Assessment of Silica Coating as a Technique for the Control of Acid Generation from Pyritic Tailings ◉

Konstantinos Kollias, Evangelia Mylona, Katerina Adam, Nymphodora Papassiopi, Anthimos Xenidis

National Technical University of Athens, School of Mining & Metallurgical Eng., Laboratory of Metallurgy, 15780 Zografou, Greece, kkollias@metal.ntua.gr

Abstract

A promising strategy for the efficient management of sulfide mine wastes is related to the formation of Si-based coating on sulfides surface to prevent oxidation. In order to elucidate the coating technology, batch and column tests involving treatment of pyritic tailings with solutions consisting of SiO_4^{-4} and H_2O_2 were performed. To assess the stability of coatings, treated samples were leached with a solution of H_2O_2. Humidity cell tests on selected coated samples were also performed for 41 weeks. Based on the results, silica coating resulted in the reduction of sulfate release by up to 91%, compared to the non-treated sample.

Keywords: Acid Mine Drainage, sulfidic wastes, pyrite, oxidation, silica coating, humidity cells

Introduction

The environmental and financial impact of acid mine drainage (AMD) has challenged the global scientific community for decades in order to understand the evolution and the controlling parameters of AMD formation and thus to provide sustainable and cost-effective preventive technologies (Öhlander et al. 2012; Rimstidt and Vaughan 2014; Pozo-Antonio et al. 2014). A promising approach for the environmentally safe management of potentially acid generating mine wastes is aiming to passivate the sulfide mineral surface through the formation of a coating layer, which block the access of oxidants (oxygen, water)(BREF 2009; Sahoo et al. 2013).

Several inorganic and organic compounds have been used for the development of artificial coating including phosphates, iron hydroxides, humic acids, polyamines, organosilanes, siloxane etc. (Zhang and Evangelou 1996; Huminicki and Rimstidt 2009; Ačai et al. 2009; You et al. 2013; Diao et al. 2013; Ouyang et al. 2015; Kollias et al. 2015). Silicates have been also used for the formation of a protective layer around pyrite particles. Silica coatings are advantageous over other types due to the abundance of silicates in the crust as well as their inert nature and limited solubility (Iler 1979; O'Neill 1994).

The methodology initially developed for the formation of silica coating included leaching of the pyritic waste using a solution containing hydrogen peroxide (H_2O_2), a silica source and pH adjustment in the range 4-6. Under these conditions, the pyrite is oxidized by H_2O_2 releasing mainly iron and sulfates in the presence of Si. The iron is hydrolyzed and iron hydroxides are precipitated on FeS_2 surface. Finally, an outer silica layer is formed on the chemically modified surface (Evangelou 1996). Later studies have shown that a coating layer containing Si and Fe can be developed on pyrite particles following treatment with solutions having variable Si concentrations (0.8-300 mM) at pH: 6-7 and variable L/S ratios (1-8600 mL/g). Silica coating was developed both in the presence and absence of H_2O_2 (Evangelou 2001; Kargbo and Chatterjee 2005; Bessho et al. 2011; Kang et al. 2017; Fan et al. 2017). However, the optimal conditions favoring the formation of coating as well as its stability are still under consideration.

Based on the above, the aim of this study is to optimize the conditions resulting in a stable Si-bearing protective layer around pyrite grains in order to increase the feasibility of the coating technology.

Materials and Methods

Pyritic tailings (Py) from Kassandra mines at Chalkidiki peninsula (Greece) were used in this study. The experiments were performed using the -2+0.074 mm and -0.125+0.074 mm size-fractions of particles. The secondary oxidation phases on the surface of pyrite grains were removed following treatment with a solution of 1 M HCl (Kollias et al. 2015). Thereafter, a representative amount of washed sample was finely ground and subjected to chemical and mineralogical analyses. Based on the results, the -2+0.074 mm and -0.125+0.074 mm size fractions contained 88% and 94% pyrite, respectively. The experimental methodology followed for the formation and characterization of silica coating is shown in Fig. 1.

For the development of silica coating, pyrite samples were treated with a solution consisting of 0.1 M H_2O_2 as oxidizing agent and 0.1-50 mM $Na_2SiO_3 \cdot 5H_2O$ as source of silicate ions. Hydrochloric acid (3 M HCl) was used to initially adjust pH to the selected values (pH: 5-8). Sodium acetate (0.2 M) was further used to buffer the coating solution to pH: 5-6, whereas Tris(hydroxymethyl) aminomethane (0.1 M) was used for adjusting pH at 7-8. Batch tests were conducted on the -0.125+0.074 mm-size sample, involving agitation on a rotary shaker (10 rpm). Based on the results of the batch tests, column tests with an up-flow mode involving continuous recirculation of the solution were conducted on the -2+0.074 mm size sample (Kollias et al. 2017). The variables studied in the batch and column tests are given in Table 1.

To investigate the coating effectiveness in suppressing oxidation, short- and a long-term tests were performed, i.e. oxidative leaching tests (24 hours) and humidity cell
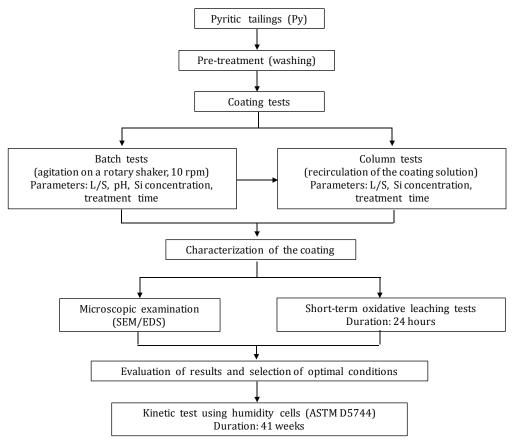

Figure 1 *Methodology used for the development of silica coating on pyrite surface and the evaluation of coating effectiveness.*

Table 1 Experimental variables for the formation of silica coating.

Parameter	Batch tests	Column tests
Particle size (mm)	-0.125+0.075	-2+0.075
Si (mM)	0, 0.1, 1, 5, 10, 25, 50	0, 0.1, 1, 5
pH	5, 6, 7, 8	6
L/S (mL/g)	5, 10, 20, 50, 100	5, 10, 20
Treatment time (h)	6, 24, 48	24, 48, 72

tests (41 weeks), respectively. The oxidative leaching tests were conducted on all the samples treated under the conditions examined in batch and column scale as well as on a "fresh" non-treated Py (i.e. washed Py sample without any coating treatment). The leaching test involved mixing of 1 g of solid samples with 100 mL of solution containing 0.1 M H_2O_2 under natural pH ($\approx$5) in the absence of buffer. The suspensions were placed for agitation on a rotary shaker (10 rpm). At 24 hours, the suspensions were filtered through a 0.45 μm filter and the filtrate was analyzed for SO_4^{-2} and Si. The oxidative leaching tests were carried out in duplicate under controlled conditions (T=20±5°C).

Based on the experimental results, humidity cell tests were conducted on the coated Py samples with the best performance in comparison with the non-treated pyrite (control test). The humidity cell tests were performed on 1000 g sample following the procedure described in ASTM D5744 (Kollias et al. 2016).

In all cases, sulfate concentrations were measured gravimetrically (Rice et al. 2012), whereas the dissolved Si in the recovered solutions was measured using Atomic Adsorption Spectroscopy-Flame Emission (2100 Perkin Elmer). Furthermore, the coated samples were air dried and examined by SEM/EDS.

Results and Discussion

Based on the results of the oxidative leaching tests, the release of SO_4^{-2} from the treated Py samples under variable conditions as well as the non-treated Py (control sample) is shown in Fig. 2. The results can be categorized in three groups, i.e. Group "A", "B" and "C".

In Group "A", the released amount of SO_4^{-2} from the treated Py samples was reduced by 7-53%, compared to the control test. It includes batch tests involving pyrite treatment with zero or very high Si concentration (50 mM) and/or low L/S (5-50 mL/g) and/or short time (6 hours). Column tests involving pyrite treatment with Si: 0 and 1 mM, L/S: 5-20 mL/g for 24-72 hours are also categorized in Group "A". Based on SEM/EDS analysis, the above treatment conditions resulted in the formation of a partial coating layer around pyrite particles.

Group "B" includes treated Py samples, for which the dissolved amount of sulfates was reduced by 63-79% compared to the control test. The batch tests of this group were performed with solutions containing Si: 0-50 mM at pH: 6 and 7 and L/S: 50 and 100 mL/g for 24 hours. Column tests were conducted with solutions of Si: 5 mM and L/S: 10 mL/g for 48 hours.

In Group "C", a reduction of sulfate release by 83-91% as compared to the control test was observed. This group includes batch tests conducted with solutions of 0.1-50 mM Si at pH: 6-7 for high L/S ratio, i.e. 100 mL/g and treatment time equal to 24 hours. Column tests involved treatment with 0.1 mM Si for 48 hours and significantly lower L/S ratio, i.e. 10 mL/g as compared to the batch tests of the group. The SEM/EDS examination indicated that there was no cracking on the coating formed at the surface of group "C" samples.

Based on the batch test results, it is seen that the main parameters affecting the formation of an effective coating layer around pyrite particles is pH, treatment time and the liquid to solid ratio. The Py sample treated with Si: 1 mM, L/S: 100 mL/g at pH: 6 for 24 h (exp. No 30) exhibited the lower dissolved amount of sulfates (i.e. 10 mmol/kg) following the oxidative leaching test.

The effectiveness of coating formed under the above conditions to inhibit pyrite oxidation was further examined in humidity cells.
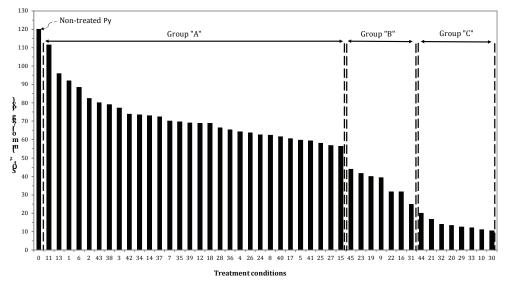
Figure 2 Comparative results of oxidative leaching tests carried out on treated pyritic tailings samples (Py) and "fresh" non-treated Py samples (mean values of duplicate tests).

The oxidation-reduction potential (ORP) versus pH of the leachates produced from the humidity cell tests is shown in Fig. 3a. pH of the leachates produced from the non-treated sample (control test) decreased from pH: 4.1 to pH: 2.7 at 4 weeks of testing. ORP values of the leachates were 400-490 mV. pH in the leachates of the Si treated sample was above pH: 4.1 after 4 weeks of testing, gradually decreased and stabilised to values 2.6±0.2 after 12 weeks of testing. The ORP values of the leachates were lower than the non-treated sample, i.e. 360-450 mV.

The cumulative amount of $S(SO_4)$ released from the Si treated and non-treated samples, expressed as a percentage of total sulfur content vs. time is shown in Fig. 3b. The evolution of dissolved $S(SO_4)$ can be distinguished in three periods, i.e. period I from 0 to 3 weeks, period II from 3 to 12 weeks and period III from 12 to 41 weeks. For the control sample, the initial dissolution rate (period I) was equivalent to 0.07% S per week, the rate was reduced to 0.03% during period II and finally the value became equal to 0.01% during period III. The observed decrease regarding the amount of S released from the non-treated Py may be attributed to the formation of a protective layer, probably consisting of iron oxyhydroxides, which suppresses the further oxidation process. The

silica treated Py resulted in slower dissolution rates and the release of sulfur corresponded to 0.02, 0.01 and 0.006% per week for periods I, II and III, respectively. The cumulative amount of sulfur dissolved from the Si treated sample at 41 weeks of testing was 0.34% and was reduced by 60%, as compared to the non-treated sample (0.85%).

Based on SEM/EDS examination of the solid residues of humidity cell tests, Si concentration at the surface of treated pyrite particles ranged from 0.30 to 0.36% as compared to 0.37% for the coated particles before the test, indicating that pyrite coating remained stable under the conditions of the weathering test. This was in agreement with the chemical analyses of leachates of the Si coated sample, which showed that silica concentration was below detection limit after 3 weeks of testing.

Conclusions

Batch tests showed that the optimal conditions of coating formation involves treatment of pyritic tailings with solutions of low Si concentration (1 mM) and L/S equal to 100 L/kg at pH: 24 h. The release of sulfates from coated pyritic material was reduced by 91%, compared to the non-treated sample (control test). Humidity cell tests indicated that the coating formed using Si solution of 1 mM remained stable after 41 weeks of leaching re-
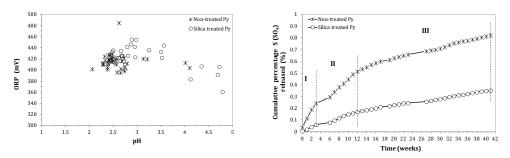
Figure 3 (a) ORP versus pH and (b) cumulative percentage of S(SO$_4$) released (%) vs. time in the leachates of treated and non-treated Py.

sulting in the reduction of SO$_4^{-2}$ dissolution rate by 60%, compared to the control sample (non-treated sample). Column experiments indicated that an efficient coating can be also established using very low Si concentration, i.e. 0.1 mM and low L/S: 10 L/kg in case that coating solution is recirculated through the pyrite bed for 48 h. Under these conditions, the amount of S oxidized was reduced by 83% as compared to the non-treated sample. The coating technique could be applied in a mineral processing plant, after ore flotation and before the disposal of the tailings. For the efficient control of acid generation from pyritic wastes, the coating method should be combined with alkaline addition to neutralize the low amount of acidity still released from the coated material.

Acknowledgements

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