Chapter Four

Discussion - Phosphate stabilisation experiments

4.1 Previous research

Phosphate stabilisation of mine waste using liquid chemical agents aims to encapsulate sulphide surfaces with stable, impermeable coatings of phosphate. The coatings can be produced by leaching the sulphides in a solution containing an oxidant, a buffer and potassium or sodium di-hydrogen phosphate (KH_2PO_4) (Huang and Evangelou, 1994; Zhang and Evangelou, 1998). Previous studies have shown that these phosphate coatings successfully inhibit further oxidation of the sulphides and prevent acid generation (Evangelou, 1995a,b; Fytas and Evangelou, 1998; Georgopoulou et al., 1996; Nyavor and Egiebor, 1995). To date, published studies of this technique have been limited to laboratory experiments on pyrite, pyrrhotite and pyritic coal waste (Evangelou, 1996, 2001; Matlock et al., 2003), and a field column experiment using pyritic tailings and coal waste (Vandiviere and Evangelou, 1998). Furthermore, unpublished laboratory studies by Woltmann (2001) have demonstrated the effectiveness of the technique to inhibit oxidation of chalcopyrite and arsenopyrite.

Phosphate stabilisation has also been utilised for the remediation of metal-contaminated soils. The technique is based on the *in situ* conversion of unstable metal-bearing phases to relatively insoluble, stable, metal-bearing phosphate species (Cotter-Howells and Caporn, 1996; Eusden et al., 2002; Ma et al., 1993; Ruby et al., 1994; Zhang et al., 1998). The research has thereby concentrated on the immobilisation of Pb in contaminated soils, taking advantage of the rapid formation and extremely low solubility product of pyromorphite ($Pb_5(PO_4)_3Cl$) (Nriagu, 1983).

Thus previous research has focussed on pure sulphide samples, pyritic coal waste and metal-contaminated soils at industrial sites. Such material is not representative of actual mine waste, especially partly oxidised waste at abandoned historic mine sites such as the Montalbion silver mine.

4.2 Experimental overview

This study has conducted phosphate stabilisation experiments in order: (a) to investigate the formation of phosphate coatings in polymineralllic, sulphidic mine waste and partly oxidised, polymineralllic mine waste, and (b) to evaluate whether the phosphate stabilisation technique could effectively control metal mobility and acid generation in these waste types. Three kinetic column leaching experiments were performed.

- Experiment 1, using polymineralllic, sulphidic waste and liquid phosphate stabiliser.
- Experiment 2, using partly oxidised, polymineralllic mine waste and liquid phosphate stabiliser.
- Experiment 3, using partly oxidised, polymineralllic mine waste and liquid as well as solid phosphate fertilisers.

Phosphate coatings and precipitates were formed in all experiments. Amorphous phosphate coatings, interpreted to be chemically connected with the underlying sulphide surface, were most abundant on chalcopyrite. Lead phosphates were the most commonly formed precipitates in experiments 1 and 2; however, granular Mn and Ca phosphate precipitates were most abundant in experiment 3. The extent of phosphate formation appeared to be dependent on cation availability, which was presumably controlled by oxidant concentration and the degree of sacrificial sulphide oxidation. In experiment 2, the dissolution of secondary sulphates contributed significant amounts of cations into solution, resulting in a greater extent of phosphate formation than experiment 1. The use of $KMnO_4$ and Trifos in experiment 3 provided high concentrations of Mn and Ca, which reacted with the phosphate anions, forming abundant phosphate coatings and precipitates.

Acid generation and metal release was inhibited to varying degrees in all experiments. This was through the inhibition of sulphide oxidation and probably due to the attenuation of dissolved metals into phosphate phases. Generally, the greater the extent of phosphate formation the greater the degree of acid generation inhibition and metal attenuation, although it is possible that metal mobility was controlled by the leachate pH alone. Lead had the lowest concentrations in the coated column leachates, which is likely a reflection of the stability of the Pb phosphates. Copper and Zn concentrations increased during the dissolution stage of experiments 1 and 2, probably due to the partial dissolution of Cu and Zn phosphates in the oxidising solution. Dissolved As and Sb were mobilised in the coated columns as a result of the circumneutral pH values.

4.3 Possible limitations of the phosphate stabilisation of partly oxidised, polyminerallic mine wastes

The overall results indicate that the phosphate stabilisation technique may represent an additional remediation tool for the prevention of AMD in partly oxidised mine wastes. However, several possible limitations of the technique have become apparent during this research and are compared with the existing literature.

4.3.1 Mobility and liberation of contaminants

The research in this study has established that the presence of an aggressive oxidant in the coating solution is required to provide sufficient cations for the formation of effective coatings through sacrificial sulphide oxidation (Section 3.3.5). However, this process also results in the liberation of acid, metals and sulphate (Matlock et al., 2003). The release of these unavoidable by-products during the coating process may be of concern regarding the disposal of unoxidised sulphidic waste. However, in the case of partly oxidised material, particularly at abandoned mine sites, the generation of acid, metals and sulphate is already occurring. Application of the coating solution to the mine waste in these situations should decrease the acid and metal release due to prevention of sulphide oxidation and the attenuation of metals. However, it may be necessary to collect and treat any leachate runoff during application of the coating solution. Otherwise, the pollution of local surface waters is likely.

This research has shown that As and Sb are preferentially mobilised from the waste due to the higher mobility of these elements at slightly acidic to circum-neutral pH values. The release of significant quantities of these elements into mine drainage waters can be induced by the addition of the coating solution to the waste. The phosphate coatings observed on tetrahedrite in experiment 3 inhibited the release of Sb, particularly in columns E and F (Section 3.5.3). The coating solutions used in these columns should be investigated further for possible use in tetrahedrite-rich wastes. The mobilisation of As was not inhibited in any experiment, despite the observed presence of phosphate coatings on arsenopyrite in most columns of all experiments. The As in the leachates may have been desorbed from Fe (hydr)oxides or released by scorodite dissolution due to the rise in pH resulting from the addition of buffered coating solutions to the waste. The chemical mobilisation of As from acidic wastes may occur during increasing pH values of mine drainage waters (Courtin-Nomade et al., 2003; Craw and Chappell, 2000). In order to prevent As contamination of mine drainage waters, the application of a separate As stabilisation method may be necessary. This may be implemented in conjunction with phosphate stabilisation or applied to the drainage of the phosphate stabilised waste. The promotion of coprecipitation/adsorption of As with ferric precipitates from drainage waters is a possible method of As attenuation (Kim et al., 2003).

The coating solution itself will become a pollutant if excess quantities of the oxidant, buffer and phosphate flow through the waste un-reacted and enter the drainage system. The release of excess phosphate into the drainage from phosphate stabilised waste will possibly lead to eutrophication of local surface waters (Hodson et al., 2000a; Traina and Laperche, 1999). A delicate balance of coating solution ingredients is required in order to ensure that adequate phosphate stabilisation of the waste occurs whilst excess chemicals do not enter the drainage. Extensive field trials will be necessary to ascertain what concentrations of coating solution ingredients will achieve this balance. In addition, careful mineralogical and chemical characterisation of the mine waste to be stabilised will be essential to determine the optimum composition of the coating solution.

4.3.2 Long term stability

The majority of amorphous phosphate coatings observed in all experiments showed abundant desiccation cracks. These cracks may reduce the effectiveness of the coatings, allowing oxidant access to the underlying sulphide (Jones et al., 2003; Nyavor and Egiebor, 1995). Close inspection of these cracks using SEM-EDS revealed that - where the coating was well developed and relatively thick (>1μm) - the cracks did not penetrate to the sulphide surface. The phosphate coating retained its integrity when well developed. Even when the sulphide was only thinly coated and showed extensive cracking, the coverage of phosphate still greatly reduced the sulphide surface area available for oxidation. This is supported by the fact that acid generation was inhibited in columns where the phosphate coating was thin and extensively cracked (Section 3.4.5). Furthermore, it is unclear whether the cracks were artefacts of sample preparation. Cracking possibly occurred due to dehydration when samples were removed from the columns, SEM stubs were constructed or when samples were placed under vacuum in the SEM. If the phosphate coatings do not crack when dehydrated under natural conditions, then concerns that the coating effectiveness may be reduced in an alternately wet and dry environment (Jones et al., 2003) are negated. Experiments investigating whether dehydrated phosphates will inhibit sulphide oxidation and acid generation are warranted.

Another possible long term problem with the phosphate stabilisation technique stems from the fact that phosphate is an essential growth ingredient for sulphide-oxidising bacteria (Jones et al., 2003). The use of aqueous phosphate on sulphidic mine wastes may promote the growth of bacteria and as a result increase bacterially mediated sulphide oxidation. No bacteria were observed in the three experiments in either the coated columns or the control columns.

However, the presence of bacteria was expected to have been ubiquitous as no bactericides were applied to the waste. It is therefore assumed that the inhibition of sulphide oxidation – as achieved by the phosphate coatings in the coated columns - occurred in the presence of sulphide-oxidising bacteria. Vandiviere and Evangelou (1998) reported inconclusive results when bacteria were added to columns containing phosphate and silicate stabilised pyritic mine waste. Oxidation was increased in phosphate stabilised columns with the addition of sulphide-oxidising bacteria in some experiments, whereas in other experiments little to no effect was observed. It is unclear whether these results were due to increased bacterially mediated pyrite oxidation or a reflection of the extent of phosphate coating. Further experimentation specifically targeting the effect of bacteria on phosphate stabilisation is required.

The long term goal of most mine site rehabilitation projects is the revegetation of the mine waste piles. However, vegetation growing on phosphate stabilised mine waste may dissolve the metal phosphates to source P for uptake if no other source of P is available (Laperche et al., 1997). Consideration of the long term stability of metal phosphates is therefore required when planning the revegetation of phosphate stabilised waste.

4.3.3 Sulphide oxidation inhibition

The observation that oxidation of arsenopyrite continued beneath a coating of $FePO_4$ in the presence of bacteria led Jones et al., (2003) to question the ability of the phosphate coatings to inhibit oxidation. These authors suggested that H_2O_2 diffusion was inhibited by the $FePO_4$ coating whereas O_2 and Fe^{3+} diffusion was not hindered by the phosphate coating. Such a hypothesis may explain why phosphate coatings inhibited pyrite oxidation in the experiments of Evangelou (1994). However, this theory fails to explain the inhibition of pyrite oxidation by phosphate coatings observed by Nyavor and Egiebor (1995) and Vandiviere and Evangelou (1998). Oxygen was used as an oxidant by these authors, applied as pressurised oxygen and dissolved in rainwater. The oxygen should have diffused through the phosphate coatings relatively easily according to Jones et al., (2003). Moreover, the phosphate stabilisation experiments using pure arsenopyrite conducted by Woltmann (2001) demonstrated that arsenopyrite oxidation by H_2O_2 was inhibited by phosphate coating. The experiments of Jones et al., (2003) formed phosphate coatings from solutions with a pH of 2.3 containing no aggressive oxidant. These conditions have been shown to be less than ideal to promote well-developed, stable phosphate coatings (Section 3.3.5) (Evangelou, 1995b). It is possible that the phosphate coatings observed by Jones et al., (2003) failed to inhibit arsenopyrite oxidation due to their poor development and resultant high permeability. A phosphate stabilisation experiment using arsenopyrite and oxygen as the dissolution stage oxidant may serve to support or dismiss the above concerns raised by Jones et al., (2003).

4.4 Future research

The previous section has highlighted the need for significant amounts of future research targeting specific limitations and criticisms of the phosphate stabilisation technique. The controlled environment of kinetic column leaching experiments is best suited to investigating these problems. However, this study has also shown that the phosphate stabilisation technique may inhibit acid generation and metal release in partly oxidised, polyminerallic mine waste on a laboratory scale. Thus long term field trials are required to investigate the phosphate stabilisation technique on a larger scale in a natural field setting.

4.4.1 Column leaching experiments

Further column leaching experiments of similar design to those used in this study are required to investigate:

- the most cost effective coating solution oxidant/buffer/phosphate combination;
- possible methods to attenuate As from the leachates and any effects these attenuation methods have on the phosphate stabilisation process (Section 4.3.1);

- the effect of dehydration and cracking on the effectiveness of the phosphate coatings to inhibit sulphide oxidation (Section 4.3.2);
- the effect of omission of $Ca(OH)_2$ from the coating process on the stability of phosphate coatings and precipitates (Section 3.4.5);
- possible reasons for the elevated SO_4^{2-} concentrations in the coated column leachates (Sections 3.3.5, 3.4.5 and 3.5.6);
- the effects of bacteria on the effectiveness of the phosphate coatings to inhibit sulphide oxidation (Section 4.3.2); and
- whether the use of O_2 as an oxidant in the dissolution stage reduces the ability of the phosphate coatings to inhibit sulphide oxidation, particularly arsenopyrite (Section 4.3.3).

4.4.2 Field trials

Phosphate stabilisation field trials should be conducted on moderately sized (~500 kg), lined waste piles of partly oxidised, polymineralic mine waste. Different combinations of phosphate coating solutions, application rates and methods should be trialled. The optimum combination of coating solution ingredients could then be ascertained, allowing stabilisation of the entire waste pile whilst preventing excess release of coating solution chemicals into the waste drainage (Section 4.3.1).

If the phosphate stabilisation proves viable in a field setting, further long term field trials should be conducted, running over several years. These trials should be designed to investigate the long term stability of the phosphate coatings and precipitates. Specific factors which should be investigated include the effects of wetting/drying cycles, vegetation, organic matter and bacteria (Section 4.3.2).

4.5 Contributions to previous research made by the phosphate stabilisation experiments

The phosphate stabilisation experiments detailed in Chapter 3 have made four significant contributions to previous published research:

Coatings on host minerals

1 Phosphate coatings were observed for the first time on galena, sphalerite, tetrahedrite, bournonite, cobaltite and stannite.

Previous published research has only described phosphate coatings on pyrite (Evangelou, 1995b), pyrrhotite (Georgopoulou et al., 1996) and arsenopyrite (Jones et al., 2003). In addition, Woltmann (2001) observed phosphate coatings on chalcopyrite and arsenopyrite.

Phosphate phase formation

2 Phosphate precipitates of metal ± alkalis were abundantly formed in the mine waste.

Extensive previous research has focussed on the formation of pyromorphite in Pb-contaminated soils. However, research involving phosphate stabilisation of other metals is limited. Chen et al., (1997) identified Zn phosphate (hopeite) formation during phosphate stabilisation experiments, and Eusden et al., (2002) reported the formation of unidentified Zn and Cu phosphates in phosphate stabilised mine waste using XRD.

Acid generation and metal release

3 Acid generation and metal release were inhibited by phosphate stabilisation of polym締merallic, sulphidic mine waste.

Previous published phosphate stabilisation experiments were conducted using pure sulphides, mine wastes containing only one major sulphide or on contaminated soils generally lacking sulphides.

Behaviour of secondary waste minerals

4 Acid generation and metal release were inhibited by phosphate stabilisation of partly oxidised, polyminerallic mine waste containing abundant secondary sulphates.

Previous phosphate stabilisation research has generally used pure sulphides or unoxidised mine waste. Where partly oxidised material was used, the soluble secondary phases were usually removed by flushing prior to treatment (Fytas and Evangelou, 1998; Vandiviere and Evangelou, 1998). The only exception to this were the experiments of Eusden et al., (2002), who used partly oxidised Pb-rich mine tailings.

The phosphate stabilisation experiments outlined in this study have demonstrated the potential of the method as a technique for the long term prevention of AMD and metal release in partly oxidised, polyminerallic mine waste. Phosphate stabilisation shows particular promise as a remediation tool at abandoned historic mine sites where abundant secondary minerals are present in the waste.