Pergamon

PII: S0883–2927(96)00015–7

Applied Geochemistry, Vol. 11, pp. 425–432, 1996

0883–2927/96 $15.00+0.00

The amelioration of acid mine drainage by an in situ electrochemical method; part 2: employing aluminium and zinc as sacrificial anodes

Gene S. Shelp*, Ward Chesworth and Graeme Spiers
Department of Land Resource Science, University of Guelph, Guelph Ontario, Canada N1G 2W1

(*Received* 21 *August* 1994; *accepted in revised form* 4 *December* 1995)

Abstract—This work represents part of an ongoing investigation of electrochemical approaches to ameliorate acid mine drainage (AMD) problems occurring at the Sherman Iron Ore Mine of Temagami, Ontario, Canada. A series of laboratory experiments were conducted using a block of massive sulphide–graphite rock from the mine site as the cathode, Al and Zn as the sacrificial anodes and acidic leachate collected from the mine site as the electrolyte. The Al anode cell failed to raise the pH of the leachate above 4.5. Excellent results, however, were obtained using a Zn anode. The electrochemical cell raised and maintained the pH of the leachate at ~6.7 which was accompanied by significant decreases in Cd, Cr, Co, Cu, and Ni to levels well within environmentally acceptable limits. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

Acid mine drainage (AMD) represents a significant environmental and financial liability. Many techniques have been devised for the amelioration of the AMD problem. These include liming, the classical technique, filtration through biological materials (e.g. Dvorak *et al.*, 1991) or wetlands (e.g. Kalin and Smith, 1991), use of bactericides (Sobek, 1987), surface coatings on the sulphides (Ahmed, 1991), engineered covers (e.g Nicholson *et al.*, 1991), flooding (Ritcey, 1991), development of raised bogs (Brown, 1991), artificial creation of Fe pan (e.g. Blenkinsopp, 1991) and use of the adsorptive properties of biofilm (Blenkinsopp, 1991). Part one of our studies (Shelp *et al.*, 1995) provides more detail and lays out the rationale of the technique which we have chosen to apply to the problem at the Sherman iron mine, Temagami, Ontario, Canada (Fig. 1). There an exposed band of sulphide-rich graphitic bedrock, described as sulphide-facies iron formation and an adjacent open pit (the South pit) containing metal-rich acidic leachate, represent potential significant environmental hazards to the surrounding aquatic ecosystems.

Our new technique uses a galvanic arrangement in which the sulphide facies of the Fe formation was converted into the cathode of an electrochemical cell by connecting the sulphide rock electrically to a scrap Fe anode immersed in the AMD of the adjacent pit. Ground water completed the circuit and an analogue experiment demonstrated how pH was raised to 5.6 by operation of the cell (Shelp *et al.*, 1995). Accompanying the rise in pH, there was a significant lowering of the concentrations of Al, Cd, Co, Cu and Ni in solution.

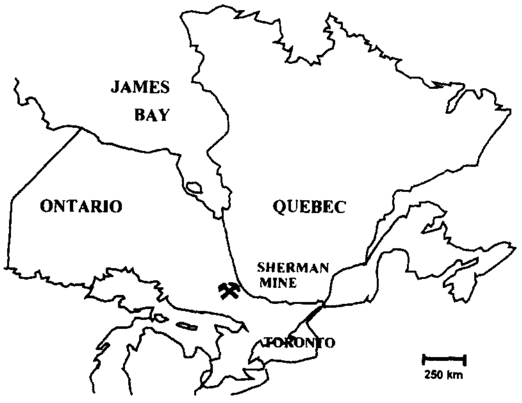

Fig. 1. Location map of the Sherman Mine Field site.

Part 2 extends the original study by presenting data obtained from electrochemical experiments employing Al and Zn as sacrificial anodes. The experiments were designed primarily to halt, or significantly inhibit the acid generating reactions, both by creating a reducing environment at the sulphide mineral surface–water–bacteria interface and by increasing the pH of AMD through conversion of H ions to H_2.

EXPERIMENTAL SETUP

A schematic diagram of the experimental cell used in the studies is shown in Fig. 2. The sulphide–graphite block, with approximate dimensions of 45 cm L by 30 cm W by 30 cm H, contained between 10 and 15% pyrite and was of fissile character with minor fractures extending through the thickness of the block. 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 head differential was maintained by an electronic level controller and peristaltic pump system. The upstream and downstream ponds contained 28 L and 41 L, respectively.

---

* Department of Land Resource Science, University of Guelph, Ontario Agricultural College, Guelph, Ontario, Canada. N1G 2W1.

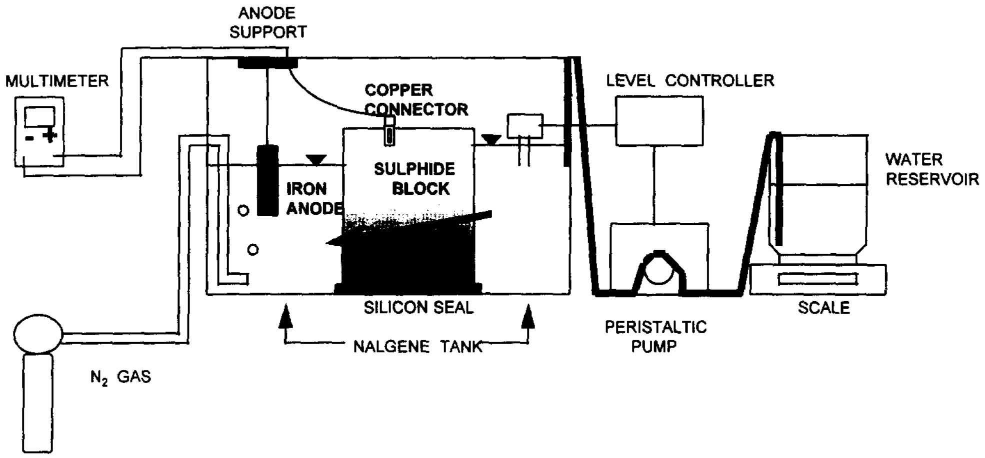

Fig. 2. Electrochemical cell setup used to test the feasibility of ameliorating AMD by cathode protection. The arrow shows the direction of flow from the upstream pond to the downstream pond. (Chemical analyses were conducted on the leachate contained within the downstream compartment.)

The sacrificial anode, suspended in the downstream pond, was attached to the semi-conductive sulphide–graphite block, the cathode, by a Cu plug assembly (Fig. 2). The downstream pond was purged with N_2 to inhibit the formation of oxide coatings on the surface of the anode. In the field this is analogous to low redox waters found in the Sherman pit at depths greater than 15 meters. The dissolved O_2 content of the pond was maintained between 1.0 and 1.2 mg/l. Aluminum was selected for testing as a potential anodic material both because of its high oxidation potential (E°—standard state), 1.706 V, and because, as shown by previous experiments, Al is effectively removed from solution during the electrochemical treatment of the leachate. Zinc was chosen both because of its high oxidation potential (E°), +0.7628 V and because of the relatively high pH, >8.0, required for the formation of amorphorous $Zn(OH)_2$ at 1×10^{-4} mol/l Zn^{2+}.

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 referencence electrode. The redox potentials presented in this paper are standardized to the hydrogen scale.

Water samples were taken periodically and analyzed for total dissolved metals such as Al, Ca, Cd, Co, Fe, K, Mg, Mn, Na, Ni, Pb, and Zn, by atomic absorption spectroscopy (AA) and inductively coupled plasma emission spectroscopy (ICP–AES), and anions by ion chromatography. Precipitate samples were collected periodically for X-ray diffraction (XRD), scanning electron microscopy (SEM–EDS) and elemental analysis (ICP–AES). X-ray diffraction analysis was conducted using a RIGAKU D/Max-A series powder X-ray diffraction system with the specimen being step-scanned from 3° to 90°2θ, at 0.02° 2θ increments with an integration time of 4 s. Precipitate samples were coated with 20 nm Au and examined by 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 2 M HCl–HNO_3.

RESULTS AND DISCUSSION

The effectiveness of the cell to reduce the hydrogen concentration of acidic leachate to pH > 5.5 is directly related to the specific phase of either Al or Zn precipitate formed. The formation of the precipitates should be accompanied by a diminution of toxic species through coprecipitation. These phenomena can be demonstrated by monitoring pH, by measuring the content of metals, such as Al, Cd, Co, Cu, Ni and Zn, in the aqueous phase, as well as for anionic species.

Aluminium anode

Physico-chemical properties of the leachate The EMF slowly rose from 950 mV to plateau at approximately 1140 mV by day 11 (Fig. 3). During the same time interval, the current slowly decreased from 4.5 mA to level off at 2.7 mA (Fig. 3), with a concomitant decrease in electrical conductivity from 2080 to approximately 1850 mS/cm (not shown).

A similar trend to that obtained by previous electrochemical cell experiments was observed, with a dramatic increase in pH during the first 4, from 3.17 to 4.34, followed by a slow rise to plateau at approximately 4.4 (Fig. 4). The pH remained constant for the following 10 days. The experiment was subsequently terminated. The reduced rate of increase in pH and the significantly lower equilibrium pH (Shelp *et al.*, 1995) are likely controlled by the formation of an Al precipitate such as amorphous gibbsite ($Al(OH)_3$) or alunite ($KAl_3(SO_4)_2(OH)_6$). During the same period, the redox potential decreased from 692 to level off at approximately 400 mV.

By day 14 the solution concentration of Fe decreased from an initial value of 11.2 to 7.0 mg/l, whereas Mn and SO_4 concentrations remained relatively constant at 5.4 mg/l and 450 mg/l, respectively. The electrochemical system appeared to reach an equilibrium solution concentration of Al at approximately 10 mg/l. Of the trace elements present in

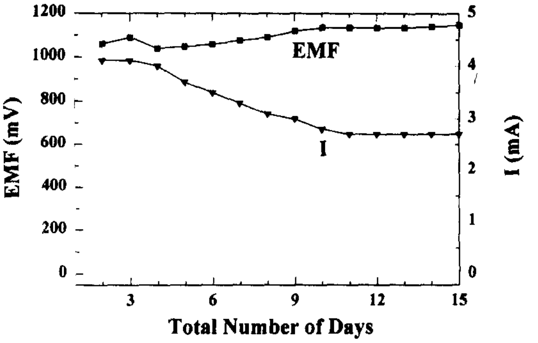

Fig. 3. Changes in EMF and current with time for the electrochemical cell experiment utilizing an Al anode.

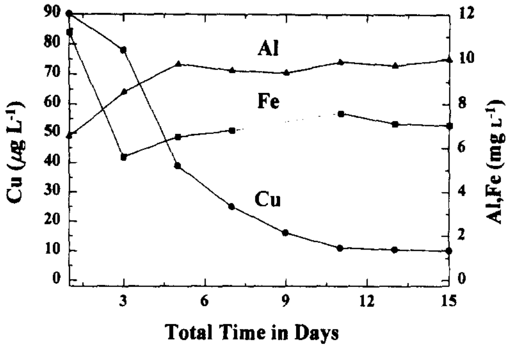

Fig. 5. Changes in Cu, Al, Fe and pH with time for the electrochemical cell experiment utilizing an Al anode.

solution, Cu alone showed a significant decrease with pH from an initial concentration of 90 µg/l at pH 3.0 to 12 µg/l by pH 4.4 (Fig. 5).

Solid phases A reddish-brown coloured precipitate was collected and analyzed by XRD, SEM–EDS, and ICP–AES. Several weak d-spacings were recorded by X-ray diffraction analysis (Table 1). The results suggest the precipitate is a crystalline material of short range order, although mineral species such as gibbsite and gypsum with characteristic d-spacings of 0.438 and 0.433 nm, and 0.756 and 0.427 nm, respectively, may be present. SEM micrographs show 2 distinct phases with a platey fine-grained mineral superimposed on an amorphous groundmass (Fig. 6). The chemical composition obtained by EDS analysis indicated an approximate atomic percent ratio of approximately 34% S, 27% Fe, 13.4% Ca, 10% Mg, 8.5% Al, 5% Si, and 2% Zn (Fig. 7). The concentrations of trace elements Co, Cu, Cd, and Ni were 62, 12, 13, and 88 mg/kg, respectively.

Table 1. XRD data for precipitates collected from the Al and Zn anode experiments

Al anode precipitate d-spacing (nm)	Zn anode precipitate	
	d-spacing (nm)	relative intensity
0.755	0.871	100
0.630	0.440	58
0.598	0.321	13
0.504	0.313	15
0.465	0.270	13
0.440	0.264	20
0.425	0.253	n.a.
0.347	0.227	16

Potential for technology development The minimum acceptable maintenance pH for a working electrochemical cell is 5.5, which represents the provincially regulated lower pH limit for the discharge of industrial waste waters. The electrochemical cell utilizing an Al anode failed to achieve this goal. Consequently, Al does not appear to be a suitable anode for the proposed technology.

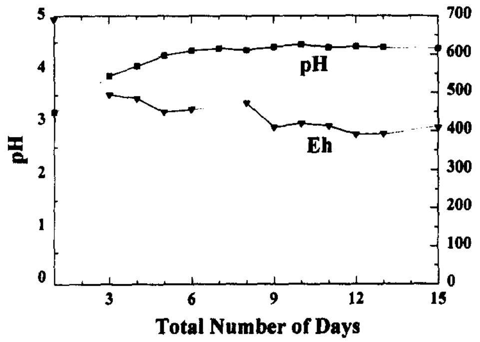

Fig. 4. Changes in pH and Eh with time for the electrochemical cell experiment utilizing an Al anode.

Zinc anode

Physico-chemical properties of the leachate The EMF decreased from a starting value of 1246 mV to plateau at approximately 400 mV by day 74 (Fig. 8), while the current rapidly decreased initially from 24 mA then slowly levelled off at approximately 1.3 mA (Fig. 8). The resulting pH data shows 3 distinctly different zones in the rate of H+ reduction (Fig. 9).

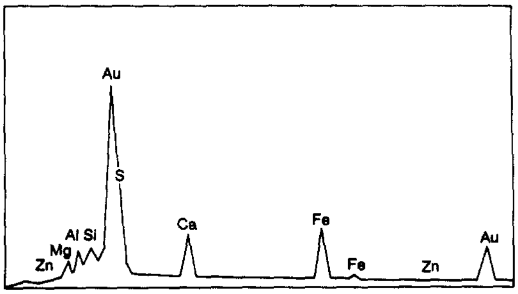

Fig. 7. Energy dispersion spectrum of the solid phase collected from the electrochemical experiment utilizing an Al anode.

An initial average rate of 2.0E−4 mol/day was recorded for the first 6 days (Zone 1), 2.0E−6 mol/day for the period day 7 to day 18 (Zone 2), and 2.8E−8 mol/day from day 19 to day 70 (Zone 3), followed by a plateau of approximately pH 6.6. Zone 1 represents an environment where little precipitation occurred. Figure 10, however, suggests that the formation of separate Al and Fe precipitates may be controlling the hydrogen reduction reaction rates of zones 2 and 3, respectively. Between pH 4.2 and 5.6, Al concentrations decreased from 11.5 to <0.5 ppm whereas Fe showed a dramatic decrease in concentration from 25 mg/l Fe at pH 5.8 to about 10 mg/l by pH 6.3 (Fig. 11). The effect of the ion concentration on the reaction rate, as stipulated by the rate law, however, has not been determined. As before, pH <5 was achieved within a week.

A concomitant reduction in Eh with an increase in pH shows the trend predicted by the Nernst relationship. Apart from S in the form of SO_4, hydrogen is the most electronegative ion present in the system. Although not identifiable, the production of $H+$ from the hydrolysis of Al and Fe is apparently controlling both the rate of $H+$ reduction to H_2, as well as the rate at which the system Eh decreases over time. The SO_4 concentration remained relatively constant at 700 mg/l.

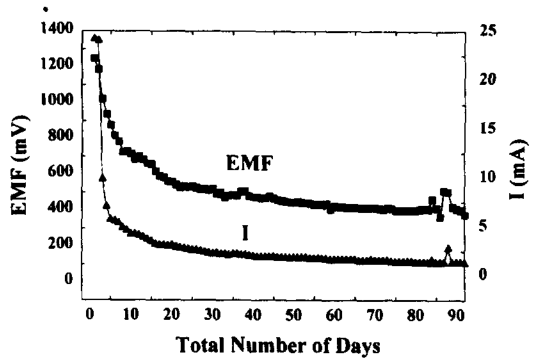

Fig. 8. Changes in EMF and current with time for the electrochemical cell experiment utilizing a Zn anode.

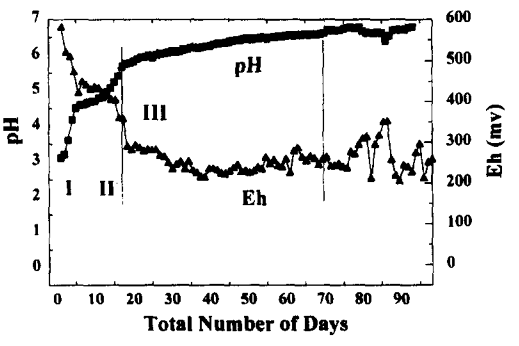

Fig. 9. Changes in pH and Eh with time for the electrochemical cell experiment utilizing a Zn anode.

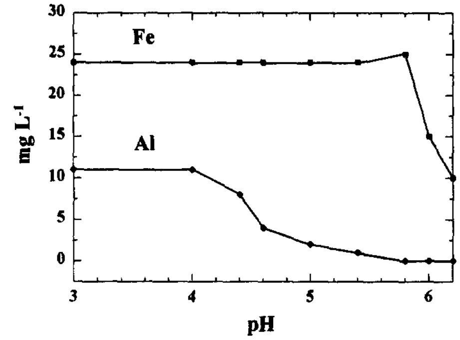

Fig. 10. Changes in Al and Fe with pH for the electrochemical cell experiment utilizing a Zn anode.

Aluminium and Fe solution concentrations appear to be strongly controlled by pH. The significant decreases in Al and Fe with increasing pH by day 19 and day 46, respectively (Fig. 11) illustrate this hypothesis. Zinc concentration continued to increase from an initial 0.5 mg/l to approximately 70 mg/l by day 91 (Fig. 12). The behaviour of trace elements is shown in Figs 13 and 14.

Solid phases

A reddish-brown coloured precipitate was collected and analyzed by XRD, SEM–EDS, and ICP–AES. Diffraction analysis indicated a mineral with predominant d-spacings at 0.87 and 0.44 nm (Table 1). The SEM micrographs show a crystalline mineral displaying a tabular structure arranged in rosettes superimposed on an amorphous groundmass (Fig. 14). The chemical composition of the complete sample obtained by EDS analysis indicated an atomic percent ratio of approximately 35% Zn, 34% O, 15.3% Al, 8.5% Fe, 4% S and 3% Si (Fig. 15). The algorithm calculated the content of O by difference (Springer, 1976). It has not been possible to positively identify the Zn mineral. The concentrations of Cd, Cr, Co, Cu, and Ni in the precipitate were 97, 166, 62, 3, and 88 mg/kg, respectively.

Potential for technology development A total of 3.1 g of Zn anode was consumed during the 3-months

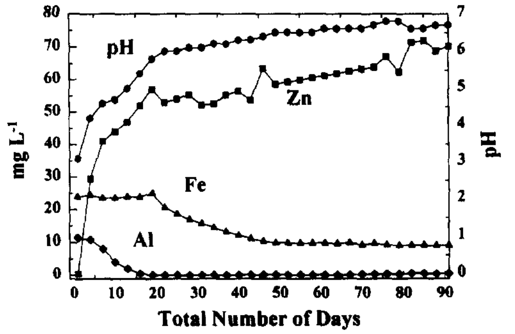

Fig. 11. Changes in Al, Fe, Zn, and pH with time for the electrochemical cell utilizing a Zn anode.

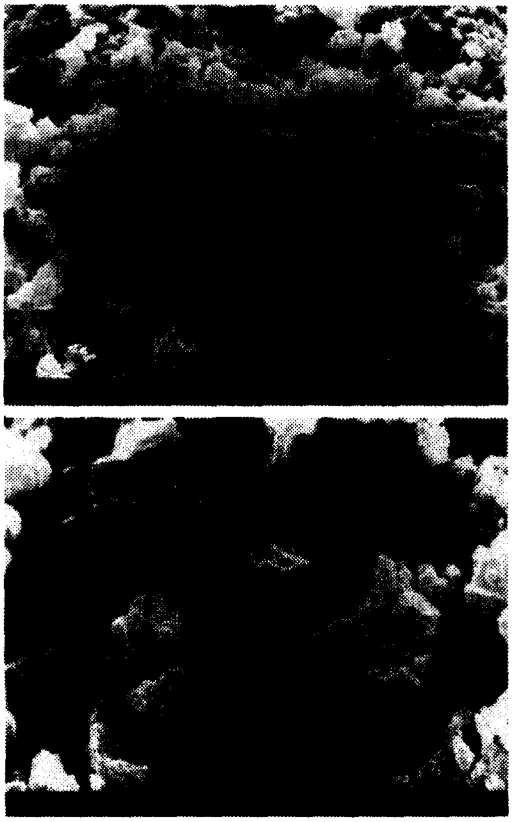

Fig. 6. SEM micrographs (a and b) showing the amorphous nature of the solid phase collected from the electrochemical cell experiment utilizing an Al anode.

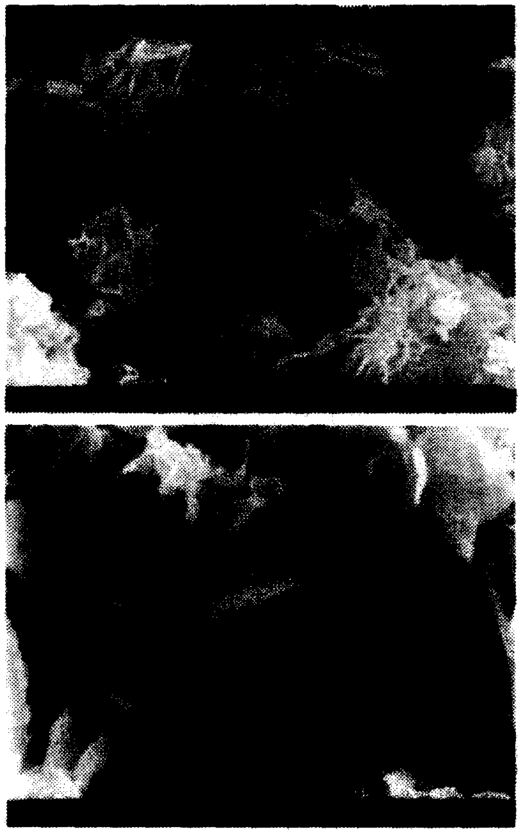

Fig. 14. SEM micrographs showing (a) rosette arrangement and (b) the petal like arrangement of the individual mineral plates (electrochemical experiment utilizing a Zn anode).

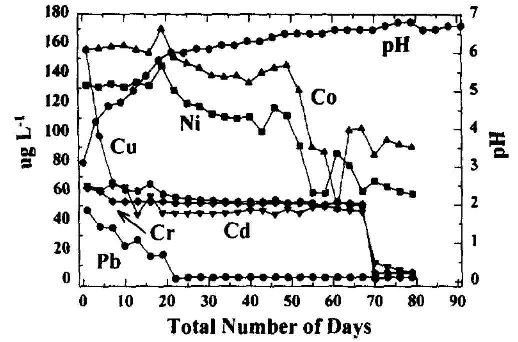

Fig. 12. Changes in Cd, Cr, Co, Cu, Pb, Ni, and pH with time for the electrochemical cell experiment utilizing a Zn anode.

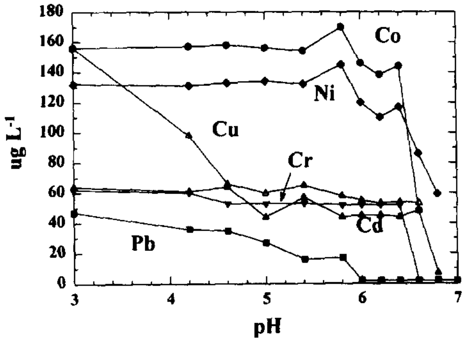

Fig. 13. Effect of pH on the solution concentrations of Cd, Cr, Co, Cu, Pb, and Ni for the electrochemical cell experiment utilizing a Zn anode.

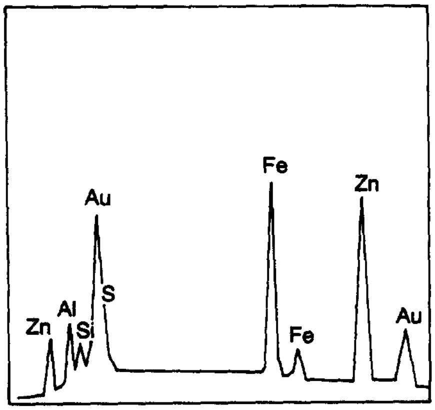

Fig. 15. Energy dispersion spectrum of the solid phase collected from the electrochemical cell experiment utilizing a Zn anode.

study which resulted in increasing the pH of 41 1 of leachate from 3.0 to a maintenance value of approximately 6.7. During that period, solution concentrations of Cd, Cr, Co, Cu, and Ni, were reduced significantly to below environmentally acceptable levels for mine effluent discharge. Although the approach shows considerable promise, the cost of Zn metal will probably prove it economically unviable. The second consideration is the unacceptable high concentration of Zn in solution under the current Eh/pH conditions. On-going work is investigating the effect of a dissolved O_2 gradient as exists in the South Pit on the formation of secondary oxide and oxyhydroxide precipitates, as well as associated coprecipitation reactions.

CONCLUSIONS

The electrochemical cell utilizing Al as the sacrificial anode failed to establish an acceptable Eh/pH environment. Experiments conducted with a Zn anode, however, showed significant reductions in both acidity of leachate and solution concentrations of dissolved trace elements. Over a period of approximately 2 months the pH of the electrochemical system rose from 3.0 to a maintenance value of 6.7 while the concentrations of Al, Cd, Co, Cr, Cu, and Ni decreased to environmentally acceptable levels. The cost of Zn may, however, preclude its use in the amelioration of AMD.

Future research will examine the effect of O_2 gradients on both the efficiency of the electrochemical cell, as well as the coprecipitation of trace elements.

Acknowledgements—The authors acknowledge the financial support of Dofasco Inc., NSERC (Natural Sciences and Engineering Research Council) and URIF (University Research Incentive Fund of the Ontario Ministry of Education and Universities, for supporting the ongoing program. Special thanks to Mr. Syd Bartle, Raw Materials Manager, Dofasco Inc. for his interest and logistical support. The enthusiastic technical support provided by Liangxue Liu, Karim Jabir and William Leveson-Gower is greatly appreciated.

Editorial handling: Dr D. D. Runnells.

REFERENCES

Ahmed S. M. (1991) Electrochemical and surface methods for the prevention of the atmospheric oxidation of sulphide tailings. In *Proc. 2nd Inter. Conf. Abatement of Acidic Drainage*, Montreal, Quebec, September 1991, Vol. 2, pp. 305–319.

Blenkinsopp S. A. (1991) The use of biofilm bacteria to exclude oxygen from acidogenic mine tailings. In *Proc. 2nd Inter. Conf. Abatement of Acidic Drainage*, Montreal, Quebec, September 1991, Vol. 1, pp. 69–377.

Brown A. (1991) Proposal for the mitigation of acid leaching from tailings using a cover of muskeg peat. In *Proc. 2nd Inter. Conf. Abatement of Acidic Drainage*, Montreal, Quebec, September 1991, Vol. 2, pp. 517–527.

Dvorak D. H., Hedin R. S., Edenborn H. M. and Gustafson S. L. (1991) Treatment of metal contaminated water using bacterial sulphate reduction: Results From Pilot Scale Reactors. In *Proc. 2nd Inter. Conf. Abatement of Acidic Drainage*, Montreal, Quebec, September 1991, Vol. 1, pp. 301–314.

Kalin M. and Smith M. P. (1991) Biological amerlioration of acidic seepage streams. In *Proc. 2nd Inter. Conf. Abatement of Acidic Drainage*, Montreal, Quebec, September 1991, Vol. 1, pp. 355–368.

Nicholson R. V., Akindunni F. F. Sydor R. C. and Gillham, R. W. (1991) Saturated tailings covers above the water table: the physics and criteria for design. In *Proc. 2nd Inter. Conf. Abatement of Acidic Drainage*, Montreal, Quebec, September 1991, Vol. 1, pp. 443–460.

Ritcey G. M. (1991) Deep water disposal of pyritic tailings—a simulation for acid predection. In *Proc. 2nd Inter. Conf. Abatement of Acidic Drainage*, Montreal, Quebec, September 1991, Vol. 1, pp. 421–442.

Shelp G., Chesworth W. and Spiers G. (1995) The amelioration of acid mine drainage by an *in situ* electrochemical method: Part 1. Employing scrap iron as the sacrifical anode. *Appl. Geochem.* **10**, 705–713.

Sobek A. A. (1987) The use of surfactants to prevent AMD in coal refuse and base metal tailings. In *Proc. Acid Mine Drainage*, Halifax, Nova Scotia, March 1987.

Springer G. (1976) Correction procedures in electron-probe analysis. In *Short Course in Micobeam Techniques*, Edmonton, Alberta.