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Electrochemical remediation of acid mine drainage

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Abstract

Acid mine drainage (AMD), which has long been a significant environmental problem, results from the microbial oxidation of iron pyrite in the presence of water and air, affording an acidic solution that contains toxic metal ions. Electrochemical treatment of AMD offers possible advantages in terms of operating costs and the opportunity to recover metals, along with cathodic reduction of protons to elemental hydrogen. This work describes the electrolysis of synthetic AMD solutions containing iron, copper and nickel and mixtures of these metals using a flow-through cell divided with an ion exchange membrane. Iron was successfully removed from a synthetic AMD solution composed of $FeSO_4/H_2SO_4$ via $Fe(OH)_3$ precipitation outside the electrochemical cell by sparging the electrolysed catholyte with air. The work was extended to acidic solutions of Fe^{2+}, Cu^{2+}, and Ni^{2+}, both singly and in combination, and to an authentic AMD sample containing principally iron and nickel.

1. Introduction

Acidic seepage from mining operations, known as acid mine drainage (AMD), is caused by microbial oxidation of sulfidic minerals such as pyrite according to Equation 1 [1]. Tailings piles are especially prone to forming AMD because of the high surface area of the crushed minerals [2]:

$$FeS_{2(s)} + \tfrac{7}{2}\,O_{2(g)} + H_2O_{(l)} \longrightarrow Fe^{2+}_{(aq)} + 2\,H^+_{(aq)} + 2\,SO^{2-}_{4(aq)} \qquad (1)$$

Environmental detriments of AMD are the toxicity of low pH to aquatic biota [3], solubilization of toxic metals such as Cu, Pb and Cd, and the deposition of $Fe(OH)_3$ downstream from the mining site due to air oxidation of Fe^{2+} [1, 4]. The latter reaction (Equation 2) is strongly pH dependent (rate $\propto [Fe^{2+}] \times pO_2 \times [OH^-]^2$) [5]; it is very slow at typical pH values of AMD, but as the AMD leaves the mining site, it becomes diluted with unpolluted water, and at pH 4–5, oxidation of Fe^{2+} becomes rapid:

$$Fe^{2+}_{(aq)} + \tfrac{1}{4}O_2(g) + H^+_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + \tfrac{1}{2}H_2O_{(l)} \qquad (2)$$

Since iron(III) is insoluble in water above pH 3 [6], $Fe(OH)_3$ forms a slimy orange precipitate on the stream bottom (Equation 3):

$$Fe^{3+}_{(aq)} + 3\,H_2O_{(l)} \longrightarrow Fe(OH)_{3(s)} + 3\,H^+_{(aq)} \qquad (3)$$

Preventative technologies for AMD include inhibition of sulfide oxidation using various coatings [7, 8], subaqueous tailings disposal [3], covering the tailings to exclude air [9], and cathodic protection of the ore body through the use of a sacrificial iron anode [10]. However, these technologies are not applicable at all sites, and there remains a need for treatment technologies. Conventional treatment of AMD involves neutralization with limestone [2, 11, 12] or quicklime [11]. Approximately one ton of sludge (dry weight) is formed per ton of limestone used; the sludge is costly to dewater and is also contaminated with whatever toxic metals were solubilized when the AMD formed.

The use of electrolysis to treat AMD by cathodic reduction of H^+ (Equation 4) has been explored several times in the past 30 years:

$$H^+_{(aq)} + e^- \longrightarrow \tfrac{1}{2}\,H_{2(g)} \qquad (4)$$

Tyco Laboratories [13] considered the oxidation of Fe^{2+} to Fe^{3+} as the anode reaction, but this approach is only practical when the stoichiometric concentrations of H^+ and Fe^{2+} in the AMD stream are nearly equivalent. Also, the use of an undivided cell in their work allowed back reduction of Fe^{3+} at the cathode. Since then, divided cells have normally been employed. Treharne and Wright [14] divided the cell with a sand barrier. Synthetic AMD flowed into the cathodic compartment where the pH was raised via proton reduction and $Fe(OH)_3$ precipitated inside the cathode compartment. Oxidation of dilute sulfuric acid at the anode (Equation

5) was claimed to produce a 'higher strength sulfuric acid' for use elsewhere, but since the sand barrier would be permeable to H^+ one imagines that proton migration from the anode would tend to nullify the loss of protons at the cathode:

$$2\,H_2O_{(l)} \longrightarrow O_{2(g)} + 4\,H^+_{(aq)} + 4e^- \qquad (5)$$

Friedrich and Knappnik [15] divided the cell using either ceramic diaphragms or ion exchange membranes, and treated synthetic AMD containing iron(III). The rise in pH led to precipitation of iron within the cell, which settled and was separated from the water stream.

Recently, we described the electrolytic reduction of synthetic AMD in a flow-through cell, using either cation- or anion-exchange membranes [1]. The anode reaction was the electrolysis of water, with sodium sulfate as the supporting electrolyte. The rise in pH of the effluent from the cathode was greatest at low flow rates and high current densities. Sparging the spent catholyte with air led to rapid oxidation of Fe^{2+} to Fe^{3+} and precipitation of $Fe(OH)_3$ outside the cell, thereby avoiding electrode fouling. 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 H^+ and SO_4^{2-} from the cathode to the anode compartments. Current efficiencies of about 50% were achieved, the loss of efficiency being accounted for by ohmic heating of the solutions. In this paper we extend the work to the electrochemical reduction of copper ($CuSO_4/H_2SO_4$) and nickel ($NiSO_4/H_2SO_4$), and their mixtures with $FeSO_4$, as well as to an authentic AMD containing principally iron and nickel.

2. Materials and methodology

Iron(II) sulfate heptahydrate (99% pure) was purchased from VWR (Mississauga, ON). Copper(II) sulfate pentahydrate and nickel(II) sulfate hexahydrate, both 98% pure, 18 mol dm^{-3} sulfuric acid and anhydrous sodium sulfate were purchased from Fisher Scientific Company (Toronto, ON). All solutions were prepared with deionized water. Graphite felt (>99% pure, 6.9 cm^2), platinum foil (4.5 cm^2) and wire (0.368 mm dia., 99.95% pure), copper plates (99.9% pure, 6.4 cm^2) and wire (1 mm dia., 99.999% pure) and lead wire (1.0 mm thick, 99.9% pure) were obtained from Alfa Aesar (Ward Hill, MA). A stainless steel plate (7.5 cm^2) and wire (1 mm dia., plate and wire composition Fe:Cr:Ni = 70:19:11) were purchased from CFF Specialties (Hamilton, ON). Nickel wire (0.5 mm dia., >99% purity) was purchased from Aldrich Chemical Company (Milwaukee, WI). Reticulated vitreous carbon (RVC) (80 pores per inch (ppi)) and all ion exchange membranes were purchased from Electrosynthesis Company (Lancaster, NY). Nafion® 417 and 450 cation exchange membranes (CEMs) were manufactured by Dupont. ESC 7000 CEM and ESC 7001 anion exchange membranes (AEMs) were produced by Electrosynthesis Company. Tokuyama Neosepta manufactured AMH, AMX and ACM AEMs.

All experiments were performed galvanostatically for 65 min using an EG&G model 173 potentiostat/galvanostat and a flow through cell divided with an ion exchange membrane (Figure 1). The synthetic or authentic AMD solutions were circulated once through the cathodic compartment; samples were not collected in the first 5 min of electrolysis. The pH of the exiting catholyte was monitored throughout each experiment. Na_2SO_4 (0.05 mol dm^{-3}) was circulated through the anodic compartment. The volume of each compartment was approximately 3 cm^3 and a flow rate of 0.6 cm^3 min^{-1} was achieved using a peristaltic pump. The anode used for all experiments was a dimensionally stabilized anode (DSA) consisting of titanium metal coated with iridium dioxide (~7.2 cm^2). Each set of experiments was carried out at a series of constant current densities at the highest of which the steady state pH of the exiting catholyte was about 10 for iron only solutions or 12 for all other solutions. The reported steady state pH was measured after 30 min of electrolysis. The potential between the cathode and anode was measured during electrolysis to monitor the depletion of ions from the solutions.

The synthetic solutions, for both single metals and mixtures, consisted of 0.01 mol dm^{-3} (558 ppm) $FeSO_4$, 0.001 mol dm^{-3} (64 ppm) $CuSO_4$, and 0.001 mol dm^{-3} (58 ppm) $NiSO_4$ in water, or 0.05 mol dm^{-3} Na_2SO_4. To each solution, either 0.53 cm^3 or 1.00 cm^3 of 18 mol dm^{-3} H_2SO_4 was added to give the solution a final approximate pH of 1.90 (0.010 mol dm^{-3}) or 1.70 (0.019 mol dm^{-3}), respectively.

Catholyte effluents containing iron were sparged with air for 45 min to precipitate $Fe(OH)_3$. In the experiments involving single metals and copper and iron

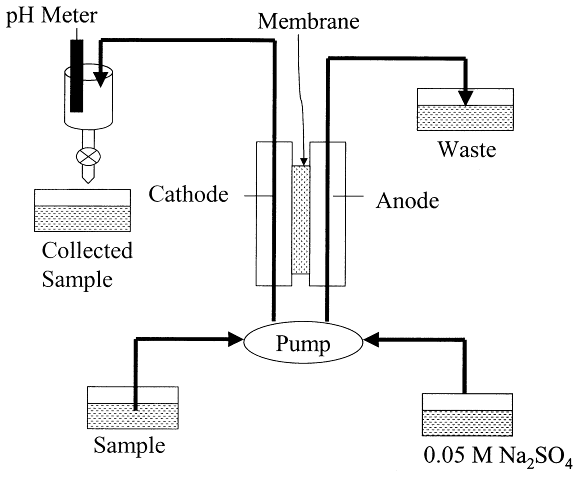

Fig. 1. Flow-through electrolysis cell.

mixtures, the metal concentration of the supernatant of the collected sample was analysed using a Perkin Elmer model 2380 atomic absorption spectrometer ($\lambda = 248.3$, 324.8 and 232.0 nm for iron, copper and nickel, respectively) and determined via a linear calibration curve. Each sample was analysed in triplicate, with each measurement consisting of an average of 10 readings. Inductively coupled plasma spectrometry (Varian Vista Pro CDD Simultaneous ICP OES, flame temperature of 10 000 K, $\lambda = 238.204$, 324.754 and 231.604 nm for iron, copper and nickel, respectively) was used to determine the metal concentrations in the samples from the electrolysis of an iron, copper and nickel mixture and an authentic AMD sample obtained from Clarabell Mine (INCO) in Sudbury, ON, Canada.

A measure of the efficiency of each electrolysis was obtained by taking the ratio of moles of protons (or iron) removed per mole of electrons passed through the solution (Equation 6). This equation is only empirical, however, because the removal of metals was not strictly electrochemical; in the case of copper and nickel hydroxide precipitation occurred along with electrodeposition. For iron, precipitation depended on pH and aeration and thus was only indirectly electrochemical. For protons, the final pH was influenced by two processes besides proton reduction at the cathode: loss of hydroxide ions by metal hydroxide precipitation, and proton (or hydroxide ion) migration through the ion exchange membrane. Percentage efficiency ε is given by:

$$\varepsilon = \frac{\text{no. moles protons or iron removed}}{\text{no. moles of electrons passed}} \times 100 \qquad (6)$$

3. Results and discussion

We previously showed that iron could be removed from a solution of $FeSO_4/H_2SO_4$ and the pH could be driven up by electrolysis followed by air sparging, the efficiency being highest at low flow rates and high current densities [1]. The anolyte solution was 0.05 mol dm^{-3} Na_2SO_4. Consistent with ferric salts being used as clarifiers in water treatment and known to settle rapidly, the $Fe(OH)_3$ was found to sink quickly to the bottom of the collection vial. Because two mol H^+ are formed for every mol Fe^{2+} removed (Equations 2 and 3), the pH must be driven up electrolytically well beyond pH 7 in order to precipitate iron quantitatively from solution, at a final pH (after iron precipitation) of 4–5. At these high pH values, the current efficiency declines due to the increasing competition between H^+ and Na^+ to migrate from the anolyte to the catholyte (cation exchange membrane, CEM), or between OH^- and SO_4^{2-} in migrating from the catholyte to the anolyte (anion exchange membrane, AEM).

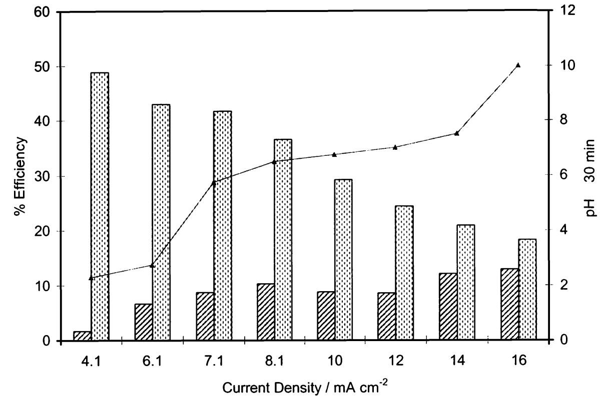

Fig. 2. pH (line) (at 30 min) and iron (left bars) and proton removal (right bars) efficiencies as a function of current density upon electrolysis of 0.01 mol dm^{-3} $FeSO_4$/0.010 mol dm^{-3} H_2SO_4 at a stainless steel cathode using a ESC-7000 CEM.

Using a Pt cathode and an ESC 7000 CEM, a current density of 14 mA cm^{-2} (70 mA) was required to remove >98% of the iron from the solution. Experimental reproducibility was investigated by carrying out seven electrolyses at 60 mA (12 mA cm^{-2}); the final pH was 6.5 ± 1 and the percentage removal of iron was (83 ± 10)%. The relatively large uncertainties are presumably due to the strong influence of pH on the solubility of $Fe(OH)_3$; much smaller uncertainties were seen in later experiments with copper. The iron removal efficiency (IRE) increased with increasing current density, until a maximum was reached (corresponding to about 90% iron removal), Figure 2. However, the efficiency in these experiments was somewhat less than with the Nafion® 417 CEM previously used [1], suggesting that the ESC-7000 CEM was more selective towards protons than sodium ions. The highest removal efficiency was achieved using the ESC-7001 AEM (at a Pt cathode, Table 1). Proton removal efficiency increased at a higher initial concentration of H^+, consistent with more efficient transfer of protons to the cathode (Table 2), with a corresponding decrease in the iron removal efficiency. With the Nafion® 417 CEM, iron was removed more efficiently at a Pt or RVC cathode than at Ni or Pb. At a stainless steel plate cathode 86% iron removal was achieved at 20 mA cm^{-2} (150 mA).

Since higher current efficiencies were previously obtained using an AEM [1], electrolyses were performed on

Table 1. Proton removal efficiencies (PREs) as a function of applied current upon electrolysis of synthetic AMD solutions containing 0.01 mol dm^{-3} $FeSO_4$/0.01 mol dm^{-3} H_2SO_4 at platinum and graphite felt cathodes using both Nafion® 450/417 cation exchange membranes (CEMs) and ESC-7001 anion exchange membranes (AEMs)

Current /mA	Pt CEM	Pt AEM	Graphite felt CEM	Graphite felt AEM
50	35	34	39	31
60	34	29	35	29
70	33	25	34	25
80	29	21	30	21
90	–	–	26	19

Table 2. Proton removal efficiencies (PREs) and iron removal efficiencies (IREs) upon electrolysis of synthetic AMD solutions containing 0.01 mol dm^{-3} $FeSO_4$/0.01 mol dm^{-3} H_2SO_4 or 0.01 mol dm^{-3} $FeSO_4$/0.019 mol dm^{-3} H_2SO_4 as a function of current density at a reticulated vitreous carbon (RVC) cathode using a Nafion®450 cation exchange membrane (CEM)

Current /mA	Current density /mA cm^{-2}	IRE 0.01 mol dm^{-3} acid	IRE 0.019 mol dm^{-3} acid	PRE 0.01 mol dm^{-3} acid	PRE 0.019 mol dm^{-3} acid
40	0.85	11	4.1	27	35
60	1.3	12	4.8	18	27
80	1.7	12	2.7	14	24

a platinum cathode using AMH, AMX and ACM AEMs and quantitative iron removal was achieved in each case (current density of 16 mA cm^{-2} (80 mA) was required for AMH and ACM and 18 mA cm^{-2} (90 mA) for AMX). Higher efficiencies were achieved because, as protons are reduced to hydrogen gas at the cathode, sulfate anions migrate to the anolyte to restore charge balance. However, as water reduction takes over from proton reduction as pH increases, OH^- ions are formed, and these compete with sulfate to cross the AEM, thus lowering the current efficiency.

Copper and nickel were also studied using about 0.001 mol dm^{-3} (64 ppm) $CuSO_4$/0.019 mol dm^{-3} H_2SO_4 and about 0.001 mol dm^{-3} (59 ppm) $NiSO_4$/0.019 mol dm^{-3} H_2SO_4 solutions. Both metals were removed from the solution via two mechanisms; deposition onto the cathode at low current densities and as the metal hydroxide when the exiting catholyte had pH > 8. In our first experiments using AEMs, the cell potential became exceedingly high during the electrolysis (>30 V), likely due to the depletion of ions in the catholyte, since protons were reduced to hydrogen gas and sulfate anions migrated to the anolyte to restore charge balance. This problem was not evident with CEMs, since Na^+ ions replace the protons lost from the catholyte. Consequently, in all subsequent experiments using an AEM, 0.05 mol dm^{-3} Na_2SO_4 was added to the catholyte as an additional supporting electrolyte, whereupon the potential difference across the cell was reduced to about 4 V.

For the $CuSO_4/H_2SO_4$ and $NiSO_4/H_2SO_4$ systems, the reduction of M^{2+} to M competes with the reduction of H^+ to H_2 at the cathode. Only about 40% of the copper was deposited onto the cathode, even though thermodynamically, copper reduction ($E^\circ = 0.337$ V, $E = 0.248$ V) is favoured over proton reduction ($E^\circ = 0$ V, $E = -0.051$ V); E was calculated on the basis of concentrations, not activities. Less than 10% of the nickel was deposited, which is consistent with less favourable thermodynamics ($E^\circ = -0.250$ V, $E = -0.339$ V). One factor that is consistent with these findings is the greater diffusivity of H^+ compared with Cu^{2+} or Ni^{2+}; another is the efficiency of mass transfer, such that practical electrolytic technology for the removal of Cu^{2+} from aqueous wastes demands the use of three-dimensional cathodes [16]. At sufficiently high current density we were able to remove >99% of both Cu and Ni from solution, but only when the steady state pH was high enough to precipitate $M(OH)_2$. In a typical experiment, the copper and nickel solutions were electrolysed at a stainless steel plate cathode using a Nafion® 450 CEM. In the case of copper, 32% was recovered through electrodeposition and 11 mA cm^{-2} (80 mA) was required to remove >96% of the copper from the solution (Figure 3). Whereas the proton removal efficiencies were moderate (~20%), those for copper and nickel were consistently low (around 1%), even though they were removed near-quantitatively. Data for proton removal efficiencies comparing iron, copper, and nickel solutions are shown in Table 3 for a stainless steel cathode: unaccountably the presence of copper in the solution depressed the proton removal efficiency. Replicate experiments suggested a reproducibility of ±10%.

Mixtures of solutions containing 0.01 mol dm^{-3} $FeSO_4$/0.001 mol dm^{-3} $CuSO_4$/0.019 mol dm^{-3} H_2SO_4 and 0.01 mol dm^{-3} $FeSO_4$/0.001 mol dm^{-3} $CuSO_4$/0.001 mol dm^{-3} $NiSO_4$/0.019 mol dm^{-3} H_2SO_4 were electrolysed using a Nafion® 450 CEM; the iron/copper solution was electrolysed at platinum, RVC and stainless steel cathodes and the iron/copper/nickel solution at stainless steel. For the iron/copper solution at stainless steel, 27 mA cm^{-2} (200 mA) was needed to remove >99% of the metals from the solution, which is higher than that needed to remove the metals from the single metal solutions. Similar results were obtained for the platinum and RVC cathodes. For the iron/copper/nickel solution, more than 98% of the metals was removed at a current density of 29 mA cm^{-2} (220 mA) (Figure 4), which is again higher than that needed to remove the metals from the single metal solutions. As before, the

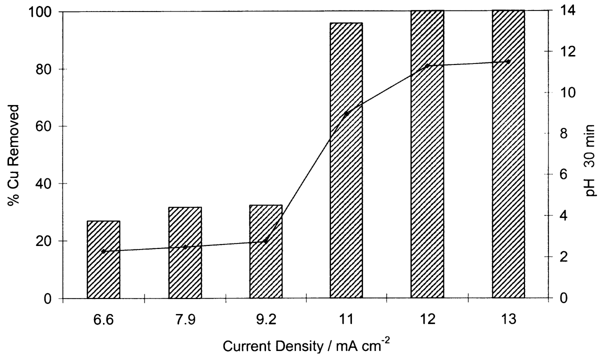

Fig. 3. pH (line) (at 30 min) and copper removal efficiency (bars) as a function of current density upon electrolysis of 0.001 mol dm^{-3} $CuSO_4$/0.019 mol dm^{-3} H_2SO_4 at a stainless steel cathode using a Nafion® 450 CEM.

Table 3. Comparison of proton removal efficiencies for 0.01 mol dm^{-3} $FeSO_4$/0.019 mol dm^{-3} H_2SO_4, 0.001 mol dm^{-3} $CuSO_4$/0.019 mol dm^{-3} H_2SO_4, and 0.001 mol dm^{-3} $NiSO_4$/0.019 mol dm^{-3} H_2SO_4 solutions at a stainless steel cathode using a Nafion® 450 cation exchange membrane (CEM)

Current /mA	Current density /mA cm^{-2}	Cu	Ni	Fe
80	11	15	23	24
90	12	14	20	21
100	13	12	18	19

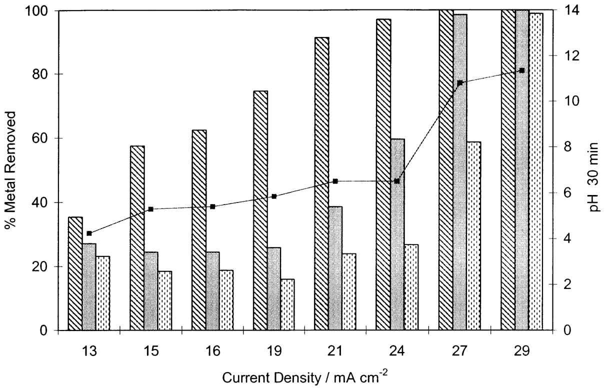

Fig. 4. pH (line) (at 30 min) and metal removal efficiency (bars, left to right Fe, Cu, Ni) as a function of current density upon electrolysis of 0.01 mol dm^{-3} $FeSO_4$/0.001 mol dm^{-3} $CuSO_4$/0.001 mol dm^{-3} $NiSO_4$/0.019 mol dm^{-3} H_2SO_4 at a stainless steel cathode using a Nafion®450 CEM.

PRE (and max IRE) for the mixture was comparable to the iron-only solution, but twice more copper and three times more nickel were deposited onto the cathode from the mixed metal solution compared to the metal-only solutions.

An authentic AMD sample from the Clarabell nickel mine, Sudbury ON, was electrolysed at a stainless steel cathode using a Nafion® 450 CEM. The sample had an initial pH of 2.5 and was a clear, orange colour, suggesting that much of the iron was present as Fe^{3+}; it contained 13.4 ppm of total organic carbon, 909 ppm iron, 104 ppm nickel and <5 ppm each of cobalt, copper and zinc (the latter three metals were not analysed for after electrolysis). More than 99% of the iron was removed at a current density of 27 mA cm^{-2} (200 mA) (Figure 5). During the electrolysis, a large amount of orange precipitate ($Fe(OH)_3$), was observed around the cathode and in the upper portion of the cathodic compartment, consistent with the iron being originally present as Fe^{3+}, which is insoluble in water above pH 3 [6]. However, less than 50% of the nickel was removed, even at high current densities (68 mA cm^{-2}), likely through electrodeposition, as the pH was not high enough to form $Ni(OH)_2$.

Electrolysis at 44 mA cm^{-2} (332 mA) removed more than 99% of the iron and 41% of the nickel from the solution. The catholyte was collected, filtered and reelectrolysed at the same current density to remove the remaining nickel; by driving the pH up to 12, more than 98% of the nickel could be removed from the AMD solution. Alternatively, the AMD solution was electrolysed at a current density of 33 mA cm^{-2} (250 mA) for 4 h, which resulted in the removal of >99% of the iron and 29% of the nickel from solution, whose pH was then 4.1. Soda ash was then added to remove >99% of the remaining nickel as a cloudy grey precipitate of $Ni(OH)_2$, although the disadvantage of this method is the need for chemical additives.

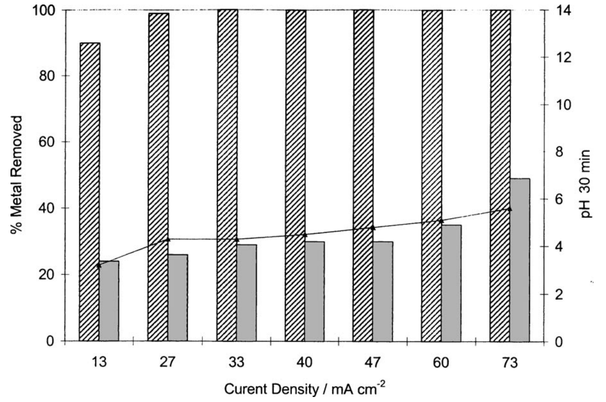

Fig. 5. pH (line) (at 30 min) and metal removal efficiency (bars, left Fe, right Ni) as a function of current density upon electrolysis of authentic AMD from Clarabell Mine, near Sudbury, Ontario as a function of current density using a Nafion® 450 CEM at a stainless steel cathode.

4. Conclusions

Our overall objectives are: (i) to raise the pH of AMD by reduction of H^+ to H_2; (ii) to capture iron, to prevent its deposition in the environment; (iii) to produce sludges outside the electrochemical cell to minimize electrode fouling; (iv) to produce an easily dewaterable sludge; (v) to transfer acidity from AMD to sulfuric acid, for use elsewhere; (vi) to lower the toxic metal content of the effluent.

The iron-only experiments achieved the first four outlined objectives. Proton reduction at the cathode combined with water oxidation at the anode effectively transferred acidity from the catholyte to the anolyte. Iron precipitated readily outside the cell as $Fe(OH)_3$, after oxygenation of the catholyte. The experiments with copper and nickel were only partly successful in that metal removal occurred more by hydroxide precipitation than electrodeposition. Electrolysis of authentic AMD was successful in removing iron from solution, but quantitative removal of nickel required reelectrolysis or chemical precipitation. Development of an electrolytic technology for AMD remediation requires more work on the chronology of electrolysis, aeration, and sludge separation, and on cell design to optimize mass transfer and permit the *in situ* separation of the sludges formed when the original AMD contains significant quantities of Fe(III).

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