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Recovery and Separation of Rare and Radioactive Elements with 5-(Diphenylphosphoryl)hexan-3-one during Phosphogypsum Processing

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Abstract—The possibility of using 5-(diphenylphosphoryl)hexan-3-one as an extractant for efficient recovery of rare-earth metals (REM), as well as uranium(VI) and thorium(IV) from breakdown phosphogypsum solutions within a single technological extraction process was demonstrated. 5-(Diphenylphosphoryl)hexan-3-one as an extractant was compared in terms of efficiency with commercially available TBP and TOPO. It is shown that the complete recovery of rare earth metals into the organic phase is achieved in three stages of depletion. There occurs an extraction purification of total rare earth metals from uranium(VI) and thorium(IV). The separation factor during extraction for U(VI) and ΣREE was $f[\Sigma\text{REE/U(VI)}] > 3000$, and in the case of thorium(IV), $f[\Sigma\text{REE/Th(IV)}] \sim 10000$. 5-(Diphenylphosphoryl)hexan-3-one can be successfully used in the extraction processing of mineral and technogenic raw materials, which enables separation and concentration of REMs.

Keywords: lanthanides, actinides, uranium, thorium, rare earth metals, extraction, recovery, separation, organophosphorus extractants, phosphoryl ketones, mineral and technogenic raw materials, phosphogypsum

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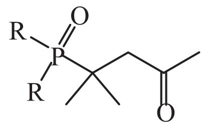
INTRODUCTION

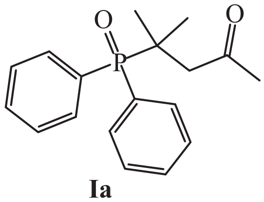
For the Russian Federation, an urgent issue is the search for new raw materials sources of rare earth elements (REE) [1, 2]. Phosphogypsum, a large-tonnage product of apatite processing in the production of extraction phosphoric acid for mineral fertilizers, can serve as one of the promising sources of REE [3–7]. In addition to rare earth elements, phosphogypsum contains uranium, thorium and emanating products of their radioactive decay, which, as environmental pollutants, are of particular danger. Thus, the recovery of REE, uranium, and thorium from phosphogypsum, as well as their separation, is an urgent radiochemical problem.

Liquid extraction is one of the most technologically advanced and efficient methods for extracting and separating rare and radioactive elements [8, 9]. At the same time, the choice of an extractant is of particular importance, the selectivity and efficiency of an extractant determines the economic feasibility of the rare metal raw material processing. When searching for new highly efficient and selective extractants among bifunctional neutral organophosphorus compounds, it was found that phosphoryl ketones **I** with alkyl and phenyl substituents at the phosphorus atom extract actinides and lanthanides from nitric acid media much more efficiently than the known neutral organophosphorus compounds (NPOCs) [10–12].

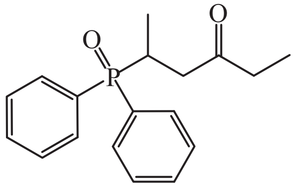


I

R = Alk, Ph



Ia



II

To establish the denticity of the complex formation of phosphoryl ketones with *f*-elements, complexes **Ia** with neodymium(III) and uranyl nitrate were studied using spectral methods and X-ray diffraction analysis [13]. At interaction with uranyl nitrate, regardless of the ratio of components, phosphoryl ketone acts as a monodentate phosphoryl ligand, generating a neutral bis-ligand complex, the structure of which is preserved in solution. When interacting with neodymium nitrate, depending on the ratio of reagents, phosphoryl ketone forms bis- or tris-ligand complexes, acting in the first of them as a bidentate ligand, and in the second, as a phosphoryl monodentate. Due to the chelate interaction of the liganding ensemble of phosphoryl ketone, based on the coordination of both PO and CO groups to the Ln^{3+} ion, compounds of this class exhibit greater selectivity towards lanthanides compared to actinides [13].

Study of the design of promising extractants of the class of phosphoryl ketones for the extraction of *f*-elementst revealed that the modification of phosphoryl ketone **Ia** to its isomeric phosphoryl ketone **II** with isomerization of the alkyl part of the phosphoryl ketone molecule can lead to a significant increase in their efficiency and selectivity as extractants. It was shown in [14] that **II** is the most efficient and selective extractant for the extraction of heavy (Ho, Yb) and light (La, Nd) lanthanides from nitric acid solutions into chloroform and for their separation. Extraction of REEs using compound **II** from the breakdown solution of phosphogypsum [15] and eudialyte concentrate was studied [14, 16]. It was of interest to determine the behavior of uranium and thorium against the background of REE extraction with ligand **II** solutions from phosphogypsum processing solutions.

EXPERIMENTAL

Starting materials. A phosphogypsum sample provided by JSC Voskresensk Mineral Fertilizers (Voskresensk) was broken down according to the procedure in [17, 18]. In this case, the REE salting out agent was calcium nitrate, and the salting out effect of $Ca(NO_3)_2$ present in solutions after breaking down at a concentration of 2 M was equivalent to that of 5 M alkali metal nitrate. The solutions obtained after breaking down the phosphogypsum also contained about 2.3 M of residual nitric acid.

Tributyl phosphate (TBP) (Aldrich, 98%), trioctylphosphine oxide (TOPO) (Aldrich, 99%), and 5-(diphenylphosphoryl)hexan-3-one (**II**) synthesized according to the procedure in [14, 19] and characterized by elemental analysis and NMR spectroscopy (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) were used as extractants. Chloroform (chemically pure grade) served as a diluent of extractants for TOPO and **II**. Nitric acid (extra pure grade) and calcium nitrate (chemically pure grade) were used to break down the phosphogypsum sample.

Extraction technique. Extraction experiments were carried out at a phase ratio of 1 : 1 for 15 min in a rotator at a rotation frequency of 100 rpm. The concentration of the sum of lanthanides, uranium, and thorium in the aqueous phase was determined by the spectrophotometric method [20] with arsenazo III on a Lambda 465 spectrophotometer. Elemental analysis was carried out by ICP-MS mass spectrometric method using an Agilent 7500ce instrument (Agilent Technologies Inc., USA) with a measurement error of 4.5%.

The distribution coefficients of REE, thorium, and uranium ($D = [M]_{org}/[M]_{aq}$) were determined as the ratio of their concentrations in the organic and aqueous phases. The separation factors of the total REE and each of the actinides were found as the ratio of their distribution coefficients.

RESULTS AND DISCUSSION

The chemical composition of the phosphogypsum sample used in the study and found according to the method [21], is present in Tables 1 and 2.

It can be seen from Tables 1 and 2 the content of lanthanides in phosphogypsum is low and does not exceed ~0.5%. Therewith, lanthanum, cerium, and neodymium are the main proportion of lanthanides in

Table 1. The chemical composition of the phosphogypsum sample. Total water content 27.8%

Oxide	CaO	SrO	Na_2O	MgO	Al_2O_3	K_2O	Fe_2O_3	TiO_2	MnO	SO_3	SiO_2	P_2O_5	F	Ln_2O_3 (total)
Content, wt %	27.90	1.63	0.27	0.18	0.17	0.10	0.03	0.02	0.005	40.17	6.79	1.15	0.35	0.44

Table 2. The content of REE oxides in a phosphogypsum sample

Oxide	Ln_2O_3 (total)	La_2O_3	CeO_2	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3
Content, wt %	0.44	0.133	0.193	0.020	0.071	0.008	0.003	0.007
Oxide	Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	Y_2O_3
Content, wt %	0.0003	0.004	0.001	0.001	0.0002	0.0004	< PO	0.017

the phosphogypsum sample, while other rare earth elements account for less than ~15%.

To estimate the number of stages of the cross-current cascade required for the complete recovery of rare earth elements from the phosphogypsum breakdown solution [22, 23], experiments were conducted both with a single phase contact and in the cross current mode. Simulation of the exhaustive stage of the cross current cascade makes it possible to estimate the number of stages required to reach the steady state or to get as close as possible to it.

In the case of using 100% TBP as an extractant, four exhaustion stages were carried out, and for an 1.33 M **II** solution in chloroform, three stages (Figs. 1 and 3).

All experiments were conducted at a ratio of phase volumes O : A = 1 : 1. Schemes presented in Figs. 1 and 3 shows that when depleted, one portion of the fresh aqueous phase contacts in cuvette 1 with a portion of the fresh organic phase. After phase separation in a separatory funnel, the depleted aqueous phase enters cuvette 2, where it contacts with a fresh portion of the organic phase. After contact in the second cuvette and phase separation, the depleted aqueous phase enters the 3rd cuvette, and then into the 4th. After each contact, the total content of REE, uranium, and thorium in the aqueous phase was determined spectrophotometrically by the express method.

Figure 2 shows the distribution coefficients of REE, uranium, and thorium upon a single contact of 100% TBP with a phosphogypsum breakdown solution.

After four stages of extraction of REE, thorium, and uranium, almost all components of the phosphogypsum breakdown solution were completely extracted into the 100% TBP phase. TBP was pre-saturated with nitric acid.

Trialkylphosphine oxides $(Alk)_3PO$, in particular TOPO, as compared to TBP and other trialkylphosphates $(AlkO)_3PO$, as a rule, have a higher extraction ability due to less electronegative substituents at the phosphorus atom compared to alkyl phosphates [24]. At the same

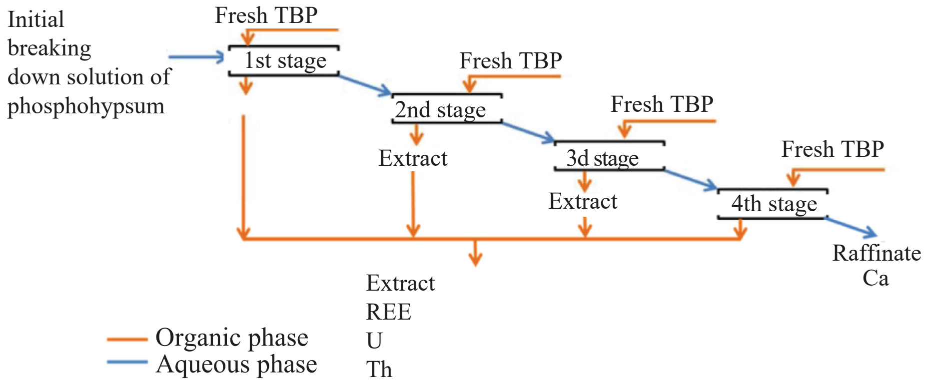


Fig. 1. Scheme of four stages of extraction depletion with 100% TBP from the break down solution of phosphogypsum.

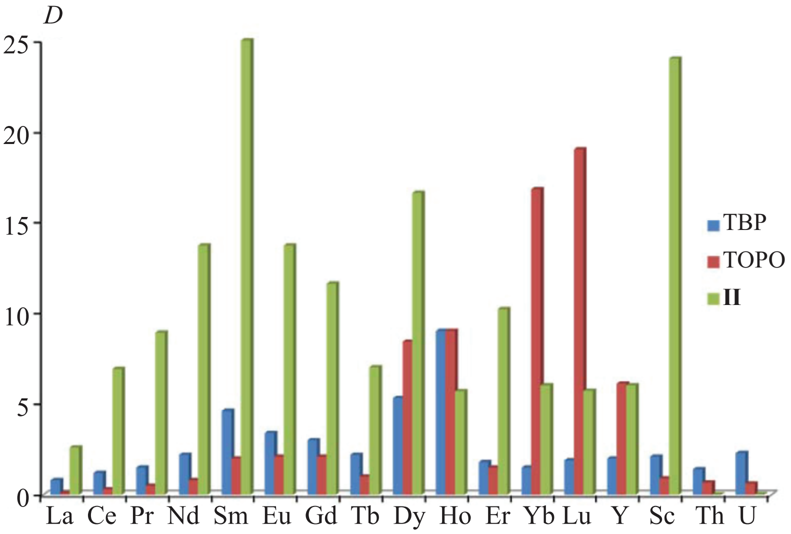


Fig. 2. Distribution coefficients of REE, uranium(VI), and thorium(IV) upon single contact of the aqueous and organic phases in the presence of 100% TBP, as well as 1.8 M TOPO and 1.33 M **II** in $CHCl_3$.

time, alkyl phosphine oxides, owing to their higher electron-donating ability, efficiently extract metals at lower acid concentrations compared to alkyl phosphates. The highest extraction ability of alkyl phosphine oxides is in the region of 1 M HNO_3, while for $(AlkO)_3PO$ the highest extraction efficiency is possible in the region of 3 M HNO_3 [25, 26]. Figure 2 exhibits the distribution coefficients of rare-earth elements during their extraction (single contact of the aqueous and organic phases) from the breakdown solution of phosphogypsum with an 1.8 M TOPO solution in $CHCl_3$. The *D* values for light REMs are found to be significantly lower than in the case of 100% TBP, although heavy REEs are better distributed into the organic phase.

Since the fact that TOPO already showed worse characteristics at one stage of extraction than the cheaper and more accessible TBP, exhaustive extraction was not performed in the case of TOPO.

To evaluate the efficiency and selectivity of phosphoryl ketone **II** for the recovery of REE, as well as U(VI) and Th(IV), a single contact of an 1.33 M solution of **II** with a phosphogypsum breakdown solution was performed.

Figure 2 shows the results of a single extraction of REE, thorium(IV), and uranium(VI) from the breakdown solution of phosphogypsum with 100% TBP, as well as solutions of 1.8 M TOPO and 1.33 M **II** in $CHCl_3$.

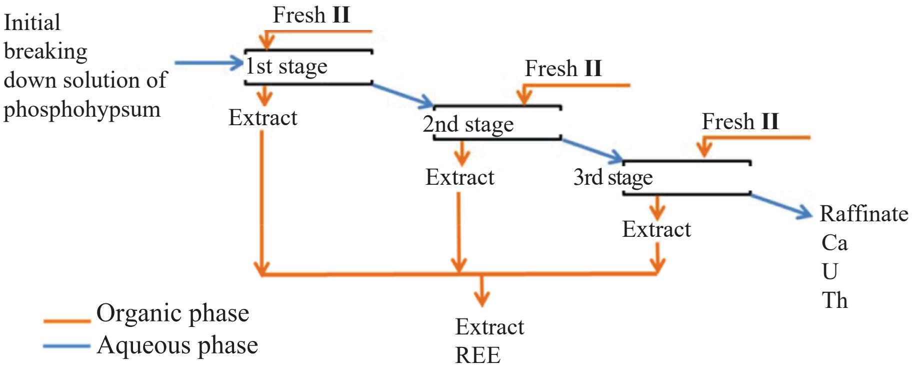


Fig. 3. Scheme of three stages of the cross-current extraction with 1.33 M **II** in chloroform from the breakdown solution of phosphogypsum.

As can be seen from Fig. 2, the extraction ability of **II** is high towards rare earth elements of both the cerium and yttrium subgroups, which distinguishes it from both TBP, which is more selective towards REES of the cerium subgroup, and from TOPO, which is selective towards the REEs of yttrium subgroup.

Extraction with a phosphoryl ketone **II** solution revealed an unexpected effect of an increase in the distribution coefficients of lanthanides (*D*) of the cerium subgroup with the maximum value of *D* corresponding to samarium. The effect obtained may be due to the low content of lanthanides in comparison with lanthanum and cerium. The differences in the extraction of the Nd(III) and Sm(III) pair are greater than expected, since the neodymium concentration in the initial breakdown solution of phosphogypsum is 250 mg/L, and that of samarium is, 39 mg/L. An important role in the efficiency of lanthanide extraction is played by the known rule for the change in the strength of lanthanide coordination complexes with an increase in the atomic number of an element in the cerium subgroup [27–29]. It should be noted that phosphoryl ketone **II** exhibits the highest efficiency with respect to pairs of heavy and light lanthanides, and especially towards Sm(III). The extraction properties of **II** were compared with the properties of well-known phosphoryl-containing extractants, TBP and TOPO, studied under the same experimental conditions (Fig. 2). Figure 2 shows that in relation to the extraction of uranium(VI) and thorium(IV), known extractants (TBP and TOPO) are more efficient. However, in contrast to them, phosphoryl ketone **II** does not exhibit extraction ability towards U(VI) and Th(IV), which is a prerequisite for the use of **II** as an extractant for the selective separation of emanating U(VI) and Th(IV) to obtain a collective REE concentrate.

Afterwards, three stages of cross current were carried out (Fig. 3) during extraction with according to the procedure described above.

It was found that under these conditions, the extraction ability of an 1.33 M **II** solution in $CHCl_3$ is significantly higher than that of 100% TBP, as a result the complete extraction of REE into the organic phase is achieved.

It should be noted that uranium(VI) and thorium(IV) are extracted into the organic phase containing phosphoryl ketone **II** much worse (in the case of a single extraction, Figs. 2 and 4), which may be a prerequisite for the extraction separation of the total REE and radioactive uranium(VI) and thorium(IV). The separation factor for

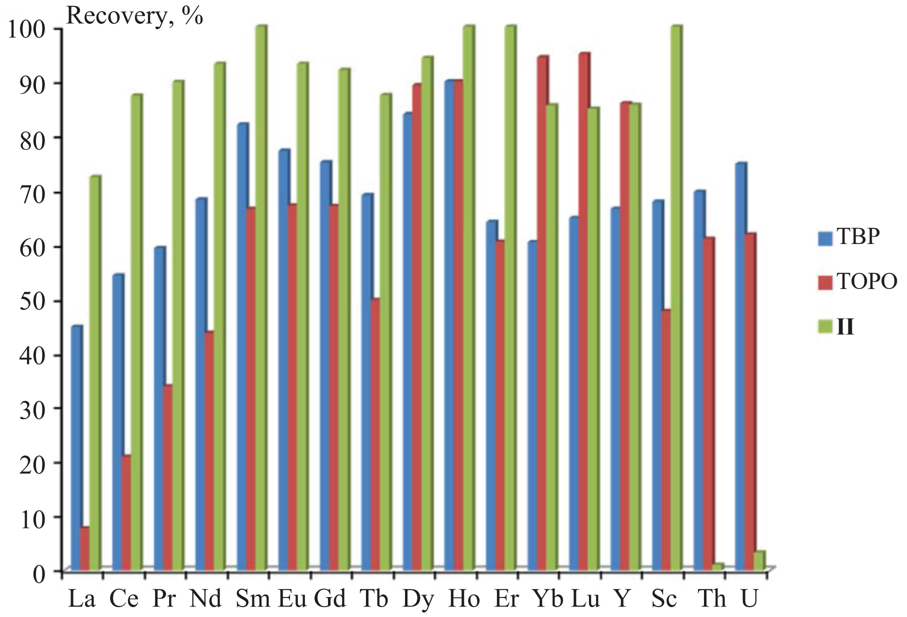


Fig. 4. Comparison of the recovery of REE, thorium(IV), and uranium(VI) upon single extraction with 100% TBP, 1.6 M TOPO, and 1.33 M **II** solutions of in chloroform.

U(VI) and the total REE was $f[\Sigma REE/U(VI)] > 3000$, and in the case of thorium(IV) $f[\Sigma REE/Th(IV)]$ ~10 000 was three times higher.

The results obtained demonstrate the possibility of using 5-(diphenylphosphoryl)hexan-3-one (**II**) as an extractant for the efficient extraction of REEs from phosphogypsum breakdown solutions, as well as their separation from radioactive uranium(VI) and thorium(IV) within a single technological process. In contrast to commercially available TBP and TOPO, the complete recovery of REMs into the organic phase is achieved in three depletion stages, while the phosphoryl ketone concentration is almost 3 times lower than the TBP concentration (3.62 M). Both of these facts lead to a significant simplification of the REMs recovery from the breakdown solution of phosphogypsum.

CONCLUSIONS

Thus, 5-(diphenylphosphoryl)hexan-3-one is a more efficient extractant of REMs than tributyl phosphate and trioctylphosphine oxide. It has a high selectivity, which allows, during the extraction of REE, to purify them from radioactive uranium and thorium with a high separation factor (for U(VI) and total REE $f[\Sigma REE/U(VI)] > 3000$, for thorium(IV) and total REE $f[\Sigma REE/Th(IV)]$ ~10 000). This reagent can be successfully used for the extraction processing of phosphogypsum and other mineral and technogenic raw materials, making it possible to extract and concentrate REEs, as well as to separate them from accompanying impurities, in particular, from radioactive uranium and thorium.

FINDING

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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