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ELECTROCHEMICAL TREATMENT OF ACIDIC AQUEOUS FERROUS SULFATE AND COPPER SULFATE AS MODELS FOR ACID MINE DRAINAGE

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Abstract—Acid mine drainage (AMD) is a serious environmental problem in the mining industry. The present work describes electrolytic reduction of solutions of synthetic AMD, comprising $FeSO_4/H_2SO_4$ and $CuSO_4/H_2SO_4$, in flow-through cells whose anode and cathode compartments were separated using ion exchange membranes. In the case of $FeSO_4/H_2SO_4$ at constant flow rate, the pH of the effluent from the catholyte increased progressively with current at a variety of cathodes, due to electrolytic reduction of H^+ ions to elemental hydrogen. Near-quantitative removal of iron was achieved by sparging air into the catholyte effluent, thereby precipitating iron outside the electrochemical cell, and avoiding fouling of the electrodes. The anode reaction was the oxidation of water to O_2, a proton-releasing process. Using cation exchange membranes and sodium sulfate as the supporting electrolyte in the anode compartment, the efficiency of the process was compromised at high currents by transport of H^+ competitively with Na^+ from the anode to the cathode compartments. Higher efficiencies were obtained when anion exchange membranes were used, and in this case no additional supporting electrolyte other than dilute H_2SO_4 was needed, the net reaction being the electrochemically driven transfer of the elements of H_2SO_4 from the cathode to the anode compartments. Current efficiencies $\sim 50\%$ were achieved, the loss of efficiency being accounted for by ohmic heating of the solutions. In the case of $CuSO_4/H_2SO_4$ and anion exchange membranes at high currents, reduction of Cu^{2+} and H^+ ions and transport of SO_4^{2-} ions out of the catholyte caused unacceptably high potentials to be generated. © 2001 Elsevier Science Ltd. All rights reserved

Key words—acid mine drainage, electrolysis, air oxidation

INTRODUCTION

AMD, an important environmental problem of the mining industry (Bunce, 1993), is caused by the biological oxidation of sulfidic minerals in waste crushed rock, leading to the production of sulfuric acid, as shown in equation (1).

$$FeS_2(s) + 3\tfrac{1}{2}O_2(g) + H_2O(l) \rightarrow Fe^{2+}(aq) + 2H^+(aq) + 2SO_4^{2-}(aq) \quad (1)$$

The organisms that cause AMD have a remarkable tolerance for acid; *Thiobacillus ferrooxidans* thrives in solutions as low as pH 1, and recent work at the Iron Mountain site in California has revealed organisms that can acidify water below pH 0 (Nordstrom *et al.*, 2000). Because the bacteria colonize the surface of the sulfides, AMD develops mainly in tailings piles, which have a high surface area available for oxidation.

Three major environmental detriments associated with AMD are the inherent toxicity of low pH to aquatic life, the solubilization of toxic metals such as lead, copper, cadmium, and arsenic that are typically found in sulfide deposits, and the deposition of unsightly slimy orange precipitates of iron oxides downstream of the mine site as a result of chemical oxidation of Fe^{2+} ions (equations (2)–(4)).

Oxidation :

$$Fe^{2+}(aq) + \tfrac{1}{4}O_2(g) + H^+(aq) \rightarrow Fe^{3+}(aq) + \tfrac{1}{2}H_2O(l) \quad (2)$$

Precipitation :

$$Fe^{3+}(aq) + 3H_2O(l) \rightarrow Fe(OH)_3(s) + 3H^+(aq) \quad (3)$$

Overall :

$$Fe^{2+}(aq) + \tfrac{1}{4}O_2(g) + 2\tfrac{1}{2}H_2O(l) \rightarrow Fe(OH)_3(s) + 2H^+(aq) \quad (4)$$

The latter reaction is strongly pH-dependent (rate $\alpha[Fe^{2+}] \times p(O_2) \times [OH^-]^2$; Snoeyink and Jenkins,

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1980). Although oxidation is imperceptibly slow at pH 1–2, it becomes rapid at pH 4–5 when the acidic stream flows away from the vicinity of the mine site and becomes diluted with uncontaminated stream water. The ferric iron thus formed immediately precipitates at this pH.

The metal composition of AMD is site specific and varies greatly between coal and metal ore mines. For example, water at pH 3.8 from an abandoned colliery (Cape Breton Development Corp., 1993) was found to contain >900 ppm of iron and 0.03 ppm of copper. However, water analyzed from the a metal ore mine at Iron Mountain, California contained an average of 26,514 ppm of iron(II) and 1253 ppm of copper (Nordstrom *et al*., 2000). Further comparisons of metal contents of the surrounding waters of these mining sites are presented in Table 1.

Technologies for dealing with AMD involve prevention or treatment. Prevention is preferable if the sulfidic tailings can be covered with soil, in order to exclude air (Maki *et al*., 1995). Otherwise, AMD is conventionally treated by neutralizing the acid with crushed limestone or slaked lime, a technology that involves material and transportation costs to ship in the neutralizing agent. About 1 tonne of sludge (dry-weight basis) is formed per tonne of limestone used. The sludge has a high (95–98%) water content, and is difficult to dewater; besides iron (20–30%) it contains hundreds of ppm of toxic elements such as arsenic, cadmium, chromium, copper, manganese, nickel, and lead, and therefore must itself be treated as a hazardous waste. Sludge treatment and disposal costs over the lifetime of a treatment facility may be an order of magnitude higher than the capital costs and the costs of the neutralization chemicals. Alternative treatment technologies thus offer the possibility of substantial savings in sludge handling costs.

Electrolysis, the use of electrical energy to drive otherwise unfavourable chemical reactions, has been suggested several times over the last 30 years as a possible remediation technology for AMD, but has not yet been commercially implemented. The essential concept is to lower acidity by reducing H^+ to elemental hydrogen at the cathode of an electrolytic cell. Originally Tyco Laboratories (1972) carried out a study for the US EPA, in which a synthetic AMD solution ($FeSO_4 + H_2SO_4$) was electrolyzed in an undivided (one-compartment) electrochemical cell, with the goal of reducing H^+ to H_2 at the cathode, while anodically oxidizing Fe^{2+} to Fe^{3+} (equations (5) and (6)) which is then precipitated (equation (3)). The problems with this approach included back-reduction of Fe^{3+} by migration to the cathode, and fouling of the electrodes by precipitation of iron inside the cell.

$$\textit{Reduction}: H^+(aq) + e^- \rightarrow \tfrac{1}{2}H_2(g) \qquad (5)$$

$$\textit{Oxidation}: Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^- \qquad (6)$$

Table 1. Comparison of metal concentrations at a coal mine site in Nova Scotia, Canada (Cape Breton Development Corp., 1993) and a metal ore mining site at Iron Mountain, California, USA (Nordstrom *et al*., 2000)

Metal	Concentration (ppm) at coal mine	Concentration (ppm) at metal ore mine
Fe (II)	527	26 514
Cu	0.08	1253
Zn	0.52	6668
Cd	0.32	54.7
Pb	1.1	4.9
As	0.45	112

Treharne and Wright (1974) used a sand barrier to separate the cathode compartment (which contained synthetic AMD) from an anode compartment in order to avoid the back-reduction that occurred in the undivided cell. Hydrogen was produced in the cathode compartment, raising the pH. The anode compartment contained pure dilute sulfuric acid as a supporting electrolyte: oxygen evolution from the anolyte (equation (7)) lowered the pH, producing a higher strength sulfuric acid for other uses.

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq)^+4e^+ \qquad (7)$$

These workers sought to precipitate iron in the cathode compartment, but because Fe(II) is much more water soluble than Fe(III), they suggested oxidizing Fe^{2+} by passing O_2 or O_3 into the catholyte. Again, this leads to precipitation in the cathode compartment and fouling of the cathode; it is also inefficient electrochemically, because the oxidant can be reduced at the cathode, and the Fe^{3+} can be back-reduced to Fe^{2+}. Additionally, it is dangerously impractical to have gaseous oxidants in close proximity with the electrolysis product H_2.

Friedrich and Knappnik (1997) electrolyzed AMD using ceramic diaphragms, porous polyethylene foils, or sulfate-selective ion exchange membranes to separate the anode and cathode compartments. These permit much closer separation between the anode and cathode than was possible in the approach of Treharne and Wright, thus greatly reducing energy losses due to ohmic heating (i^2R) of the solution. In the present work, we have studied the use of both cation and anion exchange membranes to divide the electrolytic cell.

Our research program has the following objectives for eventual application as a remediation technology:

(1) Raise the pH of AMD by reduction of H^+ to H_2 at the cathode.
(2) Capture iron at the treatment facility, preventing its escape and oxidation in the environment.
(3) Produce any sludges outside the electrochemical cell to minimize electrode fouling.
(4) Produce a denser sludge than chemical treatment, allowing for easier dewatering.

(5) Transfer acidity from AMD to sulfuric acid, which can be used elsewhere on site.
(6) Recover metals through electrodeposition, while simultaneously lowering the toxic metal content of the effluent.

This paper's specific objectives were to develop, for synthetic AMD consisting of $FeSO_4/H_2SO_4$ and $CuSO_4/H_2SO_4$, procedures for both raising the pH of the solution by cathodic reduction and, in the case of $FeSO_4/H_2SO_4$, precipitating iron in a subsequent reaction outside the electrochemical cell in order to prevent electrode fouling.

METHODOLOGY

Chemicals were analytical grade materials, purchased from Fisher Scientific Co., Toronto, ON. All electrolyses were carried out under constant current conditions, using an EG&G Model 173 Potentiostat/Galvanostat and small flow-through cells constructed in our laboratory (Fig. 1). The cell potential (i.e. the potential between the cathode and the anode) was measured for the experiments involving copper, but not for the experiments involving iron. The volume of each electrode compartment was 3.5 mL, and flow rates of 0.6–8.0 mL min^{-1} were achieved using a peristaltic pump. Cathodes were made from platinum, copper, graphite and carbon felt, with areas of 4.5, 6.4, 6.8 and 6.9 cm^2, respectively. In all experiments, the anode was a dimensionally stabilized anode (DSA) comprising Ti coated with iridium dioxide (approximately 7.2 cm^2). Separate flows of solutions were passed through the anode and the cathode compartments. In all experiments the solution flowed once through the cathode compartment (the catholyte) and was then collected, while the anolyte solution was recirculated. The pH of the catholyte was monitored as the solution exited the cell. Other measurements were taken on solutions that were collected from the catholyte when the electrolysis had been running for at least 30 min, in order to achieve a steady state.

Initial experiments involved a 602 ppm solution of iron(II) with a pH of 1.82. The removal of iron from the solution was determined by collecting a 35 mL sample of the effluent from the catholyte, into which air was then sparged for 45 min. A precipitate of Fe(III) hydroxide was formed, and when this had settled, the concentration of iron in the supernatant was determined spectrophotometrically by measuring the absorbance of the Fe(III)-SCN complex at 478 nm (Sandell, 1959). A linear calibration curve was obtained, detection limit of 0.5 ppm of iron, which represented <0.1% of the iron initially present. In the case of copper, a 64 ppm solution (copper (II) sulphate) with an initial pH of 1.63 was used. The concentration remaining in the catholyte was determined by atomic absorption spectrometry, using a Perkin Elmer model 2380 instrument, with an oxyacetylene flame, with analysis at 324.8 nm. A linear calibration curve was obtained, detection limit 0.05 ppm of copper, which represented <0.1% of the copper initially present.

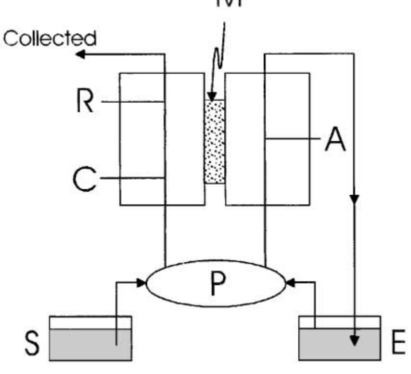

Fig. 1. Flow-through electrochemical cell. M = Membrane, R = Reference cell (Note: Experiments involving Pt cathode were not equipped with this port), C = Cathode, A = Anode, P = Peristaltic pump, S = Sample reservoir, and E = Supporting electrolyte.

RESULTS AND DISCUSSION

In the first series of experiments, the catholyte was synthetic AMD comprising ~0.01 M $FeSO_4$ (602 ppm) and 0.01 M H_2SO_4 (pH ~ 1.80), the anolyte was 0.05 M Na_2SO_4 and Nafion 417 was used as a cation exchange membrane. Passage of current through the cell caused the reduction of H^+ to H_2 at the Pt cathode, thus raising the pH of the catholyte (equation (5)). Figure 2 shows how the effluent pH of the catholyte changed with varying flow rate through the cell. The faster flow rates were ineffective (the pH remained low) because of the short residence time of the synthetic AMD in the cathode compartment. A current of 200 mA was chosen because it allowed the range of the pump speeds to be examined while significant changes of pH occurred.

Next, we studied the effect of varying the current through the cell, at a constant flow rate of 0.6 mL min^{-1}. The effluent pH increased in step with increases in the current (Fig. 3, which is based on single experiments). In this case the solution exiting the cathode compartment was sparged with air; at the raised pH of the electrolyzed solutions, Fe^{2+} was rapidly oxidized to Fe^{3+}, which precipitated as $Fe(OH)_3$ (equation (4)). Figure 3 also shows the proportion of the total iron removed from the solution following sparging the catholyte effluent with air. Air sparging of the catholyte was always carried out after the solution had exited the cell, both

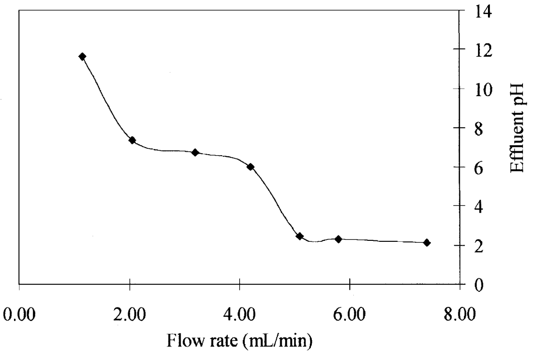

Fig. 2. Catholyte effluent as a function of flow rate: Nafion 417 CEM, 200 mA, Pt cathode.

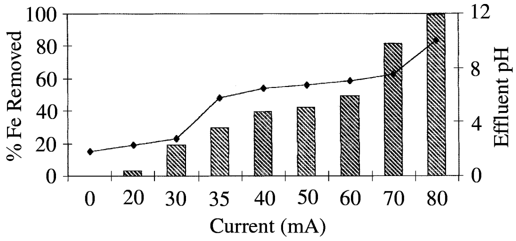

Fig. 3. Iron removal (bars) and catholyte pH (line) as a function of applied current: Nafion 417 CEM, 0.6 mL/min, Pt cathode.

to prevent cathode fouling by iron hydroxides and to avoid contact between air and the hydrogen evolved at the cathode. A current of 80 mA (the current density, calculated by dividing the current by the area of the cathode, was approximately 18 mA cm^{-2}) gave almost quantitative removal of iron. Although ferric iron precipitates almost quantitatively above pH 5 (Snoeyink and Jenkins, 1980), the pH of the catholyte must be raised well beyond this value in order to achieve efficient subsequent removal of iron from the solution, because air oxidation and precipitation of iron is a proton-releasing process (equation (4)). Practical technology will require a trade-off between raising the pH high enough to allow precipitation of $Fe(OH)_3$ but not so high that the final effluent required reacidification beofre discharge to the environment. The precipitate of $Fe(OH)_3$ settled readily; this was expected, because Fe^{3+} salts are used as filter aids in water treatment (Bunce, 1993). Clearly, the absence of high concentrations of carbonate and other metal cations was beneficial to the precipitation reaction. 12

The cathode reaction (equation (5)) leads to the loss of positive charge from the catholyte. When a cation exchange membrane is used to separate the anode and cathode compartments, Na^+ ions originating in the anolyte (Na_2SO_4) must cross the Nafion cation exchange membrane into the catholyte to restore charge balance. An idealized summary of the chemistry is that H_2SO_4 in AMD is converted to Na_2SO_4 at the cathode, while Na_2SO_4 in a clean solution is converted to H_2SO_4 at the anode.

The current efficiency for the loss of protons from the system (Table 2) is given by equation (8).

$$\frac{\text{mol H}^+\text{removed}}{\text{mol charge passed}}\times 100. \qquad (8)$$

The efficiency for the loss of iron is somewhat ambiguous, because Fe^{2+} is not removed electrochemically, but rather in a pH-dependent chemical reaction with air (equation (4)). We have chosen to report the efficiency for loss of Fe^{2+} (and later Cu^{2+}) in analogous terms as equation (8), recognizing that this is a purely empirical measure, and that it does not account for the number of electrons involved. At low current densities the current efficiency for removal of H^+ approached 50%, but at increasing current densities (and correspondingly higher steady state pH values) the current efficiency fell. There is an upper limit on the efficiency of electrolysis and on the ultimate pH that can be achieved in the catholyte, because the H^+ ions produced in the anolyte (equation (7)) compete efficiently with Na^+ to cross the membrane, and this process, H^+ migration out of the anolyte negates the cathode reaction. Further experiments were carried out using cathodes of copper, graphite, and carbon mould. In each case, the results at constant flow rate were qualitatively similar to those shown in Fig. 3, with catholyte pH increasing with current density. Carbon cathodes gave lower current efficiencies than Pt (25–30% at low current densities); copper was least satisfactory due to its higher overpotential for H_2 evolution, leading to deposition of iron on the cathode (data not shown).

Experiments were also carried out using anion exchange membranes (AEM), for which the loss of positive charge in the catholyte due to H^+ reduction is balanced by the migration of sulfate anions out of the catholyte. Figure 4 shows the result of such an experiment using the anion exchange membrane ESC 7001. As anticipated, the pH of the catholyte rose with increasing current, and significantly, the current required to achieve efficient loss of iron from the air-sparged solution was lower than in the corresponding reaction shown in Fig. 3. Table 3 shows the percent efficiency of the process at varying currents, as defined above, in this case.

Table 2. Percent current efficiency for iron and proton removal at various currents; 602 ppm initial iron solution, Nafion 417 CEM, Pt cathode, flow rate 0.6 mL min^{-1}

Current (mA)	Final iron concentration (ppm)	% Ion removed	Iron % efficiency	Final pH (steady state)	Proton % efficiency
20	582	3	1.7	2.3	48.8
30	486	19	6.7	2.8	43
35	425	29	8.7	5.8	41.7
50	347	42	8.8	6.8	29.2
60	305	49	8.6	7	24.3
70	112	81	12.1	7.5	20.9
80	3	99	12.9	10	18.3

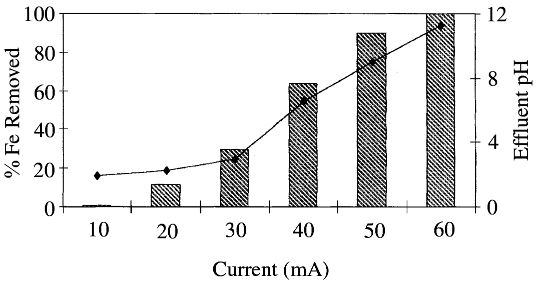

Fig. 4. Iron removal (bars) and effluent pH (line) as a function of applied current: ESC 7001 AEM, 0.6 mL/min, Pt cathode.

Under anion exchange conditions, the idealized chemistry involves loss of both H^+ and SO_4^{2-} ions from the catholyte, and gain of both H^+ and SO_4^{2-} ions in the anolyte: i.e., the net result of electrolysis is to transfer sulfuric acid from AMD into the clean anolyte. Unlike the experimental arrangement with the cation exchange membrane, sodium sulfate is not needed as a supporting electrolyte for the anolyte because sulfuric acid diluted from a previous experiment can be used as the initial supporting electrolyte. The only drawback is that if the pH of the catholyte is pushed too high, OH ions will compete with sulfate ions for transport across the anion exchange membrane, reducing current efficiency and neutralizing H^+ formed at the anode.

For the removal of copper from acidified copper sulfate solution, the catholyte was 0.01 M $CuSO_4$ (64 ppm) and 0.019 M H_2SO_4 (pH ~ 1.65). Using the Nafion cation exchange membrane we obtained results similar to the experiments with $FeSO_4/H_2SO_4$ (i.e. an increase in both catholyte pH and copper removal with increasing current). Both Cu^{2+} and H^+ ions were discharged at the cathode, and the use of a copper cathode led to deposition of the metal (Table 4). Some copper also precipitated as $Cu(OH)_2$ when the catholyte pH rose above 10. Table 4 summarizes the percent current efficiency of the process for both pH change and copper removal. At the highest currents the efficiency for copper removal drops below the maximum because of the inefficiency at high pH of transport of H^+ or OH^- through the cation or anion exchange membrane. As with $FeSO_4/H_2SO_4$, the $CuSO_4/H_2SO_4$ solutions were remediated more efficiently with the ESC 7001 anion exchange membrane (Table 5) than with the Nafion 417 cation exchange membrane. Rather similar results were obtained when a platinum cathode was used in place of a copper cathode: the efficiencies of proton removal (at low current densities) were in the order Cu cathode/ESC 7001 membrane > Pt cathode/ESC 7001 or Nafion 417 > Cu cathode/Nafion (Tables 6 and 7). In fact, if the current was set too high, use of the anion exchange membrane led to the total removal of ions from the cathodic compartment, because both H^+ and Cu^{2+} were reduced at the cathode, causing all of the SO_4^{2-} anions to migrate to the anode compartment. This greatly increased the resistance and potential differences up to 10 V were observed between the cathode and anode. Under our laboratory conditions, this problem was easily overcome by adding 0.05 M Na_2SO_4 to the $CuSO_4/H_2SO_4$ solution as a supporting electrolyte.

The work with $FeSO_4/H_2SO_4$ solutions addresses the first five of the objectives noted in the Introduction. Cathodic reduction lowered the acidity of the synthetic AMD, and pH values > 7 were readily achieved. Air sparging of the catholyte effluent allowed iron to be oxidized and precipitated outside the electrochemical cell, thereby avoiding electrode fouling and prospectively preventing escape of iron

Table 3. Percent current efficiency for iron and proton removal at various currents; 602 ppm initial iron solution, ESC 7001 AEM, Pt cathode, flow rate 0.6 mL min^{-1}

Current (mA)	Final iron concentration (ppm)	% Iron removed	Iron % efficiency	Final pH (steady state)	Proton % efficiency
10	599	1	0.5	1.9	24.6
20	532	12	6	2.3	45.9
30	425	29	10.2	3	45.5
40	219	34	16.5	6.5	36.5
50	60	90	18.7	9	29.2
60	BDL[a]	100	17.3	11.3	24.3

[a] Below detection limit.

Table 4. Percent current efficiency for copper and proton removal at various currents; 64 ppm initial copper solution, Nafion 417 CEM, Cu cathode

Current (mA)	Final copper concentration (ppm)	% copper removed	copper % efficiency	Final pH (steady state)	Proton % efficiency
80	52	18	0.2	2.8	26.8
90	47	26	0.3	4.5	25.7
100	0.4	99	1	11	23.2
110	0.2	99	0.9	11.5	21
120	0.2	99	0.8	11.5	19.3

Table 5. Percent current efficiency for copper and proton removal at various currents; 64 ppm initial copper solution, ESC 7001 AEM, Cu cathode

Current (mA)	Final copper concentration (ppm)	% Copper removed	Copper % efficiency	Final pH (steady state)	Proton % efficiency
30	62	2	0.1	2.2	46.9
40	57	10	0.2	2.5	42.8
50	0.1	99	1.9	11.4	40.3
60	0.2	99	1.6	11.8	33.6
70	0.2	99	1.4	12	28.8

Table 6. Percent current efficiency for copper and proton removal at various currents; 64 ppm initial copper solution, Nafion 417 CEM, Pt cathode

Current (mA)	Final copper concentration (ppm)	% Copper removed	Copper % efficiency	Final pH (steady state)	Proton % efficiency
30	45	29	0.9	1.9	36.7
40	44	31	0.8	2.1	36.4
50	43	32	0.6	2.3	35.4
60	45	29	0.5	2.6	34
70	42	33	0.5	4.3	33
80	0.2	99	1.2	11.1	28.9
90	0.2	99	1.1	11.5	25.7
100	0.2	99	1	11.7	23.2
110	0.2	99	0.9	11.8	21

Table 7. Percent current efficiency for copper and proton removal at various currents; 64 ppm initial copper solution, ESC 7001 AEM, Pt cathode

Current (mA)	Final copper concentration (ppm)	% Copper removed	Copper % efficiency	Final pH (steady state)	Proton % efficiency
30	55	14	0.5	2.3	39.1
40	53	17	0.4	2.4	33.3
50	43	32	0.6	7	34.2
60	0.7	99	1.6	11.8	28.6
70	0.8	99	1.4	11.9	24.5
80	0.8	99	1.2	12	21.5

into the environment. The sludge of Fe(III) hydroxide was dense and settled easily, while the use of ion exchange membranes, especially anion exchange membranes, transferred acidity from AMD to produce high quality, but relatively low strength, sulfuric acid as a byproduct in the anode compartment. Additionally, anion exchange membranes could be used without the need for additional chemicals as supporting electrolytes.

The experiments with $CuSO_4/H_2SO_4$ solutions suggest that the objective of electroseparation may be realizable, although considerable additional work will be required to show that electrodeposition is feasible with other metals, and whether electroseparation is practical when complex mixtures of metal ions are present. An alternative approach may be to deposit metals as a mixture and recover them from the cathode sludge. This work is currently in progress.

The prospective advantage of electrochemical waste remediation is the low cost of electricity by comparison with chemicals: at a cell potential of 4 V and with electricity costing 8¢ per kWh, $1.00 purchases over 100 mol of electrons. Electrochemical methods have recently been suggested for the oxidation of municipal landfill leachates (Cossu *et al.*, 1998) and the reductive treatment of chlorinated aliphatic solvents (Liu *et al.*, 1998). As prospective advantages of environmental pollution control by electrochemical remediation methods, Rajeshwar and Ibanez (1997) cite operation at ambient temperature and pressure, simple equipment with moderate capital costs, high energy efficiency, and applicability to large and small waste streams. On the negative side, deposition of material on the electrode surface may impede mass transfer, and expensive electrode materials must be avoided. Another negative factor in many electrolytic remediation processes, namely parasitic electrolysis of the solvent, is irrelevant to AMD treatment because the whole objective of the proposed technology is the electrolysis of water. Part of our ongoing work involves the evaluation of different electrode materials for both their current efficiency and their longevity. Successful technology will depend on finding electrode materials that are inexpensive and do not require frequent replacement. A key factor to investigate concerns the overpotential of different electrode materials for the liberation of gaseous hydrogen; laboratory experiments with platinum cathodes are optimal in this regard, because of their low overpotential for hydrogen evolution. Platinum is, however, far too expensive for commercial application, and we have to determine whether electrodes can be developed that will allow metal ions M^{2+} (copper, lead, nickel, etc.) to be successfully discharged at potentials separate from the discharge of H^+.

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