PYRITE OXIDATION IN COAL-BEARING STRATA THE USE OF P-BLOCKING TECHNIQUES

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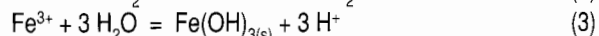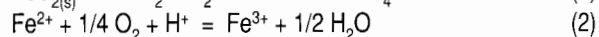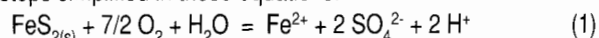e-mail: samita.roy@durham.ac.uk

ABSTRACT

Management of acidic mine drainage (AMD) can be divided into three categories; source, migration and treatment of effluent, the latter two being the most common. Migration control, includes diversion of effluent from ground water flow-paths and grouting of spoil heaps whereas treatment of the effluent involves the application of neutralizing chemicals or the cheaper passive constructed wetlands and anoxic limestone drains. These treatments are often costly, labour intensive and required throughout the lifetime of the effluent source.

In contrast, control of the source of AMD by prevention of pyrite oxidation could provide a permanent solution to the problem. Coating technologies using phosphates, acetyl acetone, lignin and sodium silicate have recently been investigated by several authors (Nyavor et al., 1995; Evangelou, 1995a). Evangelou et al., demonstrate coating pyrite with iron phosphate by applying a phosphate/hydrogen-peroxide solution decreases amount of pyrite available for oxidation (Evangelou, 1995a; Belzile et al., 1997). In this study we statistically optimise the concentration of solutions used to provide a durable Fe-phosphate coating. This procedure may then be used as a remediation technique or to study the diffusion rates of oxidising fluids within coal strata.
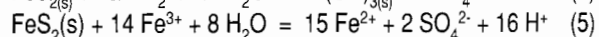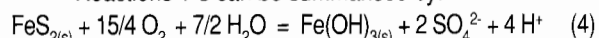
INTRODUCTION

Acid mine drainage (AMD) is a major form of water-borne pollution in catchment areas where coal or mineral-ore mining has been carried out on a large scale. The primary production mechanism for this highly toxic effluent is the oxidation of Fe-sulphides. Dewatering of mines during mineral extraction alters the reducing environment in the rock to an oxidising one by allowing downward circulation of atmospheric oxygen. Exposed inorganic sulphide minerals formed during diagenesis both within the mineralised seam and associated strata become vulnerable to oxidative attack (Casagrande et al., 1989). This attack forms soluble salts which produce acidic leachates. The exposure to oxygen is increased in spoil heaps where their relatively porous nature allows thorough infiltration by either gaseous or dissolved oxygen. Pyrite (FeS_2) is considered to be the most prolific producer of acidity as oxidation of one mole will produce 4 moles of protons (Webb et al., 1994) (reaction 4).

The process of pyrite oxidation is a result of several steps simplified in these equations:

$$FeS_{2(s)} + 7/2\ O_2 + H_2O = Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \qquad (1)$$
$$Fe^{2+} + 1/4\ O_2 + H^+ = Fe^{3+} + 1/2\ H_2O \qquad (2)$$
$$Fe^{3+} + 3\ H_2O = Fe(OH)_{3(s)} + 3\ H^+ \qquad (3)$$

Reactions 1-3 can be summarised by:

$$FeS_{2(s)} + 15/4\ O_2 + 7/2\ H_2O = Fe(OH)_{3(s)} + 2\ SO_4^{2-} + 4\ H^+ \quad (4)$$
$$FeS_2(s) + 14\ Fe^{3+} + 8\ H_2O = 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \quad (5)$$

The initial rate of reaction 1 and 2 is slow, making the oxidation of ferrous iron the rate-controlling step. In the presence of Fe-oxidising bacteria, *Thiobacillus ferrooxidaans*, dramatically accelerates reaction 1 and as pH decreases so too does the stability of Fe-hydroxide, in turn releasing ferric iron (Fe^{3+}) into solution (Nordstrom, 1982; Evangelou, 1995a; Dubrovsky et al., 1985). Ferric iron itself oxidizes ferrous iron (Fe^{2+}), (reaction 5), and the reaction becomes self-catalysing. At low pH the attack of Fe^{2+} by Fe^{3+} has been shown to dominate the oxida-

tion process (Singer et al., 1970). Pyrite oxidation by ferric iron produces four times as much acidity than by oxygen alone, highlighting ferric iron as the major culprit in the formation of AMD.

The changes in rock geochemistry initiated by mine dewatering and dumping material in spoil heaps leads to not only the decrease in pH described above, but also the release of trace metals such as Cu, Zn, Ag, Pb and As (Gray, 1997). Meteoric recharge of water tables in spoil heaps and currently dewatered mines flushes out toxic products forming along their flow-paths. This produces characteristic AMD discharges, which may go on to, cause local environmental problems if left untreated. A more serious dilemma needs to be addressed where potential closure of mines and ceasing of dewatering will lead to the flushing out of oxidation products from a much larger catchment than that adjacent to localised meteoric recharge flow paths.

CURRENT REMEDIATION STRATEGIES

Pollution by AMD may be arrested at three main stages in its production (Connely et al., 1994).

1. Source control - Initial pyrite oxidation and leaching of products is prevented.
   Current treatments include minimising the oxygen supply to the pyrite by compaction of spoil heaps, submersion of waste in mine lakes, covering heaps with a humic substrate to encourage reducing conditions, and air-sealing mine adits.
   Geochemical studies show that constriction oxygen transport to markedly slower diffusive transport by compaction or submersion of tailings is effective in minimising AMD production (Schuring et al., 1997). Physically blocking the pathway of atmospheric oxygen does not account for dissolved oxygen and Fe^{3+} in the form of Fe-hydroxide, which continue oxidizing free ferrous iron within the submersed tailings (Webb et al., 1994).

2. Migration control - Effluent is trapped as it migrates from source.
   Examples of this are covering or grouting of spoil heaps with concrete, using physical barriers to divert ground water flow from the most contaminated pathway, settling ponds which isolate effluent from local ground-water.
   As cement is weathered to ettringite in acidic conditions, the trapping of potentially acidic products is not a long-term solution (Wiggering, 1993). Similarly the use of physical barriers and diversion ditches rely on consistent groundwater flow and do not cover the eventuality of a change in flow direction or flooding of the system.

3. Release control - Effluent is collected and treated.
   Remediation of acidic high conductivity effluent includes chemical treatment to neutralize acidity and precipitate metals using chemicals such as lime and barium chlori-

de combined with aeration. The resultant sludge is often itself classed as hazardous waste (Stefanoff et al., 1994). Alternatively limestone rock, coal fly ash (Stewart et al., 1997) and phosphate rock have all been mixed into spoil heap waste to neutralize acidity or prevent pyrite oxidation by the precipitation of ferric iron in insoluble Fe-phosphates (Doolittle et al., 1997; Stewart et al., 1997; Spotts et al., 1992; Stiller et al., 1989). Unfortunately the limestone and phosphate rock usually becomes coated with Fe-hydroxide or Fe-phosphate inhibiting their effectiveness (Evangelou, 1995).

Passive treatments include the use of constructed wetlands where acidity and dissolved metals are removed by passing the AMD through various subtrates the most common of which are organic rich reducing layers where bacteria thrive, precipitating metal-sulphides and limestone substrates to neutralize acidity. The neutralisation by limestone is inhibited by Fe-hydroxide precipitation on the limestone surfaces. This is avoided by passing AMD through an Anoxic Limestone Drain (ALD) which allows neutralization and but stops the precipitation of Fe-hydroxide. The AMD still contains high concentrations soluble metals including ferric iron which will hydrolyse when the water comes into contact with the atmosphere producing further acidity (Webb et al., 1994). Combining an ALD with a wetland should therefore remove both acidity and dissolved metals. Wetlands and ALDs are designed for the pH and metal concentration of the current drainage, however, spoil heap weathering involves several buffering systems provided by the chemical breakdown of carbonates, alumino-sillicates, clays and sulphides (Wiggering, 1987). Thus the pH and chemistry of AMD from spoil heaps will remain constant for a period of time then change in a much shorter period. Changes in the properties of the effluent being treated negate the use of wetlands as a long-term solution to AMD.

Current remediation strategies are effective only in the short term and require monitoring throughout the lifetime of the pollution source. Coating technologies may provide a long-term solution with little monitoring required after the initial treatment. The development of coating technologies has included the use of acetyl acetone, humic acid, lignin, sodium silicates, Fe-phosphate, Fe-hydroxide and silica to various degrees of success (Belzile et al., 1997; Nyavor et al., 1995; Evangelou, 1995a; Wiggering, 1987).

It has been shown that a coating of Fe-phosphate can be produced on pyrite grains by using a weak oxidising solution of H_2O_2 followed by a phosphate solution to react with the released ferrous iron (Evangelou, 1995a, b) However the increase in solubility of Fe-phosphate with decreasing pH have led Vandiviere and Evangelou

(1998) to conclude that silica coatings would be less stable under fluctuating pH (Evangelou, 1995b). However, successful coating of pyrite coupled with natural buffering systems due to clay-weathering would hold pH at the higher levels required for coating stability.

A remediation strategy which involves a combination of H_2O_2 and phosphate solution could lead to an increase in acidity during initial oxidation and also contribution of excess phosphate, a pollutant itself, to ground water. In this study we will use statistical methods to optimise the initial solutions so that the minimum amount of Fe and SO_4^{2-} are released and the maximum phosphate is taken up.

METHOD AND MATERIALS

Pyrite was ultrasonically washed in de-ionised water to remove surficial dirt and sulphate phases. The sulphide was then crushed and sieved through a 150 μm mesh with the smaller portion retained. In order to obtain a leachate with minimal Fe, S and P within a short period of time a complete factorial design experiment was performed. Pyrite was immersed in all possible combinations of the following solutions; 0.08M, 0.008M, 0.0008M or 0.00M $KH_2PO_{4\ (aq)}$ and 0.015%, 0.05% or 0.00% H_2O_2. 0.1g of the <150 μm pyrite was placed in a conical flask and 10ml of hydrogen peroxide then of phosphate solutions were added to each. Duplicates of each combination were prepared plus one pyrite free blank. The flasks were left overnight then vacuum filtered through a 45 μm filter and the residue retained. Fe, S and P in the filtrate were measured by ICP-OES. To test the extent of coating the treated pyrite was reacted overnight with H_2O_2. The filtered liquid was split equally with half being back-titrated to calculate H_2O_2 loss by oxidation of exposed pyrite and the other half analysed by ICP-OES for Fe and S.

RESULTS AND DISCUSSION

Filtrate concentrations of Fe, S and P are displayed in Table 1. These are blank corrected and therefore represent the change in the analyte concentration by the end of the reaction. Fe concentration varies between 6.71-0.00 ppm, S between 14.31-0.67 ppm and P between -36.62-39.57 ppm. The negative values in P concentration should represent the uptake of P during reaction with ferric iron, however statistical analysis of variance indicates that P concentrations fall within the measurement error and no change in concentration may be concluded from these figures. Similarly, analysis of variance of S and Fe falls outside the measurement error, allowing use of these results in determining interactions within samples.

The results of this experiment are best demonstrated by plotting S against Fe concentration (Figure 1). The samples fall into three groups; a cluster of low S and Fe (trend A), a line of

Sample	Initial P (ppm)	Initial H_2O_2 (%)	Mean Fe (ppm)	Std dev Fe	Mean S (ppm)	Std dev S	Mean P (ppm)	Std dev P
A1	1240	0.015	0.02	0.01	3.02	0.86	-5.09	44.59
B1	1240	0.005	0.01	0.01	2.32	0.18	4.76	5.31
C1	1240	0.00	0.01	0.00	0.99	0.45	21.73	25.23
A2	124	0.015	0.01	0.01	3.47	0.38	-4.88	5.74
B2	124	0.005	0.01	0.00	2.13	0.16	1.59	1.93
C2	124	0.000	0.00	0.00	0.96	0.36	-4.86	1.28
A3	12.4	0.015	0.33	0.34	13.30	0.55	-2.02	0.82
B3	12.4	0.005	0.04	0.00	7.83	0.14	-0.47	0.03
C3	12.4	0.00	0.10	0.03	2.92	0.70	-0.71	0.01
A4	0	0.015	6.45	0.38	13.89	0.59	0.07	0.07
B4	0	0.005	2.68	0.01	6.63	0.13	-0.07	0.03
C4	0	0.00	1.05	0.93	3.06	1.37	-0.41	0.06

Table 1. Mean and standard deviations of blank corrected Fe, S and P concentrations for duplicate samples.

high S and low Fe (trend B) and a line where S is always twice the concentration of Fe (trend C).

Trend C can be attributed to pyrite oxidation by H_2O_2 as it is made up of the samples containing pyrite with increasing concentrations of H_2O_2. Trend B is made up of samples with low P (12.4 ppm) with increasing H_2O_2. As the amount of H_2O_2 increases Fe is precipitated by the phosphate solution but the dissolution of S is not halted, implying that oxidation is allowed to continue. The cluster at low S and Fe is made up of samples where oxidation has been inhibited and the release of both Fe and S halted. The fact that within this cluster samples still contain S where no Fe is present shows that the control of S release by this treatment is secondary via the halting of oxidation, whereas Fe is removed from solution at a faster rate. Results of testing coating success using hydrogen peroxide attack will be discussed at a later date.
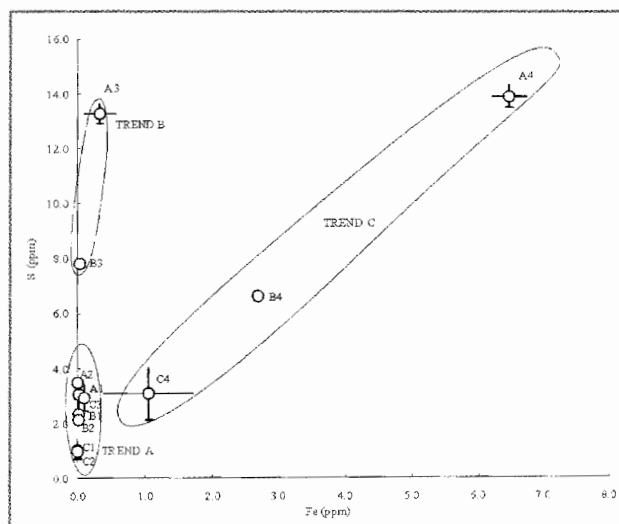

Figure 1. Mean S concentration against mean P concentration, error bars show standard error of the mean.

CONCLUSIONS

The inhibition of Fe release by phosphate precipitation is much stronger than that of S. This demonstrates the secondary nature of the control of S by halting oxidation. In inhibition of oxidation S concentration may be a possible indicator of coating success.

In order to find a combination of solutions which provides low Fe, S and P the region between 124 ppm and 12.4 ppm P at 0.005% H_2O_2 should be investigated.

WORK IN PROGRESS

Chemical testing of the durability of the coating using hydrogen peroxide attack will be further developed.

Physical presence of pyrite coating will observed using an SEM.

Coating technologies will be used to explore fluid transport through rock strata.

ACKNOWLEDGEMENTS

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