ВЛИЯНИЕ ФОНОВОГО ЭЛЕКТРОЛИТА И ПОВЕРХНОСТНО-АКТИВНЫХ ВЕЩЕСТВ НА ЭФФЕКТИВНОСТЬ ЭЛЕКТРОФЛОТАЦИОННОГО ИЗВЛЕЧЕНИЯ ТРУДНАРОСТВОРЯМЫХ СОЕДИНЕНИЙ ЕВРОПИЯ

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Европий и его соединения находят широкое применение в высокотехнологичных процессах ядерной и водородной энергетики, электронике, медицине и других сферах. В работе получены и проанализированы закономерности электрофлотационного извлечения труднорастворимых соединений европия из модельных систем. Целью работы являлось получение данных по процессу электрофлотационного извлечения труднорастворимых соединений европия (III) из модельных систем с фоновым электролитом и добавками поверхностно-активных веществ, а также установление оптимальных условий эффективного извлечения труднорастворимых соединений европия (III). Исследование проведено при комнатной температуре (20±2 °С) в непроточном электрофлотаторе периодического действия, который выполнен в виде вертикальной колонны. Площадь поперечного сечения электрофлотатора 10 см², объем обрабатываемого раствора 500 мл, высота аппарата 800 мм, вентиль отбора проб располагается на высоте 40 мм от электродного блока. Электродный блок состоит из нерастворимого анода, выполненного из ОРТА (титан с покрытием оксидом рутения) и катода, выполненного из сетки нержавеющей стали (размер ячеек 0,5×0,4 мм, толщина проволоки 0,3 мм). Массовая концентрация европия (III) определена на масс-спектрометре с индуктивно связанной плазмой марки Termo Scientific. Определение размеров частиц и гранулометрического состава, а также поверхностного заряда частиц дисперсной фазы (ζ-дзета-потенциалов) проведено с помощью лазерного анализатора частиц Photocor Compact-Z. Эффективность процесса извлечения труднорастворимых соединений Eu3⁺ оценивали по степени извлечения a (%). Объектами исследования являлись коллоидно-дисперсные системы малорастворимых соединений европия (III) в водных растворах при наличии поверхностно-активных веществ различной природы и фоновых электролитов. Исходный водный раствор содержит: С Eu3⁺ - 0,1 г/л, С фонового электролита - 1 г/л, фоновые соли: NaCl, NaNO₃, Na₂SO₄, С ПАВ - 5 мг/л. Показано, что для каждого типа растворов эффективность электрофлотационного процесса достигается при определенных рН. Установлено, что оптимальными условиями извлечения соединений европия (III) являются: объемная плотность тока, Jv = 0,4 А/л; продолжительность процесса 10 мин. Для нитратного фона степень процесса извлечения максимальна при рН 10 – 11 и наличии в растворе добавки анионного ПАВ (ОксПАВ А1218). При извлечении соединений европия (III) из системы с сульфатным фоном лучшие результаты получены при значениях рН 8 и 10, а также добавлении анионного и/или катионного (Септа ПАВ ХЭВ70) поверхностно активного вещества. Хлоридный фон показал лучшие условия для извлечения европия (III) при рН 7 с добавлением неионогенного ПАВ марки ПЭО-1500. Степень извлечения европия составляет 98-99%.
INFLUENCE OF BACKGROUND ELECTROLYTE AND SURFACE-ACTIVE SUBSTANCES ON EFFICIENCY OF ELECTRO-FLOTATION EXTRACTION OF HARDLY SOLUBLE EUROPium COMPOUNDS

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Europium and its compounds are widely used in high-tech processes of nuclear and hydrogen energy, electronics, medicine and other fields. In this work, the regularities of electrofloation extraction of hardly soluble europium compounds from model systems were obtained and analyzed. The aim of the work is to obtain data on the process of electrofloation extraction of hardly soluble europium (III) compounds from model systems with background electrolyte and the addition of surface-active substances, establishing optimal conditions for efficient extraction of hardly soluble europium (III) compounds. The research was conducted at room temperature (20 ± 2 °C) in a non-current electric flotator of periodic action, which is made in the form of a vertical column. The cross-sectional area of the electric flotator is 10 cm², the volume of the treated solution is 500 ml, the height of the apparatus is 800 mm, and the sampling valve is located at a height of 40 mm from the electrode unit. The electrode unit consists of an insoluble anode made of ORTA (titanium with ruthenium oxide coating) and of a cathode made of stainless steel mesh (cell size 0.5 × 0.4 mm, wire thickness 0.3 mm). The mass concentration of europium (III) was determined by a mass-spectrometer with inductively coupled plasma of Thermo Scientific brand. Determination of particle size and particle size distribution, surface charge of particles of the dispersed phase (ξ) were carried out using a Photocor Compact-Z laser particle analyzer. The efficiency of the process of extracting hardly soluble compounds of Eu³⁺ was evaluated by the degree of extraction α (%). The objects of study are colloid-dispersed systems of poorly soluble compounds of europium (III) in aqueous solutions in the presence of surface-active substances of various nature and background electrolytes. The initial aqueous solution contains: Concentration of Eu³⁺ = 0.1 g/l, C-background electrolyte = 1 g/l, background salts: NaCl, NaNO₃, Na₂SO₄; Cₘₙ = 5 mg/l. It has been shown that for each type of solution the efficiency of the electrofloation process is achieved at certain pH. It is established that the optimal conditions for the extraction of europium (III) compounds are: volume current density, Jv = 0.4 A/l; process duration 10 min. For nitrate background the degree of extraction is maximum at pH 10-11 and at the presence of an anionic surfactant additive in the solution (Oxy surfactant A1218). When extracting europium (III) compounds from a system with a sulphate background the best results were obtained at pH values of 8 and 10, as well as the addition of an anionic and, or cationic (Septa surfactant XEV70) surfactant. Chloride background showed the best conditions for the extraction of europium (III) at pH 7 with the addition of a non-ionic surfactant of PEO-1500 brand. The degree of extraction of europium is 98-99%.

Key words: electrofloation, background electrolyte, surface-active substances, europium, extraction degree
INTRODUCTION

Rare-earth metals are important resources for the production base in many industries, as well as in the development of innovative technologies in the nuclear power industry, optics, medicine, and chemical technology. Europium and its compounds are used in atomic reactors as a neutron absorber, hydrogen power engineering during thermochemical decomposition of water, phosphors, hybrid engines of automobiles and many other products. In medicine, europium and its compounds are used in the diagnosis of various diseases and the treatment of certain forms of cancer [1, 2].

As it is known, rare-earth metals are found in many minerals, but only monacite, bastnesite and some others are of industrial importance. The relative prevalence of rare-earth metals in nature can be judged by the composition of monacite and bastnesite. In this ore europium oxide contains an insignificant amount of 0.001%. This may indicate the relevance of developments in the field of extraction of europium and its compounds.

Metallic europium is obtained by reducing its compounds, as well as by electrolysis of the melt EuCl3.

Electroflotation is one of the promising directions for the extraction of hardly soluble compounds, due to its high efficiency [3, 4]. Positive results were obtained on the extraction of hydroxides and other hardly soluble compounds of chromium, copper, nickel, zinc, cobalt, cadmium, iron from aqueous solutions [5-8], as well as for the treatment of oily wastewater [9-11].

Ion flotation is used to extract and separate rare-earth elements [12]. Data on ion flotation of lanthanum (III) and holmium (III) from nitrate and nitrate-chloride media were obtained [13], as well as cerium (III), samarium (III), europium (III) from chloride media [14, 15]. However, this method has a number of disadvantages, including the problem of regeneration of the collector [16].

The efficiency of the electroflotation process is shown in the extraction of lanthanum, scandium, cerium [17-23].

MATERIALS AND METHODS OF RESEARCH

Electroflotation extraction of hardly soluble europium (III) compounds was carried out from model systems containing a background electrolyte, in particular, nitrate, sulfate, chloride, with a salt concentration of 1 g/l, as well as surfactant additives. All systems were studied in the range of pH 6-11.

The study was carried out at room temperature (20±2 °C) in a non-current electric flotator of periodic action [18], which is made of Plexiglas in the form of a vertical column, has a cross-sectional area of 10 cm², the volume of the solution being processed is 500 ml, and its height is 800 mm, the sampler valve is located at a height of 40 mm from the electrode unit.

The electrode unit includes an insoluble anode made of ORTA (titanium with ruthenium oxide coating) and a cathode made of stainless steel mesh with a cell size of 0.5×0.4 mm and a wire thickness of 0.3 mm. The cathode is located above the anode in order to allow free passage of the anodic oxygen bubbles into the electroflotator column.

The efficiency of the process of extracting europium (III) compounds from solution was evaluated by the degree of extraction α in percent. The degree of extraction was calculated as the ratio of the difference between the initial (c_i, mg/l) and final (c_f, mg/l) concentrations of europium (III) ions in solution to the initial concentration of europium ions.

The degree of extraction (α) is a value that indicates the efficiency of the process of metal extraction, determined by the formula (1):

\[ \alpha = \left( \frac{c_f - c_i}{c_i} \right) \cdot 100\% \]  

(1)

where α is the degree of extraction; c_i – initial metal concentration; c_f – the final concentration of the metal.

The mass concentration of europium (III) was measured on a mass-spectrometer with inductively coupled plasma brand Thermo Scientific.

In this paper, the effect of various types of surfactant substances is investigated: anionic surfactant – Oxy surfactant A1218; cationic surfactant – Septa Surfactant Hev70; nonionic surfactant – PEO-1500.

Determination of particle size and particle size distribution, as well as the surface charges of par-
particles of the dispersed phase ($\xi$-potentials) were performed using a Photocor Compact-Z laser particle analyzer. Sampling was carried out in 1 ml intervals of 5, 10 and 20 min.

RESULTS AND DISCUSSION

The formation of the dispersed phase is one of the determining stages of the electro-flotation process for the extraction of hardly soluble compounds. The conversion of europium compounds into hardly soluble forms was carried out by adjusting the pH of the medium.

Fig. 1 shows the dependence of the degree of extraction ($\alpha$) of hardly soluble compounds of europium (III) on the pH of the solution.

![Graph](image)

**Fig. 1. Dependence of the extraction degree of europium (III) compounds on the pH of a solution. Experimental conditions: $J_0 = 0.4 \ A/l$, $C_0 (\text{Eu}^{3+}) = 0.1 \ g/l$, $C(\text{background}) = 1 \ g/l$; backgrounds: 1- nitrate, 2- sulfate, 3-chloride.

It was established that the degree of extraction of europium (III) has different indicators and depends both on pH and on the composition of the background electrolyte. It can be seen from Fig. 1 that the extraction of europium compounds from the chloride background proceeds efficiently in the range of pH 6-7; from sulfate background at pH 8 and 10; nitrate background allows you to extract insoluble europium compounds with the best result in the pH range 10-11.

Taking into account the presence of several peaks and good reproducibility of the results (the error in the degree of extraction of europium compounds is $\pm 3\%$ based on the results of three measurements), when determining the values of $\alpha$ for a sulfate electrolyte, we assume that these peaks are associated with the extraction of various insoluble europium compounds at certain pH values.

The fluctuations in the curves of Fig. 1 for the chloride and nitrate background are less pronounced. It is known that the pH of the solution changes the proportion of accumulation, in this case, of europium compounds. The change in the share of accumulation of various europium compounds as a function of the pH of the solution apparently determines the wavy course of the $\alpha - \text{pH}$ curves (Fig. 1).

The influence of the nature of the background on the degree of extraction is due to the different coordination ability of the anions and the solubility of their compounds. The presence of peaks in Fig. 1 in the general case may be due to several reasons, one of which is the formation of heteroligand compounds. Evidence for the formation of such compounds may be data on the various effects of the nature of the background electrolyte on the degree of extraction of europium compounds. The formation of polynuclear complexes of europium (III) cannot be ruled out. However, this issue requires additional studies of the processes of complexation and solubility of the corresponding products.

As shown by studies of the kinetics of the electroflotation process, the maximum degree of extraction is achieved after 15 min of electrolysis. The released hydrogen and oxygen destroy the foam layer over time.

On average, the degree of extraction in all the studied solutions is 85%.

To increase the efficiency and intensify electroflotation, it is known that additives of surfactants are used.

To gain the deeper understanding of electroflotation, studies were conducted and the sizes of dispersed particles of europium (III) compounds were experimentally determined, as well as the value of the zeta potential ($\xi$).

The dependence of the particle diameter on the nature of the electrolyte at pH 10 in the form of a differential distribution function is shown in Fig. 2.

It was established that, in general, the particle size is 10-20 $\mu m$. The nature of the electrolyte does not have a noticeable effect on the size of insoluble dispersed particles, but the largest particles are observed under conditions of sulphate background. Apparently, this is associated with a higher charge of sulfate-ion, in comparison with chloride and nitrate ions.

The diameter of the bulk of insoluble particles varies from 5 to 30 $\mu m$, which is sufficient for electro-flotation extraction. But, as laboratory tests have shown, over time, the foam layer is destroyed and it is
partially transferred into the solution volume as a precipitate, which reduces the degree of extraction.

Using the Photocor Compact-Z laser analyzer, it was found that the surface charge of a particle of Eu\(^{3+}\) compounds varies depending on the nature of the anion, which is part of the background electrolyte, and the type of surfactant (Table 1).

![Graph](image)

**Fig. 2.** Dependence of the particle diameter of hardly soluble europium compounds on the nature of the electrolyte at pH 10 (differential curves) for the background: 1- sulphate, 2- nitrate, 3- chloride

**Table 1. \(\xi\) – potentials of particles of insoluble europium (III) compounds**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Zeta Potentials ((\xi)), mV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{Eu}^{2+}) + chloride pH 7</td>
</tr>
<tr>
<td>Without surfactant additive</td>
<td>4</td>
</tr>
<tr>
<td>Septa surfactant Hev70</td>
<td>-1</td>
</tr>
<tr>
<td>Oxy surfactant A1218</td>
<td>8</td>
</tr>
<tr>
<td>PEO-1500</td>
<td>-15</td>
</tr>
</tbody>
</table>

The study showed that low electroflotation activity is observed for the dispersed phase, which has a \(\xi\)-potential in the negative region or close to zero.

The use of surfactants of anionic, cationic and non-ionic types in the electro-flotation process leads to an increase in the degree of extraction (\(\alpha\)). This effect is explained by a number of known factors: the adsorption of substances on the hydrophilic surface of sparingly soluble metal compounds, which makes it even more hydrophobic. Under these conditions, the formation of large flotation complexes with a developed bulk structure and lower density is possible.

**Fig. 3.** Electroflotation extraction of hardly soluble europium (III) compounds from solutions with a nitrate background and surfactant additives. Experimental conditions: \(J_0 = 0.4\) A/l, pH 11, \(C_{\text{Eu}^{3+}}\) = 100 mg/l, \(C(NaNO_3) = 1\) g/l, \(C(\text{sulfactant}) = 5\) mg/l, 1-without surfactant, 2-Septa surfactant Hev70, 3-Oxy surfactant A1218, 4-PEO-1500

As can be seen from Fig. 3, the greatest degree of extraction is achieved with the presence of an anionic surfactant additive (Oxy surfactant A1218). It should be noted that the process is intensive and in most cases the degree of extraction (\(\alpha\)) of europium compounds reaches a maximum value of 98% in the first 5 minutes of the experiment. Table 2 shows the average sizes of dispersed particles at pH 9-11.

**Table 2. The size of dispersed particles of europium (III) in the model solution with the addition of surfactant and nitrate background**

<table>
<thead>
<tr>
<th>Model system</th>
<th>Nitrate</th>
<th>Nitrate + Septa surfactant Hev70</th>
<th>Nitrate + Oxy surfactant A1218</th>
<th>Nitrate + PEO-1500</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d_{\text{av}}, \mu m)</td>
<td>18</td>
<td>15</td>
<td>40</td>
<td>62</td>
</tr>
</tbody>
</table>

It is seen from the Table 2 that the average size of the dispersed europium particle increased in the presence of anionic surfactant and is 40 \(\mu m\). This is probably the optimum particle size for electroflotation extraction for an examined background electrolyte. The particle size when adding PEO – 1500 increased to 62 \(\mu m\), which is a rather large value. Large dispersed particles float only up to a certain point, and then, due to gravitational forces, remain in the solution volume or fall to the bottom of the electroflotation unit. When cationic type surfactants are added, the particle size for a given background remains almost unchanged and is 15-20 \(\mu m\).

It should be noted that with the addition of surfactants of all types, the aggregates of particles that
emerge on the surface and form a foam layer (flotation concentrate) have a stable structure. This makes it possible to extract the flotation concentrate without losing any insoluble europium particles.

The kinetics of the process of extracting hardly soluble europium compounds from the model system with sulfate and surfactant additives at pH 10 was experimentally determined. The results are presented in Fig. 4.

![Figure 4](image-url)

Fig. 4. Electroflotation extraction of hardly soluble europium (III) compounds from solutions with a sulphate background and surfactant additives. (a) - experimental results obtained with anionic surfactants (Oxy surfactant A1218) added to the model system. With the addition of Septa surfactant HEV70 into the solution, the process also goes intensively. The degree of extraction reaches 99%. The foam layer (flotation concentrate) has a homogeneous structure and does not collapse during the entire time of the process.

Table 3 shows the average sizes of dispersed particles of europium (III) compounds from model solutions with the addition of surfactant and sulfate background.

<table>
<thead>
<tr>
<th>Model system</th>
<th>sulfate</th>
<th>sulfate + Septa surfactant Hev70</th>
<th>sulfate + Oxy surfactant A1218</th>
<th>sulfate + Septa surfactant Hev70 + Septa surfactant Hev70</th>
<th>sulfate + Septa surfactant Hev70 + Septa surfactant Hev70</th>
</tr>
</thead>
<tbody>
<tr>
<td>d, µm</td>
<td>28</td>
<td>33</td>
<td>39</td>
<td>51 has to be added</td>
<td>51 has to be added</td>
</tr>
</tbody>
</table>

The most effective process is observed with the addition of PEO-1500, the degree of extraction at pH 7 reaches 98%.

CONCLUSION

For the first time obtained the data on the process of electroflotation extraction of hardly soluble europium (III) compounds.

Table 4. Sizes of dispersed particles of europium (III) in the model solution with the addition of surfactant and sulfate background

<table>
<thead>
<tr>
<th>Solution</th>
<th>pH 6</th>
<th>pH 7</th>
<th>pH 8</th>
<th>pH 9</th>
<th>pH 10</th>
<th>pH 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>chloride</td>
<td>80</td>
<td>89</td>
<td>40</td>
<td>82</td>
<td>71</td>
<td>40</td>
</tr>
<tr>
<td>chloride + Septa surfactant Hev70</td>
<td>82</td>
<td>84</td>
<td>80</td>
<td>93</td>
<td>91</td>
<td>90</td>
</tr>
<tr>
<td>chloride + Oxy surfactant A1218</td>
<td>58</td>
<td>63</td>
<td>56</td>
<td>42</td>
<td>89</td>
<td>88</td>
</tr>
<tr>
<td>chloride + PEO-1500</td>
<td>90</td>
<td>98</td>
<td>94</td>
<td>78</td>
<td>72</td>
<td>66</td>
</tr>
</tbody>
</table>

It has been experimentally established that the optimal conditions for electroflotation extraction of europium (III) compounds for a solution containing C(Eu<sup>3+</sup>) = 0.1 g/l, C(PEO) = 1500, the degree of extraction at pH 7 reaches 98%.

The summarized data on electroflotation extraction of hardly soluble europium compounds from model systems with a chloride background are presented in Table 4.

Table 4. The degree of extraction of insoluble europium (III) compounds from model systems with chloride electrolyte and surfactant additives

<table>
<thead>
<tr>
<th>Solution</th>
<th>pH 6</th>
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<td>78</td>
<td>72</td>
<td>66</td>
</tr>
</tbody>
</table>

The degree of extraction of europium is 98-99%.


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Поступила в редакцию 23.09.2019
Принята к опубликованию 20.03.2020

Received 23.09.2019
Accepted 20.03.2020


83