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**Samarium/cobalt separation by solvent extraction with undiluted
quaternary ammonium ionic liquids**

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Abstract

SmCo permanent magnets are used in the automotive and aircraft industries. They are preferable over NdFeB magnets for applications above 150 °C. End-of-life SmCo magnets are a valuable secondary source of cobalt and samarium. This study presents solvent extraction systems without addition of molecular diluents. Undiluted quaternary ammonium ionic liquids with chloride, thiocyanate and nitrate anions were used to extract metals from aqueous feed solutions with high chloride concentrations in order to separate the main metals (Sm/Co/Cu) present in SmCo magnets. A chloride/chloride extraction was compared with two split-anion extraction systems (*i.e.* chloride in the aqueous phase and either nitrate or thiocyanate in the organic phase). The advantage of split-anion extraction is that it can be done from a chloride solution, but with the extraction behavior of nitrate or thiocyanate solutions. Split-anion extraction was in this work applied to the separation of rare earth elements/transition metals instead of previous applications to the mixtures of rare earths. For all the systems, the selectivity of extraction, scrubbing and stripping from a multi-element solution were investigated. High separation factors (> 7500) were found for Co/Sm separations. Co(II) and Cu(II) extracted in the chloride/chloride and chloride/nitrate systems could be stripped simply by water. However, stripping of the loaded ionic liquid in the chloride/thiocyanate system with water was not feasible. The extraction mechanism for the different ionic liquids was studied by extended X-ray absorption fine structure (EXAFS). A possible explanation on the extraction behavior of samarium ions in the presence of transition metal ions (cobalt and copper) is given.

Key words

Basic extractants; magnet recycling; metal separation; rare earths; split-anion extraction.

Abbreviations

EXAFS, extended X-ray absorption fine structure; ILs, ionic liquids;
 HDEHP/D2EHPA/P204/TOPS 99, bis(2-ethylhexyl)phosphoric acid; HEHEHP/P507/PC88A,
 2-ethylhexylphosphonic acid; Cyanex 272, bis(2,4,4-trimethylpentyl)phosphinic acid; TBP,
 tri-*n*-butylphosphate; TOPO, trioctylphosphine oxide; DOS, di-*n*-octyl sulphide; [A336][Cl],
 Aliquat 336 chloride; [A336][SCN], Aliquat 336 thiocyanate; [A336][NO₃], Aliquat 336 nitrate;
 O, organic phase; A, aqueous phase; O/A, organic to aqueous phase volume ratio; TXRF, total
 reflection X-ray fluorescence; D_M , distribution ratio of the metal *M*; α , separation factor; %*E*,
 percentage extraction; %*Sc*, percentage scrubbing; %*St*, percentage stripping.

1. Introduction

Currently, most of the rare-earth magnet recycling research focuses on NdFeB magnets, whereas the evolution of recycling processes for SmCo magnets remains undeveloped. This is because they cover just 2% of the rare-earth permanent magnet market and they are only used for high-end niche applications [1]. Nevertheless, end-of-life SmCo magnets and other related waste fractions such as magnet production scrap or swarf are an important secondary source of samarium [2]. Next to samarium, the magnets also contain cobalt. Cobalt is a critical metal, economically very important due to its unique resistance to oxidation (e.g. in steel industry) and its use in cathode materials for lithium-ion batteries [3]. Other metals such as iron, copper, titanium or zirconium are sometimes added to the magnet to improve the coercivity or to modify the magnet microstructure [4], [5], [6]. Separation and recovery of metals from SmCo magnets is of interest to partially mitigate the supply risk of critical metals.

Solvent extraction is an important technique used on industrial scale to obtain high-purity metals. The separation occurs by preferential distribution of the metals between two immiscible phases, in most cases an aqueous phase and an organic phase. The aqueous feed solution contains the metal ions to be separated, while the organic phase usually contains an extractant, a diluent and a modifier [7]. In this study, ionic liquids (ILs) were used as the organic phase, without the addition of any modifier or diluent. The use of undiluted ILs as concentrated extractants consequently allows solvent extraction from highly concentrated feed solutions, which is interesting from an industrial point of view. ILs are organic salts which consist entirely of ions and traditionally have a melting point below 100 °C. There is a strong incentive by the European Union to limit the use of volatile organic compounds, which also applies for solvent extraction processes (VOC Directive 1999/13/EC; Directive 2002/3/EC on ozone in air). In this perspective it is therefore an asset that no volatile chemicals were added to the organic phase, since ILs themselves do not

evaporate. The use of low-volatile and low-flammable ILs or deep eutectic solvents is now getting more attention in the search towards more environmentally friendly and safer solvents [8]. However, often used organic solvents in solvent extraction processes such as kerosene have a high boiling point. An important issue related to the traditional solvents is their high flammability and low conductivity, resulting in the build-up of static electricity. In solvent extraction processes, ILs can be considered as safer alternatives for organic solvents [9], [10], [11], [12], [13]. Safer, mainly because ILs have an intrinsic electric conductivity, so no electrostatic charges can build up and electrostatic ignition is avoided [14].

Commercially used extractants in rare-earth separation processes are either acidic extractants (HDEHP/D2EHPA/P204/TOPS 99, HEHEHP/P507/PC88A, Versatic 10/V10, Cyanex 272), solvating extractants (TBP, Cyanex 923) or basic extractants (Aliquat 336) [7], [15], [16], [17], [18], [19], [20], [21], [22]. A lot of research has been done on solvent extraction systems with ILs, where diluents were added to lower the viscosity of the extractant. Among the studied systems, tested was a separation between rare earths and transition metals by non-aqueous solvent extraction from ethylene glycol using Aliquat 336 diluted in toluene [23]. Other authors recently presented the separation of Sm and Co relevant to SmCo magnets recycling from sulphate or chloride media by TBP, TOPS 99 and Aliquat 336, all diluted in kerosene [24]. The highest extraction efficiency of samarium (> 95%) along with little co-extraction of cobalt was achieved by TOPS 99 for both media. Cyanex 572 (a mixture of phosphinic and phosphonic acid) diluted in kerosene was applied for purification of a chloride leachate of roasted SmCo magnets to separate Sm/Co [25]. Besides the approach involving diluents, synergistic extraction systems combining various extractants without the need of diluents were also reported in the literature for the separation of rare-earth elements [20]. The possibility to separate light rare-earth elements was investigated by mixing Cyanex 272 with other extractants (TBP, TOPO, DOS, Cyanex 301,

V10, Alamine 308 and Aliquat 336). Different combinations of extractants (TOPS 99, PC88A, Cyanex 272, Cyanex 302, Cyanex 921, Cyanex 923 and Aliquat 336) were tested for the separation of Sm/Gd/Dy/Y from chloride media. However, it was concluded that mixing the extractants does not significantly enhance the separation factors of the rare earths [19]. Undiluted ILs with just a single type of anion were applied by several authors mainly from nitrate, but also chloride and sulfate solutions [26], [27], [28], [29], [30], [31], [32].

In this paper, undiluted quaternary ammonium based ILs with different anions (Aliquat 336 in its chloride, nitrate and thiocyanate form) were applied as extractants for metal extraction. Because the concentration of anions in undiluted ILs is higher than in conventional solvent extraction systems with basic extractants, a concentrated chloride feed solution could be used. The approach of working with high feed concentrations is also more convenient for industrial applications since higher extraction efficiencies are achieved. Two split-anion solvent extraction systems were studied in detail. Split-anion extraction is characterized by the presence of different anions in the aqueous and organic phase [33]. In our case, chloride anions were present in the aqueous phase and thiocyanate or nitrate anions in the water-immiscible organic phase (ionic liquid). Both thiocyanate and nitrate anions are suitable for use in combination with a chloride aqueous phase, because they have a stronger affinity for the organic phase than chloride anions ($\text{Cl}^- < \text{NO}_3^- < \text{SCN}^-$) providing a very good immiscibility of the phases [34]. As a comparison, also the solvent extraction system containing only chloride anions in both aqueous and organic phases was investigated, although this system cannot be considered a split-anion extraction. Split-anion extraction was so far only applied to the mixtures of rare earths, while in this paper separations relevant to rare earths and transition metals are given.

2. Experimental details

2.1. Chemicals

A commercial mixture of trialkylmethylammonium chlorides with trioctylmethylammonium chloride as the main component (Aliquat 336) with a moisture content of ≤ 5 wt% and quaternary content of 88.2 – 93.0%, as well as ammonium thiocyanate ($> 99\%$), ammonium nitrate ($> 99\%$) and the nonionic surfactant alkylaryl polyether alcohol (Triton X-100) were obtained from Sigma-Aldrich (Diegem, Belgium). $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%) was obtained from Strem Chemicals Inc. (Newburyport, USA), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (99%), anhydrous CuCl_2 (99%) and citric acid (99.6%) from Acros Organics (Geel, Belgium). $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ($> 99.5\%$), gallium standard solution ($1000 \text{ mg} \cdot \text{L}^{-1}$), neodymium standard solution ($1000 \text{ mg} \cdot \text{L}^{-1}$) and ammonia solution (25 wt%) were ordered from Chem-Lab (Zedelgem, Belgium). The silicone solution in isopropanol was purchased from SERVA Electrophoresis GmbH (Heidelberg, Germany), HCl (~ 37 wt%), HNO_3 (68 wt%) and ethanol (absolute) from VWR International (Leuven, Belgium). All the chemicals were used as received, without further purification. A Milli-Q Synergy UV water purification system was used to obtain ultrapure water ($18.2 \text{ M}\Omega \cdot \text{cm}$).

A chloride aqueous feed solution was used for all the solvent extraction systems in this work. A highly-concentrated metal stock solution was prepared from chloride salts mimicking the metal mass ratio present in real SmCo magnets. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ and anhydrous CuCl_2 were dissolved in ultrapure water without further acidification. The metal stock solution contained $93 \text{ g} \cdot \text{L}^{-1}$ Co(II), $92 \text{ g} \cdot \text{L}^{-1}$ Sm(III) and $8 \text{ g} \cdot \text{L}^{-1}$ Cu(II). In addition, a stock solution of $4 \text{ mol} \cdot \text{L}^{-1}$ CaCl_2 was prepared by dissolving 294 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in 500 mL of ultrapure water.

The undiluted quaternary ammonium salt Aliquat 336, $[\text{A336}][\text{Cl}]$ and its thiocyanate and nitrate analogues, $[\text{A336}][\text{SCN}]$ and $[\text{A336}][\text{NO}_3]$, were used as the organic phase in the solvent

extraction systems. [A336][Cl] was used as received for the $\text{Cl}^-_{\text{aq}}/\text{Cl}^-_{\text{org}}$ extraction system. [A336][SCN] and [A336][NO₃], which were used for the split-anion extraction systems $\text{Cl}^-_{\text{aq}}/\text{SCN}^-_{\text{org}}$ and $\text{Cl}^-_{\text{aq}}/\text{NO}_3^-_{\text{org}}$, were prepared by a metathesis reaction as described elsewhere [33], [35], [36]. [A336][Cl] was contacted three times with an equal volume of 8 mol·L⁻¹ ammonium thiocyanate (or ammonium nitrate) and shaken for 10 min. The aqueous phase was removed and the same procedure was repeated with water in order to remove excesses of salt. The effectiveness of the metathesis reaction was checked for every ionic liquid by measuring the remaining chloride content using TXRF analysis [37].

2.2. Density and viscosity of ionic liquids

The density of the prepared ILs were measured with an Anton Paar DMA 4500 M density meter and the viscosity by an Anton Paar LOVIS 2000 ME rolling-ball viscometer, both as a function of the temperature. The sample was measured in a borosilicate glass capillary (diameter 1.8 mm) with a gold-coated stainless steel ball (diameter 1.5 mm, 7.93 g·cm⁻³) at an angle of 70°.

2.3. Extraction experiments

The extraction experiments were performed in 4 mL glass vials. A 1 mL aliquot of the aqueous phase containing 0.1 mL of the metal stock solution and varying calcium chloride concentrations (0 – 3.6 mol·L⁻¹ CaCl₂; in intervals of 0.4 mol·L⁻¹) was mixed with 1 mL of undiluted ionic liquid (0.88 g [A336][Cl]/ 0.90 g [A336][SCN]/ 0.92 g [A336][NO₃]). The initial metal feed concentration in the aqueous phase was kept constant for all the experiments: 9.3 g·L⁻¹ Co(II), 9.2 g·L⁻¹ Sm(III) and 0.8 g·L⁻¹ Cu(II). Samples were shaken horizontally at 40 °C, 2000 rpm for 2 h in Turbo Thermo TMS-200 Shakers to make sure that the equilibrium was reached. Loading experiments at the volume ratio between the organic (O) and the aqueous phase (A), O/A = 0.05,

0.1, 0.25, 0.5, 0.75 and 1, were done in 40 mL vials by heating to 40 °C and stirring at 2000 rpm for 2 h in Turbo Thermo TMS-200 Shakers. After extraction, the phase separation between the loaded organic phase and the aqueous phase was accelerated by centrifugation at 2600 rpm for 10 min in a Thermo Scientific Heraeus Labofuge 200 centrifuge, or for the 40 mL vials for 15 min at 1600 rpm in a Megafuge 1.0 Eppendorf centrifuge 5804.

2.4. Metal concentration analysis

The elemental concentration in both phases was quantified by total reflection X-ray fluorescence (TXRF) spectroscopy with a Bruker S2 Picofox spectrometer. The TXRF sample preparation procedure consisted of a pretreatment step of the quartz glass carriers with 30 µL of silicone solution in isopropanol, and a drying process at 60 °C for 20 min to ensure a hydrophobic surface for the sample [30]. Sample of the aqueous phase (50 µL) was mixed with 5% Triton X-100 (850 µL), and sample of the organic phase (50 mg) was mixed with ethanol (850 µL). Then a Nd internal standard solution of 1000 mg·L⁻¹ (100 µL) was added to both. The mixtures were homogenized on an IKA MS 3 basic vibrating plate. Afterwards, 3 µL of the aqueous phase (or 1 µL of the organic phase) was added onto the sample carrier and dried at 60 °C for 30 min. All the samples were measured for 300 s. The spectrometer was operating with a Mo X-ray source at 50 kV voltage and 600 µA current [38], [39]. Experiments were performed in single runs when investigating trends. Data points which did not fit the trend were remeasured in triplicate.

The *distribution ratio* of a given metal M (D_M) was calculated as:

$$D_M = \frac{[M]_{org}}{[M]_{aq}} \quad (1)$$

where $[M]_{org}$ is the metal concentration in the organic phase and $[M]_{aq}$ is the metal concentration in the aqueous phase after extraction. Volumes of the organic phase (V_{org}) and the aqueous phase (V_{aq}) were assumed to be constant.

The metal selectivity of the extraction was expressed as the *separation factor* ($\alpha_{M1,M2}$) between two metals, $M1$ and $M2$:

$$\alpha_{M1,M2} = \frac{D_{M1}}{D_{M2}} \quad (2)$$

The percentage of metal ions extracted to the ionic liquid phase compared to the total amount is described by the *percentage extraction* ($\%E_M$):

$$\%E_M = \frac{V_{org}[M]_{org}}{V_{aq}[M]_{aq} + V_{org}[M]_{org}} \times 100 \quad (3)$$

where $[M]_0$ is the initial metal concentration in the aqueous phase.

During scrubbing, the loaded ionic liquid obtained after the metal extraction is contacted with an aqueous solution in order to remove the remaining impurities. The *percentage scrubbing* ($\%Sc_M$) was calculated as follows:

$$\%Sc_M = \frac{V_{aq}[M]_{aq}}{V_{aq}[M]_{aq} + V_{org}[M]_{org}} \times 100 \quad (4)$$

The *percentage stripping* ($\%St_M$) in the stripping phase was defined as the amount of metal removed from the organic phase to the total amount of metal in the ionic liquid before stripping $[M]_{org,0}$:

$$\%St_M = \left(1 - \frac{[M]_{org}}{[M]_{org,0}}\right) \times 100 \quad (5)$$

2.5. Analysis of the extracted complexes

The coordination structures of the complexes in the ionic liquid phase were determined by extended X-ray absorption fine structure (EXAFS) spectroscopy. Every individual ionic liquid (SCN^-_{org} , Cl^-_{org} and $\text{NO}_3^-_{org}$) loaded with a single metal Sm(III) or Co(II) was measured. The ionic liquid phases were loaded by shaking at 40 °C, 2000 rpm for 2 h in Turbo Thermo TMS-200 Shakers. Because the studied solvent extraction systems were designed and optimized with the purpose to leave Sm(III) behind in the aqueous phase, loaded organic phases were prepared at conditions that allow extraction of Sm(III) from a single metal solution. SCN^-_{org} was loaded with 2.5 g·L⁻¹ Sm(III), Cl^-_{org} with 5.8 g·L⁻¹ Sm(III) and $\text{NO}_3^-_{org}$ with 10.4 g·L⁻¹ Sm(III), all at 3.6 mol·L⁻¹ CaCl_2 . To investigate the extraction mechanism of transition metals, SCN^-_{org} , Cl^-_{org} and $\text{NO}_3^-_{org}$ were loaded with 16 g·L⁻¹ Co(II) (SCN^-_{org} at 1.2 mol·L⁻¹ CaCl_2 and other two at 3.6 mol·L⁻¹ CaCl_2). A rubber VITON spacer containing the metal-loaded IL with a thickness of 0.5 mm (for highly concentrated samples) or 2 mm (for more dilute samples) was placed between two brass holders with Kapton windows. EXAFS spectra of the K-edge of Co (7709 eV) and L_{III}-edge of Sm (6716 eV) were collected at the Dutch-Belgian Beamline (DUBBLE, BM26A), located at the European Synchrotron Radiation Facility in Grenoble (France). The energy of the X-ray beam was tuned by a double-crystal monochromator operating in fixed-exit mode using a Si(111) crystal pair. Measurements were done in a transmission mode using Ar/He gas-filled ionization chambers.

The collected EXAFS data were modeled in the program Viper [40]. Standard procedures were used for pre-edge subtraction and data normalization in order to isolate the EXAFS function (χ). The isolated EXAFS oscillations, accomplished by a smoothing spline as realized in the program Viper, were k^3 -weighted and Fourier transformed over the k -range from 2.0 to 12.9 Å⁻¹. The data

were fitted using the *ab initio* code FEFF 7.0, which was used to calculate the theoretical phase and amplitude functions that were subsequently used in the non-linear least-squares refinement of the experimental data [41]. Fitting of the data with the model was performed in r-space.

Estimated standard errors are shown between parentheses and were calculated by Viper.

3. Results and discussion

3.1. Density and viscosity of the ionic liquids

Ionic liquids are viscous and pipetting the exact volume does not work well, because relatively large volumes of the ionic liquid remain adhered to the walls of the pipette tip. Due to the high viscosity of the ILs, pipetting is a great source of errors during the experiments. In order to obtain more accurate results, the densities of the ILs were measured and the exact mass was calculated ($V = m/\rho$). The measured densities of the pure ILs at room temperature (22 °C) were: 0.89 g·mL⁻¹ for [A336][SCN], 0.88 g·mL⁻¹ for [A336][Cl] and 0.92 g·mL⁻¹ for [A336][NO₃]. As seen in Figure 1, the density decreases as a function of temperature and increases with amount of loaded metals. Furthermore, the viscosity of the water-saturated ILs was measured and compared to the loaded ionic liquid phases. Figure 2 shows that the viscosity increases upon extraction of metal ions as well. Such a high viscosity of the organic phase slows down the mass transfer and kinetics of the solvent extraction process [42]. However, the viscosity drops by a factor of 4 to 6 by heating the IL from room temperature to 40 or 50 °C. Based on the data, the temperature of 40 °C was decided for all the experiments. So instead of adding extra diluents to the systems, which would need to be recycled as well, another approach (slightly elevated temperature) was chosen to keep the advantages of a pure ionic liquid. The measured IL phases were all water-saturated, since they were contacted with an aqueous phase in all the experiments.

Figure 1: Density of quaternary ammonium based ILs (water-saturated) as a function of the temperature. Composition of the loaded ILs phases in $\text{g}\cdot\text{L}^{-1}$ for [A336][SCN]: 9.3 Co, 0.8 Cu, 0.0 Sm; [A336][Cl]: 8.1 Co, 0.7 Cu, 2.6 Sm; [A336][NO₃]: 9.0 Co, 0.8 Cu, 5.5 Sm.

Figure 2: Viscosity of pure and loaded quaternary ammonium based ILs (water-saturated) as a function of the temperature. Composition of the loaded ILs phases in g·L⁻¹ for [A336][SCN]:

9.3 Co, 0.8 Cu, 0.0 Sm; [A336][Cl]: 8.1 Co, 0.7 Cu, 2.6 Sm; [A336][NO₃]: 9.0 Co, 0.8 Cu, 5.5 Sm.

3.2. Extraction with [A336][SCN]

The composition of the feed solution containing 9.3 g·L⁻¹ Co(II), 9.2 g·L⁻¹ Sm(III) and 0.8 g·L⁻¹ Cu(II) was chosen to represent a possible SmCo₅ magnet leachate for solvent extraction [6], [43]. The separation processes with basic extractants depend on the anion concentration, so the extraction parameters can be eventually optimized again (*via* adjusting CaCl₂ addition in the aqueous phase) for different aqueous feed concentrations [12]. Therefore, the usage of undiluted ILs as concentrated extractants, *i.e.* higher anions concentration, should at the same volume phase ratio lead to higher extraction efficiencies and distribution ratios, compared to diluted ILs.

The first system tested was the Cl⁻_{aq}/SCN⁻_{org} split-anion solvent extraction system. The idea behind the split-anion principle is that some metal ions form metal complexes more easily with thiocyanate (or nitrate) anions present in the ionic liquid, rather than with chloride anions in the aqueous feed [33]. These metal ions are preferentially extracted, meaning that the source of complexing anions is the organic phase. When the metal complexes are extracted, chloride anions from the aqueous phase co-extract to the organic phase to preserve charge neutrality of both phases. CaCl₂ was therefore selected as a salting-out agent to facilitate the extraction and to limit the dissolution of IL in the aqueous phase [44].

The impact of the salting-out effect on the extraction and the distribution of Sm(III) was investigated by varying the chloride concentration in the aqueous phase (Figure 3). In the $\text{Cl}^-_{\text{aq}}/\text{SCN}^-_{\text{org}}$ system, Sm(III) was not extracted to the ionic liquid phase at low CaCl_2 concentration in the aqueous phase ($< 2 \text{ mol}\cdot\text{L}^{-1}$). Samarium and calcium both have a high affinity for the aqueous phase in this system. When the activity of water in the aqueous phase decreased due to the added salt, samarium became less hydrated and started to extract as well [33]. As shown in Figure 3, Co(II) and Cu(II) could be quantitatively extracted in a single extraction step without co-extraction of Sm(III), meaning there was no need for a scrubbing step in the $\text{Cl}^-_{\text{aq}}/\text{SCN}^-_{\text{org}}$ system.

Figure 3: Extraction percentage of Co(II), Cu(II) and Sm(III) in the $\text{Cl}^-_{\text{aq}}/\text{SCN}^-_{\text{org}}$ system as a function of the initial CaCl_2 concentration in the aqueous phase. Conditions: $O/A = 1$, 40°C , 2000 rpm, 2 h.

The concentration of the extractant (undiluted ionic liquid) was very high, which maximized the distribution ratios. The highest distribution ratios ($D \geq 400$) of Co(II) and Cu(II) were achieved at $1.2 \text{ mol}\cdot\text{L}^{-1}$ CaCl_2 (Table 1). The low distribution ratios of Sm(III) was in accordance with the literature [33], [45]. An explanation for this can be found in the coordinating ability of anions towards transition metals and lanthanides [46]. Samarium does not coordinate with Cl^- or SCN^- . It therefore has a high charge density and is strongly hydrated. Transition metal complexes have a low charge density, and are thus less strongly hydrated, giving them the propensity to report to the organic phase [45]. Consequently, separation of Sm(III) in the $\text{Cl}^-_{\text{aq}}/\text{SCN}^-_{\text{org}}$ system at $1.2 \text{ mol}\cdot\text{L}^{-1}$ CaCl_2 was efficient and very high separation factors between samarium and transition metals were obtained.

Table 1: Separation factors (α), extraction percentages (%E) and distribution ratios (D) for the $\text{Cl}^-_{\text{aq}}/\text{SCN}^-_{\text{org}}$ system. Conditions: $1.2 \text{ mol}\cdot\text{L}^{-1}$ CaCl_2 , $O/A = 1$, 40°C , 2000 rpm, 2 h.

Metal	α			%E	D
	Cu(II)	Sm(III)	Co(II)		
Co(II)	6			100.0	2400
Cu(II)		$> 400000^a$		99.8	400
Sm(III)			$>> 400000^a$	0.0	0.00

^a calculated for a value $D = 0.001$

Based on these extraction results, loading experiments were performed with $1.2 \text{ mol}\cdot\text{L}^{-1}$ CaCl_2 . Loading experiments were executed to test the metal loading in the organic phase as a function of

the volume ratio between the phases, because the concentration of the ionic liquid anion is the most crucial parameter to be optimized for a given feed solution. The complete extraction of the transition metals ($8 \text{ g}\cdot\text{L}^{-1}$ Co(II) and $1 \text{ g}\cdot\text{L}^{-1}$ Cu(II)) was achieved beginning from a 1:2 volume ratio between the organic (O) and the aqueous phase (A), $O/A = 0.5$ (Figure 4).

Figure 4: Extraction percentage of Cu(II), Co(II) and Sm(III) in the $\text{Cl}_{\text{aq}}/\text{SCN}_{\text{org}}$ system as a function of the volume ratio (O/A). Conditions: $1.2 \text{ mol}\cdot\text{L}^{-1}$ CaCl_2 , 40°C , 2000 rpm, 2 h.

Stripping of $[\text{A336}][\text{SCN}]$ was performed at the conditions $O/A = 1$, 40°C , 2000 rpm, 2 h. Water cannot be used as a possible stripping agent, because the distribution ratios for extraction from pure water ($0 \text{ mol}\cdot\text{L}^{-1}$ CaCl_2) were very high for both transition metal ions Co(II) and Cu(II) ($D > 400$) (Figure 3, Table 1). Stripping of Co(II) and Cu(II) with 1 and $4 \text{ mol}\cdot\text{L}^{-1}$ citric acid solution led to negligible stripping percentage (below 1%). After an alkaline stripping step with

an ammonia solution (25 wt%), the formation of a precipitate was observed. Precipitation stripping resulted in insoluble metal hydroxides instead of water-soluble chloride complexes. Consequently, the precipitates caused errors in metal concentration analysis for both phases. No precipitation occurred at strongly alkaline conditions ($\text{pH} > 12$), but quaternary ammonium salts are not stable in strong alkaline conditions as they can undergo Hofmann elimination [47]. Although extraction from chloride solution with the ionic liquid [A336][SCN] works well for the separation of samarium from transition metals, the difficulty to strip the metals from the loaded ionic liquid phase was a showstopper.

Moreover, there are issues with the long-term stability of the thiocyanate ion, especially in contact with strongly acidic and basic solutions [47]. The thiocyanate ion is thermally unstable in an aqueous solution. It also spontaneously forms an orange-red solid product [48]. Thiocyanate anions (in the molten state or in solution) polymerize under oxidative conditions to $(\text{SCN})_x$ (polythiocyanogen) [49]. In contact with water, thiocyanogen $(\text{SCN})_2$ quickly hydrolyzes and is also decomposed by reaction with alcohols and tertiary amines [50], [51]. A thermogravimetric analysis study of a water-free thiocyanate ILs showed no mass losses below $225\text{ }^\circ\text{C}$, so these ILs have a good short-term thermal stability in the dry state [52]. However, the photosensitivity of $(\text{SCN})_x$ is more serious for the long-term decomposition of SCN^- than its thermal stability, because thiocyanate anions are activated when exposed to light, resulting in an increased polymerization rate. ILs with thiocyanate anions have a yellow/orange color and the color which in turn darkens over time [52], [53], [54]. Color changes were noticed for [A336][SCN]. For all these reasons, it was decided to stop the further development of a solvent extraction system based on this ionic liquid.

3.3. Extraction with [A336][Cl]

The differences in affinity of metal ions for [A336][Cl] were tested for a multi-element solution containing Sm(III), Co(II) and Cu(II). Sm(III) has a high affinity for water and a small affinity for chloride anions in aqueous solutions [55], [56]. Therefore, in the $\text{Cl}^-_{aq}/\text{Cl}^-_{org}$ system, even at higher chloride concentrations, only water molecules coordinate to Sm(III). According to the literature, rare-earth ions cannot be efficiently extracted by basic extractants (e.g. quaternary ammonium salts) in their chloride form, but only in thiocyanate or nitrate form at high salt concentrations [33]. A low salt concentration in the aqueous phase leads to a low affinity of the hydrated rare-earth species for the organic phase and a high stability of the rare-earth-water complex in the aqueous phase [41]. However, at higher salt concentrations, water interacts with the cations and anions of the salt and less free water molecules are available to hydrate the Sm(III) ions. It was reported that a high concentration of salting-out agent decreases the activity of water in the aqueous phase, so that 25% Sm(III) co-extraction occurred at 3.6 M CaCl_2 , when Co(II) and Cu(II) were also present (Figure 5) [33].

Figure 5: Extraction percentage of Co(II), Cu(II) and Sm(III) as a function of the initial CaCl_2 concentration in the aqueous phase for the $\text{Cl}_{\text{aq}}/\text{Cl}_{\text{org}}$ system. Conditions: $O/A = 1$, 40°C , 2000 rpm, 2 h. The results for the volume ratio $O/A = 0.25$ are marked as “x”.

Undiluted [A336][Cl] is an effective extractant for Co(II) and Cu(II), even for extractions from concentrated chloride solutions, because these metal ions form stable anionic chloro complexes with the chloride IL. A high CaCl_2 concentration attributes to the salting-out effect and besides improving the separation between the aqueous and the organic phase, CaCl_2 takes part in the formation of chloro complexes with these two transition metal ions [57]. Because the chloride ion acts as a counter ion for the formation of an ion pair, the transition metal ions are extracted. The distribution ratio curves of Co(II) and Cu(II) are crossing, since the extraction of Cu(II) increases just up to a certain point ($2 \text{ mol}\cdot\text{L}^{-1}$). It is important to note that these experiments were not performed with a single-element feed solution, but the resulting separation was extensively influenced by the presence of three different metal cations in the initial feed composition. At low

chloride concentrations in the aqueous feed, the order of extraction efficiency was: $\text{Cu(II)} > \text{Co(II)}$, while at $3.6 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$ the order was reversed: $\text{Co(II)} > \text{Cu(II)}$. A possible explanation for the crossover of the distribution ratios can be related to the initial metal feed concentration [33]. Initially, there was a much higher concentration of Co(II) ($9.3 \text{ g}\cdot\text{L}^{-1}$) than Cu(II) ($0.8 \text{ g}\cdot\text{L}^{-1}$) in the aqueous feed. Thus, after loading of the ionic liquid with Cu(II) at high salt concentrations, the distribution ratios of Cu(II) did not increase any further, while an amount of Co(II) in the aqueous phase was still available for loading. The same trend has been reported in the literature for quaternary ammonium salts from single-element solutions [58].

Scrubbing experiments were performed to investigate the possibility of removing co-extracted Sm(III) from the IL to the scrubbing phase. Different salt concentration values were tested for scrubbing from the $[\text{A336}][\text{Cl}]$ phase (Table 2). Despite the highest scrubbing efficiencies for Sm(III) were obtained with a lower salt concentration ($2 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$), it was equally important to scrub Sm(III) selectively in order to eliminate loss of Co(II) and Cu(II) in the scrub raffinate. The highest distribution ratios and therefore the highest separation factor between Sm(III) and the transition metals, were obtained at high CaCl_2 concentrations (Figure 5, Table 3). The CaCl_2 concentration must be therefore kept high and $3.6 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$ was further used for extractions as well as scrubbing.

Table 2: Percentage scrubbing of Sm(III) from $[\text{A336}][\text{Cl}]$ as a function of the CaCl_2 concentration. Conditions: 40°C , 2000 rpm, 2 h.

CaCl_2 [$\text{mol}\cdot\text{L}^{-1}$]	$\%Sc_{\text{Sm}}$

O/A = 1	2.0	91.0
	3.0	79.0
	3.6	71.9
O/A = 0.25	3.6	56.3

Conclusions cannot be made based on the percentage scrubbing in Table 2 without considering the concentration of initially extracted Sm(III). For example, at a volume ratio $O/A = 1$ and $3.6 \text{ mol}\cdot\text{L}^{-1}$ CaCl_2 , around 25% Sm(III) was extracted to [A336][Cl] from the multi-element solution (Figure 5), while at $O/A = 0.25$ extracted was only 1% Sm(III). Although the percentage scrubbing of Sm(III) was lower at $O/A = 0.25$, in combination with lower co-extraction with Co(II) and Cu(II), it gave better results than $O/A = 1$. Therefore, for selective removal of Sm(III) from the organic phase, while retaining the transition metals in the organic phase, a volume ratio $O/A = 0.25$ was found to be suitable (Figure 6). When less IL than this optimal phase ratio ($O/A < 0.25$) was used, the transition metals were transferred to the aqueous phase together with Sm(III). When more IL than the optimal ratio ($O/A > 0.25$) was used, Sm(III) tended to stay extracted in the IL and the scrubbing efficiencies were therefore found to be lower.

Figure 6: Extraction percentage of Cu(II), Co(II) and Sm(III) in the Cl^-_{aq}/Cl^-_{org} system as a function of the volume ratio (O/A). Conditions: $3.6 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$, 40°C , 2000 rpm, 2 h.

The results for the Cl^-_{aq}/Cl^-_{org} system with $3.6 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$ are summarized in Table 3. The co-extraction of Sm(III) was reduced to about 1% at $3.6 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$ and $O/A = 0.25$. An advantage of $[A336][Cl]$ compared to $[A336][SCN]$ is that chloride anions are relatively redox stable and they cannot decompose, so the chloride system is much more stable even in strongly acidic conditions. No signs of decomposition were observed under the extraction conditions.

Table 3: Extraction percentages (%E), distribution ratios (D) and separation factors (α) for the Cl^-_{aq}/Cl^-_{org} system at the conditions $3.6 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$, 40°C , 2000 rpm, 2 h.

	Metal	α			%E	D
		Cu(II)	Sm(III)	Co(II)		
O/A = 1	Co(II)	7			99.9	> 700
	Cu(II)		> 300		99.3	> 100
	Sm(III)			> 2000	25.5	0.34
O/A = 0.25	Co(II)	6			99.8	1800
	Cu(II)		6000		98.7	300
	Sm(III)			36000	1.4	0.05

3.4. Extraction with [A336][NO₃]

The Cl⁻_{aq}/NO₃⁻_{org} system is the second split-anion solvent extraction system investigated. Upon extraction from an aqueous feed solution containing 3.6 mol·L⁻¹ CaCl₂ and O/A = 1, about 60% Sm(III) was co-extracted to the ionic liquid phase with transition metals (Figure 7). This is three times more than was observed for the Cl⁻_{aq}/Cl⁻_{org} system. In agreement with the data presented by Larsson and Binnemans on the split-anion extraction, the Cl⁻_{aq}/NO₃⁻_{org} system (Table 4) showed larger distribution ratios of Sm(III) than the Cl⁻_{aq}/SCN⁻_{org} system (Table 1) [33]. The authors compared the distribution ratios across the lanthanide series (including Sm) using the ionic liquids [A336][SCN] and [A336][NO₃] from single-element chloride solutions with a matrix of 4 mol·L⁻¹ MgCl₂. The thiocyanate ions have a stronger affinity for the ionic liquid phase than nitrate ions as can be derived from their stability constants [46]. A higher miscibility of the phases was also expected in the Cl⁻_{aq}/NO₃⁻_{org} system [34]. The optimization with respect to loading was found to be very important for process development. The authors applied the volume phase ratio O/A = 1. As shown in Table 4, the distribution ratio of Sm(III) for the Cl⁻_{aq}/NO₃⁻_{org} system (as well as for the Cl⁻_{aq}/Cl⁻_{org} system) can decrease when applying O/A = 0.25 (Figure 8).

Figure 7: Extraction percentage of Co(II), Cu(II) and Sm(III) as a function of the initial CaCl_2 concentration in the aqueous phase for the $\text{Cl}^-_{\text{aq}}/\text{NO}_3^-_{\text{org}}$ system. Conditions: $O/A = 1$, 40 °C, 2000 rpm, 2 h. The results for the volume ratio $O/A = 0.25$ are marked as “x”.

Figure 8: Extraction percentage of Cu(II), Co(II) and Sm(III) in the $\text{Cl}^-_{\text{aq}}/\text{NO}_3^-_{\text{org}}$ system as a function of the volume ratio (O/A). Conditions: $3.6 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$, 40°C , 2000 rpm, 2 h.

Table 4: Extraction percentages (%E), distribution ratios (D) and separation factors (α) for the $\text{Cl}^-_{\text{aq}}/\text{NO}_3^-_{\text{org}}$ system at the conditions $3.6 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$, 40°C , 2000 rpm, 2 h.

	Metal	α			%E	D
		Cu(II)	Sm(III)	Co(II)		
O/A = 1	Co(II)	4			99.8	400
	Cu(II)		60		99.3	> 100
	Sm(III)			> 250	60.8	1.55
O/A = 0.25	Co(II)	3			99.3	600
	Cu(II)		2500		97.8	200
	Sm(III)			7500	1.9	0.08

Selective scrubbing of Sm(III) from the ionic liquid was done by contacting the loaded organic phase with $3.6 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$. Scrubbing was slightly better for the $\text{Cl}^-_{\text{aq}}/\text{Cl}^-_{\text{org}}$ system than for the $\text{Cl}^-_{\text{aq}}/\text{NO}_3^-_{\text{org}}$ system. After only one scrubbing step, less than 1% Sm(III) remained in $[\text{A336}][\text{Cl}]$, whereas in the $\text{Cl}^-_{\text{aq}}/\text{NO}_3^-_{\text{org}}$ system less than 2% Sm(III) remained co-extracted. If the targeted purities are higher, the scrubbing step should be repeated once more. Sm(III) can be recovered from the raffinate by precipitation with oxalic acid, the oxalate $\text{Sm}_2(\text{C}_2\text{O}_4)_3$. After filtration, the precipitate can be calcined to pure Sm_2O_3 [59].

The distribution ratios of Co(II) and Cu(II) were very low ($D \sim 0.00$) at $0 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$ (Figure 7, Table 4). As a consequence, stripping of $[\text{A336}][\text{Cl}]$ and $[\text{A336}][\text{NO}_3]$ could be done with water, instead of acids or bases [33]. The possibility to strip with water is an environmental

advantage as explained by Wellens *et al.* for the separation of Co(II) from Ni(II) [31]. During the stripping with water, the extracted chloride complexes of transition metals start to form hexaaquo complexes in water. Transition metals were removed to the water phase with high stripping efficiencies: $\%St_{Co} = 99.4\%$ and $\%St_{Cu} = 87.8\%$ for [A336][Cl], and $\%St_{Co} = 99.2\%$ and $\%St_{Cu} = 82.3\%$ for [A336][NO₃]. For more complete stripping of metals, this step could be repeated two or three times. After stripping, the ionic liquid can be directly reused as the extracting phase.

To summarize, the overview of extraction results for all the three solvent extraction systems is given in Table 5.

Table 5: Overview of the extraction results at the optimized conditions for a mixed metal feed solution containing 9.3 g·L⁻¹ Co(II), 9.2 g·L⁻¹ Sm(III) and 0.8 g·L⁻¹ Cu(II).

Solvent extraction system	Co-extracted Sm [%]	Extracted Co [%]	Extracted Cu [%]
Cl ⁻ _{aq} /SCN ⁻ _{org} ^a	0	100	100
Cl ⁻ _{aq} /Cl ⁻ _{org} ^b	1	100	99
Cl ⁻ _{aq} /NO ₃ ⁻ _{org} ^b	2	99	98

^a optimized conditions: 1.2 M CaCl₂, O/A = 1; ^b optimized conditions: 3.6 M CaCl₂, O/A = 0.25

3.5. Extraction mechanism

EXAFS is a useful technique to investigate the metal extraction mechanism. In general, the extraction of metals to the IL phase can proceed *via* three mechanisms: (1) ion-pair extraction (the extraction of the metal cations with the corresponding anions from the aqueous phase

towards the ionic liquid), (2) ion exchange (anions or cations from ionic liquid or protons from the extractant are exchanged by metal ions from the aqueous phase) or (3) a combination of both [60]. For this experiment, only single-metal solutions were prepared considering the optimized CaCl_2 concentration and the volume ratio. Summary of the EXAFS study and the structures of the complexes are presented in Table 6. The isolated EXAFS function $\chi(k) * k^3$ with the model and the Fourier transform of the $[\text{CoCl}_4]^{2-}$ complex are given as a typical example in Figure 9. More EXAFS data are available as Supplementary Material.

Table 6: Complexes present in IL after extraction for the studied solvent extraction systems, results from the EXAFS measurements.

Solvent extraction system	Sm	Co
$\text{Cl}^-_{\text{aq}}/\text{SCN}^-_{\text{org}}$ ^a	$[\text{Sm}(\text{SCN})_8]^{5-}$	$[\text{Co}(\text{SCN})_4]^{2-}$
$\text{Cl}^-_{\text{aq}}/\text{Cl}^-_{\text{org}}$ ^b	$[\text{Sm}(\text{H}_2\text{O})_9]^{3+}$	$[\text{CoCl}_4]^{2-}$
$\text{Cl}^-_{\text{aq}}/\text{NO}_3^-_{\text{org}}$ ^b	$[\text{Sm}(\text{NO}_3)_5]^{2-}$	$[\text{CoCl}_4]^{2-}$

^a optimized conditions: 1.2 M CaCl_2 , O/A = 1; ^b optimized conditions: 3.6 M CaCl_2 , O/A = 0.25

(a)

(b)

Figure 9: (a) EXAFS function $\chi(k)*k^3$ (black) and model (red); (b) Fourier transform (black) and model (red) of the $[\text{CoCl}_4]^{2-}$ complex in $[\text{A336}][\text{Cl}]$, measured on the K-edge of Co (7709 eV). The data were Fourier-transformed between $k = 2.0$ and $12.9 \text{ \AA}^{-1}$ with a Gaussian rounded ends function and fitted to the model between $r = 0$ and $3 \text{ \AA}$.

All the ILs tested are labeled in the literature as ‘anion exchangers’. However, the split-anion extraction is an exceptional case, since chloride anions have to be co-extracted together with the metal ions to keep the electrical neutrality [33]. As will be discussed below, it was indeed found that the extraction mechanism of the systems studied (Table 6) occurs mainly *via* ion-pair rather than *via* an ion-exchange mechanism.

In the $\text{Cl}^-_{aq}/\text{SCN}^-_{org}$ system, the SCN^- anion has a very good coordinating ability towards transition metals and rare-earth ions [46]. Despite the stability issues associated with the thiocyanate anion, the speciation of the loaded $[\text{A336}][\text{SCN}]$ has been made. The coordination number of Co(II) was found by EXAFS to be 4, which means that it forms tetrahedral complexes with thiocyanate ligands (equation 6). Because the transition metals are extracted as -2 charged complexes, two molecules of the ionic liquid are needed for the extraction of one Co(II) ion at $3.6 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$. For low ionic strengths (SCN^- and Cl^- concentrations of $0.1 \text{ mol}\cdot\text{L}^{-1}$), $[\text{Cu}(\text{SCN})_3]^-$ anionic complexes were reported to be unstable and to be reduced to the copper(I) complex $[\text{Cu}(\text{SCN})_2]$ [61]. An increase in ionic strength from 0.1 to $1 \text{ mol}\cdot\text{L}^{-1}$ made extraction of $[\text{Cu}(\text{SCN})_3]^-$ species possible. Because the concentrations of SCN^- and Cl^- anions were much higher in our extraction experiments, the copper(II) thiocyanate complex was stable under these conditions. The speciation of Cu(II) was therefore assumed to be the same as for Co(II), since they belong to the first transition series [71]. It was shown by EXAFS that Sm(III) was possible to extract at $3.6 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$ by an ion-pair mechanism, forming a negatively charged complex with eight thiocyanate counter ions (equation 7). The species in the organic phase are marked with overbars. Symbol $M = \text{Co}$ or Cu .

In the Cl^{-}_{aq}/Cl^{-}_{org} system, cobalt was extracted as the anionic tetrachloro complex $[CoCl_4]^{2-}$ (equation 8), which holds true at high $CaCl_2$ concentration in the aqueous phase that was applied. The coordination sites of the anionic species are fully occupied by the chloride anions. According to the literature, the predominant extraction mechanism for quaternary ammonium salts is anion exchange [69], [62]. We cannot draw the same conclusion on the basis of equation 8, since the chloride anions in ionic liquid can originate either from the aqueous or the organic phase. The transition metals were therefore extracted in the Cl^{-}_{aq}/Cl^{-}_{org} system either by an ion-pair mechanism or by an anion-exchange mechanism. Sm(III) does not form complexes with chloride anions in an aqueous solution, because the stability constants of complexes of rare-earth ions with chloride anions are low [55], [63]. Instead, there is a high affinity of Sm(III) for water. This suggests that Sm(III) cannot be extracted to the ionic liquid containing chloride anions, but it does not apply when a salting-out agent is used. $CaCl_2$ as a salting-out agent consists of the non-extractable cation (Ca^{2+}) and the anion of the extractable species (Cl^{-}). So in a highly concentrated solution ($3.6 \text{ mol} \cdot \text{L}^{-1} CaCl_2$), the extractable complexes are formed as hydrated Sm(III)-containing ion pairs with chloride anions to keep the charge neutrality [64], [65]. Therefore at high salt concentrations, Sm(III) is salted-out to the ionic liquid as the $[Sm(H_2O)_9]^{3+}$ complex *via* ion-pair mechanism (equations 9 and 10).

The distribution ratios of the extracted Co(II) and Cu(II) ions in the $\text{Cl}^-_{aq}/\text{Cl}^-_{org}$ and $\text{Cl}^-_{aq}/\text{NO}_3^-_{org}$ systems depend on the chloride concentration in the aqueous phase, because even in the $\text{Cl}^-_{aq}/\text{NO}_3^-_{org}$ system, Co(II) was extracted as a chloro complex and not as a nitrate complex (equation 11). In the $\text{Cl}^-_{aq}/\text{NO}_3^-_{org}$ system, Co(II) was extracted through an anion-exchange mechanism forming $[\text{CoCl}_4]^{2-}$ complex. However, when the transition metals are extracted and subsequently stripped, the nitrate anion present in the IL is replaced by the tetrachlorocobaltate anion. The loss of IL anions to the aqueous phase due to ion exchange causes problems for a possible transformation to a continuous setup. The IL thus needs to be regenerated and cannot be reused directly for another extraction step [31], [66]. Moreover, as mentioned in the introduction, HCl is in industrial processes preferred over HNO_3 . If HNO_3 is generated in the aqueous phase, the advantage of a closed-loop process for the $\text{Cl}^-_{aq}/\text{NO}_3^-_{org}$ system is lost because of the ion-exchange mechanism. An ion-pair mechanism applies to the Sm(III) cation and the chloride anion from the aqueous phase, since they are simultaneously extracted. Sm(III) forms negatively charged complexes with nitrate ions, $[\text{Sm}(\text{NO}_3)_5]^{2-}$, and chloride ions are co-extracted to maintain the electrical neutrality (equation 12) [33].

4. Conclusions

This study contributes to indirect SmCo magnets recycling by solvent extraction, which is relevant for the recovery of individual high-purity metals instead of direct reprocessing of magnets. Solvent extraction systems with quaternary ammonium salts were tested without the addition of any diluents. In addition, the processes require a minimal use of chemicals and are environmentally friendly. The achieved extraction/scrubbing/stripping efficiencies were very high, already after a single contact. At a fine-tuned salt concentration, the $\text{Cl}^-_{\text{aq}}/\text{SCN}^-_{\text{org}}$ system allowed to reach very high extraction efficiencies of transition metals ($> 99.9\%$ Co and $> 99.7\%$ Cu) without any co-extraction of samarium. However this system seemed to have stability issues, because of the unstable thiocyanate anion. The extracted metals could not be removed efficiently from $[\text{A336}][\text{SCN}]$ due to poor stability of the quaternary ammonium salts in alkaline conditions and impossible stripping with water. On the other hand, the $\text{Cl}^-_{\text{aq}}/\text{Cl}^-_{\text{org}}$ and $\text{Cl}^-_{\text{aq}}/\text{NO}_3^-_{\text{org}}$ systems are stable even in concentrated chloride media. The best extraction and scrubbing results were achieved at $3.6 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$ and $\text{O/A} = 0.25$, also leading to very high extraction efficiencies of transition metals and only a limited co-extraction of Sm(III). As an environmentally friendly approach, the stripping of loaded $[\text{A336}][\text{Cl}]$ and $[\text{A336}][\text{NO}_3]$ could be done by water. A study of the extraction mechanism showed a different tendency in extraction of the trivalent rare-earth ion Sm(III) and the divalent transition metal ions Co(II) and Cu(II). In the split-anion extraction system $\text{Cl}^-_{\text{aq}}/\text{NO}_3^-_{\text{org}}$, transition metals were extracted *via* an ion exchange mechanism. This leads to unacceptable dissolution of nitrate ions in the aqueous phase at high salt concentrations and subsequent problems with transformation to a continuous process. The predominant extraction mechanism in the $\text{Cl}^-_{\text{aq}}/\text{SCN}^-_{\text{org}}$ and $\text{Cl}^-_{\text{aq}}/\text{Cl}^-_{\text{org}}$ systems was ion-pair

formation. The $\text{Cl}^-_{aq}/\text{Cl}^-_{org}$ system appeared to be the most viable solvent extraction system for further development to a continuous process.

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Conflicts of interest

There are no conflicts to declare.

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Table of Content Graphic

Highlights

- Metal separations relevant to recycling of SmCo magnets were investigated
- Aliquat 336 and its thiocyanate and nitrate forms were tested from chloride solutions
- Cobalt was efficiently extracted, while samarium was left in the raffinate
- Stripping from the loaded chloride and nitrate ionic liquids could be done with water
- Stripping from the loaded thiocyanate ionic liquid was difficult due to poor stability