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To the 85th Anniversary of birthday of late Yu.G. Gololobov

Recovery of Lanthanides from Digested Phosphogypsum Solutions Using a New Organophosphorus Extractant, 5-(Diphenylphosphoryl)hexan-3-one

A. M. Safiulina[a], A. G. Matveeva[b], A. V. Evtushenko[a], A. V. Lizunov[c], E. I. Goryunov[b], I. B. Goryunova[b], G. V. Bodrin[b], A. A. Semenov[c], and V. K. Brel[b]

[a] *Uralchem United Chemical Company, Open Joint-Stock Company,*
Presnenskaya nab. 6/2, Moscow, 123317 Russia

[b] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
ul. Vavilova 28, Moscow, 119991 Russia
e-mail: matveeva@ineos.ac.ru

[c] *Bochvar High-Technology Research Institute of Inorganic Materials, Open Joint-Stock Company,*
Rosatom State Atomic Energy Corporation, ul. Rogova 5a, Moscow, 123098 Russia

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Abstract—Extraction of rare earth elements from digested phosphogypsum solutions with a number of well-known organophosphorus compounds, tributyl phosphate, trioctylphosphine oxide, and bis(2-ethylhexyl)-phosphoric acid, as well as with phosphoryl ketone $Ph_2P(O)CHMeCH_2C(O)Et$, was studied. It was found that this phosphoryl ketone is the most effective reagent for obtaining the mixed lanthanide concentrate. An improved synthetic route to this compound was developed.

Keywords: phosphogypsum, lanthanides, organophosphorus extractants, phosphoryl ketones, extraction

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Due to a wide diversity of applications and low resource availability, rare earth metals rank now among the most popular chemical elements. The high demand and poor resource base stimulate the development of new ways to recover rare earth metals from various raw materials. The latter include ores with low content of rare earth metals and technogenic waste of different origin: chemical plant waste, spent nuclear fuel, discarded items and products, etc.

Significant amounts of rare earth metals are concentrated in dumped phosphogypsum,[1] a waste product of apatite concentrate processing into mineral fertilizers, which, though having a relatively low content of rare earth metals (0.3–1%), is still a valuable raw material. This is because integrated processing of phosphogypsum makes it possible to obtain, along with a rare-earth metal concentrate, high-quality building materials and incidentally solve the environmental problems that inevitably arise in cases where phosphogypsum is accumulated as a fertilizer production waste. In recent years, a number of methods were proposed for phosphogypsum processing, in particular those involving recovery of the mixed rare-earth metal concentrate [1–10]. Most often, the main stages in phosphogypsum processing schemes are leaching with mineral acids and recovery of rare-earth metal concentrate from an aqueous solution by multistage solvent extraction [11–15]. The most common agents used for the extraction are organic extractants based on neutral organophosphorus compounds (predominantly tributyl phosphate) or organophosphorus acids [predominantly bis(2-ethylhexyl)-phosphoric acid] [5, 15–17]. However, these extractants are characterized by fairly low distribution ratios

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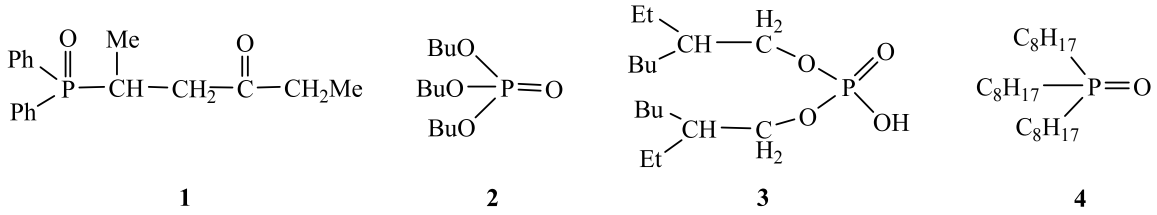
[1] Phosphogypsum is calcium sulfate contaminated with P_2O_5, F, Fe, Al, Sr, and rare-earth metal impurities, comprising most of the rare earth metals contained in apatite.

Scheme 1.



for lanthanides. The efficiency of the extraction procedures depends primarily on the correct choice of extractant, so the search for new effective and synthetically accessible reagents for the recovery of rare earth metals remains topical.

It was found recently that phosphoryl-containing ketones $R_2^1P(O)CR^2R^3CH_2C(O)Me$ (R^1 = Alk, Ph; R^2 = H, Me, Ph, Het; R^3 = H, Me) are highly effective in the extraction of lanthanides from model nitrate solutions into chloroform. In this process they significantly surpass the known extractants tributyl phosphate, trioctylphosphine oxide $(C_8H_{17})_3P(O)$, and carbamoyl-methylphosphine oxide $Ph_2P(O)CH_2C(O)\cdot NBu_2$ [18–20]. Among the phosphoryl ketones studied, 5-(diphenylphosphoryl)hexan-3-one $Ph_2P(O)CHMe\cdot CH_2C(O)Et$ extracts lanthanides most effectively [21].

Here, we studied the extraction of rare earth metals from digested phosphogypsum solutions [9] both with phosphoryl ketone **1** and well-known organophosphorus compounds **2–4** and mixtures thereof (Scheme 1).

To obtain the necessary amount of compound **1** we developed an improved version of the earlier developed procedure of one-pot synthesis of this reagent [21], which gives the target product with no less than 99% purity in virtually quantitative yield (see Experimental).

In our experiments we used a sample of phosphogypsum (hemihydrate phosphogypsum) which is a waste product of the phosphoric acid production in Voskresenskie Mineral'nye Udobreniya, Open Joint-Stock Company (Uralchem United Chemical Company, Open Joint-Stock Company). The chemical composition of the phosphogypsum sample is shown in Tables 1 and 2.

As a result of phosphogypsum digestion by the procedure described in [9] up to 98% of rare earth metals pass into the aqueous solution. The nitric acid and calcium nitrate concentrations in the resultant solution are 2.3 and 2 M, respectively. The presence of nitrates is known to enhance the extraction of rare earth metals (see, e.g. [11]). Various methods were described in the literature employed for isolating a rare-earth metal concentrate from aqueous solutions, among which solvent extraction is the most popular and workable method [22–26]. The most common extractants used for this purpose are neutral organophosphorus compounds and acids of phosphorus, as well as their synergistic mixtures [15, 16, 23, 26–28]. It should also be noted that successful use of an extractant for recovery and separation of rare earth metals from model solutions does not always mean equally successful results for real systems.

Table 1. Chemical composition of the phosphogypsum[a] sample

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)
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

[a] Total water content is 27.8%.

Table 2. Content of rare-earth metal oxides in the 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	Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	Y_2O_3
wt %	0.440	0.133	0.193	0.020	0.071	0.008	0.003	0.007	0.0003	0.004	0.001	0.001	0.0002	0.0004	–[a]	0.017

[a] Below the detection limit.

Table 3. Distribution ratio of lanthanum D_{La} in the extraction with reagent **2** in different stages of extraction from the digested phosphogypsum solution

Extraction stage no.	D_{La}
1	0.8
2	2.9
3	3.8
4	3.3

In the extraction studies, we determined for each extractant tested the number of extraction stages required for exhaustive extraction of rare earth metals. As indicator served the change in the lanthanum distribution ratio (distribution ratio $D_{\mathrm{M}} = [M]_{\mathrm{org}}/[M]_{\mathrm{aq}}$).

Tributyl phosphate **2** is the main agent that has been used for the recovery of uranium and plutonium from nuclear fuel by most countries since the 1950s [23, 26, 27]. This phosphate also extracts lanthanides(III) for which the distribution ratio tends to increase with increasing atomic number. The extraction efficiency is highly dependent on the medium: In chloride solutions D_{Ln} is significantly lower than that in a nitrate medium [16, 29].

In this study, we used individual reagent **2** for the recovery of rare earth metals from digested phosphogypsum solutions. It was found that under these conditions the exhaustive extraction of rare earth metals requires a 4-stage process (Table 3). As seen from Table 4, a four-stage extraction procedure afforded exhaustive extraction of all rare earth metals except for dysprosium (~91% recovery).

Organophosphorus acids are effective in extraction of rare earth metals in diverse media (nitric acid, sulfuric acid, hydrochloric acid, perchloric acid, etc. [16, 17, 23]), with the extraction efficiency depending fairly strongly on the acidity of the aqueous solution [30, 31]. In this regard it should be noted that synergistic mixtures of phosphorus acids with neutral organophosphorus compounds are known to extract rare earth metals more efficiently than do individual compounds in some cases [4, 12, 13, 32–34].

We found (Table 5) that acid **3**, both individually and when mixed with neutral organophosphorus compounds, is unsuitable for the recovery of rare earth metals from digested phosphogypsum solutions. The D_{La} ratios for compound **3** are 5–8 times lower than those for reagent **2**.

Table 4. Extraction of rare earth metals from the digested phosphogypsum solution with reagent **2**

Element	Content[a], mg/L			Degree of recovery[b], %	
	a_0	a_1	a_4	b_1	b_4
La	510	280	2.9	45.1	99.4
Ce	770	350	2.1	54.5	99.7
Pr	79	32	≤1	59.5	≤100
Nd	250	79	≤0.5	68.4	≤100
Sm	39	7	≤0.8	82.1	≤100
Eu	11	2.5	≤0.04	77.3	≤100
Gd	29	7.2	≤0.4	75.2	≤100
Tb	12	3.7	0.3	69.2	97.5
Dy	15	2.4	1.4	84	90.7
Ho	2	0.2	≤0.3	90	≤100
Er	5.6	2	≤0.5	64.3	≤100
Tm	≤0.4	≤0.2	≤0.3	≤50	≤50
Yb	1.6	0.63	≤0.03	60.6	≤100
Lu	0.2	0.07	≤0.01	65	≤100
Y	60	20	0.1	66.7	99.8
Sc	0.25	0.08	≤0.01	68	≤100

[a] a_0, a_1, and a_4 is the respective content of the element in the initial solution and after the first and fourth stages of the extraction cycle.

[b] b_1 and b_4 are the respective degrees of recovery of the element after the first and fourth stages of the extraction cycle.

Alkylphosphine oxides are more effective extractants than alkyl phosphates, but due to a high electron density on the oxygen in the P=O group they are very easily protonated in acidic media, whereby they fail to act as extractants. Therefore, unlike phosphates, they are used only at low acid concentrations [16, 23, 26, 27].

Under the actual experimental conditions (HNO_3 concentration 2.3 M) the lanthanum distribution ratio in the extraction with phosphine oxide **4** is 0.09, which is almost 9 times lower than in the case of phosphate 2 (Table 3). Accordingly, the degree of recovery of lanthanum is as low as 7.8%. However, in contrast to the situation with reagent **2**, heavy and light lanthanides are differently extracted by compound **4**. The degree of recovery of light lanthanides (La–Tb) with phosphine oxide **4** is lower than that in the case of phosphate **2** (cf. Tables 4 and 6), whereas heavy lanthanides (Dy, Ho, Yb, Y) are extracted by phosphine oxide **4** much more efficiently: These elements

Table 5. Distribution ratio of lanthanum (D_{La}) in the extraction with reagent **3** and its synergistic mixtures from the digested phosphogypsum solution (stage 1)

Extractant	D_{La}
Reagent **3**	0.06
Reagent **2**-reagent **3** mixture (1 : 1)	0.16
Solution of reagent **3** (1.8 M) and reagent **4** (1.8 M) in chloroform	0.095

are recovered to 86–95% in the first stage (Table 6). Nevertheless, reagent **4** is unsuitable for recovery of the mixed rare-earth metal extract from digested phosphogypsum solutions because of a low content of heavy lanthanides in phosphogypsum. Moreover, extraction with 3.6 M solution of reagent **4** in chloroform was accompanied by the appearance of a third phase.

The extraction properties of phosphoryl ketone **1** were examined earlier in model experiments on the recovery of *f*-elements from nitric acid solutions and in experiments on the recovery of rare earth metals from digested eudialyte solutions [21]. It was found that this reagent exceeds in the extraction properties both the traditional neutral organophosphorus compounds [reagents **2** and **4** and bidentate carbamoylmethylphosphine oxide $Ph_2P(O)CH_2C(O)NBu_2$] and most of related diphenylphosphoryl ketones [19–21].

Table 7 shows that D_{La} for phosphoryl ketone **1** significantly exceeds those for the other extractants tested (cf. Tables 3, 5, and 7). In particular, in the first extraction stage D_{La} for compound **1** is 3 times as large as that that for reagent **2**.

As seen from Table 8, all rare earth metals are quantitatively recovered with phosphoryl ketone **1** from the digested phosphogypsum solution after the third extraction stage.

Thus, among the organophosphorus extractants tested, the most effective for recovery of the overall extract of rare earth metals from digested phosphogypsum solutions is 5-(diphenylphosphoryl)hexan-3-one **1,** a new reagent belonging to the class of phosphoryl ketones. In contrast to the other compounds and mixtures thereof tested, reagent **1** affords exhaustive extraction of rare earth metals into the organic phase in three stages of extraction, with the ketone **1** concentration being almost three times lower than that of phosphate **2**. For these two reasons the process of the recovery of rare earth metals from digested phosphogypsum solution is significantly simplified.

Table 6. Extraction of rare earth metals from the digested phosphogypsum solution with 3.6 M solution of reagent **4** in chloroform

Element	Content[a], mg/L		Degree of recovery, %
	a_0	a_1	
La	510	470	7.8
Ce	770	610	20.8
Pr	79	52	34.2
Nd	250	140	44.0
Sm	39	13	66.7
Eu	11	3.6	67.3
Gd	29	9.5	67.2
Tb	12	6	50.0
Dy	15	1.6	89.3
Ho	2	0.2	90.0
Er	5.6	2.2	60.7
Tm	≤0.4	≤0.2	≤50
Yb	1.6	0.09	94.4
Lu	0.2	0.01	95.0
Y	60	8.4	86.0
Sc	0.25	0.13	48.0

[a] a_0 and a_1 is the respective content of the element in the initial solution and after the first stage of the extraction cycle.

EXPERIMENTAL

The ^1H and ^{31}P ($CDCl_3$) NMR spectra were recorded on a Bruker AV-400 instrument [400.13 (^1H) and 161.98 MHz (^{31}P)]. The residual proton signals of the deuterated solvent served as the internal reference (^1H), and 85% H_3PO_4, as the external reference (^{31}P).

Elemental analysis of phosphoryl ketone **1** was carried out in the Laboratory of Microanalysis, Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences.

Tributyl phosphate **2** (98%, Aldrich), bis(2-ethylhexyl)phosphoric acid **3** (97%, Aldrich), trioctylphosphine oxide **4** (99%, Aldrich), and the initial trans-hex-4-en-3-one (Aldrich) were used without further purification. Diphenylchlorophosphine (Acros) was purified by vacuum distillation just before the reaction. All the manipulations with diphenylchlorophosphine were performed under argon.

We used a sample of phosphogypsum (hemihydrate phosphogypsum) which is a waste product of the

Table 7. Distribution ratio of lanthanum (D_{La}) in the extraction with 1.33 M solution of reagent **1** in chloroform for different stages of the extraction from the digested phosphogypsum solution

Extraction stage no.	D_{La}
1	2.6
2	4.2
3	3.8

phosphoric acid production in Voskresenskie Mineral'nye Udobreniya, Open Joint-Stock Company (Uralchem United Chemical Company, Open Joint-Stock Company). The chemical composition of the phosphogypsum sample was analyzed by inductively coupled plasma optical emission spectroscopy on a Thermo Jarrell Ash IRIS Advantage mass spectrometer; digestion was carried out by the procedure described in [35]. The total water content (crystallization and hydration) in the sample was determined by the thermogravimetric method using an A&D MX-50 automatic moisture analyzer.

5-(Diphenylphosphoryl)hexan-3-one (1). A mixture of 9.3 g (94.8 mmol) of trans-hex-4-en-3-one and 20.9 g (94.7 mmol) of Ph_2PCl was maintained in the dark at room temperature for 72 h. The solidified reaction mixture was cooled to 0°C, after which 30 mL of anhydrous EtOH was added. The resulting mixture was stirred at this temperature until the formation of a homogeneous solution (~3 h), and the excess alcohol was distilled off. The residue was kept in a vacuum (~1 Torr) at 65°C for 2.5 h, dissolved in 120 mL of a CH_2Cl_2–heptane mixture (1 : 1), and filtered through 10 g of basic Al_2O_3, after which Al_2O_3 was washed with 20 mL of CH_2Cl_2. The combined filtrates were evaporated, and the residue was triturated with 70 mL of hexane; the resulting precipitate was separated, washed (2 × 90 mL) with a diethyl ether-hexane mixture (2 : 1), and dried in a vacuum (~1 Torr) at 50°C for 1 h. Yield 27.0 g (94.9%), mp 95–96.5°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.94 t (3H, $C\underline{H}_3CH_2$, $^3J_{HH}$ 7.3), 1.09 d.d (3H, $C\underline{H}_3CH$, $^3J_{HH}$ 7.0, $^3J_{HP}$ 16.4), 2.29 q (2H, $CH_3C\underline{H}_2$, $^3J_{HH}$ 7.3), 2.54–2.71 m (2H, $CHC\underline{H}_2$), 3.05–3.16 m (1H, CHP), 7.39–7.51 m (6H, *m,p*-C_6H_5), 7.72–7.82 m (4H, *o*-C_6H_5). ^{31}P NMR spectrum, δ_P 37.9 ppm. Found, %: C 71.88; H 6.99; P 10.41. $C_{18}H_{21}O_2P$. Calculated, %: C 71.99; H 7.05; P 10.31.

Study of the extraction. The phosphogypsum sample was digested by the procedure described in [9]. The HNO_3 concentration in the solution obtained after phosphogypsum digestion was 2.3 M.

Table 8. Extraction of rare earth metals from the digested phosphogypsum solution with 1.33 M solution of reagent **1** in chloroform

Element	Content[a], mg/L			Degree of recovery[b], %	
	a_0	a_1	a_3	b_1	b_2
La	510	140	1.8	72.5	99.6
Ce	770	97	1.2	87.4	99.8
Pr	79	8	≤1	89.9	≤100
Nd	250	17	≤0.4	93.2	≤100
Sm	39	≤0.8	≤0.6	≤100	≤100
Eu	11	0.75	≤0.03	93.2	≤100
Gd	29	2.3	≤0.3	92.1	≤100
Tb	12	1.5	0.5	87.5	95.8
Dy	15	0.85	≤0.2	94.3	≤100
Ho	2	≤0.3	≤0.2	≤100	≤100
Er	5.6	≤0.5	≤0.4	≤100	≤100
Tm	≤0.4	≤0.3	≤0.2	≤25	≤50
Yb	1.6	0.23	≤0.02	85.6	≤100
Lu	0.2	0.03	≤0.01	85	≤100
Y	60	8.6	0.1	85.7	99.8
Sc	0.25	≤0.01	≤0.01	≤100	≤100

[a] a_0, a_1, and a_3 is the respective content of the element in the initial solution and after the first and third stages of the extraction cycle.

[b] b_1 and b_3 are the respective degrees of recovery of the element after the first and third stages of the extraction cycle.

For preparation of solutions we used chloroform (reagent grade). The solutions of the extractants in chloroform and mixtures of the extractants were prepared by the volumetric-gravimetric method. The extraction experiments were performed in test tubes with ground-glass stoppers at a 1 : 1 organic to aqueous phase volume ratio. The phases were stirred for 15 min in an RS-60 BioSan rotator at 100 rpm. The equilibrium time for the extraction was checked by increasing the phase contact time to 60 min, during which period the distribution ratios (D_M) remained unchanged. The phase separation was achieved by centrifugation. The concentrations of the elements in the initial and the equilibrium aqueous solutions were determined by inductively coupled plasma optical emission spectroscopy using the procedure from [36]. The distribution ratios ($D_M = [M]_{org}/[M]_{aq}$) were determined by calculating the concentration in the organic phase from the difference of the concentrations for the initial and equilibrium aqueous phases. The number of exhaustion stages for the extractant selected was established based on the onset of a decrease in the distribution ratio for lanthanum (D_{La}). The lanthanum content was measured after each contact between the organic and aqueous phases. The HNO_3 concentration in the aqueous phase was determined by acid-base titration with NaOH (bromothymol blue indicator). All the experiments were performed at the temperature of 20±2°C.

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