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Selective extraction of metals using ionic liquids for nickel metal hydride battery recycling

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A new separation scheme for the recycling of metal values from nickel metal hydride batteries utilizing ionic liquids has been developed. The scheme has been optimized for synthetic solutions and uses either the ionic liquid trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) or tricaprylmethylammonium chloride (Aliquat 336). In the first stage of extraction cobalt, manganese, iron and zinc are removed from the rare earths and nickel in a metal-loaded liquor of high chloride concentration (8 M chloride). Recovery of rare earths was demonstrated on the raffinate resulting from the first extraction by extraction with the solvating extractant Cyanex 923 (10% v/v) in tricaprylmethylammonium nitrate. Cobalt and manganese were separated utilizing tricaprylmethylammonium thiocyanate.

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1 Introduction

The recycling of rare earths is of importance for helping to secure a supply of these critical metals and to guarantee their efficient use.¹ The recycling of rare earths is also recommended from the point of view of the so-called “Balance Problem”.² Most of the research activities in the field of recycling of rare earths from end-of-life consumer goods have focused on permanent magnets and phosphors of fluorescent lamps. Less attention has been paid to nickel metal hydride (NiMH) batteries, which contain substantial amounts of lanthanum, with smaller admixtures of other rare earths. The recycling of rare earths or other metal values such as nickel can be done *via* either a pyrometallurgical or a hydrometallurgical process.³ In a pyrometallurgical process, the nickel metal hydride batteries will be heated in a high-temperature furnace. Nickel reports to a metallic phase and the rare earths to the oxide slag. The metals are then recovered in further process steps. In a hydrometallurgical process, the batteries are first dismantled and the anode and cathode materials can be treated separately, by leaching with acid and extraction of the metals from the leachates by solvent extraction.⁴

In earlier work by the first author, a process for recycling nickel metal hydride batteries was developed and tested based on dissolving batteries using 8 M hydrochloric acid and utilizing Cyanex 923 to extract metals.^{4–6} The novelty of this process was primarily the focus on high metal concentrations and solvating extractants, which afforded an efficient process by

having low volumes and low sensitivity to pH. The 8 M hydrochloric acid was found to be close to optimal since it approaches the solubility limits of the dissolved battery materials and yields a high chloride matrix that can be used to extract metal-chloride complexes. The resulting composition was therefore used for the experiments described in this paper.

Previous research on NiMH recycling in chloride media includes the process developed by Zhang *et al.* whereby the batteries were dissolved in 3 M hydrochloric acid, followed by extraction of rare earths with bis(2-ethylhexyl)phosphoric acid (D2EHPA) in kerosene, and nickel/cobalt separation by extraction with trioctylamine in kerosene.⁷ Tzanetakis and Scott also developed a process in chloride media, with D2EHPA in kerosene to recover rare earths followed by electrochemical recovery of a nickel–cobalt alloy.^{8,9} Gasser and Aly investigated recovery and separation of rare earths from NiMH batteries using a synthetic adsorbent after sulphuric acid dissolution.¹⁰ Fernandes *et al.* reported a high chloride concentration process for NiMH battery recycling using TBP (tributyl phosphate), Alamine 336 (tri-*n*-octylamine), PC-88A (2-ethyl hexyl phosphonic acid mono-2-ethylhexyl ester) and oxalate precipitation.¹¹

Ionic liquids (ILs) are solvents that consists entirely of ions. They are often composed of bulky organic cations and organic or inorganic anions and they are often in a liquid state at or near room temperature. Using ionic liquids in solvent extraction by replacing classical organic solvents as diluents or extractants is potentially beneficial since ionic liquids can have more desirable properties, such as a very low vapor pressure and associated low volatility and flammability, immiscibility with water or organic solvents (depending on the composition of the ionic liquid) and the ability to dissolve a wide range of organic and inorganic compounds.^{12–24} With regard

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to solvent extraction they can serve as new extractants and have been shown to be able to increase distribution ratios and change separation factors.

In this paper, the ionic liquids trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) and tricaprylmethylammonium chloride (Aliquat 336) are used in pure form for chloro-complex separations, in nitrate form together with the solvating trialkylphosphine oxide mixture Cyanex 923 for nitrate-complex separations and in thiocyanate form for separating cobalt from manganese. These ionic liquids have suitable physical and chemical properties for use in separation processes and they are non-fluorinated. Avoiding fluorinated ionic liquids is advisable due to their high price and their persistence in nature. Aliquat 336 dissolved in molecular solvents has been shown to extract anionic complexes in chloride media through anion exchange mechanism for a number of transition metals such as cobalt, manganese and zinc.^{25–27} Cyphos IL 101 has previously been shown to be able to extract copper, cobalt, iron, manganese and zinc from chloride solutions.^{28–30}

The work presented in this paper expands the scope of previously reported hydrometallurgical processes for recycling of metals from metal hydride batteries by using ionic liquids to perform extractions on synthetic solutions simulating the composition of leachates of nickel metal hydride batteries.⁴ The benefit of using ionic liquids (Cyphos IL 101 or Aliquat 336) is that the transition metals, except nickel, can be extracted in an initial step as compared to previous work where rare earths were extracted together with the transition metals in a single step.⁴ This is a benefit, since it removes the need for a subsequent separation of rare earths from cobalt, manganese and zinc. The purity of cobalt and manganese with regard to nickel is also very high due to a very effective scrub of the ionic liquid phase containing the extracted cobalt and nickel using hydrochloric acid.

2 Experimental

2.1 Chemicals

Cyphos IL 101 is the ionic liquid trihexyl(tetradecyl)phosphonium chloride (Cytec, 97.7%). Aliquat 336 (tricaprylmethylammonium chloride) is a mixed quaternary ammonium salt containing mainly trioctylmethylammonium and tridecylmethylammonium chloride (Aldrich, 88.2–90.6%). Cyanex 923 (Cytec, 93%) is a mixture of trialkylphosphine oxides with octyl and hexyl side groups: trioctylphosphine oxide, trihexylphosphine oxide and the mixed side group versions. The ionic liquids and extractants were used as received without further purifications and the structure of the main components are shown in Fig. 1.

In order to prepare nitrate forms of the ionic liquids, they were pre-equilibrated three times with a 2.5 M KNO_3 solution to exchange the chloride ions for nitrate ions. The reduction in chloride concentration after the two first equilibrations is shown in Table 1 and is below 200 ppm. Three equilibrations

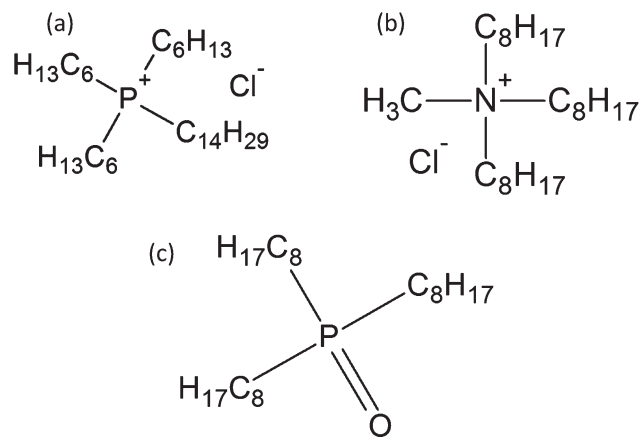


Fig. 1 Structures of the ionic liquids and extractants used in this study: (a) Cyphos IL 101; (b) Aliquat 336 (main component); (c) Cyanex 923 (main component).

Table 1 Measured chloride concentrations (in ppm) in the two phases for pre-equilibrations of Aliquat 336 and Cyphos IL 101 using an aqueous phase of 2.5 M KNO_3

Phase	Initial	After equilib. 1	After equilib. 2
Aliquat 336	>25 000	4500	160
Aqueous	—	>40 000	4100
Cyphos IL 101	>25 000	730	100
Aqueous	—	>40 000	2200

were used since this gave chloride levels in the ionic liquid phase close to the instrumental detection limits.

The following salts were used in preparation of solutions: aluminium(III) chloride hexahydrate (Acros Organics, 99%), cerium(III) chloride heptahydrate (Alfa Aesar, 99%), cobalt(II) chloride hexahydrate (Sigma-Aldrich, 97%), iron(III) chloride (Riedel-de Haën, 99%), potassium chloride (AnalaR, >99.5%), lanthanum(III) chloride heptahydrate (Sigma-Aldrich, 99.9%), magnesium(II) chloride (Sigma-Aldrich, >98%), manganese(II) chloride hexahydrate (Acros Organics, 97%), neodymium(III) chloride hexahydrate (GFS chemicals, 99.9%), nickel(II) chloride hexahydrate (Merck, >98%), praseodymium(III) chloride hexahydrate (Acros Organics, 99.9%), yttrium(III) chloride hexahydrate (Heraeus, 99.9%), zinc(II) chloride hexahydrate (Sigma-Aldrich, 99.999%), sodium nitrate (Chem-Lab, >99%), sodium citrate (Fischer, 99.5%). The salts were dissolved using pure water (MilliQ, Millipore, >18 $\text{M}\Omega\text{ cm}^{-1}$). For some strip steps ammonia (25% (w/v), Chem-lab) was used.

A Bruker S2 Picofox total reflection X-ray fluorescence (TXRF) spectrometer was used to determine the metal content in solutions. The uncertainties given are one standard deviation based on differences in triplicate measurements, *i.e.* the standard deviation for the measurement replication.

Three initial aqueous solutions were prepared for extraction studies. The first solution (solution 1) was based on the composition of mixed electrodes from a hybrid electric vehicle (HEV) NiMH battery dissolved in 8 M hydrochloric acid, as described previously by Larsson *et al.*⁵ The second solution

Table 2 Concentrations of metals in the starting solutions (in M), as measured by TXRF. Aluminium (approximately 0.1 M) and magnesium (approximately 0.04 M) were also present in all the solutions

Metal	Solution 1	Solution 2	Solution 3
Co	0.47 ± 0.01	0.06 ± 0.004	
Fe	0.04 ± 0.002	0.02 ± 0.001	
Mn	0.13 ± 0.01	0.05 ± 0.003	
Zn	0.02 ± 0.001	0.03 ± 0.001	
K	0.08 ± 0.004	0.10 ± 0.001	0.04 ± 0.02
Ni	3.0 ± 0.10	4.17 ± 0.2	3.6 ± 0.26
Y	0.04 ± 0.002	0.02 ± 0.001	0.05 ± 0.01
La	0.25 ± 0.01	0.03 ± 0.002	0.24 ± 0.05
Ce	0.08 ± 0.002	0.02 ± 0.001	0.08 ± 0.02
Pr	0.01 ± 0.0004	0.01 ± 0.001	0.01 ± 0.004
Nd	0.02 ± 0.001	0.01 ± 0.001	0.03 ± 0.003

(solution 2) was designed to contain NiMH battery metals in low concentration in a 4 M nickel chloride matrix in order to test extraction at low loading of the ionic liquid. The third solution (solution 3) was prepared in order to have additional solution where cobalt, manganese, iron and zinc had been extracted giving a solution of primarily rare earths and nickel. Concentrations for the aqueous solutions are shown in Table 2 (TXRF measurement results). Magnesium and aluminium concentrations could not be reliably determined by TXRF at the concentrations in the prepared solutions and are therefore present in the solutions in order to mimic real solutions but no extraction data could be reported. However, it is probable that neither magnesium nor aluminium will be strongly extracted by Cyphos IL 101 or Aliquat 336 in chloride solutions and that they can be scrubbed from a loaded ionic liquid.²⁸ Potassium extraction was at or below detection limits in the ionic liquid phase for all experiments.

2.2 Solvent extraction procedure

Batch solvent extraction experiments were performed using approximately 1 mL of each phase, unless other phase ratios were tested, in which case the ionic liquid volume was increased. Samples were shaken at constant temperature (30 °C) using a TMS-200 turbo thermo shaker (Hangzhou Allsheng Instruments Co., Ltd). Larger extraction experiments used 30 mL to make the treated phases for further experiments.

The distribution ratio (D) of a single metal is defined (eqn (1)) as the ratio of the total concentration in the ionic liquid phase ($[M]_{IL}$) by the total concentration in the aqueous phase ($[M]_{aq}$) after extraction and phase separation. The phase ratios are defined as the volume ionic liquid divided by the volume aqueous phase. The percentage extracted is defined in eqn (2), where V_{aq} and V_{IL} are the volumes of the aqueous and ionic liquid phases, respectively.

$$D = \frac{[M]_{IL}}{[M]_{aq}} \quad (1)$$

$$\%E = \frac{100D}{D + \frac{V_{aq}}{V_{IL}}} \quad (2)$$

3 Results

3.1 Transition metal extraction

In order to evaluate the potential of Cyphos IL 101 and Aliquat 336 for separation of manganese, iron, cobalt and zinc from the chloride liquor, initial tests were performed. The aqueous phase with reduced metal concentrations (solution 2) was used in order to avoid high loading (concentration of the extracted solute in the extracting phase). Manganese, iron, cobalt and zinc were all below detection limits in the aqueous phase after equilibration, indicating distribution ratios well above 100 and the distribution ratios for the remaining metals are shown in Table 3. The extraction of nickel and rare earths was low compared to the metals with high distribution ratios giving a good separation.

Subsequently, an experiment with the synthetic solution mimicking a real dissolved battery (solution 1) was used at a phase ratio of 1 : 1. The high loading of the ionic liquid phase significantly increased the viscosity of the phase and the distribution ratios decreased significantly as an effect of the system not being in equilibrium. The mixing became inefficient at 2200 rpm when the viscosity increased due to the high loading of the ionic liquid. To show that the equilibration time is short when the system is efficiently mixed and the viscosity is lowered by increasing the temperature a series of experiments with different equilibration times were performed (Fig. 2). This

Table 3 Distribution ratios for a synthetic 4 M NiCl₂ solution with low levels of the extractable metals (solution 2) and a phase ratio ($V_{IL} : V_{aq}$) of 1 : 1 Cyphos IL 101 and Aliquat 336. Manganese, iron, cobalt and zinc fully extracted after 30 min of mixing (2200 rpm) at 30 °C

Metal	Cyphos IL 101	Aliquat 336
Ni	0.04 ± 0.02	0.10 ± 0.005
Y	0.70 ± 0.34	0.32 ± 0.03
La	0.05 ± 0.02	0.15 ± 0.01
Ce	0.06 ± 0.02	0.15 ± 0.01
Pr	0.07 ± 0.03	0.14 ± 0.01
Nd	0.09 ± 0.04	0.15 ± 0.01

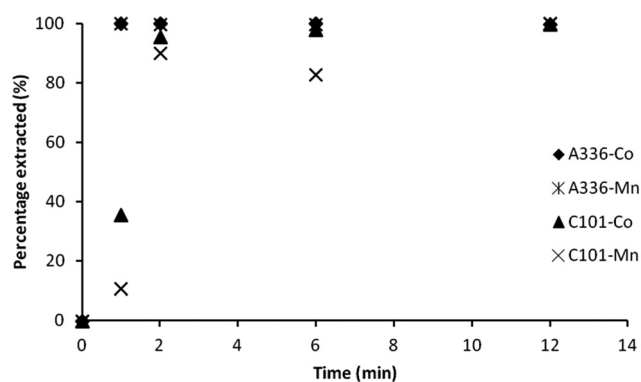


Fig. 2 Kinetics experiment showing percentage extracted for Aliquat 336 (A336) and Cyphos IL 101 (C101) at a higher mixing speed (3000 rpm) at 50 °C with a phase ratio ($V_{IL} : V_{aq}$) of 2 : 1.

Table 4 Distribution ratios for Cyphos IL 101 with solution 1 as aqueous phase at phase ratio ($V_{IL} : V_{aq}$) 2 : 1, 1 hour of mixing (2200 rpm) at 30 °C

Metal	<i>D</i>	Metal	<i>D</i>
Co	>100	Y	0.11 ± 0.03
Fe	>100	La	0.09 ± 0.02
Mn	>100	Ce	0.10 ± 0.02
Zn	>100	Pr	0.09 ± 0.05
Ni	0.06 ± 0.006	Nd	0.10 ± 0.06

demonstrated that Aliquat 336 reached equilibrium in less than 1 min and Cyphos IL 101 within 12 min.

At high mixing speeds and high temperatures full extraction of manganese, iron, cobalt and zinc was achieved down to a phase ratio of 1 : 1. The increased temperature significantly reduced the viscosity of the loaded ionic liquid and the required equilibration time, however, near room-temperature represents an interesting scenario since it shows that the process can work at ambient temperatures. Experiments with a 2 : 1 phase ratio at 1 hour of mixing (2200 rpm) were performed using Cyphos IL 101 (Table 4). The experiments indicated that the extraction of cobalt reached sufficiently high distribution ratios at these conditions. With the mixing time of 1 hour there was full extraction ($D > 100$) of iron, zinc, manganese and cobalt. Minimizing the phase ratio without compromising the extraction of manganese, iron, cobalt and zinc is preferable since the extraction of nickel and rare earths increases with increasing phase ratio. While the viscosity increases with minimized phase ratio (increased loading) leading to a technical optimal value. However, the phase ratio does not need to be determined more precisely here since the optimal value will change for a continuous process and at different mixing conditions and higher temperatures. For further experiments utilizing the extract (loaded IL), a phase ratio of 2 : 1 and 1 hour of mixing at 30 °C was used in order to ensure full extraction of the transition metals. A similar experiment with Aliquat 336 showed that a 2 : 1 ratio for 1 hour of mixing was sufficient (with similar distribution ratios) for this ionic liquid as well.

3.2 Transition metal scrubbing

Loaded Cyphos IL 101 and Aliquat 336 ionic liquid phases were created in two single-step experiments (30 mL) and this phase was used for stripping experiments. Since the extraction is dependent on the chloride concentration, an efficient scrub of the ionic liquid in order to purify the extracted metals was achieved using 8 M hydrochloric acid. The results of a scrubbing experiment to determine a suitable phase ratio are shown in Table 5, indicating that a 3 : 1 phase ratio is acceptable.

Manganese, iron, cobalt and zinc remained quantitatively extracted, while nickel and the rare earths were effectively scrubbed from the ionic liquid phase. Additionally some scrubbing of cobalt, manganese, iron and zinc would be acceptable since no material is lost, since the 8 M hydrochloric acid scrub raffinate solution could be used for dissolution of

Table 5 Distribution ratios when scrubbing loaded Cyphos IL 101 with 8 M hydrochloric acid in order to remove nickel and rare earth content at varying phase ratios ($V_{IL} : V_{aq}$). The samples were mixed (2200 rpm) for 30 min at 30 °C

Metal	1 : 1	2 : 1	3 : 1
Co	>100	>100	>100
Fe	20 ± 3	18 ± 7.5	20 ± 4.6
Mn	15 ± 1.8	15 ± 1.3	15 ± 0.8
Zn	>100	>100	>100
Ni	0.04 ± 0.02	0.02 ± 0.01	0.02 ± 0.02
Y	0.04 ± 0.02	0.01 ± 0.003	0.03 ± 0.02
La	0.02 ± 0.01	0.01 ± 0.003	0.01 ± 0.003
Ce	0.01 ± 0.02	0.01 ± 0.01	0.01 ± 0.01
Pr	0.01 ± 0.01	0.03 ± 0.02	0.02 ± 0.04
Nd	0.01 ± 0.01	0.07 ± 0.01	0.04 ± 0.04

additional battery material. Similar results were achieved for Aliquat 336 showing that an 8 M hydrochloric acid scrub gave an effective scrub of nickel and rare earths.

3.3 Transition metal stripping

Table 6 shows the results from consecutive stripping steps using pure water and how it affects the distribution ratio for the equal volume situation. The distribution ratios of the three stripped metals remain fairly high due to a relatively high chloride level in the strip. The ionic liquid phase contributes to the chloride concentration during the strip since it extracts hydrochloric acid during the scrub step and due to the chloride concentration provided by the stripped metal chloride complexes. Two steps would be sufficient to nearly quantitatively strip manganese and cobalt content with iron and zinc in the ionic liquid phase. In order to ensure that iron is not stripped a small amount of hydrochloric acid can be added to the stripping water.

The residual iron and zinc in the ionic liquid phase after a three-step water strip can be removed using sodium citrate (Table 7), which can act as an ionic liquid regeneration step. The majority of the zinc was stripped in the first step, but later steps became less efficient.

An alternative to this somewhat inefficient stripping of iron and zinc was achieved using a concentrated ammonia solution. This removed the impurities to the aqueous phase. A 5% ammonia solution at a 2 : 1 ($V_{IL} : V_{aq}$) phase ratio was used for this, but a lower concentration could be possible. The stripped iron behaved like a third phase and gathered at the bottom after centrifugation, the zinc stayed in solution. The iron and

Table 6 Distribution ratios after stripping the scrubbed Cyphos IL 101 using water, consecutive steps with 30 min of mixing (2200 rpm) at 30 °C

Metal	Step 1	Step 2	Step 3
Co	1.7 ± 0.4	0.1 ± 0.01	0.003 ± 0.0002
Fe	2.1 ± 0.3	4.5 ± 0.7	1.3 ± 0.5
Mn	0.3 ± 0.1	0.02 ± 0.001	0.01 ± 0.02
Zn	>100	>100	>100

Table 7 Distribution ratios for a Cyphos IL 101 ionic liquid regeneration step using 1 M sodium citrate solution with 30 min of mixing (2200 rpm) at 30 °C

Metal	Step 1	Step 2
Fe	0.2 ± 0.06	0.4 ± 0.04
Zn	0.9 ± 0.1	5.2 ± 0.4

zinc were both quantitatively stripped in a single step with distribution ratios below 0.01.

3.4 Separation of cobalt and manganese

Separation of the cobalt and manganese after their selective strip using water (with a low content of hydrochloric acid), giving a dilute chloride solution, was achieved using tricaprylmethylammonium thiocyanate dissolved in Aliquat 336. The thiocyanate in tricaprylmethylammonium thiocyanate can bind to the cobalt and extract it to the ionic liquid phase. To determine a suitable concentration of tricaprylmethylammonium thiocyanate a series of experiments with increasing concentration was performed at a 1 : 1 phase ratio (Fig. 3). With the requirement that the cobalt distribution exceed 10 and the manganese distribution ratios remain low a concentration of 30% was found to be adequate and was used on a 10 mL scale giving a distribution ratio for cobalt of 28 and for manganese 0.07, giving a separation factor of 400. The solution was scrubbed using water at a 10 : 1 ($V_{IL} : V_{aq}$) phase ratio to remove manganese. The cobalt was quantitatively stripped in a single step using a 10% (w/v) ammonia solution with a 1 : 3 ($V_{IL} : V_{aq}$) phase ratio. The high concentration and low phase ratio was optimized to maintain the cobalt dissolved in the aqueous solution, however, the cobalt rapidly precipitates also at these conditions and a different ammonia concentration could be suitable. The ionic liquid was used directly after stripping for cobalt and manganese separation again with similar distribution ratios (26 and 0.07 respectively).

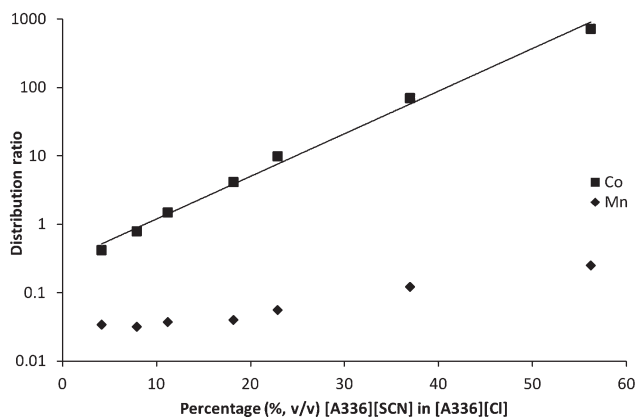


Fig. 3 Distribution ratios for cobalt and manganese in tricaprylmethylammonium chloride with a varying tricaprylmethylammonium thiocyanate content in volume percent.

3.5 Recovery of rare earths with a solvating extractant

The main goal of the rare earths recovery studies was to find a medium which has a very low extraction of nickel and from which the extracted phase could easily be scrubbed of nickel. For this purpose a solvating extractant, Cyanex 923, was used dissolved in nitrated forms of Cyphos IL 101 and Aliquat 336. This allows the ionic liquids to be used in a special way, in that the ionic liquids will supply the nitrates for the extraction without the nitrates being a component of the aqueous phase. The source of nitrates will be solely from the ionic liquid phase meaning that the availability of nitrates will be fairly low and thereby the solvating extractant was necessary since the ionic liquids themselves had slightly too low distribution ratios when used on the solutions resulting from the extraction of iron, zinc, cobalt and manganese. Adding nitrates to the aqueous phase would be unsuitable since this solution could be used for electrowinning. However, the distribution ratios can be raised using higher chloride levels, and thereby avoiding the use of the solvating extractant. Both the routes with and without solvating extractant were explored. Experiments with rare earths and increasing Cyanex 923 concentration at a phase ratio of 2 : 1 gave increasing distribution ratios (Tables 8 and 9). The distribution ratios for 25% v/v Cyanex 923 in trihexyl(tetradecyl)phosphonium nitrate at phase ratio 2 : 1 showed that it was possible to remove the rare-earth content from nickel. For the tricaprylmethylammonium nitrate experiment the mixing time for the experiment was increased to allow the sample to reach closer to equilibrium since the shorter mixing time of 30 min had very low distribution ratios for yttrium and lanthanum. The extraction of metals by trihexyl(tetradecyl)phosphonium nitrate and tricaprylmethylammonium nitrate are similar, but tricaprylmethylammonium nitrate gives larger distribution ratios for both the rare earths

Table 8 Distribution ratios for 10% and 25% v/v Cyanex 923 in trihexyl(tetradecyl)phosphonium nitrate with solution 3 as the aqueous phase, phase ratio ($V_{IL} : V_{aq}$) 2 : 1 with 30 min of mixing (2200 rpm) at 30 °C

Metal	10%	25%
Ni	0.02 ± 0.0004	0.02 ± 0.008
Y	0.70 ± 0.04	6.7 ± 3.1
La	5.8 ± 0.47	35 ± 15
Ce	30 ± 4.0	>100
Pr	9.0 ± 8.7	>100
Nd	4.8 ± 2.1	>100

Table 9 Distribution ratios for 10% and 25% v/v Cyanex 923 in tricaprylmethylammonium nitrate with solution 3 as the aqueous phase, phase ratio ($V_{IL} : V_{aq}$) 2 : 1 at 30 °C, with 1 hour of mixing (2200 rpm)

Metal	10%	25%
Ni	0.10 ± 0.032	0.091 ± 0.033
Y	2.3 ± 0.17	>100
La	13 ± 0.90	26 ± 3.8
Ce	14 ± 4.7	>100
Pr	19 ± 3.6	36 ± 4.2
Nd	8.0 ± 2.3	>100

Table 10 Distribution ratios for tricaprylmethylammonium nitrate from an aqueous phase obtained after extraction by Aliquat 336 on solution 1, for the pure aqueous phase and the aqueous phase with added anhydrous magnesium chloride (140 mg mL⁻¹). Phase ratio ($V_{IL} : V_{aq}$) 2 : 1 at 50 °C, with 1 hour of mixing (2200 rpm)

Metal	Pure	Added MgCl ₂
Ni	0.04 ± 0.004	0.08 ± 0.02
Y	0.1 ± 0.004	0.7 ± 0.08
La	1.4 ± 0.2	7.8 ± 1.5
Ce	1.4 ± 0.2	9.9 ± 1.6
Pr	0.7 ± 0.01	3.3 ± 0.29
Nd	0.5 ± 0.06	2.5 ± 0.02

and nickel, compared to trihexyl(tetradecyl)phosphonium nitrate. The higher distribution ratios for rare earths can be beneficial since a lower level of Cyanex 923 can be used and the increased extraction of nickel is not an issue since it can be scrubbed using a nitrate solution (Tables 11 and 12). After three consecutive steps with 20 : 1 of a 3 M sodium nitrate solution 99% of the nickel was stripped in the trihexyl(tetradecyl)phosphonium nitrate case. For the tricaprylmethylammonium nitrate case the scrubbing of nickel is somewhat less at the 20 : 1 phase ratio since the total amount of extracted nickel is higher. Approximately 140 mg mL⁻¹ of anhydrous magnesium chloride (approximately 1.5 M) was added to the aqueous phase before contact to sufficiently increase the rare earth distributions to be extracted with tricaprylmethylammonium nitrate without using Cyanex 923 (Table 10). However, the yttrium distribution ratios remained somewhat low ($D < 1$) and an even higher increase of chloride could be necessary to make it an efficient path.

Table 11 Distribution ratios for a 3 M nitrate scrub of loaded 25% v/v Cyanex 923 in trihexyl(tetradecyl)phosphonium nitrate, phase ratio ($V_{IL} : V_{aq}$) 20 : 1. The samples were mixed (2200 rpm) for 30 min at 30 °C

Metal	Step 1	Step 2	Step 3
Ni	0.012 ± 0.0013	0.008 ± 0.002	0.01 ± 0.003
Y	8.2 ± 1.3	8.3 ± 2.6	>100
La	5.8 ± 0.15	6.9 ± 1.9	87 ± 25
Ce	11 ± 0.24	14 ± 3.9	>100
Pr	5.2 ± 1.8	7.5 ± 2.0	82 ± 21
Nd	13 ± 0.75	20 ± 3.8	>100

Table 12 Distribution ratios for a 3 M nitrate scrub of loaded 10% v/v Cyanex 923 in tricaprylmethylammonium nitrate, phase ratio ($V_{IL} : V_{aq}$) 20 : 1. The samples were mixed (2200 rpm) for 30 min at 30 °C

Metal	Step 1	Step 2	Step 3
Ni	0.069 ± 0.004	0.034 ± 0.012	0.026 ± 0.013
Y	1.2 ± 0.26	0.9 ± 0.03	1.2 ± 0.21
La	6.9 ± 1.5	6.1 ± 0.69	8.8 ± 1.5
Ce	6.9 ± 1.6	6.5 ± 0.98	9.7 ± 1.8
Pr	5.5 ± 0.93	4.6 ± 0.14	7.3 ± 1.1
Nd	7.2 ± 1.5	5.9 ± 1.2	7.2 ± 1.1

Table 13 Distribution ratios for a water strip of the scrubbed 25% v/v Cyanex 923 in trihexyl(tetradecyl)phosphonium nitrate, phase ratio ($V_{IL} : V_{aq}$) 1 : 1. The samples were mixed (2200 rpm) for 30 min at 30 °C

Metal	Step 1	Step 2	Step 3
Y	0.61 ± 0.14	0.55 ± 0.18	0.45 ± 0.10
La	1.2 ± 0.24	1.4 ± 0.70	1.3 ± 0.17
Ce	0.54 ± 0.10	0.61 ± 0.30	0.58 ± 0.11
Pr	0.31 ± 0.08	0.32 ± 0.14	0.35 ± 0.07
Nd	0.35 ± 0.07	0.37 ± 0.18	0.37 ± 0.07

Table 14 Distribution ratios for a water strip of the scrubbed 10% v/v Cyanex 923 in tricaprylmethylammonium nitrate, phase ratio ($V_{IL} : V_{aq}$) 1 : 1. For the second step yttrium was below detection limits. The samples were mixed (2200 rpm) for 30 min at 30 °C

Metal	Step 1	Step 2
Y	0.07 ± 0.01	Nd
La	0.20 ± 0.02	0.11 ± 0.01
Ce	0.30 ± 0.04	0.17 ± 0.03
Pr	0.44 ± 0.05	0.21 ± 0.05
Nd	0.38 ± 0.05	0.22 ± 0.04

The extracted rare earths can be stripped from the resulting solution using water (Table 13) in the trihexyl(tetradecyl)phosphonium nitrate case. Lanthanum is the least stripped rare-earth and approximately 84% of the total lanthanum content is stripped over 3 stages of 1 : 1 stripping with water, this value could be improved by using more steps or adding a stripping agent. However, in the interest of maintaining an environmentally friendly process water was deemed sufficiently effective.

The stripping of rare earths from tricaprylmethylammonium nitrate could be done with either water or dilute nitric acid, 0.1 M nitric acid was used (Table 14). The lower Cyanex 923 concentration allows for a much more complete strip than the trihexyl(tetradecyl)phosphonium nitrate case. Two steps were deemed sufficient to strip the majority of the rare earths, yttrium was below detection limits in the ionic liquid in the second step, additional steps would give increased stripping.

4 Discussion

The nitrate based extraction is interesting since the nitrates necessary for the extraction is supplied solely by the ionic liquid and because the extraction mechanism is different for an ionic liquid media compared to in a molecular solvent since the extracted complex is likely charged instead of uncharged. The most likely number of nitrate ions involved in the extracted complex is 6, where this charged complex is solvated by the ionic liquids cations. This is based on the fact that in dry ionic liquids a complex with six nitrates is the most likely species of neodymium(III) when the availability of nitrate is sufficiently high.³¹ The ionic liquid cations (ammonium or phosphonium cations) have a distinct influence on the extraction process, since the distribution ratios for the rare earths are higher in the ammonium-based ionic liquid. The differ-

ences in the interactions with the ionic liquid cations is also evident from the color of the nickel complexes. The solution of the pure phosphonium ionic liquid at a 3 : 1 phase ratio after equilibration is purple, due to the presence of blue and red nickel complexes. Moreover, the color of the solution is temperature-dependent (thermochromism), the solution goes from red at low temperatures to blue at high temperatures. This is in fact one of the few examples of thermochromic ionic liquid solutions.^{32–35} When Cyanex 923 is added to the system there are no more red complexes and the solution goes from light blue to dark blue when temperature is increased. Solutions with nickel complexes in the ammonium-based ionic liquid goes from light green at low temperatures to deep blue at higher temperatures.

Two systems can be envisioned utilizing either of the tested ionic liquids Cyphos IL 101 or Aliquat 336. Choosing between the two ionic liquids requires partly a cost-based optimization since both ionic liquids are capable of extracting the desired metals and have fairly low viscosities. However, the long-term stability and the level of loss to the aqueous phase of both ionic liquids would need to be investigated in order to determine the most suitable ionic liquid. Tricaprylmethylammonium nitrate has somewhat higher distribution ratios for rare earth extraction and thereby allows for a lower level of Cyanex 923 in the process as shown. This makes Aliquat 336 the most

suitable ionic liquid to base the system on, since this also simplifies the scrub and strip steps. Essentially the two ionic liquids are interchangeable in the process with some influence on the optimization of concentrations and temperature in the different steps.

The process scheme is shown in Fig. 4 and makes use of Aliquat 336 to extract cobalt, iron, manganese and zinc. The loaded ionic liquid phase from the chloro-complex extraction is scrubbed using a concentrated hydrogen chloride solution (8 M) in order to have high distribution ratios for cobalt, manganese, iron and zinc, while scrubbing nickel and rare earths. The strip step requires lower chloride levels in order to selectively strip cobalt and manganese, while continuing to extract zinc and iron. This is achieved by the hydrochloric acid extracted in the scrub step or by adding a low concentration of hydrochloric acid to the strip solution (water). The cobalt- and manganese-rich aqueous strip can be purified from iron (if present) by contacting it with Aliquat 336 which could be re-entered into the main extraction step. The solvent regeneration step is performed using 5% ammonia in order to remove iron and zinc. The cobalt and manganese from strip 1 is separated using 30% (v/v) tricaprylmethylammonium thiocyanate in Aliquat 336 which extracts the cobalt leaving purified manganese in the raffinate (2). The cobalt-loaded ionic liquid phase is scrubbed at a high phase ratio (10 : 1) and stripped using

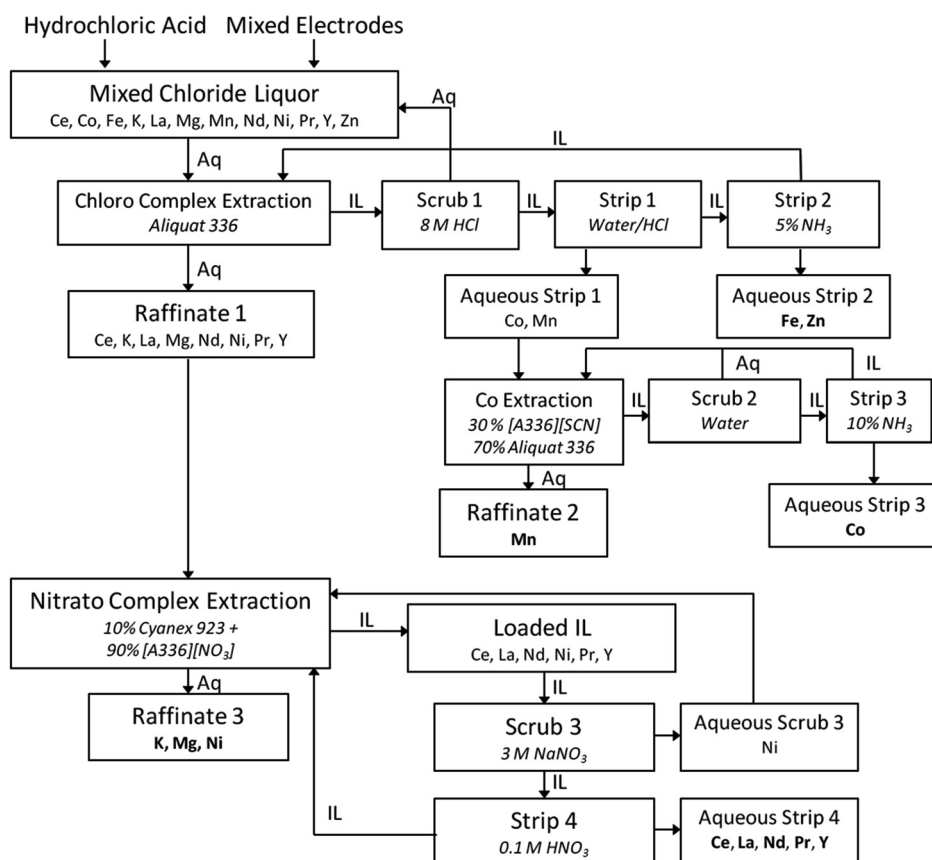


Fig. 4 Flow-sheet describing the two major steps and the resulting ionic liquid and aqueous streams.

ammonia. The raffinate (1) from the initial extraction is contacted with Cyanex 923 diluted in tricaprilmethylammonium nitrate, in order to extract the rare earths. The solvent itself supplies the nitrate ions required for the extraction, since the aqueous phase is a chloride solution. The loaded ionic liquid is scrubbed from nickel using a nitrate solution, at a phase ratio of 10:1 or more, where the rare earths remain extracted while nickel is scrubbed to the aqueous phase. This nickel-rich scrub is re-entered into raffinate 1. The re-entering of the scrub can require an optimization to ensure that any excess nitrate is extracted by the tricaprilmethylammonium nitrate phase. Any contamination of raffinate 2 during the nitrate complex extraction with nitrate ions will likely be negligible since the nitrate ions will be part of the ionic liquid or involved in complex formation with rare-earth ions. The strip could potentially be performed selectively in multiple steps at different nitrate and stripping agent concentrations in order to separate the rare earths.

To recover the metal values of the different streams as solid materials there are several available alternatives. For example, the nickel in raffinate 3 can be recovered by electrodeposition.³⁶ The aqueous strip raffinate (strip 1) rich in cobalt and manganese can also be treated by, for example, D2EHPA, PC-88A, Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid) or a mixture of these in order to separate the cobalt and manganese, the metals in the individual solutions can be recovered as hydroxides.^{37,38} The aqueous strip raffinate (aqueous strip 4) containing rare earths can be recovered by precipitation with oxalic acid.⁷ The amounts of iron and zinc obtained from the strip 2 step are small and are of low value. The expected losses of ionic liquid due to solubility in the aqueous phases is expected to be low, in the range of 10 to 40 ppm for tertiary amines can be expected and 40 to 80 ppm for Cyphos IL 101.²⁴ However, a more detailed investigation into solvent losses is needed.

5 Conclusions

The results presented in this paper show that ionic liquids can be beneficial for application in the recycling of metal values from nickel metal hydride batteries. Cyphos IL 101 and Aliquat 336 are effective in removing cobalt, manganese, iron and zinc from chloride based liquors with low co-extraction of nickel since it can easily be scrubbed using hydrogen chloride solutions. The rare earth metals can be recovered by using Cyanex 923 dissolved in the nitrated forms of Cyphos IL 101 or Aliquat 336, where the ionic liquid contains the nitrate ions for the nitrate complex extraction. Tricaprilmethylammonium nitrate is preferable since it has higher distribution ratios for the rare earths and can accommodate a lower Cyanex 923 concentration. Tricaprilmethylammonium thiocyanate in tricaprilmethylammonium chloride can be used to separate the cobalt from the manganese. A flow sheet describing the process has been proposed for the use of ionic liquids as extractants and diluents in order to separate the metals used in NiMH

batteries. The direct application of an ionic liquid to recover manganese, cobalt, iron and zinc is more efficient than directly using a Cyanex 923 based solvent. This is due to the fact that the subsequent purification of rare earths is simplified and due to the inherent benefits of using an ionic liquid as the extracting phase such as a negligible vapor pressure.

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References

- 1 K. Binnemans, P. T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton and M. Buchert, *J. Cleaner Prod.*, 2013, **51**, 1–22.
- 2 K. Binnemans, P. T. Jones, K. Van Acker, B. Blanpain, B. Mishra and D. Apelian, *JOM*, 2013, **65**, 846–848.
- 3 T. Mueller and B. Friedrich, *J. Power Sources*, 2006, **158**, 1498–1509.
- 4 K. Larsson, C. Ekberg and A. Ødegaard-Jensen, *Hydrometallurgy*, 2012, **129–130**, 35–42.
- 5 K. Larsson, C. Ekberg and A. Ødegaard-Jensen, *Waste Manage.*, 2013, **33**, 689–698.
- 6 K. Larsson, C. Ekberg and A. Ødegaard-Jensen, *Hydrometallurgy*, 2013, **133**, 168–175.
- 7 P. Zhang, T. Yokoyama, O. Itabashi, Y. Wakui, T. M. Suzuki and K. Inoue, *Hydrometallurgy*, 1998, **50**, 61–75.
- 8 N. Tzanetakis and K. Scott, *J. Chem. Technol. Biotechnol.*, 2004, **79**, 919–926.
- 9 N. Tzanetakis and K. Scott, *J. Chem. Technol. Biotechnol.*, 2004, **79**, 927–934.
- 10 M. S. Gasser and M. I. Aly, *Int. J. Miner. Process.*, 2013, **121**, 31–38.
- 11 A. Fernandes, J. C. Afonso and A. J. Dutra, *Hydrometallurgy*, 2013, **133**, 37–43.
- 12 A. E. Visser, R. P. Swatloski, W. M. Reichert, S. Griffin, R. D. Rogers and S. Griffin, *Ind. Eng. Chem. Res.*, 2000, **39**, 3596–3604.
- 13 S. Dai, Y. H. Ju and C. E. Barnes, *J. Chem. Soc., Dalton Trans.*, 1999, 1201–1202.
- 14 A. E. Visser, R. P. Swatloski, S. T. Griffin, D. H. Hartman and R. D. Rogers, *Sep. Sci. Technol.*, 2001, **36**, 785–804.
- 15 M. P. Jensen, J. Neufeind, J. V. Beitz, S. Skanthakumar, L. Soderholm and S. Skanthakumar, *J. Am. Chem. Soc.*, 2003, **125**, 15466–15473.
- 16 F. Kubota and M. Goto, *Solvent Extr. Res. Dev., Jpn.*, 2006, **13**, 23–36.
- 17 K. Nakashima, F. Kubota, T. Maruyama, M. Goto and T. Maruyama, *Ind. Eng. Chem. Res.*, 2005, **44**, 4368–4372.
- 18 A. Ouadi, O. Klimchuk, C. Gaillard and I. Billard, *Green Chem.*, 2007, **9**, 1160–1162.

- 19 N. Papaiconomou, G. Vite, N. Goujon, J.-M. Lévêque and I. Billard, *Green Chem.*, 2012, **14**, 2050–2056.
- 20 I. Billard, A. Ouadi and C. Gaillard, *Anal. Bioanal. Chem.*, 2011, **400**, 1555–1566.
- 21 P. R. Rao, K. A. Venkatesan, A. Rout, T. G. Srinivasan and K. Nagarajan, *Sep. Sci. Technol.*, 2012, **47**, 204–222.
- 22 X. Sun, H. Luo and S. Dai, *Chem. Rev.*, 2012, **112**, 2100–2128.
- 23 D. Parmentier, S. J. Metz and M. C. Kroon, *Green Chem.*, 2013, **15**, 205–209.
- 24 S. Wellens, R. Goovaerts, C. Möller, J. Luyten, B. Thijs and K. Binnemans, *Green Chem.*, 2013, **15**, 3160–3164.
- 25 B. Wassink, D. Dreisinger and J. Howard, *Hydrometallurgy*, 2000, **57**, 235–252.
- 26 T. Sato, T. Shimomura, S. Murakami, T. Maeda and T. Nakamura, *Hydrometallurgy*, 1984, **12**, 245–254.
- 27 H. Aly, M. El-Garhy and S. El-Reefy, *Microchem. J.*, 1972, **17**, 431–435.
- 28 T. Vander Hoogerstraete, S. Wellens, K. Verachtert and K. Binnemans, *Green Chem.*, 2013, **15**, 919–927.
- 29 P. Rybka and M. Regel-Rosocka, *Sep. Sci. Technol.*, 2012, **47**, 1296–1302.
- 30 S. Wellens, B. Thijs and K. Binnemans, *Green Chem.*, 2012, **14**, 1657–1665.
- 31 L. Liu, G. Tian and L. Rao, *Solvent Extr. Ion Exch.*, 2013, **31**, 384–400.
- 32 N. Aoyagi, K. Shimojo, N. R. Brooks, R. Nagaishi, H. Naganawa, K. V. Hecke, L. V. Meervelt, K. Binnemans and T. Kimura, *Chem. Commun.*, 2011, **47**, 4490–4492.
- 33 C.-D. Gu and J.-P. Tu, *RSC Adv.*, 2011, 1220–1227.
- 34 Y. Funasako, G. S. Science, T. Mochida, K. Takahashi, T. Sakurai, N. H. Rokkodai and H. Ohta, *Chem. – Eur. J.*, 2012, **18**, 11929–11936.
- 35 X. Wei, L. Yu, D. Wang, X. Jin and G. Chen, *Green Chem.*, 2008, **10**, 296–305.
- 36 D. G. E. Kerfoot, in *Handbook of Extractive Metallurgy*, ed. F. Habashi, Wiley-VCH, Weinheim, 1997, vol. 2, ch. 12.
- 37 W. Zhang and C. Y. Cheng, *Hydrometallurgy*, 2007, **89**, 160–177.
- 38 F. Wang, F. He, J. Zhao, N. Sui, L. Xu and H. Liu, *Sep. Purif. Technol.*, 2012, **93**, 8–14.