# Ion Exchange to Recover Rare Earth Elements from Acid Mine Drainage

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## Abstract

Current research addresses the study of the recovery of rare earth elements from AMD using a cationic exchange resin. The AMD has a total REE concentration of 0.35 and total impurities of 7.4 mmol $L^{-1}$ at pH 3.5. The elution was performed using 0.02 mol $L^{-1}$ $NH_4EDTA$ at pH 8.5 in systems with a loaded column and a fraction column connected in series. Elution was demonstrated to be selective for REE over impurities and to separate heavy REE from light REE. Oxalic acid precipitation proved to be highly efficient for the selective recovery of REE over Al.

**Keywords:** Cation resin, loading, elution, $NH_4EDTA$, oxalic acid.

## Introduction

Since 2011, rare earth elements (REE) have been included in the European Commission's list of critical raw materials. These materials are essential for advancing strategic sectors such as renewable energy, electric mobility, defense, and digital technologies (Bobba *et al.* 2020). In long-term decarbonization scenarios, REE are indispensable for enabling a clean energy economy. However, the global supply chain for these elements is highly vulnerable to disruptions caused by economic fluctuations and geopolitical challenges. The concentration of REE in AMD makes it a promising alternative source for REE recovery (Moraes *et al.* 2020; Middleton *et al.* 2024).

Numerous studies have investigated the separation of REE using ion exchange, demonstrating that this method is highly effective for achieving such separations. The process can be broadly described as follows: initially, the REE is adsorbed onto the resin-packed column bed. Subsequently, an eluting solution is introduced into the column, promoting individual or grouped REE desorption. Finally, the eluted REE are collected, in fractions, from the column. Various types of resins are employed during the loading and fractionation stages. Recent research on REE recovery from AMD has highlighted the effectiveness of strong acidic resins, particularly the Lewatit MDS 200H resin, owing to its remarkable loading capacity and excellent selectivity for REE compared to other metallic impurities such as aluminum, calcium, and magnesium frequently found in AMD (Felipe *et al.* 2020; José *et al.* 2024; Silva *et al.* 2024).

The eluting solution is critical in promoting the desorption of ions bound to the resin and their fractionation. Therefore, the choice of a suitable eluent is of paramount importance. Stability constants of REE complexes with specific eluents provide valuable insights into the separation efficiency and aid in identifying the most effective eluent. For instance, EDTA and DCTA, due to their high stability constants, notably enhance the separation of REE (Dezhi 2018). This study explores the recovery of REE from an AMD through the ion-exchange process, emphasizing the elution and fractionation steps using a suitable eluent to achieve selective separation of the elements, followed by precipitation of REE oxides.

## Methods

**Materials:** The AMD sample was provided by Indústrias Nucleares Brasileiras (INB) and was collected from a decommissioned uranium mine located in Caldas Municipality, Minas Gerais State, Brazil. Table 1 provides an overview of the REE concentrations (mmol $L^{-1}$) and the main metallic impurities present in the AMD. The sulfate concentration is approximately 14 mmol $L^{-1}$ (1.3 g $L^{-1}$) and pH 3.5. A detailed chemical characterization of the AMD can be found in the work by José *et al.* (2024). The resin used was Lewatit MDS 200 H, a strongly acidic cation exchange resin with sulfonic acid functional groups ($-SO_3H$), supplied by Lanxess Company.

**Loading experiments:** The loading experiments were conducted in glass columns with an inner diameter of 11 mm, wet-packed with resin Lewatit MDS 200H to a bed volume (BV) of 8 mL (6.25 g dry basis). AMD solution containing 0.35 mmol $L^{-1}$ of total REE and 7.4 mmol $L^{-1}$ of total impurities was pumped through the resin at a flow rate of 0.78 ± 0.01 mL $min^{-1}$ (residence time of 10.2 min). Samples were collected periodically by an automatic fraction collector and analyzed for chemical composition using inductively coupled plasma optical emission spectrometry ICP-OES (SPECTRO model ARCOS®).

**Elution experiments:** Elution was conducted with the loading and fractionation columns connected in series, wet-packed with the resin at BV of 8 mL and 15.5 mL, respectively. The fractionation column was pre-activated with 10% $NH_4OH$. The elution was carried out with 0.02 mol $L^{-1}$ $NH_4EDTA$ at pH 8.5, 25 ± 5 °C, a flow rate of 0.38 ± 0.02 mL $min^{-1}$, and a residence time of 21 min. Samples were collected from the effluent of the fractionation column every 45 min.

**Precipitation of oxalates:** The experiments were based on Nawab *et al.* (2022), which utilized 1.91 mol of oxalic acid per mole of total metals (REE + impurities) at a fixed pH of 2.5, adjusted with 10% $NH_4OH$. The composition of the precipitates was determined based on ICP-OES analysis (SPECTRO model ARCOS®).

***Table 1** Composition, Loading (Q) and percentage of removal of REE and Impurities from the AMD, and economic data.*

| Loading Data | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Rare Earth Elements | | | | | | | | Impurities | | |
| Elements | La | Ce | Pr | Nd | Sm | Gd | Dy | Y | $REE_{Total}$ | Ca | Al | Mg |
| AMD Molality (mmol $L^{-1}$) | 0.22 | 0.01 | 0.02 | 0.05 | 0.007 | 0.003 | 0.003 | 0.04 | 0.35 | 2.8 | 4.3 | 0.31 |
| Molar (g $mol^{-1}$) | 139 | 140 | 141 | 144 | 150 | 157 | 163 | 89 | 140 | 24 | 27 | 24 |
| AMD Composition (mg $L^{-1}$) | 30.8 | 1.4 | 2.8 | 7.2 | 1.1 | 0.5 | 0.5 | 3.6 | 47.8 | 67.2 | 116.1 | 7.44 |
| AMD Composition (%) | 2.8 | 0.1 | 0.3 | 0.6 | 0.1 | 0.04 | 0.04 | 0.5 | 4.5 | 36.1 | 55.4 | 4.0 |
| Q (mmol $g^{-1}$) | 0.174 | 0.005 | 0.012 | 0.032 | 0.004 | 0.001 | 0.001 | 0.022 | 0.25 | 0.79 | 1.71 | 0.15 |
| Q (mg $g^{-1}$) | 24.17 | 0.70 | 1.69 | 4.62 | 0.60 | 0.16 | 0.16 | 1.96 | 35.10 | 31.66 | 46.14 | 3.65 |
| Recovery (%) | 81 | 71 | 71 | 81 | 70 | 58 | 58 | 65 | 71.2 | 33.0 | 58.0 | 48.0 |
| Economic Data | | | | | | | | | | | | |
| Price for metal [1] (USD/Kg) | \$5.30 | \$5.50 | \$105.00 | \$64.50 | \$13.75 | \$25.50 | \$380.00 | \$15.00 | \$4.50 | NC | \$1.91 | \$2.26 |
| Gross Values of REE in ADM (USD/1000 L) | \$0.16 | \$0.01 | \$0.30 | \$0.47 | \$0.01 | \$0.01 | \$0.19 | \$0.05 | \$1.20 | NC | \$0.22 | \$0.02 |
| Net Values of REE in ADM (USD/1000 L) | \$0.13 | \$0.01 | \$0.21 | \$0.38 | \$0.01 | \$0.01 | \$0.11 | \$0.03 | \$0.88 | NC | \$0.13 | \$0.01 |
| Net Values of REE in ADM (USD/1000 gal[2]) | \$0.60 | \$0.02 | \$0.96 | \$1.71 | \$0.05 | \$0.03 | \$0.49 | \$0.16 | \$4.01 | NC | \$0.58 | \$0.04 |

(1) Prices: https://en.institut-seltene-erden.de/aktuelle-preise-von-seltenen-erden/; (2) gal (4.546L); NC - not calculated; LREE (La, Ce, Pr, Nd, Sm); HREE (Gd, Dy, Y).

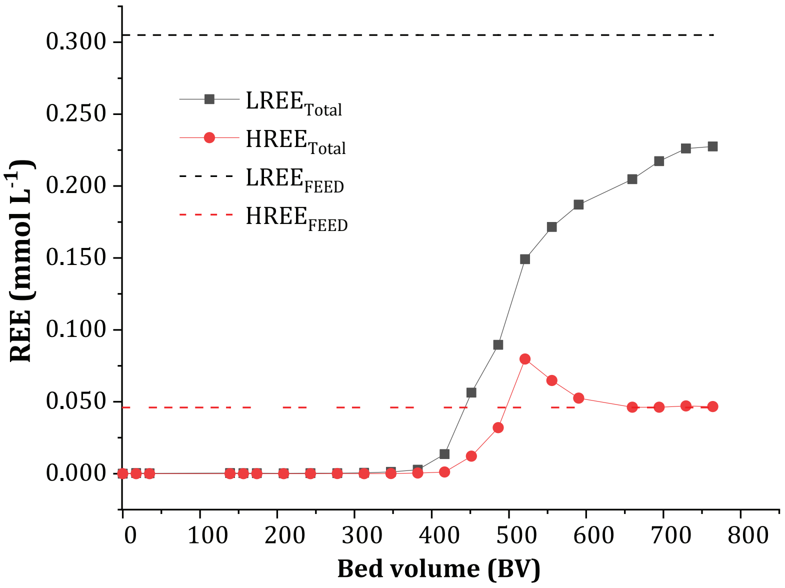

*Figure 1*

## Results and discussion

### *Loading of REE and impurities*

The loading (Q) for total REE after the percolation of approximately 800 BV of AMD was 0.25 mmol·g$^{-1}$, corresponding to 0.23 mmol·g$^{-1}$ of light REE (LREE) and 0.02 mmol g$^{-1}$ of heavy REE (HREE) (Tab. 1). These results indicate a high affinity of the resin for light REE over heavy REE, consistent with previous studies utilizing this resin for REE recovery from the same effluent (Felipe *et al.* 2020; José and Ladeira 2021; José *et al.* 2024). Regarding impurities, the loading amount was 2.7 mmol g$^{-1}$.

The loading profiles for REE were plotted based on the sum of the outlet concentrations of La, Ce, Pr, Nd, and Sm for LREE, and Gd, Dy, and Y for HREE. As previously reported, the loadings profile for LREE and HREE confirm the resin's selectivity for LREE (Fig. 1).

### *Valuation of AMD REE components*

AMD has an estimated gross REE metal value per 1000 L of approximately US$1.20, with a recoverable metal value of around US$0.88. The extractable REE value as metals per 1000 gallons of AMD is $4.01. This value falls within the mid-range of AMD treatment costs in the U.S., which vary from US$1 to US$10 per 1000 gallons (Kefeni *et al.* 2017). These values suggest that REE present in AMD could represent a potentially viable economic resource.

### *Elution and fractionation of REE and impurities*

The fractionation profiles of REE and impurities using 0.02 mol L$^{-1}$ $NH_4EDTA$ at pH 8.5 were determined (Fig. 2). It is evident that selective elution favors HREE over LREE, followed by a minor elution of aluminum. This suggests that $NH_4EDTA$ exhibits an elution selectivity order of HREE > LREE. Several studies in the literature attribute this behaviour to the preferential formation of HREE-EDTA complexes compared to those formed with LREE (La, Ce, Pr, Nd, Sm) and impurities (Al, Ca, Mg) (José *et al.* 2024; Moore 1995).

Nd, Pr, Sm, and Ce elution occurs mainly between 10 and 20 BV, while La elutes up to 30 BV, with its maximum concentration peak at 20 BV. Calcium is eluted after all REE, in the 29 to 41 BV range. The fractions of eluate were analysed for REEs and impurities, and their composition was established (Fig 3).

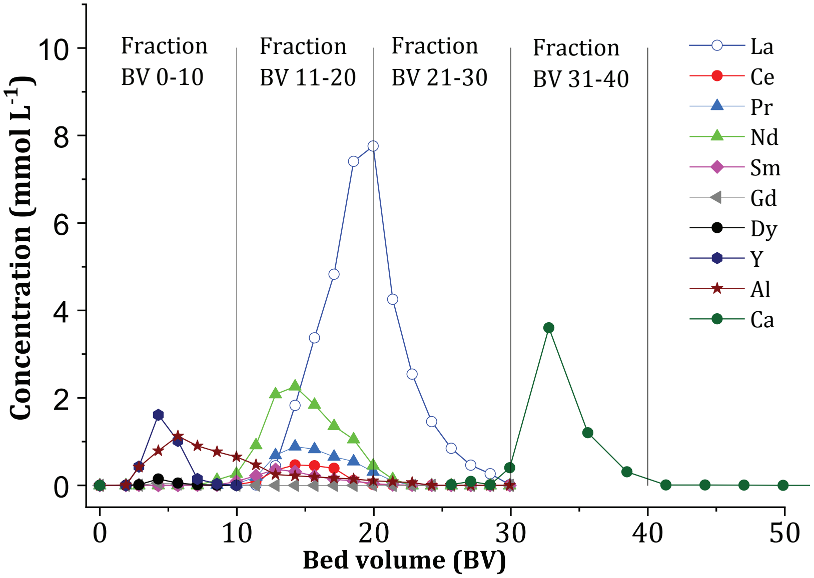

*Figure 2*

The composition of fraction 0–10 BV consists of 43% HREE, 4.6% LREE, and 52.4% Al (Fig. 3A). Similar to the loading column, the fractionation column activated with $NH_4^+$ also exhibits a preference for LREE retention over HREE retention. The fraction 11–21 BV comprises 95.5% LREE and 4.5% Al (Fig. 3B). Regarding the LRRE, La is the major component with approximately 53.5%, followed by Nd, Pr, and Sm. The fraction 21–30 BV (Fig. 3C), which concludes the elution of REE, is composed of 91.9% of La, 4.6% of (La, Ce, Nd, Pr), and 3.5% of impurities (Ca, Al). The direct comparison between the composition of the AMD and the composition of each fraction revealed that, in addition to the recovery of REE, there was separation and enrichment of heavy and light REE in distinct fractions. The composition of the last fraction, i.e., 31–40 BV, indicates an almost complete separation of Ca (Fig. 3D) from the other REE.

Each fraction of the eluate was used to produce REE oxalates through the addition of oxalic acid to one specific fraction, resulting in the formation of REE precipitates (eq. 1).

$2REE^{3+} + 3H_2C_2O_4 + 10H_2O \rightarrow REE_2(C_2O_4)_3 \cdot 10H_2O\downarrow + 6H^+$ (1)

The precipitation was carried out at pH 2.5 adjusted with $NH_4OH$. According to Nawab *et al.* (2022), at a pH of 2.5, REE precipitation reached 98.4%. Table 2 presents the composition of the solids obtained after precipitation. The precipitation process was more efficient for REE compared to impurities, particularly aluminum, which forms a stable soluble complex with oxalic acid ($Al(C_2O_4)_3^{3-}$ $Al(C_2O_4)_2^-$; $Al(C_2O_4)^+$).

The oxalate obtained from the fraction BV 11–20 was selected and then calcined at 900 °C. Fig. 4 presents the REE oxide obtained after calcination and its composition.

## Conclusions

The findings of this work established a chemical route to selective recovery of REE from AMD. This route involves adsorption using ion exchange resin, oxalate precipitation, and calcination to produce REE oxides. The results of REE and impurity loading demonstrated higher recovery efficiency for REEs. Elution experiments using 0.02 mol L$^{-1}$ $NH_4EDTA$ in a column system connected in series showed selective elution of REEs over impurities. Regarding fractionation, it was

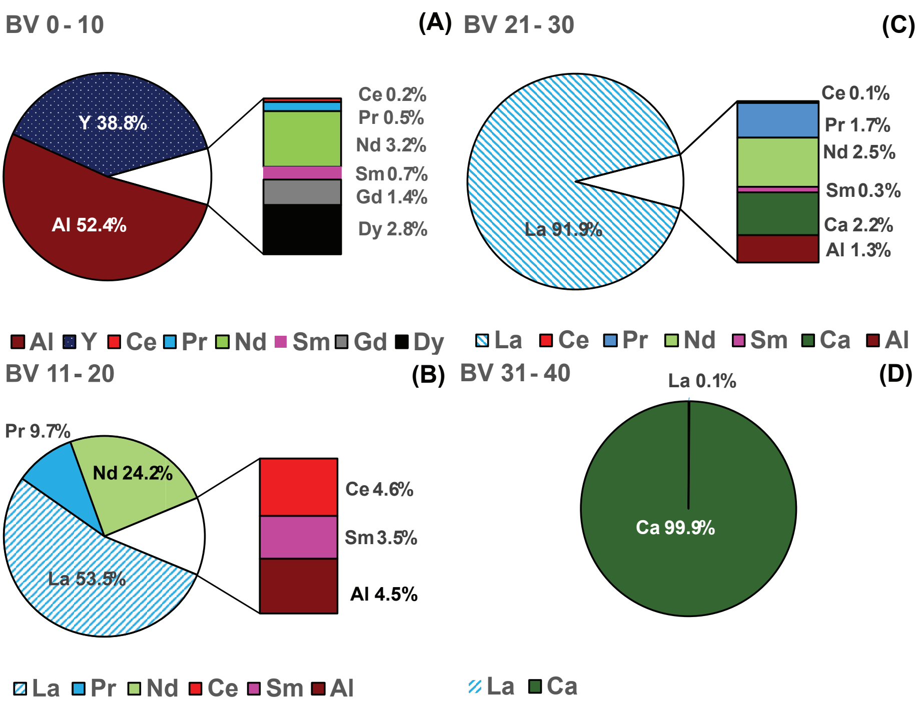

*Figure 3*

possible to obtain different eluate fractions, yielding distinct REE compositions in each collected fraction. Precipitation in oxalates was more effective and selective for REE, with aluminum accounting for only 5% of impurities in the REE oxalate. The precipitation of the eluate with oxalate acid increased the REE content from 47.6%, i.e., fraction 0 to 10 BV, to 99%. Results of the solids after calcination confirmed the efficiency of REE fractionation from AMD.

## Acknowledgements

The authors would like to thank CNPq, FAPEMIG, FINEP, INCTAcqua, INCT-Patria, RenovaMin Project, REGINA Project, INCT-Matéria, World Bank, Unipung and MCTESTP-Mozambique, for financial support and the reviewers for the valuable suggestions.

*Table 2 Composition of the precipitates obtained with oxalic acid for each fraction of the eluate.*

| Oxide | Composition of precipitate (%) | | |
|---|---|---|---|
| | Fraction 0–10 BV | Fraction 11–20 BV | Fraction 21–30 BV |
| $La_2O_3$ | 0.0 | 53.1 | 94.3 |
| $CeO_2$ | 0.7 | 4.9 | 0.1 |
| $Pr_6O_{11}$ | 2.1 | 10.8 | 1.8 |
| $Nd_2O_3$ | 13.4 | 27.4 | 2.6 |
| $Sm_2O_3$ | 2.9 | 3.8 | 0.3 |
| $Gd_2O_3$ | 6.0 | 0.0 | 0.0 |
| $Dy_2O_3$ | 9.2 | 0.0 | 0.0 |
| $Y_2O_3$ | 65.3 | 0.0 | 0.0 |
| total oxide REE | 99.6 | 99.9 | 99.1 |
| Impurities | 0.4 | 0.1 | 0.9 |

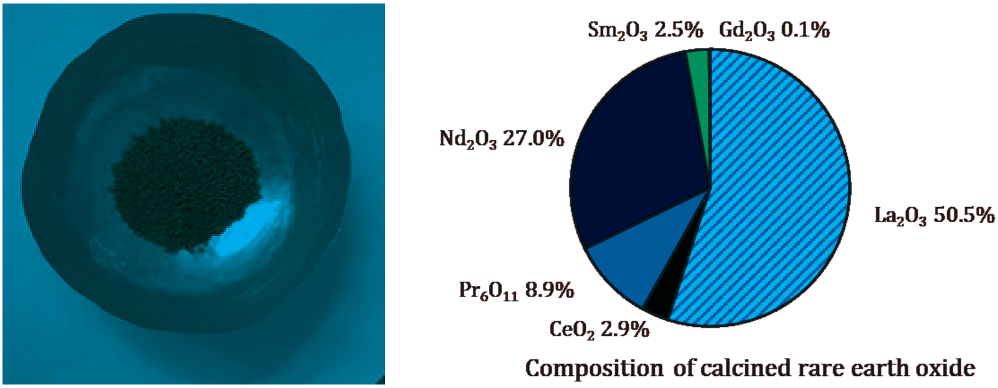

*Figure 4*

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