



Extraction of lanthanum, cerium, and neodymium using an ionic liquid and its application to rare earth leachate derived from phosphogypsum

A.H. Tilp ^{a, b}, Hesham M. Akl ^c, Abd El-Hakim T. Kandil ^c, Mohamed F. Cheira ^{d, *},
Hady Soliman Gado ^d, Bahaa A. Salah ^c

^a Department of Chemistry, College of Science, Qassim University, Buraidah, 51452, Saudi Arabia

^b Chemistry Department, Faculty of Women for Art, Science, and Education, Ain Shams University, Heliopolis, Cairo, 11757, Egypt

^c Chemistry Department, Faculty of Science, Helwan University, Egypt

^d Nuclear Materials Authority, P.O. Box 530, Maadi, Cairo, Egypt

ARTICLE INFO

Article history:

Received 13 April 2024

Received in revised form

9 June 2024

Accepted 3 July 2024

Available online 5 July 2024

Keywords:

Solvent extraction

Ionic liquid

Cyphos IL

REEs leachate

Phosphogypsum

ABSTRACT

Rare earth elements (REEs) were extracted from phosphogypsum (PG) using an indirect leaching method that produces CaCO₃. The carbonation process transforms PG into CaCO₃, and a potential source of value is the (NH₄)₂SO₄ fertilizer. The calcium carbonate byproduct is rich in REEs that are originally present in PG. Calcium carbonate, a byproduct of PG carbonation and a rich source of REEs, could dissolve in nitric acid to produce a calcium nitrate leach solution that contains RE nitrate. Subsequently, the most widely used solvent extraction technique can make use of an environmentally benign nitrate ionic liquid. Cyphos IL 101 (triethyl (tetradecyl)phosphonium chloride) is transformed into triethyl (tetradecyl) phosphonium nitrate ([P₆₆₆₁₄][NO₃]) ionic liquid by adding 2.5 mol/L potassium nitrate. The extraction examinations were tested by equilibration of 2 mL of [P₆₆₆₁₄][NO₃] with 2 mL of a synthetic solution of 1000 mg/L of individual La, Ce, and Nd to gain the optimal extraction conditions. The high extraction efficiency of La, Ce, and Nd was gained by stirring a 1/1 aqueous/organic phase ratio and 3 mol/L NH₄NO₃ (as salting out) at 800 r/min for 40 min at 50 °C to decrease the viscosity of [P₆₆₆₁₄][NO₃]. The La(III), Ce(III), and Nd(III) stripping efficiencies were examined from their loaded [P₆₆₆₁₄][NO₃] ionic liquid by 1/1 A/O ratio of acidified water, 800 r/min stirring speed, and 25 °C. After nine cycles, the extraction and stirring efficiency for the La, Ce, and Nd drop to about 80%. The extraction and stripping parameters are applied to the RE leachate from PG to gain the RE oxide with an assay of 92.67%.

© 2024 Chinese Society of Rare Earths. Published by Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

1. Introduction

Rare earth elements (REEs) are a term that describes the lanthanides, scandium, and yttrium elements. Several key components are required for the operation of modern technology. The REEs demands are expected to stay high in the next few years on a global scale, according to predictions.¹ Although REEs share many chemical characteristics, all REEs have their own unique characteristics and are frequently indispensable for certain applications. While rare earth elements have numerous possible uses, the majority of

their use is in metallurgical, polishing, magnetic, and catalytic applications.² Urban mining of manufacturing waste that includes rare earth elements, such as PG and bauxite residues, as well as recycling of waste electronic tools and neodymium magnets, should be prioritized.^{3,4} Recent price fluctuations and high demand for rare earth elements have shifted interest away from other sources and toward PG. PG's main ingredient is calcium sulfate, a byproduct of making phosphoric acid.⁵

Phosphoric acid and PG were produced during the wet processing of enhanced apatite ore with concentrated H₂SO₄. Worldwide, a ton of phosphoric acid yielded four tons of PG; the global PG production was large, with estimates ranging from 100 × 10⁶ to 280 × 10⁶ t per year.⁶ Within the wet process, the production of PG adsorbed around 80% of the REEs found in the apatite.⁷ The primary

* Corresponding author.

E-mail address: mf.farid2008@yahoo.com (M.F. Cheira).

determinant of REEs content is phosphate type. Egyptian phosphate contains approximately 700–2200 mg/kg of REEs.^{8,9}

The most frequent lixivants used for direct leaching of REEs from PG are inorganic acids such as H_2SO_4 , HCl , and HNO_3 . However, the leaching of REEs from PG is hindered by the approach's PG (CaSO_4) solubility.¹⁰ Whereas direct leaching involves the actual leaching of REEs from PG, indirect leaching involves changing the microstructure of PG into substances with potential commercial and industrial uses. When carbonation and recrystallization of PG were used, this approach demonstrated the potential for REEs leaching. These processes could make REEs extraction more appealing and economical given the high REEs concentrations in PG, which were estimated to be around 21×10^6 t, and the requirement to produce marketable products for industrial and commercial applications.¹¹ A potential method for increasing the PG's value by making CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$ fertilizer was the carbonation process. The calcium carbonate, a byproduct of the wet process in the PG, contained an abundance of REEs.¹²

Solvent extraction is one of the best methods for separating REEs into their constituent ingredients or groups.^{13–16} Solvent extraction using ionic liquids has the potential to produce more efficient and less harmful methods of separating mixtures of REEs.¹⁷ Solvents known as ionic liquids were fabricated extremely of ions. Their melting point was lower than 100 °C, and they were usually organic salts.¹⁸ Vapor pressure was negligible for ionic liquids. Solvent extraction procedures now use ionic liquids instead of using molecular diluents. It mitigated the air pollution risk resulting from organic solvent evaporation and verified the flammability of the organic phase.¹⁹

Metal ion extraction from ionic liquids was possible using a neutral extractant, such as crown ether or amine, which transferred the positively charged metal ion to the ionic liquid phase. When the cation of the ionic liquid dissolved into water and recombined with the metal's anions, the liquid's charge level dropped to zero, forming an ionic liquid. It was possible to boost the product's hydrophobicity and decrease ionic liquid loss by attaching long alkyl chains to the cation or using anions.^{20,21} Besides, various hydrophobic ionic liquids were utilized for metal ion extraction; these include Cyphos® IL 101, Aliquat 336, and Cyphos® IL 104. Molecular solvents like kerosene, toluene, and chloroform were indeed used to dilute these liquids. Diluents were used to reduce the high viscosity of ionic liquids, especially those with longer or thicker alkyl chains, to a more controllable level.^{22,23} When the viscosity was reduced, the kinetics and mass transfer were both improved. When diluents were added to pure ionic liquids for extraction, all of their advantages vanished. It was recently demonstrated that in certain instances, the viscosity could be overcome by adding water to the ionic liquid, operating at slightly higher temperatures, and using intermediate quantities of metal input.^{24–26}

Phosphonium-ionic liquids are a significant class of ionic liquids. Phosphonium-ionic liquids are distinguished from ammonium-ionic liquids by two important features: ionic conductivity and heat stability. Whether the P and N center atoms are coupled to the electron-withdrawing phenyl groups or the electron-donating octyl groups, phosphonium-based protic ionic liquids (PILs) show greater ionic conductivity and thermal stability than the comparable ammonium-based PILs. While ammonium ionic liquids are more expensive and have higher extractivity, phosphonium ionic liquids are cheaper and more thermally stable.²⁷ An ionic liquid called trihexyl (tetradecyl)phosphonium nitrate was formed as an extraction method for rare earth elements, which could be used to isolate REEs from nickel and cobalt.

In comparison to traditional solvent extraction techniques, ionic liquid techniques are more environmentally benign since they eliminate the need for volatile and flammable diluents. The ionic

liquid could be formed using a simple metathesis procedure using the commercially accessible ionic liquid trihexyl (tetradecyl)phosphonium chloride. An internally concentrated metal nitrate aqueous phase aided the extraction process by salting out the solvent.^{28–31}

Here, it was demonstrated how to construct a solvent extraction system for REEs (La, Ce, and Nd) by exchanging chloride ions in Cyphos® IL 101 to nitrate ionic liquid. The formation of CaCO_3 was an indirect process that allowed REEs to be leached from PG. The carbonation method was used to transform PG into calcium carbonate to create calcium nitrate, which contains REEs. So, by adjusting the following parameters: La, Ce, and Nd concentration [$\text{P}_{66614}][\text{NO}_3]$] amount, extraction duration, stirring speed, salting-out effect, temperature, and interfering ions, La, Ce, and Nd were selectively extracted from a nitrate leach solution. In order to obtain the best striping settings, the striping method was also used. As a final step, the appropriate parameters were used to separate REEs from the RE leachate from PG.

2. Experimental

2.1. Phosphogypsum processing

The complete dissolution of the PG sample was applied using the digestion technique for the estimation of major and trace elements.³² The leachate of PG was applied by HNO_3 before being introduced to measurement by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Prodigy high dispersion ICP, TELEDYNE - Leeman Labs USA).

2.2. Ionic liquid preparation

The $[\text{P}_{66614}][\text{NO}_3]$ (Cyphos nitrate) ionic liquid was prepared by equilibration of Cyphos chloride (Cyphos® IL 101) form with 2.5 mol/L potassium nitrate three times and then washing the ionic liquid formed with demineralized water until the negative test of chloride by silver nitrate.

2.3. Feed preparation

PG produced from west Sebaya phosphate by El-Nasr Company for Intermediate Chemicals (NCIC) Company, Fayoum Governorate, Egypt, contained REEs that were leached to nitrate leach solution. For the preparation of feed solution, a synthetic calcium nitrate of 6 mol/L was prepared after dehydration of calcium nitrate tetrahydrate by heating at 250 °C for 4 h, then left to cool in the desiccator, and then weighed. This concentration was equivalent to the amount of calcium nitrate formed when the calcium carbonate was dissolved by 37% nitric acid. The synthetic solution was mimicked by a mixture of light REEs, definitely La, Ce, and Nd, so that their total concentration was equal to 2000 mg/L, which was the maximum possible concentration of REEs in Egyptian PG.⁹

2.4. Solvent extraction investigation

The extraction trials were tested by equilibration of 2 mL of ionic liquid with 2 mL of synthetic solution of 1000 mg/L for individual La, Ce, and Nd and stirring for 40 min at room temperature with a few exceptions. Arsenazo III was used to quantify the total REEs content of the individual after the phases were separated by centrifugation in the spectrophotometric technique after the removal of calcium interference. The distribution ratio (D) is the ratio of the total concentration of rare earth ions in the two phases at equilibrium according to Eq. (1).^{33,34}

$$D = \frac{M_{\text{il}}}{M_{\text{aq}}} \quad (1)$$

In this case, the M_{il} and M_{aq} are the concentrations of REEs in the ionic liquids and the aqueous calcium nitrate solution, respectively. The distribution ratio was easily determined by measuring the concentration of RE ions in the $\text{Ca}(\text{NO}_3)_2$ phase after extraction and comparing it to the starting concentration as in Eq. (2).^{35,36}

$$D = \frac{c_i - c_f}{c_f} \times \frac{V_{\text{aq}}}{V_{\text{il}}} \quad (2)$$

c_i represents the concentration of RE ions in the feed phase prior to extraction (the initial concentration), and c_f represents the concentration after extraction (the final concentration). Both the aqueous calcium nitrate and nitrate ionic liquid phases have volumes denoted as V_{aq} and V_{il} , respectively. While the phase ratio factor was an exception, a 1:1 phase volume ratio was typically employed. The following formula was adopted for estimating the extraction percentage (E) (Eq. (3)):

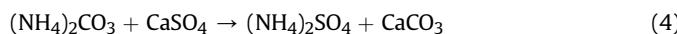
$$E = \frac{D}{D + V_{\text{aq}}/V_{\text{il}}} \times 100\% \quad (3)$$

The controlling factors, such as the pH, time, temperature, phase ratio, and the salting-out effect, were optimized. Stripping by contacting the loaded ionic liquid with stripping fluid was made, and the recyclability of the ionic liquid was investigated.

3. Results and discussion

3.1. Leaching of REEs by indirect technique

To recover REEs, it would be unfeasible and expensive to dissolve PG completely due to its limited solubility, especially since the concentration of REEs that needed to be achieved was the most diminutive. Indirect leaching modified the PG microstructure into compounds with possible commercial and industrial applications, as opposed to direct leaching, which was the actual leaching of REEs from PG. When carbonation and recrystallization of PG were applied, this technique was a promising one. In this work, PG was exploited as the secondary source of REEs in the urban mining of industrial PG waste containing REEs. The carbonation of PG was applied to the indirect leaching of REEs. PG was converted into calcium carbonate and ammonium sulfate by the carbonation process, which is one of the methods that was investigated for the purpose of assessing PG. The process is illustrated in the following equation (Eq. (4)):



The procedure resulted in the formation of calcium carbonate, which contained a high concentration of REEs initially contained in the PG. No study has reported on the recovery of REEs without PG recrystallization or crystal lattice destruction. The data make it clear that the trace amount of iron in the leach liquor was due to the most iron dissolved as ferric sulfate in ammonium sulfate solution during the carbonation process. Moreover, most of Al, Mg, Ti, etc., were removed as sulfate, while fluoride ions were also removed in the carbonation process as ammonium fluoride solution. Subsequently, 100 g of calcium carbonate was converted to a calcium nitrate solution by 400 mL of 2 mol/L nitric acid with 200 r/min stirring for 5 h at 25 °C to leach REEs into the calcium nitrate solution. The leach liquor was heated to decrease the solution volume to 200 mL. The chemical analysis of the nitrate leach liquor

obtained by indirectly leaching REEs from PG is shown in Table 1. The REEs in the leach liquor are mainly light REEs (La, Ce, and Nd ions).

3.2. Solvent extraction of La, Ce, and Nd by $[\text{P}_{66614}]/[\text{NO}_3]$ ionic liquid

3.2.1. Effect of La, Ce, and Nd concentration

A synthetic solution comprising varied amounts of distinct REEs was mixed with 2 mL of ionic liquid and 3 mol/L NH_4NO_3 at a pH of 2.5. The mixture was stirred at 800 r/min for 40 min at 50 °C to determine the individual REEs concentration. Fig. 1(a) illustrates that the extraction efficiencies remain relatively constant at 98% La(III), 96% Ce(III), and 94% Nd(III) as the concentration increases up to 2000 mg/L. However, beyond that concentration, the extraction efficiencies decrease to 90.6%, 88.4%, and 86.2% for La, Ce, and Nd, respectively, at concentration of 2500 mg/L. Evaporation is fed ideally for the increase in the initial concentrated REEs based on these variations in extraction efficacies. When the leach solution was evaporated (to 1/2), the extraction efficiency was good, i.e., 98%, 96%, and 94% for La(III), Ce(III), and Nd(III), individually. It is crucial to understand that reducing the feed concentration enhances the extraction of REEs into the ionic liquid.

3.2.2. Impact of extraction temperature

The temperature influence on the extraction efficiencies of La, Ce, and Nd was studied by stirring a 1/1 phase ratio at 800 r/min for 40 min. In contrast, the temperature varied from 30 to 70 °C. Unfortunately, it could not increase the temperature above this value because of the precipitation of calcium nitrate due to the high concentration of the working calcium nitrate. As illustrated in Fig. 1(b), the temperature significantly influences the extraction percentage. As the temperature rises, the extraction percent increases, reaching 99%, 97%, and 95% for La, Ce, and Nd within a temperature range of 50–70 °C. The sharp decrease in ionic liquid viscosity due to temperature increasing, resulting in improved contact between the two phases, could explain this increase in extraction percent. As the equilibrium of endothermic processes was moved to the right by increasing temperature, the extraction percentages of La(III), Ce(III), and Nd(III) improved accordingly. Temperature, on the other hand, makes the ionic liquid less viscous, which makes it easier to incorporate rare earth complexes into organic phases. The best possible result was achieved at 50 °C.

3.2.3. Effect of nitric acid as salting-out maker

To enhance the extraction of REEs, the salting-out effect may play a crucial role in extraction. HNO_3 and NH_4NO_3 were used to make the salting-out effect. To a set of aliquots of calcium nitrate, portions of nitric acid were added to different amounts of nitric acid, ranging from 1 to 6 mol/L. Then the extraction efficiency was monitored under the conditions of the phase ratio of 1, 1000 mg/L La, 1000 mg/L Ce, and 1000 mg/L Nd, individually, 3 mol/L NH_4NO_3 , pH 2.5, 800 r/min, 40 min, 50 °C (Fig. 1(c)). From the data, there is

Table 1
Chemical compositions of PG leach liquor.^a

Constituent	Concentration (g/L)	Constituent	Concentration (mg/L)
Ca^{2+}	15.45 ± 1.97	Cr^{3+}	3 ± 0.06
REEs ³⁺	0.255 ± 0.35	V^{5+}	1 ± 0.01
Mg^{2+}	0.15 ± 0.01	Cu^{2+}	2 ± 0.02
Al^{3+}	0.03 ± 0.001	Zn^{2+}	2 ± 0.01
Fe^{3+}	0.06 ± 0.002	Ba^{2+}	5 ± 0.09
Ti^{4+}	0.01 ± 0.001	Sr^{2+}	17 ± 0.56

^a Note: ± is SD (standard deviation).

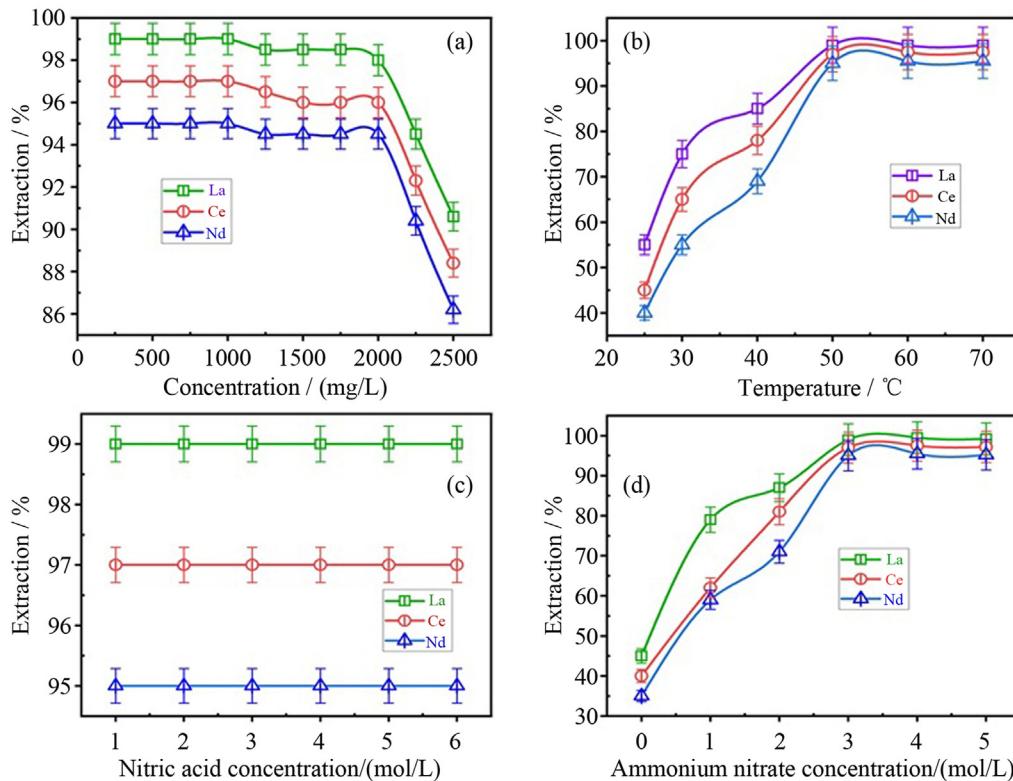


Fig. 1. (a) Effect of La, Ce, and Nd concentrations on the extraction by $[P_{66614}][NO_3]$ (3 mol/L NH_4NO_3 , A/O phase ratio of 1/1, pH 2.5, 800 r/min, 40 min, 50 °C); (b) Effect of temperature on the extraction by $[P_{66614}][NO_3]$ (1000 mg/L La, 1000 mg/L Ce, and 1000 mg/L Nd, 3 mol/L NH_4NO_3 , A/O phase ratio of 1/1, pH 2.5, 800 r/min, 40 min, 50 °C); (c) Effect of nitric acid as salting-out maker on the extraction by $[P_{66614}][NO_3]$ (1000 mg/L La, 1000 mg/L Ce, and 1000 mg/L Nd, 3 mol/L NH_4NO_3 , A/O phase ratio of 1/1, pH 2.5, 800 r/min, 40 min, 50 °C); (d) Effect of ammonium nitrate as salting-out maker on the extraction by $[P_{66614}][NO_3]$ (1000 mg/L La, 1000 mg/L Ce, and 1000 mg/L Nd, A/O phase ratio of 1/1, pH 2.5, 800 r/min, 40 min, 50 °C).

no change in the extraction efficiencies of REEs. However, they used different concentrations of nitric acid.

3.2.4. Effect of ammonium nitrate as salting-out maker

To test how well La, Ce, and Nd could be extracted, the concentration of ammonium nitrate (used as a salting out) was changed from 1 to 5 mol/L in a mixture of 2 mL of $[P_{66614}][NO_3]$ and 2 mL of a synthetic solution. The REEs concentrations were 1000 mg/L. All other parameters were maintained constant, including pH 2.5, A/O phase ratio of 1/1, and 800 r/min stirring speed, and the experiment was conducted for 40 min at 50 °C. In light of the data shown in Fig. 1(d), it was clear that the extraction efficiencies of La, Ce, and Nd increased from 45%, 40% and 35% at no added ammonium nitrate to 99%, 97%, and 95% at 3 mol/L ammonium nitrate, respectively. With increasing ammonium nitrate concentration from 3 to 5 mol/L, the extraction efficiencies were still constant. Therefore, the optimum ammonium nitrate concentration used for further experiments is 3 mol/L.

3.2.5. Impact of pH

The aqueous phase was mixed with organic ionic liquid at a ratio of 1/1, stirred at 800 r/min for 40 min at 50 °C, and then exposed to pH variations ranging from 1 to 6. The following additional parameters were kept constant: 3 mol/L NH_4NO_3 and 1000 mg/L of La, Ce, and Nd ions. As shown in Fig. S2(a), 99% La, 97% Ce, and 95% Nd extraction efficiencies were constant regardless of pH, demonstrating that pH did not affect the extraction of these elements. This means that the extractant did not alter with changes in pH. Because of the nitrate-nitric acid mixture, the salting-out effect was

negligible. However, it must be noted that they could not be separated or extracted since they precipitated at pH values higher than 6.

3.2.6. Impact of A/O ratio

An examination showed that the A/O ratio is a highly visual property that affects extraction efficiency. In addition to financial considerations, the data demonstrate that extractant concentration has a significant impact on extraction efficiency. The impact of the A/O ratio was examined on the extraction efficiency of REEs using $[P_{66614}][NO_3]$ ionic liquid at 800 r/min stirring and 50 °C for contact time of 40 min. After that, the pH of the watery mixture was brought down to 2.5, and it included 1000 mg/L of La, Ce, and Nd ions, separately. It did this not long after it set the temperature to 50 °C. After mixing, it separated the organic and inorganic components. Fig. S2(b) displays the results of monitoring the La, Ce, and Nd concentrations in the aqueous solution during this separation. The acquired data clearly indicate that the maximum extraction efficiency stays constant, primarily within the A/O ratio range of 1/1 and 1/3; however, the $[P_{66614}][NO_3]$ extractant achieved its maximum extraction at a A/O ratio of 1/1. It was anticipated that increasing the phase ratio beyond 1 would increase the percentage of extraction,³⁷ but this required a high stirring power that exceeded the parameters considered economical and experimental.

3.2.7. Stirring time impact

A series of tests was run to determine how time affects extraction percentage and procedure cost. The purpose of this was to find out how important time is in relation to these two mediums. Without a doubt, the quantity of mass transfer would grow in

proportion to the increase in stirring duration as more contact between the two phases occurs. In order to determine how contacting time affects La, Ce, and Nd extraction, a number of experiments were analyzed. At 50 °C, A/O phase ratio of 1/1 and solution pH 2.5, 3 mol/L NH₄NO₃, and 1000 mg/L of individual La, Ce, and Nd ions were mixed at 800 r/min in [P₆₆₆₁₄][NO₃] ionic liquid. From 10 to 120 min, the two phases were in contact for REEs extraction to [P₆₆₆₁₄][NO₃] ionic liquid. Fig. S2(c) shows that the extraction efficiencies of La, Ce, and Nd increased with an increasing contact time of up to 40 min for [P₆₆₆₁₄][NO₃] ionic liquid. The results show that increasing the contact duration to 120 min has no effect on the extraction efficiency. Therefore, pressing for 40 min is sufficient for maximum extraction efficacy. The subsequent tests would involve contacting the two phases for 40 min, as that is the duration required for equilibrium.

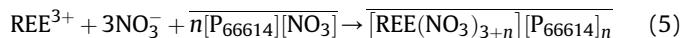
3.2.8. Impact of stirring rate

It investigated the effect of stirring rate on La, Ce, and Nd extraction efficiency by increasing the stirring speed from 200 to 1200 r/min in an aqueous phase containing 3 mol/L NH₄NO₃ and 1000 mg/L of La, Ce, and Nd ions individually and an organic phase containing [P₆₆₆₁₄][NO₃] ionic liquid. Every other variable was kept constant for 40 min at 50 °C in a A/O phase ratio of 1/1 with a pH of 2.5. As shown in Fig. S2(d), increasing the stirring rate from 200 to 800 r/min resulted in a significant increase in the extraction percentages from 40% to 99% for La ions, 45%–97% for Ce ions, and 35%–95% for Nd ions. Even after increasing the stirring speed to 1200 r/min, the extraction efficiencies remained constant. Thus, for the optimal extraction efficiency, a stirring speed of 800 r/min is enough to transfer the maximum number of REEs ions to [P₆₆₆₁₄][NO₃] ionic liquid. The ideal speed for stirring during extraction is 800 r/min.

3.3. Extraction mechanism

The fact that trivalent RE ions are capable of forming anionic complexes with bidentate nitrate ligands is the fundamental principle that underpins the extraction method of La, Ce, and Nd ions.

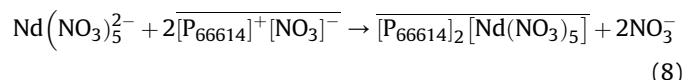
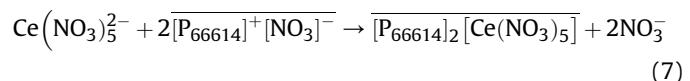
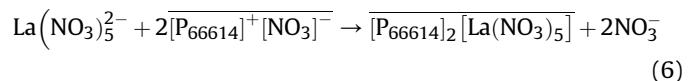
Furthermore, it was able to extract the negatively charged complexes between the nitrate ions and the rare earth ions into the [P₆₆₆₁₄][NO₃] ionic liquid. It was possible to express the general extraction mechanism for the extraction of RE ions as follows (Eq. (5)):



Experiments were conducted to determine the maximum metal loading for each of the component complex ions (La, Ce, and Nd

ions). In Fig. 2(a), La, Ce, and Nd ions were maintained at a constant level, while the quantity of [P₆₆₆₁₄][NO₃] ionic liquid was raised at a pH of 2.5 for a contact duration of 40 min at a temperature of 50 °C. When the quantity of [P₆₆₆₁₄][NO₃] ionic liquid in the extraction system is fewer than two molar ratios of the ionic liquid to the number of lanthanum, cerium, or neodymium moles, the extraction efficiencies are increased until they reach their maximum at 99% La, 97% Ce, and 95% Nd at two molar ratios.

Hoogerstraete and Binnemans²⁸ discovered earlier that the extraction process of the rare earth ions (lanthanum and samarium) produced various anionic complexes. Lanthanum (III) was extracted using the hexakis anionic complex [La(NO₃)₆]³⁻, while samarium (III) was extracted using the pentakis anionic complex [Sm(NO₃)₅]²⁻. According to this work, each mole of lanthanum, cerium, or neodymium needed two moles of [P₆₆₆₁₄][NO₃] ionic liquid to form extractant complexes by a solvation mechanism. It might be concluded that in the feed solution, lanthanum, cerium, and neodymium ions were present as pentakis anionic complexes [La(NO₃)₅]²⁻ [Ce(NO₃)₅]²⁻, and [Nd(NO₃)₅]²⁻ in the nitrate solution. Hence, these anionic complexes were extracted with [P₆₆₆₁₄][NO₃] ionic liquid. After that, the extraction of rare earth ions was maintained at the same level. It might be deduced from this that the pentakis anionic nitrate complexes of La, Ce, and Nd were gotten and produced employing two ionic liquid molecules at the maximal extraction level, as shown in the following equations (Eqs. (6)–(8)).



FTIR spectra were used to explain the extraction mechanism. It is important to discuss the differences in the FTIR spectra when the concentration of rare earth ions was relatively small. Fig. 2(b) and (c) show that the vibration modes of the extractant's cation, which correspond to the comparison bands, did not show any increase in wavenumber upon loading with REEs. It suggests that the cation of the extractant was not directly coordinated with the metal center. A CH₂ group stretching mode might be found at 2926 and 2856 cm⁻¹, which was one of the vibration modes of the cation. The broadband that is located at 3424 cm⁻¹ might be recognized as the OH stretching mode of H₂O that appears in the ionic liquid. This mode

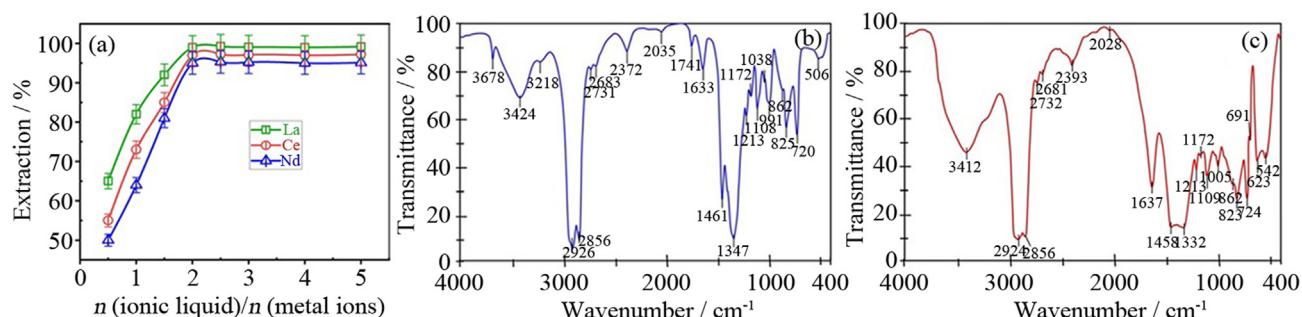


Fig. 2. (a) The number of [P₆₆₆₁₄][NO₃] ionic liquid moles on extraction efficiencies of La, Ce, and Nd anionic complexes (1000 mg/L La, 1000 mg/L Ce, and 1000 mg/L Nd, 3 mol/L NH₄NO₃, pH 2.5, 40 min contact, 800 r/min, 50 °C); (b) FTIR spectrum of [P₆₆₆₁₄][NO₃] ionic liquid; (c) FTIR spectrum of REEs/[P₆₆₆₁₄][NO₃] ionic liquid.

has manifested itself in the loaded ionic liquid as a consequence of the migration of a small quantity of hydrated calcium nitrate that has come into contact with the ionic liquid. There was also a band that could be seen at 1630 cm^{-1} was related to the bending mode of H_2O . Because the REEs were loaded and water was transferred to the ionic liquid, the band's intensity increased. All of the last remaining peaks form the NO_3 group.

Since this band is not IR active due to the great symmetry of the nonbonding nitrate, the formation of the peak at 725 cm^{-1} in the loaded ionic liquid, which corresponded to the symmetrical bending of NO_2 , is a reference to the coordination of NO_2 . The formation of this band occurred upon loading the ionic liquid with RE ions. The symmetry was reduced as a result of the coordination of the nitrate, and the peak became active in the infrared spectrum. Furthermore, the band that was related to the asymmetric stretching of $-\text{NO}_2$ was changed from 1347 to 1332 cm^{-1} , which was a determination of the bonding effect of $-\text{NO}_2$. Finally, the band of the out-plane rocking of $-\text{NO}_2$ and the N–O stretching vibration had been changed from 825 to 1461 cm^{-1} to 823 and 1458 cm^{-1} from the earlier position. The ionic liquid overloaded with REEs might have been the result of NO_2 bonding.

3.4. Stripping studies

The simplicity of the stripping procedure is one of the most important factors that determines whether or not solvent extraction is successful. The stripping process uses a suitable liquid, such as water, acid, base, or complexing agent, to extract the metals. Without a doubt, water is the best option because it is environmentally friendly. One of the benefits of this method is that it allows for the option of utilizing water in the process of stripping. When the loaded ionic liquid phase was transported into the exchange with faintly acidified water, the stripping process was accomplished. It was done in order to prevent the hydrolysis of REEs. A series of studies was conducted in order to back-extract RE ions into an aqueous phase from the REEs loaded ionic liquid. The preliminary experiments were designed to remove La, Ce, and Nd ions from the loaded $[\text{P}_{66614}][\text{NO}_3]$ ionic liquid by employing water that was faintly acidified by nitric acid. To achieve this goal, a number of pertinent parameters, including contacting time, A/O phase ratio, and temperature, were utilized in order to determine the stripping features of the RE ions that have been extracted.

3.4.1. Effect of acidity

To investigate how acidity affects the effectiveness of La, Ce, and Nd ion stripping from their loaded ionic liquid, many realistic tests were conducted spanning the acidity range of 0 – 0.1 mol/L nitric acid. Other stripping parameters used in these investigations include a contact period of 40 min , an stirring speed of 800 r/min , and an A/O phase ratio of $1/1$ at 25°C . The acquired and displayed results in Fig. 3(a) clearly show that the stripping efficiencies increased from 75.2% , 76.4% and 78.3% – 96.1% , 97.5% and 99.3% , respectively, when the acid concentration varied from 0 to 0.0001 mol/L . Acidity levels greater than 0.0001 mol/L did not noticeably enhance La, Ce, and Nd stripping. As a result, the ideal acidity for the re-extraction process is a slight acidity of 0.0001 mol/L .

3.4.2. Effect of stripping time

Under set circumstances of A/O ratio of $1/1$, 800 r/min , and room temperature, the effect of contact duration was investigated on the stripping efficiency of La, Ce, and Nd from loaded ionic liquid. The contact time ranged from 10 to 60 min , and an acidified water solution (0.0001 mol/L nitric acid) was used. The findings presented in Fig. 3(b) could be deduced that the stripping efficiency of La, Ce,

and Nd enlarged from 61.2% , 69.3% and 75.6% – 96.1% , 97.5% and 99.3% , respectively, when the contact time was increased from 5 to 40 min . Following that, a contact time that was longer than 40 min did not result in a discernible increase in the La, Ce, and Nd stripping. Therefore, a stripping time of 40 min could be deemed adequate for quantitative stripping.

3.4.3. Impact of A/O ratio

In order to investigate the impact of the A/O phase ratio on the elimination of La, Ce, and Nd from the loaded ionic liquid, several stripping parameters were examined with A/O ratio ranging from $1/3$ to $3/1$. Meanwhile, the further stripping influences were maintained in acidified water (0.0001 mol/L nitric acid) and utilized as the stripping agent for a contact time of 40 min and a stirring speed of 800 r/min at 25°C . Based on the information presented in Fig. 3(c), it could be deduced that the highest stripping efficiencies from the loaded ionic liquid were attained when the A/O ratio was equal to $1/1$ and that these efficiencies continued to be constant after that.

3.4.4. Impact of temperature

Several tests were realistic over a temperature extent of 25 – 55°C in order to study the impact of temperature on the extraction efficiency with acidified water (0.0001 mol/L nitric acid) for stripping La, Ce, and Nd ions from loaded ionic liquid. The fixed stripping conditions included a contact time of 40 min , a stirring speed of 800 r/min , and an A/O phase ratio of $1/1$. The data obtained and presented in Fig. 3(d) clearly demonstrate that the temperature rose to 55°C , and the stripping efficiencies gradually decreased from 96.1% , 97.5% and 99.3% – 77.4% , 82.3% and 84.33% for La, Ce, and Nd ions. It is possible that the exothermic reaction that occurs during the stripping process was responsible for these outcomes. As a result, the room temperature could be the optimal temperature for the re-extraction process.

3.5. Application on the recovery of REEs

For the purpose of extracting and stripping RE ions from synthetic rare earth elements solutions using the ionic liquid, the optimal settings were utilized, as indicated by the previously reported findings.²⁸ It was determined that the RE ions were extracted from the solution using the $[\text{P}_{66614}][\text{NO}_3]$ extractant, taking into account the minimal impact of interfering ions on the extraction efficiency. The results of the chemical analysis of nitrate leach liquid obtained by indirect leaching of REEs from PG are displayed in Table 1. Leach liquor contained mostly light rare earth element ions (255 mg/L REEs), such as La, Ce, and Nd ions. Moreover, the PG leach liquor contained 15.45 g/L Ca^{2+} , 150 mg/L Mg^{2+} , 30 mg/L Al^{3+} , 60 mg/L Fe^{3+} , 10 mg/L Ti^{4+} , and 17 mg/L Sr^{2+} . According to the effect of interfering ions, the metal ions in the phosphogypsum leach liquor did not interfere with the rare earth ions during the extraction process with $[\text{P}_{66614}][\text{NO}_3]$ ionic liquid extractant.

Thus, it used the PG leach liquor and the $[\text{P}_{66614}][\text{NO}_3]$ ionic liquid to recover rare earth ions. Nevertheless, to acquire high-quality RE ions, it was necessary to perform additional refinement or the addition of masking managers prior to the extraction method. The process of extraction was carried out on 1 L of the organized leach liquor, which contained 255 mg/L of RE ions and minority interfering ions. With 1 L of ionic liquid, the procedure was carried out under optimal circumstances, which included a pH of 2.5 for the PG leach liquor, stirring speed of 800 r/min , and a contact period of 40 min at 50°C .

It was used under the previously specified conditions to remove the REEs from the $[\text{P}_{66614}][\text{NO}_3]$ ionic liquid. It was used with 1 L of

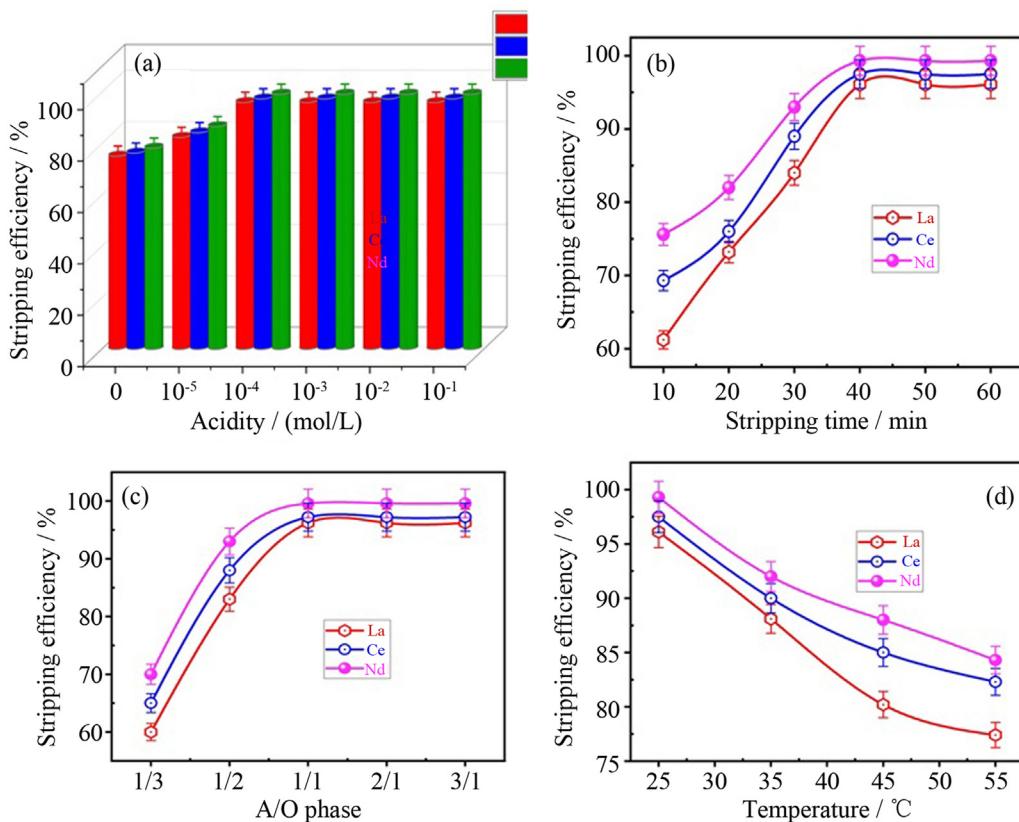


Fig. 3. (a) Effect of acidity on La, Ce, and Nd stripping efficiency from loaded ionic liquid extractant (A/O ratio of 1/1, stirring speed of 800 r/min, 25 °C); (b) Outcome of stripping time on La, Ce, and Nd stripping efficiency from loaded ionic liquid extractant (A/O ratio of 1/1, stirring speed of 800 r/min, 25 °C); (c) Outcome of A/O phase ratio on stripping efficiencies of La, Ce, and Nd from loaded ionic liquid (40 min, stirring speed of 800 r/min, 25 °C); (d) Impact of temperature on stripping efficiencies of La, Ce, and Nd from loaded ionic liquid (40 min, stirring speed of 800 r/min, A/O ratio of 1/1).

acidified water (0.0001 mol/L nitric acid, less than 1 mL concentrated acid in 1 L water solution) for a contact time of 40 min at 25 °C to agitate the working [P66614][NO₃] ionic liquid loaded with REEs, which contained 230 mg. A complete separation was achieved between the organic and aqueous phases. It was discovered that the stripping efficiency was 98.5%, and the REEs content was found to be 222 mg/L in the acidified aqueous solution.

The final phase was followed by the preconcentration route, which precipitated the REEs from the stripping solution. Consequently, oxalic acid was utilized to precipitate RE ions in the form of RE oxalate. Next, the precipitate was roasted to convert it into RE oxide. The stripping solution was subjected to concentration by evaporation until it reached a volume of 200 mL of aqueous solution to prepare an appropriate RE concentrate from the stripping

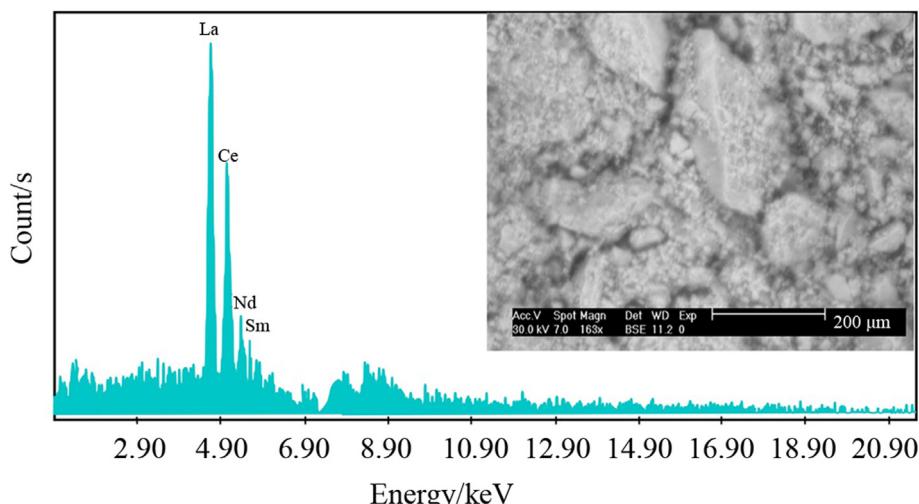
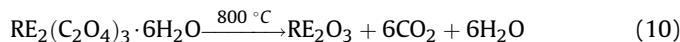
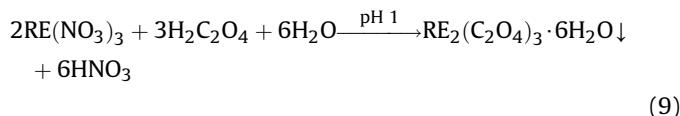


Fig. 4. SEM-EDX image of the RE oxide product.

solution. After correcting a solution of nitric acid and ammonia with pH to 1, the precipitation procedure was carried out by adding 25% oxalic acid. REEs like La, Ce and Nd precipitate as $(RE_2(C_2O_4)_3 \cdot 6H_2O$ (0.97 g), followed by roasting at 800 °C. Upon completion, the result is RE_2O_3 , which weighs 0.56 g. The following equations show the precipitation and roasting of the RE ions (Eqs. (9) and (10)).



Scanning electron microscopy (SEM) equipped with an Oxford Devices 6587 EDX microanalysis detector manufactured by Jeol of Tokyo, Japan, was used to identify the obtained RE oxide (Fig. 4). Additionally, quantitative analysis was adopted to identify the chemical components linked to the oxide formation. The acquired data revealed that the content of RE oxide was 92.67%.

4. Conclusions

For REEs recovery from PG, it would be possible and costly to dissolve PG by indirect leaching with carbonation and recrystallization into $CaCO_3$ and $(NH_4)_2SO_4$ fertilizer. The carbonation of PG initially contains a high concentration of REEs in the calcium carbonate. Calcium carbonate was converted to calcium nitrate solution by stirring it with 2 mol/L nitric acid at 200 r/min for 5 h at 25 °C. The ionic liquid Cyphos IL 101 chloride was converted to $[P_{66614}]NO_3$ nitrate ionic liquid using 2.5 mol/L potassium nitrate to extract La, Ce, and Nd from the nitrate medium. The extraction trials were tested by equilibrating 2 mL of $[P_{66614}]NO_3$ ionic liquid with 2 mL of a synthetic solution containing 1000 mg/L for each La, Ce, and Nd. This allows us to determine the ideal solvent extraction conditions, which include an A/O phase ratio of 1/1 and 3 mol/L NH_4NO_3 (as salting-out maker) at 800 r/min for 40 min at 50 °C. The stripping efficiency of La, Ce, and Nd was assessed from their loaded $[P_{66614}]NO_3$ ionic liquid using an A/O ratio of 1/1, stirring speed of 800 r/min, and 25 °C. After nine cycles, the extraction and stirring efficiencies for La, Ce, and Nd drop to about 80%. The extraction and stripping parameters were applied to the RE leachate, which results in 92.67% for RE oxide. The $[P_{66614}]NO_3$ ionic liquid exhibits a good extraction capacity and the highest affinity for La, Ce, and Nd, indicating its widespread application in the recovery of REEs from phosphogypsum and other resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jre.2024.07.005>.

References

- Goodenough KM, Wall F, Merriman D. The rare earth elements: demand, global resources, and challenges for resourcing future generations. *Nat Resour Res.* 2018;27(2):201.
- Peiravi M, Dehghani F, Ackah L, Baharlouei A, Godbold J, Liu J, et al. A Review of rare-earth elements extraction with emphasis on non-conventional sources: coal and coal byproducts, iron ore tailings, apatite, and phosphate byproducts. *Min Metall Explor.* 2021;38(1):1.
- Davris P, Balomenos E, Taxiarchou M, Panias D, Paspaliaris I. Current and alternative routes in the production of rare earth elements. *BHM Berg-Hüttenmännische Monatsh.* 2017;162(7):245.
- Liang Y, Guan B, Cao T, Liu G, Tang P, He M, et al. Study on the properties of an excess-sulphate phosphogypsum slag cement stabilized base-course mixture containing phosphogypsum-based artificial aggregate. *Construct Build Mater.* 2023;409:134095.
- Swain N, Mishra S. A review on the recovery and separation of rare earths and transition metals from secondary resources. *J Clean Prod.* 2019;220:884.
- Kandil A-HT, Cheira MF, Gado HS, Soliman MH, Akl HM. Ammonium sulfate preparation from phosphogypsum waste. *J Radiat Res Appl Sci.* 2017;10(1):24.
- Al-Thyabat S, Zhang P. In-line extraction of REE from Dihydrate (DH) and Hemidihydrate (HDH) wet processes. *Hydrometallurgy.* 2015;153:30.
- Mukaba J-L, Eze CP, Pereao O, Petrik LF. Rare earths' recovery from phosphogypsum: an overview on direct and indirect leaching techniques. *Minerals.* 2021;11(10):1051.
- Abd El-Mottaleb M, Cheira MF, Gouda GH, S AA. Leaching of rare earth elements from Egyptian Western Desert phosphate rocks using HCl. *Chem Adv Mat.* 2016;1:33.
- Orabi AS, Ismail AH, Abou El-Nour KM, Atia BM, Gado MA, Cheira MF. Nitrate-mediated kinetic leaching for rare earth elements recovery from phosphogypsum. *Anal Chem Lett.* 2023;13(5):561.
- Akfas F, Elghali A, Aboulaich A, Munoz M, Benzaazoua M, Bodinier J-L. Exploring the potential reuse of phosphogypsum: a waste or a resource? *Sci Total Environ.* 2024;908:168196.
- Safulina AM, Matveeva AG, Evtushenko AV, Lizunov AV, Goryunov EI, Goryunova IB, et al. Recovery of lanthanides from digested phosphogypsum solutions using a new organophosphorus extractant, 5-(diphenylphosphoryl) hexan-3-one. *Russ J Gen Chem.* 2015;85(9):2128.
- Xie F, Zhang TA, Dreisinger D, Doyle F. A critical review on solvent extraction of rare earths from aqueous solutions. *Miner Eng.* 2014;56:10.
- Ren Y, Polukeev VA, Kenf EV, Tkachenko LI, Alyapshev MY, Babain VA, et al. Substituted diamides of dipicolinic acid as extractants and ionophores for rare earth metals. *J Rare Earths.* 2023;41(8):1234.
- Anawati J, Azimi G. Extraction of rare earth elements from a South American ionic clay. *J Rare Earths.* 2023;41(9):1408.
- Yu G, Zeng Z, Gao Y, Ni S, Zhang H, Sun X. Separation of aluminum from rare earth by solvent extraction with 4-octyloxybenzoic acid. *J Rare Earths.* 2023;41(2):290.
- Liu Y, Chen J, Li D. Application and perspective of ionic liquids on rare earths green separation. *Separ Sci Technol.* 2012;47(2):223.
- Zein El Abedin S, Endres F. Ionic liquids: the link to high-temperature molten salts? *Acc Chem Res.* 2007;40(11):1106.
- Larsson K, Binnemans K. Separation of rare earths by solvent extraction with an undiluted nitrate ionic liquid. *J Sustainable Metall.* 2017;3(1):73.
- Dietz ML, Dzielawa JA, Laszak I, Young BA, Jensen MP. Influence of solvent structural variations on the mechanism of facilitated ion transfer into room-temperature ionic liquids. *Green Chem.* 2003;5(6):682.
- Magdalena R-R, Maciej W. In: Scott H, ed. *Ionic liquids in separation of metal ions from aqueous solutions.* Rijeka: IntechOpen; 2011.
- Inman G, Nlebedim IC, Prodius D. Application of ionic liquids for the recycling and recovery of technologically critical and valuable metals. *Energies.* 2022;15(2):628.
- Kumari A, Sinha MK, Sahu SK, Pandey BD. Solvent extraction and separation of trivalent lanthanides using Cyphos IL 104, a novel phosphonium ionic liquid as extractant. *Solvent Extr Ion Exch.* 2016;34(5):469.
- Shakeel A, Mahmood H, Farooq U, Ullah Z, Yasin S, Iqbal T, et al. Rheology of pure ionic liquids and their complex fluids: a review. *ACS Sustainable Chem Eng.* 2019;7(16):13586.
- Regel-Rosocka M, Wisniewski M. Selective removal of zinc(II) from spent pickling solutions in the presence of iron ions with phosphonium ionic liquid Cyphos IL 101. *Hydrometallurgy.* 2011;110(1):85.
- Gradwohl A, Windisch J, Weissensteiner M, Keppler BK, Kandioller W, Jirska F. Extraction of rare earth elements from aqueous solutions using the ionic liquid trihexyltetradecylphosphonium 3-hydroxy-2-naphthoate. *RSC Adv.* 2023;13(36):24899.
- Torabi M, Yarie M, Zolfogol MA, Azizian S, Gu Y. A magnetic porous organic polymer: catalytic application in the synthesis of hybrid pyridines with indole, triazole and sulfonamide moieties. *RSC Adv.* 2022;12(14):8804.
- Vander HT, Binnemans K. Highly efficient separation of rare earths from nickel and cobalt by solvent extraction with the ionic liquid trihexyl(tetradecyl) phosphonium nitrate: a process relevant to the recycling of rare earths from permanent magnets and nickel metal hydride batteries. *Green Chem.* 2014;16(3):1594.
- Li X, van de Ven JJMM, Li Z, Binnemans K. Separation of rare earths and transition metals using ionic-liquid-based aqueous biphasic systems. *Ind Eng Chem Res.* 2022;61(17):5927.
- Zhang W, Feng D, Xie X, Tong X, Du Y, Cao Y. Solvent extraction and separation of light rare earths from chloride media using HDEHP-P350 system. *J Rare Earths.* 2022;40(2):328.
- Fu Y, Huang M, Zhou Z, Li Z, Liao W, Lu Y. Separation of trivalent rare earths from nitrate medium using solvent extraction with a novel extractant 2-

- ethylhexyl ((2-ethylhexylamino)methyl) phosphonic acid. *J Rare Earths*. 2022;40(3):491.
32. Shapiro L. Rapid analysis of silicate, carbonate, and phosphate rocks: revised edition. *US Geol Surv Bull*. 1975.
33. Cheira MF, Orabi AS, Atia BM, Hassan SM. Solvent extraction and separation of thorium(IV) from chloride media by a Schiff base. *J Solut Chem*. 2018;47(4):611.
34. Hashad A, Atiti S, Cheira M, Ghonaim AK. Extraction and determination of vanadium and its application on geological samples with 8-hydroxy quinoline. *Arab J Nuclear Sci Appl*. 2011;44:27.
35. Cheira MF. Solvent extraction of uranium and vanadium from carbonate leach solutions of ferruginous siltstone using cetylpyridinium carbonate in kerosene. *Chem Pap*. 2020;74(7):2247.
36. Cheira M, Hussein G. Separation of nickel (II) from acidic media using substituted 2-amino-pyrazoloquinazolinone. *Inorg Chem Ind J*. 2013;8:156.
37. Cheira MF, Orabi AS, Hassanin MA, Hassan SM. Solvent extraction of thorium (IV) from chloride solution using Schiff base and its application for spectrophotometric determination. *Chem Data Collect*. 2018;13–14:84.