Review

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*Review*

# Rare Earths Recovery Using Ionic Liquids and Deep Eutectic Solvents

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**Abstract:** With the developments of smart technologies, the use of rare earth elements (REEs) knows a widespread use, thus, their importance as valuable and strategic metals boosted to levels never known before. Due to their scarcity in Earth crust, the recovery of these elements from secondary resources also knows further developments. Traditional pyrometallurgical and hydrometallurgical processing, though of wide use, in the recovery of these REEs, have some environmental drawbacks, thus, the development of new recovery approaches are under developments. Here, Solvometallurgy appeared as a friendly environmental technology, and ionic liquids and deep eutectic solvents resulted as a first-row chemicals to be used in the different unit operations used in solvometallurgical processing: leaching, liquid-liquid extraction, ion exchange (adsorption), precipitation and electrolysis. This manuscript reviewed the most recent literature concerning the use of ionic liquids and deep eutectic solvents in the recovery of REEs from various sources.

**Keywords:** rare earths elements; ionic liquids; deep eutectic solvents; solvometallurgy; recovery

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## 1. Introduction

Besides the use of raw material, metals can be recovered from different secondary resources. Among these, it is of special interest the processing of industrial wastes, which several times contained valuable metals. Among these metals, rare earth elements (REEs), category which includes 15 lanthanides (LNs), yttrium and scandium are included [1,2]. Due to their specific atomic structure, this group of elements presented unique optical, thermal, electrical, and magnetic properties, thus, they are widely used in various fields, including traditional industries such as glass, agriculture, ceramics, chemicals, etc., as well as high-tech industries such as energy, automotive, healthcare, nuclear industry, communications and military uses [3–7].

Against the above, these increasingly exploitations and applications have increase the presence of REEs in the environment (atmosphere, water and soil), boosting the potential risk of contamination towards organisms and humans [8].

In view of the relevance of the recovery of these REES for resource conservation, and as a real alternative to the traditional recovery (pyro or hydrometallurgical) processes, there is an increasing interest in the use of smart recovery processes, with the same efficiency and with more friendly environmental characteristics, and here the concept of Solvometallurgy arises.

If the difference between Pyrometallurgy and Hydrometallurgy relies in the use of high temperatures (Pyrometallurgy) against the use of moderate temperatures, pressure and aqueous systems in the case of hydrometallurgical processing, differentiation between Hydrometallurgy and Solvometallurgy is that the latter uses non-aqueous solvents. Most of the unit processes (leaching, solvent extraction, ion exchange, precipitation, electrolysis) in Solvometallurgy are similar to those in Hydrometallurgy, with the main difference, as it is said above, being that water is replaced by a non-aqueous solvent [9,10].

The considerations described above resulted in the use of ionic liquids and deep eutectic solvents, in Hydrometallurgy and Solvometallurgy, as cleaner alternatives to perform the recovery of REEs (and other metals) from (mainly) secondary resources. This manuscript reviews most recent (2022-June 2023) advances in the use of these two non-aqueous solvents in the recovery of, the now profitable, REEs. In Section 2, different applications of ionic liquids in the recovery of these REEs are described, whereas in Section 3 the use of deep eutectic solvents on the recovery of rare earth elements from different sources is described. The Conclusion section emphasized some future tendencies about the use of these chemicals on the recovery of these valuable and strategic elements.

## 2. Ionic Liquids

Ionic liquids (ILs) or room-temperature ionic liquids (RTILs), are a class of chemicals consisting of ions which maintained the liquid state below 100° C. They are frequently formed by an organic cation (i.e., tetraethyl ammonium, dialkylimidazolium, 1-ethyl-3-methylimidazolium) and organic or inorganic anion (i.e., chloride, nitrate, bisulphate, chlorate, thiocyanate). Moreover, ILs have relatively high viscosity and density [11].

The bulky characteristics of the organic moiety of ILs are the responsible that these chemicals presented an amply liquidous range and, thus, low volatility. The properties presented by ILs included: thermal and radioactive stability, non-volatility, non-flammability, adjustable miscibility in organic diluents and polarity. Also, these properties can be modified to match a given necessity, by changing to the appropriate cation and/or anion, to form the more specialized Task Specific Ionic Liquids (TSILs) family of chemicals. [12].

The different applications of ILs and TSILs have enhanced the development of different extraction processes: simplifying analytical methodologies, the removal of environmental contaminants, breaking of azeotropes and purification of fuels. Technologies including liquid-liquid extraction (LLE), solid-phase extraction (SPE), pressurized liquid extraction (PLE), liquid-phase microextraction (LPME) used these chemicals in a very efficient manner. Properly used, these ILs can avoid the use of chelating agents in the selective extraction of ions. Also, they can bring about mass transfer in novel miniaturized homogeneous LPME models. Other uses of this family of compounds included UV-V spectrophotometric determination of mercury ions from water samples, and the use of silica, polymers and nanoparticles, as support of ILs phases, to act as SPE adsorbents used in the removal of organic acids, amines, and aldehydes from atmospheric aerosol samples, and to remove carbon dioxide from gaseous streams, thus, widening their use in the cleaning of biogas.

ILs chemicals have been labelled as *green* compounds due to their properties, though there are also some claims against this *green* label, because there are several concerns against air, water and terrestrial pollutions. Some of these harmful properties, on living organisms, are connected with undesirable effects on cellular wall [13], though this harmfulness varies from one organism to other.

Several uses of ILs on the recovery of metals have been recently published [14–19].

### *ILs and REEs*

Several reviews [20,21] deal with the application of ILs on the recovery of these strategic elements. These reviews focused in the use of ionic liquids in the recovery of secondary resources such as e-wastes and nickel-metal hydride batteries (NiMHBs). In the case of e-wastes [20], the review included the use of IL extraction, selectivity and reusability, including several types of TSILs, and the use of diluents in the organic phase. The content of REEs (about 10% wt) in nickel-metal hydride spent batteries are usually dumped, though several approaches to recover La, Ce, Nd, and Pr, from these discarded resources are also into consideration [21].

Since REEs and some of their derivatives have several uses on smart technologies, praseodymium oxide nanoparticles ($Pr_6O_{11}$ nps) are formed by the use as templating agent of an IL (BMIM-PF6) and an alcohol [22]. The IL inhibited particle growth, whereas ethylene glycol is used as diluent of the organic phase. The as-synthesized nanoparticles presented anti-cancerigenous properties and antibacterial activity against Gram-negative bacteria K. pneumoniae and Gram-positive bacteria S. aureus.

Separation of some REEs with 1,2-hydroxypyridinone grafted ionic liquid (HOPO-IL) was investigated [23]. The extraction rate decreased when 1-octanol was used instead of the ILs. Lanthanides extraction with HOPO-IL was pH-dependent, being the metals extracted by a cation-exchange based reaction. The addition of $[NTf_2]^-$ had a minor influence on metal loading onto the organic phase, whereas the presence of $[C_4mim]^+$ had a suppressing effect on lanthanides extraction. The dependence of the extraction of these REEs on the aqueous pH value, suggested that the stripping step can be performed by solutions of acidic pH-values.

A method for recycling permanent magnet waste by betaine hydrochloride ([Hbet]Cl) solution extraction was presented [24]. The next optimum leaching conditions were obtained as leaching temperature of 200º C, reaction time of 8 h, [Hbet]Cl concentration of 0.2 mol/L, and solid–liquid ratio of 1:150 (g/mL). The above experimental values allowed to reach leaching rates of 99.8% Pr, 97.1% Nd, 95.5% Gd, 56.2% Ce and less than 0.3 % in the case of iron, the residue of the leach operation contained iron oxide. When mineral acids HCl, $H_2SO_4$ or $HNO_3$ are used to dissolve the magnet, the present procedure allowed to improve the leaching percentage and the selective separation of these elements, being the dissolution sequence in accordance with the properties of these metals. REEs are leached via the next reaction:

$$RE_2O_3 + 8[Hbet]Cl + H_2O \rightarrow [RE(bet)_8(H_2O)_4]^{6+} + 2H^+ + 8Cl^- \quad (1)$$

*Note from the authors of the review: the separation of the various REEs from the leaching solution was not described in the published manuscript.*

A method for recycling a real scrap NdFeNi magnet from computer hard disks in order to recover Nd(III) as a marketable salt and other valuable by-products was described [25]. Solvent extraction of Nd(III) and Ni(II) used the synthesized bi-functional ionic liquid (Bif–IL) [AL336][Cy572] in kerosene, based on Aliquat 336 (quaternary ammonium salt) and Cyanex 572 (phosphonic acid). When compared to Cyanex 572 alone, Bif–IL improved not only the extraction percentage of these metals but also the separation factors between Nd(III) and Ni(II), with the highest Nd/Ni separation factor of 26.3 obtained at 0.2 M HCl medium. It was determined that the extracted species are $NdCl_3(R_4NCy)_3$ and $NiCl_2(R_4NCy)_2$. Nd-loaded organic phase was stripped with 0.5 M HCl solution, and from the stripped solution, Nd(III) was precipitated with oxalic acid, further, the resulting solid was calcined to yield $Nd_2O_3$.

As part of the downstream technology development efforts in the treatment of acid mine drainage (AMD), a number of ionic liquids was synthesized and compared in the extraction of REEs including: Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th and U [26]. In the investigation, extractants and their ionic liquids showed in Table 1 were used.

**Table 1.** Extractants and ionic liquids used in the extraction of REEs from AMD.

| Extractant | Acronysm |
|---|---|
| di-2-ethylhexyl phosphoric acid | D2EHPA |
| tri(hexyltetradecyl phosphonium chloride | C101 |
| 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester | EHEHPA |
| Mixture of phosphonic acid and phosphinic acids | C572 |
| Ionic liquids | |
| trihexyltetradecylphosphonium and di-2-ethylhexyl phosphate | $[C101]^+[D2EHP]^-$ |
| trihexyltetradecylphosphonium and 2-ethylhexyl phosphate mono-2-ethylhexyl ester | $[C101]^+[HEHP]^-$ |
| trihexyltretadecylphosphonium and mixture of phosphate and phosphinate | $[C101]^+[C572]^-$ |

Kerosene was used to dissolve the above reactives in order to reduce their viscosity, and extractions were carried out with solutions of pH 4.4. Results indicated that the ionic liquids $[C101]^+[D2EHP]^-$ and $[C101]^+[EHEHP]^-$ were not better extractants for REEs than the single reactives, whereas $[C101]^+[C572]^-$ compares well with data obtained with single D2EHPA. The presence of zinc and calcium in the solution decreased the extraction of these REEs, thus, there was a necessity to minimize the presence of these two elements in the circuit. *Note from the authors of this review: no data were given about experimental variables influencing REEs extraction, and about the stripping stage. In this manuscript, the composition of Cyanex 572 differed than that given in reference [25].*

In the next reference [27], Sm and Co electrodeposition and their co-deposition in the [BMP][DCA] (BMP= 1-butyl-1-methylpyrrolidinium, DCA= dicyanamide) ionic liquid with controlled water content by electrochemical methods was investigated. It was shown that both metals can be deposited electrochemically from the corresponding single–component solutions and their deposition potential shifted positively at an increase in the water concentration, indicating deposition acceleration. From binary solutions, Sm–Co co-deposition was also observed. In these binary solutions, Sm was co-deposited at much less negative potentials than did the element from single

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solution. An increase in the water concentration resulted in inhibition of the process of Sm/Co co-deposition. The addition of water promoted Co and Sm oxidation with formation of oxides/hydroxides occurring in parallel with electrochemical deposition, the formation of these compounds resulted in fouled Sm/Co co-deposition.

Neodymium was extracted, from aqueous solutions, by trioctylphosphine oxide (TOPO) dissolved in the ionic liquid [1-Butyl-3-methylimidazolium] [Bis (trifluoromethanesulfonyl)imide] ([$C_4$mim][$Tf_2N$]) in small channel contactors [28]. A 1:6 Nd:TOPO stoichiometry was found at high initial Nd concentrations of 0.005 and 0.01 M in a 0.001 M nitric acid medium. The continuous flow extractions were carried out in channels with 0.5 and 1 mm diameter, and at equal phase mixture velocities (0.01 and 0.05 m/s), the flow pattern studies highlighted a plug flow regime, resulting in interfacial areas of up to 4900 and 2500 $m^2/m^3$ for 0.5 mm and 1mm channels, respectively. *Note from the authors of this review: no stripping data was given in the published manuscript.*

The solvent extraction of Nd (III), Sm (III) and Eu (III) by using the bifunctional ionic liquid tri-n-octyl amine-di-2-ethylhexyl phosphate ([TOA-D2]), as extractant had been investigated [29]. The extraction was performed in the presence of a complexing agent such as EDTA. The extraction of the three elements increased with the increase of the pH of the solution from 1 to 2, and tends to stabilize at pH values of 2-3 (Table 2).

**Table 2.** Percentages of extraction of REEs at various pH values.

| REE | pH 1 | pH 2 | pH 3 |
|---|---|---|---|
| Nd(III) | 33 | 69 | 69 |
| Sm(III) | 31 | 69 | 60 |
| Eu(III) | 24 | 51 | 55 |

In the three case, the extraction process was exothermic, thus, the extraction efficiency decreased when the temperature was increased from 25 to 55º C. The equilibrium data modeling also confirm the formation of solvated species with one extractant moiety. Stripping of the three elements increased with the increase of the acid concentration (HCl or $HNO_3$) from 0.02 to 0.8 M.

Having neodymium similar physicochemical properties to lanthanum, cerium and praseodymium, it was difficult to achieve the separation (and purification) of these elements, thus, various phosphate-based ionic liquids: N,N-dimethyloctylamine bis(2-ethylhexyl)phosphate ([$N_{1,1,8,H}$][DEHP]), N,N-dimethyldecylamine bis(2-ethylhexyl)phosphate ([$N_{1,1,10,H}$][DEHP]), N,N-dimethyldodecylamine bis(2-ethylhexyl)phosphate ([$N_{1,1,12,H}$][DEHP]) were synthesized and investigated for selective separation of Nd(III) from aqueous solution [30]. Under the various experimental conditions, it was found that the extraction efficiency of Nd(III) using [$N_{1,1,8,H}$][DEHP] was near 100% at pH of 4. At this pH value, the separation factor (β) values of βNd/La, βNd/Ce, βNd/Pr using this ionic liquid were 13.8, 6.9 and 3.4, respectively. Neodymium can be stripped from loaded organic phases by the use of HCl solutions, the stripping efficiency increases from neutral solution to 0.16 M HCl medium.

Two ionic liquids [A336][BTA] (BTA= dibutyl thiodiglycolamate) and [A336][OTA] (OTA= dioctyl thiodiglycolamate), both presenting low viscosities, were formed to extract Nd(III), in a selective form, using waste NdFeB magnets [31]. Better results were obtained with [A336][OTA], though in both cases the extraction increased with the increase of the pH value (1 to 3) and then (3-6) remained constant. Also, the increase of the ionic strength (NaCl addition) from 0 to 0.3 M increased the extraction efficiency. Using both ionic liquids, the extracted species responded to the $IL_2NdCl_3$ stoichiometry. Stripping was performed via precipitation with potassium oxalate. *Note from the authors of this review: this work used kinetic and extraction isotherm models than in the opinion of these reviewers are not suitable for liquid-liquid extraction science but ion exchange and adsorption processing. Thus, this manuscript must not be published with these unsense data.*

Next investigation focuses on study of the extraction of neodymium from the aqueous nitrate feed using a bifunctional ionic liquid formed by trihexylamine di-2-ethyl hexyl phosphate ($[TAHAH]^+[DEHP]^-$) in kerosene [32]. Several experimental variables including shaking time, salt concentration, aqueous phase pH, diluting agents, metal concentration, and temperature were investigated in order to investigate its influence on neodymium extraction. Results indicated that the extraction percentage increased when salt and extractant concentrations increased. The percentage of metal extraction is dependent on the pH value, increasing when the pH shifted from 1 to 3, reaching 99% at 2 M $NaNO_3$ and pH 3 using a 0.1 M solution of the ionic liquid in the organic diluent. Neodymium extraction responded to the next equilibrium:

$$Nd\left(NO_3\right)^{2+}_{aq} + 2NO_3^- + 3IL_{org} \Leftrightarrow Nd\left(NO_3\right)_3 \cdot 3IL_{org} \qquad (2)$$

This extraction process showed a negative value of ΔHº (-15 kJ/mol), indicative of heat evolution within the extraction process. The negative value (-11 kJ/mol·K) of ΔSº seemed to be indicative of a decrease in randomness as the metal is extracted into the organic phase. Metal-loaded organic phases can be stripped by the use of very diluted sulphuric acid solutions ($2 \cdot 10^{-3}$-$8 \cdot 10^{-3}$M). There was a continuous decrease in the extraction efficiency under several of extraction-stripping cycles.

Yttrium(III) was extracted, from nitrate medium, by the use of the same bifunctional ionic liquid ($[THAH]^+[DEHP]^-$) [33]. The extraction percentage of Y(III) decreased from 97% to 73% as the equilibration time increases, this being attributable to a dissociation of the extracted complex. Again, extraction increased from pH 1 to 3, and the extracted complex presented the $Y(NO_3)_3 \cdot 2IL$ stoichiometry. The variation of temperature revealed the endothermic nature of extraction process. Using 0.1 M nitric acid solution, yttrium was completely stripped from metal-loaded organic phases, however, the increase of the acid concentration up to 0.8 M decreased the stripping efficiency. Similarly to the previous reference, the extraction efficiency decreased after continuous (up to five) extraction-stripping cycles.

Benzyltributylammonium decanedioate ($[N_{444Bn}]_2[SA]$) ionic liquid was used to extract rare earths and afford the separation of Sm(III) contained in waste SmCo magnets. This investigation was carried out in acetate medium [34]. Experimental results showed that both La(III) and Nd(III) were extracted better in acetate medium, with an apparent extractability order of acetate>nitrate>chloride, being these results attributable to the low-hydrated nature of acetate ions. REEs were extracted by an ion association mechanism, with stoichiometries dependent of the aqueous medium (Table 3). Stripping results showed that 91% Nd(III) was recovered from organic phases using 1.5 M HOAc. In the case of the magnets and using a simulated synthetic solution, samarium(III) extraction increased from near 4% at pH 4 to 98% at pH 5.5, with copper(II) extraction of 87% at this same 5.5 pH value, against cobalt(II) was poorly extracted (14% at pH 5.5). Maximum separation factor Sm(III)/Co(II) reached values of 3078, however, this separation factor decreased to 148 in the treatment of a real solution coming back from the processing of magnets. *Note from the authors of this review: no stripping data were given in the manuscript in the case of Sm/Co/Cu solutions.*

**Table 3.** Species formed in the extraction of Nd(III) from various aqueous media.

| Aqueous medium | Species |
|---|---|
| Acetate | $[N_{4,4,4,Bm}]_3Nd[SA]_{1.5}(OAc)_3$ |
| Nitrate | $[N_{4,4,4,Bm}]_3Nd[SA]_{1.5}(NO_3)_3$ |
| Chloride | $[N_{4,4,4,Bm}]_4Nd[SA]_2Cl_3$ |

The next reference [35], mentioned one of the problems which one can found in the use of ionic liquids in the recovery of rare earth elements (and metals in general), and often neglected by authors. This problem arised with the same nature of ionic liquids, since during the extraction process, the ionic liquid would enter the solution in the form of ions, causing the loss of the reactive and increasing the production cost, moreover, this situation can also be considered as non-environmentally friendly. At the moment in which the manuscript was written and/or published, the use of this ionic liquids as extractants for REEs was still only in the laboratory research stage.

## 3. Deep Eutectic Solvents

The mentioned toxicity, in conjunction to their non-biodegradability properties, precluded the use of ILs as neoteric solvents with green characteristics.

ILs served as the basis of deep eutectic solvents (DESs), which formed a new class of chemicals characterized for being formed by mixtures of components forming an eutectic, the resulting product presented a melting point lower than the values presented for the pure components [36,37].

Often, DESs were considered as a subclass of ILs, due that both shared a series of physicochemical properties: low melting points, density, viscosity, low vapour pressure, absence or high flash-point values, and chemical and thermal stability; moreover, their properties can be changed to an specific use. Somewhat, the difference in the properties of DESs, with respect to those of ILs, are an advantage to compensate shortcomings of ILs, also, and since DESs can be non-ionic, this property was a clear difference between these two types of chemicals.

They were obtained by the complexation of a compound that acted as hydrogen bond acceptor (HBA), typically a quaternary ammonium salt, and either a metal salt or an organic compound that acted as hydrogen bond donor (HBD). Owing to the large combination of HBAs and HBDs possible, they can be tuned for various uses and were thus considered designer solvents.

DESs followed the nomenclature Cation$^+$X$^-$zY, where Cation$^+$ refered for a cation (e.g., ammonium, phosphonium, sulfonium) with X$^-$ being a Lewis base serving as counter ion (often halide anions) and Y being a Lewis or Brønsted acid with z molecules interacting with the anion. With the next general formulaes, one can accounted for five types of DESs:

Type I: Cation$^+$X$^-$zMCl$_x$, being M= Sn, Fe, Zn, Al, Ga or In. They were similar to metal halide/imidazolium salt systems.

Type II: Cation$^+$X$^-$zMCl$_x$·yH$_2$O, where M= Co,Cu, Cr, Ni or Fe. This type of DES differentiates from I in that they contain hydrated metal halides, which together to their relative low cost allowed to have compounds with lower melting points.

Type III: Cation$^+$X$^-$zRL, in which R is an organic radical and L= CONH$_2$, COOH or OH. This type was the most widely known and applied. Very often, these DESs used as precursors choline chloride (ChCl) and HBDs like amides, carboxylic acids and alcohols, which make them easily tunable and normally cheap and sometimes biodegradable.

Type IV: MCl$_x$ + RL = MCl$_{x-1}^+$RZ + MCl$_{x+1}^-$, here M = Al or Zn and L= CONH$_2$ or OH. In their composition inorganic cations, not forming alone low melting point eutectics, are present. ZnCl$_2$, and HBDs like urea, acetamide or different diols are normally components of this type of DESs.

Type V. This type of DES was developed from the strong interaction from the acidity difference of phenolic and aliphatic hydroxyl moieties. Clearly different to the other types, the interactions between HBAs and HBDs were non-ionic in nature and, thus, this type of chemicals was formed only by molecular compounds, i.e., the case of the thymol–menthol system.

Recently, to these types of DESs, different new terms had been added to the nomenclature of these non-aqueous solvents. Natural Deep Eutectic Solvents (NADESs) can be one of them, which refereed to type III compounds combining ChCl, as HBA, with naturally occurring carboxylic acids, sugars, aminoacids, also, water was added on some occasions as a third component. Apart from ChCl-based NADESs, others can be prepared from binary or ternary mixtures of carbohydrates with themselves (e.g., D(−)-fructose:sucrose(1:1) or D-(+)-glucose:D-(−)-glucose:sucrose(1:1:1)) or organic acids with sugar alcohols (e.g., citric acid:D-sorbitol(1:1)), among many others not requiring the presence of ChCl. NADESs were developed to explore the enhancement of the solubility of some intracelular compounds (flavonoid rutin, starch, albumin, etc.) that presented limited solubility in water. Additionally, therapeutic Deep Eutectic Solvents (THEDESs) were another type of chemicals, in which active pharmaceutical ingredients are present and having the potential interest in products where solubility problems may be avoided. Mixtures of menthol and ibuprofen had been proposed to enhance topical delivery systems.

Several reviews about the use of these DESs on the recovery of metals from various sources had been recently published [38–42].

### *Deep Eutectic Solvents and Rare Earth Elements*

It was described [43], the use of DESs (and also ILs) as high-efficient float some minerals that weree difficult to float, such as rare-earth minerals, quartz, and quartz hematite, as well as carbonate asphalt. The amount of DESs used in this field was smaller if compared with traditional flotation agents.

One of the various uses of DESs is to provide suitable media for the synthesis of REEs-bearing compounds. A DES prepared by mixing choline chloride (ChCl) and urea (1:2) was used as a synthesis medium, via the solvothermal method, of praseodymium vanadate (PrVO$_4$) nanoparticles [44]. These nanoparticles were used as a solely capable electrocatalyst for the detection of furaltadone (FLO). Despite its mutagenic and carcinogenic properties, this FLO is an antibiotic that is commonly used in the growth of aquatic organisms and livestock.

The extraction of lanthanides from nitrate media by the non-ideal solvent composed of decanoic acid ($C_{10}OOH$) and trioctylphosphine oxide (TOPO) was investigated [45]. Maximum distribution of all lanthanides (from La(III) to Lu(III) was observed for an aqueous acidity of 0.5-1 M nitric acid (Figure 1), being the extraction decreased with the increase of the organic acid concentration in the organic phase, thus, TOPO was the key-extractant for efficient extraction. *Note from the authors of this review: no stripping data were available in the published manuscript.*

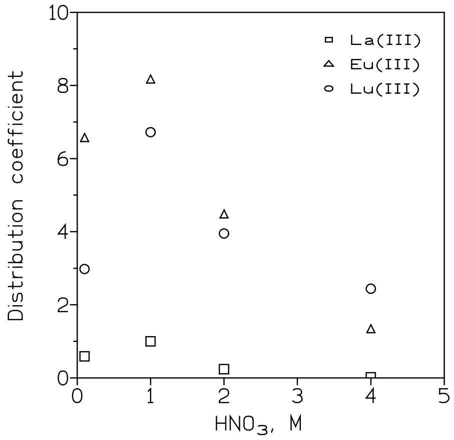

**Figure 1.** Distribution coefficients of some representative lanthanides elements at various nitric acid concentrations. $[Ln]_0$= 7.5 mmol/L. Organic phase: $C_{10}OOH$+TOPO (50% each). O/A ratio: 0.5. T: 25º C.

Deep eutectic solvents were investigated in the recovery of rare earth elements from coal flyash [46]. The mixtures of choline chloride (ChCl) with lactic acid (LA) and ChCl with para-toluene sulphonic acid monohydrate (pTSA) were used in the investigation. Firsts results showed better leaching rate when the molar ratio of ChCl:LA and ChCl:pTSA were 1:2 and 1:1, respectively. Both systems gave REE recoveries in the 85–95% range, though best results were generally obtained with the mixture ChCl:pTSA, indicative that the higher acidity provided by pTSA favorably contributed in the REEs dissolution process. Both DES systems improved about 5–8% higher dissolution than single LA, pTSA and ChCl systems, this enhancement in the dissolution is even higher, about 35%, when compared the use of these DES systems against the use of sulphuric acid, or another mineral acid (HCl, $HNO_3$). After dissolution, the leach liquor was diluted at 50% with demineralized water and REEs were recovered by direct chemical precipitation with oxalic acid.

The leaching behavior of rare earth (yttrium) carbonate before and after mechanical activation in choline chloride–urea–malonic acid deep eutectic solvents was investigated [47]. Without mechanical activation, yttrium dissolution was about 49%, against, the leaching efficiency of yttrium was increased to 85% when the activation time was 60 min, this increase being attributable to the decrease in the particle size and increasing the contact area of the reaction when mechanical activation was used. The dissolution process was controlled by chemical reaction and diffusion in the solid product layer. *Note from the authors of this review: No data about what to do with the Y-bearing DES phase.*

A strategy for the separation of yttrium from heavy rare earth elements (HREEs) based on ternary hydrophobic deep eutectic solvent (HDES) extraction had been proposed [48]. A total of 44 HDESs were prepared with four carboxylic acids as hydrogen bond donors (HBDs), bis(2-ethylhexyl) amine (BEA) as the hydrogen bond acceptor (HBA) and 1-decanol (DL) as the third component of the mixture. The prepared HDESs had the advantages of simple preparation, no purification requirement, low viscosity, low water solubility and low toxicity. Among the various compounds investigated, the DL:oleic acid (OA):BEA-based HDES with OA as the HBD presented best extraction ability, higher saturation loading capacity and better phase separation stability. The separation factors of the DL:OA:BEA (9:1:5) mixture for HREEs (Dy-Lu) and Y in an industrial Y-enriched solution are Dy/Y ≥ 3.05, Ho/Y ≥ 3.37, Er/Y ≥ 4.29, Tm/Y ≥ 6.00, Yb/Y ≥ 10.8, and Lu/Y ≥ 11.2. Extraction of these elements occurred by ion association and partial cation exchange reactions which took place simultaneously. The loaded HDES can be stripped from the organic phase with 0.2 M sodium oxalate or water.

In order to improve recovery strategies, electric field assisted mining arised as a technique to extract species from soils using green electrolytes to help in the extraction of metals. Thus, the next reference [49], evaluated the influence of various types of biodegradable electrolytes, including the use of deep eutectic solvents, in the electromining process. The soil, sampled from the northern region of Brazil, contained cerium(IV), lanthanum(III) and neodymium(III), and the DES-based solutions were prepared by mixing choline chloride and i) acetic acid, ii) citric acid and iii) oxalic acid in a 1:2 (ChCl:acid) molar ratio. Applying an electric field of 1 V/cm, and as it was somewhat expected, the use of the various electrolytes resulted in different solubilities. The maximum efficiency using only acetic acid resulted in near 70% of cerium(IV) recovery, citric acid removed 63% of lanthanum (III), and oxalic acid extracted 22% of the same rare earth. The results revealed that the use of the above DES+ acid mixtures did not improve the recovery of these REEs (Table 4), this was attributable to the possible degradation of choline chloride and to the increase of the pH in the cathodic region. *Note from the authors of this review: authors did not mention, in order to recover this valuable REEs, what to do with the resulted solutions*

**Table 4.** Recovery of REEs using ChCl:acid mixtures in an electromining process.

| Electrolyte | Ce(IV) | La(III) | Nd(III) |
|---|---|---|---|
| Acetic acid | 70 | 45 | 37 |
| ChCl:acetic acid | nil | nil | nil |
| Citric acid | 40 | 63 | 35 |
| ChCl:citric acid | 32 | 51 | 30 |
| Oxalic acid | 18 | 22 | 12 |
| ChCl:oxalic acid | nil | 2 | nil |

All the electrolytes at 0.1 M.

Similarly to ionic liquids [22], DES can be used as a medium to prepare rare earth-bearing compounds with further uses. A hydrothermal method to prepare perovskite-type potassium niobate ($KNbO_3$) through deep eutectic solvent (DES), which is further used as an electrode material for the determination of bisphenol A (BPA) was investigated [50]. This nitrate was prepared from thymol ($C_{10}H_{14}O$) and menthol ($C_{10}H_{20}O$) in a 1:1 ratio.

Cyclic voltammetry of pure $CeO_2$, $La_2O_3$, $Nd_2O_3$, and $PrO_2/Pr_2O_3$ in the deep eutectic solvent Ethaline (1:2 mixture of choline chloride and ethylene glycol) was investigated, and the electrochemical activity of these oxides were assessed [51]. Electrodissolution of pure oxides and water-leached monazite, after high-temperature pretreatment of the mineral, was carried out in a 0.1 mol/L glucose solution in Ethaline, and showed a preferential solubility of about 24% for pure $Nd_2O_3$, against, pure $CeO_2$, $La_2O_3$ and $PrO_2/Pr_2O_3$ were found to be insoluble. It was also demonstrated that that electrodissolution of the water-leached monazite was not possible because of the inert behaviour of $Ce_{1-x}Ln_xO_{2-x/2}$ solid solutions. This compound was formed due to the presence of $CeO_2$ in the product resulted from the high-temperature pretreatment of monazite at low mineral:$Na_2CO_3$ ratios. Thus, the formation of cerium oxide must be avoided as it was possible. *Note from the authors of the review: this manuscript did not give information about what to do with the resulting solutions.*

A deep eutectic solvent composed of isostearic acid (HA) and TOPO diluted in toluene was investigated for selective recovery of scandium from iron, yttrium and aluminium [52]. The use of single isostearic acid or TOPO solutions in toluene did not allow to separate these elements, however, the use of this DES solution improved the separation of scandium and yttrium for the other elements. Moreover, undiluted DES improved metal extraction, i.e., a mixture 2:1 (HA:TOPO) allowed to the selective separation of Sc(III) from Y(III) and Fe(III) at pH values near zero. Scandium was extracted by formation of $Sc(HA)_2A_3(TOPO)_5$ complex in the organic phase, releasing three protons to the raffinate. This rare earth can be stripped from loaded organic phases by the use of 2 M HCl or sulphuric acid solutions.

## Conclusions

Ionic liquids (ILs) and deep eutectic solvents (DESs) may be considered as potential substitutes to *traditional* organic reagents in synthesis, extraction and separation processes, due to their properties: low volatility, maintain as liquids in a wide range of temperatures, stability within temperature, reduced risk of inflammability and properties that can be changed to fulfil the requirements of a given process. However, green consideration of ILs is under contradiction due to that their potential harmful properties. Apparently, ILs are more toxic and cytotoxic than DESs, thus, they emerged as potential substitutes of ILs in a series of processes. However, and it is stated in a series of references their practical used, outside laboratory studies, is far to be a real situation, thus, their utility still is somewhat questionable.

Moreover, in many cases, as references dictated, the use of ILs and DESs needed the utilization of *traditional* organic diluents, specially due to the great viscosity that these chemical presented, viscosity which is increased as the metal loading in the respective organic phase increased (as some experiences from these reviewers witness).

It is worth to mention here, how some Journals published manuscripts with limited information of the process, i.e., extraction is only half of the separation/concentration process, without knowledge of the stripping stage one can not asses the usefulness of the recovery process. Nevertheless, industrialization of the dissolution/separation/concentration technologies using ILs and DESs necessitates of more information about the recovery of these strategic metals from non-synthetic wastes or real solutions coming from leaching processes of solid materials. The stability of the various ILs and DESs chemicals under continuous use is another of the points of future consideration to evaluate the usefulness of these reactives.

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