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Mathematical Modeling of Cathodic Zinc Electroextraction Processes

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Abstract. Numerical optimization techniques are widely used for solving applied problems in economics, as well as problems related to the optimization of production processes. In this paper, the Hooke-Jeeves method of direct search and numerical optimization are used to solve the problem of inverse kinetics and described the electrochemical processes for obtaining zinc powder during its leaching. Calculations are complicated by the presence of competitive processes leading to the release of zinc and hydrogen. These processes are interrelated through overvoltage at the electrode, which affects the rate of stepwise electrochemical reactions. The mathematical model of processes occurring at the electrode is governed by the Cauchy problem system. Contains relations of connections and nonnegativity constraints for the concentration of ions and molecules that participated in the reaction, as well as the rates of the electrochemical processes. The minimized functional is the sum of the squared deviations of the calculated weight of the precipitated zinc from the experimental weight at specific points in time. The initial conditions for the Cauchy problem are calculated based on the state of the system prior to the beginning of electrolysis. The calculations were verified by comparison with experimental data at time points that were not involved in the calculation of the minimized functional.

Keywords: Numerical optimization, electroextraction of zinc, heterogeneous processes.

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The continuous increase in the production of ferrous, non-ferrous and rare metals leads to the need to develop deposits with a low mineral content of minerals in the raw materials. Thus, we have to look for new methods of obtaining metal from depleted ores and waste metal. One of the methods under consideration is electroextraction. This process is used to obtain heavy nonferrous metals copper, bismuth, antimony, tin, lead, nickel, cobalt, cadmium and zinc with the lowest economic costs [1–3]. Due to the wide application of zinc for metal protection against corrosion, production of alloys and paints, use as a cementitious metal, electroextraction of zinc powder from an alkaline electrolyte has a great relevance. Electroextraction of metal powder, zinc in particular, from alkaline solutions enables rational utilization of ferrous and non-ferrous

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metallurgy and metal-working wastes reducing their hazard class. The work [4] shows the technology of powder waste processing for zinc production, and the study [5] reviews the influence of different conditions of electroextraction of zinc powders from alkaline electrolytes and reveals that there is no consensus among the authors on the influence of electrolysis conditions in terms of current yield and power consumption. It seems to be interesting to use zinc in hybrid batteries. Thus, [6] proposes a new method for creating zinc nitride hybrids as highly efficient multifunctional electrocatalysts for electrocatalysis and energy storage in Zn-air batteries. Hybrid batteries based on zinc deposition processes are also discussed in [7, 8]. When developing new and optimizing already known technologies, mathematical modeling allows to reduce the number of experiments by associating of external and internal parameters. Therefore, paper [9] presents computer modeling of Pd deposition in ethanol, calculations were performed using Vienna Ab-initio Simulation Package (version VASP 5.3.3). In the paper [10], a spatial model of the deposition of stabilized ibuprofen nanoparticles from the liquid phase is presented. Unfortunately, spatial models are quite difficult to implement and often require large computational resources. Herewith, models consisting of kinetic equations make it possible to carry out the primary analysis on the efficiency of the electrolyzer, single out the main processes and obtain individual parameters characterizing the system to solve models of higher dimensionality. Thus, if the values of rate constants of near-electrode processes are known, then the problem of predicting the precipitate yield is not particularly difficult and can be solved numerically by the Runge–Kutta method used to solve systems consisting of Cauchy problems. In paper [11], the second-order Runge–Kutta method is used to estimate transient modes of thermal reactor power. For most of the cases analyzed in this paper, the transient power values are comparable to those which calculated by other methods, and the relative deviations calculated in all cases were below the order of 10^{-2} . In the study [12], the Runge–Kutta–Felberg method was applied to investigate the effect of homogeneous-heterogeneous reactions on the surface of a rotating disk with solar heating when it is streamlined by a hybrid nanofluid. The Runge–Kutta method, in combination with other methods, can be used as part of a numerical algorithm for calculating more complex problems. When reaction rate constants are unknown, inverse problems often arise, which can sometimes be reduced to optimization problems, for example, for chemical reactors [13–16] and chemical kinetics problems in gases [17]. In this study, the inverse problem is solved when the rate constants are unknown and the mass of the precipitated metallic powder at certain time points is given. This problem is formulated and solved using the example of obtaining zinc powder during the electrolysis of sodium hydroxide solution containing sodium tetrahydroxocincate. To solve this task, an algorithm has been developed based on the Runge–Kutta method for solving a system of kinetic equations and the Hook–Jeeves direct search method with imposed constraint checking conditions for finding the rate constants of kinetic processes. The algorithm proposed by the authors, in contrast to the known statistical methods, such as regression models and interpolation methods, provides an opportunity to determine the predicted zinc mass values for a smaller number of experiments not simply in the form of a functional dependence with fitting coefficients, but directly estimate the contributions of electrochemical processes, single out limiting processes, obtain boundary conditions for the equations that calculate the concentrations of electrolyte components in the volume, directly relying on the theory of electrochemical processes.

1. Statement of the problem in mathematical terms

When leaching ores containing zinc, depending on the concentration of sodium oxide in the solution, the zinc in the electrolyte may be contained both as zinc oxide ZnO , and compound

$[Zn(OH)_4]^{(2-)}$. As shown in the paper [18], a 20% concentration of sodium hydroxide solution $NaOH$ was sufficient to make the molar ratio of the hydroxyl group OH^- ions to the contained zinc Zn sufficient for the existence of $[Zn(OH)_4]^{(2-)}$. In addition, if the concentration of the hydroxyl group $OH^{(-)}$ ions is low, then the compound $[Zn(OH)_4]^{(2-)}$ is go over zinc oxide ZnO . Thus, we describe the leaching process of zinc-containing ore as a general dissolution reaction of the form $2NaOH + Zn + 2H_2O \rightarrow Na_2[Zn(OH)_4] + H_2$.

Let us consider the processes of electrolysis at constant current between flat parallel electrodes in alkaline sodium hydroxide electrolyte containing sodium tetrahydroxocincate. The mathematical model of the charge transfer process in the interelectrode space takes into account the following features of the electrolysis of alkaline solutions and zinc electroextraction processes:

1) When the dimensions of the electrodes are larger than the interelectrode space, the resulting electric field can be considered potential and homogeneous along the electrode.

2) Sodium hydroxide is a strong base, so, neglecting the non-ideality of solutions, we can assume that $NaOH$ completely dissociates into ions $NaOH \rightarrow Na^+ + OH^-$, thus, in alkaline solutions, due to the very low concentration of hydrogen ions and the activity of hydroxonium ions H_3O^+ , the current transfer is carried out by ions Na^+ and hydroxyls OH^- .

3) Since the water dissociation constant is very small, the ionic product is small and the concentration of water can be considered constant.

4) $Na_2[Zn(OH)_4]$ in the electrolyte completely dissociates into ions $Na_2[Zn(OH)_4] \rightarrow 2Na^+ + [Zn(OH)_4]^{2-}$. This is true if the concentration of sodium hydroxide in the solution is higher than 20%.

Thus, the mathematical model will include the following equations::

1) Transfer equation (diffusion migration) for charged particles:

$$\frac{\partial C_{OH^-}}{\partial t} + \frac{\partial}{\partial x} \left(-D_{OH^-} \frac{\partial C_{OH^-}}{\partial x} - U_{OH^-} C_{OH^-} \frac{\partial \varphi}{\partial x} \right) = RC_{H_2O} \quad (1)$$

$$\frac{\partial C_{H^+}}{\partial t} + \frac{\partial}{\partial x} \left(-D_{H^+} \frac{\partial C_{H^+}}{\partial x} + U_{H^+} C_{H^+} \frac{\partial \varphi}{\partial x} \right) = RC_{H_2O} \quad (2)$$

$$\frac{\partial C_{Na^+}}{\partial t} + \frac{\partial}{\partial x} \left(-D_{Na^+} \frac{\partial C_{Na^+}}{\partial x} + U_{Na^+} C_{Na^+} \frac{\partial \varphi}{\partial x} \right) = 0 \quad (3)$$

$$\frac{\partial C_{[Zn(OH)_4]^{2-}}}{\partial t} + \frac{\partial}{\partial x} \left(-D_{[Zn(OH)_4]^{2-}} \frac{\partial C_{[Zn(OH)_4]^{2-}}}{\partial x} - U_{[Zn(OH)_4]^{2-}} C_{[Zn(OH)_4]^{2-}} \frac{\partial \varphi}{\partial x} \right) = 0, \quad (4)$$

where C_{OH^-} , C_{H^+} , C_{Na^+} , $C_{[Zn(OH)_4]^{2-}}$ are the concentrations of hydroxyl group ions, hydrogen ions, sodium ions and tetrahydroxozintkat ion, respectively, D_{OH^-} , D_{H^+} , D_{Na^+} , $D_{[Zn(OH)_4]^{2-}}$ are the diffusions of the corresponding ions,, φ is the electric field voltage, R is the constant of water decomposition rate, U_{OH^-} , U_{H^+} , U_{Na^+} , $U_{[Zn(OH)_4]^{2-}}$ are the mobility of these ions. The mobility of the hydroxyl is understood here as its average velocity at the electric field strength of 1 V/m.

Due to the fact that the water decomposition constant is small, the right side of equations (1), (2) is often zeroed out, and equations in most works are given as Nernst–Planck equations for charged particles. In addition, since the ionic product of water is constant under constant conditions, equation (2) can be replaced by the following relation:

$$K_W = C_{H^+} C_{OH^-}. \quad (5)$$

2) Poisson's equation

$$\frac{\partial}{\partial x} \left(-\varepsilon \varepsilon_0 \frac{d\varphi}{dx} \right) = F (C_{H^+} + C_{Na^+} - C_{OH^-} - C_{[Zn(OH)_4]^{2-}}), \quad (6)$$

where $\varepsilon = 1 + \chi$ is a medium permittivity which considers the polarization of medium and depends on the frequency of applied voltage, χ is a medium dielectric susceptibility, ε_0 is a dielectric constant.

When setting boundary conditions for solving the system of equations (1), (2), (4), (5), (6), it is required the knowledge of processes occurring on the electrode surface, in our case we will consider the electrodes to be inert. So, for the Poisson's equation (6), there are considered the boundary conditions of the first kind: $\varphi_l = E_{0l} + E_l$, where E_{0l} is the standard electrode potential of reaction at the electrode l , $l = \{a \text{ is the anode, } s \text{ is the cathode}\}$, at the same time, the value E_{0l} determined for the total reaction taking place at the electrode.

$$E_l = \left| \frac{\beta RT}{nF} \right| \ln \prod C_i^{\nu_j}, \quad (7)$$

where $C_i^{\nu_j}$ is the concentration of the j -th component involved in the electrode reactions at this electrode, ν_j is the stoichiometric coefficient ($\nu_j > 0$ is for oxidation, $\nu_j < 0$ is for recovery). Here, E_0 is the standard electrode potential of the reaction, but it can shift in the case of parallel reactions, thus, in the paper [19], it was noted that, for many systems, the electrode potential of the cathodic metal deposition reaction may be more negative than the one of the reversible hydrogen electrode due to polarization. The concentration of charged particles will depend on the rates of heterogeneous processes described by stage reactions. So, for example:

1) Sodium ions on the electrodes are not discharged, accumulating the concentration in the cathode space and reducing it in the anode space over time.

2) Simultaneously, at the cathode, it is released hydrogen: $2H_2O + 2e \rightarrow H_2 + OH^-$, $E_0 = -0.28V$, and zinc: $[Zn(OH)_4]^{2-} + 2e \rightarrow Zn + 4OH^-$, $E_0 = -1.216V$, in the following stepwise reactions $[Zn(OH)_4]^{2-} + 2e \xrightarrow{R_1} Zn^{2+} + 4OH^-$, $Zn^{2+} + 2e \xrightarrow{R_2} Zn$, $H_2O \xrightarrow{R_3} H^+ + OH^-$, $H^+ + OH^- \xrightarrow{R_4} H_2O$, $H^+ + e \xrightarrow{R_5} H$, $H + H \xrightarrow{R_6} H_2$.

3) At the anode, oxygen in alkaline electrolytes is released according to the following scheme of electrochemical reactions: $H_2O \xrightarrow{R_1} H^+ + OH^-$, $H^+ + OH^- \xrightarrow{R_2} H_2O$, $2OH^- + 2e \xrightarrow{R_3} H_2O + O$, $O + O \xrightarrow{R_4} O_2$.

Thus, in order to find boundary conditions for the transfer equations for particles reacting on the electrodes, it is necessary to know the rates of the stepwise processes that affect their concentration. Modeling of heterogeneous processes represents a separate type of problems, where the rate constant is determined by the characteristics of the heterogeneous system being modeled: the size of the electrodes or maybe the reacting surface area, which depends on the roughness of the electrode surface and its homogeneity, so even a small percentage of impurity can change their mechanism of course, as well as the electrolyte composition, the hydrogen ion exponent value. In this paper, the authors proposed a method that allows to find rate constants of stepwise processes, as well as to predict the yield of the substance according to the available small number of experimental yield data. Let us consider it on the example of cathodic reactions of zinc extraction with parallel hydrogen yield. When writing down the system of kinetic equations, we make the following assumptions:

First, despite the fact that these competitive reactions are not directly related, the rates of the stepwise reactions depend exponentially on the overvoltage at the electrodes (7), which in

our case, at the cathode, is

$$E_l = \frac{\beta RT}{nF} \ln \frac{C_{H^+} C_{Zn^{2+}}}{C_H C_{Zn}}. \quad (8)$$

Secondly, the structure of the metallic precipitate is determined by a number of factors, such as solution composition, presence of impurities in it, surface pretreatment, current density, etc. The works [20–22] noted the spongy and porous nature of the deposited zinc coating. Therefore, we use the porous film approximation to model zinc deposition. In the case of a porous film, it is assumed that it does not resist the reagent approaching the interface and does not affect the reaction rate; in the case of a non-porous film, the boundary layer resistance can be neglected, considering the resistance of the emitted product layer as main. Moreover, if the process is controlled by diffusion through the boundary layer, the process rate is $\omega = \frac{D}{\delta} SC$, where δ is the product layer thickness, S is the working electrode area. The thickness of the product layer in the approximation of the solution of the Yander equation can be considered proportional to time: $\frac{\partial \delta}{\partial t} = K/t$ and $\delta^2 = 2Kt$.

Third, the water association process $H_2O \xrightarrow{R_3} H^+ + OH^-$ is not taken into account in this model, since our calculations and analysis of the rates of stepwise reactions in predicting the cathodic yield of hydrogen in the electrolysis of alkaline electrolyte in [23] showed very little difference from zero in the value of the rate constant of this process. In this way, the mathematical model consists of a system describing electrochemical stepwise cathodic reactions:

$$\left\{ \begin{array}{l} \partial C_{H_2O} / \partial t = -R_3 C_{H_2O}, \\ \partial C_{H^+} / \partial t = R_3 C_{H_2O} - R_5 C_{Zn} C_H C_{H^+} / (C_{Zn^{2+}} + C_{H^+}), \\ \partial C_H / \partial t = R_5 C_{Zn} C_H C_{H^+} / (C_{Zn^{2+}} + C_{H^+}) - R_6 C_H C_H, \\ \partial C_{H_2} / \partial t = R_6 C_H C_H, \\ \frac{\partial C_{[Zn(OH)_4]^{2-}}}{\partial t} = \frac{D_{[Zn(OH)_4]^{2-}} (C_{[Zn(OH)_4]^{2-}} - C_0) R_7}{2Kt} - \frac{R_1 C_{Zn} C_H C_{[Zn(OH)_4]^{2-}}}{C_{Zn^{2+}} + C_{H^+}}, \\ \partial C_{Zn^{2+}} / \partial t = R_1 C_{Zn} C_H C_{[Zn(OH)_4]^{2-}} / (C_{Zn^{2+}} + C_{H^+}) - R_2 C_{Zn^{2+}}, \\ \partial C_{Zn} / \partial t = R_2 C_{Zn^{2+}}. \end{array} \right. \quad (9)$$

Here, $D_{[Zn(OH)_4]^{2-}}$ is the diffusion of tetrahydroxozincate ions through the porous film of the precipitate, C_0 is the concentration of these ions in the volume of the electrolyte.

This notation of the kinetic equations described by Cauchy problems implies that the rate constants of the reactions $k_i \geq 0, i = 1, \dots, 7$, factor of proportionality $K \geq 0$, and concentration values $C_j \geq 0, j = \{H_2O, Zn, H, Zn^{2+}, C_{H^+}, H_2, C_{[Zn(OH)_4]^{2-}}\}$ are positive. In order to calculate the mass of precipitated zinc residuas, it is considered zinc concentration and film volume:

$$M_{Zn} = 65,38 * C_{Zn} S \sqrt{2KT}, \quad (10)$$

where T is the final calculation time.

When selecting initial approximations for the rates of near-electrode process constants, the initial approximation of reaction rates is chosen on the basis of the ratio between the rates of stepwise reactions, stoichiometric numbers, and the rate of the limiting reaction. In addition, in the case of presence of two competitive chains of cathodic reactions, one of which proceeds with the release of a solid phase, there are observed more complex kinetic regularities, and, consequently, the initial approximations for the rate constants calculated in this way have a larger error. Initial values for the concentrations of charged particles are calculated considering

the assumptions made earlier for the state of the system before applying voltage to the electrodes. The solution of the problem to find the rate constants of the cathodic electrochemical processes and to predict the yield is based on the minimization of the functional:

$$\sum_{l=1}^n \sum_{\nu=1}^m \left(C_{l,\nu}^{experiments} - C_{l,\nu}^{calculation} \right)^2. \quad (11)$$

Here l is responsible for summation over time, while ν responsible for summation over substances which concentrations are known from experiments at certain points in time T_l , $l = 1, \dots, n$. Ideally, it is desirable to have data for both hydrogen and the mass of the precipitate, but this is usually the mass of the precipitate at several time points, and the functional takes the form

$$M(K, R_1, \dots, R_7) = \sum_{l=1}^n \left(M_{Zn,l}^{experiments} - M_{Zn,l}^{calculation} \right)^2. \quad (12)$$

2. Numerical algorithm for the study of cathodic processes

This study shows the application of the numerical optimization method to the solution of the inverse problem arising when predicting the substance yield in the solid phase by current in the case of two parallel cathodic reactions which are not directly related, using zinc deposition with attendant hydrogen release as an example. The proposed algorithm is based on the method of direct search for numerical optimization, supplemented by constraint checking, and the Runge–Kutta method used to solve the kinetic system of equations describing stepwise electrochemical reactions.

This algorithm relies on the calculation of values of the functional (11) which should be minimize. The value of this functional is calculated by numerical solution of the system of kinetic equations (9) by the Runge–Kutta method of fourth order and relation (10). From the family of explicit fourth-order Runge–Kutta methods, it was chosen a method called the classic fourth-order Runge–Kutta method was. The fourth-order accuracy is generally sufficient to match the accuracy of experimental data acquisition. In order to describe its implementation for this problem, let us introduce the following notations:

$$\vec{U}(t) = (C_{H_2O}, C_{H^+}, C_H, C_{H_2}, C_{[Zn(OH)_4]^{2-}}, C_{Zn^{2+}}, C_{Zn})^T,$$

$$\vec{R} = (R_1, R_2, R_3, R_5, R_6, R_7, K),$$

$$\vec{F}(t, \vec{R}, \vec{U}) =$$

$$= (f_1(t, \vec{R}, \vec{U}), f_2(t, \vec{R}, \vec{U}), f_3(t, \vec{R}, \vec{U}), f_4(t, \vec{R}, \vec{U}), f_5(t, \vec{R}, \vec{U}), f_6(t, \vec{R}, \vec{U}), f_7(t, \vec{R}, \vec{U}))^T.$$

Here $(\bullet)^T$ is a transposition operation, and functions $f_1(t, \vec{R}, \vec{U})$, $f_2(t, \vec{R}, \vec{U})$, $f_3(t, \vec{R}, \vec{U})$, $f_4(t, \vec{R}, \vec{U})$, $f_5(t, \vec{R}, \vec{U})$, $f_6(t, \vec{R}, \vec{U})$, $f_7(t, \vec{R}, \vec{U})$ correspond to the right-hand sides of system (9):

$$f_1(t, \vec{R}, \vec{U}) = -R_3 C_{H_2O},$$

$$f_2(t, \vec{R}, \vec{U}) = R_3 C_{H_2O} - R_5 C_{Zn} C_H C_{H^+} / (C_{Zn^{2+}} C_{H^+}),$$

$$f_3(t, \vec{R}, \vec{U}) = R_5 C_{Zn} C_H C_{H^+} / (C_{Zn^{2+}} C_{H^+}) - R_6 C_H C_H,$$

$$f_4(t, \vec{R}, \vec{U}) = R_6 C_H C_H,$$

$$f_5(t, \vec{R}, \vec{U}) = \frac{D_{[Zn(OH)_4]^{2-}} (C_{[Zn(OH)_4]^{2-}} - C_0) R_7}{2Kt} - \frac{R_1 C_{Zn} C_H C_{[Zn(OH)_4]^{2-}}}{C_{Zn^{2+}} C_{H^+}},$$

$$f_6(t, \vec{R}, \vec{U}) = R_1 C_{Zn} C_H C_{[Zn(OH)_4]^{2-}} / (C_{Zn^{2+}} C_{H^+}) - R_2 C_{Zn^{2+}},$$

$$f_7(t, \vec{R}, \vec{U}) = R_2 C_{Zn^{2+}}.$$

Thus, the system (9) will be rewritten in vector form:

$$\frac{d\vec{U}(t)}{dt} = \vec{F}(t, \vec{R}, \vec{U}),$$

where $t_0 < t \leq T$. Here, T is the maximum value of time at which the experimental value was recorded. Let us cover the time interval (t_0, T) by grid $\omega_n = \{t_0, t_1, \dots, t_i = t_0 + ih, \dots, t_n = T\}$, where $h = t_{i+1} - t_i = \text{const}$. The values in the half nodes of the grid will be denoted as: $t_{i+\frac{1}{2}} = t_i + \frac{h}{2}$. Let us introduce the grid functions $\vec{U}_i = \vec{U}(t_i)$ and $\vec{F}_i(t_i, \vec{R}, \vec{U}_i)$ in the nodes of the grid ω_n , corresponding to the numerical solution of the difference problem:

$$\vec{U}_{i+1} = \vec{U}_i + h \vec{d}_i.$$

Here,

$$\vec{d}_i = (\vec{d}_i^{(1)} + 2\vec{d}_i^{(2)} + 2\vec{d}_i^{(3)} + \vec{d}_i^{(4)}),$$

$$\vec{d}_i^{(1)} = \vec{F}_i(t_i, \vec{R}, \vec{U}_i),$$

$$\vec{d}_i^{(2)} = \vec{F}_i\left(t_{i+\frac{1}{2}}, \vec{R}, \vec{U}_i + h \frac{\vec{d}_i^{(1)}}{2}\right),$$

$$\vec{d}_i^{(3)} = \vec{F}_i\left(t_{i+\frac{1}{2}}, \vec{R}, \vec{U}_i + h \frac{\vec{d}_i^{(2)}}{2}\right),$$

$$\vec{d}_i^{(4)} = \vec{F}_i(t_{i+1}, \vec{R}, \vec{U}_i + h \vec{d}_i^{(3)}).$$

The algorithm for calculating the minimum itself is iterated through each constant (which are further considered in the description as independent coordinates) The first step of the method consists in an exploratory search around the basis point $g(K, R_1, \dots, R_i, \dots, R_7)$ by the vector of increments $\vec{H}(h, h_1, \dots, h_7)$, where h_i is a coordinate step $k_i, l = 1, \dots, 7$. In order to perform this step, for each coordinate separately, it is calculated the functional values (11) at three points: points $g(K, R_1, \dots, R_i, \dots, R_7)$ directly, and points distant from it by a step on the studied coordinate. Then, the point at which the functional takes a minimum value is taken as a new basis point. These iterations continue until the basis point stops changing. In addition, the calculation algorithm assumes that the point where the value of the coordinate or any of the concentrations in the calculation becomes less than zero is excluded from consideration. For example, for the coordinate responsible for the proportionality factor K in points $g(K, R_1, \dots, R_i, \dots, R_7)$, $g_1(K + h, R_1, \dots, R_i, \dots, R_7)$, $g_2(K - h, R_1, \dots, R_i, \dots, R_7)$, here $K - h \geq 0$, it is calculated the functional (11). Then, for the new value of the coordinate K , we take one of the values K , $K+h$, и $K-h$ at which the value of the functional (11) takes a minimum. Herewith, if $K - h < 0$, then this point is removed from consideration. The recalculation continues until the value of coordinate K stops changing, after which it is performed the transition to the next coordinate. After calculating on the last coordinate, we get a new point g' , which can both coincide with the original point $g' = g$, as well as to be different from it $g' \neq g$. Then if the original base point coincides with the newly obtained point $g' = g$, then we decrease the values of the components of the vector of subordinate gradients and continue the search around the basis point. Otherwise, if $g' \neq g$, the it is performed the search following the model. It takes the values $g', g + 2 * (g - g')$ as a new basis point, at which, once again, the value of the functional (11) is minimal. The output condition is a restriction on the size of components of increment vector \vec{H} .

When calculating the target function, we used a numerical method from the fourth-order accuracy Runge–Kutta method family, i.e. its error is $O(\Delta t^4)$, where t is time step. In order to find the target function, it was used the Hooke–Jeeves method; its accuracy is determined by setting a limit to the possible deviation of the calculated parameter values from the values of the parameters that determine the minimum of ε_i . Thus, the error of the method is $\max_i(\Delta t^4, \varepsilon_i)$.

3. Numerical calculation results

The numerical algorithm implementing the mathematical statement for zinc powder deposition was verified using the full-scale experiment described in [24]. In this experiment, it was investigated the effect of voltage applied on near-electrode processes of zinc electrodeposition in sodium hydroxide solutions on a stainless-steel cathode. Concentration of zinc ions Zn^{2+} in the prepared solution is 10 g/l. The working electrode was made from stainless steel and has an area of 1 cm². Let us use the experimental conditions to derive the initial conditions:

$$\begin{aligned} 1000 \text{ grams/l of solution gives } 80\%, \\ C_{NaOH}|_{t=0} \text{ gives } 20\%. \end{aligned}$$

Therefore, $C_{NaOH}|_{t=0} = 250 \text{ grams/l} \approx 6.25 \text{ mol/l}$. The molar mass of zinc is 65.38 g/mol, and a concentration of 10g/l gives approximately 0.153 mol/l and, following the dissolution reaction $2Na(OH) + Zn + Na_2[Zn(OH)_4] \rightarrow 2Na^+ + [Zn(OH)_4]^{2-} + H_2$, we will get $C_{NaOH}|_{t=0} \approx 0.153 \text{ mol/l}$. Furthermore, 0.153 mol/l of zinc binds only $\approx 0.306 \text{ mol/l}$ ions of the hydroxyl group, the remaining 5.944 mol/l takes part in the dissociation reaction $NaOH \rightarrow Na^+ + OH^-$, thus, $C_{OH^-}|_{t=0} \approx 5.944 \text{ mol/l}$. The initial concentration of the hydroxyl ion is not directly involved in the cathodic stepwise reactions we have singled out, but the ionic product of water shows that $C_{H^+}|_{t=0} \approx 0.168 * 10^{-14} \text{ mol/l}$ under normal conditions. Zinc is bound by a hydroxide group, and we take the values of ionic concentrations close to "zero", taking into account that the deposition of metals occurs around nuclei, and the electrochemical process of nuclei (adatoms) formation stage is different from their growth stage, which is out of our interest in fact. The concentration of zinc atoms is taken as "zero". We will take the concentration of water as $C_{H_2O} \approx 750 \text{ grams/l} \approx 41.7 \text{ mol/l}$, under normal conditions, the water contains $C_{H^+}|_{t=0} \approx 4.29 * 10^{-7} \text{ mol/l}$. We take the concentration of hydrogen ions dissolved in water close to "zero", taking into account the necessary presence of nuclei. The paper [24] shows the experimental data on zinc yield in %, calculated using the following formula given in it $\eta_{Zn} = \frac{m_i - m_0}{1.22 \times I \times t} \times 100\%$, where m_0 is the initial cathode mass in grams, m_i the mass of the cathode with zinc deposited on it at i -th point of time.

The indicators were taken every 10 minutes, I is the current strength in A, and $t = \frac{10 * i}{60}$. Since the article [24] does not provide data on the hydrogen yield, we will construct the functional using only the known mass of deposited zinc.

The calculation results were verified by comparing with the experimental data of study [24], the comparison results are shown in Tab. 1. The calculations showed the greatest discrepancy at the beginning of the electrolysis process. From this, we can conclude that the phase of nucleation has an influence at the initial stage and, its influence decreases with the expansion of zinc crystals. Thus, at the initial stage of zinc crystal growth, hydrogen is released both on the electrode and on the surface of zinc crystals, which makes the surface highly inhomogeneous. So, modes at current density 500 A/m² and 375 A/m² according to [24] have a lower rate of zinc coverage of

the electrode area than at 125 A/m² and 250 A/m² and, accordingly, a larger surface for the release of hydrogen, as well as a longer time for the release of hydrogen on the cathode material, since it is released more easily on steel than on metallic zinc. And, accordingly, more accurate information on the development of the initial stage could be obtained by taking into account the data on the hydrogen yield.

Table 1. Ranges of the experimentally obtained Zn mass and the calculated values obtained at a current of 125 A for two points (t=1 hour and t = 10 minutes)

T, min	Experimental data range [24]	Calculated values
20	0.467–0.49	0.30115
40	0.976–1.03	0.8516
60	1.495–1.6	1.564
70	1.761–1.921	1.97
100	2.49–2.6687	3.3

Conclusion

This research presents a numerical algorithm for obtaining the rate constants of heterogeneous processes for their subsequent investigation. This algorithm is verified on the problem of predicting zinc precipitation during the parallel hydrogen yield reaction. The calculation algorithm was verified on the experimental data on the mass of deposited zinc and showed good agreement with the experimental data. The calculations showed that at the initial stage the nucleation growth stage has a great influence and, accordingly, the difference in the hydrogen generation rate at the surface of the steel, of which the electrode is made, and the surface of the zinc crystal too. Further, in order to develop the model, it is of interest to study the phase of nucleation (anatomical) emergence and to include into the mathematical model the most influential nucleation processes. Since rate constants depend on factors intrinsic to the systems under study, such as heterogeneity and roughness of the electrode surface, transport coefficient of charged particles, and electrolyte concentrations, it seems inexpedient to verify the algorithm by comparing the rates of processes determined for other systems. In this case, the obtained rate constants can be used to calculate the spatial characteristics of the electrical system by models of higher dimensionality.

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Математическое моделирование катодных процессов электроэкстракции цинка

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Аннотация. Численные методы оптимизации широко используются для решения прикладных задач по экономике, а также для решения задач по оптимизации процессов производства. В данной работе методом прямого поиска численной оптимизации, а именно методом Хука–Дживса, решается задача обратной кинетики, описывающая электрохимические процессы получения порошка цинка при его выщелачивании. Вычисления осложняются наличием на электроде конкурирующих между собой процессов, ведущих к выделению цинка и водорода. Данные процессы связаны между собой через перенапряжение на электроде, влияющем на скорости стадийных электрохимических реакций. Математическая модель процессов, происходящих на электроде, описывается системой задач Коши, содержит соотношения связи и условия неотрицательности концентрации ионов, молекул, участвующих в реакции, а также скоростей электрохимических процессов. Минимизируемый функционал представляет собой сумму квадратов отклонений расчетного веса осажденного цинка от экспериментального на определенные моменты времени. Начальные условия для задач Коши рассчитываются на основе состояния системы до начала электролиза. Расчеты проверялись путем сравнения с экспериментальными данными на моменты времени, не участвующими в расчете минимизируемого функционала.

Ключевые слова: численная оптимизация, электроэкстракция цинка, гетерогенные процессы.