

A DEMONSTRATION OF THE FEASIBILITY OF TREATING ACID MINE DRAINAGE BY AN IN SITU ELECTROCHEMICAL METHOD¹

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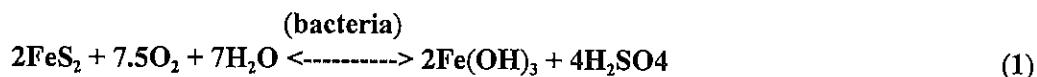
Abstract: A series of laboratory experiments were conducted to evaluate the effectiveness of an electrochemical approach to ameliorate AMD. An electrochemical cell was constructed using a block of massive sulfide-graphite rock from the Sherman Iron Ore Mine of Temagami, Ont., Canada as the cathode, scrap iron as the sacrificial anode, and acidic leachate collected from the mine site as the electrolyte. The cell raised the pH of ~41.0 L of leachate from 3.0 to a maintenance value of ~5.5. This result was accompanied by a significant decrease in redox potential from >550 to <300 mv. Furthermore, iron sulphate precipitate formed, with a concomitant lowering of Al, Ca, and Mg solution concentrations. The study clearly demonstrated the electrochemical approach to be a technically feasible and practical method of ameliorating AMD.

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

Introduction

Acid mine drainage (AMD) results from bacterially catalyzed oxidation of sulfide-rich mining wastes. AMD is considered the single greatest environmental problem facing the Canadian mining industry because of the potential threat contaminated acid waters pose to aquatic ecosystems occurring within the vicinity of both operating and abandoned mining operations.

At its simplest, the production of AMD can be described by the following stoichiometric equation:



This equation shows iron sulfide (pyrite) weathering to iron hydroxide and sulphuric acid. Methods of dealing with AMD can readily be related to this reaction. One set of methods, such as liming, organic-biological filtration systems (Dvorak 1991, Kuyucak 1991) and wetlands (Kalin 1984, 1987, 1990, 1991, Hammer 1990, Karathanasis and Thompson 1991, Stark 1991) treats the products of the reaction. A more fundamental approach is to attack the problem at the source by preventing the reactants on the left-hand side of the reaction from coming together. This approach includes bactericides (Sobek 1987), mineral coatings on the surface of sulfide grains (Nicholson 1990, Ahmed 1991), engineered covers (Collin 1990, Broman 1991, Nicholson 1991, Yanful 1991), submergence (McCready 1987, Ritcey 1991), sphagnum bogs (Brown 1991), iron-pan (Blenkinsop 1991, Ahmed 1991), and biofilm (Blenkinsop 1991).

In 1991 Dofasco Inc. and the University of Guelph began research to develop technology to ameliorate acid mine drainage problems associated with the recently decommissioned (1990) Sherman open pit iron mine, Temagami, Ont., Canada. The deposit occurs within an Algoma-type banded-iron formation (BIF). During mining a residual band of sulfide-rich graphitic bedrock, described as sulfide-facies iron formation, was exposed for approximately 2 km along the

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north side of the South Pit, one of five open pits occurring on the property. The sulfide-rich zone contains blebs, nodules, stringers, and massive lenses of pyrite up to 1.5 m wide and tens of meters long. The South Pit acidic waters were generated by the interaction of oxygenated surface water and groundwater with the sulfide-rich formation. The pH 3.0 - 3.1 waters contain high concentrations of iron, manganese, aluminum, and other metals.

Options including perpetual treatment with lime were considered to reduce the rate of oxidation of sulfide minerals. The most practical option, although expensive and possibly ultimately ineffective, involved filling the pit with the sulphidic material and then installing an impermeable material cover.

The main objective of our research is to evaluate an alternative treatment, namely, an in situ electrochemical technology designed to change AMD to within environmentally acceptable chemical levels. In equation 1, a redox reaction, electrons are produced by the forward half-reaction and consumed by the backward half-reaction. The forward reaction rate can therefore be slowed, or even prevented, by supplying electrons. This may be achieved by making the sulfide-rich rocks the cathode of an electrochemical cell and a material of greater electroactivity than pyrite the sacrificial anode. The fundamental electrochemical reaction is a transfer of electrons from the anode to the cathode. Theoretically, this transfer should inhibit acid-generating reactions by both creating a reducing environment on the surface of the sulfide mineral and also reducing the activity of *Thiobacillus ferrooxidans* by increasing the pH of the microsites through the conversion of hydrogen ions (H^+) to elemental hydrogen (H_2).

The desired effect may be illustrated (fig. 1) using Eh and pH as master variables. Acid mine drainage would plot to the upper left of the normal field of natural surface and near-surface waters. The electrochemical treatment is expected to bring the AMD to within the normal region by inhibiting the oxidation of the primary sulfide minerals while minimizing the long-term costs of amelioration. The final pH of the system should be controlled by the hydrolysis reaction for some form of iron oxyhydroxide or basic iron sulfate.

This paper presents the results of a series of laboratory experiments that demonstrate the effectiveness of the proposed electrochemical approach to ameliorate AMD.

The Experimental Setup

Figure 2 shows the experimental cell. The sulfide block shown with approximate dimensions of 45 cm L by 30 cm W by 30 cm H, was sawn from a sample of the sulfide facies iron formation, weighing approximately 1 mt, collected at the Sherman Mine site. The block had between 10% and 15% pyrite and was of fissile character with minor fractures extending through the thickness of the block. The initial step was to saturate the blocks with South Pit leachate collected at the mine in order to establish the electrical continuity required for an operating cell. The 2 L of water absorbed by the block corresponds to a porosity of approximately 4%. Subsequently, the block was placed into a Nalgene tank (fig. 2) with silicone used to establish a water tight seal along the bottom and sides of the block. A 3-cm head of water was maintained upstream to ensure that acidic leachate generated during the experiment collected in the downstream pond. The head differential was maintained by an electronic level controller and peristaltic pump system. The upstream and downstream ponds contained 27.5 and 41.3 L, respectively.

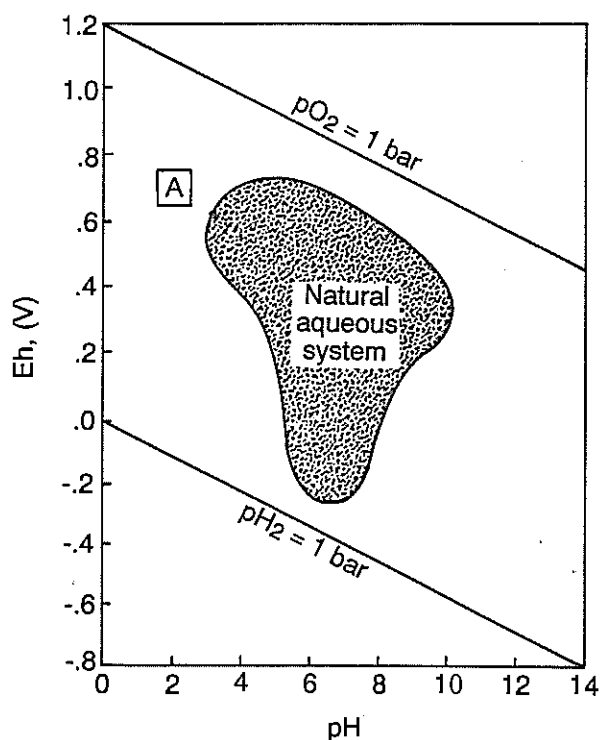


Figure 1. Eh-pH diagram showing where Sherman Mine leachate (A) plots relative to the field of natural aqueous systems (after Baas Becking et al., 1960).

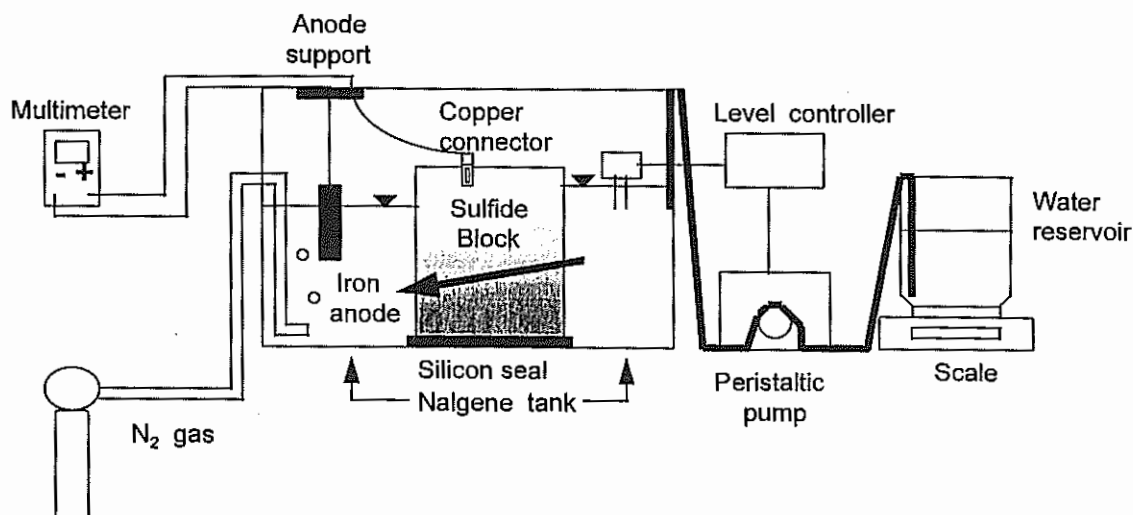
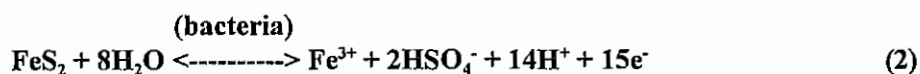


Figure 2. Electrochemical cell setup.

The sacrificial anode, suspended in the downstream pond, was attached to the semiconductive sulfide-graphite block, the cathode, by a copper plug assembly. The possibility of oxide coatings forming on the surface of the anode was reduced by generating anoxic conditions through purging the pond with nitrogen. Dissolved O_2 was maintained between 1.0 and 1.2 mg/L. Anodic materials must have standard oxidation potentials greater than that of pyrite. The oxidation potential for pyrite was calculated from equation 2, to be -376 mv .



Scrap iron was selected as the most suitable anode because it is considered both environmentally safe under natural conditions and relatively inexpensive. For iron or any other anodic material to function effectively, the cell must be capable of raising and maintaining the leachate pH above 5.5, close to the theoretical pH of rain water.

Laboratory experiments were also designed to test the ability of the cell to respond to simulated natural system perturbations. The experiment simulated an influx of acidity into the South Pit by a one time addition of ~3.5 L of AMD to the downstream pond. A multimeter was used to record EMF and current on a daily to weekly basis throughout the experiment. Redox potential (Eh) and pH were measured using an Accumet 1000 series meter with a Ag-AgCl reference electrode. The redox potentials are standardized to the hydrogen scale.

Water samples were taken periodically and analyzed for various aqueous species by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Precipitate samples were collected periodically for x-ray diffraction, scanning electron microscopy and elemental analysis. X-ray diffraction analysis was conducted using a RIGAKU D/Max-A powder diffraction system, with the specimen being analyzed from 3° to $90^\circ 2\theta$, at $0.02^\circ 2\theta$ increments with a 4 s integration time. 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 subsamples were analyzed for total metal content by ICP-AES following dissolution with 2M HCl-HNO₃.

Results and Discussion

AMD is a problem in the environment not only because of acidity but also because the solutions are rich in species inimical to the biosphere, as illustrated by the chemical analysis (table 1) of South Pit water. However, a rise in pH is

directly related to the formation of precipitates of iron phases with an accompanying diminution of toxic species by simultaneous precipitation or adsorption. We can demonstrate this by monitoring pH, Eh, and Al content in the aqueous phase. Al^{3+} is the principal ionic form of aluminum considered toxic to plant and animal species in acidic-leachate-contaminated aquatic environments.

Table 1. Chemistry of AMD from South Pit, Sherman Mine (pH=3.0)

Conc, mg/L		Conc, mg/L	
Fe	10	Ni	0.1
Al	10	SO_4^{-2}	1,500
Mn	5	Cl ⁻	7
Zn	0.16	F ⁻	1.4
Cu	0.1		

Source: Data courtesy of Syd Bartle, Dofasco Inc.

EMF and Current

The cell generated voltages exceeding 800 mV. This value can be predicted from the difference between the calculated oxidation potential of pyrite (FeS_2), -376 mV, and that of the oxidation of elemental iron to ferrous iron, +440 mV. During the latter stages of the experiment, the EMF decreased to a steady state value of ~350 mV. The current also decreased from an initial value of 25 mA to a level at ~7 mA.

pH and Redox

The pH increased linearly to between 5.4 and 5.5 after forty days (fig. 3). The redox potential of the system decreased from an initial value exceeding 550 mV to ~300 mV (fig. 3). These Eh-pH conditions approach those of reduced forms of iron and sulfur. Consequently, oxidizing reactions occurring on the sulfide mineral surface microsites will be significantly inhibited.

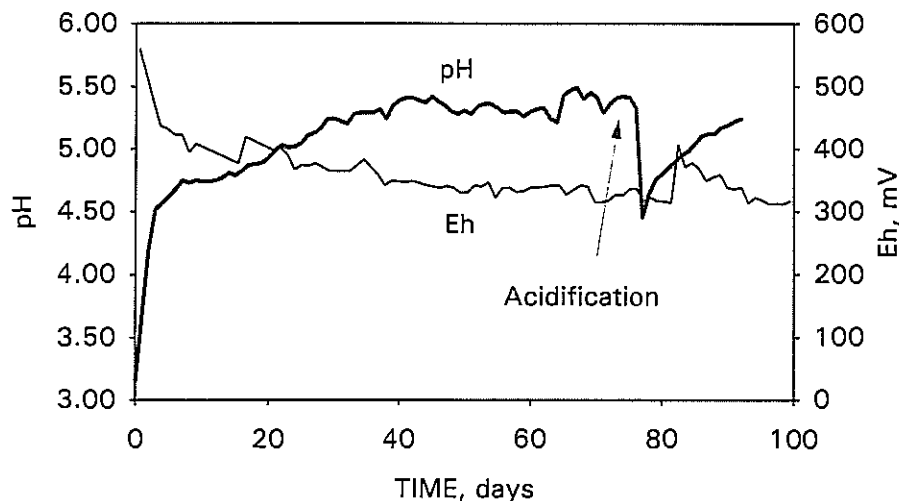


Figure 3. Changes in Eh and pH with time.

The ability of the system to respond to additional acidity following neutralization of the existing leachate was evaluated by a one-time addition, on day 77, of ~3.5 L of pH 3 leachate. The pH decreased from 5.30 to 4.45 (fig. 3) with a concomitant Eh increase from 314 to 418 mV. The pH and Eh recovered to values prior to the pH pulse within 16 days.

Precipitate Formation

When pH reached a steady-state value, a reddish-brown secondary solid phase was observed precipitating on the bottom of the experimental tank. SEM examination revealed a precipitate composed of a network of acicular crystals (fig. 4) with apparent trigonal symmetry. X-ray diffraction of specimens collected at various times throughout the experiment

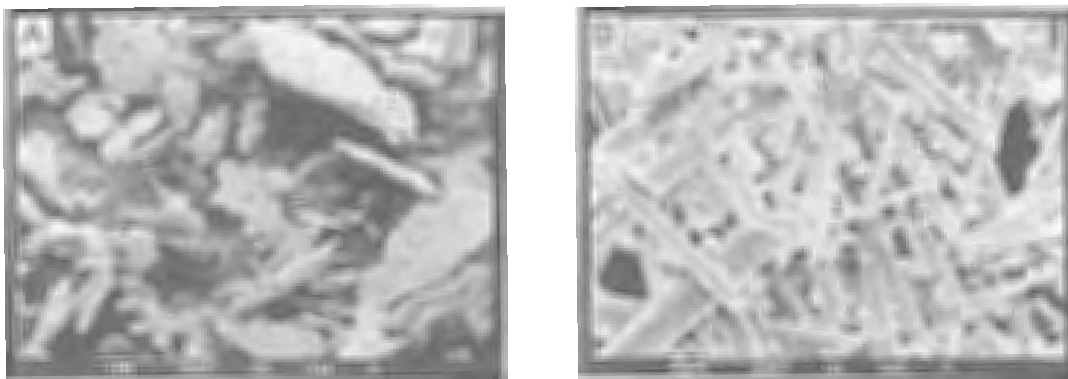


Figure 4. Scanning electron micrographs of precipitate: A) low magnification micrograph, B) higher magnification of acicular crystals within the aggregates.

revealed two predominant d-spacings at 4.75 ± 0.01 and 8.27 ± 0.01 nm. Although these two d-spacings are common to the iron sulfate hydrate mineral coquimbite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$), the crystallinity of the precipitate is insufficient to enable positive identification by X-ray diffraction. Chemical analyses indicate a modal composition of approximately 43% Fe, 18% S, 21% Ca, and 15% Mg, 0.7% Al (fig. 5).

Aluminum Chemistry

Aluminum concentration in the solution phase decreased from 10.5 mg/L to less than 0.01 mg/L within 30 days. This decrease may be caused by the precipitation of a separate Al phase or by adsorption of Al by, or incorporation into, the Fe rich precipitate. As indicated above, Al is a significant minor component of the solid phase.

Conclusion

The results of this laboratory study clearly demonstrate that the proposed electrochemical approach is an effective treatment for acid mine drainage. The electrochemical system has been shown to be capable of generating sufficient voltage and current to raise and maintain the pH of acid leachate to an environmentally acceptable level of 5.5 and to significantly reduce the redox potential, thus inhibiting the oxidation of sulfide minerals. Furthermore potentially toxic elements such as aluminum may be scavenged from solution as adsorbed or structural components during the formation of a relatively stable iron sulfate precipitate.

Future research will focus on an examination of both leachate chemistry and on the nature of solid precipitates, especially as potential scavengers for contaminant metals. Other possible anodic materials will also be examined.

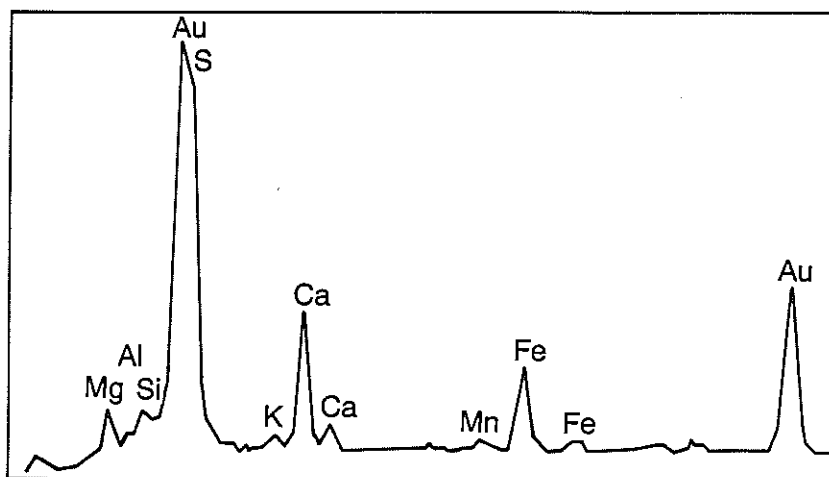


Figure 5. Energy dispersive spectrum of the iron sulfate precipitate.

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