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Review

Recovery of Rare Earth Elements (REEs) Using Ionic Solvents

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Abstract: Rare earth elements (REEs) are becoming more and more significant as they play crucial roles in many advanced technologies. Therefore, the development of optimized processes for their recovery, whether from primary resources or from secondary sources, has become necessary, including recovery from mine tailings, recycling of end-of-life products and urban and industrial waste. Ionic solvents, including ionic liquids (ILs) and deep-eutectic solvents (DESs), have attracted much attention since they represent an alternative to conventional processes for metal recovery. These systems are used as reactive agents in leaching and extraction processes. The most significant studies reported in the last decade regarding the recovery of REEs are presented in this review.

Keywords: rare earth elements; ionic liquid; deep-eutectic solvent; leaching; extraction; separation

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1. Use and Sourcing of Rare Earths Elements

Rare earth elements (REEs) as defined by the International Union of Pure and Applied Chemistry (IUPAC) include metals characterized by similar properties, namely scandium (Sc), yttrium (Y) and all the lanthanides. The latter correspond to the chemical elements listed in the periodic table of Mendeleev that have an atomic number ranging from 57 for lanthanum (La) to 71 for lutetium (Lu) [1]. REEs are often subdivided into "light rare earths elements" (LREEs) and "heavy rare earths elements" (HREEs) according to their atomic numbers. Yttrium is oftentimes associated with HREEs due to chemical similarities, including ionic radii. In some cases, the elements from samarium to terbium are considered as the "middle rare earth elements" (MREEs) [2].

With the increasing uses of these elements, global demand is growing and their access is becoming crucial, leading to diversified sources of supply (Figure 1).

The properties of REEs are linked to their electronic configuration and in particular to the specificity of their electronic 4f sublayer, which allows numerous optical transitions and gives them particular magnetic and catalytic properties [3]. REEs are mainly trivalent; however, different oxidation states can occur naturally for cerium and europium.

Due to these remarkable properties, REEs are used in many high-tech applications [4,5], such as lasers [6,7], permanent magnets [8,9] energy storage [10,11] and so on. REEs are therefore part of the so-called "technological" metals, the supply of which has become strategic, as it is threatened by the growth in world demand for these particular metals [12,13]. REEs are also considered as "critical" elements by a number of institutions, such as the EU, which has identified these elements as being of high economic importance with a high risk associated with their supply. The latter includes geopolitical considerations, such as the quasi-monopoly over the production of these elements maintained by China.

REEs are commonly mined as co-products or as by-products of other materials. Primary sources of REEs include hard rock deposits of bastnaesite as well as alluvial deposits of monazite and xenotime [14]. In addition to these ores, which contain the highest concentrations of REEs, other mineral resources can be considered, such as phosphate or apatites, which are admittedly poorer in REEs, but whose exploitation and processing in the future may be cost-effective [15,16].

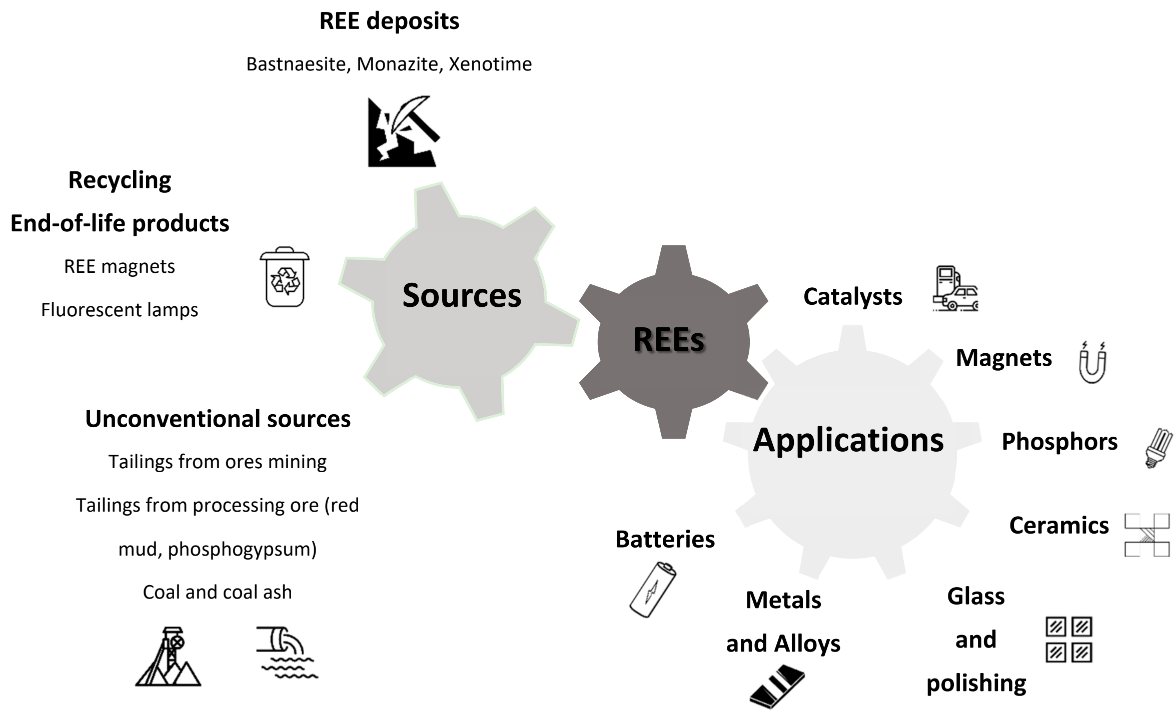


Figure 1. Use and sourcing of rare earth elements.

Due to the critical need for these materials, alternative sources need to be investigated, particularly in the context of the circular economy [17,18]. Valorisation of secondary or unconventional sources becomes more and more relevant, both from economic and environmental perspectives [19].

REE recovery from industrial landfilled stocks containing lower REE concentrations requires larger volumes. Among industrial wastes, bauxite residue (red mud) generated during the production of alumina from bauxite (the Bayer process) represents a promising source for REEs [20,21]. It is mainly composed of the metallic oxides aluminium, iron and titanium, as well as up to 1000 ppm of REEs [22,23].

Like bauxite residue, phosphogypsum, which is a waste generated by the fertilizer industry, has been identified as a significant source of REEs due to presence of these elements and the large volumes generated worldwide [24,25].

Other important secondary sources that are challenging for REE recovery are acid mine drainages (AMDs) [26] and wastewater sludges [27]. AMD and mine water from operating and closed mining sites represent a potential secondary source for many elements of economic interest, including REEs [28]. There is also significant potential for the recovery of these elements from coal and coal combustion by-products (coal fly ash) and the feasibility and implementation of industrial processes are under study [29,30].

As REEs are also present in a large amount of technological equipment, recovery from recycling of specific wastes, and in particular from waste electrical and electronic equipment (WEEE), also called urban mines, represents an unconventional and alternative source with high potential [18,31,32]. In this context, much research has recently been performed on end-of-life products containing high concentrations of REEs, such as magnets [33,34] or fluorescent lamps [35,36].

The processes currently used to recover rare earths from these natural or industrial ores (conventional and unconventional sources) consist in subjecting the ores, which have been previously crushed, to chemical treatments (with acidic or basic reagents) in order to obtain mineral concentrates. The chemical attack or leaching process is conventionally carried out by means of one or more acid reagents, including nitric acid, sulphuric acid, phosphoric acid, hydrochloric acid or a mixture of them (aqua regia). The so-called "pregnant leach solutions" are then subjected to an extraction/separation step using solvent extraction, ion exchange and/or precipitation [37].

Among such separation techniques, solvent extraction or liquid–liquid extraction is the most commonly used process for the recovery of REEs from the different sources (primary and secondary mining, waste streams, end-of-life materials and so on). The solvent extraction process consists in bringing the aqueous phase constituted by the pregnant leach solution into contact with an organic phase comprising one or more extractants, in order to achieve an efficient and selective extraction of REEs. Although widely applied on an industrial scale, liquid–liquid extraction suffers from certain limitations, such as the use of large amounts of toxic solvents and/or flammable solvents, which are a potential threat to human health and the environment [38]. For example, aliphatic diluents, such as isooctane, are classified as highly flammable liquids and vapours with safety concerns (they may be fatal if they are swallowed and enter the airways, very toxic to aquatic life, etc.), while *n*-dodecane is classified as a combustible liquid and can be used as an alternative; however, it also presents health risks. Another major issue associated with the use of organic solvents in hydrometallurgy is their loss by evaporation. Besides the economic aspect, this leads to ecological concerns. Elimination or replacement of hazardous solvents in terms of toxicity and flammability, which has a clear impact on worker safety and environmental issues, is therefore one of the main challenges for metallurgical processes.

2. Description and Properties of Ionic Solvents

Due to their quasi non-flammability [39] and non-volatility [40,41], ionic solvents, including ionic liquids (ILs) and deep-eutectic solvents (DESs), are increasingly being used as alternative diluents or extractants to conventional volatile organic compounds in extraction processes [42,43]. Recently, the term "ionometallurgy" was introduced by Abbott et al. for metallurgical processes using ionic solvents [44]. One of the interesting features of using ionic solvents is that an electrochemical process for the dissolution and the purification of metallic species can be implemented thanks to their large electrochemical window [45].

Ionic solvents can be considered as salts with melting points lower than 100 °C [46,47] and modular physical and chemical properties. Two categories can be considered: the "conventional" ILs composed of a discrete cation and anion, and DES systems formed from an eutectic mixture of Lewis or Brønsted acids and bases, which can contain a diversity of ionic species (anionic and/or cationic) [48–50].

ILs exhibit a wide variety of chemical structures, but share some common characteristics, such as bulky organic cations (ammonium, phosphonium, imidazolium, pyridinium, pyrrolidinium, piperidinium, triazolium) combined with smaller inorganic (chloride, hexafluorophosphate, tetrafluoroborate, etc.) or organic (acetate, triflate, bis(trifluoromethyl) sulfonyl imide, etc.) anions (Figure 2).

Appropriate combinations of the cation and anion allow adjustment of the physicochemical properties of the ILs (viscosity, density, hydrophilicity and solubility). The multiple possibilities make it possible to consider them as "designer solvents" that are attractive potential alternatives for organic molecular solvents [51].

In conventional approaches applied for metal extraction, ILs are usually hydrophobic to avoid their miscibility in the aqueous phases. Their hydrophobicity is governed by the length of the alkyl chain carried by the cation, as well as by the shape, symmetry and the nature of the anion associated. Typically the applied organic cations present long carbon chains, and the anions are usually hydrophobic anions such as hexafluorophosphate [PF_6^-] or bis(trifluoromethyl)sulfonyl imide [NTf_2^-]. IL density and viscosity are essential parameters to take into account in the implementation of an extraction process, as they affect the transport properties, such as diffusion [52]. Longer alkyl chain lengths result in lower density and higher viscosity while, for different anions, these parameters may evolve independently from their hydrophobicity [53]. Viscosity behaviours have also been assigned to the molecular structure of ionic liquids and to the presence of hydrogen bonding and van der Waals interactions [54]. In addition, for an identical cation, ILs based on a weak or non-coordinating anion have a lower viscosity than those composed of a complexing anion.

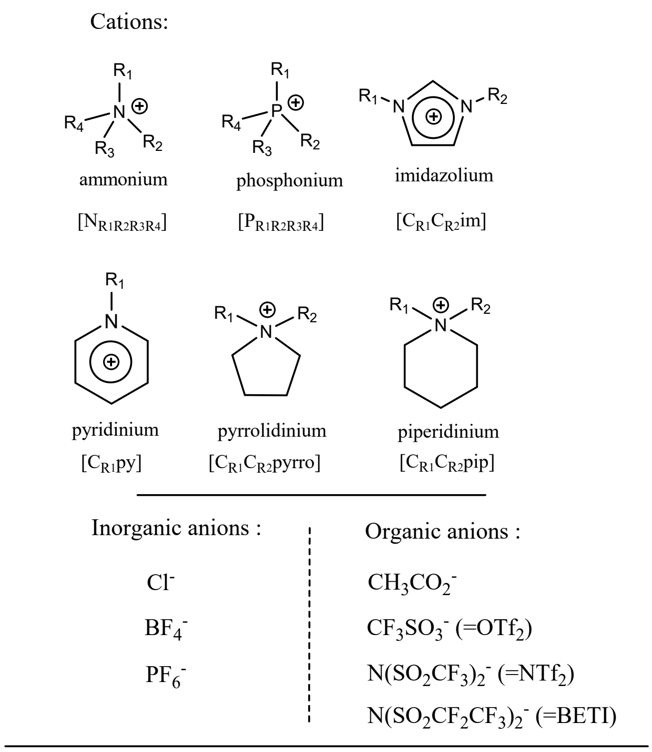


Figure 2. Structures of common cations and anions used in ILs.

Eutectic mixtures are usually considered a new class of ILs and they gained attention because some of them can be prepared from natural sources, which tends to make them more biodegradable, biocompatible and sustainable [55,56]. In this case, they are defined as natural DESs (NADESs) [57,58]. DESs usually result from a mixture of compounds that interact through hydrogen bonding, which leads to charge delocalization resulting in a depression of the melting point of the mixture [49,59–62].

A four-group classification has been proposed by Abbott et al. based on their constituents [48,49].

Types I to III DESs can be defined by the general formula $Cat^+X^-\cdot Y^-$, where:

- Cat^+ is usually a quaternary ammonium or phosphonium salt;
- X is the anionic moiety (generally a halide anion);
- Y is a metal chloride for type I, a metal chloride hydrate for type II and a hydrogen bond donor for type III.

Type IV DESs involve a metal chloride hydrate and hydrogen bond donor.

Most common DESs imply a hydrogen bond donor (HBD) and an ionic hydrogen bond acceptor (HBA), leading to type III DESs as defined by Abbott et al. [48]. DESs are mainly hydrophilic mixtures as they are based on at least one ionic species and strong hydrogen bonding interactions. Most popular DESs are based on quaternary ammonium salts and choline chloride [63] for their HBA part, and on urea, carboxylic acids, alcohols and glycols for their HBD. The most common structures of the HBA and HBD are illustrated in Figure 3. As for the ILs, judicious choices for each component allow the control of parameters such as density, viscosity, acidity or basicity, hydrophobicity, polarity, volatility and the extractability properties of the DES.

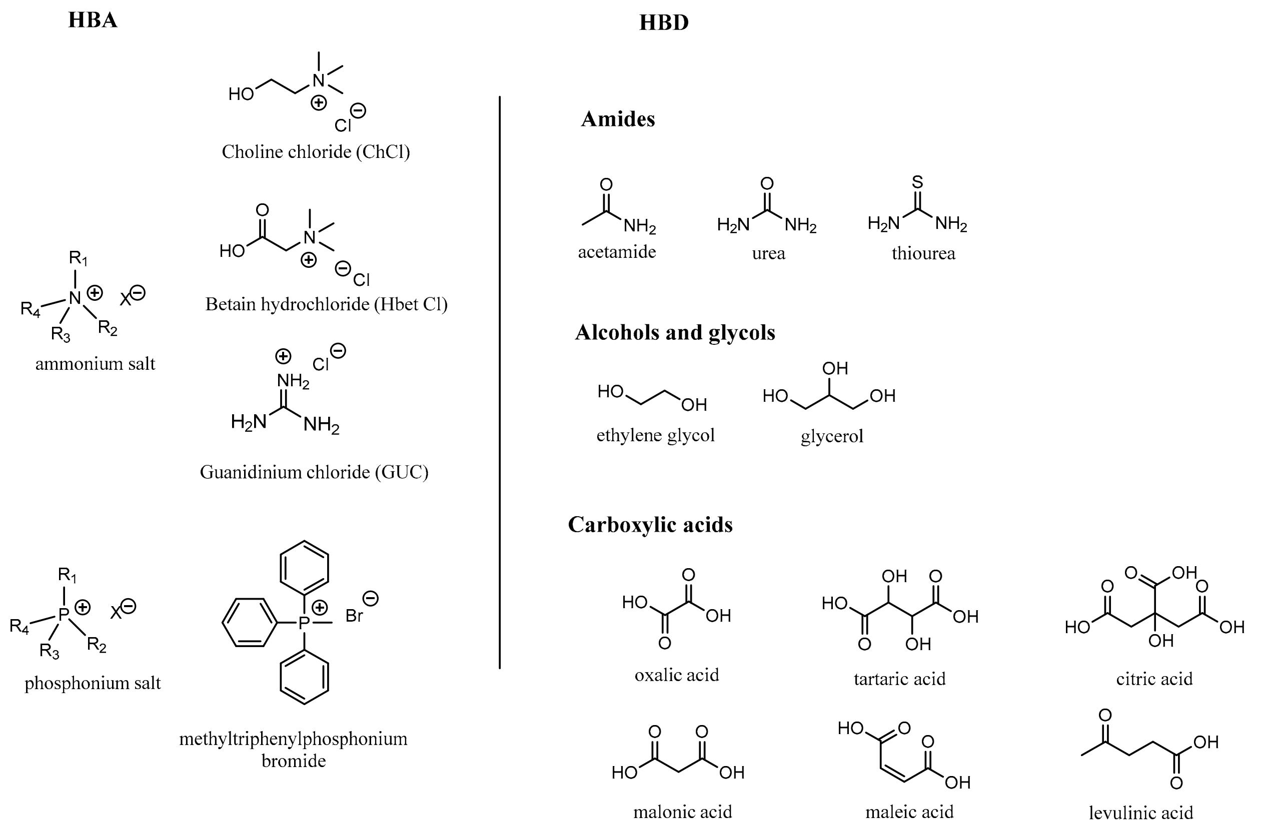


Figure 3. Structures of some hydrogen bond acceptors (halide salts) and hydrogen bond donors (amines, alcohols, carboxylic acids) used in the formation of deep-eutectic solvents.

Among these properties, the acidic character of DESs, also called acidic deep-eutectic solvents (ADESs), has been highlighted for applications in dissolution, extraction and metal electrodeposition [60]. The acidity of ADESs can be controlled with the acidity of the HBD and these DESs are often divided into two classes: Brønsted and Lewis DESs.

Also, since 2015, with the concept of hydrophobic deep-eutectic solvents (HDESs) proposed by van Osch et al. [64], interest in the synthesis and application of HDESs is strongly increasing [65–67]. It is assumed that the hydrophobic character depends on the hydrophobicity of the components forming the DES. HDESs are mainly type III, involving bulky quaternary ammonium or phosphonium halide ILs as HBAs and hydrophobic carboxylic acids as HBDs. This trend for hydrophobic eutectic mixtures was recently investigated for mixtures solely composed of non-ionic species [68,69]. A fifth class of DES has therefore been proposed to complete the Abbott classification so that it includes such fully organic hydrophobic eutectic solvents involving strong interaction between a hydrogen bond donor and a hydrogen bond acceptor [70]. These type V non-ionic DESs represent a relatively new class of eutectics which have strong potential for the recovery of REEs through solvent extraction.

3. Use of ILs and DESs for the Recovery of REEs

3.1. Leaching Processes

Conventional leaching processes are based on the use of strong mineral acids (sulphuric, nitric or hydrochloric) as well as alkali media (such as ammonia or sodium hydroxide), despite their poor selectivity and adverse effects for the environment and health. In this regard, ionometallurgy appears as an interesting alternative that deserves to be further explored. In particular, DESs and ILs have been shown to be good solvents for metal oxides [71–75]. Few examples of DES and IL systems have been proposed for the dissolution of materials that incorporate REEs (Table 1).

The solubility of metal oxides, including rare earth oxides (REOs), has been studied using ILs such as betaine bis(trifluoromethylsulfonyl)imide ([Hbet] [NTf_2]). [Hbet] [NTf_2] is a weak Brønsted acidic ionic liquid due to the carboxyl group attached to its cation. The formation of a carboxylate complex between the carboxylic acid group of the ionic liquid and the metal oxides allows the dissolution of metal oxides, which is favoured by the presence of water in the IL phase [76].

Such an [Hbet] [NTf_2] ionic liquid has been applied for the leaching of bauxite residue in order to perform a selective dissolution of REEs against iron [77]. In aqueous solution, the betainium cation exhibits the necessary acidity (higher acidity (pKa = 1.83) than acetic acid (pKa = 4.75)) for the metals' dissolution, as well as complexing properties for the metals' complexation. It has been found that the temperature is a key parameter: the efficiency is much more pronounced when dissolution is carried out at temperatures above 100 °C.

Another application of [Hbet] [NTf_2] highlighted is its role as part of the selective leaching for the recovery of REEs from iron in NdFeB permanent magnets [78]. The useful effect of the roasting of NdFeB permanent magnets, which makes it possible to avoid the formation of the insoluble ternary $NdFeO_3$ phase, was supported by leaching with an aqueous solution containing the ionic liquid [Hbet] [NTf_2] [79]. The same research group showed that the use of protic ionic liquids, such as pyridine hydrochloride (PyHCl), at high temperature (165 °C) allows the leaching of NdFeB magnets and then the recovery of the REEs by solvent extraction [80].

DES also have excellent dissolution properties due to their capacity to accept/donate protons or electrons to form hydrogen bonds [49,59]. The leaching behaviour of bastnaesite-type deposits, which are the main source of rare earths, was investigated using choline–chloride-based deep-eutectic solvents [81]. For this purpose, single-salt and multicomponent mineral mixtures of REEs (Y, La, Ce, Nd and Sm) in their carbonate form were studied. Dissolution experiments have shown that the DESs based on [choline chloride (ChCl):malonic acid (MA)] and [choline chloride (ChCl):urea + malonic acid mixture (UMA)] display higher performances in dissolving REEs. Bastnaesite ore was therefore subjected to a dissolution step using [ChCl:UMA], highlighting a potential DES system for selective dissolution of heavy REEs in comparison to light REEs and competitive elements resulting from the gangue minerals, such as Ca, Mg and Fe.

Dissolution of REOs has been investigated using a series of Brønsted acidic DESs based on polyols and organic acids [82]. Among the DESs studied, the [ethylene glycol (EG):maleic acid (Maleic) (4:1)] system was highlighted as the optimal solvent due to its strong acidity and low viscosity. Notable differences in the solubilities of REOs have been observed, with considerable solubilization ability identified for the LREEs (except for CeO_2) and MREEs in comparison to the HREEs, which allows the consideration of their separation. The solubility and separation of REE oxides and salts were also recently demonstrated by Söldner et al. [75,83] for various DESs.

NdFeB magnet leachates have also been studied with a deep-eutectic solvent. It has been shown that the complete dissolution of NdFeB magnets can be performed with [choline chloride (ChCl):lactic acid (LAC) (molar ratio 1:2)], while the dissolution is not observed in the case of [ChCl:urea] or [ChCl:ethylene glycol] [84].

It was assumed that the protons present in the lactic acid could react with the metal oxides to dissolve them, and that the coordinating abilities of lactic acid and of choline may have favoured this dissolution. After the complete dissolution, liquid–liquid extraction was applied to separate the REEs from Fe, Co and B and to separate Dy from Nd in a second step.

In a similar approach, a recovery process for simulated NdFeB permanent magnets was proposed using [guanidine hydrochloride (GUC):lactic acid (LAC)]. Such DESs exhibit a high selectivity for the dissolution of Nd in comparison to Fe. Starting from a mixture of Nd_2O_3 and Fe_2O_3 with a mole ratio of 1:7, it was found that 95% of Nd can be dissolved while less than 1% could be for Fe [85]. The particular interest of this application has also been demonstrated through a patent which is based on the use of the choline chloride/lactic acid system, thus showing the maturity of such a process for the recovery of REEs from NdFeB magnets [86].

Beyond permanent magnets, other end-of-life products, such as fluorescent lamps, have been studied using chloride-based DESs and [Hbet] [NTf_2] ionic liquid. In this case, a [choline chloride:levulinic acid (LevA) (1:3)] system was found to be appropriate for the solubility of the phase containing the REEs, such as red phosphor $Y_2O_3{:}Eu^{3+}$ (YOX) against halophosphate phosphor $(Sr,Ca)_{10}(PO_4)(Cl,F)_2{:}Sb^{3+}$, Mn^{2+} (HALO), which does not contain any REEs [87]. Extraction of REEs from the loaded lixiviant DES phase was also examined and showed that metal recovery was possible via solvent extraction, thus allowing the recycling of the DES. The [Hbet] [NTf_2] efficiency for the oxide dissolution was valued for lamp phosphor waste with the selective dissolution of YOX without dissolving the other phosphors, such as the green phosphor $LaPO_4{:}Ce^{3+}$, Tb^{3+} (LAP), the blue phosphor $BaMgAl_{10}O_{17}{:}Eu^{2+}$ (BAM) or halophosphate phosphor (HALO) [88]. Also, as an alternative to conventional sulphuric acid leach, the recovery of REEs from waste phosphor can be performed after their leaching in 1-methylimidazolium hydrogen sulphate [C_1Him] [HSO_4] and by oxalic acid precipitation [89].

Coal and coal combustion by-products have been studied as potential sources of REEs. The dissolution of coal in ILs has been recently reviewed [90] and the possibility of recovering REEs has been investigated using an IL and a DES, respectively 1-butyl-3-methylimidazolium chloride [C_1C_4im] [Cl] and a mixture of choline chloride:urea (molar ratio 1:2) [91].

Due to the low melting points of these ionic solvents, they can be used as undiluted or low-dilution leaching agents, which is very different from conventional mineral acid solutions. It implies new mechanisms that are, for now, still not well understood or mastered. Irrespective of the hydrophobic or hydrophilic character of the ionic solvent, water content seems to be a critical point for all the systems, influencing the viscosity, the dissolution rate, the selectivity and even the triggering or the inhibiting of the mechanisms, depending on the situation. Moreover, these low water content ionic systems change the nature of the pregnant leach solution, which therefore strongly affects the following steps of the metal recovery compared to conventional processes [80,84,87].

Table 1. Overview of ionic solvent for REE leaching.

Ionic Solvent	Extracted/Feed	Matrix	Author
ChCl:U + MA (1:1:0.5)	HREEs leaching against Ca, Mg and Fe	Carbonate salts	Entezari-Zarandi et al. [81]
EG:Maleic (4:1)	LREEs leaching against HREEs	REO	Chen et al. [82]
ChCl:U	LREEs leaching	REO	Söldner et al. [83]
[Hbet] [NTf_2]	REE leaching	REO	Nockemann et al. [76]
[Hbet] [NTf_2]	REE leaching against Fe	Bauxite residue	Davris et al. [77]
[Hbet] [NTf_2]	REE leaching against Fe	NdFeB magnet	Dupont et al. [78]
[Hbet] [NTf_2]	Nd leaching against Fe	NdFeB magnet	Orefice et al. [79]
[Py] [Cl]	Complete dissolution	NdFeB magnet	Orefice et al. [80]
ChCl:LAC (1:2)	Complete dissolution	NdFeB magnet	Riaño et al. [84]
GUC:LAC (1:2)	Nd leaching against Fe	NdFeB magnet	Liu et al. [85]
ChCl:LevA (1:3)	YOX phosphor ($Y_2O_3{:}Eu^{3+}$)	Fluorescent lamps	Pateli et al. [87]
[Hbet] [NTf_2]	YOX phosphor ($Y_2O_3{:}Eu^{3+}$)	Fluorescent lamps	Dupont et al. [88]
[C_1Him] [HSO_4]	YOX phosphor ($Y_2O_3{:}Eu^{3+}$)	Fluorescent lamps	Schaeffer et al. [89]
[C_1C_4im] [Cl]; ChCl:U (1:2)	Complete dissolution	Coal by-products	Rozelle et al. [91]

3.2. Solvent Extraction Processes

As mentioned before, solvent extraction or liquid–liquid extraction is the most commonly used process for the recovery of rare earth elements after the leaching step.

Since the pioneering work of Dai et al. [92] highlighting the potential of ILs for solvent extraction in the context of metal recovery, many studies have been developed showing their potential in terms of efficiency in comparison to classical organic solvents [93].

As already mentioned, solvent extraction exploits the different distribution of a solute between two immiscible liquids. In most cases, the pregnant leach solutions, which contain the REEs to be extracted, are in an aqueous phase that makes contact with the hydrophobic ILs, leading to the formation of biphasic systems [94].

Some hydrophobic ILs that are immiscible with nonpolar organic solvents can also be engaged in triphasic extraction systems and are named water/organic solvents/ILs [95]. Moreover, water-miscible ILs can also form two-phase systems with aqueous solutions in the presence of kosmotropic ions, which contribute to the stability and structure of water–water interactions, such as K_3PO_4, K_2CO_3 and $Na_2S_2O_3$ in the aqueous solution. The hydrophilic ILs can thus be separated from the aqueous phase and be further re-used [96].

Ionic liquid-based aqueous biphasic systems (IL-ABSs) are also encountered as systems for the extraction and separation of different metal species but much more marginally compared to triblock copolymer-based ABSs [97].

In conventional solvent extraction, as the hydrated metallic cations tend to stay in the aqueous solution, extractants are usually required in the organic phase to form complexes with the metal and increase its hydrophobicity. This therefore favours the transfer of the metallic ions from the aqueous phase to the hydrophobic IL phase.

It has been highlighted that, in some cases, the solvation of extractant–metal complexes is more thermodynamically favoured in ILs than in conventional organic solvents. [92] This property is a major advantage of using ILs for metal ion extractions since in many cases they exhibit significantly higher extraction performance and improved metal selectivity than conventional solvents [98]. Consequently, IL-based extraction systems have been prepared using several extractants or synergistic systems diluted in ILs, or by using task-specific ionic liquids (TSILs), which refer to ILs that incorporate the extracting moieties into the cation or the anion of the ionic liquid.

In conventional diluents, solvent extraction mechanisms are based on the molecular and supramolecular interaction properties of the extractant molecule aggregates due to their amphiphilic nature. This aptitude has also been demonstrated for the IL-based organic phase [99].

Usually, the extraction mechanisms in an IL differ considerably from those in traditional organic diluents [100,101]. ILs are capable of solubilizing neutral or charged complexes, while only neutral species (or neutral ion pairs) are extracted in conventional solvents. These extraction modes and mechanisms are based on the principle of electroneutrality. Therefore, if charged species are extracted in the IL phase, they have to be counterbalanced in the aqueous phase. Depending on the aqueous leach solutions, the nature of the extractant and of the IL involved in the extraction systems, various mechanisms can therefore be encountered, such as ion exchange, when the cations or anions of ILs might be transferred into the aqueous phase during extraction; neutral extraction; or neutral coextraction [102,103]. Three main kinds of molecular mechanisms have been identified when ionic liquids are used as extraction diluents. Taking as an example an extractant in an imidazolium-type ionic liquid, these mechanisms are illustrated within the Figure 4 and can be described as follows:

- Neutral extraction mechanism: A neutral complex is formed and extracted in the IL phase. This mechanism is similar to those encountered in conventional solvents; however, the detailed mechanisms are often different. In this extraction mode, the IL acts as a polar non-aqueous solvent [104];

- Cation exchange: This extraction mode is specific to IL systems. The IL acts as a liquid ion exchanger with cationic complexes extracted from the aqueous phase into the IL phase. Consequently, an IL cation has to be transferred to the aqueous phase while, in exchange, a metallic cation is transferred to the IL phase to respect electroneutrality [105];
- Anion exchange: This extraction mode is also specific to IL systems. An anionic extractant forms over-neutralized anionic complexes that can be transferred to the IL phase, in exchange for the transfer of an IL anion to the aqueous phase [106]. Anion exchange is less common than cation exchange.

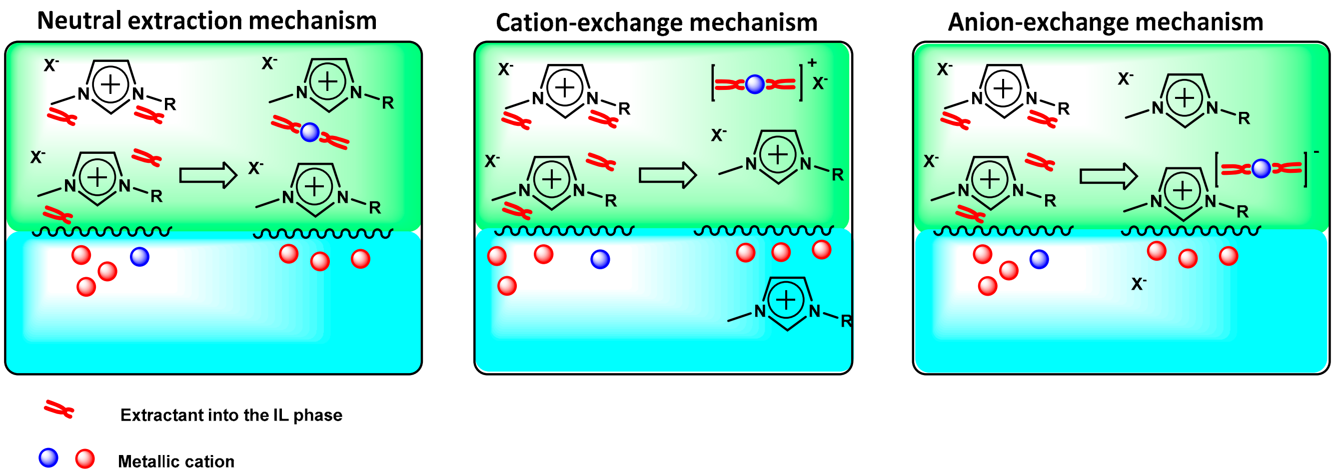


Figure 4. Schematic representation of mechanisms encountered in IL-based extraction systems.

In comparison with the extraction behaviours of conventional organic systems, the mechanism in IL-based extraction systems exhibits high complexity. In some cases, the IL-based systems involve polyvalent metals and cationic or anionic extractants or polyvalent ILs can be encountered, which leads to mixed extraction mechanisms.

Ion-exchange mechanisms are the main drawback of the IL-based extraction systems, since a part of the IL is lost in the aqueous phase and can be considered as sacrificial. The main factor influencing this exchange mechanism is the solubility in the aqueous phase of the IL component. It has been shown that hydrophobic cations can moderate these exchanges, whereas the phenomenon is increased with hydrophilic anions [107,108]. The increase of the hydrophobicity, such as the alkyl chain length of the IL cation, can lead to a switchover of the mechanism from ion exchange to neutral complex extraction [109]. Aqueous phase acidity has also been shown to play a role in the ion-exchange mechanisms of some systems [110].

3.3. IL-Based Extraction Systems for REE Recovery

Many systems, including cation exchangers (Table 2) and neutral extractants (Table 3), as well as synergistic systems (Table 4), have been studied for the recovery of REEs and have shown their potential in common solvents. This is why the feasibility of using these various systems has been implemented within the framework of IL-based extraction for the recovery of REEs [111,112]. Applications of mixtures of ILs and molecular extractants in metal solvent extraction technology have been recently reviewed by Wang et al. [113].

3.3.1. Ionic Exchangers

The cationic exchangers may exhibit a function with an acidic character (possessing a labile proton), such as carboxylic (diglycolamic acid), phosphoric (HDEHP: bis (2-ethylhexyl)phosphoric acid), phosphonic (PC-88A: 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) and phosphinic (Cyanex-272: bis(2,4,4-trimethylpentyl) acids), or they may function as chelating extractants, such as beta-diketone (HTTA: 2-thenoyltrifluoro acetone, HBA: benzoylacetone). In these cases, metal ions are complexed by the conjugate bases.

Among these extractants, numerous studies have been dedicated to the use of the beta-diketone HTTA in imidazolium-based IL ([C_1C_nim] [NTf_2]) [114–118]. Since the work of Jensen et al. with HTTA in ILs showing the presence of anionic lanthanide complexes in [C_1C_4im] [NTf_2] [106], comprehensive investigations of REE extraction have suggested the unusual extraction mechanisms of such ionic exchangers. Anionic lanthanide complexes are made possible by the exchange of the ionic liquid anions into the aqueous phase for the lanthanide complex at high HTTA concentrations, while at lower concentrations, Ln^{3+} was extracted as a neutral $Ln(TTA)_3$ complex.

Eu^{3+} chelation with HTTA into [C_1C_nim] [NTf_2] has been investigated with time-resolved laser-induced fluorescence spectroscopy (TRLFS) and highlighted that a mixture of neutral $Eu(TTA)_3$ and anionic $Eu(TTA)_4{}^-$ complexes can be encountered [114]. The stoichiometry of extracted complexes, such as the $Ln(TTA)_4{}^-$ anionic complex, was confirmed by emission profiles and spectrophotometric titration respectively for Eu^{3+}/HTTA and Nd^{3+}/HTTA complexes [115]. The role of the IL anion with regard to Ln chelates and the extraction mechanism has been evidenced for the bis(trifluoromethanesulfonyl)imide anion (NTf_2) [116], as well as nonafluoro-1-butanesulfonate ($CF_3(CF_2)_3SO_3{}^-$) [117]. The efficiency of HTTA has thus been demonstrated for various REEs [118]; other beta-diketones, such as benzoylacetone (HBA), also show the interest of this type of extractant. This aptitude for REE extraction has also been studied within the implementation of synergistic systems in combination with neutral extractants.

The feasibility for the selective recovery of REEs using [C_1C_8im] [NTf_2] with DODGAA as extractant has been demonstrated with sulphuric and nitric acid solutions [119,120].

The extraction performance of DODGAA in [C_1C_4im] [NTf_2] for REEs (Y, La, Ce, Eu and Tb) with an acidic leach solution of phosphor powders coming from waste fluorescent lamps was examined and demonstrated selective extraction toward metal impurities such as Fe, Al and Zn for both leaching nitric and sulphuric acid solutions [121].

Recently, solvent impregnated resins (SIRs) based on DODGAA and [C_1C_4im] [NTf_2] have been developed for extraction chromatography of lanthanides [122], as well as for the recovery of REEs from leach solutions of thin film phosphors [123]. Another diglycolamic acid (HDEHDGA) has been studied by Rout et al., confirming the potential of this type of extractant in ionic liquid media such as tetraoctylammonium dodecyl sulphate, [N_{8888}] [DS] [124] or methyltrioctylammonium bis (trifluoromethanesulfonyl)imide ([N_{1888}] [NTf_2]) [125].

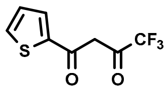
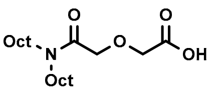
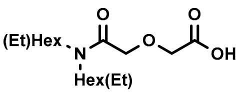
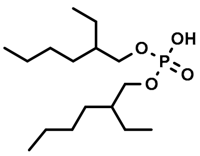
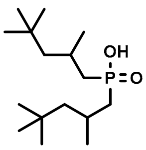
Despite Cyanex-272 and HDEHP being widely used as metal extractants, there are only a few studies reporting their use in the context of IL-based extraction systems for REE recovery. Cocalia et al. [104] have studied these extractants and described identical extraction behaviour and coordination of f-element cations using 1-decyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_1C_{10}im] [NTf_2]) and n-dodecane. Other studies have shown their potential in various ionic liquid diluents, such as [C_1C_nim] [NTf_2] and [C_1C_nim] [BETI] (n = 4–10) [126], or compared to diglycolamic acid extractant [124,125]. In some cases the conjugate bases of acidic and chelating extractants have been used to replace the IL anion in order to develop TSIL (see below).

Stripping from the extraction phase is an important aspect to take into consideration. REE extraction efficiency often depends on acid feed concentration, which usually allows the stripping of some REEs by playing with the pH. The stripping can be attributed partly to a lack of dissociation of the chelating extractant or protonation of the acidic extractant. Indeed, for acidic extractants, the extraction ability usually decreases for high acidic concentrations in the feed solution. REEs can therefore be stripped from the ionic phase by strongly acidic solutions. The stripping percentage can be gradually increased by increasing the acidity of the stripping phase.

The efficiency of the stripping is also related to the affinity of the extracting phase for the metal. Indeed, with greater affinities, the back-extraction will be more difficult. In some cases, complex-forming agents, such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), need to be added to the aqueous stripping phase.

With regard to the reuse of the ionic phase, it must generally undergo an additional clean-up step (a scrubbing step with a base, for example) in order to deprotonate the acidic extractant engaged in the ionic based-extraction system.

Table 2. Examples of acidic and chelating extractants in ILs for the recovery of REEs.

Extractants	Ionic Solvent	Extracted (Feed)	Author
 HTTA	$[C_1C_4im]$ $[NTf_2]$ $[C_1C_4im]$ $[NTf_2]$ $[C_1C_nim]$ $[NTf_2]$ n = 2–10 $[C_1C_4im]$ [NfO] $[C_1C_nim]$ $[NTf_2]$ n = 2, 4	Eu(III) chelate Nd(III) chelate Eu(III) chelate Nd; Eu ($NaClO_4^-$) Ce (NO_3^-)	Okamura et al. [114] Gujar et al. [115] Okamura et al. [116] Jensen et al. [117] Hidayah et al. [118]
 DODGAA	$[C_1C_nim]$ $[NTf_2]$ n = 4, 8, 12 $[C_1C_nim]$ $[NTf_2]$ n = 4, 8, 12 $[C_1C_4im]$ $[NTf_2]$	REEs (SO_4^{2-}) Y, Eu (NO_3^-) Y, La, Ce, Eu, Tb (SO_4^{2-}; (NO_3^-)	Yang et al. [119] Kubota et al. [120] Yang et al. [121]
 HDEHDGA	$[N_{8888}]$ [DS] $[N_{1888}]$ $[NTf_2]$	Eu (NO_3^-) Eu (NO_3^-)	Rout et al. [124] Rout et al. [125]
 HDEHP	$[C_1C_nim]$ $[NTf_2]$ n = 4–10 $[N_{8888}]$ [DS] $[N_{1888}]$ $[NTf_2]$	Ln (NO_3^-) Eu (NO_3^-) Eu (NO_3^-)	Sun et al. [126] Rout et al. [124] Rout et al. [125]
 Cyanex 272	$[N_{8888}]$ [DS] $[N_{1888}]$ $[NTf_2]$	Eu (NO_3^-) Eu (NO_3^-)	Rout et al. [124] Rout et al. [125]

3.3.2. Neutral Extractants

A typical neutral extractant has donor groups (O, S, P, N) without labile hydrogen. The extractant (a hydrophobic Lewis base) acts through its donor power, giving rise to interactions of the acceptor–donor type with the neutral metal species of the aqueous phase. The extracted species is solvated in an electrically neutral molecular form.

The most widely used solvating compounds are the neutral organophosphorus derivatives, including phosphines, phosphine oxides, phosphinates, phosphonates and phosphates. The extraction of neutral metal complexes by solvation is performed through their O-donor character [127]. This ability for the extraction and separation of REEs has also been examined in ILs.

Tri-*n*-octylphosphine oxide (TOPO) was engaged with $[C_1C_nim]$ $[NTf_2]$ (n = 4, 8) for the extraction of REEs from a nitrate medium, showing the importance of the cation of the IL in the extraction mechanism. REEs were extracted through the exchange of the metal ion and the imidazolium cations of the IL. In addition, for the IL-based TOPO extraction systems, an inversion of selectivity for the REEs was observed in comparison to an organic solvent such as *n*-dodecane, which can be explained by the difference in the coordination sphere [128].

Cyanex 923, which is a mixture of four trialkylphosphine oxides, exhibits extraction properties similar to TOPO. Cyanex 923 has been used in ionic liquid phases for the extraction of REEs from nitric acid medium using ILs containing a bis(trifluoromethylsulfonyl) imide anion ($[C_1C_4im]$ $[NTf_2]$, $[N_{1444}]$ $[NTf_2]$ and $[P_{66614}]$ $[NTf_2]$) [129], while nitrate

ILs, such as trioctylmethylammonium nitrate ([N_{1888}] [NO_3]) and trihexyl(tetradecyl) phosphonium ([P_{66614}] [NO_3]), were employed for concentrated chloride aqueous solutions [130].

Acquisition of these results led to the implementation of a process in continuous mode for the separation of Dy and Nd from chloride media using Cyanex 923 diluted in [P_{66614}] [SCN] [131].

Tri-*n*-butyl phosphate (TBP) is widely used for metal recovery. It has been employed in [N_{1888}] [NO_3] for the recovery of REEs from an aqueous nitrate phase from spent Nd-Fe-B magnets [132].

This possibility has also been investigated for Pr(III), Nd(III) and Dy(III) in aqueous phase containing a bis(trifluoromethyl-sulfonyl)amide anion with the aim of undertaking electrodeposition after their extraction by TBP in triethyl-pentyl-phosphonium [P_{2225}] [NTf_2]. A combination ion-pair and cation-exchange mechanism was observed and the direct electrodeposition of the extracted [$Nd(TBP)_3$]$^{3+}$ in the TBP IL-based system was demonstrated [133].

The efficiency and selectivity of REE(III) extraction from chloride media has also been demonstrated using the neutral extractant octyl(phenyl)-*N*,*N*-diisobutyl-carbamoylmethylphosphine oxide (CMPO) in [C_1C_4im] [NTf_2] [134,135]. A CMPO IL-based system ([C_1C_4im] [PF_6]) has been previously used for the recovery of REEs from nitrate aqueous solution with an enhancement in the efficiency in comparison to conventional organic solvents [136].

Moreover, the usual neutral organophosphorus derivatives, phosphoryl-containing podands, have been also investigated for REE recovery from a nitric acid, such as triphosphine trioxide (TPO) [137] in *N*-butyl, *N*-octyl-*N*-ethylpiperidinium bis(trifluoromethylsulfonyl) imide [C_2C_4Pip] [NTf_2] or [C_2C_8Pip] [NTf_2], or diethyl 2- [(diphenylphosphoryl)methoxy]-5-ethylphenylphosphonate [138] in [C_1C_4im] [NTf_2].

Diglycolamides (DGAs), with their tridentate O-donating ligands, have the ability to form stable complexes with lanthanides and actinides. Therefore, diglycolamide-based systems in IL have been investigated for the recovery of such metals [139]. It was found that *N*,*N*,*N*′,*N*′-tetraoctyl diglycolamide (TODGA) allows the enhancement of the extraction performance for REEs when it is diluted in [C_1C_4im] [NTf_2] in comparison to an isooctane system. Significant differences were observed in the extraction mechanisms, since a cation-exchange mechanism is involved for the TODGA-ILs systems while it is ion pair extraction in isooctane. Also, a difference in the selectivity was noticed, with a preference for MREEs in the ILs systems and HREEs in the isooctane system [140]. A kinetics study of metal transfer (Eu^{3+}) from a nitric solution to a TODGA- [C_1C_4im] [NTf_2] phase showed that it depends on the nitric acid and TODGA concentrations [141].

The possibility of transferring REEs from a Cl^- aqueous phase was investigated using the systems TODGA- [C_1C_4im] [NTf_2] [135] and TODGA- [N_{1114}] [NTf_2], or TODGA- [C_1C_4Pyro] [NTf_2], by studying the solvation of REEs with electronic absorption spectroscopy [142]. Murakami et al. [143] studied the possibility of using a TODGA- [P_{2225}] [NTf_2] system to recover REEs from an aqueous phase containing a bis(trifluoromethyl-sulfonyl)amide anion with a similar approach as in their study with TBP- [P_{2225}] [NTf_2] [133].

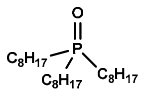
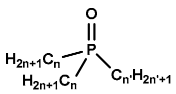
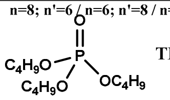
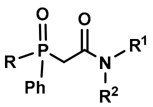
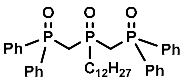
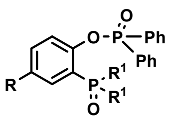
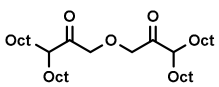
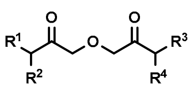
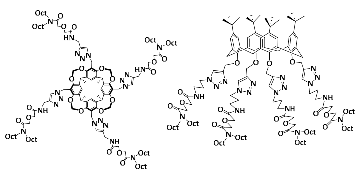
Other studies have focused on REE complexation by diglycolamides in [C_1C_8im] [NTf_2], showing that DGA ligands are bonded with the metal ion in a tridentate fashion via 2 carbonyl O atoms and one etheric O atom, as observed in organic solvent [144]. Also, a high loading of metals is possible without third phase formation, contrary to what can be observed with molecular diluents [145]. Similarly, other DGAs have been used, such as *N*,*N*′-dimethyl-*N*,*N*′-dioctyl-3-oxadiglycolamide (DMDODGA) in [C_1C_4im] [NTf_2] [146]. The use of DGAs has been studied by taking advantage of their preorganization on macrocyclic platforms, such as calix [4]arene. As demonstrated in other studies, DGA-based extraction systems result in different behaviours in ILs with regard to the efficiency and selectivity for REEs [147].

There are on-going studies investigating the use of malonamide as part of an IL-based extracting system for the recovery of REEs, with a focus on the molecular and supramolecular mechanisms involved in such systems [148,149].

As already discussed, stripping is an important step to consider for the recovery of REEs and the reusability of the ionic phase. As neutral extractants are able to extract acids, stripping can be performed by using a high acidic stripping phase. Promoting the extraction of acid in the ionic phase allows the release of metals extracted from this phase.

The mechanism of the stripping reaction is attributed to exchange of REE ions with protons in the ionic phase. However, the presence of acid in the ionic phase can have a negative impact; for systems with an NTf_2^- anion, this leads to the formation of triflimide ($HNTf_2$), which is partially lost in the aqueous stripping phase due to its high solubility in water.

Table 3. Examples of neutral extractants in ILs for the recovery of REEs.

Extractants	Ionic Solvent	Extracted (Feed)	Author
 TOPO	$[C_1C_nim]$ $[NTf_2]$ n = 4, 8	Y, Eu, Dy, Nd (NO_3^-)	Yang et al. [128]
 Cyanex 923 n=8; n'=6 / n=6; n'=8 / n=n'=6 / n=n'=8	$[C_1C_4im]$ $[NTf_2]$, $[N_{1444}]$ $[NTf_2]$, $[N_{1888}]$ $[NTf_2]$, $[P_{66614}]$ $[NTf_2]$ $[N_{1888}]$ $[NO_3]$, $[P_{66614}]$ $[NO_3]$ $[P_{66614}]$ [SCN], $[P_{66614}]$ $[NO_3]$	Nd (NO_3^-) La, Ce, Pr (Cl^-) Nd, Dy (Cl^-)	Rout et al. [129] Regadío et al. [130] Riaño et al. [131]
 TBP	$[N_{1888}]$ $[NO_3]$ $[P_{2225}]$ $[NTf_2]$	Pr, Nd, Dy (NO_3^-) Pr, Nd, Dy (NTf_2)	Kikuchi et al. [132] Matsumiya et al. [133]
 CMPO	$[C_1C_4im]$ $[NTf_2]$ $[C_1C_6im]$ $[NTf_2]$ $[C_1C_4im]$ $[NTf_2]$	REEs (Cl^-) Ce, Eu, Lu (Cl^-) REEs (NO_3^-)	Turanov et al. [134] Atanassova et al. [135] Nakashima et al. [136]
 TPO	$[C_2C_nPip]$ $[NTf_2]$ n = 4, 8	La, Nd, Eu, Dy, Yb (NO_3^-)	Turgis et al. [137]
	$[C_1C_4im]$ $[NTf_2]$	REEs (NO_3^-)	Turanov et al. [138]
 TODGA	$[C_1C_6im]$ $[NTf_2]$ $[C_1C_nim]$ $[NTf_2]$ n = 2, 4, 6 $[C_1C_4im]$ $[NTf_2]$ $[N_{1114}]$ $[NTf_2]$, $[C_1C_4Pyro]$ $[NTf_2]$ $[P_{2225}]$ $[NTf_2]$	Ce, Eu, Lu (Cl^-) La, Eu, Lu (NO_3^-) Eu (NO_3^-) Sm, Eu, Yb (Cl^-) Pr, Nd, Dy (NTf_2)	Atanassova et al. [135] Shimojo et al. [140] Sypula et al. [141] Pan et al. [142] Murakami et al. [143]
 TRDGA	$[C_1C_8im]$ $[NTf_2]$ $[C_1C_8im]$ $[NTf_2]$ $[C_1C_4im]$ $[NTf_2]$	Nd, Eu (NO_3^-) Eu (NO_3^-) La, Nd, Sm, Gd, Yb (NO_3^-)	Ansari et al. [144] Rama et al. [145] Chen et al. [146]
	$[C_2C_8Pip]$ $[NTf_2]$	La, Eu, Yb (NO_3^-)	Whebie et al. [147]

3.3.3. Combination of Extractant and Synergistic Systems

As mentioned above, many studies have demonstrated remarkable favourable changes, in terms of extraction mechanisms, efficiency and selectivity, for a variety of IL-based systems [150]. These extractants can also be used in combination to achieve, under certain conditions, synergistic systems in which the interactions of the two extractants produce a better effect than the sum of their individual effects. In some cases, the term "synergism" is used when the extractants are engaged in a simple combination to improve their efficiency or selectivity in cooperative ways. Synergistic mixtures of extractants, for which improvements of extraction efficiency have been demonstrated in organic solvents, have been studied in IL-based systems.

Taking into account the efficiency of beta-diketone (HTTA) and benzoylacetone (HBA), these extractants have been combined or engaged in synergistic systems with different neutral extractants, such as TOPO or CMPO.

Accordingly, we can notably cite the systems HTTA-TOPO [151–154], HBA-TOPO [154,155], HTTA-CMPO [156] and HBA-CMPO [157], which have all been diluted in various $[C_1C_n im]$ $[NTf_2]$.

A combination of neutral extractants has also been investigated and demonstrated that the addition of TBP to a TODGA- $[C_1C_8 im]$ $[NTf_2]$ system makes it possible to increase the efficiency for REE extraction [145], while a TODGA-CMPO mixture in $[C_1C_n im]$ $[NTf_2]$ phases highlighted antagonism behaviour in the transfer of REEs (Ce, Eu and Lu) from Cl^- aqueous solutions [135]. Recently, the selective separation of Gd(III) from Sm(III) in a nitric acid solution was described in the presence of a mixture of organophosphorus extractants (TBP-Cyanex 272 or TBP-HDEHP) in the $[C_1C_6 im]$ $[PF_6]$ [158].

Table 4. Examples of combinations of extractants in ILs for the recovery of REEs.

Extractants	Ionic Solvent	Extracted (Feed)	Author
HTTA-TOPO	$[C_1C_4 im]$ $[NTf_2]$ $[C_1C_4 im]$ $[NTf_2]$ $[P_{2225}]$ $[NTf_2]$ $[C_1C_4 im]$ $[NTf_2]$	Ln (HTTA) Sc, Y, La, Nd, Eu, Dy (NO_3^-) Pr, Nd, Dy (NTf_2) La, Eu, Lu (Cl^-)	Okamura et al. [151] Zhao et al. [152] Matsumiya et al. [153] Okamura et al. [154]
HBA-TOPO	$[C_1C_4 im]$ $[NTf_2]$ $[C_1C_4 im]$ $[NTf_2]$	Eu (Cl^-) La, Nd, Eu, Dy, Lu (Cl^-)	Okamura et al. [154] Hatakeyama et al. [155]
HTTA-CMPO	$[C_1C_n im]$ $[NTf_2]$ n = 4–10	Eu (Cl^-)	Atanassova et al. [156]
HBA-CMPO	$[C_1C_n im]$ $[NTf_2]$ n = 4, 10 $[C_1C_4 pyrro]$ $[NTf_2]$	Eu (Cl^-)	Atanassova et al. [157]
TBP-TODGA	$[C_1C_8 im]$ $[NTf_2]$	Eu (NO_3^-)	Rama et al. [145]
CMPO-TODGA	$[C_1C_6 im]$ $[NTf_2]$	Ce, Eu, Lu (Cl^-)	Atanassova et al. [135]
TBP-Cyanex 272	$[C_1C_6 im]$ $[PF_6]$	Gd, Sm (NO_3^-)	Asadollahzadeh et al. [158]
TBP-HDEHP	$[C_1C_6 im]$ $[PF_6]$	Gd, Sm (NO_3^-)	Asadollahzadeh et al. [158]

3.3.4. Task-Specific Ionic Liquids (TSILs)

As they refer to ILs that incorporate a chelating site, TSILs combine the properties of ionic liquids with those of conventional extracting compounds [159]. TSILs can therefore act both as the organic phase as well as the extracting agent, avoiding the difficulties that can be encountered through extractant/solvent miscibility. Extraction experiments have thus been performed using undiluted TSILs or diluted in an IL. The incorporation of functional groups, which act as complexation sites for the REEs, can be undertaken on the anionic or cationic parts of the IL.

- TSILs with functionalized anion (Table 5)

TSILs with functionalized anions usually exhibit an anionic chelation site, which has strong coordinating properties for the REEs. REEs can be coordinated by anions with complexation abilities, such as thiocyanate [SCN^-] or nitrate [NO_3^-], as demonstrated by various studies from Binnemans' research group. These studies are mainly focused on recycling processes, such as the recovery of REEs from magnets [160,161], batteries [162] and fluorescent lamp waste [163]. Also, the conventional IL anion can be replaced by an anionic extractant.

HDEHP is certainly one of the most useful and efficient acidic extractants. However despite the ability of ILs to solubilize a wide range of solutes, it appears that HDEHP is poorly soluble in these media [164].

To overcome such a drawback, the extractant has been engaged as an anion in various TSIL systems. The extraction behaviour of neodymium(III) from a nitrate medium was studied using 1-hexyl-3-methylimidazolium bis(2-ethylhexyl)phosphate ([C_1C_6im] [DEHP]), 1-hexyl-1-methylpyrrolidinium bis(2-ethylhexyl)phosphate ([C_1C_6pyr] [DEHP]) and tetrabutylammonium bis(2-ethylhexyl)phosphate ([N_{4444}] [DEHP]), diluted in their corresponding bis(trifluoromethylsulfonyl)imide IL [165]. Sun et al. studied various DEHP-type ionic extractants with ammonium (tetrabutylammonium [N_{4444}], tetraoctylammonium [N_{8888}]) or phosphonium (trihexyl(tetradecyl)phosphonium [P_{66614}]) cations diluted in [C_1C_nim] [NTf_2] or [C_1C_nim] [BETI]. Higher REE extraction performances were obtained in ILs with better solubilities and stabilities for REE complexes in comparison to organic solvents [166–168]. It has been highlighted that the driving force of DEHP-based TSIL extraction systems is mainly ion interaction rather than ion exchange. Also, DEHP-based TSILs have been used in a synergistic extraction using Cyanex 923 as molecular extractant, which made it possible to increase the efficiency of the separation of middle to heavy REEs (Eu^{3+}, Dy^{3+}, Er^{3+}) from light REEs (La^{3+}) [169].

Recently, more and more studies have described the use of Cyphos® IL 104 as an extracting phase. This phosphonium-based ionic liquid [P_{66614}] uses Cyanex 272 as part of the anion of the IL.

Solvent extractions of Y from chloride and nitrate solutions were investigated with this TSIL and compared to ammonium-based ionic liquids [N_{1888}] with Cyanex 272 as an anion [170]. Other studies have shown the efficiency of such systems for various REEs from various feed solutions [171,172]. Also, it has been shown that Cyphos® IL 104 can be used for the separation of rare earths, with an ionic liquid [C_1C_2im] [Cl] phase allowing an ionic liquid–ionic liquid extraction system, for the recycling of valuable metals from nickel metal hydride (NiMH) batteries [173].

Other phosphorous acidic extractants have been considered as anionic species for the development of TSILs, such as 2-ethylhexyl phosphoric acid mono(2-ethylhexyl) ester, which is named P507 or PC-88A. As an example, the extraction of mid-heavy REEs from H_2SO_4 media has been highlighted using [N_{1888}] [P507] [174]. In some cases, the TSIL is used as an extractant that can be diluted in organic solvent. This was proposed by Dutta et al. [175] for the liquid–liquid extraction of gadolinium from a nitric acid medium to an organic phase consisting of [N_{1888}] [P507] extractant dissolved in *n*-dodecane.

As shown in different studies, beta-diketones are also widely used for the recovery of REEs. They have been studied as anions for the implementation of TSIL-based extraction systems [176,177]. This extractant was used for the application of a homogeneous liquid–liquid extraction process involving a hexafluoroacetylacetone [hfac] as anion in an IL-based system involving [Ch] [hfac] and [Ch] [NTf_2]. Extraction of Nd(III) was performed by taking advantage of [Ch] [NTf_2] thermomorphic behaviour in water and of the formation of an anionic tetrakis(hexafluoroacetylacetonato)Nd(III) complex, with a choline cation as counter ion. It was accompanied by an ion exchange of three choline ions from the IL phase to the aqueous phase [177].

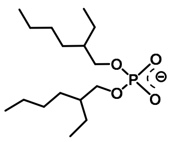
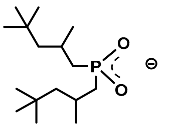
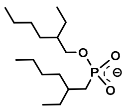
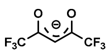
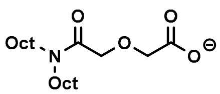
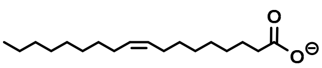
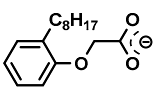
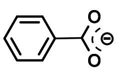
Other coordinating anions have also been considered, such as diglycolamate or carboxylate anions. A TSIL based on trioctylmethylammonium dioctyl diglycolamate [N_{1888}] [DGA] diluted in [N_{1888}] [NO_3] was proposed for the recovery of Nd(III), and it showed good extraction properties from nitrate media in comparison to chloride media [178]. Undiluted tetraoctylphosphonium oleate [P_{8888}] [oleate] was used as a bifunctional extractant for the recovery of metals from an aqueous chloride feed solution [179]. The separation of transition metals from REEs was considered by adjusting the chloride concentration and pH.

In addition, the potential of ionic liquids exhibiting a carboxylic acid group on their anion has been shown in various studies. Sec-Octylphenoxy acetic acid (CA-12) and sec-nonylphenoxy acetic acid (CA-100) have been applied in combination with trioctylmethylammonium as the bifunctional ionic liquid extractants [N_{1888}] [CA-12] and [N_{1888}] [CA-100] for the selective extraction of La(III) from REEs into a chloride medium [180].

The same system has been involved for the extraction of REEs from a nitrate medium [181]. In a similar approach, the feasibility of a selective extraction of Y(III) from a chloride medium was demonstrated using a [N_{1888}] [CA-12] system [182], with an improvement in the efficiency and phase separation when tri-n-butyl phosphate (TBP) was used as a phase modifier [183]. Another example that can be cited is the use of benzoate anion in phosphonium-based ionic liquid in the context of Nd(III) extraction from an aqueous solution of $NdCl_3$ with and without hydrochloric acid (HCl) [184].

Synergistic extraction strategies have been proposed using TSILs with functionalized anions, such as mixtures of [N_{1888}] [CA-12] and Cyphos® IL 104 for HREE separation from chloride solution [185].

Table 5. Examples of TSILs with functionalized anions for the recovery of REEs.

TSIL Anion	TSIL Cation	Extracted (Feed)	Author
 DEHP	$[C_1C_6im]^+$, $[C_1C_6pyrro]^+$ $[N_{4444}]^+$	Nd (NO_3^-)	Rout et al. [165]
	$[N_{4444}]^+$, $[N_{1888}]^+$, $[N_{66614}]^+$	REEs (DTPA-glycolic acid)	Sun et al. [166]
	$[N_{1888}]^+$	REEs (DTPA-glycolic acid)	Sun et al. [167]
	$[N_{2222}]^+$, $[N_{4444}]^+$, $[N_{6666}]^+$, $[N_{8888}]^+$, $[N_{1888}]^+$	REEs (DTPA-glycolic acid)	Sun et al. [168]
	$[N_{2222}]$	Nd, Eu, Dy, Er (Cl^-)	Sun et al. [169]
Cyphos® IL 104		Y (Cl^-,NO_3^-)	Devi et al. [170]
 Cyanex 272	$[P_{66614}]^+$	La, Nd, Gd, Lu (Cl^-)	Kumari et al. [171]
		Ce, La (NO_3^-)	Makowka et al. [172]
		Y, La, Nd, Eu, Dy, Ho, Yb ($[C_1C_2im]$ [Cl])	Rout et al. [173]
 P507	$[N_{1888}]^+$	Y, La, Gd, Tb, Tm, Yb, Lu (SO_4^{2-})	Shen et al. [174]
	$[N_{1888}]^+$	Gd (NO_3^-)	Dutta et al. [175]
 TTA	$[C_1C_nim]^+$ n = 1–17, $[C_1C_1C_4im]^+$, $[C_1C_4pyrro]^+$	Nd (NTf_2^-)	Mehdi et al. [176]
	$[Ch]^+$	Nd (NO_3^-)	Onghena et al. [177]
 DGA	$[N_{1888}]^+$	Nd (NO_3^-)	Rout et al. [178]
	$[P_{8888}]^+$	La, Nd, Sm, Dy, Er, Yb (Cl^-)	Parmentier et al. [179]
 CA-12	$[N_{1888}]^+$	REEs (Cl^-)	Wang et al. [180]
	$[N_{1888}]^+$	Y, La, Eu, Ho (NO_3^-)	Yang et al. [181]
	$[N_{1888}]^+$	REEs (Cl^-)	Wang et al. [182]
	$[N_{1888}]^+$	Y (Cl^-)	Chen et al. [183]
 BA	$[P_{66614}]^+$	Nd (Cl^-)	Panigrahi et al. [184]

- TSILs with a functionalized cation (Table 6)

A great variety of functional groups have been incorporated onto the cation of ILs, mainly hard base oxygen derivatives, since REEs are considered hard acids according to Pearson's HSAB concept.

TSILs bearing a carboxylic group have been proposed, such as hydrophobic [PF_6], which requires saponification to be considered for the extraction of yttrium [186]. Chen et al. described a pH-controlled selective separation of Nd(III) from Fe(III) by using carboxyl-functionalized imidazolium ionic liquids [$C_1(CH_2)_nCOOHim$] [NTf_2] (n = 3, 5, 7) as the solvent and complexing agent [187]. Taking advantage of carboxylic acids for the extraction of REEs, a carboxyl-functionalized phosphonium IL [$P_{444}C_1COOH$]Cl showed good extraction properties for scandium in an aqueous biphasic system (ABS) [188]. Betaine incorporates a carboxylic acid.

This functional cation, which was originally developed for the dissolution of metal oxides [76], has been also used for the extraction and recovery of REEs. Many examples of IL-based systems using [Hbet] [NTf_2] can be cited [189–191]. Homogeneous liquid−liquid extraction was implemented on the basis of the significant solubility in water and the thermomorphic behaviour of [Hbet] [NTf_2]. The [Hbet] [NTf_2]/water mixture exhibits an upper critical solution temperature (UCST) of 55 °C [190]. The extraction efficiency of the zwitterionic betaine has been highlighted for various REEs and applications [78,88,192,193]. Other Brønsted acids can be also encountered; Dupont et al. have reported the use of ILs incorporating sulfonic acid (-SO_3H) [194], alkylsulfuric acid (-OSO_3H) [195] and *N*-alkylated sulfamic acid (NH–SO_3) [196].

Neutral extractants have also been immobilized on ILs cations. Most TSILs containing neutral extractants have been studied for the partitioning of actinides/lanthanides [197]. As mentioned above, CMPO was used as the extractant in ILs for the extraction of REEs; moreover, ILs with grafted CMPO moieties have been synthesized and used for the extraction of Ln [198–200].

Phosphoryl-based TSILs, involving the introduction of coordinating P=O groups on the IL cations, were found to help Nd(III) ion extraction [201].

Solvent extraction experiments have indicated the possibility of extracting Eu(III) with diglycolamide-functionalized task-specific ionic liquids, as shown in a study of the Eu^{3+}–DGA-TSIL complex in [C_1C_4im] [NTf_2] [202]. In contrast, Yun et al. indicated that no Ln can be extracted by using a diglycolamide-grafted imidazolium IL in [C_1C_6im] [NTf_2]. It has been suggested that TSILs suppress the extraction of lanthanides because of the formation of water-soluble complexes [203].

Table 6. Examples of TSILs with a functionalized cation for the recovery of REEs.

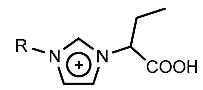
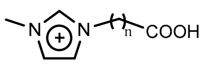
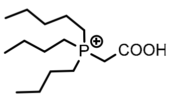
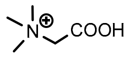
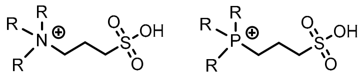
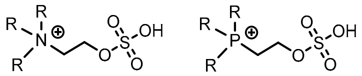
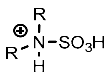
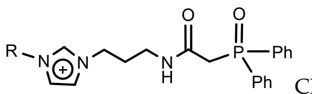
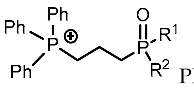
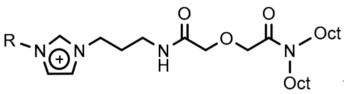
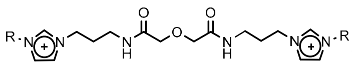
TSIL Cation	TSIL Anion	Extracted (Feed)	Author
 R = C_4H_9, C_6H_{13}, C_8H_{17} [1-alkyl-3-(1-carboxylpropyl)im]	$[PF_6]^-$	Y (NO_3^-)	Wang et al. [186]
 n =3, 5, 7 [$C_1(CH_2)_nCOOHim$]	$[NTf_2]^-$	Sm, Nd	Chen et al. [187]
 [$P_{444}C_1COOH$]	$[Cl]^-$	Sc (Cl^-)	Depuydt et al. [188]

Table 6. *Cont.*

TSIL Cation	TSIL Anion	Extracted (Feed)	Author
 [Hbet]	$[NTf_2]^-$	Nd (Cl^-)	Fagnant et al. [189]
	$[NTf_2]^-$	Nd (NTf_2^-)	Vander Hoogerstraete et al. [190]
	$[NTf_2]^-$	Nd (NTf_2^-)	Vander Hoogerstraete et al. [191]
	$[NTf_2]^-$	Sc (Cl^-, NO_3^-)	Onghena et al. [192]
	$[NTf_2]^-$	Sc (SO_4^{2-})	Onghena et al. [193]
 sulfonic acid	$[NTf_2]^-$	Dy, Nd, Sc (Cl^-)	Dupont et al. [194]
 alkylsulfuric acid	$[NTf_2]^-$	Y, Dy, Nd, La (Cl^-, SO_4^{2-})	Dupont et al. [195]
 *N*-alkylated sulfamic acid	$[NTf_2]^-$	La, Nd, Dy (Cl^-, NO_3^-)	Dupont et al. [196]
 CMPO	$[PF_6]^-$	Eu (NO_3^-)	Odinets et al. [198]
	$[NTf_2]^-$	Eu (NO_3^-)	Mohapatra et al. [199]
	$[NTf_2]^-$	La, Eu, Tb, Ho, Er, Lu (NO_3^-)	Turanov et al. [200]
 PFILs	$[PF_6]^-$, $[NTf_2]^-$	Nd (NO_3^-)	Wang et al. [201]
 DGA	$[NTf_2]^-$	Y, La, Ce, Pr, Nd, Sm (NO_3^-)	Sengupta et al. [202]
 DGA	$[NTf_2]^-$, $[BETI]^-$	La, Eu, Lu (NO_3^-)	Yun et al. [203]

4. Outlook—Open Questions and Needed Research

Ionic solvents offer an interesting alternative to the various conventionally used organic solvents and extractants and acid or alkali leaching solutions. Indeed, such systems can be used independently as solvents for the solvent leaching and extracting phases in the recovery of metallic species; these methods are part of the so-called "ionometallurgy" process.

However, in the case of REE recovery, few studies report both leaching and extraction steps using ionic solvents [80,84]. Indeed, changes in pregnant leach solution using DESs or ILs affect extraction and separation possibilities and can lead to emerging non-aqueous processes, introduced as "solvometallurgy" by Binnemans and Jones [204]. The following sections provide an overview of the potential of iono-/solvo-metallurgy for REE recovery, including the identification of potential gaps that need to be further explored.

4.1. Future of Leaching

Using ionic solvents during the leaching step often shows lower dissolution properties but higher selectivities toward targeted metals compared to the use of strong mineral acid solutions that dissolve the entire matrix. Such solvents could particularly be appropriated for low-grade REE resources, like mine tailings or industrial wastes, since complete leaching requires large amounts of chemicals and energy in these cases. Moreover, partial decomposition of the matrix by ionic solvents should theoretically reduce the difficulty and/or the number of steps during liquid–liquid extraction and then reduce the impact of recovery. In the best-case scenarios, we can imagine that the extraction step could be suppressed by efficient selective leaching. However, REE speciation in secondary sources is often overlooked. A better consideration of chemical speciation of REEs coupled with a good characterization of the hosting matrices would help in identifying the proper IL or DES system for leaching selectivity.

In addition, a concern to take into account in the context of the use of ionic solvents as leaching agents is that some of them can remain in the leaching residues, which implies the need to clean the solid residue.

4.2. Future of Liquid–Liquid Extraction

The number of studies involving IL-based extracting systems for the recovery of REEs is constantly increasing. Many studies have focused on imidazolium-based cations with hydrophobic anions, including PF_6^- and NTf_2^-, but more recent studies involve other types of cations, such as ammonium or phosphonium. Khazalpour et al. published a recent review focused on phosphonium-based ionic liquid PILs for various applications, including ion extraction and, therefore, REE recovery [205].

Recent studies rely on the use of ionic liquid-based aqueous biphasic systems (IL-ABS) to avoid having to resort to hydrophobic ILs, which are mainly based on fluorinated anions that are expensive and present a significant environmental impact. Currently, the use of this type of IL-ABS system is not well-reported for the recovery of REEs [206], except for a few examples [207,208].

In the majority of the studies for the recovery of REEs, DESs are involved in the leaching process but not as extracting phases. Hydrophobic DESs (HDESs) demonstrated promising results as extracting phases for the extraction and separation of metallic elements [209–213]. However, REE recovery has not been studied apart from a recent study showing the potential of HDES for recovery of waste SmCo magnets [214]. Also, non-ionic hydrophobic eutectics should be considered, as recent studies have proposed a hydrophobic eutectic solvent-based on TOPO as an extractant for liquid–liquid separation of uranyl nitrate from aqueous acid [215] or platinum group and transition metals in HCl media [216].

In addition, emphasis should be placed on intra-rare earth separation. A recent review devoted to this issue showed that high selectivities can be obtained when separating LREEs from HREEs; however, the separation between adjacent REEs requires more attention [217].

4.3. Electrochemical Behaviour

Beyond their efficiency for the extraction of REEs, ionic solvents can also be used for the electroleaching [218] or electrodeposition of metals from non-aqueous electrolytes [44,219]. Electrodeposition of REEs cannot be performed in aqueous solutions because the electropositivity of these metals is greater than that of hydrogen, but ILs can provide suitable conditions for their electrodeposition [220]. Therefore, the electrochemical behaviour of various IL systems and REEs have been investigated [221–224]. Zhang et al. [225] recently described the application of non-haloaluminate ILs as solvents for low-temperature electrodeposition of REEs.

Although electroleaching has been demonstrated for different metals using ionic solvents, there are only a few studies focused on REEs. Further research on this topic should therefore be further considered.

4.4. Mechanism and Predictive Models

Another open question concerns the mechanisms involved in ionic solvents, which are not fully described in most of the studies on this topic. Comprehension and prediction of solvent extraction in ionic solvents would help in identifying a priori which ionic solvent can be used to transpose the extractant systems known in conventional solvents to ionic solvents. Transposition from conventional diluents to ionic solvents would therefore become more straightforward and less expensive for industrial actors.

Recent studies have been undertaken focused on supramolecular mechanisms and the formation of aggregates [149]. In addition, the contributions of modelling and theoretical chemistry are important to take into account in order to better understand these mechanisms and acquire predictable models.

To render the application of ILs in solvent extraction predictable and reliable, it is therefore of crucial importance to understand their impact in the solvent extraction mechanisms. Specifically, it is also of prime industrial importance to use non-sacrificial ILs, for which it is necessary to be able to predict why and with which ILs ion exchange may occur or not.

4.5. Industrial Applications and Prospects

Although the performances and expectations are significant, the feasibility of these experiments when transferred from the laboratory scale to the pilot or even industrial levels is not well addressed in the various studies. One of the often reported drawbacks for ILs is their cost. Their recyclability and non-volatility make it possible to reduce the cost of use. The recovery of the extracted REEs and the recycling of the ionic phase are important in industrial separation processes. However, this point is not always investigated in detail in most studies. It is important to further investigate the stripping of REEs from the loaded ionic phase, as well as, in some cases, the scrubbing of the ionic phase before reusing it in new extracting steps.

The limitations of these processes should be taken into account, such as the loss of ionic liquid through ionic exchange in some of the systems examined. This phenomenon can be slightly mitigated by changing the pH [110] but, in practice, ion exchange is often attenuated by increasing the hydrophobic character of the ILs: by acting on the anion nature or on the length of the cation chains. This latter possibility generally leads to an increase in viscosity. The viscosities of the ionic liquids used in the extraction processes are indeed relatively high compared to the viscosities of water and traditional organic solvents, which may have an impact on the mixing, phase transfer and separation. They can also be reduced by using suitable IL mixtures [226]. The industrial applications of some ILs [227] may also be limited due to other characteristics, such as corrosiveness, hygroscopicity and, in some cases, toxicity.

The industrial applications of ionic liquids are steadily increasing in many sectors [228]: a pre-commercial permanent magnet recycling plant for REE recovery was opened in 2018 by Seren Technologies Limited, based on patents from Nockemann's group at Queen's University Belfast [229,230], and a pilot-scale plant for rare earth ore separation is currently being built.

The rise of DESs is also moving in this direction since they involve lower viscosities and cheaper precursors than the ILs, making technical considerations for the implementation of industrial process less restrictive [231]. It appears that the application of DESs for the recovery of REEs could address some of the existing challenges of ionic liquids.

4.6. Environmental Impact

The low pressure of ionic liquid vapours is often considered a major advantage of ionic liquids from an environmental point of view, and these liquids are considered as environmentally friendly alternatives to volatile organic solvents. However, the toxicity of these ionic systems must be considered [232,233]. It has been shown that the overall toxicity of ILs depends on both their cation—and particularly the cation alkyl chain length—and anion parts [234,235]. It seems important to take into account these factors when implementing IL-based extracting systems and choosing the cation and anion. Once again, this tends to encourage the use of DESs and, more particularly, NADESs. Indeed, DESs are usually known to be less toxic and more biodegradable than ILs [236]. However, statements about DESs' low toxicity are based on the low toxicities of their individual components; however, DESs are not necessarily as low in toxicity as their constituents. The toxicities of their mixtures must be taken into account [237].

Given the importance of REEs in various advanced technologies and the potential of ionic solvent recovery processes highlighted in various studies, investigation of such systems, and particularly DES systems, should continue to grow.

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

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