GEOCHEMISTRY OF OXIDISED WASTE ROCK: IMPLICATIONS FOR THE DISPOSAL OF MINE WASTE

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ABSTRACT

During a study of the Avoca mine, County Wicklow, Eire, an assessment was made of the effects of precursor lixiviant on the removal of metals and salts from partially oxidised mine waste. Based on batch tests, the partially oxidised mine waste can release high concentrations of contaminants noticeably Zn, Mn, Cd, Fe and Cu on initial contact with water. At the Avoca mine, groundwater is acidic and accentuates the oxidation process. In testwork this was simulated by using a lixiviant of similar chemistry to measured mine water chemistry. Only slightly enhanced leaching for this simulated mine water was observed compared to distilled water, due to a buffering effect by lixiviant solute content.

The solubility of most cations are strongly controlled by their mineralogy, for example Ca by gypsum. The higher than predicted solubility of Fe in one cell in the testwork was due to the presence of Fe-sulfate salts which although thermodynamically less stable than goethite appear to have a higher rate of formation and so mobilization is controlled by kinetic as well as thermodynamic factors. Even after flooding and initial flushing of the cells solute release is observed despite a decrease in redox potential. These results indicate that even after final disposal, oxidised mine waste can still generate significant concentrations of contaminants.

INTRODUCTION

Subaqueous disposal of mine waste is a common method proposed for the disposal of mine waste, particularly mine waste that is considered likely to generate Acid Rock Drainage (ARD). The disposal can be within a flooded open pit, flooded underground workings or tailings impoundment. Although this practice may reduce the potential for ARD commonly such mine waste contains sulfide oxidation products, many of which are highly soluble. Consequently on contact with water contaminants can be released to overlying water or to groundwater. The stability of secondary mineral assemblages to subsequent reactions has been evaluated by several workers over the last few years (Alpers et al., 1994; Cravotta, 1994; Bowell et al., 1996; Sadler, 1998). Despite these studies the relative release rates of metals from partially and wholly oxidised mine waste is unknown and the control of mineral species for complex polymetallic mine waste is still poorly understood.

As part of a larger study on the geochemical stability of mine waste at the Avoca mine, in County Wicklow, Eire an assessment was made of the release of chemical constituents from the mine waste to the environment on contact with water

(Bowell et al., 1997). Mining has been intermittent in the area from 1750 to 1982 with the major periods of mining being from 1750-1880 and 1958-1962. The ore has been exploited by underground and open pit methods and large waste rock dumps occur either side of the Avoca river (Platt, 1975). The Department of Energy and Wicklow County Council through European Community funding has initiated a study to reclaim the Avoca mine waste rock dumps.

GEOLOGY OF THE AVOCA MINING DISTRICT

The Avoca mineralization comprises of Ordovician age volcanogenic massive sulfide deposits. These were formed in a submarine environment at the end of a sialic volcanic event (Platt, 1977). Ore mineralization is dominated by pyrite. Associated with pyrite are chalcopyrite, bornite, chalcocite, covellite, sphalerite, galena, arsenopyrite, pyrrhotite, Ag-,Bi-,Sb- sulfosalts and tetrahedrite. The massive sulfide lenses are up to 3 m thick and occur over a strike length of up to 300 m. These mineralized lodes grade up to 13 % Cu and over 40% pyrite. The disseminated sulfide mineralization is generally more widespread and can carry <0.5-4 % Cu and up to 25% pyrite.

METHODOLOGY

The sample used specifically for this study was a composite sample of partly oxidised pyritic marginal ore. Main minerals were pyrite, sphalerite, and galena with minor chalcopyrite and numerous secondary minerals (Table 1). The partially oxidised sulfide waste rock has a high potential for both reactive acidity as reflected in the low paste pH (Table 1) and a large reservoir for acid generation as reflected by the low NNP and high NAG (Table 1).

The lixiviants used in the testwork were distilled water (cell 1) and synthetic water based on analyses of mine water from an adit and seepage from waste rock dumps (Table 2).

Parameter	Lixiviant	Mine water
pH (su)	3.25	3.61
Sulfate	1154.00	1235
Chloride	33.90	27.42
Iron	68.50	66.67
Manganese	5.50	4.26
Copper	0.58	1.55
Zinc	83.30	69.76
Sodium	6.70	10.80
Magnesium	94.10	94.81
Potassium	4.25	4.69
Calcium	11.20	3.61

All values in mg/l unless otherwise stated.
Table 2: Geochemistry of natural waters from Avoca mine and synthetic lixiviant.

Testwork protocol

The crushed (<5 mm diameter rock chips) were subjected to periodic rinsing in plexiglass cylinders that were sealed with a central drain hole at the base of the cylinder. The cells used in this testwork conformed with those proposed by previous studies as being useful in ARD assessment (SRK, 1989). The cells were loaded with approximately 3 kg of waste rock. The philosophy of the testwork was to assess the mineralogical and geochemical changes that were likely for three scenarios:
- Initial placement of waste rock (cycle 0).
- Prolonged exposure of waste rock to water (cycles 1-22).
- Flooding of mine waste (cycles 23-24).

The first cycle was designed to assess the initial flushing of soluble components from the waste rock. In the initial rinse, four pore volumes of water was used to flush the unsaturated waste rock.

The second phase of leaching was used to estimate the reactive or available solute and acid inventory and to investigate controls on metal release from the waste rock. Cycle length for this stage was fixed at three days over which time, it was found that conductivity becomes stable. At the end of each cycle the drained water volume was measured and the leachate analysed for dissolved metals, cations, As, sulfate, EC, Eh and pH.

The final cycles were designed to assess the release of constituents with a permanent water cover. In the first cycle the waste rock was saturated and a minimum of 50 cm head of water added. The sample was left like this for three days after which time an aliquot was analysed and the water volume replaced. A second sample was taken 28 days later and analysed.

All analyses were undertaken at the Division of Materials and Minerals, Cardiff University. Solution analysis was by ICPAES and flame AA. Geochemical modelling was undertaken using the geochemical codes MINTEQA2 (Allison et al, 1991).

Property	
Primary sulfides	Pyrite, sphalerite, galena, chalcopyrite
Secondary minerals	Chalcanthite, jarosite, melanterite, halotrichite, connellite, brochanthite
Gangue minerals	Quartz, chlorite, muscovite, Ca-Na feldspar, K-feldspar, amphibole, biotite, smectite, kaolinite, ankerite, siderite
Partial chemistry	0.3wt% Cu; 5.6wt% S; 0.4wt% Zn; 0.3 wt% Pb
NNP	-105 eq kg CaCO$_3$
NAG	76.5 eq kg H$_2$SO$_4$
Paste pH	2.73 su

Table 1: Characteristics of sample used in testwork.

RESULTS AND DISCUSSION

Initial leaching of the waste rock

In the four pore volume leach test significant levels of Fe, Mn, Zn, As, Cu, Cd and Al were leached in both cells (Table 3).

Parameter	Cell 1	Cell 2
pH (su)	2.04	3.24
Sulfate	957.00	1062.00
Manganese	7.80	9.10
Iron	189.00	29.50
Aluminium	148.00	50.00
Copper	6.40	5.90
Zinc	50.20	76.80
Cadmium	0.07	0.03

All values in mg/l unless stated otherwise
Table 3: Results of four pore volume extractions.

The high levels of Fe and sulfate in the leachate are most likely due to dissolution of secondary minerals that are common on the old dumps. In the case of Cu the lower leachate concentration does not necessarily mean that leaching is not occurring but that adsorption or precipitation is simultaneous to dissolution and this is reflected in the microchemistry of the precipitated Fe-Mn oxide phases that have high trace level concentrations (up to 10,000 ppm) of Co, Ni, Cu and As (Bowell et al., 1997).

This has important implications in that at low pH secondary Fe, Cu and Zn sulfates can be precipitated or trace metals and sulfate can be adsorbed by goethite. With a change in pH these elements are released leading to a secondary source of acid generation, temporarily stored in the mine waste and are much less predictable than primary sulfide oxidation.

Prolonged exposure of waste rock to water

Cyclic leaching was undertaken using a conventional seven-day cycle (3 days wet, 3 days dry, then sample). The full results of the testwork are available from the authors.

pH

Although cell 2 was treated with the lower pH water, the lowest pH is observed in cell 1. This could be because in cell 2 pH is probably buffered by ferric hydroxide at 3.25 whereas no such control exists in cell 1 and consequently distilled water will assume the pH of the prevailing mineral reactions.

During the course of cyclic leaching pH in both cells attains an equilibrium value after 5-10 cycles of 2.3-2.5 reflecting the presence of Fe sulfate salts that were observed in cell 1 and by theoretical modelling found to be near saturation early in the testwork program (Figure 1). It has been shown that water in contact with Fe-sulfate phases can have pH that is considerably lower than this (Alpers and Nordstrom, 1991; Alpers et al., 1994). An additional control on pH could also be buffering by unoxidised sulfides (Thornber, 1993).
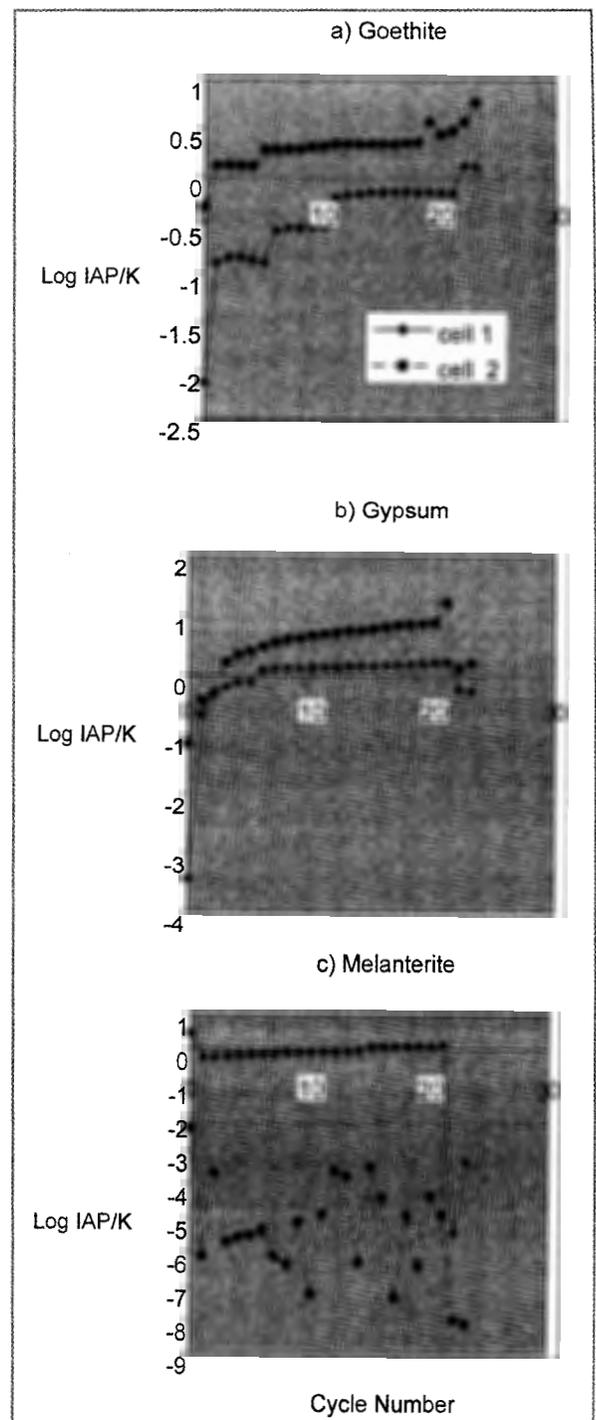
Figure 1. Saturation indices for important mineral species.

Metals

In most cases, for example Fe (Figure 2a), Mn (Figure 2b), and Zn (Figure 2c) enhanced concentrations are observed in the cell 2 leachate where enhanced sulfide oxidation and metal leaching occurs due to the lixiviants high solute levels. For Cu (Figure 2d) leaching is initially higher in cell 2 but quickly falls with leaching from both cells being similar. Aluminium leaching by contrast is higher in cell 1, possibly due to lower pH in the cell (Figure 2e). Over time as pH rises and solute concentrations increase, goethite and gypsum becomes saturated (Bowell et al., 1997) and concentration differences between the two cells decrease (Figure 2).

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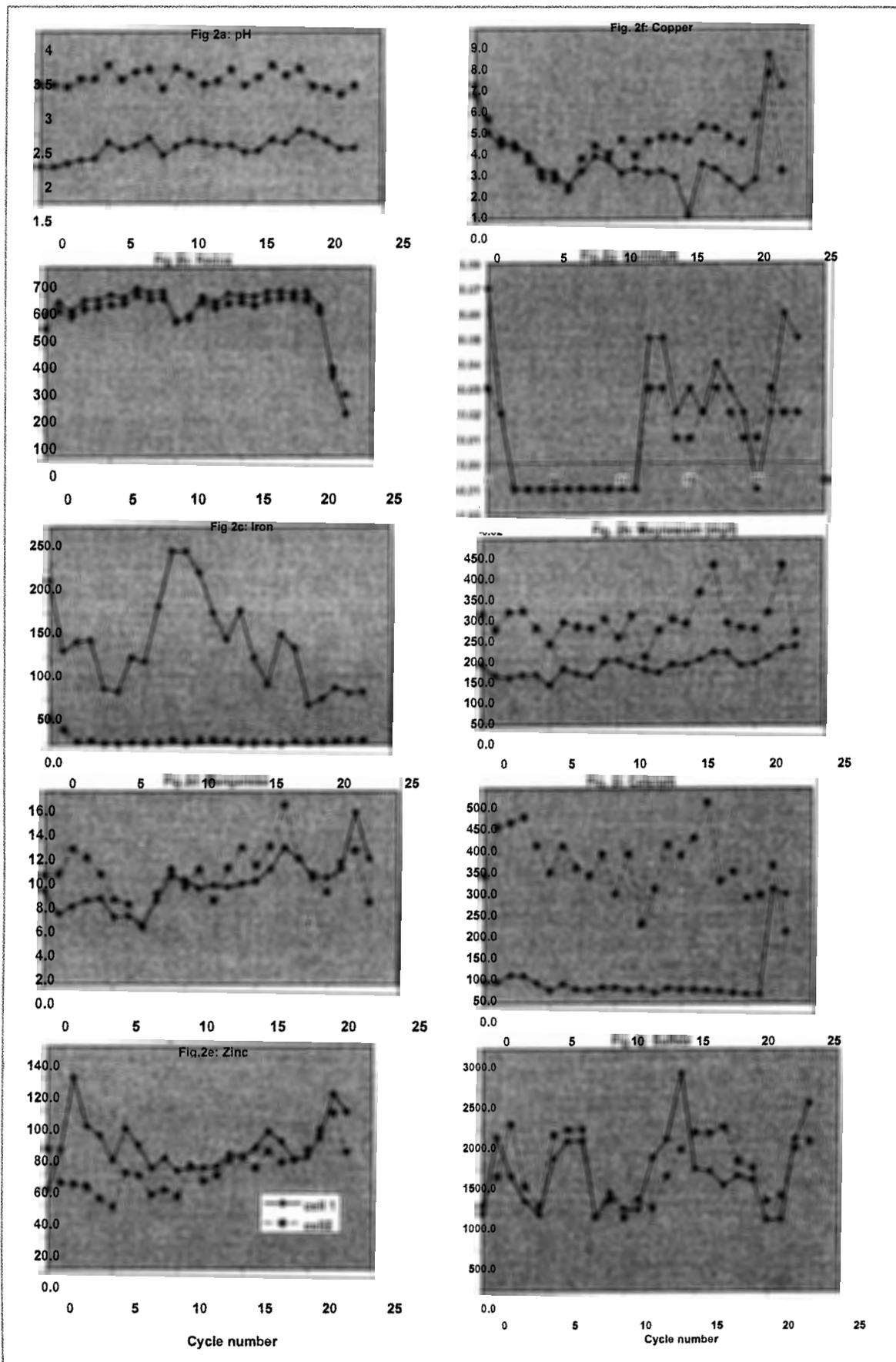
Figure 2. Results of cyclic leaching testwork. Results in mg/l unless stated otherwise.

Cations

Both Mg and Ca show high concentrations in the leachate with cell 2 reflecting a higher concentration than cell 1 (Figure 2f-g). Magnesium is leached from dissolution of minerals such as chlorite, amphibolessmectite and ankerite.

All three of these minerals have been identified in the spoil material and in the in-situ host rocks and mineralization.

Calcium chemistry in the samples is controlled, like magnesium, by dissolution of buffer minerals, in the case of calcium by calcite, plagioclase feldspar, amphiboles and clay minerals. Similarly calcium is precipitated as sulfate minerals, anhydrite ($CaSO_4$) and gypsum ($CaSO_4.2H_2O$) both of which have been identified in the samples.

Sulfate

Both samples show peaks related to sulfate leaching, often well in excess of feed concentration, indicating dissolution of sulfate minerals and sulfide oxidation. Troughs, below feed concentration in cell 2, relate to sulfate precipitation events (Figure 2j).

From MINTEQA2 speciation sulfate speciation is dominated by calcium and to a lesser extent magnesium with iron, copper and zinc sulfate complexing decreasing with time (Table 4). Other species include ferric sulfate. These are most abundant during maximum periods of sulfide oxidation in cycles 5-10.

Date	Sulfate speciation
Cycle 1	10% SO_4^{2-}; 3% $MgSO_4$; 12% $CaSO_4$; 36% $FeSO_4$; 12% $ZnSO_4$; 23% $CuSO_4$; 4% other S species
Cycle 5	15% SO_4^{2-}; 4% $MgSO_4$; 22.4% $CaSO_4$, 32.6% $FeSO_4$; 10 % $ZnSO_4$; 7.6% $CuSO_4$; 8.4% other S species
Cycle 10	18% SO_4^{2-}; 5% $MgSO_4$; 25.1% $CaSO_4$, 28.3% $FeSO_4$; 8.6% $ZnSO_4$; 6.2% $CuSO_4$; 8.8% other S species
Cycle 15	18.5% SO_4^{2-}; 5.3% $MgSO_4$; 33.7% $CaSO_4$, 26% $FeSO_4$; 8% $ZnSO_4$; 4.5% $CuSO_4$; 4% other S species
Cycle 24	20% SO_4^{2-}; 5.8% $MgSO_4$; 44% $CaSO_4$, 18% $FeSO_4$; 5% $ZnSO_4$; 4.1% $CuSO_4$; 3.6% other S species

Table 4: Sulfur speciation in Avoca cycles, cell 1 as predicted by MINTEQA2.

Less than 20% sulfate remains as free sulfate, most likely adsorbed onto mineral grains such as goethite. Secondary sulfate minerals have been recorded in the x-ray diffraction traces of the samples confirming theoretical modelling predictions that gypsum, anhydrite, goslarite, melanterite, retgesite ($NiSO_4.6H_2O$), chalcanthite and coquimbite are close to or are saturated in the testwork leachates (Bowell et al., 1997).

Flooding of mine waste

On completion of cyclic leaching, and flooding of the cells, concentration decreased in both cells for all constituents (Figure 2). It should be noted that this was a preliminary experiment and in hindsight should have been continued until Eh became reducing or that parameter concentrations stabilised. Additionally both Eh and dissolved oxygen should have been measured on the two cells. Although not completely suggesting that even when flooded metal leaching is still occurring. Because of the different experimental conditions for the flooded cells versus the standard cells, the data sets are not directly comparable. A very obvious and intentional difference is that the flooded cells are not in contact with atmospheric oxygen. However, another important difference is that the entire liquid contents of the cell are not exchanged after each cycle. Consequently, the determination of yield of the cell as measured in mg/kg is complicated by the build-up of constituents in the cell from preceding cycles (Table 5).

	Cell 1	Cell 2
Cumulative Sulfate, mg/kg Cycles 1-2	2870	2489
Cumulative Sulfate, mg/kg Cycles 3-22	28270	30277
Cumulative Sulfate, mg/kg Cycles 23-24	4343	3654
Rate increase (flooded to cyclic rinsing)	0.15	0.12
Rate increase (flooding to initial flushing)	9.85	12.14
Rate increase (cyclic rinsing to initial flushing)	1.51	1.47

Table 5: Sulfate yields in testwork leachates.

The flooded cells show that the pH values at the time of flooding were low (pH < 3), and these samples remained at low pH values throughout the remainder of the experiment.

The chemistry of the flooded cells is likely to be explained by a combination of several factors:

- The initial reservoir chemistry dominated the compositions of the samples removed from the cells and only minor variations occur in the following two cycles. Whilst this is true for cell 2, cell 1 continues to show a large increase in sulfate yield.
- Flushing of secondary minerals in the cells. This is highly likely and the important consideration here is that the flushing takes more than one cycle and could continue for a prolonged period (Alpers et al., 1994; Sadler, 1998).
- Continued sulfide oxidation. Although the convention is to assume on flooding that all oxidation is terminated the reality is that some dissolved oxygen is still present within groundwater and so oxidation can continue, all be it at a reduced rate (Lowson, 1982). However, even in anoxic conditions if a sufficiently strong oxidiser was present, such as ferric Fe at low pH then the potential exists for further sulfide oxidation. Provided unreacted conductive sulfides are in connection then theoretically, oxidation could occur over the sulfide mass. This occurs through delocalised electrons being transferred from one pyrite atom to another. Consequently, the distance

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between the anode and cathode is limited, only by the electrochemical properties of the sulfide grains (Sivenas and Beal, 1982; Thornber, 1993). This process has been shown to have geological analogues in the production of deeply weathered sulfide bodies well below the water table, such as at Kambalda, Australia (Thornber, 1975).

Consequently, even after flooding sulfide mine waste can be considered as a potential source of metals, acidity and salts for groundwater contamination.

CONCLUSIONS

In this study it has been found that the Avoca spoil material is acid generating and has a high labile metal and sulfate content. The material demonstrates different acid generating potentials depending on mineralogy of the material reflecting the nature of the spoil and length of time exposed.

Two principal acid generating mechanisms have been determined, these are sulfide oxidation and sulfate dissolution. Sulfide oxidation tends to be a more sluggish process than sulfate dissolution and is only observed after a few cycles of flushing whereas even with initial contact between mine waste and water secondary salts can be flushed from the waste.

The use of distilled water in assessing the leachability of mine waste is conservative compared to leaching with a simulated natural water in terms of acid and salt release due to some buffering potential from natural waters. By contrast natural water leaching has the potential to leach significant concentrations of metals, possibly due to the presence of complexing ligands in natural waters that would enhance mobilization. This has important implications for the assessment and modelling of mine waste behaviour and is currently being investigated further at the Division of Materials and Minerals.

Flooding of mine waste does not necessarily imply cessation of metal, acid or sulfate release or even of sulfide oxidation. From the preliminary results reported here it is possible to suggest that a combination of physical flushing and chemical oxidation-dissolution can be responsible for the continued release of metals, salts and acidity from mine waste. This has important implications for closure practice and is the subject of ongoing research in the Division of Minerals and Materials, Cardiff University.

ACKNOWLEDGEMENTS

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