CATHODIC PROTECTION OF A WEATHERING ORE BODY[1]

Gene Shelp[2], Ward Chesworth[2], Graeme Spiers[3], and Liangxue Liu[2]

Abstract: A series of laboratory-scale experiments were conducted to evaluate the effectiveness of an electrochemical approach to stop, or significantly inhibit, the oxidation of an exposed band of sulphide facies iron formation and consequently prevent the production of acid mine drainage. An electrochemical cell was constructed using a block of massive sulphide-graphite rock from the Sherman iron-ore mine in Temagami, Ontario as the cathode, scrap iron, aluminum, or zinc as sacrificial anode, and acidic leachate collected from the mine site as the electrolyte. A working electrochemical cell was successfully established in all cell configurations with EMF and current values exceeding 850 mV and 4.5 mA, respectively. Electrochemical cells utilizing iron and zinc anodes raised the pH of the electrolyte from 3.0 to 5.6 and 6.7, respectively, with concomitant decreases in redox potentials from >650 to <300 mV. The cell utilizing the aluminum anode failed to increase the pH of the electrolyte above 4.5. The inhibition of sulphide oxidation is demonstrated in the zinc anode cell experiment whereby the concentration of iron in solution remained constant at 25 mg/L until pH 5.8 at which point the concentration of iron dropped dramatically. The experiment was designed such that the cathode represented the only known source of new iron in the system.

Key Words: acid mine drainage, electrochemistry, cathode, anode, EMF, redox potential, amelioration.

Introduction

During mining of the Sherman open pit iron mine, Temagami, Ontario, Canada (Fig.1), a band of sulphide-rich graphitic bedrock, described as sulphide-facies iron formation, was exposed for approximately 2 km along the north side of the South Pit. The sulphide-rich zone contains blebs, nodules, stringers, and massive lenses of pyrite up to 1.5 m wide and tens of metres long. Acidic waters generated by the interaction of oxygenated surface water and groundwater with the sulphide-rich formation continue to fill the abandoned pit. The pH 3.0 waters, contain high concentrations of iron, manganese, aluminum and other metals.

At its simplest, the oxidation of pyrite to produce acid mine drainage (AMD) can be described by the following stoichiometric equation:

$$2FeS_2 + 7.5O_2 + 7H_2O \overset{\text{(bacteria)}}{\leftrightarrows} 2Fe(OH)_3 + 4H_2SO_4 \qquad (1)$$

In simple terms the iron sulphide (pyrite) weathers to form iron hydroxide and sulphuric acid. Current methods of dealing with AMD can readily be related to this reaction. One set of methods,

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including liming, organic/biological filtration systems (1, 2, 3) and wetlands (4, 5, 6) treats the reaction products. A more fundamental approach is to prevent the reactants on the left-hand side of the reaction from interacting. This approach includes the use of bactericides (7) mineral coatings on the surface of sulphide grains (8), engineered covers (9, 10, 11) submergence (12, 13) sphagnum bogs (14), iron-pan (8, 15) and biofilm (15).

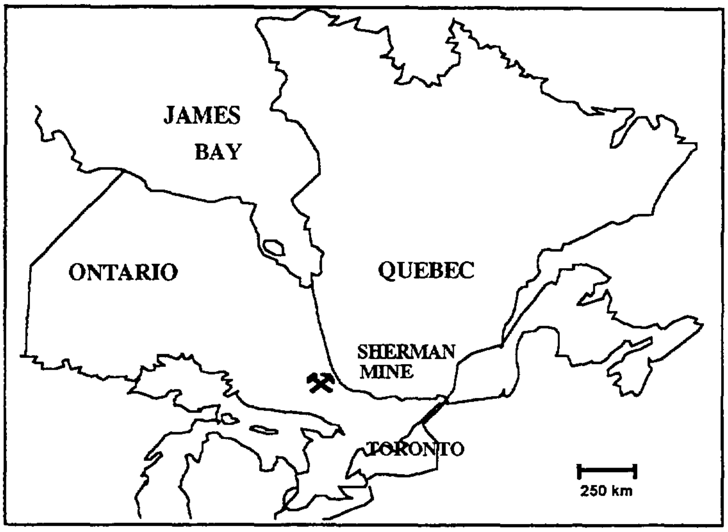

Figure 1. Location map showing the Sherman mine site

The main objective of the current research was to evaluate the potential of an in-situ electrochemical technology as an alternative treatment. Equation 1 represents a redox reaction. Referring to the associated half reactions (equations 2, 3 and 4) electrons are produced by the forward half-reaction and consumed by the backward half-reaction. The forward reaction rate can theoretically be slowed, or even prevented, by supplying electrons through the incorporation of sulphide-rich rock as the cathode of an electrochemical cell, with a material of greater electroactivity than pyrite as the sacrificial anode. The fundamental electrochemical reaction is a transfer of electrons from the anode to the cathode through the external circuit. Theoretically, this transfer should inhibit acid generating reactions by reducing both the electrode potential of the sulphide mineral, or in other words the tendency for the mineral to weather, and the activity of Thiobacillus ferrooxidans by increasing the pH of the microsites. The decrease in the hydrogen ion concentration results from the reduction of oxygen and subsequent complexation with hydrogen ions to form water (equation 5) and/or from the conversion of hydrogen ions (H^+) to elemental hydrogen (H_2) (equation 6). The Eh conditions of the system will control which of the two reactions will predominate.

$$FeS_2 + 3.5O_2 + H_2O \rightleftarrows Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (2)$$

$$Fe^{2+} + \tfrac{1}{4}O_2 + H^+ \rightleftarrows Fe^{3+} + \tfrac{1}{2}H_2O \quad (3)$$

$$Fe^{3+} + 3H_2O \rightleftarrows Fe(OH)_3 + 3H^+ \quad (4)$$

$$2H^+ + O_2 + 2e^- \leftrightarrows H_2O \quad (5)$$

$$2H^+ + 2e^- \leftrightarrows H_2 \quad (6)$$

A series of laboratory electrochemical cell experiments were conducted using a block of massive sulphide/graphite rock from the mine site as the cathode, and each of scrap iron, aluminum, and zinc as the sacrificial anode in three separate experiments. The acidic leachate collected from the mine site was the electrolyte. The laboratory testing was followed by a 10-month field trial. The focus of the research was to evaluate the effectiveness of the proposed electrochemical approach to stop, or significantly inhibit, the acid generating reactions. The results presented in this paper represent critical data that best demonstrate the possibility of converting a weathering sulphide body into the cathode of an electrochemical cell demonstrating the possibility of inhibiting the future oxidation of the ore body by a form of cathode protection.

Experimental Design

Laboratory Setup

Figure 2 is a schematic diagram of the experimental cell used in the studies. The sulphide/graphite block (45 cm by 30 cm by 30 cm) containing between 10-15 % pyrite was of fissile character with minor fractures. A 3 cm head of water was maintained in the upstream pond to ensure that acidic leachate generated during the experiment collected in the downstream pond. The upstream and downstream ponds contained 27.5 and 41.3 litres of solution, respectively.

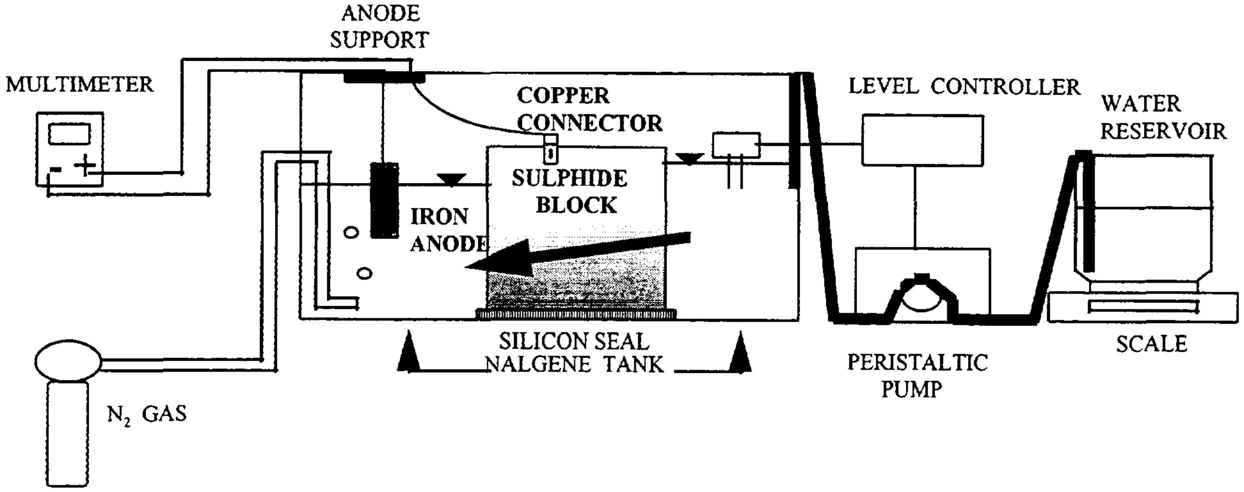

Figure 2. Electrochemical cell setup

The sacrificial anode, suspended in the downstream pond, was attached to the semi-conductive sulphide-graphite block, the cathode, by a copper plug assembly (Fig. 2). The downstream pond was purged with nitrogen to maintain the dissolved oxygen content between 1.0 and 1.2 mg/L thereby inhibiting the formation of oxide coatings on the surface of the anode and to mimic the redox conditions in the South Pit, Sherman Mine. Anodic materials were selected based on their positive electroactivity with respect to pyrite. Of the anodic materials chosen for testing, emphasis was placed on scrap iron because it is environmentally safe under natural conditions. A multimeter was used to record EMF and current throughout the experiment. The measured potential (Eh) and pH were measured using an Accumet 1000 Series meter with a Ag/AgCl reference electrode. The measured potentials were standardized to the hydrogen scale.

Water samples were taken periodically and analyzed for total dissolved metals such as Al, Ca, Cd, Co, Cr, Fe, K, Mg, Mn, Na, Ni, Pb, and Zn, by atomic absorption spectroscopy (AA) and inductively coupled plasma spectroscopy (ICP-AES). The anions, SO_4, Cl, PO_4, were analyzed by ion chromatography.

Precipitate samples were collected periodically for x-ray diffraction, scanning electron microscopic and elemental analysis. X-ray diffraction analysis was conducted using a RIGAKU D/Max-A series powder X-ray diffraction system with specimen being step-scanned from 3° to $90°2\theta$, in $0.02°2\theta$ increments with 4 s integration times. Precipitate samples were coated with 20 nm Au and examined with a Cambridge 250 scanning electron microscope equipped with a Noran thin window energy dispersive detector and a Tracor 5500 analyzer (SEM-EDS). Precipitate sub-samples were analyzed for total metal content by ICP-AES following dissolution with aqua regia.

Field Setup

In November, 1992, an attempt was made to establish a working electrochemical cell in the South Pit. The thermite process, which employs the burning of magnesium metal strips to ignite an aluminum metal/ferric oxide powder mixture (16) was used to weld a stainless steel chisel to the sulphide orebody. An insulated copper lead was attached to the chisel using a cable clamp. A second lead was clamped to a solid sulphide handle, prepared using a rock saw, to ensure the integrity of the electrical connection over time. Both leads were bolted to a scrap iron plate anode, weighing 8.062 kg, which was subsequently lowered into the anoxic zone at a depth of approximately 10 m. A control was established by suspending an additional scrap iron plate, weighing 9.443 kg, at the same depth.

Field measurements of EMF and current were taken 3 times during the test period: March 11, 1993; May 25, 1993; and August 31, 1993. Finally, the plates were weighed and visually examined for corrosion.

Results and Discussion

Laboratory Study

AMD is a problem in the environment not only because of acidity, but also because the solution contains metal species at concentrations inimical to aquatic organisms. Theoretically, the electrochemical treatment should eliminate further production of AMD by attacking the problem at the source by preventing the oxidation of the sulphide minerals. Furthermore, the resultant rise in the pH of the electrolyte of the cell is directly related to the formation of precipitates such as aluminum and iron hydroxide phases. The formation of precipitates should be accompanied by a diminution of toxic species through coprecipitation. Such phenomena can be demonstrated by monitoring EMF, current, pH, Eh, and by measuring the content of metals, such as Al, Cd, Co, Cu, Fe, Ni and Zn, and anions in the aqueous phase, and by collecting and analyzing any precipitates.

The possibility of converting a solid block of sulphide-rich bedrock into the cathode of an electrochemical cell was quickly established as starting EMF and current values were recorded at between 850 and 1250 mV and 4.5 and 24 mA, respectively (Figure 3). The fact that both EMF and current decreased with time suggests that the internal resistance of the circuit remained relatively constant as the cells proceeded towards steady state conditions.

Supporting evidence for a working electrochemical cell can be obtained by examining the changing physicochemical properties of the electrolyte. An increase in pH by the consumption of hydrogen ion by reactions described by Equations 5 and 6 is an indirect measure of the relative effectiveness of a particular cell configuration. The cell utilizing an aluminum anode failed to increase the pH of the solution above 4.5 (Figure 3). The pH of the solution was probably controlled by precipitation reactions involving the hydrolysis of aluminum. Results of x-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) identified a solid phase of short-range order with an approximate atomic percent ratio of 34% S, 27% Fe, 13% Ca, 10% Mg, 9% Al, 5% Si, and 2% Zn. The precipitate may be composed of more than one solid phase.

The solution pH of the cells with iron and zinc anodes attained steady state values of 5.6 and 6.7, respectively (Figure 3). These steady state pH levels are controlled by the precipitation of iron and zinc solid phases. The iron experiment resulted in the formation of a reddish-brown amorphous precipitate with an approximate atomic percent ratio of 35.4% S, 28.6% Fe, 24.4% Mg, 7% Al, 2.6% Si, 1.5% Mn, and 1% K. For the zinc anode experiment, diffraction analysis and SEM micrographs identified

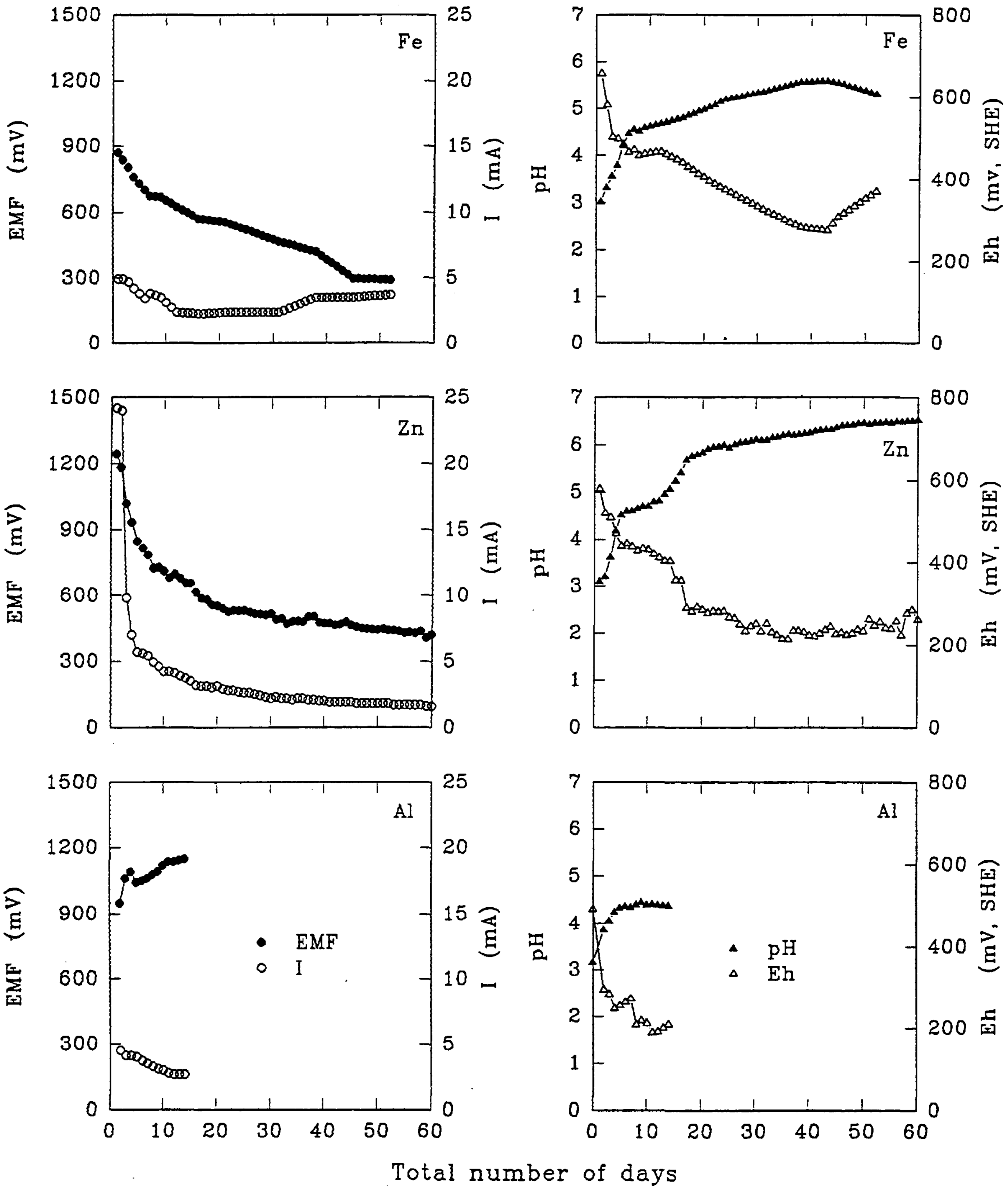

Figure 3. EMF, current, pH, and Eh temporal trends for electrochemical cell experiments utilizing iron (Fe), zinc (Zn), and aluminum (Al) anodes

a crystalline mineral displaying a tabular structure arranged in rosettes. The chemical composition calculated from EDS analysis indicated an average atomic percent ratio of 35% Zn, 34% O, 15.3% Al, 8.5% Fe, and 4% S, and 3% Si. Positive identification of the zinc mineral has not been possible.

The redox potential of the electrolyte is another indirect measure of the effectiveness of the various electrochemical cell configurations to inhibit the oxidation of the sulphide body. The relationship between redox potential and pH can be expressed by the theoretical slope (-59 mV/pH unit) derived from the Nernst equation. For iron and zinc the experimental slopes were calculated at -123mV/pH and -107mV/pH, respectively (Figure 4). The slope of the regression line for the experimental data indicates a decreasing pO_2 with time, suggestive of the presence of reduced ion species.

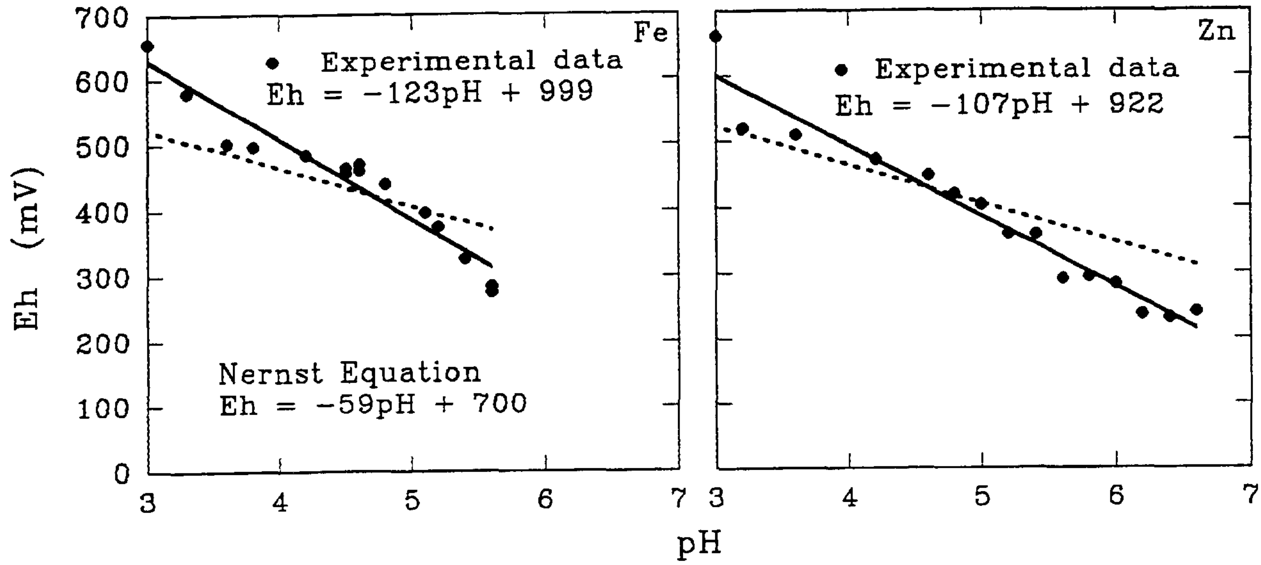

Figure 4. The Eh/pH diagrams describe the slope of the regression line (solid line) obtained from the iron and zinc anode electrochemical cell experiments. The theoretical slope derived from the Nernst equation (dashed line) is illustrated for comparison.

The solution phase trace element results obtained from the zinc anode experiment are used to describe the ability of the electrochemical cell to inhibit acid generation (Figure 5). The dramatic decrease in the concentration of iron in solution at pH 5.8 from 25 mg/L to < 10 mg/L is followed by a slow but continuous decrease (Figure 5). If the sulphide block was the only source of iron, the results suggest that the oxidation of the sulphide minerals was inhibited during the 3-month test period of this particular electrochemical cell configuration. The sulphate concentration showed a slight decrease from approximately 1400 mg/L to approximately 1000 mg/L during the same period (data not shown).

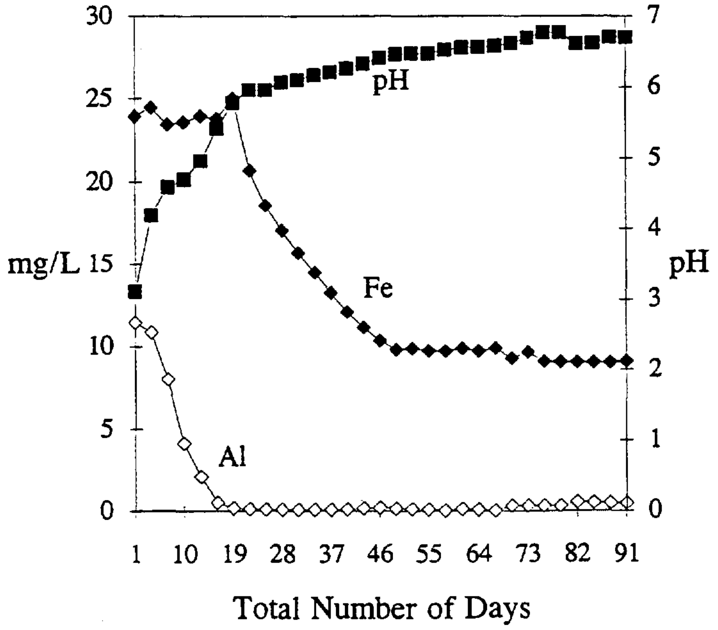

Figure 5. Temporal changes in iron, aluminum, and pH for zinc anode electrochemical cell experiment

Field Study

The laboratory experiments demonstrated that conversion of a solid block of sulphide rich bedrock into the cathode of an electrochemical cell is possible, and that the rate of oxidation of the sulphide block was reduced through a form of cathode protection. To demonstrate the possibility of establishing a working electrochemical cell under field conditions, a small scale electrochemical cell was set up at the northeast end of the South Pit. The EMF and current of the cell were monitored for 10 months. EMF readings consistently measured between 400 and 500 mV, with readings as high as 603 mV. A constant current measurement for the cell, however, was elusive, with the value recorded strongly dependent on the mineralogy present at the exact point at which the multimeter leads contacted the sulphide/graphite ore body, as well as the ambient conditions, such as water content in the vicinity of the contact. For a pyrite contact, the current generally ranged between 2 and 5 mA, whereas readings for graphite were consistently higher in the 30 to 50 mA range. After 10 months, the active anode was encrusted with an ferric iron oxy(hydr)oxide precipitate, whereas the control anode showed almost no signs of corrosion. This result was substantiated by a 400 mg reduction in the weight of the active anode, whereas an 81 mg reduction was recorded for the control anode. These results suggest that dissolution of iron is largely due to the electrochemical processes, and not to metal corrosion.

Conclusions

A sucessful laboratory study, which clearly demonstrated that a weathering ore body can be converted into the cathode of an electrochemical cell, was followed by the establishment of a working electrochemical cell at the Temagami mine site. The preliminary laboratory results suggest that further weathering of the ore body can be inhibited by electrochemical treatment. Additional experiments are currently underway to confirm this. Future research will focus on an examination of various cell configurations involving different electron sources and different cathodic materials which will include both coal deposits and sulphide-rich tailings.

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