



Combined multi-step precipitation and supported ionic liquid phase chromatography for the recovery of rare earths from leach solutions of bauxite residues



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ABSTRACT

Rare-earth elements (REEs) were efficiently recovered by a supported ionic liquid phase (SILP) after iron(III) precipitation from simulated bauxite residue (BR) leachates in sulfuric acid media, since leaching of BR with sulfuric acid is more feasible than leaching with other mineral acids. The SILP betainium sulfonylethyl(tri-fluoromethanesulfonylimide) poly(styrene-co-divinylbenzene) [Hbet-STFSI-PS-DVB] exhibits a high selectivity for the rare-earth elements (REEs) over other elements in acidic BR leachates. However, scandium(III) uptake by the [Hbet-STFSI-PS-DVB] from sulfuric acid leachates is difficult due to strong electrostatic interactions of small scandium(III) ions with sulfate anions. Sulfuric acid leachates generally contain high concentrations of base metal ions like iron(III) and this reduces the efficiency of the [Hbet-STFSI-PS-DVB] for uptake of REEs. Therefore, a precipitation step for iron(III) removal with aqueous ammonia solution was introduced, as a simple and economically viable pretreatment step of BR leachate, prior to the REEs recovery by the SILP. Iron(III) precipitation from sulfuric acid BR leachates increased the efficiency of purification by column chromatography. Additionally, scandium(III) phosphate precipitation, after iron(III) removal, was performed in order to compare and assess the optimum route for scandium(III) purification between the two common processes: selective precipitation and elution chromatography. After scandium(III) phosphate precipitation, the recovery and subsequent purification of the remaining REEs on the [Hbet-STFSI-PS-DVB] column were also examined, and resulted in a higher purity of these REEs.

1. Introduction

The rare-earth elements (REEs) greatly contribute to modern technology, but there are only few mineable REE deposits (Binnemans et al., 2018; Fernandez, 2017; Zhang et al., 2016). Their most important applications are in permanent magnets for wind turbines, electric vehicles, computer hard-disk drives and mobile phones, alloys for rechargeable batteries, high-performance aluminium and magnesium alloys, as well as lamp phosphors (Binnemans et al., 2015; Binnemans et al., 2018; Seidman et al., 2002; Riesgo García et al., 2017; Zhang et al., 2016). The high economic importance of the REEs is reflected by their leading position in the list of the critical raw materials (CRMs) of the European Commission (Binnemans et al., 2018; European

Commission, 2017). Since 2014 the REEs are no longer considered as one group in the list of CRMs, but are split into light and heavy REEs, whereas scandium was assessed separately from other REEs. In the 2017 update of the CRMs list, the light REEs were assessed as the CRMs with the highest supply risk. Moreover, the steadily growing demand for scandium (Sc), especially in high-strength aluminium alloys, necessarily increased its criticality and intensified the need for its production (Binnemans et al., 2018; European Commission, 2017; Pyrzyńska et al., 2018). Although scandium resources have been identified across the globe, its concentration in the ores is generally low, so scandium is mainly produced as a by-product during processing of various ores or recovered from previously processed tailings or residues (Narayanan et al., 2017; Ochsenkühn-Petropoulou et al., 2002;

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Pyrzyńska et al., 2018).

The scarcity of naturally occurring REEs deposits, presents an opportunity for utilization of secondary resources. In fact, in a quest for an alternative source of REEs, bauxite residue (BR), a waste material abundantly produced by the alumina industry, has recently drawn a lot of research attention. The REEs in BR are enriched by a factor of two compared to the bauxite ore (Deady et al., 2014; Ochsenkühn-Petropulu et al., 1996). It is well known that > 90% of the trace metal value in BR can be attributed to the presence of scandium (Borra et al., 2015; Liu and Naidu, 2014; Liu and Li, 2015). For instance, Greek BR is rich in scandium, with a concentration of around 120 g per tonne (Borra et al., 2015). However, the base elements, namely iron (Fe), aluminium (Al), calcium (Ca), silicon (Si), titanium (Ti) and sodium (Na), are much more abundant in BR (e.g. 5–60% of Fe₂O₃), which represents one of the major drawbacks for BR utilization in REEs recovery (Evans, 2016). Several flow-sheets are proposed for the selective recovery of REEs from the BR matrix, including alkali roasting–smelting for the separation of Al and Fe (Alkan et al., 2017; Borra et al., 2016). The residue can then be further treated by leaching with mineral acids (Ochsenkühn-Petropoulou et al., 2002). These methods are either energy-intensive, consume large volumes of chemicals, and are thus not economically feasible.

Borra et al. (2015) reported that leaching of Greek BR gave similar results for HCl, HNO₃ and H₂SO₄, with a maximum scandium leaching efficiency of 80%. However, from an economical point of view, H₂SO₄ is the preferred lixiviant (Borra et al., 2016). In our previous studies, REEs were recovered from HCl, HNO₃ and H₂SO₄ media by the supported ionic liquid phase (SILP) betainium sulfonyl(trifluoromethanesulfonylimide) poly(styrene-co-divinylbenzene) [Hbet-STFSI-PS-DVB] (Fig. 1) (Avdibegović et al., 2017; Avdibegović et al., 2018). In contrast to HCl and HNO₃ media, [Hbet-STFSI-PS-DVB] did not exhibit a very high tendency for Sc(III) uptake from H₂SO₄ media, especially in the presence of high concentrations of base elements. This issue sparked the idea of introducing a pretreatment step for BR leachates with H₂SO₄ prior to the recovery of REEs, and Sc(III) in particular, by [Hbet-STFSI-PS-DVB] column chromatography. Precipitation of highly concentrated and interfering ionic species from solutions is a commonly used treatment method in hydrometallurgy (Deblonde et al., 2016; Güler and Seyrankaya, 2016; Han et al., 2016; Mazurek, 2013; Narayanan et al., 2017; Singh et al., 2017; Yagmurlu et al., 2017b; Wang et al., 2011). The focus of the present study was to purify the REEs from a simulated H₂SO₄ BR leachate by a tandem process involving a multi-step precipitation and [Hbet-STFSI-PS-DVB] column chromatography. The precipitation steps comprised Fe(III) removal by addition of an aqueous ammonia solution and selective ScPO₄ precipitation. The tested leachate consisted of substantial concentrations of REEs (Sc, Y, Nd, Dy) and base elements (Fe, Al, Ca) which are typically difficult to separate from the REEs and present in high concentrations. Still, real BR leachates contain a variety of elements not considered in the present study which might, to some extent, cause deviation of results compared to our study with a simulated leachate. Typical BR acidic leachates comprise only several mg L⁻¹ of REEs and thousand times more concentrated base elements, so a significant loss of REEs due to co-precipitation with base elements can be anticipated (Borra et al., 2015; Evans, 2016). Procedures for selective enrichment of REEs in the BR leachate have been developed (Alkan et al., 2018; Onghena et al., 2017; Rivera et al., 2018). Since it is elaborate to obtain a substantial amount of enriched BR leachates, a simplified study with the

simulated leachate composed by realistic metal concentrations to a typical BR leachate was performed (Borra et al., 2015; Evans, 2016; Rivera et al., 2018). The main goal of this work is to give insight into the performance of the tandem process for the separation of REEs and base elements.

2. Experimental

2.1. Chemicals

HNO₃ (65%), Al₂(SO₄)₃·18H₂O (100–110%), standard solutions of scandium, yttrium, neodymium, dysprosium, lanthanum, aluminium, iron and calcium (1000 µg mL⁻¹) were purchased from Chem-Lab NV (Zedelgem, Belgium). CaSO₄·2H₂O was purchased from Vel (Leuven, Belgium). Nd₂(SO₄)₃·xH₂O (99.9%) was purchased from Alfa Aesar (Karlsruhe, Germany), DyCl₃·6H₂O (99.9%) from abcr (Karlsruhe, Germany) and YCl₃·6H₂O (99.9%) from Strem Chemicals (Newburyport, USA). H₃PO₄ (85%) was purchased from Ashland Chemicals (Columbus, USA). (NH₄)₂HPO₄ (98%) and NH₃ solution (25%) were purchased from Merck KGaA (Darmstadt, Germany). Betaine hydrochloride (99%), triethylamine (99%), and H₂SO₄ (96%) were purchased from Acros Organics (Geel, Belgium). Poly(styrene-co-divinylbenzene) (PS-DVB) sulfonyl chloride resin (0.91 mmol g⁻¹, 200–400 mesh) was purchased from RappPolymere (Tübingen, Germany). Trifluoromethanesulfonamide (98%) was purchased from J & K Scientific GmbH (Pforzheim, Germany). Dichloromethane (DCM) (p.a.) and acetone (p.a.) were purchased from Fisher Chemical (Loughborough, UK). Sc₂O₃ (99.99%) was kindly provided by Solvay (La Rochelle, France). Hydrated Sc₂(SO₄)₃ was prepared from Sc₂O₃ according to a literature procedure (Li et al., 2003). Hydrated Y₂(SO₄)₃ and Dy₂(SO₄)₃ were prepared in a similar manner from Y₂O₃ and Dy₂O₃, respectively.

2.2. Equipment

pH measurements were performed with WTW ProfiLine pH 197 series pH-meter with a Sentix 81 precision electrode. A fraction collector CF-2 (Spectrum Laboratories, Inc.) equipped with a drop sensor and an IPC 8-channel peristaltic pump (ISMATEC) was used for sampling during the chromatography studies. An inductively coupled plasma optical emission spectrometer (ICP-OES) (Perkin Elmer OPTIMA 8300) was used to measure the concentrations of the elements in solutions. The calibration solutions and all samples were prepared by dilution with 2 wt% HNO₃. Lanthanum (5 mg L⁻¹) was used as an internal standard. The following spectral lines (wavelengths in nm) in axial view were used for quantification: Fe 238.204, Al 308.215, Ca 317.933, Sc 361.383, Y 371.029, Dy 394.468, Nd 401.225, La 408.672.

2.3. Preparation of a simulated BR leachate and precipitation steps

A simulated H₂SO₄ BR feed was prepared by dissolving the sulfate salts of the REEs and base elements in water, and the pH was adjusted to 1.50, typically with a 4 mol L⁻¹ H₂SO₄ solution. The generated feed was used for column chromatography tests and for Fe(III) removal by a selective hydroxide precipitation with an ammonia solution.

Fe(III) was selectively removed by a dual-step precipitation procedure (Yagmurlu et al., 2017a, 2017b, 2018). First, the largest part of Fe(III) was precipitated by addition of 10 wt% NH_{3(aq)}, until the pH of the solution reached the value of 3.3 and then the mixture was filtered. Secondly, a 10 wt% NH_{3(aq)} was further added to the generated filtrate to remove the remaining Fe(III), until the pH of the solution reached the value of 3.7. The mixture was filtered and the solution pH was re-adjusted by dilute H₂SO₄ solution to 2.0 to aid the selectivity of the following ScPO₄ precipitation step. In this step, the remaining leachate after Fe(III) precipitation was further treated with 1 mol L⁻¹ (NH₄)₂HPO₄ solution to selectively precipitate Sc(III) as a phosphate

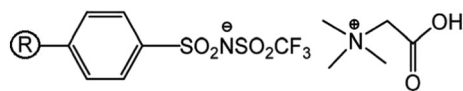


Fig. 1. Structure of the SILP betainium sulfonyl(trifluoromethanesulfonylimide) poly(styrene-co-divinylbenzene) [Hbet-STFSI-PS-DVB] for REEs recovery and separation by column chromatography.

(ScPO₄), until the equilibrium pH reached the value of 2.7.

After Fe(III) and Sc(III) precipitations, aliquots of 10 mL of the leachates were taken for column chromatography separation studies. The total dilution factors after the Fe(III) and Sc(III) precipitation steps were 1.08 and 1.15, respectively, including the additional dilutions for pH adjustments prior to column chromatography tests. These dilution factors were taken into account when calculating the precipitation percentage for each element.

The precipitation of metal ions was calculated from the Eq. (1).

$$\text{Precipitation (\%)} = \frac{c - c_1}{c} \cdot 100 \quad (1)$$

c and c_1 are the metal concentrations (mg L^{-1}) in the feed and in the solution after precipitation, respectively. c_1 is corrected by a dilution factor after the pH adjustments.

2.4. Test with the SILP in a column chromatography

The SILP [Hbet-STFSI-PS-DVB] used in chromatography studies was prepared following an earlier reported literature procedure (Avdibegović et al., 2017). A gravity flow glass column (BIO-RAD) of 30 cm length and 0.7 cm diameter was used in chromatography separation experiments. Approximately 10.8 mL bed volume (the total volume of the SILP in the column including the void volume, BV) of [Hbet-STFSI-PS-DVB] was packed in a column by a wet method (1.36 g of [Hbet-STFSI-PS-DVB], dry mass). [Hbet-STFSI-PS-DVB] was pre-conditioned with H₂SO₄ solution (pH = 1.5) prior to each experiment. For every chromatography separation, the column was loaded with 2 mL of synthetic BR leachate, of which the pH was adjusted to 1.5. An aliquot of 5 mL of H₂SO₄ (pH = 1.5) was added to remove remaining impurities in the column, prior to flowing the eluting solution through the column for the separation process. H₃PO₄ and HNO₃ were used as eluting agents, according to the previously optimized column chromatography process for the separation of REEs and base elements in BR (Avdibegović et al., 2018). During each experiment, 5 mL fractions were collected and analyzed by ICP-OES. All column chromatography experiments were conducted at room temperature with a set flow rate of 0.5 mL min⁻¹. The recovery of metal ions by [HBET-STFSI-PS-DVB] was calculated from eq. 2.

$$\text{Recovery (\%)} = \frac{c - c_2}{c} \cdot 100 \quad (2)$$

c and c_2 are the metal concentrations (mg L^{-1}) in the feed before and after column loading, respectively.

3. Results and discussion

Dual-step Fe(III) precipitation as a pretreatment of BR leachate prior to recovery and purification of REEs by the [HBET-STFSI-PS-DVB]

Table 1

Metal concentrations in the simulated H₂SO₄ BR leachates: (1) initial H₂SO₄ BR leachate, (2) after dual-step Fe(III) removal, and (3) after ScPO₄ precipitation. For comparison, the concentrations are corrected by dilution factors after pH adjustments.

Elements	H ₂ SO ₄ BR leachates		
	(1)	(2)	(3)
	Concentration (mg L^{-1})		
Al	3145	2991	2261
Fe	2942	23	7
Ca	390	390	367
Dy	31	12	9
Nd	25	22	11
Sc	16	14	5
Y	10	10	9

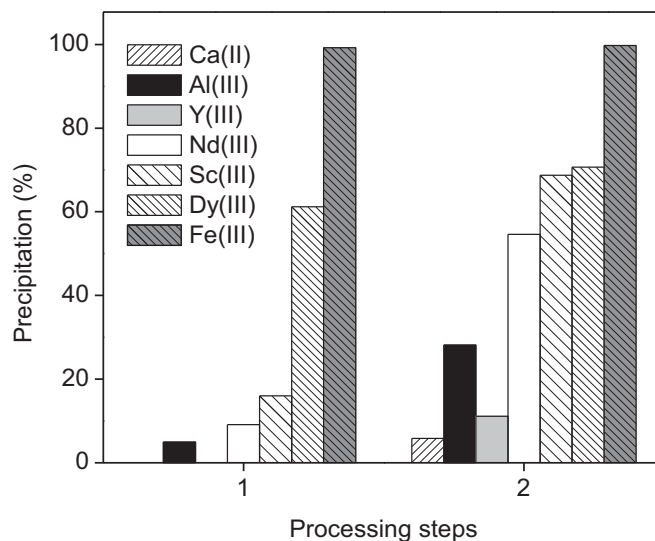


Fig. 2. Precipitation (%) of elements in: (1) Fe(III) dual-step removal with ammonia solution, and (2) ScPO₄ precipitation step with di-ammonium phosphate. The precipitation (%) was calculated relative to the concentration of elements in the simulated H₂SO₄ BR leachate.

column chromatography was examined. Three simulated BR leachates were studied: 1) H₂SO₄ leachate with very high concentrations of base elements and lower concentrations of REEs, 2) H₂SO₄ leachate after Fe(III) removal with ammonia, and 3) H₂SO₄ leachate after Sc(III) precipitation with dibasic phosphate solution from the Fe(III) depleted leachate.

3.1. Selective precipitation

Selective removal of Fe(III) was attempted in order to increase the efficiency of the SILP column chromatography operation for REEs (and especially Sc) purification from H₂SO₄ medium. An ammonia solution was used as an efficient and selective precipitating agent for the two-stage removal of Fe(III) from the solution (Yagmurulu et al., 2017a, 2017b). Then, Sc(III) was precipitated from the Fe(III) depleted solution with di-ammonium phosphate to produce a Sc concentrate.

The precipitation tests were conducted on a H₂SO₄ solution, with a composition similar to real BR leachate with enriched REEs concentrations (Table 1) (Borra et al., 2015; Evans, 2016; Rivera et al., 2018; Yagmurulu et al., 2017a, 2017b). Sc(III), Y(III), Nd(III) and Dy(III) were studied taking into consideration their concentration in BR, high

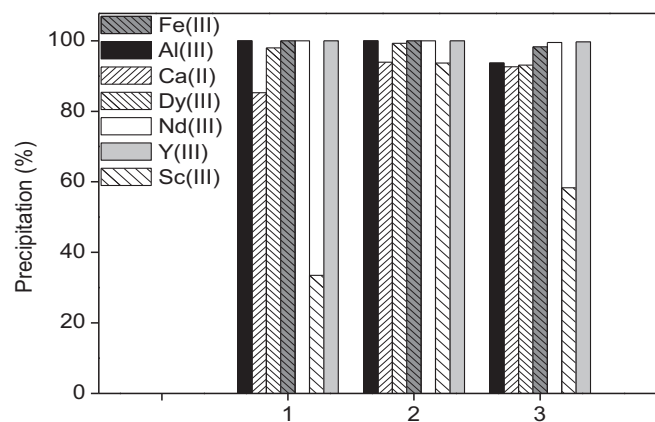


Fig. 3. Recovery (%) of elements by [Hbet-STFSI-PS-DVB] after loading of: (1) simulated H₂SO₄ BR leachate, (2) leachate after dual-step Fe(III) removal by addition of ammonia solution, and (3) leachate after ScPO₄ precipitation.

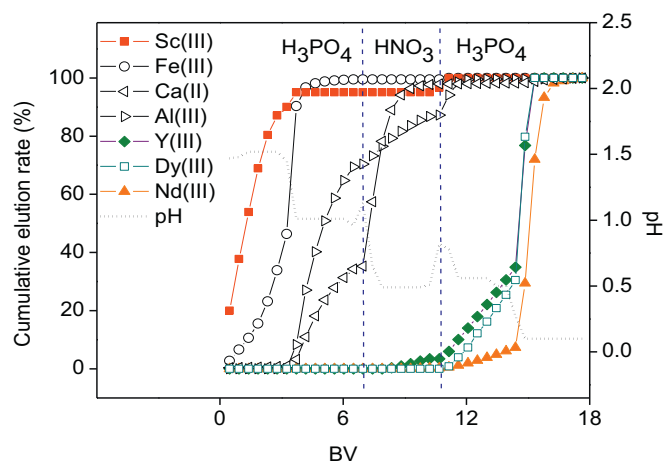


Fig. 4. pH gradient elution with H_3PO_4 and HNO_3 . Feed: 2 mL of simulated H_2SO_4 BR leachate (pH = 1.5). Flow rate 0.5 mL min^{-1} .

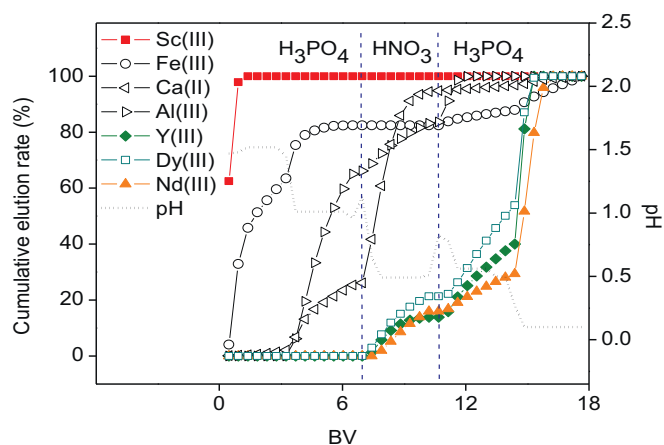


Fig. 5. pH gradient elution with H_3PO_4 and HNO_3 . Feed: 2 mL of simulated H_2SO_4 BR leachate after Fe(III) precipitation (pH = 1.5). Flow rate 0.5 mL min^{-1} .

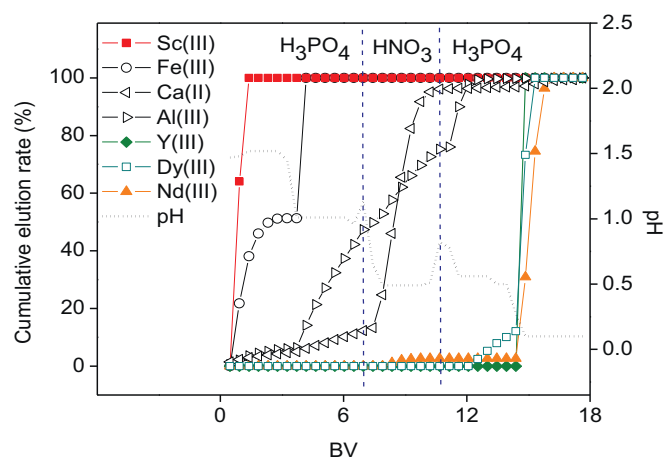


Fig. 6. pH gradient elution with H_3PO_4 and HNO_3 . Feed: 2 mL of simulated H_2SO_4 BR leachate after ScPO_4 precipitation (pH = 1.5). Flow rate 0.5 mL min^{-1} .

supply risk and economic importance (Borra et al., 2015; European Commission, 2017). Nd(III) was studied as a representative element of the light REEs and Dy(III) of the heavy REEs. In highly concentrated Fe(III) solutions, such as the simulated H_2SO_4 BR leachate, an increase in

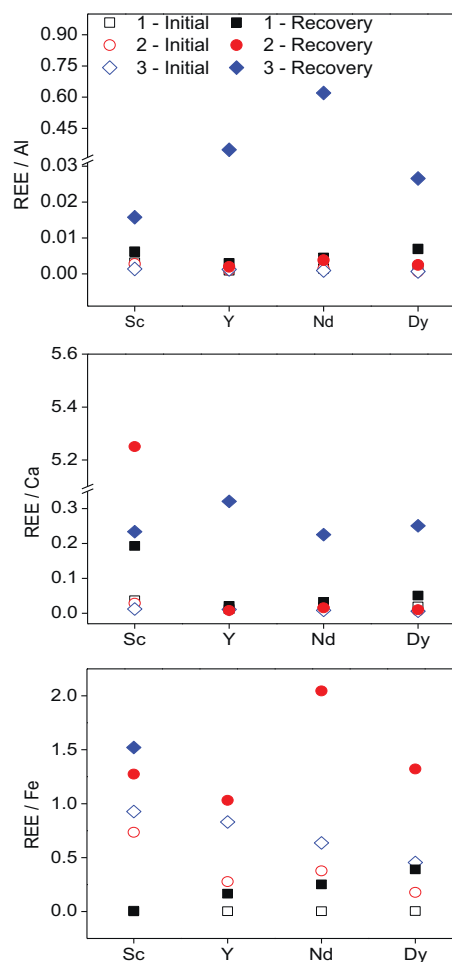


Fig. 7. Molar ratios of REEs and base elements in the feed solutions (open symbols) and after recovery and elution in the [Hbet-STFSI-PS-DVB] column (filled symbols) with: (1) simulated H_2SO_4 BR leachate, (2) leachate after Fe(III) removal, and (3) leachate after ScPO_4 precipitation.

pH favors dimerization, which proceeds according to eq. 3 (Coetzee et al., 2018).



The product $[\text{Fe}_2(\text{OH})_2]^{4+}$ undergoes polymerization and larger iron(III)-hydroxo compounds are most likely being formed by the displacement and ionization of adjacent water molecules with other iron(III)-containing monomers and oligomers. The resulting species are the precursors to self-nucleated Fe(III) oxide/Fe(III) hydroxide precipitates. These precipitates can also incorporate other ligands into the structure, such as sulfate ions.

A decrease in Fe(III) concentration from approximately 2900 mg L^{-1} to 20 mg L^{-1} (99% removal) confirmed the efficiency of the dual-step precipitation (Table 1, Fig. 2). Upon Fe(III) precipitation, 2 mg L^{-1} of Sc(III) and 19 mg L^{-1} of Dy(III) were co-precipitated (Table 1, Fig. 2). The total removal of other elements in the feed was even lower than that of Sc(III) (Fig. 2). It appears that Fe(III) precipitation step is more beneficial for the later Sc(III), Y(III) and light REEs recovery by [Hbet-STFSI-PS-DVB], due to their low co-precipitation, than for the heavy REEs. This is even more important considering that the concentration of light REEs in the BR is generally higher than that of the heavy REEs (Borra et al., 2015; Narayanan et al., 2017; Ujaczki et al., 2017). The highest of co-precipitation occurs during the second Fe(III) removal step, where minor amount of Fe(III) is being precipitated (Yagmurulu et al., 2017a, 2017b). The co-precipitated REEs can still be recovered by re-dissolving the precipitate and further

Table 2

Summary of REEs and major elements quantities in the fractions after purification by the [Hbet-STFSI-PS-DVB] column chromatography from: (1) simulated H₂SO₄ BR leachate, (2) leachate after Fe(III) removal, and (3) leachate after ScPO₄ precipitation.

REEs	Feed	m (mg)	wt%							V (mL)	Fractions
			Al	Ca	Dy	Fe	Nd	Sc	Y		
Sc	1	0.007	4.25	63.8	0.00	24.0	0.00	0.27	0.00	40.0	1–8
	2	0.020	0.00	7.92	0.00	45.5	0.00	46.6	0.00	15.0	1–3
	3	0.003	87.1	8.71	0.00	1.87	0.00	2.29	0.00	10.0	2–3
Y	1	0.004	80.2	15.8	1.10	2.59	0.07	0.00	0.17	52.5	17–28
Nd		0.002									
Dy		0.022									
Y	2	0.003	73.4	25.5	0.46	0.06	0.38	0.00	0.15	57.5	16–28
Nd		0.009									
Dy		0.011									
Y	3	0.000	93.6	4.60	1.77	0.00	0.00	0.00	0.00	22.5	27–31
Nd		0.000									
Dy		0.001									
Y	1	0.009	1.35	2.70	58.4	5.84	17.1	0.00	14.7	18.0	29–32
Nd		0.010									
Dy		0.034									
Y	2	0.005	0.49	25.6	30.7	4.30	24.6	0.00	14.3	18.0	29–32
Nd		0.009									
Dy		0.012									
Y	3	0.002	8.84	14.2	42.6	0.00	24.3	0.00	10.1	4.50	32
Nd		0.009									
Dy		0.009									
Y	1	0.004	26.9	14.3	14.7	5.30	34.2	0.00	4.53	27.0	33–38
Nd		0.028									
Dy		0.012									
Y	2	0.002	0.00	44.5	7.13	7.81	36.2	0.00	4.43	27.0	33–38
Nd		0.017									
Dy		0.003									
Y	3	0.000	8.93	48.5	10.15	0.00	32.4	0.00	0.00	13.5	33–35
Nd		0.003									
Dy		0.000									

processing of the solution by a column chromatography.

Selective precipitation of Sc(III) from the Fe(III) depleted BR leachate was studied by addition of (NH₄)₂HPO₄. After this step, 56% of Sc(III) initially present in the Fe(III) depleted BR leachate was precipitated as ScPO₄ (Fig. 2). However, during Sc(III) precipitation, the co-precipitation of other REEs increased compared to their co-precipitation rate during Fe(III) removal with ammonia. In particular, the Nd(III) co-precipitation rate increased from 9%, during Fe(III) removal, to 55% during Sc(III) precipitation. The co-precipitated REEs could eventually be recovered by re-dissolving ScPO₄ and performing [Hbet-STFSI-PS-DVB] column chromatography. The solution that can be generated in this way would have low concentrations of the base elements, due to their limited co-precipitation with Sc(III) (Fig. 2). Hence this feed composition is a convenient source for downstream processes to easily obtain high-purity fractions of REEs by [Hbet-STFSI-PS-DVB] column chromatography.

3.2. Purification of REEs by the SILP in a fixed bed column

The recovery of REEs by the SILP in column chromatography was studied by making use of the [Hbet-STFSI-PS-DVB] SILP as the solid support, since this material has a proven ability to recover REEs from acidic media (Avdibegović et al., 2017, 2018). The possibility to obtain high-purity REEs fractions by column chromatography with [Hbet-STFSI-PS-DVB] was examined for the three simulated H₂SO₄ BR leachates (Table 1).

Firstly, the simulated H₂SO₄ BR leachate was tested prior to any precipitation treatment. As expected, Sc(III) sorption from this leachate was much lower compared to that of all other elements (Fig. 3). The low affinity of [Hbet-STFSI-PS-DVB] towards Sc(III) in H₂SO₄ solution was previously explained by the high electrostatic interactions between the small Sc(III) cations and sulfate anions, which tightly retain Sc(III) in the solution (Avdibegović et al., 2017; Cotton, 2006). In addition, Sc

(III) uptake was hindered by the high concentration of base elements, especially of Fe(III) which exhibits very similar physico-chemical behavior to Sc(III). Recovery rate of the base elements from the sulfate feed was nearly complete (Fig. 3). The electrostatic interactions between sulfate anions and metal ions were less pronounced for other REEs (Y(III), Nd(III), Dy(III)) than for Sc(III), resulting in their quantitative recovery.

Since the base elements were recovered by [Hbet-STFSI-PS-DVB] to a great extent, separation from the REEs was performed by applying a pH gradient elution with H₃PO₄ (from pH 1.5 to approximately 0.0). HNO₃ (pH = 0.5) was used to specifically enhance Ca(II) elution (Fig. 4). With the applied elution profile, Sc(III) and other REEs were separated from the other elements of the simulated H₂SO₄ BR leachate in the following sequence: Sc(III) > Fe(III) > Ca(II) > Al(III) > Dy(III) ≈ Y(III) > Nd(III).

The second test was performed with the leachate obtained after precipitating Fe(III) with ammonia. Here, the Sc(III) recovery by [Hbet-STFSI-PS-DVB] increased dramatically from 33% to 94% (Fig. 3). The interaction between the carboxyl group of [Hbet-STFSI-PS-DVB] and Sc(III) ions was facilitated, since the binding sites on [Hbet-STFSI-PS-DVB] are no longer occupied by Fe(III) ions. Therefore, Fe(III) removal by precipitation as Fe(OH)₃ had a positive impact on the Sc(III) recovery from the H₂SO₄ leachate by [Hbet-STFSI-PS-DVB]. The recovery of other REEs and base elements still remained nearly quantitative (Fig. 3).

The elution sequence of the REEs recovered by [Hbet-STFSI-PS-DVB] from the feed after Fe(III) removal, followed the same trend as with the BR H₂SO₄ leachate without Fe(III) precipitation (Fig. 5). Sc(III) was eluted within the first three fractions. The remaining REEs started to partially elute already with HNO₃, although with original leachate, the REEs were only eluted with H₃PO₄ at a pH below 0.5 (Figs. 4, 5). These results indicate that ammonium ions in the feed, not consumed during the Fe(III) removal step, may have partially occupied the

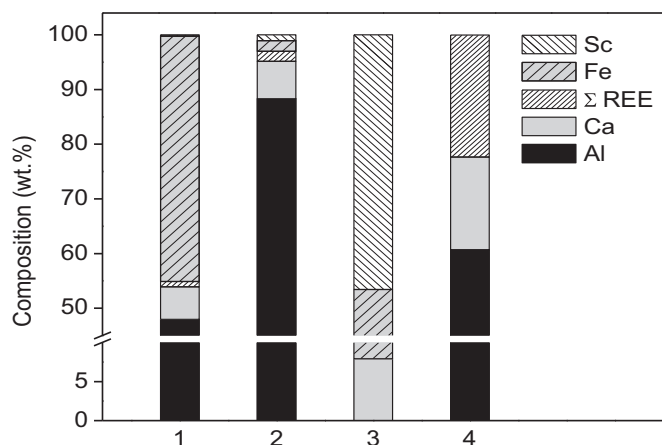


Fig. 8. Summary of the compositions (wt%) of: (1) simulated H₂SO₄ BR leachate, (2) ScPO₄ precipitate, (3) Sc(III) chromatography fractions after Fe(III) removal, and (4) REEs chromatography fractions after ScPO₄ precipitation.

available ion-exchange sites of [Hbet-STFSI-PS-DVB]. As a consequence of increased competition, the REEs migrated further through the column during the loading of the feed, and eventually started eluting earlier, already during the HNO₃ elution step.

The last tests were performed with the simulated H₂SO₄ BR leachates after two consecutive precipitation steps, where Fe(III) and Sc(III) had been extensively removed by precipitation with NH₃ and (NH₄)₂HPO₄ solutions, respectively. [Hbet-STFSI-PS-DVB] exhibited a maximum recovery of 58% of trace amount of Sc(III) that could not be sorbed and persisted in the solution (Fig. 3). Although the Fe(III) concentration in the tested feed was negligible (Table 1), presumably the presence of phosphate anions that remained after Sc(III) precipitation inhibited trace Sc(III) recovery by [Hbet-STFSI-PS-DVB]. Nevertheless, the recovery of other REEs remained remarkably high (> 98%). It must be noted that the REEs concentrations in the feed after Sc(III)

precipitation were lower than in the initial H₂SO₄ leachate and after Fe(III) removal, due to their co-precipitation (Table 1).

The elution sequence in the column chromatography for the separation of REEs and base elements from the leachate after Sc(III) precipitation was in agreement with the previous ones (without precipitation and after Fe(III) removal) (Fig. 6). The trace amount of Sc(III) recovered by [Hbet-STFSI-PS-DVB] was eluted with H₃PO₄ in only two fractions and the remaining REEs were eluted with H₃PO₄. The REEs did not migrate faster through the column than in the case with the leachate after Fe(III) removal by ammonia. The influence of ammonium ions was less pronounced in the presence of phosphate counter-ions that were primary added for Sc(III) precipitation.

3.3. Assessment of the different combinations: precipitation – SILP chromatography

In all three tested cases, the REEs collected in the fractions after [Hbet-STFSI-PS-DVB] column chromatography were largely purified from the base elements (Fig. 7, Table 2). The most efficient Sc(III) recovery and purification route was found to be by [Hbet-STFSI-PS-DVB] column chromatography after Fe(III) removal (Fig. 3). The purity of Sc(III) in the fractions obtained when performing only Fe(III) removal prior to the chromatography separation, was superior to the purity of Sc(III) concentrate obtained by the phosphate precipitation (Fig. 8). However, by ScPO₄ precipitation generally higher feed volumes can be treated per purification step in comparison with [Hbet-STFSI-PS-DVB] column chromatography, making the former process more suitable for large-scale scandium production. The amount of the feed solution treated with [Hbet-STFSI-PS-DVB] column chromatography is limited by the presence of large concentrations of base elements. Sc(III) precipitation resulted in a feed with lower concentrations of interfering elements, which was beneficial for the subsequent column chromatography separation of other REEs. As a result, the purity of the REEs fractions was better compared to the purity obtained after separation from the simulated H₂SO₄ BR leachate, before and after Fe(III) precipitation (Fig. 7, Fig. 8). Hence, the precipitation and column

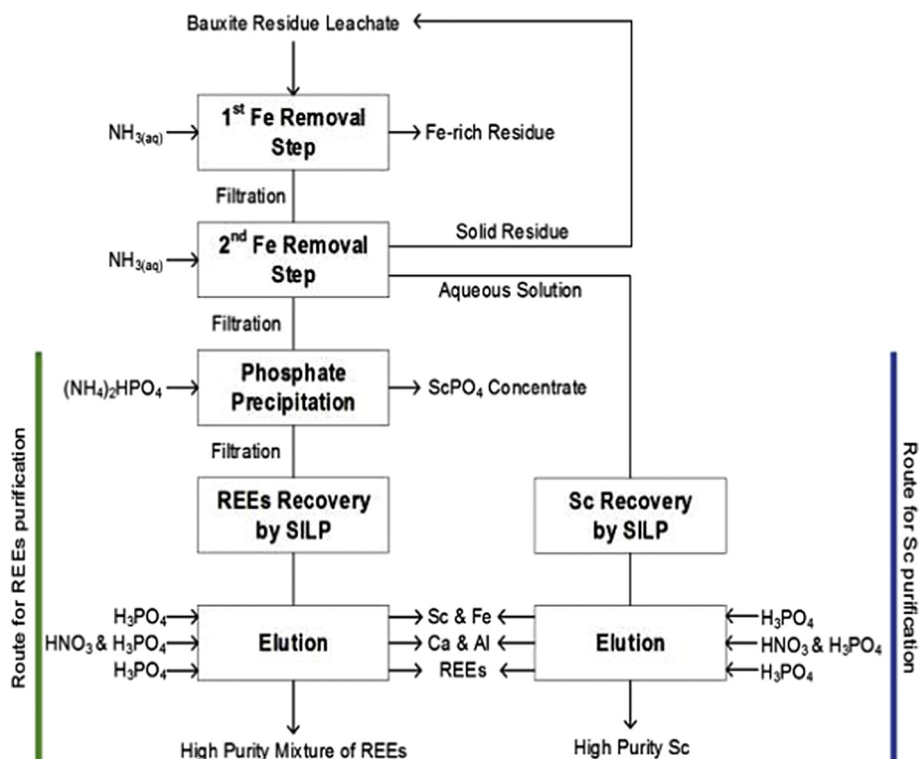


Fig. 9. Flow-sheet for REEs purification (including Sc) by a precipitation and [Hbet-STFSI-PS-DVB] column chromatography tandem processes.

chromatography tandem process enables recovery and purification of scandium and other REEs via two routes, which are split based on the resulting purity degree of REEs (Fig. 9). The proposed routes aim for simultaneous utilization of BR as a secondary source of several critical REEs, outreaching previously reported processes which are mainly focused on the recovery of a single REE, mainly scandium (Onghena et al., 2017; Roosen et al., 2016; Zhang et al., 2017).

4. Conclusions

The REEs Y(III), Nd(III) and Dy(III) were efficiently ($\approx 100\%$) recovered by [Hbet-STFSI-PS-DVB] from three simulated BR leachates: 1) H_2SO_4 leachate with very high concentrations of base elements and lower concentrations of REEs, 2) the same leachate after Fe(III) removal with ammonia, and 3) the latter leachate after additional precipitation of Sc(III) with a dibasic phosphate solution. Sc(III) recovery from the H_2SO_4 leachate by [Hbet-STFSI-PS-DVB] was only efficient after Fe(III) precipitation. A subsequent column chromatography separation step resulted in Sc(III) fractions of purity superior to $ScPO_4$ precipitate. Therefore, the precipitation of Fe(III) prior to Sc(III) recovery by [Hbet-STFSI-PS-DVB] appeared to be the most promising route to separate Sc(III) from the base elements in H_2SO_4 leachates of BR. The obtained Sc(III) purity (47%) may be further improved by an additional column chromatography cycle. The highest REEs purity (23% for the group of REEs) was achieved for the feed solution after Sc(III) precipitation. In other words, precipitation of interfering elements as a pretreatment of BR H_2SO_4 leachates boosted the efficiency of the [Hbet-STFSI-PS-DVB] column chromatography towards obtaining purified fractions of Sc(III) and other REEs.

Conflicts of interest

There are no conflicts to declare.

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