

COMMUNICATION

A continuous ionic liquid extraction process for the separation of cobalt from nickel

Cite this: *Green Chem.*, 2013, **15**, 3160

Received 29th July 2013,

Accepted 9th September 2013

DOI: 10.1039/c3gc41519h

www.rsc.org/greenchem

Sil Wellens,^{a,b} Remi Goovaerts,^b Claudia Möller,^b Jan Luyten,^b Ben Thijs^b and Koen Binnemans^{*a}

A continuous ionic liquid extraction process using the ionic liquid trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) has been developed for the selective extraction of cobalt from nickel. The performance of this continuous extraction process is competitive with that of currently applied industrial processes. Moreover, the elimination of volatile odorous compounds from the extraction phase leads to environmentally friendlier and healthier working conditions.

Introduction

Solvent extraction is one of the major hydrometallurgical techniques for the separation and purification of metals.¹ This technique has gained interest because it is possible to operate it in a continuous mode, with a high throughput and relatively simple equipment. In metal separation *via* solvent extraction a water-immiscible phase (extraction phase) is mixed with an aqueous solution containing metal ions. The metal ions are distributed between the two phases and the extraction phase is selectively enriched with one or more metals. The extraction phase contains three main components: an extractant, modifiers and a diluent. The extractant is the active species which transfers the metal ions between the two phases. Modifiers are added in order to improve the properties of the extraction phase. The diluent is an organic solvent, such as kerosene, dodecane, toluene, dichloromethane and diethyl ether, capable of dissolving the extractant. These solvents are toxic, flammable and/or volatile so that replacement of these volatile organic solvents with environmentally friendlier alternatives is a high priority, given the growing awareness of safety and environmental issues. Ionic liquids (ILs) are a possible alternative for the volatile solvents in the extraction phase, because ionic solvents are non-volatile and non-flammable.^{2,3} Ionic

liquids offer possibilities to make the hydrometallurgical process environmentally friendlier,^{4,5} and they have been investigated intensively for the extraction of metal ions.^{6–13} However, it has been shown that the ionic liquid anions and/or cations can be lost to the aqueous phase *via* an ion exchange mechanism.^{14–16} This makes the practical implementation of ionic liquids in solvent extraction difficult, both from an economical and an environmental point of view. Recently, we developed a more environmentally friendlier approach for the use of ionic liquids in solvent extraction processes, by a non-fluorinated ionic liquid playing the role of both the extractant and the diluent.¹⁷ More particularly, cobalt was selectively extracted from nickel present in an aqueous phase by using the ionic liquid trihexyl(tetradecyl)phosphonium chloride as the extraction phase, eliminating the volatile and flammable character of the extraction phase. This extraction system was also applied to the separation of iron from neodymium and of cobalt from samarium.¹⁸ These separations are relevant to recycling of rare earths from permanent magnets.¹⁹

It has been stated that the use of ionic liquids without diluents in solvent extraction processes is not practical at all, because of the high viscosity of the ionic liquid phase.²⁰ However, in this communication, we demonstrate that a continuous solvent extraction process for the separation of cobalt from nickel is possible using ionic liquids without organic diluents and that it could be competitive with current industrially applied processes after minor optimizations. To the best of our knowledge, the use of ionic liquids without organic diluents in a continuous solvent extraction process has not been described in the literature yet.

Experimental

Chemicals

Trihexyl(tetradecyl)phosphonium chloride (>97%) (Cyphos® IL 101) was purchased from Cytec Industries Inc. (Niagara Falls, Ontario, Canada). $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (>99%) were obtained from VWR (Leuven, Belgium). Hydrochloride

^aKU Leuven, Department of Chemistry, Celestijnenlaan 200F, bus 2404, B-3001 Heverlee, Belgium. E-mail: Koen.Binnemans@chem.kuleuven.be

^bUmicore, Group Research & Development, Competence Area Recycling and Extraction Technologies, Kasteelstraat 7, B-2250 Olen, Belgium

solutions were prepared from HCl (Selectipur VLSI, 36% BASF) and demineralised water. All chemicals were used as received without further purification.

Instrumentation and methods

The metal contents of the aqueous and organic phases were determined using ICP-OES (Varian Vista Pro). The chloride content was determined by potentiometric titration with AgNO_3 . The total carbon content (TOC) was measured using a Shimadzu TOC-VWP TOC analyzer. The sample preparation has been described earlier.¹⁷ Peristaltic pumps (Gilson mini-puls 3) (P1, P2, P4) and a plunger pump (CAT Labo pump – HPLH 200) (P3) were used to pump the solutions.

Experimental set up

15 L of a synthetic aqueous feed solution of Co(II) and Ni(II) with a metal concentration of 5 g L^{-1} for both metals was prepared from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 7.6 M HCl. The ionic liquid Cyphos[®] IL 101 (7 L) was presaturated with water (approximately 14 wt%) in order to keep the volume ratio of the phases constant and to decrease the viscosity of the ionic liquid phase. The ionic liquid feed was kept at a temperature of 60 °C. Five mixer-settler reactors (2.8 L) were placed in series (Fig. 1). The first reactor was filled with 1.25 L of cobalt–nickel feed, while all the other mixers were filled with 1.25 L of water. The ionic liquid was pumped (P₂) into the first reactor (MS₁) at a flow rate of 15 mL min^{-1} , while the phases were mixed. As soon as the reactor was filled, the aqueous feed solution was separately pumped (P₁) into the first mixer settler reactor at a flow rate of 14 mL min^{-1} . The start-up principle was maintained in a similar way for all other mixer-settlers. In the second reactor (MS₂), the pregnant ionic liquid was washed by pumping water (P₄) through it at a flow rate of 5.6 mL min^{-1} . In the following three mixer settlers (MS_{3–5}) the cobalt was stripped in counter current with water at a flow rate of 11.5 mL min^{-1} (P₃). All reactors were stirred at 700 rpm and the temperatures in the reactors were kept constant at 50 °C, using a heat-

conducting ribbon. After 16 hours of circulation, the water phase was analysed for the cobalt, nickel, chloride and TOC content. The ionic liquid phase was analysed for the cobalt and nickel content.

Results and discussion

Trihexyl(tetradecyl)phosphonium chloride, commercially known as Cyphos[®] IL 101, was selected as the extraction phase, both acting as a solvent and an extractant for the selective extraction of cobalt from nickel in chloride media, because of its specific properties: hydrophobic character, a melting point below room temperature, commercial availability, and the absence of fluorinated anions.²¹ This makes Cyphos[®] IL 101 an easily manageable, relatively cheap and environmentally friendly ionic liquid, which is suitable for use on an industrial scale. In an aqueous phase with high chloride concentrations, cobalt(II) will be present as an anionic tetrachlorocobaltate(II) complex (blue), whereas nickel(II) will be present as the hexaquo complex (green). The anionic tetrachlorocobaltate(II) complex is extracted to the ionic liquid phase, while the hydrated nickel(II) ion stays in the aqueous phase making it possible to separate cobalt from nickel with Cyphos[®] IL 101. The back extraction (or stripping) of cobalt from the ionic liquid is possible with water; water lowers the electrolyte concentration forcing cobalt to reform a hexaquo complex (pink).

The high viscosity of Cyphos[®] IL 101 (about 2500 cP at 20 °C)²¹ made the implementation in a continuous extraction process challenging. Both presaturating the ionic liquid with water and heating up the ionic liquid up to 60 °C reduced its viscosity (to about 100 cP)¹⁷ and made it manageable to transfer the highly viscous liquid through pumping. The experimental setup and all selected extraction parameters were carefully chosen on the basis of our previous work on the cobalt–nickel separation in a batch process.¹⁷ The actual setup is shown in Fig. 1 and the schematic representation of the



Fig. 1 Operational continuous extraction process for the separation of cobalt from nickel with the trihexyl(tetradecyl)phosphonium chloride ionic liquid (Cyphos[®] IL 101) as the extraction phase. The different stages are (from left to right): an extraction stage, a washing stage and three stripping stages in counter-current mode.

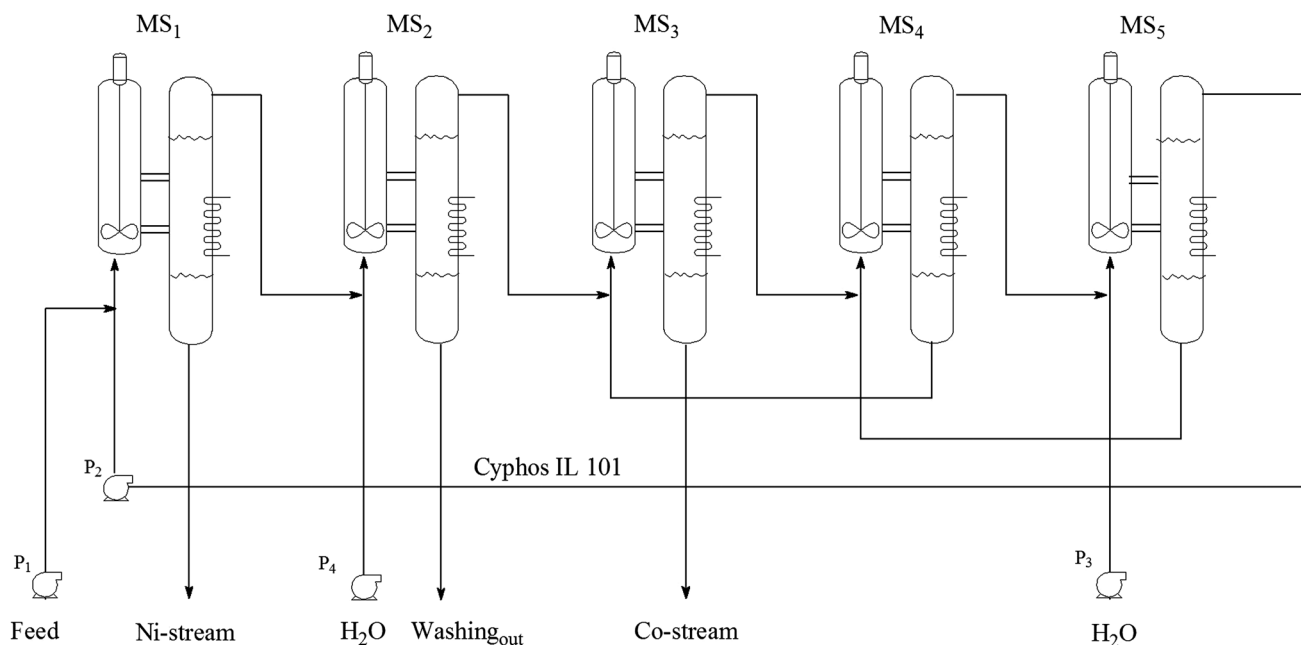


Fig. 2 Schematic representation of the continuous ionic liquid extraction process using the ionic liquid trihexyl(tetradecyl)phosphonium chloride, Cyphos[®] IL 101 (MS = mixer-settler; P = pump).

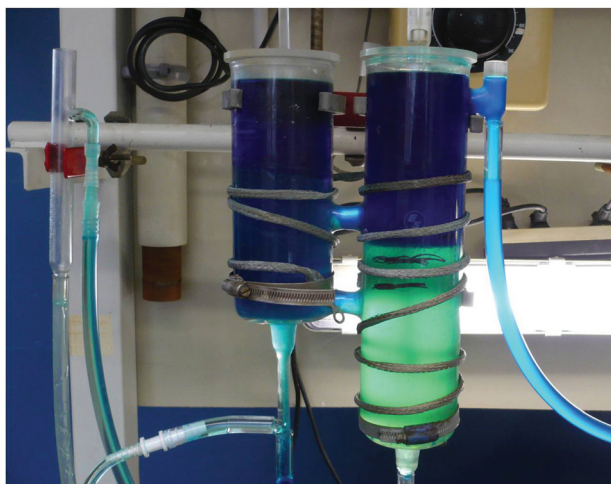


Fig. 3 Close-up of the first mixer-settler (MS_1 , not operational) in which the cobalt extraction takes place: mixing compartment (left) and phase-settling compartment (right).

continuous extraction process is shown in Fig. 2. The cobalt extraction takes place in the first reactor (MS_1), leaving nickel in the aqueous raffinate. A close-up of the first reactor is shown in Fig. 3. The ionic liquid loaded with cobalt is then washed in the second reactor (MS_2) and in the last three stages (MS_3 to MS_5) cobalt is stripped from the ionic liquid solutions using water in the counter-current mode, forming the cobalt raffinate. The regenerated ionic liquid is directly fed back to MS_1 to extract a new load of cobalt.

After 16 hours of continuous cycling, the cobalt and nickel concentrations of the different aqueous streams were analysed

(Table 1). It can be seen that the nickel raffinate contained only 21 ppm of cobalt, giving rise to a nickel purity of >99.5%. The removal of the residual cobalt impurities is discussed further in the text. After the washing stage, which was introduced to reduce the chloride content of the ionic liquid phase, the wash water contained small amounts of cobalt and nickel. These losses could be prevented by recycling the wash water back to the extraction circuit. The cobalt raffinate with a low nickel impurity level had a cobalt purity of >99.8%. Nearly all cobalt was removed from the ionic liquid phase after passing through three stripping stages.

A remark about the chloride contents before and after MS_1 has to be made: the aqueous feed had a chloride content of 7.6 M, whereas the chloride concentration in the nickel raffinate was only 6.4 M. This is because the ionic liquid that is used as the input in MS_1 originated from the after-stripping stage at MS_5 . Due to the different stripping stages, the ionic liquid at this point was saturated with water. The chloride ions in the aqueous feed redistributed into the ionic liquid and decreased the chloride concentration of the aqueous phase by 14%. Since the distribution ratio of cobalt depends on the chloride concentration, this dilution effect also decreases the extraction efficiency of cobalt.¹⁷ Further optimisation of the process is possible by using a pre-treatment step to increase the chloride concentration of the ionic liquid outlet stream of MS_5 . Pretreatment of the outlet stream with the nickel raffinate, which has a 6.4 M chloride concentration, has two beneficial effects: (1) it will increase the chloride concentration of the ionic liquid stream; (2) removal of the cobalt impurities present in the nickel raffinate will lead to a more purified nickel solution. This pretreatment is equivalent to two mixer-settlers in counter-current mode.

Table 1 Cobalt, nickel, chloride and phosphonium cation concentrations in the different aqueous streams and in the ionic liquid outlet stream

	Co (mg L ⁻¹)	Ni (mg L ⁻¹)	Cl ⁻ (M)	[P ₆₆₆₁₄] ⁺ (mg L ⁻¹)
Feed	5000	5000	7.6	— ^a
Ni raffinate (MS ₁)	21	4900	6.4	43
Wash water (MS ₂)	250	100	2.8	42
Co raffinate (MS ₃)	5000	7	0.8	77
IL outlet (MS ₅)	55	<i>n.d.</i> ^a	—	—

^a — = not measured; *n.d.* = not detected.

Reagent losses from the extraction phase to the aqueous phase are inherent to solvent extraction processes. Typical losses during an extraction process for tertiary amines in acidic media are between 10 and 40 ppm.²² In our extraction process, the loss of the phosphonium cation to the different aqueous streams was ranging from 40 to 80 ppm. These losses are thus comparable to the current state-of-the-art. However to further reduce the loss of ionic liquid cation in the aqueous phase, a salting-out process could be used,²³ and the ionic liquid could be recovered by nanofiltration.^{24,25}

The separation of cobalt and nickel by solvent extraction from chloride media is on an industrial scale applied by Xstrata Nikkelverk, (Kristiansand, Norway), Sumitomo Metal Mining (Niihama, Japan) and Eramet (Le-Havre-Sandouville, France).²⁶ The Xstrata Nikkelverk plant uses tri-*n*-octylamine as an extractant diluted in 17% of aromatic diluents.²⁷ The process makes use of four mixer-settlers in a counter-current mode to extract cobalt from the leach solution, several small mixer-settlers for the removal of nickel impurities and two mixer settler for stripping of cobalt. The leach solution used as feed contains 220 g L⁻¹ nickel and 11 g L⁻¹ cobalt. After extraction, a nickel-rich solution of 60 g L⁻¹ Ni and 0.03 g L⁻¹ Co, and a cobalt-rich solution of 0.01 g L⁻¹ Ni and 50 g L⁻¹ Co are obtained. The ionic liquid continuous extraction process presented in this communication could be further developed to a process on an industrial scale and it presents certainly a cleaner technology than the currently used industrial processes. The green credentials of a continuous ionic liquid extraction process are mainly the non-volatility and non-flammability of the ionic liquid, since the emission of odorous volatile components (diluents, modifier and extractant) are avoided. This leads to environmentally friendlier and healthier working conditions. The features of the Xstrata process can be compared with that of our continuous ionic liquid process. Although the nickel concentration is much higher in the leach solution of the Xstrata process than in our experiments, a nickel-rich feed will not have a huge influence on the results, because nickel is barely extracted. However, the extraction efficiency is affected by the cobalt concentration due to change in the viscosity of the ionic liquid phase upon extraction of cobalt. Only relatively low cobalt loadings (<20 g L⁻¹) can be used. The viscosity of the ionic liquid phase will range between 100 and 150 cP after extraction, if the initial cobalt concentration in aqueous feed is similar to that of the Xstrata

process (11 g L⁻¹).¹⁷ However, the raffinate solutions of the Xstrata process are much more purified (about ten times higher) compared to our continuous ionic liquids process. Hence, our process still needs further optimization. This optimization includes introducing extra washing steps, which allows further removal of the nickel impurities from the organic phase. As suggested earlier, the use of a second mixer settler in the counter-current mode for cobalt extraction will further reduce the cobalt content in the nickel raffinate.

Conclusions

The proof-of-principle of a continuous ionic liquid extraction process for the separation of metals has been given. Cobalt and nickel could be separated using the ionic liquid trihexyl (tetradecyl)phosphonium chloride (Cyphos[®] IL 101) as the extraction phase. The setup with one extraction step, a washing step and three counter-current stripping steps gave pure cobalt (>99.8%) and nickel (>99.5%) streams. After stripping, the ionic liquid phase was regenerated. We have shown that ionic liquids can be implemented in industrially applied solvent extraction processes with an equal or even smaller number of mixer settler stages than the state-of-the-art industrial processes. The problems associated with the inherently higher viscosity of ionic liquid phases have been solved. Our process could be made competitive with the current industrially applied processes after applying minor optimizations. The continuous ionic liquid extraction process offers a more sustainable approach to solvent extraction by eliminating volatile and odorous compounds. This leads to environmentally friendlier and healthier working conditions.

Acknowledgements

This research was supported by the Flemish Institute for the Promotion of Innovation by Science and Technology (IWT Vlaanderen) via a Baekeland PhD fellowship to Sil Wellens (IWT 090272) and by the Umicore Group Research. ICP-OES and TOC analyses were performed in the Analytical Laboratory of Umicore Group Research.

Notes and references

- 1 J. Rydberg, M. Cox, C. Musikas and G. R. Choppin, in *Solvent Extraction: Principles and Practice*, Marcel Dekker, Inc., New York, 2nd edn, 2004.
- 2 T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2083.
- 3 N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123–150.
- 4 A. P. Abbott, G. Frisch, S. J. Gurman, A. R. Hillman, J. Hartley, F. Holyoak and K. S. Ryder, *Chem. Commun.*, 2011, **47**, 10031–10033.
- 5 A. P. Abbott, G. Frisch, J. Hartley and K. S. Ryder, *Green Chem.*, 2011, **13**, 471–481.

- 6 J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser and R. D. Rogers, *Chem. Commun.*, 1998, 1765–1766.
- 7 M. L. Dietz, *Sep. Sci. Technol.*, 2006, **41**, 2047–2063.
- 8 I. Billard, Chapter 256 – Ionic Liquids: New Hopes for Efficient Lanthanide/Actinide Extraction and Separation? in *Handbook on the Physics and Chemistry of Rare Earths*, ed. J. C. G. Bünzli and V. Pescharsky, Elsevier, 2013, pp. 213–273.
- 9 Z. Kolarik, *Solvent Extr. Ion Exch.*, 2013, **31**, 24–60.
- 10 A. Stojanovic and B. K. Keppler, *Sep. Sci. Technol.*, 2012, **47**, 189–203.
- 11 P. R. Vasudeva Rao, K. A. Venkatesan, A. Rout, T. G. Srinivasan and K. Nagarajan, *Sep. Sci. Technol.*, 2012, **47**, 204–222.
- 12 D. Parmentier, S. J. Metz and M. C. Kroon, *Green Chem.*, 2013, **15**, 205–209.
- 13 N. Papaiconomou, G. Vite, N. Goujon, J. M. Leveque and I. Billard, *Green Chem.*, 2012, **14**, 2050–2056.
- 14 M. L. Dietz and J. A. Dzielawa, *Chem. Commun.*, 2001, 2124–2125.
- 15 M. L. Dietz, J. A. Dzielawa, I. Laszak, B. A. Young and M. P. Jensen, *Green Chem.*, 2003, **5**, 682–685.
- 16 I. Billard, A. Ouadi and C. Gaillard, *Dalton Trans.*, 2013, **42**, 6203–6212.
- 17 S. Wellens, B. Thijs and K. Binnemans, *Green Chem.*, 2012, **14**, 1657–1665.
- 18 T. Vander Hoogerstraete, S. Wellens, K. Verachtert and K. Binnemans, *Green Chem.*, 2013, **15**, 919–927.
- 19 K. Binnemans, P. T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton and M. Buchert, *J. Clean. Prod.*, 2013, **51**, 1–22.
- 20 A. Stojanovic, C. Morgenbesser, D. Kogelnig, R. Krachler and B. K. Keppler, Quaternary Ammonium and Phosphonium Ionic Liquids in Chemical and Environmental Engineering, in *Ionic Liquids: Theory, Properties, New Approaches*, ed. A. Kokorin, InTech, New York, 1st edn, 2011, pp. 657–680.
- 21 C. J. Bradaric, A. Downard, C. Kennedy, A. J. Robertson and Y. H. Zhou, *Green Chem.*, 2003, **5**, 143–152.
- 22 G. M. Ritcey, Development of Industrial solvent extraction processes, in *Principles and practices of solvent extraction*, ed. J. Rydberg, C. Musikas and G. R. Choppin, Marcel Dekker, New York, 1st edn, 1992, pp. 449–510.
- 23 J. R. Trindade, Z. P. Visak, M. Blesic, I. M. Marrucho, J. A. P. Coutinho, J. N. C. Lopes and L. P. N. Rebelo, *J. Phys. Chem. B*, 2007, **111**, 4737–4741.
- 24 J. Krockel and U. Kragl, *Chem. Eng. Technol.*, 2003, **26**, 1166–1168.
- 25 K. Haerens, S. Van Deuren, E. Matthijs and B. Van der Bruggen, *Green Chem.*, 2010, **12**, 2182–2188.
- 26 F. Crundwell, M. Moats, V. Ramachandran, T. Robinson and W. G. Davenport, in *Extractive Metallurgy of Nickel, Cobalt and Platinum Group Metals*, Elsevier, Amsterdam, 1st edn, 2011.
- 27 E. O. Stensholt, O. M. Dotterud, E. E. Henriksen, P. O. Ramsdal, F. Stalesen and E. Thune, *CIM Bull.*, 2001, **94**, 101–104.