

Solvent extraction in the recovery of metals from solutions: entering the third decade of XXI century

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ABSTRACT

Since its first practical application in the mid-forties of XX century on the separation and purification of metals, solvent extraction had matured in this issue, being its usefulness demonstrated by the miriade of works published along the years, and by the number of solvent extraction plants built and into production around the world. Now in the XXI century, its application is moving around a theme, in connection with the above, and related to the recovery-separation-purification of metals from raw materials, as urban mining and the treatment of metal-bearing secondary materials and wastes are. Entering the third decade of XXI century, this work reviews the most advanced contributions in the use of solvent extraction science on metals recovery from a variety of sources, as demanded by the social, environmental and profitability conditions in which the world is living nowadays.

Keywords: Solvent extraction; Metals; Recovery; Urban mining; Extraction; Stripping

1. Introduction

It seemed clear that now, entering the third decade of the 21st century, the world is living very new situations, one derived for the COVID-19 pandemic, the other with the increase in the use of new technologies which demanded more and more utilization of, until recently, less used metals, and here comes in mind, for example, the development of new 5G communications, and the increased demand of e-cars, with the subsequent appearance of spent-electric car batteries, which needed of their recycle. In these cases, and in others, the recycling of end-of-life products or the treatment of secondary metallurgical wastes, is of a necessity for social, environment and profitability point of views.

Speaking in metals terms, the great demand of these products has increase the demand of for example, rare earths, niobium and tantalum, gold and precious metals, etc., thus their recycling helps to maintain a continuous surplus of these critical metals to the manufacturers, also considering

that the raw materials containing them are not always easily accessible due to various reasons.

In practical terms, these secondary products, or wastes, very often present a great complexity in terms of their metals composition, thus it is necessary to account with the suitable technologies to address their treatment; and here hydrometallurgical processing offered adequate flexibility to treat these complex materials. In the hydrometallurgical processing of these complex wastes, and after the corresponding pre-treatment of the material, this is leached in a convenient leaching medium, in order to put in solution the metals to be recovered, thus, a subsequent separation process is needed, and here solvent extraction, as a unit operation, is useful due to its operational characteristics: selectivity, concentration capacity, possibility of the treatment of great aqueous volumes and in a very short reaction time. Probably, the negative aspects of the technology are that (i) it needs to treat clarified aqueous solutions, in order to prevent mud formation, and (ii) it is not adequate to treat very dilute metal solutions.

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In solvent extraction or liquid–liquid extraction practice, the metal-bearing aqueous feed solution and the organic phase fed a mixer in which both phases are mixed (extraction step), and the metal of interest is transferred from the aqueous to the organic phase; after settling, the aqueous raffinate is properly treated or simply goes to waste, and the metal-loaded organic phase is sent to another mixer in which it is scrubbed with an adequate aqueous solution to remove undesirable metals or impurities co-extracted in the previous extraction step. After, the metal-loaded organic phase is subjected to a stripping step in which the metal is stripped from the organic phase by a suitable aqueous solution, producing a concentrated solution of the metal, which is finally processed for metal or metal compounds production. The stripped organic phase is recycled to another extraction step, but if necessary it is properly treated before feeding this new extraction step.

The use of this unit operation in the recovery of metals from various sources is recently reviewed in the literature, summarizing Table 1 some of these most recent reviews. In the present review, the authors pretended to show the most recent published additions to the solvent extraction literature (2020–2021 y) applied to the recovery of a number of critical metals from, also, a number of sources. To gain information about how the various types of extractants removed metals from solutions, the present authors referred to a previous publication [15].

2. Solvent extraction systems

2.1. Acidic extractants

This type of extractants, also named cationic ion exchangers, extract metals by a cation-exchange mechanism, in which hydrogen atoms of the extractant molecule are exchanged for metal ions. Including in this category are some chelating-type extractants (basically oximes, oxines and β -diketones derivatives), which together to this

cation-exchange mechanism, extract metals by donation, *via* a donor atom, of an electron pair to the metal, and forming bidentate complexes with these metal ions.

The processing of a zinc plant residue in acidic medium produced a solution from which cobalt and manganese needed to be separate [16]. Prior to this separation, iron was precipitated from the solution, and LIX 984 (mixture of 5-dodecylsalicylaldehyde and 2-hydroxy-5-nonylacetophenone oxime) or DEHPA extractants, diluted in kerosene, were used for separating Co(II) and Mn(II). LIX 984 favored cobalt extraction, though metal stripping becomes more difficult, necessitating the presence of HCl in the strip phase to remove the metal from the loaded phase. With DEHPA, the strip phase was of 10–150 g/L sulfuric acid, using and O/A (organic/aqueous) phases relationship of 3, ambient temperature and 20 min of contact between both phases. The use of LIX 984 necessitates 25–250 g/L sulfuric acid and 25–200 g/L of hydrochloric acid as strip phase, 40°C and 45 min. In the final flowsheet, DEHPA is the extractant used in Co/Mn separation.

Bonded NdFeB magnets were used as source material to recover rare earth elements (REEs) [17]. After the corresponding treatment, the resultant calcine contained REE hydroxides and iron oxide, being leached at 60°C or 90°C with 20% v/v versatic acid 10 (bis-hexyl carboxylic acid) diluted in an aliphatic diluent. By this procedure, more than 95% of the REEs were dissolved with less than 1% co-dissolution of iron and 10% co-dissolution of cobalt. Precipitation-stripping of the REEs with a 1 M oxalic acid solution regenerated the extractant, and precipitated the metals. After calcination of the metal-oxalate precipitate, a mixed rare earths oxide with 98.4% wt. purity was produced. A summary of the various steps involved in the process is shown in Table 2.

The economics of hydrometallurgical treatment of low-grade chalcopyrite deposit at Sarcheshmeh Mine (Iran) as a function of ore grade and extraction recovery were investigated [18]. Preliminary capital cost and operating cost

Table 1
Some recent reviews about the use of solvent extraction in the recovery of metals from solutions

Extractant	Source	Metal	References
D2EHPA, CYPHOS IL 101	Zinc plant purification residues	Co, Zn, Cd	[1]
Not specified	Secondary Zn residues	Zn	[2]
Acid, basic, solvation	Various	Rare earths	[3]
Solvation, amines	Ore deposits, secondary sources	Ta, Nb	[4]
Ionic liquids	Waste materials	Ag, Au, PGM	[5]
Oximes	Various	Cu and others	[6]
Mixture of amines and DEHPA	PUREX raffinate	Am	[7]
Organophosphorous extractants	Various	Various	[8]
Ionic liquids	Primary and secondary sources	Nd, Sm, Eu	[9]
Acid, chelating	Mining effluents	Various	[10]
Organophosphorous extractants	Various	Ce	[11]
Amines, solvation, ionic liquids	Secondary sources	PGM	[12]
Ionic liquids	Various	f-ions	[13]
Triocylammonium based ionic liquids	Various	Cu, Cd, Zn	[14]

DEHPA or D2EHPA: di(2-ethylhexyl)phosphoric acid; CYPHOS IL 101: trihexyl(tetradecyl)phosphonium chloride.

Table 2
Various steps involved in the treatment of PCBs from computers

Step	Operation	Objective
1	Separation	Separation of the non-metallic components and yield of a metal concentrate
2	Leaching	Yield of gold and precious metals concentrate and a solution containing less valuable metals
3	Solvent extraction	Use of TBP to regulate nitric acid concentration in the solution. Recycling of this acid to step 2
4	Precipitation	Recovery of silver
5	Solvent extraction	Recovery of copper
6	Cementation	Recovery of lead from the raffinate of step 5
7	Precipitation	Recovery of nickel from the solution exiting step 6

TBP: tributyl phosphate.

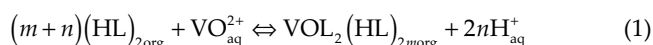
estimates were made within two options: (i) plant using a circuit of bio heap leaching of the copper ore, solvent extraction (SX) and electrowinning (EW), and (ii) that the current SX and EW facility can absorb the bio heap leaching solution; in (i) the operating cost was shown to be between US\$ 4.29/kg and US\$ 5.99/kg of copper cathode for extraction recoveries of 30% to 50%, if a construction of new SX and EW plants were required. In case (ii) the operating cost was shown to reduce from US\$ 5.36/kg to US\$ 3.66/kg, for a similar recovery range. The economic analysis showed that for an ore containing 0.28% copper, 7,000 tons/y of copper cathode production requires a total investment of 38 million US dollar. In option (i), the internal rate of return for such a plant was shown a change between -2% to 27% for copper extraction efficiencies between 30% to 50%. The sensitivity analysis of the similar plant showed that a copper selling price of US\$ 5/kg, can even make the 50% copper extraction efficiency economically unacceptable for this same option. Obviously, oximes were the extractants of choice for copper extraction, and sulfuric acid as strippant for the metal.

A pilot-scale investigation about processing a Chilean acid mine drainage by nanofiltration, to recover water, and the recovery of copper from the concentrated solution by a solvent extraction process was done [19]. 1 g/L copper solution of pH 3.5 was used in the solvent extraction investigation, being the organic phase composed of LIX 84-IC (2-hydroxy-5-nonylaceto-phenone oxime) dissolved in Escaid 110 (aliphatic diluent). The strip phase was of 30 g/L copper and 190 g/L sulfuric acid. Using two counter-current extraction stages (aqueous/organic volume phases relationship of 3.28) and one stripping stage (O/A of 5.71), 96% of copper can be recovered. The presence of calcium sulfate or antiscalant in the feed solution had a small effect on copper extraction.

In Zijinshan Mine (China), an integrated process was developed and applied to recover copper from low-grade copper sulfide ore and acid mine drainage (AMD) [20]. The process includes the main operations of milling-flotation, heap bio leaching, solvent extraction-electrowinning (HBL-SX-EW) and copper precipitation. There were two plants: (i) one which treated high copper-containing AMD from open pit and waste rock dump sites, having a composite of 1.0–1.8 g/L Cu, 4–6.5 g/L Fe and 4.5–6.5 g/L sulfuric acid, and (ii) a plant where the pregnant solution from heap bioleaching was processed, the solution was of 1–2 g/L Cu, 7–10 g/L

Fe and 7–10 g/L sulfuric acid. Each plant comprised two trains, being the capacity of each train of 600 m³/h of solution. The plants used a solution of 35–40 g/L Cu and 160 g/L sulfuric acid as strip phase, and the exiting phase to feed the electrowinning operation was of 40–50 g/L copper and 155–165 g/L sulfuric acid. Note: in the published manuscript there was not information about the extractant, and other conditions, used in the circuits. The authors of this review suggested that the extractant should be an oxime derivative.

The recovery of vanadium(IV) from acid leaching solution of spent oil hydrotreating catalyst, using bis-2-ethylhexyl phosphoric acid (P204) as an extractant, was proposed [21]. Using 20% v/v P204 in kerosene as organic phase, the single-stage maximum extraction rate of 93.5% for vanadium was obtained under the optimum extraction conditions of O/A ratio of 2, time of 8 min, temperature of 25°C and initial pH value of 2. After three stages of counter-current extraction operation the rate of vanadium extraction increased to 99.2%, with 1.0%, 2.9% and 1.9% co-extraction of iron, nickel and aluminium, respectively. It was proposed that the extraction of vanadium occurred *via* the next equilibrium:



where HL represented the extractant molecule, and m and n are two stoichiometric coefficients. 2 M sulfuric acid solution as strippant, and three stages at O/A ratio of 3 completely removed vanadium from the loaded organic phase. Note: the values of the m and n coefficients were not determined in the work. P204 was a commercial name given to DEHPA or D2EHPPA extractant.

USTB-1 extractant, (2-ethylhexyl)(2,4,4'-trimethylpentyl)phosphonic acid, dissolved in *n*-octane was investigated on the separation of cobalt from high Ni/Co ratio solutions from spent ternary cathodes leachates [22]. Its Co/Ni separation performance was superior to MEXTRAL 507P, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, and Cyanex 272 (bis(2,4,4'-trimethylpentyl)phosphonic acid). Its pH_{50} for cobalt and nickel had the values 5.4 and 7.3, respectively. At saponification ratio of 40%, the separation factor Co/Ni of USTB-1 reached 1.05×10^4 , while these of MEXTRAL 507P and Cyanex 272 were 187 and 2,697, respectively. USTB-1 had greater saturation capacity than Cyanex 272, as it loaded 99.3 mg/L of Co, while Cyanex 272 loaded 75.1 mg/L under the same conditions. Loaded

cobalt can be stripped by mineral acids, being sulfuric acid at pH 2 the most effective. USTB-1 extracted cobalt through cation exchange mechanism. Note: pH_{50} was the equilibrium pH value at which 50% metal extraction was attained.

Saponified-D2EHPA (Na-D2EHPA) diluted in kerosene, and in the presence of a modifier in the organic phase, was used in the treatment of Li_3PO_4 solutions [23]. In the extraction stage $LiR \cdot NaR$ was formed, whereas the addition of tributyl phosphate (TBP) to the organic phase resulted in the formation of $LiR \cdot NaR \cdot 0.1TBP$ species in this phase. The presence of tributyl phosphate enhanced lithium stripping, for example, using 6 M HCl as strippant 50.7% or 70.4% lithium stripping were achieved without or with the presence of TBP in the phase, respectively. Both, the formation of the saponified-DEHPA and the presence of TBP in the organic solution, promoted the rupture of the DEHPA dimer in this phase.

The next reference investigated the recovery of silver and palladium from multilayer ceramic capacitors (MLCCs) presented in waste printed circuit boards (PCBs) [24]. After the corresponding pre-treatment of the PCBs, a fine powder of MLCCs containing 0.14% Pd, 1.08% Ag, 1.76% Cu and 11.1% Ni was yielded. Firstly, nickel was selectively separated using two stages of leaching under 2 M HCl, temperature 75°C and pulp density 100 g/L. The resulting residue was washed, dried and leached in a 4 M nitric acid medium, 1 h of reaction at 80°C and the same pulp density than above; this operation resulted in 99.99% Ag and Pd recovery in the solution. From the solution, silver was recovered by precipitation with KCl, copper was extracted from the resulting solution using LIX 84IC at pH 2.2 and an O/A ratio of 1; non-extracted palladium was evaporated from the raffinate, to yield a pure salt. Copper stripping was performed using 10% sulfuric acid.

A process for the treatment of spent lithium-ion batteries was proposed using Versatic 10 acid dissolved in kerosene as organic phase [25]. After two stages of extraction, the first using 10% v/v of the extractant and pH 6.5, the second-stage with 40% v/v of versatic acid, 99.2%, 97.2% and 98.5% extraction rates resulted for nickel, manganese and cobalt, respectively. Since lithium was not extracted, it was recovered from the raffinate by precipitation with sodium carbonate.

A series of physical and hydrometallurgical operations including demagnetization, grinding, screening, leaching, precipitation and solvent extraction had been used to investigate the recovery of Nd and Dy from spent NdFeB magnets [26]. Various inorganic (HCl, HNO_3 , H_2SO_4 and aqua regia) and organic reagents (acetic acid and oxalic acid) were tested to dissolve the magnets. The recovery of Nd and Dy in the leaching solution was tested by eliminating the iron by a solution purification process involving precipitation of ferric iron in solution as hydroxide and solvent extraction with ionic liquids (ILs). The comparative studies demonstrated that the extraction efficiency of bis-2-ethylhexyl phosphoric acid (D2EHPA) was higher than trihexyltetradecylphosphonium chloride (CYPHOS IL 101) after the leaching stage. At pH 4.5 and 25°C, using 0.2 M extractant solutions, the percentages of the metals recovery were of 99% Nd and 80% Dy against near 70% each Nd and Dy for D2EHPA and CYPHOS IL 101, respectively. Note: there was not information about the stripping stage. Ionic liquids are chemicals

composed by a cation and an anion (organic or inorganic in whatever mixture) which are liquids below 100°C.

The recovery of nickel, cobalt, iron, zinc, and lanthanides from spent nickel-metal hydride batteries using formic acid as leachant was investigated [27]. The use of D2EHPA as extractant allowed to the near quantitative co-extraction of Fe(II) and Zn(II) from the leachate of pH near 1.5. Yttrium and lanthanides were precipitated as oxalates directly from the raffinate. Further, Mn(II) and Co(II) were extracted with D2EHPA at buffered pH 3 and near 5, respectively, however, about 10 wt.% of Ni(II) was co-extracted with cobalt. The remaining Ni(II) was precipitated, from the raffinate, at pH 6, and after raising the pH until 8, Al(III) was precipitated.

The solvent extraction of manganese from a solution based on lithium-ion batteries was modeled and optimized using D2EHPA as extractant and diluted in Isopar L [28]. Under optimized conditions of O/A ratio of 1.25, pH of 3.25, and an extractant concentration of 0.5 M in the organic phase, above 70% manganese extraction were reached in a single stage with a co-extraction of less than 5% cobalt, which was mostly removed in two scrubbing stages. A stripping product containing near 23 g/L Mn and 0.3 g/L Co can be yielded under optimized conditions of O/A ratio of 8, 1 M sulfuric acid solution as stripping phase, and around 13 min of contact time in one stripping stage.

A procedure to recover metal values from Sm_2Co_{17} -type magnet scrap was investigated [29]. In HCl- H_2O_2 medium, the recovery rates from the solid were 98.5% in the case of samarium and 99% for cobalt. Samarium was selectively separated from the leach liquor as a precipitated double salt using sodium sulfate. Following this first separation, iron was removed through precipitation by raising the aqueous pH to 3.0. For copper and cobalt recovery, LIX 84I (active group as LIX 84IC) dissolved in kerosene and Na-Cyanex 272 (saponified Cyanex 272), also dissolved in kerosene, were respectively used. In the case of copper, the extraction step, using a 10% v/v LIX 84I solution, comprised two stages at O/A ratio of 1 and pH 3.5, the stripping operation using 10% sulfuric acid, needed also two stages with O/A ratio of 2. In the case of cobalt, organic phases of Na-Cyanex 272 containing 5% v/v TBP were found to be more suitable for the metal recovery. With Cyanex 272 saponified at 70%, and under an extraction operation comprised one stage at pH 4 and O/A ratio of 1, 99.94% cobalt was extracted from the feed solution. The strip operation needed two stages at A/O ratio of 2, and 1% sulfuric acid as strippant. Under these conditions, 99.7% of cobalt stripping was achieved, resulting in a solution of 4.67 g/L cobalt.

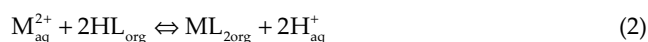
An investigation aimed to recover Ag and generation of a concentrate of precious metals (Au, Pd and Pt) from waste ICs present in PCBs of computers were carried out [30]. The concentrate yielded after the pre-treatment contained (per ton): 7 kg Ag, 5 kg Au, 110 g Pd and 4 g Pt along with Cu, Pb, Fe and Ni. Leaching of this solid was carried out in 3 M nitric acid medium at 80°C, pulp density of 50 g/L and 1 h of reaction time; this operation allowed to the recovery of more than 90% of Ag, Cu, Pb and Ni while Au, Pt and Pd remained in the residue. Solvent extraction was used to remove the acid content from the leach liquor, acid stripping from the loaded organic phase used water. From the raffinate of the previous operation, Ag was precipitated using 1 M KCl,

and copper was extracted with a 30% v/v LIX 84IC (oxime derivative) solution, at pH 2, 15 min and O/A ratio of 1. Other metals were recovered by cementation and precipitation.

A process had been reported to recover copper from waste printed circuit boards (WPCBs) using glycine solutions [31]. This option is positioned after the bulk of the aluminium, copper and iron was removed using conventional dry physical processes, but before the hydrometallurgical recovery of precious metals. Copper was recovered *via* three options: (i) hydrazine reduction, (ii) sulfide precipitation, and (iii) solvent extraction. It was found that in option (iv), Mextral 84H (active group as LIX 84IC) showed better performance than Mextral 54-100 (1-benzoyl-2-nonyl ketone) but requires more concentrated sulfuric acid solutions in the stripping stage. The ketoxime also showed greater selectivity than Mextral 54-100 with no zinc, aluminium and nickel co-extractions detected. Overall copper recoveries of 91.6% using 15% v/v Mextral 84H in kerosene followed by 200 g/L sulfuric acid stripping, and 86.7% using 30% v/v Mextral 54-100, also in kerosene, followed by 80 g/L H₂SO₄ stripping were found.

A hydrometallurgical process was developed in order to recover titanium from red mud [32]. The steps comprised in the process included: (i) leaching with 12 M hydrochloric acid, (ii) ammonia precipitation until pH 2.2, and (iii) purification by solvent extraction with 0.1 M Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid) diluted in limonene, in a O/A ratio of 1. In step (i) both iron and titanium were recovered as a precipitate, which was redissolved in step (ii), this solution was treated by the organic phase of Cyanex 301 (step iii), which extracted both metals, then the metal loaded organic phase was stripped with a 3% H₂O₂ + 0.5 M sulfuric acid mixture, which strip titanium, complete metal stripping can be obtained after two stages and O/A of 2, while 95% of the extracted iron remained in the organic phase. Recovery of titanium with a purity level exceeding 95% was found. Moreover, red mud adsorption properties were also tested for metal removal from aqueous solutions. Note: this reference contained two faults: (i) in the abstract section, it was mentioned that the diluent for the organic phase was toluene, then along the text, limonene was the used diluent and (ii) it was not mentioned in the manuscript how iron was stripped from the organic phase.

Discarded lithium-ion batteries were used as a source to the recovery of lithium, cobalt and manganese [33]. After a leaching operation, a solution containing 1.4 g/L Cu, 1.1 g/L Ni, 11.9 g/L Co, 6.9 g/L Mn and 1.2 g/L Li was rendered. Firstly, copper and nickel, were separated by solvent extraction using an organic phase of 10% v/v LIX 84-IC in kerosene and isodecanol, at equilibrium pH values of 3 and 4.6, respectively. The extraction equilibrium was represented by:



where M was copper or nickel, and HL represented the LIX 84-IC molecule. The extraction of both metals occurred *via* a cation exchange mechanism. Further, cobalt was precipitated, from the raffinate, at pH values in the 2.9–3.1 range, using undiluted ammonium sulfide solution. Manganese

was then recovered by 10% v/v D2EHPA at equilibrium pH 4.5, remaining lithium in the raffinate, manganese was stripped from the organic solution with sulfuric acid.

Cathode material from spent lithium-ion batteries (LIBs) was used to recover valuable metals contained in them [34]. By the use of 3 M HCl medium as leaching solution, the recovery of the metals from the solid material exceeding 99%. Bis(2-ethylhexyl)phosphinic acid (P227) extractant, diluted in *n*-heptane, and saponified to the NH₄⁺ form by contact with 5 M NH₃·H₂O solution, was used to co-extract transition metals directly from the leachate and separate them from lithium. The loaded organic phase with a Ni–Co–Mn ratio of 1:1:1 was completely stripping in 0.4 M HCl medium, and precipitated with oxalic acid to give Ni_{0.33}Co_{0.33}Mn_{0.33}C₂O₄, which with lithium addition and calcination was transformed to the oxide LiNi_{0.33}Co_{0.33}Mn_{0.33}O₂.

Molten pyridine hydrochloride (165°C) was used to dissolve production scrap of Nd–Fe–B permanent magnets to recover neodymium and dysprosium [35]. After the leaching step, solvent extraction was performed at high temperature (165°C) by using PC-88A (acidic extractant) or CYPHOS IL 101 (ionic liquid). PC-88A was selected due to it presented the greatest separation factors rare earths/iron (about 2410), the extractant was dissolved in *p*-cymene due to the high boiling point (177°C) which this diluent presented. In the first stage, 30% v/v PC-88A in *p*-cymene was used to extract dysprosium(III) and some neodymium(III), whereas in the second-stage undiluted PC-88A was used to extract most of neodymium(III). This element was recovered from the organic solutions by precipitation with 0.2 M oxalic acid and 10 min of reaction at room temperature, whereas the recovery of dysprosium, from the loaded organic phase from the first stage, it was not as clear since in the same conditions than above, this metal did not precipitate. A solution of 70% wt./wt. CYPHOS IL 101 in *p*-cymene was shown to efficiently extract iron(II,III) from the raffinate derived from the precious step, and the same time the leaching reagent (pyridine hydrochloride) was regenerated. Iron(II,III) was recovered from the organic phase by stripping-precipitation with a 5% ammonia solution. Note: there was not mention in the work about the real conditions for dysprosium recovery from the organic phase.

The use of Cyanex 272 and Ionquest 801 extractants diluted in ShellSol D70, and their mixtures on the extraction and separation of zinc, cobalt and nickel was investigated [36]. Both reagents performed equally in the separation Zn/Co, whereas in the system Co/Ni, Cyanex 272 performed better than Inquest 801, despite the fact Co/Ni separation factor as high as 4000 was yielded with the latter. Slope analysis determined that in the case of zinc and cobalt, the extracted complex presented a molar relationship of 1(metal):2(extractant dimer), in the case of nickel this ratio changed to 1(nickel):3(extractant dimer). The use of mixtures of both extractants presented not a clear advantage on the extraction of the three metals with respect to the results obtained with the single use of each extractant. Note: no data about the stripping stage were included in the work.

An empirical equation, such as the Alstad equation:

$$\log y^* = -AC(H_2L_2)^{1/2} \quad (3)$$

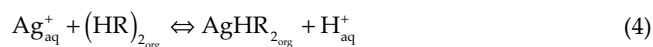
was used to elucidate the equilibrium constants in the extraction of trivalent rare earths (La, Ce, Pr, Nd, Sm, Eu, Dy and Y) with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHEHPA) [37]. In this equation, A was a coefficient that depended on the extractant, diluent and temperature, y^* represented to a coefficient for the effective concentration of the extractant, and y^* was the nominal dimer concentration of the extractant (represented by H_2L_2). The conditions used in the calculations included the dissolution of EHEHPA in a non-polar diluent, as ShellSol D70, and nitrate medium in the REEs solution, this phase presented also a constant ionic strength of 1 M, being the temperature of 25°C, also extractant dimeric concentrations 0.04–0.33 M were considered, whereas the calculations were carried out over a range of pH values. Apparent extraction equilibrium constants that reproduced the distribution ratios of the REEs with good accuracy were obtained. Further experiments at higher extractant concentrations revealed that the empirical equation was effective up to an EHEHPA dimer concentration of 0.5 M, which is significantly higher than the upper limit for the conventional dimer model. Separation factors were calculated, from the extraction equilibrium constants, for the possible pairs of REEs. Differences in the separation factors depended on the measurement conditions and were most pronounced when the difference in atomic numbers of the REEs was large, for example, for the pair Ce/Pr the value was 1.14, whereas for the pair La/Y the value was as high as 11000. Note: no mention about the stripping stage.

A hydrometallurgical route for the recovery of copper and gold from waste printed circuit boards of mobile phones was described [38]. The process comprised several steps: (i) the liberation of the metallic fractions from downsized boards, (ii) a two-stage acid leaching process to provide the separation of copper and gold from the other metals presented in the solid material, and (iii) purification of the copper and gold-bearing solutions by solvent extraction using an oxime and an amide extractants, respectively. In the first leaching step, complete dissolution of the base metals was yielded using 3 M nitric acid at 30°C, being copper selectively separate from this leach liquor by the use of ACORGA M5640 (salicylaldehyde) dissolved in kerosene. The residue from this first step, were treated with a mixture of 3 M sulfuric acid, 3 M sodium bromide and NaCl at the temperature of 70°C, resulting in the recovery of more than 95% gold. The selective separation of gold from this solution was possible by solvent extraction using 0.1 M tertiary amide extractant dissolved in toluene. Gold stripping was best accomplished with 1 M NaOH solution (quantitative stripping) than with 0.1 M NaOH solution (83% gold stripped).

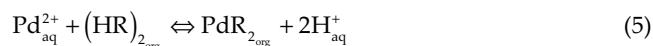
Solvent extraction operation was used in the treatment of fly ash from municipal solid waste incineration [39]. The leaching of this waste produced a solution containing zinc, cadmium and copper. Zinc was recovered by solvent extraction using Cyanex 572 (mixture of phosphinic acids) dissolved in kerosene as organic phase, and stripped from the loaded organic phase with 3 M HCl solution. Cadmium and copper were removed from the raffinate using an adsorption process by a self-assembled hierarchical hydroxyapatite (HAP) nanostructure. The solvent extraction operation allowed to a recovery rate of 91% for Zn.

Taking as a basis a vanadium slag, and further to the recovery of Cr(VI) with an amide, vanadium(V) was recovered from the raffinate using solvent extraction [40]. Extraction of this element (20.3 g/L V) from sulfate acid medium was investigated comparing the performances of D2EHPA, EHEHPA and Cyanex 272. The results demonstrated that over a 0.5–1 M range of extractants concentrations diluted in kerosene, EHEHPA (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) and Cyanex 272 were the most suitable extractants to remove vanadium from the raffinate and 99.91% vanadium could be recovered with three-stage counter-current extraction. In the case of EHEHPA and Cyanex 272, the extraction was represented by the formation of $VO_2A(HA)$ species in the organic phase, whereas in the case of DEHPA, the species formed in the organic phase had the VO_2A stoichiometry, this means that DEHPA acted as a monomer (HA), and the other two as dimers (H_2A_2). In all the cases, the extraction of VO_2^+ species into the organic phase was accompanied by the release of one proton to the raffinate. After a scrubbing step with water, vanadium stripping was accomplished with ammonium hydroxide, releasing $HV_{10}O_{28}^{5-}$ to the strip solution and formation of $NH_4A(HA)$ species in the organic phase; thus. A regeneration step with sulfuric acid was needed in order to form the acidic form of the extractant (H_2A_2), and ammonium sulfate was formed in the regeneration process. Finally, V_2O_5 product with 99.97% purity was obtained. Note: against it was written in the title of the published manuscript, the extraction of Cr(VI) was not described in the as-published article.

The recovery of spent Ag–Pd/ α - Al_2O_3 catalysts, using in the naptha-cracking process with controlled CO_2 emission, had been investigated [41]. The recovery process included a solvo-chemical recycling approach that involving the solid–liquid and liquid–liquid mass transfer phenomena. Leaching parameters was established as: 2 M HCl, 20% w/v pulp density, 90°C temperature and reaction time of 1 h. The leachate was treated for silver/palladium separation by liquid–liquid extraction with 0.15 M LIX 84-I in kerosene solution. Silver was first extracted at 2 M HCl and A/O ratio of 2.5, accordingly with the next equilibrium:



whereas palladium was next extracted at pH 2.5 and the same A/O ratio than above, the extraction equilibrium can be represented as:



Silver and palladium were stripped with 0.5 M thiourea solution and O/A ratio of 2. In the process, silver concentration increased from 15 mg/L (leach solution) to 75 mg/L (stripped solution), and palladium concentration increased from 38 mg/L (leach solution) to 186 mg/L (stripped phase).

Used NdFeB magnets were used as a source to the recovery of dysprosium and neodymium [42]. The liquid–liquid extraction step used D2EHPA, as extractant, in a two-stage process. Firstly, near 95% of dysprosium was extracted at pH 2, and 0.05 M D2EHPA, in the second-stage, Nd was

extracted at pH 4 with 0.2 M D2EHPA. Both metals can be recovered from the respective metal-loaded organic phases by acid stripping.

An approach on the liquid–liquid extraction equilibrium in metal ion extraction processes under industrial conditions and high metal ion loadings was described [43]. At the above conditions, the extractant was completely loaded (non-unreacted extractant here), and extraction curves deviate significantly from those obtained under single ion extraction. Using as an example, the extraction of Co^{2+} , Mg^{2+} and Mn^{2+} with Cyanex 272, it was shown that in the case of organic phases with an 80% excess of the extractant with respect metals concentration, the model was in accordance with the formation of MR_2 species in the organic phase.

Bis(2-ethylhexyl) dithiophosphoric acid (D2EHDTPA), diluted in dodecane, was used in the extraction and recovery of silver and gold from the acidic thiourea leachate of an ore [44]. Both metals were co-extracted according with the next general equilibrium:



with $\log K_{\text{ext}}$ of 126 and 216 for silver and gold, respectively. The metals were separated by selective stripping using 1 M thiocyanate and 0.5 M sulfuric acid in the case of silver, and after, 1 M ammonium thiosulfate for gold. In a second-step, $(\text{NH}_4)_2\text{S}_2\text{O}_3$ solution was used to recover gold. A model was developed to predict the influence of the experimental variables on the extraction and separation of these precious metals.

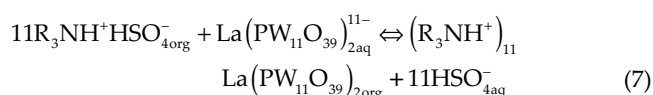
2.2. Basic extractants

Including in this type of reagents are primary, secondary and tertiary amines as well as quaternary ammonium salts. All the above compounds extracted metals which formed anionic species in the aqueous solution, thus, these basic extractants are anion ion exchangers. To extract these metal-anionic species, the primary, secondary and tertiary amines are first converted to the appropriate amine salt, which provided the anion to be exchanged with the metals species. Due to their chemical structure these basic extractants can be also considered as ionic liquids.

Leach solutions of vanadium slag was generated from ammonium sulfate roasting and water leaching process [45]. After separating titanium from the solutions, the remaining solution contained vanadium and iron. Thus, solvent extraction with trioctylamine (N235) dissolved in sulfonated kerosene was used to separate vanadium. The results indicated that in a single-stage, vanadium recovery was 86% using an organic phase of 40% v/v amine in kerosene, other variables were: initial pH of 1.23, O/A phase ratio of 1.5/1, temperature of 25°C, and an equilibrium time of 1 min. McCabe-Thiele analysis showed that over 99% of vanadium was extracted by three-stage counter-current extraction. The complex formed in the organic phase presented the next formulation $(\text{R}_3\text{NH})_4 \cdot \text{H}_2\text{V}_{10}\text{O}_{28}$. Using 1.4 M of ammonia-water, over 90% of the extracted vanadium can be stripped. The presence in the solution of impurities, such as Si, Ca, Al, Mg, and Mn on vanadium separation was negligible.

Note: against it was described in the published manuscript, the extractant was not the free N235 amine, but the cationic form of the reagent: R_3NH^+ , thus, the extractant was an ionic liquid, and the extraction of vanadium responded to an anionic exchange reaction; thus, this reference also can be part of the ionic liquids subsection of this chapter.

Scheelite mineral presented in its composition tungstate together with amounts of rare-earth metals, the leaching of this mineral with a sulfuric-phosphoric acids mixture allowed to the dissolution of all the above elements [46]. In this context, and aiming to the recovery of all these elements, a solvent extraction process was developed. First, tungsten and lanthanum were extracted from the leaching liquor using a tertiary amine (N235) dissolved in kerosene and in the presence of iso-octanol in the organic phase. This operation resulted in that 99.8% of W and 99.5% of La were extracted, using an organic phase containing 10% v/v of the amine and 10% v/v of iso-octanol in the aliphatic diluent, O/A ratio of 1:1, pH of 2.6, temperature of 30°C, and equilibrium time of 10 min. In this operation, the amine was first converted to the bisulfate salt ($\text{R}_3\text{NH}^+\text{HSO}_4^-$), by reaction of the amine with sulfuric acid, then the metal extraction proceeded as maximum lanthanum and tungsten extraction was reached after 10 min of equilibration time.



The former element was selectively stripped with 1.5 M sulfuric acid solution, at O/A ratio of 1, 10 min of contact between both phases, and 45°C. Tungsten was recovered from the W-loaded organic phase with 1.5 M ammonia-in-water solution, at O/A of 1, 10 min of equilibration and also 45°C. Note: as it can be concluded, the active extractant was again an amine salt (ionic liquid) and the previous comments also applied here.

The xenotime concentrate from the Yen Phu mine (Vietnam) were leached [47], and the recovery of uranium and thorium was investigated using the primary (N1923) and tertiary (tri-*n*-octylamine) amines dissolved in isoparaffin (IP-2028) and in the presence of *n*-decanol, acting as a modifier, in the organic phase. Experiments showed that 0.1 M primary amine organic phase extracted thorium, and 0.015 M tertiary amine phase extracted uranium, thus it was decided to use a mixture of both amines to co-extract uranium and thorium from the leaching solution. This solution was treated in a continuous counter-current extraction–scrubbing–stripping system, in order to separate both elements from accompanying metals (rare earths and iron). The basics of the investigated process were summarized in Table 3.

Trioctylamine was used to investigate its possibilities in the extraction of niobium and tantalum [48]. Prior to the extraction step, the organic phase (amine-dodecane and isodecanol) was pre-equilibrated with HF solution, which ensured that there was not interaction between the acid and the amine during the metals extraction process. Further, the aqueous solution containing both metals was treated with an organic phase of 25% amine in dodecane and isodecanol, and O/A ratio of 6 to co-extract both elements in

a single stage. Then, niobium was selectively stripped at O/A ratio of 3 with 1 M nitric acid solution, followed by a second-strip operation in which tantalum was removed from the organic phase using 10 M nitric acid as strippant. The strip operations yielded a solution of 41.8 g/L Nb and 0.92 g/L Ta, in the first stripping step, and 19.9 g/L Ta and 0.2 g/L Nb in the second-step. The key parameter to determine the niobium purity in the strip solution was the tertiary amine concentration in the organic phase (contribution 49.85%), followed by O/A ratio used in the stripping stage (contribution 47.20%). 98.88% pure niobium and tantalum of 98.08% purity were yielded from the whole operation.

A mixed process of jarosite crystallization and solvent extraction with the primary amine 7101 was used to separate iron and vanadium from titanium white waste liquid [49]. More than 97% of iron was precipitated under the best operational conditions, being vanadium best extracted by the amine in comparison of P204, Cyanex 272 and N235 extractants, whereas the extraction efficiency of vanadium reached 88.6%, with 10% Fe and, 5% Al(III) co-extraction, at pH of 2.0, and contact time of 4 min. The extraction of metals followed the order $V(V) > Fe(III) > Al(III) > Mg(II) > K(I)$. Vanadium was extracted into the amine-organic phase in the form of $H_2V_{10}O_{28}^{4-}$ polyanion, under an anion exchange mechanism. Sec-octyl alcohol was added to the amine-kerosene organic phase to improve both vanadium extraction and phases separation. Stripping with 100 g/L ammonium carbonate solution formed $(NH_4)_6V_{10}O_{28}$ solid, which was transformed to V_2O_5 . Four stages extraction and three stages of stripping were simulated by McCabe–Thiele diagrams.

2.3. Solvating extractants

The ability to extract metals are based on the solvation of neutral metal species by electron donor groups present in the extractant, thus, due to this solvation, the solubility of the metal species in the organic phase is increased.

Being palladium a component of multi-layer ceramic capacitors printed circuits boards, the recovery of this precious metal from waste boards was of interest [50]. After de-soldering, the material was dissolved in 3 M nitric acid, and a solution containing palladium and copper and iron, was obtained. This solution was processed using solvent extraction operation, being N,N' -dimethyl- N,N' -dibutyltetradecylmalonamide (BDMA) the extractant to be

used, the reagent was dissolved in toluene. With a 0.6 M extractant solution, the maximum separation factor Pd/Fe value of 2500 was achieved at 1.2 M nitric acid; however, the presence of 1 M chloride in the solution, dramatically decreased the palladium distribution coefficient from 27 to 0.06, making the solvent extraction process unusable. The co-extracted iron was scrubbed with water at O/A ratio of 5, but 7% of palladium was also lost; finally a palladium solution with 99.4% palladium purity was yielded after the stripping operation. This operation was carried out with 0.5 M sodium chloride solution at O/A of 10. From this solution, palladium was recovered as dichlorodiamine palladium(II) salt after precipitation with ammonia.

Lithium was recovered from simulated salt lake brines with high Mg/Li ratio using tributyl phosphate, $FeCl_3$ and diethyl succinate as extractant, co-extraction agent and diluent, respectively [51]. The use of TBP concentrations between 30–50% v/v, and molar ratios Fe^{3+}/Li^+ of 1.3, resulted in the highest one-stage extraction efficiency (65%) of lithium and decreased the co-extraction of accompanying metals (Mg(II), Al(III) and K(I)). Mixtures of HCl and $MgCl_2$, or HCl and NaCl were used to scrub the co-extracted metals and to strip lithium, respectively. $Mg(OH)_2$ and $MgCO_3$ were used as regeneration agents of the organic phase.

Thiophosphate- and phosphate-based extractants, 1,3-bis(diethoxythiophosphinoyloxy)benzene (Ext 1) and 1,3-bis(diethoxyphosphinoyloxy)benzene (Ext 2), respectively, were synthesized and investigated in the extraction of palladium(II) from HCl and HNO_3 media [52]. From single palladium-bearing solutions, Ext 1 (0.1 M) in 1-octanol selectively extracted 90%–99.9% Pd(II) in HCl (0.1–8 M) and 99.8% Pd(II) in HNO_3 (0.1–8 M). The variation of the A/O relationship had an influence on palladium extraction (Table 4), decreasing the extraction efficiency as the A/O ratio increased. Palladium was extracted (99%), and selectively, from a mixture of palladium, platinum, rhodium, rare earth metals, base metal ions, in 0.1 M chloride leach liquor obtained from automotive catalysts. Stripping of Pd(II) was performed using a solution of 0.1 M thiourea and 1 M HCl. Ext 2 reagent did not extract this precious metal from any of the acidic media.

The extraction of nitric acid, trivalent actinides and lanthanides with N,N,N',N' -tetra-*n*-octyl-3-oxapentanediamide (TODGA) dissolved in the aromatic diluents 1,4-diisopropylbenzene and tert-butylbenzene was investigated [53]. Nitric acid extraction proceeded with the formation of 1:1 and 2:1 HNO_3 -TODGA compounds. An(III) and Ln(III) distribution ratios were near an order of magnitude lower

Table 3
Steps in the treatment of xenotime concentrate from Yen Phu mine

Step	Objective	Results
1	Extraction of U and Th	A loaded organic phase with 2.9 g/L Th, 0.68 g/L U, 1.6 g/L REs, 0.4 g/L Fe
2	Scrubbing	A loaded organic phase without REs and Fe
3	Stripping	99% Th and U recovery

Organic phase: 0.1 M N1923 and 0.015 M TOA solution; feed phase: 0.17 g/L Th, 0.04 g/L U, 18.4 g/L REs, 1.6 g/L Fe, 32 g/L sulfate at pH 1.5.

Table 4
Influence of the A/O ratio in palladium extraction

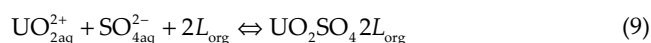
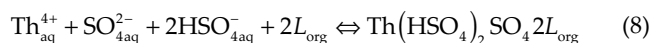
A/O	% Palladium extraction
1	99
2	80
3	60
4	40
5	20

Feed phase: 1 mM Pd in 0.1 M HCl; extractant: 0.1 M; time: 1 h.

in aromatic diluents compared to aliphatic diluents. The formed compounds in the organic phase presented 1:3 and 1:4 M(III):TODGA stoichiometries. Using TRLFS, the formation of a previously unknown 1:2 complex in organic phases loaded with Ln(III) was observed for the first time. In all the cases, the distribution ratios decreased with increasing temperature (10°C–50°C), indicating exothermic reactions. Note: the investigation did not include stripping studies.

An organic solution of 50% v/v tributyl phosphate and 20% v/v 2-octanol in kerosene was used to extract Fe(III), Ni(II) and Co(II) from a Ni(II)–Co(II) chloride solution [54]. Iron(III) extraction increased with the acidity and the chloride concentrations, for example, in 5.34 M chloride concentration and 4 M H⁺ concentration the extraction rate was greater than 99%, whereas with the same chloride concentration but 0.1 M H⁺ concentration the extraction decreased to near 55%. Nickel (II) was not extracted, and cobalt extraction was lower than that of iron(III). The iron complexes formed by TBP and 2-octanol were H₂FeCl₄·2TBP and H₂FeCl₄·5(2-octanol), and the possible compositions of Co-containing extracts were H₂CoCl₄·2TBP and H₂CoCl₄·n(2-octanol). Stripping was accomplished with water at O/A ratio of 2. An industrial waste of 26.1 g/L Fe and 57.1 g/L Co were treated in two-steps extraction operation. The results from the test indicated that 99.6% iron was extracted against less than 1.5% in the case of cobalt.

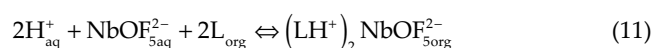
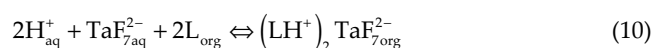
The removal of thorium and uranium from the leach solution of ion-adsorption rare earth ores by aluminum sulfate using di(2-ethylhexyl) [N-(2-ethylhexyl)aminomethyl] phosphonate (Cextrant 230) diluted in heptane was investigated [55]. The extraction of both metals occurred *via* a solvation mechanism, represented by the next equilibria:



where *L* represented the extractant molecule, and aq and org to the respective aqueous and organic phases. Uranium and thorium reached the extraction equilibrium (100% extraction) in 1 min of contact between the feed and the organic phases, whereas in the case of aluminium, lanthanum and terbium, near 5% of the metals was extracted in the same time. Also, the separation factors Th/metal and U/metal were maximized at 0.22 M HCl in the feed solution, decreasing as the acidity increased up to 3.23 M. However, the separation factors Th/REs, U/REs again increased at this 3.23 M acidic concentration. Both elements can be stripped together using 2 M HCl, or in selective form by 1 M nitric acid for uranium, and 2 M HCl for thorium. The recovery of the metals from the strip solution resulted in the formation of UO₂(NO₃)₂ or ThCl₄ compounds. By just one stage extraction, the concentrations of thorium and uranium in the simulated leaching solution decreased from 2.73 and 0.82 mg/L to less than 0.1 mg/L.

The raw ore from Penouta Mines in the North of Spain, rich in cassiterite, also contained columbo-tantalite, and was submitted to a pyrometallurgical process to separate tin, being columbo-tantalite concentrated in the resulting slags

[56]. This slag had been treated by acid leaching, using HF/H₂SO₄ mixtures, and the resulting liquor was treated by solvent extraction with Cyanex 923 (phosphine oxides mixture) dissolved in Solvesso 100 (aromatic diluent). Niobium and tantalum were co-extracted in the organic phase, and then they were separated by selective stripping. Metals loading onto the organic phase occurred *via* ion pair extraction equilibria:



The selective stripping comprised firstly, the niobium stripping with a 0.3 M NH₄F and 0.1 M aqueous ammonia solution, and secondly, tantalum stripping with 1 M NH₄F and 0.4 M aqueous ammonia solution. In both cases, the temperature was of 25°C, the O/A ratio of 1, and the equilibration time of 5 min. From the stripped solution, the metals compounds were precipitated and calcined, yielding Nb₂O₅·*n*H₂O of 98.5% purity and K₆Ta_{10.8}O₃₀ of 97.3% purity.

Scandium concentrate, generated from titanium white waste acid in sulfuric medium, was recovered by solvent extraction with trialkyl phosphine oxide (TRPO) dissolved in kerosene [57]. The results showed that the optimum extraction conditions for the recovery of the element from scandium sulfate solutions were: 10% TRPO, 5 M H₂SO₄, and A/O ratio of 1, being the contact time of 20 min. The extracted complex presented HSc(SO₄)₂·2TRPO stoichiometry. In the extraction of scandium from the leaching solution of its concentrate from titanium white waste acid, an extraction rate of up to 95.5% was obtained using the conditions of 20% TRPO, 7 M H₂SO₄, 0.5% H₂O₂, and A/O ratio of 10. Stripping with 0.4 M oxalic acid at A/O of 1 resulted in a rate of 99.9%. Calcination of Sc₂(C₂O₄)₃ at 1000°C for 2 h, produced of Sc₂O₃ with a purity of over 99.34%.

This investigation used an amide as extractant in the recovery of chromium(VI) from aqueous solutions [58]. Comparing nine amides with different alkyl groups and six diluents with different polarity, 40% v/v C₁₄H₂₉NO dissolved in Exxsol D80 were found to be the most favorable organic solution to extract chromium(VI). Results demonstrated that Cr(VI) extraction decreased with pH increases, become negligible at pH values greater than 1.26, also the increase of the temperature (20°C–70°C) decreased the extraction. Against the above, in the stripping operation, the increase of the temperature increased the rate of chromium(VI) removal from the loaded organic phase. Stripping was accomplished with water at O/A of 2. The results also demonstrated that 99.67% chromium can be extracted after six-stage counter-current extraction, being impurities, such as Na, V, Al and Mg, removed from the organic phase after three-stage cross-current scrubbing, 95.72% chromium was stripped after six-stage counter-current stripping. Since some chromium(VI) remained un-stripped, the organic phase was subjected to a contact with 1 M NaOH (O/A ratio of 20 and two stages) to remove the residual element and to completely regeneration of the extractant. The Cr₂O₃ product with 99.01% purity

was obtained and total chromium recovery from the chromium(VI) waste solution was 95.40%. Chromic and dichromate acid were extracted by forming neutral and ion association complexation with the extractant, respectively.

Coal and coal by-product were utilized as a non-traditional feedstock for rare earth production, thus a synthetic solution was prepared following the elemental composition of a strip solution generated from coarse coal refuse and used to investigate the recovery of rare earths [59]. Thus, a feeding solution containing Th, U, REEs at pH 0 were treated following the sequence shown in Fig. 1. In the first step uranium was extracted using a 5% v/v TBP in kerosene phase at an O/A ratio of 1, and raising the pH value of the feed solution to 2.5, then, the U-loaded organic phase was scrubbed, to eliminate undesirable co-extracted impurities, with 2 M nitric acid solution, and the treated organic phase was finally stripped, to recover uranium, with also 2 M nitric acid solution, but now at an O/A ratio of 2. The raffinate from the uranium- extraction step, was extracted with 40% v/v TBP in kerosene phase at an O/A ratio of 2, and the Th-loaded organic phase was stripped with water to yield a thorium solution from which the metal can be recovered.

A modified processing incorporating one-stage selective precipitation and two-stages of solvent extraction was investigated to enhance thorium and uranium recovery. The feeding was the same than mentioned above, and the steps were:

- (i) thorium precipitation at pH 2,
- (ii) uranium extraction with 50% v/v TBP in kerosene, O/A of 3 and pH 3.5,
- (iii) uranium extraction using the raffinate from step (ii), and the same conditions that in (ii),
- (iv) uranium stripping, using the organic phases from (ii) and (iii) and water as strippant at O/A of 2,
- (v) uranium stripping of the organic phase from (iv), using water at O/A of 2.

Precipitation was effective for the removal of thorium, while solvent extraction preferentially separated uranium from rare earths.

Boron removal from lithium-rich brine was investigated by solvent extraction using 2,2,4-trimethyl-1,3-pentandiol

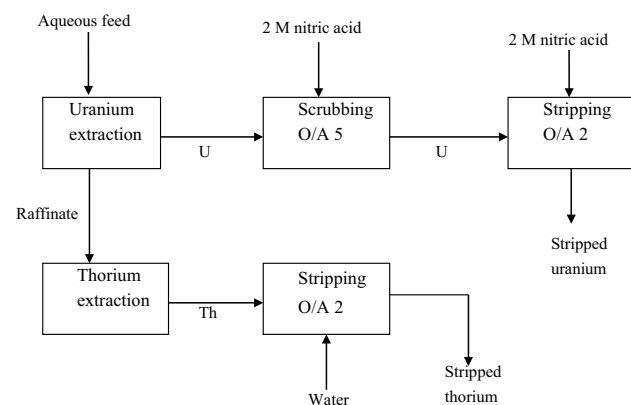


Fig. 1. Separation uranium and thorium *via* solvent extraction with TBP.

(TMPD) dissolved in 2-ethylhexanol and sulfonated kerosene [60]. During the extraction, a single TMPD molecule reacted with a single boric acid molecule to form a complex with two C–O–B ester bonds. The overall extraction efficiency reached 99.95% using a two-stage counter-current extraction. 0.2 M NaOH solution with an A/O ratio of 2 was used to strip the loaded organic phase, resulting in a 99.99% stripping efficiency.

The mineralogical studies on Black Mica raw material revealed the presence of notable high radioactive minerals such as uranium minerals (soddyite, uranophane, uranothorite, and ishkawaite), niobium-tantalum minerals (columbite and plumbopyrochlore), and rare earth elements minerals (allanite, xenotime, and monazite) [61]. Black mica sample was found to contain 1.68 g/kg U, 5 g/kg REEs, and 0.05 g/kg Nb while Ta not exceeded 5 g/kg. Sulfuric acid leaching recovered 92% of uranium under optimum leaching conditions of: 8% concentration of sulfuric acid, liquid/solid ratio of 4 at room temperature and 4 h reaction time, while REE, Nb and Ta remained in the residue. A phosphate mixture was used for the dissolution of REEs, Nb and Ta minerals, after fusion, resulting in 97.8%, 99%, and 97% leaching rates, respectively. Uranium was recovered using ion exchange technology, and REEs by precipitation, Nb and Ta was recovered by solvent extraction, in the case of niobium with 0.1 M lauryl alcohol in kerosene solution at pH 2.5 and O/A ratio of 3, tantalum was recovered from the above raffinate using the same organic phase but at pH of 2, and O/A ratio of 3. Niobium was stripped with 5 M sulfuric acid and further precipitation, whereas tantalum was stripped with water at O/A of 1, being Ta₂O₅ the final product.

Various electronic wastes were used as source to investigate the indium recovery contained in them. Solvent extraction using organic phases of Cyanex 923 dissolved in Solvesso 100 were used [62]. After separation of the non-metallic components, the metallic concentrate was leached under acidic conditions to yield a solution containing 9 mg/L indium and 0.2 g/L iron, this solution was treated at different O/A ratios with the above organic phase. The results showed that using high A/O ratios, for example, 8, iron was completely extracted from the aqueous phase, remaining indium un-extracted in the raffinate. In a second-step and using the same extractant, indium was completely removed from the aqueous solution employing a low A/O ratio, for example, 0.5. Indium was stripped from the loaded organic phase *via* sulfuric acid solutions.

Cerium(IV) was extracted from sulfate medium using Cyanex 923 in kerosene [63]. The extraction was influenced both by the variation of extractant concentration in the organic phase and the variation of the sulfuric acid concentration in the aqueous solution (Table 5). The extracted complex presented the Ce(SO₄)₂·2 L·HSO₄⁻ stoichiometry (L represented the extractant), being the extraction process exothermic in nature. Best stripping results were derived on the use of 3.5 M sulfuric acid and 0.1 M H₂O₂ solution at O/A of 1.5 and three stages. H₂O₂ served to reduce Ce(IV) to the Ce(III) oxidation state, and recover the metal as cerium(III) oxalate (Ce₂(C₂O₄)₃·xH₂O).

Triocetylphosphine oxide (TOPO), in combination with some environmental-friendly molecules to form hydrophobic deep eutectic solvents (HDEs), was used in the recovery

Table 5
Influence of Cyanex 923 and sulfuric acid concentrations on Ce(IV) extraction

[Cyanex 923], M	% Extraction ^a	[H ₂ SO ₄], M	% Extraction ^b
0.05	37	0.50	87
0.10	65	1	82
0.15	82	2	80
0.20	85		
0.25	90		

^aIn 1 M sulfuric acid;

^bIn 0.15 M Cyanex 923.

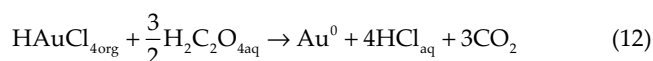
of platinum from secondary sources [64]. Among all the investigated HDEs, the TOPO/1-butanol showed, *via* ion-association mechanism, the best Pt(IV) extraction rate (98.9%) from a 1.1 g/L Pt(IV) solution. These HDEs exhibited a convenient selectivity towards Pt(IV) in the experiments using multi-elemental solutions. The extracted Pt(IV) can be completely stripped by using 0.5 M NaOH as stripping solution. Furthermore, the operating concentration of acidity and salinity was obtained as: 1.27 M HCl and 2.65 M NaCl.

Lepidolite is an important mineral resource of lithium, rubidium and cesium, being these metals extracted from the concentrate ore by sulfuric acid baking and water leaching [65]. Further, a crystallization-roasting-dissolution-solvent extraction process was developed to recover cesium from the leach solution. During crystallization, leach solution was cooled from 85°C to 35°C to precipitate most of rubidium and cesium with 98.65% and 94.59% recoveries, respectively, and in the form of RbAl(SO₄)₂·xH₂O and CsAl(SO₄)₂·xH₂O, respectively. The mixed aluminates were then roasted at 900°C to decompose them into Cs₂SO₄, Rb₂SO₄, and Al₂O₃. A further dissolution with water, of the roasted aluminates, allowed to yield a solution containing 12.51 g/L Rb(I) and 2.4 g/L Cs(I). This latter element was separated from the solution by solvent extraction, scrubbing and stripping. The extractant used in this operation was 4-tert-butyl-2-(α -methylbenzyl) phenol (t-BAMBP), and a Cs-loaded organic phase with 4.66 g/L Cs⁺ and 3.05 g/L Rb⁺ was obtained after a four-stage counter-current extraction, which represented around 99.20% of Cs(I) and 10.44% of Rb(I) extraction rates. After scrubbing and stripping of the Cs-loaded organic phase by 0.1 M sulfuric acid solution, increasing the percentage of stripping when the O/A ratio decreased; at O/A ratio of 4, a cesium sulfate solution of 16.6 g/L Cs(I) was obtained. A cesium sulfate product, with a purity of 98.47 wt.%, was then recovered by evaporation and crystallization of the stripping solution.

Two extractants, N,N'-((octylazanediy)bis(ethane-2,1-diyl))dioctanamide (L1) and N,N'-((octylazanediy)bis(ethane-2,1-diyl))di-2-methylheptanamide (L2), had been used to extract uranium from sulfate aqueous solutions [66]. The efficiency and selectivity of the extractants in dodecane/octanol (95/5% v/v) toward uranium sharply decreased as the sulfuric acid concentration in the solution increased from 0.02 M to 1 M, and levels off until a 5 M acid concentration. Using 0.02 M of L1 extractant, at 0.02 M sulfuric acid, the distribution coefficient was near 12, against, at 1 M sulfuric

acid the distribution coefficient decreased until a value of 0.3. Uranium was extracted *via* a solvation mechanism with formation of (LH)₂UO₂(SO₄)₂ species in the organic solution. In 0.1 M sulfuric acid solution and in the presence of Mo(VI), Zr(IV), Ti(IV), La(III), Ce(III) and Fe(III), the selectivity towards U(VI) is good. Uranium stripping was effective (99% stripping) when 1 M ammonium carbonate solution was used as strippant, also using 1 M sodium carbonate solution the recovery is as high as 97%, being ammonium oxalate very much less effective since the uranium recovery was of only 6%.

It was known that ethereal compounds, such as the commercially available extractant dibutyl carbitol (DBC), extracted gold(III) from acidic chloride media [67]. Thus, various aromatic ether compounds comprising an aromatic ring and aliphatic chains were prepared, and used without dilution in an organic diluent, to compare their extraction abilities toward this precious metal. Aromatic monoethers were not useful for the extraction of Au(III), but the extraction of Au(III) using aromatic 1,2-diethers increased as a function of the hydrochloric acid concentration in the aqueous phase. Using these 1,2-diethers, it was found that the shorter the aliphatic chain, the higher the extraction affinity toward gold(III). 1,2-Dimethoxybenzene (o-DMB), which had the shortest side chains, exhibited the highest extraction affinity, with this extractant gold(III), and from 5 M HCl concentration, was extracted selectively from Fe(III), Ga(III), Pd(II), Pt(IV) and a series of base metals being this performance better than using DBC. Au(III) can be recovered from the loaded organic phase by reduction with oxalic acid:

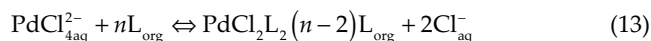


Note: the reduction of gold(III) [Eq. (3) in the published manuscript] was strangely unbalanced. Also, it was not specified how was the gold speciation in the organic phase.

This investigation presented direct Li recovery from lithium-ion batteries (LIBs) waste leachate prior to nickel and cobalt recoveries [68]. The solvent extraction system used tributyl phosphate (TBP) as extractant and iron(III) chloride as co-extractant in kerosene. Batch equilibrium experiments at room temperature were conducted with preloaded organic phase (NaCl and FeCl₃, 80% v/v TBP in kerosene) and synthetic aqueous LIBs waste leachate solution (1.3–1.5 g/L Al, 14.2–17.8 g/L Co, 1.9–2.2 g/L Cu, 0.7–0.8 g/L Fe, 2.4–2.7 g/L Li, 1.9–2.1 g/L Mn, 1.8–2.0 g/L Ni, and $E = 603$ mV Ag/AgCl). Lithium was selectively separated over divalent LIB metals (Mn, Cu, Co, Ni) and Al(III), and the extraction ability of the system is H⁺ > Li⁺ > LIBs metals. Aiming for maximum Li extraction, initial concentration of H⁺ was chosen to be 0.1 M. Substitution of MgCl₂, used in the brine systems, by AlCl₃ as chloride source increased Li extraction due to its strong salting out effect. This resulted in greater separation factors ($\beta_{\text{Li/Ni}}$ of 2825 and $\beta_{\text{Li/Co}}$ 854 using O/A ratios of 1). Loaded organic phase was purified using a mixture of 1 M LiCl+2 M AlCl₃ as scrubbing solution. Stripping with 6 M HCl, in a single-stage at O/A ratio of 5, resulted in a stripping solution with 12.26 g/L Li, 0.02 g/L Mn, 0.04 g/L Co, and 0.04 g/L Cu.

Neodymium, dysprosium, and iron were recovered from spent mobile phone camera modules via leaching and a solvent extraction procedure [69]. Nitric acid was used as leaching medium. The leachate contained Nd, Dy, Fe, Ni, Co, and B; employing a 0.5 M TOPO in kerosene solution, Nd and Dy, with a small amount of Fe, were extracted. The separation factors Nd/Fe and Dy/Fe increased with the increase of the nitric acid concentration (0.001–0.5 M) in the solution. These rare earths were extracted as $M(\text{NO}_3)_3 \cdot 3\text{TOPO}$ species, whereas in the case of iron(III), the species formed in the organic phase had the $\text{TOPOH}^+\text{Fe}(\text{NO}_3)_4$ stoichiometry. Selective stripping of Nd and Dy from the loaded TOPO phase was possible using 3 M hydrochloric acid. After removing Nd and Dy from the leachate, the remaining Fe was extracted, and separated from Co, Ni and B, using 1 M TOPO in kerosene solution at an O/A ratio of 3 and two stages, followed by stripping with 1 M oxalic acid.

The performance of three extractants: N-decyloxy-1-(pyridin-3-yl)methanimine (D-3MI), N-decyloxy-1-(pyridin-3-yl)ethanimine (D-3EI) and N-decyloxy-1-(pyridin-4-yl)ethanimine (D-4EI) diluted in toluene, in the solvent extraction of palladium from HCl medium was investigated [70]. The extraction was described by the next equilibrium:



with $n = 2, 3$. Also the possibility of forming $\text{PdCl}_3\text{L} \cdot 2\text{H}(\text{L}^+)$ species in the organic phase was described. In the above formulation, L represented the extractant molecule. Metal stripping was accomplished with a solution containing a mixture of 0.01 M thiourea and 0.1 M HCl.

The recovery of lithium from high Mg/Li salt lake brine was accomplished by the use of TBP, and NaBPh_4 and CH_2ClBr as co-extractant and diluent, respectively [71]. Under the optimal extraction conditions (molar ratio of NaBPh_4 to Li^+ of 2.0, TBP volume fraction of 50%, and O/A of 1), the one-stage extraction efficiency of Li^+ and Li/Mg separation factor reached up to 87.7% and 2260, respectively. Under optimal conditions of washing and stripping processes, the stripping efficiency of Li^+ reached up to 98.4% and lithium carbonate product could be directly obtained in the aqueous phase. The binding capacity of TBP to metal ions follows the sequence: $\text{Li} > \text{Na} > \text{K} > \text{Mg}$. Note: it was not clear that the use of CH_2ClBr as diluent make of this system as a candidate to be used under practical operational terms.

The extraction of lithium and magnesium was investigated using the Cyanex 923/ FeCl_3 or TBP/ FeCl_3 mixtures [72]. Also the use of the ionic liquid $[\text{HOEmim}][\text{Ntf}_2]$ were investigated instead of FeCl_3 . The composition of the ionic liquid was described as 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. Moreover, p-cymene was used as diluent of the organic phase. Cyanex 923 (L) extracted Mg^{2+} by salvation and formation of MgCl_2L_4 species in the organic phase, whereas TBP did not extract this element. When the ionic liquid substituted the iron(III) salt, both TBP and Cyanex 923 extracted magnesium by an ion-pair mechanism, with formation of $[\text{MgL}_2][\text{Ntf}_2]$ species in the organic phases of TBP or Cyanex 923 (L represented to any if both extractants in the previous formulation); the extraction of the above compound competed with the

extraction of lithium. Thus, the systems containing Cyanex 923 were not suitable for lithium extraction, against, the replacement of Cyanex 923 for TBP resulted in the recovery of lithium for magnesium-bearing brines. Note: no stripping results were given in the manuscript.

In this next reference [73], Au(III) extraction using a series of undiluted aliphatic ketone compounds was investigated. These chemicals showed desirable Au(III) extractability, with those bearing shorter aliphatic chains showing higher gold extractability, presenting 2-decanone the best results. With this ketone, the percentage of gold extraction increased with the increase of the HCl concentration in the aqueous feed solution, that is, 40% (0.1 M HCl), 78% (1 M HCl) and 95% (5 M HCl). From 1×10^{-3} M metal concentrations in this feed solution, only Fe(III) (84%) and Ga(III) (100%) were extracted from a 5 M HCl medium. Gold was recovered from the loaded organic phases as zero valent metal by the use of oxalic acid (0.01 to 0.1 M) solutions.

The mixture TBP/*n*-dodecane was used to resolve two issues in relation with the nuclear industry [74], these issues were based in the separation of actinides by liquid-liquid extraction technology. In the case of an organic phase loaded with uranium(VI) and thorium(IV), two streams were available: (i) one containing almost all of the thorium in the presence of uranium in a controlled ratio, and (ii) whereas the second one contained surplus uranium. Two levels were selected to control the spontaneous separation of the organic phase: (i) the addition of concentrated nitric acid, or (ii) variation in the temperature. Best results had been obtained using a decrease of the temperature in the liquid-liquid extraction process.

The extraction of U(VI), Pu(IV) and Am(III), from nitric acid solutions, using two tripodal amide extractants: N,N,N',N'',N''-hexa-*n*-octyltriloltriacetamide (HONTA) and N,N,N',N'',N''-hexa-*n*-dodecyltriloltriacetamide (HDDNTA) was investigated [75]; the extractants were dissolved in a mixture of isodecanol (10%) and *n*-dodecane (90%). In all the three cases, the extraction was represented by the next equilibrium:



Best extraction results were presented in the case of HONTA extractant, being favored the extraction of Am(III) and U(VI) as the nitric acid concentration in the feed solution decreased; in the case of Pu(IV) the extraction was stable in the 0.5–6 M nitric acid concentrations range in the feed phase. Best stripping results were yielded using a mixture of 0.5 M nitric acid and 0.5 M oxalic acid, 1 M sodium carbonate, and 1 M α -HIBA (α -hydroxyisobutyric acid) as strippants for Pu(IV), U(VI) and Am(III), respectively. Note: these three elements were extracted as their respective nitrate salts [Eq. (14)] and not as cations as one can inferred from the beginning of the abstract of the published manuscript.

TODGA (N,N,N',N'-tetraoctyl diglycolamide) is widely used in nuclear fuel reprocessing under several processes (ARTIST, i-Sanex, and EURO-GANEX). The organic solutions combines TODGA with a modifier in an aliphatic diluent, and are subjected to some kind of radiolytic degradation

due to the high radiation produced by the actinides and fission products present in the fuel [76]. The presence of nitric acid in the aqueous stream provides a slight protective effect since nitrate ions absorb the radicals, whereas the presence of 1-octanol in the organic phase seems to have a slight sensitizing effect due to a combination of a couple of competitive effects: (i) a protective effect from TODGA-octanol adducts and (ii) a sensitizing effect from an increase in the water concentration in the organic phase, which produces $\cdot\text{OH}$ radicals. In the case of lanthanides extraction, degradation products do not necessarily influence, in a negative form, the extraction properties of TODGA towards these rare earths, the above being attributable to the formation of mixed Ln-degradation compounds-TODGA complexes.

DOHyA (N,N-di-octyl-2-hydroxyacetamide) extractant diluted in *n*-dodecane was used in the liquid–liquid extraction of Zr(IV) from simulated high-level liquid waste (SHLLW) solutions [77]. DOHyA/*n*-dodecane phase showed quantitative extraction of Zr(IV) from the simulated waste solutions, however, a series of metals (La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Y, Am, Pd, Rh, Ru, Fe and Mo) was also co-extracted. All these metals, but Zr(IV) and Mo(VI), were stripped from the loaded organic phase using 0.5–1 M nitric acid solution. Zr(IV) was effectively stripped with a 0.2 M oxalic acid and 0.5 M nitric acid mixture. In the extraction process, the extracted complex presented $\text{ZrO}(\text{NO}_3)_2 \cdot 4\text{DOHyA}$ stoichiometry, being $\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ the species formed in the stripped solution.

2.4. Ionic liquids extractants

This type of reagents are chemicals composed of ions presenting a melting point below 100°C, they extracted metals *via* ion pair or ion exchange mechanisms. As it is mentioned above, amine salts can be included into this group.

In the system Au(III)-HCl-A324H⁺Cl⁻, liquid–liquid extraction experiments were used to define the extraction equilibrium and the corresponding extraction constant (K_{ext}) before its implementation in a liquid membrane operation [78]. The ionic liquid was dissolved in Solvesso 100 (aromatic diluent). The precious metal was loaded onto the organic phase by an anion exchange mechanism in which the chloride ion of the ionic liquid was exchanged for the gold(III)-chloride complex:

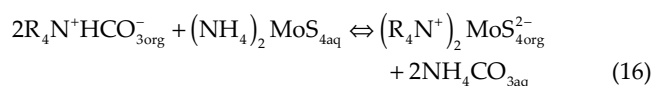


The value of $\log K_{\text{ext}}$ for the above equilibrium was of 3.11 ± 0.18 . Sodium thiocyanate solutions were used to strip gold from the corresponding organic phases.

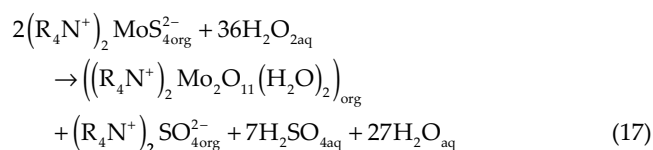
Zinc and iron were separated from the spent pickling solution by extraction with methyl trioctylammonium chloride (Aliquat 336) dissolved in kerosene [79]. Under optimal extraction conditions of 10% v/v Aliquat 336 in kerosene plus 10% v/v octanol (acting as phase modifier) and O/A ratio of 2, zinc extraction in one stage was above 92.4% and the separation coefficient $\beta_{\text{Zn/Fe}}$ could reach 273, from solutions of initial zinc concentration of 17.6 g/L, iron concentration of 141.1 g/L and 1.4 M acidity. Zinc was extracted in the form of ZnCl_4^{2-} species *via* anion exchange mechanism

between this metal species and the chloride ion of the quaternary ammonium salt. Zinc can be stripped (98.9%) in one stage using 0.5 M NaOH solutions.

Solvent extraction operation was used for the removal of molybdenum from ammonium tungstate solution [80]. The organic phase composition was of 10% v/v N263 (quaternary ammonium salt), 30% v/v iso-octanol (modifier) in kerosene. The ionic liquid was in the organic phase in the bicarbonate cycle, whereas the aqueous feed solution to the extraction step contained 178.5 g/L WO_3 , 1.3 g/L Mo and 3.3 g/L S^{2-} . Experiments were carried out in a plant comprised five extraction stages, two scrubbing stages, two oxidation stages and six stripping stages. The concentration of Mo in the raffinate was less than 0.01 g/L, and the concentration of Mo in the strip solution reached 30 g/L. Stripping used a mixture of ammonium bicarbonate and ammonium hydroxide in solution. In the oxidation step, MoS_4^{2-} extracted in the organic phase following the next equilibrium:



was oxidized to $\text{Mo}_2\text{O}_{11}(\text{H}_2\text{O})_2^-$ according to:



being this last organic phase which fed the stripping operation.

The extraction and recovery of vanadium(V) from synthetic and real leach solution of spent V_2O_5 catalyst using Cyphos IL 104 (trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate) dissolved in toluene was investigated [81]. Vanadium(V) was extracted as $(\text{R}_3\text{R}'\text{P}^+)_4\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ species and stripped from the loaded organic phase as VO_2^+ using 1 M nitric acid. The acid media of the feed solution had an influence on vanadium extraction (Table 6), decreasing the percentage of metal extraction as the acidity of the feed solution was increased. Vanadium(V) was separated from aluminium(III), titanium(IV), chromium(III), manganese(II), iron(II) and (III),

Table 6
Vanadium(V) extraction under different mineral acids

HCl, M	% Extr.	HNO_3 , M	% Extr.	H_2SO_4 , M	% Extr.
10^{-3}	90	10^{-3}	85	10^{-3}	97
10^{-2}	85	10^{-2}	80	10^{-2}	85
10^{-1}	45	10^{-1}	nil	10^{-1}	80
1	20	1	nil	1	nil

Vanadium: 0.1 g/L; organic phase: 5×10^{-3} M; Cyphos IL 104 in toluene.

molybdenum(VI) and tungsten(VI). Metals were leached from spent catalyst using alkaline leaching. McCabe-Thiele plots indicated two stages for both extraction and stripping at A/O and O/A of 3/1. Vanadium is finally recovered as V_2O_5 from the strip liquor. Note: the solvent extraction system was applied on a leach solution obtained in the treatment of a spent catalyst with a NaOH solution. However, it was not clear the scheme presented in the manuscript, since at these alkaline pH values, vanadium(V) was in the form of vanadate ion (VO_4^{3-}) and not as indicated in Eq. (10) of the published manuscript.

An ionic liquid (IL), based on tetraheptylammonium cooking oil (TC), was used in the recovery of rare earth elements from leaching liquor of ion-adsorbed-type rare earths ores [82]. Firstly, extraction performances of tetraheptylammonium oleate (TO) and tetraheptylammonium linoleate (TL) type ILs were investigated. It was shown that these ILs presented affordable extraction performances, such as short equilibration time (less than 1 min), an extraction capacity of 0.225 M and a stripping efficiency of 99%. Additionally, REEs extraction occurred in the solutions with high acidity (pH of 0.24), because the cation ($C_7H_{15}N^+$) of TO and TL formed an amine salt with hydrogen ion, of the feed solution, and decreased the acidity of this aqueous phase. An ion association mechanism of REEs extraction was responsible for the extraction, with formation of $NdCl_3(TO)_3$ species in the organic phase. In the case of TL, the stripping for Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu was effective using 3.7–5.98 M HCl solution, whereas in the case of TO, stripping was favored using 6 M HCl. TC was synthesized in water bath by mixing tetraheptylammonium bromide with saponified peanut oil. Then, comparative study of commercial extractants showed that TC had the highest REEs recovery yield of 100% from the leaching liquor. Note: apparently, the formed amine salt (ionic liquid) did not take part or affected the REEs extraction process.

The solvent extraction of scandium(III), from a concentrated sodium hydroxide solution, using an organic phase formed by the ionic liquid Aliquat 336 in OH^- form ($R_4N^+OH^-$) dissolved in kerosene, and with 10% v/v octanol as modifier were investigated [83]. The extracted species presented the next stoichiometry $R_4N^+Sc(OH)_4^-$, being the anionic exchange equilibrium exothermic and spontaneous. Stripping was accomplished with 2 M nitric acid solution. The above results were used to investigate the recovery and separation of Sc(III), and other metals, from a synthetic solution similar in composition to that expected from the leaching solution of red mud in strongly alkaline medium. In this case, scandium was extracted selectively from aluminium and calcium.

Aliquat 336 also was used to investigate the solvent extraction of vanadium from oxalic acid leachate of shale [84]. The ionic liquid was dissolved in kerosene, necessitating this organic phase the presence of TBP in order to control the formation of undesirable third phases; with organic phases containing 20% v/v TBP, this third phase did not formed. Separations factors V/AI reached maximum value (1221) employing organic phases of 40% v/v ionic liquid and 20% v/v TBP in kerosene. The results indicated that 99.06% of vanadium was extracted and 7.95% of the accompanying aluminum was co-extracted in a counter-current extraction of five stages. Vanadium was extracted *via* and anion exchange

mechanism, with formation of $(R_4N^+)_2VO(C_2O_4)_2^{2-}$ species in the organic phase. 99.32% of vanadium was stripped by 8 M HCl in a counter-current stripping comprising four stages. V_2O_5 , with a purity of 98.4%, was yielded by ammonium precipitation from the stripped vanadium solution.

The reaction of tertiary amine A327 and HCl formed the ionic liquid $A327H^+Cl^-$, and the liquid–liquid extraction of indium(III) from HCl medium by this ionic liquid dissolved in Solvesso 100 was investigated [85]. The extraction reaction was exothermic. The numerical analysis of indium distribution data suggested the formation of $A327H^+InCl_4^-$ species in the organic phase. Indium(III) was stripped from the loaded organic phase with 0.1 M HCl solutions and O/A ratio of 2. The results derived from indium(III) extraction have been implemented in a supported liquid membrane system.

Red mud was subjected to an acidic leaching operation with 9.36 M HCl, the resulting solution was extracted with an organic phase of 30% v/v Aliquat 336, 15% v/v 2-octanol in kerosene [86]. The resulted organic solution, containing about 30 g/L Fe(III), was stripped with various strippants (Table 7), NaH_2PO_4 presented the best recovery rates, however, the use of this salt in concentrations equal or greater than 2 M must be avoided, since it promoted the formation of undesirable ferric-hydroxy-phosphate precipitate. Iron stripping was optimized at O/A ratios of 2 or 4, and 10 min of contact between both phases, whereas the increase of temperature from 20°C to 50°C had little influence on iron stripping. The stripped iron(III) species presented $FeH_2PO_4^{2-}$ and $Fe(H_2PO_4)^+$ formulations. Note: in Eqs. (3) and (4) of the published manuscript, the reactions were unbalanced with respect to the electronic charges.

Different pyridinium derivatives containing an imido-amide or imine moiety: Eh3MI-PrCl (3-[1-(2-ethylhexyloxyimine)methane]-1-propylpyridinium chloride), D3MI-PrCl (3-[1-(decyloxyimine)methane]-1-propylpyridinium chloride), D3EI-PrCl (3-[1-(decyloxyimine)ethane]-1-propylpyridinium chloride) and Eh4IA-PrCl (4-[1-amine(2-ethylhexyloxyimine)]-1-propylpyridinium chloride) dissolved in toluene were used as extractants for recovery of palladium(II) and platinum(IV) from chloride aqueous medium [87]. The results of liquid–liquid extraction from one-component solutions showed that in the case of Pd(II), the extraction efficiency tended to decrease as the HCl concentration in the aqueous solution increased from 0.1 to 3 M, this was attributable to the transfer of the acid into the organic phase. In the case of Pt(IV), the extraction increased as the acid concentration increased in the aqueous phase. Also, HCl was transferred to the organic phase. Various strippants were investigated: 0.1 M ammonia, 3 M nitric

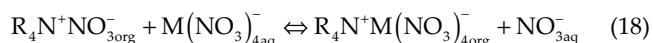
Table 7
Iron(III) stripping using various strippants

Strippant	0.5 M	1 M	1.5 M	2 M
Na_2SO_4	55–60	55–60	55–60	55–60
$NaNO_3$	55–60	55–60	55–60	55–60
$NaHPO_4$	70	83	95	90

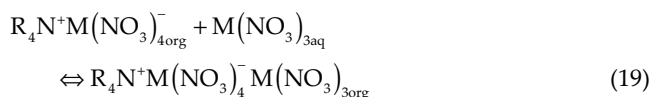
A/O ratio: 1; time: 20 min; temperature: 30°C.

acid, 3 M HCl, 0.5 M thiourea in 0.5 M HCl. Generally speaking, stripping was difficult, D3EI-PrCl was stripped with 0.1 M ammonia and Eh3MI-PrCl was best stripped with nitric or hydrochloric acids. In binary solutions, it was possible the complete co-extraction of both precious metals with D3EI-PrCl and D3MI-PrCl, whereas Eh3MI-PrCl extracted platinum selectively to palladium.

The extraction of Pr and Nd from NdFeB magnet-leaching solution using Aliquat 336 in nitrate form and dissolved in toluene was investigated under various experimental variables: Aliquat 336 concentration in the 0.30–0.85 M range, organic to aqueous phase ratio (O/A) of 3, pH in the 2.0–5 range, and varying (2.2–5.6 M) nitrate concentration in the aqueous solution [88]. The system using an extractant concentration of 0.52 M, O/A ratio of 3, aqueous pH of 2, aqueous nitrate concentration of 5.6 M, can be used in the co-extraction of both elements with percentages of extraction about 99% or 94% for Pr or Nd, respectively. The separation factor Pr/Nd was of 2.1. Also, and under the next experimental conditions: extractant concentration of 0.85 M, O/A ratio of 1, aqueous pH of 5 and aqueous nitrate concentration of 3.1 M, the system can be used to the selective separation of the elements: Pr (75% extraction) and Nd (61%), with separation factor Pr/Nd of 2.1. The extraction was attributed to the next equilibrium:



Further, a second equilibrium occurred as:

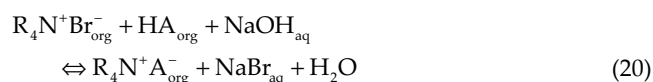


in the above equations, M stands for Pr or Nd. The presence of a supporting electrolyte (NH_4NO_3) favored the above equilibriums. It was found that the stripping of Pr and Nd from the loaded organic phase can be conducted using hydrochloric acid solutions in the 0.1–2 M concentrations range, and 5 min of equilibration between both phases.

A recycling process of cobalt from simulated solution for spent ternary lithium batteries was proposed [89]. The task-specific ionic liquids [$C_8H_{17}NH_2$][Cyanex 272] were synthesized by one-step reaction of n-octylamine and Cyanex 272 in absolute ethanol, petroleum ether or isopropyl alcohol medium. Once formed, kerosene was used for the preparation of the organic phases used in the investigation. The extraction of cobalt increased with the increase of the temperature. The pH_{50} values for cobalt and nickel extraction were 4.3 and 6.1, respectively; at these pH values, lithium extraction was about 10%. The separation factor Co/Ni was 976.9 using a two-stage cross-flow extraction, lithium was not extracted in the process. Cobalt was stripped with dilute sulfuric acid, and cobalt was finally recovered by formation of $CoSO_4 \cdot 7H_2O$.

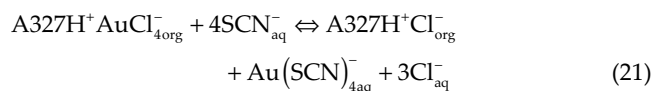
The extraction of cadmium from sulfuric acid solutions and its separation from nickel with salts of Cyanex 301 and tetraoctylammonium bromide was studied [90]. The ionic

liquid was formed by treating an equimolar mixture of both extractants in 1 M NaOH medium:



HA represented the active group of Cyanex 301, toluene was used to dissolve the ionic liquid. Extraction of cadmium was favored towards acidic pH values, for example, at pH 0, log D near 4, at pH 2, log D value was of 1. The separation coefficient cadmium/nickel reached values greater than 106. Cadmium stripping was achieved by treating the organic phase with a solution containing a mixture of ammonia and ammonium sulfate. Note: Eq. (16) was written unbalanced in the published manuscript [Eq. (1)].

The ionic liquid $A327H^+Cl^-$ is generated by reaction of the tertiary amine A327 (industrial mixture of tri-octyl and tri-decyl amines) and hydrochloric acid solutions [91]. Toluene was the medium to prepare the organic phases used in this investigation. The extraction of Au(III) by $A327H^+Cl^-$ ionic liquid was examined under various variables, including metal and ionic liquid concentrations. Results indicated that $A327H^+AuCl_4^-$ was formed in the organic solution *via* an exothermic process. Aqueous ionic strength influenced the extraction constant values, and the specific interaction theory (SIT) was used to estimate the interaction coefficient between $AuCl_4^-$ and H^+ ions in the aqueous phase. Gold(III) was stripped using thiocyanate media:



and from the strip solutions, gold was precipitated as gold nanoparticles.

The recovery of cobalt, nickel and lithium from spent lithium ion batteries had been investigated by different ionic liquids: (i) Aliquat 336 in SCN^- cycle, (ii) the ionic liquid formed by Aliquat 336 and Cyanex 272, and (iii) a mixture of Cyanex 301 and the tertiary amine Alamine 336 [92]. The resulted ionic liquids were dissolved in kerosene, with the organic phase also presenting decanol as modifier. First, cobalt was selectively extracted, from a 2 M sulfuric acid solution, over other metal ions (Mn(II), Ni(II) and Li(I)) by extraction with 0.1 M Ali-SCN and O/A ratio of 1. The cobalt in the loaded Ali-SCN was stripped (93%) by ammonia solution (5%–10%). After adjusting the raffinate pH, extraction with the ionic liquid formed in (iii), selectively extracted nickel over manganese and lithium. The presence of the amine served to regulate the proton concentration resulted from the extraction of nickel with Cyanex 301:



The extracted nickel was completely stripped by 75% aqua regia. Manganese was selectively extracted by the ionic liquid formed in (ii), after adjusting the pH of the raffinate. Co-extracted manganese was stripped with HCl solutions. The final raffinate contained only lithium.

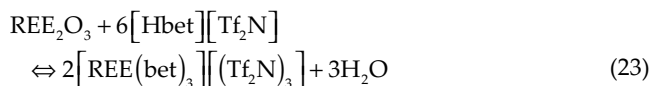
Estonian phosphorite ore (Iru deposit) was used to investigate the recovery of U, Th, and Tl contained in this raw material [93]. The solvent extraction operation used undiluted Aliquat 336 in nitrate form or undiluted DEHPA at A/O ratio of 9. Results with DEHPA were better than that derived from the use of Aliquat 336, except that Tl was not extracted by the organic-phosphoric acid. In the first step, uranium and thorium were extracted by undiluted DEHPA from 7.5 M nitric acid media, in the second-step, the raffinate from step one, at pH 1.5, was treated again with undiluted DEHPA in order to recover rare earths elements, though the selectivity was not good since various metals (Mo, Zr, Fe, Ti, V, Ga, Zn, Ca, Cd, and Pb) were more or less co-extracted. Note: This publication was very singular because very rarely undiluted DEHPA was used in solvent extraction practice. One of the proposed goals, the recovery of Tl, was not accomplished. No stripping data were provided in the publication.

The recovery of zinc, aluminium, copper, cobalt and nickel from acid mine drainage (AMD) water collected from the Portuguese Mine of Sao Domingos were investigated by the use of sixteen ionic liquids [94]. First experiments were carried out on synthetic solutions, and the most promising reagent $N_{4444}Cl$ (tetrabutylammonium chloride) was used to extract the metals from the real AMD sample. The sample was pretreated to raise the pH value until 4, and this solution (58% wt.) was treated with a mixture of the ionic liquid (24% wt.), sodium sulfate (11% wt.), 0.2% wt. of sodium thiocyanate and 68% water. The ionic liquid, now in the SCN^- cycle, extracted zinc. Thus, three cycles of selective precipitation of Zn were sequentially applied, by reusing the IL-rich phase and introducing fresh treated solution of pH 4 and sodium sulfate in each cycle. Salt-rich phases obtained after each Zn extraction and recovery cycle were collected to a new extraction system in which fresh ionic liquid and sodium thiocyanate were added to induce phase separation and the selective extraction of Cu. After the extraction step, 95% of the metal loaded in the IL-rich phase was recovered in the form of an organic-metal complex by dilution in water of this Cu-bearing organic phase (at 5:1 mass ratio).

Two new task-specific ionic liquids (TSILs): DODGA-TSIL- PF_6 and DEHDGA-TSIL- PF_6 were prepared from the corresponding acids and 1-(3-aminopropyl)imidazole [95]; these reagents were based on N,N' -dioctyl-diglycolamide (DOGDA) and N,N -di(2-ethylhexyl)-diglycolamide (DEHDGA), respectively, and were used in the extraction of Lu(III) and Y(III). As diluent of the TSIL, n -heptane was used throughout the experiments. The extraction of both metals was dependent on the pH of the aqueous solution, decreasing the percentage of extraction from pH 0.5 to 4, however, when the aqueous phase contained the mixture $HCl + NaCl = 0.4$ M, this pH-dependence was avoided. TSIL based on DODGA performed better than that based on DEHDGA. Lu(III) stripping was performed using 0.01 M HCl solutions.

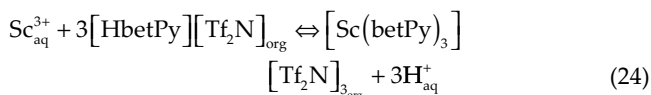
In the next work [96], the ionic liquid betainium bis(trifluoromethylsulfonyl)imide ([Hbet][Tf₂N]) for the leaching and extraction of REEs (Sc, Y, La, Ce, Nd, Eu, Dy) from different coal fly ashes was investigated. The process was based in the [Hbet][Tf₂N] thermomorphic properties with

water: upon heating water and the IL form a single liquid phase, and REEs were leached from the ashes *via* a proton-exchange mechanism



Upon cooling, the water and IL separated, and REEs were found into the ionic liquid phase, being stripped with 1.5 M HCl.

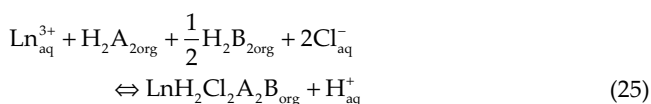
Two carboxylic acid-functionalized upper critical solution temperature (UCST)-type ILs: N -carboxymethylpyridinium bis(trifluoromethylsulfonyl)imide ([HbetPy][Tf₂N]) and N -carboxymethyl- N -methylmorpholinium bis(trifluoromethylsulfonyl)imide ([HbetMor][Tf₂N]), were used in the liquid-liquid extraction of Sc(III) [97]. In both cases, the extraction increased from pH 0.5 to 2.5, and represented by a cation exchange mechanism:



The separation factors ($\beta_{Sc/REEs}$) values were higher in the case of the pyridinium derivative than in the case of the morpholinium one (Table 8). Stripping was accomplished by the use of 1.5 M nitric acid solutions.

2.5. Mixtures of extractants

The synergistic extraction of heavy rare earths (Ho, Er, Tm, Yb, Lu) from chloride medium was investigated using the mixture of heptylaminoethylphosphonic acid mono-(2-ethyl-hexyl) ester (HEHHAP or HA) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272 or HB) in heptane [98]. The extraction efficiency of heavy rare earths and the separation factors (Table 9) between adjacent lanthanides using this mixture were better than those in the use of organic phases only containing HEHHAP or Cyanex 272 system. The rare earth extraction was determined to be a cation exchange process:



where $Ln = Yb, Lu$. The loaded metal can be stripped by HCl or H_2SO_4 . The stripping efficiency was over 90% when the concentration of HCl was in excess to 1 M.

Table 8
Separation factors Sc/REEs

	Sc/Yb	Sc/Ho	Sc/La
[HbetPy][Tf ₂ N]	749	300	214
[Hbetmor][Tf ₂ N]	499	105	153

Table 9
Separation factors for REEs

System	Cyanex 272	HEHHAP	Mixture
Ho-Dy	1.41	1.27	2.57
Y-Ho	1.47	1.41	1.60
Er-Y	1.52	0.38	2.08
Tm-Er	2.44	2.36	3.07
Yb-Tm	2.93	3.18	3.58
Lu-Dy	33.9	21.4	149

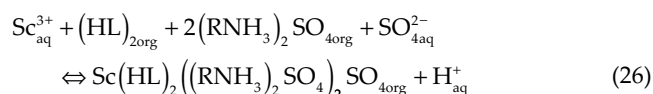
Total REEs concentration: 0.015 M; pH: 2.5; organic phase: 0.05 M mixture each extractant or 0.1 M separate extractant; diluent: heptane.

A method for recovering and separating Ce³⁺ and La³⁺ from spent fluid catalytic cracking catalyst was proposed [99]. The spent catalyst was leached with 2 M nitric acid at 80° C, and the dissolved iron was removed from the leach solution by solvent extraction with 25% v/v diisooctyl phosphinic acid in *n*-octane. Extraction of cerium and lanthane was then undertaken from the raffinate using an organic phase of 25% v/v D2EHPA and 25% v/v tri-*n*-butyl phosphate in *n*-octane. Both rare earths were stripped from the organic phase using 0.5 M sulfuric acid. Separation of Ce³⁺ from La³⁺ was then achieved by means of an in situ electrochemical oxidation coupled with a simultaneous solvent extraction process. In this process, Ce³⁺ was electrochemically oxidized to Ce⁴⁺ and removed from the aqueous phase by solvent extraction with 100 mM D2EHPA in *n*-octane, remaining La³⁺ in the aqueous solution. Finally, Ce⁴⁺ was reduced to Ce³⁺ and stripped with a mixture of 2% H₂O₂ and 0.5 M sulfuric acid.

In another process, the solvent extraction of trivalent lanthanide ions from nitric acid solutions with an organic phase comprising a mixture of two solvation extractants: tri(*n*-butyl)phosphate (TBP) and N,N,N',N'-tetra(*n*-octyl) diglycolamide (TODGA), was investigated [100]. Moreover, the ionic liquid (IL), 1-methyl-3-butyl-imidazolium bis(trifluoromethanesulfonyl)imide, was employed as diluent of the organic phase. The results revealed that the addition of TBP as a co-extractant with TODGA not only significantly enhanced the metal extraction but also allowed high intra-lanthanide ion selectivity. Maximum Eu³⁺ (lanthanides representative) was extracted from a 3 M nitric acid solution with an organic phase of 0.1 M TODGA in the ionic liquid, which also contained 0.75–1.25 M TBP. Note: stripping information was not given in the published manuscript.

A synergistic extraction of scandium(III) from a spent sulfuric acid solution of titanium dioxide production by using a mixture of bis-2-ethylhexyl phosphoric acid (P204) and primary amine (N1923) in *n*-heptane had been proposed [101]. The maximum synergistic coefficient was found to be 12.50 when the sulfuric acid concentration in the aqueous feed solution was 0.5 M, decreasing the metal extraction when the sulfuric acid concentration increased from this value until 2 M. At these high acidic concentration, the separation factors Sc/Fe and Sc/Ti were 207 and 4.29, values which compared well with those obtained with single P204 or N1923 extractants: 15.12 or 59.62 (Fe) and 4.29 or 3.34 (Ti),

respectively. The extraction of Sc(III) was explained according with the next equilibrium:



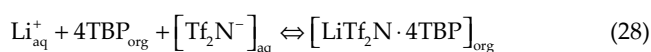
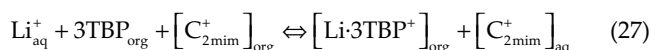
90% scandium can be stripped using a 6 M nitric acid phase, O/A ratio of 1 and 50 min of equilibration time. After three-stages counter-current extraction and stripping, and from the strip solution, Sc₂O₅ with a purity of 90% was yielded after precipitation and calcination. However, before the stripping stage, a titanium scrubbing step needed to be performed at O/A ratio of 1. Note: accordingly to Eq. (20), the amine must be transformed to the amine salt (or ionic liquid). This reaction can be accomplished prior to scandium extraction step, or in the same step by reaction of the amine with the sulfuric acid presented in the aqueous solution.

A mixed ternary solvent extraction system, consisting of TBP (tributyl phosphate), FeCl₃ and P507 (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) was used to recover lithium from real salt lake brine (East Tajinar, China), in both batch and multi-stage simulated counter-current modes [102]. The feed solution contained 5 g/L Li, 108 g/L Mg, 2.23 g/L boron and pH 0.86. Best lithium extraction results were derived when using an organic phase of 40% v/v TBP and 30% v/v P507 in kerosene, which was loaded with iron(III) in a 1.3 Fe/Li molar ratio. Metal extraction decreased with the increase in acidity (HCl) from 0 to 0.25 M, and though best extraction results were obtained with an O/A ratio of 7, in practice an O/A ratio of 4 was chosen to avoid boron co-extraction. Also, the increase of the temperature decreased lithium extraction. Prior to the stripping stage, a scrubbing step with water was needed, then water was also used as stripping in an O/A ratio of 20. In the three-stage simulated counter-current extraction tests, the recovery of lithium reached 99.8%, and in the three-stage simulated counter-current stripping tests, the obtained loaded strip liquor contained 20.9 g/L Li, 2.2 g/L Mg, and 1.6 g/L Boron. During stripping operation, the Fe³⁺ remained in the organic phase, enabling the organic phase to be directly used in the next extraction.

Lithium recovery from effluent of spent lithium batteries recycling by solvent extraction was investigated using benzoyltrifluoroacetone (HBTA, β-diketone) and TOPO, being kerosene used as diluent of the organic phase [103]. Typically, organic phases of 0.4 M HBTA and 0.4 M TOPO in kerosene were used throughout the experimentation. More than 90% of lithium could be extracted, in an exothermic process, by saponified organic phase through three-stage counter-current extraction. Saponification of HBTA increased lithium extraction, for example, with 50% saponification lithium extraction reached 67%, at 100% saponification of HBTA, the percentage of metal extraction was of 97%. The loaded organic phase was first eluted by dilute HCl solution to remove co-extracted sodium, and then stripped by 6 M HCl at an O/A ratio of 20 to obtain lithium-rich solution with 4.3 M lithium. From this solution, lithium carbonate or lithium chloride can be prepared.

The extraction of lithium in HCl or HNO₃ aqueous solutions by undiluted tri-*n*-butyl phosphate (TBP), an

imidazolium-based ionic liquid ($[C_{2min}][Tf_2N]$), or even TBP diluted in *n*-decanol was investigated [104]. The results showed that no one of the above systems were effective in the extraction of the metal from the various solutions investigated, however, the mixture of the ionic liquid with TBP provided a significant lithium extraction, being the value of the metal distribution coefficient around 30 when an organic phase of 80%–90% v/v TBP in the ionic liquid was used. The results suggested that lithium extraction into TBP-IL system occurred *via* two mechanisms: cationic exchange [Eq. (21)] and ion pair transfer [Eq. (22)]:



however, there was loss of ionic liquid by the cation exchange process, thus, it was better to mix TBP with an ionic liquid possessing low solubility in aqueous phases, for example, the system can extract lithium when a highly hydrophobic counter-ion such as (Tf_2N) was present in the aqueous phase. Note: stripping data were absent in the published manuscript.

The integration of seawater in the solvent extraction of copper was investigated. Accordingly, two oxime derivatives extractants, Acorga M5774 (ester-modified C_9 aldoxime) and LIX 984N diluted in kerosene were used in extraction of copper from a sulfate–chloride solution containing seawater [105]. The results showed a higher concentration of copper in the pregnant leach solution (PLS) as a result of using seawater; however, the concentration of Fe and the impurities that are associated with seawater, that is, Cl, Na, Mg, Ca, K were also increased. At pH 2, and using LIX 984, Acorga M5774 alone or the mixture of both extractants at 15% v/v, there was little effect on copper extraction, around 90%, with solutions containing 0–40 g/L chloride ion. Note: again, there was not information in the manuscript about copper stripping.

A mixture of TBP and P507 extractants diluted in kerosene was proposed for the separation of molybdenum and tungsten from iron in a hydrochloric-phosphoric acid solutions coming from the hydrochloric acid pre-leaching of low-grade scheelite [106]. From the various extractants accompanying to TBP, P507 showed synergistic effects on Mo and W extraction and a strong antagonistic effect on Fe extraction (Table 10). Decreasing the aqueous acidity from 1.6 to 1 M, the percentage of Mo and W extraction decreased, and also the values of the separation factors Mo/Fe and W/Fe; the same decreasing effect was observed with the increase of the A/O ratio from 1 to 6. After two-stage batch continuous extraction, 99% Mo, 94% W and 10% Fe were extracted. By washing with 2 M hydrochloric acid, most of the Fe and other impurities were removed with negligible losses of Mo and W. Upon stripping with 5 M ammonia at a 1:1 organic-to-aqueous phase ratio, almost quantitative concentrations of Mo and W were recovered from the organic phase.

Table 10
Extraction of Mo, W and Fe using various extractants

Organic phase, v/v	% Mo	% W	% Fe
20% TBP	55	80	5
40% TBP	80	90	50
20% TBP + 20% P507	95	90	10
20% TBP + 20% P204	90	70	45
20% TBP + 20% N1923	90	>95	>95

[H⁺]: 1.7 M; A/O ratio: 1; time: 10 min; temperature: 15°C.

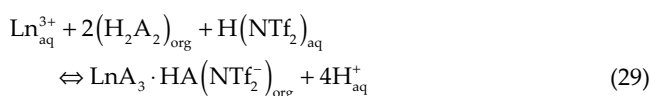
P507: phosphonic ester; P204: phosphoric acid; N1923: primary amine.

Zinc(II) was recovered from dilute ammoniacal medium using a process combining solvent extraction and electrolysis with ammonia stripping [107]. Zinc was firstly loaded into the organic phase at pH 7.56 through synergistic extraction between a β -diketone and TBP or Cyanex 923, the organic phases were diluted in kerosene. Using both mixtures, the extraction of zinc followed the same pattern: (i) increasing extraction from pH 6 to 7.5, (ii) decreasing extraction from pH 7.5 to pH 10 and (iii) increasing extraction from pH 10 to 12. Quantitative results differed, as the mixture of the β -diketone with Cyanex 923 showed extractions of 99.4% (pH 7.5), 49.7% (pH 10) and near 100% (pH 12), whereas with the mixture with TBP the results were of 75.3 (pH 7.5), 2.8% (pH 10) and near 100 (pH 12). Thus, the mixture β -diketone–Cyanex 923 appeared to be more appropriate for zinc extraction in the pH range of 6–12. Stripping was accomplished with ammoniacal solution 2–4 M; in the stripping operation the results were the reversal to these obtained in extraction: (i) with the system β -diketone–TBP, zinc was more easily stripped than in the Cyanex 923 system, (ii) the pattern was the same, increase of zinc stripping from pH 8 to pH 9.25, and decreasing again until pH 10.5, and (iii) the effectiveness using 4 M ammonia solution was greater than when 2 M solution was used. The extraction and ammonia stripping isotherms verified that Zn(II) concentration can be increased from 1.3 g/L to more than 56 g/L by using the β -diketone and Cyanex 923 mixture of extractants. Metallic zinc can be obtained by direct electrolysis from the ammoniacal stripping solution.

A solvent extraction procedure using a mixture of LIX 84-I and TBP reagents had been investigated for the separation of copper from nickel in the ammoniacal leach solutions of ABS plastic waste [108]. The interaction between LIX 84-I and TBP decreased the availability of extraction sites of LIX 84-I and increasing the bulky alkyl groups in the organic phase, the above had negative effects on nickel extraction, favoring the separation copper–nickel. The increase of ammonia concentration in the 2–5 M range, decreased copper extraction. Four counter-current stages at operational conditions of 0.5 M LIX 84-I + 0.5 M TBP, A/O ratio of 1.3 and 25°C was needed for the selective extraction of copper from real solution of ABS plastic waste (Cu = 8.14 g/L and Ni = 2.57 g/L). Loaded ammonia into the organic phase was scrubbed with a solution of pH 2 (sulfuric acid), and copper was stripped with 1 M sulfuric acid solution. Note: accordingly with the authors of this investigation, TBP did not form part of the

copper complex in the organic phase. Its usefulness was just to decrease nickel extraction.

The synergistic solvent extraction of lanthanides(III), from amide acid medium, with a mixture of di-(2-ethylhexyl)phosphoric acid (H_2A_2 as a dimer) and monoisodecyl phosphoric acid (MIDPA, H_2B_2 also in dimer form) in a phosphonium-based ionic liquid was investigated [109]. In the case of organic solutions containing only D2EHPA or MIDPA extractants, Ln(III) (Ln = Pr and Nd) was extracted as $[LnA_3HA]$ or $[LnB_3HB]$, respectively. In the case of organic phases formed by DEHPA in the ionic liquid ($[P_{2225}][NTf_2]$), the extraction equilibrium was represented by:



When MIDPA was used instead of DEHPA, the formed species were similar than in the case of using the phosphoric acid. If both reagents DEHPA and MIDPA were used together, the extraction equilibrium can be represented as:

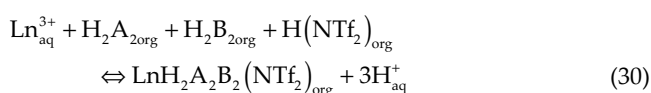


Table 11 summarizes the separation of these rare earths at various pH values of the feed solution. The process carried out on Nd-Fe-B powder consisted in the next steps:

- leaching in 1 M $H[NTf_2]$ at 343 K and 48 h,
- removal of iron using oxygen gas,
- solvent extraction with the mixture of the extractants in the ionic liquid, resulting in a raffinate rich in Nd and an ionic liquid phase rich in Dy, which was recovered as metal using an electrodeposition procedure. Note: no mention of how Nd was recovered from the raffinate, and also the fate of others rare earths (Pr, Tb) presented in the leachate.

Three-component biphasic solvent system (1:1:1) consisting of water, hexane, and isopropyl alcohol was tested for the extraction of lanthanides(III), from chloride and nitrate media, by adding different extractants to the system [110]. Bis(2-ethylhexyl)phosphoric acid (D2EHPA) and mixtures of ionic liquids (IL) dissolved in hexane were investigated as extractants. Results showed that the extraction efficiency of Ln(III) with D2EHPA increases with the addition of sodium acetate or a mixture of CH_3COONa and CH_3COOH .

Table 11
Influence of the pH on lanthanides separation factors

pH	Dy/Tb	Dy/Nd	Dy/Pr	Tb/Nd	Tb/Pr	Nd/Pr
0.19–0.21	0.78	2.45	2.51	3.13	3.22	1.03
0.29–0.31	0.73	2.97	2.90	4.09	4.00	0.98
0.39–0.41	1.08	3.90	4.98	3.60	4.58	1.28

Feed phase: 1×10^{-3} M Ln(III) in 1 M $[NTf_2]$; organic phase: 5×10^{-2} M DEHPA and 5×10^{-2} MIDPA in $[P_{2225}][NTf_2]$.

Table 12
Uses of solvent extraction technology (2020–2021) in the recovery of metals from various sources

Metal	Source
Cobalt and manganese	Zinc plant residue, batteries
Rare earths	Magnets, batteries, ores, shale, coal fly ashes, catalysts
Copper	Acid mine drainage, low grade copper sulfide ore, waste PCBs, fly ash
Vanadium	Catalysts, slags, titanium waste liquid
Cobalt	Spent ternary cathodes
Lithium	Phosphate solutions, batteries, brines, lepidolite
Silver and palladium	Capacitors, catalysts
Silver, gold and PGMs	Waste PCBs
Titanium, iron	Red mud
Nickel	Batteries, fly ash
Cadmium	Fly ash
Gold and silver	Ore
Tungsten, lanthanum and molybdenum	Scheelite mineral
Uranium and thorium	Xenotime concentrate, coal and by-product, ores
Niobium and tantalum	Columbo-tantalite concentrate
Indium	Electronic wastes
Zirconium	High-level liquid waste
Zinc, cobalt and manganese	Spent pickling solution, hot filter cake
Zinc, aluminium, copper, cobalt and manganese	Acid mine drainage
Scandium	Waste titanium production
Chromium	Rinsed electroplating wastewater

Effective separation of Ln(III) was observed by using a mixture of trioctylammonium di(2-ethylhexyl)phosphate and dicyclohexylammonium caprylate (2:1), whereas by using a mixture of trioctylammonium caprylate and dicyclohexylammonium di(2-ethylhexyl)phosphate (2:1) the Ln(III) separation did not occur. Note: no stripping information was included in the published manuscript.

The synergistic solvent extraction of Cr(VI) from rinsed electroplating wastewater was investigated using a mixture of two organophosphorus acidic extractants: bis-2,4,4-trimethylpentyl phosphinic acid (Cyanex 272) and bis-2,4,4-trimethylpentyl mono-thio-phosphinic acid (Cyanex 302) in kerosene [111]. The aqueous feed phase contained 0.043 g/L Cr(VI) at pH 3; the results showed that near quantitative Cr(VI) was synergistically reduced and extracted to the less toxic trivalent chromium a mixture concentration of 0.1 M (0.04 M Cyanex 272 + 0.06 M Cyanex 302). Cr(III) was stripped with a 7.0 M HCl solution. Note: in the range of chromium concentration in the feed phase, chromium(VI) was presented in the aqueous phase as HCrO_4^- and not as dichromate as mentioned the authors of the original paper along the manuscript and specially in Table 2 and Eqs. (5) and (6) of such publication. Also, the reduction of Cr(VI) to Cr(III) was at the cost of Cyanex 302, however, no mention about the regeneration of this reagent to its original $\text{R}_2\text{P}(\text{S})\text{OH}$ formulation was given in the published work.

A solvent extraction process was used to extract the metal species from the zinc hot filter cake (HFC) leach solution [112]. This HFC contained (w/w basis): 21.4% Zn, 0.55% Co and 8.3% Mn. First, Zn(II) was extracted up to 96% from the solution by CYANEX 302 (H_2A_2) diluted in kerosene at 25°C, O/A ratio of 1:1 and pH of 2.5. The extracted species presented $\text{ZnA}_2(\text{HA})$ stoichiometry. After Zn(II) extraction, manganese was separated from cobalt using a mixture of DEHPA (H_2R_2) and TBP (1:1 ratio) in kerosene. Around 96.6% of Mn(II), at an equilibrium pH of 4, was extracted using the extractants mixture; in this case, the extracted species presented $\text{MnR}_2 \cdot 2\text{HR}$ TBP stoichiometry. With Zn(II) and Mn(II) separated, a pure Co(II) solution remained in the aqueous phase. Note: no stripping details were given in the manuscript.

3. Conclusions

Solvent extraction technology showed its full potential as a separation-recovery technology for metals coming from very different sources, Table 12 resumes most of the findings from the present review. Besides the traditional use of solvent extraction in the production of a series of metals, for example, copper, nowadays and in the next future, solvent extraction will play a key role in one of the most important source for the recovery of some metals (rare earths, niobium, tantalum, gold, indium, PGM, etc.) as it is being urban mining, and also in the recycling of a variety of elements which occupied the daily life, being probably, the treatment of e-car batteries one of the most popular research issues. However, many of the proposed processes, as occurred in most of the literature reviewed here, are just probed in the laboratory scale, thus, their practical potential are still a chimera. Truly, the future of solvent extraction applied on the recovery of metals is alive.

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