

Recovery of rare earth elements from low concentration acidic streams using ion exchange resins

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Rare earth elements (REEs) are considered as strategically important and classified as critical raw materials, thanks to their application in modern technologies, such as electric vehicle batteries, magnets for wind turbines, smart phone screens, defence technologies and many more. Due to this growing demand, interest has shifted to low-grade sources that were previously considered to be uneconomical, such as waste streams. The REEs concentration in the pregnant leach solution produced from low grade materials is significantly lower than that obtained from treating concentrates. Conventional treatment routes, such as precipitation and solvent extraction, are not economical to treat low-grade material and innovative methods are required. Ion exchange resins with certain functionality can form a strong bond with the REE elements, allowing their extraction from acidic pregnant leach solutions without the need for neutralisation prior to ion exchange. In the current study, two cation exchange resins were tested, namely Puromet MTC1600H, with sulfonic acid functional groups, and the chelating resin Puromet TS9570, with sulfonic/phosphonic acid functional groups; these resins were evaluated for their efficiency of REE extraction from low and high acid streams generated during the leaching of phosphogypsum. The loading and elution of the REE and impurities onto these resins were studied.

INTRODUCTION

Rare earth elements (REEs) find application in various areas including magnets, catalysts, polishing powders, batteries, and others. This commodity is a backbone for the developments made in the last few decades. The REE market is experiencing sustained growth, driven primarily by the escalating production of electric vehicles, the growing clean energy sector, and the expanding construction industry. Although abundant in the earth's crust, mineable concentrations of REEs are less common, rendering the global supply chain particularly fragile. As reported by Leon and Daphne, China accounts for 63% of the world's rare earth mining (Leon and Daphne, 2023). As the demand for REE increases, industry pays attention to unconventional resources such as waste streams, low grade feed material, mine tailings and recycling as alternative sources for these elements (Figure 1).

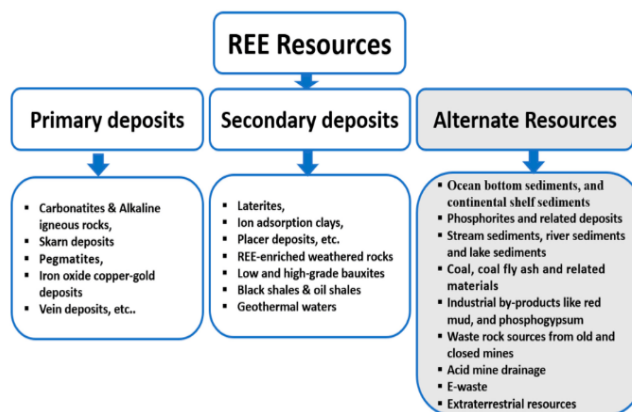


Figure 1. Different types of REE resources (Balaram, 2023).

Intensive research is currently ongoing worldwide for the development of more efficient and greener ways of extracting REE from these alternative resources. The main challenge for REE recovery from these sources is related to the low amount of REEs present in those sources, requiring the implementation of new techniques and materials related to pre-concentration steps, in which selectivity toward REEs is highly desirable (Sulfate and Sanchez, 2022).

Solvent extraction and direct precipitation are commonly applied for treatment of high concentrations of REE; ion exchange can be efficiently applied for the processing of low concentration feed solutions (Kentish and Stevens, 2001). The use of ion exchange resins for the bulk adsorption and concentration of REE has been previously investigated (Page *et al.*, 2017; El Ouardi *et al.*, 2023; Felipe, 2020; Virolaenen *et al.*, 2019). A number of ion exchange resins with different functionality show promising performance for REE recovery. Strong acid cation exchangers with sulfonic acid groups and chelating resins that contain phosphonic acid or iminodiacetic acid functional groups were used.

Page investigated the adsorption properties of chelating ion exchange resins with sulfonic, aminophosphonic (Purolite S950), mixed sulfonic/phosphonic (Purolite S957) and iminodiacetic acid (Purolite S930 Plus) functional groups with REE in the synthetic solutions prepared by dissolution of REE oxides and Al, Fe and Th salts in HCl or H₂SO₄. It was reported that the resins with sulfonic and phosphonic acid groups have high affinity for the REE and are able to efficiently extract these metals from acidic solutions even at high acid concentrations (< 0.5 M H⁺), while in the case of iminodiacetic acid resin, the weak acidic nature of the acetate functional groups results in the effective adsorption of REE only at pH>3 (Page *et al.*, 2017). Sulfonic resin displayed higher affinity for the REE and Th over the Al and Fe ions; all chelating resins adsorbed Fe and Th in preference to the REE and Al. Another advantage of the resin with sulfonic groups was higher maximal adsorption capacity (64 g/L, measured at pH 1.5); chelating resins showed much lower adsorption capacities (52 g/L, 49 g/L and 39 g/L for the resins with sulfonic/phosphonic, iminodiacetic (at pH 4) and aminophosphonic groups, respectively). Elution of the loaded resins was investigated. Iminodioacetic resin was easily eluted with diluted HCl, while sulfonic resin required 4 M HCl or M NaCl, 2 M CaCl₂ to be eluted. Elution of the chelating resin with sulfonic/phosphonic groups was the least efficient.

Filipe studied the recovery of REE from acid mine water enriched with La, Ce, Nd, Gd, Dy, and Y (to the concentration of each element of 0.35 mmol/L) by using cationic exchange resins with sulfonic groups Lewatit MDS 200 H, Dowex 50WX8 and Purolite C160). The resins tested had different total exchange capacity, ionic form and particles size. All adsorbents successfully loaded REE at pH between 1.4 and 3.4. The order of selectivity was light REE > heavy REE. The highest loading capacities were 0.212 mmol/g for La and 0.169 mmol/g for Ce for Dowex 50WX8 resin (Felipe, 2020).

Virolaenen tested strong acid cation exchangers with sulfonic groups resin (Purolite C150 and Finex CS16GC) and aminophosphonic resin (Purolite S940) for REE recovery from phosphogypsum (PG) pulp. When sulfuric acid was used as the leaching agent, all three resins showed similar behaviour and

the acid concentration affected the resin loading only slightly in the range of acid concentration between 1 and 10 g/L. The most significant impurities traced in this work were Ca, Fe, and Sr. It was found that the Ca and Sr uptake was higher for the sulfonic. On the other hand, the Fe uptake on the phosphonic resin was higher. Loadings obtained in four cross-current stages at 1.0 g/L H₂SO₄ were 19.2 g(REE)/kg(resin) and 14.7 g(Ca)/kg(resin) for the phosphonic resin and 5.6 g(REE)/kg(resin) and 67.0 g(Ca)/kg(resin) for the sulfonic resin (Virolaenen *et al.*, 2019). While adsorption property of the chelating resin was superior to that of the strong cation exchangers, the elution of REE was more difficult. 3.60 M NaCl was an efficient eluent for the strong cation exchangers, while for REE stripping from the chelating resin large volume of 4 M HCl or 0.2 M EDTA was required.

The aim of this paper is to recover REE from a pregnant leach solutions (PLS) produced from PG leaching with sulphuric acid. REE content of PG is low in comparison to the typical REE ores; it is an attractive REE source because of the large production volumes (Virolaenen *et al.*, 2019). The most common option for REE extraction from PG is sulfuric acid leach. Reasonable REE yields have been obtained with 0.5–1.0% H₂SO₄. But increasing the sulfuric acid concentration to over 20% resulted in dissolution of 73–84% REE (Virolaenen *et al.*, 2019). However, the use of strong acid comes with economic drawback. In order to upgrade REE and recover and recycle acid, adsorption of the REE from PLS using IX technology was tested. Two solutions, with low and high acid concentration were used for testwork. Two resins types with were selected for evaluation based on literature review, strong acid cation exchanger and chelating resin with sulphonic/phosphonic functionality. Both resins were expected to load REE from acidic solution and can be eluted with a concentrated chloride-containing eluent. The loading of REE and impurities and elution was tested and compared.

EXPERIMENTAL

The resins used for this study were supplied by Purolite and are commercial products. The resin properties are summarised in Table 1.

Table I. General resin properties

Resin ID	Functional group	Resin name	Matrix	Size (mm)	Water retention	Capacity
SA	Sulfonic acid	Puromet™ MTC1600H	Macroporous PS-DVB	300–1200	43–48% (H ⁺ form)	2.3 eq/L (Na ⁺ form)
SP	Sulfonic and phosphonic acid	Puromet™ MTS9570	Macroporous PS-DVB	425–1000	55–70% (H ⁺ form)	18 g/L (Fe)

Solutions used for testwork were generated during leaching of PG. They were PLSs produced by leaching of PG with 27 g/L (low acid leach) and 150 g/L H₂SO₄ (high acid leach), respectively.

The loading experiments were carried out using glass columns of 10 mm internal diameter. The volume of the resin in each column was 20 mL. The columns were fed with PLS at a flow rate of 2 BVs/h. The samples of effluent were periodically collected for chemical analysis. After loading, the resin was washed with deionised water and eluted with an eluent comprised of 2 M CaCl₂ and 0.1 M HCl. Elution was done at a flow rate of 2 BVs/h. The fractions of eluate (1 BV each) were collected for chemical analysis.

The content of REE (Ce, La, Nd and Y) and other metals in liquid samples and on resins were determined by portable Olympus DELTA Premium-50 (DP-4050) – 50 kV XRF Analyser (in gold soil mode) using external calibrations performed with standards and actual solutions analysed inductively coupled plasma mass spectrometry (ICP-MS). REE and Th content in selected samples was analysed by ICP-MS.

RESULTS

Low Acid Solution

Testwork was conducted on the PLS generated during treatment of PG with diluted sulfuric acid (27 g/L). The solution's composition is shown in Table II. It contained 425.04 mg/L REE, majority of which were light REE (LREE (La-Nd)) with a small amount of middle (MREE (Sm-Gd)), and heavy REE (HREE (Dy-Y)). The solution had 225.6 mg/L Ca and 49.2 mg/L Sr, low level of Fe and Zr as well as traces of radioactive elements, U and Th.

Table II. Low acid PLS, mg/L

Ca	Fe	Sr	Zr	Th	U	La	Ce	Pr	Nd	Sm
225.6	6.5	49.2	5.1	2.4	0.56	81.00	183.00	19.40	88.30	16.20
Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	TREE
2.96	12.40	1.31	3.94	0.43	0.85	<0.1	0.39	<0.1	14.85	425.04

This solution was passed through the columns containing the resins with strong acid sulfonic and sulfonic/phosphonic groups. The results are illustrated in Figure 2 and Figure 3.

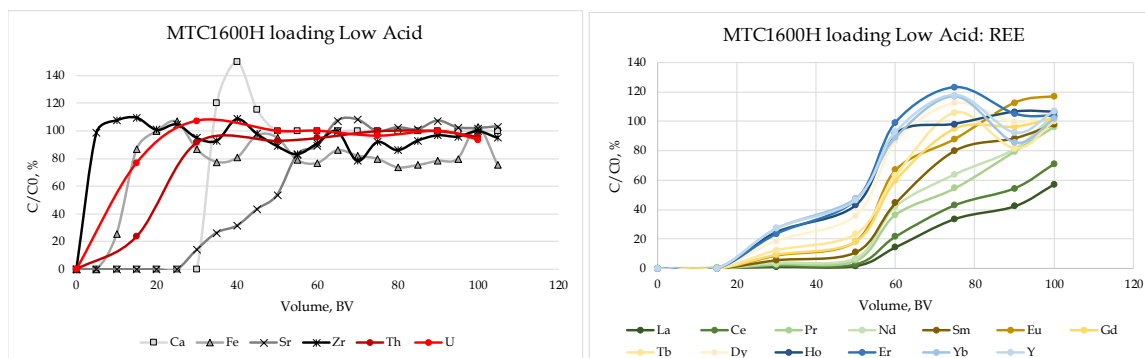


Figure 2. MTC1600H breakthrough: low acid leach.

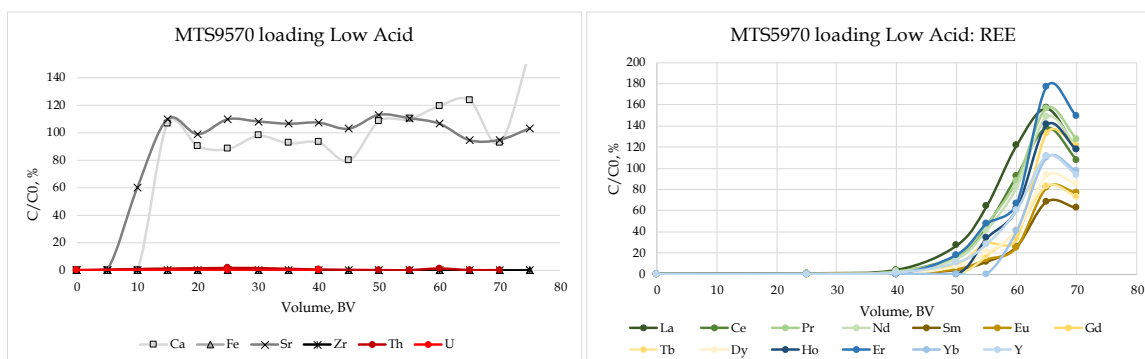


Figure 3. MTS 9570 breakthrough: low acid leach.

The rare earths were breaking through the strong acid resin MTC1600H at different volumes. HREEs broke through first at about 30 BVs, followed by MREEs and then LREEs breaking through at 75 BVs. HREEs were displaced by LREEs. Higher resin selectivity towards LREEs compared to MREEs and HREEs can be due to the smaller radius of hydration shell of the LREEs what makes it easier to access the active sites on the resin.

In the case of chelating resin MTS9570, REE started to break simultaneously at about 50 BVs of the solution passed through. Higher selectivity to MREEs and HREEs and steeper breakthrough curves

were observed for the resin with sulfonic/phosphonic mixed functionality. Overall performance of the chelating resin was poorer with lower REE loading.

Both resins co-loaded some impurities. MTC1600H showed higher Ca and Sr loading as they started to break through at 30 BVs, while in the case of MTS9570 Ca and Sr breakthrough was shorter, at 10 BVs. Advantage of MTC1600H was low co-loading of Fe (breaking through at 10 BVs) and Zr (breaking immediately). MTS9570 extracted all Fe and Zr from the solution. Moreover, MTC1600H showed low affinity to Th and U, while MTS9570 seems to be more selective for Th and U than REE.

Affinity of MTC1600H for different metals was
 LREE > MREE > HREE > Sr > Ca > Th, U, Fe > Zr
 Affinity of MTS957 for different metals was
 Th, U, Fe, Zr > MREE > HREE > LREE > Sr > Ca

The trends observed are in line with data published (El Ouardi *et al.*; Virolaenen *et al.*, 2019). Composition of the loaded resin (calculated based on eluates and eluted resin XRF analysis) is shown in Figure 4. MTC1600H had 25.26 g/L TREE and 9.82 g/L of Ca, Fe, Sr together while MTS9570 only loaded 14.45 g/L TREE and 7.75 g/L of impurities. Overall, strong acid MTC1600H resin had better performance, providing higher REE capacity and selectivity.

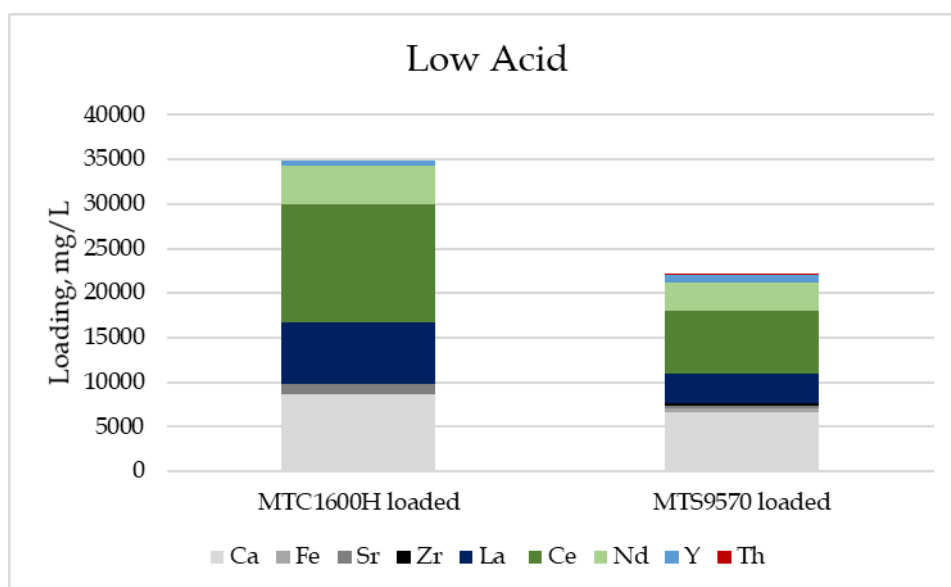


Figure 4. Loaded resins: low acid leach.

Loaded resins were stripped with acidic CaCl₂ eluent. Selection of eluent was based on the possibility of precipitation of REE with Ca(OH)₂ or oxalic acid from the eluate with the following eluate recycling; eluted resin will be in Ca form potentially acceptable for REE loading; no foreign cations (Na, K, NH₄) introduced which could cause REE double sulphate precipitation.

The first portions of eluates from both loaded resins had white precipitate. XRF scan indicated presence of high Ca and S with traces of Sr, Fe and REE, most probably gypsum.

Elution results are shown in Figure 5 and Figure 6.

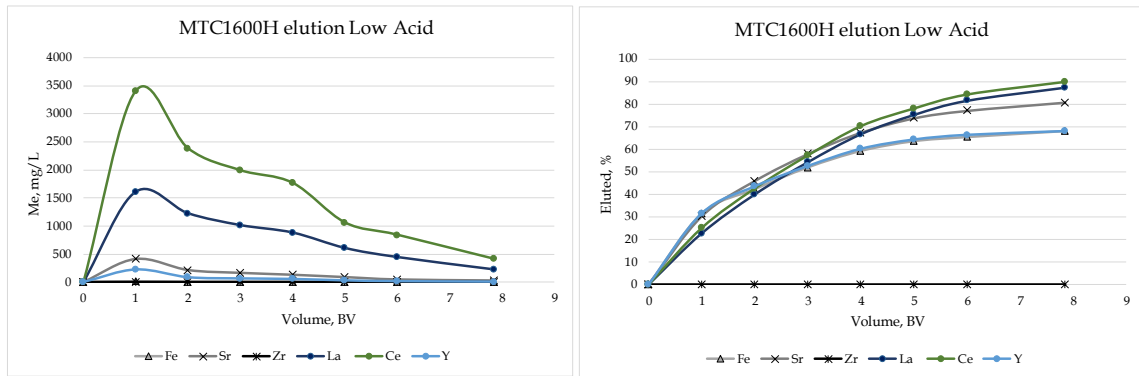


Figure 5. MTC 1600H (loaded with low acid PLS) elution.

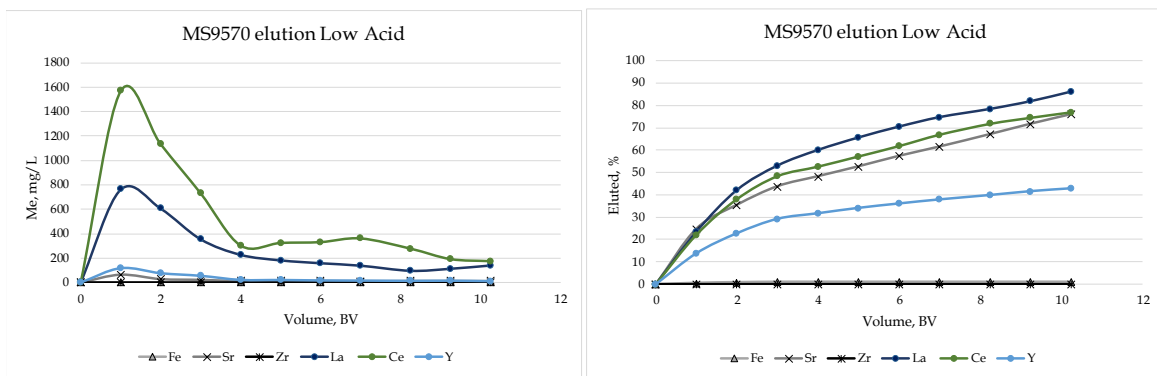


Figure 6. MTS 9570 (loaded with high acid PLS) elution.

Both resins reported high needs of acidic CaCl_2 for elution of REE and selected impurities (8–10 BV) with long tails on elution profiles. But elution peaks were higher (double) in the case of MTC1600H allowing achievement of a higher REE upgrade. It should be mentioned that in the case of MTS9570 with sulfonic and phosphonic functional groups two elution peaks were observed. The presence of these two peaks could be associated to the presence of the two different functional groups in the resins. Elution results obtained in this study are in agreement with data published by Page and Virolaene (Page *et al.*, 2017; Virolaenen *et al.*, 2019).

Eluted resins were scanned and results are shown in Figure 7, elution efficiency is presented in Table III. MTC1600H had only a small amount of REE left and high Ca (converted into Ca-form). MTS9570 had higher residual REE and non-stripped Fe, Zr, Th as well as loaded Ca.

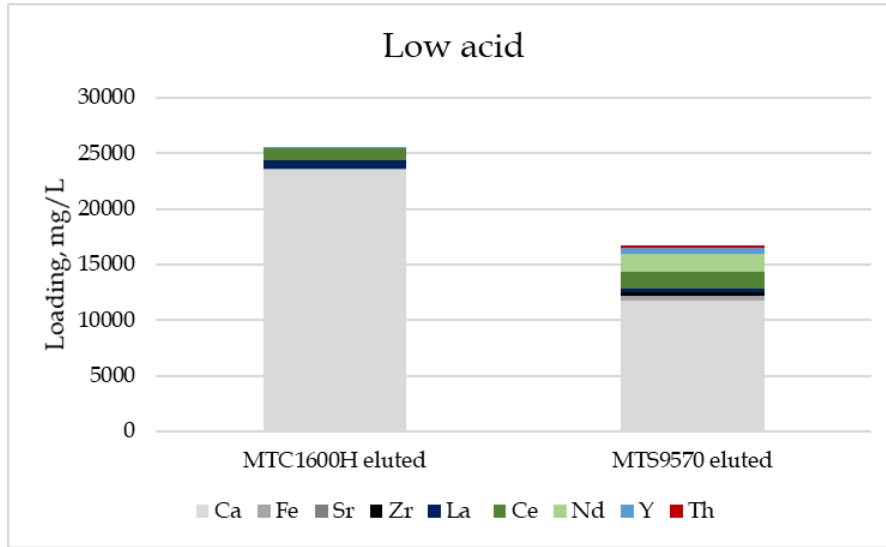


Figure 7. Eluted resins (loaded with low acid PLS).

Table III. Elution efficiency (low acid PLS), %

	Fe	Sr	Zr	La	Ce	Nd	Y
MTC1600H	88	97	n/a	85	89	100	98
MTS9570	2	98	0	85	74	38	53

High Acid Solution

PLS generated during the leach with high acid concentration was also tested for REE removal test work. The solution's composition is shown in Table IV. Acid concentration was 150 g/L. Concentration of REE and impurities was higher in high acid solution compare to the low acid PLS as higher acid concentration was applied for the leaching.

Table IV. High acid PLS, mg/L

Ca	Fe	Sr	Zr	Th	U	La	Ce	Pr	Nd	Sm
220.80	13.50	48.72	24.90	18.97	0.836	102.00	255.00	31.00	137.00	25.60
Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	TREE
5.71	23.20	2.31	6.13	0.71	1.91	<0.1	0.70	<0.1	21.00	612.26

Figure 8 and Figure 9 show results of the column loading tests.

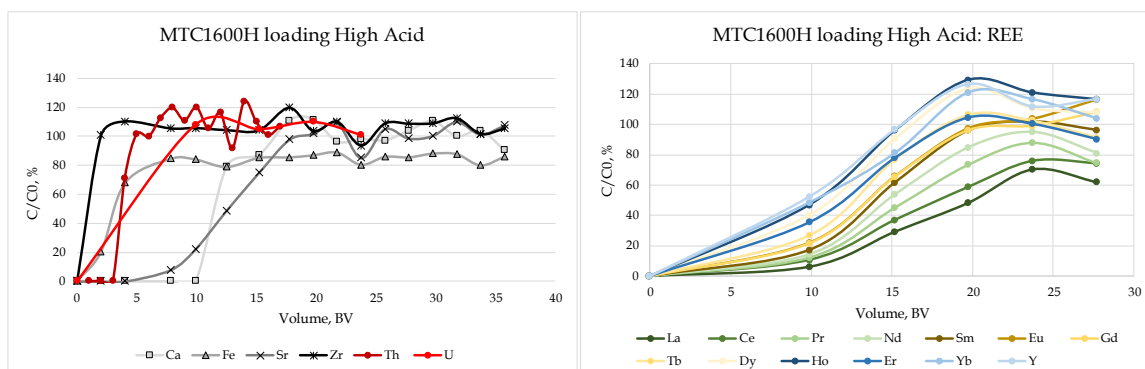


Figure 8. MTC1600H breakthrough: high acid leach.

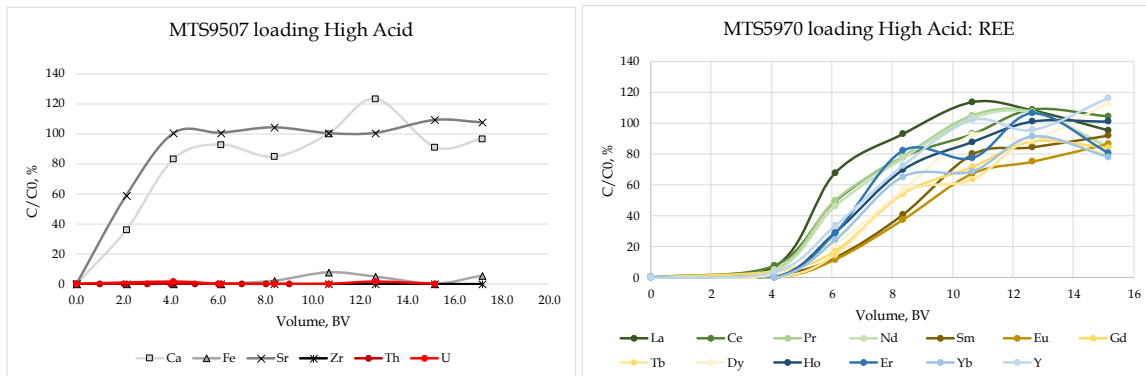


Figure 9. MTS9570 breakthrough: high acid leach.

The following was observed:

- Even at high acidity, the resins adsorbed REE and some of the impurities;
- Resins affinity to REE and impurities was the same as reported for the test with low acid PLS;
- Breakthroughs were obtained at lower volume of solution passed through the resins bed when acidity was high.

The loaded resins had composition shown in Figure 8. MTC1600H had 17.46 g/L TREE and 3.99 g/L of Ca, Fe, Sr, Th together while MTS9570 loaded 3.46 g/L TREE and 1.21 g/L of impurities.

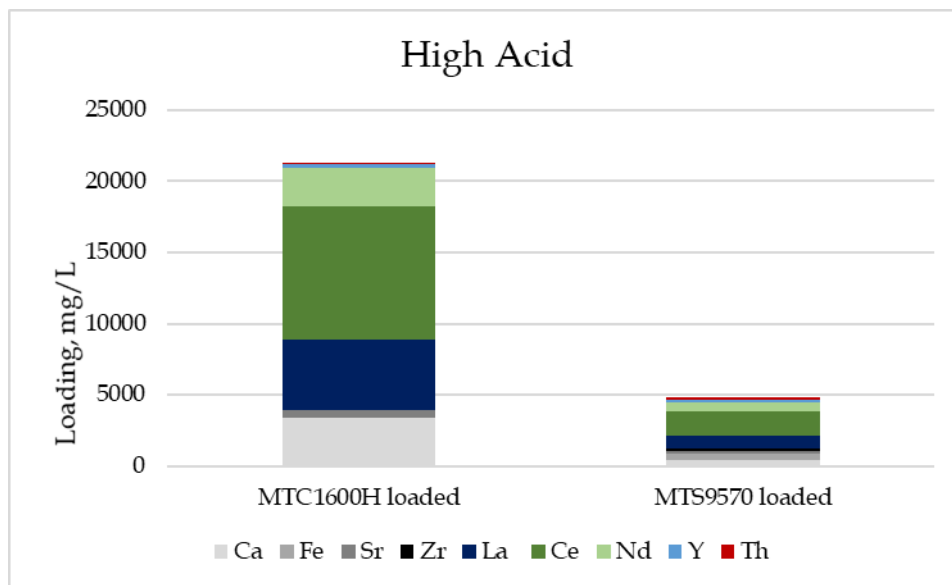


Figure 10. Loaded resins: high acid leach.

Loaded resins were stripped with acidic CaCl_2 eluent. Again, formation of precipitate (gypsum) was observed in the first portions of the eluate collected. Elution curves are shown in Figure 10 and Figure 11.

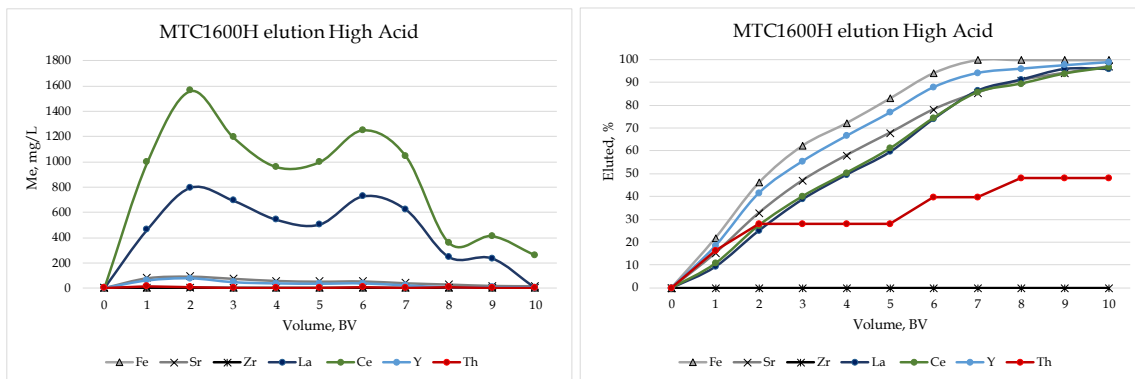


Figure 10. MTC1600H (loaded with high acid PLS) elution.

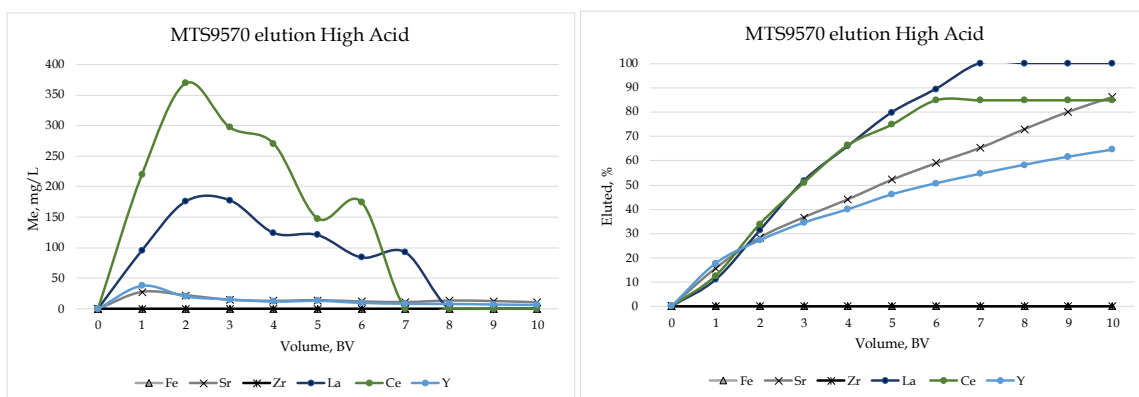


Figure 11. MTS9570 (loaded with high acid PLS) elution.

Relatively low broad elution peaks were reported for both resins tested. Eluted resins were scanned and results are shown in Figure 12, elution efficiency is presented in Table V. MTC1600H had only a small amount of REE left and high Ca (converted into Ca-form). S957 had low residual REE and non-stripped Fe, Zr, Th as well as loaded Ca.

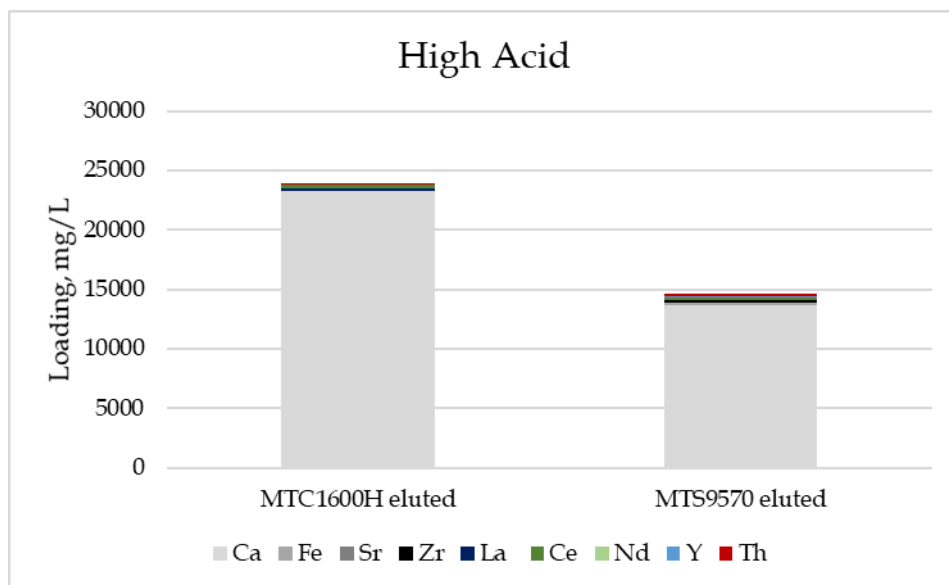


Figure 12. Eluted resins (loaded with high acid PLS).

Table V. Elution efficiency (high acid PLS), %

	Fe	Sr	Zr	La	Ce	Nd	Y	Th
MTC1600H	100	97	n/a	96	97	100	99	48
MTS9570	0	98	0	100	86	100	71	0

CONCLUSION

Two ion exchange resins, strong acid cation exchanger MTC1600H and sulfonic/phosphonic chelating resin MTS9570 were tested for REE recovery from acidic solutions obtained during PG leaching at various acid concentrations.

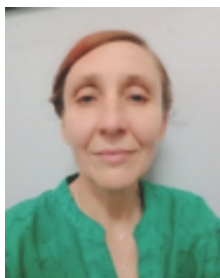
There were only two specific acid concentrations tested in this study. Both resins showed affinity to REE even at high acid concentration which allows them to be used for REE adsorption from PLS with acid recovery and reuse. Higher acid concentration negatively affected loading capacity. A broader range of conditions would further be evaluated.

The choice of resin for the REE removal would be determined by the uptake capacities and selectivity. MTC1600H showed superior REE loading capacity and selectivity over other metals presented in solution such as Ca, Sr, Zr and Th.

It was shown that both resins could be eluted with acidic CaCl₂ eluent. However, MTS9570 had Th, Fe and Zr non-stripped.

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