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Mathematical Modeling and Software for Calculating Regimes of Galvanic Wastewater Purification from Heavy and Nonferrous Metals in Devices with Flow-Through Three-Dimensional Electrodes

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Mathematical modeling and software for calculating regimes of galvanic wastewater purification from heavy and nonferrous metals in devices with flow-through three-dimensional electrodes

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***Abstract*—The paper briefly discusses progressive technologies of wastewater treatment from ions of heavy and nonferrous metals of industrial and small enterprises of urban agglomerations. An analysis of the efficiency of three-dimensional flow-through electrodes for wastewater treatment of harmful reagents is given. The mathematical models of electrochemical processes in three-dimensional flow-through electrodes as applied to extracting metals from solutions of galvanochemical industries are given. Using the developed program complex, a numerical solution of a scientific problem of practical importance has been obtained. A good correspondence between the results of calculations and experiments is shown.**

Keywords—mathematical modeling, software package, three-dimensional flow electrode, extraction of metals from galvanochemical solutions

I. INTRODUCTION

A new approach to the study of electrochemical processes in three-dimensional flowing electrodes as applied to the extraction of metals from solutions of galvanochemical production is to conduct computational experiments based on mathematical modeling and software package.

Galvano-chemical productions, with all their advantages, have a sufficient environmental hazard, which is mainly determined by the harmful impact of galvano-chemical effluents containing components of technological solutions on surface and ground water bodies, including in urban agglomerations. The exceeding of the maximum permissible concentrations (MPC) of metals in wastewater is caused by salvo discharges of electrolytes in electroplating plants. The problem of salvo discharges is caused by so-called "technical fatigue" of solutions. Such discharges lead to high water consumption, disruption of treatment facilities, a sharp increase in MPC in wastewater. The causes of deterioration of electrolytes are usually associated with the accumulation of inorganic and organic substances in them, including impurities introduced with reagents, products of electrode reactions. Conditioning of electrolytes, extraction of valuable components of electrolytes, their reuse is one of the possible ways to solve the problems of creating closed technological processes.

Until recently, in the treatment of galvanic and other wastewater the dominant direction was the treatment of the total effluent of galvanochemical production [1]. However, there are a number of publications showing that the creation of local solution processing systems gets the greatest application, as local cycles along with the solution of environmental problems provide the return of reagents and water, allowing the creation of low- and waste-free production [2,3].

II. METHODOLOGY

Among the known methods of creating local treatment systems for galvanic solutions a special place should be given to electrochemical methods of extraction of valuable components to return them into industrial cycles. Electrochemical methods satisfy the basic requirements to the processes developed for extraction of metals from solutions of galvanochemical productions: they do not require the use of reagents, the metal is obtained in the purest concentrated form and can in most cases be returned to production; the possibility of process automation is easily realized, water consumption is reduced, etc. [4–7].

One of the promising methods for solving this problem seems to be the use of apparatuses with flow-through three-dimensional electrodes (FTE) for extracting metals from solutions with low concentrations. The development of original technologies of electrodeposition of various metals based on the use of FTE is necessary for the intensification of electrochemical processes, especially in solutions with low

concentrations of electroactive components, which is achieved primarily through the use of cathode materials with a high reaction surface and the possibility of intense mass transfer in the electrode volume [4–7]. The solution of this problem is obviously promoted by the development of methods of mathematical modeling of processes in FTE and application of computational experiment. The use of mathematical modeling makes it possible to calculate and predict the results of the technological process, as well as to optimize the process by calculating the effective values of control parameters [4–6,8].

Let's assume that the flux of charged particles of the i-th grade N_i (i = 1, ..., n) in the electrolyte volume is determined by migration and convective components, which is realized in most electrochemical systems [9]:

$$N_i = z_i u_i F C_i \nabla E + C_i V. \quad (1)$$

Here z_i, C_i, u_i are, respectively, the charge, concentration and mobility of the i-th electroactive component in a pseudo-homogeneous medium; ∇E is the electric field potential gradient; V is the velocity vector of the convective transfer of the solution.

The current in the electrode-electrolyte volume is expressed by the formula:

$$j = F \Sigma(z_i N_i). \quad (2)$$

Material balance condition in the absence of a homogeneous electrochemical reaction:

$$\partial C_i / \partial t = -\nabla \bullet N_i. \quad (3)$$

Here $\nabla \bullet N_i$ is the divergence of the N_i flow.

Conversion of equations (1) – (3) using known rules of differential calculus, as well as the equation of the relationship between the change in concentration of the extractable component C_k with the partial current density j_{Sk} [10]

$$\partial C_k / \partial r = - S j_{Sk} / (|V| z_k F) \quad (4)$$

eventually leads to the following system of differential equations:

$$F \partial(\Sigma(z_k C_k) / \partial t = \nabla \bullet [-\kappa_s \kappa_l \nabla E / (\kappa_s + \kappa_t)] + S \Sigma j_{Sk}. \quad (5)$$

Here S is the reaction surface; j_{Sk} is the polarizing current density by k-component, κ_s, κ_l – conductivities of solid and liquid phases of the system. Together with natural boundary conditions:

$$[\partial E(t)/\partial n]_{\sigma c} = j(t)\rho_s, \ [\partial E(t)/\partial n]_{\sigma a} = j(t)\rho_l \quad (6)$$

$$[\partial E(t)/\partial n]_{\sigma i} = 0, \ [\partial E(t)/\partial n]_{\sigma e} = C_0. \quad (7)$$

Here n is the direction of the normal to the boundary of the reaction region, consisting of the surfaces of the cathode, anode, insulators and the electrolyte supply zone: $\sigma = \sigma_c + \sigma_a + \sigma_i + \sigma_e$; ρ_s, ρ_l are the specific resistance of the solid and liquid medium, respectively.

The system (5) – (7) makes it possible to calculate the distribution of potential, current density, and concentration of the electroactive substance in the volume of the porous electrode.

To carry out computational experiments, a software package was developed to simulate electrochemical processes in FTE. The software package is designed to calculate and analyze the parameters of the electrochemical process in the extraction of metals from electrolyte solutions on the flowing carbon fiber electrode. Type of computer: IBM PC-compatible. PC; OS: Windows XP/Vista/7/8/10. Programming language: Delphi, Object Pascal Software volume: 967 KB.

Input data for calculation are parameters of the deposited component (valence of ions, diffusion coefficient), concentration of ions of the deposited component in solution, solution flow rate, mass transfer coefficient, electrical conductivity of solid and liquid phases of the electrode-solution system, overall current density, electrode parameters (porosity, fiber radius, electrode thickness), electrolysis time.

The calculation results are: metal ion concentrations (calculation can be performed for one or two metal ions contained in the solution), distribution over the thickness (volume) of the electrode of its conductivity, metal mass, electrolyte flow rate, metal ion mass transfer coefficients, mass transfer coefficient for oxygen, potential, metal current profiles, oxygen current profile, hydrogen current profile, reduced metal current profile.

III. Results and Discussion

To illustrate the efficiency of the methods let's calculate co-deposition of gold and silver from thiourea sulfate solution with the following composition: H_2SO_4 – 0.5 mol/l, thiourea – 50 g/l, gold – 22.4 mg/l, silver – 141 mg/l (Fig. 1).

The studies were carried out with frontal (from the side of the counterelectrode) feeding of the solution into the electrode. In the first case, the electrode was composed of 12 layers of carbon fiber material (CFM) and 6 layers in the second case. The characteristics of the CFM (GDP-66-95): specific surface area is 255 cm^2/cm^3, specific electrical conductivity is 0.03 Sm/cm, and porosity is 0.95 [4–7]. The specific conductivity of the solution is 0.1 Sm/cm, the time of electrolysis is 60 min.

The experimental and calculated dependences presented in Fig. 1, as well as the consistency of the results of calculations of electrochemical functions of classical electrochemical theory allow us to conclude that the mathematical models and calculation algorithms described in this communication and in our other works [4–6] are effective for numerical studies and optimization of the control parameters of processes of metal ions extraction from industrial waste water to flowing threeedimensional electrodes for the purpose of decontaminating waste water. It should be noted that FTEs can be effectively used simultaneously for cathodic metal extraction and anodic oxidation of toxic electrolyte compounds in one electrolyser [4–7].

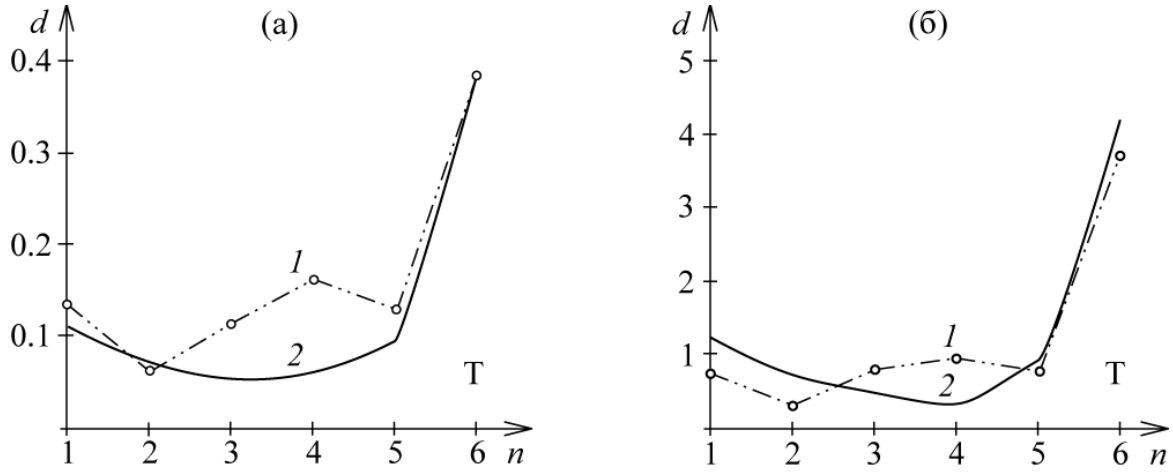

Fig. 1. Distribution of metal sludge over the thickness of the electrode: (a) – gold; (б) – silver; d – metal mass to CFM mass ratio; 1 – experiment; 2 – calculation; n – layer number; T – electrode back side; electrode thickness – 1 cm; current density – 0.2 A/m^2 , the solution flowrate – 0.56 cm/s

CONCLUSIONS

The application of mathematical modeling to study electrochemical processes in three-dimensional flowing electrodes in order to solve the problem of metal extraction from solutions of galvanochemical production, as well as the use of the developed software complex allowed to obtain a numerical solution of a scientific problem of practical importance. A good correspondence between the results of calculations and experiments is shown.

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