

# Separation and recovery of critical metal ions using ionic liquids

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**Abstract** Separation and purification of critical metal ions such as rare-earth elements (REEs), scandium and niobium from their minerals is difficult and often determines if extraction is economically and environmentally feasible. Solvent extraction is a commonly used metal-ion separation process, usually favored because of its simplicity, speed and wide scope, which is why it is often employed for separating trace metals from their minerals. However, the types of solvents widely used for the recovery of metal ions have adverse environmental impact. Alternatives to solvent extraction have been explored and advances in separation technologies have shown commercial establishment of liquid membranes as an alternative to conventional solvent extraction for the recovery of metals and other valuable materials. Liquid membrane transport incorporates solvent extraction and membrane separation in one continuously operating system. Both methods conventionally use solvents that are harmful to the environment, however, the introduction of ionic liquids (ILs) over the last decade is set to minimize the environmental impact of both solvent extraction and liquid membrane separation processes. ILs are a family of organic molten salts with low or negligible vapour pressure which may be formed below 100 °C. Such liquids are also highly thermally stable and less toxic. Their ionic structure makes them thermodynamically favorable solvents for the extraction of metallic ions. The main aim of this article is to review the current achievements in the separation of REE, scandium, niobium and vanadium from their minerals, using ILs in either

solvent extraction or liquid membrane processes. The mechanism of separation using ILs is discussed and the engineering constraints to their application are identified.

**Keywords** Critical metals · Ionic liquids (ILs) · Niobium · Tantalum · Rare-earth elements (REEs) · Vanadium · Scandium

## 1 Introduction

The European Commission published a report in July 2010 identifying a number of raw materials as “critical” to Europe’s economy [1]. “Critical” raw materials are those for which the supply into the European Union (EU) is under threat due to the rapid increase in demand and current geopolitical situations. Without supply security, the EU economy will be severely undermined. Niobium and the rare-earth elements (REEs) are into this classification because of their low substitution rate and their key role in important economic sectors.

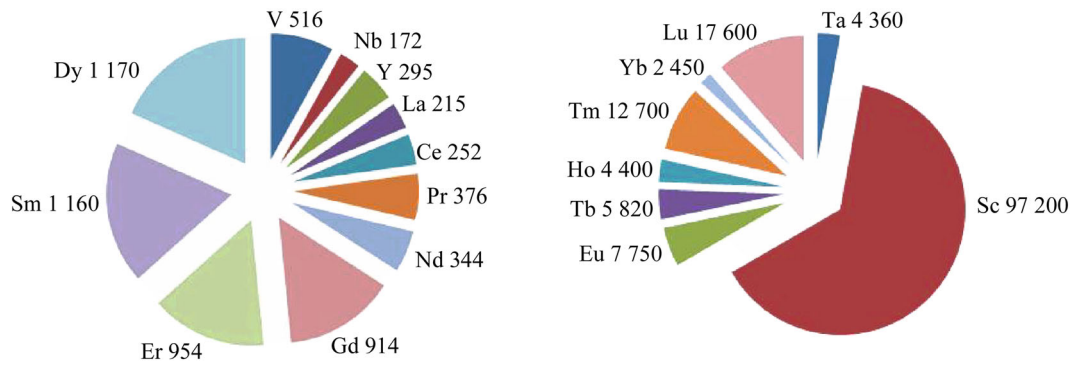
The energy required for refining these metals is shown in Fig. 1. Up to 30% of the energy required is employed in separation processes such as solvent extraction [2, 3]. In this review article, the latest developments in extractive technologies of vanadium, niobium, tantalum and REEs are presented.

### 1.1 Rare-earth sources

The REEs are a group of fifteen elements, including yttrium, belonging to the lanthanide series, with unique properties which make them essential for the development of green and energy efficient technologies [4]. According to the International Union of Applied and Pure Chemistry

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**Fig. 1** Cumulative energy demand (MJ/kg) for the extraction and processing of selected rare-earth metals [2] (The comparable energy demand for iron and steel is less than 100–1 000 times (typically below 30 GJ/t or 30 MJ/kg).)

(IUPAC) [5], the REEs can be classified into light rare-earths (LREs) (lanthanum, cerium, praseodymium, neodymium, promethium and samarium) and heavy rare-earths (HREs) (europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium). Despite being called REEs, these elements are not so rare in terms of crustal abundance, nevertheless, because of their wide distribution in low concentrations (nearly 200 minerals with less than 0.01% are known) and the difficulties associated with their extraction, they are considered rare [6]. The minerals which are currently commercially exploited are shown in Fig. 2 [7, 8].

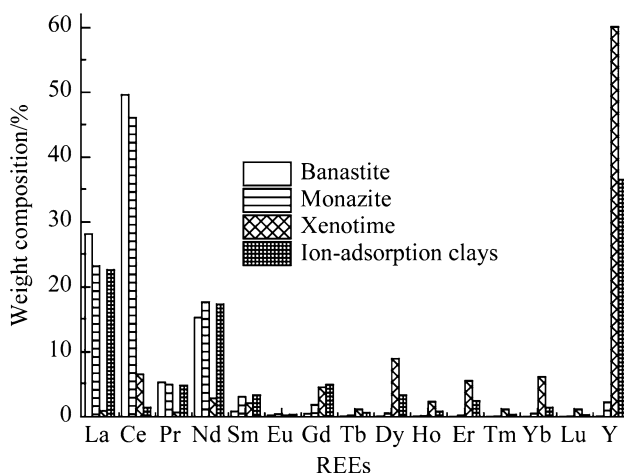
By comparison, scandium is a pre-lanthanide element with lower atomic mass than the rare-earth lanthanide series. However, due to its comparable electronic structure, its chemical properties determine its mineral association with the REEs. In this review, the scandium is included as it is distributed sparsely in trace amounts in rocks consisting of ferromagnesian minerals with an abundance of  $(5\text{--}100) \times 10^{-6}$  [9]. This is because the 3+ valance state and ionic size permit substitution with iron and aluminium

in minerals and therefore justifies its mineralogical co-existence. Ore bodies which are considered worthy of exploitation have a scandium concentration in the range of  $(2\text{--}5) \times 10^{-5}$  [9], where it can be recovered as a by-product from residues, tailings and waste liquors during production of other metals such as rare-earths, aluminium and niobium. Red mud produced in Greece and Jamaica has been reported to contain  $(1.05\text{--}1.72) \times 10^{-4}$  scandium, and therefore contain enough scandium for consideration as a secondary source [10–12].

The main commercial uses of REEs and scandium are summarized in Fig. 3.

Global production of scandium is believed to be of the order of 10 t per year. However the demand prognosis suggests that, if more becomes available, the demand in energy sector will increase.

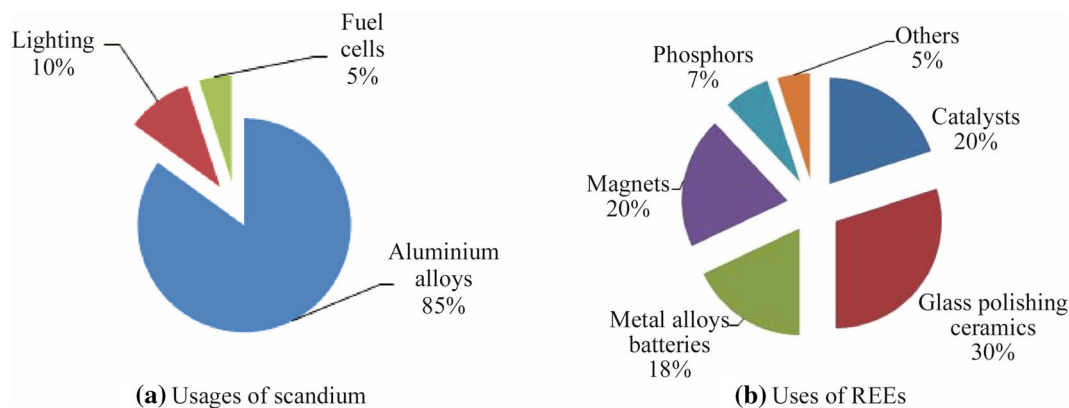
The REEs can be recycled from end-life products such as permanent magnets (Nd, Dy, Tb, Pr), fluorescent lamps, phosphors (Eu, Tb, Y, Ce, Gd, La), nickel batteries (La, Ce, Nd, Pr) and other industrial wastes; for example red mud and phosphogypsum using different pyro and hydrometallurgical approaches [14]. Scandium can also be recycled from aluminium alloys at the end of its use. However, less than 1% of the REEs and scandium are recycled in the economy at present due to inefficient collection, technological issues of extraction of such elements in end-life products and industrial wastes. Furthermore, in general there is a lack of initiatives for recycling electronic wastes and end-of-life products where valuable metal concentrations are much higher than that in the natural environments [13, 14].



**Fig. 2** Average rare-earth distribution in commercial rare-earth minerals (% of total rare-earth oxides (REOs)) [6–8]

## 1.2 Niobium and tantalum sources

Niobium has been included on the list of 20 most critical raw materials in Europe due to the risk in the security of supply and economic importance [1]. Niobium is widespread worldwide but rarely accumulates in concentrations



**Fig. 3** Usages of scandium and REEs in 2011 [13]

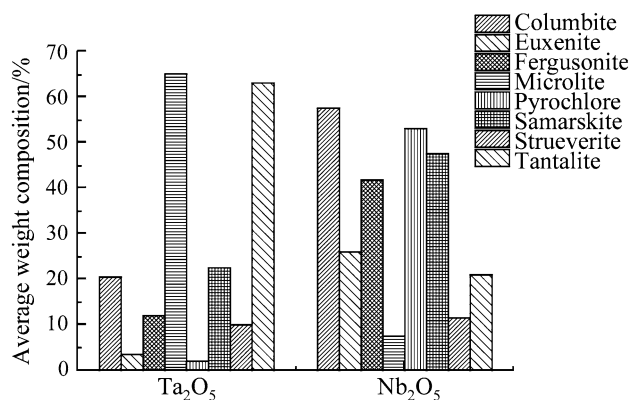
high enough for economic mining. Brazil has about 92% of global production, with Canada and Nigeria supplying the remaining 8% [15]. Almost all reserves are located in Brazil, with less than 5% located in Canada [15]. In the USA, more than 150 000 t of niobium resources have been identified [1]. And in Europe, niobium and tantalum deposits have been identified in Finland and Norway, but are not economic to exploit using conventional processes [1, 16].

The similarity in electronic structures of niobium and tantalum means that they are almost always found together in nature and require similar processes for extraction and purification, and can be substituted for one another for certain applications. Niobium and tantalum are components of hundreds of different minerals, which mainly consist of complex salts of niobic and tantallic acid together with titanium, zirconium, tin, REE, thorium, uranium and alkali-earth metals in variable ratios [17]. The most important mineral sources of niobium and tantalum may be classified as: (i) Tantaloniobates-salts of niobic and tantallic acids such as columbite and tantalite; (ii) Titanotantaloniobates in which titanium is the main component associated with niobium, tantalum and lanthanides.

In Fig. 4, the chemical composition of the main tantalum and niobium minerals is presented. Tantalite and columbite are the main sources for industrial production of tantalum and niobium, respectively [8].

The main applications of niobium and tantalum are presented in Figs. 5 and 6.

High strength low alloy steels consume most of the niobium as ferroniobium [18]. The steels are used in construction, oil and gas pipelines, and automotive industry. Niobium also has usage in special alloys for the nuclear and aircraft industries, magnets, superconductors, capacitors and catalysts. Demand for ferroniobium is set to increase, with a forecast of 8% per year [1]. This is driven mainly by the strong global demand for steel in



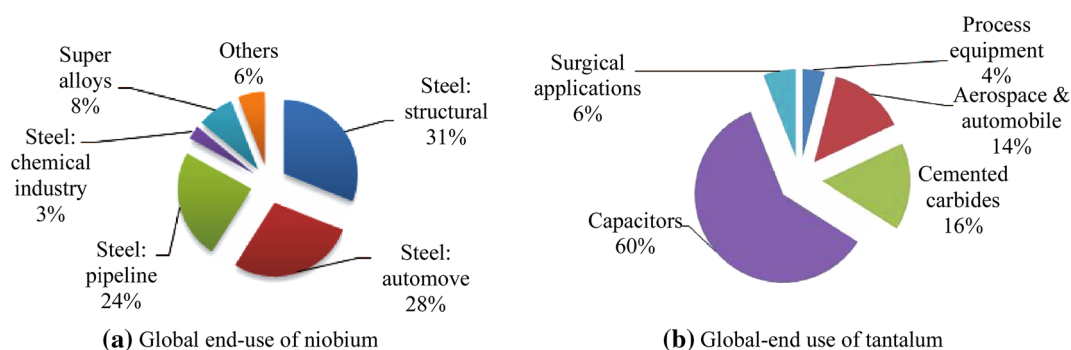
**Fig. 4** Average niobium and tantalum oxides distribution in industrial minerals [8]

construction, infrastructure and automotive applications. The major use for tantalum, as the metal powder, is in the production of electronic components, mainly capacitors and some high-power resistors. Because of the size and weight advantages, tantalum capacitors are attractive for portable telephones, personal computers, and automotive electronics [1]. Tantalum is also used to produce a variety of alloys that have high melting points, strength, and ductility for making carbide tools for metal-working equipment, superalloys for jet engine components, equipment with high corrosion resistance, nuclear reactors, missile parts, surgical instruments and implants.

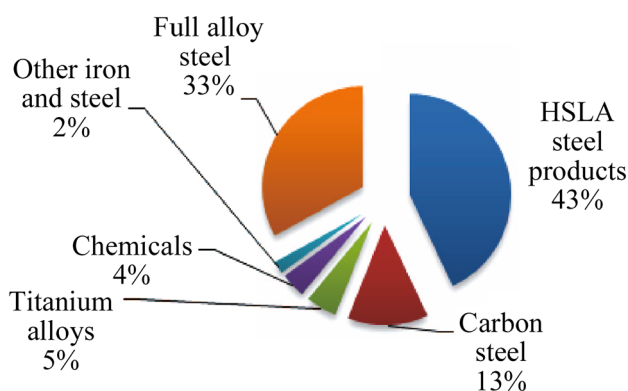
The US Geological Survey has estimated that tantalum and niobium recycling rates are around 20% [19]. Tantalum is recycled from waste and scrap like old cell phones and computers. Meanwhile, ferroniobium and niobium alloys are the main recycling sources for niobium [19].

### 1.3 Vanadium sources

Although not classed as critical in Europe, vanadium was classed as the raw material with the highest economic



**Fig. 5** Global end-uses of niobium and tantalum in 2010 [18]



**Fig. 6** Global end-use of vanadium in 2012 [20]

importance among the fifty-four candidate materials [1]. It was not considered critical due to the low risk in supply security. Like scandium, vanadium is primarily produced as a by-product, usually from the processing of titaniferous-magnetites, mineral oils, uranium-vanadium ores, phosphates and bauxites.

About 90% of the global end-use of vanadium is in the steel industry, with majority of the remaining 10% split between production of chemicals and titanium alloys [20].

Several processes for vanadium recovery and recycling have been developed. The Mineral Commodity Summaries by the US Geological Survey concluded that tool steel scrap and spent vanadium containing catalysts constitute up to 40% of global vanadium supply [21].

## 2 Solvent extraction

Solvent extraction is a well-established technique used in various chemical industries for producing pure chemical compounds including pharmaceuticals, heavy organics and metals, based on the fundamental physical chemistry of solvent-solute interaction, activity factors of the solutes in the pure phases, aqueous complexation and complex-

adduct interactions [22]. Most processes for separation and purification of REEs generally employ solvent extraction techniques, using two immiscible liquid phases to obtain a two-phase distribution of the metal ions.

### 2.1 Ionic liquids (ILs)

ILs are organic salts consisting of an organic cation and, commonly but not always, an inorganic anion. One of the main characteristics of these compounds is their low melting points (generally below 100 °C) in comparison with molten salts having melting points higher than 300 °C. The low melting points can be explained from the potential energy of interaction between ions (see Eq. (1)) [23]:

$$E = \frac{M}{4\pi\epsilon_0} \frac{Z^+Z^-}{d}, \quad (1)$$

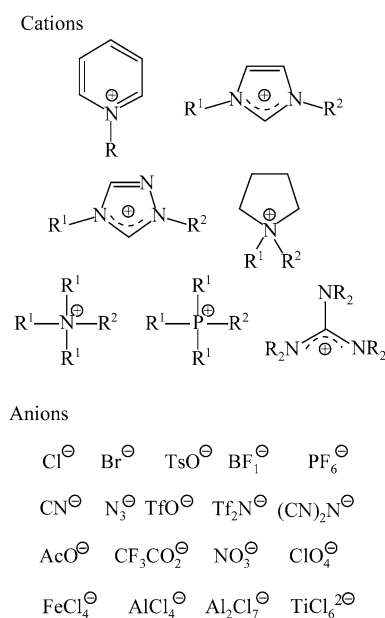
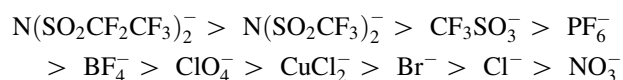
where  $Z^+$  and  $Z^-$  are the charges of the ions,  $M$  the Madelung constant,  $\epsilon_0$  the vacuum permittivity, and  $d$  the interionic distance in nanometres. An increase in the interionic distance, a lower packing efficiency (denoted by the Madelung constant), and a lower charge density is interpreted as lower lattice energy, hence lower melting point. In Table 1, the Madelung constant values of some ILs are compared with common inorganic salts.

In Fig. 7, ILs are formed by big asymmetrical ions with diffuse charge density.

These ion combinations endow ILs with interesting properties such as low vapour pressure and flammability, high dissolution power for organic and inorganic compounds, wide electrochemical windows and high thermal stability [26]. From the point of view of solvent extraction, the most important property is their water solubility because it will determine environmental and economic management related issues. The hydrophobicity of the ILs is determined by the anion. Regel-Rosocka and Wisniewski [27] proposed the following anion arrangement according to increasing hydrophobicity:

**Table 1** Madelung constant values of organic and inorganic salts [24]

| Salt                                     | Melting point/°C | Crystal type | Madelung constant |
|------------------------------------------|------------------|--------------|-------------------|
| CaF <sub>2</sub>                         | 1 418            | Cubic        | 2.524             |
| CaCl <sub>2</sub>                        | 772              | Cubic        | 2.364             |
| NaCl                                     | 801              | Cubic        | 1.474             |
| [C <sub>1</sub> mpyr][Tf <sub>2</sub> N] | 132              | Monoclinic   | 1.358             |
| [C <sub>2</sub> mpyr][TsO]               | 120              | Monoclinic   | 1.408             |
| [C <sub>4</sub> mpyr][TsO]               | 115              | Triclinic    | 1.296             |
| [C <sub>4</sub> mim][Cl]                 | 66               | Orthorhombic | 1.379             |
| [C <sub>4</sub> mim][Cl]                 | 41               | Monoclinic   | 1.345             |
| [C <sub>4</sub> mpyr][Tf <sub>2</sub> N] | -18              | Orthorhombic | 1.285             |

**Fig. 7** ILs structures [25] (Abbreviations have the following meanings: R<sup>1</sup> and R<sup>2</sup> represent linear organic chains, Tf<sub>2</sub>N = bis(trifluoromethylsulfonyl)imide, TsO = tosylate, TfO = trifluoromethanesulfonate, AcO = acetate.)

Moreover, the hydrophobicity also depends on the chemical and physical factors like the temperature. The ILs based on imidazolium cations are more water soluble with an increase of temperature, nonetheless, the presence of alkali chlorides in the aqueous solution decreases the solubility. Dilution of the ILs in organic compounds also affects the water solubility of the ILs. For example, the dilution of imidazolium ILs in tri-*n*-butyl-phosphate increases its water solubility [25–27].

ILs have been classed as green solvents for a long time because their low vapour pressure removes one exposition pathway, decreasing health impairments. However, recent

studies have put into manifest that some ILs have remarkably toxic effects across organisms and trophic levels [28].

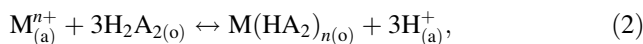
The main feature in toxicity of ILs is the “alkali chain side effect”, which is strongly related to their cationic part. An increase in the alkali chain length or hydrophobicity has proven to increase the toxicity and biodegradability of the ILs. On the other hand, the introduction of functional polar groups in the alkali chains enhances the biodegradability and reduces the toxicity [29]. Regarding the anionic part, only per-fluorinated anions and [N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sup>⊖</sup> show ecotoxicological properties [28, 29].

## 2.2 Extraction mechanisms

The extraction of metallic ions, using conventional organic solvents, has been studied for decades, and the main extraction agents and the mechanisms are described below [6, 8, 30].

### 2.2.1 Acid extractants

Acid extractants follow a cation exchange extraction mechanism which involves displacement of a hydrogen ion from the extractant by the extracted metal, forming a neutral organic soluble complex. Acid extractants commonly used are, phosphoric, phosphonic and carboxylic acids (C<sub>7</sub>–C<sub>15</sub>). They exist in dimeric form (H<sub>2</sub>A<sub>2</sub>) when dissolved in organic solvents of low polarity, therefore, the extraction can be represented by reaction (2).



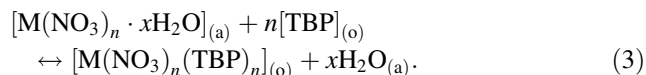
where (a) and (o) are the species present in aqueous and organic phases, respectively.

### 2.2.2 Solvating extractants

When using solvating extractants, the extractant partly or fully removes some of the water molecules from the

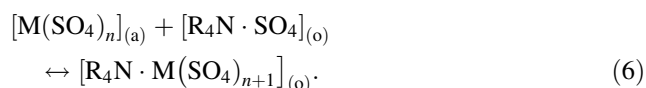
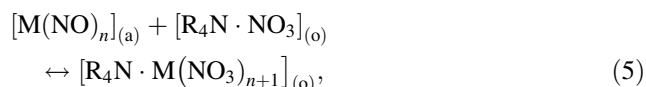
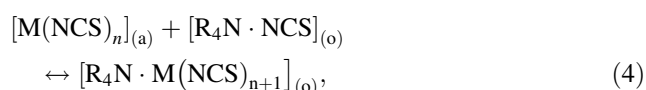


hydrated metallic ion to increase its solubility in the organic phase. One of the commonest solvating extractants is tri-butyl-phosphate (TBP). For most extraction processes employing TBP, the extraction mechanism is given as



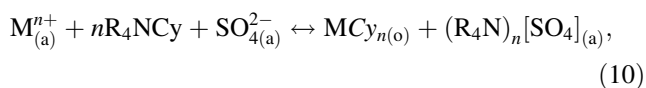
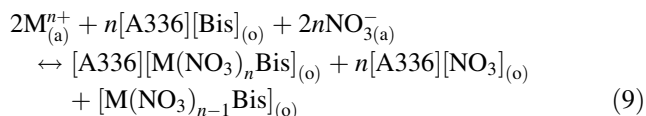
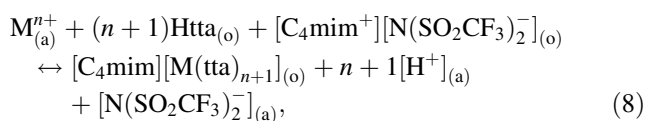
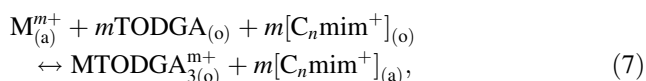
### 2.2.3 Basic extractants

Basic extractants remove metallic ions from aqueous solutions as anionic complexes by anion exchange. Long chain amines belong to this type of extractants. Extraction mechanism in thiocyanate, nitrate and sulphate media are shown in reactions (4)–(6), where  $R_4$  represents  $C_8$  to  $C_{12}$ :



Reactions (4) to (6) show that the first step of the extraction process involves the formation of an organic salt.

The extraction mechanisms in ILs are of cationic or anionic exchange nature, and less frequently, solvation of the metallic species. These mechanisms have been observed in imidazolium, ammonium and phosphonium ILs. Some examples are shown in reactions (7) to (9) [31–36]:



where TODGA is (N,N,N',N'-tetra(octyl)diglycolamide;  $C_n\text{mim}$  is the  $n$ -alkyl-methylimidazolium-cation; Htta is 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione; [A336][Bis] is tri- $n$ -octyl-methyl ammoniumbis(2,4,4-trimethylpentyl) phosphinate;  $[P_{66614}][MA]$  is tri-hexyl (tetradecyl) phosphonium N,N,N',N'-tetra(2-ethylhexyl)malonamide and  $R_4NCy$  is the general form of a quaternary ammonium

based ionic liquid. The contamination of the aqueous phase by the components of the ionic liquid in some cases (reactions (7), (8)) may be a limitation for their applicability in solvent extraction systems. However, new developments in organic synthesis are promoting ILs which mainly recover metallic ions by solvation mechanisms [37]. Castillo et al. [38] used dicarboxylic acids as anions for the extraction of divalent ions (Cd, Cu and Pb) from neutral aqueous systems via an ion exchange mechanism and their water-immiscible-halogen-free ILs minimised loss of the ILs into the aqueous phase.

### 2.3 Solvent extraction processes applied for the recovery of rare earths

The separation of REEs has been widely investigated using various types of extraction agents. Carboxylic acids such as naphthenic acid are used for the separation of yttrium from the rest of lanthanides elements. However, problems associated with compositional changes of the extraction agent and high water solubility, promoted the use of lower water solubility acids like sec-nonylphenoxy acetic acid (CA-100) and sec-octylphenoxy acetic acid (CA-12) [39]. Organophosphorous acids such as asdi-2-ethylhexylphosphoric acid (D2EHPA) diluted in toluene have been used for extracting REEs from hydrochloric solutions. The selectivity order follows the sequence  $Lu > Yb > Tm > Tb > Eu > Pm > Pr > Ce > La$ . Preston et al. [40–42] developed a continuous process for separating Sm, Eu, Gd, and Tb from La, Ce, Pr, and Nd in nitrate media. The first group was extracted using an eight counter-current stage system loaded with 15% (volume ratio) D2EHPA diluted in Shellsol AB organic phase. The organic phase was scrubbed with 1 mol/L  $HNO_3$  solution (2–4 stages) and the REEs were stripped with 1.5 mol/L HCl solution in 6–8 stages. Dy with some Tb and Gd was removed with 2.5 mol/L HCl solution in a secondary stripping of four stages. Although D2EHPA allows the REEs extraction at low pH, the recovery of the extracted metals is quite difficult due to that the prevalent chemical equilibrium existing between the aqueous and organic phases demands very acidic stripping solutions [43]. HEHEHP (2-ethylhexyl phosphonic acid mono-2-ethylhexyl), can be used to strip REEs at lower acidities compared to D2EHPA [44]. The extraction of REEs in chloride and nitrate media follows the sequence  $La < Ce < Pr < Nd < Sm < Eu < Gd < Tb < Dy (Y) < Ho < Er < Tm < Yb < Lu$  [44].

Sun et al. [45] studied the separation of rare-earth ions using the functionalized ILs tetrabutylammonium di(2-ethylhexyl)phosphate [TBA][DEHP], tri- $n$ -octylmethylammonium di(2-ethylhexyl)phosphate [A336][DEHP] and trihexyl(tetradecyl)phosphonium [THTP][DEHP], diluted in  $[C_6\text{mim}][NTf_2]$  or diisopropylbenzene (DIPB). They

found that the extraction efficiency was higher for those dissolved in  $[C_6mim][NTf_2]$  with relative distribution coefficients 100 times higher. They also reported a selectivity increase for HRRE, when compared with the conventional system using di(2-ethylhexyl)phosphoric acid (HDEHP) dissolved in the same diluents. Yang et al. [46] carried out the recycling of rare-earths from phosphor lamps after acid leaching of the phosphor powders using N, N-dioctyldiglycolamic acid (DODGAA) dissolved in the ionic liquid  $[C_4mim][NTf_2]$  and compared with PC-88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) dissolved in dodecane. The results disclosed better separation and extraction efficiency between rare-earth and transition metals using DODGAA-IL system at 30 °C in sulphate media. Rout and Binnemans [47] described similar behaviour when a trihexyl(tetradecyl)phosphonium N,N,N',N'-tetra(2ethylhexyl)malonate/trihexyl (tetradecyl) phosphonium nitrate  $[P_{66614}][MA]/[P_{66614}][NO_3]$  system was used in nitric solutions at pH 4.

Sang et al. [48] investigated the separation of  $Ce^{3+}$ ,  $Nd^{3+}$ ,  $Sm^{3+}$ ,  $Dy^{3+}$  and  $Yb^{3+}$  from nitric acid solutions with a mixture of 0.1 mol/L DEHPA dissolved in  $[C_4mim][PF_6]$ ,  $[C_2mim][PF_6]$  and  $[C_4mpyr][PF_6]$  at 40 °C. They found that for 0.01 mol/L solution of  $Ln^{3+}$ , the system had a high affinity for  $Yb^{3+}$ . Rout et al. [49] carried out the separation of  $La^{3+}$ ,  $Ce^{3+}$ ,  $Pr^{3+}$ ,  $Nd^{3+}$ ,  $Yb^{3+}$  and  $Y^{3+}$  at trace level from nitrate solutions at pH 2 using  $[C_6mim][DEHP]/[C_6mim][NTf_2]$  and  $[C_6mpyr][DEHP]/[C_6mpyr][NTf_2]$  systems, and noticed that the light rare-earths  $La^{3+}$  and  $Ce^{3+}$  were poorly extracted, meanwhile,  $Nd^{3+}$  and  $Yb^{3+}$  were strongly extracted, with  $Pr^{3+}$  being a borderline case. A similar observation was made by Yang et al. [50] when they carried out the separation of  $Nd^{3+}$ ,  $Eu^{3+}$  and  $Dy^{3+}$  with 5-octyloximethyl-8-quinolinol (HO8Q) in  $[C_8mim][NTf_2]$  as the extracting phase.

#### 2.4 Solvent extraction processes applied for the recovery of scandium

Derivation, preparation, purification, enrichment, and separation of scandium from its resources, which are typically non rare-earth minerals, are almost always achieved by employing solvent extraction processes [9]. Conventional solvent extraction processes for scandium recovery use a number of extractants including acidic organophosphorous extractants, such as TBP, D2EHPA, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (Ionquest 801) and di-2,4,4-trimethylpentyl phosphinic acid (Cyanex 272) for near-complete scandium extraction from sulphuric acid solutions. Typically, D2EHPA is used to extract scandium as Sc(III) and TBP subsequently used for preparation of high purity Sc(III) product. The TBP extraction step usually requires a high extracting aqueous acidity in the region

of 10 mol/L HCl. Li and Wang [52] showed that Cyanex 923 had a high Sc(III) extraction ability and could be directly used in waste liquor from  $TiO_2$  white pigment for scandium recovery. A summary of some of the investigations on scandium recovery is presented in Table 2.

Despite the use of ILs in extraction processes starting to gain momentum, little research has been done on their use in scandium extraction in solvent extraction processes.

#### 2.5 Solvent extraction processes applied for the recovery of niobium and tantalum

Commonly, columbite and tantalite are highly stable and can only be decomposed by digestion with concentrated hydrofluoric acid or its mixtures with sulphuric acid [8]. 1.2–2.5 t of 70% HF per ton of concentrate produced can be consumed depending on the  $Nb_2O_5:Ta_2O_5$  and FeO:MnO ratios and the processing conditions. Other problems associated with this technology are the evaporation losses of 6%–7% (volume ratio) of HF during decomposition at 250 °C, the prohibitively high recovery costs and the equipment maintenance [54–59]. During acid digestion, water soluble fluorides and oxy-fluorides are formed depending on the amount of free HF. For values lower than 35%, the predominant species are  $NbOF_n^{3-n}$  and  $TaOF_n^{3-n}$ , where  $n$  ranges among 3–6, when the HF excess overcomes 35%, the oxy-fluorides decompose to  $NbF_m^{5-m}$  and  $TaF_m^{5-m}$  fluorides [60, 61].

These fluorinated compounds readily combine with the organic molecules of the extraction agent to form extractable complexes. Only methyl-isobutyl ketone (MIBK) and TBP have been used in industrial processes [62].

MIBK can completely separate tantalum from niobium when the composition of the aqueous phase is 3 mol/L HF and 2 mol/L  $H_2SO_4$ . For higher concentrations of sulphuric acid, Okada [63] reported simultaneous extraction of both metallic ions. Agulyansky [64] related this phenomenon with the stronger Lewis acidity of niobium complexes, which requires strongest acid conditions in order to be extracted. Iron, titanium, manganese, aluminium, etc., are the common impurities associated with niobium and tantalum ores. It has been observed that the use of binary acid systems improves the separation factors between Nb, Ta and the impurities according to the following sequence:  $HF-HNO_3 > HF-H_2SO_4 > HF-HCl > HF$  [65].

Similarly to MIBK extraction, tantalum can be separated from niobium in  $HF-H_2SO_4$  systems using TBP, however, when the concentrations of  $HNO_3$ , HCl and  $H_2SO_4$  are high, the extraction efficiency of niobium decreases to levels too low for economic commercial extraction. Separation from other impurities however becomes more efficient for HF and  $HF-H_2SO_4$  systems [66].

**Table 2** Effectiveness of typical extractants on scandium extraction

| References | Extractants                                                       | Scandium recovery/% | Scandium purity/% | Comments                                                                                                                                                       |
|------------|-------------------------------------------------------------------|---------------------|-------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------|
| [51]       | TBP followed by di(1-methyl heptyl) methyl phosphate              | 93                  | 99.995            | Initially 99% Sc. 2 circuits are used.<br>12 carbons: 266.32 g/mol                                                                                             |
| [52]       | Cyanex 923 and Cyanex 925                                         | 94                  | 95                | Cyanex 923 is superior and is claimed better than TBP and HDEHP. CYANEX 923 extractant is a mixture of four trialkylphosphine oxides. Average MW is 348 g/mol. |
| [53]       | D2EHPA/TBP                                                        | 99                  | –                 | 0.05 mol/L DEHPA + 0.05 mol/L TBP<br>16 carbons: 322.43 g/mol                                                                                                  |
| [54]       | Amberlight AL-1 and AL-2                                          | 99.80               | –                 | Diluents have significant effect.<br>14 carbons: 213.4 g/mol                                                                                                   |
| [55]       | di(2ethylhexyl)dithiophosphate (Phoslex DT-8) in <i>n</i> -hexane | 97                  | –                 | No Zr is extracted.<br>16 carbons: 354.55 g/mol                                                                                                                |

There is no evidence in the literature about the use of ILs as solvent extraction agents for the separation of niobium and tantalum. However, some research regarding their individual electro-deposition from ILs has been carried out [67–70].

### 2.6 Solvent extraction processes applied for the recovery of vanadium

Vanadium can be extracted from neutral, acidic or basic solutions by solvent extraction processes [71]. Some of the relevant studies are presented in Table 3.

At an industrial scale, TBP, D2EHPA and amines are the established solvents for recovery of vanadium [75, 76]. Zhao et al. [77] developed a process that employed solvent extraction using the ILs tricaprilmethylammonium nitrate ([A336][NO<sub>3</sub>]) and organic acidified primary amine N1923 ([RNH<sub>3</sub>][NO<sub>3</sub>]) for successful separation of vanadium from chromium. Their study showed potential for application of the ionic liquid system in recovery of vanadium from industrial effluents, however there was no established commercial process that manipulated ILs as solvents for vanadium extraction.

## 3 Liquid membranes

Membranes are being widely recognized as key separation technologies and have a very important place in chemical technology where they are used in a broad range of

applications such as water purification and recovery of precious metals [78]. Their key property, which also makes them unique in separation processes, is their ability to control the permeation rate of the metal species through the membrane [79]. The two typical transport processes are cation transport and anion transport.

Regardless of transport mechanism, charge neutrality should be maintained. Both cationic and anionic transport processes occur in four similar stages.

- (i) At the phase I interface of the membrane, the guest salt is complexed with the carrier.
- (ii) The complex diffuses across the membrane.
- (iii) The release of that guest salt occurs at Phase II interface of membrane.
- (iv) The carrier diffuses back across the membrane ready to continue.

A diagrammatic illustration of the ion transport through a liquid membrane is shown in Fig. 8.

Any of the four stages of cationic or anionic transport processes can influence the rate of ion separation through the membrane. The stage with the highest resistance to ion flow is the rate controlling stage and is typically the step both chemists and engineers work on to maximise mass transport across the membrane. For a diffusion based membrane system, membrane permeability is determined by:

**Table 3** Effectiveness of different extractants on vanadium extraction

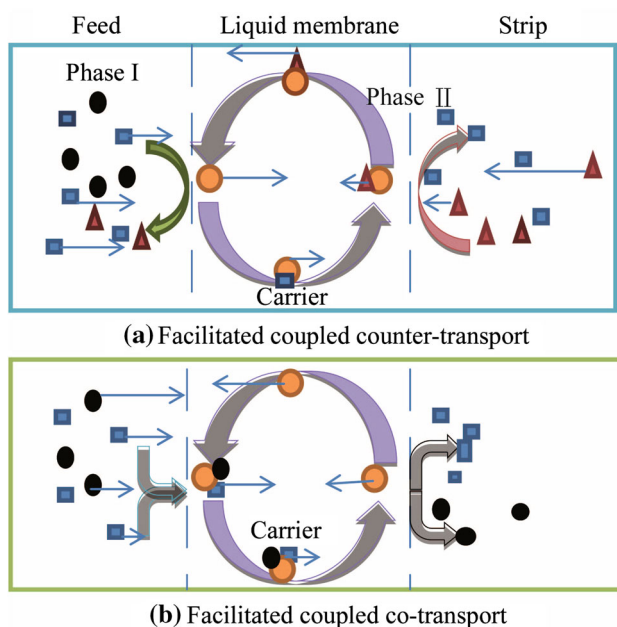
| References | Extractants      | Vanadium recovery/% | Vanadium purity/% | Comments                 |
|------------|------------------|---------------------|-------------------|--------------------------|
| [70]       | D2EHPA/TBP       | 97.7                | –                 | 16 carbons: 322.43 g/mol |
| [71]       | D2EHPA           | 99                  | 99.2              | 16 carbons: 322.43 g/mol |
| [72]       | 10% P204, 5% TBP | 85                  | 99.52             | 12 carbons: 266.32 g/mol |
| [73]       | EHEHPA           | 99.9                | –                 | 16 carbons: 306.23 g/mol |
| [74]       | Cyanex 272       | 60.5                | –                 | 16 carbons: 290.42 g/mol |



$$\frac{KD_m}{L}$$

From the formula, we can deduce that to increase permeability and selectivity of a specie across the membrane, the distribution coefficient ( $K$ ) has to be increased where possible, membrane thickness ( $L$ ) decreased and membrane diffusion coefficient ( $D_m$ ) increased [80]. Complexing the species to go across the membrane with carrier ion decreases the diffusion coefficient value due to the increase in particle size, however, the value of the distribution coefficient is increased by many orders of magnitude, resulting in facilitated transport [80]. Carrier molecules which can selectively facilitate the movement of desired molecules across the membrane without significantly lowering the diffusion coefficient are at the forefront of ionic liquid membranes research.

They can allow a single type of metal ions in a multi-metal ion solution to permeate the membrane freely while hindering permeation of other metal ions. There are several types of membrane separation processes being developed and the supported liquid membranes (SLMs) have shown huge potential in several applications. SLM consists of porous supports with a solvent impregnated inside the pores. Both organic solvents and ILs can be used in SLM, however, ILs have the advantage that they have a near-zero vapour pressure. They also have good chemical and thermal stabilities, having near-zero vapour pressures over a large temperature range [81, 82].



**Fig. 8** Facilitated coupled transport of ions through liquid membrane [80]

### 3.1 Liquid membranes in the separation of rare-earths

The potential for application of membranes, particularly the SLMs, in separation and purification of REE has been extensively investigated over the last two decades [83–88]. Usage of ILs in liquid membranes however only started getting interest in the last decade and has not yet been established for commercial exploitation [89–91]. Kubota et al. [90] developed a stable ILs based membrane for separation of rare-earth metals. Their membrane quantitatively transported Y and Eu successfully, achieving a good separation from Zn using N,N-dioctyldiglycolamic acid (DODGAA) as the mobile carrier.

### 3.2 Liquid membranes in the separation of scandium

Although potential for liquid membrane usage in scandium separation has been researched as far back as the mid 1990s [92], it has not yet been exploited. Yang et al. [92] investigated the effectiveness of electrostatic pseudo liquid membrane (ESPLIM) in pre-concentrating and separating scandium from rare-earths, aluminium and iron and found that scandium could be purified from an aqueous solution of 2.3% to nearly 96% in a single separation stage.

### 3.3 Liquid membranes in the separation of niobium and tantalum

TBP based liquid membrane processes have been studied for separation of niobium from aqueous solutions, however there is no established commercial technology for the processes [93, 94]. Campderrós and Marchese [94] studied the transportation of niobium (V) through a TBP-alamine 336 supported liquid membrane from chloride solutions and found that the process was selective for niobium and could be used for effective separation of niobium from tantalum. Buachuang et al. [95] successfully removed tantalum from a solution of tantalum and niobium using a hollow fiber supported membrane, with aliquat-336 diluted in kerosene as a carrier, providing an effective separation of the two. The use of ionic liquid membranes for niobium and tantalum separation and purification has however not been studied extensively and there are currently no industrial scale processes for separation of niobium by ionic liquid membranes.

### 3.4 Liquid membranes in the separation of vanadium

Recovery of vanadium by liquid membranes has been studied extensively over the past decade. Palet et al. [96]

recommended use of liquid membranes for removal of low concentrations ( $10^{-6}$ ) of vanadium from aqueous solutions. Chaudry et al. [97] investigated the effectiveness of tri-*n*-octyl amine cyclohexane SLMs in transporting vanadium and concluded that it was efficient for transportation of V ions. Yadav and Mahajani [98] recommended the use of liquid emulsion membrane processes as an alternative to the conventional processes employed for separation and purification of vanadium. Nosrati et al. [99] studied the transportation of vanadium from a feeding phase to an ammonia based stripping phase using the ionic liquid tri-*n*-octyl methyl ammonium chloride (TOMAC) impregnated in PTFE support membrane and found the transportation very effective. They also found that vanadium was selectively transported from its mixture with chromium ions when TOMAC was used as the carrier.

#### 4 Barriers and opportunities

ILs have great potential for revolutionising extraction processes due to their unique physical and chemical properties, however, a variety of challenges need to be addressed before ILs can be established as an alternative to conventional solvents at an industrial scale. The cost of a solvent is among the top factors taken into consideration when selecting a solvent for solvent extraction process [100]. It therefore follows that solvent losses should be minimised as high solvent losses can easily make an extraction process uneconomical. ILs have a negligible vapour pressure at temperatures below 100 °C, which decreases the solvent losses, nevertheless, the ILs cost has been an important drawback for their industrial development. However, the major cost associated with adopting ILs is the cost of the ionic liquid itself not the investment required to produce them. The economy of scale works in ILs, and their production in tons scale will decrease their prices by several orders of magnitude, making them competitive with traditional organic solvents [101].

There are usually many candidate solvents for extraction of any particular metal, therefore, as well as the solvent cost, consideration has to be given as follows:

- (i) **Selectivity.** The ability to remove and concentrate the metal solute from other metals present in the aqueous solution is desirable. ILs can be developed with specific applications in mind to match or even better the conventional organic solvents in separation and purification of valuable metals. They have been shown to be superior to conventional solvents for removal of metals such as strontium from aqueous nitrate solutions [102]. Since their properties, including selectivity, can be

tailored by changing the cation or anion, development of highly selective ILs should be achievable with adequate research.

- (ii) **Solvent safety.** Development of highly selective ILs alone is not enough. Considerations have to be given to such issues as toxicity, corrosiveness and flammability of the solvent candidates. Toxic solvents would require special measures to be taken for health considerations of plant employees and for purity of the extracted metals, depending on final use. Corrosive solvents may require expensive materials of construction for the extraction process. ILs currently being developed minimise problems associated with the environmentally unacceptable solvents that have been in use over the last century. Although ILs are generally considered safer than conventional organic solvents due to their low flammability and non-volatile nature, there are very few corrosion and toxicity data available in literature and such information is critical when developing safe commercial processes.
- (iii) **Solvent handling properties.** Density, viscosity and vapour pressure are also key engineering considerations when deciding on solvents to use for metal extraction processes. As IL is a relatively new technology, there is inadequate information on the physical properties relevant to both the handling and process design. They are however certainly highly viscous, hence high solvent regeneration and circulation rates are not easily achievable. The typically high viscosities of ILs also impede both mass transfer and capacity while a low interfacial tension solvent may lead to emulsion problems and affect the rate of mass transfer between the phases. A density difference that is too small can result in separation problems, lower capacity and larger equipment while a density difference that is too big may make it difficult to obtain the drop sizes required for efficient extraction. In view of this, process engineers and chemists need to work together in developing industrially viable ILs.
- (iv) **Solvent solubility in the raffinate phase.** High solvent solubility in the raffinate may lead to high solvent losses unless steps are taken to prevent such losses [100]. ILs have been shown to have low solubilities in typical raffinate phases [103], and if water-soluble, their recovery from raffinate phases is a relatively simple process since they can easily be recovered by water washing the raffinate.

Using ILs, these properties can be tailored for specific applications when the right combination of cation and anion is selected. During the last decade, many research efforts have been carried out to address physical properties, corrosion and toxicity data [104, 105]. However, ILs and conventional organic solvents have been used as sole extraction agents, in mixtures IL-organic extractant, diluted in organic solvents or in other compatible ILs. This heterogeneity in the extraction systems which also involves differences in equilibration time, extraction temperature, initial pH, concentration of the extraction agent and metallic ions load in the aqueous phase, make difficult their comparison and the determination on how the structure of the extraction agent affects the recovery of the metal ions.

Another key consideration that needs to be made when deciding on the best solvent is the miscibility of the two solvent with the feed. If the solvent is miscible in the feed, there usually is a need for either recovery of the solvent from the raffinate or continuous and costly replacement of the solvent.

The ease of solvent recovery also makes a key consideration to make. The solvent needs to be as pure as possible following stripping of the solute in order to permit recycling to the extractor and minimise losses and potential pollution [100]. Complexity of the solvent recovery operation is largely dependent on the mutual solubility of the two liquids (aqueous and solvent phases). Nearly immiscible solvents are generally preferred due to the ease associated with their clean-up, while partly miscible liquids may require expensive and complex unit operations such as extractive distillation for separation of the two phases. More research is required to investigate the stripping, recycle cycle and how to efficiently remove ILs from aqueous streams in order to avoid their introduction to the environment [106].

Since ILs are relatively new, there is limited literature on physical properties such as solubilities, heat capacities and viscosities, corrosion data as well as data on toxicity of ILs, making their commercialisation very challenging. Some ILs contain halogenated anions such as  $\text{BF}_4^-$ , which despite being air stable and neutral [102], can undergo hydrolysis making them less favourable at an industrial scale, leading to a need for research into alternative ILs which can match the halogenated anion's selectivity and cost. Development of ILs for most applications has been done by chemists and this may be one of the overlooked barriers to commercialisation of the technology. There is a need for both engineers and scientists to collaborate during the research and development stages in order to minimise risk associated with scale up and ensure that industrially relevant ILs are developed. Key areas of research and development where scientists and engineers can work together can be summarised as: (i) Determination of

physical properties, corrosion data and toxicity of ILs; (ii) Development of reliable thermodynamic models of phase behaviour; (iii) Recycling and reuse of ILs – development of ILs that can be recycled or reused to minimise costs; (iv) Scalability of the technology from laboratory scale to pilot plant and large scale commercial scale.

The aforementioned areas of research will not only improve the cost effectiveness of ILs but will also open up opportunities for usage of ILs in other industries such as chemical processing, pharmaceuticals, microelectronics and textiles industries, where non-volatile liquids with a wide liquidus range could work better and potentially reduce emissions and pollution [101].

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