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Recovering rare earth elements from phosphogypsum using a resin-in-leach process: Selection of resin, leaching agent, and eluent



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ABSTRACT

Phosphogypsum (PG) is an attractive secondary raw material for rare earth elements (REEs) because it is abundant and contains significant amounts of REEs. Herein, the resin-in-leach (RIL) process for REE recovery from PG was studied, and the factors affecting the yield and selectivity of conventional leaching and RIL are discussed based on the batch equilibrium data obtained using four different lixiviants, H_2SO_4 , HCl, H_3PO_4 , and NaCl. It was found that the chelating resin enabled the use of a low H_2SO_4 concentration (1 g/L) in the RIL process. The REE recovery yield and purity in the single-stage RIL process were higher when the chelating resin was used than when strong acid resins were used. The difference was significant in the multistage cross-current RIL process, where a loading of 19.2 g(REE)/kg(resin) and up to 20% purity were obtained with the chelating resin (vs. 3% in strong acid resin) after four stages. It is concluded that neither the breaking of the PG structure, nor the adsorption of calcium by the resin is necessary to enhance REE recovery. Considering the available literature and patents, this is a promising finding. REEs can be eluted from strong cation exchangers using a saturated sodium chloride solution, while EDTA or concentrated hydrochloric acid is required in the case of a chelating resin. However, Ca and REE can be further separated during elution of the chelating resin.

1. Introduction

Phosphogypsum (PG) is a by-product of phosphoric acid production via a wet process. In this process, 70–85% of rare earth elements (REEs) originally present in the phosphate rock is concentrated in the PG (Hammas-Nasri et al., 2016). PG mainly consists of calcium sulfate ($CaSO_4$) dihydrate or hemihydrate along with phosphate, fluoride compounds, and silica as the main impurities (Binnemans et al., 2015). The REE content of PG significantly varies depending on the origin of the phosphate ore; however, it is typically ca. 0.4% (Habashi, 1985).

Although the REE content of PG is roughly one tenth of that of the typical REE ores, it is an attractive REE source because of the large production volumes. European PG production is estimated as 21 Mt/year from 30 different locations, while the world production is 100–280 Mt/year (Gijbels et al., 2017). Considering the typical REE content of 0.4%, the amounts of REE locked in the waste piles annually are 84,000 tons in Europe and 400,000–1120 000 tons worldwide. The annual world production of REEs was 170,000 tons in 2018 (USGS, 2019), and the demand of REEs is expected to grow at an annual rate of almost 6%. In 2035, the demand is predicted to be over 350,000 tons.

The contents of PG is weighed toward the light REE (Yahorava et al., 2016; Hammas-Nasri et al., 2019; Binnemans et al., 2015); thus, the

most valuable REEs in PG are Nd and Pr. Although the contents of La and Ce are the highest, their market value is not very high, and thus, their value in PG is marginal. The prices of La, Ce, Pr, and Nd in February 2019 were 5.58, 5.43, 98.1, and 59.2 dollars/kg, respectively (mineralprices.com, 2019). The demands for Nd and Pr are expected to grow from 20% to 40% (until 2035) and from 7% to 11% of the total REE demand, respectively. La and Ce constitute ca. 20% and 40% of the total REE demand, respectively, and their shares are expected to decrease (Alonso et al., 2012). The growth rate of Nd demand is related to its use in permanent magnets, which are the key components in electric vehicle motors. Therefore, Nd is clearly the most interesting target element in PG.

Yahorava et al. (2016) have reviewed the various methods used for REE recovery from PG. Several mineral acids and their mixtures have been used for digestion (Cánovas et al., 2019), among which H_2SO_4 has been the most commonly used. The yield of REEs by H_2SO_4 leaching depends on the structure of PG, H_2SO_4 concentration, and the liquid-to-solid ratio. Up to 50% yields have been reported with < 10% H_2SO_4 , while reasonable yields have been obtained with 0.5–1.0% H_2SO_4 . By increasing the H_2SO_4 concentration to over 20%, 73–84% yields have been obtained. The total REE concentration in the obtained leachates was typically 200–1000 mg/L (Yahorava et al., 2016).

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The most common method for the recovery of REEs from mineral acid leachates has been solvent extraction using organophosphorus reagents, mainly tributyl phosphate (TBP) or di-(2-ethylhexyl)phosphoric acid (D2EHPA) (Safuulina et al., 2015; Cánovas et al., 2017). Ion exchange with different cation exchangers has also been suggested (e.g. Koopman and Witkamp, 2000; Saykina et al., 2016; Lokshin et al., 2015a; Xu et al., 2018). The studies on PG leachates involve the use of strong cation exchangers, and the performance of chelating resins has not been investigated yet. REE concentrates can be recovered with or without the solvent extraction or ion exchange purification process by different precipitation methods (Binnemans et al., 2015). For example, 97–99 wt% REE concentrate has been obtained by hydrolytic precipitation after ion exchange recovery with a sulfonic acid resin (Lokshin et al., 2015b).

The resin-in-leach (RIL, also called resin-in-pulp) process is a common method in the hydrometallurgical industry for recovering metals from solid raw materials in a single unit operation. In the RIL process, an ion-exchange resin is added to the pulp in the leaching reactor, and the leached metals liberated from the solid raw material are transferred to the resin. The implementation of the RIL process for the recovery of REEs from PG was first suggested in the 1990s (Padayachee et al., 1996). The researchers briefly compared different types of resins functionalized or impregnated with sulfonic and phosphonic acid, acetyl acetone, citric acid, polyethylene glycol, D2EHPA, and TBP in sulfuric acid media. Since then, the process has been studied to some extent and patents concerning the process have been filed (Kolyasnikov et al., 2012; Yavorava et al., 2016; Nechaev et al., 2018). Yavorava et al. (2016) optimized the process in sulfuric acid media using a strong cation exchanger. In addition, they discussed elution with NaCl, HCl, and CaCl₂ and presented the techno-economic analysis of the proposed flowsheet. The benefits of the RIL process are the use of dilute H₂SO₄ as a lixiviant, a higher REE recovery through a leaching reaction driven in the forward direction, and a simultaneous leaching and recovery step. Therefore, it is considered a promising option from the techno-economic point of view (Yavorava et al., 2016). After the loading of REEs and impurities, the resin can be eluted with CaCl₂, NaCl, HCl (Yavorava et al., 2016), or NH₄NO₃ (Rychkov et al., 2018; Nechaev et al., 2018), and consequently, the REE concentrate can be obtained by precipitation as described above.

Despite the above discussed research in the field, the chemistry of the RIL process, including elution, for REE recovery from PG has not been studied systematically and thoroughly. Herein, the selection of lixiviant, resin, and eluent for the recovery of REEs from PG by the RIL process is systematically studied to understand the equilibrium phenomena, and consequently, to optimize the process for industrial operation.

2. Materials and methods

2.1. Materials

The PG sample used here was obtained as a by-product of the phosphoric acid wet process from Yara Siilinjärvi plant in Finland, and the apatite ore used in the process was obtained from the same region. Before the experiments, the PG was vacuum-dried at 60 °C and powdered using a mortar and pestle. Table 1 shows the REE content of PG analyzed by inductively coupled plasma mass spectrometry (ICP-MS) after microwave digestion (analytical details are given in Section 2.5).

Table 1

REE content of phosphogypsum raw material used in the resin-in-leach experiments.

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
mg/kg	31.8	260.2	735.4	102.2	422.6	64.0	15.8	37.0	3.4	13.4

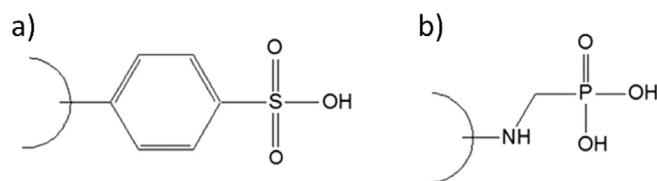


Fig. 1. Structures of the resins used in the resin-in-leach experiments. a) Sulfonic acid resin (Purolite C150 and Finex CS16GC) and b) aminophosphonic resin (Purolite S940). Adapted from Page et al. (2017).

The PG contained 1.7 g/kg total REE, 49 g/kg Ca, 0.5 g/kg Fe, and 3.8 g/kg Sr. Although the PG samples around the world often contain considerable amounts of radioactivity (Binnemans et al., 2015), it is not a concern in this case as the apatite used in the Siilinjärvi plant originated from igneous phosphate rocks (Jaakkola et al., 2012).

The ion-exchange resins studied were Purolite S940 (denoted here as CHEL), Purolite C150 (SAC1), and Finex CS16GC (SAC2). The resin structures are given in Fig. 1, and their properties are listed in Table 2.

2.2. Sorption isotherms

The properties of the cation-exchangers were studied using synthetic Nd solutions to obtain a reference for REE uptake. Sorption isotherms of Nd were determined in the absence and presence of CaSO₄ (saturated solution) to assess the competing effect of Ca. H₂SO₄ (10 g/L) was used as a background to provide similar conditions as that in the RIL experiments. The isotherms were measured by mixing 10 mg of resin with 5 mL of a Nd solution containing varying concentrations of Nd (from 60 to 800 mg/L) for 24 h at room temperature (294 ± 1 K). The concentrations of Nd before and after the experiments were measured by ICP-MS.

2.3. Resin-in-leach experiments

The RIL experiments were conducted by mixing PG (2.5 g), resin (0.5 g), and an acidic solution (20 mL) in 50 mL plastic tubes for 24 h. The acidic solutions tested were H₂SO₄, HCl, and H₃PO₄ with acid concentrations of 0.1, 1.0, 5.0, and 10 g/L. In addition, aqueous NaCl solutions (5.0, 25, and 58 g/L) were used to determine the effect of H⁺ / Na⁺ exchange in the system. After 24 h of mixing and a few minutes of settling, a liquid sample was withdrawn from the tubes using a syringe and filtered through a polypropylene membrane filter (0.45 μm) to ensure no solids passed to the sample. The resin was then separated from the liquid and residual PG using a 250 μm sieve and washed carefully with deionized water. The PG phase was washed with water saturated with CaSO₄. CaSO₄ was added to avoid the dissolution of Ca from the PG sample. Both the solids (i.e., the resin and residual PG) were dried, and the metals were completely leached by microwave digestion (see below) and analyzed by ICP-MS.

Leaching experiments were performed without the resin as a reference. In addition to the concentrations used in the RIL experiments, a 20 g/L concentration was used for each acid, and 1.0 g/L and 100 g/L concentrations were used for NaCl.

The cross-current multi-stage process was studied by contacting the same batch of resin with a fresh PG/acid mixture several times. The resin was separated from the PG slurry as described above, added to a fresh slurry of PG and acid (1.0 g/L HCl or 5.0 g/L H₂SO₄), and mixed for 24 h.

2.4. Elution of REEs and impurities from the resin

CHEL and SAC2 resins were eluted in a batch contactor using NaCl, HCl, EDTA, Na-citrate, HCl in 50% ethanol + 50% H₂O, thiourea in 1 M HCl, thiosulfate + Na₂SO₃ (2:1 M ratio), dimethyl sulfoxide, and glycine. The possible organic and inorganic eluents were screened for two

Table 2

Properties of the resins used in the resin-in-leach experiments. All resins have a poly(styrene-divinylbenzene) matrix.

Resin	Physical structure	Functional group	Type	Capacity, equiv/L	Particle size, μm
Purolite S940	Macroporous	Aminomethyl-phosphonic acid	Chelating	1.11 ^a	425–850
Purolite C150	Macroporous	Sulfonic acid	Strong cation	1.8 ^a	300–1200
Finex CS16GC	Gel	Sulfonic acid	Strong cation	1.93 ^b	275

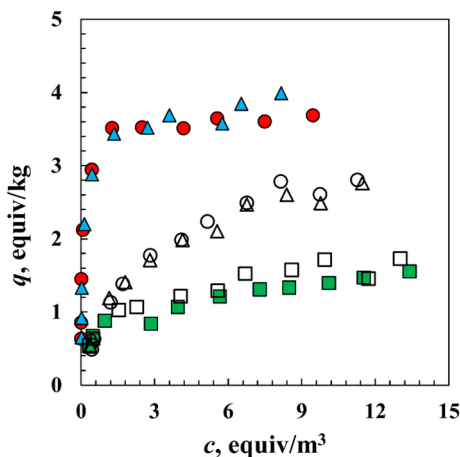
^a www.purolite.com.^b Heinonen and Sainio, 2014.

Fig. 2. Nd sorption isotherms from water with 10 g/L H_2SO_4 (filled symbols) and from saturated CaSO_4 solution with 10 g/L H_2SO_4 (open symbols). Circles: SAC1, triangles: SAC2, squares: CHEL. Phase ratio, 1:500 (kg/L); initial concentration of Nd, 60–800 mg/L; contact time, 24 h; T , 294 K.

Table 3

PG leaching without resin. The phase ratio (PG:solution) was 1:8 (kg/L), contact time was 24 h, and temperature was 294 K.

Leaching agent	c , g/L	Ca, mg/L	Total REE, mg/L	REE yield, %
HCl	0.1	695.1	2.2	1.2%
	0.5	830.8	13.1	6.9%
	1	902.9	19.8	10.5%
	5	1673.2	62.9	33.4%
	10	2245.1	77.1	40.9%
	20	3765.1	97.9	52.0%
H_2SO_4	0.1	638.6	1.5	0.8%
	0.5	552.0	7.8	4.2%
	1	773.4	8.1	4.3%
	5	662.6	62.0	32.9%
	10	744.0	81.2	43.1%
	20	710.9	76.4	40.6%
H_3PO_4	0.1	712.1	0.2	0.1%
	0.5	691.6	0.8	0.4%
	1	790.6	1.5	0.8%
	5	879.4	3.5	1.8%
	10	1112.4	5.5	2.9%
	20	1307.8	9.3	4.9%
NaCl	1	735.6	0.0	0.0%
	5	908.7	0.0	0.0%
	12	1133.1	0.0	0.0%
	25	1347.9	0.0	0.0%
	58	1854.8	0.0	0.0%
	100	3044.6	0.0	0.0%

reasons: (1) REEs do not elute easily from the aminophosphonic groups (Hérés et al., 2018), and (2) the possibility of at least partial fractionation of the sorbed metals (REE, Ca, Fe, Sr) was studied. The concentrations of eluents were so chosen that there would be a four-fold increase in each ligand with respect to the amount of REEs loaded in the resin. The contact time at room temperature was 2 h, and the liquid-to-solid ratio was 5 mL/g resin.

Column elution experiments were performed at 294 K at flowrates of 1.98–2.03 mL/min, corresponding to 6.45–7.32 BV/h, in 15-mm-diameter glass columns (YMC Europe GmbH) for the following resin-eluent combinations: SAC2–1 M NaCl, SAC2–3.60 M NaCl, CHEL–1 M HCl, CHEL–4 M HCl, and CHEL–0.2 M EDTA.

The extent of elution of each metal was calculated as the ratio of the mass of each metal eluted from the column and the loading achieved in the RIL step, as shown in Eq. (1). The loading was determined by analyzing the resin by a wet combustion method. The integral in Eq. (1) was evaluated numerically from the elution curves using the trapezoidal rule.

$$E_j = \frac{1}{q_j^{\text{RIL}}} \int_0^\infty \frac{c_j^{\text{out}}}{m_{\text{resin}}} dV_{\text{eluent}} \quad (1)$$

where E is the extent of elution of metal j , q^{RIL} is the loading of the resin after the RIL process (mg/g), V_{eluent} is the volume of the eluent fed into the column (mL), c^{out} is the concentration of the effluent discharged from the column (mg/L), and m_{resin} is the mass of resin in the column during elution (g).

2.5. Analytical methods

The solid samples were analyzed by microwave digestion in a mixture of HNO_3 and HCl (Romil SpA™ Super Purity Acid grade, $\text{HNO}_3:\text{HCl} = 1:3$, v/v) using a Milestone Ultrawave microwave digestion system. Approximately 100 mg of each sample was placed in a microwave vessel with the acid mixture, covered with a cap, and heated to 250 °C under a pressure of 80 bars.

The metals in the liquid phase were analyzed using an Agilent 7900 inductively coupled plasma mass spectrometer. All the standards used were of ICP-MS grade and the acids were as described above.

Scanning electron microscopy (SEM) was performed using a Hitachi SU3500 scanning electron microscope fitted with a ThermoScientific UltraDry SDD energy dispersive X-ray spectroscopy (EDS).

3. Results and discussion

3.1. Nd sorption isotherms from synthetic solutions

The characteristic feature of the PG RIL process is the presence of Ca close to the saturation concentration. To compare the loading capacities of the resins and to quantify the effect of Ca on the sorption of REEs in a controlled manner, the uptake of Nd was studied separately. The sorption equilibrium isotherms were determined in 10 g/L H_2SO_4 solutions for pure Nd and Nd/ CaSO_4 mixtures. Fig. 2 shows that the sorption of Nd^{3+} in the SAC resins from a 10 g/L H_2SO_4 solution is significantly high and the resin is fully loaded at low concentrations. The performances of the macroporous and gel-type resins were only slightly different. The competing effect of Ca reduced Nd sorption by the SAC resins. The Nd loading of CHEL was lower than that of the SAC resins due to the lower ion exchange capacity (Table 2). However, it remained nearly the same despite the large amount of Ca, which reveals that the REE/Ca selectivity of the CHEL resin is better than that of the SAC resins. This suggests that the coordination mechanism could be exploited in the RIL process to improve the selectivity of the resin

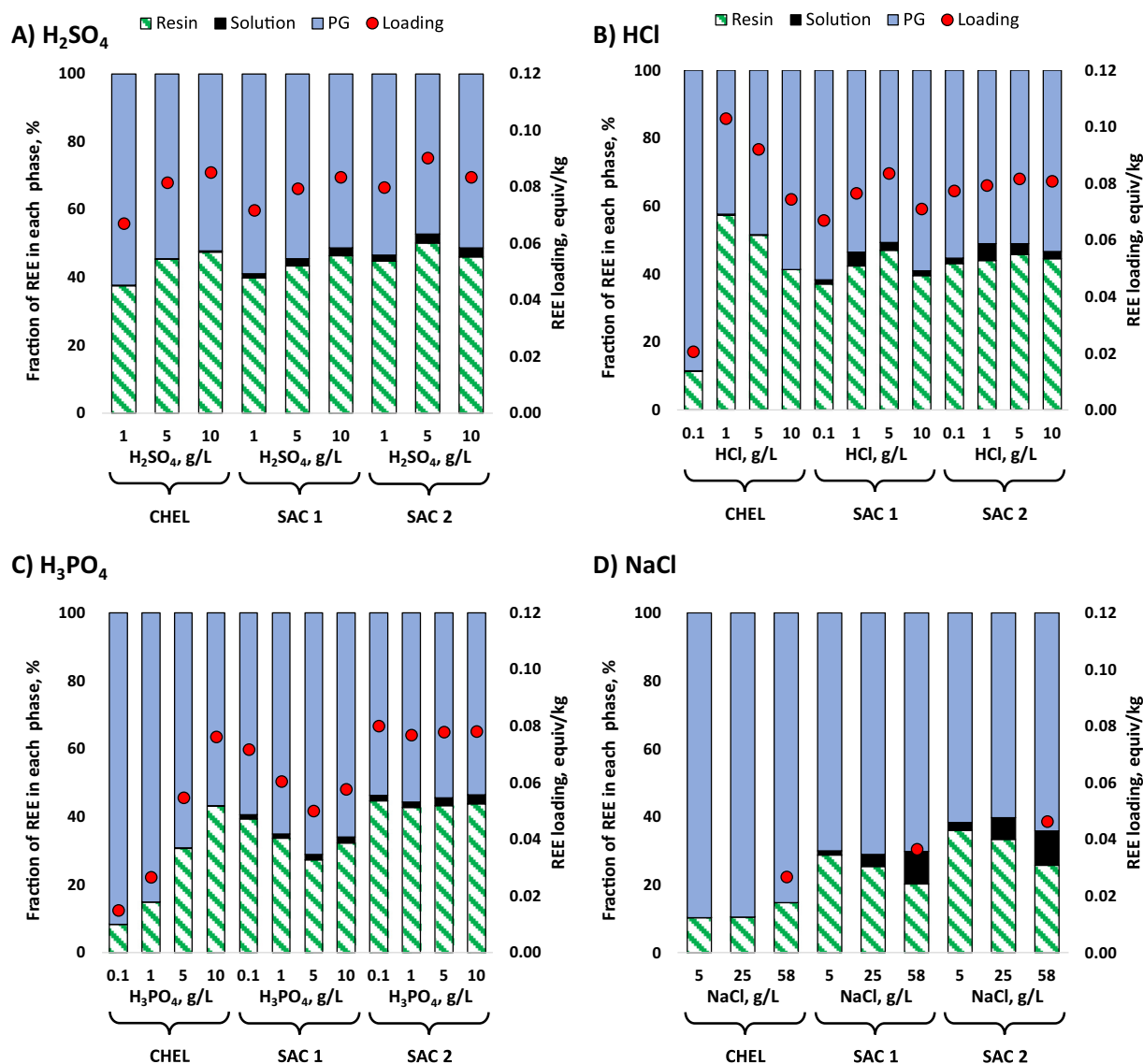


Fig. 3. REE distributions in PG, solution, and resin after one-stage RIL experiments in (a) H_2SO_4 , (b) HCl , (c) H_3PO_4 , and (d) NaCl . The total loading of REEs in the resin is shown on the right y-axis. Phase ratio (PG:resin:solution), 5:1:40 (kg/kg/L); contact time, 24 h; T , 294 K.

toward REEs over Ca.

The difference in the selectivities of the SAC and CHEL resins can be explained by their different affinities and coordination behaviors toward metal ions. For the SAC resin, the metal ion retains its hydration shell during sorption, when it is not directly in contact with the surface sulfonate groups. In this case, the attraction between the surface and metal ion mostly depends on the valence of the metal ion, and Nd with a higher charge is bound more strongly than Ca with a lower charge. However, this attraction is not comparable to the complex formation, and the high amount of Ca in the solution affects Nd sorption. In contrast, for the CHEL resin, Nd is strongly bound on the surface via several phosphonate groups, forming a highly stable complex, which is less affected by the presence of Ca ions (Page et al., 2017). Although the stability constant of a complex between the amino phosphonic group and Nd is unknown, the stability constant of the complex formed between La and a similar ligand has been evaluated to be over 100,000 times higher than that of a Ca complex (Popov et al., 2001).

3.2. Acid leaching of PG without resins

As a reference for the systematic RIL experiments, a series of batch

leaching experiments was performed without resin (Table 3). The REE yield (%) was calculated by the following equation:

$$\text{REE yield} = \frac{c_{\sum \text{REE}}^{\text{Eq}} \cdot V_L}{q_{\sum \text{REE}}^0 \cdot m_{\text{PG}}} \cdot 100\% \quad (2)$$

where $c_{\sum \text{REE}}^{\text{Eq}}$ is the total equilibrium concentration of REEs in the leaching agent (mg/L), V_L is the volume of the leaching agent (L), $q_{\sum \text{REE}}^0$ is the total initial concentration of REEs in PG (mg/kg), and m_{PG} is the initial mass of PG (kg).

The REEs could not be leached using H_3PO_4 and NaCl . However, with HCl and H_2SO_4 , reasonable yields were obtained using an acid concentration of 5 g/L or more. A maximum yield of 52% was obtained with 20 g/L HCl . It is noteworthy that HCl resulted in substantially higher Ca concentration in the leachate than H_2SO_4 did, with no significant difference in the leaching of REEs. This is because Ca dissolved in H_2SO_4 reprecipitated as gypsum, whereas the REEs remained in the liquid phase.

A motivation for the use of SAC resins in the RIL process in previous works has been the sorption of Ca to increase the driving force for PG dissolution (Yahorava et al., 2016). However, the results shown in Table 2 indicate that Ca sorption is not necessary. Therefore, the resin

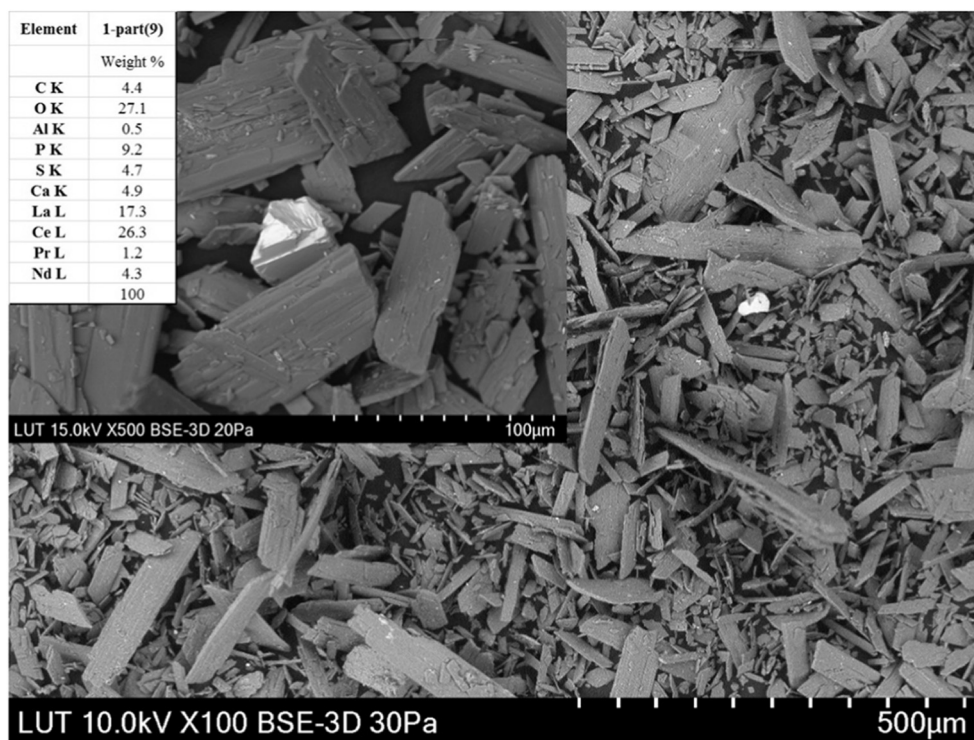


Fig. 4. SEM image of PG before leaching. Inset: elemental composition of the white crystal.

used in the RIL process can be chosen based on its selectivity toward REE over Ca and metallic impurities rather than its Ca sorption capacity.

3.3. Single-stage RIL experiments

Single-stage RIL experiments were performed in four different media (H_2SO_4 , HCl, H_3PO_4 , and NaCl) with varying acid and salt concentrations. The distribution of REE in PG, resin, and solution as a function of acid/salt concentration are presented in Fig. 3. When sulfuric acid was used as the leaching agent, all the three resins showed a rather similar behavior and the acid concentration affected the resin loading only slightly. The amount of REE in the solution phase relative to the total amount of REE in the system increased with increasing acid concentration; however, it remained below 3% for the SAC resins and below 0.5% for the CHEL resin.

Based on an earlier study (Walawalkar et al., 2016), it was expected that the leaching of REE would be more effective in HCl than in H_2SO_4 due to the limiting effect of the common anion in calcium sulfate and sulfuric acid. However, this was observed in 1.0 and 5.0 g/L HCl concentrations only for the CHEL resin. In the case of CHEL, the proton concentration in 0.1 g/L HCl was not large enough to dissolve the REE from PG, and the highest leaching was obtained in 1.0 g/L HCl. In the case of SAC resins, however, more protons were released from the resin due to the uptake of Ca, which enhanced the leaching of REE even at very low acid concentrations. Further, compared with H_2SO_4 , the amount of REE in the solution phase was higher when HCl was used with the SAC resins, especially at a HCl concentration of 1.0 g/L. Similarly, the highest Ca concentrations in the solution were measured for 1.0 g/L HCl.

In the H_3PO_4 medium, the REE uptake by CHEL increased steadily with increasing acid concentration, while the equilibrium pH decreased from 3.3 to 1.8. In the case of SAC resins, a different recovery behavior was observed. For SAC1, the recovery of REE decreased with increasing H_3PO_4 concentration. Moreover, the uptake of REE by the SAC1 resin was lower in H_3PO_4 than in H_2SO_4 and HCl. In contrast, rather similar

behaviors were observed for SAC2 in all the tested acids and acid concentrations. This can be attributed to the highest amount of protons released from SAC2, which created rather similar conditions for the leaching of REE in all the media.

In the case of NaCl, as seen in Fig. 3, the dissolution of REE from PG required more protons than those released from CHEL (solution pH was around 3), which led to low recoveries (from 10 to 15%) with a slight increase in salt concentration. However, the SAC resins released more protons, resulting in a more effective leaching of REEs.

The SEM image displayed in Fig. 4 shows that the REEs in the PG raw material are present as separate white crystals, as observed in previous works (Walawalkar et al., 2016). The crystals contained Ce, La, Pr, and Nd approximately in the ratio of 1:0.5:0.1:0.2. After leaching by H_2SO_4 in the absence of resin, the ratio changed to 1:0.4:0.1:0.35, which corresponded to a leaching order of La > Ce \approx Pr > Nd. This behavior was confirmed by analyzing the resins after the single-stage RIL experiments. After the RIL experiment using CHEL in 1.0 g/L HCl, the white REE crystals were no longer observed in the SEM analysis but were observed after RIL experiments using SAC in 10 g/L H_2SO_4 . It is thus concluded that HCl is a better leaching agent than H_2SO_4 (Table 3). The morphology of PG was retained during leaching, and the crystal surfaces were smoother than those observed in other studies (Zmemla et al., 2016). It is concluded that there is no significant selectivity between the REEs in the leaching step. Thus, the REEs should be separated from each other (optional process) in a separate step.

The most significant impurities in the PG used in this work were Ca, Fe, and Sr. In the single-stage RIL experiments, the Ca uptake was similar (~ 15 g/kg resin) for both the SAC resins and all the acids (Fig. 5). On the other hand, the Ca uptake (~ 5 g/kg) was much lower for the CHEL resin, which indicates a higher REE selectivity. As expected, the Fe loading of the CHEL resin (560–1090 mg/kg resin) was higher than that of the SAC resins. The macroporous SAC1 resin contained less Fe (27.5–205 mg/kg resin) than the gel-type SAC2 resin did (40.5–237 mg/kg). In terms of REE/Sr selectivity, the CHEL resin was better than the SAC resins with approximately 20 times lower Sr

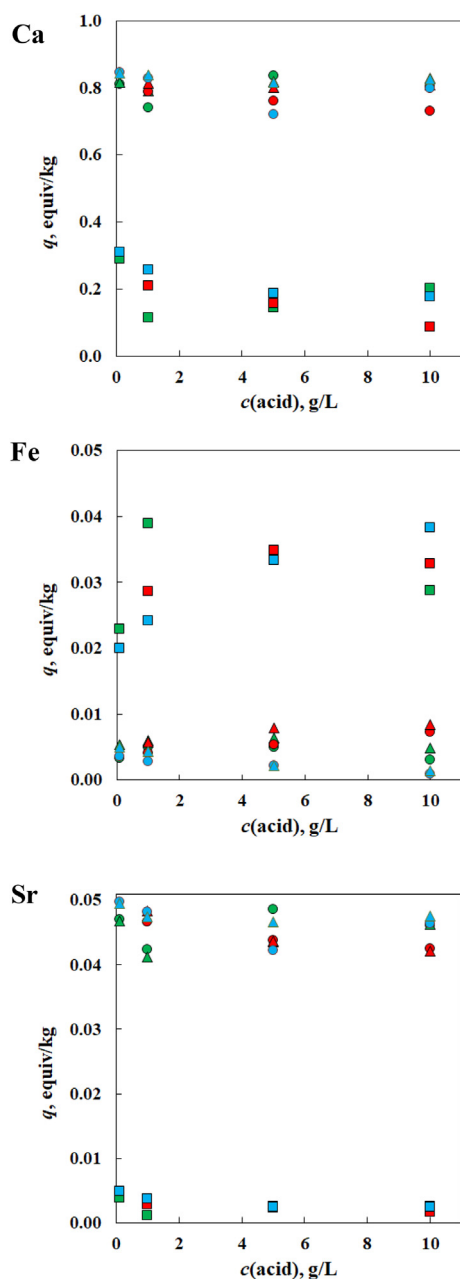


Fig. 5. Loading of Ca, Fe, and Sr metallic impurities to the resins in RIL experiments. Symbols for resins: square = CHEL, circle = SAC1, and triangle = SAC2. Colors for mineral acids: red = H_2SO_4 , green = HCl, and blue = H_3PO_4 . Phase (PG:resin:solution) ratio, 5:1:40 (kg/kg/L); contact time, 24 h; T , 294 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

loadings. In general, the uptake selectivity depends more on the resin than on the leaching agent.

3.4. Cross-current multistage RIL experiments

As the loadings in the single-stage experiments were quite low (ca. 0.1 equiv./kg at maximum), a more efficient utilization of the resins was investigated by contacting them four times with a fresh acid-PG slurry and determining the loading of resin, the purity of REEs in the loaded resin, and the yield of REEs from PG to the resin.

As can be seen in Fig. 6, the loadings are similar for the CHEL and SAC resins (~ 0.1 equiv./kg) in the first contact stage. This is consistent with the effect of Ca on the uptake of pure Nd shown in Fig. 2.

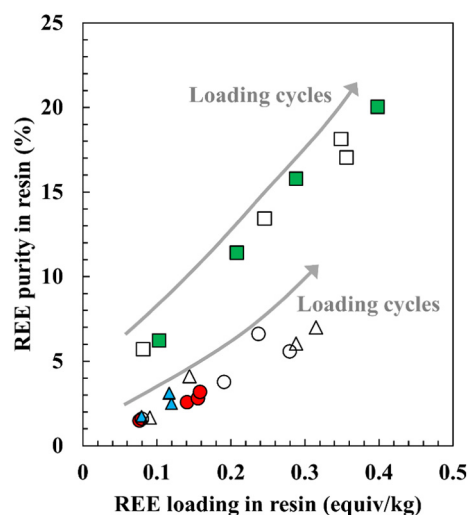


Fig. 6. Evolution of cumulative REE loading and REE purity in the resins during cross-current RIL treatment of PG with 1 g/L H_2SO_4 (filled symbols) and 5 g/L H_2SO_4 (open symbols). Circles: SAC1, triangles: SAC2, squares: CHEL. Phase (PG:resin:solution) ratio, 5:1:40 (kg/kg/L); contact time, 24 h; T , 294 K.

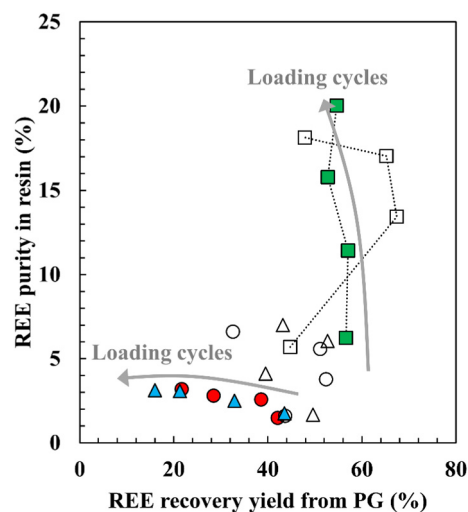


Fig. 7. REE yield from PG (per stage) and cumulative REE purity in the resins during cross-current RIL treatment of PG with 1 g/L H_2SO_4 (filled symbols) and 5 g/L H_2SO_4 (open symbols). Circles: SAC1, triangles: SAC2, squares: CHEL. Phase (PG:resin:solution) ratio, 5:1:40 (kg/kg/L); contact time, 24 h; T , 294 K.

However, in the second contact stage, the REE loading of CHEL resin (> 0.2 equiv./kg) is significantly higher than that of the SAC resins (< 0.15 equiv./kg). This is because of the better REE selectivity of CHEL. Since its Ca sorption capacity is low, there is more room for additional REEs. The same effect is observed for the purity of REE in the resin (Fig. 6). Starting from the first stage, the REE purities were much higher in the loaded CHEL resin than in the SAC resins and the difference increased with further cross-current contacts.

No significant difference was observed in the cross-current RIL performances for 1 g/L and 5 g/L concentrations of H_2SO_4 leaching agent with the CHEL resin. The performance (REE loading in particular) of the SAC resins improved significantly when 5 g/L acid was used (Fig. 6). This is because more acid is needed in the liquid phase to digest PG as the resin does not provide protons in the second and subsequent cross-current contact stages. This is consistent with the decrease in stage-wise leaching yields obtained with the SAC resins, as shown in Fig. 7. In contrast, for the CHEL resin, the yield remains high upon each contact and is not strongly dependent on the acid concentration. It is

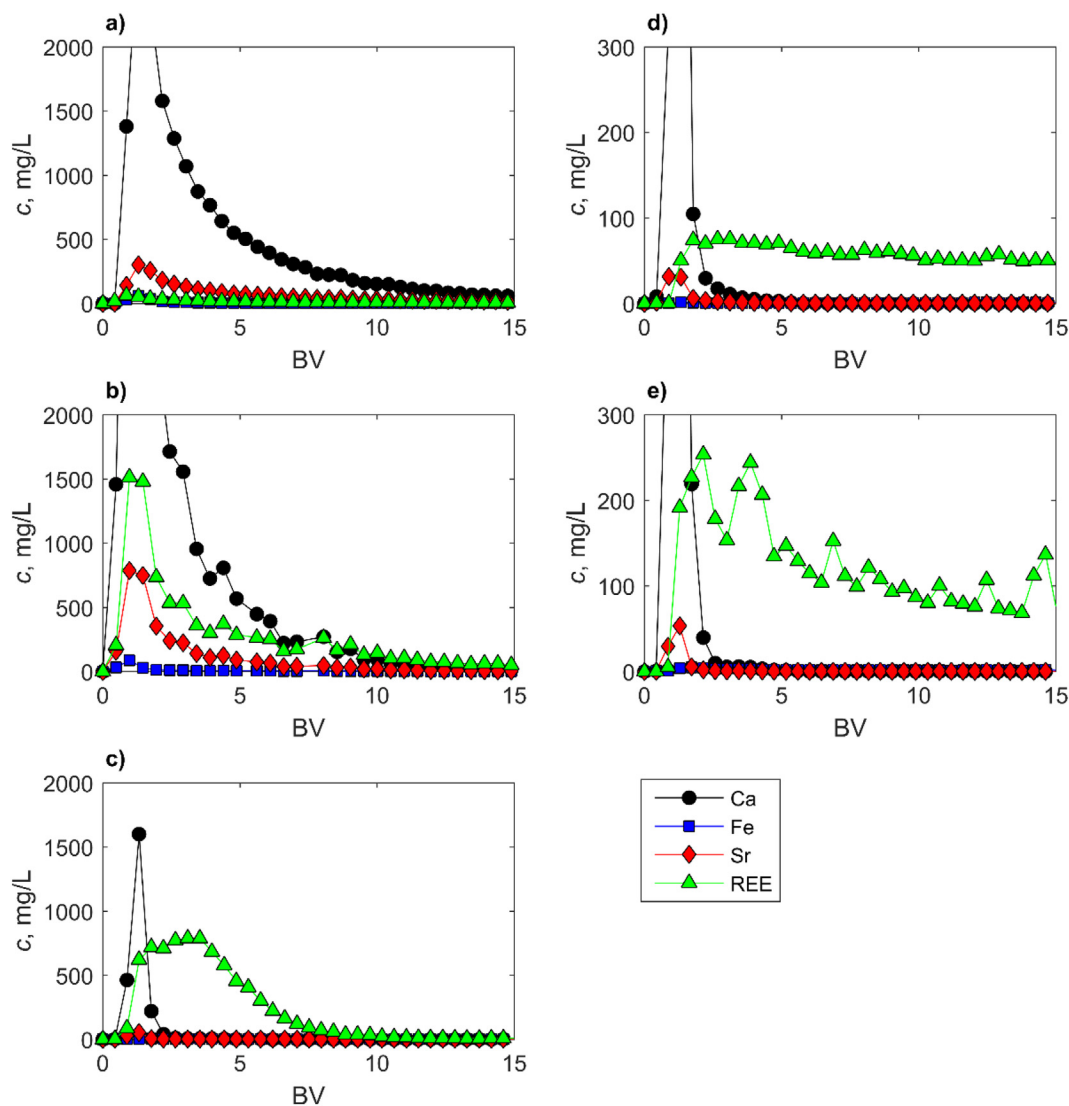


Fig. 8. Elution of metals from the RIL loaded resins. a) SAC2, 1.0 M NaCl, b) SAC2, 3.6 M, c) CHEL, 0.2 M EDTA, d) CHEL, 1.0 M HCl, and e) CHEL 4.0 M HCl. T: 294 K, flowrate: 6.45–7.32 BV/h.

Table 4

Extent of elution from RIL loaded resins with 17.3 BV of eluent. T: 294 K, flowrate: 6.45–7.32 BV/h.

Resin	Eluent	E_{REE}	E_{Ca}	E_{Fe}	E_{Sr}
SAC2	1.0 M NaCl	0.053	0.858	0.208	0.820
	3.6 M NaCl	1.000	0.823	0.316	1.000
CHEL	1.0 M HCl	0.249	0.855	0.012	1.000
	4.0 M HCl	0.599	1.000	0.048	1.000
	0.2 M EDTA	1.000	1.000	0.053	1.000

thus concluded that the CHEL resin is a better choice than the SAC resins from the point of view of acid consumption.

The yield of REEs from PG leaching varies greatly depending on the PG source. With this particular PG, the yields are very promising in the case of CHEL resin (45–75%) and good in the case of SAC resins, at least considering the 15.5–25.0% yields reported by [Yahorava et al. \(2016\)](#) by the techno-economic analysis of the RIL process.

Another promising finding of this study is the superior selectivity of the CHEL resin compared with the SAC resins. This aspect is discussed below in terms of elution of REE from the resin.

[Yahorava et al. \(2016\)](#) used the counter-current RIL mode because it is a conventional method for utilizing the separation material

efficiently. The high yield from each cross-current contact ([Fig. 7](#)) suggests that the cross-current RIL mode is a viable option when the CHEL resin is used instead of the SAC resins. This would allow a higher throughput and lower resin inventory if approximately 50–60% yield is deemed sufficient.

3.5. Elution of REEs from the resins

The purpose of the elution experiments was to maximize the REE elution efficiency and achieve higher selectivity over the Ca, Fe, and Sr metallic impurities. Toward this end, NaCl, HCl, EDTA, Na-citrate, HCl in 50% ethanol + 50% H₂O, thiourea in 1 M HCl, thiosulfate + Na₂SO₃ (2:1 M ratio), dimethyl sulfoxide, and glycine were used as eluents. Owing to the similar performances of SAC1 and SAC2, elution experiments using only SAC2 and CHEL were investigated.

It was found that NaCl and EDTA are the most efficient eluents for the SAC2 resin, while HCl and EDTA are the most efficient for the CHEL resin. Na-citrate showed effective elution and slight selectivity for REE in the case of SAC2 resin; however, precipitates were observed. The other eluents were found to be unsatisfactory and are not discussed for the sake of brevity.

The elution curves are shown in [Fig. 8](#), and the extents of elution are given in [Table 4](#). REEs efficiently eluted from SAC2 with 3.6 M NaCl but

not with 1.0 M NaCl. The elution profiles are much sharper for more concentrated NaCl, and the elution is complete in ca. 10 BV (Fig. 8a and b). As for the impurities, most of Ca and Sr were eluted from SAC2 with 1.0 M NaCl, whereas Fe could not be eluted even with 3.6 M NaCl solution (Table 4).

In the case of CHEL resin with 1.0 M HCl, Ca and Sr exhibit sharp elution peaks, while the REE elution profile is significantly tailing ($E_{\text{REE}} = 0.249$, Fig. 8d). The E_{REE} value increased to 0.599 for elution with 4.0 M HCl (Fig. 8e). The strong affinity of REE to the chelating resin causes displacement of Ca and Sr during the elution; however, the Fe profile is seen to tail similar to the REE profile. As observed in Fig. 8e, the effluent purity is high after the elution of Ca and Sr (ca. 6 BV), which demonstrates that a high selectivity can be achieved. However, the REE concentration is low because a large volume of 4.0 M HCl was required, and E_{REE} is unsatisfactory.

EDTA is a known strong chelating agent for metals, especially for Ca. Since the stability constant of CaEDTA complex is several orders of magnitude higher than that of Ca aminophosphonic complex, it was not surprising that Ca exhibited a sharp elution peak and REEs were completely eluted from the CHEL resin in approximately 10 BV. In addition, Sr was eluted to a high extent, while E_{Fe} was only 0.053 (Fig. 8c, Table 4). From the elution point of view, EDTA is the best choice as an eluent for the CHEL resin; however, the precipitation of REE from EDTA would be difficult. According to solubility calculations made with MEDUSA software (KTH Royal Institute of Technology, School of Chemical Engineering), Nd does not precipitate in 0.2 M EDTA with oxalate or carbonate, which are viable precipitation agents.

Although the elution of Fe from the SAC2 resin was better, both the resins had the same drawback of a weak Fe elution. In the case of CHEL resin, this is due to the very strong interactions between Fe and resin, which has been observed earlier (Page et al., 2017). As Fe cannot be eluted within the normal elution cycle, it would be accumulated in the resin, and needs to be removed within a certain period by some special treatment. The problem would be more challenging with the CHEL resin. Based on the eluent screening experiments, Fe could be eluted from SAC2 using a large amount of concentrated NaCl or HCl, or at least with EDTA. In addition, the uptake of Fe by the SAC resins is less significant than that by the CHEL resin (Fig. 5).

4. Conclusions

Ion-exchange resins, leaching agents, and eluents were systematically investigated for the recovery of REEs from PG by a resin-in-leach process. Based on the equilibrium batch experiments performed with and without an ion-exchange resin, it was concluded that it is not necessary to break the gypsum structure to recover REEs. Therefore, H_2SO_4 is a suitable leaching agent despite the low solubility of CaSO_4 . Similarly, the removal of Ca from the liquid phase using a strong cation exchanger is not necessary, and a more selective chelating resin can be used. High REE selectivity thus led to higher REE loadings of the resin when the same batch of resin was used in several cross-current resin-in-leach stages. With a chelating resin and 1.0 g/L H_2SO_4 , 19.2 g(REE)/kg (resin) and 14.7 g(Ca)/kg(resin) loadings were obtained in four cross-current stages, whereas with a strong cation exchanger, the loadings were 5.6 g(REE)/kg(resin) and 67.0 g(Ca)/kg(resin).

While the performance of the chelating resin was superior to that of the strong cation exchangers in the resin-in-leach step, the elution of REEs was more difficult. REEs with Ca, Sr, and a part of Fe were eluted from the strong cation exchanger with 3.60 M NaCl. A higher REE selectivity was achieved for the chelating resin using HCl and EDTA; however, the elution peak of REE tailed heavily especially with HCl, and precipitation of REEs from EDTA solution is most probably challenging.

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