Chalcopyrite leaching in sulfate–chloride media at ambient pressure

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ARTICLE INFO	ABSTRACT

In this article, experimental results on the leaching of a chalcopyrite concentrate with oxygen at ambient pressure in H_2SO_4–NaCl solutions are discussed taking into account the evolution of the solution redox potential and the concentration of ferric ions during leaching. The results indicate that leaching of chalcopyrite concentrate with particle size 12.3 μm in sulfate–chloride solutions was rapid. Over 90% copper was dissolved in 180 min at 100 °C. The results also showed that 17.7 g/l (0.5 M) of chloride ions in the leaching solution affected significantly the leaching rate as compared to leaching without chloride. The addition of 3 g/l of ferric ions to the leaching system produced a large increase in the solution potential which in turn affected negatively the leaching rate of chalcopyrite. The leaching of chalcopyrite in H_2SO_4–NaCl–O_2 media depends largely on the temperature, and the linear kinetics model $1-(1-X)^{1/3}=kt$ represents the copper dissolution well. An activation energy value of 91.2 kJ/mol was determined for the temperature range of 80 to 100 °C.

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1. Introduction

The dissolution rate of chalcopyrite in sulfate media is slow as compared to the leaching of secondary copper sulfides. This slow dissolution rate has prevented an efficient industrial leaching of this mineral in sulfate media. Alternatively, in sulfate–chloride media the leaching rate of chalcopyrite is significantly faster as compared to the leaching in pure sulfate media. This improved dissolution has been attributed to changes in the morphology of the elemental sulfur produced (Lu et al., 2000a) or to a change in the leaching mechanism involving the Cu^{2+}/Cu^+ redox couple (Carneiro and Leão, 2007). Thus, the chemical leaching with additions of chloride has been explored for the treatment of chalcopyrite containing ores (Montealegre, 2002) and concentrates (Jones and Hestrin, 1998).

1.1. Chemistry and mechanisms of chalcopyrite leaching in oxygenated media

The leaching reaction for the dissolution of chalcopyrite with oxygen in acidic aqueous solutions can be represented by:

$$CuFeS_2 + O_2 + 4H^+ = Cu^{2+} + Fe^{2+} + 2S° + 2H_2O. \tag{1}$$
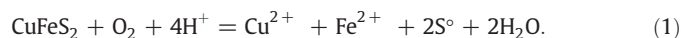
However, since this reaction produces ferrous ions, which can be oxidized to ferric ions by oxygen, the ferric oxidation of chalcopyrite can also occur as the leaching proceeds. The dissolution reaction in this case can be written as:

$$CuFeS_2 + 4Fe^{3+} = Cu^{2+} + 5Fe^{2+} + 2S°. \tag{2}$$
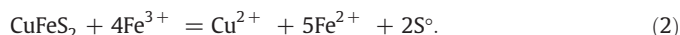
This reaction is coupled with the regeneration of the ferric ions by:

$$4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O. \tag{3}$$
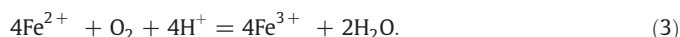
On adding reactions (2) and (3) we get the leaching reaction (1). Reaction (3) is slow at ambient pressure thus limiting the ferric ion formation in the system.

When chloride ions are present in the leaching solution, a second redox couple, the Cu^{2+}/Cu^+, can also be operative in the system. Thus cupric leaching of chalcopyrite can occur because of the greater stability of the chloro-complexes of cuprous ions compared to the chloro-complexes of cupric ions (Bonan et al., 1981). The produced cuprous ions can also be reoxidized to cupric by oxygen during the leaching. The cupric leaching of chalcopyrite in the presence of oxygen can be represented by reactions (4) and (5) where, for simplicity, copper and iron species in solution are written as simple cations instead of chloro-complex ions.

$$CuFeS_2 + 3Cu^{2+} = 4Cu^+ + Fe^{2+} + 2S° \tag{4}$$

$$4Cu^+ + O_2 + 4H^+ = 4Cu^{2+} 2H_2O. \tag{5}$$
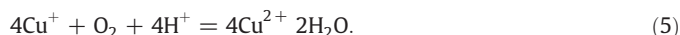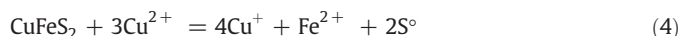
The oxidation of cuprous to cupric ions with oxygen, reaction (5), is a fast reaction (Ruiz et al., 1998; Tran and Swinkels, 1986); therefore,

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the regeneration of cupric ions can be achieved at atmospheric pressure more efficiently than ferric ion regeneration.

The oxidation of chalcopyrite by cupric ions has also been observed to occur in the last period of the ferric chloride leaching when the Fe^{3+}/Fe^{2+} ratio in the solution becomes less than about 0.2 (O'Malley and Liddell, 1987). Under these conditions, the Cu^+ concentration in the solution was found to increase sharply which was accompanied by acceleration in the leaching rate of the chalcopyrite.
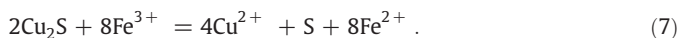
It is now widely accepted that the reason for the slow dissolution kinetics of chalcopyrite in sulfate media is the passivation of the surface of the mineral at high solution potentials although the nature of the passivating film is still a controversial issue. On this matter, the formation of various compounds on the surface of the chalcopyrite particles have been proposed as the cause for the passivation: a dense layer of elemental sulfur (Dutrizac, 1989; Muñoz et al., 1979), a metal-deficient sulfide (most commonly iron deficient sulfide) (Arce and González, 2002; Dixon et al., 2008; Lu et al., 2000b), a polysulfide, CuS_n (Hackl et al., 1995), and jarosite-type iron precipitates (Córdoba et al., 2008). Passivation of chalcopyrite has also been found in chloride media, although to a lesser degree to that in sulfate systems, which has been confirmed by electrochemical studies (Lu et al., 2000b).

In leaching of chalcopyrite there exists a solution potential zone just below the passivation potential where the leaching rate increases dramatically with increments in the solution potential (Gericke et al., 2010). Therefore, there is a narrow "potential window" for effective leaching of chalcopyrite (Córdoba et al., 2008; Kametani and Aoki, 1985). In general, the existence of this potential window has been attributed to an alternative leaching mechanism that can operate below the critical potential (passivation potential). Again, there is a controversy regarding this alternative mechanism. On this matter, Hiroyoshi et al. (2001) conducted experiments of chalcopyrite leaching with Fe^{3+}/Fe^{2+} sulfate solutions and proposed that the dissolution in the potential window occurs by a reduction/oxidation reaction mechanism, which consists of the following sequence of reactions:
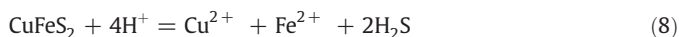
Reduction of chalcopyrite by ferrous ions:

$$CuFeS_2 + 3Cu^{2+} + 3Fe^{2+} = 2Cu_2S + 4Fe^{3+}. \tag{6}$$
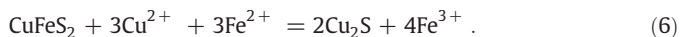
Oxidation of the intermediate Cu_2S by ferric ions:

$$2Cu_2S + 8Fe^{3+} = 4Cu^{2+} + S + 8Fe^{2+}. \tag{7}$$

Since reaction (6) is only feasible below a critical potential, this mechanism would explain the decreased reactivity of chalcopyrite at high potentials. It should be noticed that reaction (6) requires the presence of ferrous and cupric ions in the solution, and an increase in concentration of ferrous ions in the solution will favor the chalcopyrite leaching rate only when sufficient cupric ions are present. Hiroyoshi and coworkers have carried out additional research supporting this reaction mechanism (Hiroyoshi et al., 2004; Hiroyoshi et al., 2007). Recently, Yoo et al. (2010) studied the effect of chloride on chalcopyrite leaching and found that in the presence of chloride ions the leaching kinetics increased significantly which they attributed to an increase in the critical potential caused by the formation of cuprous-chloride complex ions in the system.

Velásquez-Yévenes et al. (2010a, 2010b) and Nicol et al. (2010) have proposed different mechanisms to explain the improved dissolution of chalcopyrite in the solution potential window. These researchers carried out chalcopyrite leaching experiments in dilute chloride solutions under controlled potential conditions and they found that the rate of dissolution of chalcopyrite was enhanced for solution redox potential in the range of 550 to 600 mV vs SHE. They postulated two possible mechanisms that could explain their results, both involving an acid non oxidative step followed by an oxidative step. The first mechanism includes the following sequence of reactions:

$$CuFeS_2 + 4H^+ = Cu^{2+} + Fe^{2+} + 2H_2S \tag{8}$$

$$H_2S + 2Fe^{3+} = S° + 2Fe^{2+} + 2H^+ \tag{9}$$

Or

$$H_2S + 2Cu^{2+} = S° + 2Cu^+ + 2H^+. \tag{10}$$

These authors postulate also that the H_2S oxidation by cupric ions was faster than the oxidation with ferric ions which would explain the faster kinetics observed in chloride media, as opposed to sulfate media.

The second alternative mechanism proposed by these researchers includes the formation of a "covellite-like" intermediate product:

$$CuFeS_2 + 2H^+ = CuS + Fe^{2+} + H_2S. \tag{11}$$

This reaction is followed by the oxidation of H_2S by reaction (9) or (10) and the oxidative leaching of the secondary CuS. The detection of CuS in partially reacted samples has been used as an argument in favor of this mechanism.

From this discussion, it is clear that the leaching of chalcopyrite in oxygenated sulfate and chloride media is a complex process with some controversial issues that still need to be clarified.

In this article, experimental results on the leaching of a chalcopyrite concentrate with oxygen at ambient pressure in H_2SO_4–NaCl solutions are discussed taking into account the evolution of the solution potential and the concentration of ferric ions during leaching.

2. Experimental

Chalcopyrite concentrate for the experiments was obtained from Andina Mine of CODELCO, Chile. This flotation concentrate was classified into narrow size fractions using a cyclosizer to obtain various clean size fractions. The fraction with an average size of 12.3 μm was used in the experimental work to obtain a rapid dissolution rate of chalcopyrite. The chemical analysis of this sample showed 29.2% Cu and 31% Fe. The mineralogical composition was determined using a SEM-based automated analysis system (QEMSCAN). The result showed 79% chalcopyrite, 16.5% pyrite and 2.2% covellite, the balance were gangue minerals.

Batch, isothermal leaching experiments were carried out in a 2-liter glass reactor which was equipped with variable speed stirrer, a heating mantle, a thermocouple, a fritted tube for liquid sampling and for oxygen injection to the reactor, and a water cooled condenser to minimize the loss of solution by vaporization.

In a typical experiment, the reactor was charged with 1 l of sulfuric acid–sodium chloride leaching solution. Ferric sulfate was also added to the solution in some experiments. Once the solution was heated to the test temperature, the oxygen flow rate was set, and 3 g of solid sample was charged to the reactor. The reaction was allowed to proceed and liquid samples were withdrawn at various times for copper and total iron determination by atomic absorption spectroscopy. The ferrous concentration was also determined immediately after sampling by dichromate titration and the ferric ion concentration was calculated as the difference from the total iron concentrations. This was a reliable procedure except for very small ferric concentrations in the solution. Additional samples were withdrawn at various reaction times for immediate redox potential measurements. At the end of each experiment, the solution was filtered and the residues were washed and dried. The elemental sulfur content of some of the residues was determined by Soxhlet extraction method using carbon disulfide.

3. Results and discussions

Some of the main variables that affect the leaching of chalcopyrite concentrate studied were: stirring speed, oxygen flow rate, temperature, chloride concentration, and initial ferric concentration.

3.1. Effect of the stirring speed

Leaching experiments were carried out using agitations of 360, 600 and 1000 rpm in 1 l of solution containing 20 g/l (0.2 M) H_2SO_4 and 35.5 g/l Cl^- (1 M NaCl). This solution was the standard leaching solution used thereafter. The sulfuric acid concentration of 20 g/l was chosen to prevent the precipitation of ferric iron compounds during the course of the experiments. Other experimental conditions were 100 °C, 3 g of chalcopyrite concentrate of average size 12.3 μm and oxygen flow rate of 0.3 l/min. The results showed that the stirring speed affected little the copper dissolution in the range studied. Thus, a stirring speed of 1000 rpm was used in most experiments to assure that the leaching reaction was not under mass transfer control.

3.2. Effect of oxygen flow rate and oxygen concentration

The effect of pure oxygen flow rate on the chalcopyrite dissolution was studied in the range of 0.1 to 0.5 l/min. The experiments were conducted using the standard leaching solution at 1000 rpm and 100 °C. The results showed little difference in the copper dissolution at the various flow rates in 3 h of leaching. This meant that the equilibrium saturation solubility of oxygen was attained in all the flow rates used. Therefore, an oxygen flow rate of 0.3 l/min was selected as the standard value for subsequent experiments to limit the gaseous volume leaving the reactor, thus minimizing the water losses. On the other hand, when 0.3 l/min a mixture of 79% N_2–21% O_2 was used instead of pure oxygen, the rate of copper dissolution decreased significantly as shown in Fig. 1. This large difference in the dissolution of copper obtained between 100% and 21% oxygen is due to a decrease in the oxygen concentration in the solution since the oxygen solubility in aqueous solutions is proportional to the partial pressure of oxygen in the gaseous phase (Tromans, 1998, 2000).

The variation of the solution redox potential with leaching time for 21% O_2 and 100% O_2 is shown in Fig. 2. The potential values are given with respect to the Ag/AgCl, 3 M KCl electrode. As seen in this figure, in both cases, there is a sharp initial decrease of the redox potential because, once the leaching of the chalcopyrite starts, the Fe^{3+}/Fe^{2+} and the Cu^{2+}/Cu^+ redox couples contribute to the solution potential.
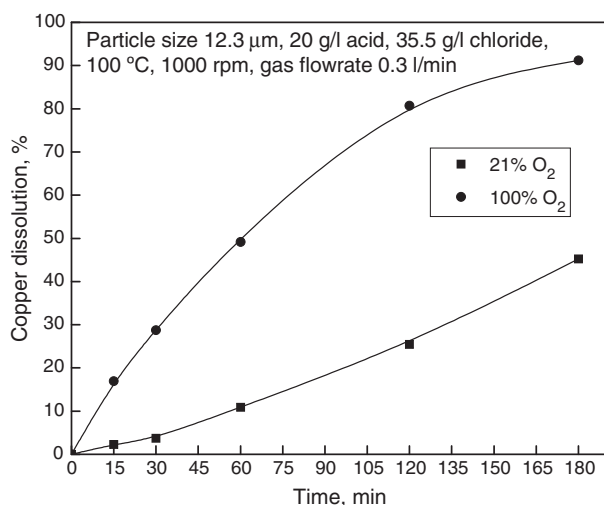

Fig. 1. Effect of oxygen concentration in the gas flow on the dissolution of copper from chalcopyrite in H_2SO_4–NaCl–O_2 solutions.
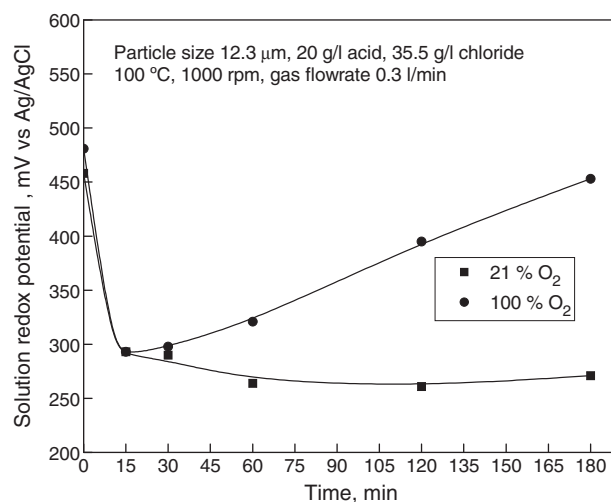

Fig. 2. Effect of oxygen concentration in the gas flow on the solution redox potential for the leaching of chalcopyrite in H_2SO_4–NaCl–O_2 solutions.

In the case of gaseous flow with 100% oxygen, we can also see that after the initial potential decrease, it increases steadily with time because the ferrous and cuprous ions are being oxidized to ferric and cupric, respectively. In contrast, the solution redox potential remains low with time at 21% oxygen, indicating that little oxidation of the leaching products occurred under this condition. The chemical analysis of the solutions confirmed that in the first case there was a buildup of ferric ions, while in the second case the formation of ferric ions was negligible during leaching. The cuprous ions concentration in solution was not determined; however, it is unlikely that a significant buildup of cuprous ions can occur since cuprous oxidation is very fast in the temperature range used in this research (Ruiz et al., 1998). Therefore, any cuprous ions formed by the cupric leaching of chalcopyrite will be rapidly reoxidized to cupric by O_2 or ferric ions. The results also suggest that ferric and/or cupric ions are more effective than oxygen in chalcopyrite oxidation. Nevertheless, the role of oxygen is very important in the leaching through the regeneration of the active oxidants of chalcopyrite.

3.3. Effect of the temperature

Experiments were conducted in the range of 80 to 100 °C using a flow rate of 0.3 l/min of pure oxygen. The results are shown in Fig. 3, where one can see that the dissolution rate of chalcopyrite increases significantly when the temperature is augmented. It can be observed that at 80 °C, the copper dissolution is slow and only 20% dissolution was obtained in 180 min, while at 90 °C, over 90% of the copper was dissolved in the same time. It is interesting to point out that the oxygen solubility in the leaching solution does not change appreciably from 80 to 100 °C as can be seen in Fig. 4, which shows the estimated solubility using the correlation proposed by Tromans (1998, 2000). Therefore, the experiments at the various temperatures were conducted at approximately the same oxygen concentration in the solution and thus, the large differences in the observed rates must be due to changes in the kinetic constants of the rate processes involved.

The variation of the solution redox potential with time at the various temperatures is shown in Fig. 5. Again, it can be observed in this figure an initial sudden drop of the solution potential followed by a subsequent increase at all the temperatures tested. The solution potential at 100 °C is the lowest in the range of temperature studied. The ferric ions and total iron concentration data for the same experiments are presented in Fig. 6. An interesting result in this figure is that the ferric ions concentration at 100 °C is very low compared to the results of 90 and 95 °C. Since the concentration of ferric ions is
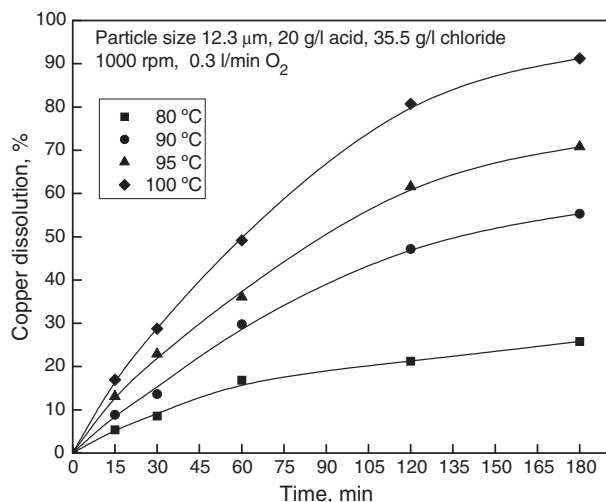
Fig. 3. Effect of the temperature on the copper dissolution from chalcopyrite concentrate in H$_2$SO$_4$–NaCl–O$_2$ solutions.

Fig. 5. Effect of the temperature on the solution redox potential during chalcopyrite leaching in H$_2$SO$_4$–NaCl–O$_2$ solutions.

given by the rate of ferrous to ferric oxidation by oxygen minus the rate of ferric ion consumption in the leaching of chalcopyrite, the lower ferric ions buildup at 100 °C can be explained by the higher leaching rate at this temperature. The corresponding calculated Fe^{3+}/Fe^{2+} ratio of the solution for 95 °C increases from 0 up to around 0.6 during the course of the reaction; while for 100 °C, the Fe^{3+}/Fe^{2+} ratio increases from 0 up to around 0.2, which is consistent with the lower solution redox potential measurements obtained for 100 °C (Fig. 5). Since ferric ions are capable of oxidizing the cuprous ions, a lower Fe^{3+}/Fe^{2+} ratio means a higher contribution of the cupric ions in the leaching of chalcopyrite with the consequent increase in the dissolution rate.

3.4. Effect of the chloride concentration

The effect of the chloride concentration was studied by adding various amounts of NaCl to the leaching solution. The results are presented in Fig. 7. It is clear that in the absence of chloride ions the chalcopyrite dissolution is very small. However, the addition of 17.7 g/l of Cl$^-$ (0.5 M) to the leaching solution produced a dramatic increase in the dissolution. Further increase in chloride concentration affects little the chalcopyrite dissolution. As expected, the experi-
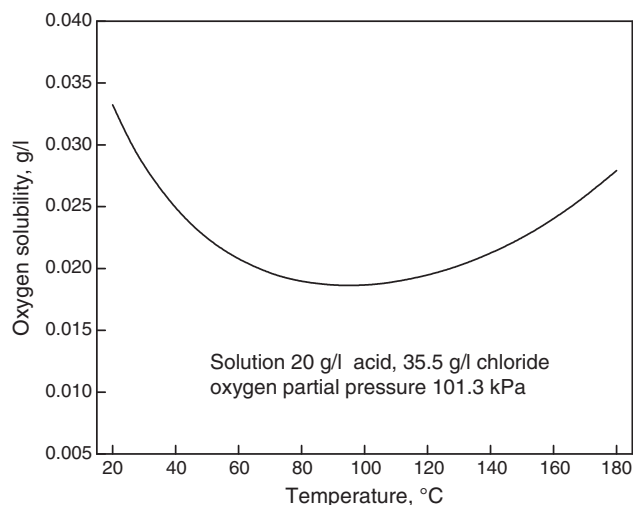
mental data concerning the redox potential and the ferric ions concentration in solution were nearly identical for the various chloride concentrations in solution in the range of 17.7 to 53.2 g/l. (0.5 M to 1.5 M).

The effect of chloride ions found in this investigation agrees well with the data reported by Lu et al. (2000a), who found that chloride concentrations over 0.5 M did not influence the leaching of chalcopyrite in sulfate–chloride solution. On the other hand, Carneiro and Leão (2007), who studied the effect of NaCl additions to the ferric sulfate leaching of chalcopyrite, found that an increase of chloride ions up to 1 M had a significant effect on the dissolution rate.

3.5. Effect of the addition of ferric ions

Experiments were carried out adding ferric ions to the leaching solution to increase the redox potential and determine its effect on the leaching rate.

Fig. 8 shows the results for the addition of 0.2 and 3 g/l of ferric ions (as sulfate salt). For 0.2 g/l of ferric ions added initially, the leaching rate increased somewhat as compared to the experiment without initial concentration of ferric ions. On the other hand, 3 g/l of ferric ions produced a large decrease in the leaching rate. The corresponding

Fig. 4. Oxygen solubility in the leaching solution as a function of temperature. Estimated by the correlation proposed by Tromans (1998, 2000).
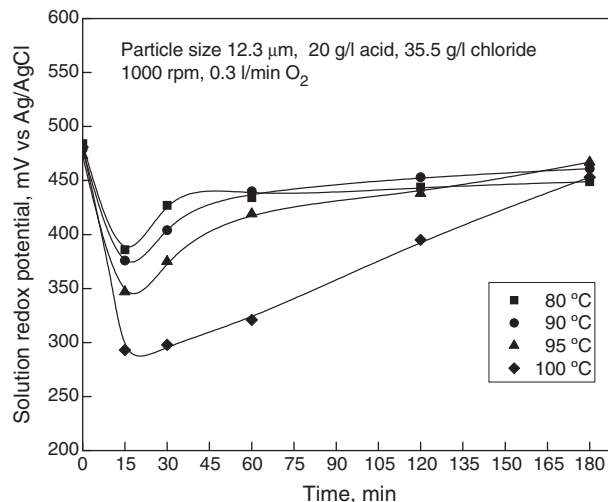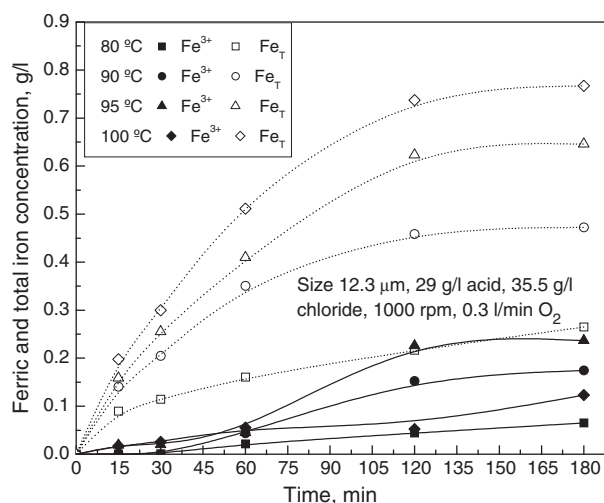

Fig. 6. Variation of Fe^{3+} concentration and total iron in solution with time during chalcopyrite leaching in H$_2$SO$_4$–NaCl–O$_2$ solutions at various temperatures.
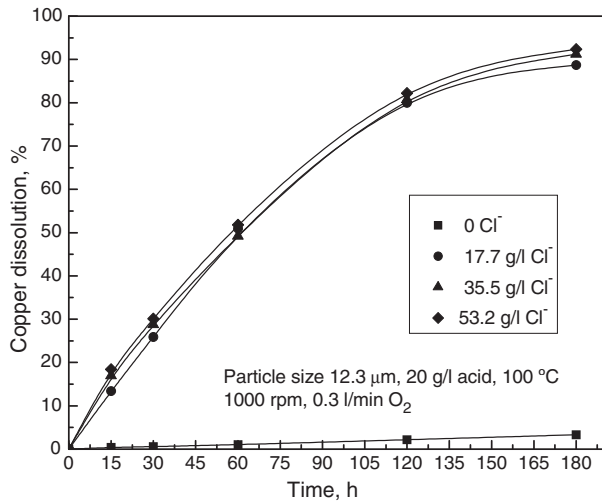
Fig. 7. Effect of chloride concentration on copper dissolution from chalcopyrite concentrate in H_2SO_4–NaCl–O_2 solutions.

Fig. 9. Effect of initial ferric concentration on the solution redox potential during chalcopyrite leaching in H_2SO_4–NaCl–O_2 media.

redox potential measurements are presented in Fig. 9. This figure shows that the leaching with 3 g/l ferric ions resulted in a very high solution redox potential, which would explain the decrease in dissolution rate obtained under these conditions. On the other hand, in the experiment with 0.2 g/l Fe^{3+}, the measured redox potentials are only slightly higher than those without ferric addition. The ferric and total iron concentrations for the same experiments are shown in Fig. 10, where we can see that for the 3 g/l ferric addition the ferric concentration in solution decreases steadily with time confirming that ferric ions are being consumed by the oxidation of chalcopyrite. The corresponding calculated Fe^{3+}/Fe^{2+} ratio for 3 g/l Fe^{3+} addition decreases from 4.2 at 15 min to 0.64 at 180 min while for 0.2 g/l Fe^{3+} addition the ratio increases from 0.03 to 0.25. This large difference in the Fe^{3+}/Fe^{2+} ratios agrees with the large difference observed in the measured solution potentials.

4. Leaching kinetics

The significant effect of temperature on the leaching of chalcopyrite in H_2SO_4–NaCl–O_2 solutions, as seen in Fig. 3, suggests that the dissolution process is controlled by a surface electrochemical reaction. Even though the analysis of the leaching residues showed that over
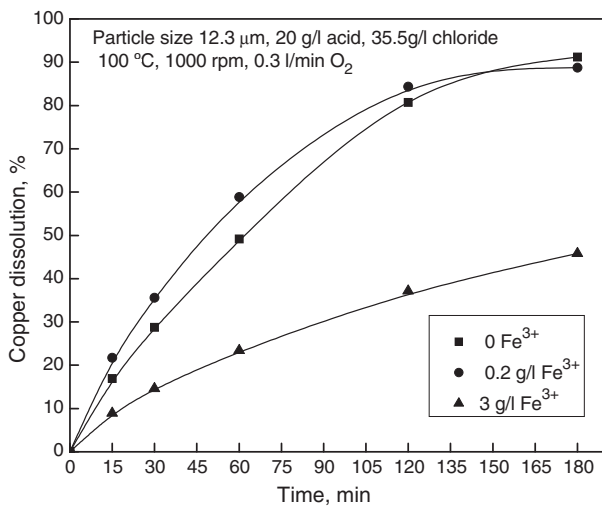
95% of the reacted chalcopyrite sulfur was oxidized to elemental sulfur, this sulfur buildup did not appear to impair the dissolution rate of the mineral. Therefore, the experimental data was analyzed by using the well known shrinking core model for surface reaction control, which for monosize particles is given by the following equation:

$$1-(1-X)^{1/3} = kt. \qquad (12)$$

In this equation, X is the fraction of copper dissolved, k is the kinetic constant and t is the reaction time. Fig. 11 shows a plot of the function $1-(1-X)^{1/3}$ vs time for the dissolution data. It can be observed in this figure a good linear relationship at all temperatures tested. This result supports the applicability of this kinetic model.

The kinetic constants for the various temperatures were determined from the slopes of the lines in Fig. 11 which were used to draw an Arrhenius plot depicted in Fig. 12. Activation energy of 91.2 kJ/mol was calculated from the slope of the curve in Fig. 11. This value is consistent with an electrochemical reaction control.

Fig. 8. Effect of ferric ion concentration in solution on the copper dissolution from chalcopyrite concentrate in H_2SO_4–NaCl–O_2 media.

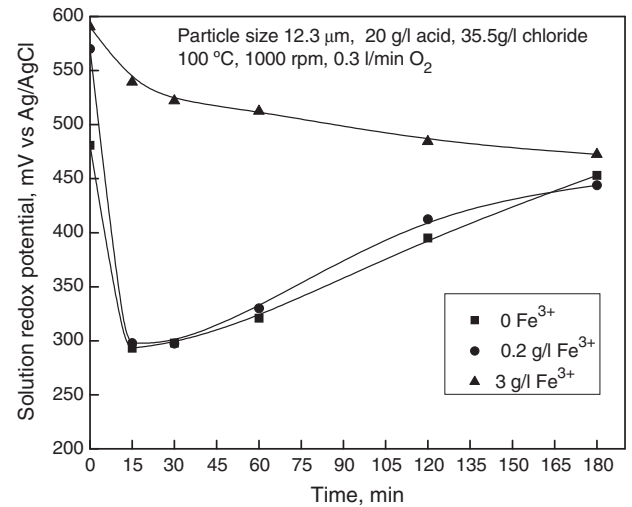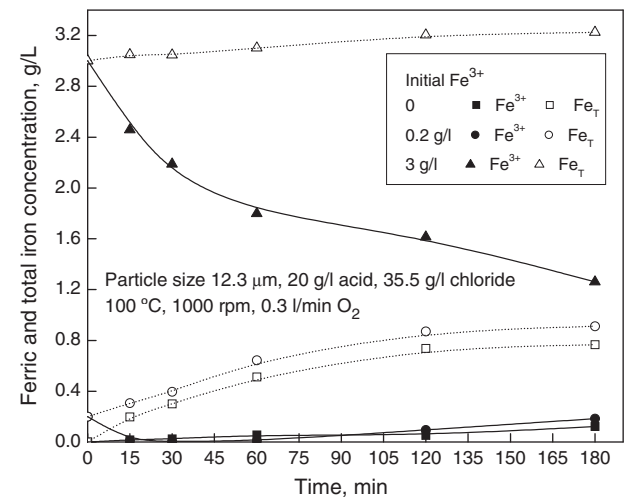**Fig. 10.** Variation of Fe^{3+} concentration and total iron in solution with time during chalcopyrite leaching in H_2SO_4–NaCl–O_2 solutions for various initial Fe^{3+} concentrations.

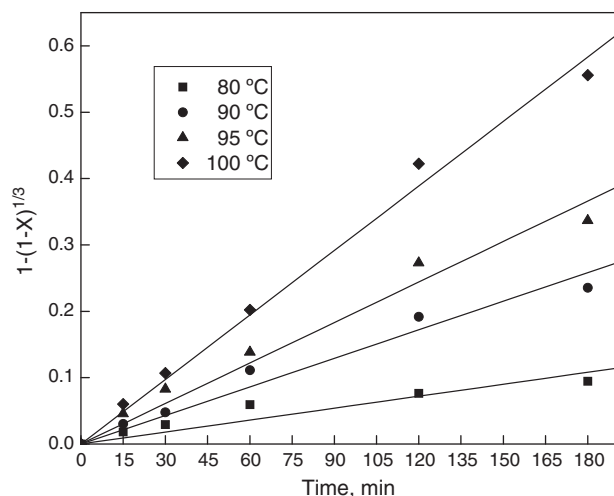**Fig. 11.** Experimental data of copper dissolution from chalcopyrite in H_2SO_4–NaCl–O_2 solutions plotted according to the linear kinetic model for monosized particles.

5. Conclusions

Based on the experimental results of chalcopyrite leaching in H_2SO_4–NaCl–O_2 solutions, the following can be concluded.

— Leaching of chalcopyrite concentrate with particle size 12.3 μm in sulfate–chloride solutions was rapid. Over 90% copper was dissolved in 180 min at 100 °C.
— The chloride ion concentration of 17.7 g/l (0.5 M) in solution had a large effect on the leaching rate compared to the leaching without chloride.
— Leaching of chalcopyrite in nitrogen–oxygen mixture with 21% oxygen decreased significantly the dissolution rate as compared to the case of 100% oxygen. This rate reduction is due to a slower oxidation of the ferrous and cuprous ions in the leaching solution because of the lower oxygen solubility at 21%.
— The addition of 3 g/l of ferric ions to the leaching system produced a large increase in the solution potential which in turn affected negatively the leaching rate of chalcopyrite.
— The leaching of chalcopyrite in H_2SO_4–NaCl–O_2 media depends largely on the temperature, and the linear kinetics model $1-(1-X)^{1/3}=kt$ represents the copper dissolution well. An activation energy value

of 91.2 kJ/mol was determined for the temperature range of 80 to 100 °C which is consistent with an electrochemical reaction control.

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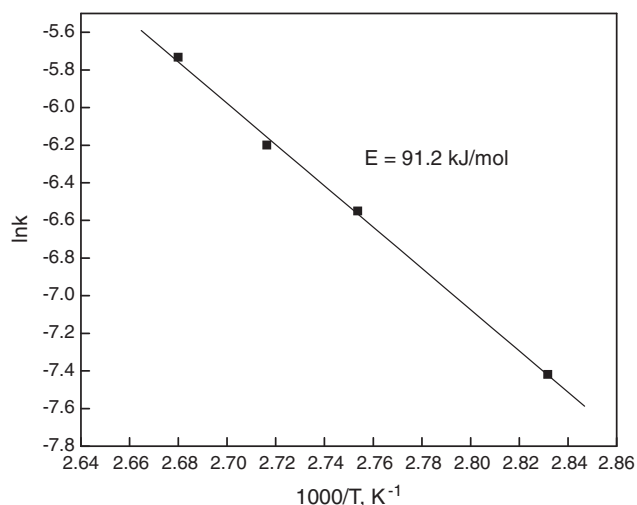

Fig. 12. Arrhenius plot for the dissolution of copper from chalcopyrite in H_2SO_4–NaCl–O_2 solutions.