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THE INFLUENCE OF THE OXIDIZING AGENTS ON THE KINETICS OF COPPER LEACHING FROM CHALCOPYRITE CONCENTRATE WITH SULPHURIC ACID

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ABSTRACT. The leaching rate constant and the apparent activation energy of chalcopyrite concentrate were investigated in sulphate media. The chemical composition (weight percent) of concentrate was: 30.38% Cu, 4.20% Zn, 1.92% Pb, 28.89% Fe and 34.49% S, respectively. The leaching time, the leaching temperature and the quantity of ferric sulphate and of oxygen as oxidizing agents were modified during the experiments. From the shape of the leaching curves, three stages of the process were observed. The apparent activation energy depends on the period of leaching as well as on the presence of ferric ion and oxygen as oxidizing agents in the leaching medium. The study intends to establish the rate controlling reaction step, according to both the activation energies, and the analytical expressions for each period.

INTRODUCTION

The most common hydrometallurgical processes for copper recovery are based on the solubilization in sulphuric medium. The sulphate-based process exhibits some potential advantages over the other systems. The sulphate leaching chemistry is generally simpler and better understood than other media leaching chemistry, and copper recovery by solvent extraction and electrowinning from sulphate medium is easier.

The dissolution of copper from chalcopyrite concentrate involves a complex mechanism. The most studied copper mineral is chalcopyrite, which leaches in sulphate medium by a parabolic kinetic [1-3], caused by the progressive formation of a sulphur layer or other products at the external surface. It behaves as a passivation layer.

From kinetic and surface science studies, the following reaction sequence has been proposed to describe the oxidative leaching and passivation of chalcopyrite in sulphate medium [3]:

$$CuFeS_2 \longrightarrow Cu_{1-x}Fe_{1-y}S_2 + x\,Cu^{2+} + y\,Fe^{2+} + 2(x + y)\,e^- \qquad \text{(fast), (1)}$$

$$y >> x,\ x + y \approx 1$$

$$Cu_{1-x}Fe_{1-y}S_2 \longrightarrow Cu_{1-x-z}S_2 + z\,Cu^{2+} + (1-y)\,Fe^{2+} + 2(z+1-y)\,e^- \qquad \text{(slow), (2)}$$

$$Cu_{1-x-z}S_2 \longrightarrow (1-x-z)z\,Cu^{2+} + 2\,S^{2+} + 2(1-x-zy)\,e^- \qquad \text{(the slowest). (3)}$$

Within the fast initial period, the iron leaches preferentially as compared to copper. An intermediate disulphide phase is formed, $Cu_{1-x}Fe_{1-y}S_2$, where $y >> x$ and $x + y \approx 1$. In the second slow stage, the disulphide phase is further oxidized to form copper polysulphide, $Cu_{1-x-z}S_2$, alternatively expressed as CuS_n where $n=2/(1-x-z)$. The copper polysulphide acts on chalcopyrite as a passive layer.

The rate controlling reaction step is the slow decomposition of the copper polysulphide to cupric ions and elemental sulphur, with the polysulphide chains restructuring to form S_8 rings. The elemental sulphur is porous enough, so that the rate is not limited by reactant/product diffusion through sulphur unless the sulphur melts during leaching when higher temperatures are used.

EXPERIMENTAL

The leaching tests were carried out on chalcopyrite concentrate obtained by flotation of ores from mines around Baia Mare. The chemical and mineralogical composition of the investigated concentrate is shown in table 1.

Table 1.

The chemical and mineralogical composition of concentrate.

Chemical composition					
Element	Cu	Zn	Pb	Fe	S
% (weight percent)	30.38	4.2	1.93	28.89	34.49
Mineralogical composition					
Mineral	Chalcopyrite ($CuFeS_2$)	Pyrite (FeS_2)	Sphalerite (ZnS)	Galena (PbS)	
% (weight percent)	85.5-86.5	5-6	6-7	2-3	

The particle size of chalcopyrite concentrate ranged between 0.071 and 0.1 mm. A solution of 8.0 N H_2SO_4 was used as leaching medium. Each leaching experiment was performed with 2 g chalcopyrite concentrate and 15 ml leaching solution therefore, with a solid/liquid ratio of 1/7.5. The leaching experiments were carried out between 20 and 60°C.

To increase the copper dissolution, ferric sulphate was added to the leaching solution, as oxidizing agent. The tested concentration of ferric sulphate in 8.0 N H_2SO_4 was of 10, 20 and 30 g/l. Also, the leaching pulp was stirred by air bubbling at 200 l/hour in a volume of 210 ml leaching agent, at the same ratio of solid/liquid. The leaching experiments were carried out at a temperature of 40 and 60°C when the oxidizing agents (Fe^{3+} and/or O_2) were used. The leaching pulp was filtrated and the copper concentration of the solution was analyzed spectrophotometrically by using cuprizon as complexing agent.

RESULTS AND DISCUSSIONS

The leaching curves, presented in figure 1, indicates three periods of leaching [4-6]. From the shape of the leaching curve, it is obvious that the leached copper pecent present a sharply increse in the initial period followed by a tendency of leveling of in the third period of the solubilization.

Similary to the shrinking-core model for gas-solid noncatalytic reactions [7], three rates are observed:

I - diffusion of reagents through the boundary layer;
II - diffusion through the layer of products;
III - reaction at the interface of the unreacted core.

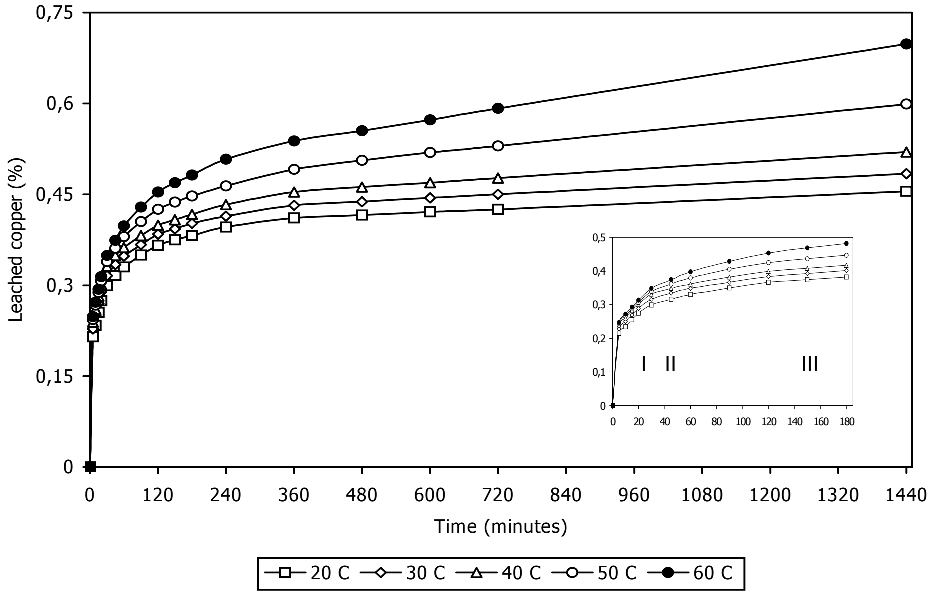

Fig. 1. *The chalcopyrite concentrate's leaching curves as a function of time at different temperatures.*

We were encouraged to use this shrinking-core model by the fact that the particle size did not vary after the leaching process. By drying the remaining solid material and separation by screening, the same size (between 0.071 and 0.1 mm) has been obtained.

It is obvious that the initial stage of solubilization is characterized by linear kinetics. Within this stage, the rate controlling reaction step is the external diffusion (the diffusion of reagents from the bulk solution to the particle surfaces).

The second period of solubilization could be described by a power function. For this leaching period, the rate controlling reaction step is the internal diffusion through the product layer adherent to the original material.

Within the third stage of solubilization, the rate controlling reaction step seems to be the chemical reaction.

The change of the leached copper percent in first, second and third period, respectively, could be described by the analytical expressions presented in table 2, where t is the leaching time, t_∞ represents the time for complete copper conversion if the process would follow the same mechanism throughout, and x is the converted fraction of copper. The ratio $\frac{1}{t_\infty}$ represents the rate constant (time^{-1}).

From the graphic representation of the functions $t/t_\infty=f(t)$, could be observed a near-linear dependences with a good enough correlation coefficients, as seen in figure 2 (a, b and c). Thus, the assumed model seems to be satisfactory.

The values of the apparent rate constants were estimated from the slopes of the straight lines obtained by using the experimental data for all three periods of chalcopyrite concentrate leaching, with sulphuric acid at 20°C.

Table 2.

The analytical expressions which describes the change of the leached copper percent in first, second and third period, respectively.

Period	*Analytical expressions*	*Time elapse* (minutes)
I	$\frac{t}{t_\infty} = 1 - (1 - x) = k_1 t$ (1)	0÷30
II	$\frac{t}{t_\infty} = 1 - 3(1 - x)^{\frac{2}{3}} + 2(1 - x) = k_2 t$ (2)	30÷180
III	$\frac{t}{t_\infty} = 1 - (1 - x)^{\frac{1}{3}} = k_3 t$ (3)	180÷1440

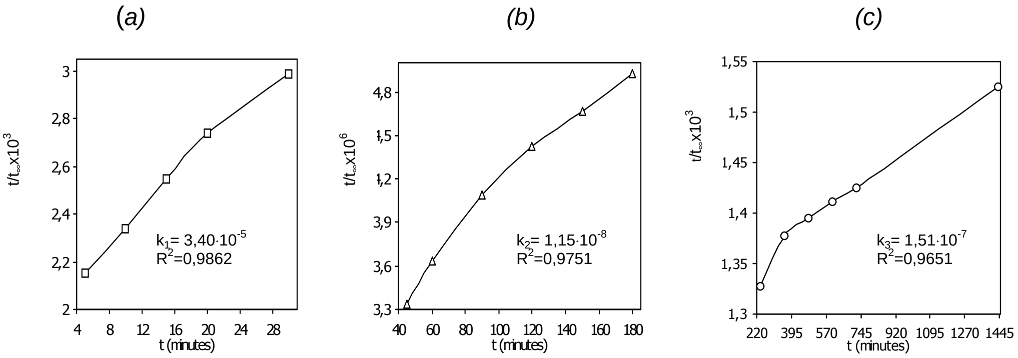
(*a*) (*b*) (*c*)

Fig.2. *The near-linear dependences t/t∞=f(t) for all three periods of chalcopyrite concentrate leaching with sulphuric acid at 20°C.*

The values of the rate constants, obtained as function of leaching temperature, for chalcopyrite concentrate solubilization curves, are listed in table 3. As seen, important enhancement of rate constant is obtained within the third and second stage, and only small enhancement within the first stage when the leaching temperature is risen. Also, it could be observed a differences between the first period rate constant value and the other two periods rate constant values. We atributed the differences to the formation of the adherent product layer to the original material, which produces the decrease of the leaching rate.

Table 3.

The values of the rate constants.

Temperature (°C)	10^5 k_1 (min^{-1})	10^8 k_2 (min^{-1})	10^7 k_3 (min^{-1})
20	3.40	1.15	1.51
30	3.56	1.23	2.00
40	3.73	1.25	2.50
50	3.84	1.67	3.33
60	4.04	2.50	5.00

The quantitative expression of the temperature influence can be obtained by the Arrhenius relation. The values of the apparent activation energies are presented in table 4.

Table 4.

The apparent activation energy.

Period	I	II	III
E_a (kJ/mol)	3.14 ± 0.002	18.76 ± 0.028	24.21 ± 0.001

To increase more the copper dissolution from chalcopyrite concentrate with sulphuric acid, oxidizing agents were added into the leaching solution. Therefore, the influence of the ferric sulphate and/or oxygen addition, as oxidizing agent, on the rate of chalcopyrite concentrate was studied. Figure 3 presents the chalcopyrite concentrate leaching curves, with sulphuric acid when using the oxidizing agent.

The rate constants and apparent activation energies, within the temperature range 40-60°C, for all of three period in the presence of oxidizing agents, are presented in table 5.

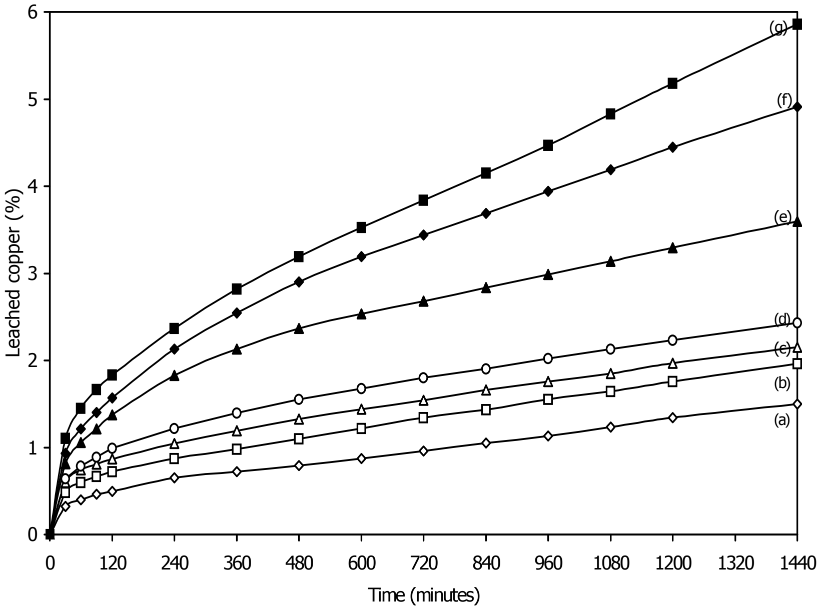

Fig. 3. *The chalcopyrite concentrate leaching curves, when using oxidizing agents, as function of time.*

(a) the addition of oxygen at 40°C; (b) the addition of oxygen at 60°C; (c) the addition of oxygen and ferric sulphate (30 g/l) at 40°C; (d) the addition of ferric sulphate (10 g/l) at 60°C; (e) the addition of ferric sulphate (20 g/l) at 60°C; (f) the addition of ferric sulphate (30 g/l) at 60°C; and (g) the addition of oxygen and ferric sulphate (30 g/l) at 60°C.

Table 5.

The rate constants and apparent activation energies, for all of three oxidizing leaching period of the chalcopyrite concentrate.

Oxidizing agents	Period	Temperature (°C)	k (min^{-1})	E_a (kJ/mol)
O_2	I	40	8.64×10^{-5}	17.2
		60	12.86×10^{-5}	
	II	40	1.58×10^{-4}	33.6
		60	3.43×10^{-4}	
	III	40	3.33×10^{-8}	47.6
		60	10.00×10^{-8}	
O_2 and Fe^{3+}	I	40	1.11×10^{-7}	65.2
		60	5.00×10^{-7}	
	II	40	1.28×10^{-8}	38.2
		60	3.09×10^{-8}	
	III	40	3.04×10^{-8}	52.1
		60	10.11×10^{-8}	

CONCLUSIONS

The obtained apparent activation energies are comparable with those found in literature: about 69 kJ/mol for ferric chloride chalcopyrite leaching, in the range of 40-100°C [8]. Also, the small leached copper percent obtained for ferric sulphate chalcopyrite (about 6% in 24 hours) can be compared with the literature values. At ferric chloride chalcopyriteleaching, in similar conditions, the leached copper percent are at about 7% [8]. The ferric chloride chalcopyrite leaching conditions was:

- the fraction of concentrate sample between 0.071 and 0.1 mm;
- the chemical composition of fraction: 32.3% Cu, 28.4% Fe, 31.9% S;
- the solid/liquid ratio of 1/25;
- the leaching agent concentration: 1.0 M $FeCl_3$ in 0.2 M HCl;
- the leaching time: 240 minutes;
- the temperature: 60°C;
- the stirring speed: 300 rpm.

The slightly increased percent for ferric chloride chalcopyrite leaching, can be explained by the fact that the ferric chloride is much more aggressive than sulphate, due to the ability to accelerate dissolution of the mineral, owing to the formation of complexes, as well as due to the fact that a high stirring speed was applied to the pulp.

The examination of the obtained rate constants and apparent activation energies leads to the following conclusions:

According to the apparent activation energy (~3 kJ/mol) in the range 20-60°C, the rate controlling reaction step within the first period of leaching is the diffusion of leaching agent from the bulk to the grain surface (external diffusion);

Within the initial stage of dissolution, fast leaching rates have been observed due to dissolution of the fine portions of chalcopyrite concentrate, the high concentration gradients at the interface, as well as the fact that the start of the process is not retarded by layers of elemental sulphur or other weak reactive products, formed on the leached surface;

The second period of leaching is much longer than the first one and the values of the apparent activation energy (~18 kJ/mol) indicate that the diffusion of reactants and products over the passivating layer (internal diffusion), as the rate controlling reaction step;

For the third period of leaching the values of the apparent activation energy (~24 kJ/mol) indicate the same rate controlling reaction step, as in second period;

The increase of the apparent activation energy (up to 50 kJ/mol), when the oxidizing agents were used, can be assigned to the change of mechanism. It is highly probable that the copper polysulphide layer can release copper (see reaction (3)) in the interaction with the oxidizing agents, and the chemical control is installed.

The same conclusions were driven when the same oxidizing agents were used for leaching of low-grade chalcocite-covellite-chalcopyrite ore in sulphuric acid media [5].

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