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LEACHING OF CHALCOPYRITE CONCENTRATE WITH SULPHURIC ACID IN ABSENCE AND PRESENCE OF OXIDIZING AGENTS

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ABSTRACT. The kinetic leaching characteristics of chalcopyrite concentrate were investigated in sulphate media. The experiments were carried out on chalcopyrite concentrate obtained by flotation of the ores from mines around Baia Mare. The concentrate has the following chemical composition: 30.38% Cu, 4.2% Zn, 1.93% Pb, 28.89% Fe and 34.49% S. Three stages of the leaching process were established. The apparent activation energy suggests a dependence on the period of leaching and on the presence of ferric ion and oxygen as oxidizing agents in the leaching solution. Also, an attempt was made to determine the rate controlling reaction step, according to both the activation energies, and the analytical expressions for each period. The parameters that were modified during experiments were: the leaching time, the leaching temperature and the quantity of ferric sulphate and of oxygen as oxidizing agents.

INTRODUCTION

Hydrometallurgical processes for chalcopyrite copper concentrates can be categorized according to the type of lixiviants used, the most common lixiviants being chloride, nitrate, ammine and sulphate. The sulphate-based processes have some potential advantages over the others in that the leaching chemistry is generally simpler and better understood, and copper recovery from sulphate media (by solvent extraction/electrowinning) is easy. Unfortunately, the sulphate processes have a critical disadvantage in that chalcopyrite leaches slower in sulphate media than in the other media. Initial reaction rates tend to decline rapidly with time, leading at the conclusion that a passivating layer forms on the mineral surface.

The study of the reaction rate between chalcopyrite and leaching agents is important because a prolongation of the leaching process considerably raises the operational costs, owing to the necessity of treating large volumes of dilute solutions.

The literature on chalcopyrite leaching concerning the theoretical and practical aspects, reveals that the dissolution of chalcopyrite is governed by a parabolic kinetic caused by the progressive formation of a compact layer of elemental sulphur or other products on the solid/liquid interface. This layer may not be entirely impermeable and it can be abraded or peeled off by the pulp stirring.

A number of papers [1-11] have reported the leaching kinetic of pure or synthetic chalcopyrite having the ferric ion as oxidizing agent. In most of these papers [3-5, 7, 8], the ferric chloride was used because its availability and recoverability, but it is also much more aggressive than sulphate, due to the ability to accelerate dissolution of the mineral owing to the formation of complexes.

The apparent activation energy depends on the period of leaching, as well as on the presence of oxidizing agents Fe^{3+} or O_2 in the leaching solution. Some attempts were made to determine the rate controlling reaction steps for each period of leaching from the kinetics. The dissolution kinetics vary sensibly with the leaching temperature, and the quantity of ferric sulphate and/or of oxygen added as oxidizing agents.

The scattering values of apparent activation energy, presented in literature, can be mainly attributed to:

- the significant variation of the different chalcopyrite concentrates reactivity with the location of origin [3];
- the presence of flotation reagents which seemed to have minor effects on the leaching behavior;
- the major difference in the electroleaching rates caused mainly by electrical conductivity variations;
- the admixtures and impurities as well as the influence of real structure of the investigated material.

EXPERIMENTAL

The leach 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 and table 2, respectively.

Table 1.

The chemical composition of concentrate.

Element	Cu	Zn	Pb	Fe	S
%	30.38	4.2	1.93	28.89	34.49

Table 2.

The mineralogical composition of concentrate.

Mineral	Chalcopyrite $CuFeS_2$	Pyrite FeS_2	Sphalerite ZnS	Galena PbS
%	85.5-86.5	5-6	6-7	2-3

The particle size of chalcopyrite concentrate ranged between 0.071-0.1 mm. As leaching medium, a solution of 8.0 N H_2SO_4 was used. Each leaching experiment was performed with 2 g chalcopyrite and 15 ml leaching solution therefore, a ratio solid/liquid of 1/7.5.

The chalcopyrite concentrate leaching experiments were carried out at the following temperatures: 20, 30, 40, 50 and 60°C. For each leaching temperature, the leaching time was: 5, 10, 15, 20, 30, 45, 60, 90, 120, 150, 180, 240, 360, 480, 600, 720 and 1440 minutes.

To increase the copper dissolution, the ferric sulphate as oxidizing agent was added to the leaching solution. The tested concentration of ferric sulphate in 8.0 N H_2SO_4 was 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 a same ratio solid/liquid. For leaching tests, in which the oxidizing agents (Fe^{3+} and/or O_2) were used, the leaching temperatures were 40 and 60°C.

After filtration, the copper concentration in solution was analyzed by spectrophotometric method.

RESULTS AND DISCUSSIONS

The leaching results of chalcopyrite concentrate, in the temperature region of 20-60°C, at atmospheric pressure, are represented in figure 1.

The shape of the leaching curves indicates three periods of leaching. The attempt to treat the first two periods as one resulted in a exponential dependence with an exponent less than one, it is not recommended, because from figure 1 it is obvious that the initial stage is characterized by linear kinetics.

The change of the leached copper percent in that first period could be described by the analytical expression:

$$c_1 = k_1 t \tag{1}$$

where c_1 is the leached copper percent in time t ($t \leq 0.3333$ h), and k_1 is a constant representing the slope of the respective plot (% of leached copper/h).

The second period could be described by a power function having the form:

$$c_2 = c - c_1 = k_2 (t - t_1)^a \tag{2}$$

where c is the total leached copper percent in time t (in this case $t \in$ [0.5-4 h), k_2 is a constant representing the intercept on the ordinate axis in the log-log plot, a is the coefficient related to the slope in the log-log plot, and c_1 is the maximum leached copper percent in first period at time t_1 (t_1 = 0.333 h).

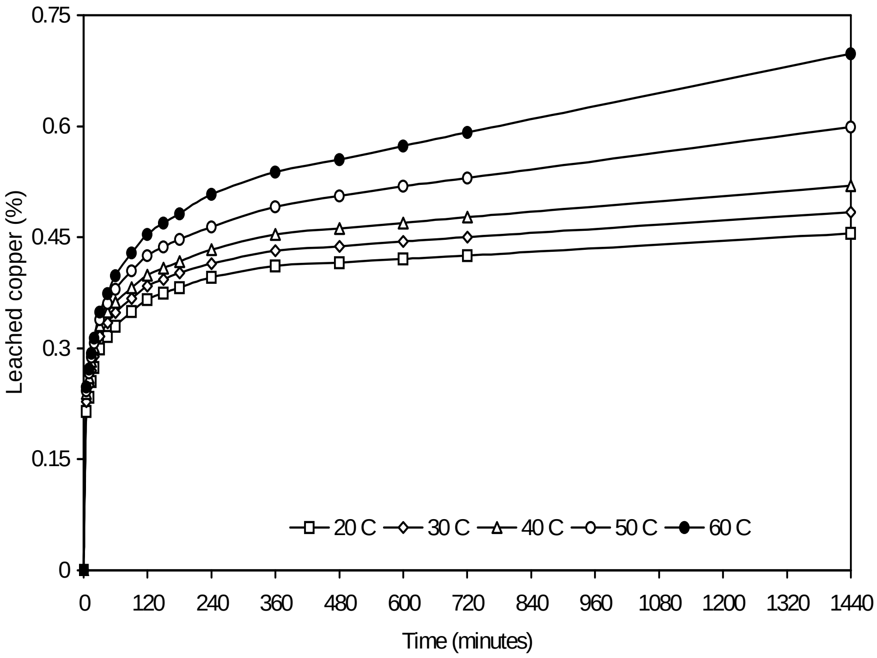

Figure. 1. The chalcopyrite concentrates leaching curves as a function of time at different temperatures.

The third period was characterized by linear kinetics, the corresponding analytical expression having the form:

$$c_3 = c - c_2 = k_3(t - t_2) \quad (3)$$

where c is the total leached copper percent in time t (in this case $t \geq 6$ h), k_3 is constant representing the slope of the respective plot (% of leached copper/h), and c_2 is the maximum leached copper in the second period at t_2 ($t_2 = 4$ h).

The experimental data for all the three periods of chalcopyrite concentrate leaching, with sulphuric acid at 20°C, are given in table 3. The bolded values of this table represent the values of c_1 and t_1 of equation (2), and c_2 and t_2 of equation (3), respectively.

The values of the rate constants k and exponents a, obtained as function of temperature, for chalcopyrite concentrate leaching curves are listed in table 4.

Table 3.

The experimental data of chalcopyrite concentrate leaching with sulphuric acid at 20°C.

First period			Second period						Third period				
c_1 (%)	t (h)	k_1 (%/h)	c (%)	t (h)	C_2 (%)	$t-t_1$ (h)	k_2 (%/h^a)	a	c (%)	t (h)	c_3 (%)	$t-t_2$ (h)	k_3 (%/h)
0.215	0.083	0.237	0.299	0.50	0.025	0.167	0.0668	0.521	0.411	6	0.015	2	0.00226
0.234	0.167		0.316	0.75	0.042	0.417			0.416	8	0.020	4	
0.255	0.250		0.330	1.00	0.056	0.667			0.421	10	0.025	6	
0.274	0.333		0.350	1.50	0.076	1.167			0.425	12	0.029	8	
			0.366	2.00	0.092	1.667			0.455	24	0.059	20	
			0.375	2.50	0.101	2.167							
			0.384	3.00	0.110	2.667							
			0.396	4.00	0.122	3.667							

Table 4.

The values of the constants *k* and exponents *a*.

Temperature (°C)	Period			
	I	II		III
	k_1 (%/h)	k_2 (%/h^a)	a	k_3 (%/h)
20	0.237	0.0668	0.521	0.00226
30	0.243	0.0698	0.504	0.00288
40	0.249	0.0733	0.484	0.00365
50	0.255	0.0860	0.522	0.00590
60	0.263	0.1000	0.561	0.00891

Accordingly, with the results represented in figure 1, the leaching of chalcopyrite in acidic media is characterized by an increase with temperature. The quantitative expression of the temperature influence can be obtained by the Arrhenius relation represented in figure 2.

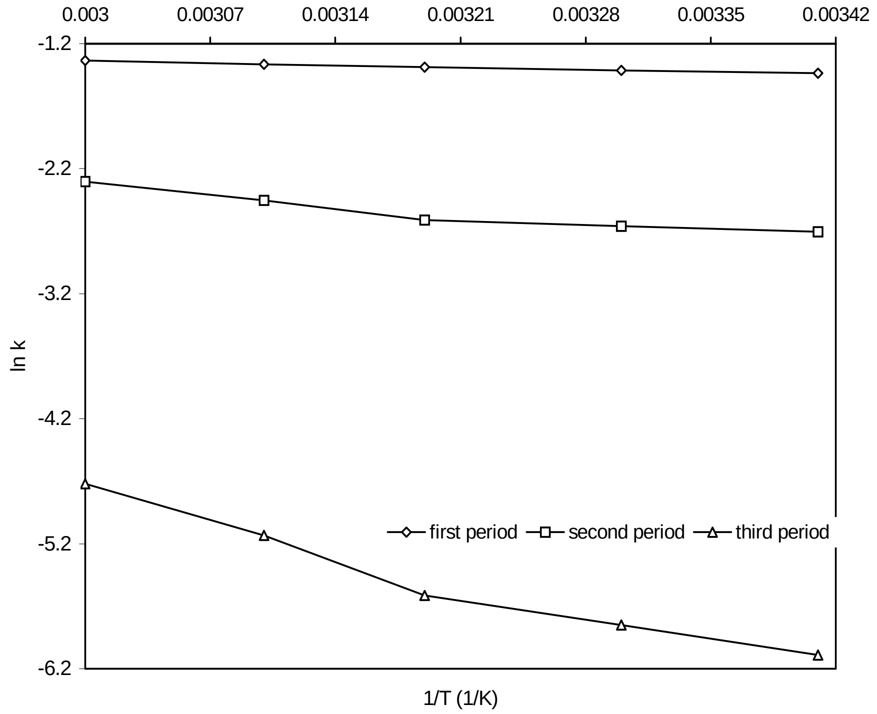

Figure. 2. The dependence of apparent activation energy on the period of leaching

The values of apparent activation energy, obtained from the Arrhenius plot showed in figure 2, are presented in table 5.

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

Table 5.

The apparent activation energy.

Period of leaching	Temperature range (°C)	E_a (kJ/mol)
I	20-60	2.023
II	20-40	3.538
	40-60	13.446
III	20-40	18.267
	40-60	38.707

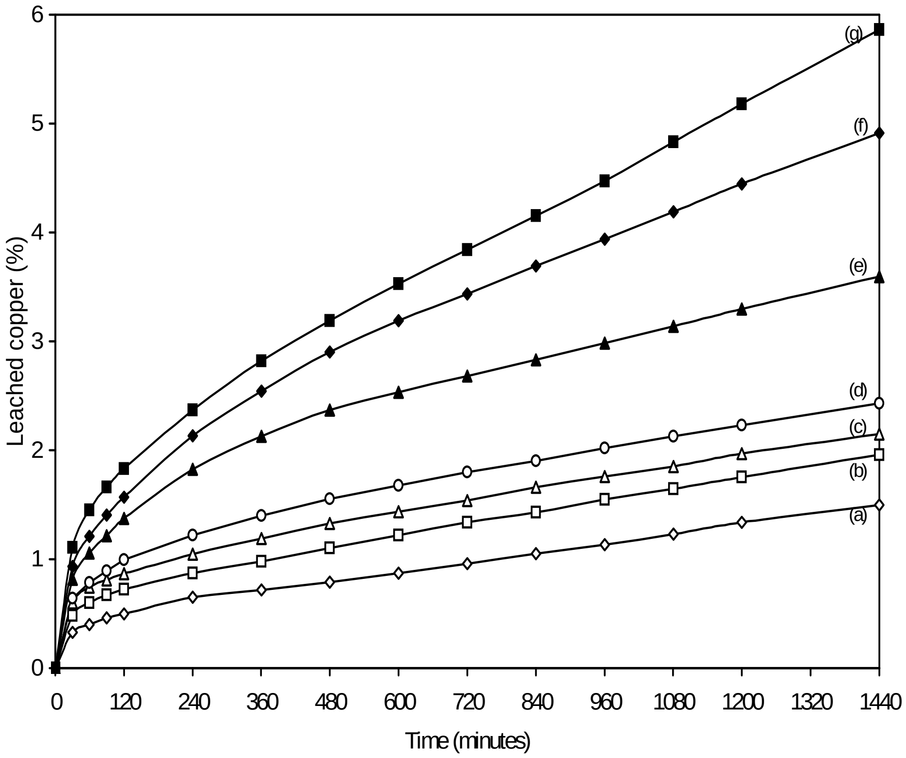

Figure. 3. The chalcopyrite concentrate leaching curves, using oxidizing agents, as function of time.

The shapes of the oxidative leaching curve points out an increase of the second period time until 480 minutes in (c)–(g) cases. The rate constants *k* and apparent activation energies, in the range of temperature 40-60°C, for third period of chalcopyrite concentrate leaching, with sulphate acid, in the presence of oxygen or oxygen and ferric sulphate (30 g/l), are presented in table 6.

Table 6.

The rate constants and apparent activation energies, for third period of chalcopyrite concentrate leaching.

Oxidizing used agents	Temperature (°C)	k_3 (%/h)	E_a (kJ/mol)
oxygen	40	0.0223	38.894
	60	0.0523	
Oxygen and ferric sulphate (30 g/l)	40	0.0547	52.675
	60	0.1763	

CONCLUSIONS

The obtained apparent activation energies are comparable with these found in literature: about 69 kJ/mol for ferric chloride chalcopyrite leaching, in the range 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, which are about 7% [8] for ferric chloride chalcopyrite leaching, in the similar conditions (the fraction of concentrate sample: 0.071-0.1 mm; the chemical composition of fraction: 32.3% Cu, 28.4% Fe, 31.9% S; the ratio solid/liquid: 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 leached copper percent for ferric chloride chalcopyrite leaching, a little increased, 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 by the fact that a high stirring speed was applied to the pulp.

The examination of the rate constants, exponents and apparent activation energy values obtained leads to the following conclusions:

(a) according to the apparent activation energy (~2 kJ/mol) in the range 20-60°C, the rate controlling reaction step in the first period of leaching is diffusion of leaching agent from bulk solution to the grain surface (external diffusion);

(b) in the initial stage of dissolution, fast leaching rates have been observed due to dissolution of the fine portions of chalcopyrite, 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, formed on the leached surface;

(c) the second period of leaching is much longer than the first, and the values of the apparent activation energy (~3.5 kJ/mol in the range 20-40°C, and ~13.5 kJ/mol in the range 40-60°C, respectively) indicates the diffusion of reactants and products over the passivating layer (internal diffusion), as the rate controlling reaction step;

(d) the analytical form of the expression describing the kinetics of leaching in the third period indicates linear kinetics, and the values of the apparent activation energy (~18 kJ/mol in the range 20-40°C, and ~39 kJ/mol in the range 40-60°C, respectively) indicates the same rate controlling reaction step, like in second period;

(e) the same behavior was observed when the oxidizing agents were used;

(f) the increase of the apparent activation energy for the third period, when the oxidizing agents were used, can be ascribed to the change of chemical reaction mechanism.

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