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1 **Recovery of metals from waste electrical and electronic equipment** 2 **(WEEE) using unconventional solvents based on ionic liquids**

3
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10 **Abstract**

11 Waste electrical and electronic equipment (WEEE) is the fastest growing type of waste globally and is
12 an important challenge due to its heterogeneity, intrinsic toxicity and potential environmental impact.
13 However, WEEE also represents an important secondary source of critical and valuable elements and
14 must be viewed as a resource within the context of a circular economy. The use of ionic liquids (ILs) to
15 recover metals from WEEE is reviewed with a special emphasis on the use of ILs in leaching and solvent
16 extraction processes. The advantages of ILs as a reaction medium compared to existing conventional
17 solvents lies in their tuneability and potential environmental benefits. Many studies have used ILs for
18 the selective extraction and purification of metals from WEEE, particularly from waste fluorescent lamp
19 phosphor and batteries containing rare-earth elements with promising results. However, significant
20 barriers remain to the commercial use of ILs for treating WEEE and key barriers to progress are
21 identified. In particular more focus is required to improve upstream collection and separation of WEEE,
22 as this would greatly increase the potential to use selective, more efficient, ILs for metal recovery.
23

24 **Keywords:** Critical materials; Ionic liquids; WEEE; Solvent extraction; Leaching; Hydrometallurgy
25

26 **1. Introduction**

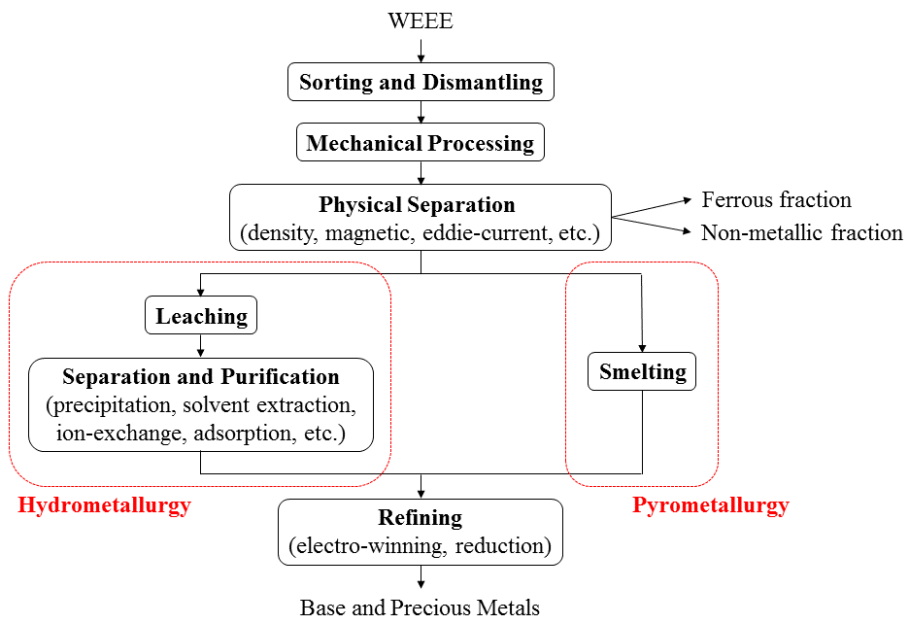
27 As organisations are looking for ways to mitigate the effects of human activity on the
28 environment, recent global trends point towards a shift from the historically prevailing linear economic
29 model, whereby goods are manufactured, consumed and disposed, to a circular economic model
30 promoting reuse and recycling. The primary tenet of the circular economy is the concept of value
31 recovery: all waste possesses an inherent value, which if properly managed can be extracted. In this
32 new context of global environmental remediation, sustainable, effective and affordable waste
33 management is an issue of critical importance.

34 Waste electrical and electronic equipment (WEEE) is the fastest growing waste stream globally
35 and is an important challenge due to inherent value, heterogeneity and potential environmental impact
36 (Ye et al., 2009; Ogondo et al., 2011). Essential constituents of many EEE products, in particular

37 information technology (IT) and communication equipment, are base metals (Fe, Cu, Al, etc.) as well
 38 as important concentrations of precious metals (Au, Ag, Pd) and specialty metals (In, Sb, Te, Ta, rare
 39 earth elements (REE), etc.) all highly interlinked in a complex composition (Hagulken, 2006). Many
 40 WEEE streams or components of WEEE contain higher concentrations of valuable metals than their
 41 primary ore and as such represent an opportunity as secondary ‘ores’. This is especially true as metals
 42 are finite commodities with a limited availability for human use. Mining rates of most metals are at a
 43 historical maximum whilst the average ore grade has decreased over the last hundred years for both
 44 base and precious metals (Mudd, 2010). The reduced availability of minable deposits and the
 45 concentration of these deposits in a limited number of countries results in an imbalance between supply
 46 and demand, making the current practice unsustainable in the long term. In addition, there is a growing
 47 legislative pressure on the proper handling and recycling of WEEE, with the collection and recycling
 48 targets recently increased as part of the EU WEEE Directive (2012/19/EU).

49 Current processes to recover value from WEEE can be complex and involve high water and energy
 50 consumption and/or the production of large quantities of hazardous effluents (Cui & Zhang, 2008,
 51 Tuncuk et al., 2012). WEEE recycling occurs in three major stages: (1) disassembly, (2) upgrading
 52 using mechanical and/or metallurgical processing to increase the desirable materials content of the
 53 waste, and (3) refining by purification of the upgraded material by metallurgical processing (Cui &
 54 Forssberg, 2003). A schematic flow-diagram of the major stages in WEEE processing is given in Figure
 55 1.

56



57

58

Figure 1. Simplified schematic of the major stages of WEEE recycling.

59

60 Although both hydro- and pyro- metallurgy have advantages, hydrometallurgy is often favoured
61 over traditional pyrometallurgy by industry due to an ability to recover metals from a variety of
62 challenging sources, including low grade ores, mixed metal ores and secondary sources such as WEEE.
63 Furthermore, hydrometallurgy allows the use of low process temperatures and recycling of reagents
64 (Wilson et al., 2014). Conventional industrial processing of WEEE requires extraction and separation
65 techniques that use aggressive acid or alkali digestion, can involve multi-stage separation procedures,
66 produce large aqueous waste streams which require further treatment, and in the solvent extraction
67 process, make use of solvents which are potentially flammable, volatile and toxic.

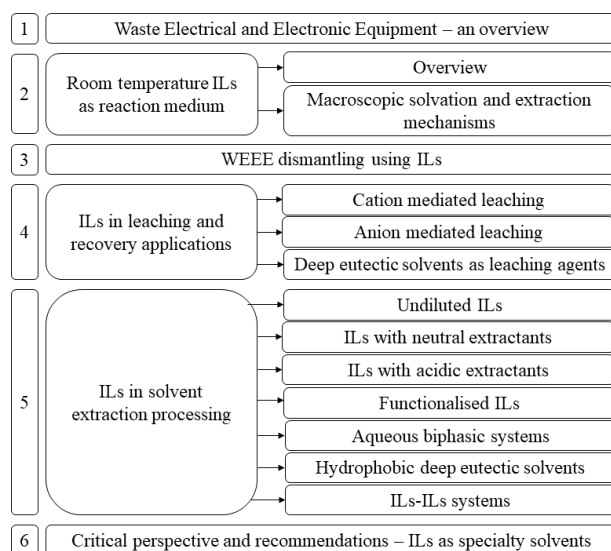
68 Ionic liquids (ILs) are solvents composed of ions with properties intermediate between molten
69 salts and organic solvents and are attracting significant interest due to potential environmental benefits
70 and tailorability compared to conventional solvents (Earle & Seddon, 2000; Rogers & Seddon, 2003).
71 They have been applied in a number of industrial processes and products (Plechkova & Seddon, 2008)
72 and if properly selected, ILs could offer an environmentally friendly alternative to current
73 hydrometallurgical WEEE recycling processes by minimizing waste generation and acid consumption
74 whilst maintaining selective leaching. Since the proposal of ILs as environmentally friendly media
75 compared to volatile organic solvents for liquid-liquid extraction (Huddleston et al., 1998), the use of
76 ILs for solvent extraction remains the most widely researched field in IL mediated metal processing.
77 Solvent extraction (or liquid-liquid extraction) is the favored option for metal separation and involves
78 the preferential two-phase distribution of a solute between mutually immiscible liquid phases usually
79 consisting of an aqueous acidic solution and an aliphatic organic solvent.

80 Due to their versatility and growing popularity, the use of ILs for metal separation has been
81 reviewed by previous authors (Dietz et al., 2006; Lee, 2006; Han & Armstrong, 2007; Abbott et al.,
82 2011; Tian et al., 2010; Hiramaya, 2011; Stojanovic & Keppler, 2012; Sun et al., 2012; Kolaric, 2013)
83 whilst the use of the immobilized IL in metal extraction was reviewed elsewhere (Stojanovic & Keppler,
84 2012; Vidal et al., 2012). The use of ILs for the electro-deposition of metals was previously reviewed
85 by the research groups of Abbott et al. (2006; 2011; 2013), Smith et al. (2014) and Endres et al. (2002;
86 2008). Furthermore, a detailed description of the fundamental governing principles dictating metal
87 extraction to IL (Watanabe et al., 2014; Janssen et al., 2015; Katsuta et al., 2016; Papaiconomou et al.,
88 2016) as well as specific applications for certain classes of ILs such as acidic ILs (Amarasekara, 2016)
89 or temperature responsive ILs (Qiao et al., 2017) are also available. Nevertheless, there is currently no
90 review focusing on the use of ILs for the recovery of value from WEEE despite the increasing number
91 of publications on this field in the last five years.

92 This review is divided into six sections, with the schematic review outline presented in Figure
93 2. After an introduction of the current WEEE recycling and ILs, the discussion follows the typical
94 sequence in WEEE processing, starting with dismantling, followed by leaching and finishing with
95 solvent extraction. The first provides a brief overview of metal recycling from WEEE highlighting the
96 metals of critical interest for recovery and the challenges to date. The second addresses the general

97 properties of ILs as reaction medium with an emphasis on metal-ILs extraction mechanisms. The third
 98 and fourth sections present the application of IL-derived solvents to the solvato-metallurgical
 99 processing of electronic waste, namely their use for the dismantling and leaching of WEEE. In the case
 100 where the reviewed literature presents a recovery methodology, this will be presented in conjunction
 101 with its leaching to promote the application of a one solution for the elective leaching and recovery of
 102 metals from WEEE. The fifth section reviews the use of unconventional solvents based on ILs in solvent
 103 extraction processes relevant to WEEE recycling. This section represents the largest body of reviewed
 104 works and covers both the use of traditional IL solvent extraction processes as well as non-conventional
 105 systems such as hydrophobic deep eutectic solvents (DES) and aqueous biphasic systems (ABS).
 106 Finally, a critical assessment on the use of ILs for metal extraction from WEEE is conducted with
 107 guidelines provided based on the reviewed literature to maximise its beneficial application. The focus
 108 is on recovery of metals from WEEE rather than plastic or glass components, with emphasis on ILs
 109 used in leaching and solvent extraction. In this review, the ILs are discussed according to their
 110 application. As such, one IL used both in leaching and in solvent extraction applications will be
 111 presented in two different section although care is taken to avoid overlap. Although not within the scope
 112 of this review, some relevant examples on the application of ILs for the recovery of metals from primary
 113 ores are presented to enrich the discussion. Current hydrometallurgical treatment of WEEE borrows
 114 heavily from principles developed by the mining industry; innovative techniques developed for the
 115 latter can be transferred to the extraction of value from WEEE.

116



117

118

Figure 2. Schematic outline of the review.

119

120 **2. Waste Electrical and Electronic Equipment (WEEE)**

121 Global WEEE generation is estimated at 20-50 million tonnes per year and is increasing at a 3-
 122 5 % rate (Ogondo et al., 2011). In 2005, WEEE already represented approximately 8 % of municipal
 123 solid waste (Widmer et al., 2005). Annual WEEE production in the European Union (EU) increased
 124 from 6.5 Mt in 2004 to 12 Mt in 2015 (Goosey, 2004, Baldé et al., 2015). An important distinction must
 125 be made between WEEE and e-waste. Although many authors use the terms interchangeably, Robinson
 126 (2009) describes WEEE as “discarded appliances that use electricity” including traditionally non-
 127 electronic goods such as refrigerators and ovens. WEEE designates any wastes that fall under the
 128 jurisdiction of the European WEEE Directive (2002/96/EC) as set out in Table 1. E-waste is a sub-
 129 fraction of WEEE that encompasses “waste electronic goods, such as computers, televisions and cell
 130 phones”. These goods primarily fall under category 3 and 4 of the WEEE Directive.

131

132 **Table 1.** Classification of WEEE into ten categories according to the European WEEE Directive
 133 (2002/96/EC). The highlighted rows correspond to the e-waste subsection of WEEE.

No.	Category	Example
1	Large household appliances	Refrigerator, oven, washing machine
2	Small household appliance	Toaster, microwave, vacuum cleaner
3	IT and telecommunications equipment	Mobile phone, computer, computer screen
4	Consumer equipment	Television, radio, speaker
5	Lighting Equipment	LED, gas discharge lamps
6	Electrical and electronic tools	Power drill, electric screw driver
7	Toys, leisure and sports equipment	Treadmill, game console
8	Medical devices	MRI, dialysis
9	Monitoring and control instruments	Thermocouple, smoke detector
10	Automatic dispenser	Vending machine, cash distributor

134

135 Global WEEE is exponentially increasing due to (1) population growth, (2) economic growth
 136 and the resulting improvement in living standards, (3) decrease in product lifespan and (4) the increase
 137 in everyday commodities containing microprocessors. One consequence of increasing EEE on the
 138 market is the blurring of the traditional borders between classical electrical equipment and electronic
 139 equipment. Over 98% of all programmable microprocessors are now embedded in commodities that are
 140 not associated with computers (Hilty, 2005).

141 WEEE is a complex, heterogeneous waste stream containing over 1000 different substances (Ye et
 142 al., 2009) and is primarily composed of plastics (34.6 wt.%), electronic components (23.5 wt.%) and
 143 ferrous metals (15.6 wt.%) (Dimitrakakis et al., 2009). Essential constituents of many EEE products, in
 144 particular IT and communication equipment, are base metals (Fe, Cu, Al, etc.), precious metals (Au,
 145 Ag, Pd) and speciality metals (In, Sb, Te, Ta, rare earth elements (REEs), etc.) (Hagelucken, 2006). Due

146 to their significant metal concentration, EEE production has an important impact on global demand for
 147 metals and is an important driver of metal scarcity. Essential constituent of many EEE are metal with
 148 reserves often concentrated in a handful of countries creating a potential supply risk. This is exemplified
 149 by the substantial increase of most of rare earth oxides (REOs) prices in 2011 due to the implementation
 150 during the previous year in China of a REOs export quota policy (Tan et al., 2015). Imbalances between
 151 metal supply and demand in conjunction with the importance of a metal for continued economic growth
 152 has inspired the concept of metal criticality (Graedel et al., 2015). Multiple methodologies have
 153 attempted to assess the criticality of materials with widely varying results (Erdmann & Graedel, 2011,
 154 Bujis et al., 2012).

155 A selection of previous studies assessing raw material criticality is presented in Table 2. These
 156 studies primarily focus on the criticality of materials from a European or U.S. perspective. It is important
 157 to remark that criticality varies geographically, and certain materials labelled as critical in EU are likely
 158 to change if other countries such as China are considered. The most comprehensive studies are those
 159 originating from the European Commission (2014) and from Graedel et al. (2012, 2015). These reports
 160 include a temporal dimension (assessment of current and future criticality) and estimate material
 161 criticality based on multiple factors including (but not limited to) economic importance, supply risk,
 162 vulnerability to supply restriction, substitutability and environmental impact. Although material
 163 criticality is a fluid concept with temporal and geographical variations, certain metal groups appear in
 164 most of the presented studies, namely indium, antimony, REE, platinum group metals (PGM),
 165 magnesium, manganese and niobium. Recovery of these elements is of major importance to minimise
 166 their environmental impact and for the continued growth of the EEE industry and green industry.

167

168 **Table 2.** Selection of previous studies assessing raw material criticality.

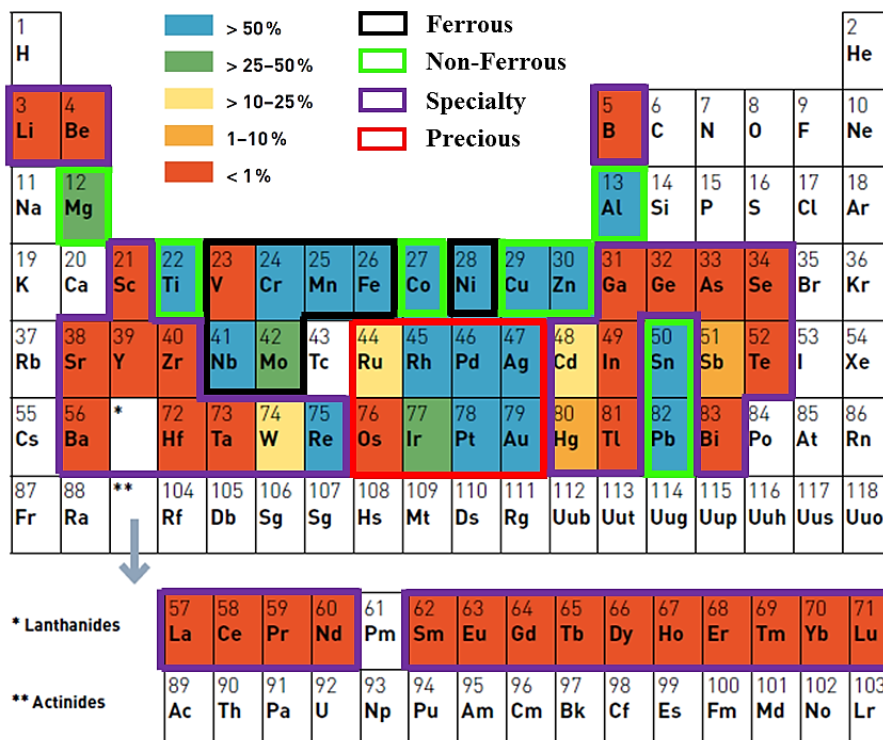
Study	Critical Material
NRC (2008)	In, Mn, Nb, PGM, REE
Morley & Eatherley (2008)	Au, Rh, Pt, Sr, Ag, Sb, Sn
Oko-Institut (2009)	Te, In, Ga, REE, PGM, Ta, Li, Ge, Co
U.S. DoE (2010)	REE (Dy, Nd, Tb, Eu, Y), In
Erdmann & Graedel (2011)	REE, PGM, In, W
Graedel et al. (2012)	Results grouped by mineral family. Eg. for 'copper family': As = Gd > Ag > Se ≈ Cu > Te
European Commission (2014)	Sb, Be, Co, fluorspar, Ga, Ge, graphite, In, Mg, Nb, PGM, REE, Ta, W
Graedel et al. (2015)	In, As, Tl, Sb, Ag, Se, Au, PGM, Mg, Cr, Mn, Rh, REE

169

170 In 2007, demand for indium, antimony, tin, copper, silver, cobalt and selenium for use in EEE
 171 accounted for an estimated 79.2, 50.0, 32.7, 30.0, 30.0, 19.0 and 17.1% of total production of these
 172 metals (Hagelüken & Buchert, 2008). Many WEEE streams and components of WEEE contain greater
 173 concentrations of valuable metals than the primary ore. It is estimated that the annual replacement value
 174 of the materials found in WEEE disposed of in the UK alone is ~£1.3bn, with £400m either hoarded or
 175 landfilled (Haig et al., 2012). The quantity of precious metal in WEEE generated solely in the UK is
 176 estimated at about 50 tonnes per year. For example, phosphor powders used in fluorescent lamps
 177 contains elevated concentration of REE including Eu. Binnemans et al. (2013) estimate that waste
 178 fluorescent lamps will contain up to 25,000 tons of REEs by 2020.

179 The primary factors influencing the recyclability of a metal from WEEE are the volume of the waste,
 180 the price of the metal and the purity of the element and ease of recovery. For many electrical products,
 181 innovation is associated with an increase in the number of elements used. In the 1980's, 11 elements
 182 were contained in Intel® printed circuit boards (PCBs), compared to ~60 in the 2000s (Johnson et al.,
 183 2007). Additional elements are often present at low concentrations but have important specific
 184 functions. New high-strength permanent magnets or new alloys with enhanced physical and chemical
 185 properties are obtained using lanthanide elements (Graedel, 2011; Binnemans et al., 2013). Recovery
 186 of these metals from WEEE is seldom considered due to the technological and economic challenges
 187 involved (Reck & Graedel, 2012). A consequence of the rising number of elements in WEEE is that
 188 individual metal recycling rates can be divided into three categories. Recent global estimates of end-of-
 189 life recycling rates for 60 metals and metalloid (UNEP, 2011) are presented in Figure 3.

190



191

192 **Figure 3.** Global estimates of end-of-life recycling rates for 60 metals and metalloid in 2008 (adapted
193 from UNEP, 2011).

194

195 The first category of metal corresponds to ‘base metals’ (Fe, Cu, Sn, Ni, Zn, Al and Pb), with end-
196 of-life recycling rates (EOL-RRs) at >50 wt.%. These are the main metals in WEEE, are often found in
197 relatively pure elemental form and benefit from mature recycling infrastructure (Khaliq et al., 2014).
198 The second category corresponds to ‘precious metals’ with EOL-RRs of ~50-60 wt.%. This includes
199 some platinum group metals, Au and Ag, which despite low concentrations have high economic value
200 (UNEP, 2011; LME, 2016). The recycling rates are positively skewed due to the high recycling rates
201 of industrial catalysts and jewellery. This significantly masks lower EOL-RR from WEEE in the EU
202 (Chancerel et al., 2009; Hagelüken, 2012). Platinum group metal recycling rates from WEEE, such as
203 Pd(II) from PCBs were only 5-10 wt.% in 2011. EOL-RRs for other elements from WEEE are restricted
204 by low collection rates due to export of WEEE to countries with primitive treatment technologies and
205 disposal of WEEE in municipal solid waste (Hagelüken, 2012). The final category consists of ‘specialty
206 metals’ that are characterised by low recycling rate, typically below < 1 wt.% (UNEP, 2011). Many
207 metals in this category are labelled as critical (see Table 2). These are used in low concentrations and
208 extensively mixed making separation often economically unviable (Du & Graedel, 2011; Reck &
209 Graedel, 2012). Recovery of these metals represents a major challenge to achieve a circular economy
210 due to increasing use in EEE and the current linear management system.

211 Frustratingly, a significant portion of most strategic metals in e-waste is lost during the collection,
212 sorting and mechanical separation stages. In turn, this decreases the financial viability of any recovery
213 process through the dilution of precious metal content by commingling with other types of lower-value
214 e-waste. Small high-value e-waste such as mobile phones suffer from low end-of-life recycling rate as
215 they are often either improperly disposed in municipal waste bins or stored forgotten in a drawer.
216 Mechanical treatment options suffer from the ‘concentration dilemma’, i.e. the recovery yield for a
217 specific metal decreases with the rising purity of that metal in the output stream (Hagulken, 2006). The
218 unintended co-separation of minor metals during mechanical pre-treatment unavoidably can lead to
219 substantial losses before it ever reaches any hydrometallurgical processes. A substance flow analysis of
220 a full-scale pre-processing facility shows that 60 wt.% of the Cu reach output fractions from which it
221 may potentially be recovered. This decreases to 25.6 wt.% for Au and Pt and only 11.5 wt.% for Ag
222 (Chancerel et al., 2009).

223 The ILs covered in this review are for the most part limited to the recovery of value from PCBs,
224 waste fluorescent phosphor, nickel metal hydride batteries and permanent magnets. Research has
225 focused on these waste types due to (i) their high inherent metallic value and (ii) their ease of
226 procurement as an ‘uncontaminated’ waste. These e-wastes have well established collection and sorting

227 processes, with some even separated at source due to legislative pressure. Fluorescent tubes, which
228 contain rare-earth rich phosphor powder, are classified as a hazardous waste in the European Union due
229 to their mercury content. As such, fluorescent lamps benefit from a dedicated collection and separation
230 chain, ensuring a high content of REE, phosphorus and antimony. In contrast, indium and tantalum can
231 be found in high concentration in indium-tin oxide film in flat screen and in capacitors respectively.
232 However as these are small components of a larger waste, their current recycling barriers make the
233 recovery of these metals from large scale WEEE treatment facilities difficult.

234

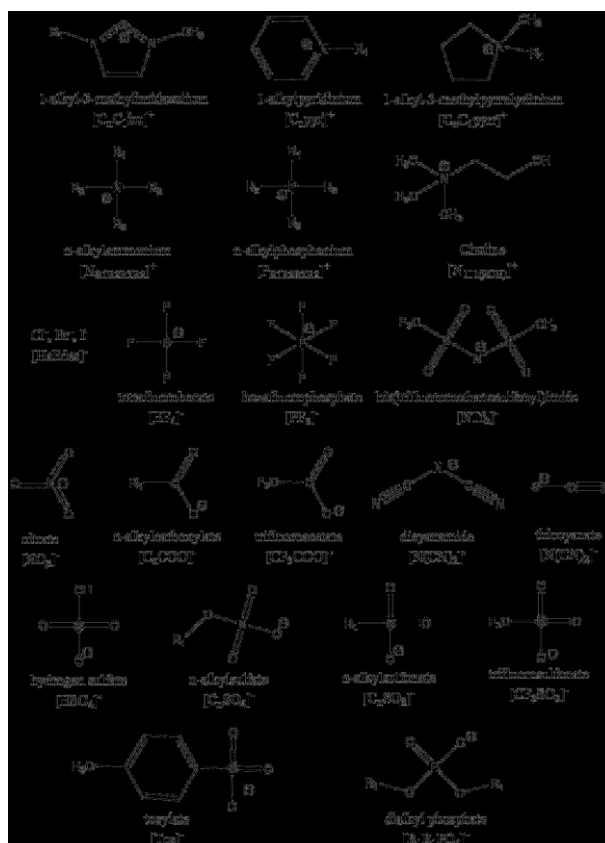
235 **3. Room temperature ILs as reaction medium**

236 **3.1. Overview**

237 Room temperature ILs are a class of solvents consisting of organic cations and organic or inorganic
238 anions with melting points below 100°C (Earle & Seddon, 2000). Due to their unique physical and
239 chemical properties, ILs have generated considerable scientific interest over the last 20 years. In this
240 section, solvation interactions within ILs are discussed prior to a more detailed assessment of ILs for
241 the recovery of metals from WEEE with special emphasis on hydrometallurgical processes. The
242 discussion is limited to second and third generation ILs and will not cover ILs based on chloroaluminate
243 anions.

244 The majority of chemical reactions occur in solution, with the solvent properties influencing its
245 suitability as a reaction medium. ILs are solvents composed exclusively of ions and as such their
246 solvation behaviour differs from that of neutral molecular solvents (hexane, acetone, DMSO, etc) and
247 aqueous, or partially ionized, solvents. ILs (generally) consist of large asymmetrical cations and simple
248 coordinating anions. The low degree of packing efficiency, induced by the size and lack of symmetry
249 of the cation, in conjunction with a lower cationic (and occasionally anionic) charge density, caused by
250 delocalization of the partial charge over the whole ion, drastically reduces the lattice energy of the salt
251 resulting in lower melting points (Seddon, 1997). This low melting point distinguishes ILs from
252 conventional molten salts like molten sodium chloride ($T_m \geq 801$ °C), which are characterised by a high
253 charge density and packing efficiency. Commonly used cations and anions for ILs and their
254 abbreviations are provided in Figure 4. For the sake of clarity and to enable meaningful comparisons
255 between different systems, ILs will be referred according to their structure and not their commercial
256 name. ILs comprised of the other anions listed in Figure 4 display varying degrees of hydrophobicity
257 depending on the cation's alkyl chain length. The hydrophobicity of an IL is of particular relevance for
258 its application as an extraction and separation media. It is important to state that all ILs are hygroscopic,
259 regardless of their hydrophobicity, and water may make up a significant molar percentage of an IL.

260



261
 262 **Figure 4.** Schematic of selected cations and anions from common ILs and DES and their abbreviations.

263
 264 Many solvent properties, including hydrophobicity, polarity and viscosity to name a few, are
 265 important to an IL's performance and applicability as a reaction medium. In ILs, these 'bulk properties'
 266 are altered by either varying the anion or the cation and this has led ILs to be labelled as 'designer
 267 solvents' (Freemantle, 1998; Huddleston et al., 2001). Many of these properties have been extensively
 268 reviewed elsewhere (Ohno, 2005; Koel et al., 2007; Endres et al., 2008, Freemantle, 2009; Hallet &
 269 Welton, 2011) and will not be discussed here.

270
 271 **3.2. Macroscopic solvation and extraction mechanisms**

272 In this section, a brief synopsis of the fundamental governing principles dictating metal-IL
 273 interaction and extraction is given, particularly as no new extraction mechanisms were reported
 274 compared to older existing work. For an in-depth analysis, the reader is referred to the review of Janssen
 275 et al. (2015). The overall solvation property of a system results from the sum of the possible solute-
 276 solvent interactions and depends on the cation and anion of the IL, as well as the solute. Charged
 277 complexes can be highly soluble in ILs, allowing for a wider range of metal speciation compared to
 278 molecular solvent in which generally only neutral complexes are soluble. The ionic nature of ILs results
 279 in metal extraction mechanisms from an aqueous phase that are not possible in conventional organic

280 solvents such as ion-exchange mechanisms involving ions of the IL, which can lead to the degradation
281 of the IL. Both charged and neutral metal complexes can be highly soluble in ILs (Jensen et al., 2002).
282 The most conclusive method for the determination of metallic species in IL is single-crystal XRD
283 analysis (Nockemann et al., 2010). However, due to the low vapour pressure and melting point of ILs,
284 acquisition of suitable crystal structure is often impossible and in-situ techniques are required. These
285 are reviewed by Abbott et al. (2008) and will only be listed here. The most widely used technique to
286 probe metallic complexes in ILs is extended X-ray absorption fine structure (EXAFS), with certain
287 studies also using Raman, UV-vis and FAB-MS spectroscopic techniques.

288 When discussing metal-IL interaction, a distinction must be made between positively and negatively
289 charge metal complexes. For positively charged metal complexes, typically the IL anion dictates the
290 chemistry of the system because it interacts with the generally more Lewis acidic metal solute. Anion
291 selection determines the Lewis acidity and coordination ability of an IL, with metal salts being poorly
292 soluble in ILs with strongly Lewis acidic/practically non-coordinating anions. Chloride, nitrate and
293 sulphate, are strongly Lewis basic/strongly coordinating anions whilst the fluorinated anions $[\text{BF}_4]^-$,
294 $[\text{PF}_6]^-$ and $[\text{NTf}_2]^-$ are acidic and only weakly coordinating (Wasserscheid & Welton, 2008). ILs
295 incorporating strongly coordinating anions exhibit significantly greater metal dissolution potential than
296 those with acidic anions (Abbott et al., 2005; Pereira et al., 2012). Complexation of the metal with the
297 IL anion controls the metal speciation and therefore its reactivity, solubility, redox potential and colour
298 (Abbott et al., 2011). The metal counter-anion also plays an important role in determining solubility in
299 a particular IL. The Hofmeister series (or the lyotropic series) provides a general indication of the
300 hydrophobicity of an anion. In ascending order, it reads: $[\text{SO}_4]^{2-} \leq \text{Cl}^- \leq \text{Br}^- \leq [\text{NO}_3]^- \leq \text{I}^- \leq [\text{ClO}_4]^- \leq$
301 $[\text{SCN}]^- \leq [\text{NTf}_2]^-$ and reflects the charge density and hydration numbers of the different anions (Dupont
302 et al., 2015). Metal salts containing hydrophilic anions of high charge density are unlikely to dissolve
303 in poorly coordinating hydrophobic ILs such as $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$. The solubility of inorganic salts in ILs
304 with a common anion is greatly improved, both for hydrophilic and hydrophobic anions (Pereira et al.,
305 2012).

306 In many cases, metal ions, including the precious metals present in WEEE, form negatively charged
307 complex species once dissolved in an acidic solution. For instance, Pt(IV) forms various
308 polychloroplatinate(IV) complexes such as $\text{PtCl}_5(\text{H}_2\text{O})^-$ or PtCl_6^{2-} in aqueous solutions of HCl. Pt(II),
309 Pd(II) and Rh(III) form similar polychlorometallate complexes, depending on the concentration of HCl
310 in water. In such cases, ILs are much more efficient at extracting these ions. Precious metals are
311 successfully extracted using undiluted ILs such as $[\text{C}_n\text{C}_1\text{im}][\text{NTf}_2]$ and their pyridinium or
312 pyrrolidinium homologues (Papaiconomou et al. 2012; 2013; 2014; 2015; Watanabe et al., 2015).
313 Functionalized ILs, also known as task specific ILs (TSILs), are ILs with an added functional group
314 covalently bonded to either the cation or anion which confer certain desired properties useful for
315 selective metal extraction (Fagnant et al, 2013). Derivatization of the IL cation to incorporate task-

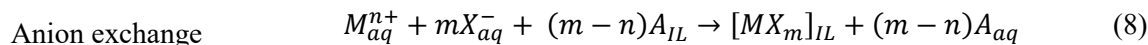
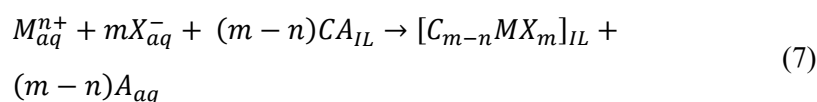
316 specific functionalities such as metal ligating groups provide an efficient way to maximise metal
 317 solvation (Visser et al., 2001). For example, substitution of the cationic alkyl chain in $[C_nC_{1im}][PF_6]$
 318 with either urea-, thiourea-, and thioether- alkyl groups can result in an increase in the extraction of
 319 Cd(II) from aqueous solution by several orders of magnitude (Visser et al., 2002).

320 Major developments in the use of ILs in solvent extraction can be divided into three main categories:
 321 ILs used as the diluting hydrophobic phase in conjunction with a traditional extractant; selective
 322 extraction of metals through IL anion interaction; and task specific ILs (Abbott et al., 2011).
 323 Electroneutrality is the governing principle behind the multiple potential extraction mechanisms in ILs
 324 as the net charge of the aqueous and IL phases must remain constant (Janssen et al., 2015). A brief
 325 overview of the potential extraction mechanisms for a metal cation (M^{n+}) from an aqueous solution
 326 containing an anion (X^-) to an IL phase (C^+ - IL cation; A^- - IL anion) containing a ligand (L or HL if
 327 protonated) is described in Table 3. A commonly used category of hydrophobic ILs in solvent extraction
 328 are those incorporating the $[NTf_2]^-$ anion. These ILs often require the addition of an extractant to
 329 increase the hydrophobicity of the metal complex to facilitate the extraction of a hydrated metal cations
 330 (Zhao et al., 2005). For example, many studies have reported enhanced extraction efficiency and
 331 selectivity for REEs on substitution of conventional organic diluents by hydrophobic ILs (Nakashima
 332 et al., 2004; Shimojo et al., 2008; Shen et al., 2011). The structure and abbreviation for the main
 333 extractants discussed in this work are presented in Figure 5.

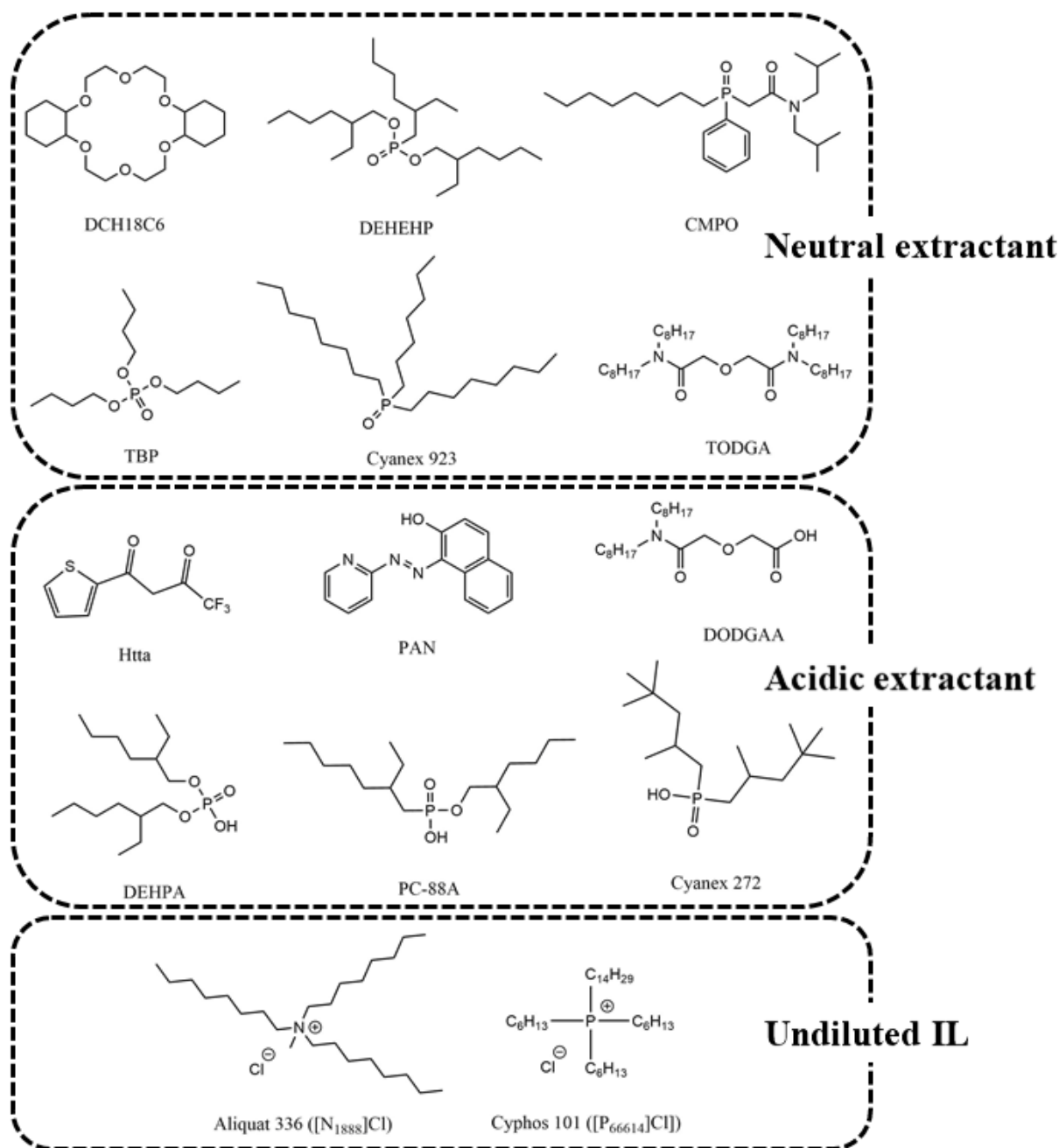
334

335 **Table 3.** Multiple extraction schemes for the transfer of metal cations from an aqueous phase to an IL
 336 phase.

Extraction mechanism	General extraction scheme	No.
ILs + extractants		
Neutral extraction	$M_{aq}^{n+} + nHL_{IL} \rightarrow [M \cdot (L)_n]_{IL} + nH_{aq}^+$	(1)
	$M_{aq}^{n+} + mL_{aq} + nX_{aq}^- \rightarrow [M \cdot (L)_m \cdot (X)_n]_{IL}$	(2)
Ion exchange	$M_{aq}^{n+} + mL_{aq} + nC_{IL}^+ \rightarrow [M \cdot (L)_m]_{IL}^{n+} + nC_{aq}^+$	(3)
	$M_{aq}^{n+} + (n + 1)HL_{aq} + [C][A]_{IL} \rightarrow [M \cdot (L)_{n+1}]_{IL}^- \cdots [C]_{IL}^+ + (n + 1)H_{aq}^+ + A_{aq}^-$	(4)
	$M_{aq}^{n+} + mL_{aq} + (n + 1)X_{aq}^- + [C][A]_{IL} \rightarrow [M \cdot (X)_{n+1} \cdot (L)_m]_{IL}^- \cdots [C]_{IL}^+ + A_{aq}^-$	(5)
Neat ILs		
Ion pair	$M_{aq}^{n+} + mX_{aq}^- + (m - n)C_{aq}^+ \rightarrow [C_{m-n}MX_m]_{IL}$	(6)



337



338

339 **Figure 5.** Schematic of selected neutral and acidic extractants and primary undiluted ILs presented in
 340 this work and their abbreviations.

341

342 These equations do not represent all potential extraction mechanisms in ILs but rather provide an
343 overview of the various extraction schemes possible whilst preserving electroneutrality. The extraction
344 mechanisms in solvent extraction systems with a ligand dissolved in the IL can be broadly divided into
345 two categories: neutral extraction and ion-exchange extraction. Neutral extraction can proceed through
346 the formation of a neutral metal-ligand complex either via deprotonation of the ligand (Ext. 1),
347 formation of a charge neutral complex with aqueous solution anions and extraction of a neutral metal-
348 cation/anion ion-pair (Ext. 2). For metal extraction proceeding through an ion exchange mechanism,
349 the IL cation is released to the aqueous phase to compensate for the incoming positive charge of the
350 metal complex (Ext. 3-5). In the case of TSILs, the functionalized component of the IL acts as the ligand
351 (Jensen et al., 2003). It is possible for multiple extraction mechanisms to co-exist within similar solvent
352 extraction systems. The factors determining the relative importance of an extraction scheme include
353 hydrophobicity of the IL cation (Jensen et al., 2002; Dietz et al., 2003) and anion (Jensen et al., 2003;
354 Luo et al., 2006) and the hydration energy of the aqueous metal complex (Garvey et al., 2012;
355 Wankowski & Dietz, 2016). The composition of the aqueous phase can also influence the extraction
356 efficiency for a particular solvent extraction. The water miscibility of four hydrophobic ILs was found
357 to increase with addition of the cations $\text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ and anions $[\text{ClO}_4]^- > \text{I}^- >$
358 $[\text{NO}_3]^- > \text{Cl}^- > \text{F}^- > [\text{SO}_4]^{2-}$ as predicted by the Hofmeister series (Dupont et al., 2015).

359 The most widely used solvent extraction systems involve use of either ion-exchange extractant
360 classified into acidic (eg. carboxylates, sulfonates, phosphates) and basic extractant (primary to
361 quaternary amines), solvating extractant (or neutral extractant) possessing ketone, ether, ester or alcohol
362 functional groups and/or coordinating extractant (or chelating extractant) (Free, 2013). These will be
363 discussed in the following section. Whilst a single extractant can often saturate the coordination sphere
364 of a metallic cation as well as produce a charge neutral and hydrophobic complex, on occasion a
365 combination of two extractants is required. If the resulting distribution ratio is greater for the combined
366 extractant than the sum for the individual extractants employed, the system benefits from a synergistic
367 extraction mechanism (Stepinski et al., 2005). In addition to increasing the extraction efficiencies,
368 synergistic extraction systems can also improve the separation factors between two different metals.
369 Such systems have been used effectively in conjunction with ILs, and the presence of two extractants
370 can result in a change of extraction mechanism compared to when the extractants are individually
371 employed (Zhu et al., 2015; Petrova, 2016).

372 In the case where no extractant is used and the metal ion forms negatively charged complex ions
373 with anions present in the aqueous phase, either originating from the acid used, or added on purpose in
374 the solution, the extraction mechanisms can be discussed in a similar way as that detailed above.
375 Because electroneutrality must be respected, two main possible extraction mechanisms, hydrophobic
376 ion pair formation or anion exchange, occur (Ext. schemes 6 to 8). In the case of the formation of
377 hydrophobic ion pairs, two versions exist in the literature, one using cations from the IL that are in the

378 IL phase, and another one using cations that are dissolved in the aqueous phase (Ext. 6 and 7).
379 Strikingly, even though anion exchange and ion pair formation were discussed as two distinct
380 mechanisms, most recent studies show that these are actually linked together because a hydrophobic
381 IL, as any salt, exhibits a limited, though non negligible, solubility in water. The typical solubility of
382 $[C_8C_1im][NTf_2]$ is around 10^{-3} mol.L⁻¹. In other terms, the solubility product of hydrophobic ILs is not
383 negligible (Chapeaux et al., 2007; Mazan et al., 2014). In an anion exchange mechanism, an anion of
384 the IL is transferred to the aqueous phase. Because the solubility of the IL is then exceeded, this
385 necessarily yields the transfer of an IL ion pair initially dissolved in the aqueous phase towards the IL
386 phase. This results as the co-extraction of a metal complex with a cation of the IL, that is, the formation
387 of a hydrophobic ion pair (Ext. 8).

388 In the following sections, the use of ILs at different stages of WEEE recycling is reviewed, with
389 particular emphasis on the use of ILs as solvents for leaching and liquid-liquid extraction processes.
390 The use of IL for the electro-deposition of metals has previously been reviewed by Abbott et al. (2006;
391 2011; 2013; Smith et al., 2014) and Endres et al. (2002; 2008) and will only be briefly addressed due to
392 the potential for IL-based solvents as a medium for the ‘one-pot’ leaching and deposition of metals. It
393 is important to note that not all reported studies use actual waste but often focus on simulated solutions
394 or mixtures containing a few elements. The use of ILs covered in this review is for the most part focused
395 on the recovery of value from PCBs, waste fluorescent phosphor, nickel metal hydride batteries and
396 permanent magnets. From the literature reviewed, optimised process flowsheets are proposed for these
397 wastes and are presented in Section 7.

398

399 **4. WEEE dismantling using ILs**

400 Current research on the use of ILs as WEEE dismantling agent is limited to the disassembly of
401 electrical components and epoxy resin from waste PCBs. PCBs are complex and challenging materials
402 due to their heterogeneous nature. PCBs are comprised of either: (1) an epoxy resin-based plastic
403 reinforced with glass fibres coated with a copper layer (FR-4 type PCB) or (2) a single layer of fibreglass
404 or cellulose paper and phenolic resins coated with a copper layer (FR-2 type PCB). The resin board is
405 overlaid with microelectronic components such as semiconductor chips and capacitors plus solder,
406 which is a Pb-Sn alloy (Zeng et al., 2013; Zhu et al., 2012c).

407 Previous research focused on the separation of the electrical components from the waste PCBs and/or
408 dissolution of the epoxy resin using the water soluble ILs $[C_2C_1im][BF_4]$ and $[C_4C_1im][BF_4]$. Separation
409 of the electrical components from waste PCBs relies on the high thermal stability of the IL used. The
410 welding point temperature for Pb and Pb-free solders is 215 °C (Zeng et al., 2013). By heating PCB
411 chips in the IL at 240 to 250 °C for 10 to 30 minutes, at 45 to 150 rpm, the solder was melted and
412 recovered from the board along with the previously attached electrical components. Under these

413 conditions, over 90 wt.% of the electronic components were separated from the PCBs and XRD analysis
 414 of the recovered solder indicates no structural changes (Zhu et al., 2012b; Zhu et al., 2012c; Zeng et al.,
 415 2013). The IL can be successfully recycled, and cost analysis of the process indicates that the process
 416 becomes financially viable for waste PCB amounts over 3 kt (Zeng et al., 2013). Heating of the bare
 417 board in [C₂C₁im][BF₄] for 10 minutes results in the complete dissolution of the polymeric materials
 418 and the delamination of the glass and copper foils. H¹-NMR analysis indicates that H-bond formation
 419 plays an important role in the dissolution of the bromine epoxy resins by [C₂C₁im][BF₄]. The IL was
 420 successfully regenerated by the addition of water, resulting in the formation of a precipitate which was
 421 confirmed as bromine epoxy resin by FTIR (Zhu et al., 2012a; Zhu et al., 2012c).

422

423 5. ILs in leaching and recovery applications

424 In this section, several methods for leaching metal ions and recovering them under a solid form
 425 (either as oxide or salts) will be detailed. The methods presented here will not deal with liquid-liquid
 426 extraction. The dissolution of metals and metal salts is the first step in hydrometallurgical processes
 427 (Figure 1). The state of elements in WEEE is diverse, with elements present as elemental metals, oxides,
 428 sulphates, phosphates, carbonates and others. The selection of an appropriate leaching agent depends
 429 on the waste matrix and value of the final product and should effectively act as a concentrating step by
 430 only selectively solubilising elements of interest prior to further separation and recovery steps. Selection
 431 of a suitable leaching medium can help reduce the complexity and number of downstream processing
 432 steps. Research on metal dissolution using unconventional solvents based on ILs has focused on DES
 433 and ILs incorporating Brønsted acidic functional groups and/or ILs based on strongly Lewis basic
 434 anions. However, some metal oxides including Ag₂O, NiO, CuO and ZnO were found to dissolve in
 435 imidazolium-based ILs with a hydrogen atom in the C² position of the imidazolium ring through the
 436 formation of carbene complexes (Wellens et al., 2014b). Selected example of IL used in leaching and
 437 recovery applications are summarised in Table 4.

438

439 **Table 4.** Selected example of ILs used in leaching and recovery applications of metals from WEEE and
 440 ores.

Waste matrix	Metals investigated	Ionic liquid / oxidant	Reference
Electric arc furnace dust	ZnO, PbO, Fe ₂ O ₃ , Al ₂ O ₃	[N _{111(20H)}]Cl:urea	Abbott et al. (2009)
Brass ash	ZnO, CuO, Cu ⁰	<u>IL</u> : [C ₄ C ₁ im][HSO ₄] <u>Oxidant</u> : H ₂ O ₂ or KHSO ₅	Kilicarslan et al. (2014)

Metals and alloys	Fe ⁰ , Cu ⁰ , In ⁰ , Zn ⁰ , Ga ⁰ , Sb ⁰ , Au ⁰ , Pt ⁰ , Ge ⁰ , Ta ⁰ , Sm ⁰ , Dy ⁰ , GaAs, InAs	[P ₄₄₄₁₄][Cl ₃]	Li et al. (2018)
Ore	Sulfidic ore containing Au, Ag, Cu, Zn, Fe, Pb	<u>IL</u> : [C ₄ C ₁ im][HSO ₄] w/ thiourea <u>Oxidant</u> : Fe ₂ (SO ₄) ₃	Whitehead et al (2004a)
Sulfidic ore / synthetic oxide ore	CuFeS ₂ , FeS ₂ , ZnS / SiO ₂ , CaSO ₄ , Fe ₂ O ₃ , Al ₂ O ₃ , MnO ₂ , TiO ₂ , AuO, AgO	<u>IL</u> : [C ₄ C ₁ im][X] (X = Cl ⁻ , [C ₁ SO ₃] ⁻ , [SCN] ⁻ , [HSO ₄] ⁻) w./ thiourea <u>Oxidant</u> : Fe ₂ (SO ₄) ₃	Whitehead et al. (2007)
Ore	Sulfidic ore containing Au, Ag, Cu, Zn, Fe, Pb	<u>IL</u> : [C ₄ C ₁ im][X] (X = Cl ⁻ , [HSO ₄] ⁻) w./ thiourea, chloride, bromide or iodide <u>Oxidant</u> : Fe ₂ (SO ₄) ₃ or KHSO ₅	Whitehead et al. (2009)
Ore	CuFeS ₂ , FeS ₂ , ZnFeS	<u>IL</u> : [C ₄ C ₁ im][HSO ₄] <u>Oxidant</u> : H ₂ O ₂	Dong et al. (2009)
Fluoride ore / synthetic ore	RECO ₃ F, RE ₂ O ₃ , RE ₂ (CO ₃) ₃	[N _{111(2(OH))}][NTf ₂] in [C ₄ C ₁ im][NTf ₂]	Freiderich et al. (2015)
Synthetic ore	Cu-Zn powder and crushed Ga-As wafer	<u>IL</u> : [N _{111(2OH)}]Cl:EG (1:2) <u>Oxidant</u> : Iodine	Abbott et al. (2015)
Ore	Sulfidic ore containing Au, Ag, Te, Fe	<u>IL</u> : [N _{111(2OH)}]Cl:EG (1:2) <u>Oxidant</u> : Iodine	Jenkin et al. (2016)
Ore	Chalcopyrite	<u>IL</u> : [C _n C ₁ im][HSO ₄] (n=1,4) <u>Oxidant</u> : O ₂	Carlesi et al. (2016)
Ore	Bauxite ore containing REE(III), Ti(IV), Si(IV), Al(III), Fe(III), Ca(II)	[N _{111(2(O)OH)}][NTf ₂]	Davris et al. (2016)
Ore	Pyrite, arsenopyrite	[N _{111(2OH)}]Cl:EG (1:2)	Abbott et al. (2017)
PCB	Cu ⁰	<u>IL</u> : [C ₄ C ₁ im][HSO ₄] <u>Oxidant</u> : H ₂ O ₂	Huang et al. (2014)
PCB	Cu ⁰ , Zn ⁰ , Pb ⁰	<u>IL</u> : [(C ₄ SO ₃ H)C ₁ im][X] (X = [OTf] ⁻ , [HSO ₄] ⁻), [C _n C ₁ im][HSO ₄] (n = 1, 4) <u>Oxidant</u> : H ₂ O ₂	Chen et al. (2015a,b,c)
PCB	Cu ⁰	<u>IL</u> : [(SO ₃ H)C ₄ pyr][HSO ₄] <u>Oxidant</u> : O ₃	Zhang et al. (2018)
NdFeB magnets	Nd ₂ O ₃ , Dy ₂ O ₃ , CoO, Fe ₂ O ₃	[N _{111(2(O)OH)}][NTf ₂]	Dupont & Binnemans (2015a)
NdFeB magnets	CoO, Fe ₂ O ₃ , B ₂ O ₃ , Nd ₂ O ₃ , Dy ₂ O ₃ , Pr ₂ O ₃ , Gd ₂ O ₃	[N _{111(2OH)}]Cl:lactic acid (1:2)	Riaño et al. (2017)
Synthetic phosphor mix	Y ₂ O ₃ :Eu ³⁺ (YOX), (Sr,Ca) ₁₀ (PO ₄) ₆ (Cl,F) ₂ :Sb ³⁺ , Mn ²⁺ (HALO)	[N _{111(2(O)OH)}][NTf ₂]	Dupont & Binnemans (2015b)

Synthetic phosphor mix & oxides	CuO, NiO, ZnO, MnO, MnO ₂ , Co ₃ O ₄ , Fe ₂ O ₃ , La ₂ O ₃ , Nd ₂ O ₃ , Dy ₂ O ₃ LaPO ₄ :Ce ³⁺ , Tb ³⁺ (LAP) BaMgAl ₁₀ O ₁₇ (BAM)	[N _{R1R2(H-SO3H)}][NTf ₂]	Dupont et al. (2016b)
Waste phosphor	Y ₂ O ₃ :Eu ³⁺ (YOX), (Sr,Ca) ₁₀ (PO ₄) ₆ (Cl,F) ₂ :Sb ³⁺ , Mn ²⁺ (HALO)	[C ₆ C _{1im}][HSO ₄]	Schaeffer et al. (2017)
Crude In(OH) ₃	In(III), As(V), Ca(II), Cd(II), Fe(III), Pb(II), Zn(II), trace elements	[N _{111(2(O)OH)}][NTf ₂]	Deferm et al. (2018)

441 RE – rare earth, EG – ethylene glycol,

442

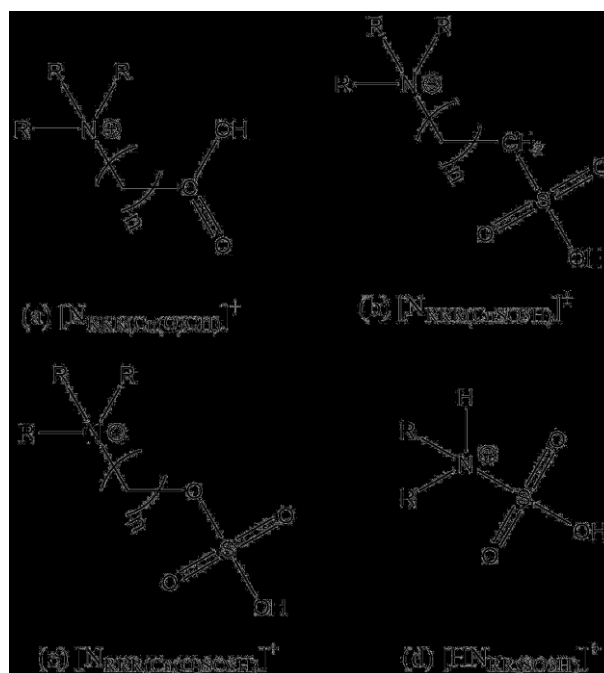
443 5.1. Cation mediated leaching

444 Many metal salts are insoluble in common hydrophobic ILs due to the hydrophilic nature of the
445 metallic cation and the weakly coordinating nature of the anion; metals and metal oxides are only
446 generally soluble in strong acidic or alkali aqueous solutions. First synthesised by Nockemann et al.
447 (2006), [N_{R11(2(O)OH)}][NTf₂] (R - imidazolium, pyridinium, pyrrolidinium, piperidinium, morpholinium,
448 and quaternary ammonium) are a group of betaine-based TSIL bearing a carboxyl group capable of
449 selectively solubilising REO, UO₂, ZnO, CdO, HgO, NiO, CuO, PdO, PbO, MnO, Ag₂O and some
450 metal hydroxides. Insoluble or very poorly soluble oxides are Fe₂O₃, CoO, Al₂O₃ and SiO₂ (Nockemann
451 et al., 2008a). The solubility of metal oxides in [N_{R11(2(O)OH)}][NTf₂] is high due to the formation IL-RE
452 stoichiometric compounds as indicated by single crystal XRD studies (Nockemann et al., 2008b;
453 Nockemann et al., 2009). Another interesting property of [N_{111(2(O)OH)}][NTf₂] is the presence of an upper
454 critical solution temperature (UCST) for the binary mixture of [N_{111(2(O)OH)}][NTf₂]/H₂O (Nockemann et
455 al., 2006). ILs with an UCST are said to exhibit thermomorphic behaviour, with the two immiscible
456 phases forming one homogeneous phases above the UCST. A two-phase system is re-established by
457 lowering the solution temperature to below the UCST. ¹H-NMR investigation attributes the presence of
458 a UCST to the temperature-dependent hydration and hydrogen-bond formation between the carboxylic
459 group of the [N_{111(2(O)OH)}]⁺ cation and the nitrogen atom of the [NTf₂]⁻ anion (Nockemann et al., 2008a).
460 Conditions above the UCST reduce the viscosity of the solution and accelerate mass transfer, resulting
461 in higher extraction efficiencies. Extracted metals were stripped from [N_{111(2(O)OH)}][NTf₂] by contacting
462 with an acidic aqueous solution, allowing the IL to be recycled for reuse.

463 The thermomorphic properties of [N_{111(2(O)OH)}][NTf₂] were used for the recovery of Nd₂O₃, Dy₂O₃
464 and CoO from waste NdFeB magnets in a combined leaching-extraction step (Dupont & Binnemans,
465 2015a). After roasting in a microwave, waste NdFeB magnets were leached at 80°C in a
466 [N_{111(2(O)OH)}][NTf₂]-H₂O solution. The leach solution was cooled and returned to a biphasic system
467 whereby the REE and Co were distributed in the aqueous phase whilst Fe remained in the IL phase.

468 Addition of oxalic acid to the solution precipitated the REE and Co while transferring Fe to the aqueous
469 phase as a soluble oxalate complex. The REEs and Co were separated by selectively leaching Co from
470 the oxalate precipitate using aqueous ammonia before calcining the RE oxalate to yield a 99.9 % pure
471 Nd_2O_3 and Dy_2O_3 mix. Dupont and Binnemans (2015b) also used $[\text{N}_{111(2(\text{O})\text{OH})}][\text{NTf}_2]$ for the recovery
472 of yttrium and europium oxide from simulated waste phosphor powder yielding a 99.9% pure final
473 $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ product after oxalate precipitation and calcination. The water content of the TSIL played a
474 crucial role in the effectiveness and selectivity of the leaching process. Under water-poor conditions
475 (<5 wt.% H_2O in the IL) YOX phosphor dissolves much more than HALO phosphor, but YOX leaching
476 efficiency also decreases with decreasing IL water content. The leaching selectivity of water-poor
477 $[\text{N}_{111(2(\text{O})\text{OH})}][\text{NTf}_2]$ was attributed to the inability of the IL to solvate anions due to the lack of suitable
478 coordination mechanisms. As the dissolution of oxides generates no anions, YOX phosphor easily
479 dissolves in $[\text{N}_{111(2(\text{O})\text{OH})}][\text{NTf}_2]$ whilst the phosphate and chloride metal salt of HALO phosphor do not.
480 The selectivity of $[\text{N}_{111(2(\text{O})\text{OH})}][\text{NTf}_2]$ for REEs was also exploited for their recovery from bauxite
481 residue containing the impurities Ti(IV), Si(IV), Al(III), Fe(III) and Ca(II) (Davris et al., 2016). In
482 addition, $[\text{N}_{111(2(\text{O})\text{OH})}][\text{NTf}_2]$ was shown to be an effective leaching agent for the purification of the
483 critical element In(III) (Deferm et al., 2018). At the optimal conditions of 3 hrs leaching time at 80°C
484 in a 1:1 $[\text{N}_{111(2(\text{O})\text{OH})}][\text{NTf}_2]:\text{H}_2\text{O}$ mixture, 99 wt.% of $\text{In}(\text{OH})_3$ was leached and separated ($D > 100$)
485 from Al(III), Ca(II), Cd(II), Ni(II) and Zn(II). Additional pre-hydrolysis and hydrolysis steps including
486 the reduction of Fe(III) to Fe(II) were required to separate In(III) from the co-extracted Fe(III), As(V)
487 and Pb(II). MgCl_2 was added as a salting-out agent to minimise the loss of the hydrophilic cation to
488 aqueous phase during extraction but its addition was found to negatively impact the separation of In(III)
489 from the other elements suggesting a compromise is required.

490



491

492 **Figure 6.** Structures of Brønsted acidic TSIL-derived from (a) betaine, (b) sulfonic acid, (c) sulfuric
 493 acid and (d) sulfamic acid.

494

495 Three groups of zwitterionic, strongly Brønsted acidic TSILs with functionalized cations
 496 incorporating sulfonic acid groups ($pK_a \sim -2.0$), alkylsulfuric acid groups ($pK_a \sim -3.5$) and sulfamic
 497 acid groups ($pK_a \sim 2.0$) can solubilise large stoichiometric amounts for a wide range of metal oxides
 498 (Dupont et al., 2015; Dupont et al., 2016a, Dupont et al., 2016b). The general structure for these cations
 499 is presented in Figure 6. This includes the inert oxides CoO , Co_3O_4 , Fe_2O_3 , TiO_2 , Al_2O_3 , Cr_2O_3 and
 500 WO_3 , which were not previously soluble in $[N_{111(2(O)OH)}][NTf_2]$. A 40 wt.% solution of the sulfamic IL
 501 $[HN_{22(SO_3H)}][NTf_2]$ diluted in $[C_2C_{1im}]Cl$ was able to leach over 90 wt.% of the notoriously inert
 502 fluorescent lamp phosphors $LaPO_4:Ce^{3+}, Tb^{3+}$ (LAP) and $BaMgAl_{10}O_{17}$ (BAM) (Dupont et al., 2016b).
 503 The natural hydrophilicity of ILs incorporating these polar and very acidic functional groups was
 504 overcome by using long alkyl chains in combination with the $[NTf_2]$ anion. Alkylsulfuric and sulfamic
 505 ILs with cationic alkyl chains shorter than $n=3$ were found to be fully miscible in water. Alkyl chains
 506 containing 6 or more carbons were required to compensate for the greater hydrophilicity of the sulfonic
 507 group. Interestingly, sulfonic and alkylsulfuric IL with short alkyl chains were shown to form aqueous
 508 biphasic system in the presence of sulfuric acid and NaCl respectively. Similarly to $[N_{111(2(O)OH)}][NTf_2]$,
 509 metal extraction in these super-acidic TSIL with long alkyl chains is controlled by a proton exchange
 510 mechanism and is therefore pH sensitive. As the acidic proton is exchanged for the metal ion, the
 511 electronic balance is maintained, and extraction occurs generally without transfer of IL cations or anions
 512 to the water phase. Comparison of hydrophobic sulfonic and alkylsulfuric IL metal extraction shows
 513 that the extraction efficiency of the latter is intermediate between carboxyl-functionalized ILs such as

514 [N_{111(2(O)OH)}][NTf₂] (poor extraction for most metal ions), and sulfonic acid ILs which fully extract most
515 studied metal ions from chloride solutions (>80%) (Dupont et al., 2016a). This trend follows the
516 functional group charge density R-COO⁻ < R-OSO₃⁻ < R-SO₃⁻. Interestingly in these systems, RE ions
517 are extracted in the reverse order (La(III) > Nd(III) > Dy(III) > Lu(III)) than the one expected based on
518 their charge density. This is attributed to the sterical hindrance from the functional groups and long
519 alkyl side chains which causes REEs with smaller radius to be less efficiently coordinated (Dupont et
520 al., 2015). The doubly acidic task-specific pyridinium-based IL incorporating a sulfonic acid moiety
521 [(SO₃H)C₄pyr][HSO₄] was used to replace H₂SO₄ in a slurry electrolytic system for the one step
522 leaching and recovery of Cu(II) from waste PCBs (Zhang et al., 2018). A 20% increase in Cu(II)
523 recovery to 90.9 wt.% was obtained when 10% H₂SO₄ was replaced by [(SO₃H)C₄pyr][HSO₄].
524 However, a further increase in the IL concentration to 40 wt.% resulted in the decrease in the Cu(II)
525 recovery rate and current efficiency due to the increase in solution viscosity. In addition, lower quality
526 deposits were obtained at these high concentrations due to the strong competitive absorption of the IL
527 cation at the cathode inhibiting deposition. The deposit was identified as a mixture of Cu⁰, CuO and
528 Cu₂O for a 10 wt.% concentration of [(SO₃H)C₄pyr][HSO₄] with H₂SO₄ and O₃ as oxidant.

529 Although the hydrophobic IL trihexyl(tetradecyl)phosphonium chloride ([P₆₆₆₁₄][Cl]) is insoluble in
530 water, [P₆₆₆₁₄][Cl] can adsorb up to 13.5 wt.% of water at room temperature. [P₆₆₆₁₄][Cl] saturated with
531 concentrated HCl was used to dissolve CaO, NiO, MnO, CoO, CuO, ZnO and Fe₂O₃. Addition of HCl
532 resulted in a large decrease in IL viscosity and allowed the solubilisation of metal oxides. UV-Vis
533 analysis indicated the presence of Ni(II), Cu(II), Fe(III), and Co(II) in [P₆₆₆₁₄][Cl] as anionic
534 tetrachlorometallate complexes, whilst Ca(II) is unable to form anionic complexes and remains as a
535 hydrated calcium ion. Separation of the solubilised elements using a stripping HCl solution was based
536 on the tendency of Ni(II) and Ca(II) to form aqua complexes regardless of HCl concentration and the
537 partial stripping of Co(II) and Mn(II) at low HCl concentrations. Ni(II) and Ca(II) were first stripped
538 using 6 M HCl before subsequent removal of Co and Mn from Fe, Zn and Cu by contacting the saturated
539 IL with a water and ammonia solution (Wellens et al., 2014a).

540

541 **5.2. Anion mediated leaching**

542 [HSO₄]⁻-based IL including [C₄C₁im][HSO₄] were successfully used to recover Cu from waste
543 PCBs (Huang et al., 2014) and chalcopyrite ore (Dong et al., 2009; Chen et al., 2015a), Cu and Zn from
544 brass ash (Kilicarslan et al., 2014), leaching of Au, Ag, Cu and base metals from ores (Whitehead et al.,
545 2004a; Whitehead et al., 2007; Whitehead et al., 2009) and YOX phosphor from waste fluorescent tubes
546 (Schaeffer et al., 2017).

547 The recovery of yttrium europium oxide from waste fluorescent tube phosphor by a simple efficient
548 low-cost IL process was developed using [C₄C₁im][HSO₄] (Schaeffer et al., 2017). The waste phosphor

549 containing Y(III), Eu(III), Tb(III), La(III) and Gd(III) was first pre-treated to concentrate its rare earth
550 content. Larger glass particles were removed by sieving through a 25 μm sieve whilst soluble Ca(II),
551 Ba(II), Sr(II) were partially removed by contacting the phosphor with a dilute HCl solution for 1hr.
552 Leaching of REEs was optimised by systematically varying the leaching temperature, the
553 $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]:\text{H}_2\text{O}$ ratio, leaching time and solid to liquid ratio. Under the optimised conditions of
554 1:1 wt. $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]:\text{H}_2\text{O}$ solution, a solid:liquid ratio of 5%, a mixing speed of 300 rpm, a leaching
555 temperature of 80°C and leaching time of 4 h, the percentage of Y, Eu and Ca leached is 91.6wt.%,
556 97.7wt.% and 24.9wt.%, respectively. The low leaching efficiency of Tb(III), La(III) and Gd(III)
557 compared to Y(III) and Eu(III) is due to the former being as highly stable phosphate salts whilst the
558 latter are found as oxides. The REEs in the leachate were precipitated by the addition of oxalic acid at
559 a molar ratio (OA:REE) of 1.5 and a solution pH of 0.9. Luminescence analysis of the recovered oxide
560 product after calcination indicates that the recovered yttrium europium oxide has the potential to be
561 directly reused as YOX phosphor. The stability and recyclability of the IL was demonstrated over four
562 leaching/precipitation cycles.

563 A recent comparison of six ILs incorporating $[\text{HSO}_4]^-$ and $[\text{CF}_3\text{SO}_3]^-$ on the leaching efficiency of
564 Cu, Zn and Pb respectively from waste PCBs found that greater leaching efficiency could be achieved
565 using $[\text{HSO}_4]^-$ and that inclusion of an acidic group on the alkyl chain of the cation increased Cu and
566 Zn leaching (Chen et al., 2015a; Chen et al., 2015b). Leaching results indicate that all six IL acids could
567 successfully recover Cu and Zn under the test conditions with almost 100 wt.% recovery except for
568 $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$. Kinetic analysis of the dissolution process using the shrinking core set of equations
569 indicates that in the case of Cu and Zn dissolution by $[\text{HSO}_4]^-$ and $[\text{CF}_3\text{SO}_3]^-$ ILs, the reaction rate is
570 controlled by diffusion processes and not by the surface chemical reaction. However, the study of Pb is
571 of minimal interest because of the aqueous insolubility of PbSO_4 , with little to no recovery recorded for
572 the $[\text{HSO}_4]^-$ and $[\text{CF}_3\text{SO}_3]^-$ ILs tested (Chen et al., 2015c). Quantitative Cu extraction from waste PCBs
573 using $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ was also achieved under the leach conditions: 1 g PCB powder (particle size of
574 0.1–0.25 mm), 25 mL 80% (v/v) $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, 10 mL 30 wt.% H_2O_2 , solid: liquid ratio of 1:25,
575 70°C and 2 hours. Kinetic analysis of the leaching process determined that this was diffusion controlled
576 with an activation energy of 25.4 $\text{kJ}\cdot\text{mol}^{-1}$ (Huang et al., 2014). None of these cited studies investigated
577 the concomitant leaching of other elements or the recovery of Cu once in solution despite the interesting
578 work of Zhang and Hua, which extensively studied the deposition of Zn (Zhang & Hua, 2009; Zhang
579 et al., 2009a; Zhang & Hua, 2011; Zhang & Hua, 2012) and Cu (Zhang et al., 2009b) from aqueous
580 sulphate solutions with $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ or $[\text{N}_{4444}][\text{HSO}_4]$ (Zhang et al., 2015) as additives. Both ILs
581 were found to inhibit electro-reduction, leading to finer and more levelled deposits. In contrast,
582 dissolved ZnO in $[\text{C}_1\text{C}_1\text{im}][\text{CF}_3\text{SO}_3]$ was recovered by electro-deposition, with high current efficiencies
583 both in neat and aqueous IL solutions. FTIR and Raman spectroscopy indicated that Zn(II) is stabilised
584 by 1-methylimidazole rather than the IL anion (Liu et al., 2015).

585 Many of the species of interest are present in their elemental form and must be oxidised prior to
586 solubilisation. The solubility of oxygen in ILs is of crucial interest as it may determine the leaching rate
587 and efficiency. The solubility of oxygen in neat imidazolium-based IL with $[\text{HSO}_4]^-$ anion is similar or
588 even superior to that in water, decreases with increasing temperature, and is anion dependent. Larger
589 anion-cation pairings leave larger 'holes' appropriate for oxygen residency compared to more compact
590 ion-pairings. In addition, dipolar interactions between oxygen and the IL anion, influenced by the shape
591 and surface charge density on the anion, are also likely to result in increased oxygen solubility
592 (Whitehead et al., 2007). Common oxidants used with $[\text{C}_n\text{C}_1\text{im}][\text{HSO}_4]$ include hydrogen peroxide
593 (H_2O_2), potassium peroxydisulfate (KHSO_5) and Fe(III). Iron(III) is a mild oxidant and unlikely to
594 affect the stability of the IL. However, none of the reported studies using $[\text{C}_n\text{C}_1\text{im}][\text{HSO}_4]$ as lixiviant
595 have investigated the potential denaturalization of the IL after a leaching cycle in the presence of strong
596 oxidants such as H_2O_2 . Results from previous research suggest that $[\text{C}_n\text{C}_1\text{im}][\text{HSO}_4]$ is readily degraded
597 by H_2O_2 (Domínguez et al., 2014). The length of the alkyl chain has a dramatic effect on the stability
598 of imidazolium-based ILs to degradation by stoichiometric amounts of H_2O_2 , with greater resistance
599 conferred by longer alkyl chains. Furthermore, ILs bearing methanesulfonate and methylsulfate anions
600 are oxidised faster than those with chloride or acetate anions. A compromise between metal extraction
601 and IL recovery is required under such circumstances

602 An innovative class of ILs containing trichloride anions (Cl_3^-) with oxidative properties capable of
603 releasing chlorine was synthesised by bringing chlorine gas into contact with the corresponding chloride
604 (Cl^-) ILs at room temperature (Li et al., 2018). These were prepared with a range of cations with no
605 degradation of the latter observed. An additional benefit from the conversion of the IL anion Cl^- to Cl_3^-
606 is the accompanying reduction in the IL viscosity due to the lower electrostatic attraction between the
607 cation and the Cl_3^- ion. Taking $[\text{P}_{44414}]\text{Cl}_3$ as a representative IL, dissolution experiments were
608 performed for 12 metals and 2 alloys in solutions at 25 °C containing molar ratio of metal:IL of 1:8.
609 Whilst the dissolution time was found to greatly vary between metals tested, 8 metals commonly found
610 in WEEE Cu, Fe, In, Zn, Ga, Au, Ge and Sb along with the alloys InAs and GaAs could be dissolved
611 in the tested IL. EXAFS analysis revealed that these metals exist as anionic chloride complexes in the
612 IL.

613

614 **5.3. Deep eutectic solvents (DES) as leaching agents**

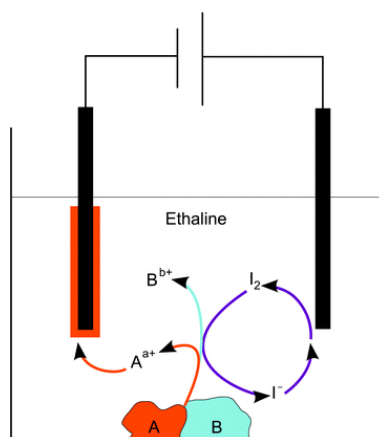
615 DES are usually composed of two chemicals, typically one hydrogen bond donor (HBD) and one
616 hydrogen bond acceptor (HBA), exhibiting high melting points. Once combined in specific
617 stoichiometric ratios, the mixture melts and forms a homogeneous liquid phase. The DES under
618 consideration in this review are those based on at least one IL homologues, namely a quaternary
619 ammonium salt, choline chloride ($[\text{N}_{111}(\text{2OH})]\text{Cl}$) being the most common, and a HBD such as urea,

620 carboxylic acids or polyols (Smith et al., 2014). DES exhibit unusual solvent properties that are
621 dependent on the selection of the HBD and HBA and their respective molar ratio. The considerable
622 attraction of DES stems from low synthesis cost, low environmental toxicity and solubility for a wide
623 range of metal oxides (Abbott et al., 2002; Abbott et al., 2004).

624 Metal oxide solubility in DES is influenced by the extent of H-bonding interactions, with compounds
625 able to donate or accept electrons or protons to form H-bonds displaying high solubility (Abbott et al.,
626 2002). The solubility of 17 metal oxides in the elemental mass series Ti through to Zn was reported,
627 with $[N_{111(2OH)}]Cl$:malonic acid displaying the greatest solubility for the tested elements after HCl
628 (Abbott et al., 2006). Most ionic transition metal oxides are soluble in DES whilst covalent metal oxides
629 such as SiO_2 and Al_2O_3 are insoluble in all tested DES to date. Judicious selection of an appropriate
630 HBD allows for the selective leaching of certain elements from a mixed oxide matrix. For example,
631 Fe_3O_4 is soluble and CuO insoluble in $[N_{111(2OH)}]Cl$:oxalic acid eutectic whilst the opposite behaviour
632 is observed when the HBD is changed to phenylpropionic acid (Abbott et al., 2004). Furthermore,
633 compounds that are known to form DES with choline chloride were successfully used for the leaching
634 of Mn, Li, Co, and Ni using either L-tartaric acid (He et al., 2017) and lactic acid (Li et al., 2017)
635 highlighting the untapped potential of DES as leaching agents. In addition to suitability for metal oxide
636 leaching, a growing number of studies employ DES as electrolytes for metal electro-deposition,
637 allowing for the development of a 'one pot' solvatometallurgical process. A large number of metals
638 including Zn, Ni, Cu, Co, Sn, Se, In, Sm, Pd, Fe, Ag and Pb were successfully deposited from DES
639 (Abbott et al., 2013; Smith et al., 2014; Zhang et al., 2016).

640 The establishment of a comparable electrochemical series for 17 redox couples referenced to the
641 $Fe(CN)_6^{3-/4-}$ couple in the DES $[N_{111(2OH)}]Cl$:urea and $[N_{111(2OH)}]Cl$:EG shows that some redox potentials
642 shift considerably in DESs compared to aqueous solution, particularly the oxophilic p-block elements
643 such as Ga and Sb, Cu and the chlorophilic late transition elements including Ag, Pd and Au. The high
644 chloride concentration in DES electrolytes acts as an environmentally benign stabilising ligand used to
645 adjust metal speciation, thereby controlling solubility and deposition properties, making DES excellent
646 separation and recovery media (Abbott et al., 2011b). The determination of the electrochemical series
647 served as the basis for the recovery of value from synthetic wastes matrices and ores (Abbott et al.,
648 2015; Jenkin et al., 2016). Iodine was selected as the electrocatalyst due to its fast electron transfer,
649 reversibility, high rates of mass transport, high solubility in DES, and environmental compatibility in
650 reduced form (Abbott et al., 2011b; Abbott et al., 2015). The redox potential of I_2/I^- in a $[N_{111(2OH)}]Cl$:EG
651 DES was found to be more positive than that of most common metals. The developed system depicted
652 in Figure 7 could oxidize Cu and Zn from 1:1 Cu-Zn powders, As and Ga from crushed Ga-As wafer
653 and Au and Ag from gold-bearing ores (Abbott et al., 2015, Jenkin et al., 2016).

654



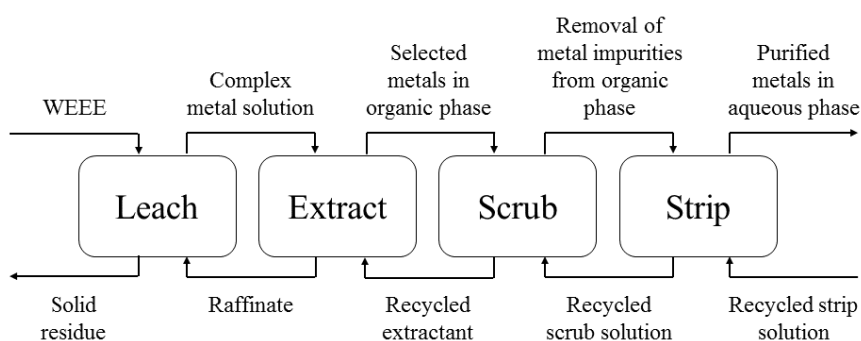
655
 656 **Figure 7.** Schematic diagram of the separation and recovery of two elements, A and B, using iodine
 657 as an electrocatalytic oxidation agent in $[N_{111}(20H)]Cl:EG$. Reproduced from Abbott et al. (2015) with
 658 permission from The Royal Society of Chemistry.

659

660 6. ILs in solvent extraction processing

661 Solvent extraction (or liquid-liquid extraction) is the favored option for metal separation and
 662 involves the preferential two-phase distribution of a solute between mutually immiscible liquid phases,
 663 usually consisting of an aqueous acidic solution and an aliphatic organic solvent. The ILs used in solvent
 664 extraction must be water immiscible to promote recovery of the metal and prevent the loss of the IL to
 665 the aqueous phase. Metal extraction from the aqueous phase results from the formation of hydrophobic
 666 M^{n+} -ligand complexes and their migration to the hydrophobic phase (Fray, 2000; Rydberg et al., 2004).
 667 A schematic of the typical process steps in the recovery of metals from leach solutions using solvent
 668 extraction is presented in Figure 8.

669



670
 671 **Figure 8.** Schematic of the typical process steps in the recovery of metals from leach solutions using
 672 solvent extraction.

673

674 This section is divided according to the application of the IL-based solvent, with a division being
675 made between traditional solvent extraction processes and more recent advances. First, the use of
676 undiluted IL acting as both the extractant and hydrophobic phase in traditional solvent extraction is
677 presented. Secondly, the application of IL as hydrophobic diluting phase in conjunction with neutral
678 and acidic extractant is discussed. Finally, the application of TSIL in solvent extraction for the recovery
679 of metals from WEEE is addressed. Following this review of more ‘traditional’ solvent extraction
680 processes, the use of IL-based aqueous biphasic system applied to WEEE valorisation is discussed as
681 well as the developing field of hydrophobic DES and triphasic IL-IL systems for the simultaneous
682 separation of different metal groups. Because of the large volume of publications on the topic, the
683 discussion will be limited to a selected number of extraction systems directly addressing the recovery
684 of metal from WEEE or the separation of critical metal groups relevant to recycling of WEEE. The
685 major studies involving the use of ILs in solvent extraction processes for the recovery of metals from
686 WEEE are summarised in Table 5.

687

688 **Table 5.** Reported IL used in solvent extraction processes for the recovery of metals from WEEE and
689 ores (NMHB – nickel metal hydride battery, FLP – fluorescent lamp phosphor).

Waste substrate	Elements recovered	Extractant	Diluent	Reference
Synthetic NMHB leach solution	Co, Ni, Fe, Mn, Zn, K, Mg, REE	(3) Cyanex 923 (4) [N ₁₈₈₈][SCN]	(1) [P ₆₆₆₁₄]Cl (2) [N ₁₈₈₈]Cl (3) [N ₁₈₈₈][NO ₃] (4) [N ₁₈₈₈]Cl	Larsson & Binnemans (2014)
Synthetic NMHB leach solution	Co, Ni, Fe, Mn, Zn, REE	Cyanex 923	[N ₁₈₈₈][NO ₃]	Larson & Binnemans (2015a)
Synthetic NdFeB and SmCo magnet leach solution	Nd, Sm	[(C _n COOH) _{C₁} im][NTf ₂]		Chen et al. (2015d)
NdFeB magnet	Pr, Nd, Dy	TBP	[N ₁₈₈₈][NO ₃]	Kikuchi et al. (2014)
NdFeB magnet	Nd, Dy, Co, Cu, Fe, Mn		[P ₆₆₆₁₄]Cl	Vander Hoogerstraete et al. (2014)
NdFeB magnet	Nd, Sm, Fe, Co		[P ₆₆₆₁₄][NO ₃]	Riaño & Binnemans (2015)
NdFeB magnet	Nd, Sm, Pr, Gd, Fe, Co, B	(1) [N ₁₈₈₈][SCN] (2) Cyanex 923	Toluene Toluene	Riaño et al. (2017)

Simulated FLP solution	REE	[N ₁₈₈₈][PC-88A] & [N ₁₈₈₈][DEHPA]		Yang et al. (2012)
FLP	La, Ce, Eu, Gd, Tb, Y	DODGAA	[C ₄ C ₁ im][NTf ₂]	Yang et al. (2013)
Commercial HALO phosphor	Sb, Ca		[N ₁₈₈₈]Cl	Dupont & Binnemans (2016)
Bastnäsite leach solution	Ce, F	DEHEHP	[C ₈ C ₁ im][PF ₆]	Zuo et al. (2009)
Bastnäsite and monazite	La, Ce, Nd, Th, Ca, Mn, Fe, Mg	[N ₄₄₄₄][DEHPA]	[EtNH ₃][NO ₃] / [C ₂ C ₁ im][SCN] / [C ₄ C ₁ im][BF ₄].	Azizi & Larachi (2018)
Salt Lake brine	Li, Mg	TBP	[C ₄ C ₁ im][NTf ₂]	Shi et al. (2016)
Bauxite residue	Sc, Fe, Ti, Si, Ca, Al		[N _{111(2(O)OH)]][NTf₂]}	Onghena et al. (2017a)

690

691 6.1. Undiluted ILs

692 Recent research on the application of ILs in solvent extraction has focused on simple IL extraction
693 systems without added complexing ligand. Hydrophobic ILs based on [NTf₂]⁻ and cation imidazolium,
694 pyrrolidinium or pyridinium have been shown to extract aqueous metal cations without the need for
695 additional ligands (Kozono & Ikeda, 2007). Regarding metals found in WEEE, these ILs were found
696 to be efficient at extracting precious metals such as Au(III), Pt(IV) or Ir(IV) from acidic aqueous
697 solutions containing large amounts of HCl (Génand-Pinaz et al., 2013; Papaiconomou et al., 2012 &
698 2014; Yang et al., 2014; Tong et al., 2015; Kubota et al., 2017). Furthermore, separation of Au(III) from
699 Pt(IV) and from Pt(IV) and Pd(II) is achieved using [C₄C₁im][NTf₂] and [C₈C₁im][NTf₂], respectively
700 (Papaiconomou et al., 2012; 2014).

701 Linear quaternary ammonium ILs and quaternary phosphonium ILs have also been extensively
702 studied and used in complete recycling processes of WEEE. ILs based on these cations and a wide
703 variety of anions including chloride, bromide, dicyanamide (Svecova 2015, Svecova 2016), nitrate,
704 dioctyl diglycolamate (Rout & Binnemans, 2014a), *N,N,N',N'*-tetra(2-ethylhexyl)malonate, *N,N,N',N'*-
705 tetra(2-ethylhexyl)malonamide (Rout & Binnemans, 2014b) or oleate (Parmentier et al., 2015a) were
706 studied. The hydrophobic fatty acid based IL tetraoctylphosphonium oleate ([P₈₈₈₈][C₁₇COO]) displays
707 a high affinity for first row transition metals in chloride media (Parmentier et al., 2015a) and was
708 employed in a continuous selective metal extraction process for the recovery of cobalt from two mixed
709 salt solutions (Co/Na, Ca/Co/K) (Parmentier et al., 2015b). The ammonium alternative to

710 [P₈₈₈₈][C₁₇COO], tetraoctylammonium oleate ([N₈₈₈₈][C₁₇COO]), was used in the solvent extraction of
711 Co(II), Ni(II) and Zn(II) with success. Comparison of Co(II), Ni(II) and Zn(II) extraction with the IL
712 as well as the IL precursors (sodium oleate and tetraoctylammonium chloride) indicates that Co(II) and
713 Ni(II) at low chloride concentration are extracted via the IL anion whilst Zn(II) can be extracted both
714 via the oleate anion and via the tetraoctylammonium cation of the IL. Slope analysis and EXAFS
715 measurements reveal that Ni(II) and Co(II) are extracted via the formation of [N₈₈₈₈⁺][M(C₁₇COO)₃⁻]
716 complexes with M being Co(II) or Ni(II). In contrast, Zn(II) was extracted via a different extraction
717 mechanism, in which the Zn(II) ion was extracted by two IL moieties as [N₈₈₈₈⁺]₂[MCl₂(C₁₇COO)₂²⁻]
718 (Parmentier et al., 2016). This example highlights the need to determine the dominant extraction
719 mechanisms as this can shed light on the higher distribution ratio for one metal compared to another.
720 Other interesting phosphonium- and ammonium-based ILs for the extraction of transition metals include
721 those containing a thiosalicylate or thiocyanate anion (Leyma et al., 2016; Rout & Binnemans, 2016).
722 The latter was used for the separation of transition metals from rare earth elements, a separation relevant
723 for the recycling of permanent magnets, nickel metal hydride batteries and lamp phosphors. The
724 extraction of metal ions from a chloride or nitrate solution with a thiocyanate IL is an example of “split-
725 anion extraction”, where different anions are present in the aqueous and IL phase. As per the Hofmeister
726 series, the [SCN]⁻ prefers the IL phase compared to the Cl⁻ and [NO₃]⁻ ions and does not exchange to
727 the aqueous phase, allowing it to preferentially coordinate the 3d transition metals.

728 Trihexyl(tetradecyl)phosphonium chloride ([P₆₆₆₁₄]Cl) is a commercially available, non-fluorinated
729 IL consisting of an organophosphorous-based cation with a chloride anion - *cf.* Figure 5. Due to the four
730 long alkyl chains, [P₆₆₆₁₄]Cl has no reported surfactant properties, in contrast to some of the shorter
731 alkyl chain quaternary phosphonium salts alternatives, thereby enhancing phase separation (Bradaric et
732 al., 2003). [P₆₆₆₁₄]Cl functions by an anion exchange mechanism; and it can be used undiluted,
733 eliminating the need for molecular solvents. The extraction experiments have primarily been conducted
734 from aqueous chloride medium. [P₆₆₆₁₄]Cl IL shows great promise for the extraction of metal ions and
735 has been studied for the extraction of Zn(II), Fe(II/III), Co(II) as well as REE(III), Au(III), Hg(II),
736 Pd(II), Pt(IV), Bi(III), Re(IV) and U(IV). For example [P₆₆₆₁₄]Cl, or [P₆₆₆₁₄]Br, extract almost
737 quantitatively Pd(II) and Pt(IV) from aqueous solutions of HCl (Papaiconomou et al., 2015; Kubota et
738 al., 2017). Distribution coefficients as high as 200 for Rh(III) are obtained in aqueous solution
739 containing 1 mol.L⁻¹ HCl, while Rh(III) remains preferentially in the aqueous phases when the
740 concentration of HCl exceeds 6 mol.L⁻¹ (Svecoca et al., 2016). Aliquat 336 ([N₁₈₈₈]Cl) is a well-
741 established quaternary ammonium extractant capable of extracting a range of metal ions through anion
742 exchange or formation of a neutral extraction complex (Černá et al., 1992).

743 [P₆₆₆₁₄]Cl and its nitrate derivative trihexyl(tetradecyl)phosphonium nitrate were employed in
744 separations relevant to the recycling of rare earths from permanent magnets and Co from Ni metal
745 hydride batteries. Wellens et al. (2012) demonstrated that Co(II) could be selectively separated from

746 Ni(II), Ca(II) and Mg(II) in 8 M HCl aqueous chloride concentration using [P₆₆₆₁₄]Cl with a separation
747 factor of ≥ 104 . Co was extracted as the tetrahedral tetrachlorocobaltate complex, [CoCl₄]²⁻. Co(II) was
748 separated from the co-extracted Mn(II) by four stripping cycles with water. [P₆₆₆₁₄]Cl was found to be
749 the best option as the IL phase compared to [N₁₈₈₈]Cl, [P₈₈₈₈]Br, [P₆₆₆₁₄]Br and [P₄₄₄₁₄]Cl as it is a
750 compromise between commercial availability, separation characteristics and ease to handle the IL. This
751 process has been up-scaled to provide a proof-of-principle for the continuous IL separation process of
752 Co(II) from Ni(II) (Wellens et al., 2013). A similarly high Co/Ni separation ratio was achieved using
753 [P₆₆₆₁₄]Cl from sulphate media with the extraction proceeding via a split-anion mechanism. Co(II)
754 present in the IL phase was stripped using water and the IL regenerated by contacting with CaCl₂
755 (Onghena et al., 2017b).

756 [P₆₆₆₁₄]Cl was also employed for the removal of Co(II) and Fe(III) from Sm(III) and Nd(III)
757 respectively in chloride solutions (Vander Hoogerstraete et al., 2013). Separation factors of 5.0×10^6
758 and 8.0×10^5 were obtained for Nd/Fe and Sm/Co respectively at HCl concentrations of 8.5-9 M. The
759 REE(III) remain in the aqueous phase while Co(II) and Fe(III) are extracted as anionic tetrachloro-
760 complexes in the IL. The distribution of Co(II), Mn(II) and Fe(III) to the IL increased with increasing
761 HCl concentration until 8.5-9 M while Zn(II) and Cu(II) decrease with increasing HCl concentrations.
762 However, Al(III), Cr(III), Ni(II), Mg(II), and Ca(II) could not be separated from REEs. After extraction,
763 Co was easily stripped from the IL with water although Fe could only be stripped by forming a water-
764 soluble iron complex with ethylenediaminetetraacetic acid (EDTA). Using the IL
765 trihexyl(tetradecyl)phosphonium nitrate, prepared from [P₆₆₆₁₄]Cl, REEs were separated from Co(II)
766 and Ni(II) (Vander Hoogerstraete & Binnemans, 2014). The separation of Sm(III) from Co(II) and
767 La(III) from Ni(II) were studied. Extraction of the REEs is facilitated by an inner salting-out effect of
768 a highly concentrated metal nitrate aqueous phase. After a scrubbing step using 7.5 M of NH₄NO₃, the
769 purity of REEs in the loaded IL phase was 99.9%. Complete stripping and regeneration of the IL was
770 achieved using pure water. Extraction of REE by [P₆₆₆₁₄][NO₃] from nitrate solution occurs by formation
771 of a neutral complex Ln(NO₃)_{3+n}(P₆₆₆₁₄)_n, while La and Sm exist as the anionic [La(NO₃)₆]³⁻ and
772 [Sm(NO₃)₆]³⁻ complexes in the IL. The high negative charge of the extracted complexes and the
773 resulting electrostatic interactions have a pronounced effect on the viscosity of the IL phase.

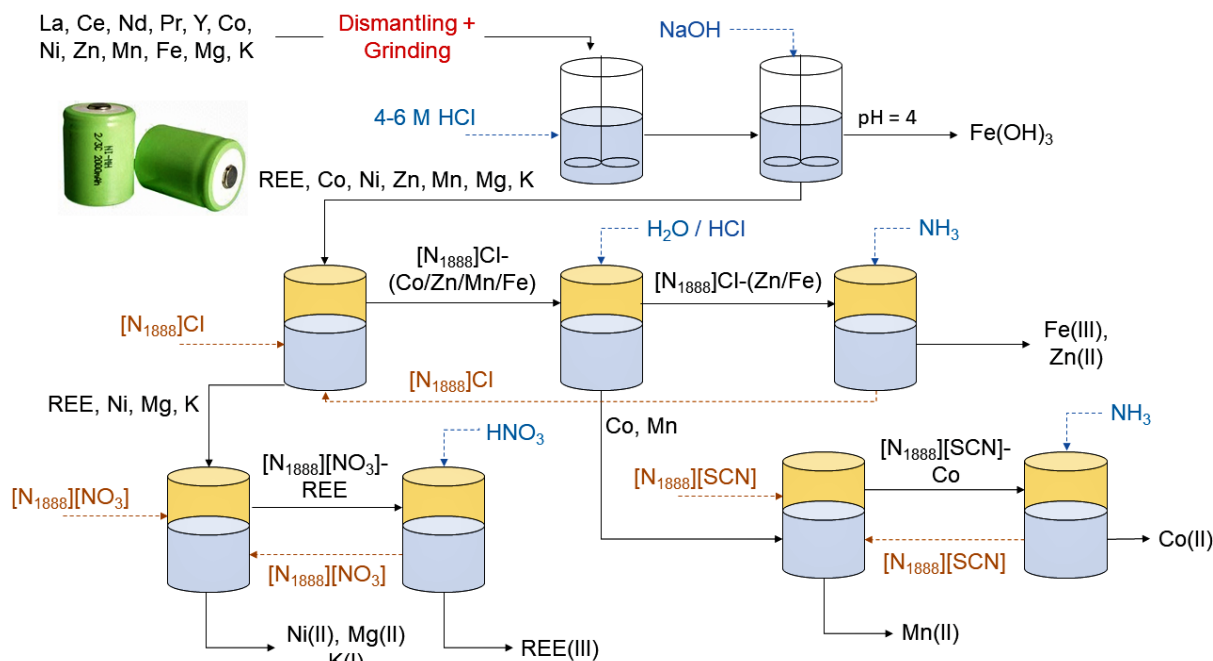
774 [P₆₆₆₁₄]Cl was used for the recovery of REEs from waste NdFeB permanent magnets in a seven-step
775 process (Vander Hoogerstraete et al., 2014). This included (1) crushing and milling the magnet into
776 coarse powder, (2) roasting to transform the metals into the corresponding oxides, (3) selective leaching
777 of the REEs with HCl leaving Fe in the solid residue by raising the pH of the leach solution above 2,
778 (4) extracting Co(II), Cu(II) and Mn(II) into [P₆₆₆₁₄]Cl 101 leaving the REEs in the aqueous phase, (5)
779 precipitating the REEs by the addition of oxalic acid, (6) recovering the precipitate by filtration and (7)
780 calcining the oxalate precipitate to yield rare-earth oxides. Roasting the waste magnet prior to
781 dissolution was found to facilitate dissolution and reduces the HCl consumption, with ≥ 90 wt.% of

782 Nd₂O₃ and Dy₂O₃ extracted compared to ≤ 25 wt.% of Fe₂O₃. A 3.5 M NH₄Cl was added to the leachate
783 as a salting-out agent to prevent the extraction of the REEs into the IL. An alternative process for the
784 extraction and separation of RE and other valuable elements from used NdFeB permanent magnets was
785 proposed by Riaño & Binnemans (2015) using [P₆₆₆₁₄][NO₃]. After roasting, the used magnets were
786 dissolved in HNO₃. At the end of the leaching process, the solution pH was raised to 4 to remove Fe by
787 precipitation. The remaining Nd(III) and Sm(III) were separated from Co(II) using [P₆₆₆₁₄][NO₃].
788 Evaluation of the extraction parameters indicated that pH had little influence on the process selectivity,
789 Co(II) extraction was suppressed at high metal loading concentrations and addition of NH₄NO₃ salted in
790 the REEs. After scrubbing Co(II) using NH₄NO₃, the loaded Nd(III) and Sm(III) were separated by
791 stripping the IL phase using an EDTA and 10 M NH₄NO₃ solution. The preferential interaction of
792 EDTA with Dy allowed for extraction to the aqueous phase whilst a high NH₄NO₃ concentration
793 suppresses stripping of Nd. At 70 °C, 0.03 M EDTA and 10 M NH₄NO₃, 79.8% and 4.0% of Dy
794 and Nd were stripped. Addition of concentrated HNO₃ to the stripping solution dissociated the weaker
795 [Nd(EDTA)]⁻ complex and facilitated its back extraction into the IL yielding a final Dy solution. All
796 elements were precipitated as oxalate salts and calcined. Although this process is complicated due to
797 the many steps involved, over 99% of Co, Nd and Dy are recovered as oxide with >99.5 % purity.

798 Larsson and Binnemans (2014) attempted the selective recovery of metals from a synthetic nickel
799 metal hydride battery leach solution using four IL systems: [P₆₆₆₁₄]Cl, [N₁₈₈₈]Cl, 10% v/v Cyanex 923
800 (neutral extractant) in [N₁₈₈₈][NO₃] and 30% v/v [N₁₈₈₈][SCN] in [N₁₈₈₈]Cl. A simplified process
801 flowsheet is presented in Figure 9. This process clearly shows the potential of ILs to recover metals
802 from complex aqueous solutions using careful selection of the ILs and understanding their influence on
803 the metal extracted complex (chloride vs. nitrate, etc).

804

805



806

807

808

Figure 9. Flow-sheet describing recovery of metals from waste nickel metal hydride batteries using ILs (adapted from Larsson & Binnemans, 2014).

809

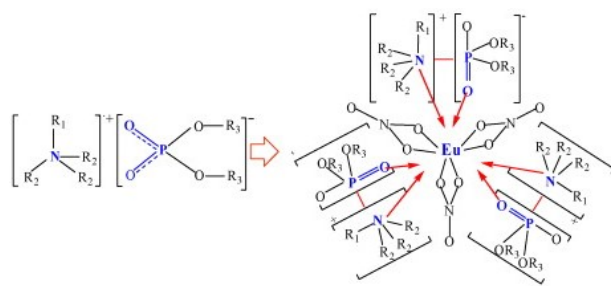
810 The feasibility of an efficient solvent extraction process for the purification of the critical element
 811 indium from a chloride medium was demonstrated using [P₆₆₆₁₄]Cl and [N₁₈₈₈]Cl. Results from single-
 812 element extraction studies indicate that the phosphonium IL [P₆₆₆₁₄]Cl outperformed [N₁₈₈₈]Cl with
 813 higher distribution ratio obtained across the entire HCl concentration range due to the greater
 814 hydrophobicity of [P₆₆₆₁₄]Cl. Maximum extraction occurred at 5 M HCl for both ILs, with the extraction
 815 mechanism assigned to the evolution of indium speciation as a function of chloride concentration and
 816 the formation of anionic chlorindate complexes at high HCl concentration. A percentage stripping over
 817 99% was reached for the 0.5 M HCl-[P₆₆₆₁₄]Cl system if 4.5 equivalents of NaOH were used. Two
 818 successive extraction/stripping cycles indicate that the IL can be recycled for reuse in liquid/liquid
 819 extraction of indium(III) without any loss of activity and with little loss of [P₆₆₆₁₄]Cl. Multi-element
 820 extraction studies show [N₁₈₈₈]Cl is the preferred IL for the separation of In(III) from As(III), Mn(II)
 821 and Ni(II), taking advantage of the low affinity of these metals for the IL phase at lower HCl
 822 concentrations. However, In(III) could not be separated from cadmium(II), iron(III), lead(II), tin(IV)
 823 and zinc(II) in a single step and additional scrubbing and stripping steps appear necessary (Deferm et
 824 al., 2016).

825 [N₁₈₈₈]-based ILs were used for the recovery of antimony and REEs from simulated waste phosphor
 826 from fluorescent lamps. Phosphor powder used in fluorescent lamps is a mixture of individual
 827 phosphors, namely HALO (Ca_{4.86}Mn_{0.10}Sb_{0.04}Sr_{0.004}(PO₄)₃Cl_{0.10}F_{0.90}), YOX (Y_{1.92}Eu_{0.08}O₃) and other
 828 constituents. Dupont and Binnemans (2016) considered the leaching and recovery of Sb from HALO
 829 phosphor only. Commercial HALO phosphor was completely leached using dilute HCl and extracted

830 as the anionic tetrachloroantimonate(III) complex (SbCl_4^-) using $[\text{N}_{1888}]\text{Cl}$ by an anion exchange
 831 mechanism. Quantitative extraction of Sb(III) was achieved from the leach solution containing Sr(II),
 832 Ca(II) and Mn(II) even in the absence of addition chloride ions. Mn(II) was only extracted at very high
 833 chloride concentrations ($\geq 4 \text{ M NaCl}$), whilst Sr(II) and Ca(II) do not form anionic chloro-complexes
 834 under the tested experimental conditions and were therefore not extracted. The loaded IL phases was
 835 scrubbed with 1 M NaCl prior to Sb(III) stripping using a NaOH solution at pH 7. The residual Ca in
 836 the leach solution was precipitated by addition of NaOH to yield a valuable calcium phosphate apatite
 837 precipitate.

838 Yang and co-workers (2012) used “bifunctional IL extractants” (Bif-ILEs) prepared from $[\text{N}_{1888}]\text{Cl}$
 839 and the commercial organophosphorus acid extractants, di-(2-ethylhexyl)phosphoric acid (DEHPA)
 840 and di(2-ethylhexyl)orthophosphinate (PC-88A), to extract REEs from a simulated solution of a
 841 fluorescent powder containing a high concentration of $\text{Al}(\text{NO}_3)_3$. $[\text{N}_{1888}][\text{DEHPA}]$ and $[\text{N}_{1888}][\text{P507}]$
 842 possess binary functional groups, one each on the cation and anion, through which complexation can
 843 occur. The extraction performance of the synthesized $[\text{N}_{1888}][\text{DEHPA}]$ and $[\text{N}_{1888}][\text{P507}]$ Bif-ILEs was
 844 compared to that of neutral organophosphorus extractants di(1-methylheptyl)methyl-phosphonate, TBP
 845 and Cyanex 923 in *n*-heptane. It was found that the sequence of extractability for REE(III) is Cyanex923
 846 $> [\text{N}_{1888}][\text{DEHPA}] = [\text{N}_{1888}][\text{PC-88A}] > \text{di}(1\text{-methylheptyl})\text{methyl-phosphonate} > \text{TBP}$. The extraction
 847 using $[\text{N}_{1888}][\text{DEHPA}]$ and $[\text{N}_{1888}][\text{PC-88A}]$ was thought to occur through the unshared electron pair of
 848 $\text{P}=\text{O}$ in the $[\text{PC-88A}]^-$ or $[\text{DEHPA}]^-$ groups and the N lone electron pair of the $[\text{N}_{1888}]^+$ group to form
 849 macromolecular extracted complexes (Figure 10).

850



851

852 **Figure 10.** The proposed structure of $[\text{N}_{1888}][\text{DEHPA}]$ and its coordination environment with Eu(III)
 853 (Sun et al., 2010).

854

855 The coexisting Al_2O_3 in the fluorescent powder was changed to a salting-out agent ($\text{Al}(\text{NO}_3)_3$) in the
 856 extraction process and this increased the extraction efficiency of REEs. Using a counter-current
 857 extraction process at a 4:1 organic to aqueous phase ratio and $\text{pH} = 0.56$, the REE recovery of 95.2
 858 wt.% was achieved in stages 5-7. However, the use of Bif-ILEs had some drawbacks, namely the
 859 addition of 10% isopropanol modifier to prevent the formation of a third-phase on extraction and the

860 important viscosity of the IL phase after extraction (Yang et al., 2012). Another study using the same
861 Bif-ILEs systems found that $[N_{1888}][PC-88A]$ and $[N_{1888}][P204]$ were suitable for the separation of
862 heavy REEs in nitrate medium and the separation of light REEs in chloride medium (Guo et al., 2014).
863 EXAFS studies attributed the synergistic effect of bifunctional IL extractant $[N_{1888}][DEHPA]$ for REE
864 extraction to the greater stability and hydrophobicity of the metal complex formed. In addition,
865 extraction was shown to proceed via co-extraction of the aqueous phase counter anion to produce a
866 neutral complex in the IL phase (Sun et al., 2010).

867

868 **6.2. Neutral extractants**

869 The use of neutral extractant in conjunction with an IL diluent system for the recovery of aqueous
870 metal complexes is the best studied extraction phenomenon involving ILs (Dai et al., 1999). Extraction
871 using neutral extractant proceeds via an ion-exchange mechanism whereby to compensate for incoming
872 positively charged metal cation into the IL, an IL component is released to the aqueous phase to
873 maintain charge neutrality. This was reported for a wide range of neutral ligands including crown ethers
874 (Dietz & Dzielawa, 2001; Jensen et al., 2002; Dietz et al., 2003; Jensen et al., 2003; Dietz & Stepinski,
875 2005; Garvey et al., 2012; Hawkins et al., 2012), phosphine oxide ligands (Kubota et al., 2009; Petrova,
876 2016), phosphate ligands (Billard et al., 2011; Zhu et al., 2015), diglycolamide ligands (Shimojo et al.,
877 2008; Shen et al., 2011), calixarene ligands (Luo et al., 2004) and others (Figure 5).

878 Systematic studies on the extraction of alkaline and alkali earth cation with DCH18C6 crown ether
879 extractant in $[C_nC_{1im}][NTf_2]$ show that the predominant extraction mechanisms, ion-exchange or
880 neutral complex extraction, depend on the hydrophobicity of the IL cation, the Lewis acidity of the
881 metal ion and the aqueous phase nitrate anion concentration (Hawkins et al., 2012; Wankowski & Dietz,
882 2016). Jensen et al. (2002) reported that for such systems, the cation exchange extraction mechanism is
883 not driven by the strength of metal-extractant complexation but by the energetically favourable
884 solvation energy obtained from the release of the IL cation to the aqueous phase. Although the IL
885 components can be recovered from the aqueous solution by 'salting-in', this adds an extra step to the
886 recovery process and decreases its economic viability. The toxicity of low concentrations of the cation
887 in waste water must also be considered. Increasing the cationic alkyl chain or incorporating fluorinated
888 groups does not fully prevent IL loss (Dietz & Stepinski, 2005) but increases the toxicity of the released
889 IL ion (Pham et al., 2010). In addition, the stripping of loaded neutral extractants in IL is problematic
890 and requires aggressive stripping solutions (Regel-Rosocka & Wisniewski). These factors have limited
891 the application of IL containing neutral extractants for the recovery of value from aqueous streams.

892 One system, the neutral extractant Cyanex 923 dissolved in $[N_{1888}][NO_3]$, has been applied to recover
893 of metals (Co, Ni, Fe, Mn, Zn, REE) from a synthetic Ni metal hydride battery leach solution (Larson
894 & Binnemans, 2015a). Cyanex 923 is a mixture of trialkylphosphine oxides with octyl and hexyl side

895 groups. Addition of 15 % Cyanex 923 (v/v) in $[N_{1888}][NO_3]$ increased the distribution ratio of the test
896 metals and allowed higher extraction efficiencies and Co-Ni separation factors compared to direct
897 application of $[N_{1888}][NO_3]$ alone. Over 98 wt.% of extracted Ni was scrubbed using a $MgCl_2$ solution
898 prior to stripping Co and Mn from the IL phase using a 3M $NaNO_3$ solution. In further stripping steps,
899 REE were removed using a 1 M HCl strip before the remaining Fe and Zn were stripped using a 1 M
900 HNO_3 solution. The separation of Co from Mn in the strip solution using $[N_{1888}][SCN]$ dissolved in
901 $[N_{1888}][NO_3]$ (40% v/v) was also investigated. This research represents an example of “split-anion
902 extraction”, whereby the aqueous and organic phases possess different anions, allowing the use of a
903 complexing anion in the organic phase that forms an extractable metal complex. This removes the
904 necessity to add a significant concentration of complexing anion in the aqueous phase and facilitates
905 metal stripping (Larson & Binnemans, 2015b). Similarly, Kikuchi and co-workers (2014) extracted
906 REE derived from NdFeB magnets from aqueous nitrate solution using TBP diluted in $[N_{1888}][NO_3]$.
907 Aqueous nitrate added as $NaNO_3$, was found to salt-in the REE and increase the distribution of the latter
908 to the IL phase. The presence of Fe(III) in solution has a negative effect on the overall REE extraction
909 efficiency and selectivity. After removal of Fe from the system, the Nd(III) concentration in the IL
910 phase reached $160\text{ g}\cdot\text{L}^{-1}$ after three loading cycles (Kikuchi et al., 2014).

911 The IL 1,3-dihexylimidazolium nitrate $[C_6C_6im][NO_3]$ was shown to preferentially extract light rare
912 earth elements over 1st row transition metals and this was applied with moderate success to the
913 separation of Sm(III)/Co(II) and La(III)/Ni(II) pairs from nitrate media, a separation relevant to the
914 recycle of these metals from WEEE. Due to the high co-extraction of Co (30%) and to a lesser extent
915 Ni (15%), successive scrubbing steps using 6M $NaNO_3$ solution were required. Interestingly,
916 $[C_6C_6im][NO_3]$ presents an UCST phase behaviour, with the IL being fully miscible with water at
917 temperature above 90 °C (Depuydt et al., 2017).

918

919 **6.3. Acidic extractant**

920 Acidic extractants are Brønsted acidic molecules containing a protonated functional group such as
921 an alkylcarboxylic acid, alkylphosphoric acid or alkylsulfuric acid group. Coordination of an acidic
922 extractant with a metal cation usually proceeds via deprotonation of the ligand and formation of a charge
923 neutral complex. The pKa of the extractant dictates the ability to deprotonate, thereby influencing the
924 extraction behaviour. By altering the pH of the aqueous solution, selectivity of metal ion extraction can
925 be controlled. In comparison to neutral extractants, extraction behaviour using acidic extractant is easier
926 to predict and back-extraction of the loaded organic phase can be achieved by contacting with an acidic
927 solution and regenerating the extractant (Cocalia et al., 2005; Free, 2013). The full potential of ILs to
928 solvate charged species is properly utilised if neutral complexes are extracted. Acidic extractants
929 commonly used in conjunction with ILs are shown in Figure 5.

930 Although widely tested on synthetic aqueous solutions, few studies have used acidic extractants
931 diluted in ILs for the recovery of metals from WEEE. The only example consists of the recovery of
932 lanthanides present in waste fluorescent lamps phosphor using *N,N*-dioctyldiglycolamic acid
933 (DODGAA) in [C₄C₁im][NTf₂] (Yang et al., 2013). DODGAA, is an anionic extractant possessing a
934 carboxyl and carbamoyl group linked together by an ether chain reported to exhibit high selectivity for
935 REEs, especially the lighter lanthanides (La(III) to Gd(III)) (Shimojo et al, 2014). In a 1st processing
936 step, Y and Eu oxides were leached using a 5 M H₂SO₄ solution at 100 °C. The solid residue was leached
937 a second time using 5 M HNO₃ solution for 6 hours at 100 °C to recover the difficult to extract RE
938 phosphate (La, Ce and Tb). The extraction efficiency of DODGAA in [C₄C₁im][NTf₂] was compared
939 to that of the carboxylic extractant PC-88A in dodecane for the recovery of the REE present in both
940 leach solutions. DODGAA in [C₄C₁im][NTf₂] provided greater selectivity and extraction efficiencies
941 for the REEs than PC-88A at similar pH. Y, Eu, La and Ce were separated from the metal impurities
942 Fe, Al and Zn, although some Ca was co-extracted. Stripping was easily achieved using a dilute acidic
943 solution, and UV spectroscopy of the aqueous phase confirmed minimal loss of the IL cation. The
944 extractant-IL system was recycled and reused five times with no appreciable loss in efficiency (Yang
945 et al., 2013). DODGAA has been shown by other researchers to extract REEs by deprotonation of three
946 ligands and the formation of a charge neutral complex (Shimojo et al, 2014).

947 Non-task-specific protic ILs can also on occasion extract metals without the need for additional
948 complexing agents. Reyna-González and co-workers (2010; 2012) studied the extraction Cu(II) from
949 an aqueous phase to the protic ILs 2-butylthiolonium bis(trifluoromethanesulfonyl)amide
950 ([[(C₄S)C₁im][NTf₂]) and 3-butylpyridinium bis(trifluoromethanesulfonyl)imide ([[3-C₄pyr][NTf₂]).
951 During the extraction process the H atom attached to the N atom of the cationic ring is released to yield
952 neutral amine capable of interacting with Cu(II) and water molecules to form a labile copper(II) system.
953 The presence of water in the IL is important to promote incorporation of hydrated Cu(II) complexes.
954 Due to the release of protons to the aqueous phase as well as the hydrophobicity of the cation, release
955 of [3-C₄pyr][NTf₂] to the aqueous phase was not recorded during extraction (Reyna-González et al.,
956 2012). High selectivity of Cu(II) compared to Co(II), Ni(II), and Fe(II) was achieved using
957 [(C₄S)C₁mim][NTf₂] (Reyna-González et al., 2010).

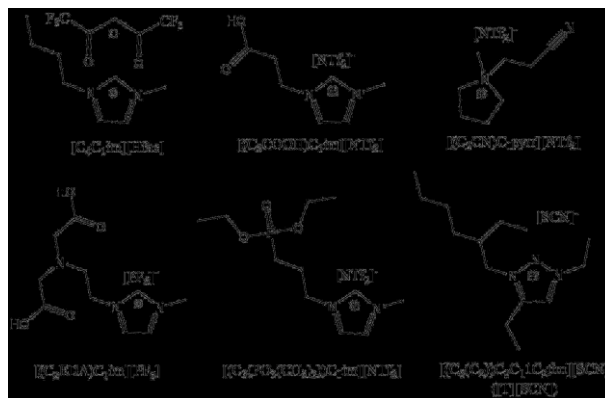
958

959 **6.4. Functionalized ILs**

960 Functionalized ILs, or TSILs, represent ILs incorporating a functional group on their anionic or
961 cationic components that acts as metal complexation site, allowing ILs to function as a solvent and
962 complexing agent. The cation is most often the functionalized moiety due to easier synthesis, which
963 simply requires a quaternization reaction between a ‘functionalised’ alkyl halide and a nucleophile
964 (tertiary amine, phosphine, etc.). The structure of the TSILs in this section are shown in Figure 11.

965 TSILs with functionalized anions most often include strongly coordinating species such as
966 alkylphosphate (Rout et al., 2013), alkyldiglycolamate (Rout et al., 2012), β -diketonate (Mehdi et al.,
967 2010), salicylate, thiosalicylate or benzoate (Stojanovic et al., 2010) anions. TSILs are covered in
968 greater detail in the reviews by Lee (2006) and Chiappe and Silvio (2014).

969



970

971 **Figure 11.** Selected examples of TSILs used in metal ion extraction.

972

973 The use of ILs as a simultaneous solvent and extraction media limits the ion-exchange extraction
974 mechanism and prevents the unwanted partitioning of the IL components or extractant to the aqueous
975 phase compared to extraction systems where the IL is solely used as a diluent. However, this is only
976 valid for ILs with functionalized cations, as extraction with some IL containing functionalised anions
977 proceeds on occasion via cation-exchange (Medhi et al., 2010). The principal factors limiting the
978 applicability of TSILs are their high viscosity, cost, complicated synthesis and unknown toxicity
979 compared to conventional ILs (Visser et al., 2001; 2002). In addition, further understanding of the
980 extraction mechanisms and characterisation of the extracted complex are required, with crystal structure
981 studies being a popular analysis method for TSIL-metal complexes (Harjani et al., 2006; Mehdi et al.,
982 2010; Nockemann et al., 2010a; Nockemann et al., 2010b).

983 TSILs incorporating a ‘hard’ base oxygen derived functional group such as a carboxylate, ketone or
984 phosphonate are used in metal extraction and separation processes. TSILs have been used to recover
985 REE(III) from fluorescent lamps as well as REE(III) and Co(II) from waste permanent magnets. The
986 use of $[N_{111}(2(O)OH)][NTf_2]$ for such applications was partially described in Section 5.1. In addition,
987 $[N_{111}(2(O)OH)][NTf_2]$ was employed for the solvent extraction of scandium. A primary study showed that
988 Sc(III) and Fe(III) could be selectively separated from La(III), Ce(III), Nd(III), Dy(III), Y(III), Al(III),
989 Ti(IV), Ca(II) and Na(I) in chloride solutions using $[N_{111}(2(O)OH)][NTf_2]$ as the IL displays a poor affinity
990 towards these elements (Onghena & Binnemans, 2015). The findings from this study were subsequently
991 applied by the same authors to the recovery of scandium from ‘sulfation-roasted’ leachates of bauxite
992 residue (Onghena et al., 2017a). The distribution ratio of Sc(III) found in this study was much lower

993 than those reported from chloride media (Onghena & Binnemans, 2015). This was assigned to the high
994 sulphate concentration in the leachate and the competing coordination between the sulphate and betaine
995 ligands to Sc(III). As expected, the extraction of Sc(III) by $[N_{111(2(O)OH)}][NTf_2]$ is heavily pH dependent.
996 At the following extraction conditions: pH = 2.4 and O/A = 1:5, 84 wt% of Sc(III) was extracted
997 compared to 23 wt% for Al(III), 4.3 wt.% Fe(III) and 2.6 wt.% Ca(II). The co-extracted metals were
998 scrubbed using dilute HCl solution prior to contacting the IL phase with 3 M H₂SO₄. The composition
999 of the resulting strip solution is 90% Sc(III), 8% Al(III), 0.7% Fe(III) and the lanthanides with 0.5%.
1000 Finally, scandium was precipitated from the strip solution by addition of oxalic acid and calcined for a
1001 final oxide product with a purity of 98% (Onghena et al., 2017a).

1002 Chen et al. (2015d) assessed the recovery of Nd(III) from Fe(III) and Sm(III) from Co(II) from
1003 synthetic NdFeB and SmCo permanent magnet leach solutions using 1-alkylcarboxylic acid-3-
1004 methylimidazolium bis(trifluoromethylsulfonyl)imide IL ($[(C_nCOOH)C_1im][NTf_2]$ ($n = 3, 5, 7$),
1005 (Figure 11). Separation of the REE from Fe(III) and Co(II) was found to be primarily pH dependent
1006 and the extraction efficiency of all the investigated metal ions increased with increasing aqueous phase
1007 pH, reaching as high as 99%. In addition, the extraction efficiency increased with a decrease in alkyl
1008 chain length at lower pH. By careful tuning of the aqueous solution pH, Sm(III) and Nd(III) could be
1009 selectively separated from Co(II) and Fe(III) respectively, with separation factors in the range 10^4 – 10^5 .
1010 Like the carboxy-functionalised $[N_{111(2(O)OH)}][NTf_2]$, REE extraction proceeds via de-protonation of the
1011 carboxylic group and formation of a 1:3 REE:IL charge neutral complex. The IL was easily stripped in
1012 a single step by dilute aqueous HCl or oxalic acid (Chen et al., 2015d).

1013 Novel 1,2,3-triazolium ILs with $[SCN]^-$ or iodide anions (Figure 11) were synthesized for the
1014 extraction of transition metals and REEs from HCl medium (Raiguel et al., 2017). These ILs exhibited
1015 better properties compared to imidazolium ILs, namely low viscosity, low solubility in water and high
1016 base stability. The ILs incorporating the 3,5-diethyl-1-(2-ethylhexyl)-4-methyl-1,2,3-triazolium ([T]
1017 cation with an iodide anion displayed a high extraction efficiency for Cu(II), moderate extraction
1018 efficiencies towards Fe(III), Co(II), Ni(II) and La(III), Nd(III) and Dy(III). After substitution of the
1019 iodide anion for thiocyanate, close to quantitative extraction is obtained for the transition metals and
1020 low to medium extraction of the REE(III). EXAFS analysis of Cu(II) speciation in [T][I] after loading
1021 with CuCl₂ indicates its presence as the $[CuCl_2]^-$. Upon extraction, the redox-active Cu(II) is reduced to
1022 Cu(I) whilst I⁻ is oxidized to I₂ which in turn reacts with remaining I⁻ to form I₃⁻. The high base stability
1023 of [T][I] was used in the separation of Cu(II), Zn(II) and Fe(III). Addition of Na₂CO₃ precipitated 98%
1024 of Zn(II) and Fe(III), leaving Cu(II) in the IL.

1025

6.5. Aqueous biphasic systems for metal extraction

An alternative to traditional solvent extraction for the extraction metals is the use of ILs in aqueous biphasic system (ABS). ABS are mainly composed of water, and can be formed, when combining in the right proportions, an inorganic salt and a hydrophilic IL, which creates two immiscible – but reversible – aqueous phases (a salt-rich and an IL-rich phases). Since such systems are obtained with hydrophilic ILs, the range of potential compounds that can be explored for the extraction is significantly enlarged and unlocks the full potential of ILs as designer solvents. As the IL-rich phase consists of an aqueous solution of IL, a much lower amount of IL is required, thus reducing the overall process cost. In addition, the environmental impact of the use of ILs is diminished as less amounts are used and hydrophilic ILs are significantly less toxic and more biodegradable than their hydrophobic counterparts. Finally, ABS overcome the high viscosity of many ILs due to the presence of water thereby increasing the reaction kinetics and transport phenomena. The extraction of metals using polyethylene glycol-based ABS is well established (Rogers et al., 1993). Aqueous solutions of ILs and their combination with ABS have been extensively used with success to extract and purify biomolecules from biomass (Freire et al., 2012). Despite this, there are few reports on the use of IL-based ABS for the extraction of metals. One of the main limitations of ABS for metal extraction is the difficult handling of metal ions with high sensitivity to hydrolysis and/or precipitation as most reported ABS experiments were carried out using slightly acidic or alkaline solutions, with pH typically ranging from 5 to 13. A full review of metal extraction using ABS is available elsewhere (Billard, 2016).

An important development in the applicability of ABS extraction to the recovery of metals from acidic WEEE leachates is the recent proof-of-concept for acidic ABS (AcABS) in which the inorganic acid itself, in this case HCl, replaces the salt as the driver of ABS formation (Gras et al., 2018). The use of the leachate solution itself as a salting-out agent allows for the simultaneous leaching and separation of critical metals, thereby simplifying the extraction and stripping processes. These systems display several advantages over other extracting solvents. Unlike classical systems based on an organic solvent and an extracting agent, the IL-based AcABS [P₄₄₄₁₄]Cl-HCl-H₂O exhibits a thermomorphic behavior with a well pronounced LCST, i.e. the biphasic mixture becomes biphasic by heating above a certain temperature for a given HCl concentration. This system was applied to the extraction of Fe(III), Pt(IV) and Co(II) from concentrated HCl solutions and to the separation of the critical transition metal pair Co(II) from Ni(II). Extraction of Co(II), Fe(III) and Pt(IV) proceeds as in the traditional two-phased systems based on [P₆₆₆₁₄]Cl via anion exchange with the IL anion. An additional benefit of this AcABS is the poor miscibility of the IL in the HCl-rich phase, ensuring quantitative recovery of the IL after extraction. The traditional ABS also based on [P₄₄₄₁₄]Cl with NaCl was shown to selectively separate Co(II) and Ni(II) in chloride media (Onghena et al., 2015). [P₄₄₄₁₄]Cl exhibits a large biphasic region, with just 5 wt% NaCl capable of inducing an ABS in a solution containing 40 wt.% IL. The [P₄₄₄₁₄]Cl-NaCl-H₂O system also displays a LCST phase behavior in water.

1062 An interesting IL-surfactant-water microemulsion system based on the IL [P₆₆₆₁₄]Cl and the
1063 surfactant Triton 100 (TX100) was developed extraction and separation of Au(III), Pd(II), and Pt(IV)
1064 from acidic chloride media (Tu Nguyen et al., 2017). A number of factors were assessed including the
1065 microemulsion structure, temperature, surfactant concentration, IL concentration, extraction time,
1066 chloride concentration, and pH. Metal extraction was found to proceed through an anion exchange
1067 mechanism between the anionic chlorometallate complexes and the IL anion. A five-step methodology
1068 was elaborated for precious metal recovery consisting of (i) mixing the feed solution with the IL-based
1069 microemulsion, (ii) inducing TX100-[P₆₆₆₁₄]Cl / aqueous phase splitting by heating to 90 °C, (iii) phase
1070 separation, (iv) stripping and (v) regeneration. Following this simple protocol, 99.9% of precious metals
1071 were selectively recovered at optimized condition. A two-step stripping process was successfully
1072 performed based on stripping of Au(III) using an aqueous solution of sodium thiosulfate followed by
1073 the recovery of Pd(II) and Pt(IV) with a thiourea-HCl solution. The performance of the system after
1074 five extraction-stripping cycles was found to decrease by approximately 9% for all three metals tested.

1075 Similarly to the results reported using the hydrophobic [P₆₆₆₁₄][NO₃] (Vander Hoogerstraete &
1076 Binnemans, 2014), Nd(III) was selectively separated from Co(II) and Ni(II) using an ABS comprised
1077 of [P₄₄₄₄][NO₃] and NaNO₃ as phase former (Chen et al., 2018) based on the ability of lanthanides to
1078 form anionic nitrate complexes. The extraction efficiency was primarily influenced by the aqueous
1079 nitrate concentration, with the Nd(III) extraction efficiency increasing from less than 15 % in aqueous
1080 solution containing no NaNO₃ to quantitative Nd(III) extraction for NaNO₃ greater than 0.3 g.L⁻¹. An
1081 increase in the NaNO₃ content of the aqueous phase also resulted in increased separation factors 10³
1082 and above when [NaNO₃]=0.6 g.L⁻¹. In contrast, IL concentration had little effect on the extraction
1083 yield: for a 1 mL feed solution containing 1 g.L⁻¹ of Nd(NO₃)₃ quantitative extraction of Nd(III) was
1084 obtained for all IL concentration tested (0.2-0.6 g). After separation of the IL rich phase, extracted
1085 Nd(III) was recovered by contacting with an aqueous solution of sodium oxalate such that the Nd(III)
1086 to oxalate molar ratio was of 1.5. However, a sharp drop in extraction efficiency over repeated cycles
1087 was observed with only 85.4 % of extraction efficiency achieved after only three cycles. NaNO₃ was
1088 found to be a better salting out agent than NH₄NO₃ whilst [N₄₄₄₄][NO₃] has a smaller biphasic region
1089 compared to [P₄₄₄₄][NO₃], in accordance with the more hydrophobic nature of phosphonium cations
1090 over ammonium ones. As with the [P₄₄₄₁₄]Cl system previously described, a strong LCST-type
1091 temperature dependent behavior of the binodal curve was observed as the temperature was increased
1092 from 15 °C to 35 °C.

1093 The ABS composed of the carboxyl-functionalized phosphonium IL [P_{444(C10OH)}]Cl (80 wt.%)
1094 and a 16 wt.% NaCl solution was employed as the salting-out agent for the selective extraction of Sc(III)
1095 (Depuydt et al., 2015). Whilst the viscosity of the pure IL was over 20000 cP at room temperature, the
1096 viscosity of the IL-rich phase in the employed ABS was drastically decreased to 400 cP. REEs do not
1097 form anionic chloride complexes, the extraction of Sc(III) was shown to proceed via deprotonation of
1098 three IL-cations (pK_a= 2.32) to form zwitterionic compounds that can coordinate scandium(III) ions in

1099 a 3:1 ratio. The pH was varied from 3.33 to 0 in the aqueous feed solution containing 5 mmol kg⁻¹ of
1100 Sc and 16 wt % of NaCl to determine the influence of the pH on the solubility of the IL cation in the
1101 water-rich phase. ¹H NMR analysis of the aqueous phase indicates that the solubility of the IL cation
1102 increases with decreasing pH from approximately 5.8 wt.% at pH=6.8 to 10.5 wt.% at pH=0. The
1103 zwitterionic form of the [P₄₄₄(C₁₀OH)]⁺ is more hydrophobic than its protonated counterpart, thus, a lower
1104 solubility is observed at higher pH values since low pH values prevent deprotonation of the cation.
1105 Quantitative stripping of IL-rich phase was achieved after addition of oxalic acid at a molar ratio of 1.5.
1106

1107 **6.6. Hydrophobic deep eutectic solvents (DES)**

1108 Whilst the use of hydrophilic DES is well documented at the laboratory scale for many applications,
1109 the use of hydrophobic DES for the liquid-liquid extraction of metals is relatively recent and opens the
1110 possibility for the substitution of expensive hydrophobic ILs.

1111 A hydrophobic DES composed of a x:1 (x=2-4) molar ratio of decanoic acid and lidocaine was
1112 investigated for the extraction of the transition and alkaline metals Co(II), Zn(II), Ni(II), Cu(II), Fe(II),
1113 Na(I), Li(I) and K(I) from chloride media (Van Osch et al., 2016). The physical properties of the DES
1114 are described, and single element extraction studies show that most transition metal cations are extracted
1115 with high efficiencies although some Fe(II) was found to precipitate and the DES phase forms a gel
1116 after extraction of Mn(II). The loading capacity of the DES is higher than that of corresponding ILs
1117 composed of fatty acids and quaternary ammonium salts. The higher the decanoic acid to lidocaine
1118 ratio, the higher the decrease in the distribution ratio because of the greater hydrophobicity of the DES.
1119 Contrary to what might be expected, the majority of the chloride remains in the aqueous phase. This is
1120 reasoned through the interaction between the protonated lidocaine and the chloride anion: it is likely
1121 that lidocaine hydrochloride is formed, which has a higher water solubility in comparison to lidocaine
1122 itself. Thus, metal extraction proceeds via an ion-exchange reaction in which upon extraction of the
1123 metal ion to the DES phase, protonated lidocaine is transferred simultaneously to the water phase. The
1124 loaded DES phase was stripped using sodium oxalate, and the regenerated DES was recycled. Due to
1125 the loss of lidocaine upon metal extraction, the DES cannot be recycled indefinitely. Although the 3:1
1126 and 4:1 molar ratio decanoic acid to lidocaine DES could be reused a second time without any drop in
1127 Co(II) distribution coefficient, a drastic drop in D for the 2:1 DES was observed. In addition, the water
1128 phase became turbid for all DES ratio.

1129 Quaternary tetraheptylammonium- and menthol-based hydrophobic DES containing carboxylic
1130 acids, lauric acid, decanoic acid, oleic acid and ibuprofen, were investigated for the recovery of indium
1131 from chloride and oxalate media (Tereshatov et al., 2016). DL-menthol:lauric acid based DES were
1132 found to be ineffective extracting agents. However, all [N₇₇₇]⁺ based DES were successful in extracting
1133 In(III), with the [N₇₇₇]:ibuprofen (7:3 molar ratio) DES displaying the highest distribution ratio.
1134 Furthermore, all [N₇₇₇] based DES display the same extraction behaviour in HCl and oxalate solution

1135 respectively, suggesting that the fatty acid alkyl chain does not influence In(III) extraction. In both
1136 media, In(III) extraction is dictated by its speciation. Similarly to In(III) extraction in the IL [P₆₆₆₁₄]Cl
1137 (Deferm et al., 2016), the DES preferentially extracts the anionic complexes [InCl₄(H₂O)₂]⁻ and
1138 [In(C₂O₄)₂]⁻ in chloride and oxalate solution respectively (Tereshatov et al., 2016) through ion-pairing
1139 with the [N₇₇₇₇]⁺ cation as deprotonation of the carboxylic acid is assumed to be suppressed at the
1140 experimental pH used. Diethylene triamine pentaacetic acid was used to strip the loaded DES.

1141

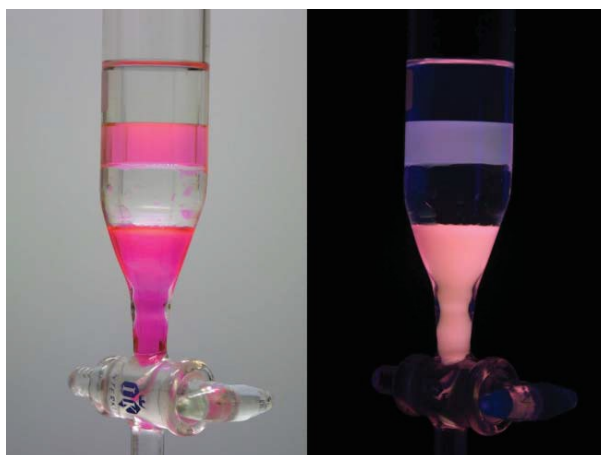
1142 **6.7. Ionic liquid – ionic liquid solvent extraction**

1143 Systems composed of two different immiscible ILs allow for the development of new separation
1144 processes and the potential for the formation of ternary or quaternary IL systems for extraction as
1145 exemplified in Figure 12.

1146 Arce et al. (2006) and Neves et al. (2017) demonstrated that if large enough structural or chemical
1147 differences exists between two ILs, then this ion mixture may yield a biphasic mixture at room
1148 temperature. For example, mixtures of [P₆₆₆₁₄]Cl and [C_nC₁im]Cl were found to be ‘immiscible’ in the
1149 temperature range 298 to 458 K, where the *n* was smaller or equal to 5, with only approximately 10
1150 mol% of imidazolium ion salt dissolved in the phosphonium phase for [C₂C₁im]Cl (Arce et al., 2006).
1151 These findings were expanded upon by Neves et al. (2017) for systems with 4 ions showing that six
1152 pairs of cholinium- and phosphonium-based aprotic ILs ([N_{111(2OH)}][NTf₂]⁻ and [P₆₆₆₁₄][X]⁻ where
1153 X=[Cyanex272]⁻, [C₉COO]⁻, [NTf₂]⁻, [N(CN)₂]⁻, Br⁻ and Cl⁻) were able to form biphasic systems. The
1154 formation of an IL liquid-liquid system is cation driven: only mixtures of two ILs with significantly
1155 structurally different IL cations or of highly different hydrogen-bond acidity can undergo liquid-liquid
1156 demixing. The IL anion does not have a significant impact on the creation of a binary systems but plays
1157 an important role in defining the mutual solubility magnitude, which was suggested to linearly depend
1158 on the volume of the IL anion. In all cases except for systems formed by ILs with a common anion,
1159 significant ion exchange occurs, the extent of which correlates with the ILs cohesive energy (Neves et
1160 al., 2017).

1161

1162



1163
 1164 **Figure 12.** A stable tetraphasic mixture of (from top to bottom): pentane, $[P_{66614}][NTf_2]$, water and
 1165 $[C_2C_1im][NTf_2]$. The pink colouration is due to rhodamine B dye, which is soluble in the ionic layers.
 1166 The figure on the left was taken in daylight and the figure on the right was taken under illumination
 1167 from UV light (254 nm). Reproduced from Arce et al. (2006) with permission from The Royal Society
 1168 of Chemistry.

1169
 1170 This principle was successfully used to separate cobalt from nickel and REEs from nickel
 1171 respectively using the biphasic system $[C_2C_1im]Cl$ and $[P_{66614}]$ -bis(2,4,4-trimethylpentyl)phosphinate
 1172 (Wellens et al., 2013; out et al., 2014). A solubility of 9.2 wt% (or 31 mol%) of $[C_2C_1im]Cl$ in
 1173 $[P_{66614}][P_{RROO}]$ was determined from 1H -NMR peak analysis peaks. The solubility of $[P_{66614}][P_{RROO}]$ in
 1174 $[C_2C_1im]Cl$ was found to be below the detection limit (Wellens et al., 2013).

1175 Vander Hoogerstraete and co-workers (2015) demonstrated a proof of principle for the separation
 1176 of tin(II), scandium(III) and yttrium(III) using the ternary IL system composed of $[N_{111(2(O)OH)}][NTf_2]$ -
 1177 H_2O - $[P_{66614}][NTf_2]$. A ternary system was required for this separation as it is known that tin(II) and
 1178 scandium(III) extraction by carboxylic ligands display the same pH dependent behaviour.
 1179 $[N_{111(2(O)OH)}][NTf_2]$ was selected over $[N_{111(2OH)}][NTf_2]$ as one of the phases due to its significantly larger
 1180 triphasic region. Initial biphasic tests showed that Sc(III) and Sn(II) could be separated from Y(III) in
 1181 the $[N_{111(2(O)OH)}][NTf_2]$ - H_2O system at pH 1.0 whilst 80% of Sn(II) was extracted to the IL phase in the
 1182 $[P_{66614}][NTf_2]$ - H_2O in the presence of the neutral tributylphosphate (TBP) ligand whilst the REEs
 1183 remained mainly in the aqueous phase. A pH below 1, along with the addition of 1M $MgCl_2$ to the
 1184 aqueous phase, was required to suppress tin hydrolysis and prevent $[P_{66614}][NTf_2]$ -TBP emulsions. In
 1185 the ternary system, the best separation was obtained at low chloride concentrations without pH
 1186 adjustment and at high TBP concentration in the $[P_{66614}][NTf_2]$ phase. Under these conditions (20 wt.%
 1187 TBP, 0.25 M $MgCl_2$), 89 % of tin was extracted to the $[N_{111(2(O)OH)}][NTf_2]$ phase, 89% of Y(III) remained
 1188 in the aqueous phase and 85% of Sc(III) was extracted to the $[P_{66614}][NTf_2]$ phase. Although not
 1189 conclusive, these encouraging results underline the versatility of ILs and the possibilities available for
 1190 IL-IL liquid-liquid extraction.

1191 The IL-IL mineral separation of rare-earth minerals (bastnäsite and monazite) from Ca, Mn, Fe and
1192 Mg rich samples (ankerite, dolomite and calcite) was attempted (Azizi & Larachi, 2018). Specifically,
1193 [N₄₄₄₄][DEHPA] was added as a droplet phase in three different ILs used as a continuous phase,
1194 ethylammonium nitrate ([EtNH₃][NO₃]), [C₂C₁im][SCN] and [C₄C₁im][BF₄]. These ILs were selected
1195 as i) [N₄₄₄₄][DEHPA] displays a far superior affinity for the REEs compared to the other ILs, ii) the
1196 droplet phase viscosity is lesser than that of the continuous phases and iii) the droplet phase and
1197 continuous phase must display minimal solubility with one-another. The optimal system of
1198 [N₄₄₄₄][DEHPA] dispersed in [C₂C₁im][SCN] was shown to outperform froth flotation and traditional
1199 liquid-liquid mineral separation for the recovery of RE minerals. DFT analysis found that anionic
1200 moiety of [N₄₄₄₄][DEHPA] directly interacts with the metal cations on the mineral surfaces through
1201 covalent bonds resulting in very favourable interaction energies compared to the other ILs.

1202 Although not technically an IL-IL extraction system, the solvent extraction of Co, Fe and B from
1203 waste NdFeB magnets in DES [N_{111(20H)}]Cl:lactic acid using [N₁₈₈₈][SCN] was successfully achieved
1204 and scaled-up over multiple mixer-settlers (Riaño et al., 2017). The dissolution of Co, Fe, B, Nd, Dy,
1205 Pr and Gd oxides from crushed and roasted rare-earth permanent magnets (NdFeB) was attempted using
1206 three different DES: [N_{111(20H)}]Cl:urea (1:2), [N_{111(20H)}]Cl:EG (1:2) and [N_{111(20H)}]Cl:lactic acid (1:2).
1207 At a liquid to solid ratio of 20 mL.g⁻¹, 70 °C leaching temperature and 24 hr leaching time, over 80
1208 wt.% of all the target elements were lixiviated using [N_{111(20H)}]Cl:lactic acid and little to no dissolution
1209 occurred in [N_{111(20H)}]Cl:urea and [N_{111(20H)}]Cl:EG. This contrast in leaching efficiency was assigned to
1210 the ability of the lactic acid moiety to deprotonate and form the metal complex M(CH₃CHOHCOO)_{n,DES}
1211 (where n is the metal oxidation state). Interestingly, whilst the water content had no influence on the
1212 leach efficiency of the non-roasted magnet, it does have an important influence on the leaching of the
1213 roasted oxides with a decrease in leaching efficiency with increasing water content. Almost no Fe and
1214 Co are recovered at 80 wt.% (L/S=12.5 mg.L⁻¹, 70 °C, and 24 hr) water content due to their hydrolysis.
1215 Recovery of the target metals from the DES [N_{111(20H)}]Cl:lactic acid (1:2) without water is achieved
1216 using a two-stage solvent extraction procedure. In this procedure, the DES phase was employed as the
1217 more polar phase for solvent extraction and the IL [N₁₈₈₈][SCN] diluted in toluene as the less polar
1218 phase. Co(II), Fe(III) and B(I) were separated from the REE(III) in an initial solvent extraction stage
1219 using [N₁₈₈₈][SCN]. EXAFS analysis indicates that cobalt is extracted as the complex [Co(SCN)₄]²⁻ in
1220 [N₁₈₈₈][SCN] whilst iron is extracted as [N₁₈₈₈][FeCl₄]. In a second stage, Nd was separated from Dy
1221 using the acidic extractant Cyanex 923 in toluene. Cyanex 923 was selected ahead of D2EHPA due to
1222 the difficulty in stripping Dy(III). The less polar phases were recycled and reused a second time with
1223 little loss in efficiency although boron extraction declined due to presence of chloride anion in
1224 [N₁₈₈₈][SCN] resulting from anion-exchange.

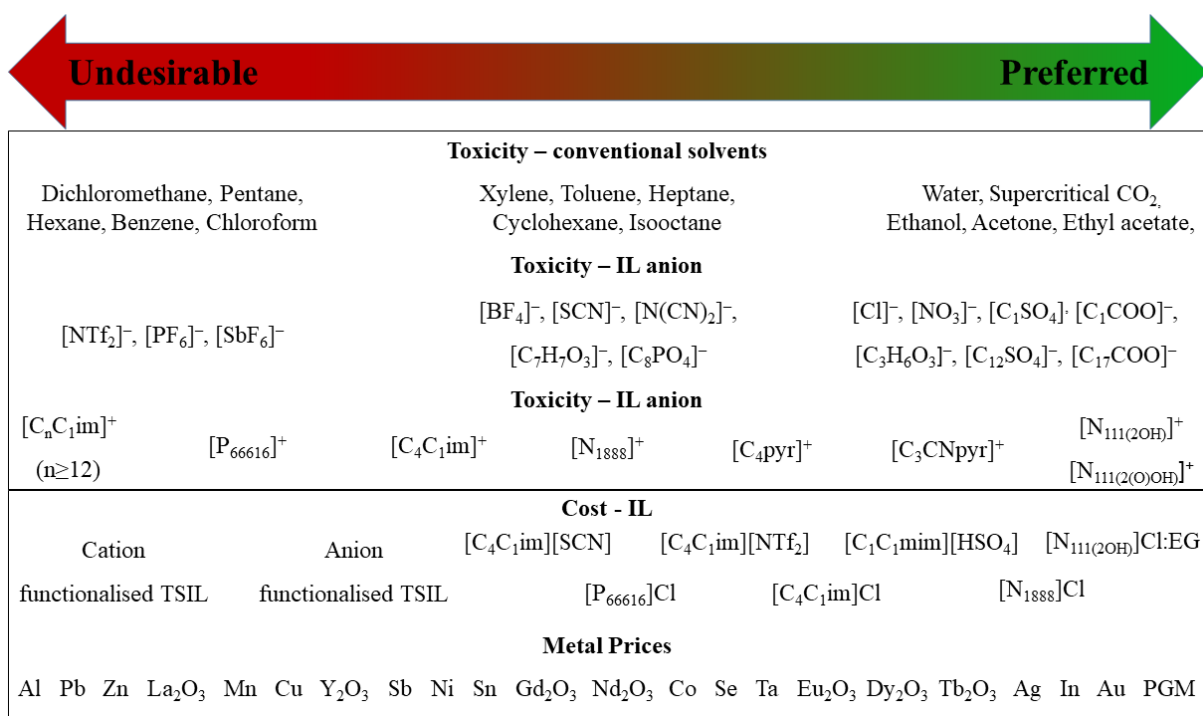
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1226 **7. Critical perspective and recommendations – ILs as specialty solvents**

1227 **7.1. Ionic liquids – the case for application-specific solvents**

1228 The publications reviewed here demonstrate the growing application of ILs for the treatment of
 1229 WEEE. Despite these promising results, few studies have made the jump from laboratory to industrial
 1230 scale. In this section, the major obstacles currently preventing the use of ILs in metal extraction
 1231 processes are highlighted. The selection of ILs is usually justified based on their green credentials,
 1232 namely their tunability, low vapour pressure, non-flammability and high stability. However, ILs also
 1233 suffer from some important disadvantages preventing their industrial application such as their high
 1234 viscosity, corrosiveness, hygroscopicity, toxicity and their higher cost compared to molecular solvents.
 1235 As such, a more nuanced perspective is required when considering the use of an IL and the following
 1236 issues must be addressed prior to any successful application. The discussion is summarised in Figure
 1237 13. All data here presented is qualitative and should be used just as a guideline. Based on the guidelines
 1238 presented in Figure 13 and the literature reviewed in the previous Sections, optimised process
 1239 flowsheets are proposed for the valorisation of the inherent metallic value in fluorescent lamp phosphor
 1240 waste (Figure 15) and nickel metal hydride battery waste (Figure 16).

1241



1242

1243 **Figure 13.** Qualitative toxicity and cost scale for the judicious selection of ILs for metal extraction

1244

- 1245
- How to design ILs more environmentally benign than currently used molecular solvents?

1246 The structural modifications that confer hydrophobicity to ILs are the same that increase their
1247 toxicity. Thuy Pham and co-workers (2010) reviewed the toxicity of common ILs across multiple
1248 trophic levels and found that toxicity seemed to be determined mainly by the cationic component and
1249 that it correlates directly with the length of the cationic alkyl-chain(s). In addition, ILs incorporating
1250 polar functional groups in the alkyl side chain such as ether, hydroxyl and nitrile moieties displayed
1251 lower cytotoxicity compared to those with simple alkyl side chain. Regarding the anionic effects,
1252 fluorinated anions, particularly $[\text{NTf}_2]^-$, are generally more toxic than their halogenated counterparts
1253 (Viboud et al., 2012). In addition, some fluorinated anions have been shown to hydrolyse and can
1254 release the toxic product HF as a result of decomposition (Swatloski et al., 2003; Freire et al., 2010).
1255 The authors show that $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$ and $[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$, two of the most widely used ILs, decompose
1256 in contact with water. The decomposition reaction leads to the formation of toxic HF.

1257 The “greenness” of molecular solvents is well documented according to multiple criteria. An
1258 established guide to green solvent selection is the ‘Pfizer solvent selection guide’ which classifies
1259 common organic diluents like hexane, benzene or petroleum spirits as undesirable (Byrne et al., 2016).
1260 In this context, it makes little sense to label the substitution of hexane in the organic phase by
1261 $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ as environmentally friendly. ‘Greener’ alternatives include the substitution of
1262 imidazolium ILs to pyridinium-based ILs, the use of large fatty acid as anions over fluorinated anions
1263 to confer the IL hydrophobic properties and – if possible – the application of DES. Water-miscible ILs
1264 with shorter cationic alkyl chains can be salted-out to form a reversible biphasic system suitable for
1265 metal extraction. It is also worth considering that many ILs act both as the hydrophobic phase and
1266 extractant, thereby potentially reducing their over whole toxicological impact. Aliquat 336 ($[\text{N}_{1888}]\text{Cl}$)
1267 stands out as such an example. However, IL systems in which metal extraction proceeds via a cation-
1268 exchange mechanism should be avoided.

1269 • Can ILs be designed to offer an improvement compared to existing industrial practices?

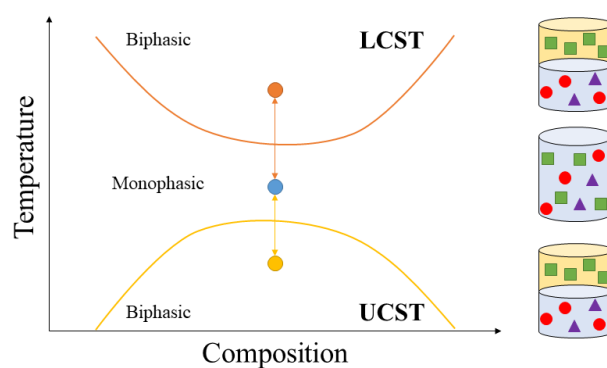
1270 In other words, is there any advantage in using IL over existing solvents, either through increased
1271 selectivity, more favourable kinetics and thermodynamics or through process simplification? E-waste
1272 represents a variable and heterogeneous waste stream, with product composition changing between
1273 manufacturers and product iterations. Current industrial hydrometallurgical methods for the recovery
1274 of metals from e-waste borrow heavily from tried and tested processes established in the mining industry
1275 for the extraction of metals from ores (Cui & Zhang, 2008). Any proposed IL-based approach needs to
1276 be robust and flexible to adapt to such variable conditions. Many of the studies reviewed here report
1277 distribution and separation factors superior to those obtained in conventional organic systems.
1278 Problematically, most of these IL studies only focused on simulated systems. Such an approach risks
1279 missing interactions that occur only in complex systems such as in leachates from WEEE from a waste
1280 treatment facility and ignores the role of trace contaminants. Physical separation processes, the
1281 preliminary step in all waste treatment facilities (Figure 1), are never 100% efficient due to the overlap

1282 between different physical properties, with impurities being entrained in the output stream. An example
1283 of a problematic trace contaminants is the extraction of Fe(III) from chloride solutions by phosphonium-
1284 based ILs. Fe(III) is strongly and efficiently extracted from even dilute chloride solutions and its
1285 stripping can prove problematic (Cui et al., 2015). This in turn can complicate the regeneration of the
1286 IL and lower the extraction efficiency of target metals.

1287 The high viscosity of ILs and especially DES is a well identified barrier to their application due to the
1288 increased cost of pumping and slow mixing processes and kinetics of mass transfer. Certain ILs,
1289 particularly those that operate by an anion-exchange mechanism, are known to significantly increase in
1290 viscosity after metal extraction due to strong intermolecular interactions. For example, the viscosity of
1291 water saturated [P₆₆₆₁₄]Cl at 60 °C increases from 95 cP to approximately 800 cP after contacting with
1292 a feed solution containing 40 g.L⁻¹ Co(II) (Vander Hoogerstraete et al., 2013). The problem of viscosity
1293 can be partially overcome by saturating the IL with water and operating at higher temperature and/or
1294 lower feed concentrations. ABS and thermomorphic ILs fully overcome the issues associated with
1295 viscosity by tuning their water miscibility through varying the salt concentration and temperature
1296 respectively.

1297 This tuneable and reversible water miscibility is extremely desirable in homogeneous liquid-liquid
1298 extraction. Performing the extraction in a monophasic solution prior to separation of the phases through
1299 a change in temperature reduces the viscosity of the solution and accelerates mass transfer, resulting in
1300 higher extraction efficiencies. This is schematically illustrated in Figure 14; ILs can either display LCST
1301 or an UCST.

1302



1303

1304 **Figure 14.** Schematic illustration of LCST or UCST behaviour and its application to homogeneous
1305 liquid-liquid extraction.

1306

1307 The synthesis of ILs exhibiting thermomorphic behaviour requires a balance between the
1308 hydrophilicity and hydrophobicity of the ions. The appearance of an LCST for [P₄₄₄₄]- and [N₄₄₄₄]-based
1309 ILs was shown to vary with anion selection (Khono & Ohno, 2012). Depuydt and co-workers (2017b)

1310 recently synthesised a range of phosphonium IL with dioctyl sulfosuccinate (DOSS) as anion. Whilst
1311 [P₄₄₄₄][DOSS] is hydrophobic, incorporation of three ethylene glycol moieties to the cation lowers the
1312 hydrophobicity of [P_{444(EG3)}][DOSS]. [P_{444(EG3)}][DOSS] has an LCST of 19 °C in water and was shown
1313 to efficiently extract both divalent and trivalent metals. Furthermore, the presence of additional ions in
1314 solution can alter the LCST or UCST temperatures due to the strong polar/electrostatic interactions
1315 between the water, IL and the ions. The UCST and LCST of [N_{111(2(O)OH)}][NTf₂] and [P₄₄₄₁₄][Cl]
1316 significantly decrease after loading with REEs (Schaeffer et al., 2016) and after addition of NaCl to the
1317 aqueous phase respectively (Onghena et al., 2015). The ability to separate an aqueous IL solution into
1318 two phases by varying the temperature or by addition of salting-out salts allows for the potential
1319 development of metal recycling processes combining leaching and extraction of metal ions.

1320 • Are IL-based processes economically viable?

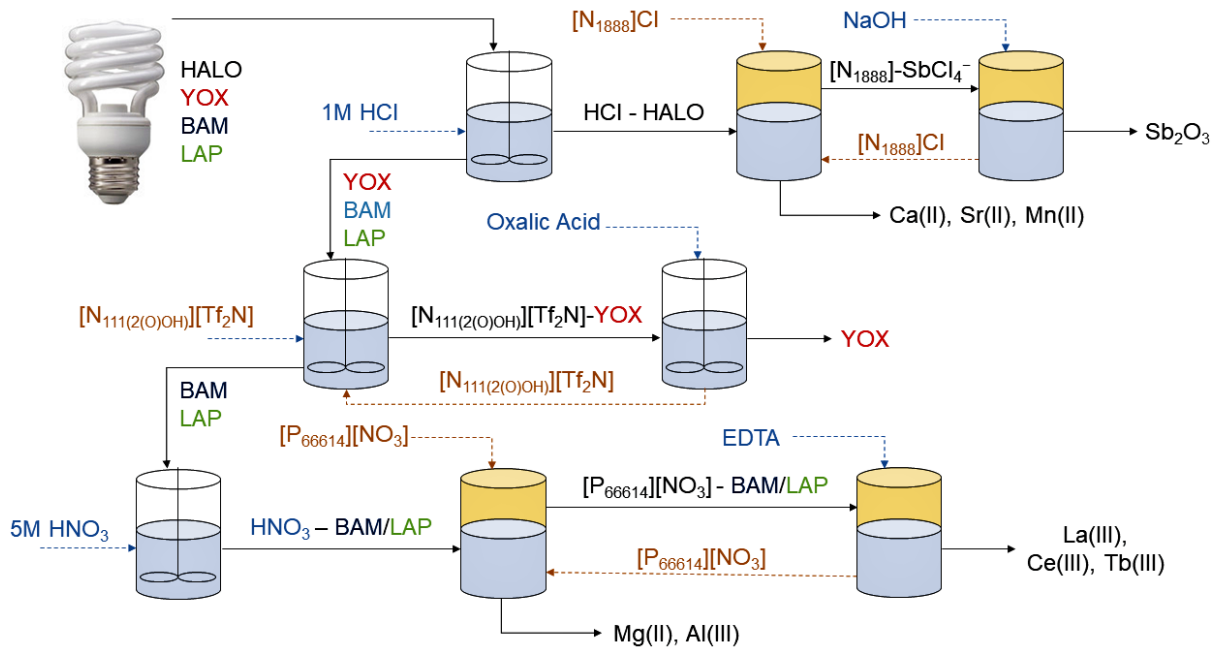
1321 The most cited of all barriers to IL application is their high initial cost; ILs normally fall in the range
1322 of 5 –20 times more expensive than molecular solvents (Plechkova & Seddon, 2008). Although prices
1323 for small quantities should not be used as a guide to commercial utility, at the time of writing the retail
1324 price on the Sigma-Aldrich website for [C₄C₁im][SCN], [C₄C₁im][NTf₂], [C₄C₁im][C₁COO] and
1325 [C₄C₁im]Cl is €2880 kg⁻¹, €1505 kg⁻¹, €776 kg⁻¹ and €288 kg⁻¹ (Sigma Aldrich, 2017). The economic
1326 sustainability of ILs is greatly improved if the IL is recycled. Due to their low vapour pressure and
1327 thermal and chemical stability, ILs are theoretically recyclable over numerous application cycles. It is
1328 estimated that 10 to 20 recycle and application cycles gives them the same cost per cycle as conventional
1329 organic solvents, and over 50 recycles makes them significantly cheaper (Plechkova & Seddon, 2008).
1330 As such, all research should aim to demonstrate the stability and recyclability of their ILs over multiple
1331 cycles. In addition, the solubility of well-known hydrophobic fluorinated ILs notably increases in the
1332 presence of inorganic acids such as HNO₃, HClO₄ and HCl (Fu et al., 2016, Mazan et al., 2016). This
1333 can lead to the irreversible loss of the IL to the aqueous phase during solvent extraction, lowering the
1334 environmental and financial sustainability of the process. A mass balance should be performed at each
1335 stage of the process to quantify overall IL losses and to determine which operation(s) primarily
1336 contribute.

1337 However not all ILs are expensive, especially at an industrial scale. Chen and co-workers (2014)
1338 demonstrated through process modelling that the price of the Brønsted acidic IL triethylammonium
1339 hydrogen sulphate ([N₂₂₂][HSO₄]) and 1-methylimidazolium hydrogen sulphate ([HC₁im][HSO₄]) on
1340 an industrial scale was of \$1.24 kg⁻¹ and \$2.96–5.88 kg⁻¹, making these significantly cheaper than
1341 fluorinated ILs. In addition, DES along with tetraalkylammonium and tetralkylphosphonium salts are
1342 intrinsically cheaper than imidazolium-based ILs (Plechkova & Seddon, 2008). [N₁₈₈₈][Cl] and
1343 [N_{111(2OH)}][Cl] (the starting component of most DES) currently retail at €92 kg⁻¹ and €58 kg⁻¹ respectively
1344 (Sigma Aldrich, 2017). As in all cases, a compromise must be made between the IL/DES selection
1345 (cation and anion selection, functionalisation, etc.), its intended application (leaching, extractant,

1346 hydrophobic diluent, medium for electrodeposition, etc.) and the price of the target metal. Whilst the
1347 use of more expensive IL can be economically justified for the recovery of In, Ag, Au, PGM and some
1348 rare earth elements, the application of fluorinated ILs for the leaching of La_2O_3 makes little economic
1349 sense.

1350 The IL-based solvents covered in this review are for the most part limited to the recovery of value
1351 from PCBs, waste fluorescent phosphor, nickel metal hydride batteries and permanent magnets. To
1352 highlight the great strides made over the last years on the potential of IL-derived solvents for WEEE
1353 treatment, optimised process flowsheets are proposed for the extraction of value in fluorescent lamp
1354 phosphor waste (Figure 15) and nickel metal hydride battery waste (Figure 16). The versatility of
1355 quaternary phosphonium- and ammonium-based ILs for metal extraction based on the selective
1356 formation of anionic metal complexes in various leaching solution (chloride, nitrate, etc.) is fully
1357 exploited. When possible, solvent extraction processes were substituted for their ABS counterpart based
1358 on similar IL cations to further reduce the environmental impact and take advantage of the
1359 thermomorphic properties of phosphonium ILs. The substitution by ABS also simplifies the metal
1360 recovery process as electrodeposition of easily reduced metals or precipitation are possible directly from
1361 the IL-rich phase. The use of the more expensive $[\text{N}_{111}(\text{2}(\text{O})\text{OH})][\text{NTf}_2]$ is justified based on its great
1362 selectivity for YOX phosphor dissolution and the high price of the recovered Eu(III). Through careful
1363 analysis of the waste matrix, selective sequential leaching steps can be designed in order to solubilise
1364 elements of interest at each stage and simplify their purification. Furthermore, the addition of pre-
1365 treatment steps such as mechanical activation, conversion of metals to oxides and/or the hydrolysis of
1366 Fe(III) greatly increases the recovery yields and simplifies the downstream purification of the other
1367 anionic chlorometallates. In all cases, closed-loop systems are suggested to recycle the IL, thereby
1368 improving the ecological and economic aspects of the proposed processes.

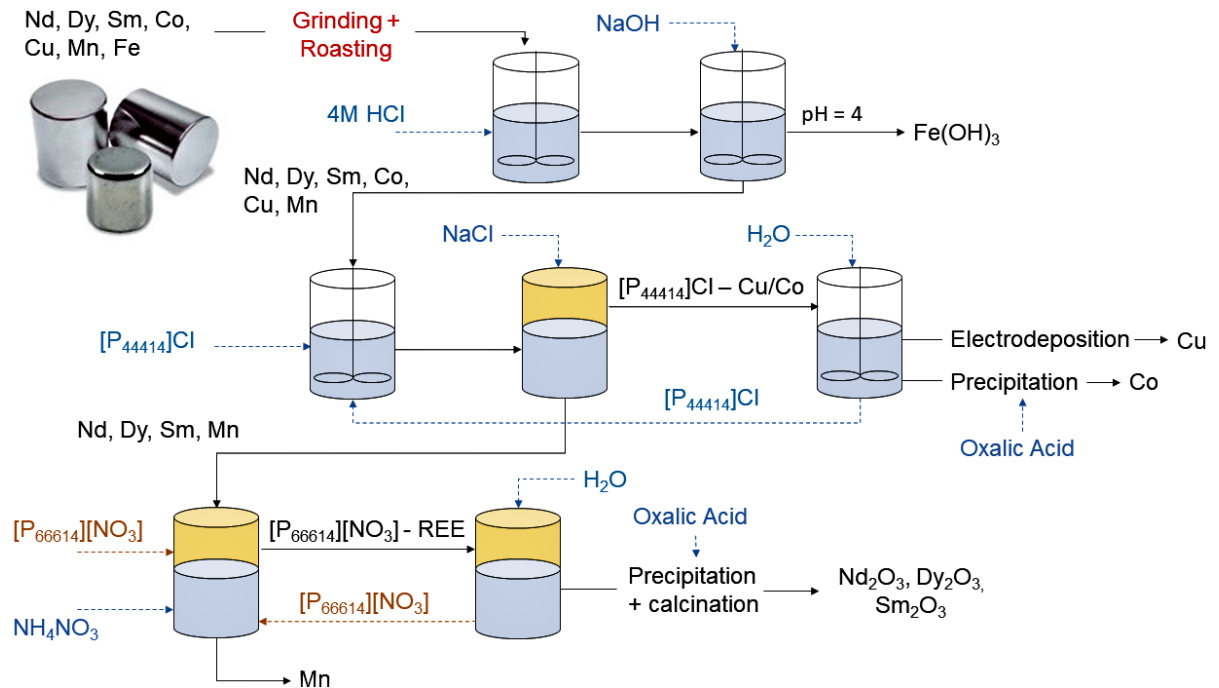
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1370

1371 **Figure 15.** Suggested simplified process flow diagram for the recovery of antimony and REE from
 1372 waste phosphor.

1373



1374

1375 **Figure 16.** Suggested simplified process flow diagram for the recovery of cobalt, copper and REE from
 1376 waste NdFeB magnets.

1377

1378 **8. Conclusions**

1379 WEEE is a global problem issue but also a potentially opportunity due to its high content of valuable
1380 metals. The physico-chemical characteristics of ILs mean they have potential applications in the
1381 recovery of metals from WEEE. Many experimental and theoretical studies have identified appropriate
1382 IL systems for the selective extraction and purification of metals from WEEE. The extraction
1383 performance of many IL systems has been characterised, allowing selection of a particular IL for a
1384 specific metal possible. Quaternary ammonium ILs, DESs and ILs-based ABS were highlighted as the
1385 most promising solutions due to their low environmental impact, competitive price, compositional
1386 flexibility and operational facility. However, significant barriers remain to commercial exploitation of
1387 ILs for metal recovery from WEEE. There is a lack of IL application to actual WEEE waste streams, as
1388 many researchers have worked on simulated systems and this risk missing interactions that occur with
1389 trace components present in WEEE. A further barrier is the high initial cost of many ILs and particularly
1390 fluorinated ILs. Despite high recyclability, the capital investment required has limited the use of ILs to
1391 extraction of high value metals from WEEE and use in systems where a high metal purity is achieved.
1392 Improved upstream collection and sorting to minimise the volume of commingled WEEE would allow
1393 more selective use of ILs.

1394

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1401 **References**

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