THE INTENSIFICATION OF COMPACT COPPER ELECTROWINNING PROCESS BY INCREASING VERTICAL CURRENT DENSITY AND DISTRIBUTION UNIFORMITY

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The process of compact copper electrowinning, which includes improving the anode construction and current mode and allows almost a two-fold increase in the working current density, was designed. It was shown that the use of an anode construction with a bottom horizontal part in a form of rectangular prongs allows the deposition of compact copper at a maximal current density of 5.7 A/dm^2, which is almost two times greater than that used in most industrial copper electrowinning processes. The specific power consumption for proposed compact copper electrowinning process with solution exhaustion for copper from 0.8 to 0.5 M at the average current density 4.74 A/dm^2 is 2.98 kW·h/kg. The corresponding value of specific power consumption is in the range of values obtained for electrowinning processes that are carried out without any additional measures for intensification. The appearance of obtained copper deposit is in a good agreement with modeling data of secondary current density distribution that confirms applicability of the proposed model for a cell with improved anode construction.

The achievement of uniform current distribution in industrial electrowinning cells is an important practical problem. Non-uniform current distribution leads to reduction of maximal applicable current density and productivity of electrowinning process. The working current density which is frequently used for compact copper electrowinning equals 3 A/dm^2 (for a Cu^{2+} concentration in the solution of 45 – 50 g/dm^3) [1]. In the case of higher current densities, there is an undesirable risk of local development of disperse and dendritic deposits over the entire cathodic surface because of non-uniform current density distribution.

Under production condition, the secondary current distribution, which depends not only on geometrical parameters of electrowinning cell but also on the cathode polarizability and conductivity of electrolyte, is commonly realized. The secondary current density distribution is more uniform compared to the primary one, while in the case of processes where the current efficiency is not dependent upon the current density, it is the same with metal distribution over the surface of cathode. There is a striking difference between the vertical and horizontal current density distribution in large-scale electrowinning cells with vertical plate parallel electrodes. The horizontal unconformity of current density distribution is realized in the form of edge effect (edge weakness), which is caused by a local increase in current on the cathode edges because of lateral current transfer through the space between electrode edges and side walls of the cell [2]. The technological methods that are commonly used for oppression of horizontal unconformity of current distribution are the following ones: electrode edge screening; optimization of electrode edges screens dimensions, electrolyte composition, correlation between cathode and anode widths. However, the most significant limiting factor for maximal working current density is unconformity of vertical current density distribution [3, 4]. The vertical unconformity of electric conductivity distribution of the solution and cathode polarization, which are the main reasons for the non-uniform current distribution in industrial electrowinning cells, can be caused by unconformity of fluid flow movement [4] and vertical stratification of gas filling within the interelectrode space [5, 6]. The intensive electrolyte overflowing through the cell, air sparging, sparging with oxygen which anodicaly evolves [3, 7, 8] was practically used for overcoming unconformity of vertical current distribution and intensification of

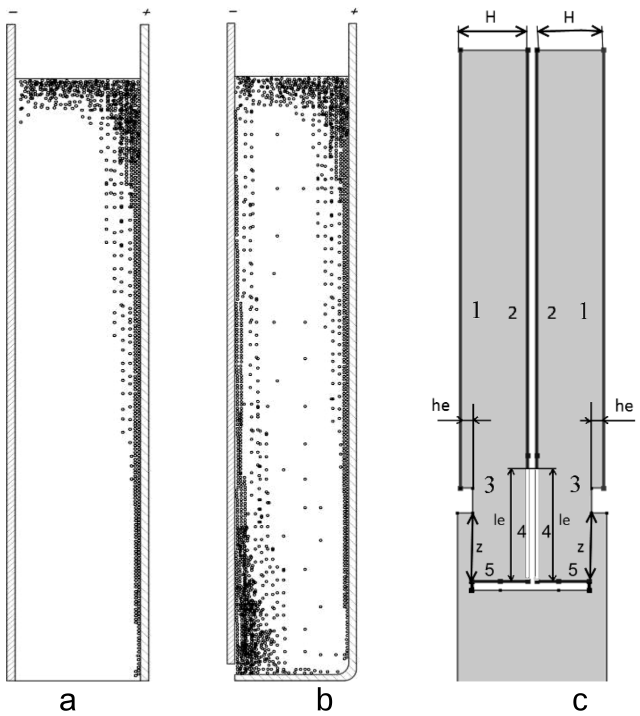


Fig. 1. Sectional view (longitudinal) of vertical copper electrowinning cell model: (a) – typical option; (b) – cell with modified anode construction; (c) – main elements of cell model with modified anode construction: 1 – exposed cathodic surfaces, 2, 5 – exposed anodic surfaces, 3 – cathodic screen, 4 – anodic screen.

electrowinning and refining processes. The sparging with oxygen which anodicaly evolves is the most promising way of copper electrowinning process intensification because of no additional material costs for the installation of compressor equipment and electricity for its operation.

According to literature data the profile of gas filling of the inter electrode space in electrowinning cells with vertical plate parallel electrodes may have a view shown in Fig. 1 a, while gas filling level may vary from 2 % at the bottom to 20 % at the top of cell [5].

In [7] the sparging with oxygen, which evolves on the auxiliary horizontal anode placed at the top of the cell, was proposed for intensification of copper refining process. To implement this method of sparging in electrowinning cells, the modification of anode construction by supplying a lower horizontal anode part edge under the cathode was proposed (fig. 1 b). Under certain circumstances the balancing of vertical distribution of gas filling and electric conductivity in the interelectrode space can be realized due to exploitation of enhanced anode construction. Moreover, the vertical balancing of distribution of mass-transfer coefficient through the intensification of the fluid motion in the near-cathode layer due to the upward movement of oxygen bubbles could takes place [3, 4].

Therefore, the use of the improved anode construction may enhance the uniformity of vertical distribution of current density to a significant extent due to oppression of its causes. But according to [2], if the anode length is much greater than that of cathode, the local increase of the current density will be observed at the edge thereof. The intensity of this edge effect will depend on the geometrical position of the anode bottom part with regard to the bottom part of the cathode.

Consequently, the aim of this study is optimization of the constructive elements of the cell in order to achieve uniform current density distribution and intensification of the compact copper electrowinning process from sulfate solution. For this purpose the modeling of secondary current distribution in the interelectrode space of electrowinning cell must be carried out.

Research мethodology

The calculation of distribution of potential and current density in the interelectrode space and distribution of current density at the surface of the electrodes was consisted in [9, 10] solving the differential Laplace equation with the given boundary conditions. In the general form the solution of this differential equation is generally described as functional dependence [10]:

$$i_{norm} = \frac{i_{lok}}{i} = f(KBa, KBk, \sum \frac{x_i}{y_i}), \qquad (1)$$

where, i_{lok} is the local current density, i is the average working current density, i_{norm} is the normalized current density; KBa, KBk is the Wagner number for anodic and cathodic processes, $\sum \frac{x_i}{y_i}$ is the set of geometric relationships of electrowinning cell parameters (the width and length of the electrodes, interelectrode distances, sizes of gaps between electrode edges and side walls of the cell). The software «COMSOL MULTIPHYSICS 4.3», which allows the computation of differential equations by the finite element method, was applied in this work. The above software integrated the multiphysical “Model of zinc electrowinning cell”, whose details are given in [10, 11] and which was hereby used as the basis for the “Model of copper electrochemical extraction adaptation”. In order to study specific effect which structural parameters of a cell may have on the current density distribution in 2D inter electrode space, the gas filling and solution composition have been considered as homogeneous, therefore conductivity of the solution in 2D inter electrode space has been considered isotropic by its character. The boundary conditions (modeling parameters) required for solving the Laplace differential equation are given in table.

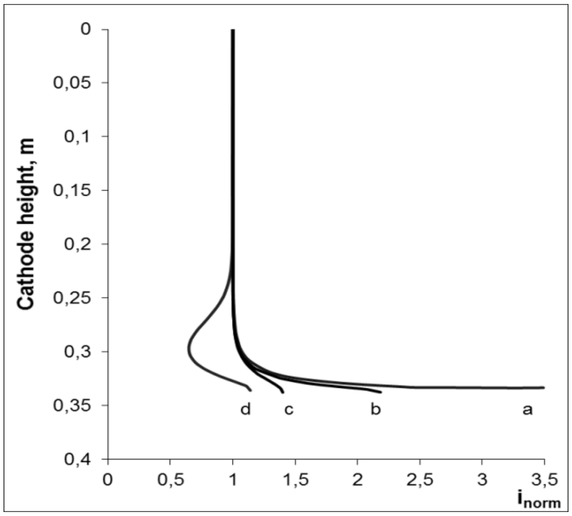
Table. Parameters (boundary conditions) for simulative modeling of secondary current distribution

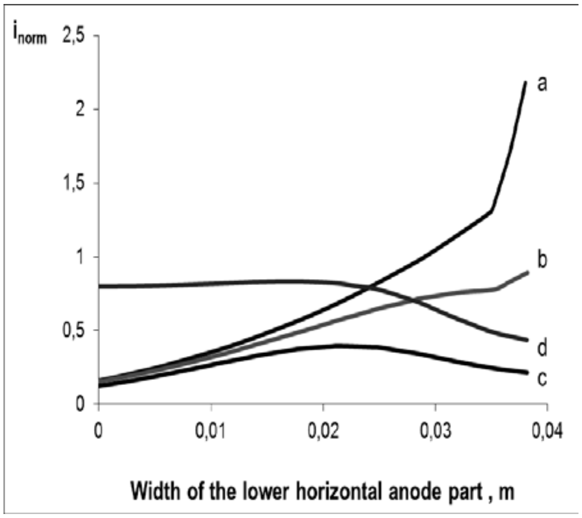
Solution composition, M		Electrode reactions	Kinetic equations	Kinetic and other physicochemical parameters of system
$CuSO_4$	H_2SO_4	cathode: $Cu^{2+} + 2e = Cu$	$i_{Cu^{2+}} = i_{0,Cu^{2+}} e^{\frac{2 \cdot \alpha_{K,Cu^{2+}} \cdot F \cdot \eta_{Cu^{2+}}}{R \cdot T}}$	The linear part of polarization curves in coordinates overvoltage (η) – ln(i) describes by following equation - η = -0.0359ln(i) – 0.1125; Exchange current density of copper reduction - $i_{0,Cu^{2+}}$ = 4.36·10^{-2} А/дм^2; Charge transfer coefficient $\alpha_{K,Cu^{2+}}$ =0.34; Exchange current density of anode oxygen evolution – i_{0,O_2} = 0.0089·10^{-2} А/дм^2 [10, 11]; Charge transfer coefficient – α_{K,O_2} = 0.4 [10, 11]; Electric conductivity of solution with corresponding composition is 12 См/м [12];
0.8	0.31	anode: $H_2O=2H^+ + 0,5O_2+ 2e$	$i_{O_2} = i_{0,O_2} e^{\frac{2 \cdot (1-\alpha_{K,O_2}) \cdot F \cdot \eta_{Cu^{2+}}}{R \cdot T}}$	

The study of effect which the anode with proposed construction (fig.1 b) may have on the value of the local current density i_{lok} within the area of vicinity of cathode edges and lower horizontal part of anode was carried out by variation of cathode screen thickness (he) (fig.1.c). The height of cathode screens (fig. 1 c, 3) was 5 mm, the height of anode screens (le) was 60 mm, the interelectrode distance H= 50 mm.

For the purpose of compact copper electrowinning test there was used a pilot plant consisting of Flex Kraft rectifier (nominal voltage 12V, ampere load 360A); rectangular 9,5 dm^3 electrowinning cell with cathode (15 dm^2 rectangular plate of X10CrNiTi18-9 steel) and anode (15,6 dm^2 lead plate) was applied. The electrowinning process was carried out with current mode described in [13].

Results and Discussion





Dimensions of electrowinning cell constructive elements (mm): thickness of the cathode screens (he) – no cathode screens (a); 5 (b), 20 (c), 10 (d); the lower vertical part of anode screened le = 60 mm (d); distance from cathode edge to the horizontal part of anode (z) – 10.

Fig.2. Normalized current density distribution graph (cathodic height along).

Fig. 3. Normalized current density distribution graph (within the bottom horizontal part).

With reference to simulation results it has been found that when using a proposed form of the anode, the edge effect within the area in the vicinity of the edge of cathode is of prominent character, i.e. normalized current density (i_{lok}) is about 3.5 times higher than the average value for a cathode (Fig. 2a). However, the i_{lok} at the edge of anode bottom horizontal part, which is responsible for the intensity of the oxygen evolution is about two times higher than the average value for anode (Fig. 3a). To reduce the edge effect intensity, the screening of the cathode lower edge was used. It was found (fig. 2 b, 2 c) that increasing the cathode screen thickness leads to reduction of the edge effect intensity. With increasing the screen thickness from 5 to 20 mm the normalized current density at the bottom edge of the cathode is reduced from 2.4 to 1.4. However, the excessive screen thickness (fig. 2 c) leads to distancing of oxygen flow from the cathode surface, and thus the intensity of oxygen evolution and intensity of mixing of solution will reduce. The above is confirmed by a decrease in the normalized current density at the edge of the emerging part of anode from 0.85 (Fig. 3b) to 0.4 (Fig. 3d).

As a result of simulative study it was found that significant inhibition of local current density increasing at the lower part of the cathode is made possible through additional screening of the anode bottom vertical part (fig. 2 d, 3 d).

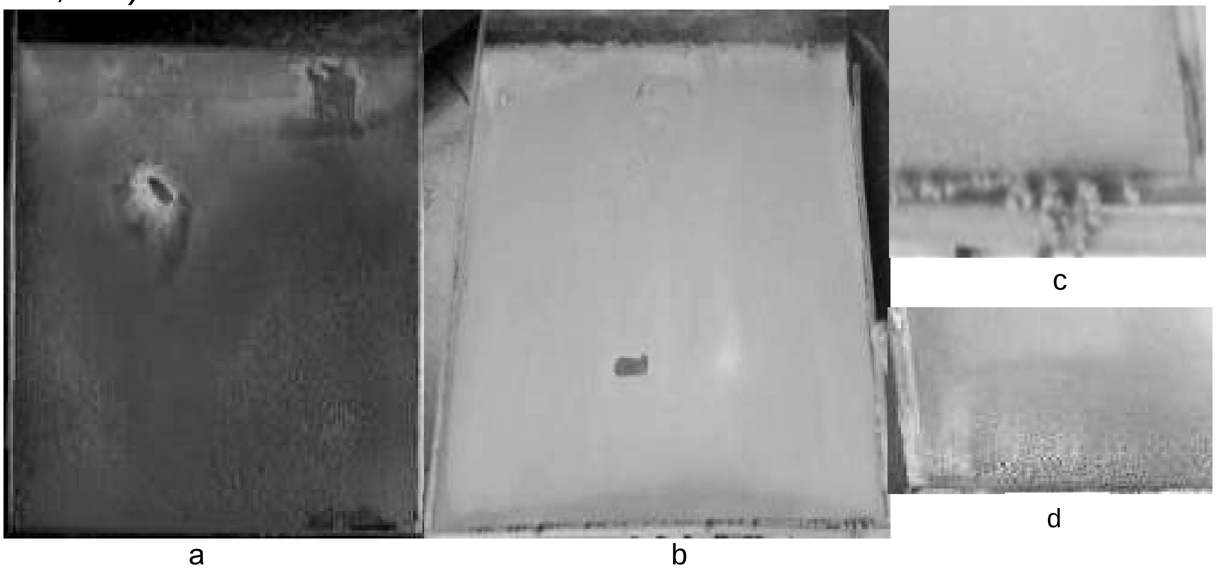


Fig.4. Cathodes with copper deposits (a, b) and fragments of the bottom deposits parts (c, d) obtained in an unimproved electrowinning cell (a), using the improved anode construction in the solution without additives (b, c) and with involving Fe^{3+}, Co^{2+} ions and gelatin mixture in the solution.

The electrowinning experiments performed in the semi-industrial cell with highly productive current mode, described in previous work [13], it has been found as follows. The rough sponge like deposits were obtained in a cell with plate parallel electrodes (fig. 1 a) at the average current density 4,7 A/dm^2, only at the top part of the cathode the compact copper appeared (fig. 4 a). The implementation of the modified anode construction (fig. 1 b) slightly improved the copper deposit quality in comparison with that using an unimproved anode. Namely, the width of compact copper area at the top part of cathode was increased almost two-fold and the deposit at the bottom part of the cathode became more compact.

For further enhancement of the obtained results, increasing the gas emission intensity by performing the horizontal bottom anode part in the form of rectangular prongs was proposed [14]. On the one hand, this will result in increased current density within the area in the vicinity of the edges of the horizontal bottom anode part. On the other hand, such sharp corners and edges prongs will intensify the oxygen evolution in these locations. The use of the anode with the prong-type construction of bottom horizontal part and the cathode with a screened bottom part (by a screen of 5x5 mm^2) allowed to significantly improve the cathode copper deposit quality (fig. 4, b). As shown in (Fig. 4 b) the slight edge effect as single dendrites and globular outgrowth is observed at the very bottom edge of the cathode. The measurement of cathode deposit upon removal from the cathodic plate showed that that it was the same both in the bottom and top parts thereof (about 200 μm). Such appearance of deposit (Fig. 4 b) is in a good agreement with modeling data of current density distribution (Fig. 2 b) and can confirm achievement of uniformity of vertical gas filling and electric conductivity distribution of the solution within the interelectrode space when using anode with a lower horizontal part in the form of rectangular prongs. Consequently, the proposed model of the secondary current density distribution may be applicable for the copper electrowinning cell with improved anode construction.

Substantial oppression of the negative influence of the edge effect at the bottom of the cathode (fig. 4 c) was achieved by involving Fe^{3+}, Co^{2+} ions and gelatin mixture in the hydrometallurgical solution [14]. The exhaustion of solution for copper from 0.8 to 0.5 M with obtaining quality compact copper deposits can be achieved at such basic technological parameters of the electrochemical extraction process: the average current density 4.74 A/ dm^2; maximal current density in the first stage (if the degree of extraction at each stage is 10%) 5.7 A/dm^2; current efficiency ~ 95%; the average cell voltage at 3.66 V; specific power consumption 2.98 kW·h / kg. Purity of obtained copper was 99.96 - 99.98%.

Conclusions

The comparison of results of the current density distribution simulative study with the results of electrowinning experiments allows a statement that improvement of cathode copper deposits quality is due to increasing the vertical uniformity of current density and metal distribution on the cathode surface. The above may be partly explained by achieving uniformity of vertical distribution of gas filling, solution composition and finally electric conductivity thereof.

The use of the improved anode construction with the lower horizontal part in the form of rectangular prongs has allowed compact copper deposition with values of the current density which are about twice as high as those the existing industrial electrowinning technologies can provide.

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