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Recovery of scandium from sulfation-roasted leachates of bauxite residue by solvent extraction with the ionic liquid betainium bis(trifluoromethylsulfonyl)imide

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Abstract

Bauxite residue (red mud) is a waste product of the alumina refining in the Bayer process and contains significant concentrations of critical metals, including scandium. Greek bauxite residue contains exploitable levels of scandium and is thus considered a suitable source for its production. A process was developed to recover scandium from Greek bauxite residue using a combination of sulfation-roasting-leaching and solvent extraction with the hydrophobic ionic liquid betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf₂N]. Sulfation-roasting-leaching was the preferred leaching technique to dissolve scandium from bauxite residue because of the low acid consumption, good selectivity towards scandium and low co-dissolution of the major elements. The scandium concentration in the leachate was increased by applying multistage leaching, during which the obtained leachate is contacted multiple times with freshly roasted material. In a next step, scandium was selectively extracted from the obtained leachate with [Hbet][Tf₂N]. To improve the separation between scandium and iron, Fe(III) was reduced to Fe(II) by addition of ascorbic acid to the sulfate leachate prior to extraction. The phase ratio and pH of the extraction were optimized to achieve high extraction and the concentration of scandium in the ionic liquid phase. Co-extracted metal ions were scrubbed from the loaded ionic liquid phase by HCl and the purified scandium was removed by stripping with H₂SO₄. Scandium was recovered from the strip solution by precipitation together with sodium. Finally, the entire process was performed on lab scale as a proof-of-principle.

Keywords: scandium, solvent extraction, ionic liquids, bauxite residue, red mud, multi-stage leaching

Highlights:

- A full process was designed to recover scandium from bauxite residue.
- Scandium is leached by sulfation-roasting-leaching and multi-stage leaching.
- [Hbet][Tf₂N] was used for the extraction of scandium from the leachate.
- Separation between Fe and Sc was improved by reduction of Fe(III) to Fe(II).

1. Introduction

In the Bayer process for the production of alumina, aluminium is leached from the bauxite ore using NaOH at elevated temperatures and pressures [1]. The residue of the Bayer process is called *bauxite residue* (BR) or *red mud* (RM), because of its red ferric oxide color. Bauxite residue consists mainly of ferric oxide, aluminium (hydr)oxides, silica, titania and calcium carbonate and should not be considered as waste, since it contains many valuable components, including trace concentrations of critical elements such as the rare earths [2-4]. Currently, few examples of the commercial valorization of bauxite residue exist [5]. On the contrary, bauxite residue is mainly treated and stockpiled in large ponds and tailings [2]. Due to its vast volumes, high alkalinity and elevated radioactivity (TENORM, technologically-enhanced natural occurring radioactive material), storage of bauxite residue is not without risks or costs. The spillage accident in Ajka, Hungary in 2010 is an example of the damage bauxite residue can cause to the neighboring environment [6,7].

Studies on the reprocessing and valorization of bauxite residue can be divided into four groups: (1) extraction of the major components such as aluminium, iron and titanium, (2) recovery of trace elements such as scandium, (3) production of building materials including cement and geopolymers and (4) other applications such as soil amelioration and acid mine drainage [8-17]. In view of (near) zero-waste valorization and the development of a sustainable process, the solution for the bauxite residue challenge lies in a combination of these applications [18,19]. Recovery of trace elements focuses mainly on the rare earths and more specifically on scandium, because of its high market value [18-20]. Depending on the bauxite source, bauxite residue contains on average 60–120 ppm of scandium, making it a viable source for scandium production [12,21]. Selective separation of scandium from the major elements in bauxite residue is challenging due to the low scandium concentration and similarities in the chemical behavior of Sc(III), Fe(III) and Al(III) [22,23]. Scandium can be recovered from bauxite residue either by direct hydrometallurgical methods or by a combination of hydrometallurgical leaching with a pyrometallurgical pretreatment [12,22,24]. Direct leaching with strong acids (H_2SO_4 , HCl, HNO_3) has been studied extensively and generally results in good leaching of the rare earths, including scandium, with only limited dissolution of iron [10,12,22,23,25,26]. However, the major drawbacks are the low rare-earth concentrations in the leachate, the high acid consumption and the co-dissolution of silica, calcium and aluminium, which complicates further processing and purification of the leachate. Combined processes such as sulfation-roasting [8,9] and iron smelting [27] prior to leaching, or the use of specialized leaching agents

such as ionic liquids [17] and bioleaching [28,29] have shown enhanced performance in the selective recovery of scandium and the rare earths from bauxite residue. Recovery and purification of scandium from the obtained leachates is generally performed using either solvent extraction or ion-exchange chromatography, or a combination of the two techniques [30-37]. Solvent extraction of scandium from acidic solutions is most commonly performed with traditional acidic or neutral organophosphorus extractants in organic diluents, although carboxylic acids and basic amines have been studied for extraction from solutions with low acidity as well [37]. Due to the generally high extractability of scandium, stripping of the loaded organic phase requires harsh conditions such as high concentrations of strong mineral acids.

In view of the current awareness of the damaging properties of volatile organic compounds (VOCs) on the Earth's environment and atmosphere, many research groups are searching for alternatives for the traditional solvents used in solvent extraction. One of these alternatives are ionic liquids. Ionic liquids (ILs) are liquids that consist entirely of ions with a melting temperature near room temperature [38,39]. Some of their more general properties are a broad liquidus range, broad electrochemical window and negligible volatility. Apart from their "green" character, ionic liquids are also intrinsically safer to work with in solvent extraction. Traditional diluents are known to show an increased risk of solvent fires due to the combination of their flammability and the build-up of static electricity, while the ionic character and low flammability of ionic liquids lowers these risks [40]. Few studies focus on the use of ionic liquids for the extraction of scandium, and often, ionic liquids are merely used as diluents for traditional extractants [41-43]. Recently, our group described the application of the functionalized ionic liquid betainium bis(trifluoromethylsulfonyl)imide, abbreviated as betainium bistriflimide or [Hbet][Tf₂N], in solvent extraction (Figure 1) [44]. Because of its hydrophobic character and the presence of the carboxyl-function on the cation, this ionic liquid is a suitable metal-ion extractant that does not require a diluent. It has already been applied in the extraction of various metal ions and in homogeneous liquid-liquid extraction due to its remarkable temperature-dependent phase behavior [45-48]. [Hbet][Tf₂N] showed very good performance towards the extraction of scandium, even at low equilibrium pH values and stripping of extracted scandium can be easily achieved [48]. Moreover, the selectivity of [Hbet][Tf₂N] towards the most important elements present in bauxite residue leachates was investigated by extraction studies on synthetic solutions. Most of the major elements, including Al, Na, Ca and Ti, together with the lanthanides and Y, were almost not extracted at low pH values. However, Fe(III) showed an extraction behavior very similar to that of Sc(III).

In this paper, we describe the application of [Hbet][Tf₂N] for the recovery of scandium from real leachates of bauxite residue, obtained via the combined sulfation-roasting-leaching process which was recently developed by Borra *et al.* [9].

Figure 1: Chemical structure of betainium bis(trifluoromethylsulfonylimide), [Hbet][Tf₂N]. (one-column figure)

2. Experimental

2.1 Products

L-Ascorbic acid (99%), potassium thiocyanate ($\geq 99\%$) and nitric acid ($\geq 65\%$) were purchased from Sigma-Aldrich (Diegem, Belgium), betaine hydrochloride (99%) and sulfuric acid (96%) were obtained from Acros (Geel, Belgium), hydrochloric acid (37%) from Fisher Scientific (Aalst, Belgium) and sodium hydroxide (pellets) from VWR (Haasrode, Belgium). Lithium bistriflimide was obtained from IoLiTec (Heilbronn, Germany). Single-element ICP standard solutions of all used elements (Sc, Fe, Ti, Ca, Na, Al, Y, La, Ce, Nd, Rh, In, 1000 $\mu\text{g}\cdot\text{mL}^{-1}$ in nitric acid) were obtained from Chem-Lab (Zedelgem, Belgium). The bauxite residue used for all experiments was provided by Aluminium of Greece (Agios Nikolaos, Greece). A description of its origin and preprocessing can be found in the paper of Borra *et al.* [10].

2.2 Instrumentation

Ultrapure water (18.2 M $\Omega\cdot\text{cm}$) was used for all dilutions and prepared using a Sartorius Arium Pro ultrapure water system. A Memmert oven and Heraeus muffle furnace were used during the sulfation (120 °C) and roasting (700 °C) of the bauxite residue. A Gerhardt Laboshake was used for the bauxite residue leaching (160 rpm, 25 °C, 24 h) and an Eppendorf Thermomixer C with a 15 mL SmartBlock for shaking of the extraction mixtures (1000 rpm, 25 °C, 15 min). The pH measurements were performed using a Mettler-Toledo SevenCompact pH meter

combined with a Hamilton Slimtrode pH-electrode. UV-VIS absorption spectra were recorded in dual-beam mode on a Varian Cary 5000 spectrometer in a 0.1 mm quartz cuvette, with ultrapure water as the blank. Scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDX) was performed on a Philips XL30 with an acceleration voltage of 10.0 keV. Elemental analysis of both the aqueous and ionic liquid phases was performed using a Perkin Elmer Optima 8300 inductively coupled plasma optical emission spectrometer (ICP-OES) in dual view, with a GemTip CrossFlow II nebulizer, a Scott Spray Chamber Assembly, a sapphire injector and a HybridXLT ceramic torch. . The calibration curve was constructed by fitting through the origin using one standard solution of 5 mg·L⁻¹ Sc, Fe, Ca, 2 mg·L⁻¹ Y, La, Ce, Nd, Dy, Ti and 50 mg·L⁻¹ Na, Al. A quality control was performed using two QC solutions of 0.005 and 0.05 mg·L⁻¹ Sc, Y, La, Ce, Nd, Dy, Ti; 0.1 and 1 mg·L⁻¹ Ca, Fe; and 1 and 5 mg·L⁻¹ Na, Al respectively, with 90% and 110% as the criteria for QC recovery. Samples of both the aqueous and ionic liquid phases were prepared in duplicate by 200-fold dilution with a 2 vol% HNO₃ solution. This 2 vol% HNO₃ solution was also used for the dilutions of the standard solutions, QC solutions and as a calibration blank. As internal standard, In and Rh (both 5 mg·L⁻¹) were added to the samples, the calibration solution and the QC solutions. The following analytical lines (in nm) were used for the calculations, without correction for the internal standard: Sc 361.383, Fe 239.569, Ti 334.941, Ca 317.931, Na 589.601, Al 308.216, Y 371.027, La 408.677, Ce 413.764, Nd 406.111, Dy 353.169.

2.3 Sulfation-roasting-leaching experiments

The sulfate leachates were prepared by the combined sulfation-roasting-leaching process described by Borra *et al.* [9]. Before starting the process, the bauxite residue was dried at 105 °C for 12 h and the dried sample was passed through a 500 µm sieve. The sulfation-roasting-leaching (SRL) process consisted of five steps. First, the dried bauxite residue (50 g) was added to an equal mass of sulfuric acid (95%, 50 g, 27.2 mL) diluted in 20 mL of water and properly mixed by stirring to improve the reaction speed between the acid and the red mud (acid mixing). The mixture was moistened with more water (approximately 20 mL) to ensure homogeneous mixing. In the second step (drying), the mixture was heated at 120 °C for at least 12 h to complete the sulfation reaction of the bauxite residue. In the third step (roasting), the mixture was subsequently roasted at 700 °C for 3 h, unless stated otherwise. In the fourth step (leaching), the roasted sample was leached in a 5:1 liquid-to-solid (L/S) ratio by mixing with 250 mL of water and shaking for 24 h (160 rpm, 25 °C). During the fifth and final step (filtration), the residue was separated from the leachate by vacuum filtration over a Buchner filter. The

percentage of dissolution of the rare earth elements (REE) and major elements was calculated according to equation (1):

$$dissolution (\%) = \frac{C_M}{C_{M,in}} \cdot \frac{m_S}{m_L} \quad (1)$$

with C_M the concentration of the element in the leachate determined with ICP-OES, $C_{M,in}$ the concentration of the element in the original bauxite residue, m_S the initial mass of the bauxite residue and m_L the mass of water used during the leaching.

Multi-stage leaching was performed by repeating the entire SRL process five times, but instead of leaching with water during the second and following cycles, the leachate of the previous cycle was used as the liquid phase. Since a small volume of the leachate is lost during filtration, the volume of the leachate after filtration is less than 250 mL. Therefore, extra water was added in each cycle to maintain a 5:1 L/S ratio. Each cycle, 210 mL of the leachate of the previous cycle was mixed with 40 mL of ultrapure water and used as the liquid phase for leaching. All other steps were performed in the same way as described above.

2.4 Solvent extraction experiments

Before extraction, the sulfate leachate was first pretreated with ascorbic acid to reduce Fe(III) to Fe(II). An aliquot of a 0.2 M ascorbic acid solution in water was added to the filtered leachate to obtain a final concentration of 15 mM, and the mixture was gently shaken by hand until the yellow color of Fe(III) disappeared.

The extraction experiments were performed by mixing water-saturated [Hbet][Tf₂N] with the reduced leachate, together with NaOH or H₂SO₄ to adjust the pH. [Hbet][Tf₂N] was synthesized according to the method described by Nockemann *et al.* [49]. The organic-to-aqueous (O/A) phase ratio θ was controlled by taking into account the solubility of the ionic liquid in water, and is defined by equation (2), with V_{IL} and V_{AQ} the volume of the ionic liquid phase and aqueous phase, respectively.

$$\theta = \frac{V_{IL}}{V_{AQ}} \quad (2)$$

An initial volume ratio of water-saturated [Hbet][Tf₂N]-to-leachate of 11:9 was required to obtain a final O/A phase ratio of 1. Next, the extraction mixture is shaken at room temperature for 15 min and allowed to settle on the lab bench for at least 1 h. Finally, the ionic liquid phase is separated from the aqueous phase and analyzed with ICP-OES. The metal extraction and separation between two metals A and B were evaluated by calculating the distribution ratios D , separation factor α_B^A , and the percentage extractions % E , using equations (3-5):

$$D = \frac{C_{IL}}{C_{AQ}} \quad (3)$$

$$\alpha_B^A = \frac{D_A}{D_B}, \text{ with } D_A > D_B \quad (4)$$

$$\%E = \frac{C_{IL}V_{IL}}{C_{IL}V_{IL} + C_{AQ}V_{AQ}} \cdot 100 \quad (5)$$

with C_{IL} , V_{IL} and C_{AQ} , V_{AQ} the equilibrium metal concentration and volume of the ionic liquid and aqueous phase, respectively.

Similarly, scrubbing and stripping were performed by contacting the loaded ionic liquid phase with a solution of HCl, HNO₃ or H₂SO₄ (various concentrations were tested). The acid solution was presaturated with [Hbet][Tf₂N] to control the phase ratio. The mixtures were shaken at room temperature for 15 min and allowed to settle for at least 1 h. Finally, the ionic liquid phase is separated from the aqueous phase and analyzed with ICP-OES. The scrubbing and stripping efficiency % S is defined by equation (6):

$$\%S = \frac{C_{AQ}V_{AQ}}{C_{IL}V_{IL} + C_{AQ}V_{AQ}} \cdot 100 \quad (6)$$

Extraction, scrubbing and stripping screening experiments were always performed in single runs to determine the optimal conditions. The full process experiments were performed in triplicate and the errors were determined as the standard deviations on the results.

3. Results and discussion

3.1 Sulfation-roasting-leaching experiments

The first step of the process to recover scandium from bauxite residue is the dissolution of scandium from the solid bauxite residue by leaching. In order to make solvent extraction more viable, the final scandium concentration in the leachate should be high. Furthermore, the leaching procedure should be selective towards scandium, leaving the major elements, including iron, aluminium, silicon, calcium and titanium, in the residue. Direct leaching with concentrated acids is not favorable due to the high acid consumption, the high level of leaching of the major elements and the low scandium concentration in the final leachate [50]. The sulfation-roasting-leaching process designed by Borra *et al.* tackles these issues and was therefore chosen as the leaching technique in this work. The major advantages of the sulfation-roasting-leaching are: (1) limited leaching of the major elements Fe, Ti and Al; (2) no or very limited leaching of silica, which improves filtration; (3) low acid consumption and possibility for acid regeneration; and (4) less waste water generation. Furthermore, the pH of the residue after water leaching is close to neutral, which e.g. facilitates further purification by solvent extraction. A full discussion including the roasting mechanism and a cost analysis, can be found in the literature [9,50]. In order to check the performance of the sulfation-roasting-leaching on a 50 g scale, the influence was studied of the roasting temperature on the leaching of the major elements and the rare-earth elements, including scandium (Figure 2). During roasting, the unstable sulfates, such as iron(III) sulfate and titanium(IV) oxysulfate, are decomposed to their corresponding oxides, while the rare-earth sulfates remain stable. The composition of the leachates was determined and the results were compared to those described by Borra *et al.* for sulfation-roasting-leaching on a 1 g scale. Regardless of the larger scale, the influence of the roasting time on the leaching of the major elements and the rare earths, including scandium, was comparable to the results of Borra *et al.* (Figure 3). Dissolution of iron and aluminium was reduced with increasing roasting time to 0.1% and 5%, respectively, after 3 h of roasting. Sodium was completely dissolved, titanium dissolution was very low and the leaching of calcium remained constant over time because CaSO_4 has a limited solubility in water. The

dissolution of the lanthanides and yttrium slightly increased with prolonged roasting times, while the dissolution of scandium drastically decreased. This is due to the lower decomposition temperature of $\text{Sc}_2(\text{SO}_4)_3$ compared to the sulfates of the other rare earths, i.e. $\text{Sc}_2(\text{SO}_4)_3$ partially decomposed at 700 °C while the sulfates of the other rare earths remained stable [9]. The slight increase in the dissolution of the lanthanides and yttrium is most likely caused by the decrease in concentration of $\text{Al}_2(\text{SO}_4)_3$ and Na_2SO_4 in the leachate, which increased the solubility of the rare earth sulfates. Only the results of the lanthanides lanthanum, cerium and neodymium, together with yttrium, are reported here because they are the most concentrated rare earths in the bauxite residue. The results of dysprosium are also reported because of its economic importance. Since the chemical behavior of the lanthanides is known to be very similar, the results of the other (less concentrated) lanthanides are omitted. The optimal roasting time was found to be 3 h, since in these experimental conditions, the leaching of scandium is still reasonably high (almost 60%) with a good selectivity over iron. Shorter or longer roasting times are not preferred since a shorter time would result in a high co-leaching of iron whereas a longer time results in a reduction in scandium leaching.

Figure 2: Different stages of the sulfation-roasting process: (a) after mixing of bauxite residue with concentrated H_2SO_4 , (b) after drying for 12 h at 120 °C and (c) after roasting at 700 °C for 4 h. (one-column figure)

Figure 3: Effect of roasting time on the leaching of (a) major elements and (b) the rare earths (H_2SO_4 -to-bauxite-residue ratio: 1:1, roasting temperature: 700 °C, leaching 24 h, 160 rpm, 25 °C, L/S ratio: 5:1). (one-column figure)

Single-stage sulfation-roasting-leaching limits the final concentration of scandium in the leachate to approximately $14 \text{ mg}\cdot\text{L}^{-1}$. Therefore, *multi-stage leaching* was applied to increase the scandium concentration in the leachate [51,52]. In this leaching technique, the obtained leachate is filtered and repeatedly contacted again with fresh solid sample in multiple leaching stages. Consequently, a more concentrated leachate is obtained and less water and acid are consumed. The roasted sample was always prepared by mixing with sulfuric acid, as described in section 2.3. The leaching was always performed in a 5:1 L/S ratio. The composition and pH of the leachate after each stage are summarized in Table 1. The scandium concentration increased in each stage and the recoveries of scandium were as expected. With each stage, the recovery of scandium decreased, mostly due to the losses of the liquid phase during filtration and the leaching was stopped after five stages. Nevertheless, the scandium concentration increased from $13.6 \text{ mg}\cdot\text{L}^{-1}$ in cycle 1 to $47.7 \text{ mg}\cdot\text{L}^{-1}$ in cycle 5, a more than three-fold increase. So it can be concluded that the multi-stage leaching was successful in concentrating scandium for further processing and purification using solvent extraction. Note that the concentration of iron did not show a clear increasing trend. It is associated with the equilibrium pH, which is determined by the complex equilibrium between hydrolysis and (re-)dissolution of mainly Fe(III) and Al(III). Iron(III) sulfate does not completely decompose to oxides at 700 °C and the

sulfates that were not decomposed, dissolved during the leaching, resulting in hydrolysis and the subsequent dissolution of aluminium oxide.

Tabel 1: Concentrations of rare earths and major elements (expressed in $\text{mg}\cdot\text{L}^{-1}$) in the leachate after the different sulfation-roasting-leaching cycles (H_2SO_4 to bauxite residue ratio: 1:1, roasting temperature: 700 °C, leaching 24 h, 160 rpm, 25 °C, L/S ratio: 5:1). (two-column table)

cycle	1	2	3	4	5
pH	3.12	2.76	2.83	2.75	3.08
Sc	13.6±0.2	25.1±0.1	35.7±0.1	40.0±0.1	47.7±0.1
Fe	59±1	506±1	511±5	432±2	271±1
Ti	<0.5	<0.5	<0.5	<0.5	<0.5
Ca	540±10	593±3	576±6	644±3	585±7
Na	3850±30	7100±700	11700±500	14200±700	16100±6
Al	1078±1	2960±50	3800±100	4600±10	4360±60
Y	12.7±0.2	12.3±0.1	20.0±0.3	16.8±0.1	25.1±0.1
La	16.0±0.2	16.0±0.2	22.9±0.3	19.9±0.2	25.1±0.1
Ce	44.4±0.8	42.9±0.7	55.6±0.9	47.3±0.7	53.8±0.3
Nd	11.0±0.1	10.7±0.3	12.8±0.1	11.1±0.1	11.5±0.1
Dy	2.09±0.01	1.38±0.04	2.4±0.1	1.39±0.03	2.65±0.01

3.2 Reduction of Fe(III) to Fe(II)

To selectively extract and recover scandium, the sulfate leachate is contacted with [Hbet][Tf₂N]. This ionic liquid is known to show a high selectivity for the extraction of Sc(III) over the majority of the other ions present in the leachate, except for Fe(III) [48]. Since the selectivity of extraction with [Hbet][Tf₂N] is mainly based on charge density of the metal cation, Sc(III) and Fe(III) both show the same extraction as a function of pH. To improve the separation between scandium and iron, the influence of the reduction of Fe(III) to Fe(II), the latter having a lower charge density, was investigated [53]. Ascorbic acid (vitamin C) was chosen as the reducing agent since it performs well in the Fe(III) reduction in aqueous solution. Moreover, ascorbic acid is non-toxic, biological and cheap [54-59]. Addition of a stoichiometric amount of ascorbic acid reduces Fe(III) in an aqueous solution to Fe(II), according to Scheme 1.

Scheme 1: Reduction of Fe(III) by ascorbic acid to Fe(II) and dehydroascorbic acid. (one-column scheme)

Figure 4 visually shows the Fe(III)-to-Fe(II) reduction process. Potassium thiocyanate was added to the solution as an indicator, turning the leachate deep red, since Fe(III) forms strongly colored complexes with thiocyanate ions in solution (Figure 4, left) [60]. The disappearance of the red color of the iron(III) thiocyanate complex after addition of ascorbic acid (Figure 4, right) clearly shows that all Fe(III) has reacted and is no longer present in solution, since the complexes with Fe(II) in solution are almost colorless. Even without the addition of thiocyanate, the reduction could be followed visually. The presence of Fe(III) gave the leachate a faint yellow color, which completely disappeared after addition of ascorbic acid.

Figure 4: Sulfate leachate before (left) and after (right) addition of ascorbic acid. A small amount of KSCN was added to the leachate as an indicator for the presence of Fe(III) in solution (red color). (one-column figure)

Furthermore, UV-VIS spectra were recorded to check the reduction (Figure 5). The spectrum of the leachate showed an absorption band at 289 nm, corresponding to Fe(III) in solution. Upon

addition of ascorbic acid to the leachate (15 mM), the 289 nm absorption band was no longer present, while the absorption band of ascorbic acid was visible at 244 nm because an excess was added [54,55,59]. The solution was then stored in a vial with a closed screw-cap and a sample was taken to record the spectrum 5 h, 24 h, 7 days and 14 days after the addition of ascorbic acid. As can be seen, the intensity of the band at 244 nm, hence also the concentration, of ascorbic acid decreased with time, while the intensity of the Fe(III) band at 289 nm remained negligible. This indicates that Fe(II) was probably oxidized back to Fe(III) by reaction with dissolved oxygen gas, which on its turn reacted with the remaining ascorbic acid to Fe(II) [61]. The relative absorbance data are summarized in Table 2, together with the relative concentration of Fe(III) in the reduced solution compared to the untreated leachate. The concentration was calculated using the absorbance at 320 nm, instead of the maximum absorbance at 289 nm, to largely cancel out the effect of the tail of the band of ascorbic acid. In conclusion, the concentration of Fe(III) remained very low ($< 10\%$), even after two weeks of storage in a closed vial. Nevertheless, it is advisable to perform the extraction with [Hbet][Tf₂N] immediately after the reduction.

Figure 5: UV-VIS spectra of the initial sulfate leachate (solid black line), the sulfate leachate after addition of ascorbic acid (15 mM) as a function of the storage time (dashed and dotted black lines), and a 15 mM solution of ascorbic acid (solid grey line). (one-column figure)

Table 2: Comparison of the UV-VIS absorbance data at 289 nm and 320 nm of the leachate before and after reduction showing the stability of Fe(II) in the sulfate leachate in a closed vial after reduction by ascorbic acid (15 mM) as a function of time. (one-column table)

	A _{289 nm}	A _{320 nm}	%Fe(III) ^a
ascorbic acid 15 mM	0.035	0.005	2
initial leachate	0.362	0.270	100
0 h after reduction	0.026	0.009	3
5 h after reduction	0.028	0.013	5
24 h after reduction	0.031	0.018	7
7 days after reduction	0.041	0.023	8
14 days after reduction	0.039	0.022	8
^a relative Fe(III) content compared to that of the pure leachate, based on the absorbance measured at 320 nm (A _{320 nm}).			

It should be noted that addition of a chemical reducing agent has the disadvantage that it is difficult to recover after reaction and thus contaminates the aqueous feed solution. Therefore, other reduction methods could be investigated in the future, including electrochemical and photochemical reduction and the use of redox resins [62-65]. Nevertheless, a chemical reducing agent such as ascorbic acid has been proven efficient and straight-forward in use on lab scale and provides a proof-of-concept of the effect of Fe(III) reduction on the extraction.

3.3 Extraction experiments

To investigate the influence of the reduction of Fe(III) by ascorbic acid on the extraction of the different metal ions present in the sulfate leachate, solutions with different concentrations of ascorbic acid were added to the leachate. Next, these pretreated leachates were contacted with [Hbet][Tf₂N] in a 1:1 O/A phase ratio and the extraction was quantified by calculating the distribution ratio D as a function of the ascorbic acid concentration in the pretreated leachate (Figure 6). The extraction of iron decreased significantly from $D = 1$ without the addition of ascorbic acid to $D = 0.02$ at ascorbic acid concentrations of 8 mM and more. This clearly showed that a stoichiometric amount of 0.5 moles of ascorbic acid with respect to the Fe(III) concentration (870 mg·L⁻¹, 16 mM) is sufficient to suppress the extraction of iron and to strongly improve the separation of scandium and iron. In all further extraction experiments,

Fe(III) was always reduced with an excess of ascorbic acid, namely 15 mM, to assure that iron remained in its Fe(II) state throughout the experiment.

Figure 6: Influence of the addition of ascorbic acid on the distribution ratios of Sc, Fe, Ti, Ca, Al, Na and the rare earths Y, La, Ce, Nd, Dy (Σ REE) for the extraction from the sulfate leachate by [Hbet][Tf₂N]. 1:1 O/A phase ratio, equilibrium pH = 1.4. (one-column figure)

Besides the decrease in iron extraction, Figure 6 also showed that the extraction of the other tested elements remained constant and was not affected by the addition of ascorbic acid. Note that Figure 6 plots ' Σ REE', instead of Y(III), La(III), Ce(III), Nd(III) and Dy(III) separately. Since the lanthanides and yttrium all behave very similar, they are not reported separately. Instead, the concentrations of these elements in the aqueous phase and ionic liquid phase are summed and the distribution ratio is calculated for the sum of these elements, which is labeled as ' Σ REE'. It should also be noted that the distribution ratio of Sc(III) is much lower than in the extraction experiments performed from synthetic chloride solution, as described in earlier work [48]. This might be explained by the presence of the high sulfate matrix in the leachates. The stability constants of the successive coordination of sulfate to Sc(III) in solution are high, $\log K_1 = 4.04 \pm 0.03$ for $\text{Sc}^{3+} + \text{SO}_4^{2-} \rightarrow [\text{ScSO}_4]^+$, and $\log K_2 = 1.66 \pm 0.04$ for $[\text{ScSO}_4]^+ + \text{SO}_4^{2-} \rightarrow [\text{Sc}(\text{SO}_4)_2]^-$ [66]. Sulfate coordination thus competes with the coordination of betaine ligands of the ionic liquid and subsequent extraction to the ionic liquid phase. Similar observations were described in the literature for the influence of chloride on extraction of transition metals with carboxylic acid extractants [67,68]. Both Preston and Verhaege described

that by addition of chloride to the aqueous phase, the entire extraction curve of the studied transition metal ions shifted to higher pH values, and, consequently, higher equilibrium pH conditions were required in the presence of chloride in the aqueous phase to achieve the same distribution ratios as with an aqueous phase that contained no chloride.

The equilibrium pH of the extraction mixture with [Hbet][Tf₂N] was increased by addition of NaOH to the aqueous phase. [Hbet][Tf₂N] shows a remarkable pH-dependent phase behavior in contact with water. The betaine cation of [Hbet][Tf₂N] is a relatively weak acid with a pK_a of 1.83 [69]. Upon contact with water or an aqueous solution, the hydrophobic [Hbet][Tf₂N] will partially dissolve in the aqueous phase, where it deprotonates resulting in a buffer system. Upon addition of base to the mixture, more ionic liquid deprotonates and dissolves in the aqueous phase with a slight increase in the equilibrium pH as a result. Moreover, addition of even more base will finally result in the complete dissolution of the ionic liquid in the aqueous phase, resulting in a homogeneous mixture, which is not useful for solvent extraction. Therefore, the pH can only be varied over a limited range. Taking into account these considerations, the influence of the equilibrium pH on the extraction was investigated by addition of NaOH or H₂SO₄ (Figure 7). D_{Sc} was increased from 0.1 without pH control by NaOH or H₂SO₄ (pH 1.40) to 25 at pH 2.40. Although the distribution ratios of the other metal ions also increased with increasing pH, the separation between Sc(III) and the other metal ions became larger with increasing pH, since the distance between the curves of two different elements in Figure 8 is a graphical measure of the separation between these two metal ions. The results of the rare earth elements of extractions below pH 1.30 have been omitted since their concentration in the ionic liquid phase were below the detection limit of 0.1 mg·L⁻¹. Remarkably, the extraction mixture is still biphasic at pH 2.40, which would not be the case if the aqueous phase would be just water with NaOH. The high concentration of sulfate salts has a positive effect on the phase separation, as described before by Dupont *et al.* [70]. Moreover, the phase ratio did not show dramatic visual changes at higher NaOH concentrations.

Figure 7: Influence of the aqueous equilibrium pH on the extraction of Sc, Fe, Ti, Ca, Al, Na and the rare earths Y, La, Ce, Nd, Dy (Σ REE) from the sulfate leachate by [Hbet][Tf₂N]: distribution ratio D versus equilibrium pH. 1:1 O/A phase ratio, $[\text{NaOH}]_{\text{aq, in}} = 0\text{-}1$ M, $[\text{H}_2\text{SO}_4]_{\text{aq, in}} = 0\text{-}1$ M. (one-column figure)

Next, the influence of the phase ratio O/A on the extraction was investigated. Lowering the phase ratio could have the advantage of improving the extraction process because of the concentration effect of scandium in the ionic liquid phase, under the condition that % E remained the same. Moreover, more leachate could be processed with a smaller amount of ionic liquid. To quantify the influence of the phase ratio O/A on the extraction, different volumes of water-saturated [Hbet][Tf₂N] were mixed with the same volume of leach solution at constant NaOH concentration (0.25 M) and the resulting distribution ratios were plotted versus the phase ratio O/A (Figure 8). For all tested elements, the distribution ratios decreased with increasing phase ratio. The equilibrium pH did not remain constant but also decreased with increasing phase ratio, which was expected. Less ionic liquid in the extraction mixture implied less acidic protons, so a higher equilibrium pH. Consequently, the change in distribution ratio was completely caused by the change in pH (Figure 9). Furthermore, the percentage extraction of Sc(III) remained approximately constant because of the combined effect of the increasing pH and decreasing O/A phase ratio. Thus, essentially the same absolute percentage of scandium ions (~ 50 %) is extracted, regardless of the amount of ionic liquid present in the extraction mixture. It can be concluded that lowering the phase ratio has several advantages with regard

to the scandium recovery process: (1) five times higher concentration of scandium in the ionic liquid phase (concentration effect), (2) higher pH values while consuming less NaOH and (3) less ionic liquid consumption.

Figure 8: Influence of the phase ratio O/A on the extraction of Sc, Fe, Ti, Ca, Al, Na and the rare earths Y, La, Ce, Nd, Dy (Σ REE) from the sulfate leachate by [Hbet][Tf₂N]: distribution ratio D versus phase ratio O/A. [NaOH]_{aq} = 0.25 M. The equilibrium pH is indicated with a dotted line. (one-column figure)

Figure 9: Distribution ratio as a function of pH for extraction of Sc from the sulfate leachate by [Hbet][Tf₂N]. Black: phase ratio O/A varied between 0.1 and 5, [NaOH]_{aq} constant at 0.25 M, grey: [NaOH]_{aq} varied between 0 and 0.5 M, phase ratio O/A constant at 1:1. (one-column figure)

From the experimental data on the influence of the pH and the phase ratio, optimal conditions for the extraction of scandium from the sulfate leachate were determined, which were always applied in further experiments. The NaOH concentration was set to 0.5 M and the phase ratio was set to 1:5 O/A. These conditions were tested in triplicate and the results are summarized in Table 3. The majority of scandium was extracted (more than 80%), while most of the other elements remained in the raffinate. The titanium extraction of 61% is not an issue since the absolute concentration in the leachate was very low (< 0.5 mg·L⁻¹).

Table 3: Distribution ratio D , percentage extraction % E and separation factor $\alpha_M^{Sc} = D_{Sc}/D_M$ for the extraction of Sc, Fe, Ti, Ca, Al, Na and the rare earths Y, La, Ce, Nd and Dy from the reduced sulfate leachate by [Hbet][Tf₂N] under the optimized extraction conditions: phase ratio O/A 1:5, [NaOH]_{aq,in} = 0.5 M, pH_{aq,eq} = 2.44 ± 0.01.^a (two-column table)

M	C_{aq} (mg·L ⁻¹)	C_{IL} (mg·L ⁻¹)	D	% E	α_M^{Sc}
Sc	4.33 ± 0.05	114 ± 4	26 ± 1	84.0 ± 0.5	1
Fe	107 ± 1	23.9 ± 0.8	0.22 ± 0.01	4.3 ± 0.2	118 ± 2
Ti	0.08 ± 0.01	0.62 ± 0.02	8 ± 2	61 ± 5	3.4 ± 0.6
Ca	400 ± 5	54.4 ± 3.0	0.14 ± 0.01	2.6 ± 0.2	193 ± 13
Na	23800 ± 1500	6560 ± 260	0.28 ± 0.03	5.2 ± 0.5	95 ± 8
Al	2510 ± 43	3770 ± 120	1.5 ± 0.02	23.1 ± 0.2	17.5 ± 0.4
Y	15.3 ± 0.3	11.1 ± 0.2	0.73 ± 0.02	12.7 ± 0.2	36.1 ± 0.7
La	14.4 ± 0.2	10.7 ± 0.3	0.74 ± 0.03	12.9 ± 0.4	36.4 ± 1.0
Ce	30.3 ± 0.4	26.5 ± 0.6	0.78 ± 0.01	14.9 ± 0.2	30.1 ± 0.7
Nd	3.06 ± 0.09	7.17 ± 0.1	1.18 ± 0.02	19.1 ± 0.3	22.2 ± 0.8
Dy	1.74 ± 0.01	2.78 ± 0.03	1.60 ± 0.01	24.3 ± 0.2	16.4 ± 0.4

^a errors determined via triplicate experiments

The optimized conditions mentioned above refer to a one-stage batch extraction, where a balance is made between the extraction of scandium and the required volume of ionic liquid. However, when the extraction process would be applied in a counter-current continuous

process, the latter optimized extraction parameters no longer apply. A McCabe-Thiele diagram was constructed to determine the number of stages and the optimum phase ratio required to extract 99% of Sc(III) from the sulfate leachate (Figure 10) [71]. Extraction from the leachate was performed at different phase ratios O/A (between 0.1 and 10), where the equilibrium volume of the aqueous phase was set at 1 mL and the volume of the ionic liquid phase was varied. The equilibrium pH was kept constant by the addition of 0.15 mL of NaOH solutions with concentrations between 0 and 2 M. The initial scandium concentration was equal to $32 \text{ mg}\cdot\text{L}^{-1}$. The optimal phase ratio depends on multiple parameters. A high phase ratio has the advantage that more scandium is extracted in one step and less extraction stages are required, which largely reduces the investment and operational costs. However, the less extractable elements, such as iron, also show an increased %*E* and the scandium purity in the ionic liquid phase decreases [71]. Furthermore, a small phase ratio implies that less ionic liquid has to be loaded in the system and the concentration of NaOH required to maintain the optimal pH is lower. The cascade in the McCabe-Thiele diagram at phase ratios O/A 1:1 and 1:2 indicated that the number of stages required to extract 99% of the scandium are 3 and 4, respectively (Figure 10). Thus, in order to keep the number of stages low, the optimal phase ratio for continuous counter-current extraction of scandium is 1:1.

Figure 10: McCabe-Thiele diagram for the extraction of Sc from the sulfate leachate with the ionic liquid [Hbet][Tf₂N]. (one-column figure)

3.4 Scrubbing and stripping

The extracted scandium is purified and recovered from the ionic liquid phase by scrubbing and stripping in order to allow further processing and the re-use of the ionic liquid. Scrubbing is usually performed by contacting the organic phase with a scrubbing solution of which the conditions, such as pH and salt concentration, are similar to the conditions of extraction. In this way, metal ions with a low preference for the organic phase, but a high concentration in the feed solution, will diffuse back from the ionic liquid phase to the aqueous scrub phase [71]. The sulfate leachate contains approximately 2 M of sulfate ions. Therefore, first, a 2 M Na₂SO₄ solution was tested for the scrubbing of the loaded [Hbet][Tf₂N] phase at a 1:1 O/A phase ratio. The equilibrium pH was controlled to be the same as during extraction. The results showed good scrubbing of the co-extracted elements Al, Na, Ca, and Fe (> 80%). However, also a significant part of the extracted scandium was scrubbed (30 %), which is undesirable and can be explained by the high stability constants for coordination of the sulfate anion to scandium. Therefore, the use of Na₂SO₄ as a scrubbing agent should be avoided. Secondly, the scrubbing and stripping performance of the three most common mineral acids were tested, namely HCl, HNO₃ and H₂SO₄, as a function of the acid concentration (expressed as normality (N), Figure 11). The scrubbing and stripping of most elements was the same for all three acids, except for scandium, where H₂SO₄ showed a higher scrubbing and stripping efficiency at lower normalities, than HCl and HNO₃. Thus, as expected, H₂SO₄ should be avoided as a scrubbing agent since too much scandium would be lost. The two remaining options, HCl and HNO₃, showed similar scrubbing performance, but HCl is the cheapest acid and is thus the preferred scrubbing agent. Figure 12 displays the scrubbing efficiencies of the loaded ionic liquid phase as a function of the HCl concentration and shows that the preferred scrubbing conditions are 0.5 M of HCl, since it combines good scrubbing of Fe, Ca, Al, Na and the rare-earth elements with a low scrubbing percentage of scandium. The best stripping acid was H₂SO₄ since it showed better stripping of scandium at lower concentrations (expressed as normality, Figure 11). The better performance of H₂SO₄ is most likely caused by the better coordinating ability of sulfate anions towards scandium, compared to chloride and nitrate anions. To further increase the concentration of scandium in the final strip solution and to lower the consumption of chemicals, the stripping of scandium was also tested at higher O/A phase ratios (Table 4). The 3 M H₂SO₄ solution showed good stripping performance (> 99%) up to a phase ratio of 5:1. At a phase ratio of 10:1, the amount of acid in the mixture is too low and the stripping performance dropped drastically to

< 10%. The optimized stripping conditions were therefore set to 3 M of H_2SO_4 and an O/A phase ratio of 5:1.

Figure 11: Comparison of the stripping efficiency of H_2SO_4 ($\blacktriangle$), HCl ($\blacksquare$) and HNO_3 ($\bullet$) and as a function of the acid concentration for the stripping of Sc from a $[\text{Hbet}][\text{Tf}_2\text{N}]$ -phase loaded by extraction from the sulfate leachate under optimized extraction conditions. Stripping mixture: 1:1 O/A phase ratio. (one-column figure)

Figure 12: Influence of the HCl concentration (0.1 - 3 M) on the scrubbing and stripping of Sc, Fe, Ca, Al, Na and the rare earths (Σ REE) Y, La, Ce, Nd, Dy from a [Hbet][Tf₂N]-phase, loaded by extraction from the sulfate leachate under optimized extraction conditions. Stripping mixture: 1:1 O/A phase ratio. (one-column figure)

Table 4: Stripping of scandium from an ionic liquid phase loaded by optimized extraction of the sulfate leachate with [Hbet][Tf₂N], with 3 M H₂SO₄ as a function of the O/A phase ratio Θ . (one-column table)

Θ	%S
1:1	99.9
2:1	99.8
5:1	97.9
10:1	9.6

3.5 Full process on batch scale

A conceptual flow sheet has been constructed for the selective recovery of scandium from the bauxite residue (Figure 13), based on the optimized parameters determined during the parameter study described above. The entire batch process was performed on a lab scale to examine the feasibility of the flow sheet. The elemental composition (%) of the different phases throughout the process are depicted in Figure 14. Sodium is omitted from the graph since NaOH is added during extraction and precipitation, so its attribution to the composition will give a wrong impression of the purity of scandium. As visualized in Figure 14, the ionic liquid phase after extraction contained, apart from scandium, mostly aluminium, and some iron and calcium. Although its distribution ratio is low, aluminium extraction was significant due to the high concentration in the leachate. These co-extracted metal ions were scrubbed with HCl in three stages. During the first scrubbing stage, most of the acid is consumed for neutralization of the deprotonated ionic liquid. This was clear from the equilibrium pH, which was equal to 1.7, while the pH of the second and third scrubbing stage were 0.9 and 1.0. Three stages were required to remove the high aluminium concentration in the ionic liquid phase, but two stages were already sufficient to scrub the co-extracted calcium, iron, yttrium and the lanthanides. As a consequence of the conditions required to scrub aluminium, also a significant percentage of

scandium was scrubbed from the ionic liquid phase (~ 50 %). The purified ionic liquid phase is then contacted with a 6 N solution of H_2SO_4 . The obtained strip solution contained $185 \text{ mg}\cdot\text{L}^{-1}$ of scandium with a purity of 90%. The main impurity was aluminium (8%), iron (0.7%) and the lanthanides (0.5%). Finally, scandium was precipitated from the strip solution. Many different inorganic precipitation methods for scandium exist, including hydroxide, carbonate, fluoride, (double) sulfate and oxalate. Oxalate and hydroxide precipitation are interesting methods because the precipitate can easily be converted to a commercial oxide product by calcination. Hydroxide precipitation is said to be more quantitative than oxalate precipitation. Furthermore, the solubility of scandium oxalate is increased by addition of competing coordinating ligands in the solution, such as betaine on our case [66]. On the other hand, aluminium also precipitates as a hydroxide by addition of a base such as NaOH, with similar pH-dependent hydrolysis behavior as scandium. Consequently, the strip solution should be free of aluminium to obtain a pure scandium hydroxide precipitate. Although, at highly alkaline pH ($> \sim \text{pH } 12$), the most thermodynamically stable species is $\text{Al}(\text{OH})_4^-$, as can be concluded from its Pourbaix diagram [72], once an aluminium precipitate is formed, it is problematic to redissolve it again as $\text{Al}(\text{OH})_4^-$, and elevated pressures and temperatures might be required. Since both precipitation agents have advantages and drawbacks, a combination of both was applied to precipitate scandium from the strip solution. NaOH was first added, after which the formed precipitate was redissolved in sulfuric acid and again precipitated by addition of oxalic acid and NaOH. Metal analysis of the final precipitate with ICP-OES showed only the presence of scandium and sodium and some traces of titanium, lanthanum, cerium and iron. Without taking into account the sodium content, the purity of scandium in the precipitate was 98%. Finally, the precipitate was analyzed with SEM-EDX (Figure 15). Various different crystal phases could be distinguished, indicating that the precipitate consisted of different compounds. The elemental composition of the different crystals was determined with EDX and showed, besides scandium, significant concentrations of oxygen, sodium and sulfur, which might indicate the presence of sodium sulfate. This is remarkable, since it was expected that the precipitate consisted of scandium oxalate. Probably, the presence of sodium and sulfur can be explained by the precipitation of Na_2SO_4 , which maximum solubility product was exceeded because of the addition of NaOH to the 3 M H_2SO_4 strip solution. Furthermore, it is not completely clear in which manner scandium precipitated out of solution. The most likely options are precipitation as a scandium oxalate salt, as double sulfates with sodium ($\text{NaSc}(\text{SO}_4)_2$ and $\text{Na}_3\text{Sc}(\text{SO}_4)_3$), which are also known to be insoluble in water, or as a mixture of both [66]. Further in-depth analysis is required, but this was outside the scope of this article.

Figure 13: Schematic overview of the recovery process of scandium from bauxite residue based on the combined sulfation-roasting-leaching and solvent extraction with the ionic liquid [Hbet][Tf₂N]. Red and blue arrows indicate the flow of the ionic liquid phases and the aqueous phases respectively. (one-column figure)

Figure 14: Summary of the composition (%) of the different phases during the optimized process. L: sulfate leachate after 5-stage leaching, EX: ionic liquid phase after extraction (O/A 1:5, pH 2.5), SC1: ionic liquid phase after scrubbing step 1 (O/A 1:1, 0.5 M HCl), SC2: ionic liquid phase after scrubbing step 2 (O/A 1:1, 0.5 M HCl), SC3: ionic liquid phase after scrubbing step 3 (O/A 1:1 0.1 M HCl), ST: aqueous phase after stripping (O/A 5:1, 3 M H₂SO₄), PR: precipitate after precipitation with NaOH (pH 12.5). Sodium was omitted since it is added during extraction and precipitation. (one-column figure)

Figure 15: SEM images of the precipitate formed from the strip solution after addition of NaOH and oxalic acid.

3.6 Reuse of the ionic liquid

The reuse of the ionic liquid was tested by comparing the extraction of scandium with freshly prepared and with recycled [Hbet][Tf₂N], which has already been used for extraction of sulfate leachate. The recycled [Hbet][Tf₂N] was obtained after running through the optimized process as depicted in Figure 13 and was reused as such, without an extra washing or preconditioning step after the stripping. The performance of the recycled ionic liquid was shown to be the same as freshly prepared ionic liquid. The equilibrium aqueous pH was slightly lower (pH 2.40 versus pH 2.48) in the extraction with the recycled ionic liquid, although the same concentration of NaOH was added to both mixtures. This could be explained by the stripping acid which was partially retained in the ionic liquid phase. However, the difference is only small, so an extra washing step before reusing the ionic liquid is not necessary.

4. Conclusion

A combined pyrometallurgical-hydrometallurgical process was developed to recover scandium from Greek bauxite residue. Scandium was selectively leached from the solid bauxite residue material using a combination of sulfation, roasting and leaching. By applying multi-stage leaching, the concentration of scandium in the final leachate was increased three times compared to single-stage leaching. Furthermore, acid and water consumption in the sulfation-roasting-leaching is low. Scandium was subsequently purified from the obtained sulfate leachate by solvent extraction with the ionic liquid betainium bis(trifluoromethylsulfonyl)imide. This extraction system was proven to be selective for Sc(III) over the major elements and the rare-earth elements present in the leachate. The separation between scandium and iron was improved by reduction of Fe(III) to Fe(II) with ascorbic acid. Extraction, scrubbing and stripping were optimized to achieve high scandium extraction and good separation. Furthermore, the scandium concentration in the system was increased by applying a phase ratio O/A of 1:5 during extraction and 5:1 during stripping. After stripping, the recovered ionic liquid could be reused as such, without loss in performance. Finally, the complete optimized process was executed in batch mode to give the proof-of-principle of the process. Scandium was recovered and purified from the strip solution by precipitation. Apart from the host elements of the precipitate, including sodium, the scandium purity was 98%.

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Graphical abstract