

Ferric chloride leaching of chalcopyrite: Synergetic effect of CuCl_2

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Abstract

This work presents a study of the leaching of chalcopyrite in acidic ferric chloride. Two chalcopyrite samples (natural chalcopyrite crystal and chalcopyrite concentrate) were leached under different conditions. The effects of stirring speed and temperature were investigated. It was found that agitation had a negative effect on copper recovery from chalcopyrite during the leaching process. This is explained by the fact that cupric chloride complexes are formed during the leaching process where cupric ion is considered as a stronger oxidant than ferric ion. Agitation sweeps away the cupric chloride complexes formed, whereas, under stagnant conditions cupric chloride complexes accumulate at the reaction interface causing enhanced dissolution of copper. The overall leaching reaction was found to be sensitive to temperature. The shrinking core model was fitted to the data and it was found that the leaching process was controlled by chemical reaction with activation energy of 69 kJ/mole.

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1. Introduction

Chalcopyrite is one of the most important copper minerals in terms of scale of use and availability. Generally, chalcopyrite is treated by pyrometallurgical processes often in reverberatory furnaces or by using flash smelting techniques (Davenport et al., 1976). However, recently, there has been interest in the hydrometallurgical leaching of sulphide minerals due to the requirement to avoid SO_2 emissions and the fall in demand for H_2SO_4 produced as a by-product during smelter operations (Dutrillac, 1989a,b). Conversion of SO_2 to H_2SO_4 requires a high capital cost, which often

can not be justified economically, whereas, elemental sulphur formed during ferric ion leaching can be discarded with the tailings without the environmental problems encountered in the disposal of SO_2 produced by smelting operations (Lu et al., 2000). In addition, there is a need to process lower grade sulphide concentrates that cannot be economically treated by smelting technology (Peacey et al., 2003).

The most common lixiviants used for chalcopyrite leaching are chloride, sulphate, amine and nitrate. Despite the favorable kinetics of ammonia leaching and the formation of hematite out of solution, this process consumes considerable amounts of ammonia due to the formation of $(\text{NH}_4)_2\text{SO}_4$, which subsequently needs to be decomposed (Habashi and Toor, 1979; Tiwari et al., 1980). In addition, the process requires

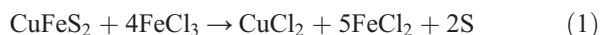
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special handling equipment due to the explosive nature of ammonia and oxygen mixtures (Tiwari et al., 1980). Nitric acid is a powerful oxidizing agent which can successfully dissolve many sulphide minerals with acceptable kinetics. However, it is very expensive and small losses can adversely influence the economics of the process (Habashi, 1993).

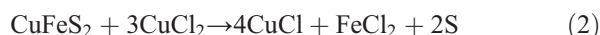
From an economic point of view the most practical oxidants are ferric ions (Dutrizac, 1992). However, the leaching rate of chalcopyrite is very slow when using ferric sulphate and is also slow in ferric chloride media. Therefore, several methods have been used to increase reaction rates, by separation or oxidation of sulphur to soluble sulphuric acid, such as: organic extracting additions, sulfidizing chalcopyrite activation, mechanical activation, the use of ozone as an oxidant (Havlik and Kammel, 1995), the use of promoters (silver ions, surfactants, carbon particles, iron powder or hematite) (Hiro Yoshi et al., 2000), and leaching in presence of nanosized silica (Misra and Fuerstenau, 2005).

Chloride systems involve the use of hydrochloric acid as a leaching reagent to prevent hydrolysis with ferric chloride as the oxidant. Reaction (1) is reported to represent the dissolution of chalcopyrite in ferric chloride (O'Malley and Liddell, 1987). When compared to ferric sulphate based leaching, this system is quicker and more aggressive, ferric chloride can be regenerated, and pyrite is not attacked (Godocikova et al., 2002). Chlorides are corrosive but this can be overcome by the use of polymers and plastic materials. In addition, the iron is dissolved and has to be separated (Habashi and Toor, 1979). However, elements like Ag, Pb, As, and Sb are soluble in chloride media and can report to the final product (Dutrizac, 1992).



Several researchers have investigated chloride leaching (Dutrizac, 1978; Dutrizac, 1981; Palmer et al., 1981; O'Malley and Liddell, 1987; Dutrizac, 1990; Havlik and Kammel, 1995; Havlik et al., 1995) and there are several processes (pilot and large laboratory scale), which involve the use of chloride systems. These include the CYMET process, Cuprex process, Cominco process, Mintek process, Outokumpu process (recently renamed as Outotec Oyj HydroCopper® process), and Intec process (Peacey et al., 2003). The only commercial process was the CLEAR process which again was closed in 1982 due to major problems including: gypsum fouling in the tank house, silver contamination of the final product and washing of the final product (Dutrizac, 1992; Peacey et al., 2003). The most recent chloride

process is HydroCopper® developed by Outotec Oyj® which has recently reached the commercial scale in Mongolia (Hyvarinen and Hamalainen, 2005). This process is based on the use of cupric chloride as an oxidant where chalcopyrite is reported to dissolve according to the reaction (2) (Lundstrom et al., 2005).



The aim of this work is to examine the catalytic action of cupric ions during leaching of chalcopyrite in ferric chloride. Additionally, it is attempted to study the effect of agitation on this catalytic action.

2. Materials and methods

2.1. Materials

Two different samples of chalcopyrite were used in this study. The first sample was prepared from copper sulphide ore obtained from Kennecott Utah Copper Corporation (KUCC) in North America. The ore was crushed and then concentrated by two stages of froth flotation. The second sample was prepared from natural high purity chalcopyrite crystals obtained from mineral dealer Gregory, Bottley & Lloyd (GBL), London, UK. Both samples were wet sieved to prepare several size fractions. Samples of the size fractions used in this study were totally digested for chemical analysis which was carried out by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The chemical analysis of the samples is shown in Table 1. All chemicals used in this study were of reagent grade (HCl-33% (AnalarR®), FeCl₃ and CuCl₂ (Merk®)). Milli-Q ultrapure water (18.2 MΩcm⁻¹) was used for making up solutions and washing glassware.

The samples were also characterized by XRD analysis using a computer controlled Hiltonbrooks® generator with a Philips® PW 1050 diffractometer with an automatic divergence slit, and Cu anode producing X-rays of wavelength $\lambda = 1.54056 \text{ \AA}$. The diffractometer was operating at 40 kV and 20 mA, and automatic routines allowed scanning for values 2θ from 5° to 95° using a step size of 0.05° and scan speed of 2°/min. The diffraction data was analyzed by Diffraction Technology "Traces V.3®" X-ray analytical software. Identification of the minerals contained in the sample was achieved by comparison

Table 1
Chemical analysis of chalcopyrite samples

Material	Cu, %	Fe, %	S, %	Zn, %
Chalcopyrite concentrate	31.08±0.37	29.09±0.32	33.35±0.51	0.16±0.00
Chalcopyrite crystal	34.29±0.09	29.44±0.36	35.00±0.45	0.15±0.00
Theoretical composition	34.62	30.43	34.95	0

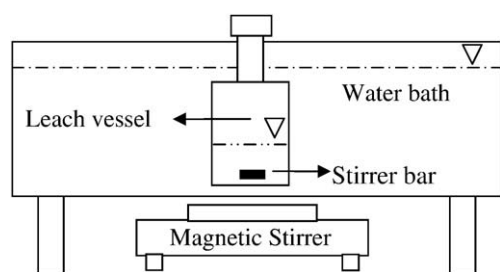


Fig. 1. Experimental set up for conventional leaching in closed vessel.

with a database (Joint Committee on Powder Diffraction Standards-International Centre for Diffraction Data (JCPDS-ICDD)). Chalcopyrite concentrate was found to contain only chalcopyrite and pyrite whereas the sample prepared from chalcopyrite crystal was found to contain chalcopyrite only.

2.2. Experimental procedure

Two leaching systems were used in this study. The first set of leaching experiments was carried out in a 500 ml leaching vessel with a five neck lid. The vessel was immersed in a thermostatic water bath which controls the temperature within ± 1 °C. 250 ml of the leaching solution was heated to the required leaching temperature and then 1 g of chalcopyrite was added to the leaching solution which was leached for 3 h. Samples (2 ml aliquots) were periodically withdrawn for chemical analysis. The degree of agitation of the mixture was maintained using a two-bladed anchor glass propeller. Agitation was applied to suspend the particles and prevent their caking and to eliminate any possible gross solution inhomogeneities. The shaft of the propeller passed through the central neck in the lid and was connected to a variable speed stirrer supplied with a digital tachometer and speed control.

The second set of experiments was similar to the one described above but with the following modifications (see Fig. 1): the agitation was applied using a magnetic stirrer which was arranged underneath the thermostated water bath, the leaching vessel used was a single neck flat bottomed supplied with screw type plastic cover which can be tightly closed so that no escape of vapor and any gases or ingress of air was possible. This vessel was fixed firmly within the water bath. The set of experiments carried out using this setup will be referred to as “closed vessel experiments”.

100 ml of 0.5 M FeCl_3 –0.5 M HCl was poured in the vessel and immersed in the water bath for about 10 min (to allow the solution to reach the required temperature (90 °C)). The vessel was opened and about 0.4 g of chalcopyrite concentrate (< 25 μm) was added to the leaching solution. The vessel was then tightly closed. After 3 h leaching time, the vessel was removed from the water bath and samples for ICP and titration analysis were taken. Ferrous ions concentration was determined by titration using potassium dichromate as titrate and sodium diphenylamine sulfonate as an indicator.

Two leaching experiments were carried out using the set up shown in Fig. 1. In one experiment the leaching mixture

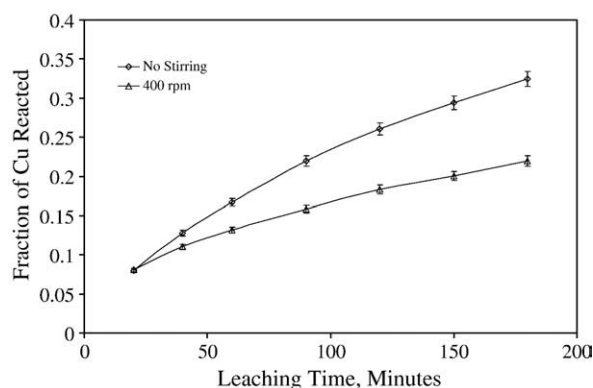


Fig. 2. The effect of stirring speed on the copper recovery from chalcopyrite crystal when leached in ferric chloride (C_{FeCl_3} : 0.5 M, $T=90$ °C, < 38 μm).

was agitated using a stirrer bar at a stirring speed 700 rpm. The second experiment was carried out under stagnant conditions. Each of these experiments was repeated twice to allow assessment of reproducibility.

3. Results and discussion

3.1. Effect of agitation

The effect of agitation on the copper recovery from chalcopyrite crystals when leached in ferric chloride was studied at a temperature of 90 °C in 0.5 M FeCl_3 –0.5 M HCl. The results are shown in Fig. 2. Unexpectedly, agitation had a negative effect on the amount of copper extracted. Due to a limitation on the quantity of chalcopyrite crystals available this phenomenon was investigated further using chalcopyrite concentrate. Similar results for chalcopyrite concentrate were obtained and are shown in Fig. 3.

At low stirring speeds (less than 300 rpm) it was observed that the chalcopyrite particles tended to coagulate as shown in Fig. 4. The phenomenon of coagulation was found to be more

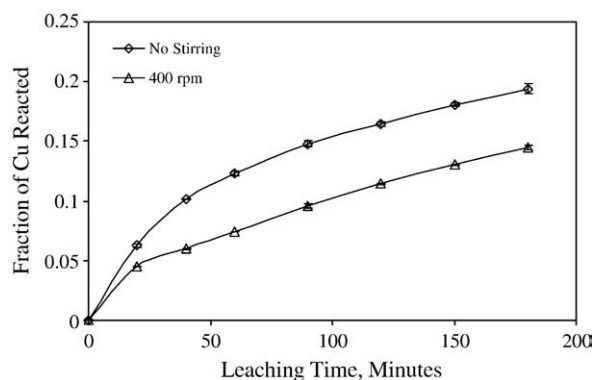


Fig. 3. The effect of stirring speed on the copper recovery from chalcopyrite concentrate when leached in ferric chloride (C_{FeCl_3} : 0.5 M, $T=90$ °C, < 25 μm).

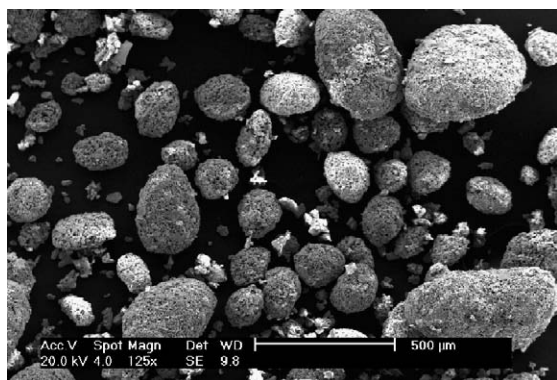


Fig. 4. Coagulation of chalcopyrite particles at low stirring speeds when leached in acidified ferric chloride at a temperature of 90 °C.

evident for chalcopyrite concentrate than chalcopyrite crystal. This coagulation disappears at stirring speeds >350 rpm. Coagulation of chalcopyrite and pyrite has been recently investigated by Mitchell et al. (2005) in froth flotation separations. They found that the two minerals heterocoagulate in acidic medium which make their separation by flotation at pH below 4 impossible. This is why coagulation is more apparent in chalcopyrite concentrate which contains both chalcopyrite and pyrite.

3.2. Effect of temperature

The effect of temperature upon copper recovery from chalcopyrite crystals leached in ferric chloride was studied using particles with a size of <38 μm leached at temperatures of, 70, 80 and 90 °C for 3 h. The experimental results are shown in Fig. 5. As shown in this graph, the copper recovery is highly sensitive to temperature. About 7.4% of copper was extracted from chalcopyrite at a temperature of 70 °C in 3 h leaching time, whereas, about 22% was recovered at a temperature of 90 °C after the same period of time.

The kinetics of chalcopyrite leaching in acidic ferric chloride have been assessed on the basis of the shrinking core model as sulphur is produced on the surface of chalcopyrite

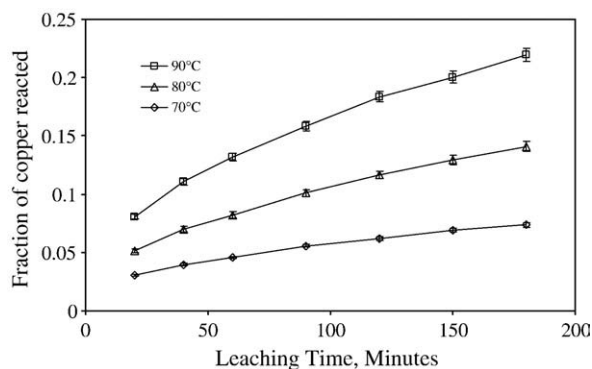


Fig. 5. The effect of temperature on the leaching of chalcopyrite crystal in ferric chloride as a function of time (C_{FeCl_3} =0.5 M, particle size <38 μm).

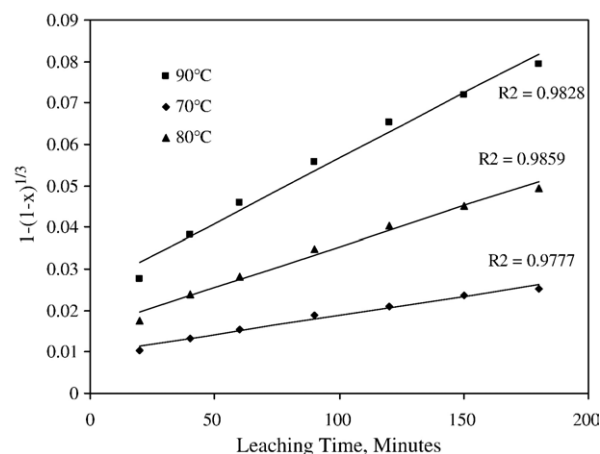


Fig. 6. Plot of $1-(1-X)^{1/3}$ vs. leaching time at different temperatures (C_{FeCl_3} =0.5 M, particle size <38 μm, stirring speed 400 rpm).

particles. This model considers that the leaching process is controlled either by diffusion of reactants through the solution boundary layer or through a solid product layer, or by surface chemical reaction. The dissolution of copper was found to follow linear kinetics according to Eq. (3):

$$1 - (1 - X)^{1/3} = k_s t \quad (3)$$

Where X is the fraction reacted at time t (min), and k_s is the apparent rate constant (1/min).

When Eq. (3) was applied to the data shown on Fig. 5, it gave a good linear fit, as shown in Fig. 6, with a correlation coefficient higher than 0.98. The quasi-linear fit in Fig. 7 seems to support the fact that the reaction is chemically controlled.

3.3. Quantification of sulphate formation

As opposed to ferric sulphate, in ferric chloride leaching of chalcopyrite, it is possible to measure sulphate ions present in the leaching solution formed as a result of sulfur oxidation.

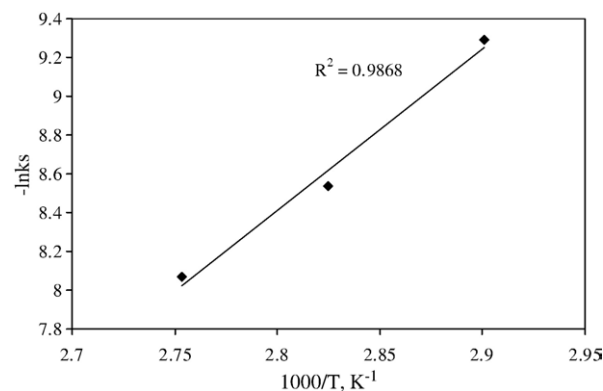


Fig. 7. Arrhenius plot of the conventional leaching of chalcopyrite in ferric chloride based on the apparent rate constants calculated from Fig. 6.

Table 2

Amount of sulphate sulphur dissolved in the leaching solution when chalcopyrite crystal was leached under conventional conditions (0.5 M FeCl₃–0.5 M HCl, <38 µm)

Leaching time, h	S dissolved in leaching solution (SO ₄ ²⁻) mg/g		
1	1.1±0.1	1.4±0.1	0.9±0.7
2	1.4±0.4	1.8±0.1	1.1±0.2
3	1.4±0.2	2.0±0.3	1.3±0.7
T, °C	80	90	90
Stirring speed, rpm	400	0	400

This is because the matrix of the leaching solution is chloride based. The source of sulphate could be a result of sulphide oxidation to sulphate and/or as a result of the dissolution of any sulphates which were formed prior to leaching. In this study, it was attempted to measure the sulphate present in the ferric chloride leaching solution by ICP. The experimental results are shown in Table 2.

3.4. Ratio of Fe/Cu

The molar ratio of Fe²⁺/Cu²⁺ for the dissolution of chalcopyrite crystal in ferric chloride is shown in Table 3. The theoretical molar ratio of Fe²⁺/Cu²⁺ as calculated from reaction (1) is 5. The experimental results show that this ratio is close to 5 especially after taking into account the amount of ferric ions consumed in sulphur oxidation to the sulphate state.

The quantity of sulphate formed is estimated to be less than 6% of the total oxidized sulphide. This is in agreement with the values reported in the literature (Dutrizac, 1992).

3.5. Experimental results of the closed vessel

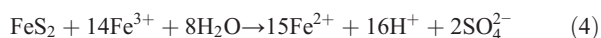
The experimental results of the leaching experiments performed in the closed vessel are presented in Table 4. The leaching experiments were carried out using chalcopyrite concentrate of particle size <25 µm. As found for the open vessel, the copper recovery was higher without agitation. About 24% of copper was recovered in the closed agitated vessel compared to about 41% copper recovered without agitation. The estimated amount of sulphate formed during the leaching process of chalcopyrite concentrate in the closed vessel conditions was found to be more than three times higher when stirring was applied. Surprisingly, the copper recovery increased from about

19%, in the open vessel case (Fig. 3), to about 42% in the closed vessel under stagnant conditions (Table 4). Under agitated and closed vessel condition, the copper recovery was also raised from about 16 to 24%.

The negative effect of agitation on the recovery of copper from chalcopyrite is surprising. Traditionally, one can expect an increase in the conversion when the diffusion through liquid film layer is eliminated by agitation. One would expect high conversion under stagnant conditions if the chemical reaction is a very fast exothermic reaction. In this case, the heat released due to the chemical reaction would rise the temperature at the reaction interface so that the actual reaction temperature is higher than the bulk one. The heat of formation calculated for chalcopyrite oxidation by ferric chloride (reaction (1)) is about 165 kJ/mole. This enthalpy value does not suggest that the rise in temperature at the solid surface, due to the exothermic reaction, is high enough to give an enhanced copper recovery. Furthermore, the apparent rate constant calculated for chalcopyrite leaching at a temperature of 90 °C is about $5.23 \times 10^{-5} \text{ s}^{-1}$ as calculated from the kinetic data in Fig. 6. This is not high enough to expect a measurable rise in temperature at the reaction interface.

On the other hand, in the closed vessel where a minimal amount of oxygen could participate in the oxidation reaction, the situation is different (see Table 4). The amount of sulphate generated in solution is much higher when stirring is applied (more than 220% higher).

The amount of iron generated in the closed vessel is slightly higher under non agitated conditions (only 10% higher), whereas, the copper recovery is more than 180% higher under stagnant conditions (Table 4). The XRD and chemical analysis of chalcopyrite concentrate shows that it contains some pyrite. It is estimated that the chalcopyrite concentrate contains about 5% pyrite as calculated from the chemical analysis. This means that pyrite could participate in the leaching process although it is known that pyrite is of slow reactivity in chloride systems (Dutrizac, 1992). The oxidation of pyrite is known to generate mainly sulphate rather than elemental sulphur according to the following overall reaction 4 (Dutrizac, 1989a,b; Rimstidt and Vaughan, 2003).



Therefore, it is possible to suggest that the high level of sulphate in the leaching solution is associated with pyrite oxidation. Generation of sulphate during chalcopyrite oxidation

Table 3

Molar ratio of reaction products as measured or calculated when chalcopyrite was leached in 0.5 M FeCl₃–0.5 M HCl for 3 h at standard conditions

T, °C	Stirring, rpm	Cu ²⁺	Fe ²⁺	SO ₄ ²⁻	Fe required to oxidize S to SO ₄ ²⁻	Fe ²⁺ /Cu ²⁺	Fe ²⁺ /Cu ²⁺ corrected	SO ₄ ²⁻ / S + SO ₄ ²⁻ , %
		Measured			Calculated			
		mmole/g chalcopyrite						
90	0	1.71	8.59	0.06	0.43	5.02	4.81	3.5
90	400	1.16	5.51	0.04	0.29	4.76	4.55	3.4
80	400	0.74	3.92	0.04	0.31	5.28	4.92	5.7

Table 4

Amount of sulphate sulphur dissolved in leaching solution when chalcopyrite concentrate was leached in 0.5 M FeCl₃–0.5 M HCl for 3 h at 90 °C (closed vessel)

	Stirring	Fraction of Cu reacted, %	Cu ²⁺ , Measured	Fe ²⁺	SO ₄ ²⁻	Fe required to oxidize S to SO ₄ ²⁻ Calculated	Fe ²⁺ /Cu ²⁺	Fe ²⁺ /Cu ²⁺ corrected	$\frac{SO_4^{2-}}{S + SO_4^{2-}}, \%$
			mmole/g chalcopyrite						
Rep 1	Yes	24.5	1.20	10.54	0.56	3.90	8.80	5.54	32
Rep 2	Yes	23.7	1.16	9.91	0.41	2.87	8.56	6.01	26
Rep 1	No	40.2	1.97	10.65	0.18	1.28	5.42	4.76	9
Rep 2	No	42.0	2.05	11.29	0.18	1.26	5.49	4.88	8

is negligible and could reach up to 5% of the total oxidized sulphide sulphur (Dutrizac, 1990).

The above facts suggest that agitation had a negative effect on chalcopyrite leaching whereas it had positive effect on pyrite oxidation. Pyrite when oxidized in acidic media produces sulphate. From the experiments in the closed vessel under agitated conditions where the oxygen in the system is limited, it can be seen that SO₄²⁻ concentration steadily increases. This fact suggests that the oxygen source in sulphate is not only from the dissolved oxygen but also from water. This supports the proposed model for pyrite oxidation by Rimstidt and Vaughan (2003). Furthermore, the presence of SO₄²⁻ in the solution suggests formation of several intermediate products such as: S₂O₃²⁻, SO₃¹⁻, HSO₃¹⁻, S₄O₆²⁻ and S₃O₆. However, these species are not stable and could not be measured (Parker et al., 2001).

The arguments presented above do not address two issues. These are the higher recovery of copper under non agitating conditions in both open and closed vessels and also the considerable increase in copper recovery in the closed vessel under non agitating conditions compared to that from the open vessel. Regarding the first issue, one can present the following hypothesis: Under stagnant conditions the Fe³⁺ concentration is high (0.5 M). Due to the slow reaction kinetics of chalcopyrite leaching in ferric chloride, it can be assumed that the Fe³⁺ concentration across the liquid film layer is equal to the bulk concentration. Furthermore, according to reaction

(1), cupric ions are produced in the form of complexes like [CuCl]⁻, [CuCl]⁰ and [CuCl₃]⁻, which are known to be a powerful oxidants (Hirato et al., 1987; Lundstrom et al., 2005). The chalcopyrite oxidation reaction using cupric ions proceed according to reaction (2):

Under non agitation conditions, it is possible that cupric chloride complexes accumulate at the reaction surface within the liquid film layer (see Fig. 8). The rate of chalcopyrite oxidation by cupric chloride salt solution is dependant on Cu²⁺ concentration. According to Hirato et al. (1987) the reaction rate of chalcopyrite in cupric chloride was found to be half order [CuCl₂]^{0.5}. Therefore, with no agitation, reaction (1) proceeds with a faster rate than the agitated case, whereas agitation may reduce the concentration of Cu²⁺ at chalcopyrite surface by diluting it with the bulk solution. Furthermore, chalcopyrite leaching in cupric chloride is faster than leaching with ferric chloride at equal concentrations of both (Parker et al., 1981; Hirato et al., 1987).

It can therefore be concluded that the enhanced reaction rate of chalcopyrite dissolution in ferric chloride without agitation is due to chalcopyrite oxidation by two parallel reactions (reactions (1) and (2)). If the action of cupric chloride complexes is the only reason behind the enhanced recovery then this phenomenon would diminish if a sensible amount of CuCl₂ salt is added to the leaching system.

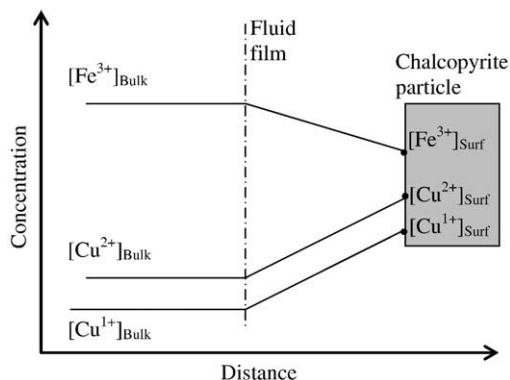


Fig. 8. Mass transfer of reactants and products of chalcopyrite leaching in ferric chloride with no agitation.

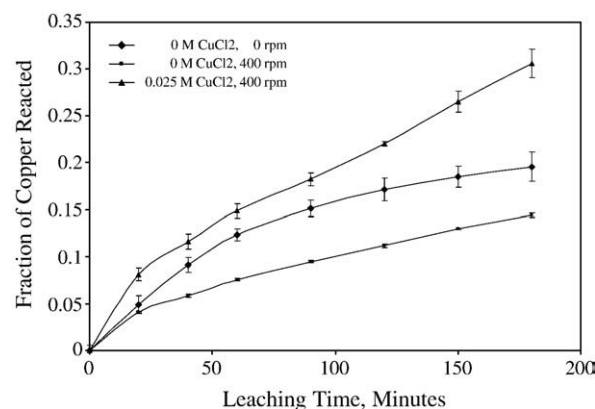


Fig. 9. The effect of agitation on the leaching of chalcopyrite concentrate in ferric chloride in presence and absence of cupric chloride (C_{FeCl_3} : 0.5 M, $T=90$ °C, <25 μ m).

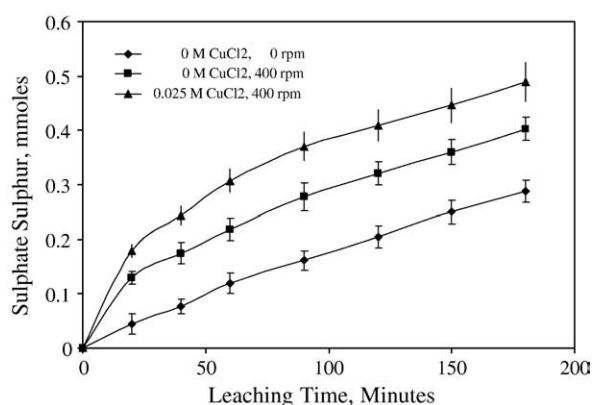


Fig. 10. The effect of stirring on the amount of SO_4^{2-} generated when chalcopyrite concentrate leached in ferric chloride in presence and absence of cupric chloride (C_{FeCl_3} : 0.5 M, $T=90^\circ\text{C}$, $<25\ \mu\text{m}$).

3.6. Effect of cupric chloride addition on FeCl_3 leaching of chalcopyrite

In order to confirm that the higher copper recovery obtained when chalcopyrite was leached in acidic ferric chloride under stagnant conditions, an additional experiment was performed. In this experiment chalcopyrite concentrate was leached in 0.5 M FeCl_3 –0.5 M HCl containing 0.025 M CuCl_2 and the results compared to that without cupric chloride addition under stagnant and agitated conditions as shown in Fig. 9. Again the copper recovery was found to be higher under stagnant conditions. However, the addition of cupric chloride salt to the leaching system significantly increased the copper recovery under agitation.

Similarly, the amount sulphate sulphur measured in the leaching solution was found to have the same trend as for the copper recovered as shown in Fig. 10. It is also interesting to note that the amount of sulphate formed as a result of concentrate

leaching at stirring speed 400 rpm is higher than that of at stagnant conditions. This is opposite to those results obtained when chalcopyrite crystal was leached (see Table 4). This is due to the presence of pyrite in chalcopyrite concentrate which produces more sulphate at higher rotation speeds.

It is now evident that the enhanced recovery of copper from chalcopyrite when leached in acidified ferric chloride at stagnant conditions is caused by the catalytic effect of cupric ions produced by reaction (1). It acts as a second oxidant for chalcopyrite and its accumulation at the reaction interface in the absence of agitation magnifies the effect. The catalytic action of cupric ions was observed by Mulak et al. (2001) when leached millerite in ferric chloride.

This result indicates that most kinetic studies that have been carried out for the purposes of determination of the activation energy of reaction (1) could be misleading due to the fact that the overall leaching involves two reactions. It is suspected that the results produced by those who carried out their experiments with a low solid/ liquid ratio could have produced values of activation energy closer to the true values than those which used a high solid/liquid ratio. It is possible that this issue explains the significant scatter in published values of activation energy for chalcopyrite leaching in ferric chloride as seen in Table 5. These values range from 1.1 to 87 kJ/mol. The scatter in the data could also be related to the fact that some authors did not consider the two mechanisms for chalcopyrite leaching in ferric chloride proposed by Havlik and Kammel (1995). Additionally, such scatter may also be attributed to the method of calculation especially when the conversion is far from unity. This latter can lead to an error in determining the rate-limiting step and therefore an incorrect calculation of the apparent rate constant and activation energy (Prosser, 1996).

It is therefore, very important to take into account the existence of cupric chloride in the leaching solution when evaluating data produced during leaching experiments when formation of cupric chloride complexes is possible. This is especially true in the latter stages of leaching.

Table 5
Summary of investigations on chalcopyrite leaching in ferric chloride

Material	Temperature range, $^\circ\text{C}$	E_a kJ/mol.	Author
Synthetic	25–75	38 ± 4	(Ammou-Chokroum et al., 1977)
Natural	30–100	42 ± 4	(Dutrizac, 1978)
Synthetic	50–100	46 ± 4	(Dutrizac, 1978)
Natural	60–106	50	(Ermilov et al., 1969)
Natural monosize, 0.2 M HCl , 0.1 FeCl_3	75–96	62	(Palmer et al., 1981)
Natural, 1M HCl , 3M NaCl , 0.1 FeCl_3	82.5–96	83	(Palmer et al., 1981)
Natural	55–85	69	(Majima et al., 1985)
Natural of an offgrade copper concentrate in 4M FeCl_3 –2M HCl	~ 65–110	37.4	(Ngoc et al., 1990)
Natural	40–90	73 ± 1.5	Buttinelli (1993)
Natural	3.5–80	55 ± 5	(Havlik et al., 1995)
Natural	3.5–45	1.1	(Havlik and Kammel, 1995)
Natural	45–80	69	(Havlik and Kammel, 1995)
Natural, with addition of CCl_4	45–80	31.2	(Havlik and Kammel, 1995)
Natural, 1.0M FeCl_3 , 1M NaCl , 0.25 HCl	60–90	68	(Maurice and Hawk, 1998)
Natural, pentlandite– CuFeS_2 concentrate, 1.0M FeCl_3 , 1M NaCl , 0.25 HCl	70–90	86.7 ± 10	(Maurice and Hawk, 1999)
Museum grade natural chalcopyrite crystal, 0.1M FeCl_3 , 0.2 M HCl	52–85	69	(Hirato et al., 1986)

Referring back to the kinetic study presented above, the value of activation energy for the dissolution of chalcopyrite in ferric chloride was calculated and compared to the literature data presented in Table 5. This is due to the negative influence of agitation on the leaching kinetics of chalcopyrite dissolution in ferric chloride caused by the catalytic action of cupric ions. If the stirring inhibits the action of Cu^{2+} , (mainly at earlier stages of leaching) then the process would involve more than one reaction which again is difficult to account for in the shrinking core model. Nevertheless, the value of activation energy estimated for chalcopyrite dissolution in ferric chloride is found to be about 69 kJ/mole. This value is in good agreement with some of the published literature values presented in Table 5, especially the values reported by Majima et al. (1985), Havlik and Kammel (1995), Maurice and Hawk (1998) and (Hirato et al., 1986).

Finally, there is currently no explanation for the considerable increase in copper recovery when chalcopyrite is leached in a closed vessel. A systematic study is currently underway to investigate this interesting result.

4. Conclusions

In this work, the dissolution kinetics of chalcopyrite in ferric chloride have been investigated. It was found that the dissolution rate increased with an increase in temperature. However, agitation of the leaching mixture caused a reduction in copper recovery. This was explained by the fact that agitation results in removal of the cupric chloride complexes formed at the reaction interface between chalcopyrite particles and ferric ions. The cupric ion acts as a second oxidant in the dissolution reaction. Its concentration under stagnant conditions at the reaction interface is high enough to produce a positive effect on the overall reaction rate. The additional effect of cupric ions at stagnant conditions was confirmed by addition of cupric chloride salt to the leaching system. In this case, as expected, agitation enhanced the reaction rate by breaking up the fluid film layer around chalcopyrite particles.

By fitting the shrinking core model to the kinetic data, it was found that the overall activation energy of chalcopyrite dissolution in ferric chloride was about 69 kJ/mole, which is in general agreement with several of the reported literature.

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