Solvometallurgical route for the recovery of Sm, Co, Cu and Fe from SmCo permanent magnets

Martina Orefice, Heleen Audoor, Zheng Li, Koen Binnemans⁎

KU Leuven, Department of Chemistry, Celestijnenlaan 200F, P.O. Box 2404, B-3001 Leuven, Belgium

ARTICLE INFO

Keywords:
SmCo magnets
Metal recovery
Samarium
Non-aqueous solvent extraction
Solvometallurgy

ABSTRACT

A solvometallurgical recycling route for the recovery of samarium, cobalt, copper and iron from SmCo magnets was developed. The SmCo magnets were first crushed and milled to powder size and then leached in a 2 mol L⁻¹ hydrochloric acid solution in ethylene glycol. Afterwards, cobalt, copper and iron were extracted from the leachate with 50 wt% Aliquat 336 in toluene, which was pre-saturated with 37 wt% HCl. The non-aqueous solvent extraction system improved the extraction efficiency of cobalt. The extraction was optimized by evaluating the extraction rates, the effects of temperature, feed/solvent ratio and the hydrochloric acid concentration. Through the construction of a McCabe-Thiele diagram it was possible to calculate the number of stages required for continuous extraction. Cobalt was recovered from the loaded solvent by stripping with a 0.5 mol L⁻¹ aqueous hydrochloric acid solution. Copper was recovered by stripping with a 5 vol% aqueous ammonia solution, whereas iron precipitated under these conditions. The solvent could be reused after regeneration, i.e. evaporation of water and ammonia and reintegration of toluene and HCl. The samarium left in the raffinate was extracted by 20 vol% Cyanex 272 in n-dodecane. Finally, samarium was recovered from the loaded Cyanex 272 by precipitation stripping with a 0.2 mol L⁻¹ aqueous oxalic acid solution. The purity of the recovered cobalt chloride was 98.3 wt% and that of samarium oxalate was 99.4 wt%.

1. Introduction

SmCo permanent magnets were introduced in 1967 by Strnat and co-workers, using SmCo₅ magnetic alloys [1,2]. Although these SmCo₅ magnets have a very high coercivity, $H_c$, independently of the manufacturing process, they show a low saturation magnetization, in contrast to magnets made of the Sm₂Co₁₇ alloy [3]. The advantages of the two alloys can be combined in a composite structure. In this case, the main phase is the Sm₂Co₁₇ phase, usually with addition of copper and iron to decrease the cobalt content and to increase the saturation magnetization [4,5]. The Sm₂Co₁₇ phase domains are surrounded by the SmCo₅ phase [6,7]. The Curie temperature ($≥ 747 °C$) and the maximum operating temperature ($≥ 250 °C$) of SmCo permanent magnets strongly exceed those of NdFeB permanent magnets. Therefore, SmCo magnets are used for high-temperature applications, such as turbomachinery and motors of high-end electric cars [8–10]. Another difference with NdFeB magnets is that the supply risk and price instability of SmCo magnets do not depend on the rare-earth element, Sm, but rather on the cobalt in the magnet alloy. In fact, the limited market volumes of SmCo magnets ensure that the samarium supply it not at risk [11]. The cobalt abundance in the Earth’s crust is comparable to that of neodymium [12]. The cobalt market is wider and clearly in the ascendency, owing to the rapid rise of lithium ion batteries, in which cobalt is typically used in the cathode material [1]. A burgeoning risk of a supply crunch in cobalt poses one of the key threats to forecasts for increasing electric vehicle adoption [13].

End-of-life SmCo magnets are a very good secondary resource for cobalt and samarium. Several studies have been published recently concerning the recovery of samarium and cobalt from SmCo magnets [14–20]. Despite some differences in the leaching and/or in the separation steps, all reported processes are based on hydrometallurgy. Since recently, an alternative to traditional hydrometallurgy is appearing: i.e. solvometallurgy, which can be considered as a new branch in extractive metallurgy [21]. A metal-processing route is defined as being "solvometallurgical" if water is largely replaced by an organic solvent. This implies different options: leaching in concentrated inorganic or organic acids [22,23], mineral acids diluted in organic solvents as lixiviant or the use of ionic liquids both in leaching and in non-aqueous solvent extraction processes [24]. Solvometallurgy can be combined with hydrometallurgy into an optimized flow sheet [25–27].

In this paper, we describe a solvometallurgical route for indirect recycling of SmCo scrap to recover samarium, cobalt and copper. The...
process involves a combination of solvoleaching and non-aqueous solvent extraction.

2. Experimental

2.1. Materials

Ethylene glycol (EG) (99.5%) and n-dodecane (≥99.0%) were purchased from Acros Organics (Geel, Belgium), while hydrochloric acid (37 wt% solution in water) and ammonia solution (25 wt% NH₃ solution in water) were obtained from VWR Chemicals (Haarnd, Belgium). Nitric acid (65 wt% solution in water) and ICP standard solutions of cobalt, copper, europium, iron, samarium and zirconium (1000 mg L⁻¹ in 3–5 wt% HNO₃) were supplied by ChemLab (Zedelgem, Belgium). Toluene (99.0%) and sodium hydroxide pearls (≥99.0%) were obtained from Fisher Scientific (Mellebeke, Belgium). The ionic liquid Aliquat® 336 (a commercial mixture of methyltriocylammonium chloride and methyltridecylammonium chloride, with the former dominating), and oxalic acid (99%) were obtained from Sigma–Aldrich (Diegem, Belgium). The extractant Cyanex® 272 (bis{(2,4,4-trimethylpentyl)phosphinic acid) was purchased from Cytec Industries (Vlaardingen, Netherlands) and lithium chloride (≥99%) from Carl Roth GmbH (Karlsruhe, Germany). Samarium(III) chloride hexahydrate (99.9%) was supplied by Strem Chemicals Inc. (Kehl, Germany). All the chemicals were used as received, without any further purification. Ultrapure water (resistivity 18.2 MΩ cm) was obtained from a Millipore device. Demagnetized SmCo permanent magnets were kindly provided by Magnetik Ljubljana d.d. (Slovenia).

2.2. Instrumentation

SmCo magnets were first crushed by a hydraulic press and subsequently reduced into powder by a Fritsch Planetary Mill Pulverisette 7. Automatic shaking sieves, Analysette 3 Spartan by Fritsch, were used to collect fractions of the milled powder. The particle size distribution of the SmCo powder was determined by a laser diffractrometer, i.e. Malvern Masterizer 3000. The morphology of the SmCo powder was studied by scanning electron microscopy (SEM) using a Philips XL30 FEG electron microscope. The mineralogical composition was determined by X-ray diffraction (XRD) using a Seifert 3003 T/T device (Seifert Analytical X-ray). Metal concentrations in the aqueous hydrochloric acid and in EG–HCl solutions were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES), i.e. model Perkin Elmer Optima 8300. Data were processed by the software Syngistix 1.0.1.1275.

All the experiments were carried out in glass vials. For the leaching tests, setups of aluminum blocks, magnetic stirring bars and heating—stirring plates (IRE, RCT basic) were used. The solvent extraction and stripping experiments were carried out in a thermo-controlled TMS-300 Turbo Thermo Shaker Incubator (nemusLIFE). The acid-saturated solvent extraction X-ray fluorescence (TXRF) spectrometer: a droplet of the solvent was added on a quartz carrier, which was dried in an oven at 60 °C, prior to the analysis [28]. The data analysis was performed using the Picofox 7.5.3.0 software.

2.3. Pre-treatment and characterization of SmCo permanent magnets

The bulk solids were reduced to coarse particles by a hydraulic press and then milled in a planetary ball mill. The applied conditions for milling were: stainless steel pots and balls (diameter 10 and 1 mm), charge ratio = 3/1 balls-to-powder, speed = 600 rpm, milling time = 5 min with 5 min pause, cycles = 3, solvent = ethanol. The parameters applied to record the diffractogram of the crystalline structure of the milled, unsieved SmCo powder were: 2θ = 20°–90°, radiation = Cu Kα, acceleration voltage = 40 kV, acceleration current = 40 mA, a step size of 0.02° and a counting time of 1 s per step, spin mode. The X’Pert HighScore software was used to analyze the collected data by comparison with the ICDD (International Centre for Diffraction Data). The analytical conditions for the particle size distribution were: suspending fluid = water; incident wavelength: λblue = 470 nm and λred = 632.8 nm. The chemical composition of the magnets was determined in the following way: about 125 mg of magnet material was dissolved in 10 mL of 37 wt% HCl by stirring at 80 °C until the solid was completely dissolved. An aliquot of the solution was diluted 1000 times in volume for analysis of the major elements cobalt, copper, iron, samarium and zirconium via ICP-OES.

2.4. Solvometallurgical leaching of SmCo magnet powder

As for the leaching, the HCl concentration in EG and the liquid/solid (L/S) ratio (mL g⁻¹) were first optimized. The effect of the HCl concentration in EG on the leaching time was tested by varying this concentration using the following values (mol L⁻¹): 6, 4, 3, 2.5, 2, 1.1. A L/S ratio of 20/1 was chosen for these tests. Subsequently, the L/S ratio was varied in the range of 4/1, 5/1, 10/1, 20/1 by adding the relevant amounts of magnet powder to 1 mL of 37 wt% HCl diluted in EG. A comparison with an aqueous solution of 37 wt% HCl was made at the following conditions: HCl concentration in water = 2 mol L⁻¹ and L/S ratio = 20/1. All leaching tests were conducted by stirring the mixtures at 300 rpm at 80 °C until complete dissolution of the powder was observed.

2.5. Solvent extraction experiments

Two equivalent solutions of leachate from, respectively, 2 mol L⁻¹ hydrochloric acid in EG and 2 mol L⁻¹ hydrochloric acid in water were stirred for 60 min at 40 °C, in each case with an equal volume, 2 mL, (feed/extract volume ratio, or F/E = 1/1) of Aliquat 336 50 wt% diluted in toluene. These and all the following solvent extraction tests were performed by shaking the vials at 1000 rpm in TMS-300 Turbo Thermo Shaker Incubators. After settling, the metal concentrations in the raffinate were measured by diluting the solutions 1000 times in volume in 2 vol% HNO₃ and analyzing them with ICP-OES. The fraction extracted (%E) was calculated using the formula:

\[
\%E = \left(1 - \frac{n_E}{n_F}\right)100
\]

where \(n_E\) and \(n_F\) are the moles of metal in the feed and in the raffinate, respectively. The effect of 37 wt% HCl in the ionic liquid was also tested. Solvent extraction was performed on the leachate in EG at the same conditions as reported above (F/E = 1/1, T = 40 °C, t = 60 min.) with Aliquat 336 50 wt% diluted in toluene saturated with 37 wt% HCl. All further tests were performed with Aliquat 336 50 wt% diluted in toluene saturated with 37 wt% HCl, also referred to as “solvent”. An equal mass of Aliquat 336 50 wt% in toluene and 37 wt% HCl was mixed together and then centrifuged at 4000 rpm for 5 min. The effect of both the temperature and the F/E ratio with respect to the %E were evaluated by performing two extractions at room temperature, for 60 min and F/E = 1/1 and 1/2. The extraction rate was analyzed with a series of extractions at room temperature, F/E = 1/2 and mixing times: 1, 2, 5, 10, 20, 30, 60 min. Finally, a McCabe–Thiele diagram was constructed to calculate the number of stages that are required for the full extraction of the transition metals. The equilibrium curves were drawn by varying the F/E ratio in the following range = 4/1, 2/1, 1/1, 1/2, 1/4, 1/8, 1/16. Other operating parameters were: T = room temperature, t = 60 min. The operating lines were drawn assuming no
transition metals in the raffinate and constant flows in the mass balances, as is the case in non-volatile diluted systems
\[ y = \left( \frac{F}{E} \right) (x - x_0) \]  
(2)

where \( y \) and \( x \) are the metal concentrations (mg L\(^{-1}\)) at any stage, in the solvent and in the feed respectively, and \( x_0 \) is the metal concentration in the raffinate in the last stage, which is 0 for complete stripping. The results from the McCabe–Thiele diagrams were validated by performing a lab-scale test with three stages at a F/E ratio of 1/2. The total volume in each stage varied between 20 and 16 mL, while the mixing time was 60 min at room temperature.

2.6. Metal recovery from the loaded solvents

The next steps in the flow sheet consisted of the removal of cobalt, copper and iron from the loaded solvent, which allows to recover the metals and to regenerate the solvent. Only the extract with the highest metal concentration, i.e. the one obtained after the first extraction stage, was considered for stripping studies. Cobalt was stripped from the solvent by aqueous HCl to subsequently recover the cobalt as chloride salt. Different HCl concentrations, 0.5, 1.0, 2.0 and 4.0 mol L\(^{-1}\), were tested at the following conditions: volume ratio of solvent/stripping agent (E/S) = 1/1, temperature = room temperature, shaking speed = 2000 rpm and shaking time = 30 min. The solvcat was purified by removing iron and copper using a 5 vol% of concentrated aqueous ammonia solution, at the following working conditions: E/S ratio = 1/1, temperature = room temperature, and shaking time = 30 min. The stripping yields were calculated using Eq. (3):

\[ \%S = \left( 1 - \frac{n_{LS}}{n_{RS}} \right) \times 100 \]  
(3)

where \( n_{RS} \) and \( n_{LS} \) are the moles of metal in the stripping feed and in the loaded stripping agent, respectively. The precipitate was separated by filtration, washed with water and ethanol and dried in a vacuum oven at 50 °C for at least 3 h. Subsequently, the precipitate was re-dissolved in 37 wt% HCl to determine the purity via ICP-OES analysis. The Aliquat 336-based solvent was regenerated by drying it for 1 h at 50 °C in vacuo on a rotary evaporator, and by adding once more both the toluene and the 37 wt% HCl. The regenerated solvent was then, tested in four consecutive cycles of one stage solvent extraction, stripping and regeneration. Samarium was recovered from the raffinate via extraction with Cyanex 272. A solution of 2 mol L\(^{-1}\) NaOH was used to adjust the pH and the extraction was carried out until a pH of about 7.0 was reached. The other operating parameters were: F/E ratio = 1/1, room temperature. A first test was performed on a model solution of 141.35 g of SmCl\(_3\)·6H\(_2\)O in EG to which HCl and water were added to reproduce their content in the real leachate. In a second test, the real 2 mol L\(^{-1}\) HCl in EG raffinate after the three stages extraction described above was tested. Samarium was recovered from the loaded Cyanex 272 as an oxalate salt by precipitation stripping with a 0.2 mol L\(^{-1}\) aqueous oxalic acid solution. The stripping parameters, in the latter case, were: E/S = 1/1.5; mixing time = 10 min, room temperature.

As for samarium, direct precipitation from the EG – HCl solutions was also investigated by adding an aqueous solution of oxalic acid (1 mol L\(^{-1}\)) to the raffinate in a molar ratio oxalic acid/samarium = 1.5, 2, 3, 5, 7.5, 10 and 12.5.

3. Results and discussion

3.1. SmCo permanent magnets characterisation

The magnets were received in the shape of discs of about 0.5 cm in diameter. They were crushed and then reduced to powder by wet planetary ball milling, to enhance the interfacial area and, consequently, the leaching rates. In contrast to NdFeB permanent magnet powders, the SmCo powders are not pyrophoric, which implies that milling of SmCo magnets is safer with respect to NdFeB magnets.

In Fig. 1, the particle size is reported in terms of volume distribution. The results collected by the laser diffractometer indicate that all the particles have a diameter smaller than the smallest sieve size, i.e. \( \leq 45 \mu m \). More specifically, the distribution curve corroborates that 90% of the particles (in numbers) have a diameter \( \leq 40 \mu m \).

However, when the magnet powder was manually sieved, two fractions were obtained: \( \leq 45 \mu m \) and \( 45 \mu m < d_p < 400 \mu m \), with \( d_p \) = particle diameter. Investigations by SEM, in Fig. 2(a) and (b), confirmed that no particles larger than 20 \( \mu m \) were detected; the particles which did not pass the 45 \( \mu m \) sieve at the first moment were very likely agglomerates of smaller particles. When the particle size is reduced, the specific surface area increases inversely proportional to the particle radius. Consequently, the surface forces, such as electrostatic forces, increase as well and the particles commonly tend to aggregate to minimize such forces [30].

The X-ray diffractogram of the milled magnet powder is reported in Fig. 3, revealing the composite microstructure. It can be observed that the milling treatment did not lead to the formation of metal oxides. As already discussed, both Sm\(_2\)Co\(_{17}\) and SmCo\(_5\) are present because of the particular manufacturing process, as first described by Mishra et al. [7]. A third phase was detected, where iron partially substitutes cobalt in the rare-earth–transition metal alloy.

In Table 1, the composition of the treated SmCo permanent magnets is reported in terms of the major elements cobalt, copper, iron, samarium and zirconium. About 1 wt% of the composition corresponds to minor elements (aluminum, chromium, gallium, gadolinium, manganese, nickel and zinc), which is in accordance with the data provided by the manufacturer.

Interestingly, the iron content is similar to the samarium content, which is quite high: both samarium and iron represent one fifth of the total composition (wt%). However, one should also remember that the atomic mass of samarium is about three times higher than the atomic mass of iron. Hence, the molar fraction of iron in these SmCo permanent magnets is about three times higher than that of samarium.

Copper, iron and zirconium are common additives to Sm\(_2\)Co\(_{17}\) magnets [6,7]. Addition of iron allows to decrease the cobalt content, while maintaining a good maximum energy product, \( BH_{\text{max}} \). Copper, usually 4–8 wt%, and zirconium, about 2–3 wt%, represent important additions to increase the intrinsic coercivity, \( IH_c \), and the Curie temperature.
3.2. Leaching and solvent extraction

After being characterized, the milled SmCo magnet powder was directly used for the leaching test. A non-aqueous solution of HCl in EG as lixiviant was tested to explore the opportunities of solvometallurgical leaching. EG is considered to be a green solvent. Moreover, it is a protic solvent, it has a high boiling point (197.3 °C) and it is not volatile. As such, it can be considered as a valuable alternative to water. According to the definition of solvometallurgy, the water content in the flow streams should be ≤50 vol% [21]. However, when concentrated hydrochloric acid is added to the system, water is unavoidably introduced. Nevertheless, a 1/1 mixture of 37 wt% hydrochloric acid in EG already falls within the ≤50 vol% restriction. The influence of the HCl concentration in EG with respect to the leaching of the magnets was evaluated. Complete dissolution of the SmCo magnet powder was obtained with all the tested concentrations of the inorganic acid in the organic solvent: (mol L\(^{-1}\)) 6, 4, 3, 2.5, 2, 1.1. Nevertheless, an absolute minimum in terms of water and acid content versus leaching time was found when the 5/1 ratio was used. This corresponds to a leaching time of about 150 min, a hydrochloric acid concentration of 2 mol L\(^{-1}\) and a water content of about 10 vol%. All the tests were conducted at 80 °C, with 0.250 g of SmCo magnet powder and L/S = 20/1. Once the best conditions were obtained for the non-aqueous system (2 mol L\(^{-1}\) HCl in EG), a comparative test was performed with a solution of 2 mol L\(^{-1}\) HCl in water. The non-aqueous system did not prove to be better than the aqueous one, since the time for complete dissolution was the same in the two cases. This suggests that the activity of 37 wt% HCl is not affected by the diluent, being either water or EG, very likely because the non-aqueous system still contains about 10 vol% water. At the same time, the higher viscosity of the non-aqueous system has a negligible effect on the mass transfer: the leaching kinetics are very likely dominated by an external transport mechanism, for which the flow rate is more important than the fluid parameters [31]. Solvent extraction with the ionic liquid Aliquat 336 was studied to purify the leachate from the transition metals. The ionic liquid Aliquat 336 was selected as extractant for its known affinity to transition metals in chloride media and because of its commercial availability, allowing to save on any synthesis or purification step. Aliquat 336 is a commercial mixture of quaternary ammonium compounds, with trioctylmethylammonium chloride as the main component. It is a basic extractant, which extracts metals in their corresponding anionic complexes. The associated extraction mechanism is a solvating mechanism, although one cannot exclude an anion exchange mechanism [32,33]. The ionic liquid was diluted to 50 wt% with toluene to decrease its viscosity. As for the extraction tests, the effect of the aqueous and non-aqueous feed on the percentage of extraction, %E, was studied. The results are shown in Table 2.

On average the extraction of cobalt occurs four times more efficient

---

### Table 1

Elemental composition (in wt%) of the major elements in the SmCo permanent magnets as determined by ICP-OES. Traces include Al, Cr, Ga, Gd, Mn, Ni and Zn.

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>47.9</td>
</tr>
<tr>
<td>Cu</td>
<td>4.9</td>
</tr>
<tr>
<td>Fe</td>
<td>22.6</td>
</tr>
<tr>
<td>Sm</td>
<td>20.9</td>
</tr>
<tr>
<td>Zr</td>
<td>2.8</td>
</tr>
<tr>
<td>Traces</td>
<td>0.9</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
</tr>
</tbody>
</table>

### Table 2

Percentage extraction, %E (%) of cobalt, iron and samarium at different mixing times, t (min), from the EG based leachate, %E\(_{\text{EG}}\) and from the water based leachate, %E\(_{\text{H2O}}\).

<table>
<thead>
<tr>
<th>t (min)</th>
<th>%E(_{\text{EG}}) (%)</th>
<th>%E(_{\text{H2O}}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>46</td>
<td>10</td>
</tr>
<tr>
<td>60</td>
<td>48</td>
<td>12</td>
</tr>
<tr>
<td>120</td>
<td>47</td>
<td>11</td>
</tr>
<tr>
<td>30</td>
<td>16</td>
<td>19</td>
</tr>
<tr>
<td>60</td>
<td>13</td>
<td>18</td>
</tr>
<tr>
<td>120</td>
<td>13</td>
<td>18</td>
</tr>
</tbody>
</table>

*a Experimental conditions: feed = 2 mol L\(^{-1}\) HCl in EG; metal concentrations in the feed: [Co] = 23108.9 mg L\(^{-1}\), [Fe] = 11636.6 mg L\(^{-1}\), [Sm] = 11651.6 mg L\(^{-1}\); solvent = Aliquat 336; T = 40 °C; F/E = 1/1.
in the EG-based system than in the water-based system: i.e. %E of 47% vs. 11%. The reason for this difference is that, in the case of EG, chloride anions preferentially coordinate to the cobalt ions, rather than to the water molecules. Hence, the charge density of the ion is higher and the extraction is enhanced. It is remarkable that samarium was not extracted under any of the tested experimental conditions. A very good separation of transition metals from rare earths in EG solutions by Aliquat 336 has already been reported by Li et al. [26]. In fact, the rare-earth elements do not tend to form anionic chloro-complexes and, in these conditions, they are not extracted by basic extractants. Vander Hoogerstraete et al. have recently demonstrated that rare-earth ions are weakly extracted from chloride solutions by basic extractants, but not via a mechanism of anionic complexes [33].

In all following experiments, 2 mol L\(^{-1}\) HCl in EG was selected as lixiviant. The following solvent extraction tests were all carried out for 60 min. On the basis of the work of Wellens et al., the solvent was saturated with 37 wt% hydrochloric acid to enhance the extraction of metals by providing chloride ions [34]. The results are displayed in Table 3. The saturation of the solvent with HCl also avoids losses of HCl to the more polar phase, i.e. in the feed solution, by extraction towards the Aliquat phase. The HCl concentration in the more polar phase will even increase due to back-extraction, since the HCl concentration in the saturated solvent was considerably higher with respect to the one of the feed solution. To provide a proof-of-concept, the test was carried out at a very high feed/extract ratio (F/E), i.e. 4/1. Only trace amounts of samarium were extracted, while the %E of the transition metals significantly increased: an increase in extraction percentage of almost 60% was observed for cobalt and almost 40% for iron, when the solvent is saturated with HCl compared to the previous case without HCl. This is due to the higher chloride concentration in the system. However, iron is not a valuable metal and there is little interest in its recovery, since it has a negligible supply risk [35]. The mixture of extractant (Aliquat 336), diluent (toluene) and additive (37 wt% hydrochloric acid) is referred to in the text as “solvent”. It has to be noticed, however, that these %E’s are lower than those reported above or further in the text, because of the high F/E ratio used.

Based on these findings, Aliquat 336 diluted 1/1 (in mass) in toluene and saturated with 37 wt% HCl was selected as solvent. Table 4 summarizes the effect of the temperature and the F/E ratio with respect to the %E. An operating temperature of 40 °C is not advisable since the %E only increased slightly in the case of iron and decreased for cobalt. The effect of the F/E ratio is more significant than the effect of the temperature, as expected. In particular, the extraction of cobalt is almost quantitative, exceeding 95%, in one step when using a F/E ratio of 1/2. This would mean that a higher solvent volume leads to a higher operating cost. Nevertheless, different options exist to recycle the solvent after stripping of the metals (vide infra), circumventing this drawback.

At this stage, the optimum solvent has been defined as well as the temperature and the F/E ratio. Afterwards, the extraction time was examined to evaluate if the mixing time of 60 min could be reduced (Fig. 4). The same leachate was used for the six different kinetic tests to assure more homogeneous results.

The minimum mixing time corresponds to the time at which the equilibrium of the system is reached, i.e. when the %E as a function of the time reaches a constant value. Unfortunately, the equilibrium was not reached with less than 60 min of mixing. This time is much longer than that previously reported with respect to the extraction of metals via the ionic liquid Aliquat 336 [25,36,37]. This is most likely caused by the higher viscosity of the two phases compared to traditional solvent extraction systems. Enhancing the mixing could improve the mass transfer, hence accelerating the process. For industrial applications, the duration of the full recycling process does not only depend on this non-aqueous solvent extraction step. Each extraction stage is, in fact, still faster than the leaching step, for which a complete dissolution time of about 150 min was observed with no significant differences between the non-aqueous and aqueous systems (vide supra).

Finally, the number of stages required for the total separation of cobalt, copper and iron from samarium was calculated with the McCabe–Thiele method. The equilibrium concentration of a single element in both the raffinate and the extract phase, at different F/E ratios, are plotted. The operating line is drawn by defining the working conditions, i.e. the F/E ratio. McCabe–Thiele diagrams of cobalt and iron are presented in Fig. 5(a) and (b), respectively. The equilibrium curves were drawn by varying the F/E ratio in the following range = 4/1, 2/1, 1/1, 1/2, 1/4, 1/8, 1/16. Such ratios were chosen to describe

### Table 3

<table>
<thead>
<tr>
<th>Solvent</th>
<th>%E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A336/toluene</td>
<td>57</td>
</tr>
<tr>
<td>37 wt% HCl sat.-A336/toluene</td>
<td>64</td>
</tr>
</tbody>
</table>

* Experimental conditions: feed = 2 mol L\(^{-1}\) HCl in EG; metal concentrations in the feed: \([\text{Co}]=23108.9 \text{mg L}^{-1}, [\text{Fe}]=11636.6 \text{mg L}^{-1}, [\text{Sm}]=11651.6 \text{mg L}^{-1}\); \(T=40^\circ\text{C}, F/E (\%)=4/1\); mixing time = 60 min.

### Table 4

<table>
<thead>
<tr>
<th>%E (%)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>F/E ratio (%)</th>
<th>%E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/1</td>
<td>40</td>
</tr>
<tr>
<td>1/1</td>
<td>RT</td>
</tr>
<tr>
<td>1/2</td>
<td>RT</td>
</tr>
</tbody>
</table>

* Experimental conditions: feed = 2 mol L\(^{-1}\) HCl in EG; metal concentrations in the feed: \([\text{Co}]=23108.9 \text{mg L}^{-1}, [\text{Fe}]=11636.6 \text{mg L}^{-1}, [\text{Sm}]=11651.6 \text{mg L}^{-1}\); solvent = 37 wt% HCl saturated–Aliquat 336 50 wt% in toluene; mixing time = 60 min. RT = room temperature.

### Fig. 4

%E (%) as a function of the mixing time, t (min), of cobalt (■), iron (○) and samarium (●) from the SmCo magnets leachate. Operating conditions: feed = 2 mol L\(^{-1}\) HCl in EG; metal concentrations in the feed: \([\text{Co}]=23108.88 \text{mg L}^{-1}, [\text{Fe}]=11636.63 \text{mg L}^{-1}, [\text{Sm}]=11651.63 \text{mg L}^{-1}\); solvent = 50 wt% Aliquat 336 solution in toluene saturated with 37 wt% HCl; F/E = 1/2, T = room temperature, mixing speed = 1000 rpm.
the equilibrium for solutions (raffinate and extract) from very concentrated to very diluted. The operating line had a slope equal to the operating F/E of 1/2. since at F/E = 1/1 the operating line crossed the equilibrium curve.

Whereas, with a F/E ratio = 1/2, two stages are necessary to extract about 98% cobalt from the leachate, three stages are required for iron extraction. Since cobalt and iron occur together in the extract stream, the total number of extraction stages, to completely separate all the transition metals from the rare-earth elements, adds up to three. At the high F/E ratio of 4/1, the McCabe–Thiele diagram for cobalt shows saturation of the solvent, which the corresponding diagram for iron does not display. In fact, the cobalt concentration in the solvent drops by 21% at higher cobalt concentrations in the raffinate, i.e. also at higher F/E ratios. This is depicted in Fig. 5(a).

The three-stage process was tested in the lab to corroborate if all cobalt and iron could be quantitatively extracted. Fig. 6 reports the %E TOTAL (%), of cobalt (■), copper (●), iron (▲) and samarium (♦) from the SmCo magnets leachate. Operating conditions: feed = 2 mol L⁻¹ HCl in EG; metal concentrations in the feed: [Co] = 23108.88 mg L⁻¹, [Fe] = 11636.63 mg L⁻¹, [Sm] = 11651.63 mg L⁻¹; solvent = 50 wt% Aliquat 336 solution in toluene saturated with 37 wt% HCl; mixing time (min) = extraction equilibrium time = 60, operating F/E ratio = slope of the operating line = 1/2; T = room temperature.

Based on the preceding results, the first two steps of the flow sheet, leaching and solvent extraction of the transition metals, have now been defined. The leaching conditions are: lixiviant = 2 mol L⁻¹ HCl in EG, L/S (mL g⁻¹) = 20; time for complete dissolution (min) = 150; T (°C) = 80. The conditions of the non-aqueous solvent extraction are: solvent = 50 wt% Aliquat 336 solution in toluene saturated with 37 wt% HCl; mixing time (min) = 60; F/E = 1/2, T = room temperature, which varied in all the tests between about 25 °C and 28.5 °C. The next stage is to recover samarium from the raffinate of 2 mol L⁻¹ HCl in EG and cobalt from the extract of 50 wt% Aliquat 336 solution in toluene saturated with 37 wt% HCl. Furthermore, iron has to be stripped from the solvent, which can be recycled to the first stage of the non-aqueous solvent extraction.

3.3. Rare-earth recovery from the raffinate

Conventionally, the raffinate from the solvent extraction is an aqueous solution. When the solution has a mono-element character, or when the solubility is different for the distinct dissolved elements, the most straightforward method to recover the metals from the raffinate is via precipitation. At lab-scale, the rare-earth metals are usually precipitated as oxalates by the addition of oxalic acid to the aqueous raffinate. Subsequently, the oxalates are converted to oxides via calcination. To the best of our knowledge, solubility and precipitation of rare-
earth elements in EG solutions have not been investigated in detail [38]. To explore this, varying volumes of a 1 mol L\(^{-1}\) aqueous solution of oxalic acid were added to 1 mL of raffinate to obtain the following ratios: \(n(\text{oxalic acid})/n(\text{samarium}) = 3, 5, 7.5, 10\) and 12.5. Precipitation was only observed in the sample containing the highest amount of oxalic acid, i.e. \(n(\text{oxalic acid})/n(\text{samarium}) = 12.5\). A qualitative TXRF analysis of the raffinate after precipitation revealed that it still contained samarium. Therefore, it is concluded that rare-earths precipitation as oxalates in an EG solution is not a suitable recovery option, because a large amount of chemicals were required and full precipitation of the rare-earth elements was not feasible. As an alternative, a non-aqueous solvent extraction step was studied to recover samarium from the EG-based leachate.

Different commercial extractants were tested: first a mixture predominantly made up of trietylphosphine oxides (Cyanex 923), and then a mixture mainly made up of bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272). Once more, the choice went out to a commercially available extractant, allowing to keep the process as convenient as possible in view of subsequent upscaling. Cyanex 923 was not suitable, because the significant amount of water in the feed solution, the 2 mol L\(^{-1}\) HCl in EG rich in samarium, lowers the extraction. Furthermore, a high concentration of chloride anions it required to coordinate the extracted samarium [26]. As for the acidic extractant Cyanex 272, this one only works at pH above 4, which implies that the acid in the feed solution has to be neutralized, for example by adding a solution of sodium hydroxide. In addition, the extraction mechanism consists of cation exchange: the phosphinic acid releases protons in order to complex the samarium ion. As a consequence, the pH diminishes but the extraction efficiency drops accordingly.

Solvent extraction of samarium from the 2 mol L\(^{-1}\) HCl in EG solution was carried out with a solution of 20 vol% Cyanex 272 in n-dodecane with a dropwise addition of a 2 mol L\(^{-1}\) sodium hydroxide solution to reach a neutral pH at equilibrium. Extraction from a model solution of samarium chloride hexahydrate in EG corroborated that 87.2% of samarium was extracted in one stage with an equilibrium pH of 7.6. In case of the real leachate, the %S was even higher, 99.5%, albeit with a much higher equilibrium pH, i.e. 10.3. It is worth noticing that the feed solution needs to contain water to control the pH. In both cases the samarium was finally recovered by precipitation stripping with a 0.2 mol L\(^{-1}\) aqueous oxalic acid solution added in a E/S ratio of 1.5, because of the stoichiometry of the samarium oxalate, \(\text{Sm}_2(\text{C}_2\text{O}_4)_3\). In less than 10 min, all the samarium was precipitated and the recovered precipitate obtained a purity of 99.4 wt% for the model solution, and of 99.3 wt% for the real leachate. To the best of our knowledge, this is the first study, which describes a non-aqueous solvent extraction of rare-earth elements from a real leachate by using molecular extractants. In fact, Cyanex 272 has already been tested to recover rare-earth elements but from an aqueous chloride solution: in those cases the %S fluctuated between 85% and 99% [39–41]. Moreover, none of the cited studies report about rare earths recovered as precipitates (only rare-earths stripped in solution are mentioned).

### Table 5

<table>
<thead>
<tr>
<th>[HCl] (mol L(^{-1}))</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>%S (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>95</td>
<td>98</td>
<td>91</td>
<td>99</td>
</tr>
<tr>
<td>Cu</td>
<td>7</td>
<td>1</td>
<td>3</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0.0</td>
</tr>
<tr>
<td>x (wt%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%S (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

* Operating conditions: metal concentrations in the extract: [Co] = 22565.45 mg L\(^{-1}\), [Cu] = 2523.19 mg L\(^{-1}\), [Fe] = 10899.17 mg L\(^{-1}\) stripping agent = 0.5, 1.0, 2.0 and 4.0 mol L\(^{-1}\) aqueous HCl, T = room temperature, F/E (–) = 1/1, mixing time (min) = 30.

#### 3.4. Transition metal recovery from the solvent and reusability of the solvent

The transition metals were separated from the loaded solvent in two steps: (1) stripping of cobalt with an aqueous solution of HCl, and (2) stripping of copper with an aqueous solution of ammonia. In the second step, precipitation stripping of iron occurred as well. Since the thermodynamics are not influenced by the concentration, the stripping of cobalt, copper and iron was studied solely on the extract from the first extraction stage. As for cobalt stripping, the feed is the extract after stage I, whereas the copper and iron stripping feed is the raffinate from the cobalt stripping process. Aqueous HCl solutions of, respectively, 0.5, 1.0, 2.0 and 4.0 mol L\(^{-1}\) were tested to recover cobalt as a chloride salt. Although cobalt can be extracted with water as well, the presence of HCl prevents the stripping of copper and, especially, of iron. The results are reported in Table 5. In Fig. 8 the obtained gradient in cobalt stripping is highlighted by the different colors of the solutions.

As expected, a higher HCl concentration in the stripping agent leads to a lower %S (%) for cobalt, which drops to < 20% at 4 mol L\(^{-1}\) HCl. The same trend is followed for the stripping of copper and iron. In contrast, the purity of the stripped cobalt in the loaded stripping agent generally increases while increasing the HCl concentration. The solution of 0.5 mol L\(^{-1}\) HCl was selected as a sound stripping agent. In fact, it presented the highest %S (%) among those reported and, although it is less pure in cobalt than the solution at 1 mol L\(^{-1}\) HCl, it is also obviously less acidic than the latter one. It has to be noticed that such stripping step, as the following steps, was not optimized yet and a lower HCl concentration might be chosen, offering a compromise between stripping yields and stripping selectivity, when upscaling the process.

Electrowinning can be used to recover cobalt from a chloride solution at pH ≤ 4. Although this option is also applied at large scale, it was not tested here because out of the scope of the present work [42]. Subsequently, the stripped solution of 50 wt% Aliquat 336 solution in toluene saturated with 37 wt% HCl was rich in copper and iron, and was purified with an ammonia solution. Three phases were collected: (1) an upper liquid phase containing the purified solvent; (2) a lower liquid blue phase, corresponding to the aqueous copper(II) amine

![Fig. 8. Loaded stripping aqueous HCl (bottom phase) and raffinates (top phase) at different aqueous HCl concentrations: from left to right, 0.5, 1.0, 2.0 and 4.0 mol L\(^{-1}\). The gradient in metal concentration is clearly shown by the gradient in the green and pink shadows (see Table 5).](image-url)
solution, and (3) a dark-orange precipitate of iron(III) hydroxide. The removal yields of copper and iron were respectively 98.9% and 99.8%. Both the copper(II) amine solution and the iron(III) hydroxide precipitate were 100% pure in copper and iron, respectively. The purity of the metal precipitates were: 99.4 wt% for samarium, 98.3 wt% for cobalt and 100 wt% for iron and copper. The oxalate to the oxide via calcination was not investigated, since this is already widely reported [43,44].

The flow sheet in Fig. 11 summarizes the overall process and highlights its simplicity, consisting of only six unit operations: (1) leaching in 2 mol L$^{-1}$ hydrochloric acid in EG; (2) solvent extraction with 37 wt% HCl–saturated Aliquat 336 diluted in toluene; (3) stripping of cobalt using an aqueous solution of hydrochloric acid; (4) stripping of copper and precipitation stripping of iron with an aqueous ammonia solution; (5) extraction of samarium in Cyanex 272 and (6) precipitation stripping of samarium with oxalic acid. The reusability of the 50 wt % Aliquat 336 diluted in toluene saturated with 37 wt% HCl solvent is also highlighted. The solvometallurgical steps are marked in green full lines, while the hydrometallurgical ones in blue dashed lines.

4. Conclusions

A solvometallurgical process was developed to recover samarium, cobalt and copper from SmCo permanent magnets. Firstly, the bulk magnets were reduced to a powder to increase the specific surface area and the leaching kinetics. Secondly, the SmCo powder was leached in a solution of 2 mol L$^{-1}$ hydrochloric acid in EG. Thirdly, cobalt, copper and iron were extracted by 50 wt% Aliquat 336 diluted in toluene saturated with 37 wt% hydrochloric acid. A comparison was made with an aqueous solution of 37 wt% hydrochloric acid as lixiviant, in terms of leaching and of extraction efficiency. At this stage, the rare-earth element (Sm) was separated from the transition metals. The latter metals were recovered from the solvent by stripping with 0.5 mol L$^{-1}$ aqueous HCl for cobalt and 5 vol% ammonia for copper and iron. The reusability of the solvent was demonstrated. Samarium was extracted from the leachate by 20 vol% Cyanex 272 in dodecane and a 2 mol L$^{-1}$ NaOH solution to adjust the pH. Finally, samarium was recovered by precipitation stripping with 0.2 mol L$^{-1}$ oxalic acid. Although it was tested, metal precipitation did not occur in the non-aqueous phase, i.e. the last step of the designed process has to be a hydrometallurgical process. The purity of the metal precipitates were: 99.4 wt% for samarium, 98.3 wt% for cobalt and 100 wt% for iron and copper.
Acknowledgements

The research leading to these results received funding from the European Community’s Horizon 2020 Programme (HE2020–2014–2019) under Grant Agreement no. 674973 (MSCA-ETN DEMETER) and from the European Research Council (ERC) under the European Union’s Horizon 2020 Research and Innovation Programme: Grant Agreement 694078—Solvometallurgy for critical metals (SOLCRMET). This publication reflects only the authors’ view, exempting the Community from any liability.

The authors want to thank Magneti Ljubljana d.d. (Slovenia) for providing the SmCo permanent magnets, Tony Debecker and Kevin Wieringakx for crushing the magnets, Dr. Jeroen Jordens for the particle size measurements, Dr. Jeroen Snikers for the SEM and EDS analysis, Dr. Nagaphani Kumar Batchu for the very helpful discussion and Dr. Biene Ongenna and Dr. Peter Tom Jones for reviewing and editing the manuscript.

Conflict of interest

There are no conflicts to declare.

References

[3] H. Sanderson, N. Hume, VW fails to secure long-term cobalt supply for electric
[5] K. Binnemans, P.T. Jones, Solvometallurgy: an emerging branch of extractive met-
[10] E. Padhan, K. Sarangi, Recovery of Nd and Pr from NdFeB magnet leachates with bi-


K. Binnemans, P.T. Jones, Solvometallurgy: an emerging branch of extractive met-


S. Wellness, T. Vander Hoogerstraete, C. Möller, B. Thijs, J. Luyten, K. Binnemans, Dissolution of metal oxides in an acid-saturated ionic liquid solution and in-


B. Wissink, D. Dreisigier, J. Howard, Solvent extraction separation of zinc and cadmium from nickel and cobalt using Aliquat 336, a strong base anion exchanger, in the chloride and thiocyanate forms, Hydrometallurgy 57 (2000) 235–252, https://doi.org/10.1016/S0304-386X(00)00116-X.


R.S. Gärtner, M.M. Seckler, G.J. Witkamp, Solid phases and their solubilities in the

1039/c7ra09144c.

E. Padhan, K. Sarangi, Recovery of Nd and Pr from NdFeB magnet leachates with bi-


