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EXTRACTION OF RARE-EARTH ELEMENTS FROM THE COMPOSITION OF KARATAU PHOSPHORITES

Abstract. Karatau phosphorite concentrate is a perspective and unique raw material for complex processing, which allows to obtain strontium, rare earth metal and fluorine compounds along with the main product - phosphorus fertilizers. In spite of the obvious ecological expediency of complex processing of phosphorite, actually, there is the only industrial scheme involving associated extraction of rare-earth elements, strontium and the utilization of fluorine, based on the decomposition of phosphorite with nitric acid.

This article presents the results of a study of the decomposition of the Karatau phosphorites (Kokzhon and Koksu deposits) with hydrochloric and nitric acids in a ratio of 1: 1, with an increase in temperature to 85-90 °C, for 30 minutes with vigorous stirring. The chemical composition of the products obtained was determined by titrimetric, gravimetric, photocolorimetric, potentiometric methods.

Analysis of the samples showed that the mass fraction of rare-earth elements in the concentrate obtained by extraction with nitric acid was 27%, hydrochloric acid - 36% and the extraction rate of rare-earth elements with respect to their content in phosphorite was 75%. It is possible to obtain 20-36 kg of rare-earth metal concentrate in the processing of 1 ton of phosphorite

Key words: rare earth elements, extraction, phosphorites, decomposition, concentrate.

Introduction. Rare-earth metals are one of the most scarce and demanded types of mineral raw materials, since they are used in various areas, including radio electronics, engineering, nuclear industry, chemical sector, defense industry, etc., and the global demand for them multiple exceeds the market offer [1-4, 13]. The production of rare and rare-earth metals is a promising area of industrial-innovative development of Kazakhstan aimed at creating high-tech industries.

Karatau phosphorite concentrate is a promising and unique raw material for complex processing, which allows to obtain compounds of strontium, rare earth elements and fluorine along with the main product - phosphorus fertilizers [5, 6]. In spite of the obvious ecological expediency of complex processing of phosphorite, actually, there is the only industrial scheme involving the associated extraction of rare-earth elements, strontium and utilization of fluorine, based on the decomposition of phosphorite with nitric acid [7].

The aim of this work is to develop an efficient method for extracting rare-earth elements from the Karatau phosphorites.

Methods. According to the physicochemical properties of Kokzhon, Koksu phosphorite flour (standard grinding, moisture content 0.1-0.3%) has a bulk density (t/per m^3): 1.10-1.20 on the conveyor, 1.45-1.50 when freshly poured in railway carriage, up to 1.6 after transportation by railway and 1.8-2.0 after a long-term storage in the warehouse. Dry Kokzhon, Koksu phosphorite flour is very fluid, flows like a liquid at an angle of 15-20°. Being humidified to 0.75-1.5% flour loses fluidity and is capable of caking.

The isolation of rare-earth elements from phosphate concentrate obtained by processing of phosphorites from Kokzhon and Koksu deposits has been investigated.

Prior to the beginning of the main studies, X-ray diffractometric analysis of chemical composition of the initial phosphorite has been carried out on the automatic diffractometer DRON-3 with $Cu_{K\alpha}$ radiation, β-filter. Conditions for shooting diffraction patterns: U = 35 kV; I = 20 mA; shooting θ-2θ; detector 2 gr/min. X-ray phase analysis on a semi-quantitative basis was performed on the diffraction patterns of powder samples using the method of equal weights and artificial mixtures. Quantitative ratios of crystalline phases were determined. Interpretation of the diffractograms was carried out using the ICDD file data: powder diffractometry database PDF2 (Powder Diffraction File) and diffractograms of pure minerals.

The essence of the method lies in the fact that the residual solid phase is subjected to secondary decomposition. 1 kg of the phosphate rare earth concentrates and 200 g of finely ground secondary pulp were fed to the reactor. 3.0 liters of 2N nitric acid were added to this mass. The isolation was carried out by heating in 2 N nitric acid (sample №1), in 2 N hydrochloric acid (sample №2) at solid-liquid ratio of 1: 2.5-3.5 in the presence of oxalic acid (50 wt. % excess above stoichiometry when converted to oxides of rare earth elements). The precipitate of oxalates was separated by filtration, washed with water and calcined [8-12].

1.0 ml of the liquid phase was diluted with distilled water in a volumetric flask of 100 ml. 5-10 ml aliquots were taken for chemical and physico-chemical composition analysis: for determination of total nitrogen, sodium nitrite and P_2O_5, calcium and magnesium oxide, iron, aluminum, chlorine and etc. The solid phase had been first dried at room temperature, then in an oven at a temperature of 80-850 °C and the mass fraction of moisture was determined.

Two different samples were tested (decomposition of phosphorites with 2 N nitric acid and decomposition of phosphorites with 2N hydrochloric acid). 10 ml of concentrate were poured into a 100 ml flask, then diluted with distilled water and mixed thoroughly. An aliquot of the solution obtained was analyzed by atomic emission spectroscopy on Agilent 4200 MP-AES [8].

Then it was reanalyzed by atomic-emission spectroscopy on a DFS-13 diffraction spectrograph with a grating of 500 strokes per mm and a linear dispersion of 0.4 nm/mm, manufactured in Russia. Excitation of the spectra was carried out in an electric arc at current strength 14 A, detection of spectra in the ultraviolet region 230-345 nm was carried out on PFS-03 photographic plates which are sensitive in this wavelength interval. GSO 8670-2005 (SGD-2A), GSO 3484-86 (SGXM-2) were used as reference samples. The research was carried out in the K. I. Satpayev Scientific Research Institute of Geological Sciences in Almaty.

Results and discussion. The Karatau phosphorite contains up to 5-7% of the rare-earth elements 70% of which are transferred to a precipitate of calcium sulfate during sulfuric acid decomposition. Along with rare-earth elements, the precipitate contains small amounts of fluoride and phosphate ions. The resulting sediment is a waste of the of mineral fertilizer production [14-20], called "phosphogypsum", and forms gigantic mountains around the plants for processing of Karatau phosphorites (Taraz city).

Table 1 – Results of semi-quantitative X-ray phase analysis of crystalline phases of the original phosphorite.

Mineral	Formula	Concentration, %
Gypsum	$Ca(SO_4)(H_2O)_2$	43.5
Quartz	SiO_2	33.8
Bassanite	$CaSO_4 \cdot 0.5H_2O$	19.8
Mica	$KAl_2(AlSi_3O_{10})(OH)_2$	2.9

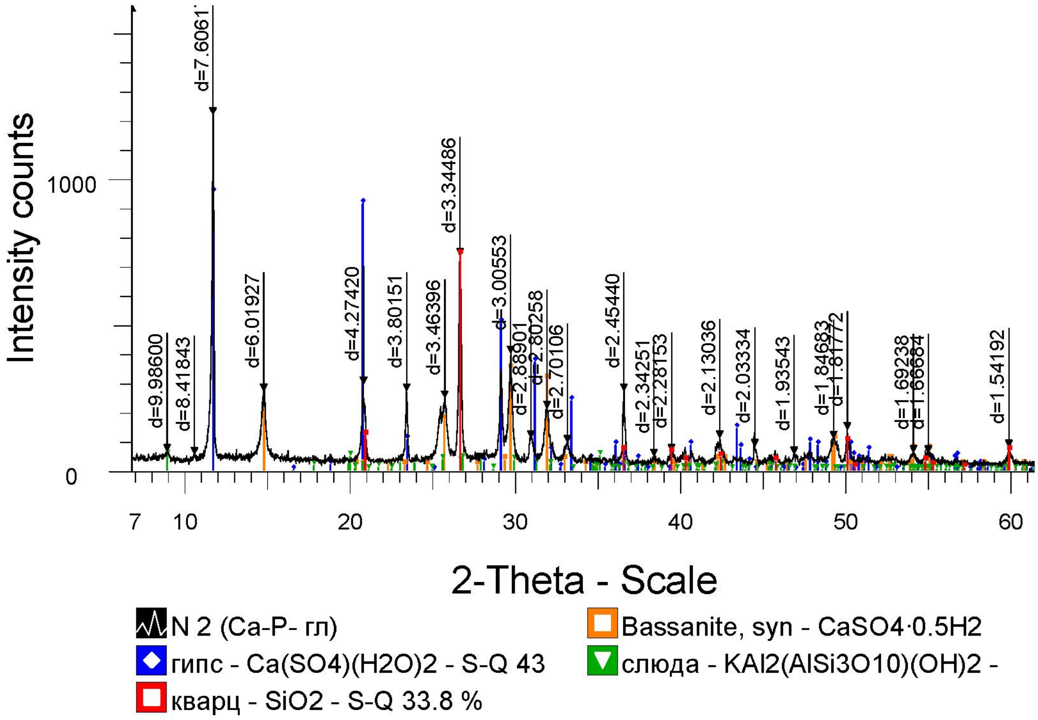

Figure 1 – Diffractogram of a sample of initial phosphorite (Ca-P-clay)

Table 2 – Determination of rare-earth element content in the Karatau phosphorite by atomic emission spectroscopy (Agilent 4200 MP-AES)

#	Sample	Label element, nm	Concentration	Unit	SD	%, RSD
1	Sample№1. Decomposition of phosphorites 2 nHNO_3	Se (196,026)	0,27	Ppm	0,08	29,76
		Zn (213,857)	0,15		0,00	1,68
		Cd (228,802)	0,00		0,00	>100
		Sr (407,771)	8,19		0,03	0,42
		Ba (455,403)	1,48		0,00	0,20
		Cu (324,754)	0,06		0,00	0,48
		Ni (352,454)	0,31		0,00	0,61
		As (193,695)	0,73		0,22	29,81
		Co (340,512)	0,53		0,01	1,06
		Pb (405,781)	-0,12 mu		0,00	1,75
		Mo(379,825)	0,08		0,00	1,05
		Mn(403,076)	17,73 o		0,05	0,29
		Cr (425,433)	0,27		0,01	2,47
		Al (396,152)	13,70 o		0,79	5,78
2	Sample№2. Decomposition of phosphorites 2 nHCl	Se (196,026)	-0,28 u		0,12	43,27
		Zn (213,857)	0,25		0,00	0,83
		Cd (228,802)	0,00		0,00	>100,00
		Sr (407,771)	10,28		0,05	0,49
		Ba (455,403)	0,36		0,00	0,19
		Cu (324,754)	0,12		0,00	0,23
		Ni (352,454)	0,23		0,00	0,60
		As (193,695)	0,75		0,35	46,98
		Co (340,512)	-0,02u		0,00	5,48
		Pb (405,781)	-0,27 mv		0,01	2,24
		Mo(379,825)	0,05		0,00	4,17
		Mn(403,076)	20,44		0,03	0,14
		Cr (425,433)	0,43		0,04	9,69
		Al (396,152)	73,34 o		5,64	7,69

The data presented in the table prove that the highest efficiency in the decomposition of phosphorites with mineral acids is achieved when hydrochloric acid is used (2N HCl). For example Se - 43.27 against 29.76 with nitric acid; As -46.98 vs. 29.81; Cr - 9.69 vs. 2.47, etc.

Table 3 – Summary data on the chemical analysis of secondary concentrates of Karatau phosphorites, decomposed in nitric and hydrochloric acid

#	Content of mass fraction, %													
	Moist.	P_2O_5	Cl^-	C_2H_2	SO_4^{2-}	F^-	SiO_2	CaO	MgO	Fe_2O_3	Al_2O_3	Tot. nitrogen	$NaNO_2$	NO_3^-
2 n HNO_3 (liquid phase)	–	1,9	7,92	0,0112	2,06	0,77	20,9	0,145	0,014	0,03	0,002	4,23	2,07	17,4
2 n HNO_3 (solid phase)	9,17	0,13	2,64	0,114	2,06	1,52	11,4	0,0207	0,014	0,02	0,06	1,29	1,93	0,02
Summary, %	–	2,03	10,52	0,1252	4,12	2,29	32,3	0,1657	0,028	0,05	0,062	5,52	4,00	17,42
2 n HNO_3 (liquid phase)	–	0,8	61,8	0,0082	2,06	0,42	23,46	0,103	0,028	0,03	0,003	1,53	2,06	–
2 n HNO_3 (solid phase)	8,28	0,5	7,92	0,152	2,26	1,615	22,83	0,014	0,014	0,01	0,06	2,23	2,08	–
Summary, %	–	1,3	69,72	0,1602	4,32	2,035	46,29	0,117	0,042	0,04	0,063	3,76	4,14	–

It can be seen (table 3) that after secondary decomposition of pulp, it still contains valuable elements, which can be used as fertilizers.

Samples of secondary concentrates of Karatau phosphorites, decomposed in nitric and hydrochloric acids, were studied by IR spectroscopic method. In figure 2, weakly pronounced bands characteristic of phosphoric acid with frequencies of 2319 cm^{-1} and medium pronounced bands characteristic of nitrate ions with frequencies of 694 cm^{-1}, 729 cm^{-1}, 879 cm^{-1} are observed.

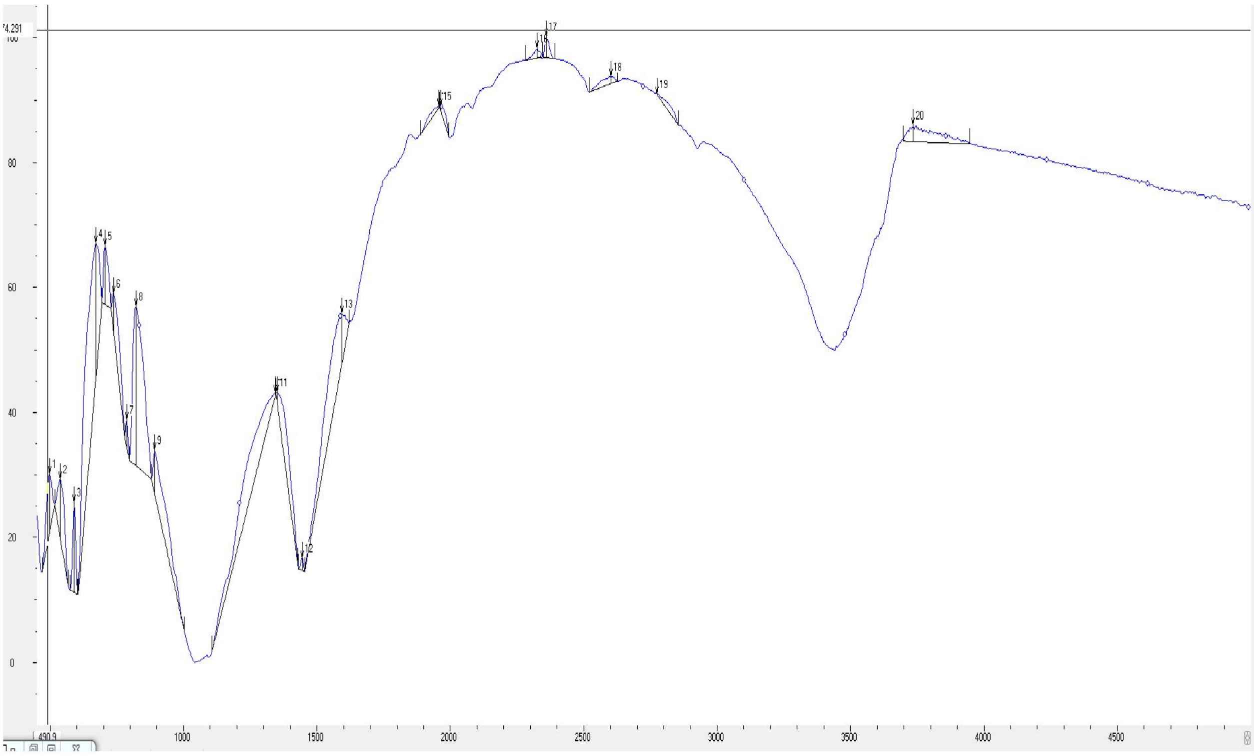

Figure 2 – IR spectra of solutions obtained by decomposition of Karatau phosphorites with nitric acid. The abscissa axis is the oscillation frequency (cm^{-1}), the ordinate – transmission (%)

The IR spectra of solutions obtained by decomposition of Karatau phosphorites with hydrochloric acid (figure 3) show medium-pronounced bands characteristic of phosphoric acid with frequencies of 2144 cm^{-1}, 2403 cm^{-1}, as well as weakly pronounced bands of 2673 cm^{-1}, corresponding to phosphoric acid.

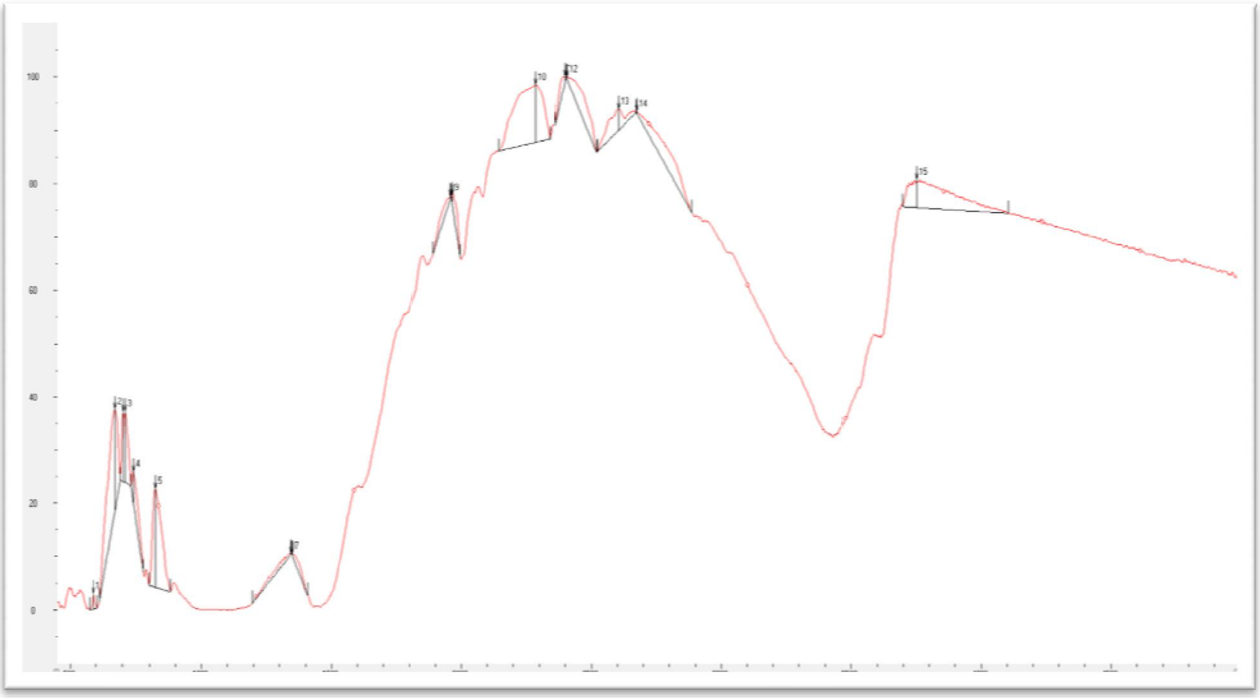

Figure 3 – IR spectra of solutions obtained by decomposition of Karatau phosphorites with hydrochloric acid. The abscissa axis is the oscillation frequency (cm^{-1}), the ordinate axis is the transmission (%)

The results of chemical and physicochemical analysis of the liquid and solid phases of products, obtained by decomposition of Karatau phosphorites with nitric and hydrochloric acids, confirm and supplement each other and show that the main products are phosphates, nitrates and calcium chlorides. The product also contains rare-earth elements with a mass fraction of 23-36% with respect to the initial content in phosphorite.

Conclusions. The results of chemical composition study of Karatauphosphorite include rare-earth elements within Se - 23,0-29,76%, Zn - 0,5-1,68%, Sr - 0,42-2,0%, Ba - 0.20-2.8%, Cu - 0.48-3.6%, Ni - 0.61-0.75%, As - 29.81-32.0%, Co - 1.06-2,10%, Pb - 1.75-2.0%, Mo - 0.8-1.05%, Mn - 0.29-0.35%, Cr - 2.47-3.8%, Al - 5.78-7.9% Y-(yttrium) - 0.007-0.15%, Yb-(ytterbium) - 0.005-0.7%, La-(lanthanum) - 0.025-0.15%, Ce-(cerium) - 0.05-0.30%, Gd- (gadolinium) - 0.002%, Nd-(neodymium) - 0.04-0.05%, Sm-(samarium) - 0.01%, Eu-(europium) - 0.001%, Tb-(terbium) - 0.005%, Dy-(dysprosium) - 0.01%, No- (golya) - 0.001%, Er-(erbium) - 0.01%, Lu-(Lutetium) - 0.001%, Tm-(thulium) -0.0001-0.10%, Pr-(praseodymium) - 0.02%, etc.

The initial Karatauphosphorites contain 23.23% of the sum of rare-earth elements (in terms of oxides), the content of the mass fraction of% CaO, P_2O_5, and also the compounds of iron and aluminum. When processing 1 ton of phosphorite obtaining of about 20-36 kg of the sum of rare-earth element concentrate is possible. The mass fraction of rare-earth elements for decomposition with hydrochloric acid is 36%, and with nitric acid is 27%. The recovery of REE in the concentrate is ~ 75% with respect to the initial content in phosphorite.

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ҚАРАТАУ ФОСФОРИТТЕРДІҢ ҚҰРАМЫНАН СИРЕК-ЖЕР ЭЛЕМЕНТТЕРДІ БӨЛІП АЛУ

Аннотация. Қаратау фосфорит концентраты – кешенді қайта өңдеуге қажетті перспективалық және бірегей шикізат, одан фосфорлы тыңайтқыш сияқты негізгі өнімнен басқа, стронцийдың қосылыстары, сирек жер элементтерін және фторды алуға мүмкіндіктері бар. Фосфоритті кешенді қайта өңдеудің айқын экологиялық негіздемесіне қарамастан, қазіргі уақытта сирек жер элементтерін, стронцийды және фторды жолай бөліп алу үшін жалғыз өндірістік сызбасы бар, ол фосфоритті азот қышқылымен ыдыратуға негізделген.

Бұл мақалада Қаратау (Көкжон, Көксу кен орындары) фосфориттерін тұз және азот қышқылдарымен ыдыратуын ара-қатынасы 1:1, температураны 85-90^{0}С дейін жоғарылатқанда, 30 минут аралығында қарқынды түрде араластыру арқылы зерттеу нәтижелері келтірілген. Алынған өнімдердің химиялық құрамы титриметриялық, гравиметриялық, фотоколориметриялық, потенциометриялық әдістермен анықталды.

Алынған нысандардың талдауы бойынша концентраттағы сирек жер элементтерінің массалық үлесі азот қышқылымен бөліп алғанда 27%, ал тұз қышқылымен 36% құрады, сирек жер элементтерін концентраттан бөліп алу ~ 75% фосфориттің құрамындағы қатынасына қарай 1 тонна фосфоритті қайта өңдеу барысында 20-36 кг сирек жер элементтерінің концентрат сомасын алуға мүмкіндігі бар.

Түйін сөздер: сирек жер элементтері, бөліп алу, ыдырату, концентрат.

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ИЗВЛЕЧЕНИЕ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ ИЗ СОСТАВА ФОСФОРИТОВ КАРАТАУ

Аннотация. Каратауский фосфоритовый концентрат – перспективное и уникальное сырье для комплексной переработки, позволяющее получить, помимо основного продукта – фосфорных удобрений, соединения стронция, редкоземельных элементов и фтора. Несмотря на явную экологическую целесообразность комплексной переработки фосфорита, в настоящее время существует единственная промышленная схема, предусматривающая попутное извлечение редкоземельных элементов, стронция и утилизацию фтора, основанная на разложении фосфорита азотной кислотой.

В данной статье представлены результаты исследования разложения фосфоритов Каратау (месторождения Кокжон и Коксу) соляной и азотной кислотами в соотношении 1:1, при повышении температуры до 85-90 °С, в течение 30 минут с интенсивным перемешиванием. Химический состав полученных продуктов определяли титриметрическим, гравиметрическим, фотоколориметрическим, потенциометрическим методами.

Анализ полученных образцов показал, что массовая доля редкоземельных элементов в концентрате при извлечении азотной кислотой составила 27%, соляной кислотой – 36%, извлечение редкоземельных элементов в концентрат ~ 75 % по отношению к содержанию в фосфорите. Существует возможность получения 20-36 кг суммы концентрата редкоземельных элементов при переработке 1 т фосфорита.

Ключевые слова: редкоземельные элементы, извлечение, фосфориты, разложение, концентрат.

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