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An environmentally friendlier approach to hydrometallurgy: highly selective separation of cobalt from nickel by solvent extraction with undiluted phosphonium ionic liquids

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A green solvent extraction process for the separation of cobalt from nickel, magnesium and calcium in chloride medium was developed, using undiluted phosphonium-based ionic liquids as extractants. Cobalt was extracted to the ionic liquid phase as the tetrachlorocobaltate(II) complex, leaving behind nickel, magnesium and calcium in the aqueous phase. Manganese is interfering in the separation process. The main advantage of this ionic liquid extraction process is that no organic diluents have to be added to the organic phase, so that the use of volatile organic compounds can be avoided. Separation factors higher than 50 000 were observed for the cobalt/nickel separation from 8 M HCl solution. After extraction, cobalt can easily be stripped using water and the ionic liquid can be reused as extractant, so that a continuous extraction process is possible. Up to 35 g L^{-1} of cobalt can be extracted to the ionic liquid phase, while still having a distribution coefficient higher than 100. Instead of hydrochloric acid, sodium chloride can be used as a chloride source. The extraction process has been upscaled to batch processes using 250 mL of ionic liquid. Tri(hexyl)tetradecylphosphonium chloride, tri(butyl)tetradecylphosphonium chloride, tetra(octyl)phosphonium bromide, tri(hexyl)tetradecylphosphonium bromide and Aliquat 336 have been tested for their performance to extract cobalt from an aqueous chloride phase to an ionic liquid phase. Tri(hexyl)tetradecylphosphonium chloride (Cyphos IL 101) turned out to be the best option as the ionic liquid phase, compromising between commercial availability, separation characteristics and easiness to handle the ionic liquid.

Introduction

Liquid-liquid extraction (solvent extraction) is a very important technique for metal ion separations, both on a laboratory scale (sample preparation prior to chemical analysis) and on an industrial scale (hydrometallurgical processes for extraction and purification of metals).¹⁻⁴ Solvent extraction offers several advantages over competing techniques, such as ion-exchange processes. Advantages include the ability to operate in a continuous mode, to employ only relatively simple equipment and small quantities of reagents, and to achieve a high sample throughput. The method is very flexible because the extraction process can be tailored by a suitable choice of the process parameters, e.g., the nature and concentration of the extractants, the composition of the aqueous and organic phase, etc. The traditional liquid-liquid extraction process makes use of water-immiscible organic solvents, many of which are flammable, volatile or toxic. Examples of solvents are kerosene, dodecane, toluene, dichloromethane,

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chloroform and diethyl ether. The growing awareness of safety and environmental impact related with the use of these organic solvents renders their replacement with less noxious alternatives desirable. There is presently an increasing research activity in the field of the development of sustainable separation processes, including those based on ionic liquids.⁵⁻¹⁰ Ionic liquids (ILs) are solvents that consist entirely of ions.¹¹⁻¹⁴ Typically, they are organic salts with a melting point below 100 °C. Major advantages of ionic liquids for application in solvent extraction processes are their low volatility and low flammability. In 1998, Rogers and co-workers were the first to suggest that ionic liquids may be suitable as the basis for novel liquid-liquid extraction processes.¹⁵ They demonstrated that a variety of ionisable and non-ionisable aromatic molecules are transferred from water into the ionic liquid $[C_6 mim][PF_6]$, with distribution ratios of more than 1000 in some cases, e.g., for the extraction of 4,4'dichlorobiphenyl.

Although ionic liquids have proved to be interesting and useful solvents for the extraction of neutral organic compounds, including natural products, the high expectations have only been partially met in the case of application of ionic liquids for solvent extraction of metal ions. First of all, the transfer of hydrated metal ions from an aqueous phase to a hydrophobic ionic liquid phase is unfavourable, so that extractants have to be

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used. The mechanisms for extraction of metal ions into ionic liquids are in many cases different from what is observed for extraction into molecular solvents. The main problem is that extraction of metal ions from an aqueous phase into an ionic liquid phase often takes place via an ion-exchange mechanism.^{16,17} This means that upon extraction ionic liquid components are solubilised in the aqueous phase. Ionic liquid cations are lost during extraction of a metal ion with a neutral extractant such as a crown ether, whereas ionic liquid anions can be lost during extraction of anionic metal complexes. These losses of ionic liquid by solubilisation in the aqueous phase are a serious problem that hampers the general application of ionic liquids for liquid-liquid extraction processes.¹⁸ Although these losses of ionic liquid can be reduced by structural variation of the ionic liquid, e.g., by increasing the alkyl chain length or fluorination of the alkyl chain, these modifications often have a negative effect on the distribution ratios and the extraction efficiency.¹⁹ Because water-immiscible ionic liquids are required for solvent extraction, the choice of the ionic liquid is limited to hydrophobic ionic liquids.²⁰ These ionic liquids often contain fluorinated anions, such as the hexafluorophosphate (PF_6) or the bis (trifluoromethylsulfonyl)imide (Tf_2N^-) anion.²¹ Fluorinated ionic liquids are quite expensive, so that the use of ionic liquids for classic solvent extraction processes cannot be justified from an economical point of view, especially not because the advantages of ionic liquids for these applications are limited to their low volatility and flammability. Moreover, there are concerns about the toxicity of these ionic liquids and hexafluorophosphate anions are not stable against hydrolysis.²² Examples of nonfluorinated ionic liquids that are not miscible with water are Aliquat 336²³ and tri(hexyl)tetradecylphosphonium chloride (Cyphos[®] IL 101).²⁴ Although these ionic liquids have been used in solvent extraction studies of metal ions, they are never applied in a pure state, but they are dissolved in diluents such as toluene or kerosene.²⁵⁻³¹ The diluents largely decrease the viscosity of the organic phase and thus accelerate the kinetics of the solvent extraction process, but the diluents are also volatile organic solvents. Therefore, the advantages of using ionic liquids for solvent extraction are lost. The diluents can be omitted by impregnating a solid support with the ionic liquid, but this practice has often a negative effect on the capacity of the ionic liquid for separation of metal ions.^{32,33} Ionic liquids with non-fluorinated anions have also been used for the dissolution of metal oxides or for the leaching of metals from ores or industrial waste products.34-39

In this paper, we show that an efficient solvent extraction process for the separation of cobalt and nickel from a chloride medium can be developed by using phosphonium ionic liquids. The separation of cobalt and nickel by solvent extraction is an important industrial hydrometallurgical process.^{40–49} In our method, the phosphonium ionic liquid acts as an undiluted extractant. No addition of volatile organic solvents to the organic phase is required. The optimum extraction parameters have been determined. With separation factors higher than 50 000, this solvent extraction process is more efficient than industrial processes currently in use. The process has been scaled up to 250 mL batches of ionic liquid. Attention has been paid to the stripping of cobalt from the ionic liquid phase and to the recycling of the ionic liquid.

Experimental

Chemicals

Tri(hexyl)tetradecylphosphonium chloride (>97%) (Cyphos[®] IL 101) was purchased from Cytec Industries Inc. (Niagara Falls, Ontario, Canada). Tri(butyl)tetradecylphosphonium chloride (>95%), tetra(octyl)phosphonium bromide, tri(hexyl)tetradecylphosphonium bromide were purchased from IoLiTec (Heilbronn, Germany) and Aliquat 336 was obtained from Fluka (Sigma-Aldrich Co, Bornem, Belgium). $CoCl_2 \cdot 6H_2O$ (>97%), MnCl₂·4H₂O (>99%) and MgCl₂·6H₂O (>99%) were purchased from Merck (Overijse, Belgium), NiCl₂·6H₂O (>99%) and CaCl₂·2H₂O (>98%) were purchased from VWR (Leuven, Belgium). Hydrochloride solutions were prepared from HCl (Selectipur VLSI, 36% BASF) and demineralised water. Potassium oxalate monohydrate was purchased from ACROS Organics (Geel, Belgium). All chemicals were used as received, without further purification.

Instrumentation and analysis methods

The water content of the ionic liquid after the extraction was determined with a Mettler Toledo DL 39 Karl Fischer Coulometer. The viscosity was measured using a falling ball type viscosimeter (Gilmont Instruments). Absorption spectra were measured with a Varian Cary 5000 spectrophotometer. A quartz cuvette with an optical path length of 0.1 mm was used. The HCl concentration of the organic phases after extraction was determined by a titration method. A solution of potassium oxalate (0.15 M, 100 mL) was prepared. An additional portion of 2 g of solid potassium oxalate was added to ensure an excess of oxalate. The solution was stirred and the pH was adjusted to a value of 5.75 to 6 with HCl (1 N). The solution of the sample (1 mL) was added to the oxalate solution to avoid precipitation of Co(OH)₂ and titrated with sodium hydroxide (0.2 N) until the original pH value was reached. The metal contents of the aqueous and organic phases after extraction for the lab scale experiments were determined using a bench top total reflection X-ray fluorescence (TXRF) spectrometer (Picofox S2, Bruker). For analysis of the aqueous phase by TXRF, aqueous samples (1 mL) were measured after addition of gallium as an internal standard. The samples were diluted with MilliQ50 water (if necessary). A small aliquot of 10 µL (solution) was applied on a quartz glass carrier, dried by evaporation in a hot air oven (80 °C) and measured with a measurement time of 200 s. For the determination of the metal content in an organic phase by TXRF, a certain weight of the extracted phase $(\pm 0.5 \text{ g})$ was diluted in dioxane (20 mL). Gallium was added to the solution as an internal standard. A small aliquot of 5 µL solution was applied on a quartz glass carrier, dried by evaporation in a hot air oven (60 °C) and measured with a measurement time of 400 s. The metal contents of the aqueous and organic phases after extraction for the batch scale experiments were determined using ICP-OES (Varian Vista Pro). For analysis of the aqueous phase by ICP-OES, the samples were diluted in 10 vol.% HCl. A calibration curve was prepared for the concentration range for $0-10 \text{ mg L}^{-1}$ and scandium was used as an internal standard. The spectra were measured with a power of 1.4 kW, an argon

flow of 15 L min⁻¹ and an auxiliary flow (Ar) of 1.5 L min⁻¹. For analysis of the organic phase by ICP-OES, the organic samples were decomposed with a mixture of H_2SO_4 and HNO_3 in a quartz beaker on a heating plate. H_2SO_4 and HNO_3 were evaporated and the residue was dissolved in 10 vol.% HCl before measurement as described for aqueous solutions. The total carbon content (TOC) was measured using a Shimadzu TOC-VWP TOC analyzer. The organic carbon was converted to CO_2 by addition of an oxidizing acidic solution (60 g of $Na_2S_2O_8$ and 15 mL of H_3PO_4 (85%) in 500 mL of water) in a heated UV reactor (80 °C). The formed CO_2 was carried *via* a carrier gas flow (N₂, 200 mL) to a non-dispersive infrared detector, where CO_2 was measured. A calibration curve was prepared to relate the detector signal to the CO_2 concentration and hence to the corresponding carbon concentration of the sample.

Small-scale extraction experiments

To determine the distribution coefficients as a function of the cobalt concentration present in the feed solution, an aqueous solution of Co(II) with a hydrochloric acid content of 8 M containing CoCl₂·6H₂O with the desired metal concentration (5 to 50 g L^{-1}) was prepared and tri(hexyl)tetradecylphosphonium chloride was used as extraction phase. 5 mL of the aqueous solution and 5 mL of the ionic liquid phase were stirred for 10 min at 60 °C. The cobalt concentration in the aqueous phase was analysed. For the extraction at a 4 M sodium chloride concentration, an aqueous solution containing CoCl₂·6H₂O and NiCl₂·6H₂O (at a concentration of 5 g L^{-1}) and with a NaCl content of 4 M was prepared. Tri(hexyl)tetradecylphosphonium chloride was used as the extraction phase. 5 mL of the aqueous solution and 5 mL of the ionic liquid phase were stirred for 10 min at 60 °C. The metal content of both phases was analysed after centrifugation (3000 rpm, 10 min). To test the performance of the ionic liquids tri(butyl)tetradecylphosphonium chloride, tetra(octyl)phosphonium chloride, tri(hexyl)tetradecyl phosphonium bromide and Aliquat 336 for the extraction of cobalt and nickel, an aqueous 8 M HCl solution containing CoCl₂·6H₂O and NiCl₂·6H₂O (with a metal concentration of 5 g L^{-1}) was prepared. 5 mL of the aqueous solution and 5 mL of the ionic liquid phase were stirred for 10 min at 60 °C. The metal content of both phases was analysed after centrifugation (3000 rpm, 10 min).

Batch-scale extraction experiments

Extraction batch test 1: An aqueous solution of Co(II) and Ni(II) with a metal concentration of 5 g L^{-1} was prepared from CoCl₂·6H₂O and NiCl₂·6H₂O in 8 M HCl. The aqueous solution (250 mL) was poured in a jacketed reactor vessel (500 mL) and the liquid extraction reagents tri(hexyl)tetradecylphosphonium chloride (250 mL) was added. After intensively stirring at 1040 rpm for 10 min at 60 °C, equilibrium was reached and the phases were allowed to settle. Both phases were analyzed for their metal content after centrifugation (3000 rpm, 10 min).

Extraction batch test 2: An aqueous solution of 8 M HCl (250 mL) was poured in a jacketed reactor vessel (500 mL) and the ionic liquid extractant tri(hexyl)tetradecylphosphonium

chloride (250 mL) was added. Equilibrium was reached after intensively stirring at 1040 rpm for 10 min at 60 °C and the phases were allowed to settle. After phase separation, the organic phase (now loaded with water and hydrochloride) was reused as extraction phase and an extraction was performed, as described for extraction batch test 1 (see above). The metal content of the two phases was analysed after centrifugation (3000 rpm, 10 min).

Extraction batch test 3: An aqueous 8 M HCl solution containing CoCl₂·6H₂O, NiCl₂·6H₂O, MnCl₂·4H₂O, CaCl₂·2H₂O, and MgCl₂·6H₂O with a metal concentration of 5 g L⁻¹ was prepared. The aqueous solution (500 mL) was poured in a jacketed reactor vessel (1 L) and the extraction phase tri(hexyl)tetradecylphosphonium chloride (500 mL) was added. Equilibrium was reached after intensively stirring at 1040 rpm for 10 min at 60 °C and the phases were allowed to settle. The metal content of the two phases was analysed after centrifugation (3000 rpm, 10 min).

Stripping conditions: Water (40 mL) as the stripping phase was poured in a jacketed reactor vessel (250 mL), and the extraction phase from extraction batch test 2 containing Co(II) (circa 5 g L⁻¹, 80 mL) was added. After intensive stirring at 1040 rpm for 10 min at 60 °C, the phases were allowed to settle. The cobalt concentration in the aqueous phase was measured after centrifugation (3000 rpm, 10 min). The organic phase was recycled after each stripping step and reused until no residual cobalt could be detected in the ionic liquid phase.

Distribution coefficients and separation factor

The distribution coefficient for cobalt D_{Co} was calculated as follows:

$$D_{\rm Co} = \frac{[\rm Co]_0 - [\rm Co]_{aq}}{[\rm Co]_{aq}} \tag{1}$$

where $[Co]_0$ is the initial cobalt concentration in the aqueous phase before extraction and $[Co]_{aq}$ is the cobalt concentration in the aqueous phase after the extraction. Distribution coefficient for nickel D_{Ni} was calculated using the following equation:

$$D_{\rm Ni} = \frac{[\rm Ni]_{\rm org}}{[\rm Ni]_0 - [\rm Ni]_{\rm org}}$$
(2)

where $[Ni]_0$ is the initial nickel concentration in the aqueous phase before extraction and $[Ni]_{org}$ is the nickel concentration in the organic phase after the extraction. The efficiency of separation of cobalt from nickel is described by the separation factor β :

$$\beta_{\rm Ni}^{\rm Co} = \frac{D_{\rm Co}}{D_{\rm Ni}} \tag{3}$$

The distribution coefficient for manganese (D_{Mn}) is defined in a way similar to that of cobalt (eqn (1)), whereas the distribution coefficients for calcium (D_{Ca}) and magnesium (D_{Mg}) were defined in a way similar to that of nickel (eqn (2)).

Results and discussion

Tri(hexyl)tetradecylphosphonium chloride (Cyphos[®] IL 101 or $P_{66614}Cl$) was selected for the extraction experiments with cobalt





Fig. 1 Structure of tri(hexyl)tetradecylphosphonium chloride (P₆₆₆₁₄Cl).

and nickel, because it is a room-temperature ionic liquid and because it is one of the few examples of non-fluorinated ionic liquids that are largely immiscible with water (Fig. 1). Moreover, this ionic liquid is commercially available and has no surfactant properties, in contrast to quaternary ammonium and phosphonium salts with one long alkyl chain and three short alkyl chains. The absence of surfactant properties enhances the phase separation after mixing of organic and aqueous phase. Although cobalt is often extracted from sulphate medium, it was decided to switch to chloride medium to have in the aqueous and ionic liquid phase the same anion. Cobalt(II) chloride hexahydrate (CoCl₂·6H₂O) was used as the cobalt source, and nickel(II) chloride hexahydrate (NiCl₂·6H₂O) as nickel source. Typically, the extraction experiments were performed at 60 °C to reduce the viscosity of the ionic liquid phase. Phosphonium ionic liquids are known to be very viscous at room temperature.^{50,51}

In a first series of experiments, the optimal chloride concentration was determined by varying the HCl concentration of the feed solution. It was found that the extraction efficiency of cobalt increases with increasing chloride concentration, with a maximum at a chloride concentration of 8 M (Fig. 2). This decrease in efficiency of extraction of cobalt(II) at high HCl concentration has also been observed by other authors for extraction of cobalt(II) by quaternary ammonium salts.⁵² This behaviour is attributed to the extraction of the excess HCl, probably in the form of the hydrogen dichloride ion, [HCl₂]^{-.53} The extracted cobalt(II) species is the tetrahedral tetrachlorocobaltate(II) complex, $[CoCl_4]^{2-}$. This species was identified by optical absorption spectroscopy in the aqueous phase and in the ionic liquid phase, on the basis of its typical absorption spectrum (Fig. 3). The absorption band in the visible region with different submaxima, due to the spin orbit coupling, can be assigned to the ${}^{4}T_{1g}(P) \leftarrow {}^{4}A_{2}$ transition. ^{54,55} The molar absorptivity ε values are in the typical range for tetrahedral cobaltate(II)



Fig. 2 Distribution coefficient of cobalt(II) as a function of the HCl concentration.



Fig. 3 Absorption spectrum of the ionic liquid phase after extraction, containing bis(tri(hexyl)tetradecylphosphonium) tetrachlorocobaltate(u). The absorption spectrum is typical for the $[CoCl_4]^{2-}$ anion.

complexes, with values ranging between 10^2 and 2×10^3 L cm⁻¹ mole⁻¹. These absorptivity values are clearly distinct from the values for octahedral cobalt(II) complexes, which range between 5 and 40 L cm⁻¹ mole⁻¹ for the ${}^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}$ transition. The $[CoCl_4]^{2-}$ ion is also found upon dissolution of anhydrous CoCl₂ in the ionic liquid 1-butyl-3-methylimidazolium chloride.⁵⁶ Ionic liquids with the $[CoCl_4]^{2-}$ have been described in the literature.^{57,58} The extraction mechanism of cobalt to the ionic liquid phase can be described as an anion exchange mechanism, in which the $[CoCl_4]^{2-}$ complex which is present in the aqueous phase at high chloride concentrations is extracted into the ionic liquid phase. During the extraction process, for every $[CoCl_4]^{2-}$ unit extracted to the ionic liquids phase, two chloride ions are released from the ionic liquid phase to the aqueous phase:

$$\operatorname{CoCl}_4]^{2-} + 2\overline{[P_{66614}]Cl} \to \overline{[P_{66614}]_2[\operatorname{CoCl}_4]} + 2Cl^- \quad (4)$$



Fig. 4 Distribution coefficient of nickel(II) as a function of the HCl concentration.

 Table 1
 Results of the extraction after extraction batch tests 1 and 2

	Batch test 1	Batch test 2^a
$ \frac{[\text{Co}]_{\text{aq}} (\text{mg L}^{-1})}{[\text{Ni}]_{\text{org}} (\text{mg L}^{-1})} D_{\text{Co}} D_{\text{Ni}} \beta_{\text{Ni}}^{\text{Co}} $	11 (±0.5) 44 (±2.7) 460 (±21) 0.0088 (±0.0006) 52 000 (±2800)	$14 (\pm 1.4) \\ 43 (\pm 3.6) \\ 360 (\pm 32) \\ 0.0087 (\pm 0.0007) \\ 41 000 (\pm 3300)$

^a Using an ionic liquid phase, saturated with water and HCl.

where the bars denote species in the organic (ionic liquid) phase. The extraction efficiency of nickel(II) linearly increases with increasing chloride concentration, but the absolute values of the distribution coefficient remain low (Fig. 4). The highest selectivity between cobalt and nickel was obtained at 8 M HCl concentration.

A batch extraction experiment with 250 mL of ionic liquid was performed with an aqueous 8 M HCl solution containing a mixture of cobalt and nickel (both at 5 g L^{-1}) (extraction batch test 1). The cobalt concentration in the aqueous phase, nickel concentration in the organic phase after extraction, the distribution coefficients and separation factor are given in Table 1. The data show that cobalt is preferentially extracted to the ionic liquid phase, while nickel remains in the aqueous phase. When the physical properties of the ionic liquid phase are compared before and after extraction (Table 2), it can be concluded that water and hydrochloric acid are partly co-extracted to the ionic liquid phase. This can be explained by the ionic nature of the ionic liquid, which attracts water molecules to their surroundings (solvation shell). The absorption of water by the ionic liquid is responsible for the sharp decrease in viscosity (from 280 to 101 cP at 60 °C) and makes the ionic liquid phase much easier to handle during the extraction process. Due to the extraction of water and HCl to the ionic liquid phase, the volume of the aqueous phase decreases. This change in volume can easily be prevented by saturating the ionic liquid with water and HCl before the extraction reaction. In extraction batch test 2, the ionic

Table 2 Physical properties of the ionic liquid before and after extraction batch test 1 (at $60 \text{ }^{\circ}\text{C}$)

	Before extraction	After extraction
Water content (wt%)	0.1	7.7
HCl content (wt%)	0	5.2
Viscosity (cP)	280	101
Density $(g m L^{-1})$	0.87	0.91
Phase separation time (s)		90

liquid phase was equilibrated by a 8 M HCl solution before the start of the extraction experiment (Fig. 5, Table 1). It should be realized that also in a continuous extraction process, the ionic liquid phase will be saturated by the acidic water solution. The physical properties of the ionic liquid before and after extraction are presented in Table 3. By using an ionic liquid phase saturated by the aqueous 8 M HCl solution, the ratio of the volumes of the aqueous and the ionic liquid phase remains constant. When these results are compared with the results of extraction batch test 1 (Table 1), a decrease in the distribution coefficients of cobalt is observed. Because ± 15 wt% less ionic liquid is present due to the absorption of water and HCl (±15 wt%), the concentration ratio between the ionic liquid and cobalt present in the feed solution decreases. This situation is actually the same as having 15% more cobalt in the feed solution. An experiment with 15% extra cobalt in the feed solution was carried out and this led to the same results. This result also agrees with the observation that the distribution coefficient decreases with increasing cobalt concentrations in the feed solution (see further).

When the extraction is performed with an aqueous feed solution containing besides cobalt and nickel also manganese, magnesium and calcium (extraction batch test 3), no good separation of cobalt and manganese could be obtained. Manganese is coextracted together with cobalt. Magnesium, calcium and nickel remain in the aqueous phase and can thus be separated from cobalt and manganese. To end up with a pure cobalt solution, manganese needs to be removed from the aqueous feed before the extraction step. Distribution coefficients for cobalt and the other elements are given in Table 4. Due to the higher viscosity of ionic liquids, compared to classical organic solvents, entrainment of ionic liquid in the water phase can be an issue. A higher viscosity can hinder the phase separation during settling. Loss of ionic liquid in the water phase needs to be avoided because of ecological and economic reasons. The total organic content was measured in the aqueous phase after extraction. The data show that only very small quantities of the ionic liquid are lost towards the aqueous phase. For instance, the concentration of the ionic liquid in the aqueous phase after extraction was only 4.2 mg L^{-1} for extraction batch test 1, <40 mg L^{-1} for extraction batch 2 and 11 mg L^{-1} for extraction batch test 3. Cobalt can be stripped from the ionic liquid phase by water. Four steps are required to strip the total cobalt content of the ionic liquid. The percentage of cobalt stripped from the ionic liquid is reported in Table 5. The stripping of cobalt is possible because water will wash the excess of chlorides from the ionic liquid phase, leading to transformation of the tetrachlorocobaltate(II) complex to the hexaaquocobalt(II) complex. After four stripping steps, no HCl remains in the ionic liquid phase and the ionic liquid phase



Fig. 5 Top: batch scale reactor before extraction batch test 2. Bottom: batch scale reactor after extraction batch test 2; (upper phase = ionic liquid). It is can be observed that cobalt(II) is extracted as the dark blue tetracobaltate(II) complex to the ionic liquid phase, while the green hydrated nickel(II) ions remains in the aqueous phase.

contains 15 wt% of water. This ionic liquid phase can be reused to extract a new load of cobalt from an aqueous solution. An

 Table 3
 Physical properties of the ionic liquid before and after extraction batch test 2, using an ionic liquid phase, saturated with water and HCl

	Before extraction	After extraction
Water content (wt%)	8.7	6.9
HCl content (wt%)	6.0	5.8
Viscosity (cP)	95	101
Density $(g m L^{-1})$	0.90	0.91
Phase separation time (s)		90

Table 4DistributioncoefficientsDforcobalt(II),nickel(II),manganese(II),magnesium(II),and calcium(II)

Element	D
Co	450
Ni	0.0062
Mn	30
Mg	0.0014
Ca	0.0056

 Table 5
 Percentage of cobalt that is stripped to aqueous phase

Stripping step	Amount of cobalt stripped (%)		
1	2.5		
2	28		
3	52		
4	17.5		
Total	100		

additional purification step can be done by scrubbing the ionic liquid phase with an aqueous solution of 8 M HCl to remove coextracted nickel from the ionic liquid phase.

The theoretical cobalt loading capacity of the ionic liquid is 50 g L^{-1} . In this case, all the chloride anions of the ionic liquid phase are completely converted into the tetrachlorocobaltate(II) anion. To compensate the double negative charge of this anion, two phosphonium cations are required. At higher cobalt concentrations longer stirring times are needed to reach equilibrium. This is shown in Fig. 6 where the distribution coefficient of cobalt was plotted as a function of stirring time when a feed solution of 30 g L^{-1} cobalt was used. The fact that longer stirring times are required can be explained by the increased viscosity due to higher cobalt concentration in the ionic liquid phase. The increase in viscosity with increasing cobalt concentration is shown in Fig. 7. To determine the distribution coefficients as a function of the cobalt concentration the following stirring times were used: 10, 20, 60 and 120 min respectively for cobalt concentrations of 5–15 g L⁻¹, 20–25 g L⁻¹, 30 g L⁻¹, 35–50 g L⁻¹. When the distribution coefficient of cobalt is plotted as a function of the cobalt concentration of the aqueous feed, the distribution coefficient of cobalt decreases with increasing cobalt concentration of the feed solution (Fig. 8). Since cobalt is present as the $[CoCl_4]^{2-}$ complex, more tetrachlorocobaltate(II) is loaded on the organic phase upon extraction. Because double charges have higher repulsive forces to each other than single charges there are more repulsive forces built up in the ionic



Fig. 6 Distribution function of cobalt as a function of time for a feed solution of 30 g L^{-1} cobalt.



Fig. 7 Viscosity of the ionic liquid phase after extraction at 60 $^{\circ}$ C as function of cobalt concentration in the feed solution.

liquid phase This will result in displacement of the doubly charged tetrachlorocobaltate(II) complex from the ionic liquid.

Other chloride sources instead of hydrochloric acid can be used for the selective extractions of cobalt. Another extraction was performed using sodium chloride as chloride source. First the optimal chloride concentration was determined by varying the NaCl concentration of the feed solution. At higher concentrations (5 M) sodium chloride is precipitating in the aqueous phase upon extraction. It was found that the extraction efficiency of cobalt and nickel are increasing with increasing chloride concentration. (Fig. 9). The highest separation for cobalt over nickel could be obtained with a concentration of 4 M NaCl. This is a quite low chloride concentration compared to the extraction with the feed solutions saturated by 8 M HCl. The reason for this can be found in the salting out effect. By using sodium chloride as chloride source, nickel will be pushed to the ionic liquid phase, but to a much lower extent than cobalt. A good separation of



Fig. 8 Distribution coefficient as a function of the cobalt concentration in the aqueous feed solution.



Fig. 9 Distribution coefficient of cobalt and nickel as a function of the sodium chloride concentration.

cobalt and nickel can still be obtained under these conditions. In Table 6 the extraction results using sodium chloride are shown. The advantage of using sodium chloride solutions over hydrochloric acid solution is that they are less aggressive media, cheaper and lower concentrations of chloride are needed.

Other phosphonium based ionic liquids can be used as extraction phases provided that they are largely immiscible with the aqueous phase. Three other phosphonium ionic liquids were tested for their extraction characteristics: tetra(octyl)phosphonium bromide ($P_{8888}Br$) and tri(butyl)tetradecylphosphonium bromide ($P_{44414}Cl$) and tri(hexyl)tetradecylphosphonium bromide ($P_{66614}Br$). These phosphonium ionic liquids were selected because of their hydrophobic nature and commercial availability. A disadvantage of the ionic liquids $P_{8888}Cl$ and $P_{44414}Cl$ is that they are solid at room temperature and re therefore more difficult to handle. The ionic liquid $P_{66614}Br$, where the chloride anion from Cyphos IL 101 is replaced with bromide, is liquid at room temperature. The results of the

$\begin{bmatrix} \text{Co} \end{bmatrix}_{\text{aq}} (\text{mg } \text{L}^{-1})$	$21 (\pm 3)$
$D_{\rm Co}$	$240 (\pm 29)$ 0 020 (+0 0010)
$\beta_{\rm Ni}^{\rm Co}$	12 000 (±1000)

Table 7 Extraction results for the separation of cobalt and nickel using different ionic liquids as the extractant phase

$\mathrm{P}_{8888}\mathrm{Br}$	P ₄₄₄₁₄ Cl	P ₆₆₆₁₄ Br	P ₆₆₆₁₄ Cl
11	180	11	11
23	300	39	44
450	27	450	460
0.0046	0.064	0.0078	0.0088
98 000	420	58 000	52 000
3.8	23.4	7.3	7.7

phosphonium extraction phase were compared with those of tri-(hexyl)tetradecylphosphonium chloride. From the results given in Table 7, when using P₈₈₈₈Br as the extraction phase, a separation factor of nearly 10^5 is achieved. When the water content in the organic phase is measured after extraction (Table 7), less water is extracted to the ionic liquid phase and less nickel ends up in the ionic liquid phase. P₈₈₈₈Br is a less polar ionic liquid, and therefore its hydrophobicity increases, leading to a lower uptake of water and better separation efficiency. When P₄₄₄₁₄Cl is used as the extraction phase poor separation efficiency for cobalt over nickel was observed compared to P66614Cl. The separation factor is 10^2 times lower. When the water content is measured after extraction, 23.4 wt% of water is extracted to the ionic liquid phase. The extraction of water is responsible for the decrease in separation efficiency between cobalt and nickel. With increasing water content more nickel was found in the ionic liquid phase and cobalt is extracted in a lower extend to the ionic liquid phase when less hydrophobic ionic liquids are used. With the third phosphonium ionic liquid, P₆₆₆₁₄Br, the extraction results are comparable to these of P₆₆₆₁₄Cl. Likewise the water content in the ionic liquid phase after extraction are comparable. However, for the industrial application of this process it is better to use the chloride ionic liquid because the ionic liquid can easily be generated after extraction, with the bromide ionic liquid this is much more difficult. In general other phosphonium ionic liquids could be used as extraction phase for the separation of cobalt from nickel. Enhanced extraction results are expected with increasing hydrophobicity. The performance of the phosphonium chloride Cyphos IL 101 and an ammonium ionic liquid Aliquat 336 as extraction phase for the separation of cobalt from nickel were compared. Both ionic liquids are commercially available. Recently, the nitrate version of Aliquat 336 has been used as the organic phase for the extraction of rare earths with the phosphine oxide extractant Cyanex 925.59 The extraction results are shown in Table 8. When Cyphos IL 101 is used as extractant instead of Aliquat 336 at 8 M HCl, the separation factor is at least 20 times higher. Using the phosphonium ionic liquid has thus superior extraction characteristics. This can be explained by the increased hydrophobicity of the phosphonium ionic liquid.

Table 8 Extraction results after extraction using Aliquat 336 and Cyphos IL 101 as extraction phase

	Aliquat 336	Cyphos IL 101	
$[Co]_{ac}$ (mg L ⁻¹)	60	11	
$[Ni]_{org}$ (mg L ⁻¹)	160	44	
D_{C_0}	80	460	
D _{Ni}	0.03	0.0088	
$\beta_{\rm Ni}^{\rm Co}$	2500	52 000	

Conclusions

Cobalt can selectively be separated from nickel, magnesium and calcium with solvent extraction using phosphonium-based ionic liquids as extraction reagents. A separation of factor of 5×10^4 . 8×10^4 , 3×10^5 is observed for Ni, Ca and Mg, respectively. After extraction cobalt can easily be stripped using water where four stripping steps are required to strip the total cobalt content. After stripping the ionic liquid can be reused as the extraction phase, which makes it possible to do the extraction in a continuous process. Up to 35 g L^{-1} of cobalt can be extracted to the ionic liquid phase while still having a distribution coefficient of more than 10^2 . Instead of hydrochloric acid, sodium chloride can be used as a chloride source. Phosphonium ionic liquids can be made more hydrophobic by lengthening the alkyl chains so that their miscibility with water will become negligible. An advantage associated with the use of (phosphonium) ionic liquids as the extraction phase is that volatile organic compounds are avoided and this offers a greener approach to solvent extraction. By doing extractions on a batch scale set-up, the practical implementation of ionic liquid as extraction phase has been proved. Three phosphonium and one ammonium ionic liquids were compared for their extraction capabilities where tri(hexyl)tetradecylphosphonium chloride in particular seems to be superior and the best option as ionic liquid phase as a compromise between commercial availability, separation characteristics and the ease to handle the ionic liquid. This work shows that fluorine-free ionic liquids cannot only be used for solid-liquid extraction and leaching of ores or industrial solid wastes, but also as undiluted organic phases in conventional liquid-liquid extraction for the separation of metal ions.

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