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PETROCHEMISTRY AND PETROLEUM PROCESSING

Electrochemical Decomposition of Chelate Complex of Ethylenediaminetetraacetic Acid with Cobalt

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Abstract—The exponential reduction of the concentration of cobalt ions in the solution with time accompanied by the release of aluminum ions is observed during the electrolysis of aqueous solutions containing Co-EDTA using aluminum electrodes. The conditions and physical and chemical mechanism of the process are under discussion.

Keywords: liquid radioactive waste, Co-EDTA, electrolysis

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INTRODUCTION

The operation of nuclear power plants involves the significant pollution of steam generators and heat exchangers as a result of the deposition of poorly soluble salts and corrosion products to be removed by chemical treatment. The use of chelating agents for this purpose is based on their ability to interact with metal ions in a wide range of pH values and form stable water-soluble chelate complexes [1]. The presence of these complexes in liquid radioactive wastes (LRWs) makes it very difficult to clean them . Thus, the ions of ^{60}Co radioactive isotope form a stable soluble compound with ethylenediaminetetraacetic acid (EDTA), namely, Co-EDTA, which leads to the extremely inefficient extraction of cobalt with ion-exchange resins and selective sorbents usually used for cleaning LRWs [2].

The mentioned chelate complex should be decomposed to remove cobalt ions from aqueous solutions. Various methods based on oxidation may be used for this purpose [2–4].

Electrolysis of model water solutions that contain Co-EDTA using aluminum electrodes has been shown in [5] to result in the destruction of the chelate complex, with a multiphase residue containing cobalt that had precipitated and the concentration of the latter in the solution that had decreased by two orders of magnitude. The aim of the present work was to study the electrochemical process used to clean aqueous solutions from cobalt ions, as well as to determine the relationship between the modes of electrolysis and the pH values and the composition of the solution.

EXPERIMENTAL

Plates made of AD0 aluminum (99.5 at % of Al) were used as electrodes. The solution was prepared by dissolving the weighted sample of analytical-grade $CoCl_2 \cdot 6H_2O$ in distilled water, and analytical-grade $Na_2H_2C_{10}H_{14}N_2O_8 \cdot 2H_2O$ salt was used as a chelating agent. The pH value of the final solution was 2.5 and the initial concentration of cobalt in the solution $C =$ 1751 mg L^{-1}.

The cathode-to-anode area ratio was $S_c/S_a = 3$ and the initial temperature of electrolyte was set at 25°, with the process parameters was $I = 4$ A and $U = 200$ V. The process was performed in two modes, i.e., for 2 min with a break to cool after 1 min (mode 1) and for 2 min continuously (mode 2). The precipitate was separated by filtration, the pH value of the solution was measured, the solution was cooled to room temperature, and the process continued again.

An automatic instrument with the computer processing of results was used as a source of polarizing voltage of electrodes. An electrochemical cell and electrolyte was not cooled during the process.

The pH value of the solution was measured using a Multitest IPL-102 pH-meter/ion-meter equipped with a ESK-10601/7 glass electrode standardized by buffer solutions. The content of cobalt and aluminum ions in the solution was determined by atomic absorption spectrometry (AAS) on a Solar 6M spectrometer.

A Bruker D8 ADVANCE X-ray diffractometer with CuK_α-radiation was used for X-ray analysis of dry residue, with identification of X-ray patterns being performed using an EVA software with a PDF-2 powder database. Micrographs of the residue were obtained by a LEXT3100 optical microscope and the elemental composition was determined on a Hitachi S5500 high-

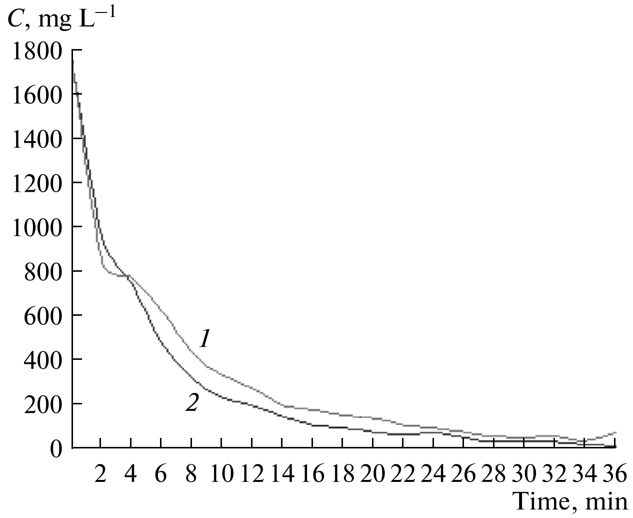

Fig. 1. Concentration of Co ions in the solution depending on duration of the process performed (*1*) in the mode with a break to cool and (*2*) continuously.

resolution scanning electron microscope equipped with an attachment for energy dispersive analysis (Thermo Scientific).

RESULTS AND DISCUSSION

The reduction of the concentration (*C*) of cobalt ions in the solution is described by the exponential dependence on the process time (Fig. 1). The lower the concentration of Co in electrolyte, the greater the amount of electricity required to extract it from the solution. The total time of the electrochemical process to reduce *C* to 18.24 (mode 1) or 79.32 mg L^{-1} (mode 2) is equal to 36 min. Figure 1 shows that mode 1 (with a break to cool the solution) leads to a significantly higher decrease in the concentration of Co in the solution (curve *1*).

The electrochemical extraction of cobalt is accompanied by a reduction in the mass of electrodes (Fig. 2), which indicates the release of aluminum into the solution followed by formation of $Al(OH)_3$ precipitate. The mass of the anode decreases more than that of the cathode during the process, that is, $\Delta m_a/\Delta m_c = 1.9$.

It was mentioned above that the electrolysis product is characterized by a complex multiphase composition (Fig. 3). $CoAl_2O_4$, $CoO \cdot OH$, CoO (or Co_2O_3 and Co_3O_4), and $Al(OH)_3$ phases commonly occur [5], along with amorphous organic products of the electrochemical decomposition of EDTA. In some cases, $Co(OH)_2$ peaks are also observed instead of the peaks of $CoO \cdot OH$ heterogenite and $Al_2O_3 \cdot H_2O$ takes place instead of $Al(OH)_3$. A change in the current density due to variations in the S_c/S_a cathode-to-anode area ratio does not lead to any changes in the phase composition of products.

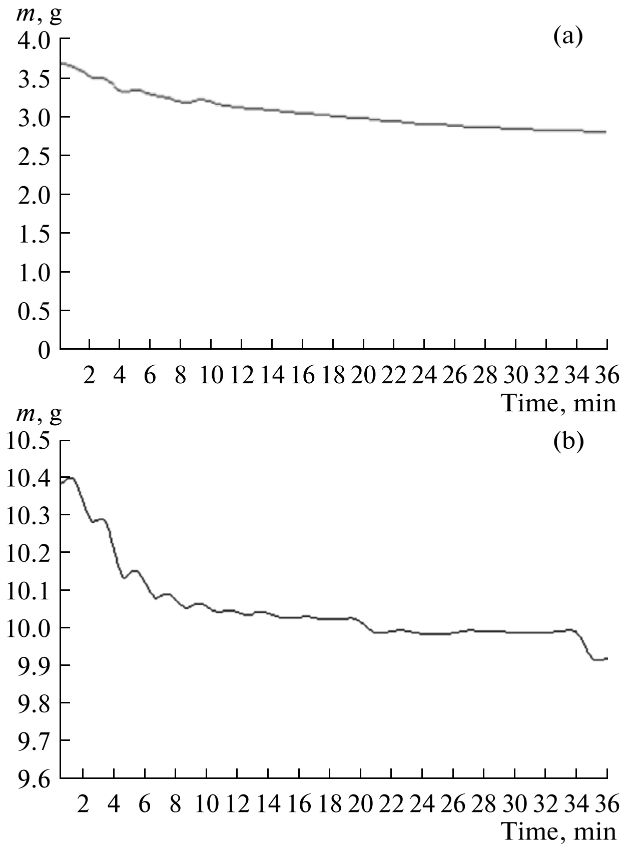

Fig. 2. Dependence of mass of (a) the anode and (b) the cathode on duration of the process.

According to energy-dispersive analysis, the content of C and O (excluding hydrogen) in the precipitated residue is as high as 80–90%, while Al and Co make up the rest.

Atomic absorption analysis indicates that part of the aluminum remains in the solution and its concentration changes significantly, increasing or decreasing at different stages of the process (Fig. 4). This circumstance may be due to the periodic formation of a hydroxyl film on the cathode, which leads to the passivation of the electrode, while it is possible to peel the film off and dissolve it. Similarly, the oxide film is occasionally forms and dissolves on the anode [6]. The irregular reduction of the mass of electrodes may be explained by the same factors (see the fluctuation of curves in Fig. 2).

As the aluminum concentration increases, the solution becomes a gel. This result indicates the accumulation of fine insoluble particles in the solution, with these particles being likely to be AlOOH metahydroxide (SL = 3.98×10^{-15} at 25°C) or equilibrium $Al_2O_3 \cdot xH_2O \cdot yOH^-$ oxides containing the variable number of hydroxyl groups. After keeping the treated solution at 25°C for 24 h, a light flocculent precipitate appears due to the formation of less soluble $Al(OH)_3$ phase (SL = 2.63×10^{-34} at 25°C) and the pH value slightly decreases by 0.2–0.4.

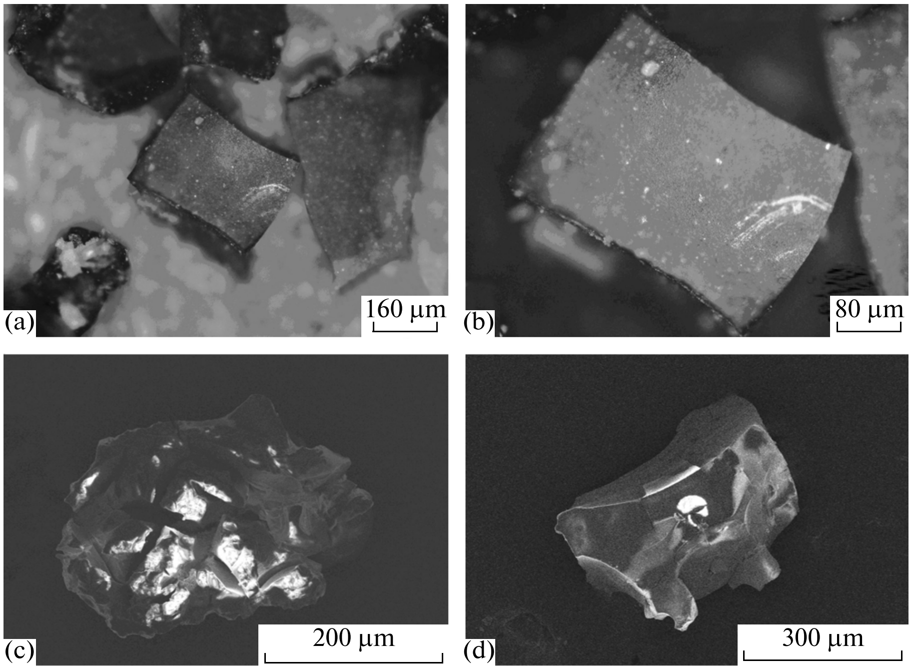

Fig. 3. Micrographs of crystals formed during electrolysis and obtained with (a, b) an optical microscope and (c, d) a scanning electron microscope.

The pH value of the solution also changes depending on time from 2.5 (for the initial solution) to 4.5 (Fig. 5). The detailed examination shows the correlation between the curves, which indicate a change in the pH and those that indicate the dependence of the aluminum concentration in the solution. An increase in the pH to 4.5 observed after electrolysis for 2 min may result from the release of Al^{3+} ions from the anode into the solution to form $AlCl_3$ accompanied by the release of $3H^+$ protons from the cathode. The further increase in the aluminum concentration in the solution leads to the hydrolysis of $AlCl_3$ salt and precipitation of $Al(OH)_3$, which in turn induces a reduction in the pH value. Thus, changes in the curves of Al concentration in the solution (Fig. 4) and the solution pH (Fig. 5) are due to alternate processes of the accumulation of Al in the solution and its subsequent release in the form of $Al(OH)_3$.

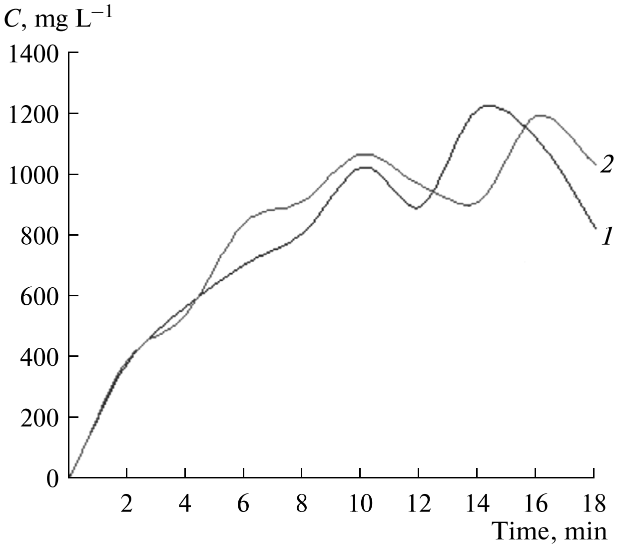

Fig. 4. Concentration of Al ions in the solution depending on duration (τ = 18 min) of the process performed (*1*) in the mode with a break to cool and (*2*) continuously.

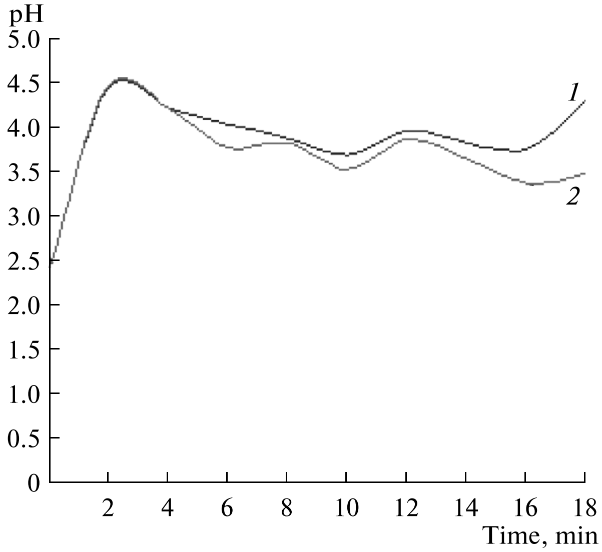

Fig. 5. pH value of the solution depending on the duration (τ = 18 min) of the process performed (*1*) in the mode with a break to cool and (*2*) continuously.

The separation of the solution volume to the anode and cathode regions by a diaphragm to prevent active stirring (Fig. 6) makes it possible to find that the products of the electrochemical process release at the cathode. The bluish green (closer to green) color of precipitate indicates the formation of cobalt oxides due to the dehydration of $Co(OH)_2$. An increase in the current and the duration of the process leads to the boiling of the solution and the precipitation of products as a bright-pink residue of cobalt hydroxide.

The above results suggest the following mechanism of the cleaning process. The negatively charged $(Co\text{-}EDTA)^{2-}$ complex decomposes at the anode during the electrochemical process under the influence of two factors, i.e., a high temperature at the near-anode region and a locally low pH, as the stability of metal chelate complexes is significantly reduced in the acidic medium [1]. The first stage of thermal degradation of the chelate complex in the solution consists of the dissociation of the complex followed by the destruction of free ligand as follows [1]:

$$[Medta]^{2-} \cdot M^{2+} + edta^{4-},$$

$$edta^{4-} \longrightarrow \text{degradation products.}$$

Co^{2+} cation interacts with OH^- to be released as $Co(OH)_2 \cdot Al^{3+}$ at the cathode and form $Al(OH)_3$ hydroxide. In the case of the boiling solution, the formation of spinels based on Co and Al ($CoAl_2O_4$) and characterized by variable composition is due to a high temperature of the near-electrode regions.

The products of the degradation of the free EDTA ligand may be different depending on the temperature, the nature of cation, and the pH value. The cations of 3*d* transition metals being used, iminodiacetic acid, *N*-(2-hydroxyethyl)iminodiacetic acid, ethylene glycol, dimethylamine, glycine, glycolic acid, and carbon dioxide are the most typical degradation products [1]. The composition of the organic component of the degradation products of the chelate complex, as well as the influence of the salt environment on the extraction of cobalt and the pH value of the solution will be determined in future studies.

Thus, it was found that the decrease in the concentration of cobalt ions in the solution is described by the exponential time dependence and accompanied by the release of aluminum ions into the solution. The periodic cooling during the electrochemical process leads to the more efficient cleaning of the aqueous solution. Cations of Co and Al metals precipitate in the form of hydroxides, oxides, and spinels of variable composition. Periodic changes in the pH value are due to the release of aluminum into the solution (increase in the pH), followed by the precipitation of $Al(OH)_3$ (decrease in the pH).

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Fig. 6. Co-EDTA solution (separated by a diaphragm, with the cathode being on the left) after the electrochemical process.

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