

Exploring the Potential for Rare Earth Element Recovery from Coal Mine Acid Mine Drainage using Ion Exchange Technology

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Abstract

Rare earth elements (REEs) are crucial in multiple industrial applications, but their limited distribution in the Earth's crust has led to worldwide supply shortages. A sustainable alternative is recycling REEs from waste streams, such as mine-impacted water. This study examined the REE concentration in coal mine acid mine drainage (AMD) and used ion exchange (IX) technology to extract them. Results showed that the collected AMD contains Ce, La, Nd, Gd, Pr, Dy and Y which amount to approximately €1 /m³ in value, and that cationic resin effectively extracts more REEs from AMD than chelating resin. Iron in AMD lowers the adsorption capacity of resins and may need to be removed before REE extraction. This study provides a proof of concept for REE extraction using IX technology, potentially allowing for reduced costs of AMD treatment, generation of profits, and promotion of a circular economy in the mining industry.

Keywords: Rare earth elements (REEs); acid mine drainage (AMD); ion exchange technology; circular economy.

Introduction

Treatment costs for mine impacted waters are amongst the highest in the industrial wastewater treatment sector, with limited sustainable options available to date (Brewster *et al.*, 2020). Interestingly, many acid mine drainage (AMD) sources contain significant amounts of lanthanides and actinides (commonly referred to as rare earth elements (REEs) (Vaziri Hassas *et al.*, 2023)) which remain a valuable resource because of their critical use in many high-tech industrial and commercial products. The recovery of REEs from AMD is an important development in AMD processing as it has the potential to offset the traditionally high treatment costs associated with remediation. Global REEs supply challenges as well as their abundance

in many AMD streams, may even allow for revenue generation from AMD sources and thus deserves consideration in the mining wastewater sphere.

There are several techniques that have been used to recover metal ions from AMD including staged chemical precipitation, solvent extraction, cloud point extraction, ion flotation, ion-exchange (IX), adsorption, molecular recognition technology, magnetic separation and membrane filtration (Mwewa *et al.*, 2022). Of these techniques, IX using resins is considered an environmentally sustainable option, as none of the toxic organic solvents employed in other types of metal recovery are used (Felipe *et al.*, 2021). Moreover, in some AMD streams REEs are found in small amounts, and IX technology is particularly efficient for treating large volumes

of acidic water containing metals in trace concentrations (Simate & Ndlovu, 2014).

IX is the formation of ion pairs on functional groups attached to a crosslinked polymer matrix. Ions in solution can exchange with ions attached to the functional groups, via electrostatic attraction. Higher charged ions and ions with a small, hydrated radius are most strongly held (Dahman *et al.*, 2017). REEs form mainly trivalent cations and therefore the chemistry of adjacent REEs are very similar and difficult to separate. As the atomic weight of the REE increases, the f-orbitals are filled, reducing the atomic (and ionic radii) of the elements (known as "Lanthanide Contraction") (Hubicki *et al.*, 1968). In water solutions, cations are hydrated which results in a stronger attraction, and a subsequent increase in hydrated ionic radius with atomic weight. Strong Acid Cation (SAC) resins will have selectivity sequence from the light to the heavy lanthanides: $>Ce^{3+}>Eu^{3+}>Lu^{3+}>Y^{3+}>Fe^{3+}$. The differences are small, and so it is difficult to separate adjacent Lanthanides. Chelating resins have interactions with the F-orbitals and so the selectivity effect is amplified and the selectivity sequence is reversed: $Fe^{3+}>Y^{3+}>Lu^{3+}>Eu^{3+}>Ce^{3+}$ (Hubicki *et al.*, 1968).

Although IX has been used for AMD treatment in the past (Chen *et al.*, 2022; Vecino *et al.*, 2021), the use of cationic resins in the enrichment of a variety of REEs has not been studied in depth. The kinetics of these systems are of importance to large scale implementation or practical applications, and thus research which delves into the mechanisms of REE extraction from AMD is much needed in the water treatment and the REE sphere.

The aim of this research was to explore this concept by studying the use of IX in REE recovery from coal mine AMD waste, and to investigate the behaviour of this extraction and recovery. The behavioural parameters which were identified as important in this study, were (i) isotherm parameters, (ii) batch kinetics, (iii) breakthrough capacities and (iv) desorption behaviour. In addition, (v) determining the concentration of REEs in an AMD dam as well as coal samples taken from the area surrounding the AMD

dam, were identified as important to discern the availability of REEs in coal, and the leachability of these REEs into surrounding water bodies. The kinetic and isotherm studies were deemed important as they will likely aid in understanding the adsorbent-adsorbate interaction and diffusion, providing insights into the mechanisms of REE extraction and recovery from AMD.

Materials and Methods

Resin was sourced from CWENGA technologies, South Africa. Lewatit® MonoPlus TP 207 (a weakly acidic, macroporous cation exchange resin with chelating iminodiacetic acid groups designed for the selective extraction of metal cations from weakly acidic to weakly basic solutions), and Lewatit® MonoPlus S 108 H (a strongly acidic, gelular cation exchange resin also with beads of uniform size and based in a styrene-divinylbenzene copolymer), were chosen due to their metal removal and water demineralization applications. Acid mine drainage from a coal mine storage dam in Emalahleni, Mpumalanga was used. Fresh AMD samples were taken from the dam and stored in a temperature-controlled room, while a coal/rock sample was obtained from the area surrounding the AMD dam and analysed directly.

The behavioural parameters of the IX system were tested in the following manners:

1. **AMD REE content:** Samples were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectroscopy (ICP-MS) at two external laboratories (University of Johannesburg and De Bruyn Spectroscopic Solutions, South Africa).
2. **Coal tailings metal content:** Coal samples were analyzed for metals content at the University of Johannesburg, using X-ray fluorescence (XRF), X-ray diffraction (XRD) and ICP-MS.
3. **Isotherm Parameters:** The two resins were tested with AMD samples (which were diluted to different concentrations and placed into 900 mL bottles containing 45 mL S108H or 64 mL of TP207). The bottles were agitated

for 3 days at 23°C, at an RPM of 200. The liquid portion in the vessels was filtered and analyzed using ICP-OES and ICP-MS. The data were fitted to four different adsorption models (isotherms). The Freundlich, Langmuir, Temkin, and Dubinin–Radushkevich isotherms were applied to fit the isothermal data.

4. **Batch Kinetics:** 900 mL AMD and 45 mL of S 108H resin, or 800 mL AMD and 64 mL of TP 207 resin, were decanted into plastic bottles. The bottles were agitated on a shaking table for 4 h at 23°C. Liquid samples were collected at different time intervals and filtered for analysis using ICP-OES and ICP-MS. Pseudo-First-order (PFO), Pseudo-Second-order (PSO), Elovich, and Intra-particle (IP) models were used to assess the kinetic data.

5. **Breakthrough capacity and desorption behaviour:**

- a. AMD was passed through the S 108H resin at a rate of 12.7 BV/h. Samples were collected after 28 bed volumes (BV) had passed through the column. Samples were assayed for Fe, Ca, Mg and REEs using ICP-OES and ICP-MS. Iron, Calcium and Magnesium were focused on as these were found in high concentrations in the AMD samples used for this study.
- b. AMD was passed through the TP 207 resin at a rate of 6.6 BV/h. Samples were collected after one bed volume. Samples were assayed for Fe, Ca, Mg and REEs using ICP-OES and ICP-MS.
- c. Loaded S 180H resin was treated with 0.01M of EDTA solution passed through at 6 BV/h. Samples were collected after 0.3 bed volumes and assayed for Fe, Ca, Mg and REEs. A stronger solution of EDTA (0.14M and 0.27M) was tested on a fresh batch of resin.
- d. A similar experiment was run for the TP 207 resin using sulfuric acid instead of EDTA solution; the concentration of sulfuric acid used in the second stage was 2% and in the third stage was 5%. Deionized water

was used to rinse the resin in the first section. 10% and 15% sulfuric acid solution were used to increase the desorption efficiency in two new allotments of AMD and resin.

The models which were assessed are discussed in detail in Appendix A.

Discussion

AMD and Coal Tailings REE content

The concentrations of Y, La, Ce, Pr, Nd, Gd and Dy in AMD were 1.97 mg/L, 0.67 mg/L, 6.02 mg/L, 0.28 mg/L, 1.64 mg/L, 0.87 mg/L, and 0.33 mg/L respectively. The same elemental concentrations found in waste coal/rock samples were 7.3 mg/kg, 15 mg/kg, 66 mg/kg, 3.3 mg/kg, 13 mg/kg, 1,9 mg/kg, and 1,4 mg/kg respectively. A further Sm content of 2.29 mg/kg was found in the waste rock. Using current market values for the REEs (IndiaMart, 2022; Institut Seltene Erden, 2022), the potential recovery of REEs per m³ of AMD and per thousand kilograms of waste rock processed (without taking into account cost of treatment or transport) is at least €1 /m³ and €4.34 /1000 kg respectively (Galal, 2023; Statista, 2023). It should be noted that only the data for REEs with a statistical standard deviation of less than 30% among measurements from the same source are presented above. Any REE concentration which was deemed statistically inaccurate was omitted from this study, therefore the potential recovery is assumed to be higher than the results presented in this paper. Once the initial REE content was found, extraction and recovery using IX was then evaluated.

Isotherm Parameters/Equilibrium Models

Behaviour of the less acidic resin (TP207) notably aligned to the Langmuir model for all elements, except for Y and La (please see Appendix A, Table A1 and A2 for model assessment). Both of these elements aligned to the Temkin isotherm model. The results indicated that the Langmuir model could potentially be used for modelling resin adsorption of Fe, Ce, Nd, and Gd in an AMD system, while the Temkin model is best suited for modelling Y and La adsorption on the same resin.

The Langmuir model (for both the weak and strong acidic resins) showed promise in defining the behavior of the adsorption system experiments for the range of REE metals from an AMD solution, with the Temkin model showing potential in governing or defining the TP207's adsorption of Y and La. For both systems, the Temkin modelling showed coefficients of determination higher than that of the Freundlich and the Dubinin–Radushkevich models. It is thus hypothesized that under conditions where the Langmuir isotherm fails, Temkin can be used to model the system in a relatively accurate way. When comparing both resins using the Langmuir Isotherm, the maximal adsorption was seen to be consistently higher using the S 108H.

In the case of the Gd, the adsorption on the S 108 H was over 5 times more than on the TP 207 resin. Interestingly, the Langmuir constant (K), which indicates the extent of interaction between adsorbate and the surface, was seen to be higher in the TP 207

than in the S 108 H resin (although both resins present fairly high values for this constant). This shows that (i) there is a strong interaction between adsorbate and adsorbent for both resins (with REEs in AMD) and (ii) that the ratio of adsorption to desorption rates at this temperature is higher on the TP 207, than on the S 108H resin. Although the Freundlich Isotherm did not display high enough coefficients of determination to be considered in alignment with the data obtained, the intensity of adsorption (n) was consistently over 1 which indicates favourable sorption for both resins.

Batch Kinetics

The data obtained (Appendix A – Table A3 and A4) from the batch kinetic experiments from both resins unequivocally displayed PSO behaviour. The calculated equilibrium adsorption capacity (qe) using the PSO model (138 for Ce on S 108H, and 39 for Ce on TP 207) most closely aligns with the experimental

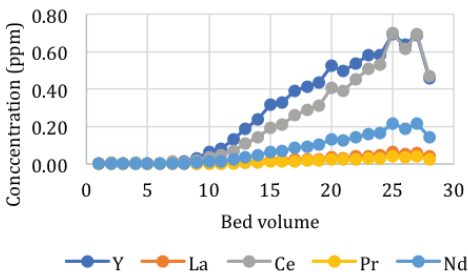


Figure 1 Breakthrough capacity of MonoPlus S 108 H resin at a rate of 12.7 BV/h (for Fe, Ca, and Mg)

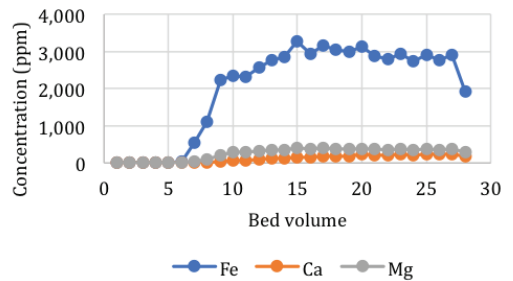


Figure 2 Breakthrough capacity of MonoPlus S 108 H resin at a rate of 12.7 BV/h (for a range REEs)

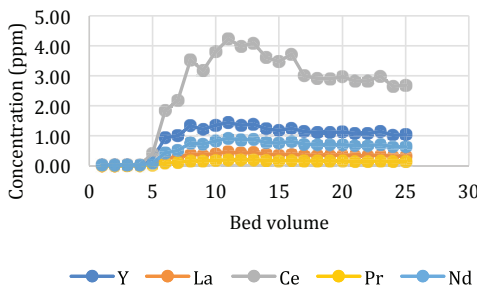


Figure 3 Breakthrough capacity of MonoPlus TP 207 resin at a rate of 12.7 BV/h (for a range REEs)

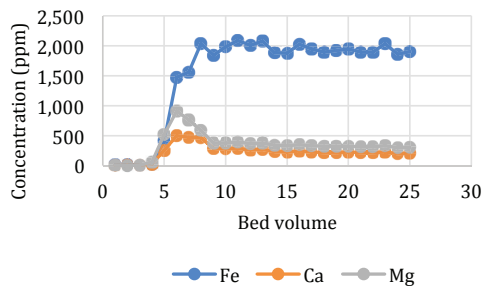


Figure 4 Breakthrough capacity of MonoPlus TP 207 resin at a rate of 6.6 BV/h (for Fe, Ca, and Mg)

value (137 and 42,6 respectively)– confirming the applicability of the PSO model. These results likely mean that the rate-limiting step is chemical sorption or chemisorption in both these systems. This can be confirmed using microscopic or spectroscopic methods. This step predicts the behaviour over the entire range of adsorption. The adsorption

Breakthrough

Figure 1 and Figure 2 show a graphical representation of the breakthrough data. Y, Ce, and Nd begin to show breakthrough between 8 and 9 BV, while La and Pr show breakthrough after approximately 11 – 12 BVs. Fe shows breakthrough much sooner than Ca, Mg, and the range of REEs (at a BV of 6), which indicates that this resin is saturated with Fe much sooner than the REEs.

The S 108H resin achieved adsorption of 80% for all REEs with the exception of Th. Conservatively, €0.8 of REEs can practically be removed from 1 m3 of AMD using IX with S 108 H resin. The same method was followed for TP 207 resin; however, the AMD was passed through the column at 6.6 BV/h and samples were collected after one bed volume. Fe, Mg and Ca reached breakthrough on the TP 207 resin at a BV of 4, while the first REEs broke through at a BV of 5 (Figure 3 and Figure 4).

The adsorption of Fe was shown to be much more competitive using the TP 207 (Fe is more likely to be adsorbed by the resin, potentially preventing, or reducing the adsorption of other REEs). As a result, this resin is not practical to use under these

conditions. Fe removal prior to IX may improve this function. Breakthrough occurs at lower BV values for all elements using this resin. This is an indication that its maximum adsorption capacity is much lower than that of S 108H. The maximum adsorbent capacity of the TP207 was lower than the S 108H resin, with the maximum adsorption being of Ce at 44.35%.

Desorption

The highest concentration of EDTA used for desorption was a 0,27 M solution. Although there was a link between strength of EDTA solution and the extent desorption, the highest concentration was not deemed effective for elution of the S 108H resin because the average desorption of the range of REEs was 40%. It is known that temperature plays an important role in EDTA reactivity (Çiçek & Keskin, 2015), so conducting this step at a higher temperature of between 50 and 70 °C could improve desorption. However, as this technology aims to generate a profit or revenue stream, use of high temperature or other energy intensive processes are not desirable. The TP 207 desorption system presented more favourable results with an average desorption of 80% (for REEs) using a 15% sulfuric acid solution. Figure 3 shows how the desorption ratio/percent is influenced by the strength of the acid eluant – this is similar for the EDTA solution. The concentration of the eluant can therefore be used as a variable parameter to increase the desorption of the various REEs from the resin.

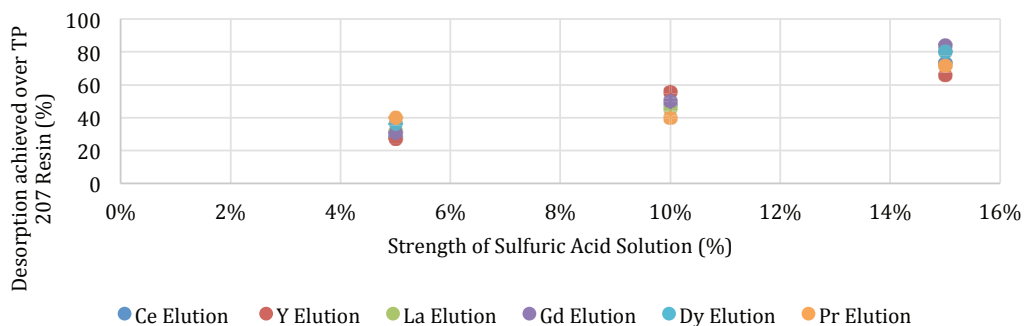


Figure 5 Relationship between amount of desorption over the TP 207 resin and the strength of the sulfuric acid eluant

Conclusions

Coal mine AMD contains significant amounts of REEs and could generate substantial revenue if extracted and processed correctly. In countries where AMD is produced in megalitres per day, this could result in either (i) sizeable cost recovery before or after water treatment or (ii) profit generation. Cationic and chelating ion exchange resins can be used effectively to extract REEs from AMD. The cationic resin displays a greater adsorption efficiency for the range of REEs tested, with adsorption of over 80% (up to 95%) of REEs found in AMD, while the chelating resin displayed between 33% and 45% adsorption. The cationic resin showed a greater affinity for adsorption of the REEs – in some cases adsorbing up to 5 times more than the chelating resin.

Adsorption of REEs conforms to the Langmuir isotherm model. Both chelating and cationic resin adsorption (of the range of REEs tested in this study), conform to Langmuir isotherm behaviour, with only the adsorption of Y and La on the chelating resin conforming better to the Temkin isotherm model.

The IX system (both cationic and chelating resins) followed a pseudo-second order kinetic model with regard to adsorption of all REEs tested. The adsorption rate in this type of system is thus dependent on adsorption capacity not on concentration of adsorbate. Desorption of the REEs from the chelating resin was successful using a 1,53 M sulfuric acid solution. Desorption of the REEs from the surface of the cationic resin was deemed unsuccessful using a 0,27 M solution of EDTA. Elution requires further investigation in this instance.

It was noted that the presence of iron in AMD lowers the adsorption capacity of the resins used in this study. Iron may need to be removed in a pre-treatment step to make extraction of the REEs more efficient and more cost effective. Although further research is required to (i) evaluate the removal of other REEs that could be contained in AMD from different mine sources, (ii) optimise the elution of REEs from the resins, post adsorption (or extraction), and (iii) determine effective methods of iron removal that do not

affect (or minimally affects) REE content, these findings provide a successful proof of concept for the application of this technology. Extraction of REEs from AMD using ion exchange technology has the potential to reduce the cost of AMD treatment, generate a profit, and contribute to developing a circular economy in the mining industry.

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