

Destruction of Co-EDTA Complexes by the Electrochemical Treatment of Water-Based Solutions

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Abstract—This work reports the main findings of the studies related to the problem of liquid radioactive waste utilization conducted at the Institute of Chemistry, Far Eastern Branch, Russian Academy of Sciences, in 2013–2018. It has been shown that, during the electrochemical treatment of model aqueous solutions containing Co-EDTA, the complex is destroyed and cobalt precipitates in the form of oxides, hydroxides, and spinel of variable compositions.

Keywords: liquid radioactive waste, complexes, Co-EDTA, electrochemical treatment

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INTRODUCTION

The problem of environmental pollution in the handling of radioactive waste generated by the nuclear industry enterprises and power reactors of nuclear transport installations during their operation and in emergencies is a key factor in the development of the nuclear energy sector [1–3]. Without a reliable solution to the problems connected with the treatment of liquid and gaseous waste, the decontamination of solid radioactive waste, and the curing and immobilization of radionuclides, their danger can exceed any economic benefits from the use of atomic energy. Among the three aggregate states in which radioactive waste can be formed, liquid radioactive waste (LRW) is the most common. Therefore, its treatment and disposal are the most important environmental problems not only in Russia, but throughout the world.

The most effective and widely used methods of LRW treatment are sorption methods based on the interaction of radioactive ions in solution with various sorbents. Among the most long-living radionuclides ¹³⁷Cs, ⁶⁰Co, and ⁹⁰Sr, ions of the radioactive isotopes of cesium and strontium can be effectively extracted by sorption [4–10].

For the deactivation of equipment for complexing radioactive isotopes and heavy metals in solutions, complexes that dissolve scales are often used. The use of complexes for this purpose is based on their ability to interact with metal ions in a wide pH range and form stable water-soluble complexes [11]. The inevitable presence of such complexes in liquid radioactive waste significantly complicates their treatment. In

particular, ions of the radioactive isotope ⁶⁰Co form a stable soluble compound, Co-EDTA, with ethylenediaminetetraacetic acid (EDTA), resulting in ineffective cobalt recovery by ion-exchange resins and selective sorbents commonly used for LRW treatment [1].

To remove cobalt ions from solutions, the destruction of cobalt complex Co-EDTA is necessary. For this purpose, various approaches based on the oxidation of complex are used: the use of hydrogen peroxide (H₂O₂), ozonation, and permanganate oxidation. Currently, relatively new methods for the destruction of cobalt complexes, such as hydrothermal oxidation and ultraviolet and microwave treatment, are being actively developed [12–16].

Scientists from the Institute of Chemistry, Far Eastern Branch, Russian Academy of Sciences, are working on an alternative approach to the destruction of Co-EDTA and the extraction of cobalt ions based on the electrochemical treatment of the solution.

EXPERIMENTAL

Model solutions containing Co-EDTA were prepared by dissolving stoichiometric amounts of CoCl₂ · 6H₂O and sodium EDTA salt Na₂H₂C₁₀H₁₄N₂O₈ · 2H₂O in distilled water. To remove free Co²⁺ ions, solutions were additionally treated with silicate sorbents, characterized by a high sorptive capacity of cobalt. The remaining cobalt ions were considered bound to the Co-EDTA complex. During electrolysis, Al plates of AD0 alloy (99.5 at % Al) were used as elec-

Table 1. Initial concentration of Co^{2+} ions and pH in model solutions

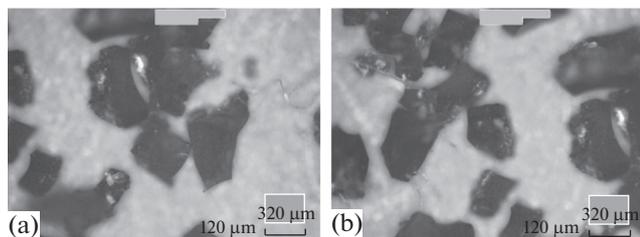
Solution	Co^{2+} concentration, mg/L	pH
1 – without salt background	2050	2.08
2 – 0.01 mol/L NO_3^-	1895	4
3 – 0.1 mol/L NO_3^-	1571	2.34

trodes. An electrochemical cell with a volume of 100 mL was used.

To study the effect of the current density on the treatment effectiveness, electrolysis was performed with the varying surface area of the cathode S_c and the anode S_a . The S_a area was constantly kept 1600 mm², while S_c was 1660, 4800, and 9600 mm². Hence, the ratio $S_a : S_c$ was 1 : 1, 1 : 3, and 1 : 6. The process parameters were as follows: $I = 4$ A, $U = 200$ V, initial temperature $t = 25^\circ\text{C}$. After 120 s of treatment, the temperature reached 95–98°C. After every 120 s of continuous treatment, the process was stopped, solutions were cooled to room temperature, and the precipitate was filtered. After that, pH and the concentration of Co^{2+} and Al^{3+} ions were controlled. Then the process was repeated until the total processing time τ 960 s was reached.

Automatic installation for micro-arc oxidation with computer processing of the results was used as a source of polarizing voltage. During the process, the electrochemical cell was cooled with flowing water. To determine the precipitation area, the electrochemical cell with the solution was divided by perforated plexiglass into cathodic and anodic compartments. It does not block the solution flow, but prevents the active mixing of the electrolyte when it is heated during treatment.

To evaluate the salt effect, two solutions with the maximum concentration of NO_3^- 0.01 and 0.1 mol/L were used. Solutions were prepared by adding NaNO_3 to the model solution containing Co-EDTA to make

**Fig. 1.** Microphotographs of precipitates formed during the electrochemical treatment of model solutions.

the NO_3^- content of 0.01 and 0.1 mol/L. The initial concentration of cobalt and pH of the solutions after preparation were different (Table 1).

The pH of the solution was measured using a MULTITEST IPL-102 pH meter/ionomer with an ESK-10601/7 glass electrode calibrated by buffer solutions. The content of cobalt and aluminum ions in solutions was determined by atomic absorption spectrometry (AAS, a Solar 6M spectrometer).

The dry precipitate was examined by X-ray phase analysis on a Bruker D8 ADVANCE X-ray diffractometer using $\text{CuK}\alpha$ radiation. The X-ray diffraction patterns were analyzed by the EVA program using the PDF-2 database. Microphotographs of the precipitate were obtained with a LEXT 3100 optical microscope.

RESULTS AND DISCUSSION

It should be noted that the term “electrochemical” does not precisely reflect the essence of the treatment method under study. According to the conditions of the processing, the method itself is closer to the well-known plasma electrolytic oxidation (PEO) [17]. Despite the similarity of the technological aspects of the proposed solution processing with the electrochemical process, the main factors for the destruction of cobalt complexes are an extreme pH change in the electrode region and high current densities in the local breakdown zones of the anodically polarized surface of the electrode, which result in a sharp temperature and pressure increase in these zones. These factors are especially manifested at high polarization potentials; therefore, the high voltage on the electrodes when compared to standard electrochemical methods is one of the main features of the proposed treatment process.

Composition of the Products of Electrochemical Process

Precipitates formed during the treatment of solutions have a complex multiphase composition (Fig. 1). The most typical phases are CoAl_2O_4 , $\text{CoO} \cdot \text{OH}$, CoO (in some cases, Co_2O_3 and Co_3O_4), and $\text{Al}(\text{OH})_3$ [18], along with amorphous organic products of the decomposition of ethylenediaminetetraacetic acid (Fig. 2). This indicates that, during the electrochemical process, the Co-EDTA complex is destroyed and Co^{2+} ions react with the products of the process. It is known that, during the thermolysis and oxidation of EDTA, the formation of a range of products is possible which can interact with both cobalt and aluminum in the solution.

It should be noted that, after annealing at 1000°C, the precipitate has a bright blue color, which is due to the formation of $\text{Al}_{0.27}\text{Co}_{0.73}(\text{Al}_{0.73}\text{Co}_{1.27})\text{O}_4$ spinel [18]. In addition to the cobalt–aluminum spinel, the X-ray diffraction pattern of the precipitate after annealing shows Co_3O_4 peaks and an X-ray amor-

phous phase. This may be of interest for the synthesis of cobalt–aluminum spinel materials, which are synthesized purposefully for use as pigments in the manufacture of paints and nonferrous ceramics, as well as in catalysis [19, 20].

Composition of the Solutions after Electrochemical Process

After the first 120 s of treatment, the concentration of cobalt ions decreased from 1750 mg/L to 1130 mg/L and then decreased continuously with time, following a parabolic dependence (Fig. 3). Computer processing of the parameters recorded during the electrochemical process established that, as the concentration of Co^{2+} in the electrolyte decreases, the amount of electricity required to remove it from the solution increases: to precipitate 1 μg Co, it is required to spend 2.75 W·s and 17 W·s, respectively [18]. After a total treatment duration of 960 s, the concentration C decreased to 90 mg/L.

The solution treatment is accompanied by the dissolution of aluminum electrodes and the release of aluminum ions into the solution, which then precipitate in the form of $\text{Al}(\text{OH})_3$ hydroxide. According to atomic absorption analysis, part of aluminum remains in the solution, while its concentration varies quite significantly (Fig. 4), increasing or decreasing at different stages of the process. This is possibly due to the periodic formation of a hydroxyl film at the cathode, facilitating the passivation of the electrode and then the peeling off and release into the solution. Similarly, an oxide film is periodically formed and dissolved on the anode. Table 1.@

As the concentration of aluminum increases, the solution becomes gel-like, indicating the accumulation of finely dispersed insoluble particles in the solution, which, presumably, are AlOOH metahydroxides ($K_{\text{sp}} = 3.98 \times 10^{-15}$ at 25°C) or oxides associated with a variable equilibrium number of Al_2O_3 hydroxyl groups $x\text{H}_2\text{O} \cdot y\text{OH}^-$. During the aging of the treated solution (24 h at 25°C), a light precipitate, associated with the formation of a less soluble $\text{Al}(\text{OH})_3$ phase ($K_{\text{sp}} = 2.63 \times 10^{-34}$ at 25°C), is formed, accompanied by a slight (0.2–0.4) decrease in pH.

The curve of the pH in the solution also changes from 2.5 (initial solution) to 4.5 (Fig. 5). A detailed examination reveals a good correlation between the curves of pH fluctuation and the concentration of aluminum in the solution. First, after 2 min of electrolysis, an increase in pH to 4.5 is observed, which can be explained by the release of Al^{3+} ions into the solution at the anode with the formation of AlCl_3 , accompanied by the release of three 3H^+ protons. A further increase in the concentration of aluminum in the solution leads to hydrolysis of AlCl_3 and precipitation of $\text{Al}(\text{OH})_3$, which, in turn, contributes to a partial

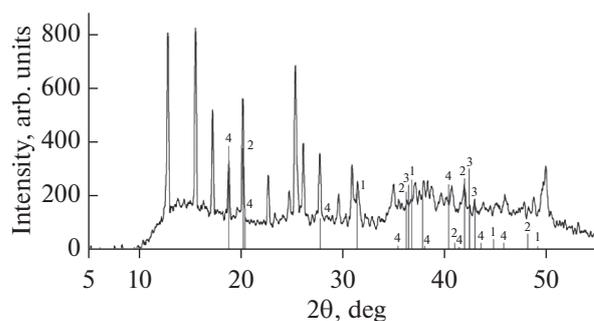


Fig. 2. XRD pattern of precipitate after drying at 100°C . Peaks correspond to [18]: (1) CoAl_2O_4 , (2) $\text{CoO} \cdot \text{OH}$ (heterogenite), (3) CoO , and (4) $\text{Al}(\text{OH})_3$.

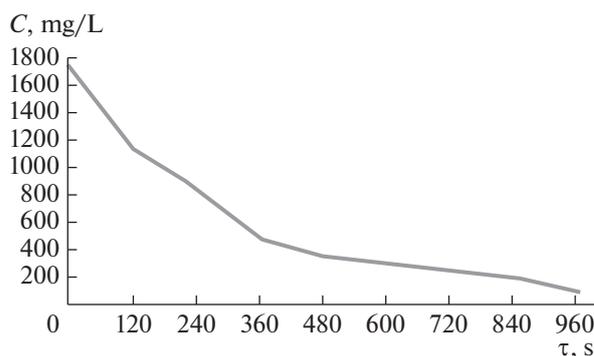


Fig. 3. Dependence of the concentration of Co^{2+} ions on the duration of the solution treatment.

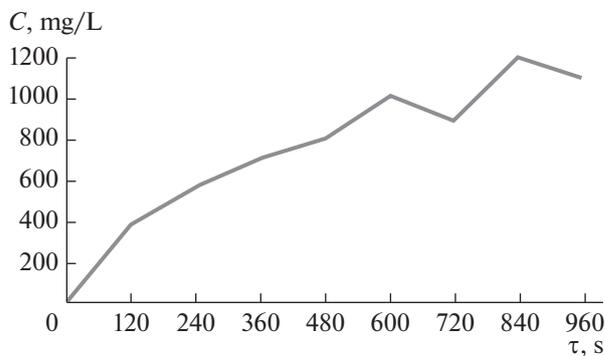


Fig. 4. Dependence of the concentration of Al^{3+} ions on the duration of the solution treatment.

decrease in pH. Thus, fluctuations seen in the curves of the Al concentration in the solution (Fig. 4) and the pH of the solution (Fig. 5) are explained by the successive processes of Al accumulation in the solution and its subsequent release in the form of $\text{Al}(\text{OH})_3$. All pH and ion concentrations were measured at room temperature.

Separation of the solution volume into the anode and cathode compartments by a partition that prevents

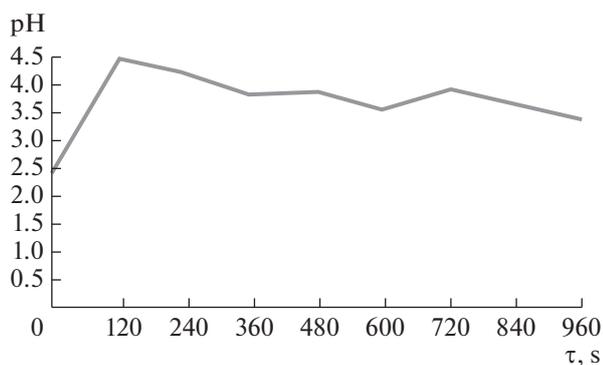
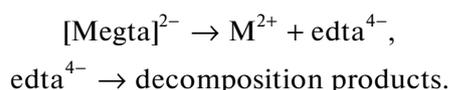


Fig. 5. Dependence of pH on the duration of the solution treatment.

active mixing made it possible to establish that products of the electrochemical process are formed on the cathode [21]. The precipitate has a blue-green (closer to green) color, indicating the release of cobalt oxides, which are formed due to dehydration of $\text{Co}(\text{OH})_2$. An increase in either the duration or current density of the process leads to the boiling of the solution. In this case, the products precipitate in the form of a bright pink precipitate corresponding to cobalt hydroxide.

These findings suggest the following treatment mechanism. During the electrochemical process, a negatively charged $(\text{Co-EDTA})^{2-}$ complex is destroyed at the anode as a result of the action of two factors, which are the high temperature and low pH values, since the stability of metal complexes is significantly reduced in the acidic conditions. During thermal decomposition of the complex in the solution, according to [11], at the first stage, its dissociation is observed, followed by the destruction of the free ligand:



Further, the Co^{2+} cation interacts with OH^- and is precipitated on the cathode in the form of $\text{Co}(\text{OH})_2$. As noted above, Al^{3+} also forms $\text{Al}(\text{OH})_3$ hydroxide. The formation of Co- and $\text{Al}(\text{CoAl}_2\text{O}_4)$ spinels with variable composition is due to the high temperature of the electrode regions.

The decomposition products of the free EDTA ligand can vary depending on temperature, the nature of the cation, and pH value. In the case of the transition 3d metal cations, the most characteristic products are iminodiacetic and hydroxyethyliminodiacetic acids, ethylene glycol, dimethylamine, glycine, glycolic acid, and carbon dioxide [11].

To evaluate the effect of current density on the treatment efficiency, the process was carried out at various ratios of the anode S_a and the cathode S_k surface ($S_a : S_k = 1 : 1, 1 : 3, \text{ and } 1 : 6$) (Fig. 6). As the cath-

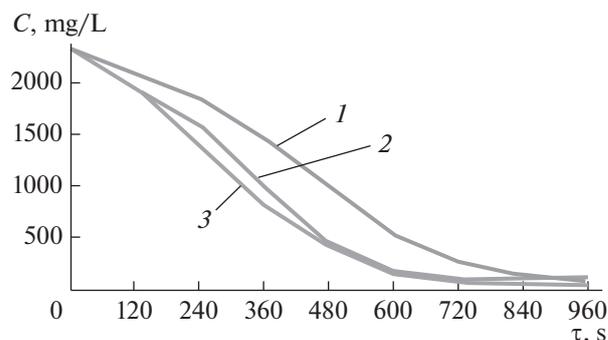


Fig. 6. Dependence of the concentration of Co^{2+} ions on the duration of the solution treatment with a varying electrode ratio: $S_a : S_k = (1) 1 : 1, (2) 1 : 3, \text{ and } (3) 1 : 6$.

ode area increases, the density of the anode current increases too, resulting in a sharper decrease in the Co^{2+} concentrations in the studied solutions; i.e., the removal of cobalt ions from solutions increases. After 240 s of the process with the ratio $S_a : S_k = 1 : 1$ and $1 : 6$, $C(\text{Co}^{2+}) = 1959 \text{ mg/L}$ and 1379 mg/L , respectively. However, after 960 s of treatment, the concentration of all three solutions equalizes around 100 mg/L .

Effect of Salt Background on Electrochemical Process

According to [1], the chemical composition of LRW is rather complex and can vary widely depending on the reagents used for decontamination and the specific operations that precede the formation of waste. Therefore, the influence of the salt background on the treatment process should be taken into account when selecting the treatment methods for high-salt LRW.

To assess the effect of the salt background, two solutions with limiting concentrations of NO_3^- 0.01 and 0.1 mol/L were analyzed. The results of the electrochemical processing of these solutions were compared with the results of the processing of the model solution without a salt background.

Figure 7 shows the dependencies of the concentration of Co^{2+} ions in the three solutions with different salt backgrounds on the processing duration. As can be seen, in all cases after 960 s of the electrochemical treatment, a decrease in the concentration of cobalt ions is observed by approximately an order of magnitude, but solutions with a high content of NO_3^- showed lower performance (see Fig. 7, curve 3). This is explained by a change in the pH of the solutions (Fig. 8). An increase in pH is observed during the electrochemical treatment of the solutions in all cases, but the presence of NO_3^- anion contributes to a greater pH shift to the alkaline region. With the increasing pH of the solutions, the stability of the Co-EDTA complex also increases [11].

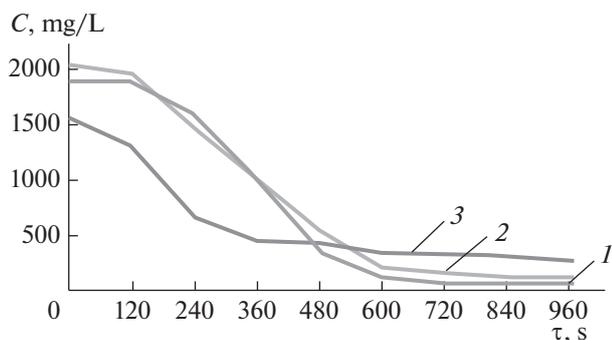


Fig. 7. Dependence of the concentration of Co^{2+} ions on the duration of the solution treatment. (1) Initial solution, (2) 0.01 mol/L NO_3^- , and (3) 0.1 mol/L NO_3^- .

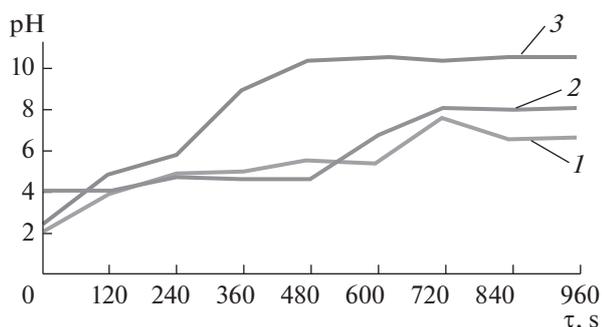


Fig. 8. Dependence of pH on the duration of the solution treatment. (1) Initial solution, (2) 0.01 mol/L NO_3^- , and (3) 0.1 mol/L NO_3^- .

CONCLUSIONS

In our series of works [18, 21, 22], the following conclusions were drawn:

(i) during the electrolysis of aqueous solutions containing Co-EDTA using aluminum electrodes, the concentration of Co^{2+} ions in the solution decreases in a parabolic manner depending on the processing time;

(ii) the treatment is accompanied by the release of aluminum ions into the solution, and cobalt precipitates as part of a multiphase precipitate. This precipitate contains oxidized and hydrated forms of cobalt and aluminum with organic products of the Co-EDTA complex destruction;

(iii) the formation of spinel based on Al and Co occurs as a result of annealing and oxidation of the initial precipitate at 1000°C ;

(iv) a decrease in the concentration of Co^{2+} ions increases the amount of spent electricity, and increasing anodic current density results in the increased release of cobalt ions from solutions;

(v) the presence of a salt background (using the NO_3^- anion as an example) in solutions containing Co-

EDTA promotes an increase in pH during electrochemical treatment, thereby “stabilizing” soluble metal-containing compounds in solutions, which, in turn, should increase the energy consumption of the LRW purification process.

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REFERENCES

1. Ryabchikov, B.E., *Ochistka zhidkikh radioaktivnykh ot-khodov* (Purification of Liquid Radioactive Wastes), Moscow: DeLi Print, 2008.
2. Harada, S. and Yanagisawa, M., Evaluation of a method for removing cesium and reducing the volume of leaf litter from broad-leaved trees contaminated by the Fukushima Daiichi nuclear accident during the Great East Japan Earthquake, *Chemosphere*, 2017, vol. 172, pp. 516–524.
3. Wu, Y., Zhang, X.X., Wei, Y.Z., and Mimura, H., Development of adsorption and solidification process for decontamination of Cs-contaminated radioactive water in Fukushima through silica-based AMP hybrid adsorbent, *Sep. Purif. Technol.*, 2017, vol. 181, pp. 76–84.
4. Jeon, C., Removal of cesium ions from aqueous solutions using immobilized nickel hexacyanoferrate-sericite beads in the batch and continuous processes, *J. Ind. Eng. Chem. (Amsterdam, Neth.)*, 2016, vol. 40, pp. 93–98.
5. Genevois, N., Villandier, N., Chaleix, V., Poli, E., Jauberty, L., and Gloaguen, V., Removal of cesium ion from contaminated water: Improvement of Douglas fir bark biosorption by a combination of nickel hexacyanoferrate impregnation and TEMPO oxidation, *Ecol. Eng.*, 2017, vol. 100, pp. 186–193. <https://doi.org/10.1016/j.ecoleng.2016.12.012>
6. Gordienko, P.S., Shabalin, I.A., Yarusova, S.B., Suponina, A.P., and Zhevtun, I.G., Sorption of cesium ions by nanostructured calcium aluminosilicates, *Russ. J. Phys. Chem. A*, 2016, vol. 90, no. 10, pp. 2022–2028. <https://doi.org/10.1134/S0036024416100125>
7. Lieberman, R.N., Green, U., Segev, G., Polat, M., Mastai, Y., and Cohen, H., Coal fly ash as a potential fixation reagent for radioactive wastes, *Fuel*, 2015, vol. 153, pp. 437–444.
8. Gasser, M.S., Mekhamer, H.S., and Abdel Rahman, R.O., Optimization of the utilization of Mg/Fe hydrotalcite like compounds in the removal of Sr(II) from aqueous solution, *J. Environ. Chem. Eng.*, 2016, vol. 4, pp. 4619–4630.
9. Ghaly, M., El-Dars, F.M.S.E., Hegazy, M.M., and Abdel Rahman, R.O., Evaluation of synthetic Birnesite utilization as a sorbent for cobalt and strontium removal from aqueous solution, *Chem. Eng. J.*, 2016, vol. 284, pp. 1373–1385. <https://doi.org/10.1016/j.cej.2015.09.025>

10. Yarusova, S.B., Gordienko, P.S., Krysenko, G.F., and Azarova, Yu.A., Sr²⁺ sorption by synthetic and technogenic silicate materials, *Inorg. Mater.*, 2014, vol. 50, no. 6, pp. 599–605.
<https://doi.org/10.1134/S002016851406020X>
11. Dyatlova, N.M., Temkina, V.Ya., and Popov, K.I., *Kompleksy i kompleksy metallov* (Complexes and Complexonates of Metals), Moscow: Khimiya, 1988.
12. Seliverstov, A.F., Lagunova, Yu.O., Milyutin, V.V., and Ershov, B.G., Recovery of ⁶⁰Co from EDTA-containing aqueous solutions, *Radiochemistry*, 2013, vol. 55, no. 4, pp. 388–391.
<https://doi.org/10.1134/S1066362213040085>
13. Ku, Y., Wang, L.-S., and Shen, Y.-S., Decomposition of EDTA in aqueous solution by UV/H₂O₂ process, *J. Hazard. Mater.*, 1998, vol. 60, pp. 41–55.
14. Lee, H.-C., In, J.-H., Hwang, K.-Y., and Lee, C.-H., Decomposition of ethylenediaminetetraacetic acid by supercritical water oxidation, *Ind. Eng. Chem. Res.*, 2004, vol. 43, no. 13, pp. 3223–3227.
<https://doi.org/10.1021/ie049952u>
15. Lin, Q., Pan, H., Yao, K., Pan, Y., and Long, W., Competitive removal of Cu–EDTA and Ni–EDTA via microwave-enhanced Fenton oxidation with hydroxide precipitation, *Water Sci. Technol.*, 2015, vol. 72, no. 7, pp. 1184–1190.
<https://doi.org/10.2166/wst.2015.329>
16. Liu, X., Fan, J.-H., Hao, Y., and Ma, L.-M., The degradation of EDTA by the bimetallic Fe–Cu/O₂ system, *Chem. Eng. J.*, 2014, vol. 250, pp. 354–365.
<https://doi.org/10.1016/j.cej.2014.04.028>
17. Gordienko, P.S., Dostovalov, V.A., and Efimenko, A.V., *Mikrodugovoe oksidirovanie metallov i splavov* (Microarc Oxidation of Metals and Alloys), Vladivostok: Dal'nevost. Fed. Univ., 2013.
18. Gordienko, P.S., Zhevtun, I.G., Shabalin, I.A., and Yarusova, S.B., Study of the composition and thermal behavior of the products of electrolysis of aqueous solutions of the Co–EDTA chelate, *Khim. Tekhnol.*, 2013, vol. 14, no. 11, pp. 693–698.
19. Li, D., Ding, Y., Wei, X., Xiao, Y., and Jiang, L., Cobalt-aluminum mixed oxides prepared from layered double hydroxides for the total oxidation of benzene, *Appl. Catal., A*, 2015, vol. 507, pp. 130–138.
<https://doi.org/10.1016/j.apcata.2015.09.038>
20. Deraz, N.M. and Fouda, M.M.G., Synthesis, structural, morphological properties of cobalt-aluminum nano-composite, *Int. J. Electrochem. Sci.*, 2013, vol. 8, no. 2, pp. 2756–2767.
21. Gordienko, P.S., Zhevtun, I.G., Shabalin, I.A., Yarusova, S.B., and Dmitrieva, E.E., Electrochemical decomposition of chelate complex of ethylenediaminetetraacetic acid with cobalt, *Theor. Found. Chem. Eng.*, 2015, vol. 49, pp. 786–789.
<https://doi.org/10.1134/S0040579515050073>
22. Gordienko, P.S., Zhevtun, I.G., Yarusova, S.B., Shabalin, I.A., Vasilenko, O.S., Yudakov, A.A., Paramonov, A.N., and Amelichkin, D.A., Effect of the salt background of solutions containing Co–EDTA on the electrochemical recovery of Co²⁺ ions, *Ekol. Khim.*, 2015, vol. 24, no. 3, pp. 176–180.

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