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Improvement of chalcopyrite atmospheric leaching using controlled slurry potential and additive treatments

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Abstract: In this study, the synergistic effects of the oxidation-reduction potential (ORP) of leaching slurry and additives (pyrite, sodium chloride and silica) on chalcopyrite atmospheric leaching were investigated. According to the best results of leaching experiments, in the optimum ORP range of 410-430 mV, galvanic (pyrite mass ratio of 4:1), chemical (1.5 mol/dm^3 sodium chloride concentration), galvanochemical (pyrite mass ratio of 4:1 and 1.5 mol/dm^3 sodium chloride concentration) and mechanical (30 g/dm^3 silica concentration) treatments provided 29.8, 46.4, 48.6 and 6.7% increase in the copper recovery, respectively. In galvanic treatments, effective surface corrosion of chalcopyrite was the reason for enhanced chalcopyrite dissolution. In chemical and galvanochemical treatments, considerable surface porosity of chalcopyrite was responsible for accelerated leaching. Also, in mechanical treatments, removing the remained passive layer from the chalcopyrite surface improved leaching. SEM results showed extensive porosity in the chalcopyrite surface in the presence of pyrite and sodium chloride and even more porosity in the presence of their combination. SEM results also showed obviously clean surface of chalcopyrite in the presence of silica. The comparison of ORP-assisted and non-ORP-assisted experiments showed that there were 8, 5.2, 3.9 and 0.5% more copper recoveries in galvanic, chemical, galvanochemical and mechanical treatments with ORP assistance, respectively. The reason was the fewer chalcopyrite surface passivation, which caused the additives to perform better.

Keywords: *chalcopyrite, improved leaching, controlled oxidation-reduction potential, additive treatment, pyrite, sodium chloride, silica*

Introduction

Chalcopyrite is the most important copper ore mineral in the world, which covers about 70% of the world total copper resources (Zeng et al., 2013). Currently, copper from this mineral is mostly produced by pyrometallurgical methods after producing chalcopyrite concentrate through flotation (Cordoba et al., 2008a). However, due to environmental problems such as sulfur dioxide emission and high capital investment, hydrometallurgical methods are drawing more attention nowadays (Misra and

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Fuerstenau, 2005; Mahajan et al., 2007). Hydrometallurgy as an alternative for pyrometallurgy has many advantages such as lower environmental pollutions, the ability of processing low-grade ores and simple residue control (Xian et al., 2012). Despite the mentioned advantages for hydrometallurgical alternatives, because of passivation, chalcopyrite strongly resists atmospheric leaching (Ghahremaninezhad et al., 2015) and bioleaching (Bevilaqua et al., 2013).

The leaching medium is an important factor in hydrometallurgical processing of chalcopyrite. Four different mediums such as sulfate, chloride, nitrate and ammonia are mostly used. The sulfate media is the most important among them because of lower capital cost, simple leaching chemistry and higher copper recovery by solvent extraction and electrowinning (Eghbalnia and Dixon, 2011). However, chalcopyrite leaching in the sulfate media has slow kinetics due to surface passivation which leads to hindered dissolution (Clauber, 2008). The most detected compositions of the passive layer include elemental sulfur, jarosite and metal-deficient polysulfide (Zhao et al., 2015).

Recently, it has been reported that the concentration ratio of ferric to ferrous ions as the oxidation-reduction potential (ORP), is one of the most important factors during the hydrometallurgical processing of chalcopyrite. It has been suggested that this factor can improve the chalcopyrite dissolution rate (Sandstrom et al., 2005; Cordoba et al., 2008b; Gericke et al., 2010). Another study by Cordoba et al. (2008a) indicated that the ORP factor can prevent the formation of some passivation composites like jarosite, but it cannot completely prevent the formation of elemental sulfur. Furthermore, some other studies have been done for improving chalcopyrite dissolution using additives such as silver (Sato et al., 2000; Hu et al., 2002), activated carbon (Liang et al., 2010), sodium chloride (e.g. Carneiro and Leao, 2007; Bevilaqua et al., 2013), manganese dioxide (Xiao et al., 2008), pyrite (Dixon et al., 2008; Nazari et al., 2011) and etc. in leaching and bioleaching processes. However, there were no or not enough attention paid to controlling and also reducing the chalcopyrite surface passivation before using additives in leaching and bioleaching processes. In addition, the combined roles of additives, especially in the optimum range of ORP, need to be investigated.

In the present study, leaching experiments were performed in atmospheric pressure. For the aim of reducing chalcopyrite surface passivation, the oxidation-reduction potential (ORP) of leaching slurry was controlled and optimized in the range that surface passivation reduces (details not shown here). Then, additives were used in the optimum ORP range to accelerate leaching. The methods of ORP-assisted galvanic, chemical, galvanochemical (galvanic + chemical) and mechanical treatments were studied. Furthermore, the effects of mentioned methods on chalcopyrite particles were studied by SEM-EDS analyses of leaching residues. Eventually, the results of ORP-assisted treatments were compared with the treatments with no ORP assistance.

Experimental

Materials

Chalcopyrite and pyrite samples were gathered from Mazraeh copper mine located in East Azerbaijan province, and the silica sample was collected from Mizoj silica mine located in Qazvin province of Iran.

Chemicals used in leaching experiments include sulfuric acid (95-97%) supplied from Merck, iron (III) sulfate hydrate (97%) from Sigma Aldrich, and iron (II) sulfate heptahydrate (100%), sodium chloride (100%), hydrogen peroxide (30%) purchased from Merck. The experiments were conducted in distilled water.

Methods

Sample purification and concentration

Chalcopyrite and pyrite samples were crushed in three steps, that is jaw, cone and roller crushers, respectively. Then, the samples were primarily ground in a ball mill to reach the desired particle size for magnetic separation (80% less than 300 µm) as a purification method from iron ores. After magnetic separation, the samples were ground again in the ball mill to reach the final particle size of 80% less than 75 µm for chalcopyrite and 80% less than 63 µm for pyrite. The samples were concentrated by flotation twice and produced concentrates were washed with distilled water and acetone to be cleaned of flotation chemicals. The concentrates were dried in a vacuum oven at 70 °C for 6 hours after washing (to avoid any possible oxidation). A silica sample was also crushed in three steps (jaw, cone and roller crushers, respectively), and then was ground in a disk mill to reach the particle size of 100% less than 210 µm afterward. The final sample was washed with distilled water and dried at 70 °C for 5 hours.

Leaching

Leaching experiments were performed in atmospheric pressure in a 600 cm^3 glass reactor equipped with three baffles made of 316L stainless steel (glass baffles were used in the presence of sodium chloride). For heating and stirring the leaching slurry, a hotplate with magnetic stirrer (Dragon MS7 H550 Pro) was used. An integrated temperature sensor (PT1000) was also used for precise temperature control. All of the experiments were performed with 500 cm^3 distilled water, 0.4 mol/dm^3 sulfuric acid, 0.11 mol/dm^3 total iron, and 15 g/dm^3 chalcopyrite concentrate.

To start the leaching experiment, the reactor was initially filled with distilled water and sulfuric acid and the solution was mildly stirred and heating commenced. When the solution temperature reached the desired point, iron sulfates were added to the solution. After a few minutes, pH and ORP values were set, the chalcopyrite concentrate was added to the solution and stirring was increased to final speed. For additive containing experiments, pyrite and silica were added a few minutes after chalcopyrite concentrate and sodium chloride was added a few minutes before the chalcopyrite concentrate. The initial solution potential was set by the concentration ratio of Fe^{3+}/Fe^{2+} from iron sulfates, and during leaching experiments the potential was controlled in desired range by adding hydrogen peroxide to the slurry. For measuring the pH and ORP, a desktop multimeter with pH and ORP probes was used. The solution was sampled by a 5 cm^3 syringe, and then filtered (Whatman grade 42 filter paper), diluted by deionized water and sent for an atomic absorption analysis to determine the copper content. Evaporation losses were recovered by adding distilled water to the slurry.

Sample examining and measuring methods

Mineralogical and chemical compositions of mineral samples were determined by X-ray diffraction (XRD) (Philips X'Pert Analytical) and X-ray fluorescence (XRF) (Philips Magix-Pro), respectively. Copper content of solution samples was determined by atomic absorption (AA) (GBC 902 double beam). The pH and ORP values were measured by a desktop multimeter (AZ 86505) and an ORP probe (AZ 86P5) (Pt vs. Ag/AgCl). Surface analyses of leaching residues were done by scanning electron microscope (LEO 1450 VP).

Results and discussion

Composition analyses results of concentrates and samples

The mineralogical analyses of chalcopyrite and pyrite concentrates showed that the chalcopyrite concentrate contained 95.6% chalcopyrite and 4.4% pyrite, and pyrite concentrate contained 96.9% pyrite and 3.1% chalcopyrite. Also, mineralogical analysis of silica sample indicated that the sample contained 100% silica (d_{100} less than 210 μm). Chemical compositions of chalcopyrite and pyrite concentrates are displayed in Table 1.

Table 1. Chemical composition of concentrates

Component	% Cu	% Fe	% S	% SiO_2	% Al_2O_3	% CaO	% MgO	% other	% Total
Chalcopyrite conc.	32.4	30.2	34.7	1.5	0.4	0.1	0.2	0.5	100
Pyrite conc.	1.5	45.3	51.9	0.6	0.4	0.1	0.1	0.1	100

ORP-assisted galvanic treatments by pyrite

In ORP-assisted galvanic treatment experiments, regarding to an upper rest potential of pyrite compared to chalcopyrite (363 mV for chalcopyrite and 464 mV for pyrite [Pt vs. Ag/AgCl] (Mehta and Murr, 1983)), galvanic interactions between these two minerals in the optimum ORP range (410-430 mV [Pt vs. Ag/AgCl]) were employed for enhancing chalcopyrite dissolution. Four different pyrite to chalcopyrite (Py/Ch) mass ratios of 2:1, 3:1, 4:1 and 6:1 were investigated in these experiments. In Figure

1a, the copper recovery is shown as a function of Py/Ch mass ratio. The pH and ORP values during experiments are also shown in Fig. 1b and 1c, respectively.

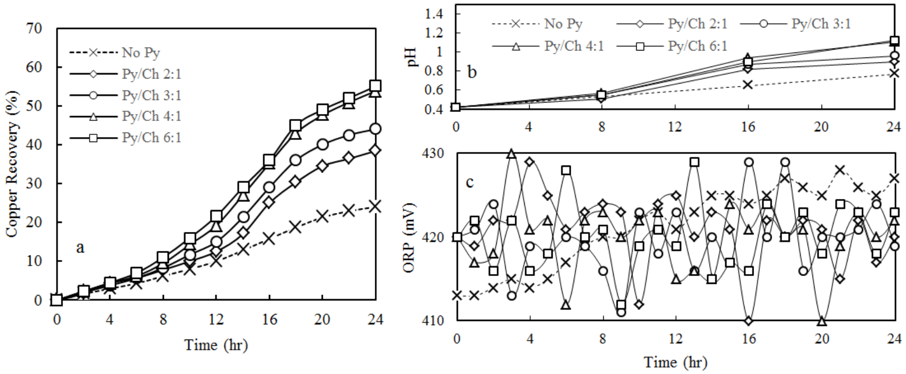


Fig. 1. (a) Copper recovery for different Py/Ch mass ratios, (b) pH, and (c) ORP values during leaching experiments. Conditions: temperature of 80 °C, 0.11 mol/dm^3 total iron, 0.4 mol/dm^3 sulfuric acid (initial pH of 0.42), potential range of 410-430 mV [Pt vs. Ag/AgCl], 850 rpm stirring speed

As can be seen in Fig. 1a, increasing the Py/Ch mass ratio in the optimum ORP range led to significant increase in the copper recovery and extraction rate. The copper extraction rate and recovery enhanced as the Py/Ch mass ratio increased from 2:1 to 4:1, but when the pyrite content exceeded the ratio of 4:1, no more positive effect was observed. The copper recovery for Py/Ch mass ratios of 2:1, 3:1, 4:1 and 6:1 were 38.4, 44, 53.8 and 55%, respectively after 24 hours. In ferric sulfate media, the total leaching reaction of chalcopyrite is:

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0. \quad (1)$$

This total reaction can also be expressed as anodic and cathodic half-cell reactions (Eghbalnia and Dixon, 2011):

$$CuFeS_2 \rightarrow Cu^{2+} + Fe^{2+} + 2S^0 + 4e^- \quad (2)$$

$$4Fe^{3+} + 4e^- \rightarrow 4Fe^{2+} . \quad (3)$$

When there is only chalcopyrite, both anodic (2) and cathodic (3) half-cell reactions occur on the chalcopyrite surface simultaneously. In the presence of pyrite, the anodic surface of chalcopyrite expands by transferring the reduction reaction of ferric ions (Eq. 3) from the chalcopyrite surface to the pyrite surface which leads to promoted chalcopyrite leaching kinetics through more anodic surface corrosion (Tshilombo, 2004). When the Py/Ch mass ratio increases, galvanic interaction between chalcopyrite and pyrite and also surface corrosion of chalcopyrite enhances. By enhancing the surface corrosion, the surface porosity increases which facilitates the diffusion of leaching agents through the chalcopyrite surface and thereafter leaching is accelerated. According to the literature, galvanic interactions between chalcopyrite and pyrite due to the difference in their rest potentials play an important role in accelerating chalcopyrite dissolution. In a galvanic cell, chalcopyrite acts as an anode and its dissolution is accelerated, while pyrite acts as a cathode and is galvanically protected (Dixon et al., 2008; Nazari et al., 2011; Nazari et al., 2012; Ahmadi et al., 2012).

ORP-assisted chemical treatments by sodium chloride

Three different sodium chloride concentrations of 0.5, 1.0 and 1.5 mol/dm^3 were used in the optimum ORP range (410-430 mV [Pt vs. Ag/AgCl]) for ORP-assisted chemical treatment experiments. In Figure 2a, the copper recovery is shown as a function of sodium chloride concentration. Figure 2b shows the pH values during experiments. About the ORP change trends during experiments, it can be said that a narrow increase in ORP from 410 to around 428 mV with some variations could be seen during the experiments, while all of the ORP values were controlled in the mentioned optimum range.

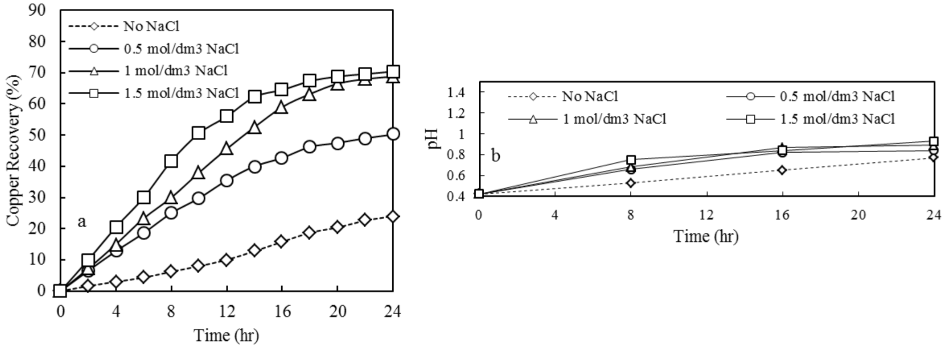


Fig. 2. (a) Copper recovery for different sodium chloride concentrations, (b) pH values during leaching experiments. Conditions: temperature of 80 °C, 0.11 mol/dm^3 total iron, 0.4 mol/dm^3 sulfuric acid (initial pH of 0.42), potential range of 410-430 mV [Pt vs. Ag/AgCl], 850 rpm stirring speed

As shown in Fig. 2a, sodium chloride (chloride ions) had a significantly positive effect on chalcopyrite dissolution in the optimum ORP range. By increasing the sodium chloride concentration from 0.5 to 1.5 mol/dm^3, the copper recovery increased significantly. In addition, the copper extraction rate increased noticeably with increase in the sodium chloride concentration. The copper recovery for 0.5, 1.0 and 1.5 mol/dm^3 sodium chloride was 50.2, 68.8 and 70.4%, respectively after 24 hours. A number of studies (Winand, 1991; Lu et al., 2000; Kinnunen and Puhakka, 2004; Skrobian et al., 2005; Herreros and Vinals, 2007; Carneiro and Leao, 2007; Liang et al., 2012) have investigated the effect of chloride ions on chalcopyrite leaching. Carneiro and Leao (2007) studied the assisted leaching of chalcopyrite by sodium chloride and found that a porous and crystalline sulfur layer formed in the presence of chloride ions which facilitated the diffusion of reagents through the reacting product layer and improved the leaching kinetics. Based on another report, chalcopyrite leaching in the chloride media provided faster rate than leaching in the sulfate media (Kinnunen and Puhakka, 2004). Furthermore, it has been reported that the activation energy for chalcopyrite dissolution in the chloride media (42 kJ/mol) was lower than the activation energy in the sulfate media (75 kJ/mol) (Liang et al., 2012). The results of ORP-assisted chemical treatment by sodium chloride indicated that sodium chloride successfully eliminated the negative effect of the remained passive layer and effectively promoted the chalcopyrite dissolution.

ORP-assisted galvanochemical treatment by pyrite and sodium chloride

In the galvanochemical treatment experiment, pyrite and sodium chloride were used together in the optimum ORP range (410-430 mV [Pt vs. Ag/AgCl]) and the overall effect was investigated. In Figure 3a, the copper recovery is shown in the presence of pyrite, sodium chloride and both. The pH and ORP values can also be found in Figs. 3b and 3c, respectively.

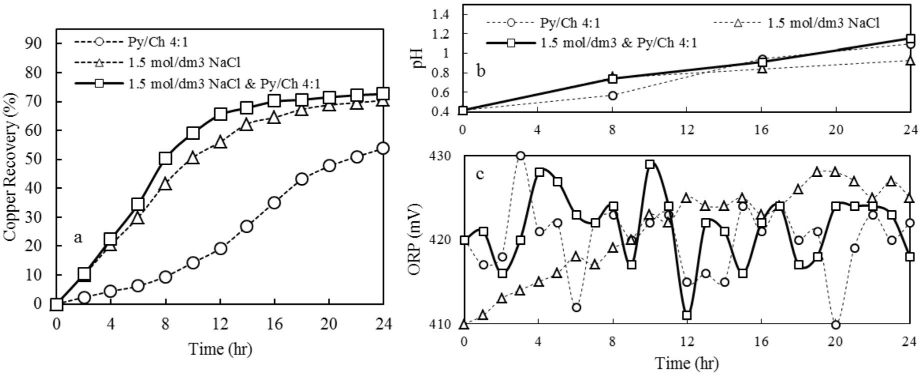
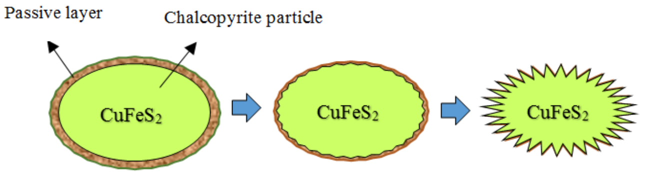


Fig. 3. (a) Copper recovery in the presence of pyrite, sodium chloride and both, (b) pH and (c) ORP values during leaching experiments. Conditions: temperature of 80 °C, 0.11 mol/dm^3 total iron, 0.4 mol/dm^3 sulfuric acid (initial pH of 0.42), potential range of 410-430 mV [Pt vs. Ag/AgCl], 850 rpm stirring speed

As can be seen in Fig. 3a, using pyrite (Py/Ch mass ratio of 4:1) in parallel with sodium chloride (1.5 mol/dm^3) in the optimum range of ORP increased the copper extraction rate obviously. Thus, it can be concluded that the combined role of pyrite and sodium chloride is stronger that their individual roles and can accelerate the chalcopyrite dissolution more. The copper recovery in the presence of both additives was 72.6% after 24 hours.

The improvement sequence for leaching in galvanic, chemical and galvano-chemical treatments in the optimum range of ORP is illustrated in Fig. 4. As can be seen in Fig. 4, the improvement in leaching occurs in two steps which are described in parts (b) and (c). The scheme of Fig. 4 will also be better illustrated by SEM photos of leaching residues.



a) Free leaching (no ORP control and no additive). Passive layer forms

b) Leaching with ORP control. The passive layer reduces

c) Leaching with ORP control and additive treatment. The surface becomes porous and the dissolution enhances

Fig. 4. The scheme of improvement in chalcopyrite leaching by the aid of ORP control and accelerating additives

ORP-assisted mechanical treatments by silica

Silica is an inert mineral with high hardness and very good abrasive feature. By attention to chalcopyrite surface passivation during the leaching process, the abrasive feature of silica was used to destroy and clean the passive layer formed on the chalcopyrite surface. For this aim, four different concentrations of silica (10, 20, 30 and 40 g/dm^3) were investigated in the optimum ORP range (410–430 mV [Pt vs. Ag/AgCl]) for ORP-assisted mechanical treatment experiments. In Figure 5a, the copper recovery is displayed as a function of silica concentration. Figure 5b displays the pH values during experiments. For describing the ORP change trends during experiments, it can be stated that despite some variations in the ORP values, the overall trend was slightly ascendant. All of the ORP values were controlled in the mentioned optimum range, while the majority of them were in the range of 420–429 mV.

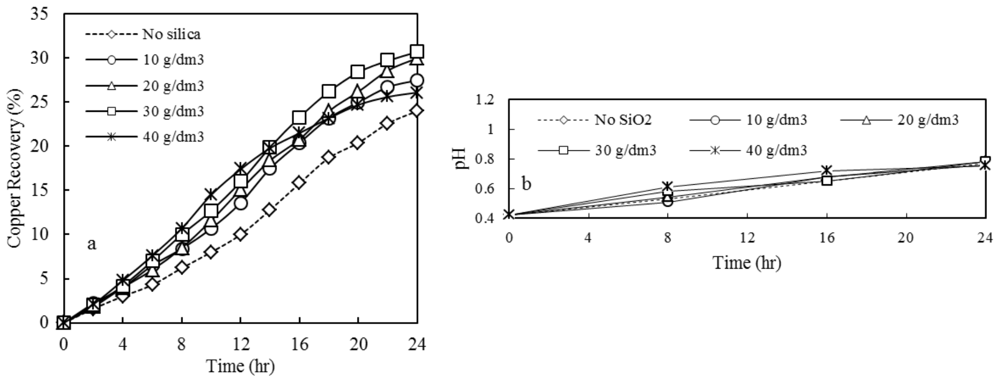


Fig. 5. (a) Copper recovery for different concentrations of silica, (b) pH values during leaching experiments. Conditions: temperature of 80 °C, 0.11 mol/dm^3 total iron, 0.4 mol/dm^3 sulfuric acid (initial pH of 0.42), potential range of 410-430 mV [Pt vs. Ag/AgCl], 700 rpm stirring speed

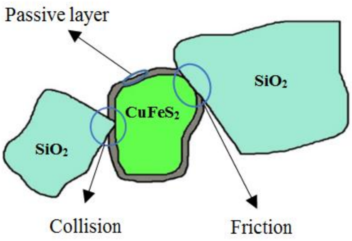


Fig. 6. Scheme of role of silica in cleaning chalcopyrite surface

Figure 5a shows that the presence of silica in the optimum range of ORP had a positive effect on chalcopyrite dissolution and copper recovery. As illustrated in Fig. 6, the increase in the copper recovery was due to combination of the two mechanisms of mechanical friction and collision between silica particles and chalcopyrite which eliminated the remained passive layer through the turbulence of leaching slurry. The scheme of Fig. 6 is also better exhibited by SEM photo of leaching residues where the surface of chalcopyrite particles remained clean in the presence of silica. As the chalcopyrite surface is clean, there is a better contact between the chalcopyrite surface and leaching agents which causes chalcopyrite to be leached more effectively. By increasing the silica concentration from 10 to 30 g/dm^3 the copper recovery increased, but more increase in the silica concentration had no more positive effect. The copper recovery in the presence of 10, 20, 30 and 40 g/dm^3 silica were 27.5, 30, 30.7 and 26.1% respectively after 24 hours, while the recovery in the absence of silica was 24%. Dong et al. (2013) also studied the effect of quartz addition on chalcopyrite bioleaching in shaking flasks. They found that quartz had significant positive effect on the copper extraction by erosion on the surface of chalcopyrite. They also reported that copper extraction in bioleaching at 50 g/dm^3 quartz concentration increased about 20% compared to bioleaching in the absence of quartz.

Comparison of ORP-assisted and non-ORP-assisted treatments

To evaluate the superiority of ORP-assisted treatments, experiments under the same conditions except ORP control (no ORP assistance) in the presence of best-resulted amounts of additives were performed. In Figure 7, the copper recoveries are shown for no ORP assistance and ORP-assisted treatments.

By attention to Fig. 7, the ORP-assisted treatments provided better performance and more copper recovery. As shown in Fig. 7, the effect of ORP was not the same in the presence of all additives. The ORP had more noticeable effect in the presence of pyrite, sodium chloride and combination of them, but less effect in the presence of silica. The assistance of ORP resulted in 8, 5.2, 3.9 and 0.5% more copper recoveries in galvanic, chemical, galvanochemical and mechanical treatments respectively. Consequently, it can be stated that the ORP-assisted treatments are superior to non-ORP-assisted treatments.

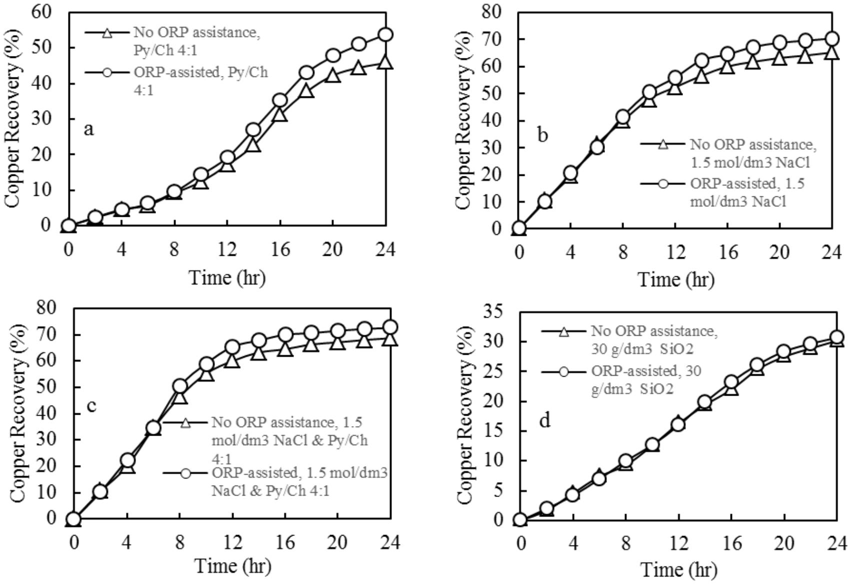


Fig. 7. Copper recovery for non-ORP-assisted and ORP-assisted treatments in presence of best-resulted amounts of additives

SEM-EDS results

Secondary SEM micrographs of leaching residues are shown in Figs. 8a and 8c to 8f. In Figure 8a, chalcopyrite particles are shown in the absence of additives and in the optimum range of slurry ORP (410–430 mV [Pt vs. Ag/AgCl]). As can be seen, there was no extensive passivation and the chalcopyrite surface remained cleaner. However, the surface was covered by some metal deficient sulfide (a compound with high sulfur and lower iron and copper content) which was detected by the EDS analysis shown in Fig. 8b. In Figure 8c, chalcopyrite particles are shown in the presence of pyrite (Py/Ch mass ratio of 4:1) (ORP-assisted galvanic treatment). Under this condition, due to galvanic interactions between chalcopyrite and pyrite, the chalcopyrite surface was effectively corroded and destructed, while the pyrite remained inert. In Figure 8d, chalcopyrite particles are displayed in the presence of sodium chloride (1.5 mol/dm^3 concentration) (ORP-assisted chemical treatment). As can be seen, sodium chloride made remarkable porosity in the surface of chalcopyrite. In Figure 8e, chalcopyrite particles are displayed in the presence of both pyrite and sodium chloride (Py/Ch mass ration of 4:1 and 1.5 mol/dm^3 sodium chloride concentration) (ORP-assisted galvanochemical treatment). Under this condition, the chalcopyrite surface was highly porous and the destruction of chalcopyrite particles was higher. Sodium chloride (chloride ions) had no noticeable effect on pyrite as shown in Fig. 8e. Because of the more noticeable effects of the ORP-assisted galvanic, chemical and galvanochemical treatments, SEM photos of them (Figs. 8c-e) are shown with larger magnification to see the surface of chalcopyrite with more details. In Figure 8f, chalcopyrite particles are shown in the presence of silica (30 g/dm^3 concentration, 700 rpm stirring speed) (ORP-assisted mechanical treatment). As shown, the surface of chalcopyrite particles remained obviously clean because of mechanical friction and collision on the surface. The metal deficient sulfide was also detected on the chalcopyrite surface in the presence of pyrite, sodium chloride and much less in the presence of silica.

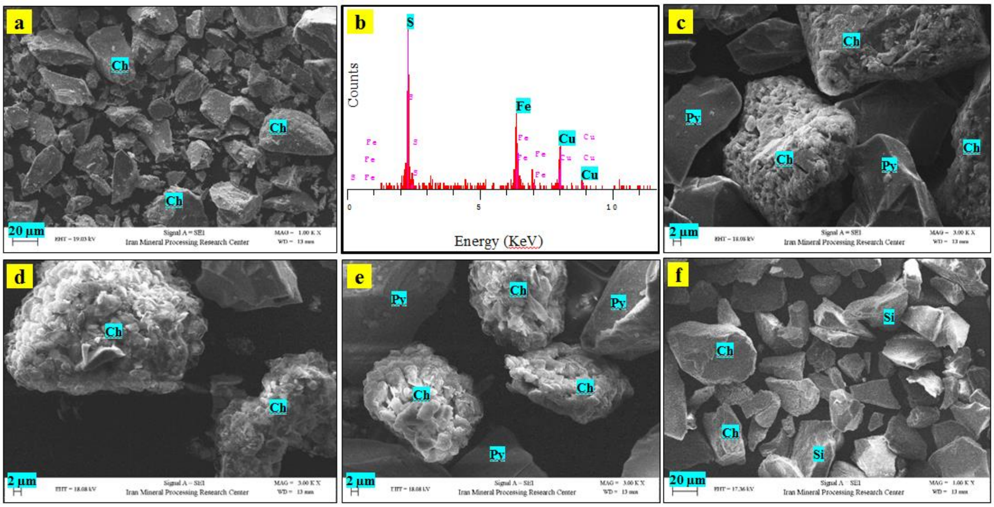


Fig. 8. (a) Chalcopyrite particles in the absence of additives and in the ORP range of 410-430 mV; (b) EDS analysis of chalcopyrite surface in the absence of additives (410-430 mV); (c) chalcopyrite particles in the presence of pyrite ratio of 4:1 (410-430 mV); (d) chalcopyrite particles in the presence of 1.5 mol/dm^3 sodium chloride (410-430 mV); (e) chalcopyrite particles in the presence of pyrite ratio of 4:1 and 1.5 mol/dm^3 sodium chloride (410-430 mV); (f) chalcopyrite particles in the presence of 30 g/dm^3 silica (410-430 mV).

Conclusions

In this study, ORP-assisted treatments using additives in the optimum range of ORP were investigated. In order to reduce passivation of the chalcopyrite surface, the ORP was firstly optimized (results not shown here). In the next step, treatments by the additives of pyrite, sodium chloride and silica were employed in the optimum range of ORP as ORP-assisted treatments to accelerate chalcopyrite dissolution. The results of leaching experiments revealed that the ORP-assisted treatments significantly improved the chalcopyrite dissolution rate and copper recovery. In ORP-assisted galvanic treatments by pyrite, the chalcopyrite surface was effectively corroded (SEM result) due to galvanic interactions which accelerated the leaching process. The copper recovery for the Py/Ch mass ratio of 4:1 reached the value of 53.8%, while the recovery was only 24% in the absence of pyrite. In ORP-assisted chemical treatments by sodium chloride, chemical reactions on the chalcopyrite surface were accelerated and that also caused significant porosity in the chalcopyrite surface (SEM result) which enhanced leaching. In the presence of 1.5 mol/dm^3 sodium chloride concentration, the copper recovery increased to 70.4%. Moreover, the results of leaching experiment in the presence of both pyrite and sodium chloride (ORP-assisted galvanochemical treatment) indicated that the overall effect of both additives was stronger than their individual effects and the porosity of surface was more in the presence of both (SEM result). The copper recovery reached 72.2% under this condition (Py/Ch mass ratio of 4:1 and 1.5 mol/dm^3 sodium chloride concentration). In ORP-assisted mechanical treatments by silica, the collision and friction between silica particles and chalcopyrite surface improved leaching by cleaning the surface (SEM result) from the remained passive layer. The copper recovery increased from 24% in the absence of silica to 30.7% in 30 g/dm^3 silica concentration. To examine the superiority of ORP-assisted treatments to non-ORP-assisted ones, experiments were performed under the same conditions but with no ORP control. The comparison results undoubtedly confirmed the superiority of ORP-assisted treatments. It is worth mentioning that all of the experiments were conducted three times and the average of them were reported.

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