

## Preventing oxidation of iron sulfide minerals by polyethylene polyamines

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### Abstract

This paper presents some important findings on the passivation of pyrite and pyrrhotite minerals. Polyethylene polyamines, such as triethylenetetramine (TETA), diethylenetriamine (DETA), used alone in dilute solutions or combined with potassium amyl xanthate (p.a.x.) can provide an effective protective layer for sulfidic ores and significantly reduce the penetration of atmospheric oxygen and the oxidation of these ores. Experimental studies were carried out systematically on both small particles and coarse samples using both diluted hydrogen peroxide solutions and atmospheric oxygen as oxidants. In all cases, a remarkable diminution of oxidation of the coated samples was observed. The study also demonstrates that solutions of polyethylene polyamines such as DETA and TETA are relatively strong reducing agents while showing good buffering capacities as well because of their nucleophilic functional groups. These properties give them additional advantages over other coating agents. The presence of these compounds also prevents the proliferation of the bacterium *Acidithiobacillus ferrooxidans* that plays an important catalyzing role in the oxidation of sulfides and acid mine generation. Polyethylene polyamines are effective coating agents to prevent surface oxidation of sulfidic minerals.

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**Keywords:** Sulfide ores; Acid rock drainage; Oxidation; Surface modification; Redox reaction

### 1. Introduction

The oxidation of sulfide minerals not only generates serious environmental damages by producing acid mine drainage and releasing toxic trace metals (Lowson, 1980; Bierens de Haan, 1991; Belzile et al., 1997a,b) to the environment but the rapid oxidation process, particularly for pyrrhotites, also causes important economic losses by reducing the efficiency of metals extraction (Belzile et al., 2004). The time delay between blasting and mineral processing can cause significant surface oxi-

dation of sulfide rock piles, which can in turn remarkably reduce the extractability of metals. The warm and humid environment of underground mines presents favorable conditions for oxidation processes. The estimated economic loss due to this process alone is huge in the mines of Inco Limited. How to effectively prevent, or slow down oxidation processes of sulfide minerals still remains an important issue for both mineral extraction and environmental protection.

To retard the oxidation process of sulfides, it is essential to block the contact with oxygen or other possible oxidizing agents. For years, many methods have been tested to reduce the oxidation of sulfide minerals, including the application of lime (Caruccio et al., 1988), or covering mine wastes with dry or organic materials such as clay, peat, sludge and compost (Nicholson et al., 1989; Pierce et al., 1994; Belzile et al., 1997a,b) or water

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Table 1  
Chemical, physical and mineralogical properties of studied pyrrhotite samples

Sample properties	Copper Cliff #3 (CC3)	McCreedy (McC)	Garson #3 (G3)	Garson #5 (G5)	46H6497	Simulation ore
Cu	0.77	0.54	0.40	0.31	0.57	0.86
Ni	5.19	4.53	3.89	3.63	0.05	3.17
Fe	53.30	56.00	44.20	49.05	49.70	42.33
S	33.40	33.00	27.8	31.35	31.65	26.27
SiO <sub>2</sub>	2.59	0.39	11.74	6.79	2.25	13.21
Al <sub>2</sub> O <sub>3</sub>	0.21	<DL	3.38	1.58	0.08	3.59
CaO	0.51	0.20	1.93	1.18	0.76	1.02
MgO	0.05	<DL	1.48	1.49	2.66	1.41
Hex Po/tot Po (SD)	10 (±10)	5 (±5)	55 (±5)	5 (±5)	80 (±10)	5 (±5)
Specific area (m <sup>2</sup> /g)	0.26	1.02	1.22	1.26	2.47	Not available

All chemical and mineralogical properties are in weight percentage.

## 2.2. Surface coating on pyrite samples

Preliminary studies with pyrite samples were done by measuring and comparing oxidation extents of pristine and pre-oxidized samples after coating with solutions of various concentrations of diethylenetriamine (DETA, Aldrich), potassium amyl xanthate (p.a.x., American Cyanamid) or mixtures of both. All chemicals used in the studies were dissolved in double deionized water (DDW) and prepared daily. For direct coating, about 20 mg samples were precisely weighed in a 50 mL glass beaker and 0.2 mL of coating solution was added. Samples were rinsed well with the coating solution and allowed to dry overnight. Sample pre-oxidation was done by adding 10.0 mL of 0.3% w/w (0.124 M) H<sub>2</sub>O<sub>2</sub> into a beaker containing 30.0 mg of pyrite sample. The pre-oxidation was conducted at 22 °C for 2 h. The sample was then filtered through a 0.22 µm membrane. The filtrate was collected and acidified to pH 2 with HCl and iron in the filtrate was measured by flame atomic absorption spectrometry (FAAS). This allowed us to estimate how much pyrite was oxidized and the oxidized iron was dissolved upon acidification during the pre-oxidation step. The particles collected on the membrane were rinsed thoroughly with double deionized water (DDW) and allowed to dry in a vacuum desiccator. Once the particles were dried, 0.2 mL of coating solution was added on the particles carefully so that all particles were in contact with the solution.

After the coating step, the particles were subjected to an oxidation process in 10.0 mL of 3.0% w/w (1.24 M) H<sub>2</sub>O<sub>2</sub> for 2 h at 22 °C. After a 2-h oxidation, the process was stopped by adding 0.134 g of sodium oxalate into the solution, followed by 0.4 mL of 0.25 M HCl to adjust the pH to 2. Sodium oxalate has been for long used as an effective reducing agent to extract and dissolve oxidized iron from mineral surfaces (Chao, 1984; Bigham et al., 1990) into solution. The extraction step lasted for 1 h with occasional stirring of the sample solution; the particles were then filtered through a 0.22 µm membrane. The filtrate was collected and the amount of oxi-

dized iron in the filtrate was determined by FAAS. Quadruplicate samples were carried out for each experimental treatment.

## 2.3. Surface coating on pyrrhotite samples

Pyrrhotites are minerals that are much readily subjected to oxidation compared to pyrite; therefore a fast oxidation becomes an even more serious problem for mineral extraction or environmental protection. Experimental work was done to determine if DETA or DETA-p.a.x. could also reduce the oxidation rate of pyrrhotite samples. In this part of the work, triethylenetetramine (TETA, Fisher Scientific) was introduced as another coating agent.

To compare the coating effectiveness between pristine and pre-oxidized samples, 50.0 mg sample was pre-treated with 5.0 mL 0.1% w/w (0.041 M) H<sub>2</sub>O<sub>2</sub> for 30 min at 20 °C. Each sample was filtered and rinsed with DDW, and the filter with collected particles was dried overnight in a desiccator. Then, a 0.5 mL coating solution was added directly on the filter and the extra coating solution was removed through filtration. The filter containing the coated particles were dried overnight and then put into a 5.0 mL of 0.5% w/w (0.207 M) H<sub>2</sub>O<sub>2</sub> solution for a 2-h oxidation period. The oxidation process was then stopped and the oxidized iron was extracted by 5.0 mL of 0.2 M sodium oxalate (pH 2) for 1 h.

For direct sample coating without pre-oxidation, 0.1 mL coating solution was added directly to the sample in a glass beaker. After the coating solution has dried out, the oxidation was performed with 10.0 mL 1.0% w/w (0.41 M) H<sub>2</sub>O<sub>2</sub> for 2 h. The extraction steps were the same as above except that the volume of oxalate solution was 10.0 mL. The oxidized iron in the leachate was measured by FAAS. The method of standard addition was performed to investigate possible matrix interferences of sodium oxalate and sulfate on iron analysis, neither positive nor negative interferences were found. Controls (without coating treatment) were systematically carried in each test.

#### 2.4. Surface coating on coarse pyrrhotite rock samples

For this experiment, approximately 40 kg of pyrrhotite-rich rock from Inco Limited was collected and crushed into two size classes, one between 3.4 and 6.7 mm and the other between 6.7 and 9.5 mm. Sub-samples composed of 225 g of the small size fraction and 275 g of the larger one were disposed in 1 L plastic boxes. For samples to be coated, 20.0 mL of coating solution was added. Nothing was added on dry controls while wet controls received 20.0 mL of DDW. All these samples were allowed to dry in a fume hood overnight. The samples were then kept in a chamber made of plastic film. Warm water baths were operated inside the chamber to maintain the temperature and humidity at  $30 \pm 5$  °C and  $85 \pm 10\%$ , respectively. At selected times, 150 mL of 0.2 M sodium oxalate was added to sub-samples and pH was adjusted to  $\sim 2$  with a volume of 3.0 M HCl. The volume of HCl was slightly different for different samples:  $\sim 8.0$  mL for controls,  $\sim 11.0$  mL for 1% TETA, 2% TETA and 2% DETA and  $\sim 13.0$  mL for 3% TETA respectively, because of the alkaline nature of these polyamine solutions. The extraction of the oxidized iron by  $\text{Na}_2\text{C}_2\text{O}_4$  was done for 30 min with occasional hand stirring. The filtration was done on  $0.45 \mu\text{m}$  membranes. The iron concentration in the filtrate was measured by FAAS. The standard addition method was performed on the extracted solution and no matrix interferences were observed. Triplicate samples were carried out for each different concentration.

#### 2.5. Estimation of reducing potential of TETA

Titration of TETA with hydrogen peroxide was performed according to an iodometric method (Harris, 2003) to estimate the reducing power of polyethylene polyamines. In principle, when TETA and an excessive quantity of  $\text{H}_2\text{O}_2$  are mixed together, the concentration of  $\text{H}_2\text{O}_2$  should decrease if a redox reaction occurs. Therefore by measuring the concentration of  $\text{H}_2\text{O}_2$  before and after the reaction, we can estimate whether such a reaction occur or not. In this experiment, the concentrated  $\text{H}_2\text{O}_2$  solution was precisely weighed in a 250 mL glass flask, and then a precise amount of TETA was added into the solution. After reaction, the excess of  $\text{H}_2\text{O}_2$  concentration was determined. The estimated number of mmol of  $\text{H}_2\text{O}_2$  that has reacted with TETA can be calculated by difference.

### 3. Results and discussion

To compare the effectiveness of passivation with the different coating agents and treatments, the concept of oxidation extent (%) was used:

Oxidation extent (%)

$$= \frac{\text{Weight of oxidized sulfide sample}}{\text{Weight of sulfide sample}} \times 100 \quad (1)$$

For pure pyrite, a definite chemical formula  $\text{FeS}_2$  exists, therefore the weight of oxidized pyrite can be calculated based on the amount of oxidized iron determined. For pyrrhotite, the conversion to weight of oxidized sulfide sample was made by the percentage of iron oxidized in that sample divided by the fraction of iron in the original sample. For instance, in sample 46H6497 (from Ward's Geology), the proportion of iron was 49.7% w/w and if the determined oxidized iron in the experiment was 12.09% in the sample, then the oxidation extent (%) would be 12.09 divided by 0.497, therefore the oxidation extent of that sample under the specific experimental conditions was calculated as 24.33%.

When comparing the coating effectiveness between samples with and without pre-oxidation treatment, a problem emerged as some small particles subjected to the pre-oxidation treatment were removed during this pre-oxidation step. In this case, not only the surface but also the particle size distribution had been modified during the pre-oxidation step. Consequently a direct comparison of the oxidation extent (%) between coating on the pristine samples and coating on the pre-oxidized samples would be biased. To overcome this difficulty, a second parameter, the passivation efficiency (%), was introduced:

Passivation efficiency (%)

$$= \frac{\text{Oxidation extent}_{\text{control}} - \text{Oxidation extent}_{\text{coated}}}{\text{Oxidation extent}_{\text{control}}} \times 100 \quad (2)$$

This way, the relative comparison between different coating conditions could be made and the direct comparison of oxidation extent (%) was avoided.

#### 3.1. Coating effectiveness on pyrite samples with DETA and DETA-p.a.x.

Preliminary tests with different concentrations and combinations of coating solutions were performed on pristine samples. With p.a.x. alone, the oxidation extent level was the same as controls, therefore it cannot be used as a coating agent alone. However, with even very low concentrations of DETA or DETA-p.a.x., remarkable passivation results were obtained (Table 2). When samples were pre-oxidized before coating, the passivation efficiency was further improved (Table 3).

Oxidation extents (%) presented in Table 3 are significantly lower than those of Table 2. This is partially caused by the elimination of smaller particles in the pre-oxidation step. In order to have a better estimation of the oxidation extent and passivation efficiency, the

Table 2

Comparison of oxidation extents between different coating treatments on pristine Huanzala pyrite samples (20 mg sample with 0.2 mL coating agent added directly on the sample particles)

Coating agent (%)	Control (0)	p.a.x. + DETA (0.2% + 0.2%)	p.a.x. + DETA (0.4% + 0.6%)	DETA (1.0%)
Oxidation extent (%)	36.1	25.3	8.2	8.8
SD ( $n = 4$ )	0.7	1.6	0.6	0.2
RSD %	1.9	6.3	7.3	2.3
Passivation efficiency (%)	—	30.4	77.0	74.6

Table 3

Comparison of oxidation extents between different coating treatments on pre-oxidized Huanzala pyrite samples (coating conditions as in Table 2)

Coating agent (%)	Control (0)	p.a.x. + DETA (0.2% + 0.2%)	p.a.x. + DETA (0.4% + 0.6%)	DETA (1.0%)
Oxidation extent (%)	25.7	6.1	4.0	4.1
SD ( $n = 4$ )	1.4	0.7	0.2	0.2
RSD %	5.3	11.0	4.7	6.3
Passivation efficiency (%)	—	76.2	84.6	84.1

amount of pyrite sample lost in form of dissolved iron during pre-oxidation was measured. For a total of 30.0 mg pyrite sample, about 0.3 mg was lost during the pre-oxidation step. Therefore in the calculation of oxidation extent (%) this fraction was subtracted from the numerator in Eq. (1).

The results show that even very low concentrations of DETA or DETA-p.a.x. can remarkably lessen the oxidation of pyrite by hydrogen peroxide. The passivation efficiency was greatly improved when samples were pre-oxidized by a diluted  $H_2O_2$  solution. The creation of an iron oxide layer has been proved to be a good way of promoting the coating efficiency (Belzile et al., 1997a,b). Scanning electron microscopy (SEM) pictures (not shown) also pointed out that a much larger surface had been generated after the sample pre-treatment thus creating favorable conditions for a better coating on pyrite samples.

### 3.2. Coating effectiveness of pyrrhotite samples with TETA, DETA and DETA-p.a.x.

Further coating experiments were done with pyrrhotite samples using polyethylene polyamines. Because the oxidation of pyrrhotite samples can occur much faster than that of pyrite, experimental conditions were adjusted accordingly. Samples Garson #3 and McCreedy were chosen to test whether a pre-oxidation step could enhance the effectiveness of surface coating for pyrrhotite. In this experiment, 0.2% (v/v) solutions of DETA, TETA or combined reagents were used. The detailed experimental protocol is given in Section 2.3. The results demonstrated that a pre-oxidizing step did not have a clear advantage over direct coating of pyrrhotite samples (Fig. 1). This is likely due to the higher reactivity of pyrrhotite samples compared to pyrite. During the crushing, milling and storage processes, a layer of oxide had already been formed. It was found that the

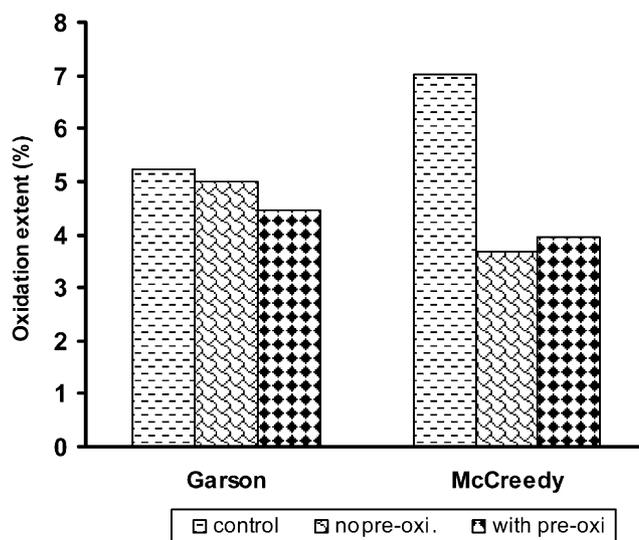


Fig. 1. Comparison between pre-oxidation and non-pre-oxidation treatments before coating. Pre-oxidation was performed on 60 mg sample with 5.0 mL of 0.1% (w/w)  $H_2O_2$  (0.04 M) for 30.0 min at room temperature. Further oxidation was carried out in 5.0 mL of 0.5% (w/w)  $H_2O_2$  (0.207 M) at 25 °C for 2 h.

oxidation of pyrrhotite sample was 8.7%, 6.5%, 3.8%, 2.9% and 2.7% for samples 46H6497, McCreedy, Garson #3, Garson #5 and Copper Cliff #3 respectively, after sample preparation and storage in a vacuum desiccator for certain time, whereas pyrite samples remained very stable with only little oxidation (<2.5%) for even several years with the same sample preparation and storage conditions.

Fig. 1 also indicates that the coating effectiveness varies significantly between the two samples. This phenomenon has been further confirmed by other sets of experiments in which a direct addition of 0.1 mL of coating solution was applied (Fig. 2). The oxidation extents of control samples (TETA 0%) 46H6497 and G5

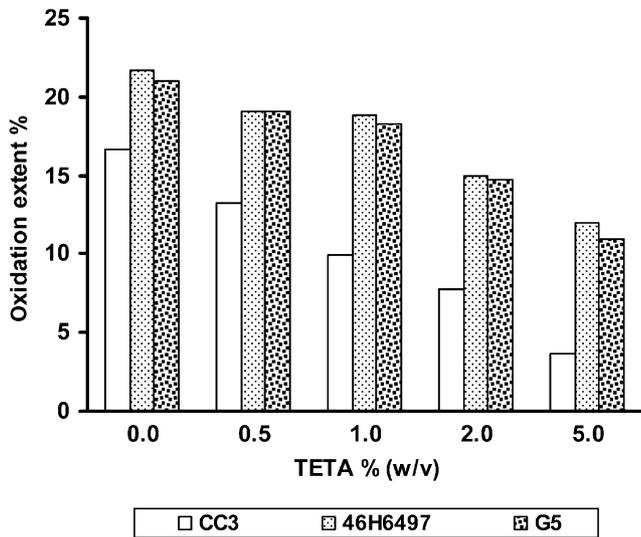


Fig. 2. Comparison of coating effectiveness with different concentrations of TETA. 0.1 mL of TETA was added directly on 60 mg samples. Oxidation was done with 10.0 mL of 1.0% (w/w) H<sub>2</sub>O<sub>2</sub> (0.414 M) for 2 h at 25 °C. To stop oxidation, 10.0 mL of 0.2 M Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> was added at pH 2 and oxidized iron was extract with occasional stirring for 1 h.

were significantly higher than that of CC3 indicating that the chemical reactivity of the first two samples was much higher than that of sample CC3. When samples were coated with different concentrations of TETA, the oxidation extents of CC3 dropped much more quickly compared to those of G5 and 46H6497. These discrepancies in chemical reactivity and coating effectiveness are attributed to the individual chemical and mineralogical nature of each sample and to specific experimental conditions. For example, when the above three samples were subjected to an 18-h oxidation with H<sub>2</sub>O<sub>2</sub>, results showed that CC3 was more resistant to oxidation, whereas 46H6497 and G5 were rather similar and more sensitive to such conditions (Fig. 3). However,

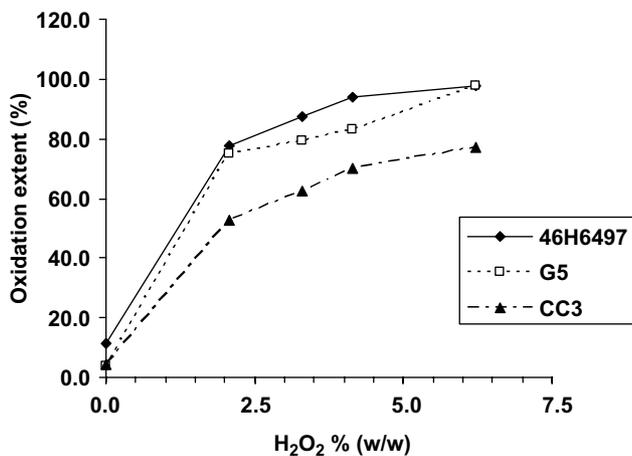


Fig. 3. Comparison of reactivities of Copper Cliff #3, Garson #5 and 46H6497. 10.0 mL of H<sub>2</sub>O<sub>2</sub> at various concentrations was added into 60 mg samples and oxidation lasted for 18 h at 25 °C.

when the oxidation strength was reduced by using 0.5% (w/w) H<sub>2</sub>O<sub>2</sub> (0.207 M) for a shorter time, the chemical reactivity of G5 and 46H6497 was remarkably differentiated, whereas CC3 still remained the most stable to oxidation among the three samples (Fig. 4). The high reactivity of 46H6497 is likely due to its very large specific surface and possibly to the high percentage of hexagonal pyrrhotite which has been suggested to be more vulnerable to oxidation (Orlova et al., 1988). The difference in coating effectiveness between different types of pyrrhotites could be partially due to their surface, chemical and mineralogical properties which require further studies. The reproducibility of coating operations was examined with triplicate experiments and it was proven

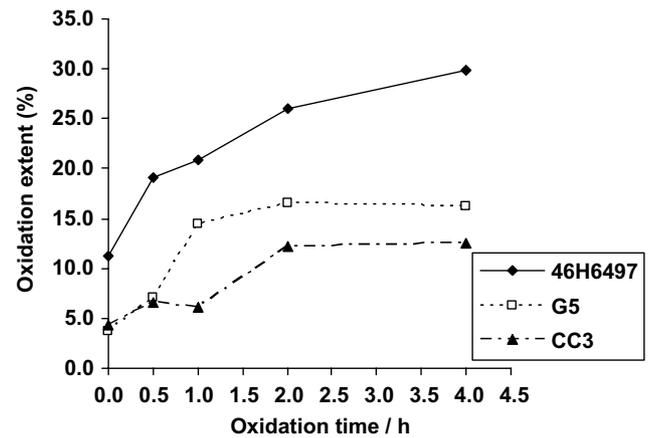


Fig. 4. Oxidation reactivities of CC3, G5 and 46H6497 under milder oxidation conditions and at different reaction times. 10.0 mL of 0.5% (w/w) H<sub>2</sub>O<sub>2</sub> (0.207 M) was added into 50 mg samples and oxidation was carried at 25 °C for different times.

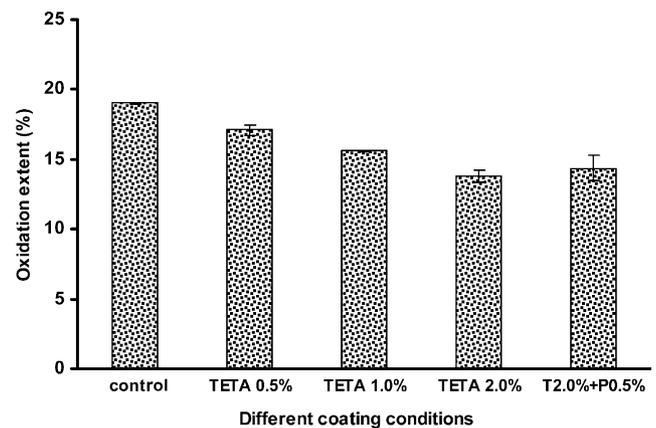


Fig. 5. Triplicate coating study with Garson #5. 0.1 mL of coating agent was applied on 60 mg samples. Oxidation with 10.0 mL of 1.0% (w/w) H<sub>2</sub>O<sub>2</sub> (0.414 M) was performed at 25 °C for 2 h on dried particles. In the last bar, T and P stand for TETA and potassium amyln xanthate respectively.

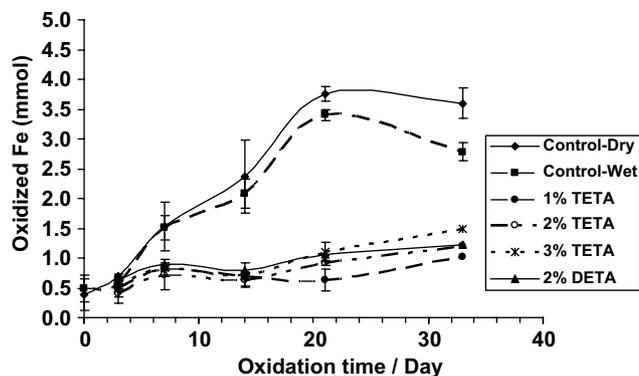


Fig. 6. Simulation studies with coarse samples on a large scale basis. Each 500 g individual sample resulted from the combination of 225 g of samples between 3.35 mm and 6.68 mm in size and 275 g of samples between 6.68 mm and 9.51 mm. Oxidation was carried under atmospheric conditions inside a chamber with controlled humidity at  $85 \pm 15\%$  and temperature at  $30 \pm 5^\circ\text{C}$ .

satisfactory as shown in Fig. 5 with SDs between 0.08% and 0.89%.

### 3.3. Coating experiments with coarse pyrrhotite rock samples

The surface coating was then applied to coarse materials on a larger scale. The experiment showed that excellent passivation results were achieved for both TETA and DETA (Fig. 6). The contrast between coated and control samples was visually remarkable. After 33 days of atmospheric oxidation, a yellow rusty color of iron oxides covered the whole surface of control samples whereas the surface of coated samples remained deep dark and showed no sign of oxidation. Higher con-

centrations of TETA did not seem more effective than lower ones. It was also noticed that wet controls looked less oxidized than dry control samples, particularly when the oxidation time was prolonged. This could be due to two reasons: after 20 days of oxidation, a good layer of oxidized iron was formed on the surface of control samples and protected them from further oxidation; secondly, although TETA and DETA have relative high boiling points, some vapors could still reach the surface of these control samples, particularly in a relatively large scale experiment where nearly a hundred samples were gathered in a limited space at relatively high temperature and moisture and for a long time. The surface of wet controls would likely be more favorable to this secondary coating process. Over 33 days of experiment, there was no visible degradation of the coating layer, indicating that these polyethylene polyamines were relatively stable under the controlled conditions.

### 3.4. Estimation of the reducing capacity of TETA with $\text{H}_2\text{O}_2$

Polyethylene polyamines contain several nucleophilic groups with nitrogen; therefore they should possess some reducing capacity. To examine this chemical property, redox titrations of  $\text{H}_2\text{O}_2$  with thiosulfate were performed. In one series of experiments, two different volumes of 30.0% (w/w) (12.41 M)  $\text{H}_2\text{O}_2$  were reacted separately with 100% (v/v) TETA for one hour. After the reaction, 50.0 mL of DDW was added into the reaction system and the remaining  $\text{H}_2\text{O}_2$  was titrated with  $\text{Na}_2\text{S}_2\text{O}_3$ . In another series of tests, the molar ratio between  $\text{H}_2\text{O}_2$  and TETA was kept approximately

Table 4  
Investigation of redox reactions between  $\text{H}_2\text{O}_2$  and TETA by iodometric titration

Experimental conditions	$\text{H}_2\text{O}_2$ (mmol)	TETA (mmol)	Consumed $\text{Na}_2\text{S}_2\text{O}_3$ (mmol)	$\text{H}_2\text{O}_2$ reacted With TETA (mmol)	Avg SD (RSD%)
<i>Reaction with concentrated <math>\text{H}_2\text{O}_2</math></i>					
$\text{H}_2\text{O}_2$ :TETA 12:1	11.81	1.097	4.508	9.553	9.632
	11.79	1.048	4.163	9.711	0.079
	11.75	0.999	4.239	9.631	(0.82)
$\text{H}_2\text{O}_2$ :TETA 1.2:1.0	1.23	1.103	0.548	0.952	0.980
	1.20	1.023	0.342	1.030	0.043
	1.20	1.006	0.479	0.957	(4.427)
<i>Reaction with diluted <math>\text{H}_2\text{O}_2</math> (<math>\text{H}_2\text{O}_2</math>:TETA = 1.3:1.0)</i>					
0.5 h Reaction	0.880	0.674	1.42	0.170	0.229
	0.842	0.671	1.08	0.302	0.067
	0.830	0.679	1.23	0.215	(29.30)
1.0 h Reaction	0.844	0.682	1.35	0.169	0.123
	0.825	0.677	1.63	0.010	0.098
	0.834	0.671	1.29	0.189	(79.96)
2.0 h Reaction	0.842	0.670	1.49	0.097	0.063
	0.834	0.679	1.68	-0.006	0.059
	0.857	0.668	1.52	0.097	(94.89)

constant at 1.3:1.0. However the concentration of  $H_2O_2$  was first diluted with 50.0 mL of DDW, then TETA was introduced and the reaction was allowed to proceed for 0.5, 1.0 and 2.0 h, respectively. Titrations were performed as above. In all experiments, the reagent blanks without TETA were always carried and 100% recoveries of  $H_2O_2$  were obtained. The results are presented in Table 4. Although the reaction is not quantitative, the titration results still present an instructive picture on the nature of the reaction between  $H_2O_2$  and TETA. Several conclusions can be made based on these experiments: (1) in the reaction, TETA does play a role of reducing agent, because it can provide electrons in the redox reaction; (2) in the presence of a larger quantity of concentrated  $H_2O_2$ , each molecule of TETA provided several electrons (see experiment  $H_2O_2$ :TETA = 12:1), suggesting that not only all nitrogen atoms were oxidized, but also some of  $CH_2$ -bonds. (3) when the molar ratio of participants is around 1.0:1.0 (see experiment  $H_2O_2$ : TETA = 1.2:1.0), approximately 1 mol of TETA reacted with 1 mol of  $H_2O_2$ ; (4) this reaction is incomplete; (5) the kinetics of this reaction is very much depending on the concentration of  $H_2O_2$ ; in a diluted system, the oxidation reaction seems remarkably inhibited.

#### 4. Conclusion

Polyethylene polyamines are efficient coating agents in preventing the oxidation of pyrite and pyrrhotite. All samples coated with TETA or DETA demonstrated a significant decrease in oxidation. The diluted solutions (1.0% w/v or less) of TETA or DETA could be easily sprayed on surfaces of blasted rock piles to allow the formation of a protective layer while waiting for transportation outside the mines for milling and extraction. This would mean an important economic return with a simple and easy application of a protective diluted solution. There are many advantages of using polyethylene polyamines as coating agents. They are already used in the floatation processes, therefore they should not cause any unwished effects. They possess large potential as reducing agents which consequently prevent the oxidation by air or  $Fe^{3+}$ . They are basic substances and behave as such in neutralizing protons produced during oxidation processes and they seem to adsorb strongly on the surface of coated sulfidic ores as there was no observable degradation of the coating layer after 33 days of experiment under  $85 \pm 15\%$  humidity and  $30 \pm 5$  °C. A later work also showed that polyethylene polyamines also effectively inhibited the proliferation of the bacterium *Acidithiobacillus ferrooxidans*, which is known to play a catalyzing role in the oxidation of sulfidic ores. Although both TETA and DETA can slow down the oxidation of sulfide minerals,

TETA can be more attractive than DETA as a coating agent. The former contains one more alkyl functional group than DETA which should make it less hydrophilic. All studied pyrrhotite samples exhibited hydrophobic properties. The higher hydrophobic nature of TETA should be advantageous for surface coating. In addition, the higher molecular weight of TETA makes it less volatile (b.p. 277 °C at 760 mmHg) than DETA (b.p. 207 °C at 760 mmHg). This means that it will produce fewer vapors that could affect working conditions. Because TETA or DETA is used in the floatation process, the particles coated with TETA or DETA should be also more resistant to atmospheric oxidation, therefore the tailings could be less sensitive to acid drainage problem. More systematic studies on the adhesiveness of the coating on the surface of sulfide minerals are needed to estimate its sustainability under natural weather conditions.

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