

НАФТОГАЗОПРОМИСЛОВЕ ОБЛАДНАННЯ

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MATHEMATIC MODELLING OF THE COPPER RECOVERY PROCESS FROM WASTEWATERS USING A GRAPHITE VOLUMIC ELECTRODE I. POLARISATION CURVES

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В статье анализируются основные параметры, что характеризуют электролитический процесс с порошковым катодом (зернистость частиц покрытия, форма текущего питателя и места, где он расположен) за формами кривых поляризации. Полученные экспериментальные данные показывают, что графитный порошок с зернистостью в диапазоне -0.2 ± 0.125 см имеет более однородные кривые поляризации

The paper analyses the influence of main parameters that characterized an electrolytic process with powder cathode (granularity of the bed's particles, the form of current feeder and the place where she is located and fluidization) on shapes of polarization curves.

The obtained experimental data show that graphite powders with granularity in range -0.2 ± 0.125 cm has the most uniform polarization curves

Introduction

Pollution on environment is a major problem, even for the countries indirectly confront with bad consequences of technological progress. That is why, the spill of wastewater coming from industrial plants and mining activities pose major problems because of environment contamination. The reglementations from 1986 of Clean Water Act (CWA) and Safe Drinking Water Act (SDWA), specify 13 metals, including Cu, Pb, Hg, as major pollutant of wastewater and set the maximum admitted limits of these at ppb level [1-3]. Often, the missing of performance technologies and efficient cleaning plants leads to high concentration of pollutant agents in wastewater, followed by ecological accidents. That is the reason for the advanced cleaning of wastewater becomes more and more important.

Utilization of electrochemical methods, especially of these based by volumic electrodes (tridimensional electrodes, 3D) represents an advantageous strategy.

Between the electrodes categories knotted as 3D electrodes [4], this paper presents the cathodes made by graphite powders and study the

parameters that influence the shape of polarization curves, that have a very important impact on electro-extraction efficiency.

Experimental

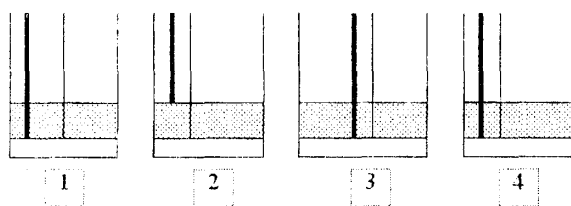
The experiments have been made using a glass electrolysis cell, by 25 cm high and 6 cm internal diameter, equipped with three electrodes (two work electrodes and one reference electrode).

The cathode were made by graphite powders with granularity in ranges -0.6 ± 0.4 cm ($206 \text{ cm}^2/\text{g}$ specific mass area) and -0.2 ± 0.125 cm ($1204 \text{ cm}^2/\text{g}$ specific mass area). A plastic sieve, located at 2 cm from electrolyte entrance orifice, to avoid "entrance hydrodynamic effect" [5] supported them. We can't use powders with lower granularity, although are strongly recommended by their higher specific mass area (over $1500 \text{ cm}^2/\text{g}$).

Theirs particles are easily flowed by the electrolyte and a part of them, because of collision with anode, are polarized and the copper from theirs surface are anodic dissolved. The other part, are evacuated with electrolyte and clogging the pipes. We try to agglomerate the particles using sedimentation and coagulation agents (acryl-



1. Type A of current feeder



2. Type B of current feeder

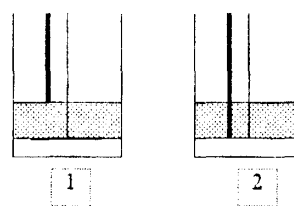


Figure 1 - The location of reference electrode in cathodic bed made by graphite powders; electric wire that polarised the current feeder; reference electrode

Table 1 - The circulation rates of electrolyte, v , and highs of fixed and fluidized beds, h_{exp} , for optimal volumic weight of each analyzed graphite powders granularity

Granularity	Fixed bed		Fluidized bed					
	v cm/s	h_{exp} cm	v cm/s	h_{exp} cm	v cm/s	h_{exp} cm	v cm/s	h_{exp} cm
-0.6+0.4 cm; $m_{optim} = 12 \text{ g (0.017 g/cm}^3\text{)**}$	2	3.8	2.3*	4.1	2.5	4.3	2.8	4.5
-0.2+0.125 cm; $m_{optim} = 8 \text{ g (0.011 g/cm}^3\text{)**}$	1	1.3	1.3	1.8	1.5*	2	1.8	2.6

* optimum fluidisation rate for each granularity;

** optimal volumic weight of cathodic bed

amide, aluminum sulfate). Because they are adsorbed on the surface of powder particles, insulate them, reduce the electrical conductivity of the cathodic bed and increase the energetic consumption of the process.

Polarization of cathodic bed were made using two type of current feeders, symbolized with A and B. The type A current feeder was an electrical wire, insulated around to electrolyte contact area to avoid the current losses in electrolyte. The type B current feeder, a sieve copper, played in the same time, the role of powder's support.

The anode, represented by 2 MoNiCr 175 stainless steel sieve, had a diameter about 4 cm.

We worked in potentiostatic conditions, assured by a Wenkin ST-72 potentiostat.

Reference electrode, made by a copper wire were inserted in a Lugging capillary and located in different areas of cathodic bed (Figure 1).

Was processing about 1.5 l waste electrolyte, coming from copper electro-extraction plant, with contains: 0.2 g/l Cu^{2+} , 0.12 g/l Zn^{2+} , tracers of Pb^{2+} , $\text{pH} = 2$. The circulation of electrolyte, from the bottom to the top of the cell, made with an S 16/50 liquid pump, was regulated to assure both fixed and fluidized bed regimes.

In Table 1 are presented the circulation rate of electrolyte for fixed and fluidized bed regimes for each optimal volumic weight of analyzed granularity [6].

Discussion of experimental results

In Figures 2-7 are represented the influences of applied polarisation, type of current feeder, position in bed of reference electrode and

hydrodynamic conditions on current density in cathodic bed, i_b , for each analysed granularity. A general view of these, show that, no matter of granularity, the values of i_b increase with applied polarisation, but the shape of curves depends by the size of particles. In case of graphite powders with large dimensions (-0.6+0.4 cm), the increases of i_b are slow and irregular, and that make difficult to observe the diffusion limiting current, i_L , and to choose the work polarisation. The irregular increases of i_b with applied polarisation are directly reflected in non-uniform discharge rate of Cu^{2+} on cathode, followed by negative consequences on recovery efficiency [6].

The increases of i_b in case of graphite powders with low dimensions (-0.2+0.125 cm) are uniform and their values are higher (Figures 3, 5). The plates that indicate the diffusion limiting current, i_L , are larger and more obviously.

The value of polarisation when the system reach diffusion limiting current, i_L , depends by the diameter of particles, implicitly correlated with their specific mass area: high value for the graphite powders with granularity in range -0.6+0.4 cm, and considerable lower for the graphite powder with fine granularity (-0.2+0,125 cm), as is present in Table 2 (Figures 2, 3).

Significant importance have the position of particles in cathodic bed and the type of current feeder. Using a type A current feeder and graphite powder in range -0.6+0.4 cm, the experimental data show important differences between i_b values recorded in different regions of the cathodic bed.

The most favoured particles, from the charge transfer point of view, are those located near to current feeder (position 3 for type A current feeder



and position 2 for type B of current feeder – Figure 1). This observation is supported by the higher values of i_b obtained in this area (Figures 2-5).

Table 2. Values of polarization to reach of diffusion limiting current, i_L , for analyzed graphite powders; type A current feeder; fixed bed regime; position 3 of electrode in cathodic bed (Figure 1).

Granularity	Value of polarization to reach diffusion limiting current, i_L
-0.6+0.4 cm	1480 mV
-0.2+0.125 cm	340 mV

The lower values of i_b recorded in the others areas of the cathodic bed, show an important current losses. These are favoured by the low specific mass area of the particles and by the high porosity of cathodic bed induced by the larger diameter of the graphite particles. From the charge transfer point of view, the most disadvantaged are the particles located to the top of the cathodic bed, directly contacted with electrolyte. There, the current losses are induced especially because of “edge effect” [7-9] (high difference between electrical conductivity of cathodic bed and electrolyte).

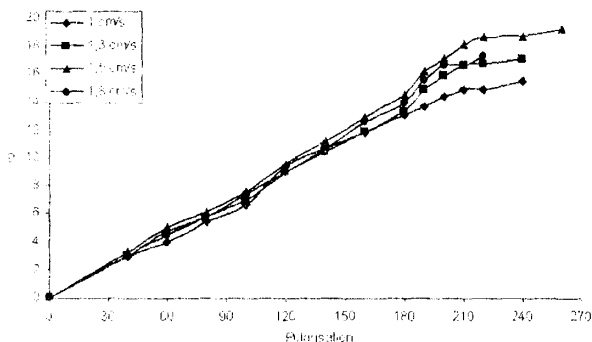


Figure 2. Variation of i_p ($\mu\text{A}/\text{cm}^2$) in different areas of the bed (Figure 1) vs. applied polarisation (mV); grafit powder with granularity in range -0.6+0.4 cm; type A of current feeder; fixed bed regime

Graphite powders directly contacted with current feeder will have only one polarisation on their surface, cathodic one in this case. In case of powders distanced by the current feeder, especially those from at the top of cathodic bed, the polarisation process is more complicate.

Whether inside of cathodic bed the electrical potential is almost constant, in solution, because of her non-homogeneity, appear a potential gradient that determined a double polarisation of the same particle (bipolar particle). On one side, the particle has an anodic polarisation and on the other side, a cathodic one. The two charges are mutual compensate and the whole particle is electrical neutral. On each polarised side of particle, takes place the specific electrochemical reaction. As long as the distance between the current feeder and

particles increases, the probability of existing the bipolar particles is higher, process reflected in low extraction efficiency [6].

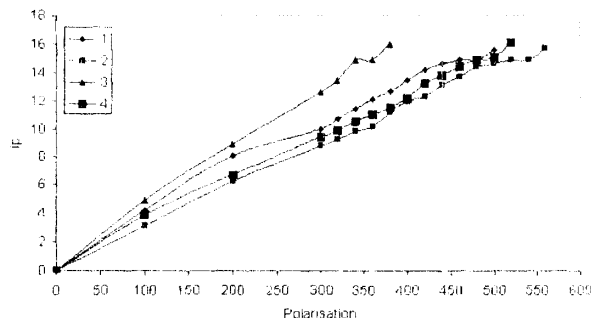


Figure 3. Variation of i_p ($\mu\text{A}/\text{cm}^2$) in different areas of the bed (Figure 1) vs. applied polarisation (mV); grafit powder with granularity in range -0.2+0.125 cm; type A of current feeder; fixed bed regime

We improve the charge transfer using a type B current feeder (Figures 4, 5). The shape of polarisation curves is regular, even in case of graphite powders with high granularity (Figure 4). Uniformity of current curves, determined by a uniformity of current field, is directly reflected in linearity of extraction curves [6]. On the other side, a uniform distribution of current field, because of type B current feeder, doesn't entirely compensate the high current losses that take place in cathodic bed with large granularity (-0.6+0.4 cm). We noticed high differences between the i_p values recorded in different areas of cathodic bed (Figure 4). These are smaller than the situation we used type A current feeder, and decrease as the granularity of powders is lower. As long as the dimensions of particles decrease, simultaneously with increase of their specific area, the structure of cathodic bed is closer to a continuous one. That is characterised by a high electrical conductivity and reduced current losses, reflected in closer values of i_b recorded in different areas of the cathodic bed. In case of -0.2+0.125 cm granularity, the polarisation curves are very closed one to another, even superposed (Figure 5), indicating the closer or identical values of i_b in different areas of the bed.

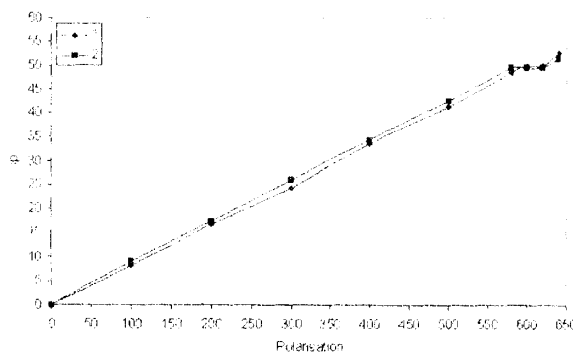


Figure 4 - Variation of i_p ($\mu\text{A}/\text{cm}^2$) in different areas of the bed (Figure 1) vs. applied polarisation (mV); grafit powder with granularity in range -0.6+0.4 cm; type B of current feeder; fixed bed regime



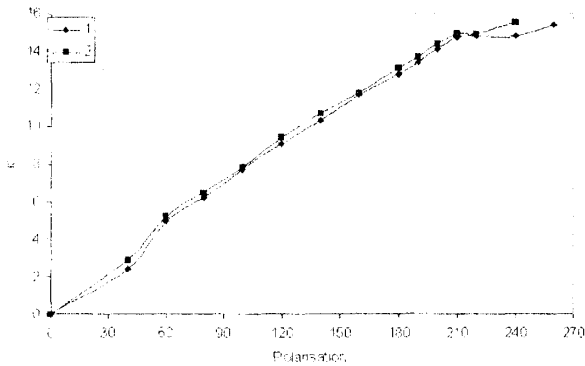


Figure 5 - Variation of i_p ($\mu\text{A}/\text{cm}^2$) in different areas of the bed (Figure 1) vs. applied polarisation (mV); grafit powder with granularity in range $-0.2+0.125$ cm; type B of current feeder; fixed bed regime

A detailed analysis of type and position of current feeder is very important from economical point of view. As the current losses are lower, the current fraction effectively used for Cu^{2+} extraction is higher and extraction and current efficiencies are higher.

The influence of homogeneity of current field spreads in fluidisation regime (Figures 6, 7). Increases of i_b are reducing in case of graphite powders with high dimensions and type A current feeder utilisation. Improvement of mass transfer coefficient with faster circulation of electrolyte doesn't compensate the current losses caused by the increase of bed's porosity. Favourable effect induced by the homogenous electric field provokes by the type B current feeder is expressed by an important increase of i_b , especially in case of fine granularity. High contacted area between the particles with granularity in range $-0.2+0.125$ cm, correlate with increase of active specie transport, compensate the current losses and allow more intensive fluidisation [6].

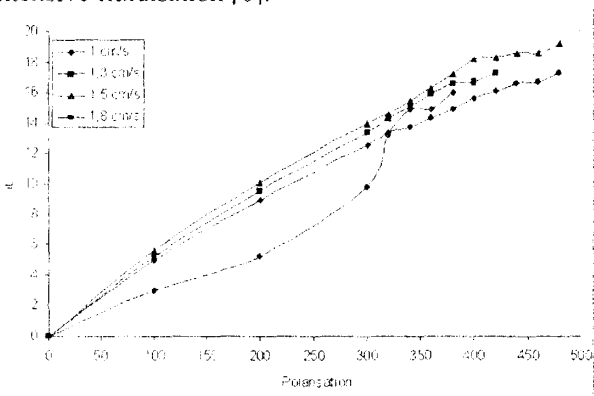


Figure 6 - Variation of i_p ($\mu\text{A}/\text{cm}^2$) vs. applied polarisation (mV) for different circulation rate of electrolyte; grafit powder with granularity in range $-0.2+0.125$ cm; type A of current feeder; position 3 of the electrode in bed (Figure 1)

Our experimental results concerning the diffusion limiting current, $i_{l,d}$, present a good agreement with aspects from others papers [10,

11]. Up to a specific circulation rate of the electrolyte, the value of $i_{l,d}$ rises because of improvement the charge transfer induced by increasing of collision frequency between particles and current feeder. Over that rate, at developed fluidization, large distances between particles reduce the collision frequency, reflected in slow charge transfer, increase the current losses in electrolyte correlate with low values of i_b .

Conclusions

Uniformity of polarization curves, correlate with low current losses in cathodic bed and high values of i_b obtained at 2 cm/s circulation rate of electrolyte (Table 1), recommends as optimum in copper recovery from dilute solution the graphite powders with granularity in range $-0.2+0.125$ cm. Experimental aspects support this conclusion. According to them [6], an electrolysis about 200 minutes at $0.014 \text{ mA}/\text{cm}^2$, with graphite powder cathode in range $-0.2+0.125$ cm leads, leads to an extraction efficiency of copper about 80%.

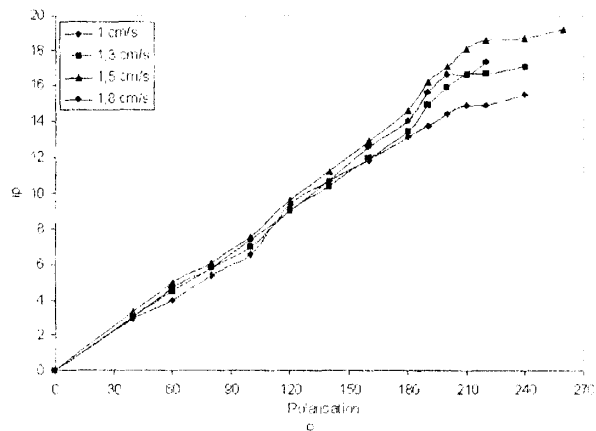


Figure 7 - Variation of i_p ($\mu\text{A}/\text{cm}^2$) vs. applied polarisation (mV) for different circulation rate of electrolyte; grafit powder with granularity in range $-0.2+0.125$ cm; type B of current feeder; position 2 of the electrode in bed (Figure 1)

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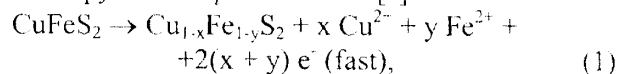
The leaching characteristics of low-grade chalcocite-covellite-chalcopyrite ore from the Cavnic Mine were investigated in sulphate media. The chemical composition of ore was: 0.37% Cu, 1.50% Zn, 2.00% Pb, 0.38 g/t Au, 45.70 g/t Ag, 7.52% Fe, 7.92% S and 53.40% SiO₂. During the experiments, the following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

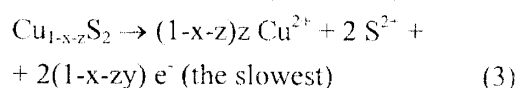
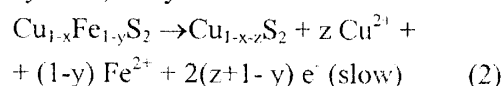
In the last years there has been a renewed interest for copper recovery by processing the low-grade ores or complex ores with hydrometallurgical methods. The most common hydrometallurgical processes for copper recovery are based on the solubilization in sulphuric medium. The sulphate-based processes 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-chalcopyrite 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]:



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



Within the fast initial period, the iron leaches preferentially as compared to copper. An intermediate disulphide phase is formed, $\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_2$, where $y \gg x$ and $x + y \approx 1$. In the second slow stage, the disulphide phase is further oxidizer to form copper polysulphide, $\text{Cu}_{1-x-z}\text{S}_2$, alternatively