MATHEMATIC MODELLING OF THE COPPER RECOVERY PROCESS USING A VOLUMIC ELECTRODE

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Abstract: 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.

Key words: Volumic electrode, recovery of copper, polarization curves

1. INTRODUCTION

Pollution on environment is a major problem, even for the countries indirectly confront with bad consequences of technological progress. The spill of wastewater coming from industrial plants and mining activities poses major problems because of environment contamination. 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 [1], 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.

2. 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 cm²/g specific mass area) and -0.2 + 0.125 cm (1204 cm²/g specific mass area). A plastic

sieve, located at 2 cm from electrolyte entrance orifice, to avoid "entrance hydrodynamic effect" [2] 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 coagulation agents (acryl-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 an electrical wire, insulated around to electrolyte contact area to avoid the current losses in electrolyte.

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).



Fig. 1. The location of electrodes in cathodic bed made by graphite powders;

electric wire that polarised the current feeder; ______ reference electrode. Was processing about 1.5 l waste electrolyte, with contains:0.2 g/l Cu²⁺, 0.12 g/l Zn²⁺, tracers of Pb²⁺, 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 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 [3].

Table 1. The circulation rates of electrolyte,	v, and highs of fixed	d and fluidized beds	, h _{exp} , for optimal
volumic weight of each analized graphite po	owders granularity		-

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

^{*} optimum fluidisation rate for each granularity; ** optimal volumic weight of cathodic bed.

3. RESULTS AND CONCLUSIONS

In Figures 2 - 4 are represented the influences of applied polarisation, position in bed of reference electrode and hydrodynamic conditions on current density in cathodic bed, i_b , for each analysed granularity.

A general view shows 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 also to choose the work polarisation.



Fig. 2. Variation of $i_p (\mu A/cm^2)$ in different areas of the bed vs. applied polarisation (mV); graphite in range -0.6+0.4 cm; fixed bed



Fig. 3. Variation of $i_p (\mu A/cm^2)$ in different areas of the bed vs. applied polarisation (mV); graphite in range -0.2+0.125 cm; fixed bed



Fig. 4. Variation of $i_p (\mu A/cm^2)$ vs. applied polarisation (mV) for different circulation rate of electrolyte; graphite in range -0.2+0.125 cm; position 3 of electrod

The irregular increases of i_b with applied polarisation are directly reflected in non-uniform discharge rate of Cu²⁺, followed by negative consequences on recovery efficiency [3]. 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). 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 has the position of particles in cathodic bed. For 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 – Fig. 1). 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. Considering the charge transfer, 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" [4-6] (high difference between electrical conductivity of cathodic bed and electrolyte).

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, appears an potential gradient that determined a double polarisation of the same particles (bipolar particles). On one side, the particles have an anodic polarisation and on the other side, a cathodic one. The two charges are mutual compensate and the particles are electrical neutral. On each polarised side of particles, 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 [3].

The influence of homogeneity of current field spreads in fluidisation regime (Figure 4). Increases of i_b are reducing in case of graphite powders with high dimensions. Improvement of mass transfer coefficient with faster circulation of electrolyte doesn't compensate the current losses caused by the increase of bed's porosity. 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 [3].

Our experimental results concerning the diffusion limiting current, i_L , present a good agreement with aspects from others papers [7, 8]. Up to a specific circulation rate of the electrolyte, the value of i_L , 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 .

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], after about 200 electrolysis minutes at 0.014 mA/cm², with graphite powder cathode in range -0.2+0.125 cm, leads to an extraction efficiency of copper about 80%.

5. REFERENCES

1.F. Goodridge şi A.R. Wright, "Porous Flow-Through and Fluidized Bed Electrodes", în *A Comprehensive Treatise of Electrochemistry*, J. O'M Bockris, B.E. Conway, E. Yeager şi R.E. White (eds.), vol. 6, Plenum Press, New York, (1981), 393.

2.G. Jinescu, "Procese hidrodinamice și utilaje specifice în industria chimică", Editura Didactică și Pedagogică, București, (1983).

3. A. Mihai – Recuperarea electrochimică a cuprului din ape de deversare, Teză de doctorat – Universitatea Babeş Bolyai – Cluj Napoca, 2000;

4. T. Huh. și J.W. Evans, J. Electrochem. Sci. Tech. 2 (1987) 308.

5. A.I. Masliy și N.P. Poddubny, J.Appl. Electrochem., 28 (1998) 589.

6. W.H. Smyrl, J. Electrochem. Soc., 1 (1989) 132.

7. F. Goodridge şi A. Wright, "Comprehensive Treatise of Electrochemistry", Y. Eager, J.O'M. Bockris, B.E. Conway and S. Sarangapari (eds.), vol. 6: "Electrodic Transport", Plenum Press, New York, (1983), 393.

8. T. Huh, J.W. Evans, J. Electrochem., 134 (1987) 308.