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LEACHING OF LOW-GRADE CHALCOCITE-COVELLITE-CHALCOPYRITE ORE WITH SULPHURIC ACID IN ABSENCE AND PRESENCE OF OXIDIZING AGENTS

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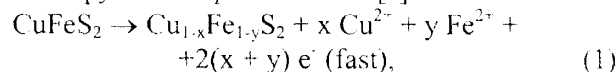*nbancila@univer.ubm.ro*

The leaching characteristics of low-grade chalcocite-covellite-chalcopyrite ore from the Cavnic Mine were investigated in sulphate media. The chemical composition of ore was: 0.37% Cu, 1.50% Zn, 2.00% Pb, 0.38 g/t Au, 45.70 g/t Ag, 7.52% Fe, 7.92% S and 53.40% SiO₂. During the experiments, the following parameters were modified: the leaching time, the leaching temperature and the quantity of ferric sulphate and of oxygen as oxidizing agents. 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
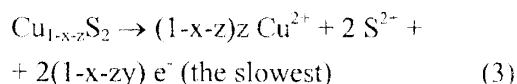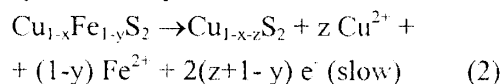
Introduction

In the last years there has been a renewed interest for copper recovery by processing the low-grade ores or complex ores with hydrometallurgical methods. The most common hydrometallurgical processes for copper recovery are based on the solubilization in sulphuric medium. The sulphate-based processes exhibits some potential advantages over the others systems because the leaching chemistry is generally simpler and better understood, and copper recovery by solvent extraction and electrowinning from sulphate medium is easier. The dissolution of copper from the low-grade chalcocite-covellite-chalcopiryte ore involves a complex mechanism.

The most studied copper mineral is chalcopyrite, which in sulphate medium leaches by a parabolic kinetic [1-3], caused by the progressive formation of a sulphur layer or other products at the external surface. It behaved as passivation layer. From the 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]:

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

where: $y \gg x$, $x + y \approx 1$

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

$$Cu_{1-x-z}S_2 \rightarrow (1-x-z)z\ Cu^{2+} + 2\ S^{2+} +$$
$$+ 2(1-x-zy)\ e^- \text{ (the slowest)} \quad (3)$$

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 $y \gg x$ and $x + y \approx 1$. In the second slow stage, the disulphide phase is further oxidizer to form copper polysulphide, $Cu_{1-x-z}S_2$, alternatively

Table 1 - The chemical composition of low-grade ore.

Element	Cu (%)	Pb (%)	Zn (%)	Au (g/t)	Ag (g/t)	Fe (%)	S (%)	SiO$_2$ (%)
Cavnic Mine Ore	0.37	1.50	2.00	0.38	45.70	7.52	7.92	53.40

Table 2 - The mineralogical composition of low-grade ore.

Element	Compounds	Mineralogical composition reported at ore	Mineralogical composition reported at element
Cu (%)	sulphates	0.003	0.80
	carbonates and oxides	0.013	3.49
	chalcocite and covellite	0.144	38.70
	chalcopyrite	0.212	56.98
Pb (%)	sulphates	0.140	9.33
	carbonates	0.110	7.33
	sulphides	1.010	67.33
	oxidic compounds	0.240	16.00
Zn (%)	sulphates	0.005	0.27
	carbonates and oxides	0.065	3.24
	silicates	0.080	3.98
	sulphides	1.855	93.49

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 was considered 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 that the rate is not limited by reactant/product diffusion through sulphur unless the sulphur melts during leaching when higher temperatures are used. The attempts to dissolve of chalcocite with acidic ferric sulphate solutions has proved that the process occurs in two stages [4-6]:

$$Cu_2S + 2\ Fe^{3+} = Cu^{2+} + CuS + 2\ Fe^{2+},$$
(4)

$$CuS + 2\ Fe^{3+} = Cu^{2+} + S + 2\ Fe^{2+}.$$
(5)
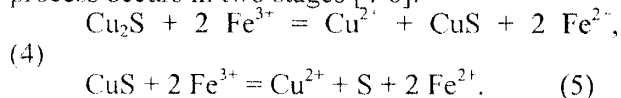
Afterwards, in presence of the ferric sulphate added to leaching of natural chalcocite the following sequence of reactions has been identified [7]:

$$5\ Cu_2S = 5\ Cu_{1.8}S + Cu^{2+} + 2\ e^-,$$
(6)

$$5\ Cu_{1.8}S = 5\ Cu_{1.2}S + 3\ Cu^{2+} + 6\ e^-,$$
(7)

$$5\ Cu_{1.2}S = 5\ S + 6\ Cu^{2+} + 12\ e^-$$
(8)
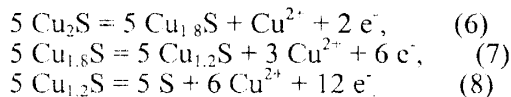
The intermediate product $Cu_{1.8}S$, digenite, was found to be rapidly formed. At 30°C and 48x65 mesh Cu_2S, particles were completely covered to $Cu_{1.8}S$ after 3.5 minutes in 0.03M ferric sulphate solutions. The final product at 30°C, and low ferric sulphate concentrations, was blue remaining covellite, $Cu_{1.2}S$, which leaches at a much slower rate. Normal covellite, CuS, was never observed as a product of reaction at 30°C. At higher temperature values (75°C) the final product was cupric ion.

The kinetics of synthetic covellite dissolution in aqueous acidic ferric sulphate solutions reveals a linear dependence of dissolved copper concentration upon the leaching time, with the exception of the initial induction period which was very short [8-10].

Experimental

The investigations were carried out by using samples of low-grade chalcocite-covellite-chalcopyrite ore obtained from the Cavnic Mine. The chemical and mineralogical composition of the investigated ore is given in table 1 and table 2, respectively.

The fraction 100-160 μm of low-grade ore was separated by screening and used for leaching. A solution of 8.0 N H_2SO_4 was used as leaching medium. Each leaching experiment was performed with 2 g low-grade ore and a ratio solid/liquid of 1/7.5. The low-grade chalcocite-covellite-chalcopyrite ore leaching experiments were carried out at various temperature values. 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 spectrophotometrical method using cuprizon as complexing agent.

Results and discussions

The leaching results of low-grade chalcocite-covellite-chalcopyrite ore, in the temperature range of 20-60°C, at atmospheric pressure, are presented in figure 1.
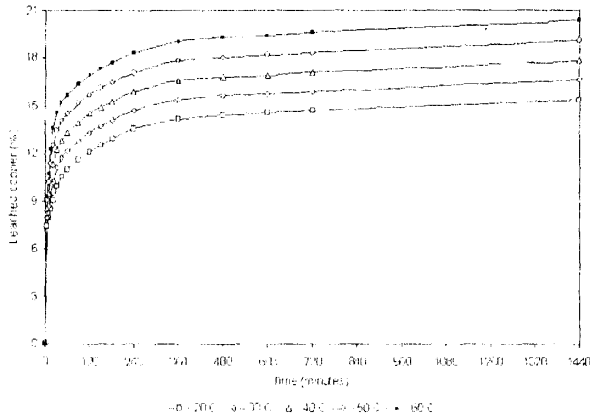

Fig. 1 - The low-grade chalcocite-covellite-chalcopyrite ore leaching curves as a function of time at different temperatures

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:

$$c_1 = k_1 t , \qquad (9)$$

where c_1 is the leached copper percent in time t (t ≤ 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:

$$c_2 = c - c_1 = k_2 \left(t - t_1 \right)^a , \qquad (10)$$

where c is the total leached copper percent in time t (in this case t ∈ [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).

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

$$c_3 = c - c_2 = k_3 \left(t - t_2 \right), \qquad (11)$$

where c is the total leached copper percent in time t (in this case t ≥ 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 low-grade chalcocite-covellite-chalcopyrite ore 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 low-grade chalcocite-covellite-chalcopyrite ore leaching curves are listed in table 4.

Accordingly, with the results represented in

Table 3 - The experimental data of low-grade chalcocite-covellite-chalcopyrite ore 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	c (%)	t (h)	c_3 (%)	t-t_2 (h)	k_3
7.42	0.083			10.00	0.50	0.90	0.167			14.10	6	0.62	2	
7.95	0.167	6.7		10.57	0.75	1.47	0.417			14.35	8	0.87	4	0.065
8.50	0.250			11.00	1.00	1.90	0.667	1.95	0.566	14.48	10	1.00	6	
9.10	0.333			11.51	1.50	2.41	1.167			14.61	12	1.13	8	
				11.88	2.00	2.78	1.667			15.33	24	1.85	20	
				12.30	2.50	3.20	2.167							
				12.75	3.00	3.65	2.667							
				13.48	4.00	4.38	3.667							

figure 1, the leaching of low-grade chalcocite-covellite-chalcopyrite ore in acidic media is characterized by an increase with temperature. The quantitative expression of the temperature influence can be obtained by the Arrhenius relation. The values of apparent activation energy, obtained from the slope of linear plots are presented in table 5.

To increase the copper dissolution from low-grade chalcocite-covellite-chalcopyrite ore 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 low-grade chalcocite-covellite-chalcopyrite ore was studied too.

The low-grade chalcocite-covellite-Table 6. The rate constants and apparent activation energies, for third period of low-grade chalcocite-covellite-chalcopyrite ore leaching.chalcopyrite ore leaching curves, with sulphuric acid using the

following conditions, are presented in figure 2: (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; (G) the addition of oxygen and ferric sulphate (30 g/l) at 60°C.

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 low-grade chalcocite-covellite-chalcopyrite ore leaching, with sulphate acid, in the presence of oxygen or oxygen and ferric sulphate (30 g/l), are presented in table 6.

Conclusions

The examination of the rate constants and

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	6.7	1.95	0.566	0.065
30	8.9	2.43	0.485	0.066
40	11.1	2.72	0.457	0.068
50	13.8	2.73	0.471	0.070
60	17.5	3.06	0.440	0.072

Table 5.The apparent activation energy

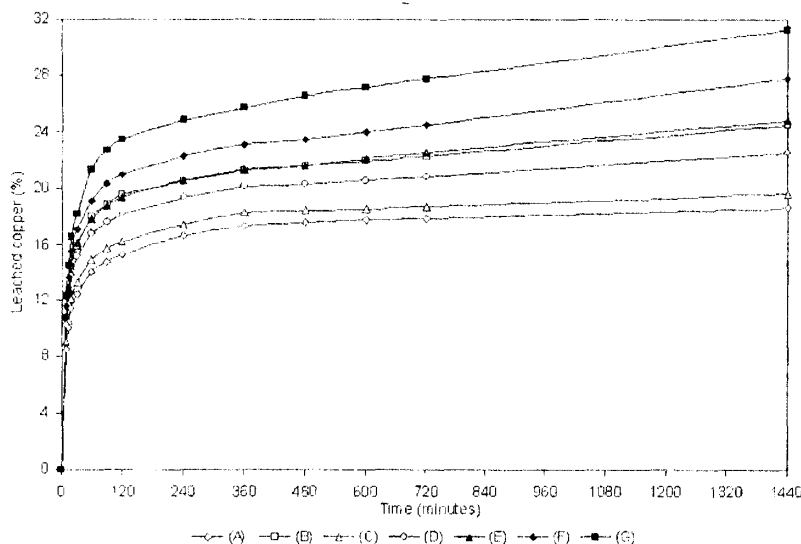| Period of leaching	Temperature range (°C)	E_a (kJ/mol)
I	20-60	19.0
II	20-60	8.3
III	20-60	2.1

Figure 2 - The low-grade chalcocite-covellite-chalcopyrite ore leaching curves, using oxidizing agents, as function of time

Table 6 - The rate constants and apparent activation energies, for third period of low-grade chalcocite-covellite-chalcopyrite ore leaching

Oxidizing used agents	Temperature (°C)	k_3 (%/h)	E_a (kJ/mol)
oxygen	40	0.069	
	60	0.182	42.0
oxygen and ferric sulphate (30 g/l)	40	0.077	
	60	0.300	58.9

apparent activation energy obtained values leads to the following conclusions:

According to the apparent activation energy (~19 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);

In the initial stage of dissolution, fast leaching rates have been observed due to dissolution of the fine portions of low-grade chalcocite-covellite-chalcopyrite ore, 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, and the values of the apparent activation energy (~8 kJ/mol) indicates the diffusion of reactants and products over the passivating layer (internal diffusion), as the rate controlling reaction step;

In the third period, the values of the apparent activation energy (~2 kJ/mol) indicates the same rate controlling reaction step, like in second period;

The increase of the apparent activation energy for the third period, when the oxidizing agents were used, can be ascribed to the change of mechanism. It is highly probable that the copper polysulphide layer can release copper ions (see eqs. (3), (6)-(7)) in the interaction with the oxidizing agents, and the chemical control is installed.

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