

1.2 Alternative Treatment Technologies

While lime neutralization is the conventional treatment technology for acidic mineral effluents, there is a wide range of technologies available for treating acid mine drainage before discharge including some new and yet to be proven techniques (e.g. electrodialysis, liquid membranes, etc.). Significant attention has been directed towards metals recovery and sludge recycling to smelters with limited success (8, 9, 26). As a result, potentially recoverable metal values still report to disposable sludge. For example, at a specific mine site in British Columbia, AMD carries approximately 100,000 kg of Cu per year with an estimated value of $250,000. Similar quantities of Zn and Cd are also present. Table 2 summarizes important information on chemical characteristics of selected acidic mineral effluents in Canada. The focus in this survey is on high metal concentrations, where metal and by-product recovery is potentially feasible.

Table 2 shows that there are sites with relatively high copper concentrations (exceeding 200 mg/L), high zinc concentrations (exceeding 1 g/L) and very high iron and sulphate concentrations (several g/L). There is insufficient information on the Fe^{2+}/Fe^{3+} ratio in the acidic mineral effluents and existing data are rather unreliable, since high Fe^{2+} concentrations are suspected in the effluents. Solution acidity is related to hydrolyzing cations and the natural pH has been reported by as low as 1.8.

Table 2. Chemical Characteristics of Selected Acidic Mineral Effluents in Canada

Company	Cu	Pb	Zn	Ni	Al	Fe_{total}	Fe^{2+}	SO_4^{2-}	pH	Acidity (mg $CaCO_3$/L)	Susp. Solids (mg/L)	Flowrate (m^3/hr)
	(mg/L)											
Brunswick Mining (underground) (7,27)	9.57	2.58	1,027	NA	NA	1,202	NA	8,591	2.71	6,955	186	800
Brunswick Mining (surface) (7,27)	49.2	1.16	538	NA	NA	718	NA	4,454	2.73	4,200	65.0	280
Heath Steele Mines (27)	19.9	1.31	105	NA	NA	68.7	NA	1,018	3.01	746	3,007	NA
Equity Silver Mines (overall) (28,29)	125.8	NA	79	NA	1,000	1,028	46.5	8,800	2.46	8,700	NA	80
Equity Silver Mines (waste rock) (30)	791	NA	350	NA	NA	NA	NA	NA	2.4	44,100	NA	NA
Gibraltar (waste rock) (30)	257	NA	NA	NA	183	71	NA	NA	3.1	2,675	NA	NA
Westmin (open pit) (30)	10	NA	51	NA	20	72	NA	NA	3.0	423	NA	NA
Westmin (waste rock) (30)	13	NA	74	NA	36	9.5	NA	NA	3.8	397	NA	NA
Sullivan (tailings) (7,30,31)	NA	5.3	76	NA	71	817	NA	NA	2.7	995	75	1,000
Britannia (mine) (30)	43	NA	32	NA	NA	45	NA	NA	2.7	494	NA	NA

NA - not available

Table 2 (Cont'd)

Company	Cu	Pb	Zn	Ni	Al	Fe_{total}	Fe^{2+}	SO_4^{2-}	pH	Acidity (mg $CaCO_3$/L)	Susp. Solids (mg/L)	Flowrate (m^3/hr)
	(mg/L)											
Duthie (tailings) (30)	138	NA	1,360	NA	NA	13,300	NA	NA	1.9	NA	NA	NA
Anyox (tailings) (30)	3.1	NA	5.9	NA	150	1,650	NA	NA	NA	NA	NA	NA
Mt. Washington (waste rock) (30)	77	NA	NA	NA	50	7.2	NA	NA	3.4	431	NA	NA
Wedge Mine (closed) (32)	55	NA	580	NA	NA	2,100	NA	NA	3.5	NA	NA	NA
Les Mines Gallen (33)	0.26	NA	530	NA	NA	865	NA	NA	3.5	NA	NA	NA
Chester Mine (23)	100	NA	100	NA	NA	300	NA	NA	NA	NA	NA	NA
GECO (23)	3.4	NA	120	NA	NA	460	NA	NA	3.9	NA	NA	NA
Inco Nolin Creek (34)	6.7	NA	NA	19.8	NA	35.6	NA	NA	4.3	NA	NA	1,500
Mattabi Mines (waste rock) (35)	715	3.8	4,480	0.5	751	1,630	NA	18,387	2.2	NA	NA	NA
Mattabi Mines (tailings) (35)	19	4.2	1,630	2.1	61	2,360	NA	7,528	1.8	NA	NA	NA

Metals cannot be destroyed and unless recovered they end up in a lime sludge which still presents a disposal problem. Consequently, emphasis is shifted to treatment techniques which facilitate the recovery of metal contaminants and other by-products from acid mine drainage. This is the focus of this project, where investigations into selected treatment technologies may lead to economically attractive alternatives. The Phase I (a) report is based on a literature review of these treatment technologies. This rather narrow project scope has been selected following consultations with MEND members. The possible need of pre-concentration (e.g. by freeze desalination, reverse osmosis, etc.) and polishing steps (e.g. wetlands, ion exchange, sulphide precipitation, sodium borohydride addition, carbon and peat adsorption, etc.) should be tested and evaluated in other projects.

Four process technologies have been selected for further evaluation, based on their development potential by CANMET. These process technologies will contribute to the development of an overall treatment flowsheet. The technologies under investigation are: a) biosorption of metals, b) chemical treatment, c) electrowinning and d) ion exchange and solvent extraction.

2.0 BIOSORPTION OF METALS

Some microorganisms and aquatic and terrestial plants have the ability to accumulate heavy metals to levels that exceed normal background concentrations. Such metal enrichment by biological systems has been used to detect environmental contaminations and to prospect for subsurface ore deposits. Biological systems accumulate heavy metals by three distinct mechanisms:

- bioaccumulation - in this process the metal ions are taken across the cellular membranes and may be bound intracellularly by metallothionines or may be metabolically reduced to a non-toxic valence state;
- physical entrapment - due to the protective slime layer or extracellular capsule produced by aquatic plants and microorganisms, suspended solids containing metal ions may be incorporated in or adhere on the capsular or slime material;
- biosorption - the cellular wall of both plants and microorganisms contains many anionic charged groups which may react with metal ions, thus this mechanism is dependent on the cation exchange capacity of the cell wall components.

2.1 Aquatic Plants and Algae

In 1973, Gale et al. reported that aquatic plants exposed to effluents of lead mines in the Missouri Lead Belt could accumulate high concentrations of heavy metals. Later, Gale and Wixson (1978) reported that the loading capacity of several aquatic algae ranged from 505-836 ppm lead, 510-695 ppm of zinc, 39-46 ppm of copper and 10,353-14,287 ppm of manganese when exposed to a lead smelter effluent.

Kalin (1991) reported the successful use of biological polishing with macrophytic algae in the effluents of a zinc/copper mine in northern Ontario. After implementation of the biological polishing the zinc concentrations in the Decant Pond have been reduced to less than 5 mg/L which is much lower than the levels obtainable with liming alone. Kalin (1988) has also implemented the use of "Chara" in the biological polishing of alkaline mine effluents and have shown that this macrophyte will accumulate significant quantities of uranium, radium 226, nickel and copper. Their efforts are now concentrated on the development of biological polishing systems for acidic mine drainage.

P. Lane and Associates (1991) have shown that species indigenous to an abandoned gold mill tailings accumulate as much as 10,000 ppm As and 16 ppm Hg in their tissues. Campylium stellata (a moss) accumulated high levels of metals, 4,000 ppm arsenic and 7.7 ppm of mercury. Of the terrestrial plants, horsetails and cattails accumulated the largest quantities of As and Hg, but growth is suppressed as the metals accumulated in the plant tissue.

Darnall et al. (1989) have reported on the use of a commercially available immobilized algal absorbant to recover precious metals from geothermal waters and for the recovery of base metals from contaminated groundwater. The new immobilized algal absorbant was specially formulated for high temperature tolerance (greater than 165°C) for the recovery of metals from geothermal waters. About 90% of the gold was recovered from geothermal waters at 190°C through 14 loading and elution cycles. Further studies showed that both Ag and Pt, present in the ppb range, where completely bound by the algal absorbant. Base metals (Cd, Cu and Hg) were removed from contaminated groundwater containing trichloroethylene and dichloroethylene using algal absorbant. In all cases the effluent after treatment met drinking water guidelines in regard to metal content.

2.2 Fungi and Yeasts

As environmental concerns are raised regarding the release of toxic metal ions into the environment from mining and milling operations, the number of research groups assessing biosorption as an economic means of removing metals from solution and possibly recovering the metals has increased exponentially. Most groups have concentrated their efforts on the use of fungi and yeasts as biosorbants for several reasons. Many pharmaceutical and food industry processes produce fungal and yeast biomass as a waste product that could be acquired very economically. Secondly, yeast and fungi are easily cultured and can utilize wastes from other industries as nutrients. Thirdly, compared to bacterial growth, large volumes of biomass can be produced quickly.

Townsley et al. (1986) reported that Penicillium spinulosum and Aspergillus niger, two filamentous fungi, could remove up to 99% of the heavy metals from contaminated effluents. One of the effluents tested contained 43 ppm copper, the other contained 14.5 ppm gold, 0.3 ppm silver and 40. 5 ppm copper. These effluents had to be neutralized to pH 5.0 to 5.5 to obtain maximum loading, but temperature had little or no effect on the metal removal capability of the biomass. Metal loading was reduced by 25% at pH 3.5 and was reduced by about 80% at pH 2.0.

Ross and Townsley (1986) reported that detergent treatment of fungal biomass greatly increased the loading capacity for copper and to a lesser extent increased the loading of cadmium at pH 5.5. However, these studies were carried out using mono-metallic solutions in a physiological buffer.

Townsley et al. (1986) reported that Trichoderma virides biomass on a molochite column could remove about 75% of the copper from a chalcopyrite bacterial leach liquor containing 6-127 ppm of copper. The copper could be recovered from the biomass by elution with 1M HCl. However, Tsezos (1986) has presented evidence that dilute mineral acids destroy the biomass and a sequential reduction in the loading capacity occurs following elution with mineral acids.

Kiff and Little (1986) grew Aspergillus oryzae on the surface of foam support particles which were placed in a glass column for the removal of cadmium from a mono-metallic solution. The initial solution contained 1 ppm of cadmium sulphate and the maximum loading of the fungal biomass was 2 mg Cd/g biomass. For industrial application of biosorption the studies must be conducted on multi-ion solutions or most preferably on actual industrial effluent solutions.

Yakubu and Dudeney (1986) reported on the use of pelletized Aspergillus niger in a fluidized bed column to adsorb uranium from a pure uranyl nitrate solution at pH 4.0. The loaded uranium was eluted with 0.1 M HNO_3 and a 12 fold concentration of uranium was achieved.

The most detailed study of biosorption has been that of Tsezos and a variety of co-workers on the biosorption of uranium from bacterial leach liquors by immobilized Rhizopus arrhizus. Over the last decade, Tsezos (1982-1991) has described the site of uranium binding within the cell wall and the competitive interactions between uranium, iron and aluminum. He has also developed an immobilization procedure which has little or no effect on metal binding capacity of the biomass and has determined the precise point within the fungal growth curve for recovery of biomass having the optimal uranium loading capacity. This detailed study has progressed to intermediate pilot plant studies on the recovery of uranium from a complex bacterial leach liquor. Uranium biosorption is optimal at pH 4.0 and loadings are generally in the range of 150-300 mg U/g of immobilized biomass. Complete recovery of the uranium can be accomplished by elution with a dilute solution of sodium carbonate. Following elution a forty-fold concentration of uranium has been achieved when the influent feed ranges from 100-150 ppm uranium.

In contrast to fungal biomass, where the addition of a carbon source has little affect on the uptake or binding of metal ions, yeast shows an increased uptake and adsorption of metals in the presence of glucose. Thus for yeast, metal uptake is an energy-dependent process (Gadd et al., 1987). Gadd (1986) reported that Saccharomyces cerevisiae (bread yeast) could accumulate up to 160 nmol Zn/mg dry wt. in the presence of 50 mM glucose at 25°C, but that uptake of Zn was substantially reduced at 4°C or in the presence of antimycin A. He further stated that glucose analogues or metabolic inhibitors or electron transport uncouplers would inhibit the metal ion uptake. As yeast requires energy for metal ion accumulation at levels high enough to provide an economic metal removal or recovery process, further discussion of their use will not be pursued.

2.3 Bacteria

Beveridge (1986) has conducted extensive basic research on the binding of metals to bacterial cell walls. The cell walls of Gram positive bacteria are composed of peptidoglycan and teichoic acid. Metal ions bind exclusively to the phosphate moieties within the teichoic acid and via the COO^- groups of the peptidoglycan polymer. Once the metals bind, they act as nucleation sites and additional metal ions precipitate until the interpolymer spaces of the cell wall are filled with metal. In contrast, the Gram negative cell walls are composed of peptidoglycan (about 1/6 the amount present in Gram positive organisms) and lipopolysaccharides. The metal ions bind to the phosphate groups of the lipopolysaccharides and to the carboxyl groups of the peptidoglycan. Due to the differences in the cell wall structure, Gram positive cells have a much greater metal loading capacity than the Gram negative cells.

Sterritt and Lester (1986) have shown that the metal binding capacity of sewage sludge is directly related to the soluble and colloidal bacterial exopolymer content of the sludge. They reported that the metal loading capacity of bacterial exopolymers extracted from the sewage sludge had a slightly higher metal loading capacity on a dry weight basis and that the exopolymer loading capacity increased with increased sludge age. In contrast, the sludge itself showed a reduced metal loading capacity with increased age. They also reported that the exopolymer of Zoogloea ramigera could accumulate 300 mg Cd/g of exopolymer and 400 mg Cu/g of exopolymer. As bacterial exopolymers are predominantly polysaccharides, the metals are assumed to bind to the free carboxyl groups of these polymers.

Advanced Mineral Technologies Inc. (AMT) developed and marketed the AMT-Bioclaim™ process which was based on the use of immobilized bacterial biomass particles which were utilized in either fixed-bed canisters or in fluid-bed reactor systems for wastewater treatment and metal recovery (Brierley et al., 1986). They reported that these granules have a high capacity for metal cations (86 mg Ag/g; 394 mg Au/g; 214 mg Cd/g; 152 mg Cu/g; 601 mg Pb/g and 137 mg Zn/g) with greater than 99% removal of metal ions from solutions containing 10-100 ppm of metal ions per litre. These metal recovery agents (MRA) adsorb metal cations over the temperature range of 4-90°C. Brierley (1990) stated that most of the biologically based biosorbants utilize non-living biomass as many industrial effluent streams, contaminated groundwaters, landfill leachates and process streams are potentially lethal to the organisms. These solutions may contain lethal levels of metal ions, surfactants, be highly variable in pH and salt concentrations therefore precluding the use of living organisms.

Geesey and Jang (1990) in their discussion of metal binding by bacterial exopolymers speculate that genetic manipulation of the bacteria will result in the increased production of polysaccharide and lipopolysaccharide polymers which contain the specific chemical moities for the binding or chelation of a specific metal ion.

Recent studies by Costerton et al. (1991) have indicated that bacterial isolates from a nickel mine drainage system have exceedingly high loading capacities for nickel. These cells do not take up iron, but will accumulate lesser amounts of cobalt. Nickel adsorption is maximal at pH 7.0, but a substantial increase in the Ni loading/g of biomass was observed after a brief exposure of the cells to pH 4.0 prior to the metal adsorption at pH 7.0. Further studies are required to confirm these preliminary findings and to assess the potential use of these organisms to remove nickel from mine effluents.

2.4 Sewage Sludge

Morper (1986) reported on the use of anaerobic sewage sludge in an upflow anaerobic sludge bed to treat metal laden solutions. During the treatment of polluted waste water from brandy production (COD 35,000 mg/L and containing 20 mg/L Cu) the sludge in the lower zone of the reactor contained 9,000 ppm of copper. Microbial reduction of sulphate to sulphide with the subsequent precipitation of copper sulphide is assumed to be the major mechanism of metal removal.

Subsequent studies have shown that the sewage sludge system is also efficient in removing precious metals from solution. On treating a silver containing effluent, the sludge adsorbed up to 54 g Ag/kg of sludge and for gold the maximum loading was about 43 g Au/kg of sludge. The metal values can be recovered from the sludge by incineration followed by dissolution of the metals from the ash using aqua regia. Morper states that the elucidation of the mechanism of metal removal will be very difficult to ascertain as sewage sludges are ill-defined, inhomogeneous mixtures consisting of various viable anaerobic and facultative bacteria, dead microbes, cell debris, organic cell lysis products as well as dissolved and insoluble inorganic matter.

3.0 CHEMICAL TREATMENT

Several chemical methods can be utilized to recover/recycle metals and other by-products from acid mine drainage and diminish hazardous wastes in an efficient, effective and economically viable manner. The chemical methods of interest involve: a) copper cementation with iron, b) selective sulphate and iron removal, and c) metal removal/recovery (e.g., Ni, Zn). These methods are addressed separately initially and subsequently they are interconnected into an integrated effluent treatment process.

3.1 Copper Cementation with Iron

Copper cementation on iron has been used successfully in hydrometallurgical processes for commercial copper production for several centuries (62). However, it is only recently (since 1965) that extensive studies have been performed to improve process understanding and performance (63-73).

The copper cementation reaction on iron can be written as follows:

$$Cu^{2+} + Fe \rightarrow Fe^{2+} + Cu$$

Cementation reactions involve simple electrochemical precipitation of a noble metal from solutions of its salts on a more electropositive metal. This type of reaction is heterogeneous in nature, involving the direct nucleation and growth of metal in elemental form upon a suitable substrate or precipitant metal (70). A visual presentation of copper cementation on iron is given in Figure 2 (74).

According to this model, cupric ions are transported to and reduced on the growing copper deposits attached to the iron surface. The electrons required to reduce the cupric ion are transferred from the anodic site on the iron surface by conduction in the iron and deposited copper. Iron is oxidized to ferrous ions at the anodic sites, thus liberating the electrons necessary for cupric ion reduction. The solubilized iron diffuses into the bulk solution through the copper deposit. Transport of cupric ions through a limiting boundary layer is believed to be the rate controlling process even in the presence of a significant deposit (64-66,69,71-74). This view of cementation applies to systems that produce a porous deposit. If the pores of the deposit become closed due to metal deposition, the reaction rate may be retarded instead of enhanced (68,70,75) and the model of Figure 2 will not apply.

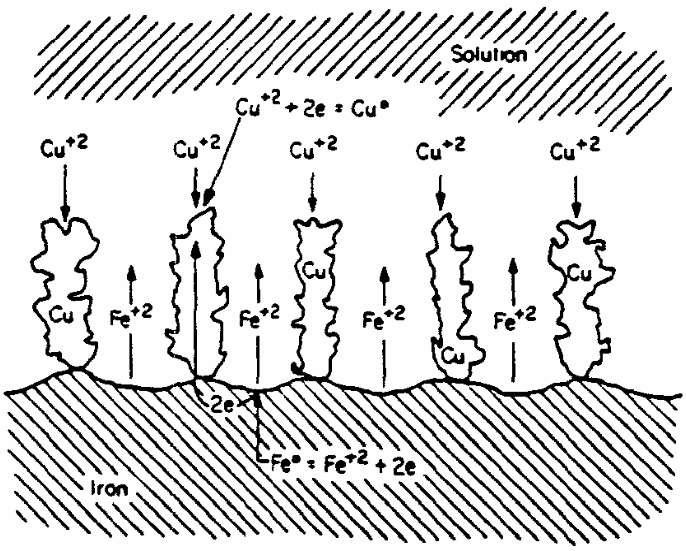


Figure 2. Electrochemical Cells Formed During Copper Cementation on Iron (74).

This difference in deposition mechanism appears to be due to the experimental apparatus or the copper cementation reactor utilized. It is an extremely important factor in achieving fast cementation kinetics and minimum residual copper in dilute solutions such as acid mine drainage.

Theoretically, for each kg of copper cemented 0.88 kg of iron is consumed. However, in reality, iron consumption amounts to an average of 1.4 to as much as 3.2 kgs per kg of copper produced. The various side reactions taking place (70) are considered responsible for this high iron consumption:

$$2Fe^{3+} + Fe \rightarrow 3Fe^{2+} \qquad (2)$$

$$2H^{+} + Fe \rightarrow Fe^{2+} + H_2\uparrow \qquad (3)$$

$$Fe + 1/2O_2 + 2H^{+} \rightarrow Fe^{2+} + H_2O \qquad (4)$$

$$2Fe^{2+} + 1/2O_2 + 2H^{+} \rightarrow 2Fe^{3+} + H_2O \qquad (5)$$

$$Cu + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} \qquad (6)$$

Minimization of these side reactions is essential in any copper cementation approach. In general, factors affecting copper cementation on iron include: stirring rate, copper ion concentration, hydrogen ion concentration (solution pH), temperature, atmosphere, iron surface area and ionic strength of the solution (64-66,68-74). These factors should be taken into account in the design of efficient copper cementation reactors.

Significant efforts have been made to develop these cementation reactors (74,76-83). The devices used for copper cementation from concentrated solutions (1-30 g Cu/L) are launder precipitators, horizontal or vertical drum precipitators and funnel precipitators (79).

Cementation launders, while simple in design and operation, require extensive manual handling, need significant plant space, produce low purity copper (60-70% copper) and have high iron consumption. Drum precipitators have higher cementation rates and lower iron consumption compared to launder precipitators, while high capital costs, high energy consumption and increased equipment wear and tear are experienced. Funnel precipitators developed by Kennecott Copper Co., offer numerous advantages over the other cementation systems, because of their efficiency, lower iron consumption, low manual work requirements and high automation capability. Disadvantages are lower cementation rates and utilization of expensive iron powder. Newer developments have attempted to address these drawbacks (79,80,82,83).

Until now research and development in copper cementation reactors has been conducted with concentrated solutions. Preliminary investigations at CANMET have used relatively dilute solutions (i.e., acid mine drainage). Since conventional reactors either produced limited success or prohibitive capital and operational costs, further efforts were focused on developing novel cementation reactors by exploiting the process factors that the control copper cementation. Two reactors were tested initially with very encouraging results (84). The first reactor is based on the concept of solution flowing with high speed through a tubular annulus. Tests with synthetic solutions proved that copper can be successfully removed from solution, leaving 1 mg/L residual copper concentration. The second reactor utilizes the draft tube approach and the initial investigations show very fast kinetics and high efficiency. Further work is required to optimize both the reactor design and the applicable process variables.

The presence of high ferric ion (Fe^{3+}) concentration in the feed will significantly increase the iron consumption during copper cementation. Iron is mainly in its ferrous (Fe^{2+}) state in acid mine drainage. Copper recovered from the cementation reactor is in the metallic form with some iron contamination. Iron can be effectively removed by leaching the cementate with dilute sulphuric acid at room temperature (85).

In another development, a method to recover copper from wastewaters with granular iron based on a controlled potential approach has been presented (86).

Following copper removal/recovery by cementation, iron oxidation and precipitation could follow. This is a necessary step before other metals (Zn, Ni,...) could be recovered, since iron is usually a major interferent.

3.2 Selective Iron Removal

The main objective in this process step is to remove iron, and most of the sulphate from acid mine drainage, while leaving the heavy metals (e.g., Ni, Zn) in solution for subsequent recovery. Common practice in acidic solution is oxidation of Fe^{2+} to Fe^{3+} by molecular oxygen and lime is added to precipitate ferric oxides and/or hydroxides as well as gypsum.

Iron oxidation and hydrolysis for iron control in hydrometallurgical operations have been studied extensively (87-105). Commonly tested industrial solutions are acidic, highly concentrated and at elevated temperatures. Limited information is available for dilute solutions such as acidic mineral effluents, treated at near ambient temperatures.

To selectively precipitate iron, while maintaining the concentrations of the other metals, iron must be oxidized from Fe^{2+} to Fe^{3+}, since the Fe^{3+} ion precipitates at a much lower pH (92,94). Therefore, any iron in the ferric state in the effluent will also precipitate. The oxidation of Fe^{2+} to Fe^{3+} by oxygen has a slow reaction rate for solutions of high acidity (88,99,103). Same acid is consumed in this chemical reaction:

$$2Fe^{2+} + 1/2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \qquad (7)$$

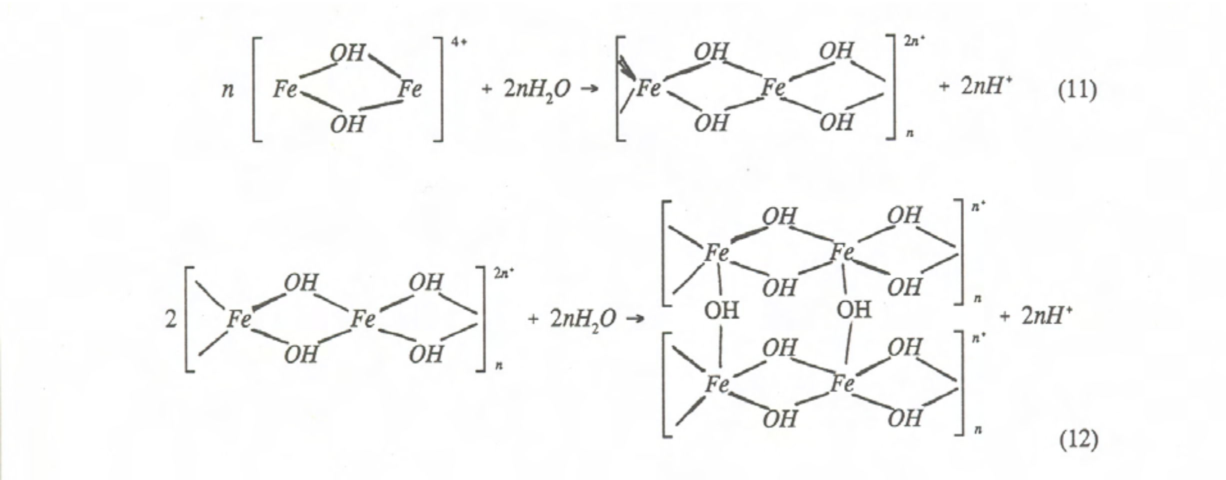
This reaction is greatly accelerated by the presence of copper ion, which acts as a catalyst (88,103):

$$2Fe^{2+} + 2Cu^{2+} \rightarrow 2Fe^{3+} + 2Cu^+ \qquad (8)$$

$$2Cu^+ + 1/2O_2 + 2H^+ \rightarrow 2Cu^{2+} + H_2O \qquad (9)$$

When a base is added to the acidic solution containing ferric ions, a rapid formation of hydroxyl complexes takes place. The mechanism by which a soluble entity is transformed into a solid precipitate is very complex and not all steps are well understood. A potential route for iron hydrolysis (91, 98, 101, 105) is given below:

$$2Fe^{3+} + 2H_2O \rightarrow Fe_2(OH)_2^{4+} + 2H^+ \qquad (10)$$


(11)

(12)

or

$$Fe^{3+} + 2H_2O \rightarrow FeO.OH + 3H^+ \qquad (13)$$

The rate at which these steps evolve depends on temperature, Fe^{3+}/OH ratio, pH, iron concentration, ionic strength as well as the specific anions and cations present (98). The presence of sulphate ions in high concentrations (i.e., acid mine drainage) promotes iron complexation and dramatically affects iron hydroxyl polymer composition and reaction rates (90,97,101,104). Attempts to simulate acid mine drainage chemistry (106,107) have been hampered due to the large number and ill-defined iron complexes formed in the presence of high sulphate concentrations.

Chemical species such as sulphate, copper, nickel and zinc ions are known to be encapsulated or adsorbed at the surface of hydrous iron oxides (98,108). This is also true for acidic mineral effluents, where heavy metals coprecipitation should be reduced. The existing practice of acid mine drainage neutralization with excess lime addition is clearly undesirable because of the iron gel formation that has poor filtering and settling properties. A well controlled addition of slaked lime would allow to work below supersaturation levels, in a heterogeneous environment, where crystal formation would be prompted (100).

Initial tests performed at CANMET (84) show that complete iron removal is feasible in simulated AMD solutions at pH close to 5.0. However, most of the copper content coprecipitates. In view of this fact, tests were performed at higher temperatures (25-80°C) showing that pH and temperature are the most important process factors. Copper removal, again, reached high extraction levels (~60%), while nickel and zinc remain largely in solution. These tests show that when the copper content in AMD is significant, it should be recovered in a step preceding iron precipitation. An iron precipitate (~50% Fe), where iron hydrous oxide and gypsum are the main components, is safely disposed of or can be used as a by-product. It is expected that the economics of heating AMD will not be favourable.

Two of the most promising approaches in by-product generation are: a) production of ferric sulphate for coagulation or effluent treatment, and b) utilization of iron precipitate in mine backfill. Ferric sulphate solution is produced by treating the precipitate in a dilute sulphuric acid solution. Initial tests have been performed at McGill University (35). Tests to produce concrete from lime neutralization sludge, combined with other materials, has produced encouraging results at CANMET. Other investigators (109) have developed a method to process this sludge and produce calcium sulphate hemihydrate or anhydrite that is successfully utilized in mine backfill. Other potential uses include: production of pigments, magnetite, additions to smelter charges, road bed and bricks, etc.

Finally, some attempts have been made in our laboratories to produce high quality gypsum. Following copper cementation with iron, slaked lime was added to raise the pH to 4.5-5.0. Because all iron is in the ferrous form following copper cementation, the calcium sulphate precipitate contains small quantities of iron. The introduction of oxygen or air, in the next step, triggers a fast oxidation and precipitation of ferric iron. Serious limitations of this approach are that only ~10% of the sulphate ions were removed and that the market value of this by-product is very low.

3.3 Metal Removal/Recovery (Ni, Zn,...)

Heavy metal recovery from dilute acidic solutions has been the subject of numerous publications applying a broad range of process technologies. Some of these technologies are presented in this report (e.g., biosorption, electrowinning, solvent extraction and ion exchange). A few investigations have been reported with selective heavy metal hydroxide precipitation in acidic effluents, mostly in combination with other techniques (110-113). Certain selectivity is possible through metal hydroxide precipitation (94,110) by controlling the oxidation state of the metals and the pH of the solution. Introduction of higher temperatures (113) and complexing agents (111) can greatly assist in the separation of heavy metals during neutralization of acid mine drainage. Furthermore, coordination with other techniques discussed in this report will enhance selectivity in metal removal/recovery.

A mine wastewater containing 6.5 mg/L nickel at pH 7.4 was tested at CANMET (84) for nickel removal and recovery. A series of studies with bioadsorbants and resins showed that nickel could be loaded from mine wastewater, producing purified water. Subsequent elution with sulphuric acid solution produced an acidic, concentrated nickel solution. Lime neutralization was applied with the objective to produce a nickel hydroxide precipitate suitable for custom smelting. Concentrated synthetic solutions were prepared and processed in a two-stage approach. The first stage involved lime neutralization up to a pH of 4.5, so that significant quantities of sulphates precipitated as gypsum ($CaSO_4.2H_2O$), followed by a second stage of lime addition for nickel hydroxide formation. Selected results from this testwork are presented in Table 3. Apparently, nickel precipitation in the second stage took place in less than 10 minutes, while zinc was removed in even shorter times (~5 min). An X-ray diffraction analysis of the precipitates revealed the presence of nickel hydroxide ($Ni(OH)_2$), nickel hydroxide hydrate ($Ni(OH)_2.3/4H_2O$) and calcite ($CaCO_3$). The precipitates are poorly crystallized but they settle fast and filter easily. These neutralization tests demonstrated the feasibility of producing a recyclable nickel hydroxide precipitate from this particular mine wastewater.

Zinc removal in a stage preceding nickel recovery has been tested by applying higher temperatures (~90°C). It appears that separation of zinc and nickel is feasible, as it was also stated elsewhere (113). In the same investigation nickel was recovered as $NiSO_4.7H_2O$ following a full evaporation of the water. This by-product satisfied the requirements for electroplating applications.

Table 3. Nickel Precipitation from a Synthetic Concentrated Nickel Solution*

	Time (min)	Ph	Temp (°C)	$[Ni]_{sol}$ (ppm)	Ni_{extr} (%)	$[Zn]_{sol}$ (ppm)	Zn_{extr} (%)
Stage 1	0	0.5	24	16,250	0	623	0
	30	4.5	30	16,250	0	639	0
Stage 2	0	5.0	30	16,250	0	639	0
	5	6.8	31	16,250	0	2.5	99.6
	10	7.7	33	0.3	100	0.5	99.9
	30	10.0	31	0.3	100	0.5	99.9
	60	10.0	28	0.3	100	1.0	99.8

*16.25 g/L Ni, 0.62 g/L Zn, 1M H_2SO_4, lime addition

4.0 ELECTROWINNING

4.1 Introduction

Increased consideration is being given to electrolytic processes for the removal/recovery of metals from dilute process streams. In comparison to the various physical and chemical waste water treatment methods, electrowinning systems offer several advantages. These include: low capital costs with high return rates, low operating costs, no sludge generation, no chemicals are required, the standards for effluents can be met, water consumption is reduced, maintenance and operation are facile, saleable products are possible and combination with other techniques such as ion exchange to more economically recover less noble metals is feasible.

4.2 Process Engineering

The development of electrolytic cells for metal recovery from dilute solutions dates from the mid-1960's when several major advances in electrochemical engineering occurred. In conventional electrowinning cell systems with vertical electrode plates the throughput per unit cell volume is limited by both the small electrode surface area and insufficient mass transfer conditions. Advances in mass transfer processes together with the introduction of new electrode materials resulted in novel cathode designs with improved mass transfer characteristics that have overcome these drawbacks. These novel cell designs provided the high space-time yield required for metal recovery from dilute solutions: the high yield is achieved by increasing the surface area of the cathode and by minimizing the boundary layer thickness through improved mass-transfer conditions achieved by agitation of the electrolyte and/or the electrode.

Many electrochemical cell systems based on either large surface area electrodes and/or enhanced mass transfer have been designed and developed in recent years. These cells are all capable of electrowinning metals from dilute process solutions and some of them have achieved commercial application, particularly in the plating and circuit board manufacturing industries. According to their operational specialty these electrolytic cells (or electrolytic reactor systems) can be grouped as follows:

- cells with extended surface area cathodes (E.S.E., Swiss-Roll, Fixed-Bed, HSA reactor),
- cells with rigorous electrolyte agitation (ECO, Chemelec), and
- cells with large surface area cathodes and intense agitation (Fluidized-bed, rotating cylinder and impact-rod-reactor).

These electrochemical reactor systems have also been classified in terms of concentrator cells and direct recovery cells. The concentrator cells either produce directly concentrated solutions from dilute effluents (electrodialysis) or metal deposits (Swiss-Roll, E.S.E., Fixed-bed, HSA) from which the metal is recovered. The metal is recovered by chemical dissolution to yield a concentrated solution or is anodically stripped and deposited on cathodes as in commercial electrorefining. The concentrator cells have stationary electrodes with extended cathode surface areas of various shapes and dimensions. The electrodes may be metal strip or mesh wound up in a spiral, helix or cylindrical configuration; e.g., Swiss-Roll or ESE (extended surface electrode) cell. These cells have shown promising metal recoveries in laboratory and pilot tests and can operate at fluid velocities up to 10 m/s. An example of a concentrator cell is the HSA reactor system which is being developed by ECO corporation under the name ECO-MRS. This technology is being used in the metal finishing industry to remove metals from wastewater. Commercial applications of this technology in the mining industry both for metal recovery as well as for waste water treatment are under investigation. The technology uses carbon fibers as the working electrode in an electrochemical reactor. The unique characteristic of a carbon fiber electrode is the enormous increase in electrochemical mass transfer rate while maintaining a controllable and uniform electrode potential over the entire electrode surface. The area of the carbon fiber electrode bed is many magnitudes larger than that of a flat plate electrode, ~13000X greater. This enormous active area, coupled with the tortuous flow pattern in the multi-layered carbon-fiber assembly, results in a system that is capable of recovering trace metals from process rinses to almost undetectable ppm concentrations with low power consumption.

The treatment process begins with electrodeposition followed by electrorefining. In the electrodeposition mode the dilute, metal bearing solution, which functions as the electrolyte in the HSA reactor, is pumped and continuously recirculated in a closed-loop flow circuit through porous carbon-fiber cathode assemblies. As metal deposition progresses, the cathodes maintain a steady removal efficiency until most of the active surface area in the carbon fibers is occupied with deposited metal. At this point the loaded cathodes are exchanged with those in the electrorefining cell where they are regenerated by anodic stripping of accumulated metal.

During the refining process, the dissolved metal ions migrate through a permanent electrolyte in the cell and deposit onto stainless steel starter sheets. The metal is periodically stripped from the starter sheets as a saleable product. These two processes are controlled independently yet function simultaneously to achieve minimal operation time. By switching cathodes between the two processes, they are used repeatedly thus eliminating the expense of "one use" consumable devices.

Direct recovery cells produce metal directly from dilute solutions in powder, particulate or even in coherent form. In the ECO cell, metal is deposited above the limiting current density as a powder on a rapidly rotating-cylinder cathode. Mass transfer rates 1000X higher than those of conventional cells and copper removal from effluents from 400 to <2 ppm have been attained using the ECO cell.

The Chemelec Cell uses an array of expanded mesh cathodes with alternate precious metal oxide coated (DSA) planar anodes in an undivided cell. This cell uses a bed of fluidized glass beads to enhance mass transfer. It has been used successfully to recover metal values from a variety of feed solutions including metal finishing, printed circuit board and photographic industries. The Chemelec cell has been developed with the prime intention of recovering non-precious metals from electroplating rinse waters. The Chemelec cell can produce hard adherent deposits even at very low metal concentrations due to the superior agitation provided by the fluidized bed, which acts in a scouring manner to prevent soft deposits. An even flow through the bed is achieved by pumping the solution through a slotted distributor plate located at the bottom of the cel. Some care with prefiltering of solution is necessary to prevent blocking of the distributor.

4.3 Applications and Economics

Electrochemical reactors, particularly the Chemelec cell and the HSA reactor, have shown great promise for treating waste streams from metal finishing operations. These streams contain a range of metals including copper, cadmium, lead and chromium, cyanides and some organics. Optimum performance of a metal recovery cell installed in electroplating line is achieved when the first rinse tank after the plating tank is a dragout (static rinse). The contents of the dragout tank are continuously recirculated through the cell and back to the tank. Thus, the concentration of metal in the dragout is kept to less than 500 ppm ensuring that very little metal contamination is carried by the work into the running water rinses that normally follow dragout.

One of the more promising strategies described for treating chemical waste from printed circuit board manufacturing is based on a combination of ion-exchange and electrowinning. The dilute metal-bearing process rinse streams are first separated and treated by an ion-exchange process. The high concentration waste sources are treated directly with an electrowinning cell using planar stainless steel cathodes in a tank cell with membrane isolated anodes and turbulence promotion. Metal concentrations are reduced from 5-20 g/L down to 200-500 mg/L. The residual solution after treatment is recycled through the ion-exchange process to remove the remaining metals.

Another area where the HSA reactor system has shown promise is in the treatment of barren bleed streams after conventional Merrill Crowe precipitation of gold with zinc. The HSA reactor system was used to remove impurity metals from the barren stream, thus liberating free cyanide which could be recycled back to the leaching stage.

Although the Chemelec and HSA reactor systems have received extensive testing in the above mentioned areas, published economic data are lacking. However, the energy required for electrolysis using a Chemelec cell to recover 1 kg of metal is in the 6-10 kWh range while the energy required for pumping is 1.5-10 kWh. These operating costs can be off-set by the value of the recovered metal which can be substantial and can lead to a short pay-back time. It has also been noted that the running costs of a Chemelec cell to recover 20 tonnes/ year copper are estimated at £75/ton with a capital cost of ~£10,000 (1975 figures). Projected annual operating costs of a HSA type reactor system including electrical power, other utilities and labour were given as $11,000.00 in 1988.

4.4 Application to Acid Mine Drainage (AMD)

The promising results obtained with the Chemelec Cell and HSA reactor systems on the recovery of metals from dilute process streams suggest that this technology may also be applicable to removing/recovering metals such as Cu, Cd and Zn from acid mine drainage waters. However, some laboratory testwork is necessary to determine how effective these systems will be for AMD solutions that contain a considerable concentration of iron as compared to other metal contaminants. Such tests should determine if the iron present affects the efficiency of Cu recovery or if its presence in the electrolyte prevents zinc deposition. These tests would also provide necessary information on the current efficiency and power requirements for recovering the various metals. The feasibility of combining ion-exchange and electrowinning technologies for the treatment of acid mine drainage should also be examined.

5.0 ION EXCHANGE AND SOLVENT EXTRACTION

A literature search was done on the use of ion exchange and solvent extraction for the treatment of acid mine drainage. This was done at the CANMET/MSL library through the computerized Chemical Abstracts system. Over 600 titles were reviewed for applicability to the present problem. The full papers or patents were obtained and reviewed for the most appropriate titles.

Ion exchange (IX) methods have been proposed for the extraction of several metals from the AMD water. The recovery of copper, nickel, cobalt, arsenic, mercury, and uranium appear to be technically and economically feasible. Processes for water recovery, i.e. complete desalination of the acid mine drainage water, have been developed and are commercially available. Solvent extraction (SX) is inherently less suitable for the treatment of AMD and, therefore, has received considerably less attention. However, in very recent years, important advances have been announced in the removal of acids and metals from effluents by SX.

5.1 Ion Exchange

Ion exchange has been a useful process in many industrial areas. The earliest and still the most common application is the production of high purity water (Bolto and Pawlowski, 1987). Ion exchange is also an important method for handling wastewaters in the metal finishing industry (Bolto et al., 1986). In view of its extensive application, IX for water recycle can be considered a mature technology whose use is well documented. A newer field of application is the use of either weak acid or chelating resins for the removal of objectionable heavy metals from effluent prior to discharge to the environment (Karrs et al., 1986).

Kemmer and Beardsley (1971) compare ion exchange with other alternative techniques to treat wastewater from mining and mineral processing. In their view, past ideas of the economic limit for recovery of metals from leach liquors should be re-evaluated in view of increasing needs for pollution control. The loss of heavy metals from a processing circuit to the sewer system creates a difficult problem of removal from the combined wastewaters before discharge to streams or lakes. It is more practical to remove these metal ions from selected waste streams before they reach the sewer, and ion exchange may provide the means of doing this whereby the recovery of metal values during regeneration may pay the cost of the process. A more recent comparative study (Wilmoth et al., 1978) concludes that lime neutralization is cheaper than both reverse osmosis and conventional ion exchange for the treatment of AMD, but the two latter techniques are slightly more efficient in removing trace metals. They did not consider environmental aspects, potential revenue from metal production, or advanced IX systems.

Ion exchange resins can be classified as 1) anionic, 2) cationic, and 3) chelating. The first two types are used extensively to purify water. Anionic resins are useful for extracting amphoteric elements (arsenic) or metals that form sulphate complexes (uranium). Cationic resins can have either sulphonic or carboxylic functionality. They are essentially non-selective and will extract most polyvalent cations including calcium, magnesium and iron. Chelating resins are relatively new products that have high selectivity for some specific metals. These resins are more expensive and less characterized than the conventional types.

This literature survey revealed two basic approaches to the treatment of AMD by ion exchange:

1. The selective removal of heavy metals from the AMD solution, and
2. Water recovery, which involves the total removal of both anions and cations from the AMD, to produce potable water.

5.1.1 Selective removal of heavy metals

In this case, the objective of the process is to remove a particularly valuable or highly toxic metal, which would otherwise report to the sludge disposal site. This reduces the environmental impact of the sludge and may generate some revenue if the metal is valuable. The AMD solution must still be treated for disposal by lime neutralization or other means.

The following metals have been investigated:

Copper, Nickel, Cobalt

The extraction of copper, nickel and cobalt is probably the most promising of all the potential applications of ion exchange to metal recovery from AMD. In addition to their relatively high value, these metals can be extracted directly from the unmodified AMD solution. The affinity of most resins for copper is very high and they will extract this metal at considerably low pH. The affinity for cobalt and nickel is somewhat smaller, but still favourable at the natural pH of most AMD solutions. The low pH decreases the interference from calcium and magnesium to a large extent. The presence of ferric iron is more troublesome because it is extracted strongly by most resins (ferrous iron is only moderately extracted). Several chelating resins have been developed that exhibit a fair to good selectivity for copper, cobalt and nickel over ferric iron.

Selected Literature: The extraction of copper and other metals from AMD solutions were studied with sulphonic cation resins (Lucas, 1980; Slater et al., 1978). In the presence of large amounts of calcium and iron, the recovery of copper, nickel or cobalt using the sulphonic (Weaver and Winger, 1958) and the carboxylic (Gilmore, 1970) cationic resins was difficult. The separation of copper from calcium is sometimes possible at relatively low pH (Anonymous, 1971; Gilmore, 1977). The extraction of copper and other metals has been studied with the following chelating resins: Picolylamine (Grinstead, 1984; Riveros and Chassé, 1991), Imino-diacetate (Díaz and Mijangos, 1987; Mijangos and Díaz, 1990), Amidoxime (Loureiro et al., 1988). The CARIX process can remove Ni^{2+} from dilute solutions with an IX system that uses carbonic acid for regeneration (Ma et al., 1989). The separation of nickel from cobalt in sulphate medium with a picolylamine resin was reported by Rosato et al. (1984). Prisbrey et al. (1980) were able to reduce the concentration of copper and cobalt to acceptable levels at Blackbird Mine (Idaho) using a fluidized ion exchange system.

Zinc, Cadmium, Lead

These metals are less amenable to extraction than the previous group. As a rule, IX resins do not extract zinc, cadmium and lead at low pH, which is the case of AMD solutions. Chelating resins have an affinity for zinc, cadmium and lead, but they also extract ferric iron. For these reasons, it is unlikely that these metals can be removed from a typical, unmodified AMD solution. The best approach would be to eliminate iron and calcium by neutralizing to pH 7 and extract zinc, cadmium and lead from the supernatant. If no other metals are present, the conventional neutralization to pH 10, and consequent lime consumption, may be avoided. Under some conditions, significant losses by co-precipitation with iron may occur.

Selected Literature: Gilmore (1977) describes a process to recover zinc from AMD solution containing small amounts of calcium and magnesium. The extraction of cadmium from a partially neutralized AMD solution with a chelating resin has been recently reported (Riveros and Chassé, 1991). The extraction of zinc and lead has been studied with an aminoxime resin (Loureiro et al., 1988) and with picolylamine, iminodiacetate, and carboxylic resins (Zhu et al., 1990). The CARIX process is reported to be able to remove Cd^{2+} from dilute solutions with an IX system that uses carbonic acid for regeneration (Ma et al., 1989).

Uranium, Thorium, Radium

If present in AMD, the recovery of these metals becomes mandatory for ecological reasons. The recovery of uranium and thorium is facilitated by their almost unique ability to form stable complexes with sulphate ions. Thus, these two metals can be readily extracted and separated with anionic resins, which will not extract other metals. Radium has received less attention because it can be efficiently eliminated by precipitation, but its adsorption on experimental chelating resins appears to be technically feasible.

Selected Literature: The extraction of uranium with anionic resins has been reported (Gilmore, 1979A; Gilmore 1979B). Sarkar (1984) presents an economic analysis of IX processes for the recovery of uranium from mine water. Mine water solution containing uranium and thorium was treated in a fluidized bed using a strong-base resin (Lucas, 1980). Subsequently, the treatment of mine water containing 100 ppm uranium was investigated in an underground pilot plant at a mine site (Lucas et al., 1981). Palmer et al. (1984) described the use of a continuous system for recovering uranium from mine water. The recovery of radium by ion exchange has been reported (Gilmore, 1981; Gilmore, 1982). Itzkovitch and Ritcey (1979) discussed the alternatives to remove radium and other radionuclides from uranium effluents.

Arsenic

Arsenic is not efficiently removed by lime neutralization due to its amphoteric nature. Besides, the high toxicity of this element provides a good incentive for removing it rather than allowing it to precipitate in the sludge. Arsenic is amenable to extraction with anionic resins, both weak- and strong-base. Recent reports indicate that some inorganic adsorbents can be used to extract arsenic.

Selected Literature: The removal of arsenic from waste waters was reported to be feasible with a strong-base resin above pH 5 and with a weak-base resin at pH 2-3 (Lee and Rosehart, 1972). Two resin systems using a strong acid cation resin followed by weak base resin were effective in removing metals including arsenic (Wilmoth, 1978). Inorganic adsorbents, prepared by precipitating $Fe(OH)_3$ on titanium and aluminum oxides, were used to remove arsenic from synthetic and deep well waters (Hlavay et al., 1984).

Mercury

The direct removal of mercury from acidic solutions has been attempted with various resins. The best results were obtained with resins containing thiol and isothiouronium functionality. Although no studies were found on the removal of mercury from AMD, the chances for resins use are good for this application.

Selected Literature: Strong cation resins combined with sulphide precipitation is efficient in the removal and recycling of heavy metals such as mercury from waste solutions (Raiter, 1978). Calmon (1979) discusses the use of resins containing thiol, isothiouronium or thiocarbamate groups for the recovery of mercury. A process for the selective extraction of mercury has been developed (de Jong and Rekers, 1974). Tests by Law (1971) indicated that an isothiouronium resin can reversibly pick up both inorganic and organic bound mercury without interference from iron, nickel, copper, zinc, or lead.

Miscellaneous

Various other developments have been reported. These include: the extraction of less common metals, experimental resins, and new processes or improvements on old processes.

Selected Literature: Gott (1978) reported a pilot-plant campaign to remove molybdenum from waste water with a weak-base resin. A hydroxamic polymer highly selective for iron was developed (Winston et al., 1980). Gilmore (1974) has summarized various methods for recovering cesium. Ma et al. (1989) described a new method for regenerating resins loaded with cations from wastewaters. The most important feature of the method, which is known as the CARIX process, is the use of non-polluting chemicals, such as carbon dioxide and magnesium hydroxide. An experimental selective resin for selenium has been reported (Tanaka et al., 1983). Raiter (1978) has developed an inexpensive method to recover metals from the eluate. This is an attempt to reduce the cost of the reagents used by IX systems.

Equipment

In principle, the extraction of metals from AMD could be done simply by allowing the AMD water to pass through fixed-bed columns containing the resin. The elution can be done in these same columns, which minimizes the resin losses. This simple system has been successfully used in many plants. However, much progress has been made recently towards the development of continuous ion exchange (CIX) systems. The main advantage of CIX over fixed-bed columns is a significant reduction in the resin inventory. This could make a large difference in capital expenditure, especially if the more expensive chelating resins are being considered. Also, CIX systems have a better tolerance to the presence of suspended solids than fixed-bed columns.

Selected Literature: Holliday (1972) stated that, although the control system of a CIX may be more elaborate than an automatic fixed bed plant, the total plant costs could be less in some cases. Lucas (1980) described the application of a single-stage fluidized bed column to the following systems: removal of base metals from mine water; cyanide removal from gold mill waste; uranium removal from sulphuric acid leach liquor; and uranium removal from mine water. Slater et al. (1978) designed and operated a continuous ion exchange pilot plant to recover copper from a waste stream. Hendry (1982) reported on a continuous countercurrent ion exchange process for the desalination of mineralized effluents and brackish water. A fully automated continuous system is presented by Himsley and Bennett (1984).

5.1.2 Water recovery

In this approach, all the dissolved solids are removed from the AMD solution, so that water is produced which is suitable for domestic use. This may be an important consideration in some locations because the water resulting from lime neutralization is only suitable for aquatic life but not for domestic or industrial use due to its high salinity.

Several processes have been proposed, all of which are technically feasible. Since the economic considerations are important, great efforts have been made to reduce the consumption of reagents, which is invariably the largest expense of all these processes. The most promising system for treating AMD is the so-called "modified DESAL" process, although the SUL-BISUL and the SIROTHERM also show some potential. The modified DESAL process is an adaptation of the original DESAL process, which has been very successful for the treatment of brackish water. The original DESAL process employs a three-column system consisting of a weak-base cation resin in the bicarbonate form, a weak-acid cation resin in the hydrogen form, and another weak-base anion resin, but in the free base form. In the first bed, anions are removed and replaced with HCO_3^- ions. Cations are removed in the second unit and replaced by H^+ ions. In the third bed, the H_2CO_3 is removed by hydroxide ions which converts the resin to the bicarbonate form. In practice, when the system is regenerated, the flow is reversed and the third bed becomes the first. The DESAL process is ideally suited for saline waters which are alkaline and contain little iron, and is therefore not suitable for AMD. In the Modified DESAL process only the first step of the DESAL process is employed, i.e. a weak-base anion resin in the bicarbonate form. This resin effectively removes the sulphate anion as well as any free mineral acidity. The effluent water is then aerated to oxidize the ferrous iron to ferric iron and to remove carbon dioxide gas; treated with lime to remove the metallic salts; and filtered as is normally required for producing potable water. Interestingly, calcium and magnesium are in the bicarbonate form which enables them to be removed as insoluble compounds through the lime softening process.

The SUL-BISUL process employs two resins, a strong cation exchange resin and a strong anion exchange resin. The AMD feed is first passed through the cation exchanger (hydrogen form resin) which removes the metal ions and exchanges these for H^+ ions. The product water from this exchange reaction contains sulfuric acid. This eluate is then passed through a strong base exchange resin in the sulphate form. Because of the low pH, high acidity of the feed, sulphate ions in solution and the resin are converted to the bisulphate form. The unusual feature of this process is the removal of sulfate from feed water by anion exchange using only water with a little added alkali as the regenerant.

The SIROTHERM Process is an ion-exchange process which utilizes hot water rather than chemicals as the regenerant and has distinct advantages in terms of operating costs, energy requirements and effluent disposal. These thermally regenerable ion exchange resins, available commercially as SIROTHERM resins, contain both weak acid and weak base functionality within the one bead. They will adsorb significant quantities of salt at ambient temperatures and release salt on heating to 70 to 90°C. (Stevens, 1977)

Selected Literature: Various methods for the treatment of acid mine drainage waters and water recovery have been evaluated by Penn Environmental Consultants (1973). The genesis of the modified DESAL process was reported by Kunin (1970) and Downing and Kunin (1968). The SUL-BISUL process has been discussed by Intorre et al. (1974) and Zaban et al. (1972). Wilmoth and Scott (1976) discussed the economics of water recovery methods. Intorre et al. (1974) reported on research carried out at the Acid Mine Drainage Demonstration Plant located at Hawk Run, Pennsylvania. The goal of this research was the conversion of acid mine drainage wastes to potable water by ion exchange processes. Holmes and Kreusch (1972) conducted laboratory studies on synthetic AMD using five IX systems, including the Modified DESAL and the SUL-BISUL processes. Cost estimates for various cases were included. The modified DESAL system and a "two-resin" system were found most promising. Research aimed at establishing the parameters for setting up large-scale plants is reported by Holmes et al. (1972) and Intorre et al. (1974).

5.2 Solvent Extraction

Solvent extraction, as a technique for treating AMD, has received very little interest. One main objection to this technique is that it becomes highly energy-intensive if the concentration of the target metal is low, as is often the case with AMD. Also, it is generally thought that SX has the potential of introducing organic contamination to the effluent solutions, which may have a negative impact on aquatic life and the rest of the environment. The latter notion does not take into account the recent progress in solvent extraction equipment, which can greatly minimize the losses of organic matter. Also, activated carbon has proven to be successful in removing dissolved organics from the raffinate.

Solvent extraction may have some potential in the selective extraction of metals if these are present in relatively high concentrations. For example the recovery of copper may be realized with better selectivity and much faster kinetics with solvent extraction than with ion exchange, if the concentration of copper is 100 ppm or more.

Two interesting new developments are a process to remove and concentrate acid from waste streams and a liquid extractant to remove metals from effluents.

Selected Literature: Reinhardt (1975) and Gallacher (1980) described several solvent extraction processes to treat industrial waste effluents. Recently, Monsanto Inc. has introduced an extractant which it claims is capable of extracting many metals from effluents (Rathie, 1991). Eyal et al. (1990) discussed a solvent extraction process to extract and concentrate mineral acids from effluents.

5.3 Conclusions

The treatment of AMD with ion exchange can be divided into two areas: 1) the selective extraction of some heavy metals and 2) the conversion of the AMD into potable water.

Among the many metals that may be found in AMD solutions, the selective extraction of copper, nickel, cobalt, uranium and mercury appear to be the most feasible. However, major interferences may arise if ferric iron, calcium and/or magnesium are present in high concentrations. In this case, selective resins will offer better performance, but they are more expensive and not properly characterized.

The recovery of other metals, such as arsenic, zinc, cadmium and lead, is less likely to be successful due to the low pH of most AMD solutions. However, it is possible to extract some of the metals from the partially neutralized AMD solution, provided that they are not co-precipitated with ferric iron.

The removal of heavy metals from effluents by adsorption offers important advantages over the conventional precipitation process: 1) less long-term environmental impact of the effluent sludge, 2) a reduction in lime consumption as the usual final pH of 9-10 may not be necessary, 3) a reduction in the size of the settling ponds.

The recovery of potable water or complete desalination of AMD solutions can be accomplished by a number of proven processes. In general, IX water recovery processes are more expensive than lime neutralization, but, unlike the latter, they produce water that is suitable for industrial and domestic purposes. This is an important consideration in some geographical areas.

Solvent extraction is considered less suitable than IX for the treatment of AMD and this is clearly reflected in the lack of literature on this topic. However, solvent extraction is being successfully applied to the treatment of metal finishing wastes and this technology could easily be modified for the treatment of AMD waters. Recent progress in equipment and extractants may prompt much more interest in widening the applications of solvent extraction.

6.0 CONCLUSIONS AND RECOMMENDATIONS

Waste management sites containing hundreds of millions of tonnes of acid generating sulphide tailings are found throughout Canada. The generation of acid from these tailings continues long after cessation of mining activities. The management of these sites and treatment of acidic drainage adds to the overall mining costs and poses a long term liability. Lime neutralization methodology is utilized extensively producing voluminous sludge that contains the metal contaminants mainly as unstable metal hydroxides.

The objective of this MEND project is to investigate alternative treatment techniques which facilitate recovery of metals and other by-products from acid mine drainage. This approach is evaluated with the production of high quality effluents, generation of a satisfactory revenue and minimization/elimination of hazardous sludges.

The literature review carried out in this report covers four disciplines: biosorption, chemical treatment, electrowinning and ion exchange with solvent extraction. It is apparent that extensive expertise has been accumulated in an attempt to recover metals from concentrated as well as dilute acidic solutions. The need to focus this knowledge in the AMD situation is obvious. Certain metal concentrations in AMD (see Table 2) show that metal recovery could be economically feasible.

Detailed laboratory investigations should be carried out to study the recovery of various by-products, develop a treatment process flowsheet and evaluate the economic and environmental benefits. The focal points in this research are: a) to define the recoverable metals, and b) to establish a multi-disciplinary approach, where various research techniques are efficiently utilized. These investigations will result in the development of a specific treatment flowsheet that could resemble the flowsheet in Figure 3. This schematic consists of several unit operations that involve:

- metals recovery, employing copper cementation, and electrowinning or ion exchange for copper, nickel, cobalt, arsenic, etc.;
- iron and sulphate removal, with oxidation of ferrous ion by aeration and partial solution neutralization; and
- metals recovery, utilizing biosorption, chemical treatment, electrowinning or ion exchange, or a combination of these techniques.

It is recommended that AMD samples from two milling operations be utilized.

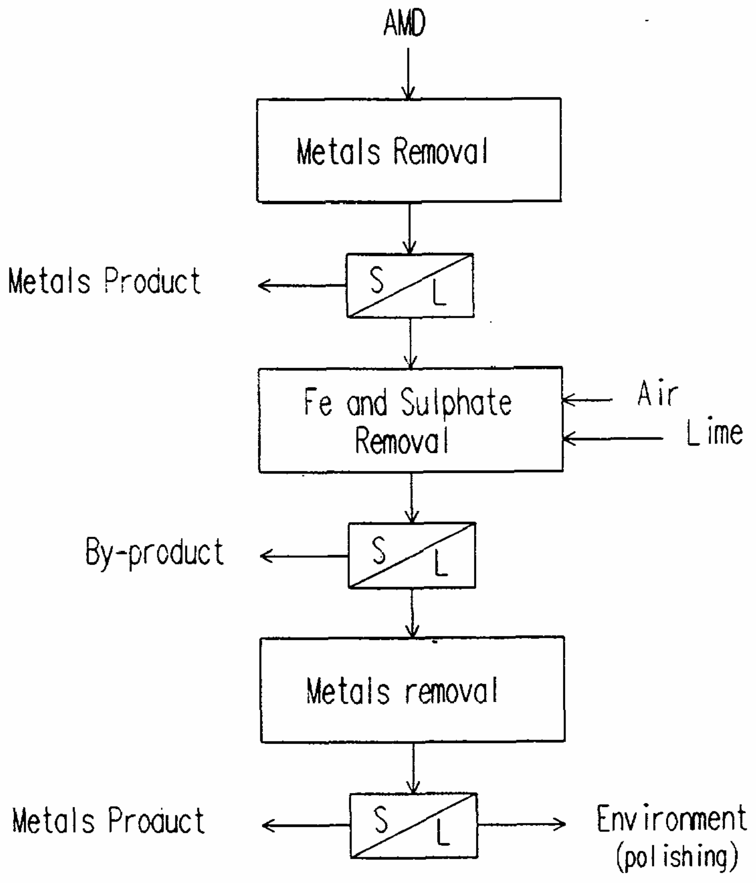


Figure 3. Potential AMD Treatment Process Schematic.

The need and feasibility of pre-concentration and polishing steps in this process flowsheet will be evaluated in a later stage.

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STUDY ON METALS RECOVERY/RECYCLING FROM ACID MINE DRAINAGE

SUPPLEMENT

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SUPPLEMENT

The literature review carried out in the main report revealed numerous processes to recover valuable metals from dilute acidic solutions. These processes should be evaluated for their applicability to AMD. There was a request to supplement the work by focusing on specific contaminants (i.e., Cu, Fe, Ni, Zn), critically assess the published techniques, offer specific recommendations and propose a focused research.

The criteria utilized in this supplemental evaluation were:
- the specific metals;
- economics;
- technical feasibility; and
- treated effluent quality.

BIOSORPTION OF METALS

CANMET has pilot plant data on the biosorption of uranium using immobilized Rhizopus arrhizus and has shown that a forty-fold concentration can be achieved with 100% recovery and that at least 16 loading/elution cycles can be achieved with the same biomass.

Current contract research at the University of Calgary has resulted in the isolation of indigenous bacteria from a nickel operation which preferentially bind nickel and cobalt with minimal binding of iron. Further studies are underway to determine the maximum loading capacity for nickel by immobilized biomass. If the results of the current study are encouraging, a pilot plant study should proceed. This may lead to a commercial process in 18-24 months.

Biosorption of other metals would require longer term research and commercial use would require a minimum of three to five years of research and process development. One would have to isolate bacteria or fungi that have a high specificity for a specific metal ion, low uptake of iron and that would adsorb metal ions at acidic to neutral pH's.

The targets in the development of this technology are: high metal specificity, high metal uptaking and low manufacturing costs, compared to metal selective resins. Selective nickel removal from AMD by immobilized biomass should be a research priority. Capital and operating costs are similar to those presented later in this Supplement for ion exchange technology. The benefits anticipated from the use of biosorption are associated with the development of a biomass significantly less expensive than the corresponding resin.

CHEMICAL TREATMENT

The chemical methods of interest to AMD treatment were presented in the main report and include:

- copper cementation with iron;
- selective iron removal; and
- metal removal/recovery (e.g., Ni, Zn).

Copper Cementation with Iron

CANMET investigations have shown that copper removal by cementation from dilute acidic solutions, such as AMD, is technically feasible. The critical question to be answered is: what is the lowest residual copper concentration in the treated effluent that can be achieved in a cost efficient manner?

Commercial copper cementation reactors have been designed to operate in concentrated solutions and are expected to have high operating costs in dilute solutions. There is an apparent need for new cementation reactors designed especially for dilute solutions (i.e., AMD). In the specific case of Equity Silver Mines in B.C. lost copper value in AMD exceeds $300,000 annually.

Order of magnitude capital and operating cost estimates (accuracy ±40%) have been carried out by CANMET on a process to recover copper from a Mattabi Mine acid mine drainage. The copper cementation process was designed to treat a solution flow of 500 m^3/h containing 0.5 g/L. This flow rate translates into 250 kg copper/h or 6 tonne copper/d. The cementation plant consisted of conventional cone type cementation vessels with 99% copper recovery. The estimated fixed capital cost is: **$4,300,000**. The anticipated operating costs (**$613,200/year**) will consist of iron replacement and pumping expenses. A copper precipitate will be produced which could be sent to a smelter or a refining operation. Although overall copper recovery costs should remain lower than the expected revenues, other benefits exist such as reduced sludge volume, reduced sludge contamination and improved sludge stability.

Investigations with a novel copper cementation reactor at CANMET have indicated that copper concentrations can be effectively reduced from 150 mg/L or higher to less than 5 mg/L. Copper is readily recovered in its metallic form with some iron contamination. The high costs to establish lower levels of copper concentration show that lime utilization is necessary to meet environmental standards. The initial ratio of Fe^{2+}/Fe^{3+} in AMD will play an important role in iron consumption during copper cementation. Ferrous ion will be dissolved with cementation in AMD and it should be removed in a later stage.

Copper recovery by cementation with iron appears to be a very promising AMD treatment technology. Thus, it is proposed to proceed to bench scale studies that involve the following areas:

a) **testing the new cementation reactor** to:
  - improve cementation kinetics;
  - decrease residual copper;
  - minimize iron consumption and overall costs; and
  - establish conditions for pilot plant design.

b) **comparison studies** between the new cementation reactor and a conventional precipitator.

c) **an economic evaluation** to establish a minimum acceptable copper concentration in AMD for copper recovery.

Selective Iron Removal

Iron is the most common metal contaminant in AMD in concentrations often exceeding 1.0 g/L. Iron removal takes place in any effluent neutralization methodology. High volume (1-2% solids) lime neutralization sludge is formed because of the polymerization of iron precipitates.

A well controlled ferrous to ferric oxidation and lime neutralization process will result in:
- complete iron removal;
- maximum sulphate removal;
- minimum heavy metal entrainment; and
- better precipitate quality.

The use of this precipitate for mine backfill appears possible, while other uses such as a material for road construction, pigments, etc. should be also examined.

Since iron removal from AMD by precipitation appears inevitable, research work to improve this treatment step is necessary. This research work should be directed towards:

i) **optimization of iron removal parameters**, such as:
  - rate of ferrous oxidation;
  - final solution pH;
  - rate of lime addition;
  - flocculation/coagulation schemes; and
  - seeding materials.

ii) **by-product generation**.

Mineralogical analysis and surface chemistry investigations will enhance process chemistry understanding and efficient process development. Successful completion of this work will result in the elimination of the sludge disposal problem.

Metal Removal/Recovery (Ni, Zn, ...)

Iron removal from AMD results in solutions, containing residual heavy metals such as nickel and zinc. The method of metal recovery depends on the particular location and the final product use.

In the case of high metal concentrations, a metal hydroxide precipitate can be formed which will be recycled to a smelter. Increased gypsum and water contents are expected to be a liability. Further work on sludge volume, filterability and quality is necessary.

Capital and operating cost estimates (± 40%) were carried out by CANMET with a Mattabi Mine acid mine drainage for a process to:

- recover copper by cementation with iron;
- neutralize acid with lime to pH 6 and precipitate iron and aluminum; and
- neutralize acid with lime to pH 11 and precipitate zinc, nickel and lead.

The process was designed to treat a solution flow of 500 m^3/h having a pH of 2.2 and containing 0.5 g/L copper, 3.1 g/L zinc, 0.525 g/L aluminum, 0.00035 g/L nickel and 0.0027 g/L lead. The precipitated metal hydroxides are recovered in two settling ponds. Pond 1 contains iron and aluminum and pond 2 zinc, nickel and lead. In addition to the metal hydroxides both ponds will contain gypsum. The objective is to recycle sludge from the second pond to a nearby smelter.

The plant operates 24 h/d, 365 d/y, and is considered to be an addition to an existing complex, so that the cost of other external facilities and utilities are excluded. The estimated capital cost for neutralization and precipitation is **$1,971,000** and the estimated operating cost is **$4,584,000**, which translates to $1.05/$m^3$ **soln**. The large operating cost for neutralization and precipitation is due to the lime requirement, with 20% excess, 92 ton/d calcium oxide @ $130/ton. Not included in the above operating costs is a charge for removal and disposal from the settling ponds of 108,000 ton/y of mixed gypsum and metal hydroxide precipitates. On a contract basis, this work could add $200,000 to $300,000 or more per year to the operating costs.

If metal pre-concentration is required to produce a usable solid product, then ion exchange or biosorption should be considered. These techniques will result in a highly purified effluent and a small volume of concentrated solution, which would be further processed.

ION EXCHANGE AND SOLVENT EXTRACTION

Ion exchange represents a potentially useful technique for the treatment of acid mine drainage waters. In particular, the following applications have the most potential:

1. **The selective extraction of heavy metals before neutralization**. The removal of heavy metals by adsorption rather than by precipitation reduces the environmental impact of the AMD solution. Some revenue may be generated depending on the nature and amount of metal to be recovered. The metals most amenable to this procedure are copper, nickel, cobalt and mercury.

2. **The removal of sulphate before neutralization**. This approach would have the following advantages: elimination of gypsum precipitation, easier recovery of metals, and improved quality of the effluent water. However, there may be several disadvantages. For example it requires a two-stage operation such as sulphate removal and effluent treatment and expected costs will be significantly higher than lime neutralization.

3. **The removal of soluble metals after neutralization**. According to normal practice, AMD solutions are neutralized to pH 9-10 to ensure the precipitation of the least basic metals such as zinc, lead and cadmium. The proposed approach would consist of neutralizing to pH 7 to precipitate iron and aluminum, followed by extraction of the soluble metals with ion exchange resins. A potential problem will be that of the co-precipitation of certain metals with the iron and gypsum. The control and mitigation of such co-precipitation must be further studied.

Solvent extraction can in principle be used for the same application as ion exchange. Solvent extraction offers better kinetics and selectivity, and it has favourable economics compared to ion exchange technology (see Table 1). However, there is a potential problem of organic entrainment in the effluent that should be treated.

Economical Aspects

Although ion exchange is generally considered to be expensive, the revenue from the recovered metals can offset to a large extent the operating costs. More importantly, ion exchange offers important environmental benefits because the metals are recovered in a reusable form.

One of the major expenses is the cost of the resin itself. Modern selective resins cost about $10-15 a litre. Thus, the capital cost of an IX plant tends to be significantly high. Capital cost estimates, similar to copper cementation estimates presented earlier, were performed at CANMET, for the selective recovery of copper with ion exchange. Solution flows of 500 m^3/h with 0.5 g/L copper were used. The specified ion exchange resin had the following characteristics:

- load weight 20 kg copper/m^3;
- adsorption time 1 to 2 h;
- resin cost \$15,000/m^3.

The plant extracted 95% of the copper and consisted of one set of three columns, two absorbing with the third being eluted. The required bed volumes of resin were 4 at 250 m^3 each. Based on these values, the estimated fixed capital costs were:

Ion exchange plant:	\$ 5,000,000
Resin @ \$15,000/m^3:	\$15,000,000
Total fixed capital:	\$20,000,000.

These capital costs do not include installations for copper recovery from the eluates.

However, these resins have minimal attrition losses, particularly in dilute solutions such as AMD. The main operating expenses (**\$2.5 M/year** when EW is included) are the chemicals used for regeneration and resin replacement. In the case of AMD, the main chemical will be sulphuric acid.

Overall Research Plan

The following research program is proposed:

1. Select one or two typical AMD solutions.
2. Study the extraction of metals from the unmodified solution with various selective resins. The study would include elution from the resin and final recovery of valuable metals. The metals most likely to respond to this treatment would be copper, cobalt and nickel.
3. Evaluate the technical and economic aspects of this approach. Make recommendations about the continuation of the project.

The successful completion of this program could signal an interest to proceed with two other aspects:

1. Study the adsorption of residual metals from a solution neutralized to pH 7. The most likely metals to be found would be zinc, lead and cadmium.
2. Study the extraction of sulphate from the feed solution and determine its influence on the subsequent lime neutralization. Expected benefits: no gypsum, better metal precipitation and easier precipitate recovery, improved quality of the water (useful for industrial and domestic use). Anticipated disadvantages are: process complications and higher costs.

ELECTROWINNING

Electrowinning in concert with ion exchange offers the potential of recovering saleable metals from acid mine drainage solutions.

A high mass transfer (HMT) electrowinning cell may be used to electrowin **nickel** from the IX eluate. The pH would have to be adjusted and maintained at 3-4 during nickel electrowinning to prevent excessive hydrogen evolution.

HMT cell technology may be also employed to recover **zinc** cathode from the IX eluate. The spent electrolyte from the zinc electrowinning cell would be used for stripping the IX resin.

The costs incurred by electrowinning are significant. These costs can be significantly reduced by using smaller cathodes (say 2ft x 2ft), which could be removed by hand if necessary. Decreasing the anode-cathode separation will reduce the IR drop across the cell, thus reducing the energy consumption and improving agitation. It also reduces the size of the cell needed for a given cathode area requirement. The limiting current density for electrowinning is proportional to the metal concentration in the electrolyte. Concentration proportional current control, i.e., the current density is automatically varied on a real-time basis in proportion to the metal concentration, allows the cell to be operated as close as possible to the limiting current density at all times, thereby minimizing the capital costs.

Although selective electrowinning is a promising technology, a long-term research commitment is required to arrive to the desirable results. Canadian mineral industry needs a short to medium-term research for improvements to AMD treatment process.

PRELIMINARY COST ESTIMATES

Order of magnitude capital cost (accuracy ± 40%) and operating cost estimates have been prepared at CANMET for the recovery of copper from Mattabi Mine acid mine drainage solution by ion exchange-electrowinning (IX-EW), solvent extraction-electrowinning (SX-EW) and cementation processes. The processes were designed to treat a solution flow of 500 m^3/h containing 0.5 g/L copper. This flow rate translates into 250 kg copper/h or 6 tonne copper/d. The plants operate 24 h/d, 350 d/y. The SX-EW and IX-EW plants recover 95% of the copper and copper cementation almost 100%. These plants are considered to be additions to existing complexes and the cost of other external facilities and utilities are excluded. The cost estimates appear as follows:

Table 1. Preliminary Cost Estimates for the Recovery of Copper from a Mattabi AMD

Technology	Fixed Capital Cost ($'000s)	Annual Operating Cost ($'000s)
SX-EW	14,565	2,193
IX-EW	24,745 (15,000 for resin inventory)	2,520
Cementation	4,300	613

These cost estimates should be utilized with caution, since:

- conventional plant technology has been used, without a full appreciation of the AMD solution characteristics; and
- new cost efficient techniques have not been taken into account, due to lack of sufficient data.

Nevertheless, existing trends are apparent. These estimates are valid for copper recovery from Mattabi AMD, and extrapolation to other metal values should be avoided.

AMD TREATMENT PROCESS DEVELOPMENT

Detailed laboratory investigations should be carried out to study the recovery of metals, develop a treatment process flowsheet and evaluate the economic and environmental benefits. The need to establish a multi-disciplinary approach, where the previously discussed techniques are efficiently utilized, is obvious.

The research work is proposed to be structured in two stages: the first stage will be a short-term research resulting in a process flowsheet that can be readily applied in lime neutralization plants. The second stage will involve medium-term research leading to a sophisticated process flowsheet where alternative technologies are applied. Both of these stages are dependant to the solution characteristics and location of each AMD occurrence.

For the short-term stage, the process flowsheet will resemble the flowsheet in Figure 1. This schematic consists of several unit operations that involve:

- **copper removal** with conventional cementation reactors, producing a copper sludge to be recycled to a smelter;
- **iron precipitation** with oxidation of ferrous ion by aeration and partial solution neutralization,

producing an iron sludge to be safely disposed; and

- **metals precipitation** by raising the solution pH and generating a sludge that can possibly be recycled to a smelter.

The drawbacks of this approach include larger sludge volumes, maintenance problems due to scaling and low value and quality of sludges produced. However, metal toxicity will be minimized and some revenue will be generated.

The process flowsheet generated by the medium-term research will be similar to the flowsheet in Figure 2. The main unit operations are as follows:

- **selective metal removal before neutralization**, that could involve:
    - copper cementation with a novel reactor,
    - copper removal with a selective resin,
    - nickel and cobalt removal with selective resins, if the solution characteristics are favourable, and
    - nickel and cobalt removal with selective biomass; and
- **selective iron removal**, with the utilization of improved precipitation techniques.

Finally, another unit operation should be investigated in the future, that is:

- **metal removal following neutralization**, with the use of ion exchange.

The need and feasibility of pre-concentration and polishing steps in AMD treatment will be evaluated in a later stage.

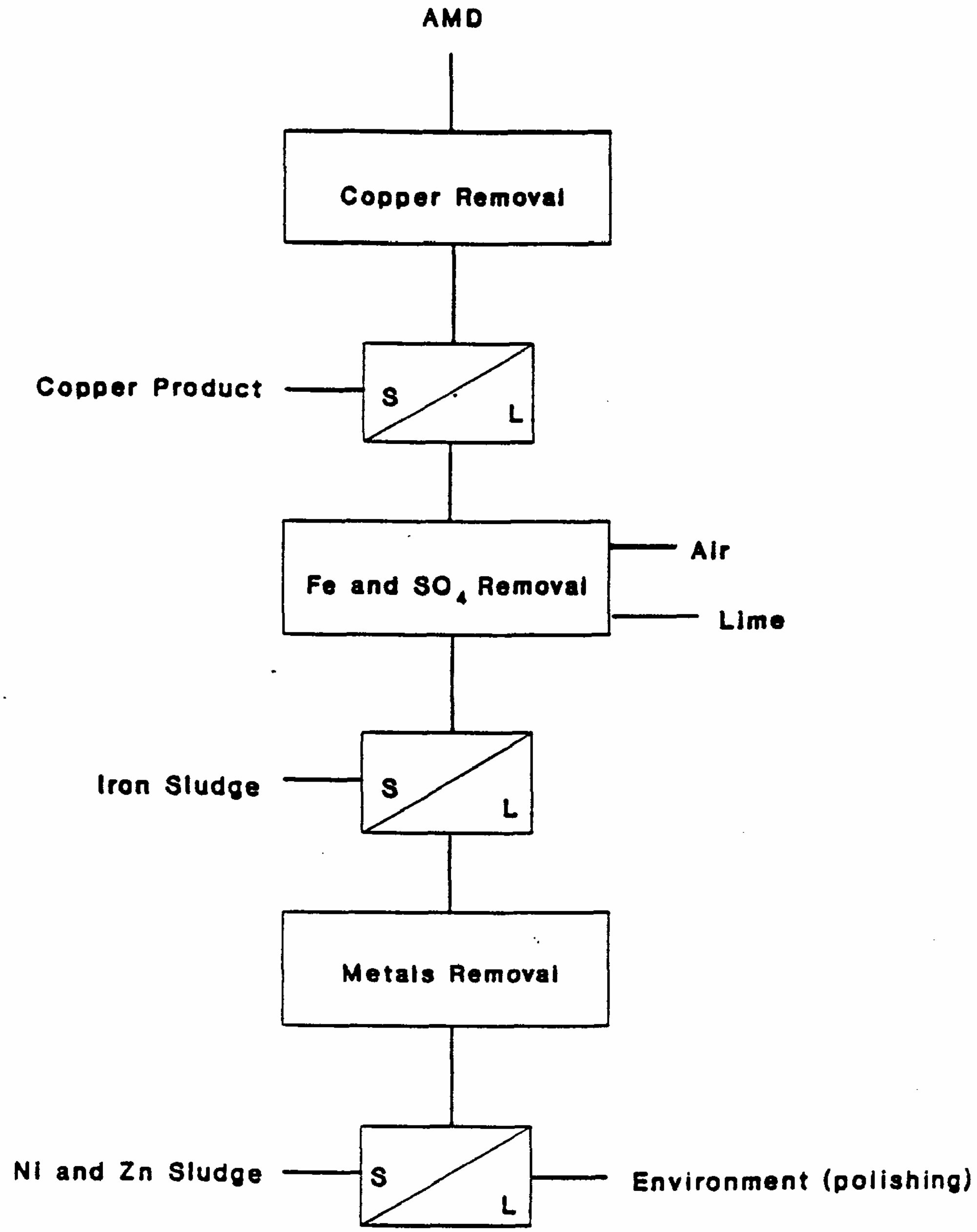

Figure 1: Potential AMD treatment process schematic.
(Short-term approach: 3-6 months research)

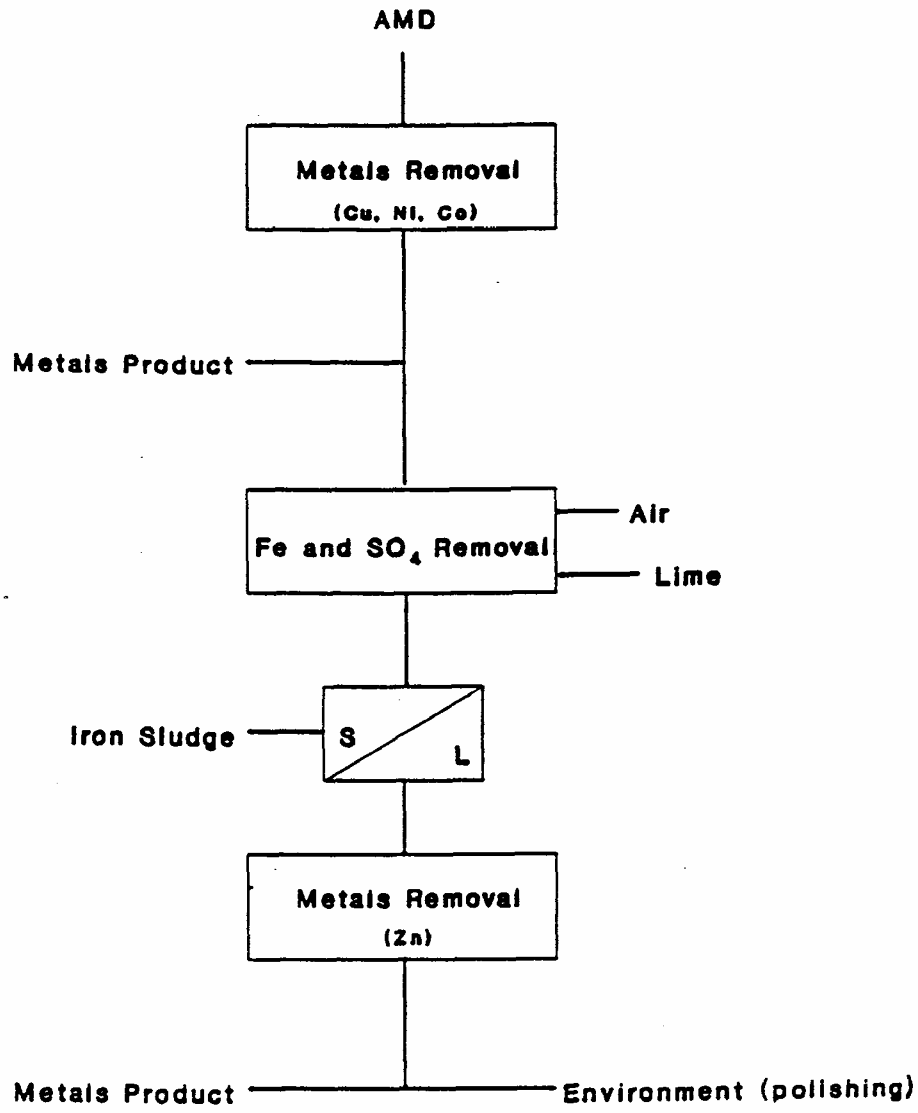

Figure 2: Potential AMD treatment process schematic.
(Medium term approach: 1-3 years research)