

## NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN  
SERIES OF GEOLOGY AND TECHNICAL SCIENCES

ISSN 2224-5278

Volume 2, Number 440 (2020), 87 – 95

<https://doi.org/10.32014/2020.2518-170X.35>

**B. Kenzhaliyev<sup>1</sup>, D. M. Yesimova<sup>1</sup>, T. Y. Surkova<sup>1</sup>,  
A. Soemowidagdo<sup>2</sup>, L. U. Amanzholova<sup>1</sup>, N. B. Egorov<sup>3</sup>**

<sup>1</sup>Satbayev University, Institute of Metallurgy and Ore Benefication, Almaty, Kazakhstan;

<sup>2</sup>Yogyakarta State University, Indonesia;

<sup>3</sup>Tomsk Polytechnic University Tomsk, Russia.

E-mail: bagdaulet\_k@satbayev.university;

d.yessimova@satbayev.university; arianto\_ls@uny.ac.id;

## TRANSFORMATION OF THE RARE EARTH ELEMENTS AND IMPURITY ELEMENTS COMBINATIONS IN THE COURSE OF pH PREGNANT SOLUTION MODIFICATION

**Abstract.** Currently, the scientific and engineering progress is mainly associated with the rare earth elements application. A lot of spheres of effective REEs use are numbered as in military so the civil industries. Additional raw materials sources of the REEs concentration and probable extraction are explored due to the increased demand in the last two decades. The man-made mineral formations (MMF) after phosphate ores processing is one of them. The REEs' content reaches 5.0%. The MMF processing technology consists of the following stages: a feedstock development; pregnant solutions treatment from impurities; and the REEs concentrate extraction. A loss of 30% of REEs at the second stage is the main failure, which is due to their co-precipitation with the impurity elements at pH pregnant solution adjustment. To find means and methods of making the REEs co-precipitation lower the solutions and residues generated in the course of pH standardized test solutions modification set based on the REEs and impurity elements content in the pregnant solutions have been studied by the physical and chemical methods. As part of studies, the pH initial solutions were improved within the values range of 1.7-4.0 pH by sodium hydroxide and ammonia. According to a counteracting solution, the various ways of combinations transformation of the REEs and impurity elements are provided. Appropriate conditions of pregnant solutions treatment are determined at driving to the least of the REEs co-precipitation based on the results.

**Key words:** rare earth elements, man-made mineral formations (MMF), pH solution, physical and chemical researches.

**Introduction.** Increasing demand for the REEs is explained by its application in various spheres. The rare grounds are the major asset to the production of the material for the high technology spheres of consumption, such as electron and electro-optic branches, information technology, biomedicine, environment protection, energy-saving [1-3].

Increased demand for the REEs in the last two decades forces them to find out the new raw sources containing the REEs and to improve the methods of their extraction [4-11]. Among these are the man-made mineral formations after the phosphate uranium ores processing the REEs concentrate is acquired from in SARECO LLP – an affiliate of Kazatomprom NAC [12-14].

**Research procedure.** The standardized test solutions of the following composition were used as the feedstock, g/dm<sup>3</sup>: Fe-5.5; P - 7.2; La -2.1 and Fe-5.5; P - 7.2; CE -2.1. pH value of the solutions equaled 0.6.

The REEs sulphates of chemically pure qualification, state standard 6-09-4676-83 and sodium orthophosphate reagent grade qualification, state standard 245-76 were used to prepare the standardized test solution. Considering the feedstock contains Fe in various modifications we have synthesized and identified oxide ferrum hydroxide and the standardized test solution of the above composition has been prepared based on it.

X-ray phase analysis identified the synthesized substance as a mixture of Fe<sub>2</sub>O<sub>3</sub> • H<sub>2</sub>O and Fe<sub>3</sub>O<sub>4</sub> • H<sub>2</sub>O.

Sodium hydroxide of the reagent grade qualification, state standard 4328-77, 25% of ammonia, of reagent grade qualification, state standard 3760-79 were used as the reagents to counteract the standardized test solution. Sulfuric acid was used as well of chemically pure qualification in this study, state standard 4204-77.

The standardized test solution adjustment to the determined pH values was carried out with sodium hydroxide and ammonia. The adjusted solution at a certain pH, after 0.5 hours, was filtered; the filtrate and the precipitate were analyzed to have components by physical and chemical methods.

**Methods of analysis.** The REEs quantitative content was determined using an atomic emission spectrometer with an inductively coupled plasma Optima 8300DV, and phosphorus and iron according to the generally accepted methods [15]. The solutions spectra were obtained by Infrared Fourier spectrometer "ALPHA" in the spectral range of 4000–400  $\text{cm}^{-1}$  PLATINUMATR module. The precipitation spectra of the 1st and the 2nd series of the experiments were obtained using Infrared Fourier spectrometer ALPHA, ALPHA-T module (pellets with KBr) and Avatar 370 (Nujol Mull) in the 4000-400 $\text{cm}^{-1}$  spectral range.

The X-ray phase analysis method data were obtained using a D8 ADVANCE (Bruker) Set of Cu Ka radiation, a tube voltage of 40 kV, a current of 40 mA. The processing of the obtained diffractogram data and the calculation of the interplanar distances were carried out using the EVA software. The Search/match program with the powder diffractometric database of PDF-2 was used to sample decoding and phase search.

**The results of researches.** The REEs content within the man-made mineral formations used by SARECO LLP to obtain a concentrate exceeds 5.0% and may well compete with the mineral. The light group elements are predominate. The main impurities are iron, phosphorus, magnesium, calcium, aluminum in a smaller amount.

The technology of Man-made Mineral Formations (MMF) processing with obtaining the REEs concentrate includes the following processing stages: raw materials development; pregnant solutions treatment from impurities; obtaining the REEs concentrate.

The REEs lost is mostly remarkable at the second stage - pregnant solutions treatment from impurities. This stage involves the ferric iron and phosphorus precipitation, the most representative impurity elements, as well as, to a lesser extent, aluminum, calcium and magnesium. Up to 30% of the REEs are co-precipitated together with the above elements, which are subsequently difficult to separate from impurities and isolate from the sediment. In this regard, the REEs co-precipitation reducing issue during the pregnant solutions treatment from impurities is challenging for production.

In order to find a method of the REEs co-precipitation reducing of the rare-earth elements with impurities, their performance in the process of pH change of the pregnant solution is necessary to be studied.

After examining the statistical data of the individual elements content in the pregnant solutions over the year, we have prepared the standardized test solutions that, by the main components (iron, phosphorus, REEs total), duplicate the original pregnant from sulfuric acid leaching of MMF. The lanthanum concentration in the first solution and cerium in the second was equal to the REEs total. These elements were chosen to take into account the REEs composition in the pregnant solution, where the light group prevails.

Considering that the main components of the pregnant and standardized test solutions are iron, phosphorus and the REEs, the iron orthophosphates and the REEs can be assumed to be produced while adjusting the pH values. The literature references speak of pH orthophosphates formation of the individual REEs varies widely. Thus, the pH formation of praseodymium orthophosphate –  $\text{PrPO}_4 \cdot n\text{H}_2\text{O}$  – is 1.5, the samarium orthophosphate –  $\text{SmPO}_4 \cdot n\text{H}_2\text{O}$  – 1.7; gadolinium orthophosphates –  $\text{GdPO}_4 \cdot n\text{H}_2\text{O}$  and ytterbium -  $\text{YbPO}_4 \cdot n\text{H}_2\text{O}$ . At the same time, the iron phosphates formation is observed at pH 1.5-1.7 [16-18]. Based on the literature data, we have chosen the alteration range of pH solution varying from 1.7-4.0.

As part of the study, the initial standardized test solutions were successively counteracted to pH values of 1.7; 2.5; 3.2; 4.0 by sodium hydroxide in the first set of experiments and ammonia in the second. As mentioned above, the improved solution was filtered, the filtrate and sediment were analyzed for the content of the component by chemical method, and the states of their availability were analyzed by IR spectroscopic and X-ray diffraction methods. The results of chemical analysis of the initial solutions and after improving the pH values by sodium hydroxide are provided in table 1.

Table 1 – Precipitation rate of rare earth and impurity elements by the sodium hydroxide depending on pH solution

pH solution	A precipitation rate,%			A precipitation rate,%		
	Fe	P	La	Fe	P	Ce
1.7	89.0	44.7	25.0	90.0	40.7	22.8
2.5	91.9	48.3	79.8	93.9	47.3	80.9
3.2	95.2	49.9	85.7	94.1	50.9	91.7
4.0	99.0	51.1	98.1	98.9	58.1	95.0

As of the table as far as the pH values of standardized test solutions increase from 1.7 to 4.0, the iron sedimentation rate increases to almost 98–99%, phosphorus increases to 45–50%, the rare earth's sediment intensively in the 1.7-3.2 pH range, then the sedimentation process slows down. At a pH value of 1.7, the degree of co-precipitation of the REEs is 25–26%, and at 2.5 is over 80%.

IR spectroscopic studies of the initial lanthanum-containing solution and adjusted at different pH values have testified that in the spectrum of the initial solution (a) there are absorption bands of  $\nu$  (OH) -  $3359\text{ cm}^{-1}$  valences, bending  $\delta$ HOH- $1632\text{ cm}^{-1}$  fluctuations of molecular water. The ion hydrosulfate -  $\text{HSO}_4^-$ , coordinated by the metal —  $1175, 1045, 880, 579\text{ cm}^{-1}$  [19].

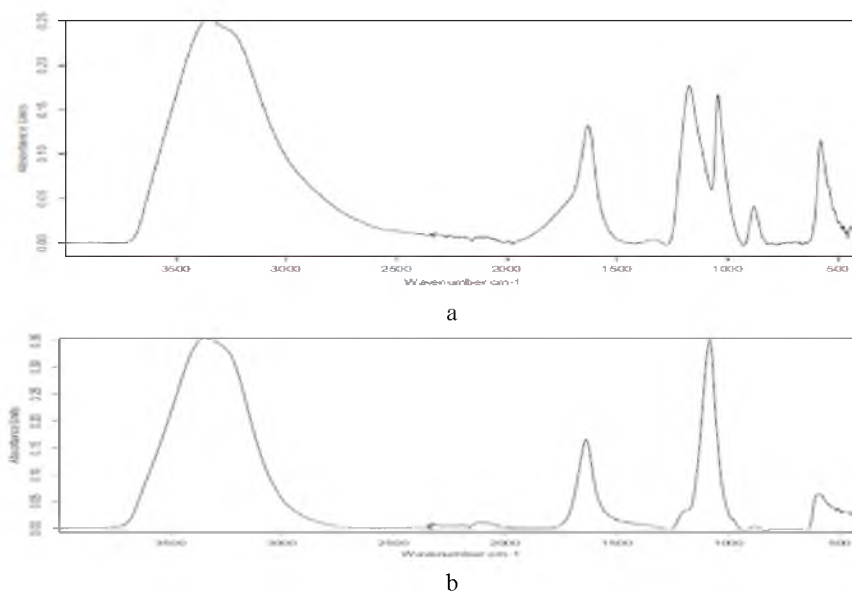


Figure 1 – IR spectra of the initial standardized test solution (a) and adjusted at 1.7 pH (b)

The solution spectrum obtained at 1.7 pH differs from the previous one. The spectrum shows absorption bands of  $\nu$  (OH) -  $3354\text{ cm}^{-1}$  valence, and bending  $\delta$ HOH- $1640\text{ cm}^{-1}$  fluctuations of the molecular water [20].

An ion sulfate -  $[\text{SO}_4]^{2-}$  -  $1085, 981, 604\text{ cm}^{-1}$  [18, 19] prevails over an ion hydrosulfate -  $\text{HSO}_4^-$  -  $1189, 887, 587\text{ cm}^{-1}$  [18]. Phosphate absorption band appears: a  $[\text{PO}_4]^{3-}$  group -  $1085\text{ cm}^{-1}$  [21].

The spectra of improved at pH 2.5; 3.2; 4.0 solutions should be noted to have a similar profile, a shift of the  $\nu_3$   $[\text{SO}_4]^{2-}$  band to the long-wavelength region is observed with increasing content of  $[\text{PO}_4]^{3-}$  ions, which indicates a change in the concentration of the component. The  $\nu$  [OH] $^-$  and  $\nu_3$   $[\text{SO}_4]^{2-}$  band intensity redistribution give evidence of the salt background change of the solution.

IR spectroscopic studies of precipitations obtained in the process of pH changing of the initial standardized test lanthanum-containing solution are provided in figure 2 and table 2.

An analysis of the studies performed the sediment spectrum obtained at pH standardized test lanthanum-containing solution adjusting to pH = 1.7 one fluctuation band  $\nu_3$  ( $\text{F}_2$ ) and two bands  $\nu_4$  ( $\text{F}_2$ ) of the tetrahedral ion  $[\text{SO}_4]^{2-}$  describing the sulfate symmetry phase ion D<sub>2</sub>, which corresponds to  $\text{Na}_2\text{SO}_4$  thenardite is traced. As the pH of the initial solution changes from 1.7 to 4.0, the intensity of the

fluctuation band  $\nu_3$  (F2) increases and at 3.2 and 4.0 pH it splits into two (figure 2), its intensity increases 3 times (table 2), respectively another sulfate phase dominates.

An increase of the  $\nu_3$  band intensity may indicate both an increase in the sulfate content and the formation of a new sulfate phase, for example, REE double sulfates. If a phase can be stated as an impurity at 1.7 and 1.8pH, then at 3.2 and 4.0pH is as an established independent phase.

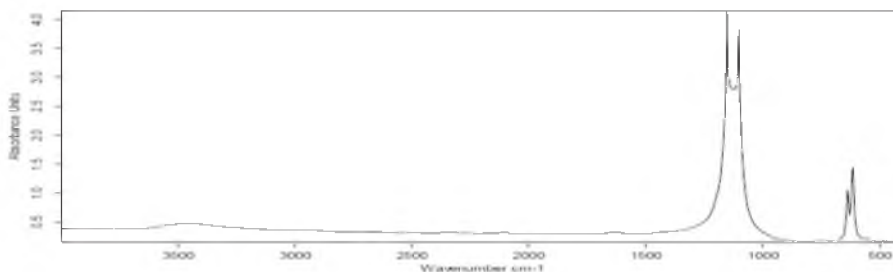


Figure 2 – IR spectra of a sediment obtained at 4.0 pH precipitation by sodium hydroxide

Table 2 – Bands intensity values of the IR spectra of sediments obtained by pH standardized test solution adjustment

pH value	Fluctuation frequencies $\nu_3$	Relative intensity	Fluctuation frequencies $\nu_4$	Relative intensity
10-10 1.7	1128.67	1.194	638.24	0.107
			616.94	0.560
13-13 1.8	1128.55	1.391	637.96	0.127
			616.71	0.623
14-14 2.5	1129.97	1.555	638.21	0.143
			617.04	0.669
15-15 3.2	1148.40	3.852	638.36	0.425
	1106.35	0.933	616.98	1.210
16-16 4.0	1154.78	3.936	638.41	0.464
	1104.06	1.118	616.94	1.289

The double salt availability is confirmed by the X-ray phase analysis according to which the main components of the lanthanum-containing sediment are the double salt of  $\text{NaLa}(\text{SO}_4)_2$  and sodium sulphate - Thenardite -  $\text{Na}_2\text{SO}_4$ .

X-ray diffraction data maintain that the iron in the sediment is Iron Oxide Sulphate Hydrate -  $\text{Fe}_{14}\text{O}_3(\text{SO}_4)_{18} \cdot \text{H}_2\text{O}$ ; Iron Phosphate -  $\text{FePO}_4$  and Iron Oxide -  $\text{Fe}_2\text{O}_3$ , i.e. in the process of pH solution adjustment, iron is partially transformed into ferric iron phosphate and sulfate of a complex composition.

The study of cerium-containing solutions with comparable concentrations of components and pH values has demonstrated the similar results.

Thus, the data obtained speak of that in the course of pH initial solution (pH = 0.6) process adjustment the hydrosulfates are transformed into sulfates with the subsequent formation of double sulfates of the rare-earth elements, phosphates from hydro and dihydrogen phosphates into orthophosphates, with the formation of iron orthophosphate. The iron is present also in the form of sulfate of complex composition.

At the second stage of the research, the initial lanthanum and cerium containing solutions were adjusted with ammonia.

Changes in the composition of the precipitate obtained in the process of adjusting the initial solution with ammonia are most clearly seen in the example of cerium-containing solutions.

Figure 3 shows the precipitation spectra obtained in the process of improving the pH of the initial cerium-containing standardized test solution.

It follows from the figure that an increase in the intensity of the absorption bands is observed in the ranges of sulfate ion and phosphate ion fluctuations with increasing pH values in the range of 1.7–4.0. In view of overlapping the absorption areas of the sulfate ion and the phosphate ion, an increase in the total

content of the compounds that comprise these groups is possible to observe. A redistribution of the intensities of the bands was observed at wavenumbers of 1148, 1107, 1063, 615, 596, 574  $\text{cm}^{-1}$ , which is due to the ratio variation of the salts present in the samples. In the long-wavelength area of all spectra, a peak at 596  $\text{cm}^{-1}$  was recorded corresponding to the  $\text{NaCe}(\text{SO}_4)_2 \cdot (\text{H}_2\text{O})$  compound. In the spectra of the samples obtained during precipitation, in the pH range of 2.2-4.0, a peak is observed at a wavenumber of 615  $\text{cm}^{-1}$ , which falls within the range of fluctuation of  $\nu_4$  sulfate-ion in sodium sulfate, ammonium sulfate and  $\nu_4$  phosphate-ion fluctuation is in the  $\text{CePO}_4$  compound [19–23].

According to X-ray phase analysis, in all samples of cerium-containing sediments a double salt of  $\text{NaCe}(\text{SO}_4)_2 \cdot (\text{H}_2\text{O})$  compound, cerium orthophosphate  $\text{CeO}_4$ , and iron in the form of  $\text{FeO}(\text{OH})$  compound are available.

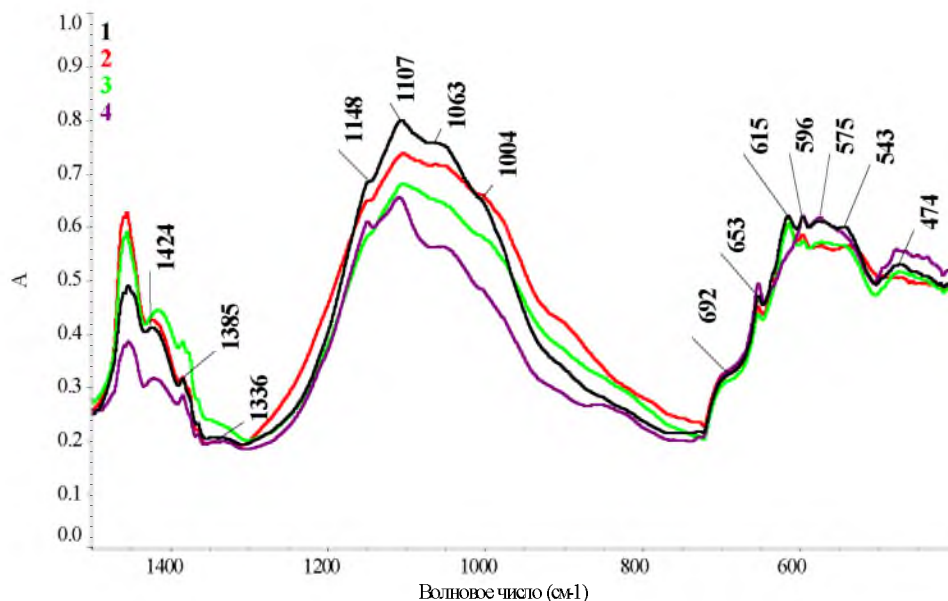


Figure 3 – IR precipitate spectrum obtained at 1.7 pH by ammonia precipitation of 1-4 pH values, respectively: 1.7; 2.2; 3.2; 4.0

By the ammonia precipitation the double salt is may be assumed to be formed due to sodium ions of a standartized test solution introduced in the form of sodium orthophosphate and its amount is limited by the sodium concentration in the solution. Double salt of lanthanum or cerium with ammonia under these conditions is not formed. Excess REEs is mixed with phosphorus into the REEs orthophosphate.

Thus, according to the researches and the results, the transformation of the compound of the rare-earth elements can be assumed to proceed not in the same manner when pH values are adjusted by sodium hydroxide and ammonia. Provided that in the first case, the formation of double salts prevails, in the second is REEs orthophosphate.

At the same time, the literary sources [17] reveal the solubility of the double salts of rare-earth elements increases with a decrease in the temperature of their precipitation. In this regard, we carried out the precipitation of the impurity elements from the pregnant solution at 1.7 pH by sodium hydroxide under standard conditions and during cooling. The results are provided in table 3 and in figure 4.

Table 3 – Source data of the REEs content in the pregnant solution

pH	Content mg / l							
	La	Ce	Dy	Er	Eu	Gd	Ho	Lu
0,6	102	103	58.0	27.0	3.9	65.0	13.1	5.1
	Nd	Pr	Sm	Tb	Tm	Y	Yb	
	132	41.3	34.0	9.9	4.7	43.6	26.6	

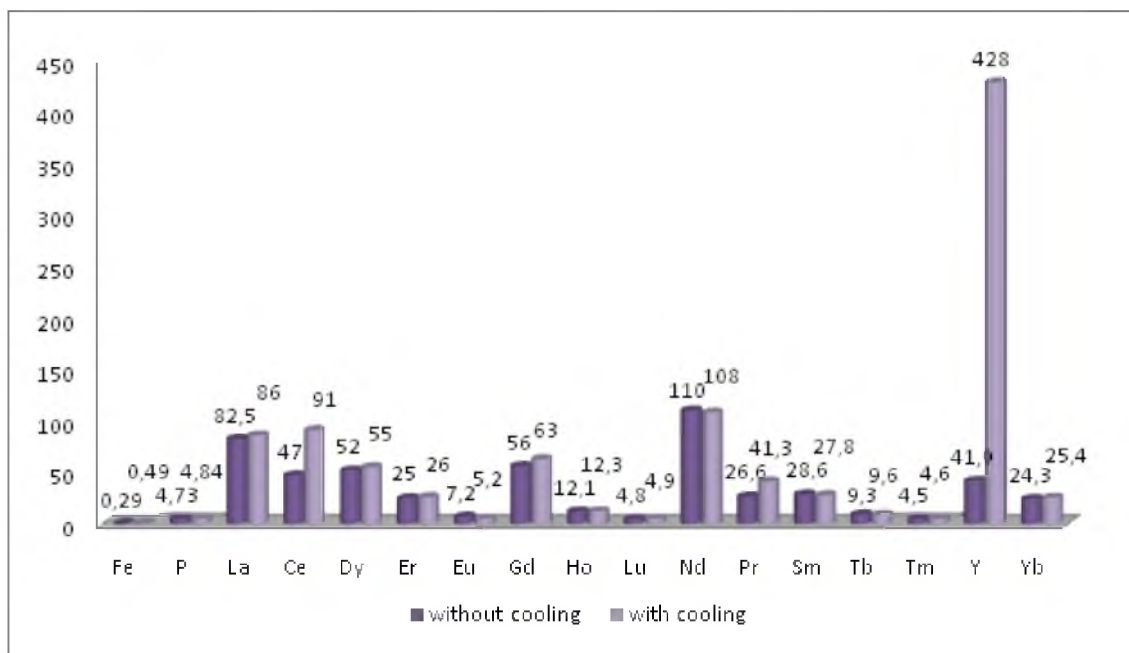


Figure 4 – Individual REEs precipitation, depending on the conditions

The given results make it clear the solution is under cooling within the precipitation of impurity elements process, leads to the solubility of the rare-earth elements sulfates increase, and their co-precipitation with sediment decreases. The data provided demonstrate the content of all rare-earth elements in the solution in the process of pH solution values improvement under the cooling conditions is higher than under standard conditions, but to the different extent. This is especially evident as concerns cerium and yttrium and, to a lesser extent, lanthanum, dysprosium, gadolinium and praseodymium. This effect is not observed when improving the pH solution values with ammonia.

Thus, using this technique in production to achieve the desired results, the precipitation is preferably carried out with sodium hydroxide, or in the 2 stages with sodium hydroxide to 1.0 pH and then ammonia to 1.7 pH.

**Conclusion.** The development and improvement of technology in the metallurgy for the production of rare and rare earth metals for different industries has been carried out by Kazakhstani scientists [24-28]. These studies of standardized test solutions were conducted to resolve co-precipitation issue of the REEs, which compound is mainly duplicate the initial pregnant MMF after sulfuric acid leaching. The improvement of pH standardized test solutions was in the range of 1.7-4.0 by sodium hydroxide and ammonia.

The sediment and filtrate after the standardized test solutions adjustment were analyzed to have components content by chemical method and the states of their availability were analyzed by IR spectroscopic and X-ray diffraction methods. Irregular combinations were observed in the process of pH improvement by various counteracting reagent as the results provided. Double salts prevail affected by sodium hydroxide, and ammonia is the REEs orthophosphate is prevailed.

Considering the double sulphates of the REEs possess abnormal properties, their solubility increases when the solution temperature decrease (Figure 4) – the impurity elements precipitation when cooling in production will result in the REEs co-precipitation decrease. To reach the result precipitation is preferable by sodium hydroxide or in the second stage by sodium hydroxide to 1.0 pH value and further by ammonia to 1.7 pH value.

**Б. Кенжалиев<sup>1</sup>, Д. М. Есимова<sup>1</sup>, Т. Ю. Суркова<sup>1</sup>,  
А. Сумовидагдо<sup>2</sup>, Л. У. Аманжолова<sup>1</sup>, Н. Б. Егоров<sup>3</sup>**

<sup>1</sup>Satbayev University, Металлургия және кен байыту институты, Алматы, Қазақстан;

<sup>2</sup>Джокьякарта мемлекеттік университеті, Индонезия;

<sup>3</sup>Томск политехникалық университеті, Томск, Ресей

### **ҮРДІСТЕ ӨНІМДІ ЕРІТІНДІДЕГІ рН ӨЗГЕРУІНЕ ҚАРАЙ, СИРЕК КЕЗДЕСЕТІН ЖӘНЕ КІРМЕ ЭЛЕМЕНТТЕР ҚОСЫЛЫСТАРЫНЫҢ ӨЗГЕРТІЛУІ**

**Аннотация.** Сирекжер элементтеріне (СЖЭ) жоғары сұраныс оның түрлі салада пайдаланылуымен байланысты. СЖЭ қолданыстың жоғарытехнологиялық - электрондық және электрооптикалық, ақпараттық технологиялар, биомедицина, қоршаған ортаны қорғау, энергияны үнемдеу сияқты салаларына арналған материалдар өндірісінде негізгі актив болып табылады.

Соңғы жиырма жылдың ішінде СЖЭ деген сұраныстың артуына байланысты, оларды концентрлеу және мүмкіндігінше бөліп алу үшін қосымша шикізаттар іздестіріліп келеді, оларды бөліп алу әдістері жетілдірілуде. Осылардың біріне, фосфатты уран кендерін қайта өңдегенде пайда болатын техногенді минералды түзілімдер (ТМТ) жатады, олар «SARECO» ЖШС – «Қазатомпром» ҰАК филиалында алынады. Ондағы СЖЭ-ің үлесі 5,0 %-ды құрайды және минералмен толықтай бәсекелесе алады. Құрамында жеңіл элементтердің топтары басым. Негізгі қоспалары болып темір, фосфор, магний, кальций және аз мөлшерде алюминий табылады. ТМТ технологиясын қайтадан өңдеу, келесідей: бастапқы шикізатты ашу; өнімді ерітінділерді қоспалардан тазалау; СЖЭ концентрациясын алу сияқты бөлімдерінен тұрады. Бұл технологияның негізгі кемшіліктерінің бірі, екінші сатыда, демек өнімді ерітіндінің рН реттеу кезінде қоспа элементтерімен қоса олардың бірге шөгілуіне байланысты шамамен 30 % СЖЭ жоғалады.

СЖЭ-нің бірге шөгілуінің төмендету тәсілдері мен олардың жолдарын іздеу үшін, өнімді ерітінділердегі сирекжер және қоспа элементтердің үлестік көрсеткіштерімен, әрі модельді ерітіндідегі үрдістер рН өзгеруінен қалыптасқан шөгінділер мен ерітінділердің құрамы, физикалық-химиялық әдістермен зерттелінді.

Зерттеу барысында, бастапқы ерітінділердің рН деңгейі 1,7 – 4,0 аралығындағы, аммиак және натрий гидрототығымен реттелінді. Бейтараптау–ерітіндісімен сирекжер және қоспа элементтер қосылыстарының өзгертулеріндегі әртүрлі жолдары көрсетілді. Алынған зерттеу нәтижелерімен, СЖЭ анағұрлым төмен бірге шөгілдіргендегі өнімді ерітінділерді тазалаудың оңтайлы жағдайы анықталды.

Келтірілген қорытындылардан ерітіндіні тұнбалау кезінде суыту СЖЭ сульфаттарының ерігіштігін арттыруға және олардың тұнбамен бірге шөгуін төмендетуге әкелетінін түсінуге болады. Алынған мәліметтер рН мәнін жақсарту кезінде ерітіндіде барлық СЖЭ болуының стандартты шарттарға қарағанда суыту кезінде түрлі дәрежеде жоғары екенін көрсетеді. Бұл, әсіресе, церий мен иттрийге, және аз мөлшерде лантан, диспрозий, гадолиний және празеодимге қатысты анық. Бұл көрініс амиагы бар ерітіндінің рН мәнін жақсарту кезінде байқалмайды.

Осылайша, бұл технологияны қажетті нәтижеге жету үшін өндірісте қолданғанда, тұндыруды натрий гидрототығымен немесе 2-ші кезеңде натрий гидрототығымен 1,0 рН-қа дейін, ал кейін аммиакпен 1,7 рН-қа жүргізу қажет.

**Түйін сөздер:** сиреккездесетін элементтері, техногенді минералды түзілімдер (ТМТ), рН ерітіндісі, физикалық-химиялық зерттеу.

**Б. Кенжалиев<sup>1</sup>, Д. М. Есимова<sup>1</sup>, Т. Ю. Суркова<sup>1</sup>,  
А. Сумовидагдо<sup>2</sup>, Л. У. Аманжолова<sup>1</sup>, Н. Б. Егоров<sup>3</sup>**

<sup>1</sup>Satbayev University, Институт металлургии и обогащения, Алматы, Казахстан;

<sup>2</sup>Джокьякартский государственный университет, Индонезия;

<sup>3</sup>Томский политехнический университет, Томск, Россия

### **ТРАНСФОРМАЦИЯ СОЕДИНЕНИЙ РЕДКОЗЕМЕЛЬНЫХ И ПРИМЕСНЫХ ЭЛЕМЕНТОВ В ПРОЦЕССЕ ИЗМЕНЕНИЯ рН ПРОДУКТИВНОГО РАСТВОРА**

**Аннотация.** Растущий спрос на редкоземельные элементы (РЗЭ) объясняется его применением в различных сферах. РЗЭ являются основным активом в производстве материалов для высокотехнологичных сфер потребления, таких как электронная и электрооптическая отрасли, информационные технологии, биомедицина, защита окружающей среды, энергосбережение.

В связи с возросшим в последние два десятилетия спросом на РЗЭ, изыскиваются дополнительные сырьевые источники их концентрирования и возможного извлечения, совершенствуются методы их получения. Одним из них являются техногенные минеральные образования (ТМО) от переработки фосфатных урановых руд, которые приобретаются в ТОО «SARECO» – филиал НАК «Казатомпром». Содержание в них РЗЭ достигает 5,0 % и вполне может конкурировать с минералом. Группа легких элементов преобладают. Основными примесями являются железо, фосфор, магний, кальций, алюминий в меньшем количестве. Технология переработки ТМО включает следующие переделы: вскрытие исходного сырья; очистка продуктивных растворов от примесей; получение концентрата редкоземельных элементов. Одним из основных недостатков данной технологии является потеря почти 30% РЗЭ на второй стадии, в связи с соосаждением их с примесными элементами при корректировке pH продуктивного раствора.

Для поиска путей и способов снижения соосаждения РЗЭ были изучены физико-химическими методами составы растворов и осадков, образующихся в процессе изменения pH модельных растворов, сформированных на основе данных о содержании редкоземельных и примесных элементов в продуктивных. В ходе исследований pH исходных растворов корректировали в диапазоне значений pH 1.7-4.0 гидроксидом натрия и аммиаком. Показаны разные пути трансформации соединений редкоземельных и примесных элементов в зависимости от раствора-нейтрализатора. На основании полученных результатов определены оптимальные условия очистки продуктивных растворов при минимизировании соосаждения РЗЭ.

Приведенные результаты дают понять, что раствор при охлаждении в процессе осаждения примесных элементов приводит к увеличению растворимости сульфатов РЗЭ и уменьшению их соосаждения с осадком. Представленные данные демонстрируют содержание всех РЗЭ в растворе в процессе улучшения значений pH раствора в условиях охлаждения выше, чем в стандартных условиях, но в разной степени. Это особенно очевидно в отношении церия и иттрия и, в меньшей степени, лантана, диспрозия, гадолиния и празеодима. Этот эффект не наблюдается при улучшении значений pH раствора с аммиаком.

Таким образом, используя эту технологию в производстве для достижения желаемых результатов, осаждение предпочтительно проводят гидроксидом натрия или на 2-й стадии гидроксидом натрия до 1,0 pH, а затем аммиаком до 1,7 pH.

**Ключевые слова:** редкоземельные элементы, техногенные минеральные образования (ТМО), pH раствора, физико-химические исследования.

#### Information about the authors:

Kenzhaliyev Bagdaulet, Doc.of Eng., Professor, Vice-Rector for Research, Satbayev University; General Director – Chairman of the Board, Institute of Metallurgy and Ore Benefication, Almaty, Kazakhstan; bagdaulet\_k@satbayev.university; <https://orcid.org/0000-0003-1474-8354>

Yesimova Dinara Muratbekovna, Master of Eng. in Metallurgy, Engineer, Satbayev University, Institute of Metallurgy and Ore Benefication, Almaty, Kazakhstan; [d.yessimova@satbayev.university](mailto:d.yessimova@satbayev.university); <https://orcid.org/0000-0002-1582-6732>

Surkova Tat'yana Yur'evna, Candidate of Eng., Senior Researcher, Satbayev University, Institute of Metallurgy and Ore Benefication, Almaty, Kazakhstan; [t.surkova@satbayev.university](mailto:t.surkova@satbayev.university); <https://orcid.org/0000-0001-8271-125X>

Soemowidagdo Arianto, PhD, Yogyakarta State University, Indonesia; [arianto\\_ls@uny.ac.id](mailto:arianto_ls@uny.ac.id); <https://orcid.org/0000-0001-7489-8050>

Amanzholova Leila Uralovna, Candidate of Eng., Senior Researcher, Satbayev University, Institute of Metallurgy and Ore Benefication, Almaty, Kazakhstan; [l.amanzholova@satbayev.university](mailto:l.amanzholova@satbayev.university); <https://orcid.org/0000-0002-9582-3522>

Egorov Nikolay Borisovich, Candidate of Chemistry, Associate Professor, Division for Nuclear-Fuel Cycle School of Nuclear Science and Engineering, Tomsk Polytechnic University, Tomsk, Russia; [egorov@tpu.ru](mailto:egorov@tpu.ru); <https://orcid.org/0000-0002-3875-9798>

#### REFERENCES

- [1] Naumov A.V. (2008) Review of the world market of rare-earth metals // News of universities. Non-ferrous metallurgy [Obzor mirovogo rynka redkozemel'nyh metallov Izvestija vuzov. Cvetnaja metallurgija] 1: 22-31. ISSN: 0021-3438
- [2] Mihajlov V.A. (2010) Rare Earth Ores [Redkozemel'nye rudy mira] Kiev. ISBN:978-3-540- 70777-6
- [3] Gorshkov K.V.A., et al., (2017). Heat-sensitive pick-up cable for fire alarm systems in aircraft, chemical reactors, industrial enterprises. Patent RF, no RU2605548-C1.
- [4] Bochevskaja E.G., Abisheva Z.S., Karshigina Z.B., Turdalieva B.D., Kvjatkovskaja M.N. (2016) The behavior of rare earth elements during nitric acid leaching of slag from phosphorus production // Complex use of mineral resources [Povedenie redkozemel'nyh jelementov pri azotnokislom vyshhelachivanii shlaka fosfornogo proizvodstva Kompleksnoe ispol'zovanie mineral'nogo syr'ja] 1: 9-16. [www.kims-imio.kz](http://www.kims-imio.kz)
- [5] Seryh V.I., Kopobaeva A.N. (2019) Patterns of placement of rare-metal deposits of Central Kazakhstan // News of the National Academy of Sciences of the Republic of Kazakhstan. Series of geology and technical sciences [Zakonomernosti



razmeshhenija redkometall'nyh mestorozhdenij Central'nogo Kazahstana // Izvestija nacional'noj akademii nauk respubliki kazahstan. Serija geologii i tehnikeskikh nauk]. 2019. Vol. 1, N 433. P. 143-150 (in Russ.). ISSN 2224-5278. <https://doi.org/10.32014/2019.2518-170X.18>

[6] Shokobaev N.M., Zhurinov M.Zh., Zhumabaeva D.S., Ivanov N.S., Abil'magzhanov A.Z. (2018) Development of a sorption technology for the extraction of rare-earth metals from solutions of underground downhole leaching of uranium. News of the National Academy of Sciences of the Republic of Kazakhstan. Series of geology and technical sciences [Razrabotka sorbcionnoj tehnologii izvlechenija redkozemel'nyh metallov iz rastvorov podzemnogo skvazhinnogo vyshhelachivaniya urana // Izvestija nacional'noj akademii nauk respubliki kazahstan. Serija geologii i tehnikeskikh nauk]. 2018. Vol. 6, N 432. P. 77-84. (in Russ.). ISSN 2224-5278. <https://doi.org/10.32014/2018.2518-170X.37>

[7] Abhilash Sinha S., Sinha M.K., Pandey B.D. (2014) Extraction of lanthanum and cerium from Indian red mud // International Journal of Mineral Processing. 127: 70–73. <https://doi.org/10.1016/j.minpro.2013.12.009>

[8] Borra C.R., Mermans J., Blanpain B., Pontikes Y., Binnemans K., Van Gerven T. (2016) Selective recovery of rare earths from bauxite residue by combination of sulfation, roasting and leaching // Minerals Engineering. 92: 151-159. <https://doi.org/10.1007/s40831-016-0103-3>

[9] Ksenofontov B.S., Kozodaev A.S., Taranov R.A., Vinogradov M.S., Senik E.V., Voropaeva A.A. (2016) Rare-earth metals leaching from coal ash and their concentration // Safety in the technosphere [Vyshhelachivaniya redkozemel'nyh metallov iz ugol'noj zoly i ih koncentrirovaniya // Bezopasnost' v tehnosfere] 1:48-55. ISSN: 2307-0595

[10] Hammam-Nasri Ines, Horchani-naifer Karima, Ferid Mokhtar, Barca Donatella (2016) Rare earths concentration from phosphogypsum waste by two-step leaching method // Rare earths concentration from phosphogypsum waste by two-step leaching method. 149: 78-83. <https://doi.org/10.1007/s42250-019-00048-z>

[11] Todorovsky D., Terziev A., Milanova M. (1997) Influence of mechanoactivation on rare earths leaching from phosphogypsum // Hydrometallurgy. 45:13-19. <https://doi.org/10.1007/s12598-017-0952-3>

[12] Kenzhaliev B.K., Surkova T.Ju., Julusov S.B., Pirmatov Je.A., Dulenin A.P. (2017) Obtaining a concentrate of rare-earth elements from waste and industrial products of the uranium industry. Complex use of mineral resources [Poluchenie koncentrata redkozemel'nyh jelementov iz othodov i promproduktov uranovoj promyshlennosti Kompleksnoe ispol'zovanie mineral'nogo syr'ja] 1:70-77. [www.kims-imio.kz](http://www.kims-imio.kz)

[13] Bekturganov N.S., Najmanbaev M.A., Surkova T.Ju. (2010) Prospects for the development of the rare-earth sub-industry in Kazakhstan // Non-ferrous metals [Perspektivy razvitiya redkozemel'noj podotrasli v Kazahstane. Cvetnye metally] 4:48-50. ISSN: 0372-2929

[14] Uzhkenov B.S., Kajupov S.K. (2005) Technogenic mineral formations of mining enterprises, the possibilities of their use and geological and economic characteristics [Tehnogennye mineral'nye obrazovaniya predpriyatij gomopromyshlennogo proizvodstva, vozmozhnosti ih ispol'zovaniya i geologo-jekonomicheskaja harakteristika] Almaty.

[15] RMG 22772.4-96 Manganese udds, concentrates and agglomerates. Standards Publishing House [Rudy margancevyje, koncentraty i aglomeraty. Izdatel'stvo standartov] Minsk 1998.

[16] Lokshin Je.P., Taraeva O.A. (2008) Purification of phosphorus hemihydrate from phosphorus // Chemistry in the interests of sustainable development [Ochistka fosfopolugidrata ot fosfora // Himija v interesah ustojchivogo razvitiya]. T. 16. N 5. P. 553-558.

[17] Bol'shakov K.A. (1978) Chemistry and technology of rare and trace elements [Himija i tehnologija redkih i rassejannyh jelementov] M.: Vysshaja shkola 361 p.

[18] Turaev N.S., Zherin I.I. (2005) Chemistry and Technology of Uranium. CNIIATOMINFORM [Himija i tehnologija urana. M.: CNIIATOMINFORM], 407 p. ISBN 5-7262-0526-5

[19] Farmer V.C. (1974) «The Infrared Spectra of minerals», MINERALOGICAL SOCIETY, 41 QUEEN'S GATE. London, 539 p. ISBN 0903056054

[20] Nakamoto K. (1966) Infrared Spectra of Inorganic and Coordination Compounds: Translated from English [Infrakrasnye spektry neorganicheskikh i koordinacionnyh soedinenij: Per. s angl.] M.: Mir. 412 p.

[21] Kazicyna L.A., Kupletskaia N.B. (1971) The use of UV, IR and NMR spectroscopy in organic chemistry [Primenenie UF, IK i JaMR spektroskopii v organicheskoi himii], M., V.Sh., g. 264 p.

[22] Kenzhaliev B.K., Surkova, T.Y., Berkinbayeva, A.N., Dosymbayeva, Z.D., Chukmanova, M.T. (2019) To the question of recovery of uranium from raw materials News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology and Technical Sciences 1 (433):112-119 <https://doi.org/10.32014/2019.2518-170X.14>

[23] Kenzhaliyev B.K. (2019). Innovative technologies providing enhancement of non-ferrous, precious, rare and rare earth metals extraction. Complex Use of Mineral Resources [Kompleksnoe Ispol'zovanie Mineral'nogo Syr'ja]. 3 (310), 64–75. Available at: <https://doi.org/10.31643/2019/6445.30>

[24] Kenzhaliyev B.K., et al., (2019) To the question of the intensification of the processes of uranium extraction from refractory raw materials. Metalurgija, Vol. 58. P. 75-78.

[25] Kenzhaliev B.K., et al., (2019). Production of Very Fine, Spherical, Particles of Ferriferous Pigments from the Diatomaceous Raw Material of Kazakhstan. Glass and Ceramics, 76 (5-6), 194–198. Available at: <https://doi.org/10.1007/s10717-019-00163-w>

[26] Kapsalamova F.R., et al., (2019) Structural and phase transformations in wear resistant Fe-Ni-Cr-Cu-Si-B-C coatings. Journal of the Balkan Tribological Association, 25 (1). P. 95-103.

[27] Yessengaziyev A., et al., (2019) Research of the leaching process of industrial waste of titanium production with nitric acid. Journal of Chemical Technology and Metallurgy, 54 (5). P. 1061-1071.

[28] Koyzhanova A.K., et al., (2019). Research on the technology for recovering gold from spent heap leaching ore piles. Obogashchenie Rud. Vol. 2019, Issue 3, 2019. P. 54-59. Available at: <https://doi.org/10.17580/or.2019.03.09>