APPLICATION OF HYDROLYTIC PRECIPITATION
FOR SEPARATION OF RARE-EARTH AND IMPURITY ELEMENTS

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ABSTRACT

The growth in the consumption of the rare-earth elements is primarily due to its use in the science-driven industries. The search for additional sources of raw materials requires to study the possibility of a by-product recovery process of rare-earth elements from uranium-containing raw materials. The present research aims at the preparation of productive solutions after the opening of uranium-containing raw materials and extraction of uranium, molybdenum and vanadium from them. The content of the rare-earth elements in these solutions is 50 mg/dm³ - 100 mg/dm³. In addition, there is an increased content of iron and aluminum. Iron has a particularly negative effect on sorption extraction. The method of hydrolytic deposition is proposed to remove Fe, Al. The study of the process kinetics provides to determine the optimal conditions for its conduct. The rare-earth elements can be recovered by sorption or extraction from the purified solutions.

Keywords: rare-earth elements, impurity elements, hydrolytic precipitation, sorption.

INTRODUCTION

The increase of the global demand in respect to rare earth elements (REE) is primarily due to the improvement of technology in virtually all industries and the use of rare-earth products in the creation of new high-tech materials and products of unique characteristics that are often the decisive factor in the modern competitive economy. The increase in REE demand, in turn, requires the search for additional sources of raw materials. Taking into consideration the fact that uranium raw materials contain REE in particular, the by-product extraction of ones from the productive solutions increases the profitability of the main production and contributes to the receipt of additional valuable products. But an increased content of impurity elements, especially iron, is noted in productive solutions.

The methods of separation of impurity (Fe, Al) and REE described in the literature are based on the precipitation of iron and aluminum by alkali metal hydroxides or ammonium hydroxide. As a rule, this is a process of hydrolytic deposition [1]. The authors of ref. [2] propose a method for purifying industrial uranium-containing solutions from iron by partial precipitation of ferric iron and subsequent recovery of the divalent state product. Taking into account the initial composition of the productive solutions, in which the iron content (7,76 g/dm³) is many times higher than that of REE (50 mg/dm³ - 100 mg/dm³), the application of the method described in ref. [2] is ineffective, while that presented in ref. [1] needs to be improved. The present communication studies the method of hydrolytic deposition for the separation of rare-earth and impurity elements applied to these productive solutions

EXPERIMENTAL

Research objectives
Solutions obtained after the opening of uranium-containing raw materials and extraction of uranium, molybdenum and vanadium contained there were used. Their compositions was as follows, g/dm³: Fe - 7,76, Al - 8,71, Σ_{REE} - 0,087.

The content of individual REE referred to (mg/dm³):

La - 3,3, Ce - 10,0, Y - 37,2, Dy - 5,1, Pr - 3,4, Nd - 16,2, Sm - 3,9, Gd - 8,6.

The aim of the research was to separate the impurity elements from the REE elements through a further sorption recovery process.

Method of procedure

Hydrolytic precipitation of the impurity elements was carried out at 50°C, 70°C and 90°C in correspondence with a procedure described in ref. [1]. The initial solution was heated up to the given temperature, neutralized to the pH = 4 and cooled. It was analyzed at defined intervals for the rare-earth and impurity elements content. Then the residuum was separated from the solution using a filter, and the solution obtained was directed for REE sorption.

Sorption from purified solutions was carried out following the established procedures [2].

The concentration of REE was determined by Perkin Elmer (USA) 2001 emission spectrometer 'Optima 2000 DV' with inductively coupled plasma.

The phase composition of the residues was determined by "Bruker D8 Advance" X-ray diffractometer.

RESULTS AND DISCUSSION

The data reported in ref. [4] show that industrial solutions contain substantial quantities of iron and aluminum, adversely affecting the sorption and extraction recovery process of REE.

The hydrolytic process of multivalent metals precipitation is the most efficient precipitation method, especially in case of iron

In this case, the research of the thermal hydrolysis kinetics is of a practical interest because it contributes to identifying the factors of greatest impact on the rate and degree of elements deposition.

The results referring to the hydrolytic impurity elements deposition are shown in Table1. As evident it is preferred to carry out the process at 50°C because the precipitates partial dissolution which requires a higher temperature.

The changes of REE concentrations in the process of the thermal hydrolysis at 50°C are listed in Table 2. It is seen that rare-earth and impurity elements co-deposition is observed even at the 15th min. Within the first hour of thermal iron hydrolysis reaches 95 %, aluminum

Table 1. Kinetics of hydrolytic deposition of impurity elements.

Time, min	Content in the solution, g/dm^3								
	Fe	Al	V	Fe	Al	V	Fe	Al	V
	Temperature 50 $^\circ$C			Temperature 70 $^\circ$C			Temperature 90 $^\circ$C		
15	0.47	5.52	0.014	0.48	8.04	0.013	0.44	8.42	0.012
30	0.31	4.91	0.012	0.34	7.81	0.012	0.28	8.13	0.011
60	0.26	4.73	0.011	0.28	7.62	0.011	0.23	8.01	0.010
120	0.21	4.42	0.010	0.31	7.73	0.010	0.25	8.21	0.011
240	0.20	4.41	0.009	0.35	8.01	0.010	0.36	8.31	0.011

Table 2. Kinetics of hydrolytic deposition of REE at 50°C.

Time, min	Content in the solution, g/dm^3							
	La	Ce	Y	Dy	Pr	Nd	Gd	Sm
15	3.14	9.15	30.08	5.01	3.22	15.74	8.28	3.82
30	2.94	8.64	28.57	4.57	3.05	13.66	7.49	3.71
60	2.71	8.11	26.01	4.23	2.91	12.63	7.35	3.53
120	2.69	8.07	25.87	4.01	2.89	12.47	7.08	3.31
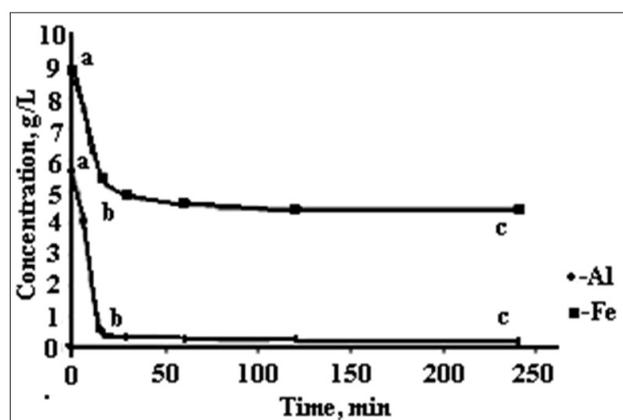
Fig. 1. Changes of impurity elements concentrations in the thermal hydrolysis process.

Fig. 2. The determination of a kinetic constant fot the thermal hydrolysis process.

deposition exceeds 50 %, that of vanadium exceeds 90 %, while Σ_{REE} is about 20 %.

Considering that the initial solutions are complex systems, it is preferred to suggest a mass crystallization. The rate of the latter is a composite function of many variables. The general view of the dependences obtained in case of the iron and aluminum is presented in Fig. 1.

It is seen from the figure that the induction period is indistinctive for this process. The crystallization rate is described by formal kinetics equations as shown in ref. [5]. The equation advanced by Fischer for the crystallization rate is as follows:

$$-\frac{dC}{d\tau} = \frac{K\alpha^n S}{V},$$

where C is the concentration of the substance actually being crystallized in the solution, S stands for the crystal surface, V is the volume of solution, α is the absolute oversaturation, while **K** and **n** stand for the kinetic constant and the chemical reaction order, correspondingly.

At V = 1 and $\alpha = C - C_{н}$, the equation above is rearranged to:

$$-\frac{dC}{d\tau} = K(C - C_{н})^n S$$

Constant **n** which designated the chemical reaction order depends on the dissolved substance properties, the oversaturation, the temperature, the stirring rate. It is determined by the number of the crystal nucleation modes and the growth orientations, as well as by the law of growth.

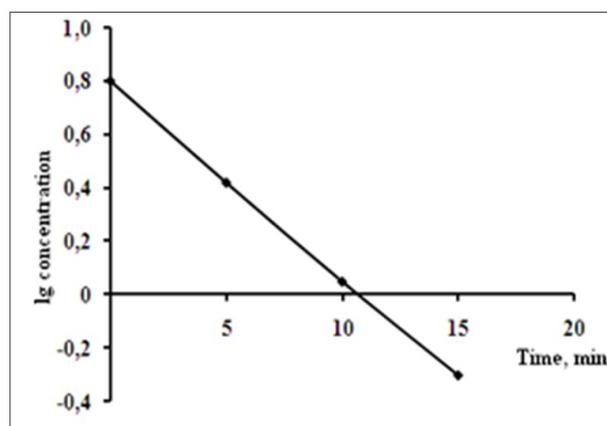The analysis of the kinetic curves in Fig. 1 shows

that the iron deposition runs at higher rates as compared to aluminum. Thus, the iron concentration in the solution decreases by 95 % within 30 min of the process while the aluminum concentration decreases only by 45 %.

The kinetic curves may be conventionally divided into two sections - **ab** and **bc.** Based on the experimental data, we managed to calculate the order of the reaction, the values of the kinetic constant and the effective activation energy for iron within the **ab** section - it deposits at a higher rate, which means that it is determining the system.

The order of the reaction and the kinetic rate constant are determined graphically. The dependence of the logarithm of the concentration change versus time (Fig. 2) is linear. This indicates that the reaction proceeds as a first order one. The rate constant determined on the ground of the slope is found equal to $1.69.10^{-3}$ min $^{-1}$.

The kinetic constant is calculated at three temperature values. This provides the determination of the effective activation energy in correspondence with the Arrhenius equation $K = A_0 e^{-E/RT}$. The dependence of lgK versus 1/T is linear as expected with tgα = - E 2.303R. The value of 41.5 kJ/mole evidences that the reaction occurs within the kinetic area, as shown in ref. [6]. According to the research data, it is possible to state that the hydrolytic precipitation of the impurity elements is a first-order reaction running within the kinetic area of the process.

The data obtained show that the process of hydrothermal impurity elements precipitation using technogenic solutions of uranium-containing raw materials has to take place at 50ºC. Shock cooling of the solution is

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required to intensify the process.

Many industrial solutions contain mechanical impurities, which may serve as nucleating and crystallization centers. The facilitation of the crystallization process depends on the size of the foreign particles and the affinity of their crystalline structure to the structure of the solution-crystallized salt. Aiming a verification in this respect, the hydrolytic precipitation process is carried out in presence of a seeding agent. In fact, the deposit obtained in the course of the preceding experiment acted such. The X-ray phase analysis carried out shows the content of an amorphous phase, trivalent iron oxide, and the complex compounds $AlFeO_3$, $Na_3Fe(SO_4)_3$. Hence, it is evident that the presence of a seeding agent contributes to the formation of larger precipitate crystals.

The solutions pretreatment requires sorption proceeding. Thus, the slump is filtered, while the solution is subjected to REE sorption carried out at static conditions in KU-2-8n and KKh-100 ionites-assisted media. It is found that the scrutinized elements are lined according to sorption decrease as follows: Ce-Y-La-Sm-Dy. Based on the study data, we managed to calculate the distribution factors for the individual REE sorption in KU-2-8n ionite: Y - 0.55; Ce - 0.41; Sm - 0.35; Dy - 0.34; La - 0.31 while on KKh -100 ionite, ones are as follows: Y - 0.58; Ce - 0.46; Sm - 0.38; Dy - 0.35; La - 0.32. This data proves that REE distribution factors in KKh-100 ionite are higher in comparison to the KU-2-8n ionite. Elements as Pr, Nd and Gd are not practically absorbed, i.e., the partial rare-earth elements separation is possible in the sorption process.

CONCLUSIONS

The process of separation of rare-earth and impurity elements from solutions obtained in leaching of uranium-bearing ores is studied. Hydrolytic deposition is applied. The kinetic study of the process provides to determine the values of the rate constant, the reaction order, the activation energy and to select the optimal conditions.

A possibility of subsequent sorption extraction of rare-earth elements from purified solutions is demonstrated.

The investigation reported is a new stage of the study of rare-earth elements extraction from the uranium-containing raw material.

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