PASSIVATION OF PYRITE OXIDATION BY ORGANIC COMPOUNDS.

Yu-Wei CHEN, Nelson BELZILE* & Douglas E. GOLDSACK
Department of Chemistry & Biochemistry and CIMMER
Laurentian University
Sudbury, Ontario P3E 2C6 CANADA

Abstract

Several techniques have been developed and used to limit acid mine drainage (AMD) and acid rock drainage (ARD) resulting from the oxidation of sulphidic mine wastes. Passivation involves the coating of particles or rock surfaces with a substance or a combination of substances, which render them impenetrable to oxidative attack. In this study, we have examined the effectiveness of two organic compounds used in the milling process on two types of pyrite with and without an iron oxide layer. Aqueous solutions of the two organic compounds, diethyletriamine (DETA) and potassium amyl-xanthate (PAX) were tested separately and in combined solutions of various concentrations. The results clearly showed that a combined solution containing 0.4%(w/v) PAX and 0.6%(w/v) DETA was the most effective and could reduce the oxidation of pyrite by more than 75%. When pyrite samples were pre-oxidized to form a thin iron oxide layer, the efficiency of the same passivating solution increased to 85%. The passivation mechanisms resulting from the combination of these two coating agents and the possible large-scale application of this technique will be briefly presented.

Key Words: pyrite, oxidation, passivation, iron oxides, coating agents

1. Introduction

The oxidation of sulphide tailings is a cause of underground and surface water acidification and of trace metal contamination. It is one of the most important environmental concerns for the mining industry and the various government agencies in Canada [1,2]. A large number of studies have been done to monitor and predict geochemical processes in sulphide tailings [3-5]. Laboratory experiments have been performed to understand the kinetics of pyrite and pyrrhotite oxidation [6-9]. Concurrently, many researchers have been investigating various methods to retard or prevent the oxidation process of sulphides tailings including liming, dry, wet and organic covers [2]. Some attention has also been given to the surface coating of sulphide minerals by inorganic and organic compounds [10-12]. It has been shown that the surface coating of sulphide minerals with commercial chemicals or natural compounds such as lignin and humic acids can effectively reduce the oxidation rate of pyrite to various degrees. In this study, we have investigated the passivation capabilities of two products used in the milling process at Inco Clarabelle Mill in Copper Cliff, more specifically, the potassium amyl xanthate (PAX) and diethylenetriamine (DETA).

PAX has been conventionally used as a collector in the flotation of metallic sulphide ores [13] and the interaction mechanisms between xanthate and pyrite or pyrrhotite surfaces have been studied by many workers [14,15]. Recently, Inco limited has introduced DETA into its milling operation as a pyrrhotite depressant [16]. However, the effects of these two compounds as coating agents for inhibiting sulphide minerals oxidation have never been studied.

Diethylenetriamine is a relatively strong baseand the presence of this polyamine can create buffering conditions to neutralize the protons produced by the oxidation of sulphides:

$$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH_2 + H_2O \Longleftrightarrow H_2N\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{NH_2}\text{-}CH_2\text{-}CH_2\text{-}NH_2 + OH^-$$

$pK_1 = 3.89$

$$H_2N\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{NH_2}\text{-}CH_2\text{-}CH_2\text{-}NH_2 + H_2O \Longleftrightarrow H_2N\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{NH_2}\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{NH_3} + OH^-$$

$pK_1 = 4.60$

Besides its buffer capacity, DETA is one of the most widely used polyethylene polyamines as reactive hardeners in epoxy resin formulation, mainly employed for protective coatings, electrical embedments and adhesives. It is also found that alkali-metal xanthates reacting with lower alkylamines in the presence of catalysts can produce water insoluble compounds [17]. Because of the above interesting chemical and physical features of these two compounds, a series of primary studies was conducted to investigate their potential capacities as coating agents.

2. Methodology

A schematic diagram of the analytical procedure for non pre-oxidized and pre oxidized tests coated pyrite is given in Figures 1and 2 respectively. Controls, i.e. non oxidized or uncoated samples were always carried through all series of tests.

2.1 Sample Preparation

Two high purity pyrite samples (one from Huanzala, Peru purchased from Ward's Natural Science Inc. and the other from the Nanisivik mine on Baffin Island, N.W.T., Canada) were ground manually and sieved through a 230 mesh sieve (ϕ=62µm). Ground samples were stored in a vacuum desiccator. Due to the very slow oxidation rate of pyrite under normal atmospheric conditions, the oxidation studies were done using different concentrations of hydrogen peroxide (see Figure 1) at room temperature. To terminate the oxidation process, the samples were either rapidly vacuum-filtered, rinsed with double distilled (DD) water, dried and stored in a vacuum desiccator (for Fourier transform infra red, FTIR or scanning electron microscopy, SEM analyses) or treated with a reducing solution of sodium oxalate (0.05 - 0.10 M) adjusted at pH 2, filtered (0.22µm), washed and stored. With the last procedure, the dissolution of oxidized iron is rapid and complete and the concentration of iron in the filtrate can be measured by flame atomic absorption spectrometry (FAAS).

The coating agents PAX (American Cyanamid) and DETA (Aldrich) were dissolved in DD water and prepared daily. Coating tests were done using two different approaches: with and without prior oxidation of the pyrite surface (Figure 1). When the coating agents were applied on non oxidized pyrite particles, it was done by adding 0.2 mL of different coating solutions (PAX and DETA in different concentrations and proportions) to 20.0 mg of dried particles. The beakers containing coated particles were covered with a watch glass and left overnight to dry the solvent. The coated samples were then stored in a vacuum desiccator and made ready for FTIR and SEM analysis, or for the oxidation reaction by 10.0 mL of 3.0% H_2O_2 for 2h at room temperature.

In another series of tests, pyrite particles (30.0 mg) were previously oxidized with 10.0 mL of 1.0% H_2O_2 for 2h. After the removal of the solution by filtration (0.22µm), the pre-oxidized particles were dried and coated with 0.2 ml of the different coating solutions directly on the filter and treated as described previously.

2.2 Instrumentation

The particle size distributions of the ground and sieved pyrite particles were determined using a Leeds & Northrup Microtac FRA. The coated and uncoated particles were analyzed by Fourier Transform Infra Red Spectroscopy (FTIR) on a Perkin-Elmer Series 1600 (4 cm^{-1} resolution, scanning number 64). A JEOL JSM-6400 Scanning Electron Microscope (SEM) was used to observe the morphological state of the studied particles. Particles were attached on a black glue tape and covered by a thin gold film. The extent of oxidation under various conditions was measured through the concentration of formed iron oxides, which were dissolved completely after the addition of the oxalate solution. The dissolved iron was analyzed by a Perkin-Elmer Model 603 Atomic Absorption Spectrometer (FAAS) in an air-acetylene flame.

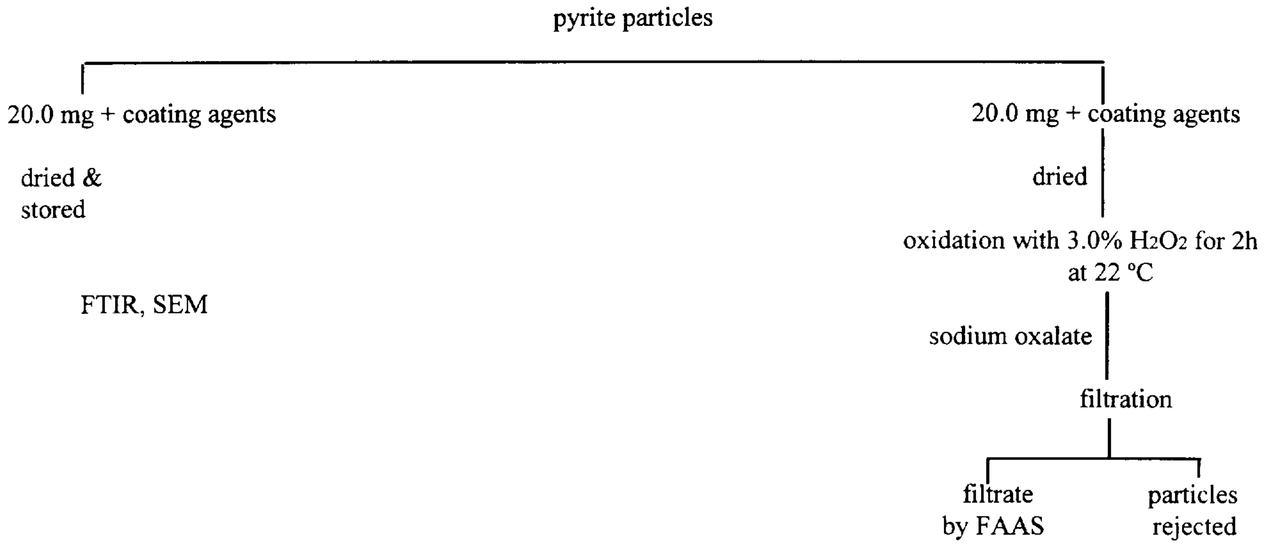

Fig. 1. Schematic diagram of the analytical procedure for the oxidation study of non pre-oxidized pyrite particles.

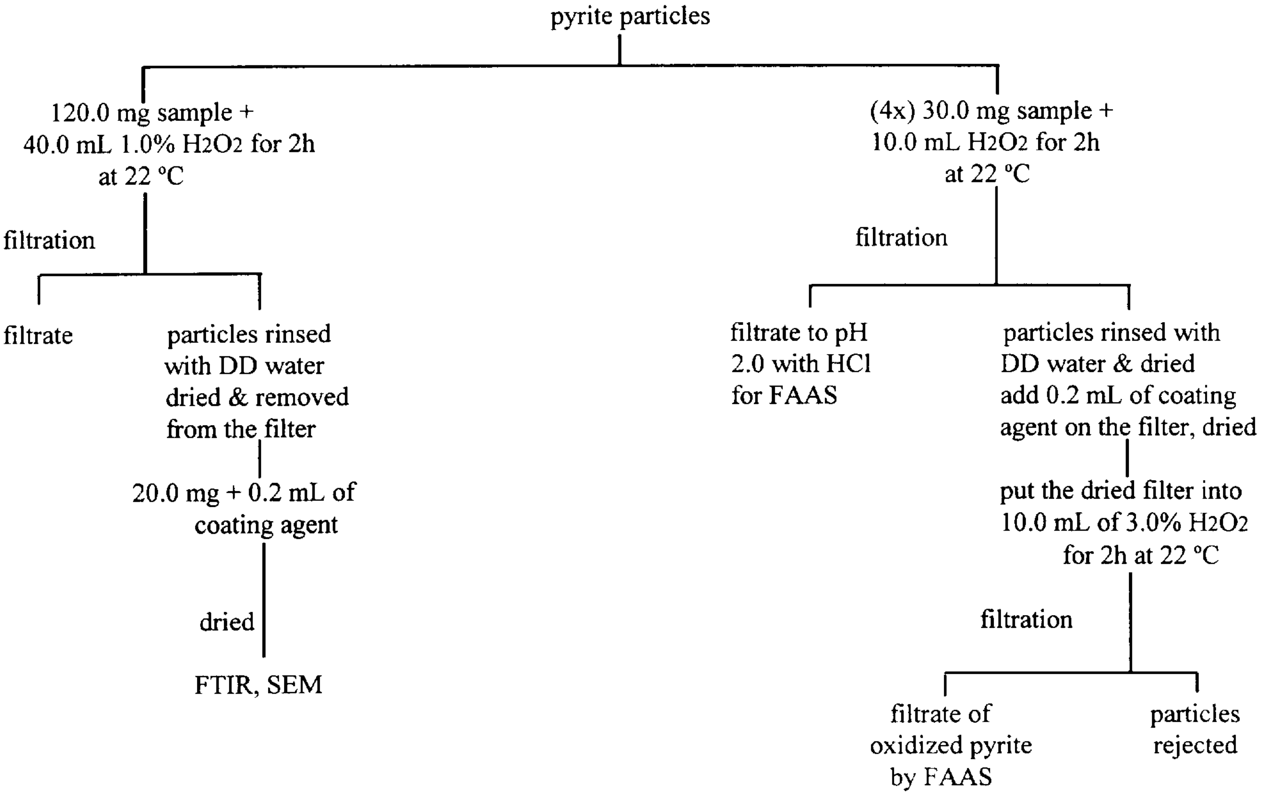

Fig. 2. Schematic diagram of the analytical procedure for the oxidation study of pre-oxidized pyrite particles

3. Results and Discussion

3.1 Particle Characteristics

The particle size distribution of Huanzala and Nanisivik pyrite samples were very similar having both a major fraction (38% in mass) in the 48-68 μm range and only about 10% of particles in the 6-17 μm and 80-160 μm range respectively. The purity of both samples was determined by FAAS after a complete digestion in 16M HNO_3. The values are:

for Huanzala 99.50 ± 2.40 % (n=12)
for Nanisivik 99.36 ± 2.31 % (n=12)

To determine the level of oxidation introduced by grinding and storage, a fraction of the two pyrite samples was extracted with 10.0 mL of 0.2M sodium oxalate solution at pH 2.0 for 1h. After analysis by FAAS, it was found that the atmospheric oxidation was only 0.2 % after grinding and 2 months of storage in a vacuum desiccator.

3.2 Oxidation by Hydrogen Peroxide

3.2.1 Uncoated samples

Four concentrations of H_2O_2 (5, 8, 10 and 15%) were first tested on uncoated particles and the corresponding degrees of oxidation (after 16h) were measured and studied by FTIR and SEM. Infrared spectra of oxidized Huanzala and Nanisivik samples indicated that (1) the characteristic IR absorption peak of pyrite diminished consistently with deeper oxidation while (2) the absorbing intensities of $FeSO_4.7H_2O$ or Fe(III) oxyhydroxysulphate increased with the increasing strength of the oxidant. The SEM analysis showed that both untreated samples possessed intact surfaces. The particle surfaces were more and more etched as the oxidation level increased. The details on FTIR and SEM analyses can be found in the reference by Chen et al.[18] The oxidation extent (OE) was calculated by equation 1 and the results are given in Table 1.

$$\text{oxidation extent (OE in \%)} = \frac{\text{weight of oxidized pyrite}}{\text{initial weight of pyrite}} \times 100 \qquad [1]$$

Table 1. Oxidation extent[1] of pyrite at different H_2O_2 concentrations

H_2O_2 conc (% v/v)	Huanzala	Nanisivik
5.0	54.4	53.1
8.0	58.2	56.6
10.0	63.7	61.7
15.0	63.1	61.6

[1] according to equation 1.

The results of Table 1 show that although the concentration of H_2O_2 was increased by three times, the oxidation of pyrite did not increase proportionally. This suggests a protective action of the iron oxide layer formed by the oxidation of FeS_2.

3.2.2 Non pre-oxidized coated particles

The passivation capacity of five different solutions of coating agents was tested on unoxidized pyrite particles according to the scheme presented in Figure 1a. The results are given in Table 2. The presence of the coating agents on pyrite was confirmed by FTIR with a decrease of the pyrite peak at 417 cm^{-1} and the appearance of the characteristic IR peaks of PAX and DETA at ~585 cm^{-1}, between ~1450 and 1600 cm^{-1} and between ~2850 and 2950 cm^{-1}. In the particular case of the 2% PAX solution, a radical modification of the pure PAX spectrum was observed suggesting a significant interaction between the pyrite surface and PAX. The SEM study revealed significant morphological modifications of the particulate system after the coating treatment. The agglutinating properties of both agents were evident and the level of agglutination seemed to depend on the concentration of coating agent and on the strength of agitation exerted during the treatment. However, it appears that the good adhesive properties of PAX do not reflect a passivation capacity for PAX alone (Table 2).

Table 2. Oxidation extent[1] of pyrite with different coating agents

Coating Agent (conc in % w/v)	Huanzala	Nanisivik
Uncoated (control)	38.0	38.1
DETA (0.2)	34.2	27.6
DETA (1.0)	9.9	9.2
PAX (0.2)	38.7	36.9
PAX (1.0)	36.3	36.3
DETA (0.1) + PAX (0.2)	27.3	25.9

[1] according to equation 1.

When it is combined with DETA, even at very low concentrations, PAX exhibited a promising capacity to reduce oxidation. Different combinations of the two reagents were investigated on Huanzala pyrite and the results are presented in Table 3.

The oxidation extent (OE) of pyrite was significantly reduced when DETA and PAX were combined as passivation agents. The best combination in our study was with 1.0% DETA and 0.4% PAX. To check the analytical reproducibility and precision of the analysis, four replicates of Huanzala samples were processed for three different combinations of coating agents (Table 4). The passivation efficiency (PE) is then defined as (equation 2):

$$\text{passivation efficiency (PE in \%)} = \frac{\text{OE control} - \text{OE coated}}{\text{OE control}} \times 100 \qquad [2]$$

Table 3. Oxidation extent[1] of non pre-oxidized Huanzala pyrite[2] with different combinations of the two coating agents

DETA conc. (% w/v)	PAX (0.2% w/v)	PAX (0.4% w/v)
0.2	-	17.7
0.4	22.9	-
0.6	9.7	8.9
0.8	10.6	10.2
1.0	9.3	7.9

[1] according to equation 1.

[2] the oxidation of the control was 35.0%

The higher the PE, the stronger the oxidation inhibition capacity of the studied coating system will be. The analytical precision and relative standard deviation obtained in this study (Table 4) are well below the limit of analytical allowance.

Table 4. Oxidation extent[1], analytical precision and passivation efficiency[2] of non pre-oxidized Huanzala pyrite with different combinations of the two coating agents

Coating Agent (in %w/v)	Control	PAX (0.2) + DETA (0.2)	PAX (0.4) + DETA (0.6)	DETA (1.0)
OE (%)	36.1	25.3	8.2	8.8
std dev.	0.7	1.6	0.6	0.2
relat.std dev.	1.9	6.3	7.3	2.3
PE[2] (%)	-	30.4	77.0	74.6

[1] according to equation 1.

[2] according to equation 2.

3.2.2 Pre-oxidized coated particles

In this experiment (Figure 1b), Huanzala pyrite samples were pre-oxidized by a 1%(v/v) H_2O_2 solution for 2h before any coating treatment. After the coating treatment by various combinations of the passivation agents, the oxidation extent was measured on four replicates which were performed independently from the pre-oxidation step to the end of the analysis.

The FTIR spectra of pre-oxidized coated pyrite samples were very similar to those of non pre-oxidized coated samples. The adhesion of the two coating agents on pyrite is once again confirmed by the appearance of the characteristic IR peaks of PAX and DETA at ~585 cm^{-1}, between ~1450 and 1600 cm^{-1} and between ~2850 and 2950 cm^{-1}. The SEM analysis revealed that most of the very small pyrite particles were completely oxidized and removed from the samples during the dissolution step. The morphological state of remaining larger particles was not much different from that of non pre-oxidized coated ones. A lower degree of agglutination of pre-oxidized particles may be attributed to the partial removal of small particles in the pre-oxidation step.

Table 5 presents the average oxidation extent values under different coating treatments after pre-oxidation. The calculation of OE and PE is given after subtracting the weight of pre-oxidized pyrite (13.6 ± 0.3% of the initial amount). The comparison of Table 4 and Table 5 clearly indicates the remarkable decrease of the oxidation extent of pre-oxidized samples. For all pre-oxidized coated pyrite samples, significantly higher values of passivation efficiency were measured when compared to the non pre-oxidation treatment. It is particularly obvious for the combination of 0.2% PAX and 0.2% DETA coating agent. It has already been observed that the formation of a thin layer of iron oxides can reduce the oxidation rate [9] and that their strong adsorbing properties [19] can favour the attachment of coating compounds on the surface of pyrite particles.

Table 5. Oxidation extent[1], analytical precision and passivation efficiency[2] of pre-oxidized Huanzala pyrite coated with different combinations of the two coating agents

Coating Agent (in %w/v)	Control	PAX (0.2) + DETA (0.2)	PAX (0.4) + DETA (0.6)	DETA (1.0)
OE (%)	25.7	6.1	4.0	4.1
std dev.	1.4	0.7	0.2	0.3
relat.std dev.	5.3	11.0	4.7	6.3
PE[2] (%)	-	76.2	84.6	84.1

[1] according to equation 1.

[2] according to equation 2.

The passivation efficiency of these two combined coating agents could be related to the formation of a water insoluble compound at the surface of pyrite particles. Such a compound has already been identified when alkali-metal xanthates react with lower alkylamines in the presence of catalytic amounts of nickel to produce dialkythionocarbamates as in equation 3 [17]:

$$(CH_3)_2\text{-C-O-C-}S_2\text{-Na} + CH_3\text{-}CH_2\text{-}NH_2 \xrightarrow{Ni^{2+}} (CH_3)_2\text{-C-O-C-NS-}CH_2\text{-}CH_3 + NaSH \qquad [3]$$

If such a reaction can occur during the passivation process, the by-product SH^- could play the role of a strong base ($pKb1 = 0.11$) to neutralize protons in an acidic environment.

Conclusion

Our experiments have demonstrated the remarkable function of oxidation inhibition of diethylenetriamine (DETA) and of the mixture of DETA with potassium amyl xanthate. Coating performed on slightly pre-oxidized pyrite surfaces significantly enhanced the efficiency of oxidation inhibition of these coating agents. Since the two compounds are already used in the milling/flotation process, we can suppose that they can a significant role in decreasing the reactivity of rejected pyrrhotite. We can also imagine that a combined solution of both products in proportions respecting what was determined in our study (i.e. 0.4% PAX and 0.6% DETA, all w/v) could be used and sprayed over tailing areas to retard the oxidation process. Our results clearly showed that the passivation treatment is much more efficient on pre-oxidized particles. Such a treatment can be easily combined with other remediation techniques involving the creation of an oxygen barrier.

The FTIR study revealed obvious modifications of DETA and PAX after the coating treatment, however, further studies will be necessary to identify the exact mechanisms occurring between the two reagents and the surface of pyrite particles.

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