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LEACHING OF LOW-GRADE CHALCOCITE-COVELLITE-CHALCOPYRITE ORE WITH SULPHURIC ACID. THE INFLUENCE OF THE OXIDIZING AGENTS ON THE KINETICS OF COPPER LEACHING

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ABSTRACT. The leaching characteristics of low-grade chalcocite-covellite-chalcopyrite ore from the Cavnic Mine were investigated in sulphate medium. 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% SiO_2. 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]:

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

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

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

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 oxidizer 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 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]:

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

$$CuS + 2\,Fe^{3+} = Cu^{2+} + S + 2\,Fe^{2+}. \qquad (5)$$

Afterwards, in presence of the ferric sulphate added to leaching of natural chalcocite the following sequence of reactions has been identified [7]:

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

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

$$5\,Cu_{1.2}S = 5\,S + 6\,Cu^{2+} + 12\,e^-. \qquad (8)$$

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.

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

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.

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

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.

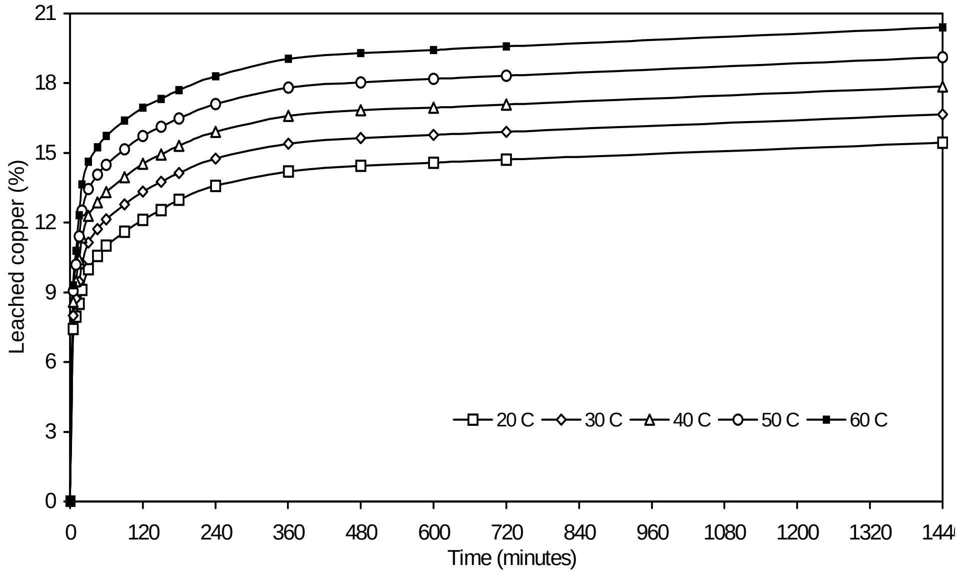

Fig. 1. The low-grade chalcocite-covellite-chalcopyrite ore leaching curves as a function of time at different temperatures.

The shape of the leaching curves indicates three periods of leaching. Making an analogy with the shrinking-core model for gas-solid noncatalytic reaction [11], the three rates - diffusion of reagents through the boundary layer, diffusion through the layer of product, and reactions at the interface of unreacted core – are observed. We were encouraged to use this shrinking-core model by the fact that particle size did not modify after the leaching process. By drying the remaining solid material and separation by screening, the same size (100-160 μm) has been obtained.

It is obvious that the initial stage of solubilization is characterized by linear kinetics. In this stage, the rate controlling reaction step is the external diffusion (the diffusion of reagents from the bulk solution to the particle surfaces). The change of the leached copper percent in this initial period could be described by the analytical expression:

$$\frac{t}{t_\infty} = 1 - (1 - x) = k_1 t \qquad (1)$$

where *t* is the leaching time (for this period $t \in 5 \div 30$ minutes), t_∞ represents the time for complete copper conversion if the process followed the same mechanism throughout, and *x* is the copper fractional recovery. The ratio $1/t_\infty = k_1$ represents the rate constant (time^{-1}).

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

$$\frac{t}{t_\infty} = 1 - 3(1-x)^{\frac{2}{3}} + 2(1-x) = k_2 t \qquad (2)$$

where *t* (for this period $t \in 45 \div 240$ minutes), t_∞ and *x* have the same signification as for the first stage. Now, the rate controlling reaction step is the internal diffusion through the product layer adherent to the original material.

The third period was characterized by the following analytical expression:

$$\frac{t}{t_\infty} = 1 - (1-x)^{\frac{1}{3}} = k_3 t \qquad (3)$$

where *t* (for third period $t \in 360 \div 1440$ minutes), t_∞ and *x* with the previous signification like on equations (1) and (2). In this stage, the rate controlling reaction step seems to be the chemical reactions.

The experimental data for all the three periods of low-grade ore leaching, with sulphuric acid at 20°C, are presented in table 3. The apparent rate constant has been obtained using a standard least-square method. The linear dependence described by eqs. (1)-(3) is quite good, with correlation coefficients of 0.9970, 0.9866 and 0.9880 respectively.

Table 3.

The experimental data of low-grade ore leaching with sulphuric acid at 20°C.

First period			Second period			Third period		
x	t min	$10^3 k_1$ min^{-1}	x	t min	$10^5 k_2$ min^{-1}	x	t min	$10^6 k_3$ min^{-1}
0.0742	5	1.05	0.1057	45	1.37	0.1420	360	4.12
0.0795	10		0.1100	60		0.1445	480	
0.0850	15		0.1161	90		0.1458	600	
0.0910	20		0.1212	120		0.1471	720	
0.1000	30		0.1254	150		0.1543	1440	
			0.1298	180				
			0.1358	240				

The values of the rate constants, obtained as function of leaching temperature, for low-grade chalcocite-covellite-chalcopyrite ore solubilization curves, are listed in table 4. As seen, important enhancement of rate constant is obtained within the first stage, and only small enhancement within the following two stages as temperature values was risen.

Table 4.

The values of the rate constants.

Temperature °C	10^3 k_1 min^{-1}	10^5 k_2 min^{-1}	10^6 k_3 min^{-1}
20	1.05	1.37	4.12
30	1.29	1.54	4.28
40	1.55	1.69	4.30
50	1.86	1.83	4.44
60	2.30	1.96	4.69

Linear Arrhenius relation can express the quantitative dependence on the temperature. From the linear plots the values of apparent activation energy were determined. They depend upon the period of leaching and are given in table 5.

Table 5

The apparent activation energy.

Period	Temperature range (°C)	E_a (kJ/mol)
I	20-60	15.7
II	20-60	7.2
III	20-60	2.4

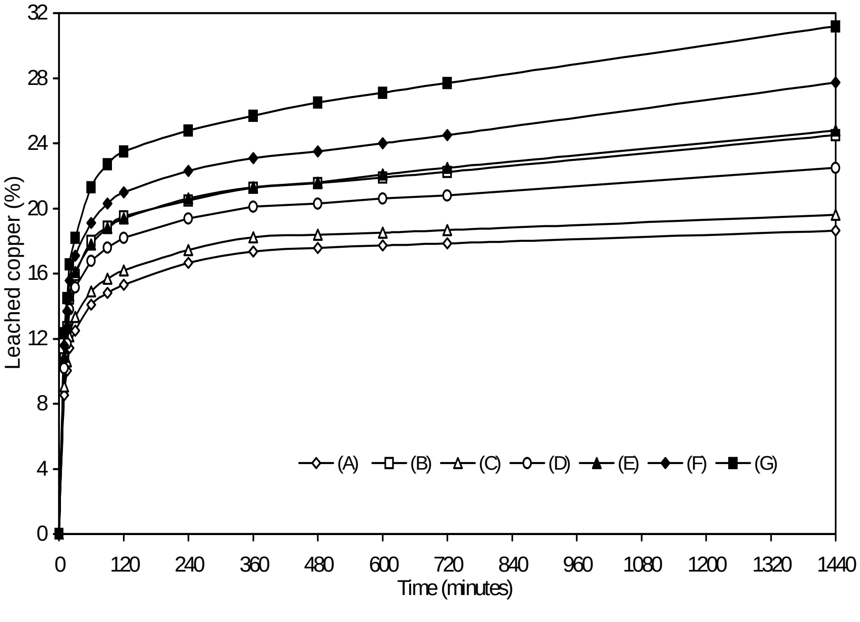

Fig. 2. The low-grade chalcocite-covellite-chalcopyrite ore leaching curves, using oxidizing agents, as function of time.

Table 6.

The R^2 values, for all of three oxidizing leaching period of the low-grade chalcocite-covellite-chalcopyrite ore.

Time range (minutes)	R^2								
	$k_1t = 1-(1-x)$		$k_2t = 1-3(1-x)^{\frac{2}{3}} + 2(1-x)$					$k_3t = 1-(1-x)^{\frac{1}{3}}$	
	10÷20	10÷30	30÷240	30÷360	60÷240	60÷360	60÷120	240÷1440	360÷1440
40°C, O_2	0.9991	0.9355	0.9061	0.9017	0.9824	0.9649	0.9937	0.8787	0.9928
40°C,O_2, Fe^{3+}	1.0000	0.9393	0.8902	0.8979	0.9651	0.9632	0.9861	0.9018	0.9996
60°C, O_2	0.9990	0.9392	0.8058	0.8254	0.9175	0.9374	0.9892	0.9917	0.9982
60°C, Fe^{3+}	0.9991	0.9391	0.8519	0.8552	0.9209	0.9295	0.9809	0.9978	0.9984
60°C, O_2, Fe^{3+}	0.9997	0.9402	0.7887	0.7944	0.8944	0.9107	0.9826	0.9950	0.9986

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 chalcopyrite concentrate was studied too. The low-grade chalcocite-covellite-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;and the addition of ferric sulphate (30 g/l) at 60°C; The data handling using the eqs. (1)-(3), in order to split the points into three periods, leads to the R^2 values presented in table 6. From these values it can be observed a decrease of second period leaching time at 60°C, when oxidizing agents are used.

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 7.

Table 7

The rate constants and apparent activation energies, for all of three oxidizing leaching period of the low-grade chalcocite-covellite-chalcopyrite ore.

Oxidizing agents	Period	Temperature °C	k min^{-1}	E_a kJ/mol
O_2	I	40	2.09×10^{-3}	10.6
		60	2.67×10^{-3}	
	II	40	1.58×10^{-5}	35.9
		60	3.62×10^{-5}	
	III	40	4.40×10^{-6}	45.9
		60	12.68×10^{-6}	
O_2 and Fe^{3+}	I	40	2.24×10^{-3}	13.8
		60	3.08×10^{-3}	
	II	40	1.68×10^{-5}	59.4
		60	6.62×10^{-5}	
	III	40	4.92×10^{-6}	64.2
		60	21.66×10^{-6}	

CONCLUSIONS

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

(a) According to the apparent activation energy (~16 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 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;

(c) The second period of leaching is much longer than the first, and the values of the apparent activation energy (~7 kJ/mol) indicates the diffusion of reactants and products over the passivating layer (internal diffusion), as the rate controlling reaction step;

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

(e) The increase of the apparent activation energy for the second and 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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