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# Solvometallurgy: An Emerging Branch of Extractive Metallurgy

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**Abstract** This position paper introduces the reader to the concept of solvometallurgy, the term used to describe the extraction of metals from ores, industrial process residues, production scrap, and urban waste using non-aqueous solutions. Here, non-aqueous is not used to imply anhydrous, but rather a low water content. The unit operations are as follows: solvent leaching; separation of the residue; purification of the leach solution by non-aqueous solvent extraction or non-aqueous ion exchange; and metal recovery by precipitation or electrolysis in non-aqueous electrolytes. Solvometallurgy is similar to hydrometallurgy in that both the branches of extractive metallurgy use low-temperature processes, but with solvometallurgy, there is no discrete water phase. Both branches use organic or inorganic solvents (excluding water in the case of solvometallurgy). However, for solvometallurgical processes to be sustainable, they must be based on green solvents, which means that all toxic or environmentally harmful solvents must be avoided. Solvometallurgy is complementary to pyrometallurgy and hydrometallurgy, but this new approach offers several advantages. First, the consumption of water is very limited, and so the generation of wastewater can be avoided. Second, the leaching and solvent extraction can be combined to form a single step, resulting in more simplified process flow sheets. Third, solvent leaching is often more selective than leaching with acidic aqueous solutions, leading to reduced acid consumption and fewer purification steps. Fourth, solvometallurgy is useful for the treatment of ores rich in soluble silica (e.g., eudialyte) because no silica gel is formed. In short, solvometallurgy is in a position to help develop the near-zero-waste metallurgical processes, and with levels of energy consumption that are much lower than those with the high-temperature processes. The Technology Readiness Level (TRL) of this emerging branch of extractive metallurgy is still low (TRL = 3–4), which is a disadvantage for short-term implementation, but offers a great opportunity for further research, development, and innovation.

**Keywords** Ionometallurgy · Lyometallurgy · Non-aqueous solvent extraction · Solvometallurgy · Solvent leaching · Sustainable metallurgy

## Introduction

Until a few centuries ago, mankind made use of only seven metals—copper, tin, iron, gold, silver, lead, and mercury—in pure form or in the form of alloys (e.g., bronze) [1]. In the early nineteenth century, metallic zinc began to be produced, although this metal had been used for centuries as a component of brass. All these metals were produced from high-grade ores by the high-temperature, pyrometallurgical processes. However, once the rich ore deposits began to run out, there was no alternative but to start mining lower-grade ores, which could not be processed into a concentrate using the beneficiation methods that were employed at that time. This became a serious problem at the turn of the twentieth century and led to the development of mineral processing (e.g., froth flotation) and

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hydrometallurgical processing (e.g., leaching, ion exchange, and solvent extraction) [2]. Hydrometallurgy makes use of water as a solvent, and operates at much lower temperatures (20–200 °C) than pyrometallurgy (>300 °C) [3]. Hydrometallurgical processes were originally developed for the extraction of copper and gold, but the extraction of uranium from low-grade ores after World War II gave a boost to the development of hydrometallurgy.

Hydrometallurgical flow sheets are now important for the extractive metallurgy of the rare-earth elements (REEs), zirconium, niobium, tantalum, gallium, indium, platinum-group metals (PGMs) zinc, and copper. The aluminum industry has also contributed to the development of hydrometallurgy; for example, the Bayer process, used to prepare pure alumina from bauxite ore, is the oldest example of a commercialized, high-pressure hydrometallurgical process. For the production of iron, pyrometallurgy is the dominant technique, whereas the flow sheets for the extraction of many other metals are based on a combination of pyrometallurgical and hydrometallurgical process steps. For instance, after sintering and roasting the ore concentrate (i.e., a pyrometallurgical process), the calcine can be leached by an acid (i.e., a hydrometallurgical process). Hydrometallurgy is used only in the first parts of the flow sheet, and metal production is finalized quite often by pyrometallurgy.

As the demand for metals increases, the metallurgical industry has to rely increasingly on low-grade ores. In fact, industry is currently considering whether to recover metals from industrial process residues (e.g., bauxite residue, goethite, jarosite, phosphogypsum) or mine tailings, which were considered as waste until recently. Pyrometallurgical methods are often incapable of treating these residues in an economic way, because the metal concentrations are too low. Likewise, most hydrometallurgical processes are not very suitable for the recovery of metals from low-grade ores, tailings, or industrial residues with low concentrations of valuable metals, because leaching with aqueous solutions of acids suffers from a poor selectivity. This means that not only are the metals of interest dissolved, but also large parts of the matrix or gangue minerals go into solution, which leads to unnecessary acid consumption and generation of impure leachates. Alkaline leaching is more selective, but not all metals of interest can be solubilized by alkaline lixiviants. Furthermore, alkaline leaching causes the dissolution of large amounts of silica. The processing of urban waste (e.g., waste electric and electronic equipment, WEEE) by hydrometallurgical processes has some specific issues. For instance, the dissolution of metals and alloys from scrap through the use of acids will form large volumes of flammable hydrogen gas, while the dissolution of semiconductor materials such as gallium arsenide can generate highly toxic arsine gas. The recovery of metals from mine tailings, industrial process residues, and urban waste helps to close the materials loop and to establish a circular economy. Figure 1 shows the different materials' streams in the zero-waste approach to metal-containing waste streams: (1) direct (pre-consumer) recycling of metal scrap and swarf generated during the production of metal-based (intermediate) products; (2) (post-consumer) recycling and/or urban mining of, respectively, flows and stocks of complex, multimaterial, metal-containing products (for example, a hybrid electric vehicle); (3) landfill mining of historic urban solid waste; (4) metal recovery from flows of industrial process residues from primary and secondary metal productions; and, finally, (5) metal recovery from stocks of landfilled mining waste and industrial process residues. The zero-waste vision implies that for (4) and (5), the residual mineral matrixes are valorized in building or engineered materials. In combination with the extraction of metals from low-grade ores, an optimized material's flow also helps to slow the depletion of our natural resources.

In cases where pyrometallurgical or hydrometallurgical processes fail to efficiently extract metal values from low-grade ores, mine tailings, industrial process residues, or urban waste, we could turn to solvometallurgy, which constitutes a branch of extractive metallurgy that is complementary to both pyrometallurgy and hydrometallurgy. *Solvometallurgy* makes use of processes involving the non-aqueous solvents. These non-aqueous solvents can be molecular organic solvents, ionic liquids, deep-eutectic solvents (DESs), but also the inorganic solvents such as liquefied ammonia, concentrated sulfuric acid, or supercritical carbon dioxide. High-temperature molten salts and liquid metals are excluded if they require temperatures above 300 °C. Non-aqueous solvents do not imply anhydrous conditions, but rather a low water content. Some solvometallurgical processes must take place in the absence of water, while for other processes, a low water content is required. Strictly speaking, conventional solvent extraction, which is based on the preferential distribution of metal ions between an aqueous phase and a water-immiscible organic phase, is not a solvometallurgical process because of the presence of an aqueous phase.

The original concept of solvometallurgy dates from the late 1940s and early 1950s when researchers in the United States were developing processes to recover uranium from the uranium ores through leaching with organic mixtures such as acetone-HCl or alkylphosphoric acids in kerosene [4–9]. At that time, the term "*lyometallurgy*" was introduced to describe solvent-based leaching processes, derived from the Greek word *lyein*, meaning to loosen or to dissolve. Other suggested terms included "*anhydrometallurgy*" and the contradictory "*non-aqueous hydrometallurgy*." Later, solvometallurgical methods were used for
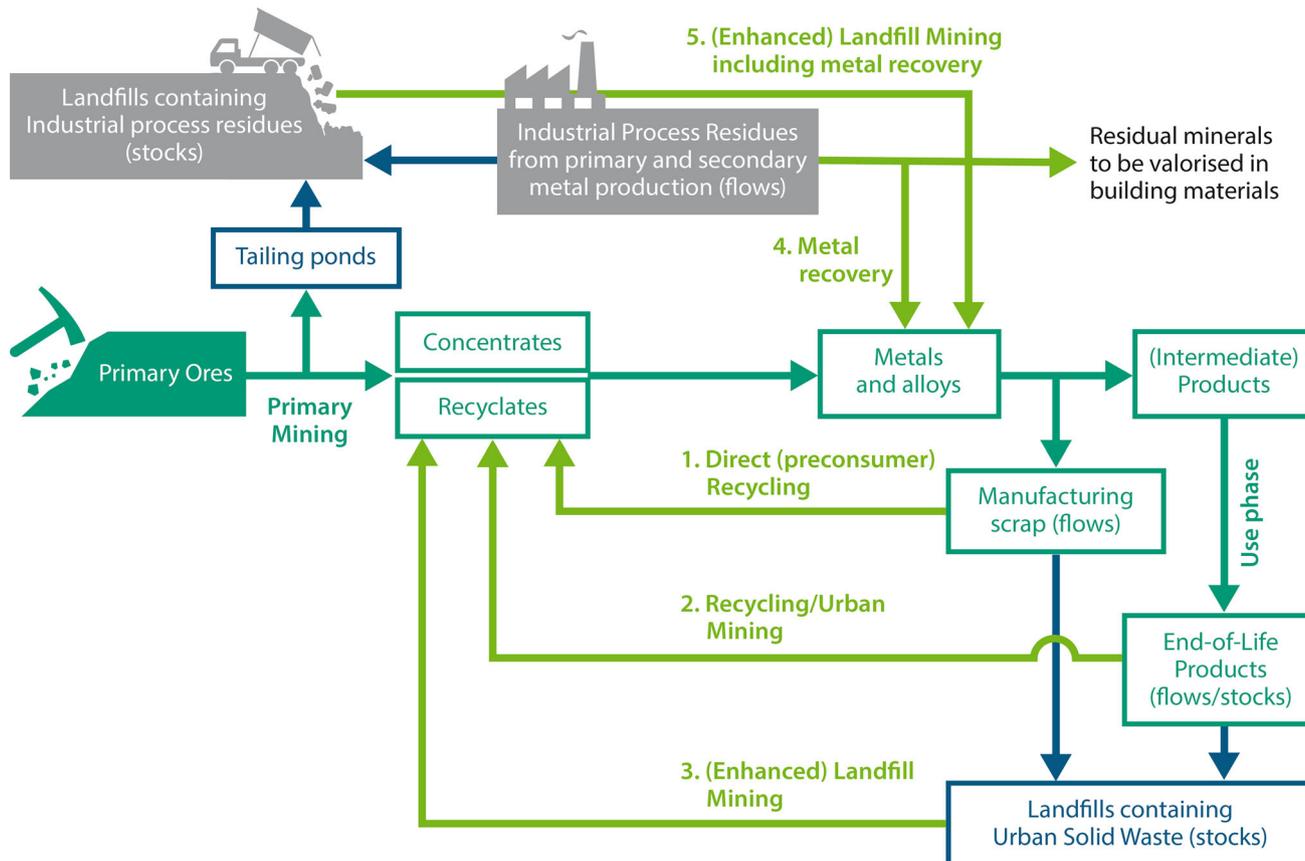
**Fig. 1** Zero-waste approach to metal-containing waste streams (Color figure online)

the recovery of copper from chrysocolla, a largely amorphous copper silicate [10–12]. It was also realized that solvometallurgy could be useful for the reprocessing of spent nuclear fuel [13]. Sastri reviewed the possibility of using organic solvents and chelating agents for the processing of ores [14]. In 1985, in his book on ion solvation, Marcus used the term "*solvometallurgy*" to describe the extension of hydrometallurgy to solvents other than water [15]. Russian researchers also applied the solvometallurgical methods to recover metals from complex silica-rich ores (e.g., eudialyte), urban waste, and pellets of nuclear fuel [16–19]. In recent years, there has been progress in the use of ionic liquids and deep-eutectic solvents in metallurgical processes, ranging from leaching, to solvent extraction, and the electrodeposition of metals [20–23]. The term "*ionometallurgy*" was coined for metallurgical processes involving the ionic solvents [24], but ionic-liquid processes are solvometallurgical as well. Although we could consider hydrometallurgy to be part of solvometallurgy (since water is a solvent), we want to make a clear distinction between hydrometallurgy (based on water as solvent) and solvometallurgy (based on non-aqueous solvents).

In this paper, we describe the concept of solvometallurgy and its potential applications in extractive metallurgy. An overview of solvometallurgical unit processes is provided, and ten reasons are presented to highlight why solvometallurgy is a useful complement to hydrometallurgy and pyrometallurgy. Because we realize that several hurdles must be overcome before solvometallurgy will become commonplace in extractive metallurgy, the main challenges facing this new approach are discussed. Selected examples of solvometallurgical processes reported in the scientific literature and the patent literature are described. Attention is paid to the selection and disposal of the solvents, because the use of green solvents is a must for the development of sustainable solvometallurgical processes.

## Solvometallurgical Unit Processes

Most of the unit processes in solvometallurgy are very similar to those in hydrometallurgy, with the main difference being that the water is replaced by a non-aqueous solvent. Table 1 shows a comparison of the

**Table 1** Comparison of hydrometallurgical and solvometallurgical processes

|  | Hydrometallurgy | Solvometallurgy |
| --- | --- | --- |
| Leaching | Leaching with aqueous solutions of acids or bases, or aqueous solutions of chelating agents | Leaching with acid-saturated neutral or basic extractants, acidic extractants, chelating extractants diluted in nonpolar organic solvents; acid-saturated polar solvents; halogens in organic solvents |
| Solvent extraction | Distribution between an aqueous phase and an immiscible organic phase | Distribution between two immiscible organic phases |
| Ion exchange | Ion exchange between the resin and aqueous solutions | Ion exchange between the resin and non-aqueous solutions |
| Precipitation | Precipitation by reagent addition, control of pH, evaporation of water | Precipitation by reagent addition, addition of anti-solvent, evaporation of solvent |
| Electrolysis | Electrodeposition of metals at the cathode from an aqueous electrolyte | Electrodeposition of metals at the cathode from a non-aqueous electrolyte |

hydrometallurgical and solvometallurgical processes. Some solvometallurgical processes make use of solvent–water mixtures, but the solvent concentration is assumed to be at least 50 vol%, because otherwise the phase should be considered as an aqueous phase with added solvent, rather than as a non-aqueous phase. It is important to note that the word solvent can have different meanings in solvometallurgy, and therefore the intended meaning must be derived from the context. The most general meaning of solvent is that of an organic phase, as opposed to an aqueous phase in hydrometallurgy. A solvent can contain different components, such as the extractant, the diluent, and dissolved acids. The diluent is an organic solvent, the main purpose of which is to obtain an organic phase with a reasonably low viscosity, if the extractant is a viscous liquid. According to the more strict definition, the term solvent is used to indicate the diluent.

## Solvent Leaching

In hydrometallurgy, leaching (solid–liquid extraction) mainly involves: (1) mineral acids such as $H_2SO_4$, $HNO_3$, or HCl, (2) bases such as $NH_3$ or NaOH, or (3) chelating agents such as EDTA or citric acid. These lixiviants are used in diluted or concentrated forms. In solvometallurgy, one approach to carrying out leaching is with solutions of mineral acids in water-miscible (polar) organic solvents, such as acetone, methanol, ethanol, isopropanol or ethylene glycol [4, 25–28]. HCl is often selected as the acid. Anhydrous solutions of HCl in an organic solvent can be prepared by saturating the solvent with HCl gas and diluting with solvent until the appropriate HCl concentration. It is also possible to use organic acids such as formic acid or acetic acid in undiluted form or diluted with small amounts of water. Other lixiviants are deep-eutectic solvents (DESs) [29].

Another approach to solvent leaching is the use of water-immiscible (nonpolar) organic solvents with dissolved extractants. Here, the lixiviant is very similar to the organic phase used in solvent-extraction processes [6, 9, 10–12]. If an acidic extractant is used, such as a dialkylphosphoric acid (e.g., D2EHPA) or a carboxylic acid (e.g., Versatic acid), the organic phase can be applied directly for the solvent leaching of a solid material, without the need to add a mineral acid. Higher selectivities for leaching can be achieved by using solutions of chelating extractants as lixiviants. Some examples include α-hydroxyoximes (e.g. LIX® 63), β-hydroxyaryloximes (e.g. LIX® 65 N), β-diketones (e.g. LIX® 54), and 8-hydroxyquinolines (e.g. Kelex® 100). In Fig. 2, the structures of some commonly used extractants are shown.

If a neutral extractant such as tri-*n*-butyl phosphate (TBP) is used, in general the solvent cannot be used directly for the solvent leaching of a solid material, because the neutral extractants are poor lixiviants. However, very powerful lixiviants can be obtained by bringing an organic phase containing TBP into contact with a concentrated aqueous solution of a mineral acid ($H_2SO_4$, $HNO_3$, HCl) [13, 30, 31]. During this conditioning step, TBP will extract the acid molecules as well as a certain amount of water. Whereas the extraction of acids by TBP is often an unwanted phenomenon in solvent extraction (because this process competes with the extraction of metal ions), the affinity of TBP for strong acids is an asset during solvent leaching, because a highly acidic organic phase can be obtained. TBP–$H_2SO_4$, TBP–$HNO_3$ and TBP–HCl are useful lixiviants in solvometallurgy. TBP can be used in undiluted form or it can be diluted in an organic solvent to reduce its viscosity. The strength of the TBP-based lixiviant can be tuned by varying the acid concentration in the conditioning step. TBP can be replaced by other neutral extractants such as Cyanex® 923, which is a commercial mixture of trialkylphosphine oxides [32]. We could also consider using the 8-hydroxyquinoline derivative Kelex® 100 saturated with mineral acids as a lixiviant [33]. The nitrogen atom in the quinoline ring is relatively basic and
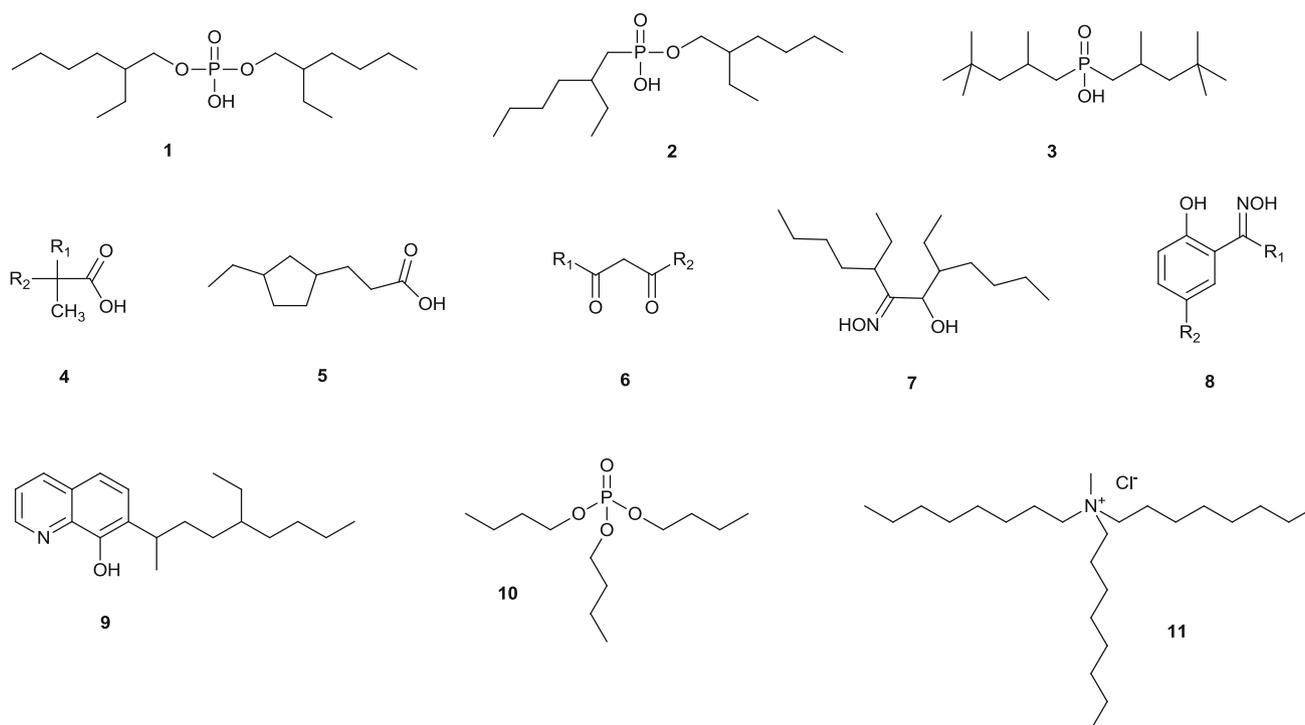
**Fig. 2** Structures of extractants: bis(2-ethylhexyl)phosphoric acid, D2EHPA (*1*), (2-ethylhexyl)phosphonic acid, mono(2-ethylhexyl) ester (*2*), bis(2,4,4-trimethylpentyl)phosphinic acid, Cyanex® 272 (*3*), Versatic acid (*4*), naphthenic acid (*5*), β-diketone (*6*), 5,8-diethyl-7-hydroxydodecane-6-oxime, LIX63 (*7*), β-hydroxyaryloxime (*8*), Kelex® 100 (*9*) tri-n-butylphosphate, TBP (*10*), Aliquat® 336 (*11*)

has a strong tendency to bind acids. The strong tendency to extract acids is a disadvantage when using Kelex® 100 for conventional solvent extraction, but it is an advantage when using this extractant for solvent leaching.

Basic extractants are anion exchangers, and they are not very suitable for solvent leaching, unless they are combined with mineral acids. In undiluted form, they can be considered as ionic liquids. The ionic liquid trihexyl (tetradecyl)phosphonium chloride (Cyphos® IL 101), saturated with concentrated HCl [34] as well as the ionic liquid betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf$_2$N] have been used to dissolve different metal oxides [35]. Instead of Cyphos® IL 101, a quaternary ammonium chloride such as Aliquat® 336 could also be used.

A promising system for solvent leaching is *n*-octanol/HCl; this was originally developed by Russian researchers to chemically attack resistant ores such as titanomagnetite [36]. *n*-Octanol is a cheap solvent and has a very low solubility in water (<0.1%). This system has a low density, resulting in good hydrodynamics and a rapid phase separation from water. The lixiviant is stable over time and is reasonably stable toward concentrated mineral acids. The maximum concentration of HCl in *n*-octanol is 5.2 mol/L at 20 °C [36].

In some cases, the dissolution of metal oxides is enhanced by a change in the oxidation state. For instance,

MnO$_2$ is much easier to dissolve in an acid solution when a reducing agent is present. An example of a reducing lixiviant for use in solvometallurgy is methanol-HCl [27, 37]. For the dissolution of metals in their elemental state, an oxidative dissolution process is required. This can be achieved with solutions of chlorine, bromine or iodine in organic solvents (vide infra).

Solvent leaching has a number of routes (Fig. 3) [6]. The organic extractant phase can be brought into direct contact with the solid material; this approach is called "*direct solid leaching*." The solid can be a crushed and grinded ore, but it can also be a fine-grained industrial process residue, or even a solid that is obtained by the dehydration of aqueous leachates or by precipitation from aqueous leachates. After the solvent leaching, the liquid organic phase and the solid residue can be separated by filtration, decantation, or centrifugation, followed by washing of the solid residue with the diluent or with another organic solvent to reduce the amount of solvent retained by the solid particles. Alternatively, the solid material can be brought into contact with both a concentrated mineral acid (typically concentrated H$_2$SO$_4$) and the organic phase. The mineral acid acts as a solubilizing agent. It is also possible to digest the ore first with the mineral acid (i.e., an acid cure), before the damp solid is brought into contact with the organic phase. This approach,
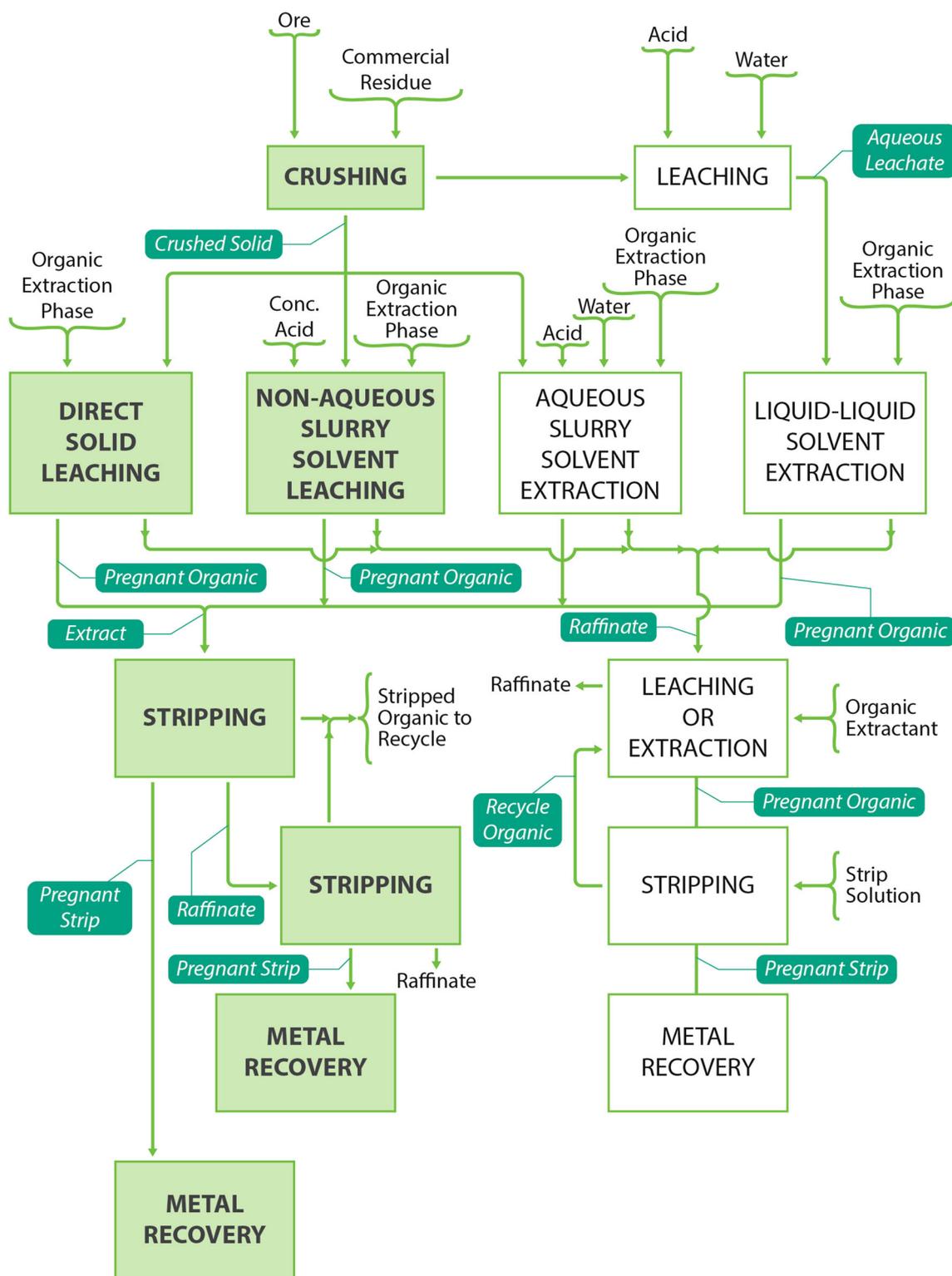
**Fig. 3** Comparison of different approaches to solvent leaching involving hydrometallurgical leaching/extraction methods. Direct solid leaching and non-aqueous-slurry solvent leaching are solvometallurgical processes, while aqueous-slurry solvent leaching is not. Figure adapted from Ref. [6] (Color figure online)

with the addition of a concentrated acid and an organic extracting phase to the solid material, is called "*non-aqueous-slurry leaching*," because the acid and the solid

form a slurry with a low water content. After leaching, the liquid organic phase and the solid residue can be separated by filtration, decantation, or centrifugation, followed by

washing of the solid residue with a solvent, just as in the case of direct solid leaching. "*Non-aqueous-slurry leaching*" should not be confused with "*aqueous-slurry solvent extraction*," which is also known as "*solvent-in-pulp extraction*" [38]. In the latter approach, an organic extraction phase is brought into contact with a slurry of the solid material and an aqueous phase. After leaching, the organic phase can be separated from the aqueous phase and the solid residue after phase disengagement by simple decantation. However, an aqueous raffinate is also obtained, which then needs to be treated further. "*Aqueous-slurry solvent extraction*" is not considered as a solvometallurgical method, because of the presence of a discrete aqueous phase. It is important to note that in the three approaches, i.e., direct solid leaching, non-aqueous-slurry leaching, and aqueous-slurry solvent extraction, the metallurgical unit operations of leaching and solvent extraction are combined into a single step. This is a form of process intensification, compared with the traditional approach, where leaching and solvent extraction are carried out as two separate steps. After solvent leaching, both direct solid leaching and non-aqueous-slurry leaching give an organic-pregnant leach solution in which the metals of interest are dissolved. The metals can then be recovered from this organic phase using different approaches, depending on the polarity of the organic phase. If the organic phase contains a solvent with low polarity, the organic phase can be treated in the same way as a loaded organic phase in solvent extraction, using a scrubbing step with an aqueous solution to remove the co-dissolved impurities and a stripping step to recover the valuable metals. The stripping step can be carried out with an aqueous stripping solution or with a stripping reagent (for precipitation stripping). In principle, the aqueous phase can be replaced by a polar organic phase, which is immiscible with the less-polar phase. If the solvent leaching is performed using a polar organic phase, the metals can be recovered by precipitation, non-aqueous ion exchange, the use of a solid adsorbent (e.g., activated charcoal), or by non-aqueous solvent extraction with an immiscible organic phase.

**Non-Aqueous Solvent Extraction**

Solvent extraction (SX) is a very important technique in hydrometallurgy for the separation and purification of metals such as cobalt, nickel, copper, zinc, uranium, REEs, and PGMs [39]. In conventional solvent extraction, the metal ions are distributed between an aqueous phase and a water-immiscible organic phase, in general with the aid of an extractant (also called the extracting agent). Because the various metal ions distribute differently between the aqueous and organic phases, mixtures of metal ions can be

separated by solvent extraction. It is clear that an aqueous phase is present in all the hydrometallurgical solvent-extraction processes. This could give the impression that all the solvent-extraction systems must involve an aqueous phase. However, this is not correct: all that is required are two mutually immiscible liquid phases. Solvent-extraction systems can also consist of (1) two mutually immiscible molten salts, (2) a molten salt and a molten metal, (3) a molten salt and an organic solvent, or (4) two mutually immiscible organic solvents.

An important point with respect to solvometallurgy is the possibility to perform solvent extraction with two immiscible molecular organic solvents, two immiscible ionic liquids, or combinations thereof (Fig. 4). It is obvious that we cannot speak about the aqueous phase and the organic phase, as is the case with conventional solvent extraction. It is better to use the terms more-polar phase and less-polar phase. The solvent pairs for non-aqueous solvent extraction need to fulfill the following requirements: (1) ability to form two immiscible phases and have low mutual solubility of the two solvents; (2) exhibition of rapid phase separation after mixing; (3) demonstration of good solubility of the extractant in the less-polar phase and poor solubility of the extractant in the more-polar phase; and (4) demonstration of good solubility of the to-be-extracted metal salts in the more-polar phase and good solubility of the extracted metal complexes in the less-polar phase. The first condition is the most difficult to fulfill because most organic solvents are mutually miscible. However, several guidelines are available for the initial selection of solvent pairs, such as reported miscibility data [40, 41], the Hildebrand solubility parameter $\delta$ for solvents [42], and the mixotropic series [43, 44]. The mixotropic series is a useful tool: the further the two solvents are apart in the series, the lower is their mutual solubility [43, 44]: concentrated aqueous salt solutions > mineral acids > water > lactic acid > formamide > morpholine > formic acid > nitromethane > acetonitrile > acetic acid > methanol > glycolmonoethylether > ethanol >
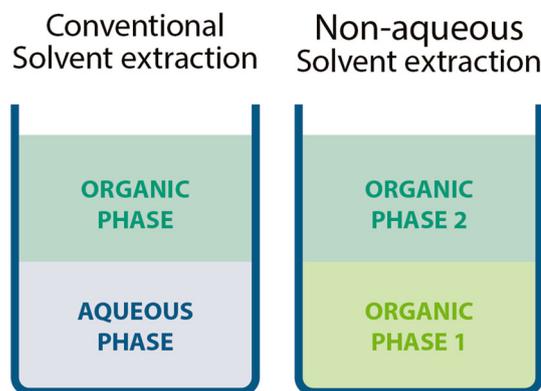


**Fig. 4** The principle of non-aqueous solvent extraction (*right*) compared with conventional solvent extraction (*left*) (Color figure online)

propanol > phenol > aniline > acetone > dioxane > tetrahydrofuran > pyridine > ethyl acetate > methyl ethyl ketone > diethyl ether > dichloromethane > tetrachloroethylene > chloroform > dichloroethane > trichloroethane > benzene > toluene > carbon tetrachloride > carbon disulfide > cyclopentane > cyclohexane > 2,2,4-trimethylpentane > heptane > hexane > paraffin oil.

The solvents at the beginning of the series have a very high polarity, whereas the solvents at the end of the series have a low polarity. Although the miscibility can be tested by simple test-tube experiments, the mutual solubility must be quantitatively measured using Fourier transform infrared (FTIR) spectroscopy, gas chromatography (GC) or nuclear magnetic resonance (NMR) spectroscopy. The mutual solubility is a function of the temperature and the concentration of dissolved salts. Two solvents that are totally miscible in the pure state can phase-separate after the addition of metal salts. For instance, ethanol is miscible with all conventional organic solvents. However, the phase separation of a mixture of ethanol and $n$-dodecane occurs upon the addition of 1 M LiCl. Higher LiCl concentrations result in the phase separation of mixtures of ethanol and aromatic solvents. Examples of immiscible solvent pairs are methanol–dodecane, formamide–dodecane, acetonitrile–dodecane, and ethylene glycol–dodecane. The ionic liquids 1-ethyl-3-methylimidazolium chloride and trihexyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl)phosphinate form a pair of immiscible non-aqueous solvents as well [45]. Another immiscible pair of ionic liquids are betainium bis(trifluoromethylsulfonyl)imide and trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide [46]. It is important to realize that the extractant dissolved in the less-polar phase can have an influence on the mutual miscibility of the two organic solvents; two solvents that are mutually immiscible can become partly miscible after dissolving an extractant in the less-polar phase. Moreover, some extractants can also extract solvent molecules from the more-polar phase.

Although non-aqueous solvent extraction has not received much attention so far, it offers several advantages over conventional aqueous solvent-extraction systems. First of all, the approach is applicable to the separation of covalent metal compounds such as halide complexes of $p$-block elements ($SiCl_4$, $GeCl_4$, $SbCl_3$) and early $d$-block elements ($ZrCl_4$, $HfCl_4$, $NbCl_5$, $TaCl_5$), as well as organometallic compounds. These compounds hydrolyze in water, and the hydrolysis reaction can be vigorous. Second, there is the opportunity to carry out separations that are not efficient in an aqueous solution because of the differences in the extraction mechanism.

## Non-Aqueous Ion Exchange

Ion exchange (IX) is an often-used method for the removal of metal ions or metal salts from aqueous solutions.

Typically, ion exchanges are carried out using functionalized, crosslinked, polystyrene-derived resins. The strongly acidic cation-exchange resins have sulfonic acid functional groups, whereas the strongly basic cation-exchange resins have quaternary ammonium groups. Whereas solvent extraction is more often used to recover metals from concentrated solutions, ion exchange is typically used for the recovery of metals from dilute aqueous solutions. Many studies have been devoted to the effect of adding polar organic solvents to the aqueous phase, because the presence of an organic solvent can lead to a stronger adsorption of metal ions by the ion-exchange resin and to higher selectivities in separation processes [47]. On the other hand, there are relatively few studies on ion exchange in non-aqueous solvents. Ion-exchange resins must swell in the solvent used in order to adsorb and exchange the ions at a sufficiently rapid rate. In general, ion-exchange resins swell well in water, even if the resin has a relatively high degree of crosslinking. However, commonly used ion-exchange resins might not swell sufficiently in a non-aqueous solvent, leading to a slowing down or inhibition of the ion-exchange reaction. Another reason is that the compounds must exhibit some ionic dissociation, which means that a polar solvent with a relatively high dielectric constant $\varepsilon_r$ must be used. An exception is anion exchangers with relatively basic anions, which can bind neutral metal complexes through adduct formation. For instance, an anion exchanger in the chloride form can bind nondissociated $CoCl_2$ dissolved in an organic solvent by the formation of a complex anion [48].

Solvents that can be used instead of water in ion-exchange processes include the lower alcohols (methanol, ethanol, propanol, isobutanol, and $n$-butanol), polyalcohols (ethylene glycol, propylene glycol, glycerine), ethers (diethyl ether, dioxane, tetrahydrofuran), ketones (acetone, methyl ethyl ketone), organic acids (formic acid, acetic acid), pyridine, DMF and DMSO [47]. To these solvents, mineral acids can be added, for example, $H_2SO_4$, $HNO_3$, HCl or HBr. Often, mixtures of these solvents with water are used instead of non-aqueous solvents. However, as mentioned above, the liquid phase must consist of at least 50 vol% of organic solvent if we are to consider the ion-exchange process as a solvometallurgical process. An example of an exotic solvent for ion exchange is molten urea [49].

A major advantage of non-aqueous ion exchange is that more metal ions form anionic complexes with chloride or nitrate ions in organic solvents than in water, which means that more metals can be recovered using an anion exchanger from an organic solution than from an aqueous solution. A typical example is the trivalent rare-earth ions. These do not form anionic complexes with chloride ions in aqueous solutions and form only anionic complexes with nitrate ions in the presence of very high nitrate

concentrations. However, the rare-earth ions readily form anionic complexes with chloride or nitrate ions in organic solvents such as methanol. Other metal ions that only form anionic complexes with chloride ions in organic solvents are thorium(IV), nickel(II), calcium(II) and chromium(III).

Cation exchangers in the protonated ($H^+$) form can be used to recover metal ions from the leachate after direct solid leaching with a solution of a mineral acid in a polar organic solvent, such as HCl in acetone. Anion exchangers in the chloride form can be used to recover metal chloride salts from organic solvents, even from those with a lower polarity, as long as the swelling of the resin is sufficient. Another approach to removing salts from organic solvents is to use dual or mixed beds of cation and anion exchangers [50].

## Precipitation or Crystallization

An alternative approach in hydrometallurgy to the recovery of dissolved metals from the leachate—in addition to solvent extraction, ion exchange or adsorption by activated charcoal—is crystallization or precipitation. Crystallization results from evaporation of the aqueous phase until the aqueous solution becomes saturated and the metal salts start to form crystals. Precipitation can be achieved by increasing the pH to form insoluble hydroxides, or by adding a precipitation agent such as sodium carbonate to precipitate insoluble metal carbonates. Metals can be recovered in metallic form by cementation (for instance by adding iron scrap to a $CuSO_4$ solution) or by reduction with hydrogen gas [1]. In principle, most of these methods can be applied to recover metal salts dissolved in organic solvents, although it is important to realize that water must be present for the precipitation of metal hydroxides. An alternative approach to crystallize or precipitate metal compounds from organic solutions is through the addition of an anti-solvent that is miscible with the solubilizing solvent. It is important to keep in mind that metals must be reduced to the metallic state. Precipitation is needed only if purification or further separation from contaminants is required.

## Electrolysis in Non-Aqueous Electrolytes

The electrowinning of metals can be achieved from aqueous electrolytes or from molten salts. It is often used to recover copper, nickel, and zinc from aqueous solutions. A typical example of an electrowinning process based on molten-salt electrolytes is the Hall–Héroult process for producing aluminum metal. Electrolysis can also be used for the electrorefining of metals, by anodic dissolution of the metal and electroreduction of the metal at the cathode. Another use of electroreduction is covering metallic

objects with a thin protective or decorative layer of another metal (i.e., electroplating). An example is the coating of a steel plate with a layer of zinc for corrosion protection. Many fundamental studies have been devoted to the electrodeposition of metals from non-aqueous electrolytes, but very few of them have been applied on an industrial scale. There are several reasons for this lack of industrial interest. First of all, non-aqueous electrolytes with dissolved conducting salts have a much lower conductivity with respect to aqueous electrolytes, so that the electrodeposition rates are much slower. Second, there are serious safety issues associated with many organic electrolytes, especially if they are based on volatile solvents such as diethyl ether. Third, sacrificial anodes have to be used, because otherwise the organic solvents in the electrolyte bath will decompose. Most of the technologies developed for the electrodeposition of metals from non-aqueous solvents are about the electrorefining or electrodeposition of metal coatings, not about electrowinning. One of the few examples of the electrowinning of metals from non-aqueous solvents is the electrowinning of zinc and lead from deep-eutectic solvents after the leaching of these metals from electric-arc-furnace (EAF) dust [51]. These deep-eutectic solvents also make it possible to deposit hard chrome layers from chromium(III) salts, which is only possible from carcinogenic chromium(VI) salts when using aqueous electrolytes [52]. The electrodeposition of aluminum layers from non-aqueous electrolytes containing organo-aluminum compounds is applied on an industrial scale by companies such as AlumiPlate Inc. in Minneapolis, MN (www.alumiplate.com) and Rasant–Alcotec in Overath, Germany (www.rasant-alcotec.de). The electrodeposition or electrorefining of metals from non-aqueous electrolytes is interesting for metals that cannot be deposited from aqueous electrolytes, e.g., aluminum, or which can only be deposited with low current efficiencies from aqueous solutions, e.g., germanium. There is a large body of literature on the electrodeposition of metals from ionic liquids, but most of this research is fundamental studies [23, 53, 54].

## Organic Solvents for Solvometallurgy

### Green Solvents

It is clear that the solvent plays a crucial role in solvometallurgy and that careful solvent selection is essential. However, the selection of the best solvent for a solvometallurgical process is not only based on performance. Stability, the possibility to recycle the solvent, and economics, because environmental impact, safety, and toxicity must also be considered. The sustainability of a solvometallurgical process is closely related to the solvent

on which the process is based. A sustainable solvometal-lurgical process cannot make use of harmful and dangerous solvents. Such solvents must be avoided, even if they would perform well in a specific leaching or extraction process. A large number of organic solvents are commercially available at a reasonable cost, but not all of these solvents are useful in solvometallurgical processes. Table 2 lists the most relevant organic solvents for solvometal-lurgy, divided into three classes: (1) preferred, (2) usable and (3) undesirable, according to the Pfizer "traffic light" solvent-selection guide [55]. If possible, the solvents listed in the first column of Table 2 should be used (= preferred solvents). If no suitable solvent is found in the first column, a solvent listed in the second column can be tried (= usable solvents). However, solvents listed in the third column of Table 2 (= undesirable solvents) must be strictly avoided for the development of sustainable solvometallurgical processes. These solvents either have a very low flash point, easily form explosive peroxides, are ozone-depleting substances, have other environmental issues, they are toxic

or they are carcinogenic. There is little ambiguity about the list of solvents in the third column, in the sense that all these solvents are problematic. The division of solvents among the first two columns is, however, more arbitrary, because the sustainable character of a solvent is determined by several criteria, including workers' safety, process safety, and environmental concerns. For more information on solvent-selection guides, the reader is referred to the literature [55–59]. It is important to realize that these solvent-selection guides were drawn up for the chemical and pharmaceutical industries and not for extractive metal-lurgy. Nevertheless, many conclusions have general validity.

Ionic liquids and deep-eutectic solvents are not listed in Table 2 because the properties of these solvents are very much dependent on the composition. The compositional range here is too wide to draw any general conclusions. However, these solvents are often considered as green solvents because of their nonvolatility, low flammability, and, in general, low toxicity.

**Table 2** Solvent-selection guide

| Preferred | Usable | Undesirable |
|---|---|---|
| water | cyclohexane | pentane |
| methanol | methyl cyclohexane | hexane(s) |
| ethanol | heptane | diisopropyl ether |
| 2-propanol | isooctane | diethyl ether |
| 1-propanol | toluene | dichloromethane |
| 1-butanol | xylenes | dichloroethane |
| tert-butanol | acetonitrile | chloroform |
| 1-octanol | 2-methyltetrahydrofuran | dimethyl formamide (DMF) |
| glycerol | cyclopentyl methyl ether | pyridine |
| polyethylene glycol (PEG) | dimethyl sulfoxide (DMSO) | N-methylpyrrolidone (NMP) |
| polypropylene glycol (PPG) | ethylene glycol | dimethoxyethane (DME) |
| acetone | acetic acid | dioxane |
| methyl ethyl ketone (MEK) | methanesulfonic acid | tetrahydrofuran (THF) |
| methyl isobutyl ketone (MIBK) | | petroleum spirits |
| diisobutyl ketone (DIBK) | | benzene |
| γ-valerolactone | | nitrobenzene |
| ethyl acetate | | carbon tetrachloride |
| isopropyl acetate | | carbon disulfide |
| isobutyl acetate | | |
| isoamyl acetate | | |
| dimethyl carbonate | | |
| diethyl carbonate | | |
| propylene carbonate (PC) | | |
| propylene glycol ethers | | |
| propylene glycol ethers acetates | | |
| biodiesel | | |
| (biodegradable) GTL solvents* | | |

*GTL = gas-to-liquid

Volatile solvents might appear to be very useful because they can be recycled by distillation. However, they contribute a great deal to smog formation and present health risks through inhalation. Many volatile solvents have a low flash point, are flammable, and can even form explosive mixtures with air. If possible, distillation should be avoided as a recycling method for organic solvents because this technique is energy intensive and requires the use of volatile solvents. It is, therefore, recommended to explore nonthermal techniques for solvent recuperation rather than distillation. An example of such a technique is *organic solvent nanofiltration* (OSN), also known as *solvent-resistant nanofiltration* (SRNF), which is a pressure-driven membrane technique [60].

The environmental impact of a solvent requires more attention when the solvent is used in a system that is open to the environment, rather than a fully closed system. A solvent used in an open system should be nonvolatile and have a low toxicity. In the case of solvents used for leaching in open systems (e.g., for heap leaching), the biodegradability, i.e., the breakdown of chemical compounds by microorganisms, of the solvent is an asset. Water-soluble esters, ketones, alcohols, and glycol ethers are readily biodegradable, while hydrocarbon solvents often have a much slower biodegradability due to their poor solubility in water, but there are differences in the degradation rate for the different classes of hydrocarbons. The order of susceptibility to biodegradation is: *n*-alkanes > branched alkanes > low-molecular-weight aromatics > cyclic alkanes. Chlorinated and fluorinated solvents are, in general, poorly degradable. Several ionic liquids have a poor biodegradability, although other types of ionic liquids have been specifically designed to be biodegradable [61]. On the other hand, biodiesel is an easily biodegradable and nontoxic solvent. Biodiesel is a mixture of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats [62, 63]. It has been successfully tested as a diluent in solvent-extraction studies [64–67]. Soybean oil methyl esters have also been investigated as a diluent for solvent-extraction systems [68]. Soybean oil consists of a mixture of fatty acids, with the vast majority of the fatty-acid component being linoleic acid, an 18-carbon, long-chain fatty acid with double bonds at carbon atoms 9 and 12. Glycerol is a side product formed during the production of biodiesel, and it is a good solvent for many metal salts [69]. It can also be used as a starting product for the production of other green solvents such as alkyl glycerol ethers [70].

Methanesulfonic acid (MSA) is an example of a strongly acidic organic solvent that can be considered as a green solvent [71]. Methanesulfonic acid has a low toxicity, is readily biodegradable, and is part of the natural sulfur cycle. In general, metal methanesulfonate salts have a very high solubility in water so that they are often considered as a metal source in the preparation of aqueous electrolytes for metal deposition.

A new class of solvents that shows great promise for applications in solvometallurgy is solvents prepared by gas-to-liquids (GTL) technology [72]. GTL solvents are prepared from natural gas using the Fischer–Tropsch process. The GTL process consists of three stages. In the first stage (syngas reforming), the natural gas is partially oxidized to create synthesis gas (syngas), a mixture of hydrogen and carbon monoxide, which is then purified. In the second stage (the Fischer–Tropsch reaction), the syngas is converted by a catalyst to a long-chain, heavy paraffinic liquid, the Fischer–Tropsch wax, which consists of a mixture of many compounds. In the third stage (product upgrading), the oxygen-containing products and alkenes are hydrogenated to alkanes. Through hydrocracking and isomerization, the paraffins are converted into smaller alkanes with a very characteristic branching pattern. Using distillation, fractions with a different distillation range are obtained. The GTL solvents consist mostly of iso-paraffins and normal paraffins, with only very small amounts of cyclic paraffins. They contain small amounts of impurities such as sulfur, olefins, and polycyclic aromatics. They are almost odorless, due to their low aromatic and naphthenic content. Shell offers a range of commercial GTL solvents with different distillation ranges (GS190, GS215, GS250, GS270, GS310). The solvents with the higher distillation ranges have the lowest volatility, but they also have a higher viscosity (although it must still be considered as a relatively low viscosity). A very interesting property of these solvents is their good biodegradability [73, 74]. GTL solvents were found to exhibit more than 60% biodegradation over the required 28-day test period, with the degradation continuing after the 28 days toward complete degradation. Therefore, they are considered to be readily biodegradable according to the OECD 301F guideline. GTL solvents have better biodegradation scores than comparable petroleum-derived solvents because of the lower proportions of aromatics and/or naphthenics in the GTL solvents.

Organic solvents tend to degrade over time. In general, this is a disadvantage compared with water. In many cases, organic impurities can be removed by a washing step with water or with an organic solvent. In other cases, solvents can be purified by distillation, even though this is an energy-intensive process. This purification process cannot be repeated endlessly, and at any given moment, the solvent has to be replaced by a fresh batch of solvent. At the end of the lifetime of the solvent, safe disposal is required. The best approach is to burn the spent solvent, with heat recuperation. The disposal by incineration is one of the reasons why halogenated solvents must be avoided.

Halogenated solvents cannot readily be handled in most incinerators.

Although inorganic solvents (with the exclusion of water, of course) can in principle be used for solvometallurgical processes, inorganic solvents are generally of little use in this context because they are too reactive, too dangerous, too toxic or too difficult to handle. Examples include liquid ammonia, liquid sulfur dioxide, anhydrous hydrogen fluoride, thionyl chloride, sulfuryl chloride, phosphoryl chloride, dinitrogen tetroxide, and antimony trichloride. Concentrated sulfuric acid is an inorganic solvent, but it is not used in solvometallurgy as a solvent, but rather for ore acidification (acid curing of ores). Supercritical $CO_2$ could find applications in the field of non-aqueous solvent extraction and solvent leaching [75–78]. Of particular interest are the promising combinations of supercritical $CO_2$ with TBP-HNO$_3$ and supercritical $CO_2$ with fluorinated β-diketones as solvents for direct solid leaching [79–83]. $CO_2$ becomes a supercritical fluid at its critical temperature (31.10 °C) and critical pressure (72.8 atm) [84]. Any supercritical fluid expands to fill a container, but it has a density that is similar to that of a liquid.

## Ionic Liquids (ILs) and Deep-Eutectic Solvents (DESs)

*Ionic liquids* (ILs) are a special class of solvents that consist entirely of ions [85, 86]. This differentiates ionic liquids from both conventional organic solvents, which consist of neutral molecules, and from salt solutions, which consist of a mixture of neutral molecules and ions. Many researchers define ionic liquids as organic salts with a melting point below 100 °C, but this definition is too restrictive, and the threshold of 100 °C (the normal boiling point of water) is arbitrary. There are many examples of ionic liquids with melting points above 100 °C that have properties very similar to those of low-melting ionic liquids. Of course, low melting points are an advantage, and the *room-temperature ionic liquids* (RTILs) are preferred. The typical cations in ionic liquids are organic cations with one or more alkyl chains. Examples include 1-alkyl-3-methylimidazolium, *N*-alkylpyridinium, *N*-alkyl-*N*-methylpyrrolidinium, tetraalkylammonium, and tetraalkylphosphonium cations. Anions can be inorganic, such as chloride, bromide, iodide, thiocyanate, tetrafluoroborate, hexafluorophosphate, bis(trifluoromethylsulfonyl)imide (=bistriflimide), or organic, such as acetate or benzoate. By combining these cations and anions, a wide range of ionic liquids can be obtained (Fig. 5). A special type of ionic liquids is the "liquid metal salts" that have a metal-containing cation. Molten-salt hydrates also belong to this class of ionic liquids [87]. In molten-salt hydrates, all the water molecules are strongly coordinated to the metal ions so that there are no free water molecules in the melt. Examples include $CaCl_2 \cdot 6H_2O$, or $Mn(NO_3)_2 \cdot 6H_2O$. Also worth mentioning are the functionalized ionic liquids in which a functional group is covalently attached to the ionic liquid cation. In the past, these ionic liquids were often called "task-specific ionic liquids" [88]. However, "functionalized ionic liquids" is nowadays the preferred term. A well-known example of a functionalized ionic liquid is betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf$_2$N], which contains a carboxylic acid functional group (Fig. 6) [35].

Although the physicochemical properties of ionic liquids are very dependent on the chemical composition of the ionic liquid, we can also make some generalizations. First



**Fig. 5** Common anion cations and anions in ionic liquids
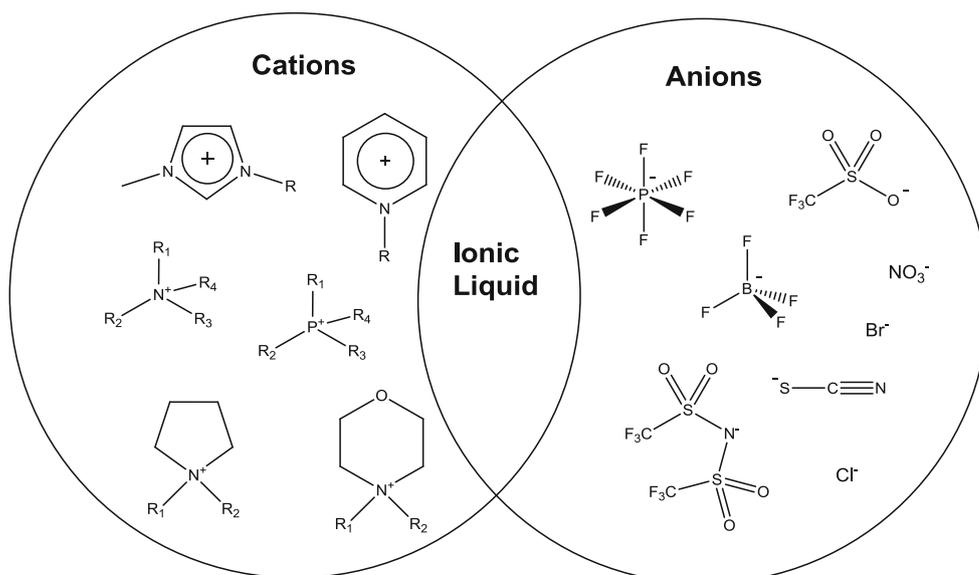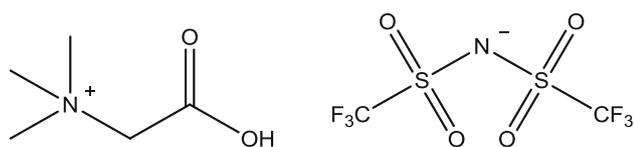
Fig. 6 Structure of the ionic liquid [Hbet][Tf$_2$N]

of all, many ionic liquids have a nonmeasurable vapor pressure at room temperature, although some ionic liquids can be distilled in a high vacuum at high temperatures. Ionic liquids often have a very wide *liquidus* range; it is not uncommon to have ionic liquids that are fluid over a range of more than 250 °C, which is much wider than the 100 °C range of water. Ionic liquids are intrinsic electrical conductors, and they can have an electrochemical window of more than 4 V (the electrochemical window of water is just 1.23 V). Ionic liquids are good solvents for many classes of inorganic and organic compounds. Compared with molecular organic solvents, ionic liquids have a much higher viscosity, which can hamper mass transport and slow down the rate of chemical processes. However, the viscosity of ionic liquids reduces dramatically upon heating or the addition of a small amount of a molecular co-solvent.

A drawback of many ionic liquids is their high price, and this has hindered the development of ionic-liquid processes on an industrial scale. A cheap alternative to ionic liquids are the *deep-eutectic solvents* (DESs) [22, 29, 89, 90], of which there are many different types. Most of them are mixtures of choline chloride and a hydrogen-bond donor (urea, ethylene glycol, malonic acid) or mixtures of choline chloride with a hydrated metal salt. A typical feature of a DES is that it has a much lower melting point than each of its individual components. Popular DESs are those obtained by mixing chloride and urea in a 1:2 molar ratio, or choline chloride and ethylene glycol in a 1:2 molar ratio. These solvents are liquid at room temperature. Choline chloride is produced on a large scale and is used as chicken feed. Due to the low cost of DESs, it is much easier to use them on a large scale than ionic liquids. Although DESs often have a significant water content, their properties are generally different from those of aqueous solutions. As mentioned before, hard chrome layers can only be electrodeposited from aqueous electrolytes using toxic chromium(VI) salts, whereas the metal can be deposited from DESs containing the much-less-toxic chromium(III) salt. In fact, a DES electrolyte for chromium deposition can be prepared by simply mixing CrCl$_3$·6H$_2$O and choline chloride [91], or by mixing CrCl$_3$·6H$_2$O and urea [92]. Although deep-eutectic solvents cannot be considered as ionic liquids, as they are mixtures of ions and smaller or larger amounts of neutral molecules, their properties are very similar to those of conventional ionic liquids. For this reason, they are often described as ionic-liquid-like solvents, or just as ionic liquids. Due to their water content, the electrochemical window of DESs is smaller than that of conventional ionic liquids.

The most obvious applications for ionic liquids and deep-eutectic solvents in solvometallurgy are in the electrodeposition of metals from non-aqueous electrolytes. Commonly used ionic liquids for electrodeposition are 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, [C$_4$mim][Tf$_2$N], or *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [BMP][Tf$_2$N], as well as several deep-eutectic solvents [23]. Other applications of these ionic solvents in solvometallurgy are as solvents for solvent leaching and in non-aqueous solvent extraction. As mentioned in the introduction, the term "*ionometallurgy*" is used for solvometallurgical processes based on ionic liquids or deep-eutectic solvents [24].

## Ten Good Reasons to Use Solvometallurgy

We recommend considering solvometallurgy for those cases where the application of traditional methods of extractive metallurgy is difficult or problematic. If existing processes are working well, there might be no need to consider alternative processes based on the use of non-aqueous solvents. However, there are many cases where solvometallurgy could make a difference. We have identified ten reasons to use solvometallurgy (Table 3), and these are discussed in more detail below.

| Table 3 Ten good reasons to use solvometallurgy | |
|---|---|
| | Reason 1. Very limited water consumption |
| | Reason 2. Reduced energy consumption |
| | Reason 3. Process intensification |
| | Reason 4. Reduced consumption of acids |
| | Reason 5. Higher selectivity for leaching |
| | Reason 6. Fewer problems with silica gel formation |
| | Reason 7. Suitable for the treatment of low-grade ores, mine tailings, and industrial process residues |
| | Reason 8. Useful for the treatment of urban waste |
| | Reason 9. Compatibility with bioleaching |
| | Reason 10. New separation processes |

**Reason 1. Very Limited Water Consumption**

Because no bulk aqueous phase is present in a solvometallurgical process, the consumption of water can be limited to a strict minimum. In some solvometallurgical processes, a small amount of water is essential, but the water volumes are always small compared to the volumes of organic solvents, and in most cases no discrete aqueous phase is present. If no water is consumed in a solvometallurgical process, it also implies that no wastewater is generated, and that there are no issues with wastewater treatment. Solvometallurgical processes have the potential to recover metals from ore deposits in arid areas, where it is difficult to guarantee a sufficient supply of process water. This is very relevant for exploiting copper mines in the Atacama Desert in Chile. Likewise, solvometallurgical processes can also be operated in (mobile) stand-alone units that can be used to recover metals from small ore deposits at remote locations.

**Reason 2. Reduced Energy Consumption**

Solvometallurgical processes offer the opportunity to treat, at ambient temperatures, ores that otherwise have to be heated to high temperatures to convert them to oxides before they can be further processed. A good example is the calcination of carbonate ores. By means of chlorine gas dissolved in an organic solvent, it is possible to chlorinate ores at ambient temperatures, instead of using chlorination or carbochlorination at high temperatures. The possibility to work at room temperature or at slightly elevated temperatures results in a considerably reduced energy consumption compared with pyrometallurgical processes, which are typically carried out at temperatures above 300 °C. In general, organic solvents have a lower heat of vaporization than water, so that less energy is required to distil the organic solvent (for solvent recycling) than to distil the same volume of water. However, as mentioned elsewhere in this paper, the use of volatile organic solvents and distillation must be avoided, whenever possible.

**Reason 3. Process Intensification**

Solvometallurgy allows for process intensification, because different unit operations (e.g., leaching and solvent extraction) can be combined, and this reduces the number of process steps. A combination of mechanical activation (e.g., by ball milling) and solvometallurgy allows the treatment of resistant ores such as columbite, tantalite, and pyrochlore under much milder conditions (ambient temperatures, no HF) with respect to traditional metallurgical methods [18].

**Reason 4. Reduced Consumption of Acids**

Even if acid curing of the ore is used as a pretreatment step prior to solvent leaching, the total acid consumption can be much lower than that in the case of conventional leaching. This is because a larger excess of acid is often used in conventional acid leaching and because protons can be provided by the extractant in the case of solvent leaching with acidic extractants. Hydrometallurgical processes with acid leaching are not very compatible with carbonate-rich ores and especially not with those rich in calcite or dolomite, because the dissolution of the carbonate gangue material consumes large amounts of acids. This is relevant if the minerals in a carbonate matrix cannot be separated from the gangue by flotation, e.g., in the case of the uranium ore carnotite. By solvent leaching the ore minerals, the carbonate gangue materials can be left largely untouched. Because solvent leaching is more selective than leaching with aqueous solutions of mineral acids, it is possible to avoid the co-dissolution of unwanted metals such as iron, which also leads to a reduction in the consumption of acids (see also Reason 5).

**Reason 5. Higher Selectivity for Leaching**

In general, leaching with aqueous solutions of mineral acids ($H_2SO_4$, $HNO_3$, HCl) suffers from low selectivity. Besides the targeted metals, many unwanted metals are co-dissolved. This poor selectivity leads not only to a higher consumption of acids (see Reason 4), but also to extra process steps for the removal of impurities from the leachate. Solvent leaching can, in principle, offer a higher selectivity than leaching with aqueous solutions of acids, especially if chelating extractants are used, such as the LIX® family of extractants.

**Reason 6. Fewer Problems with Silica Gel Formation**

For the recovery of technological metals such as rare earths, zirconium, tantalum, or niobium, we are forced to rely more and more on ores with a complex composition and a high content of soluble silica, because of the depletion of ores with a simpler chemical composition. A good example is eudialyte, $Na_{15}Ca_6(Fe,Mn)_3Zr_3(Si,Nb,REE)Si_{25}O_{73}(OH,Cl,H_2O)_5$. The leaching of such minerals with mineral acids dissolves the silica as silicic acid. This dissolved silica is gradually transformed by polymerization into colloidal silica, and these colloids can aggregate to form a gel. Gel formation in a leachate makes the filtration for solid–liquid separation impossible. Dissolved silica can also interfere with solvent extraction, because it causes the formation of extremely stable emulsions during the mixing of the aqueous and the

organic phases. These emulsions can be stable for weeks or even months. Silica colloids can also block the pores in ion-exchange resins. Dissolved silica is not only a problem in the case of acidic leaching; it is even more so in the case of alkaline leaching, because silica has a higher solubility in alkaline solutions. Because water is required for the formation of silicic acid, it is evident that the leaching of silica-rich ores with non-aqueous solvents leads to much lower solubilization of the silica and hence to fewer problems with silica gel formation.

### Reason 7. Suitable for the Treatment of Low-Grade Ores, Mine Tailings, and Industrial Process Residues

As mentioned in the introduction, the depletion of high-grade ores with a simple composition necessitates the shift to low-grade ores, mine tailings, and industrial process residues that contain only low concentrations of valuable metals and often have a complex composition with several mineral phases. Conventional leaching with aqueous solutions of mineral acids lacks selectivity, leading to the consumption of large amounts of acid and the co-dissolution of unwanted impurities. In particular, the co-dissolution of the matrix is a major problem. Solvometallurgical processes are suitable for the recovery of metals from low-grade ores (e.g., nickel laterites), tailings from primary mining, or industrial process residues (e.g., bauxite residue, goethite, or jarosite) because of their intrinsic higher selectivity (see also Reasons 4 and 5).

### Reason 8. Useful for the Treatment of Urban Waste

In ore deposits, the metals typically occur in complex polymetallic sulfide or oxide ores, whereas the metals of the urban mine are typically present in the form of alloys. Examples are the rare-earth permanent magnets, which consist of neodymium-iron-boron or samarium-cobalt alloys. The direct reuse of these alloys is often not possible, and the mixture of constituting metals needs to be separated into the individual elements. In hydrometallurgical recycling methods, the alloys are dissolved in aqueous solutions of strong mineral acids ($H_2SO_4$, HCl, $HNO_3$). This step can be unsafe because of the formation of flammable hydrogen gas during the metal dissolution. In the case of arsenic-containing alloys (e.g., GaAs), there is a danger of formation of highly toxic arsine gas ($AsH_3$). The acidic attack dissolves the whole mass of the alloy, so that selective leaching is impossible, and large volumes of acid are consumed. This is a problem with the recovery of rare earths from neodymium-iron-boron magnets, since 70 wt% of the magnet alloy consists of iron. The pyrometallurgical recycling of metals often involves a high-temperature chlorination step to transform the metals into the corresponding chlorides, followed by fractional distillation or sublimation, or by further hydrometallurgical processing (e.g., solvent extraction) after the dissolution of the chlorides in water. This approach is not energy efficient, and it is difficult to obtain high-purity compounds by distillation or sublimation. The hydrometallurgical process steps make the flow sheet more complicated, and they can be carried out only in very acidic solutions to avoid hydrolysis and the precipitation of the metals. After purification by solvent extraction, the dissolved metals have to be converted into anhydrous chlorides, fluorides, or oxides before they can be further processed to the metal, for instance, by electrolysis in molten salts. The flow sheets for the recycling of valuable metals from production scrap and end-of-life consumer goods (Fig. 1) can be shortened and made to be more energy efficient by using solvometallurgy if (1) the chlorination is carried out with chlorine gas dissolved in an organic solvent rather than in a chlorine gas stream at high temperatures, (2) the water in the hydrometallurgical process steps is replaced by organic solvents, and (3) the electrolysis is carried out in organic electrolytes instead of molten salts.

### Reason 9. Compatibility with Bioleaching

Although the aim is to recover 100% of the organic solvent after the solvent leaching, complete recovery of the solvent is impossible and some traces of solvent will always remain adhered to the particles of the solid residue, even after a washing step with another organic solvent. However, the solid residue obtained after the solvent leaching can be treated in a subsequent step with bioleaching. This bioleaching step can further enhance the recovery of metals from the residue. Based on differences in the reactivity between the solvent leaching and the bioleaching steps, metals other than those solubilized in the solvent-leaching step can be solubilized in the bioleaching step. More importantly, the solvent traces left after solvent leaching are rich in carbon and could serve as a nutrient for heterotrophic microorganisms (bacteria and fungi), which need organic supplements for growth and energy supply. In this way, the solid residue can be cleared from any solvent traces left behind after the solvent leaching. It is of course necessary that the solvents used for the solvent leaching are not toxic to microorganisms. Of course, it is preferable for the solvents to be biodegradable. Nonpolar solvents with a good biodegradability include some gas-to-liquid solvents (GTL solvents) prepared using the Fischer–Tropsch synthesis from natural gas, such as the GS series of solvents produced by Shell (e.g., GS250). In addition, biodiesel could be used as a biodegradable nonpolar solvent in solvometallurgical processes.

**Reason 10. New Separation Processes**

Some separation processes can only be carried out in the absence of water. An example is the electrowinning of reactive metals in non-aqueous electrolytes (electrodeposition of aluminum or very pure indium), which is possible in high-temperature molten salts, but not in aqueous solutions. Another example is the purification of LiCl [19, 93], which is very soluble in many organic solvents, in contrast to the other alkali-metal chlorides. Alcohols are particularly good solvents for LiCl, due to the formation of stable solvates such as $LiCl \cdot 3CH_3OH$ in methanol or $LiCl \cdot 4C_2H_5OH$ in ethanol. By treating mixtures of alkali-metal chlorides with absolute ethanol, LiCl goes into solution, whereas NaCl and KCl do not.

## Examples of Solvometallurgical Processes

### Solvent Leaching of Low-Grade Uranium Ores

The concept of solvometallurgy originates from research activities in the United States shortly after World War II, aimed at recovering uranium from domestic uranium ores. These were typically low-grade uranium ores with a $U_3O_8$ content of less than 1%, such as low-lime sandstone ores containing carnotite, autunite, torbernite, and uranophane or high-lime carnotite ores containing high concentrations of calcite ($CaCO_3$) gangue material. Carnotite is a secondary uranium-vanadium ore with the chemical formula $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$ that occurs extensively on the Colorado Plateau. The recovery of uranium from high-lime carnotite ores is very challenging because conventional hydrometallurgical processes based on acid leaching are often not economic due to the large quantities of acid consumed, resulting from the co-dissolution of the calcite gangue material. Three different solvometallurgical processes for uranium recovery from low-grade ores have been disclosed [9] (Fig. 7): (1) the TBP process; (2) the acetone-HCl process, and (3) the alkyl phosphoric acid process. Of these three processes, the alkyl phosphoric acid process is the only one that consumes less than the stoichiometric amount of acid with respect to the lime content, and it is thus the most suitable process for the recovery of uranium from high-lime carnotite ores. However, all three processes consume much lower amounts of water than hydrometallurgical processes.
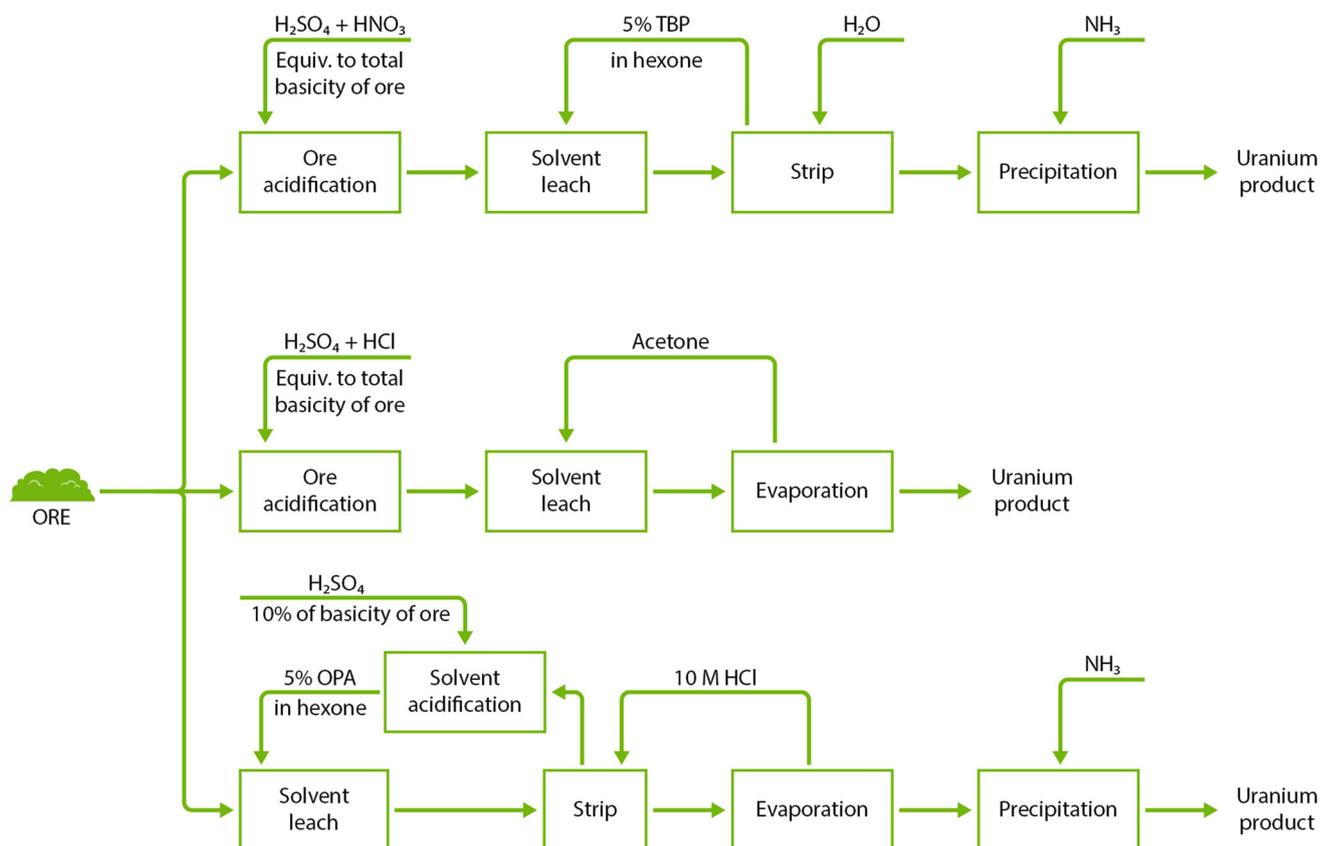


Fig. 7 Flow diagrams for the solvent leaching of uranium from ores. Adapted from Ref. [9] (Color figure online)

The *TBP process* uses tri-*n*-butylphosphate (TBP) to extract uranyl nitrate and gives a high-grade uranium concentrate [7]. The uranium ore is crushed to a particle size of less than 10 mesh, mixed with concentrated $H_2SO_4$ and a small amount of water, and cured for about 1 h to dissolve the uranium in the form of uranyl sulfate and to neutralize any of the lime that the ore might contain. The amount of acid used in this step is equivalent to that required for a conventional acidic leaching step, but the water requirements are much lower. The ore-acidification step produces a damp, friable mass into which all of the acid solution is absorbed. No liquid phase remains or separates from the ore over time. This acid-curing step is carried out with about 80% of solids present. After the pretreatment, the ore is wetted with an $NH_4NO_3$ solution to convert the uranyl sulfate into uranyl nitrate (nitrate-conditioning step) and the damp mass is leached with a 5 vol% solution of TBP in kerosene or hexone (methyl isobutyl ketone). Kerosene or hexone is used as a diluent to obtain a solvent with a sufficiently low viscosity. By adding $NH_4NO_3$ to the acid-cured ore, a nearly complete recovery of uranium from the ores is possible. The solvent can be brought into contact with the ore by agitation in a mixing tank, by percolation through a column or by spraying it on the ore, while the ore travels on a moving belt (Fig. 8). About 4000–11,000 L of solvent are required per ton of ore. The leach residue is washed with a volatile organic solvent to recover the entrained TBP and kerosene. The uranium can be easily stripped from the loaded organic phase by water to give a uranyl nitrate solution. Precipitation with an ammonia solution gives ammonium



**Fig. 8** Solvent leaching with a moving belt contactor. Adapted from Ref. [9] (Color figure online)

diuranate, which can be calcined to drive off the ammonia and to yield high-purity $U_3O_8$. The advantages of the process are that (1) a small volume of water is used, (2) the uranium stripping from the solvent is straightforward and (3) a minimum number of steps is required to produce a high-grade $U_3O_8$ concentrate from a low-grade uranium ore. The disadvantages are that (1) the ore-acidification step consumes the same amount of acid as required for a conventional hydrometallurgical leaching step, (2) the pretreatment is not effective for uranium ores requiring an oxidizing agent for good uranium dissolution, and (3) the economic recovery of TBP and kerosene is difficult.

The *acetone-HCl process* is based on the high solubility of uranyl chloride in acetone [4, 94, 95]. The ore is crushed to 10 mesh and first treated with concentrated HCl or with a mixture of concentrated HCl and $H_2SO_4$ to solubilize uranium. The cured ore is fed into a pool of acetone in an enclosed extractor. Uranium, iron, vanadium, and calcium are dissolved in acetone as chloride complexes. Anhydrous ammonia gas is bubbled through the loaded acetone phase, and the dissolved metals precipitate as hydroxides. The hydroxide precipitate is removed by filtration, and the regenerated acetone is returned to the extractor. The final concentrate is of a low grade and contains about 10–15% $U_3O_8$. Since acetone is not selective for uranyl chloride dissolution, the process is used primarily for upgrading low-grade ores. The advantage of the process is the small volume of water required. Therefore, the process could be useful for upgrading ores using relatively small installations in remote areas. The disadvantages are that a gas-tight system is needed to minimize the acetone losses and that HCl is required. HCl is more expensive than $H_2SO_4$ and it causes more corrosion problems. The precipitated hydroxides are bulky and of low grade.

The *alkyl phosphoric acid process* uses alkyl phosphoric acids and $H_2SO_4$ for the extraction of uranyl ions from the ores [5, 9]. This process is well suited to the recovery of uranium from high-lime carnotite ores. The process was optimized for OPA, a mixture of mono- and dialkylphosphoric acids, but other alkyl phosphoric acids such as bis(2-ethylhexyl)phosphoric acid (D2EHPA) can be used as well. The ground ore is passed on a moving belt, and a solvent is sprayed on it. The solvent is an acidified solution of an alkyl phosphoric acid in a diluent. The solvent percolates through the ore bed and dissolves the uranium. The solvent entrained by the solid residue is washed with fresh diluent at the discharge end of the moving belt. This solvent-leaching strategy is highly dependent on several process parameters. The most important parameters are the type and concentration of the solvent, the amount and type of the acid, the type of diluent, the phase ratio of solvent to ore, and the contact time during the leaching. The contact time can be short, i.e. 10–20 min. The preferred acid is
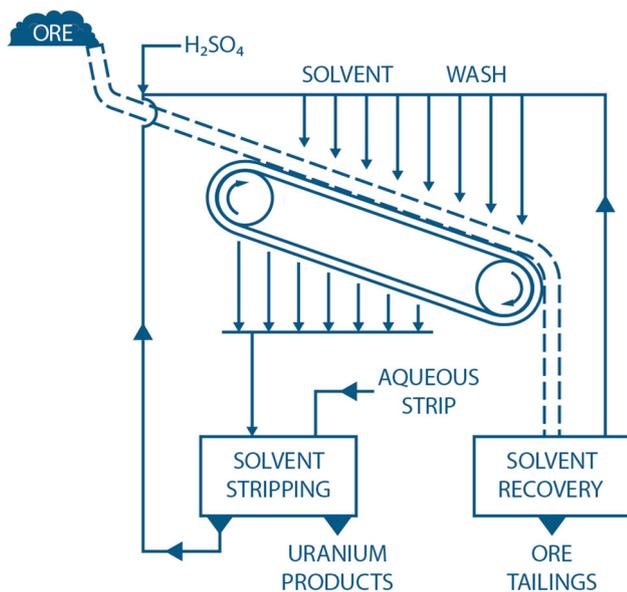
H$_2$SO$_4$, and concentrated H$_2$SO$_4$ (96%) is used to reduce the amount of water. Upon reacting the H$_2$SO$_4$ with the ore, a coating of CaSO$_4$·2H$_2$O (gypsum) is formed around the calcite particles. This isolates the calcite particles and prevents any further consumption of H$_2$SO$_4$. On the other hand, the coating of uranyl sulfate formed on the surface of the uranium minerals can be dissolved by the organic solvent. The freshly exposed surface of the uranium mineral particles further reacts with H$_2$SO$_4$ and the process continues until the entire uranium mineral particle is dissolved. Only about one-tenth of the stoichiometric amount of H$_2$SO$_4$ that would be required to dissolve all of the uranium minerals and calcite is needed. For this reason, the alkyl phosphoric acid process is very suitable for the recovery of uranium from high-lime carnotite ore. The amount of H$_2$SO$_4$ that is used also affects the loss of alkyl phosphoric acid to the solid residue. When no H$_2$SO$_4$ is used, a considerable amount of alkyl phosphoric acid is deposited on the ore, and this cannot be recovered by washing the residue with a diluent. The best efficiencies are observed by adding H$_2$SO$_4$ to the solvent before or during the contact of the solvent with the ore. Acid curing of the ore before contact with the solvent causes local neutralizations and the consumption of larger amounts of acid. The best uranium recoveries are obtained with methyl ethyl ketone (MEK) as the diluent, but isopropyl ether (IPE) has a lower solubility in water. Although kerosene would be a desirable solvent because of its low solubility in water and its relatively high flash point, the use of kerosene results in slow slurry-settling rates, higher alkyl phosphoric acid losses, and more difficult solvent recovery from the solid residue. In the final step, uranium can be stripped from the loaded solvent using a 10 M HCl solution.

## Solvent Leaching of Copper Ores

One of the principal oxidized copper ores is chrysocolla, which is a poorly defined hydrated copper(II) silicate with varying composition, often represented by the formula CuSiO$_3$·2H$_2$O. The recovery of copper from chrysocolla by direct acid leaching is challenging because of the formation of silica gel. Raghavan and Fuerstenau developed a solvometallurgical process for the recovery of copper from chrysocolla by leaching it with the extractant LIX® 63 dissolved in kerosene, in the presence of a small amount of aqueous ammonia solution [10–12]. LIX® 63 is a selective extractant for the extraction of copper from ammoniacal solutions and its active component is 5,8-diethyl-7-hydroxy-6-dodecanone oxime. The authors were able to leach 70–75% of the copper from the ore using an ammonia content that is only about one-quarter of the stoichiometrically required amount for leaching with ammoniacal solutions. The facts that chrysocolla is a

porous solid and that the pores are filled with capillary condensed water are crucial to the success of the method. Removal of the water from the pores by heating led to much lower leaching efficiencies. The nonporous synthetic CuO gave poor results as well. Ammonia is believed to enter the pores and react with the copper(II) to form the $[Cu(NH_3)_4]^{2+}$ complex, which diffuses to the entrance of the pores on the surface of the ore particles where it reacts with LIX® 63 dissolved in kerosene. Ammonia is regenerated during this reaction and returns to the aqueous phase within the pores. This process was also applied to ocean-floor manganese nodules to recover copper, nickel and cobalt, but the leaching efficiencies were poor unless a reductive treatment at 600 °C was first applied. In that case, a recovery of 71% for nickel, 69% for copper, and 44% for cobalt could be achieved.

The copper(I) ion is more strongly solvated by organic nitriles such as acetonitrile (CH$_3$CN) than by water, whereas most other cations, including copper(II) ions and protons, are more strongly solvated by water than by acetonitrile. As a consequence, copper(II) is a strong oxidizing ion in acetonitrile or in acetonitrile–water solutions, because it has a strong tendency to be transformed into the copper(I) ion. This observation was used by Parker to develop a process to recover copper from copper(I) sulfides, such as the ore minerals chalcocite, digenite, or bornite, without the need to transform the sulfides beforehand into oxides by roasting [96]. CuSO$_4$ oxidizes Cu$_2$S to sulfur in the presence of acetonitrile, and the acetonitrile can be recycled by distilling the acetonitrile–water mixture. When the volume ratio of cetonitrile to water becomes too low, copper(I) is no longer stable and is disproportionate to copper metal and copper(II). The reactions are

$$\text{Leach: } Cu_2S + 2Cu^{2+} + 8CH_3CN \rightleftarrows 4\left[Cu(CH_3CN)_2\right]^+ + S \tag{1}$$

$$\text{Distil: } 4\left[Cu(CH_3CN)_2\right]^+ \rightarrow 2Cu + 2Cu^{2+} + 8CH_3CN \tag{2}$$

$$\text{Net: } Cu_2S \rightarrow 2Cu + S \tag{3}$$
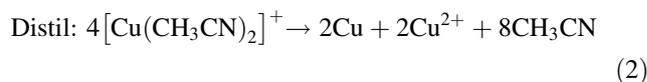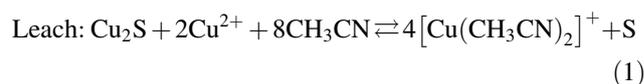
The advantage of using CuSO$_4$ as the oxidizing agent is that no other metals are introduced in the pregnant leach solution, as in the case of leaching with Fe$_2$(SO$_4$)$_3$ as an oxidizing agent. Because acetonitrile and CuSO$_4$ can, in principle, be recycled, it would be possible to develop a closed-loop leaching process based on this technology. One drawback of the process is that a high liquid-to-solid ratio is needed: about 40 g of acetonitrile is required to recover 1 g of copper. The liquid-to-solid ratio can be reduced, but this leads to the formation of CuS instead of sulfur. This reaction can also be carried out in an acetonitrile–water solution, with the acetonitrile being removed by

distillation. In water, copper(I) is unstable and undergoes a rapid disproportionation. The relevant reactions are

$$\text{Leach: } Cu^{2+} + Cu_2S + 4CH_3CN \leftrightarrows CuS^* + 2\left[Cu(CH_3CN)_2\right]^+ \tag{4}$$

$$\text{Distil: } 2\left[Cu(CH_3CN)_2\right]^+ \rightarrow Cu + Cu^{2+} + 4CH_3CN \tag{5}$$

$$\text{Net: } Cu_2S \rightarrow Cu + CuS^* \tag{6}$$
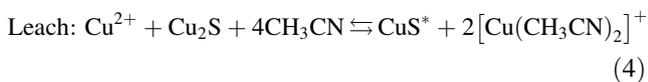
CuS* is activated copper(II) sulfide that can be leached, for instance, by air in the presence of $H_2SO_4$, with $CuSO_4$ and acetonitrile acting as catalysts:

$$CuS^* + H_2SO_4 + 1/2O_2 \xrightarrow{Cu^{2+}/CH_3CN} CuSO_4 + S + H_2O \tag{7}$$
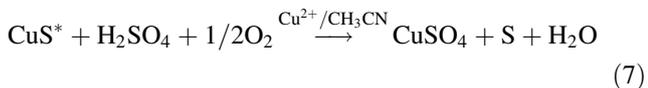
$Cu_2S$ can be dissolved in an acetonitrile solution, not only by oxidative dissolution with $CuSO_4$, but also by $H_2SO_4$ in anhydrous acetonitrile [97]:

$$Cu_2S + 2H^+ \rightleftarrows 2Cu^+ + H_2S \tag{8}$$

The solubility product of $Cu_2S$ in acetonitrile is a factor of about $10^{40}$ higher than the corresponding value in water (about $10^{-25}$ in a 1-M $H_2SO_4$ at 25 °C). The driving forces are the strong solvation of the $Cu^+$ ion in acetonitrile and the poor solvation of the $H^+$ ion in acetonitrile. After the dissolution the copper can be recovered from the solution by the addition of water so that $Cu^+$ disproportionates into $Cu^{2+}$ and Cu. The $H_2S$ can be oxidized to $H_2SO_4$, which can then be used in the leaching process. Not only $Cu_2S$, but also NiS and AgS are soluble in acidified acetonitrile, but these processes have not yet been investigated in detail.

The ores containing cuprite ($Cu_2O$) can be dissolved by $H_2SO_4$ in the presence of acetonitrile [96]:

$$Cu_2O + 4CH_3CN + H_2SO_4 \leftrightarrows \left[Cu(CH_3CN)_2\right]_2SO_4 + H_2O \tag{9}$$
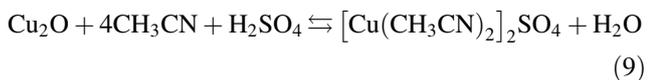
Copper can be recovered from the oxidized copper ores by solutions of $SO_2$ in water, in the presence of acetonitrile [96]:

$$\text{Leach: } 2CuO + 4CH_3CN + SO_2 \leftrightarrows \left[Cu(CH_3CN)_2\right]_2(SO_4) \tag{10}$$

$$\text{Distil: } \left[Cu(CH_3CN)_2\right]_2(SO_4) \rightarrow Cu + CuSO_4 + 4CH_3CN \tag{11}$$
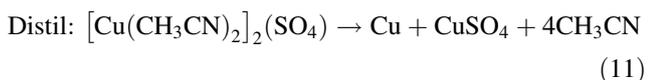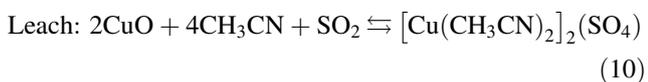
Acetonitrile is recovered by distillation, and this leads to the disproportionation of copper(I). The advantage of this method is that the $SO_2$ can be converted into sulfate, which means that the method can be coupled with the roasting of sulfidic ores. In general, a roasting plant has to be coupled to a sulfuric acid plant to avoid the release of $SO_2$ to the atmosphere. In this case, the $SO_2$ can be used for the reductive dissolution of metal oxides, such as CuO. Parker and coworkers have investigated the metallurgical applications of copper(I) in acetonitrile–water solutions in detail (cuprous metallurgy) [98–100].

A process has been proposed to recover copper, silver, and lead from copper-lead-silver dross from a blast furnace [97]. $CuSO_4$ in 50% acetonitrile–water in the presence of $H_2SO_4$ can oxidize copper and silver. However, lead is not attacked by this reagent because of the formation of a protective layer of $PbSO_4$. Silver can be cemented from the solution by the addition of copper powder, while copper is precipitated by distilling the acetonitrile. A process flow sheet has been developed for the refining of copper from scrap copper, cement copper, and reduced copper from the roasted chalcopyrite (Fig. 9) [98]. This flow sheet is also applicable to the refining of silver and to the recovery of copper from copper sulfides (CuS and $Cu_2S$).

A remark has to be made about acetonitrile and other organic nitriles. Although these compounds contain the cyano group (−CN), they do not behave like ionic cyanides such as NaCN or KCN, which release the highly toxic hydrogen cyanide (HCN) gas when in contact with acid. Organic nitriles are relatively stable compounds, but they can be metabolized to hydrogen cyanide. However, the metabolism of acetonitrile is much slower than that of other aliphatic nitriles (propionitrile, butyronitrile, acrylonitrile) so that acetonitrile has a relatively low toxicity [101, 102].

The dissolution of chalcopyrite ($CuFeS_2$) in acidic aqueous solutions at near-ambient temperatures and at atmospheric pressure proves to be a challenge because of the surface passivation. For this reason, the leaching of chalcopyrite is typically performed under oxidizing conditions or at high temperatures and pressures. Solis-Marcial and Lapidus found that the formation of a passivation layer could be limited by leaching with $H_2SO_4/H_2O_2$ in the presence of acetone or ethylene glycol in the aqueous phase [103]. The enhanced recovery of copper was attributed to the greater stability of the copper(I) ion in organic solvents. In a follow-up study, those authors investigated the leaching of chalcopyrite by $H_2SO_4$ in the presence of alcohols (methanol, isopropanol) using different oxidants ($H_2O_2$, $CuSO_4$, $O_3$) [104]. Also, the addition of acetic acid instead of an alcohol resulted in good copper extraction, but the addition of formic acid did not [105]. This negative result can be explained by the oxidative degradation of formic acid by the oxidizing agents.

## Recovery of Zinc From Industrial Process Residues

A solvometallurgical process has been developed for the recovery of zinc from different chloride-containing solid residues: zinc ash from galvanizing baths, and flue dusts
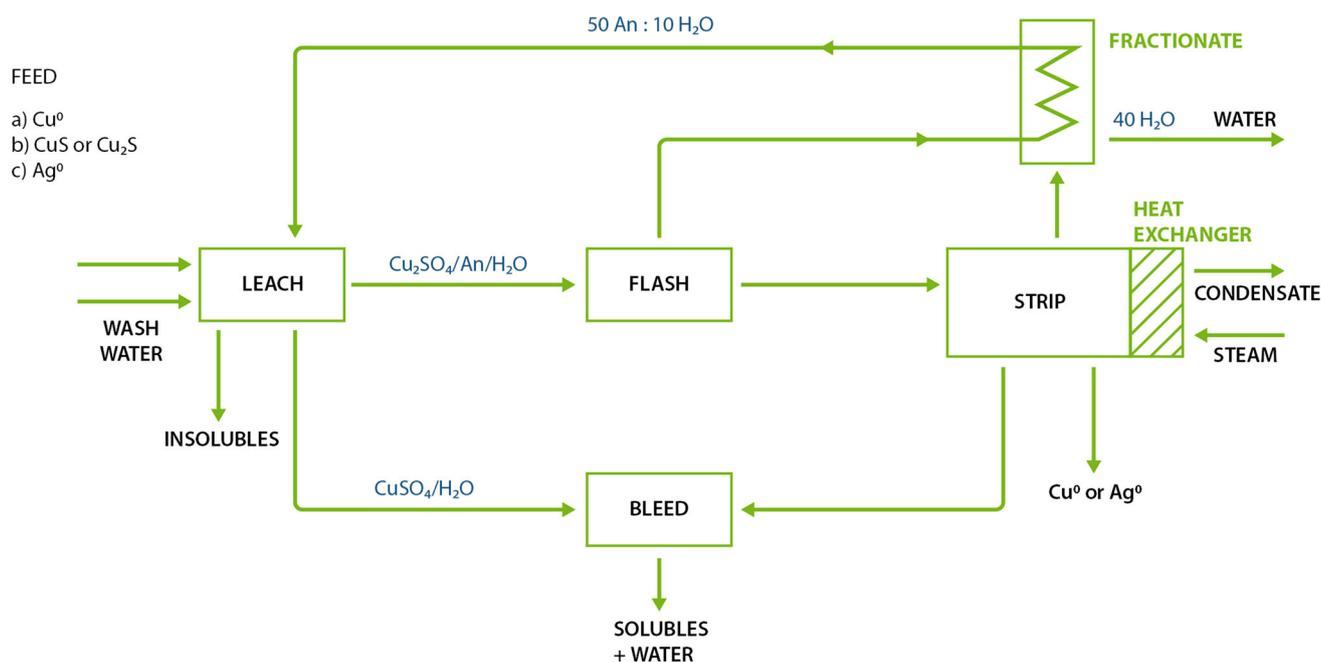
**Fig. 9** Flow sheet of a continuous process to refine copper and silver, or to recover copper from copper sulfides by leaching with $CuSO_4$ in acetonitrile–water (An:$H_2O$) mixtures. Adapted from Ref. [98] (Color figure online)

from the zinc smelting and Waelz processes [106]. The zinc ash is formed when the molten metallic zinc in a galvanizing bath is oxidized on the surface of the bath. This zinc ash, which floats on top of the molten zinc, is a mixture of zinc oxide and small metallic zinc particles. It contains various impurities (e.g., iron and lead), but also relatively large amounts of chloride compounds originating from the chloride fluxes used in the galvanizing process. The zinc flue dusts are formed in different pyrometallurgical processes such as the zinc smelting and Waelz processes, in which the zinc is volatilized after the reduction of zinc-containing materials by carbon in a rotary kiln. The flue dusts consist mainly of ZnO, but also contain oxides of lead, tin, copper, and iron, as well as zinc chloride. The solvometallurgical process is based on the reaction of the fine-grained zinc oxide with acidic extractants, and in particular with carboxylic acids such as naphthenic acids and Versatic acid. The carboxylic acids are used as a 30% solution in an aliphatic diluent. The co-dissolved chlorides can be easily scrubbed from the organic phase by washing with water. After this washing step, the organic phase is chloride-free and contains only the dissolved zinc carboxylate salt. Zinc can be stripped from the loaded organic phase by $H_2SO_4$, resulting in an aqueous solution of $ZnSO_4$, from which zinc metal can be recovered by electrolysis. Alternatively, the $ZnSO_4$ can be obtained in crystalline form ($ZnSO_4 \cdot 7H_2O$) by stripping the organic phase with an excess of $H_2SO_4$. After the stripping of zinc from the organic phase by $H_2SO_4$, the carboxylic acid is

regenerated and returned to the process for leaching a new batch of zinc-containing solid material. After the leaching, the solid residue is freed from contaminating organic material by a wash with hot water and with a $Na_2CO_3$ solution. The residue after the leaching of the zinc ash contained mainly metallic zinc particles. The solid residue obtained after leaching of the flue dust was very rich in lead.

The leaching step with Versatic acid can be combined with a solvent-extraction step to separate the zinc from the iron [107, 108]. Zinc calcine obtained by roasting zinc oxide was leached with a 30% solution of Versatic acid in an aliphatic diluent. After a subsequent contact between the zinc-containing organic phase and an iron-containing aqueous zinc sulfate solution, an exchange between the zinc and iron takes place. The iron is thereby transferred to the organic phase, where it is present as an iron(III) versatate complex. With this exchange, an equivalent amount of zinc passes from the organic phase into the aqueous zinc sulfate solution. In this manner, the iron is removed completely from the zinc sulfate solution through a contact between the two immiscible phases in one or more stages depending on the technical procedure of the liquid–liquid extraction process. Iron can be stripped from the organic phase by bringing it into contact with sulfuric acid or another mineral acid in one or more stages. Versatic acid can thereby be regenerated into its acid form and is again ready to be loaded with zinc when reacted with solid ZnO (calcine). Instead of Versatic acid, other acidic extractants

such as D2EHPA can be used. This approach is not limited to the removal of iron from zinc sulfate solutions; it is also possible to separate zinc from copper.

## Recovery of Metals From Complex Ores

During the past two decades Russian researchers have developed several processes for the recovery of valuable metals from refractory ores and ores rich in soluble silica (e.g., eudialyte) that are difficult to treat using conventional hydrometallurgical processes [17, 19]. A common feature of these solvometallurgical processes is the combination of mechanical activation with solvent leaching. It was found that the leaching efficiency was considerably improved with this mechanical activation step. The mechanical activation can be performed before the leaching step, but the two steps can also be combined into a single step, by grinding the ore in the presence of the reactive solvent. Reactive grinding can be considered as a type of mechanochemical reaction. Mechanical activation can be carried out by ball milling. The mechanical preactivation of the ore before bringing it into contact with the solvent seems to be the most promising one.

The combination of mechanical activation and solvent leaching with TBP–HNO₃ was used to extract the rare earths and zirconium from eudialyte [17]. Eudialyte becomes more amorphous during mechanical activation and this strongly affects the tendency of metal ions to be leached from the ore. It was found that mechanical activation for a short period of time (0.5–3 min) was particularly effective in improving the recovery of the metals. The mechanical activation was associated with static distortions of the crystal lattice and the rearrangement of large structure-forming cations. Interestingly, prolonged activation led to poorer leaching efficiencies compared with the leaching of the nonactivated ore. In the absence of water, the silica from the eudialyte does not form silicic acid or nonfilterable silica gel, but the silica was released in larger aggregates, which could be easily filtered.

A solvometallurgical process was developed for the recovery of uranium and vanadium from refractory brannerite ore [109]. In the first step, the granulated ore was treated with concentrated $H_2SO_4$ at 250 °C. In the second step, the sulfated product was leached with a mixture of 0.1-M bis(2-ethylhexyl)phosphoric acid (D2EHPA) and 0.1-M tri-*n*-butylphosphate (TBP) in tetrachloroethylene (TCE). It was found that leaching could be achieved only by the addition of a small amount of water, which is needed to form an invisible layer on the surface of the solid particles (wetting of the surface). Of course, the use of the halogenated solvent TCE is not recommended.

Kopkova has found that a titanomagnetite concentrate could be decomposed by an organic solvent consisting of *n*-octanol saturated with concentrated HCl [36]. Titanomagnetite has an inverse spinel structure and is very resistant to chemical attack, but it could be a potential resource for titanium and vanadium. Besides titanomagnetite, the concentrate also contained antigorite, amphibole, and ferroactinolite. By treating the ore concentrate with *n*-octanol/HCl, $FeCl_3$ and vanadium chlorides were extracted to the organic phase, while titanium oxychloride remained in the aqueous microphase that was formed in situ. This aqueous microphase is a crucial part of the solvometallurgical process. Water is formed in the chemical reaction between the metal oxide and HCl. This water is separated from the *n*-octanol phase.

## Ionometallurgical Processes

Ionometallurgy makes use of ionic liquids as solvents. A cyanide-free leaching system based on ionic liquids was developed for the recovery of gold and silver from sulfidic ores consisting of chalcopyrite, pyrite, and pyrrhotite [110, 111]. The room-temperature ionic liquid 1-butyl-3-methylimidazolium hydrogensulfate, [BMIM][HSO₄] was used as the solvent for the leaching agent thiourea and the oxidant $Fe_2(SO_4)_3$. The recovery of gold at 50 °C was similar to that of the aqueous system $H_2SO_4$/thiourea/$Fe_2(SO_4)_3$ (≥85%), but the recovery of silver was significantly higher (≥60%). The ionic liquid could be recycled after the selective stripping of gold and silver by activated charcoal. Reuse of the ionic liquid in four successive ore-treatment steps did not lead to degradation of the ionic liquid or lower recovery yields. Ionic liquids with a longer alkyl chain than the butyl chain in [BMIM][HSO₄] gave poorer recovery yields, and this was attributed to the higher viscosity of these ionic liquids, resulting in a slower mass transfer. [BMIM][HSO₄] also allowed for an efficient recovery of copper (∼85%) from chalcopyrite, with the limited co-dissolution of iron (∼8%) [111]. The most efficient lixiviant for copper recovery was 100% [BMIM][HSO₄]; the addition of water decreased the recovery yield. The selective recovery of gold and silver could also be achieved with the ionic liquid 1-butyl-3-methylimidazolium chloride, [BMIM]Cl, in combination with sodium iodide (NaI) and potassium peroxomonosulfate (KHSO₅, Oxone®) [112]. The ionic liquid [BMIM][HSO₄] was found to be effective for the leaching of copper from chalcopyrite at temperatures from 70 to 90 °C, but not below 70 °C [113]. This suggests a high activation energy for the leaching reaction. Dissolved oxygen is required for the oxidative dissolution of chalcopyrite. With optimized parameters, 88% of the copper could be recovered. The oxidative leaching of chalcopyrite was carried out with [BMIM][BF₄] using $Fe(BF_4)_3$ as the oxidant [114]. Leaching was faster in the ionic liquids than

in water, even if the ionic liquid was diluted with water. The rapid recovery of copper (45% Cu dissolution after 30 min) was observed in vacuum conditions at 100–120 °C, where water and sulfur were removed to a cold trap. Electrum (AuAg alloy), galena (PbS), chalcopyrite ($CuFeS_2$), and tellurobismuthite ($Bi_2Te_3$) could be dissolved in the deep-eutectic solvent choline chloride:ethylene glycol (1:2) (Ethaline®), using iodine as the oxidizing agent [115]. Pyrite ($FeS_2$), calaverite ($AuTe_2$), sperrylite ($PtAs_2$), and moncheite ($PtTe_2$) could not be dissolved under these conditions, but preliminary tests showed that they could be dissolved in this deep-eutectic solvent by electrolysis (anodic dissolution).

Bauxite residue (also known as red mud) is the solid-waste residue formed during the extraction of alumina from bauxite using the Bayer process. The main components of bauxite residue are $Fe_2O_3$, $SiO_2$, $Al_2O_3$, and $TiO_2$, but bauxite residue also contains significant concentrations of rare-earth elements (REEs) and especially scandium. In fact, bauxite residue could become a major source of scandium [116]. The ionic liquids 1-ethyl-3-methylimidazolium hydrogensulfate, [EMIM][HSO$_4$] and betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf$_2$N] were used for the high-temperature leaching of bauxite residue [117–119]. The leaching parameters were optimized to maximize the REE recovery, while reducing the co-dissolution of iron. [Hbet][Tf$_2$N] was found to be the most suitable ionic liquid, because the REE can be easily stripped from this water-immiscible ionic liquid by an acidic aqueous solution and at the same time, the ionic liquid is regenerated. A disadvantage of this process is the high price of the fluorinated ionic liquid [Hbet][Tf$_2$N].

The ionic liquid [BMIM]Cl and the deep-eutectic solvent choline chloride:urea (1:2 molar ratio) were used for the recovery of REEs from coal byproducts using ion exchange, but the ionic liquid and the deep-eutectic solvent did not show any advantages over leaching with an aqueous ammonium sulfate solution [120].

[BMIM][HSO$_4$] was tested for the recovery of copper and zinc from brass ash (brass dross) [121]. The brass ashes consisted mostly of metal oxides (ZnO, CuO), although a significant part of the copper was present as metallic particles. Zinc almost completely dissolved in a 50 wt% [BMIM][HSO$_4$] solution in water without any added oxidant, but the recovery of copper was low. The addition of $H_2O_2$ to the ionic-liquid solution led to an 82% recovery of copper, and at the same time the dissolution of zinc was found to be faster. After the dissolution of ZnO in the ionic liquid [BMIM][HSO$_4$] without added oxidant, metallic zinc could be recovered from the leachate by electrodeposition [122]. Tests with the protic ionic liquid 1-methylimidazolium hydrogensulfate showed that aqueous solutions of the ionic liquid gave a better recovery of

zinc and copper than the concentrated ionic liquid [123]. [BMIM][HSO$_4$] was used for leaching copper from waste printed-circuit boards (WPCBs) [124]. An almost complete recovery of copper was possible with 30% $H_2O_2$ as the oxidizing agent.

Deep-eutectic solvents (DESs) have been explored for the selective dissolution of metals from mixed-metal oxides [125]. Different types of DESs showed different types of behavior for dissolving metal oxides. The solubilities of a series of $3d$ transition-metal oxides in DESs based on malonic acid, urea, and ethylene glycol have been compared [126]. In general, the malonic-acid-based DESs showed the highest solubility for metal oxides. The DES choline chloride:oxalic acid (1:1) can solubilize up to 0.341 mol/L of $Fe_3O_4$ at 50 °C. A process has been developed to extract the lead and zinc from electric arc furnace (EAF) flue dust, originating from the remelting of steel scrap [51, 127]. The dust forms when volatile metals such as lead and zinc are vaporized at the high operating temperature of the EAF. About 15–20 kg of dust is formed per ton of steel. The DES choline chloride:urea (1:2) can selectively dissolve zinc oxide and lead oxide, while having a negligible solubility for iron oxides [127]. After the dissolution, lead and zinc could be recovered by electrodeposition. However, the high viscosity of the DES ($\sim 800$ cP at 25 °C) resulted in impeding the pumping and a more difficulty in the separation of the DES from the undissolved solids by filtration. The viscosity could be reduced by adding ethylene glycol to the DES [51]. A DES with the composition choline chloride: ethylene glycol: urea in the molar ratios 1:1.5:0.5 had a viscosity of 56 cP at room temperature. A dust loading of up to 7 wt% was used, with a digestion time of at least 24 h. Hardly any iron was co-dissolved (<1 ppm). Lead was recovered from the DES by cementation with zinc dust, and $ZnCl_2$ could be precipitated by adding an $NH_3$ solution. The electrowinning of zinc showed that the process was very slow and that the current efficiency was low. The $I_2/I^-$ redox couple is a strong oxidizing agent in the DES choline chloride: ethylene glycol (1:2 molar ratio) [24]. A process has been developed to dissolve polymetallic waste using an electrocatalytic oxidation by iodine [128]. After the oxidation, the iodide is reoxidized to iodine at the anode. The electrocatalytic method was demonstrated for copper/zinc powder mixtures, gallium arsenide (GaAs) and a sulfidic ore containing gold and silver.

Different ionic liquids have been tested for the dissolution of metal oxides. For instance, [Hbet][Tf$_2$N] was originally developed for the selective dissolution of metal oxides [35]. This ionic liquid is very useful for the dissolution of many metal oxides including rare-earth oxides, $UO_3$, CuO, ZnO, etc., but not $Al_2O_3$ and iron oxides. Similar carboxylic-acid-functionalized ionic liquids

showed a similar dissolution behavior for metal oxides [129], but of these ionic liquids [Hbet][Tf$_2$N] is the easiest to prepare. Several strong Brønsted acid ionic liquids were developed for solubilizing metal oxides and other inorganic compounds. These include sulfonic-acid-functionalized ionic liquids [130], alkyl sulfuric acid ionic liquids [131] and sulfamic-acid-derived ionic liquids [132]. Dupont and Binnemans developed an innovative process based on the ionic liquid [Hbet][Tf$_2$N] to selectively recover the red lamp-phosphor Y$_2$O$_3$:Eu$^{3+}$ (YOX) from lamp-phosphor waste without dissolving other components of the waste powder (other phosphors, glass particles, and alumina) [133]. A selective dissolution of YOX is useful because this phosphor contains 80 wt% of the REEs present in the lamp-phosphor waste, although it only represents 20 wt% of the total mass of lamp-phosphor waste. This recycling process is a major improvement compared with state-of-the-art hydrometallurgical processes where the halophosphate (HALO) phosphor (Sr,Ca)$_{10}$(PO$_4$)$_6$(Cl,F)$_2$:Sb$^{3+}$,Mn$^{2+}$ is inevitably leached when attempting to dissolve the YOX. Since the HALO phosphor can make up as much as 50 wt% of the lamp-phosphor waste powder, this dissolution process consumes large volumes of acid. After the dissolution, yttrium and europium can be recovered through a single stripping step with a stoichiometric amount of oxalic acid or by bringing the ionic liquid into contact with an HCl solution. Precipitation stripping with oxalic acid has the advantage that there is no loss of ionic liquid to the water phase and that the yttrium/europium oxalate can be calcined as such to reform the red Y$_2$O$_3$:Eu$^{3+}$ phosphor, effectively closing the loop after only three process steps. The YOX prepared from the recycled yttrium and europium showed luminescent properties that were very similar to those of the original phosphor. The resulting recycling process for lamp-phosphor waste consumes only oxalic acid and features a selective leaching, a fast stripping, and an immediate revalorization step. The conditions are mild, the ionic liquid is reusable, and no additional wastewater is generated. The flow sheet of the recycling process is shown in Fig. 10.

Powder samples of the oxides UO$_2$, UO$_3$, Nd$_2$O$_3$, Eu$_2$O$_3$ and Pr$_6$O$_{11}$ could be dissolved in the ionic liquid [BMIM][Tf$_2$N] after the addition of HNO$_3$ [134]. This work was carried out to explore the possibility of the direct dissolution of spent nuclear fuel in ionic liquids, with the aim to recover uranium and the rare earths from the ionic liquid by solvent extraction into a supercritical CO$_2$ phase. UO$_2$ could be dissolved oxidatively in different tetrachloroferrate(III) imidazolium ionic liquids, diluted in chloride ionic liquids [135]. Earlier work on the applications of ionic liquids for the processing of spent nuclear fuel have been reviewed by Binnemans [136]. The acidic ionic liquid *N,N*-dimethylacetamidium
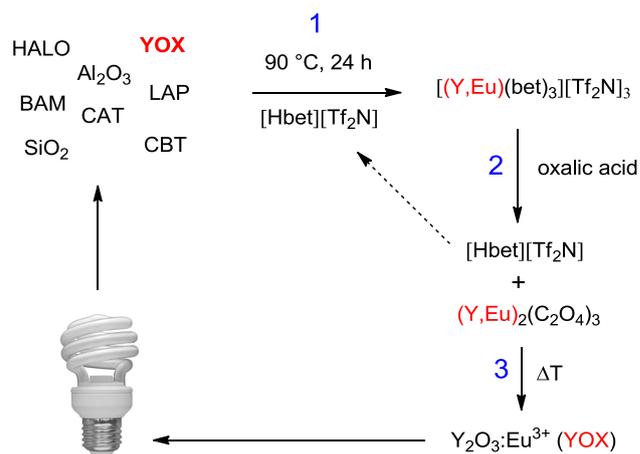


**Fig. 10** Overview of the proposed recycling process for lamp-phosphor waste, based on the selective dissolution and revalorization of Y$_2$O$_3$:Eu$^{3+}$ (YOX) with the protonated functionalized ionic liquid [Hbet][Tf$_2$N]. Step 1: selective dissolution of YOX, step 2: stripping with pure oxalic acid (regenerates the ionic liquid), step 3: direct re-synthesis of YOX. Reproduced with permission from Ref. [133]. Published by the Royal Society of Chemistry (Color figure online)

bis(trifluoromethylsulfonyl)imide diluted in the ionic liquid [BMIM][Tf$_2$N] was used to dissolve rare-earth oxides, rare-earth carbonates, rare-earth fluorocarbonates, and a bastnasite concentrate prepared by froth flotation [137]. The ionic liquid trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) saturated with concentrated HCl was used to dissolve CaO, NiO, MnO, CoO, CuO, ZnO, and Fe$_2$O$_3$ [34]. The dissolved metals could be selectively stripped by bringing the loaded ionic-liquid phase into contact with aqueous solutions of different chloride concentrations. Ag$_2$O, CuO, ZnO, and NiO could be dissolved in different imidazolium ionic liquids via carbene formation [138]. Perhalide ionic liquids have been used for the oxidative dissolution of metals [139]. Mercury could be dissolved in the ionic liquid 1-butyl-3-methylimidazolium tribromide, [BMIM][Br$_3$]. Also, copper and antimony showed a good solubility in this ionic liquid, whereas aluminum, titanium, and tungsten showed a poor solubility.

Most of the experiments with ionic liquids have been carried out at temperatures below 100 °C. However, some studies showed that ionic liquids with a melting point above 100 °C can also be useful for applications in extractive metallurgy. In 1936, Audrieth and coworkers tested the use of molten pyridinium hydrochloride (formed in a reaction between pyridine and HCl) for the dissolution of metals, metal oxides, and metal salts [140]. Pyridinium hydrochloride has a melting point of 144.5 °C and boils at 219–221 °C. Of the tested metals, Al, Cd, Ca, Mg, Zn, Cu, Mn, Ni, Sn, Pb, and Fe could be dissolved. It is interesting to note that metallic copper can be dissolved in pyridinium hydrochloride, while it cannot be dissolved in concentrated HCl. Of the oxides, Sb$_2$O$_3$, BaO, Bi$_2$O$_3$, CdO, CoO, Cu$_2$O,

CuO, $Fe_2O_3$, HgO, PbO, MgO, $MnO_2$, NiO, $MoO_3$, and $V_2O_5$ were found to be soluble, while $WO_3$ and $U_3O_8$ reacted slowly, and $Ta_2O_5$, $SnO_2$, $ThO_2$, and $TiO_2$ did not react. The carbonates $BeCO_3$, $CaCO_3$, $PbCO_3$, and $MnCO_3$ reacted readily with pyridinium hydrochloride. Hollebone and coworkers tested molten pyridinium hydrochloride for the treatment of ores, including refractory niobium ores [141]. Finely divided pyrochlore was only poorly soluble (30% dissolved after 18 h at 160 °C), but the $Nb_2O_5$ that formed after the fusion of pyrochlore in molten NaOH readily dissolved. After pyridinium hydrochloride was sublimated in vacuum at 180 °C, $NbCl_5$ was obtained. On the other hand, ferrocolumbium readily dissolved in molten pyridinium hydrochloride without any pretreatment. CuS could be dissolved as well, with the release of $H_2S$.

## Non-Aqueous Solvent Extraction

Only very few studies on non-aqueous solvent extraction have been reported in the literature, and most have been performed to study fundamental aspects of coordination chemistry in solution and were not aimed at separating mixtures of metal compounds. Earlier authors have recognized the potential of non-aqueous solvent extraction, but the lack of outstanding results led to just a small number of follow-up studies. Nevertheless, non-aqueous solvent extraction offers some interesting opportunities, for instance, the possibility of separating metal compounds that hydrolyze in water.

The distribution of $ZrCl_4$ and $HfCl_4$ between acetonitrile and isoamyl ether was investigated with the aim to separate hafnium from zirconium [142]. However, it was found that the separation factors were too small to be of practical use. Several metal salts (chloride, bromide, thiocyanate, and nitrate) were extracted to a diethyl ether phase that was equilibrated with a second immiscible phase, being ethanolamine, formamide, or adiponitrile [143]. These solvents could extract nearly all metal complexes from the ether phase with an extraction efficiency of more than 90%. Only tin(IV) chloride showed a higher affinity for the ether phase. Thallium(III) was separated from Ga(III), In(III), Fe(III), Sn(II) and Sn(IV) by extracting the elements first from an aqueous 2-M HBr solution with methylisobutyl ketone (MIBK), followed by stripping of the MIBK layer using a 1.5-M HBr solution in formamide [144]. All the thallium(III) remained in the MIBK layer, while all the other metal ions were transferred to the formamide layer. Iron(III) can be extracted from methanol or DMSO using D2EHPA in $n$-octane [145]. It was observed that equilibrium was reached much more slowly than in the case of extraction from an aqueous solution. Zinc(II) and cadmium(II) were extracted from ethylene glycol (with added HBr or LiBr) using trioctylphosphine oxide (TOPO)

dissolved in benzene [146], while the extraction behavior of zinc(II) was also studied for extraction from ethylene glycol (with added HCl or LiCl) using TOPO dissolved in toluene [147]. A later study investigated the behavior of zinc(II) in the extraction system consisting of diethylene glycol and TOPO dissolved in decaline [148].

Recently, Foreman studied the extraction of the transition-metal ions and the rare-earth ions from the deep-eutectic solvent choline chloride : lactic acid (1:2) [66]. The transition-metal ions were extracted using the quaternary ammonium salt Aliquat® 336 dissolved in an aromatic diluent and in biodiesel, while the rare-earth ions were extracted using D2EHPA dissolved in aliphatic diluents. The extraction using Aliquat® 336 was found to be more sensitive to the water content of the DES than when using D2EHPA. Batchu et al. developed a solvent-extraction process for rare earths that involved two immiscible organic phases [149]. The more-polar organic phase was ethylene glycol with the dissolved rare-earth nitrate salts and $LiNO_3$, while the less-polar phase was a solution of the neutral extractant Cyanex® 923 dissolved in $n$-dodecane. Compared with aqueous feed solutions, the light rare-earth elements (LREEs) were less efficiently extracted, and the heavy rare-earth elements (HREEs) were more efficiently extracted from an ethylene glycol feed solution, resulting in a better separation of the HREEs from the LREEs. The separation factors between neighboring elements were higher for extraction from the ethylene glycol solution than those for extraction from an aqueous solution.

## Oxidative Dissolution of Metals in Non-Aqueous Solvents

The oxidative dissolution of metals in organic solvents was originally developed for the analysis of alloys, because this method allows for the selective dissolution of the metal, while having little effect on the oxide and other non-metallic impurities. For instance, bromine-ethyl acetate and bromine-methanol mixtures have been used for the dissolution of uranium alloys. Bromine-methanol has also been used for the dissolution of zirconium, thorium, titanium, and beryllium alloys, and also as an etchant for semiconductors. Many studies have been devoted to the dissolution of gold in organic solvents. Typical solvents are dihalogen-halide-polar aprotic organic solvent (DMF, DMSO, acetonitrile) mixtures [150–152] or dihalogen-halide-nonpolar solvent (aromatics, chloroform) mixtures [153, 154]. The halide can be an alkali-metal halide or an organic halide salt (e.g., a quaternary ammonium halide). Palladium reacts with iodine in DMF [155]. Mixtures of $SOCl_2$ with pyridine, DMF, pyrimidine, or imidazole are able to dissolve gold, silver, and palladium. These solvents are called "*organic aqua regia*" because they have similar solvent
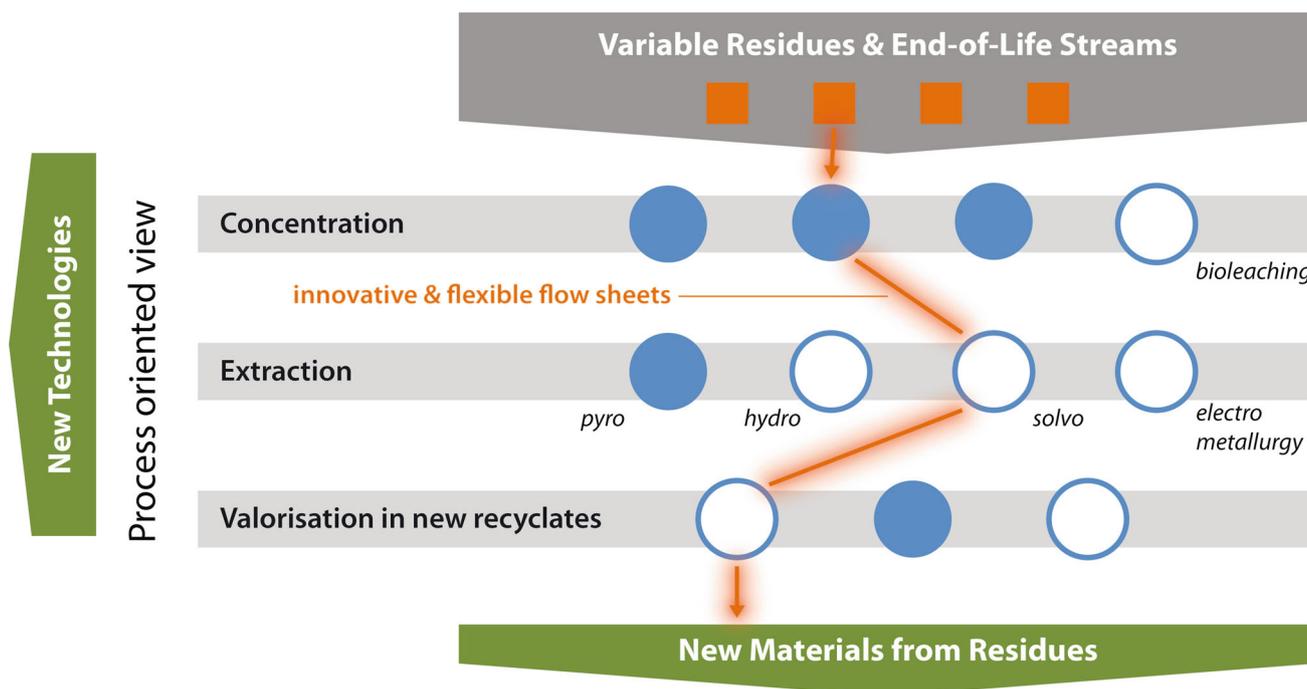
**Fig. 11** Toolbox for the treatment of low-grade ores, tailings, and industrial process residues by combining different innovative technologies. Figure adapted from the SIM MaRes programme: http://www.sim-flanders.be/research-program/mares (Color figure online)

properties to *aqua regia* [156, 157]. Interestingly, "*organic aqua regia*" cannot dissolve platinum, whereas *aqua regia* can, so that platinum–palladium separations are possible with these organic solvent mixtures. Charge-transfer complexes of dithioxamides with dihalogens are powerful reagents for the dissolution of noble metals [158–160]. A mixture of iodine and the S-donor tetraethylthiuram disulfide can dissolve gold [161]. DMF-$Cl_2$ can dissolve zirconium [162], while uranium metal can be dissolved in TBP-TCE-$Cl_2$ or TBP-TCE-$NO_2$ (TBP = tributyl phosphate, TCE = tetrachloroethylene) [163, 164]. As mentioned in the section on ionometallurgical processes, polyhalide ionic liquids with the tribromide anion are able to dissolve elemental mercury [139].

## Solvometallurgy as Part of the Metallurgical Toolbox

Solvometallurgy is complementary to pyrometallurgy and hydrometallurgy. It can be part of an integrated flow sheet combining different technologies in extractive metallurgy for cases where traditional pyrometallurgical and hydrometallurgical methods fail to efficiently extract the metal values from low-grade ores, mine tailings, and industrial process residues. The integration of these technologies into flow sheets in order to select an optimal

treatment for a specific resource or waste stream is the so-called 'toolbox' idea. The toolbox consists of a broad range of existing and to be developed "metallurgical unit operations," following a value-chain approach, from pretreatment, to metal extraction, metal recovery, and (residual) matrix valorization. These unit operations can be coupled into an integrated flow sheet that is optimized for a specific resource stream (Fig. 11). The toolbox can include both more established metallurgical technologies and innovative developments in pyrometallurgy (plasma and fuming technologies), hydrometallurgy (advanced leaching with the pretreatment of the solids), biometallurgy (selective bioleaching) and solvometallurgy. Optimal beneficiation of the secondary ore material and valorization of the residue, through novel treatment routes, and after metal extraction, contribute to the closure of the material loop for the studied material streams.

## Challenges

Solvometallurgy is a promising new approach to extractive metallurgy with several advantages, but there are still several problems that need to be solved before solvometallurgical processes can be applied on a large scale in industry.

One problem is the high price of the organic solvents and extractants compared with water and mineral acids. Therefore, it is important that these solvents and extractants can be recycled at the end of the process so that the consumption of reagents is a minimum. The recycling of solvents is also mandatory from an environmental point of view. As mentioned elsewhere, it is better not to use distillation for the recovery of solvents, but to use instead more energy-efficient membrane processes.

For health, safety, and environmental reasons, organic solvents that are highly toxic should not be considered for developing solvometallurgical processes. Examples include benzene, nitrobenzene, chloroform, carbon tetrachloride, carbon disulfide, and HMPA. Also solvents with a very low flash point such as diethyl ether must be avoided. Although volatile solvents might seem to be of interest because they can be easily recovered after the reaction by distillation, they should be avoided in open systems. One must be cautious when combining concentrated $HNO_3$ with organic solvents, because concentrated $HNO_3$ is a strong oxidizing agent, and bringing it into contact with organic solvents might cause fires or even explosions. Also protic nitrate ionic liquids can be dangerous when heated [165].

Ionic liquids and deep-eutectic solvents are very promising classes of solvents for solvometallurgical processes because of their reactivity in solvent leaching, intrinsic electrical conductivity in electrodeposition processes and very low vapor pressure (and hence low flammability and very high flash point). However, these solvents suffer from a high viscosity, especially if their water content is low. A high viscosity hampers the mass transport and slows down the chemical reactions occurring during leaching, solvent extraction, or electrodeposition. A high viscosity also makes solid–liquid separations more difficult. Of course, many aspects of working with viscous liquids are challenging from the chemical engineering point of view.

Solvometallurgy can benefit from knowledge in the fields of coordination chemistry in non-aqueous solvents [166] or the solvation of ions in non-aqueous solvents [15]. Through a better understanding of the interactions between metal ions or metal complexes and the molecule in the solvent phase, more efficient and selective solvometallurgical processes can be developed. Although an enormous amount of information is available on metal ions in aqueous solutions, very little information is available on metal ions in non-aqueous solvents. Moreover, we must be aware of the fact that even small amounts of water can significantly change the system, especially in those cases where the metal ions have a very strong tendency to bind water molecules, such as in the case of the trivalent rare-earth ions. In anhydrous acetonitrile, acetonitrile molecules will bind to rare-earth ions, but even in the presence of a small amount of water, the rare-earth ions will be coordinated by the water molecules. This is the phenomenon of *preferential solvation*. This can also occur with other solvent mixtures. For solvometallurgy, a good knowledge of the solvation of metal ions in different solvents and the preferential solvation of these metal ions in solvent mixtures is of great importance.

Comparatively few solvometallurgical processes have been described in the literature, in contrast to the large number of hydrometallurgical and pyrometallurgical processes. Therefore, the full potential of solvometallurgy still needs to be unlocked. So far, no solvometallurgical processes applied in industry have been disclosed (with the exception of the electroplating of aluminum from non-aqueous electrolytes). The Technology Readiness Level (TRL) of solvometallurgical processes is still low. On the TRL scale defined by the European Commission, which ranges from TRL 1 (basic principles observed) to TRL 9 (actual system proven in operational environment), most solvometallurgical processes have a TRL of 3 (experimental proof-of-concept) or 4 (technology validated in the lab). It is important that the sustainability of metallurgical flow sheets with solvometallurgical unit processes is assessed from the very beginning of the process design.

## Conclusions

Solvometallurgy is a new branch of extractive metallurgy that can complement pyrometallurgy and hydrometallurgy. Solvometallurgical processes are similar to hydrometallurgical processes, but with the aqueous phase replaced by a non-aqueous phase. Therefore, it is important to realize that conventional solvent extraction cannot be considered as a solvometallurgical process because of the presence of a discrete aqueous phase. An obvious advantage of solvometallurgy is the reduced use of water and the avoidance of problems with wastewater treatment. However, because the solvation of metal ions in organic solvents differs from their solvation (hydration) in water, the efficiency and selectivity of non-aqueous solvent extraction and non-aqueous ion exchange can be different from those observed for the analogous processes with aqueous solvents. By direct solid leaching or non-aqueous-slurry solvent leaching, the processes of leaching and solvent extraction can be combined into a single step, leading to process intensification. However, solvometallurgical processes require a careful selection of the most suitable solvents, and special attention has to be paid to the recovery of solvents after solvent leaching. The solvents must have a low toxicity, a low flammability and a low environmental impact. They should also be biodegradable so that any solvent traces left on the solid residues can be destroyed by

heterotrophic microorganisms. This offers the opportunity to combine solvent leaching and bioleaching with heterotrophic microorganisms because these microorganisms can use the solvent traces as nutrients for their growth. The residues obtained after solvent leaching, with or without applying an additional bioleaching step, can be used as the input materials for the preparation of building materials or for cementitious binders. Solvometallurgical unit operations can be considered as part of the metallurgical toolbox for the treatment of low-grade or complex ores, tailings, industrial residues, and urban waste. As such, solvometallurgy can contribute to the integrated, near-zero-waste, metallurgical processing of different secondary resources. The technology readiness level (TRL) of this emerging branch of extractive metallurgy is still low (TRL = 3–4), which is a disadvantage for short-term implementation, but a great opportunity for research, development, and innovation.

# References

1. Habashi F (1997) Handbook of extractive metallurgy. Wiley, Weinheim
2. Anderson C, Dunne R, Uhrie J (2014) Mineral processing and extractive metallurgy: 100 years of innovation. Society for Mining Metallurgy and Exploration (SME), Englewood
3. Hayes P (2003) Process principles in minerals and materials production, 3rd edn. Hayes Publishing Co, Sherwood
4. Kimball R, Ewing R (1957) Uranium recovery from ores with hydrochloric acid and acetone. US Patent 2800387
5. Grinstead RR (1959) Process for the recovery of metals from high-lime carnotite ores. US Patent 2869980
6. Grinstead RR (1958) Process for utilizing organic orthophosphate extractants. US Patent 2860031
7. Galvanek P (1959) Process of recovering uranium from its ores. US Patent 2875023
8. Bloecher FW Jr (1950) Lyometallurgical tests on Marysvale uranium ores. Mineral Engineering Laboratory, Massachusetts Institute of Technology, Watertown, Report MITG-252
9. Bailes R, Magner J (1957) Direct solvent leaching of uranium ores. Mines Mag 47(June):51–54
10. Raghavan S, Fuerstenau DW (1993) A lyometallurgical process for leaching copper from chrysocolla. In: Hydrometallurgy fundamentals, technology and innovations, Proceedings of the Milton E., Wordsworth (IV) Int. Symposium on Hydrometallurgy, pp 283–297
11. Raghavan S, Harris I, Fuerstenau DW (1979) Lyometallurgical treatment of porous oxidized ores. In: Prepr Pap—Int Miner. Process Congr 13th. Panst. Wydawn. Nauk.-Wroclaw, pp 743–774
12. Raghavan S, Harris I, Fuerstenau DW (1981) Lyometallurgical treatment of porous oxidized ores. In: Dev. Miner. Process. pp 960–992
13. Tomijima H, Tsukui K, Okoshi Y (1966) Direct dissolution of water-insoluble uranium compounds by contact with neutral organic solvents pretreated with nitric acid. US Patent 3288568
14. Sastri V (1975) Selective leaching of metals from ores with organic solvents and chelating agents. J Sci Ind Res 34:663–665
15. Marcus Y (1985) Ion solvation. Wiley, New York
16. Chekmarev AM, Chizhevskaya SV, Buchikhin EP (2000) Solvometallurgy as a novel trend in XXI century metallurgy. Khim Tekhnol. 2–7
17. Chizhevskaya SV, Chekmarev AM, Klimenko OM, et al (1994) Non-traditional methods of treating high-silicon ores containing rare elements. In: Hydrometallurgy'94. Springer, Dordrecht, pp 219–228. doi: 10.1007/978-94-011-1214-7_13
18. Chizhevskaya SV, Chekmarev AM, Povetkina MV, et al (2001) New extraction technologies for the treatment of rare metal raw materials using mechanochemical methods. In: Solvent Extraction for the 21st Century, Proceedings of ISEC '99, Barcelona, July 1999, Society of Chemical Industry, London, pp 805–809
19. Chekmarev A, Chizhevskaya S, Buchikhin E, Cox M (2001) Solvometallurgical methods in the treatment of rare and nonferrous metal raw materials. In: Proceedings VI Southern Hemisphere Meeting on Mineral Technology/XVIII Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa (VI SHMMT/XVIII ENTMM), May 2001, Rio de Janeiro, Brazil, pp 441–444
20. Park J, Jung Y, Kusumah P et al (2014) Application of ionic liquids in hydrometallurgy. Int J Mol Sci 15:15320. doi:10.3390/ijms150915320
21. Tian G, Li J, Hua Y (2010) Application of ionic liquids in hydrometallurgy of nonferrous metals. Trans Nonferrous Met Soc China 20:513–520. doi:10.1016/S1003-6326(09)60171-0
22. Smith EL, Abbott AP, Ryder KS (2014) Deep eutectic solvents (DESs) and their applications. Chem Rev 114:11060–11082. doi:10.1021/cr300162p
23. Endres F, MacFarlane D, Abbott A (2008) Electrodeposition from ionic liquids. Wiley, Weinheim
24. Abbott AP, Frisch G, Gurman SJ et al (2011) Ionometallurgy: designer redox properties for metal processing. Chem Commun 47:10031–10033. doi:10.1039/c1cc13616j
25. Ozdemir S, Girgin I (1991) Decomposition of scheelite in acid-alcohol solutions. Miner Eng 4:179–184. doi:10.1016/0892-6875(91)90034-S
26. Girgin I, Erkal F (1993) Dissolution characteristics of scheelite in HCl-$C_2H_5OH$-$H_2O$ and HCl-$C_2H_5OH$ solutions. Hydrometallurgy 34:221–230. doi:10.1016/0304-386X(93)90036-D
27. Jana R, Singh D, Roy S (1993) Hydrochloric acid leaching of sea nodules with methanol and ethanol addition. Mater Trans JIM 34:593–598. doi:10.2320/matertrans1989.34.593
28. Wongnawa S, Boonsin P, Sombatchaikul T (1997) Determination of impurities in ilmenite ore and residues after leaching with HCl-ethylene glycol by energy dispersive X-ray fluorescence (EDXRF) spectrometry. Hydrometallurgy 45:161–167. doi:10.1016/S0304-386X(96)00071-0
29. Abbott A, Boothby D, Capper G et al (2004) Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids. J Am Chem Soc 126:9142–9147. doi:10.1021/ja048266j
30. Duan W, Zhu L, Jing S et al (2007) Study on properties of TBP-$HNO_3$ complex used for direct dissolution of lanthanide and

actinide oxides in supercritical fluid $CO_2$. Chin J Chem 25:319–322. doi:10.1002/cjoc.200790062

31. Kumar B, Kumar S, Sampath M et al (2011) Direct dissolution of $UO_2$ and in situ extraction by TBP-$HNO_3$ and TiAP-$HNO_3$ organic solutions at atmospheric pressure. J Radioanal Nucl Chem 288:443–445. doi:10.1007/s10967-010-0941-6

32. Dziwinski E, Szymanowski J (1998) Composition of CYANEX 923, CYANEX 925, CYANEX 921 and TOPO. Solvent Extr Ion Exch 16:1515–1525. doi:10.1080/07366299808934592

33. Gareil P, Debeler S, Bauer D (1989) Composition analysis of Kelex-100, an industrial chelating agent, by liquid-chromatography and mass-spectrometry. Hydrometallurgy 22:239–248. doi:10.1016/0304-386X(89)90054-6

34. Wellens S, Vander Hoogerstraete T, Moller C et al (2014) Dissolution of metal oxides in an acid-saturated ionic liquid solution and investigation of the back-extraction behaviour to the aqueous phase. Hydrometallurgy 144:27–33. doi:10.1016/j.hydromet.2014.01.015

35. Nockemann P, Thijs B, Pittois S et al (2006) Task-specific ionic liquid for solubilizing metal oxides. J Phys Chem B 110:20978–20992. doi:10.1021/jp0642995

36. Kopkova EK, Shchelokova EA, Gromov PB (2015) Processing of titanomagnetite concentrate with a hydrochloric extract of n-octanol. Hydrometallurgy 156:21–27. doi:10.1016/j.hydromet.2015.05.007

37. Jana R, Singh D, Roy S (1995) Alcohol-modified hydrochloric-acid leaching of sea nodules. Hydrometallurgy 38:289–298. doi:10.1016/0304-386X(94)00069-F

38. Ritcey G (1983) Solvent extraction—projection to the future. Sep Sci Technol 18:1617–1646. doi:10.1080/01496398308056118

39. Rydberg J, Cox M, Musikas C, Choppin G (2004) Solvent extraction principles and practice, 2nd edn. Marcel Dekker, New York

40. Drury JS (1952) Miscibility of organic solvent pairs. Ind Eng Chem 44:2744. doi:10.1021/ie50515a065

41. Jackson WM, Drury JS (1959) Miscibility of organic solvent pairs. Ind Eng Chem 51:1491–1493. doi:10.1021/ie50600a039

42. Reichardt C (2003) Solvents and solvent effects in organic chemistry, 3rd edn. Wiley, Weinheim

43. Hecker E (1954) Auswahl von Lösungsmittelsystemen zur Multiplikativen Verteilung. Chimia 8:229–236

44. Hecker E (1955) Verteilungsverfahren im Laboratorium. Verlag Chemie, Weinheim

45. Wellens S, Thijs B, Moller C, Binnemans K (2013) Separation of cobalt and nickel by solvent extraction with two mutually immiscible ionic liquids. Phys Chem Chem Phys 15:9663–9669. doi:10.1039/c3cp50819f

46. Vander Hoogerstraete T, Blockx J, De Coster H, Binnemans K (2015) Selective single-step separation of a mixture of three metal ions by a triphasic ionic-liquid-water-ionic-liquid solvent extraction system. Chem Eur J 21:11757–11766. doi:10.1002/chem.201500825

47. Marcus Y (1973) Ion exchange in nonaqueous and mixed solvents. In: Ion exchange and solvent extraction. Marcel Dekker, New York, pp 1–119

48. Katzin L, Sullivan J (1958) Separation of inorganic salts from organic solutions. US Patent 2840451

49. Sansoni B (1956) Spezifischer Ionenaustausch durch unterschiedliche Solvatation in nichtwässerigen Lösungsmitteln: Kobalt-Nickel-Trennung in geschmolzenem Harnstoff. Angew Chem 68:117–119

50. Kennedy J, Davies RV (1959) The adsorption of inorganic salts by amine resins from organic solvents. J Inorg Nucl Chem 12:193–198. doi:10.1016/0022-1902(59)80110-X

51. Abbott AP, Collins J, Dalrymple I et al (2009) Processing of electric arc furnace dust using deep eutectic solvents. Aust J Chem 62:341–347. doi:10.1071/CH08476

52. Smith EL, Fullarton C, Harris RC et al (2010) Metal finishing with ionic liquids: scale-up and pilot plants from IONMET consortium. Trans Inst Met Finish 88:285–291. doi:10.1179/174591910X12856686485734

53. Abbott AP, McKenzie KJ (2006) Application of ionic liquids to the electrodeposition of metals. Phys Chem Chem Phys 8:4265–4279. doi:10.1039/b607329h

54. Endres F (2002) Ionic liquids: solvents for the electrodeposition of metals and semiconductors. ChemPhysChem 3:144–154. doi:10.1002/1439-7641(20020215)3:2<144:AID-CPHC144>3.3.CO;2-R

55. Alfonsi K, Colberg J, Dunn PJ et al (2008) Green chemistry tools to influence a medicinal chemistry and research chemistry based organisation. Green Chem 10:31–36. doi:10.1039/b711717e

56. Henderson RK, Jimenez-Gonzalez C, Constable DJC et al (2011) Expanding GSK's solvent selection guide—embedding sustainability into solvent selection starting at medicinal chemistry. Green Chem 13:854–862. doi:10.1039/c0gc00918k

57. Jessop PG (2011) Searching for green solvents. Green Chem 13:1391–1398. doi:10.1039/c0gc00797h

58. Alder CM, Hayler JD, Henderson RK et al (2016) Updating and further expanding GSK's solvent sustainability guide. Green Chem 18:3879–3890. doi:10.1039/c6gc00611f

59. Welton T (2015) Solvents and sustainable chemistry. Proc R Soc Math Phys Eng Sci. doi:10.1098/rspa.2015.0502

60. Marchetti P, Solomon MFJ, Szekely G, Livingston AG (2014) Molecular separation with organic solvent nanofiltration: a critical review. Chem Rev 114:10735–10806. doi:10.1021/cr500006j

61. Coleman D, Gathergood N (2010) Biodegradation studies of ionic liquids. Chem Soc Rev 39:600–637. doi:10.1039/b817717c

62. Singh SP, Singh D (2010) Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: a review. Renew Sustain Energy Rev 14:200–216. doi:10.1016/j.rser.2009.07.017

63. Hoekman SK, Broch A, Robbins C et al (2012) Review of biodiesel composition, properties, and specifications. Renew Sustain Energy Rev 16:143–169. doi:10.1016/j.rser.2011.07.143

64. Wang W, Yang H, Liu Y et al (2011) The application of biodiesel and sec-octylphenoxyacetic acid (CA-12) for the yttrium separation. Hydrometallurgy 109:47–53. doi:10.1016/j.hydromet.2011.05.010

65. Liu Y, Zhu L, Sun X, Chen J (2010) Toward greener separations of rare earths: bifunctional ionic liquid extractants in biodiesel. AIChE J 56:2338–2346. doi:10.1002/aic.12149

66. Foreman M (2016) Progress towards a process for the recycling of nickel metal hydride electric cells using a deep eutectic solvent. Cogent Chem 2:1139289. doi:10.1080/23312009.2016.1139289

67. Li Z, Smith KH, Stevens GW (2016) The use of environmentally sustainable bio-derived solvents in solvent extraction applications-A review. Chin J Chem Eng 24:215–220. doi:10.1016/j.cjche.2015.07.021

68. Spear SK, Griffin ST, Granger KS et al (2007) Renewable plant-based soybean oil methyl esters as alternatives to organic solvents. Green Chem 9:1008–1015. doi:10.1039/b702329d

69. Gu Y, Jerome F (2010) Glycerol as a sustainable solvent for green chemistry. Green Chem 12:1127–1138. doi:10.1039/c001628d

70. Garcia JI, Garcia-Marin H, Mayoral JA, Perez P (2010) Green solvents from glycerol. Synthesis and physico-chemical

properties of alkyl glycerol ethers. Green Chem 12:426–434. doi:10.1039/b923631g

71. Gernon M, Wu M, Buszta T, Janney P (1999) Environmental benefits of methanesulfonic acid: comparative properties and advantages. Green Chem 1:127–140. doi:10.1039/a900157c

72. Wood DA, Nwaoha C, Towler BF (2012) Gas-to-liquids (GTL): a review of an industry offering several routes for monetizing natural gas. J Nat Gas Sci Eng 9:196–208. doi:10.1016/j.jngse.2012.07.001

73. Hughes C, Whale G, Mead C (2015) Investigation into the biodegradability of various hydrocarbon solvents. Royal Dutch Shell Report 1–1

74. Eadsforth CV, Dirkzwager H, Maase B (2008) Compositional analysis and environmental performance of LAS produced from GTL normal paraffin and different alkylation routes. Tenside Surfactants Deterg 45:194–201. doi:10.3139/113.100376

75. Mekki S, Wai C, Billard I et al (2005) Cu(II) extraction by supercritical fluid carbon dioxide from a room temperature ionic liquid using fluorinated beta-diketones. Green Chem 7:421–423. doi:10.1039/b502190a

76. Chen Y, Mariba ERM, Van Dyk L, Potgieter JH (2011) A review of non-conventional metals extracting technologies from ore and waste. Int J Miner Process 98:1–7. doi:10.1016/j.minpro.2010.10.001

77. Baek DL, Fox RV, Case ME et al (2016) Extraction of rare earth oxides using supercritical carbon dioxide modified with tri-n-butyl phosphate-nitric acid adducts. Ind Eng Chem Res 55:7154–7163. doi:10.1021/acs.iecr.6b00554

78. Fu J, Chen Q, Shen X (2015) Stripping of uranium from an ionic liquid medium by TOPO-modified supercritical carbon dioxide. Sci China Chem 58:545–550. doi:10.1007/s11426-014-5162-3

79. Shimizu R, Sawada K, Enokida Y, Yamamoto I (2005) Supercritical fluid extraction of rare earth elements from luminescent material in waste fluorescent lamps. J Supercrit Fluids 33:235–241. doi:10.1016/j.supflu.2004.08.004

80. Tomioka O, Enokida Y, Yamamoto I (1998) Solvent extraction of lanthanides from their oxides with TBP in supercritical carbon dioxide. J Nucl Sci Technol 35:515–516. doi:10.1080/18811248.1998.9733901

81. Tomioka O, Meguro Y, Enokida Y et al (2001) Dissolution behavior of uranium oxides with supercritical $CO_2$ using $HNO_3$-TBP complex as a reactant. J Nucl Sci Technol 38:1097–1102. doi:10.1080/18811248.2001.9715141

82. Enokida Y, Tomioka O, Lee S et al (2003) Characterization of a tri-n-butyl phosphate-nitric acid complex: a $CO_2$-soluble extractant for dissolution of uranium dioxide. Ind Eng Chem Res 42:5037–5041. doi:10.1021/ie030010j

83. Vincent T, Mukhopadhyay M, Wattal PK (2009) Direct in situ supercritical fluid extraction of neodymium ion from its oxide using thenoyltrifluoroacetone-tributyl phosphate-methanol in carbon dioxide. J Supercrit Fluids 48:230–237. doi:10.1016/j.supflu.2008.10.022

84. Laintz K, Wai C, Yonker C, Smith R (1992) Extraction of metal-ions from liquid and solid materials by supercritical carbon-dioxide. Anal Chem 64:2875–2878. doi:10.1021/ac00046a039

85. Welton T (1999) Room-temperature ionic liquids. Solvents for synthesis and catalysis. Chem Rev 99:2071–2083. doi:10.1021/cr980032t

86. Plechkova NV, Seddon KR (2008) Applications of ionic liquids in the chemical industry. Chem Soc Rev 37:123–150. doi:10.1039/b006677j

87. Emons H (1988) Structure and properties of molten-salt hydrates. Electrochim Acta 33:1243–1250. doi:10.1016/0013-4686(88)80155-5

88. Davis J (2004) Task-specific ionic liquids. Chem Lett 33:1072–1077. doi:10.1246/cl.2004.1072

89. Abbott A, Capper G, Davies D et al (2003) Novel solvent properties of choline chloride/urea mixtures. Chem Commun. doi:10.1039/b210714g

90. Zhang Q, Vigier KDO, Royer S, Jerome F (2012) Deep eutectic solvents: syntheses, properties and applications. Chem Soc Rev 41:7108–7146. doi:10.1039/c2cs35178a

91. Abbott A, Capper G, Davies D, Rasheed R (2004) Ionic liquid analogues formed from hydrated metal salts. Chem Eur J 10:3769–3774. doi:10.1002/chem.200400127

92. Abbott AP, Al-Barzinjy AA, Abbott PD et al (2014) Speciation, physical and electrolytic properties of eutectic mixtures based on $CrCl_3 \cdot 6H_2O$ and urea. Phys Chem Chem Phys 16:9047–9055. doi:10.1039/c4cp00057a

93. Brown P, Jacob S (1981) Process for purification of lithium chloride. US Patent 4274834

94. Ewing R, Kiehl S, Bearse A (1955) Nonaqueous extractive methods for Western uranium ores. Final report to the U.S. Atomic Energy Commission, Contract No. AT-(49-1)-635, Battelle Memorial Institute, Columbus Ohio

95. Rosenbaum J, Clemmer J, Lennemann W (1956) Innovation in processing uranium ores. Final report to the U.S. Atomic Energy Commission, Contract No. AT-(49-1)-635, Bureau of Mines. Intermountain Experiment Station, Salt Lake City

96. Parker A (1973) Hydrometallurgy of copper and silver in solvent mixtures. Search 4:426–432

97. Parker A (1972) Solvation of ions—some applications. Proc R Aust Chem Inst 39:163–170

98. Parker A (1981) Solvation of ions—applications to minerals and energy. Pure Appl Chem 53:1437–1445. doi:10.1351/pac198153071437

99. Avraamides J, Muir D, Parker A (1980) Cuprous hydrometallurgy 6, activation of chalcopyrite by reduction with copper and solutions of copper(I) salts. Hydrometallurgy 5:325–336. doi:10.1016/0304-386X(80)90023-7

100. Preston J, Muir D, Parker A (1980) Cuprous hydrometallurgy 8. Solvent extraction and recovery of copper(I) chloride with organic nitriles from an iron(III), copper(II) chloride, 2-step oxidative leach of chalcopyrite concentrate. Hydrometallurgy 5:227–241. doi:10.1016/0304-386X(80)90041-9

101. Johannsen F, Levinskas G (1986) Relationships between toxicity and structure of aliphatic nitriles. Fundam Appl Toxicol 7:690–697. doi:10.1016/0272-0590(86)90119-3

102. DeVito S (1996) Designing safer nitriles. ACS Symp Ser 640:194–223. doi:10.1021/bk-1996-0640.ch010

103. Solis-Marcial OJ, Lapidus GT (2013) Improvement of chalcopyrite dissolution in acid media using polar organic solvents. Hydrometallurgy 131:120–126. doi:10.1016/j.hydromet.2012.11.006

104. Solis-Marcial OJ, Lapidus GT (2014) Chalcopyrite leaching in alcoholic acid media. Hydrometallurgy 147:54–58. doi:10.1016/j.hydromet.2014.04.011

105. Solis-Marcial OJ, Lapidus GT (2014) Study of the dissolution of chalcopyrite in sulfuric acid solutions containing alcohols and organic acids. Electrochim Acta 140:434–437. doi:10.1016/j.electacta.2014.07.041

106. Thorsen G, Grislingås A, Steintveit G (1981) Recovery of zinc from zinc ash and flue dusts by hydrometallurgical processing. JOM 33(1):24–29. doi:10.1007/BF03354397

107. Thorsen G, Svendsen HF, Grislingås A (1984) The integrated organic leaching—solvent extraction operation in hydrometallurgy. In: Bautista RG (ed) Hydrometallurgical process fundamentals. Springer, Boston, pp 269–292. doi:10.1007/978-1-4899-2274-8_10

108. Thorsen G (1980) Extraction and separation of metals from solids using liquid cation exchangers. US Patent 4200504

109. Chekmarev AM, Buchikhin EP, Parygin IA, Smirnov KM (2011) Patterns of extractive leaching of uranium and vanadium from an ore. Theor Found Chem Eng 45:776–778. doi:10.1134/S0040579511050046

110. Whitehead J, Lawrance G, McCluskey A (2004) 'Green' leaching: recyclable and selective leaching of gold-bearing ore in an ionic liquid. Green Chem 6:313–315. doi:10.1039/b406148a

111. Whitehead JA, Zhang J, Pereira N et al (2007) Application of 1-alkyl-3-methyl-imidazolium ionic liquids in the oxidative leaching of sulphidic copper, gold and silver ores. Hydrometallurgy 88:109–120. doi:10.1016/j.hydromet.2007.03.009

112. Whitehead JA, Zhang J, McCluskey A, Lawrance GA (2009) Comparative leaching of a sulfidic gold ore in ionic liquid and aqueous acid with thiourea and halides using Fe(III) or $HSO_5^-$ oxidant. Hydrometallurgy 98:276–280. doi:10.1016/j.hydromet.2009.05.012

113. Dong T, Hua Y, Zhang Q, Zhou D (2009) Leaching of chalcopyrite with Bronsted acidic ionic liquid. Hydrometallurgy 99:33–38. doi:10.1016/j.hydromet.2009.06.001

114. McCluskey A, Lawrance G, Leitch S et al (2002) Ionic liquids and metal ions: from green chemistry to ore refining. ACS Symp Ser 818:199–212. doi:10.1021/bk-2002-0818.ch016

115. Jenkin GRT, Al-Bassam AZM, Harris RC et al (2016) The application of deep eutectic solvent ionic liquids for environmentally-friendly dissolution and recovery of precious metals. Miner Eng 87:18–24. doi:10.1016/j.mineng.2015.09.026

116. Binnemans K, Jones PT, Blanpain B et al (2015) Towards zero-waste valorisation of rare-earth-containing industrial process residues: a critical review. J Clean Prod 99:17–38. doi:10.1016/j.jclepro.2015.02.089

117. Davris P, Balomenos E, Panias D, Paspaliaris I (2014) Leaching of rare earths from bauxite residues using imidazolium ionic liquids. In: Proceedings of the 1st European Rare Earth Resources Conference (ERES 2014), Milos (Greece), 4–7 September 2014, pp 241–252

118. Davris P, Balomenos E, Panias D, Paspaliaris I (2015) The use of ionic liquids for rare earth element extraction from bauxite residue. In: Proceedings of the Bauxite Residue Valorisation and Best Practices Conference 2015, Leuven (Belgium), 5–7 October 2015, pp 323–330

119. Davris P, Balomenos E, Panias D, Paspaliaris I (2016) Selective leaching of rare earth elements from bauxite residue (red mud), using a functionalized hydrophobic ionic liquid. Hydrometallurgy 164:125–135. doi:10.1016/j.hydromet.2016.06.012

120. Rozelle PL, Khadilkar AB, Pulati N et al (2016) A study on removal of rare earth elements from U.S. coal byproducts by ion exchange. Metall Mater Trans E 3:6–17. doi:10.1007/s40553-015-0064-7

121. Kilicarslan A, Saridede MN, Stopic S, Friedrich B (2014) Use of ionic liquid in leaching process of brass wastes for copper and zinc recovery. Int J Miner Metall Mater 21:138–143. doi:10.1007/s12613-014-0876-y

122. Kilicarslan A, Saridede MN (2015) Recovery of metallic values from brass waste using Bronsted acidic ionic liquid as leachate. JOM 67:2739–2746. doi:10.1007/s11837-015-1510-9

123. Kiliçarslan A, Saridede MN (2015) Application of 1-methylimidazolium hydrogen sulfate ionic liquid to the oxidative leaching of copper and zinc in industrial brass dross. In: Energy technology 2015. The Minerals, Metals & Materials Society, Warrendale; John Wiley & Sons, Hoboken, pp 209–215. doi: 10.1002/9781119093220.ch23

124. Huang J, Chen M, Chen H et al (2014) Leaching behavior of copper from waste printed circuit boards with Bronsted acidic ionic liquid. Waste Manag 34:483–488. doi:10.1016/j.wasman.2013.10.027

125. Abbott A, Capper G, Davies D et al (2005) Selective extraction of metals from mixed oxide matrixes using choline-based ionic liquids. Inorg Chem 44:6497–6499. doi:10.1021/ic0505450

126. Abbott AP, Capper G, Davies DL et al (2006) Solubility of metal oxides in deep eutectic solvents based on choline chloride. J Chem Eng Data 51:1280–1282. doi:10.1021/je060038c

127. Abbott AP, Capper G, Davies DL, Shikotra P (2006) Processing metal oxides using ionic liquids. Miner Process Extr Metall 115:15–18. doi:10.1179/174328506X91293

128. Abbott AP, Harris RC, Holyoak F et al (2015) Electrocatalytic recovery of elements from complex mixtures using deep eutectic solvents. Green Chem 17:2172–2179. doi:10.1039/c4gc02246g

129. Nockemann P, Thijs B, Parac-Vogt TN et al (2008) Carboxyl-functionalized task-specific ionic liquids for solubilizing metal oxides. Inorg Chem 47:9987–9999. doi:10.1021/ic801213z

130. Dupont D, Raiguel S, Binnemans K (2015) Sulfonic acid functionalized ionic liquids for dissolution of metal oxides and solvent extraction of metal ions. Chem Commun 51:9006–9009. doi:10.1039/c5cc02731d

131. Dupont D, Renders E, Binnemans K (2016) Alkylsulfuric acid ionic liquids: a promising class of strongly acidic room-temperature ionic liquids. Chem Commun 52:4640–4643. doi:10.1039/c6cc00094k

132. Dupont D, Renders E, Raiguel S, Binnemans K (2016) New metal extractants and super-acidic ionic liquids derived from sulfamic acid. Chem Commun 52:7032–7035. doi:10.1039/c6cc02350a

133. Dupont D, Binnemans K (2015) Rare-earth recycling using a functionalized ionic liquid for the selective dissolution and revalorization of $Y_2O_3$:$Eu^{3+}$ from lamp phosphor waste. Green Chem 17:856–868. doi:10.1039/c4gc02107j

134. Billard I, Gaillard C, Hennig C (2007) Dissolution of $UO_2$, $UO_3$ and of some lanthanide oxides in BumimTf$_2$N: effect of acid and water and formation of $UO_2(NO_3)_3^-$. Dalton Trans. doi:10.1039/b706355e

135. Yao A, Chu T (2013) Fe-containing ionic liquids as effective and recoverable oxidants for dissolution of $UO_2$ in the presence of imidazolium chlorides. Dalton Trans 42:8413–8419. doi:10.1039/c3dt32832e

136. Binnemans K (2007) Lanthanides and actinides in ionic liquids. Chem Rev 107:2592–2614. doi:10.1021/cr050979c

137. Freiderich JW, Stankovich JJ, Luo H et al (2015) Dissolution of the rare-earth mineral bastnaesite by acidic amide ionic liquid for recovery of critical materials. Eur J Inorg Chem. doi:10.1002/ejic.201500509

138. Wellens S, Brooks NR, Thijs B et al (2014) Carbene formation upon reactive dissolution of metal oxides in imidazolium ionic liquids. Dalton Trans 43:3443–3452. doi:10.1039/c3dt53024h

139. Rogers R, Holbrey J (2012) Ionic liquid solvents of perhalide type for metals and metal compounds. US Patent Application 20120090430

140. Audrieth LF, Long A, Edwards RE (1936) Fused "onium" salts as acids. reactions in fused pyridinium hydrochloride. J Am Chem Soc 58:428–429. doi:10.1021/ja01294a012

141. Hollebone B, Morgan W, Wiles D (1967) The use of molten pyridinium chloride in the thermal treatment of ores of niobium (columbium) and other refractory metals. Trans Metall Soc AIME 239:97–99

142. Larsen E, Trevorrow L (1956) The systems formed by zirconium and hafnium tetrachloride with acetonitrile and isoamyl ether. J Inorg Nucl Chem 2:254–259. doi:10.1016/0022-1902(56)80052-3

143. Latimer G (1963) Distribution of ion pairs between immiscible nonaqueous solvents. Anal Chem 35:1983. doi:10.1021/ac60205a062

144. Dean J, Eskew J (1971) Solvent extraction with two immiscible organic solvents: separation of thallium(III). Anal Lett 4:737–743

145. Borshch N (1987) Extraction of iron(III) from polar nonaqueous solvents and some particularities of liquid extraction of metal ions in such systems. J Anal Chem USSR 42:857–861

146. Matsui M, Aoki T, Inoue O, Shigematsu T (1975) Nonaqueous liquid-liquid extraction. Extraction of zinc and cadmium from ethylene glycol solution of bromide by trioctylphosphine oxide. Bull Inst Chem Res Kyoto Univ 52:652–657

147. Matsui M, Aoki T, Enomoto H, Shigematsu T (1975) Non-aqueous liquid-liquid extraction—extraction of zinc from ethylene-glycol solution of chloride by trioctylphosphine oxide. Anal Lett 8:247–255

148. Matsui M, Doe H, Hirade T, Shigematsu T (1979) Non-aqueous liquid-liquid extraction—extraction of zinc from methanol-water solution of chloride by trioctylphosphine oxide in decaline. Anal Lett A 12:1385–1397

149. Batchu NK, Vander Hoogerstraete T, Banerjee D, Binnemans K (2017) Non-aqueous solvent extraction of rare-earth nitrates from ethylene glycol to n-dodecane by Cyanex 923. Sep Purif Technol 174:544–553. doi:10.1016/j.seppur.2016.10.039

150. Nakao Y (1992) Dissolution of noble-metals in halogen halide polar organic solvent systems. J Chem Soc Chem Commun. doi:10.1039/c39920000426

151. Nakao Y, Sone K (1996) Reversible dissolution/deposition of gold in iodine-iodide-acetonitrile systems. Chem Commun. doi:10.1039/cc9960000897

152. Nakao Y (1997) Three procedures of reversible dissolution/deposition of gold using halogen-containing organic systems. Chem Commun. doi:10.1039/a704171c

153. Nakao Y (1991) Dissolution of metals in halogen cetylpyridinium halide-benzene systems. J Chem Res S 228–229

154. Mortier T, Persoons A, Verbiest T (2005) Oxidation of solid gold in chloroform solutions of cetyltrimethylammonium bromide. Inorg Chem Commun 8:1075–1077. doi:10.1016/j.inoche.2005.08.015

155. Buchikhin E, Kuznetsov A, Chekmarev A, Lavrent'ev I (1999) Reaction of metallic palladium with iodine in dimethylformamide. Russ J Coord Chem 25:416–417

156. Lin W, Zhang R-W, Jang S-S et al (2010) "Organic aqua regia"-powerful liquids for dissolving noble metals. Angew Chem Int Ed 49:7929–7932. doi:10.1002/anie.201001244

157. Wei L (2012) Recovery of high-purity Pt from Pt-Au bimetallic nanoparticles using organic aqua regia. Rare Met 31:92–95. doi:10.1007/s12598-012-0469-8

158. Serpe A, Artizzu F, Mercuri ML et al (2008) Charge transfer complexes of dithioxamides with dihalogens as powerful reagents in the dissolution of noble metals. Coord Chem Rev 252:1200–1212. doi:10.1016/j.ccr.2008.01.024

159. Serpe A, Bigoli F, Cabras M et al (2005) Pd-Dissolution through a mild and effective one-step reaction and its application for Pd-recovery from spent catalytic converters. Chem Commun. doi:10.1039/b415799k

160. Bigoli F, Deplano P, Mercuri M (1998) A powerful new oxidation agent towards metallic gold powder: N,N'-dimethylperhydrodiazepine-2,3-dithione (D) bis(diiodine). Synthesis and X-ray structure of [AuDI$_2$]I$_3$. Chem Commun. doi:10.1039/a806158k

161. Serpe A, Marchio L, Artizzu F et al (2013) Effective one-step gold dissolution using environmentally friendly low-cost reagents. Chem Eur J 19:10111–10114. doi:10.1002/chem.201300940

162. Chekmarev AM, Buchikhin EP, Sidorov DS, Koshcheev AM (2007) Zirconium dissolution by low-temperature chlorination in dimethylformamide. Theor Found Chem Eng 41:752–754. doi:10.1134/S0040579507050521

163. Buchikhin EP, Kuznetsov AY, Vidanov VL, Shatalov VV (2006) Reaction of metallic uranium with NO$_2$ in TBP. Radiochemistry 48:459–461. doi:10.1134/S1066362206050080

164. Buchikhin EP, Kuznetsov AY, Vidanov VL et al (2005) Non-aqueous chlorination of uranium metal in tributyl phosphate. Radiochemistry 47:263–265. doi:10.1007/s11137-005-0084-8

165. Wellens S, Thijs B, Binnemans K (2013) How safe are protic ionic liquids? Explosion of pyrrolidinium nitrate. Green Chem 15:3484–3485. doi:10.1039/c3gc41328d

166. Gutmann V (1968) Coordination chemistry in non-aqueous solutions. Springer, Vienna