PYRRHOTITE COATING TO PREVENT OXIDATION ⁽¹⁾

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Abstract: This paper presents the results of a research project on phosphate coating of pyrrhotite to prevent oxidation. The first phase of this research project evaluated the new technology on a pyrrhotite tailings sample. A series mini-columns of 0.9 cm of diameter and big columns of 5.7 cm of diameter filed with the tailings sample were treated with a coating solution composed of H_2O_2, KH_2PO_4 and sodium acetate (NaAc). H_2O_2 oxidizes the pyrrhotite and produces Fe^{3+} so that iron phosphate precipitates as a coating on pyrrhotite surfaces. Results so far have shown that coating is complete and protects pyrrhotite from oxidation. Long term experiments are still in progress in order to test coating resistance over time.

Key words: Acid mine drainage, iron phosphate coating, pyrrhotite oxidation.

Introduction

Acid Mine Drainage (AMD) is the result of the oxidation of sulphide minerals when calcareous material is not present in sufficient quantities to neutralize acidity. The principal components of AMD generation are: reactive sulphide minerals, oxygen and water. The resulting drainage is characterized by low pH and high concentrations of sulphate ions, ferric ions and base metal ions. At a pH lower than 3.5 iron-oxidizing bacteria catalyze and accelerate the oxidation of sulphide. The most common bacteria species able of catalyzing the oxidation reactions are *Thiobacillus ferrooxidans* and *Th. thiooxidans*. The final products of the reactions are protons, ferrous ions, sulphate ions and/or free sulphur (Appelo and Postma, (2); DrabkowskI, (8); Draft A.R.D. Tech. Guide, (9); Dugan, (10); Filion, et al., (14); Herlihy, et al., (17); Singh and Bhatnagar, (24); Yanful, (26)).

In the case of pyrrhotite the mineral is initially oxidized by oxygen. The ferrous iron produced can be further oxidized to ferric iron which in high pH environments precipitates as a series of amorphous iron oxides/hydroxides, further reducing the pH. Any ferric iron that does not precipitate may further oxidize the sulphide mineral. Chemical oxidation of sulphide by Fe^{3+} is faster than oxidation by oxygen. Thus, while oxidation is initially a slow process, as acid production continues, and the pH drops below 3.5, the rate of oxidation accelerates as the activity of Fe^{3+} in solution increases (Blowes, et al., (3); Buckley and Woods, (4); Elberling, et al., (11); Nicholson and Scharer, (22); Nicholson, et al., (23)). At low pH acidophilic bacteria catalyze pyrrhotite oxidation directly or indirectly, by accelerating the oxidation of ferrous into ferric ions and an oxidation cycle is established. The result is a rapid oxidation of pyrrhotite at low pH (Kandemir, (19); Miller and Risatti, (21)).

Many methods have been proposed for preventing or at least reducing AMD generation, but most of them are costly, short-term solutions or difficult to apply. A proposed remediation technology is the so-called "coating technology". By this technique the sulphide waste is coated with ferric phosphate, a highly acid-stable mineral, which is the main component of the coatings created on steel to prevent metal corrosion.

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The coating process is based on the hypothesis that if an iron-sulphide waste is treated with a phosphate solution containing low concentrations of hydrogen peroxide (H_2O_2), oxidation will take place and the ferric ions released will react with the phosphate ions forming a passive coating on the sulphide mineral surfaces. Thus sulphide oxidation and acid production would stop (Evangelou,(12); Evangelou and Huang, (13)).

The method was first applied to pyrite particles where it appeared to be a long-term, simple and cost effective solution for the prevention of Acid Mine Drainage (AMD) generation. The purpose of the present study is to examine the feasibility of creating a similar iron phosphate coating on pyrrhotite surfaces to prevent oxidation and AMD generation. The effectiveness and resistance of the established coating as well as different ways for improving the strength and the performance of the coating are tested.

Theory

Pyrrhotite oxidation by H_2O_2

When H_2O_2 is the oxidizing agent the oxidation of pyrrhotite can be written as (Fytas, et al., (16)):

$$\begin{array}{c} Fe_{1-x}S + 3.5H_2O_2 \rightarrow (1-x)Fe^{3+} + SO_4^{2-} + H^+ + 3H_2O \\ Fe_{1-x}S \Downarrow \Uparrow H_2O2 \\ Fe^{2+} \end{array} \qquad (1)$$

which is an autocatalytic process since Fe^{3+} produced by the oxidation, can oxidize pyrrhotite as well. During this oxidation process the presence of hydrogen peroxide results in higher potentials, so the iron-deficient layer of pyrrhotite decomposes to form elemental sulphur, rather than sulphate as an oxidation product. As a result the elemental sulphur levels are higher than those expected from literature (Buckley and Woods, (5)). On the other hand, the concentration of iron ions is expected to be lower, again because of the presence of H_2O_2 (Domvile, et al., (6)).

When phosphate, under the form of $H_2PO_4^-$, is present along with H_2O_2 pyrrhotite oxidation can be written as (Fytas, et al., (16)):

$$Fe_{1-x}S+3.5H_2O_2+(1-x)H_2PO_4 \rightarrow (1-x)FePO_4+SO_4^{2-}+(3-2x)H^++3H_2O \qquad (2)$$

According to reaction (2) if the solution is supersaturated with respect to iron phosphate, iron will precipitate either as a discrete phase or as a coating on pyrrhotite surfaces, depending of the degree of supersaturation. In order for iron phosphate to precipitate as coating, supersaturation should be relatively high.

Materials and methods

In order to verify the feasibility of establishing an iron phosphate coating on pyrrhotite, experiments were carried out under laboratory conditions. The sample used consisted of 80-95% (wt) pyrrhotite and comes from the magnetic flotation tailings of the Strathcona mill in Ontario (FALCONBRIDGE Ltd.). Its specific gravity was found to be 4.4 and its pH was 8 to 9. Particle size distribution of the sample was fine, with 65% finer than 37 microns. The fine size distribution should result in increased pyrrhotite oxidation rate and reactivity (Kargi, (20)).

Prior to the coating process, pyrrhotite was mixed with silica in order to increase the hydraulic conductivity of the sample. The mixture was loaded into columns of different diameters depending on the research phase. Glass wool was placed at the bottom of each column, as a filter, to avoid solid losses through the bottom of the column.

Two series of experiments were performed. During the first research phase the pyrrhotite/quartz mixture was loaded into micro-columns of 0.9 cm of diameter and 25 mL of volume. During the second research phase the pyrrhotite/quartz mixture was loaded into columns of 5.7 cm of diameter. Micro-column scale was first chosen to minimize channelling problems that could result in incomplete contact between the solid and the solution.

The coating process followed five steps, as performed by Evangelou and Huang (12) for the coating of pyrite. After each column was loaded with the proper silica/pyrrhotite mixture, it was subjected to the following steps:

1. washing with a HCl solution;
2. washing with distilled water;
3. washing with the coating solution;
4. stabilizing with a $Ca(OH)_2$ solution, 800 mg/L; and
5. leaching with a strongly oxidizing solution.

The experiments were carried out at room temperature. Table I illustrates the steps followed during the application of the coating process.

Table I : Steps of the coating process

Process	Micro-column (0.9 cm diameter)	Large column (5.7 cm diameter)	Objective
Loading	20g quartz 5g pyrrhotite	500-100g quartz 100g pyrrhotite	
surface preconditioning	30 mL HCl (2M)	2L HCl (2M)	dissolving the oxides and hydroxides formed on pyrrhotite surfaces
Rinsing	30 mL distilled water	2L distilled water	increasing the pH
coating	H_2O_2, KH_2PO_4, NaAC: hydrogen peroxide oxidizes pyrrhotite, orthophosphate provides the necessary phosphate for coating and NaAC buffers the pH. Concentrations vary according to the experiment	H_2O_2, KH_2PO_4, NaAC: hydrogen peroxide oxidizes pyrrhotite, orthophosphate provides the necessary phosphate for coating and NaAC buffers the pH. Concentrations vary according to the experiment	Establishing coating on pyrrhotite surfaces
Stabilizing	$Ca(OH)_2$ 60 mL	$Ca(OH)_2$ 2L	

The pyrrhotite sample from Strathcona was already partially oxidized and iron oxides/hydroxides or hydrated iron sulphates had already precipitated on the pyrrhotite surface, significantly reducing the kinetics of the coating process by providing a physical barrier between reactants. Leaching with HCl dissolves all these oxides/hydroxides and prepares pyrrhotite surfaces for the next step (Stiller, et al., (25)). Subsequently the loaded sample was washed with distilled water to increase the pH. The same preconditioning process was applied on the control (not coated) columns.

The sample was then coated by using a solution containing H_2O_2, sodium acetate (NaAC) and KH_2PO_4 in various concentrations. The H_2O_2 in the coating solution was essential to induce the initial oxidation and produce the Fe^{3+} ions, necessary for the iron phosphate formation. One of the most important requirements during this process was to buffer the coating solution at a pH of between 5 to 6, to allow iron phosphate precipitation on the pyrrhotite particles (Evangelou, (12)). Sodium acetate was used as a buffering agent. The phosphate containing reagent was introduced under the form of ortho-phosphate (KH_2PO_4) (Hoffmann, et al., (18)). The coating solution collected at the bottom of the column was analyzed for pH and total iron. Once the coating process was over, the coating was stabilized by washing the mineral mixture in the column with a $Ca(OH)_2$ saturated solution (800 mg/L).

In order to examine the resistance of the coated pyrrhotite to oxidizing conditions, each coated column was leached with a solution containing H_2O_2 in concentrations ranging from 0.017M to 0.2M. A non-coated preconditioned column was leached in the same way to provide a background for comparisons. H_2O_2 was chosen because it creates an extremely oxidizing environment. In the H_2O_2 solution concentration of dissolved oxygen is much higher than that occurring naturally, so the leaching process is shorter (Domvile, et al., (6)). Moreover by increasing or decreasing the concentration of H_2O_2, the power of the oxidizing environment and so the oxidation rate can be changed (Finkelman and Giffin, (15)). Distilled water saturated in oxygen with bacterial inoculation was used only once, but it has been observed in this case that the oxidation process needs more time and the tests become too long to evaluate.

During leaching with the oxidizing solution, leachates were taken at different time intervals to verify the oxidation status of each sample. Leachate samples were analyzed for pH, total iron and sulphate, because these are the three primary chemical parameters indicative of AMD and pyrrhotite oxidation (Adams, et al., (1)). Sulphate was measured by colorimetry and total iron by atomic absorption spectrophotometry. The pH was measured with a pH meter just after the leachate was collected.

Some of the coated samples were examined by scanning electron microscopy and X-ray scanning in order to observe iron phosphate coating on the pyrrhotite surfaces.

Results and discussion

Experiments in the micro-column scale

During this research phase different compositions of the coating solution were tested. The concentrations of the coating reagents were ranged from: 0.0M to O.4M H_2O_2; 0.02M to 0.2M NaAC; and 0.01M to 0.2M KH_2PO_4.

From all these experiments it was concluded that H_2O_2 is a necessary element for pyrrhotite coating, as figure 1 illustrates. When hydrogen peroxide is absent the coated sample respond to oxidation similarly to the uncoated one.

The optimum H_2O_2 concentration for the micro-columns was found to be 0.2M . For higher H_2O_2 concentrations the coating solution acts more as an oxidizing agent. For lower hydrogen peroxide concentrations, initial oxidation of the sample is negligible, ferric iron produced is not sufficient and iron phosphate coating cannot be formed.

Sodium acetate (NaAC) is another important element in the coating solution. The optimal concentration during the tests was 0.2M. At this concentration pH during coating is buffered between 5 and 6 and iron phosphate can precipitate as coating on pyrrhotite surfaces.

A combination of pyrrhotite coating and phosphate rock around the grains acts as a better inhibitor of pyrrhotite oxidation than coating alone, as figure 2 illustrates. Phosphate coating reinforces itself with time by precipitating more iron phosphate on pyrrhotite grains. Similar results can be obtained when phosphate ions are added to the oxidizing solution during leaching.

As the KH_2PO_4 concentration in the coating solution increases from 0.05M to 0.2M coating quality improves. Thus for this experimental scale the optimal coating conditions established are: 0.2M H_2O_2, 0.2M NaAC, and 0.2M KH_2PO_4.

For these concentrations SEM examination shows that a coating has been established on pyrrhotite surfaces in the form of several superimposed uniform layers which totally cover pyrrhotite grains of all sizes (photograph 1). The SEM examination also shows the formation of elemental sulphur. This is in accordance with the remarks of Nicholson and Scharer (22); Blowes, et al., (3) and Buckley and Woods (5), especially for the higher oxidation potentials such as those reached when H_2O_2 is used.

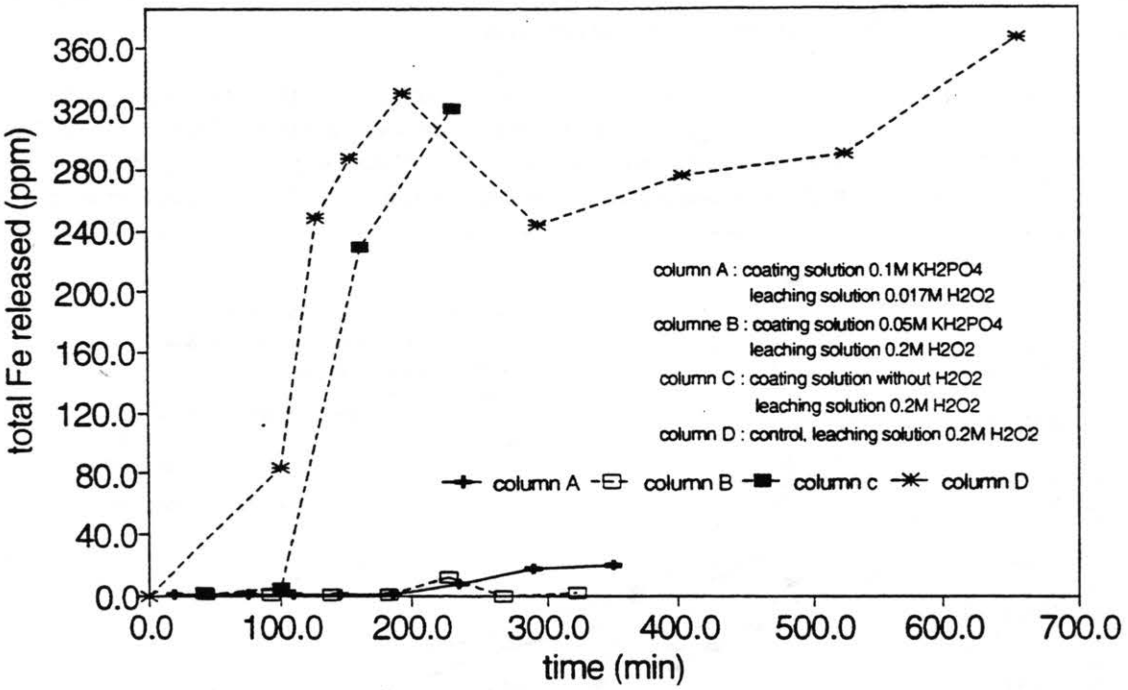


Figure 1: Total iron during leaching (micro-column scale)

<u>Experiments in large columns</u>

In order to test the scale effect on coating conditions larger columns of 0.9 cm of diameter were coated under the conditions established during the previous experimental phase.

As the coating process proceeded in a larger scale it was observed that during coating the mineral in the columns was strongly oxidized during coating. This time pH was not a good indication of oxidation since NaAC strongly buffers the system. Total iron concentrations in the coating samples were also very low. This means that total iron is a good oxidation index either since phosphate acts as an iron chelating agent that complexes iron and produces iron phosphate ($FePO_4$) and other iron phosphate species (Hoffmann, et al., (18)). As a result there is an accumulation of Fe^{3+} in the form of phosphate precipitate in each column. In the small columns we did not encounter such problems because oxidation during coating is negligible.

Photograph 1 : Large coated pyrrhotite grain(micro column scale)

In order to estimate the degree of oxidation during coating, the liquid samples were analyzed for sulphate which is a better oxidation index than iron for the coating process. From these analyses it was observed that at the end of coating, sulphate production increases exponentially reaching up to 26000 ppm. This extremely high sulphate concentration proves that excessive oxidation has taken place during coating which is undesirable.

Upon changing the scale of the experiments from the micro columns to the larger ones the behaviour of the mineral mixture during coating changed probably because the flow patterns of the solution changed as well. In the large columns there is no problem with the oxygen bubbles generated by hydrogen peroxide because bubble diameter is negligible compared to the column diameter. Thus circulation of the coating solution in the larger columns is more even and the contact between the solid and the solution is more complete. As a larger part of the solid comes into contact with the coating solution the degree of oxidation increases and oxidation becomes easier to observe. H_2O_2 is the reagent responsible for the oxidation during coating thus its concentration in the coating solution (0.2M) in the case of large columns should be reduced, otherwise the solution acts more like an oxidizing agent than as a coating one. A concentration of 0.01M H_2O_2 was chosen for the coating solution in subsequent tests.

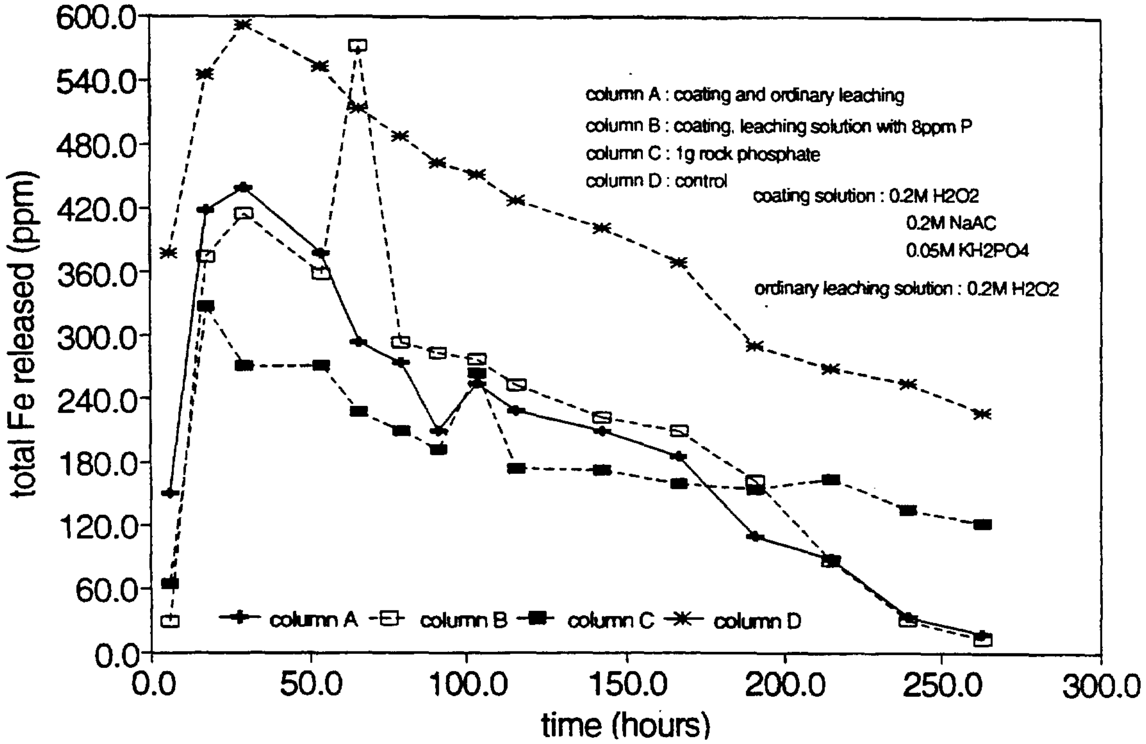


Figure 2: Total iron during leaching (micro-column scale)

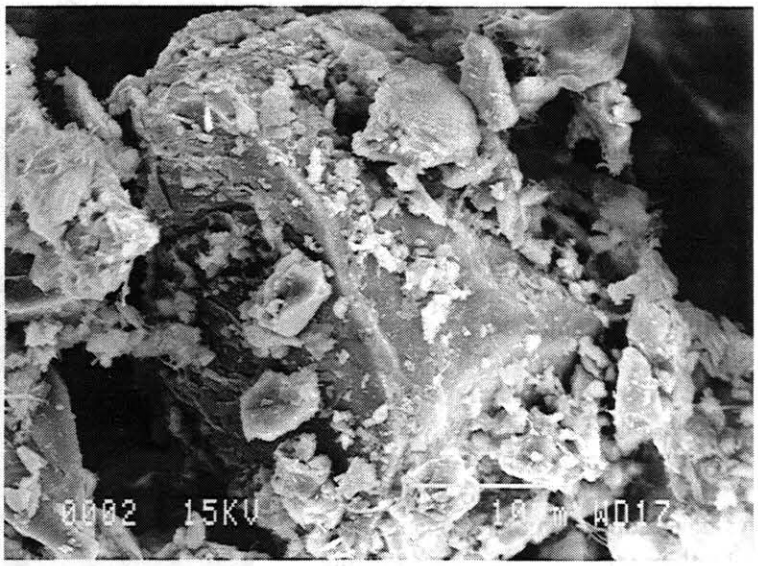
Thus the tested concentrations of the coating solution for the large columns scale were: 0.01M H_2O_2, 0.2M NaAC and 0.2/0.3M KH_2PO_4. For these concentrations oxidation of the mineral mixture during coating was negligible and sulphide concentrations at the bottom of the columns were kept to levels lower than 35ppm.

SEM examination of the samples coated in the large columns has shown that a coating has been established on pyrrhotite surfaces (photograph 2). This coating appears to be a uniform layer around the grains of pyrrhotite particles of all sizes. By SEM examination it was also observed that coating is better and more complete for the lower phosphate concentration.

In order to test the coating resistance the coated sample was leached with a highly oxidizing solution containing 0.2 M H_2O_2. As figure 3 illustrates the coated material responds to oxidation better than the uncoated one as the coated material produces lower concentrations of total iron for at least seven weeks.

It must be emphasized here that sulphate is a good index of pyrrhotite oxidation only during the coating process since free sulphur is not formed under these conditions. During leaching total iron is a better index of oxidation than sulphate. There is no phosphate in the leaching solution than can precipitate iron in the leachate. Also during leaching free sulphur is formed preferentially to sulphate, due to the higher oxidation potentials obtained in the presence of H_2O_2.

Thus for the large-scale experiments the optional coating concentrations were found to be: 0.01M H_2O_2, 0.2M NaAC and 0.2M KH_2PO_4.



Photograph 2:Fully coated pyrrhotite grain (large scale experiments)

<u>Cost estimation</u>

If the coating process is applied to fresh, not oxidized, tailings, there is no need for any specific equipment thus the major part of the expense is the cost of the reagents in the coating solution. For the concentrations established in the large experimental scale the cost of reagents for coating would be very high.

However it should be emphasized here that during these coating experiments no effort has been made to optimize the quantities of reagents. The only objective was to achieve the best coating quality possible.

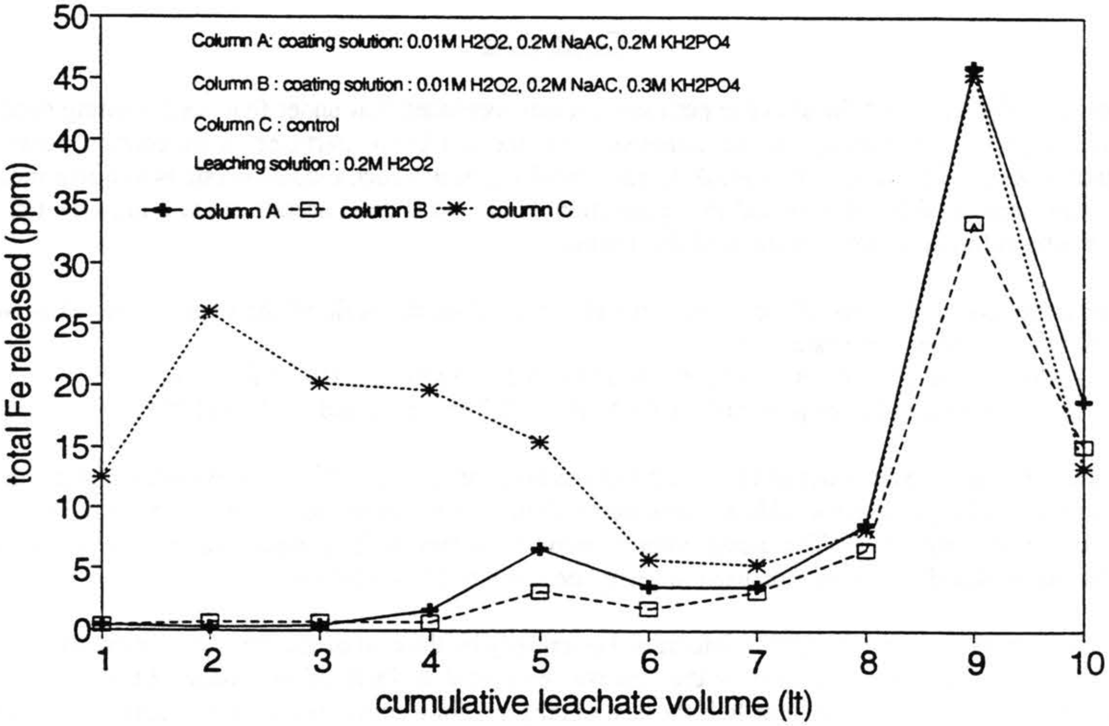
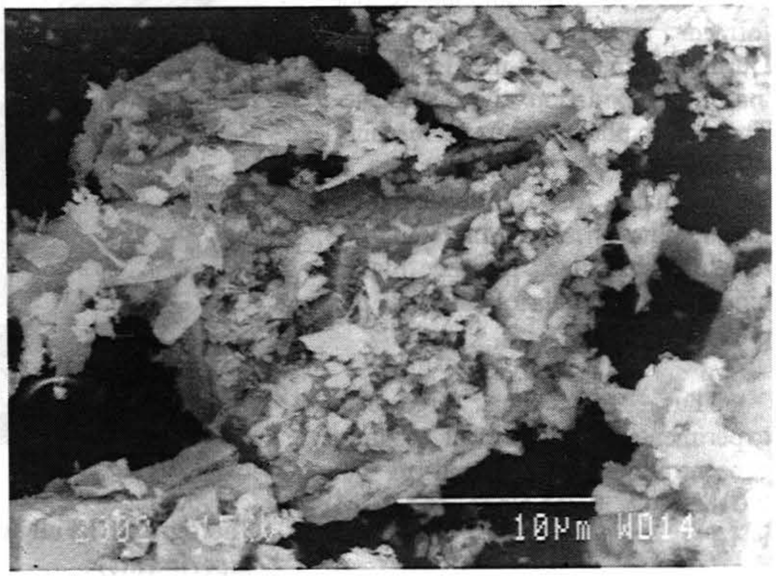


Figure 3: Total iron during leaching (large scale experiments)

Therefore no recycling of the coating solution has been tried. In order to arrive at a more cost-effective result another experiment was carried out. During this experiment 0.5L of coating solution were used to coat 500gr of sulphide waste. This coating solution was recycled through the loaded column to ensure that all of the H_2O_2 and KH_2PO_4 would be used. The concentrations of the coating solution were the optimal concentrations established during the large-scale experimental phase. SEM examination of a sample treated this way shows that iron phosphate coating is established on pyrrhotite surfaces. Moreover all pyrrhotite grains were completely coated as photograph 3 illustrates. In these conditions the reagents cost drops to about 14$ per tonne of waste. This value assumes complete consumption of the reagents in the coating solution. This is a worst case scenario, since part of the reagents are not consumed and remain in solution. This cost was estimated for tailings containing 95% pyrrhotite. In practice pyrrhotite is not more than 30% of the total volume of tailings. So for the treatment of 1 tonne of waste material the cost should be about 4$ to 5$. As a point of reference it can be mentioned that one tonne of pyrrhotite produces up to 1.1 tonne of sulphuric acid which needs 0.62 tonnes of lime, to neutralize. Assuming a cost of 55$ per tonne of lime in order to treat one tonne of pyrrhotite by conventional neutralization, the cost of reagents is of the order of 34$ per tonne pyrrhotite.



Photograph 3:Coated pyrrhotite particle (recycling of coating solution)

Conclusions

Based on the results of the above experiments, it can concluded that under functional coating conditions, a complete phosphate coating can be established on the pyrrhotite particles. This coating controls the oxidation process of pyrrhotite by stabilizing pH around 4 (pH at which oxidation rate is at a minimum) and by reducing considerably sulphate and iron generation. H_2O_2 and sodium acetate are two important elements in the coating solution for the formation of this coating.

The functional concentrations of the coating solution depend on the scale of the experiment. Thus two sets of functional conditions were established:

a. micro-columns (4 g of pyrrhotite) 0.2 M H_2O_2, 0.2 M NaAC and 0.2 M KH_2PO_4;
b. large columns (100g of pyrrhotite) 0.01 M H_2O_2, 0.2 M NaAC and 0.2 M KH_2PO_4;

If the pyrrhotite waste is not already oxidized preconditioning with HCl is not necessary. A combination of coating and phosphate rock addition acts better than coating alone, as under these conditions coating reinforces itself with time. The same improvement is achieved if a small concentration (8ppm) of phosphorous is added to the solution used to verify the stability of the coating.

The cost of the coating method is determined essentially by the cost of the reagents. Based on the optimal conditions established in the laboratory the cost was estimated at 4$ to 5$ per tonne of tailings containing 30% pyrrhotite. This cost is less than half the cost of reagents for a conventional neutralization with lime.

Iron phosphate coating seems to be a promising technology for the abatement of AMD generation by pyrrhotite tailings. It has the potential to be applied as a long term solution alone or be combined with another prevention method. For example in a tailings site, iron phosphate coating could be applied in order to stop pyrrhotite oxidation until the end of the mine life when the tailings site will eventually be flooded. In this way the subaqueous deposition will be reinforced by phosphate coating, as there are indications that not treated pyrrhotite can oxidize even in a subaqueous environment. However further experiment should be carried out in order to evaluate coating resistance on a long term basis.

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