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Technical Paper

Metallurgy

Silicate micro-encapsulation of pyrite to prevent acid mine drainage

K. Fytas and **P. Bousquet**, Laval University, Quebec City, Quebec

KEYWORDS: Acid mine drainage, Silicates, Tailings, Leaching, Oxidation.

Paper reviewed and approved for publication by The Metallurgical Society of CIM.

ABSTRACT

Acid mine drainage (AMD) is a serious environmental problem that preoccupies the Canadian mining industry. Considerable amounts of money are spent every year in an effort to prevent or reduce the acid mine drainage phenomenon. AMD occurs when sulphide minerals (e.g., pyrite) contained in rock are exposed to air and water and subsequently oxidize to produce low pH water. This acid effluent has the potential to mobilize any heavy metals contained in the rock. Coating the sulphide minerals with silicates is a new promising technology to reduce AMD. Pyrite is treated with a solution containing H_2O_2, *sodium silicate and a buffering agent.* H_2O_2 *oxidizes a small part of pyrite producing ferric iron* (Fe^{3+}) *ions. These ions subsequently react with the silicate ions to produce ferric hydroxide-silica that precipitates on the pyrite surface producing a passive coating. This silicate coating can protect the grains of pyrite from oxidation. This paper presents a series of experiments that confirm that silicate coating can considerably reduce AMD.*

Introduction

Acid mine drainage (AMD) resulting from the oxidation of sulphide minerals is the most serious environmental problem facing the Canadian mineral industry today. In Quebec alone, 21 abandoned mine sites have been classified as hazardous because of acidic drainage. It has been estimated that the total cost of reclamation of acid producing mine sites across Canada will be about $5 billion. AMD occurs when sulphide minerals (contained in mine waste or mill tailings) are exposed to air and water. It is extremely acidic (pH as low as 2) and has the potential to mobilize heavy metals (iron, lead, copper, zinc, nickel, cobalt, etc.) that may be contained in the tailings rock or elsewhere. Such effluents pose an instant threat to the ecological balance when discharged into lakes and rivers.

The reaction involved in AMD can be illustrated by the following reaction of pyrite oxidation:

$$FeS_2 + 7/2\,O_2 + H_2O \rightarrow Fe^{2+} + 2\,SO_4^{2-} + 2H^+ \quad ..\ (1)$$

The Fe^{2+} produced can be further oxidized by O_2 into Fe^{3+}, which in turn will precipitate as $Fe(OH)_3$ and lower the pH at the same time. Any Fe^{3+} from the previous reaction that does not precipitate may be used to oxidize additional pyrite (Evangelou, 1995; B.C. AMD Task Force, 1998).

Oxidation of pyrite is initially a slow process and most of the released iron ends up as iron hydroxide due to the relatively high pH on pyrite surfaces. As acid production continues and pH in the vicinity of pyrite surface drops below 3.5, formation of iron hydroxide is hindered and activity of free Fe^{3+} in solution increases. At low pH, an acidophilic, chemoautotrophic, iron-oxidizing bacterium (thiobacillus *ferrooxidans*) catalyzes and accelerates the oxidation of Fe^{2+} into Fe^{3+} by a factor higher than a million. Thus, due to the participation of bacteria, reduction of Fe^{3+} to Fe^{2+} by pyrite and oxidation of Fe^{2+} to Fe^{3+} by atmospheric oxygen constitute an effective oxidation cycle. Through this iron oxidation-reduction cycle, electrons are readily transferred from FeS_2 to the atmospheric oxygen, causing rapid oxidation of pyrite at low pH.

Currently, acid mine drainage produced by Fe-sulphide oxidation is controlled by several approaches: 1) application of limestone or rock phosphate; 2) application of bactericides in the form of slow release pellets; 3) creation of fully anoxic environments by using clay liners, plastic liners, asphalt, etc; and 4) establishments of wetlands. The first acid drainage remediation technology slows down the production of acid drainage; it does not stop it, and has a short life span due to its coating potential (armouring) by iron oxides. The problem associated with the second approach is that acid mine drainage is suppressed for relatively short periods, whereas, chemical oxidation is not completely stopped. Liner technologies, another form of acid mine drainage control, can be cost prohibitive as well as ineffective over time due to deterioration. Wetland technologies are effective in treating the symptoms of pyrite oxidation when low levels of acidity are involved. However, wetlands as an acid mine drainage amelioration technology has limitations when high levels of acidity are involved and many question the long-term effectiveness of such systems.

A new acid mine drainage remediation technology has recently been developed by the

Kostas Fytas
is a professor in the Department of Mining, Metallurgical and Materials Engineering, Laval University, Quebec City. He has extensive teaching and research experience on computer applications in mining, mine ventilation and on environmental problems in the mining and metallurgical industries. In the past, he has been involved in various research and consulting projects related to mine ventilation, acid mine drainage and reserve estimation techniques. He has recently been involved in developing the Eolaval mine ventilation package. He has published numerous papers related to mine ventilation, ore reserve estimation and environmental problems in mining and metallurgical industry. He is a member of CIM, SME and the Quebec Order of Engineers.

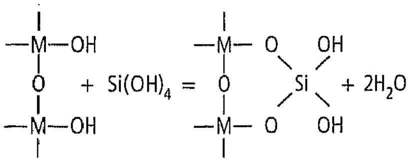
Pierre Bousquet
graduated in 1995 in geological engineering at Laval University. He worked for the Ministère des Ressources Naturelles du Québec as a senior geologist in 1997. He obtained his M.Sc. in mining engineering in 2000 at Laval University. He is now a Ph.D. candidate at the University of Waterloo.

University of Kentucky by which sulphide minerals such as pyrite are coated with ferric coatings that can prevent either O_2 or Fe^{3+} from further oxidizing pyrite (Evangelou and Zhang, 1995; Zhang and Evangelou, 1998). The coating process (also known as micro-encapsulation) involves reacting pyrite with a soluble coating agent (phosphates or silicates) in the presence of low concentrations of an oxidizer (such as H_2O_2 or hypochlorite).

The oxidizer will first attack the surface of the pyrite grains releasing ferric ions. These ferric ions will react with the coating agent creating a ferric phosphate or silicate coating on pyrite particles. These two kinds of coatings have been tested in the laboratory and they seem to inhibit pyrite oxidation under acid conditions. So far, these coatings have been tested on coal preparation residues in the Eastern United States and on gold and base metal tailings in Quebec and Ontario (Fytas et al., 1998a, 1998b).

According to comparative long-term laboratory testing between phosphate-coated and silicate-coated pyrite conducted at the University of Kentucky, it seems that silicate coatings are much more resistant under extreme conditions (low pH) (Vandiviere and Evangelou, 1998).

The silicate coating technique, patented by Evangelou (1996), involves the use of sodium silicate, $Na_2SiO_3 \cdot 5H_2O$, as a coating agent. The coating solution also contains a buffer agent, sodium acetate, to keep the pH in the 5 to 6 range, and an oxidizing agent, hydrogen peroxide or calcium hypochlorite, to release iron in the solution. This technology is based on the capability of an aqueous silica solution to precipitate on metal (M) hydroxide by the following reaction (Iler, 1979):


..(2)

The oxidizing agent, (e.g., hydrogen peroxide) attacks the surface of the pyrite which releases ferrous ions in the solution that will be further oxidized to ferric ions. Because of the buffered solution, the ferric ions precipitate on the pyrite surface as iron hydroxide. Silica in solution reacts with the iron hydroxide to form a ferric hydroxide-silica barrier that will protect the pyrite from oxygen and ferric iron.

As Zhang and Evangelou (1998) have described, the silica coating is a good barrier against the oxidation of pyrite by hydrogen peroxide and proved to be a good sink for ferric ions. The silica coating is also more resistant against acidic surroundings and friendlier to the environment than phosphate coating.

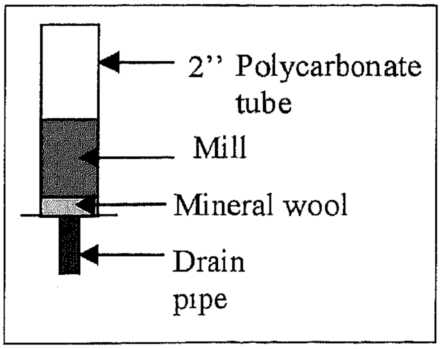
This paper describes the results of a research project involving testing of silicate coating technology on the pyrite tailings from the Bouchard-Hébert mine (Cambior) in Quebec (Fytas et al., 1999a, 1999b). The objective of this project is to test the effectiveness and long-term resistance of the silicate coating on mine tailings.

Materials and Methods

Tailings Preparation

In order to verify the feasibility of establishing an iron silicate coating on pyritic tailings, laboratory experiments were carried out on a non-oxidized fresh tailings sample from the Bouchard-Hébert mine. This mine belongs to the mining company Cambior Inc. The pyritic tailings contain 41.5% Fe, 0.42% Mg and 32% S. An X-ray diffraction analysis confirmed that the most common minerals found in the tailings are: pyrite, muscovite, quartz, and siderite. In some of the experiments, industrial limestone (0 to⅛ in. and of 70% purity) was mixed with tailings to control the pH during the coating process. The mixture was loaded into columns of 5.7 cm in diameter and 50 cm in height. A drainpipe of 2 cm in diameter was inserted and glued through the bottom of the column. A 1 in. thick mineral wool cushion was also placed at the bottom of the column in order to prevent loss of the sample during the coating and lixiviation experiments (Fig. 1).

Fig. 1. Typical column used.



Silicate Coating

Silicate coating solutions consisted of various concentrations of sodium silicate (coating agent) and hydrogen peroxide (as an oxidizer). Acetic acid was added to obtain acidic conditions. Columns D and E were loaded with a mix of 371.9 g of mill tailings and 28.7 g of industrial limestone. Column D was treated with one litre of coating solution containing 0.01 M hydrogen peroxide, and 0.11 M sodium silicate with a non-buffered pH of 12.5. Column E was treated in the same way but without hydrogen peroxide. Columns F, G and H were all doubled and loaded with 200 g of mill tailings, and during coating, 10 g of industrial limestone were added to prevent silica from creating a gel. Columns F, G and H were treated in stages.

The first stage consisted of passing 0.5 litres of coating solution (buffered to pH 5 to 6) containing 0.11 M sodium silicate in column F, 0.125 M sodium silicate in column G, and 0.14 M sodium silicate in column H. The second stage of coating treatment consisted of passing another 0.5 litres of the same coating solution (with a non-buffered pH of 12.5) for each column. Columns I and J were treated with solutions consisting of 0.13 M and 0.15 M of sodium silicate, respectively, using two stages like the preceding treatment, but limestone was mixed to the tailings like columns D and E (10.8 gr of calcium carbonate in the form of industrial limestone). Table 1 summarizes th coating treatment details for each column. Tw control columns were used containing 200 g o untreated tailings.

In order to test coating resistance, the coated samples were leached following coating. Leaching was carried out on a weekly basis on all columns. Coated columns were divided into two groups: those leached with de-ionized water and those leached with a 0.01 M hydrogen peroxide leaching solution. 250 ml of leaching solution was being poured into the columns each time and the leachates were collected after four days.

Chemical/Surface Analyses and Data Treatment

Following coating, all columns were sampled and characterized using a scanning elec-

Table 1. Treatment summary

Column	Mill Tailings (g)	Pyrite (moles)	Sodium Silicate (M)	Hydrogen Peroxide (M)	Calcium Carbonate (g)	Solution Volume (L)	pH
Control	200	1	0	0	0	0	
D	371.85	1.86	0.11	0.01	20.05	2	12.6
E	371.85	1.86	0.11	0	20.05	2	12.6
F	200	1	0.11 and 0.11	0	7	0.5 and 0.5	5.95 and 12.5
G	200	1	0.125 and 0.125	0	7	0.5 and 0.5	5.53 and 12.5
H	200	1	0.14 and 0.14	0	7	0.5 and 0.5	5.75 and 12.5
I	200	1	0.13 and 0.13	0	10.8	0.5 and 0.5	5.62 and 12.5
J	200	1	0.15 and 0.15	0	10.8	0.5 and 0.5	5.98 and 12.5

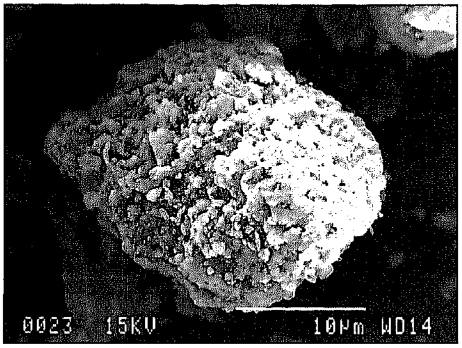
tron microscope, and the coated pyrite surfaces were verified with micro probing. The leachates were measured for pH with an electronic pH meter. Moreover, they were analyzed for iron using atomic absorption spectrophotometry and for sulphate using turbidometry with barium chloride ($BaCl_2$).

Experimental Results and Discussion

Scanning electron microscopy was used as a means to verify the success or failure of the coating process for each set of concentrations. Columns D and E showed some mixed results regarding coating. The presence of sodium silicate precipitates was also confirmed during micro probing. It was noticed that the consistency of the coating was good, with some pyrite parts still undercoated.

Columns F, G and H showed a mix of coating and precipitation of sodium silicates. The consistency and quality of coating increase as sodium silicate concentrations in the coating solution are increased. However, many pyrite grains were still partially naked after coating. About 20% to 30% of the pyrite was qualified as being coated. Columns I and J showed mainly sodium silicate precipitates on pyrite. Figure 2 shows a sample of a well-coated grain of pyrite.

Fig. 2. Sodium silicate coating on pyrite.



pH Measurements

The pH of the leachates collected after each leaching cycle was measured. The results of pH evolution through time are presented in Figures 3, 4, 5 and 6 (3 and 4 representing leaching with de-ionized water and 5 and 6, leaching with hydrogen peroxide). Columns D, E, I and J showed the best results since the beginning of the leaching process, especially column D. Columns F, G and H were discontinued because of bad results. Scanning electron microscopy showed that it was not a ferric hydro-silicate that coated the pyrite in these columns, but precipitates of the coating agent, sodium silicate.

It can be observed in Figures 3 and 5 that the pH of the leachates coming out from columns D and E varies widely compared to the control. In Figure 3, the pH starts as high as 12.5 to decrease to 2.5 for both columns. The pH of the control column was maintained between 3.7 and 2. Overall, we can notice a roller coaster progress. In fact, the pH does decrease to 2.5 for columns D and E, but it increases again to pH 6 to 7. What is more surprising is that the pH of the de-ionized water varies around 4.5. Such behaviour was witnessed during other experiments that involved tailings (Vandiviere and Evangelou, 1998). This behaviour can be explained as a re-establishment of the silica coatings (Vandiviere and Evangelou, 1998). Therefore, this may imply that the sodium silicate in columns

Fig. 3. pH of leachates, columns D and E (de-ionized water).

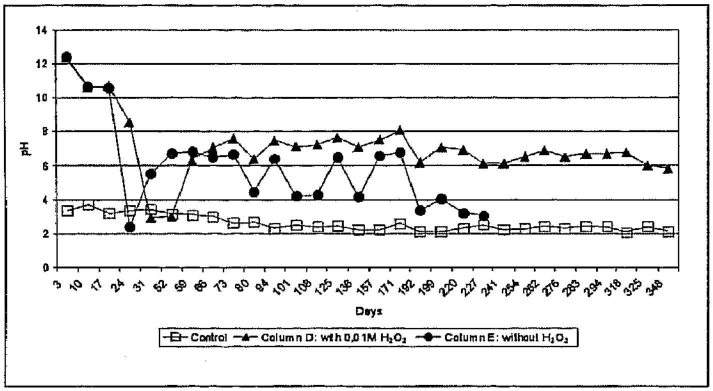


Fig. 5. pH of leachates, columns D and E (0.01 M hydrogen peroxide)

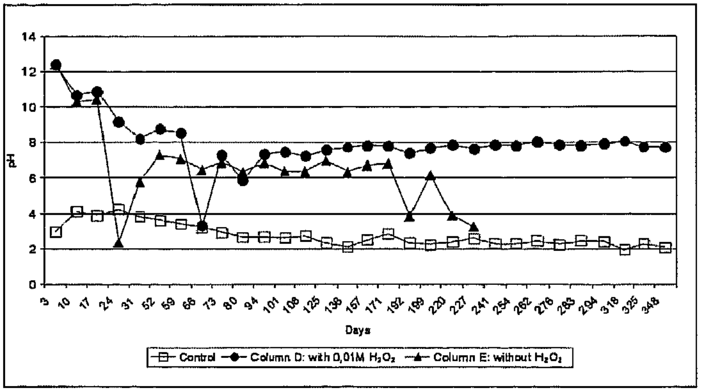


Fig. 4. pH of leachates, columns I and J (de-ionized water).

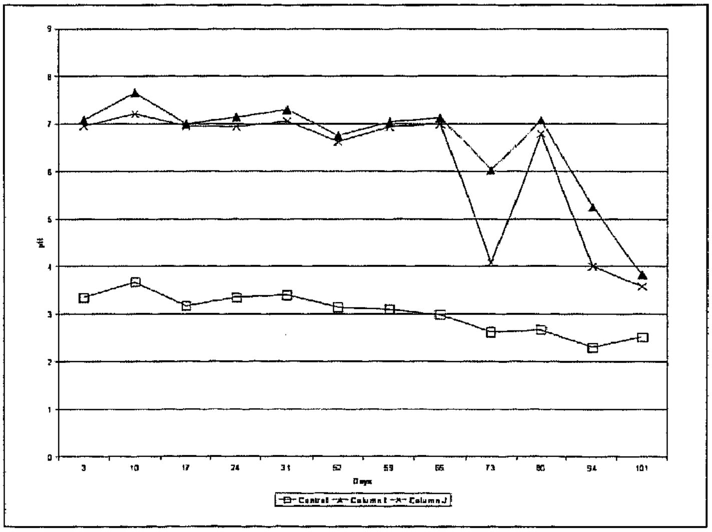


Fig. 6. pH of leachates, columns I and J (0.01 M hydrogen peroxide).

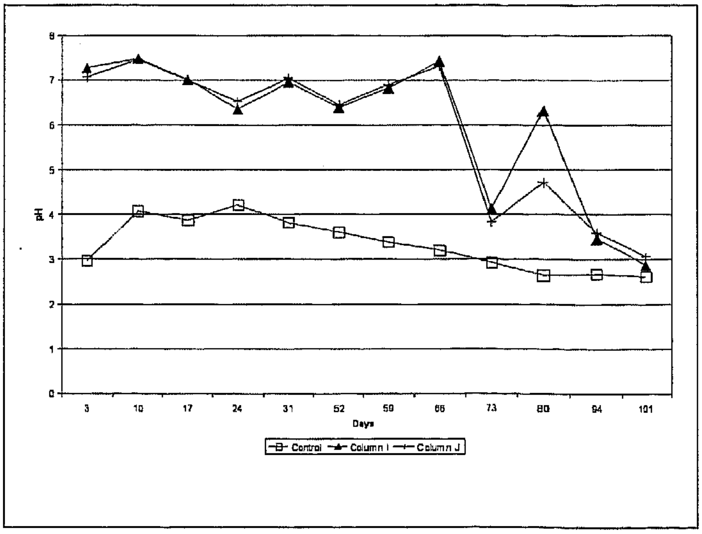


Table 2. Iron accumulations of leachates

Columns	Cumulative Iron Produced (De-ionized Water Leaching) (ppm)	Cumulative Iron Produced (0.01 M H_2O_2 Leaching) (ppm)
Control (101 days)	851.8	1230.6
I (101 days)	30.8	242.8
J (101 days)	81	155.2
Control (227 days)	5132.4	4478
E (227 days)	1096.5	187.8
Control (348 days)	8194.4	7209.8
D (348 days)	7.4	15.6

Table 3. Qualitative evaluation of the coating's performance depending on the cumulative values of iron and sulphate ions

Column	Coating Conditions			Water Leaching Performance	H_2O_2 Solution Leaching Performance	Leaching Duration (days)
	Silicates (M)	H_2O_2 (M)	Special Conditions			
D	0.11	0.01	9% calcite	Excellent	Excellent	348
E	0.11		9% calcite	Very good	Very good	227
F	0.11		10 g of limestone	Mediocre	Average	125
G	0.125		10 g of limestone	Very good	Mediocre	125
H	0.14		10 g of limestone	Very good	Mediocre	125
I	0.13		Two stages	Good	Good	101
J	0.15		Two stages	Good	Good	101

D and E have dissolved in the solution, but formed again as a ferric hydro-silica coating on a permanent basis. Since a silica solution pH varies around 12.5, this hypothesis is possible. Lately, the pH of the leachates of column E started to decrease dramatically, implying that pyrite coating in this column has failed. Therefore, leaching of column E was terminated on day 227.

As far as columns I and J are concerned, it can be observed in Figures 4 and 6 that the pH of both columns showed a promising high-low-high behaviour. However, the pH dropped again showing that the coating did not reform as hoped. After 101 days of leaching, columns I and J were terminated.

Leaching Results

Leachates were analyzed for iron using atomic absorption spectrophotometry. The results are reported in Table 2. It can be observed in this table that the cumulative iron from the leachates collected from columns D and E are well below the cumulative iron of the control column. In fact, the cumulative iron coming out of the columns are minimal at best. Column E started to show some fatigue during the 192nd day of testing. Overall, this demonstrates that silicate coating effectively retains the iron that comes from pyrite oxidation. Moreover, iron concentrations didn't increase with the drop of pH, suggesting that the sodium silicate precipitates dissolved and reformed under the form of a ferric hydroxide-silica coating. As for columns I and J, the cumulative iron in the leaching process stays quite low, implying that the coating inhibits the dissolution of the iron in the columns. Again, during the 73rd day, a little peak of iron concentration was observed. With the pH drop, this can be explained by the dissolution of the sodium silicate precipitates in the columns and the recreation of the hydro-silicate coating. Therefore, the iron concentrations are quite low in all columns implying a good resistance of silicate coating.

A qualitative appreciation of the coating's performance was attempted based on the comparison between the iron and sulphate leachate accumulations of the individual columns and those of the control column. A point system was devised according to which points are attributed to each column depending on the following rules:

- If the cumulative value of the column is higher than the control by more than 500 ppm = 1 point
- If the cumulative value of the column is higher by less than 500 ppm = 2 points
- If the cumulative value of the column is lower by less than 500 ppm = 3 points
- If the cumulative value of the column is lower by more than 500 ppm = 4 points

The points gained by each column are then added and qualified by the number of points gained: 8 points (excellent); 7 points (very good); 6 points (good); 5 points (average); 4 points (passable); 3 points (bad); and 2 points (mediocre). These are reported in Table 3.

It can be seen in Table 3 that coating performed well under the water leaching in columns D, E, G, H, I and J. Under the hydrogen peroxide leaching, columns D, E, F, I and J demonstrated good behaviour, delaying the pyrite's oxidation. Overall, the silica coating showed that it could withstand leaching for at least three months.

Conclusions

Based on these experiments, it can be concluded that a ferric hydroxide-silica coating can be established on the pyrite particles. This coating controls the oxidation process of pyrite by stabilizing the pH around 6 to 7 and by reducing considerably both sulphate and total iron production. Silicate coating seems to be a promising technology for the abatement of AMD generation by pyrite tailings. It has the potential to be applied as a long-term solution alone or to be combined with another prevention method (e.g., sub-aqueous deposition). However, further leaching experiments should be carried out in order to evaluate coating resistance on a long-term basis.

Acknowledgments

The authors would like to thank the Societé CAMBIOR Inc. and the Natural Science and Engineering Research Council of Canada (NSERC) for their financial support during the research project and for their permission to publish the research results. In particular, thanks are due to Serge Vezina, director of environment and research at Cambior for his continuous interest and encouragement.

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