

Article

Recovery of Uranium, Thorium, and Other Rare Metals from Eudialyte Concentrate by a Binary Extractant Based on 1,5-bis[2-(hydroxyethoxyphosphoryl)-4-ethylphenoxy]-3-oxapentane and Methyl Trioctylammonium Nitrate

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Citation: Safiulina, A.M.; Lizunov, A.V.; Semenov, A.A.; Baulin, D.V.; Baulin, V.E.; Tsivadze, A.Y.; Aksenov, S.M.; Tananaev, I.G. Recovery of Uranium, Thorium, and Other Rare Metals from Eudialyte Concentrate by a Binary Extractant Based on 1,5-bis[2-(hydroxyethoxyphosphoryl)-4-ethylphenoxy]-3-oxapentane and Methyl Trioctylammonium Nitrate. *Minerals* **2022**, *12*, 1469. <https://doi.org/10.3390/min12111469>

Academic Editor: M. Akbar Rhamdhani

Received: 30 August 2022

Accepted: 14 November 2022

Published: 20 November 2022

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Abstract: Eudialyte-group minerals are of scientific interest as important concentrators of rare elements (mainly Zr and REE) in apatitic alkaline rocks and a potential source of REE, Zr, Hf, Nb, and Ta for industrial use. Extraction of uranium(VI), thorium(IV), zirconium(IV), hafnium(IV), titanium(IV), and scandium(III) by a binary extractant based on 1,5-bis[2-(hydroxyethoxyphosphoryl)-4-ethylphenoxy]-3-oxapentane and methyl trioctylammonium nitrate from eudialyte breakdown solutions is studied. Extraction isotherms were obtained and exhaustive extraction was investigated. It is shown that uranium, thorium, hafnium, zirconium, scandium, and titanium are almost completely recovered in two-stage extraction by a mixture of 1,5-bis[2-(hydroxyethoxyphosphoryl)-4-ethylphenoxy]-3-oxapentane and methyltrioctylammonium nitrate in 1,2-dichloroethane. Quantitative characteristics were compared for uranium(VI), thorium(IV), zirconium(IV), hafnium(IV), titanium(IV), and scandium(III). It was shown that the extraction efficiency of the metals by the binary extractant based on 1,5-bis[2-(hydroxyethoxyphosphoryl)-4-ethylphenoxy]-3-oxapentane and methyltrioctylammonium nitrate in 1,2-dichloroethane is much higher in comparison with the commercially available tributyl phosphate.

Keywords: eudialyte; actinides; lanthanides; extraction; recovery; separation; organophosphorus extractants; phosphoryl podands; mineral processing

1. Introduction

Technological progress is related with the increased consumption of rare and rare earth metals (RMs and REMs) due to their use in functional and engineering materials in a number of technologies and technical devices: in optics, electronics, energy storage systems, reactor industry for different applications, transport vehicles, etc. [1–3]. The absence of the alternatives for RM and REM and the limited concentrations in ore deposits, as well as problems with their delivery and distribution, led to a surge of their prices [4,5]. These problems stimulated the search for new approaches for the production of rare metal concentrates from low-grade ores and industrial wastes [6–11].

Eudialyte-group minerals (EGMs) are of significant scientific and industrial interest as important concentrators of RM and REM in apatitic alkaline rocks [12–14]; therefore, these

minerals are considered as important concentrators of rare elements (mainly Zr and REE) in agpaite alkaline rocks and a potential source of REE, Zr, Hf, Nb, and Ta for industrial use [15–26]. EGMs are characterized by the following general crystal chemical formula: $[N(1)_3N(2)_3N(3)_3N(4)_3N(5)_3]\{M(1)_6M(2)_3M(3)M(4)Z_3(Si_9O_{27-3x}(OH)_{3x})_2(Si_3O_9)_2\emptyset_{0-6}\}X(1)X(2)$, where $M(1) = {}^{VI}Ca, {}^{VI}Mn^{2+}, {}^{VI}REE, {}^{VI}Na, {}^{VI}Fe^{2+}$; $M(2) = {}^{IV,V}Fe^{2+}, {}^{V,VI}Fe^{3+}, {}^{V,VI}Mn^{2+}, {}^{V,VI}Na$, and ${}^{IV,V}Zr$; $M(3)$ and $M(4) = {}^{IV}Si, {}^{VI}Nb, {}^{VI}Ti$, and ${}^{VI}W^{6+}$; $Z = {}^{VI}Zr, {}^{VI}Ti$; $\emptyset = O, OH$; $N(1)–N(5)$ are extra-framework cations ($Na, H_3O^+, K, Sr, Ln, Y, Ba, Mn^{2+}, Ca$) or H_2O ; $X(1)$ and $X(2)$ are extra-framework water molecules, halide (Cl^-, F^-) and chalcogenide (S^{2-}) anions, and anionic groups (CO_3^{2-}, SO_4^{2-}); $x = 0–1$; coordination numbers of key sites of the framework are indicated with Roman numerals [27–29]. Because of the complex microporous crystal structure of EGMs, the components are distributed between the different crystallographic sites (Figure 1), which has an influence on the search for the efficient schemes of the decomposing of EGMs and the extraction of RMs and REMs.

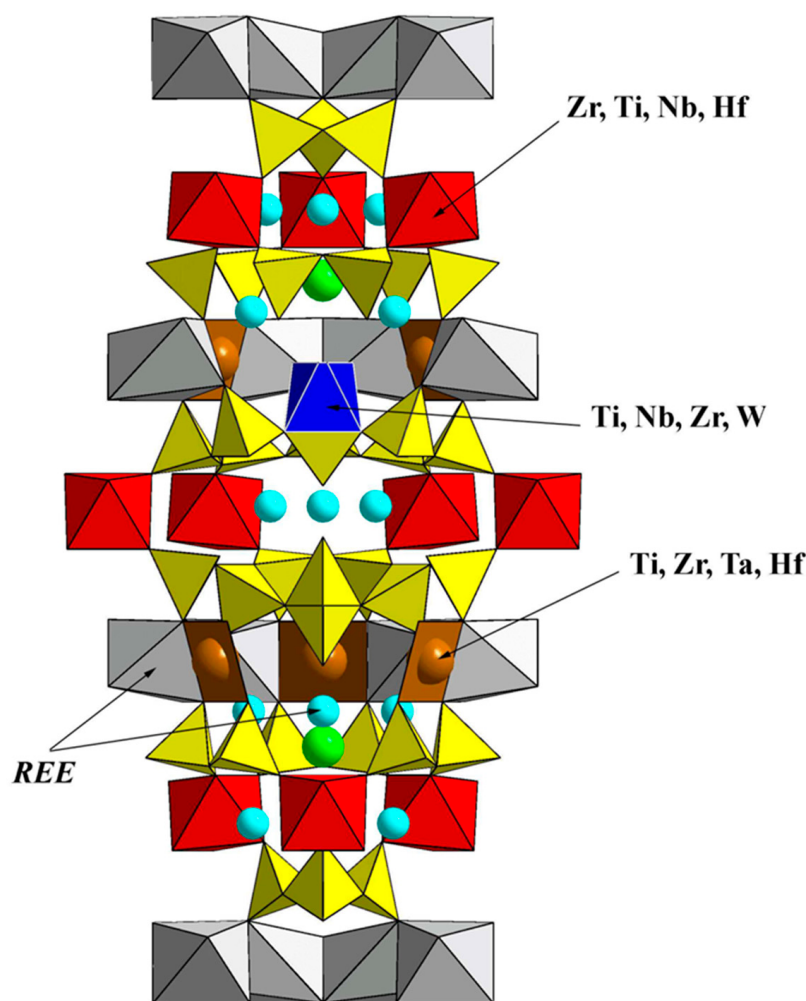


Figure 1. The general view of the crystal structure of EGMs and the distribution of RMs and REMs over the different crystallographic sites.

Herein, EGMs are silicates of sodium, calcium, and zirconium [15,30–33] which contain up to 2.5% of lanthanides [34]. Moreover, they are characterized by a high content of “heavy” yttrium subgroup metals. EGMs are widespread in mineral deposits of the Kola Peninsula [15] and contain, in addition to REMs, valuable zirconium and scandium, and also uranium and thorium. Moreover, EGMs are easily broken down by acids even without additional activation, which facilitates their processing [15,30–33].

Meanwhile, the processing of raw materials containing RMs and REMs of both natural and industrial origin results in the formation of low-activity radioactive waste (RAW), mostly owing to the presence of emanating uranium and thorium. Regulatory agencies require that RAW has to be stored with further disposal [35], which significantly decreases the economic efficiency of the production of concentrates and other RM- and REM-based products [6].

Owing to this, the prefractionation of ore concentrates is required for a selective recovery of emanating uranium and thorium and further processing of the obtained REM concentrate [10,11,35,36]. To solve this problem, the liquid extraction method with the organic compounds as extractants (that can selectively bind uranium and thorium) is used. This allows to obtain REM solutions with a low content of U(VI) and Th(IV) [36–38]. Now, widely used extractants are neutral, anionic, and cationic organophosphorus compounds [38,39], but the application of binary extractants consisting of stoichiometric mixtures of cation- and anion-exchange extractants has also been described [40,41].

The available extractants, however, do not always allow to achieve efficient fractionation. Therefore, a search for highly selective extractants for uranium and thorium recovery in the presence of REMs remains important.

Earlier, we studied the extraction ability of phosphoryl podands, acidic semiethers of diphosphonic acids (Figure 2), with respect to actinides and lanthanides in nitric acid media [42–47].

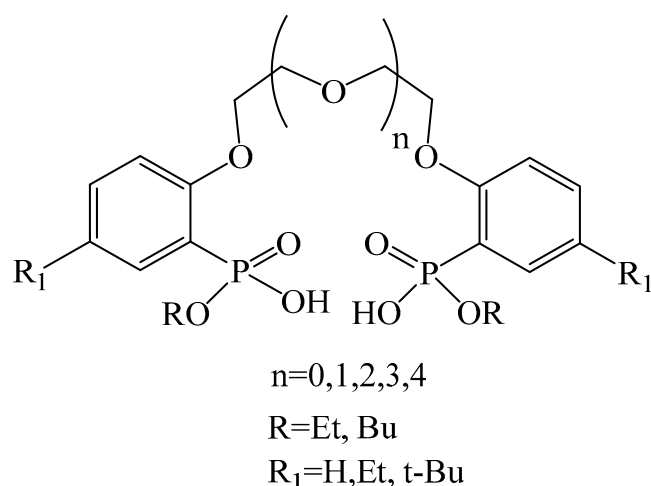


Figure 2. Molecular structures of the studied acidic phosphoryl podands.

In [45], the influence of the length of the polyether chain in the studied phosphoryl podand on the extraction efficiency of f-elements was investigated. It was shown that podands containing a diethyleneglycol fragment as their polyether chain are characterized by the highest uranium and thorium extraction ability in nitric acid media. The recovery of f-metals is also significantly affected by addition of alkyl groups to the terminal fragments of the phosphoryl podand molecule, as they enhance its lipophilicity and also improve the compatibility with the solvent [46]. U/La and Th/La extraction separation factors were calculated (Table 1) at 0.04 M HNO₃ on the basis of the results obtained in [46] for 1,5-bis[2-(hydroxyethoxyphosphoryl)-4-ethylphenoxy]-3-oxapentane (H₂L).

Table 1. Separation factors of the pairs of uranium(VI)—lanthanum(III) and thorium(IV)—lanthanum(III).

Ligand Concentration, M	F (U/La)	F (Th/La)
0.01	4200	60,000
0.001	14,200	14,333

The factors are sufficiently high, which is a prerequisite for further application of this ligand for extraction of uranium and thorium from eudialyte processing solutions. Earlier, we studied an extraction of uranium(VI), thorium(IV), and lanthanum(III) into 1,2-dichloroethane by binary extractants based on stoichiometric mixtures of diphosphonic acids (1,5-bis[2-(dioxypophoryl)phenoxy]-3-oxapentane or 1,5-bis[2-(dioxypophoryl)-4-ethylphenoxy]-3-oxapentane) and trioctylamine [47]. Conditions of extractant regeneration after re-extraction were found, which made their repeated application possible.

This work continues our systematic study of the recovery of RMs and REMs from eudialyte-group minerals and evaluates the extraction system based on phosphoryl podand H_2L and methyltrioctylammonium nitrate (MTOAN) (Figure 3) in 1,2-dichloroethane for uranium and thorium extraction and concentration from eudialyte leaching solutions to provide a basis for the technology of waste conditioning in production of RMs and REMs from natural and industrial raw materials. The use of 1,2-dichloroethane as diluent is necessary because the chosen phosphoryl podand is soluble only in heavy-halogen-containing solvents.

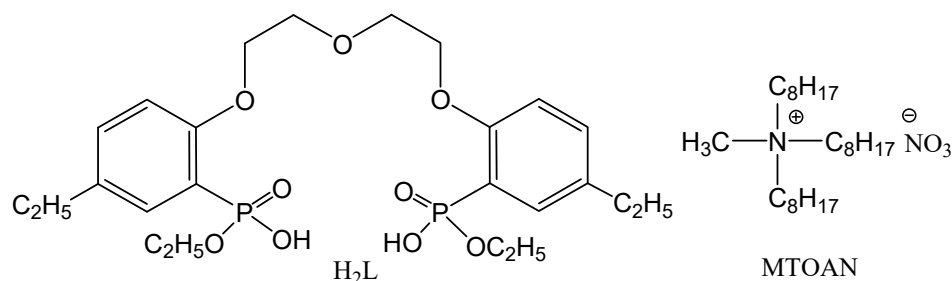


Figure 3. Molecular structures of 1,5-bis[2-(hydroxyethoxyphosphoryl)-4-ethylphenoxy]-3-oxapentane and methyl trioctylammonium nitrate.

2. Materials and Methods

1,5-bis[2-(hydroxyethoxyphosphoryl)-4-ethylphenoxy]-3-oxapentane (Figure 3), synthesized according to the method described in [46], was used. The melting point as well as 1H and ^{31}P NMR spectra were in good agreement with the literature data. 1,2-dichloroethane (chemically pure grade), tributyl phosphate (99.5%, Ekos-1), and methyl trioctylammonium nitrate (Sorbent-Tekhnologii OJSC) (Figure 3) were used. The absence of chloride ion in MTOAN was confirmed by the negative test with silver nitrate. Nitric acid (ultrahigh purity grade) and twice distilled water were also used. All solutions were prepared by the volume–weight method.

The eudialyte concentrate from the Lovozero ore mining and refining plant was used. Before the breakdown, the granulometric and elemental composition of the concentrate were determined. The granulometric composition of the eudialyte concentrate was studied by the method of low-angle laser light scattering (LALLS, laser diffraction) using an Analyzette 22 Compact diffractometer (Fritsch). The calculation of the particle size distribution was performed using the Fraunhofer theory. The average size of particles obtained as described above was 120 μm ; the size of ca. 90% of particles was in the range of 30 to 200 μm .

Elemental analysis of the eudialyte concentrate was carried out by X-ray fluorescence spectrometry with an ARL Advant’X wavelength dispersive XFA spectrometer. The Uni-Quant software was used without any correction. The results in wt.%, excluding oxygen, are presented in Table 2 and the weight percentages of individual components per total REM weight are given in Table 3.

Table 2. Elemental composition of the eudialyte concentrate.

Element	Si	Al	Fe	Zr	Mn	Ca	Na	K	Ti
wt. %	49.97	11.65	11.55	8.67	3.81	3.13	2.63	2.01	1.96
Element	Sr	Cl	Nb	Mg	P(V)	Hf	Ba	Mo	Ta
wt. %	1.25	0.675	0.503	0.309	0.292	0.122	0.064	0.039	0.031
Element	S	Ni	Y, La–Lu	La–Nd		Y, Sm–Lu		Y	
wt. %	0.023	0.017	1.22	0.77		0.45		0.403	

Table 3. Weight fractions of REM groups and some individual REMs in the eudialyte concentrate per total REM weight.

Elements	La–Nd	Ce	Sm–Lu + Y	Y
wt. %	63.2	0.40	36.8	0.40

Footnote: The sensitivity of the X-ray fluorescence spectrometry analysis is not sufficient for the determination of scandium.

Analysis of the elemental composition of liquid samples was carried out by ICP-MS using an Agilent 7500 ce device (Agilent Technologies Inc., Santa Clara County, CA, USA) with the measurement error of 4.5%. The organic phase composition was not analyzed. The elemental content in the organic phase was determined from the mass difference.

The nitric acid concentration was determined by a potentiometric titration using a T50 Mettler Toledo automatic titrator. The electrode couple was calibrated using standard buffer solutions with pH of 1.68, 4.01, and 9.21 (Mettler Toledo) (values at 20 °C). The concentration of NaOH solution was determined by potentiometric titration using 0.1 M HCl (fixanal).

Because the final solution after the leaching of the eudialyte concentrate contained more than 11 M HNO₃, the obtained nitric acid solution of metals (Table 4) was diluted four times (2.84 M HNO₃) and the obtained solution was used in extraction experiments and with the extractant solution in 1,2-dichloroethane, prepared as follows. The ratio between H₂L phosphoryl podand and MTOAN in the 1,2-dichloroethane solution was 1:2 and the H₂L concentration in the solution was 0.05 M.

Extraction was carried out in glass flasks using a stirring device at 80 rpm for 20 min. The time period during which the extraction equilibrium was established was verified by increasing the phase contact duration up to 120 min and determining that the distribution coefficients remained constant. Phase layering was achieved by centrifugation. After the phase separation, the metal cation concentration in the aqueous phase was determined by ICP-MS. All experiments were carried out at the temperature of 20 ± 1 °C.

The distribution coefficients for extraction ($D = [M]_{org}/[M]_{aq}$) were determined at constant extractant concentrations (0.05 M by H₂L in 1,2-dichloroethane) and constant initial metal concentrations in the experiment (Table 4).

Powder X-ray patterns were obtained using a Rigaku MiniFlex600 (CuKα₁₊₂ radiation, 40 kV/15 mA, Bragg–Brentano geometry) in the 2θ range of 3–90° with a step interval of 0.02° and a counting time of 2°/min. The identification of all minerals was performed using powder diffraction files of the International Centre for Diffraction Data—ICDD, PDF2 database. The phase quantification procedure involved the identification of the mineral phases followed by subsequent quantitative phase analysis of all datasets using the full profile Rietveld method implemented in the RietveldToTensor software [48].

Table 4. Elemental content in the solution after the leaching of a eudialyte ore concentrate.

Element	Detection Limits (DL), mg/L	Content of Elements in the Solution after Eudialyte Leaching, mg/L	Element	Detection Limits (DL), mg/L	Content of Elements in the Solution after Eudialyte Leaching, mg/L
Li	0.003	0.20	Sn	0.006	0.22
Be	0.001	0.54	Sb	0.003	0.056
B	0.1	0.65	Cs	0.001	0.086
Na	0.6	4153	Ba	0.006	1.3
Mg	0.6	14.9	La	0.001	72.9
Al	0.4	2032	Ce	0.002	159
S	2	33.4	Pr	0.0004	19.4
K	0.6	510	Nd	0.0008	78.5
Ca	0.6	1572	Sm	0.0007	21.6
Sc	0.01	0.63	Eu	0.0006	7.0
Ti	0.2	29.2	Gd	0.0005	21.8
Cr	0.06	0.19	Tb	0.0005	4.0
Mn	0.02	489	Dy	0.0007	25.3
Fe	0.7	701	Ho	0.0006	5.3
Co	0.02	0.053	Er	0.0003	15.0
Ni	0.06	0.17	Tm	0.0004	2.3
Cu	0.07	0.39	Yb	0.0006	13.7
Zn	0.08	4.1	Lu	0.0004	1.8
Rb	0.01	3.3	Hf	0.001	44.1
Sr	0.005	34.9	Ta	0.003	0.016
Y	0.005	119	W	0.003	0.050
Zr	0.002	2107	Bi	0.0009	0.020
Tl	0.0003	0.012	Th	0.0006	2.5
Pb	0.006	27.0	U	0.0005	2.1

3. Results and Discussion

Sulfuric acid leaching of the eudialyte concentrate occurs with large losses of zirconium and other REMs, as these elements are captured by a silica gel [15,49]. Formation of hardly soluble silica gels also complicates the filtration process. Formation of a poorly filterable silica gel precipitates in the course of eudialyte decomposition is the chief problem in the course of eudialyte concentrate leaching. In order to intensify the recovery of REMs, as well as uranium, thorium, and other REMs, from the eudialyte concentrate to the solution, we decided to perform the leaching under heating in nitric acid with the maximal possible concentration.

The leaching of a eudialyte concentrate (10 g) was carried out in 13.8 M HNO₃ (S:L = 1:10), under stirring at the temperature of 80 °C for 72 h. This ratio S:L 1:10 was justified by the concentration of nitric acid more than 10 mol/L in the solution after eudialyte leaching. In this medium (with the acidity more than 10 mol/L), the formation of oxozirconium cations is minimal, which contributes to the formation of third phases during extraction. Nitric acid decomposition of eudialyte concentrate results under the described conditions in dissolution of REM, zirconium(IV), and also emanating uranium(VI) and thorium(IV) and formation of amorphous, well-coagulated silica, which provides good pulp filterability. It should also be pointed out that the leaching under the described condi-

tions leads to dissolution of zirconium in the form of complexes of Zr^{4+} ion. The content of oxo cations ZrO^{2+} and $Zr_2O_3^{2+}$ in a highly concentrated nitric acid (HNO_3) solution is minimal [50].

The method of X-ray fluorescence spectrometry was used to study the eudialyte concentrate and also the dry residue after the leaching. Figure 4 shows the mappable fractions of elements before and after breakdown of the eudialyte concentrate. An almost two times increase in the percentage of silicon and a significant decrease in the content of metals (iron, zirconium, and others) was observed. It should also be mentioned that the overall RM content in the dry residue decreased considerably in comparison with the ore concentrate.

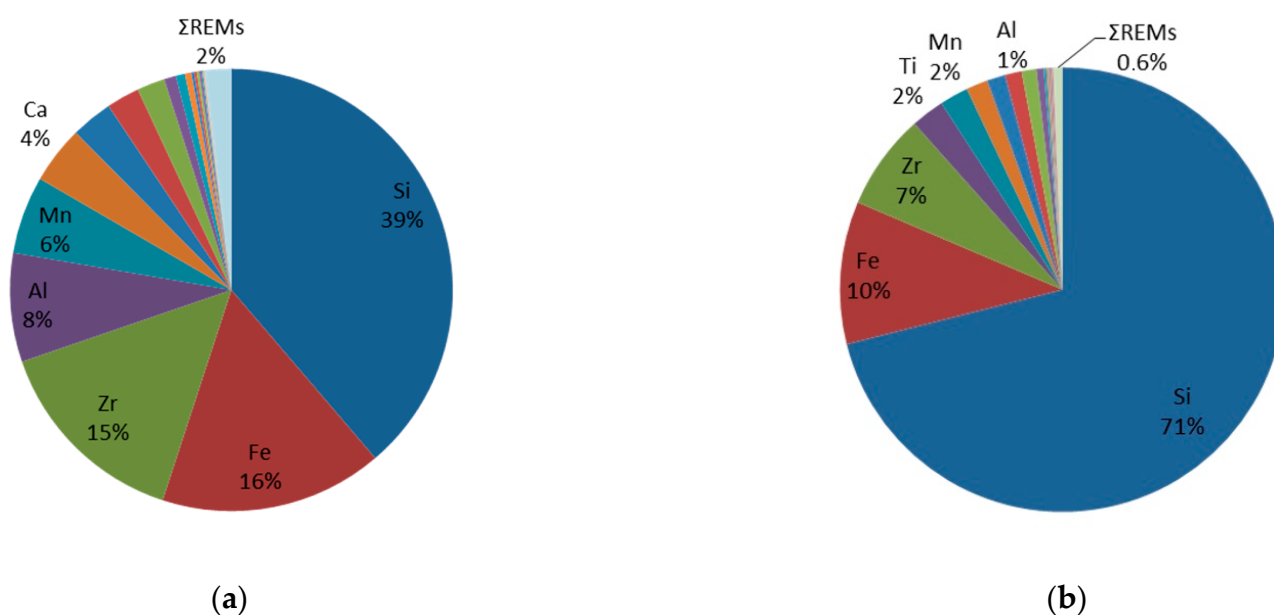


Figure 4. Distribution of element fractions before (a) and after (b) the eudialyte ore concentrate breakdown.

Table 4 contains the elemental composition of a nitric acid solution of 11.6 M HNO_3 obtained after the leaching of the eudialyte concentrate.

The mineral composition, determined by XRPD, is shown in Figure 5.

The obtained quantities for the minerals present in the eudialyte ore concentrate were (in wt.%): eudialyte—38, orthoclase—21.1, nepheline—12.8, albite—9.2, microcline—6.5, aegirine—4.2, amphibole—3.4, diopside—2, sodalite—1.7, titanite—0.7, and loparite—0.4. Visualization of the fit is given in a difference plot in Figure 6a. The obtained quantities for the minerals present in the eudialyte ore concentrate after breakdown were (in wt.%): eudialyte—29.6, orthoclase—26.7, albite—16.1, aegirine—10.2, microcline—7.7, amphibole—4.8, diopside—2.8, titanite—1.8, and sodalite—0.3. The powder X-ray analysis demonstrates that after leaching from the eudialyte concentrate, loparite and nepheline disappear, while the silicate part of nepheline becomes amorphous and forms a halo. The amount of eudialyte decreases to ~25 wt.%. According to the peaks, it seems that albite becomes less prevalent than potassium feldspars (microcline and orthoclase); however, this is not observed by the quantitative analysis. The reason for this is not so clear, probably because the albite peaks do not overlap with other minerals at $2\theta = 27.9^\circ$ (the same can be also observed at $2\theta = 14^\circ$).

Together with the traditional extractants for REM recovery and separation, binary extractants are used that can be classified as ionic liquids (IL): organic salts that are liquid at room temperature [40,51–54].

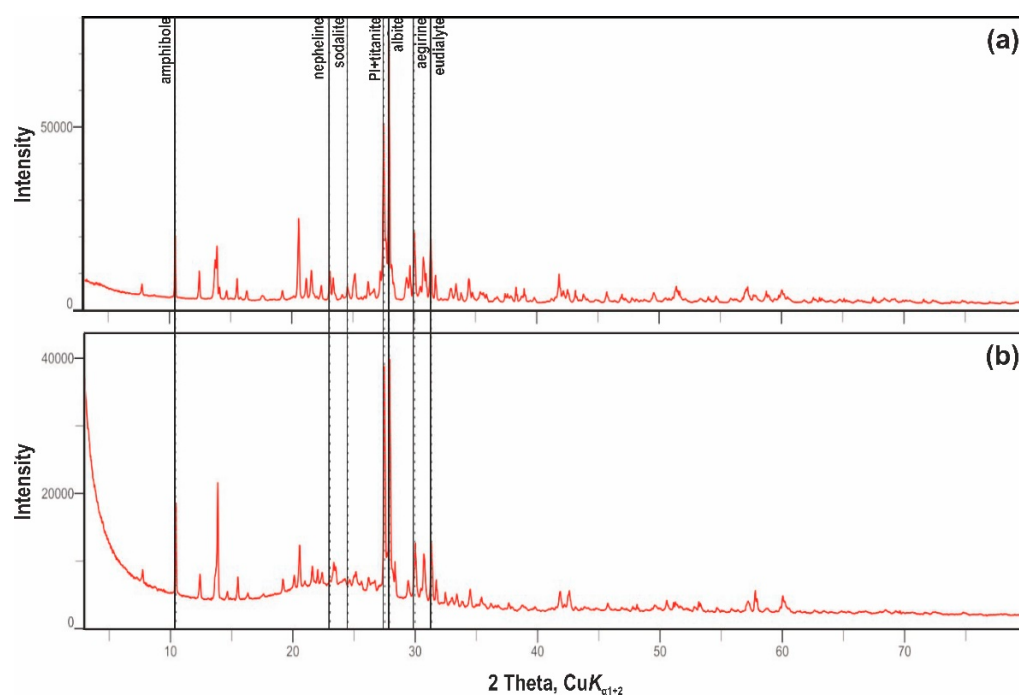


Figure 5. X-ray powder diffraction patterns of the eudialyte ore concentrate before (a) and after (b) breakdown.

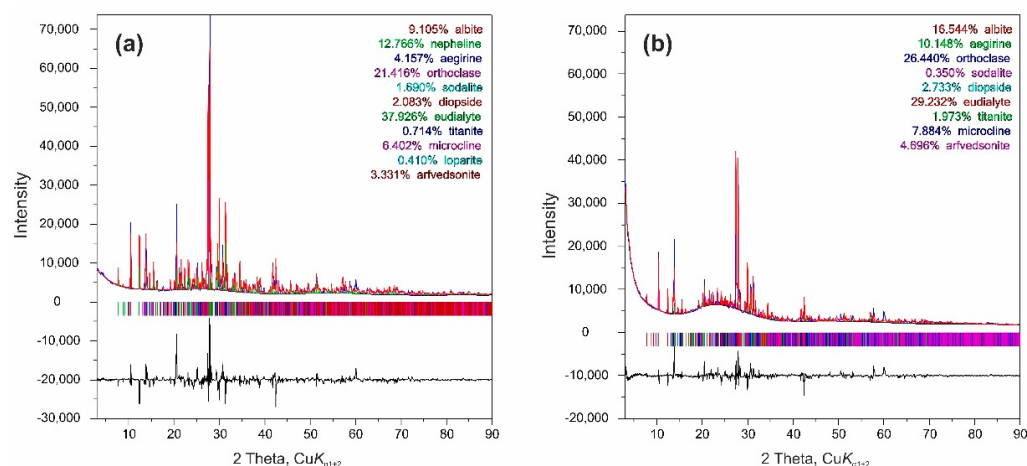
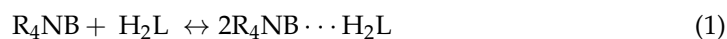
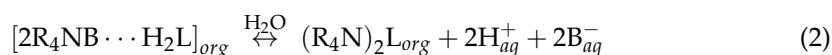


Figure 6. Rietveld refinement plot for eudialyte ore concentrate before (a) and after (b) breakdown.

When the mixtures of quaternary ammonium base R_4NB and acidic phosphoryl podand H_2L in a homogeneous organic solution are used, the following interaction between the components by formation of H-bonds between the quaternary ammonium salt and acidic phosphoryl podand is determined:



In heterogeneous aqueous–organic systems, thermodynamically stable ionic pairs are formed that consist of an organic cation and an organic anion [40,51–54]. When the aqueous phase is added into the extraction system, the mineral acid anions B^- and the hydrogen ion are extracted into the aqueous phase due to their high hydration energy:



The $(R_4N)_2L$ ion pair is formed in the organic phase and its extraction properties are determined mainly by the properties of the organic acid and base [40,51–54].

Due to the fact that the solubility of the H_2L phosphoryl podand in dichloroethane does not exceed 0.01 M, we decided to perform the target metal recovery from the eudialyte concentrate breakdown solution in the form of ionic pairs of the acidic phosphoryl podand and basic MTOAN. A decreasing of the pH of the aqueous phase upon contact with an organic solution containing acidic phosphoryl podand and MTOAN was not observed, since the podand concentration was very low (0.05 mol/L). The ionic interaction between the acidic podand and basic MTOAN improves the compatibility with the solvent and, therefore, enhances the solubility of the podand and also of the forming complexes in the course of extraction in heavy 1,2-dichloroethane. It is necessary to point out that the extraction ability of quaternary ammonium bases, in particular MTOAN, is considerably affected by the acidity of the medium. It is found that the extraction ability of MTOAN decreases drastically at an increase in the concentration of H^+ ions in the aqueous phase, and, vice versa, the ability of MTOAN to extract metals into the organic phase grows in the range of low H^+ concentrations [55]. Under the experimental conditions described in our case, the extraction ability of the ion pair is determined solely by the properties of the phosphoryl podand extracting f-elements in such media as that under our experimental conditions [44–46].

A preliminary experiment consisted of a single extraction stage to assess the extraction ability of the organic ion pair $(R_4N)_2L$ in 1,2-dichloroethane with regard to metal ion extraction into the solution after eudialyte leaching.

The results of a single extraction stage are presented in Table 5. Most elements are not extracted into the organic phase (Table 5). Meanwhile, scandium, titanium, zirconium, hafnium, uranium, and thorium are extracted into the organic phase much better than other metals. It should be pointed out that scandium, zirconium, hafnium, uranium, and thorium are practically completely extracted into the organic phase in a single stage, irrespective of the initial content of this metal ion in the aqueous solution. Titanium is recovered much worse, by ca. 66%.

All further extraction experiments were carried out using the solution obtained by the eudialyte concentrate leaching, and all analyses of the solutions after extraction were performed using ICP-MS. Due to a negligible extraction of alkali earth, alkali, rare earth, and other heavy metals, the data on these elements are not presented, while the results of extraction studies of scandium, titanium, zirconium, hafnium, uranium, and thorium are given in detail.

It is expedient to study the extraction equilibrium when metal ions are extracted into the organic phase of a two-phase aqueous–organic system containing the eudialyte breakdown solution and the organic ion pair $(R_4N)_2L$ solution in 1,2-dichloroethane, and also to obtain extraction isotherms. The extraction equilibrium of uranium(VI), thorium(IV), hafnium(IV), and zirconium(IV) was studied using the method of phase volume change. This method allows using multicomponent solutions without any risk of not achieving equilibrium by any component. The obtained isotherm, however, is correct only in the concentration range of the studied solutions. Table 6 contains the scheme of changes in the volumes of the organic and aqueous phases.

Figure 7 shows the extraction isotherms for U(VI), Th(IV), Hf(IV), and Zr(IV). For scandium and titanium, no extraction isotherms could be obtained under the described experimental conditions, as the ions of these metals are practically completely extracted. It should be pointed out that the use of the $(R_4N)_2L$ ion pair in 1,2-dichloroethane as an extractant allows to concentrate uranium(VI) up to 1.2 mg/L. Accounting for the initial 0.5 mg/L content of uranium(VI) in the solution, more than four times more concentration is achieved as a result of several extraction contacts. A similar result is also achieved in the case of thorium(IV). The content of Th(IV) in the initial solution is 0.56 mg/L. According to the obtained isotherm, thorium is concentrated up to 1.77 mg/L after several contacts, i.e.,

approximately four times more, which is in good agreement with the goal of emanating uranium and thorium recovery and concentration.

Table 5. Results of a single metal recovery stage from the eudialyte breakdown solution by the $(R_4N)_2L$ ionic pair solution in 1,2-dichloroethane (0.05 M by H_2L).

Element	Initial Solution, mg/L	Raffinate, mg/L	D	Recovery %	Element	Initial Solution, mg/L	Raffinate, mg/L	D	Recovery, %
Li	0.055	0.055	0	0	Sn	0.048	0.009	4.51	81.9
Be	0.14	0.14	0	0	Sb	0.019	0.019	0.04	3.89
B	0.43	0.43	0	0	Cs	0.023	0.023	0	0
Na	1083	1083	0	0	Ba	0.30	0.30	0	0
Mg	3.3	3.3	0	0	La	18.4	18.4	0	0
Al	495	495	0	0	Ce	39.7	39.7	0	0
S	8.4	8.2	0	0	Pr	4.9	4.9	0	0
K	119	119	0	0	Nd	19.7	19.7	0	0
Ca	420	420	0	0	Sm	5.0	5.0	0	0
Sc	0.16	0.01	15.1	93.7	Eu	1.6	1.6	0	0
Ti	7.2	2.5	1.93	65.8	Gd	5.4	5.4	0	0
Cr	0.16	0.081	0.91	47.7	Tb	0.97	0.97	0	0
Mn	127	127	0	0	Dy	6.2	6.2	0	0
Fe	186	163	0.14	12.5	Ho	1.3	1.3	0	0
Co	0.033	0.02	0.67	40.1	Er	3.6	3.6	0	0
Cu	0.17	0.17	0	0	Tm	0.53	0.51	0.02	2.1
Zn	1.0	1.0	0	0	Yb	3.3	3.2	0.05	4.4
Rb	0.81	0.81	0	0	Lu	0.42	0.40	0.06	5.5
Sr	8.5	8.5	0	0	Hf	10.3	0.090	114	99.1
Y	29.6	29.6	0	0	W	0.009	0.006	0.53	34.7
Zr	522	4.4	118	99.1	Tl	0.003	0.0003	7.96	88.8
Pb	6.7	6.7	0	0	Th	0.56	0.0006	979	99.9
Bi	0.0043	0.0035	0.22	17.9	U	2.0	0.025	78.3	98.7

Table 6. Volume phase ratios.

Contact No.	Organic Phase Volume, mL	O/A Ratio		Aqueous Phase Volume, mL
		O	A	
1	25	5	1	5
2	20	4	1	5
3	15	3	1	5
4	10	2	1	5
5	5	1	1	5
6	5	1	2	10
7	5	1	3	15
8	5	1	4	20
9	5	1	5	25

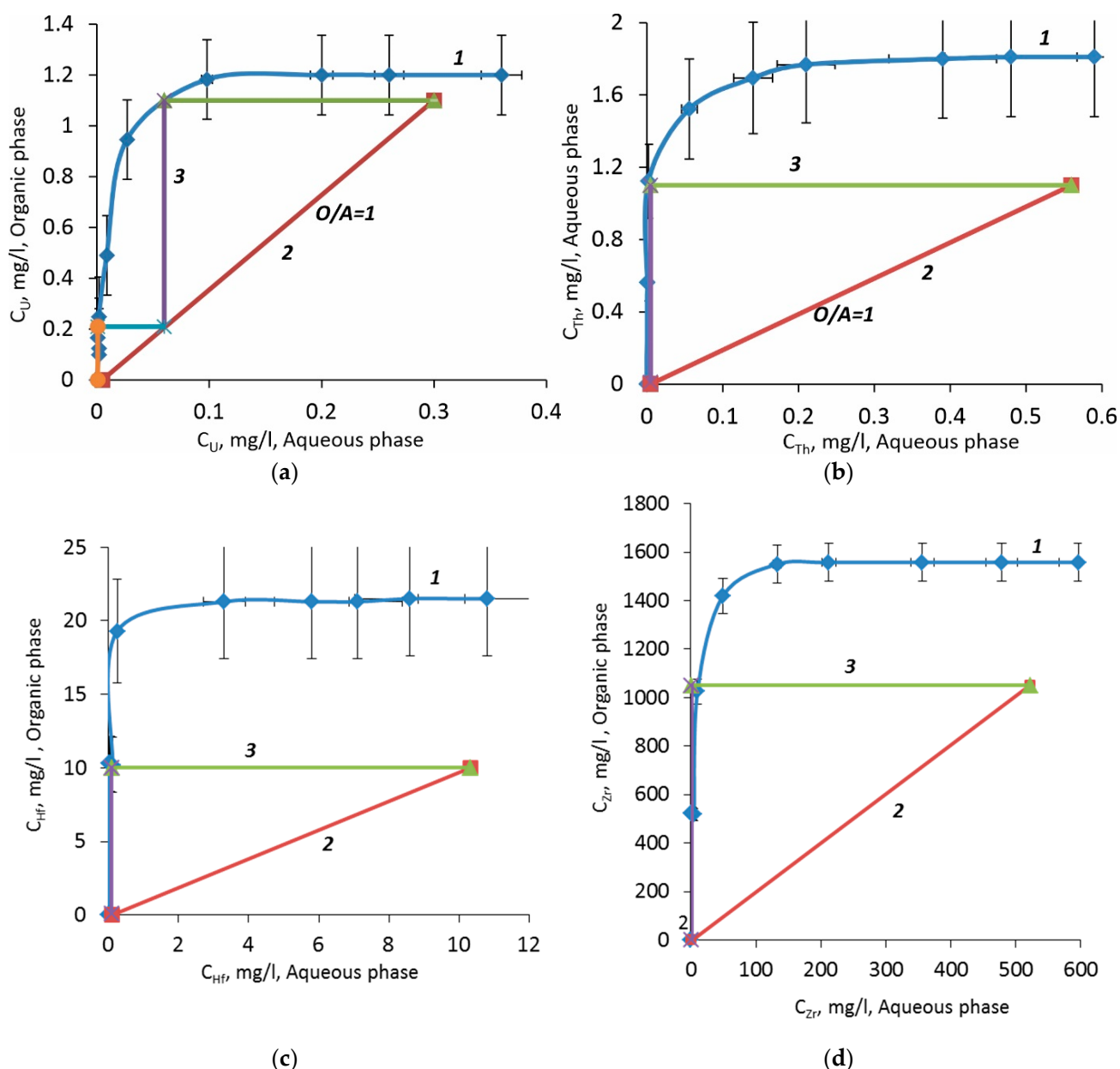


Figure 7. Extraction isotherm of U(VI) (a), Th(IV) (b), Hf(IV) (c), and Zr(IV) (d) from the eudialyte breakdown solution (2.84 M HNO_3) by a $(\text{R}_4\text{N})_2\text{L}$ ionic pair solution in 1,2-dichloroethane (0.05 M by H_2L) at 20 °C (1), working line (2), and extraction stage (3). For the calculation of the error bars, random and non-excluded, as well as the device error for determination of the concentration of metal ions, were taken into account. The study was carried out using at least three independent experiments. The total error of the results was $\sim 18.4\%$, taking into account the non-excluded and random components.

Despite that the extraction of titanium(IV) and scandium (III) was almost complete, it was not possible to obtain extraction isotherms. At a ratio of aqueous and organic phases of 1:1, titanium(IV) is extracted by 66%; however, at a ratio of 1:2, it is completely extracted and the saturation of the organic phase occurs quite quickly. In the case of scandium, the saturation of the organic phase occurs even faster.

The graphical calculation of the number of theoretical extraction steps of U(VI), Th(IV), Hf(IV), and Zr(IV) from the eudialyte concentration breakdown solutions by a $(\text{R}_4\text{N})_2\text{L}$ ion pair was carried out using the McCabe–Thiele method, which is based on constructing

the equilibrium and working lines, as well as the steps of the metal concentration gradient in the organic and aqueous phases. Figure 7 shows the extraction isotherms of target U(VI), Th(IV), Hf(IV), and Zr(IV) and the results of a graphical calculation. The working line was drawn according to the composition of the initial solution and the ratio of the flows of the organic and aqueous phases (O:A = 1:1). Based on the graphical calculation shown in Figure 7, the two stages for the complete extraction from the aqueous phase were obtained for uranium(VI), whereas for thorium(IV), hafnium(IV), and zirconium(IV), only one contact stage is sufficient for the quantitative extraction of the metals into the organic phase containing the $(R_4N)_2L$ ionic pair solution in 1,2-dichloroethane (0.05 M by H_2L). According to the theoretical calculation, it was assumed that two extraction stages are sufficient for the complete extraction of U(VI), Th(IV), Hf(IV), and Zr(IV) eudialyte concentration breakdown solutions. This assumption is in good agreement with the results of the experiment (according to the scheme shown in Figure 8) of a two-stage extraction contact for the complete extraction of target U(VI), Th(IV), Hf(IV), and Zr(IV) from the solutions.

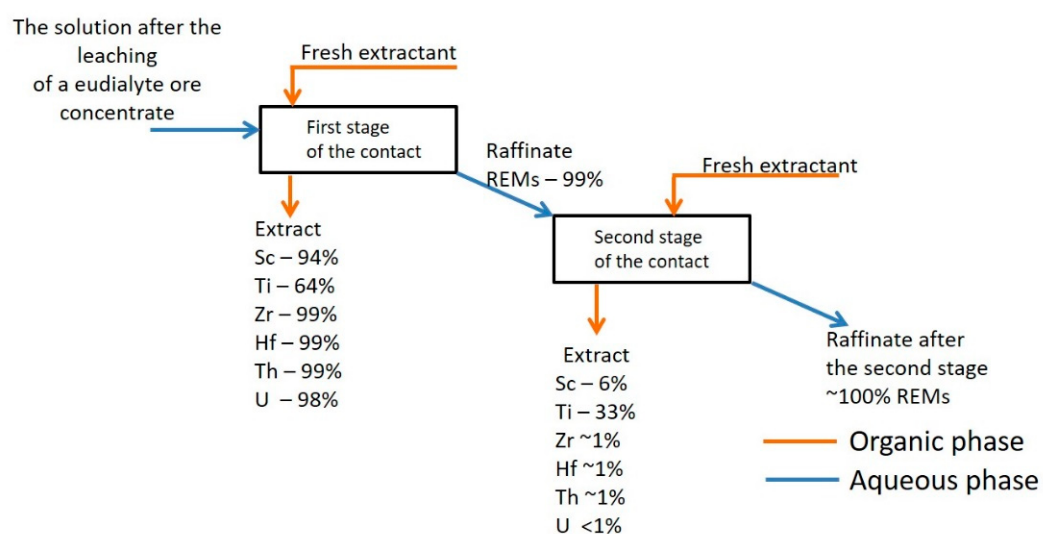


Figure 8. Scheme of two-stage exhaustive extraction.

During the experiment, express control of the distribution of elements was performed spectrophotometrically with arsenazo III until constant absorbance was achieved at the wavelength of 650 nm. The results of exhaustive extraction are presented in Table 7.

Table 7. Results of exhaustive metal extraction from eudialyte concentration breakdown solutions by an organic solution of the $(R_4N)_2L$ ion pair in 1,2-dichloroethane (0.05 M by H_2L) in 1,2-dichloroethane.

Element	Initial Solution, mg/L	1st Stage Extraction Raffinate, mg/L	1st Stage Extraction Degree, %	2nd Stage Extraction Raffinate, mg/L	2nd Stage Extraction Degree, %
Sc	0.16	0.01	93.8	<DL	~100
Ti	7.2	2.5	65.8	0.2	97.2
Zr	522	4.4	99.2	1	99.8
Hf	10.3	0.090	99.1	0.032	99.7
Th	0.56	0.0006	99.9	<DL	~100
U	2.0	0.025	98.7	0.0033	99.8

The target metals were recovered completely in two extraction stages. Moreover, the bulk of uranium(VI), thorium(IV), zirconium(IV), hafnium(IV), and scandium(III) was extracted into the organic phase in the first stage, while the first-stage extraction of Ti(IV) yielded not more than ca. 66% and the second stage resulted in practically complete extraction.

The loaded organic phase was directed for re-extraction with a solution of ~2 mol/L sulfuric acid, which leads to the destruction of the extracted complexes in the organic phase and the moving out of the extracted metal ions into an aqueous solution containing ~2 mol/L H₂SO₄. After re-extraction and additional washing, the reversed extractant can be returned to the extraction stage. Thus, it is possible to recycle the flows of organic and aqueous phases further to obtain concentrates of rare earth metals and emanated uranium and thorium together with zirconium, hafnium, and titanium.

The efficiency and selectivity of using the (R₄N)₂L extraction ion pair with respect to target metals, particularly uranium(VI) and thorium(IV), were compared with those of the commercially available tributyl phosphate (TBP). For this, an extraction experiment was carried out under similar conditions from a eudialyte extraction solution. The results are presented in Table 8.

Table 8. Comparison of the extraction ability of the (R₄N)₂L ionic pair with 30 vol.% TBP in 1,2-dichloroethane.

Element	Initial Solution, mg/L	Ionic Pair (R ₄ N) ₂ L in 1,2-dichloroethane (0.05 M by H ₂ L)			1.19 M (30%) TBP in 1,2-dichloroethane		
		Raffinate, mg/L	D	%	Raffinate, mg/L	D	%
Sc	0.161	<DL	-	~100	0.160	0.004	0.4
Ti	7.20	2.46	1.9	66	7.20	0	0.04
Zr	522.1	4.36	118	99	432	0.21	17.2
Hf	10.33	0.090	114	99	8.60	0.20	16.8
Th	0.564	<DL	-	~100	0.154	2.7	72
U	1.952	0.025	78.3	99	0.197	8.9	89

To compare the ability of TBP and the (R₄N)₂L ion pair to extract elements from eudialyte concentration breakdown solutions, the experiment was carried out under the same conditions, using the same solvent. In the case of using of TBP as an extractant, a partial extraction of rare earth elements (~30%) into the organic phase is possible. Such behavior can be observed in the analysis of raffinates when TBP is used as an extractant: the concentration of REE in raffinates decreases, which indicates their transition to the organic phase. The further use of TBP will lead to a redistribution of REE in phases, which will significantly complicate the further design of the technological scheme. On the other hand, the use of the (R₄N)₂L ion pair makes it possible to isolate the emanating of uranyl and thorium ions into a separate fraction and isolation of macrocomponents (titanium, zirconium, hafnium), and to obtain a concentrate of rare earth metals in a separate fraction.

4. Conclusions

The quantitative characteristics in the case of extraction with the studied extraction ion pair are much higher than those of TBP under similar experimental conditions. The recovery ratio for extraction of target metals from the eudialyte breakdown solution by a 1.19 M TBP organic solution in 1,2-dichloroethane for Zr(IV) and Hf(IV) does not exceed 20%, while Sc(III) and Ti(IV) are practically not extracted. In the case of uranium(VI) and thorium(IV), employing the TBP solution as an extractant results in the extraction ratio of actinides into the organic phase above 70%. Application of an ion pair (R₄N)₂L (0.05 M by H₂L) in 1,2-dichloroethane leads to quantitative recovery of target metals from the eudialyte concentrate breakdown solution, to the exclusion of titanium(IV) with its single-stage extraction degree not exceeding 66%.

Thus, the extraction ability of the (R₄N)₂L ion pair (0.05 M by H₂L) in 1,2-dichloroethane for recovery and concentration of emanating uranium(VI) and thorium(IV) and also other rare metals from a nitric acid breakdown solution of eudialyte concentrate is much better than that of the commercially available TBP. The obtained results can become a basis for a new industrial technology of waste conditioning in production of rare and rare earth

metals from natural and industrial waste. This section is not mandatory but can be added to the manuscript if the discussion is unusually long or complex.

Author Contributions: Conceptualization, A.M.S.; methodology, A.M.S. and V.E.B.; formal analysis, A.M.S., A.V.L., A.A.S., D.V.B., and S.M.A.; writing—original draft preparation, A.M.S., V.E.B., and S.M.A.; writing—review and editing, A.M.S., V.E.B., A.Y.T., S.M.A., and I.G.T.; supervision, A.Y.T. and I.G.T. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Ministry of Science and Higher Education of Russia (grant agreement № 075-15-2020-782).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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