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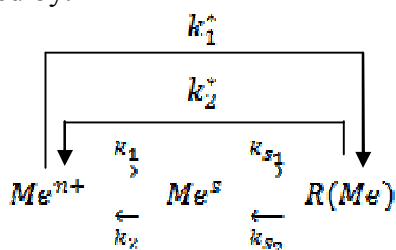
MATHEMATICAL MODEL OF ELECTROREDUCTION OF METALS ON AMALGAM ELECTRODES OF LIMITED VOLUME

A mathematical model of electrode processes in systems with amalgam electrodes of limited volume is considered. The influence of the concentration values of the supporting electrolyte solution (background) on the peak height of dissolution is researched. The mechanism of the influence of the double electric layer on the kinetics of dissolution of metal amalgam is offered. Data obtained by mathematical model allow to calculate basic characteristics of amalgam extraction of valuable metals from metal-containing wastes.

Key words: mathematical model, amalgam electrodes of limited volume, double electric layer, metal-containing wastes.

A mathematical modeling of electrode processes in systems with amalgam electrodes of limited volume is performed in the research [1].

The scheme of amalgam electroextraction of a metal from low concentrated metal systems (wastes), dissolved in water, can be represented by:



where Me^{n+} — volumetric body (metal ions in the bulk solution); Me^s — surface body — metal (ion of metal) on the surface of the mercury foam; k_1 — kinetic constant of surface body formation Me^s ; k_2 — kinetic constant of separation Me^s from the surface of the mercury foam; k_{s1} — kinetic constant of metal reduction from the surface body Me^s ; k_{s2} — kinetic constant of metal tarnishing by surface body Me^s ; k_1^* — kinetic constant of metal reduction by free surface of

electrode; k_2^* — kinetic constant of metal tarnishing by free surface of electrode;

Hereinafter $k_2^* = k_a$.

This process is described by diffusion, surface and kinetic equations in the bulk solution and on the surface of the amalgam mercury-foam electrode and in its volume.

Dissolution of metal from amalgam is the basic stage of electroextraction of metals from aqueous multicomponent metal solution. Velocity of this stage (and of the whole process) depends first of all on scanning velocity of potential and kinetic constant of electroextraction. Provided that, characteristic of metal nature is peak potential.

Theoretical correlation of peak potential and kinetic constant of electrochemical dissolution stage of metal dissolution from amalgam is suggested in the work [2]:

$$\varphi_p = \frac{RT}{\beta Z F} \cdot \ln(\omega) + \frac{RT}{\beta Z F} \cdot \ln\left(\frac{l}{k_a} \cdot \frac{\beta Z F}{RT}\right), \quad (1)$$

where φ_p — peak potential; R — absolute gas constant; T — system temperature; β — coefficient of charge transfer; Z — body of

electrons taking part in electrode process; F — Faraday constant; ω — scanning velocity of potential; δ — thickness of electrode mercury foam.

Peak potential increases linearly with the logarithm of scanning velocity of potential. According to this correlation, the greater kinetic constant (i.e. to a lower activation energy of the process) corresponds to a smaller peak potential (more negative), and vice versa.

In the study of the influence of supporting electrolyte concentration value (background) in solution on the height of dissolution peak [3] it was discovered that change in concentration of the background causes also the potential shift of the peak. Moreover, increase of background concentration results in decrease of peak potential, accelerating the process of metal dissolution.

Figure 1 shows the correlation of peaks potentials φ_p and natural logarithm of scanning velocity $\ln(\omega)$ for ions Zn^{2+} , Cd^{2+} and Pb^{2+} . Linear correlations confirm formula (1). From the slope of these curves the value β can be estimated.

Such regularity at first sight seems paradoxical: background cations under the influence of the negative field of electrode concentrate at its surface, forming double electric layer (DEL), and must prevent metal ions yielding from amalgam.

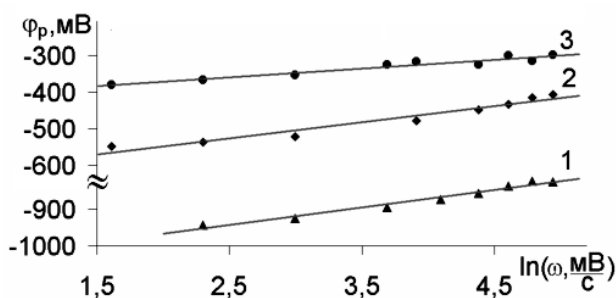


Figure 1 — Correlation of peak potential φ_p and $\ln(\omega)$ for ions Zn^{2+} (1), Cd^{2+} (2) and Pb^{2+} (3).

In addition, the rise of coefficient of charge transfer β under increasing of background concentration is discovered.

In the description of DEL it is divided into two parts: a dense layer comprising solvated counterions (CI), almost closely drawn to the electrode surface, and diffuse layer, formed by ions, located at a greater distance from the electrode, than CI. In highly concentrated solutions (more than 0.1 M), diffusion layer is practically absent: all ions DEL are concentrated in dense part [4]. In this case, the electrochemical kinetics of metal ions yielding from amalgam into solution is affected only by CI of the dense layer.

Metal in amalgam can be represented in the form of ions Me^{n+} , which, like mercury ions, are immersed into electron gas environment. The process of metal dissolution from amalgam into solution is stepwise. At first ion diffuses in the volume of mercury to its boundary (Figure 2, a) and takes marginal position (Figure 2b). Thus, it loses some of the kinetic energy and acquires a certain potential (surface) energy [5], which increases its time on the amalgam surface. In this position, the separation of the ion of metal from mercury is prevented by the activation barrier of ionization, which is reduced with approaching of the electrode potential to the potential of metal dissolution in the process of inversion. Removal of ion Me^{n+} from the surface of the amalgam occurs in the direction of reaction coordinate of its ionization. At decreasing of activation barrier ion Me^{n+} may take more remote location from mercury atoms penetrating into the volume of solution. Such penetration leads to a positive micropotential causing local rearrangement of the dense layer CI: background cations replace anions (Figure 2, b, c). To implement such rearrangement it is necessary that the time of metal ion remaining on the surface of electrode in the process of diffusion drift was much more than the time of rearrangement of the CI content in the field of micropotential. Thus penetrated into a dense layer anions create in turn negative potential ψ (Figure 2, c), which reduces the activation barrier of separation of metal ion from the surface of the mercury electrode. Detachment occurs at a distance δ , proportional to the radius of the solvated ion (Figure 2, c).

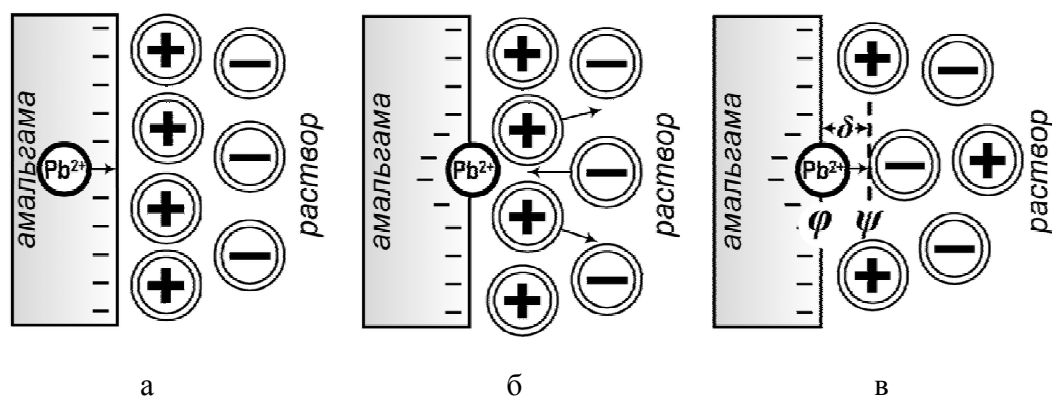


Figure 2 — Stages of the dense part DEL rearrangement in the process of metal dissolution from amalgam

The timing parameters can be estimated as follows. Period between the acts of diffusion drift of metal in the volume of amalgam is

estimated as $\tau_v = \frac{s_{\text{Hg}}^2}{6D_{\text{Pb(Hg)}}} = \tau_0 \exp\left(\frac{W_v}{kT}\right)$ [5],

where $D_{\text{Pb(Hg)}}$ — diffusion coefficient of metal in amalgam, W_v — activation energy of drift act in the volume, k — Boltzmann constant, τ_0 — average period of the fluctuations in the position of temporary equilibrium, and s_{Hg} — average distance between the positions of temporary equilibrium, defined by interatomic distance in amalgam. Value s_{Hg} for mercury is approximately $3 \cdot 10^{-8}$ cm according to the evaluation by the formula:

$s_{\text{Hg}} = 3 \sqrt{\frac{\mu_{\text{Hg}}}{N_A \rho_{\text{Hg}}}}$ [5], where μ_{Hg} and ρ_{Hg} —

molar mass and mercury density respectively, N_A — Avogadro's constant.

The time of metal ion remaining on the surface of mercury is estimated as $\tau_s = \tau_0 \exp\left(\frac{W_s}{kT}\right)$, where W_s — activation energy for the act of metal diffusion transition from the surface position to volumetric. The correlation of τ_s and τ_v is: $\frac{\tau_s}{\tau_v} = \exp\left(\frac{W_s - W_v}{kT}\right)$.

Diminution of energies $W_s - W_v$ is defined by the surface tension coefficient of mercury

σ_{Hg} : $W_s - W_v = 2\pi r_{\text{Pb}}^2 \sigma_{\text{Hg}}$, where r_{Pb} — ion radius Me^{n+} , and $2\pi r_{\text{Pb}}^2$ — area of the hemisphere. Thus: $\frac{\tau_s}{\tau_v} = \exp\left(\frac{2\pi r_{\text{Pb}}^2 \sigma_{\text{Hg}}}{kT}\right)$.

Time of rearrangement τ_e of CI content in the field of micropotential can be estimated from the velocity of ion migration u in electric field with E intensity, connected by the relation: $u = bE$, where b — ion mobility [4]. E intensity of Coulomb field $2e$ of ion Me^{n+} (e — elementary charge) is defined by the formula: $E = \frac{2e}{4\pi\epsilon_0\epsilon r^2} = \frac{e}{2\pi\epsilon_0\epsilon r^2}$, where ϵ_0 —

electrical constant, ϵ — relative dielectric constant of water, r — distance from Coulomb field. Thus: $u(r) = \frac{be}{2\pi\epsilon_0\epsilon r^2}$. Differential

of ion displacement dr in time dt is equal to: $dr = u(r)dt = \frac{be}{2\pi\epsilon_0\epsilon r^2} dt$. Time of displacement

at distance from r_b to r_f (required time τ_e) is defined by integral:

$\tau_e = \int_{r_b}^{r_f} \frac{2\pi\epsilon_0\epsilon r^2}{be} dr = \frac{2\pi\epsilon_0\epsilon}{3be} (r_f^3 - r_b^3)$. Evaluation

for the situation when background cation leaves the dense part of DEL passing the distance equal to the thickness of the dense layer h (wherein $r_b = h$, $r_f = 2h$) leads to the ex-

pression: $\tau_E = \frac{14\pi\epsilon_0\epsilon}{3be}h^3$. Value of h is usually considered to be equal to the sum of the diameter of the solvent molecules (diameter of water molecule is equal to 0.276 nm [6]) and ion radius [7].

It is possible to describe the dependence of peak potential of metal dissolution from potential ψ numerically, using the correlations outlined in the work [2]. Within the frames of two proved approximations a kinetic equation for the concentration of C_{Red} of reduced form of metal Red in the volume of amalgam was derived:

$$\frac{dC_{\text{Red}}}{d\varphi} = -\frac{k}{\omega l} C_{\text{Red}} \cdot \exp\left(\beta \frac{ZF}{RT} \varphi\right), \quad (2)$$

where: k — kinetic constant of ionization, ω — rate of potential inversion, l — thickness of the mercury-foam electrode (MFE). Adopted approximations: Red concentration is constant across the width of mercury-foam electrode; analytical signal is generated only by ionization reaction. In view of potential impact $\psi(\varphi, C_f)$, which may generally depend on φ as well as on concentration of background electrolyte C_f , the expression (2) becomes [4]:

$$\frac{dC_{\text{Red}}}{d\varphi} = -\frac{k}{\omega l} C_{\text{Red}} \cdot \exp\left(\beta \frac{ZF}{RT} [\varphi - \psi(\varphi, C_f)]\right). \quad (3)$$

The second derivative of equation (3) can be written as:

$$\frac{d^2C_{\text{Red}}}{d\varphi^2} = \frac{k}{\omega l} \cdot \exp\left(\beta \frac{ZF}{RT} [\varphi - \psi]\right) \cdot \left[\frac{dC_{\text{Red}}}{d\varphi} + C_{\text{Red}} \cdot \beta \frac{ZF}{RT} \left(1 - \frac{\partial \psi}{\partial \varphi}\right) \right]. \quad (4)$$

Since the analytical signal is proportional to the derivative $\frac{dC_{\text{Red}}}{d\varphi}$, peak potential φ_p can

be found on condition that $\frac{d^2C_{\text{Red}}}{d\varphi^2} = 0$. Substitution in (4) the value of the derivative (3) and equating the result to zero determines the required formula for peak potential:

$$\varphi_p = \frac{RT}{\beta ZF} \ln\left(\beta \frac{ZF}{RT} \omega \frac{1}{k}\right) + \psi(\varphi_p, C_f) + \frac{RT}{\beta ZF} \ln\left(1 - \left(\frac{\partial \psi(\varphi_p, C_f)}{\partial \varphi}\right)_{\varphi_p}\right). \quad (5)$$

To test the experimental data the task of the certain type of a function $\psi(\varphi, C_f)$ is needed. In the classical works on electrochemistry a theoretical derivation of the equation of the double layer is outlined and approximate formulas for potential ψ are given. Unless taking into account weak dependence of ψ on the electrode potential, then in the case of 1–1-valent of background electrolyte with a high concentration for potential, created by anions, the following approximate formula is valid:

$$\psi \approx \psi_0 - \frac{RT}{F} \ln(C_f), \quad (6)$$

where ψ_0 — invariable. In this case, the functional dependence of peak potential on the concentration of the background electrolyte is as follows:

$$\varphi_p(C_f) = \frac{RT}{\beta ZF} \ln\left(\beta \frac{ZF}{RT} \omega \frac{1}{k}\right) + \psi_0 - \frac{RT}{F} \ln(C_f). \quad (7)$$

Thus, the proposed mechanism explains the influence of DEL on kinetics of dissolution of metal from amalgam, and mathematical model of dependence of the peak potential on the concentration of the background after its experimental confirmation will allow to calculate main characteristics of amalgam extraction of valuable metals from metal-containing wastes and evaluate ecological-economic efficiency of the use of metal-containing wastes as secondary raw materials.

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МАТЕМАТИЧЕСКАЯ МОДЕЛЬ ЭЛЕКТРОВОССТАНОВЛЕНИЯ МЕТАЛЛОВ НА АМАЛЬГАМНЫХ ЭЛЕКТРОДАХ ОГРАНИЧЕННОГО ОБЪЕМА

Рассмотрена математическая модель электродных процессов в системах с амальгамными электродами ограниченного объема. Исследовано влияние величины концентрации раствора индифферентного электролита (фона) на высоту пика растворения. Предложен механизм влияния двойного электрического слоя на кинетику растворения металла из амальгамы. Полученные с помощью математической модели данные позволяют рассчитать основные характеристики амальгамного извлечения ценных металлов из металлосодержащих отходов.

Ключевые слова: математическая модель, амальгамные электроды ограниченного объема, двойной электрический слой, металлосодержащие отходы.

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МАТЕМАТИЧНА МОДЕЛЬ ЕЛЕКТРОВІДНОВЛЕННЯ МЕТАЛІВ НА АМАЛЬГАМНИХ ЕЛЕКТРОДАХ ОБМЕЖЕНОГО ОБ'ЄМУ

Розглянута математична модель електродних процесів в системах з амальгамними електродами обмеженого об'єму. Досліджено вплив величини концентрації розчину індиферентного електроліту (фону) на висоту піку розчинення. Запропонований механізм впливу подвійного електричного шару на кінетику розчинення металу з амальгами. Отримані за допомогою математичної моделі дані дозволяють розрахувати основні характеристики амальгамного вилучення цінних металів з металовмісних відходів.

Ключові слова: математична модель, амальгамні електроди обмеженого об'єму, подвійний електричний шар, металовмісні відходи.