

# Towards Sustainable Recovery of Rare Earth Elements from Acidic Mine Waters: A Circular Treatment Approach Integrating Selective Precipitation and Ion Exchange

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## Abstract

Acidic Mine Waters (AMWs) pose a great environmental risk due to their acidity and metal content. Traditional treatments neutralize acidity but produce hazardous sludge. This study introduces a sustainable, circular approach for treating AMWs, focusing on recovering valuable Rare Earth Elements (REEs) and other Critical Raw Materials (CRMs). Using AMWs from the Aznalcóllar Open Pit (SW, Spain), metals like Fe, Al, and Zn were removed through precipitation and sulfide formation, achieving >99% efficiency. Ion exchange resins separated heavy and light REEs, which were recovered as >90% pure oxalates. This eco-friendly process minimizes sludge, mitigates pollution, and supports CRM demand, demonstrating global applicability.

**Keywords:** Acid mine waters, rare earth elements recovery, heavy rare earth elements, light rare earth elements, selective precipitation, ion exchange, TP272, S930, rare earth elements oxalates

## Introduction

Rare Earth Elements (REEs), despite their importance for modern technologies, are scarce, and only a few countries (China, USA and Myanmar) hold reserves (Ayora *et al.* 2016; Voncken 2016). Due to their increasing demand and cost, the European Union (EU) has classified them as Critical Raw Materials (CRMs). Therefore, to reduce the dependency on other countries, the EU is promoting treatment schemes to recover CRMs from secondary sources through circular economy processes (León *et al.* 2021).

Acidic Mine Waters (AMW) are a by-product of the mining industry, which result from the oxidation of sulfide minerals such as pyrite (Sánchez-Andrea *et al.* 2014). Not only they are characterised by their acidic pH,

but also by their high concentration of REEs (several orders of magnitude higher than in other water sources) (Ayora *et al.* 2016). Due to that, they represent a great environmental hazard. Conventional AMW treatment focus on prevention or remediation. However, green technologies such as selective precipitation or ion exchange (IX) are being explored for metal recovery (Simate and Ndlovu 2014).

By using selective precipitation, metals can be recovered as hydroxides (Hermassi *et al.* 2022), sulfides (Luptáková *et al.* 2010) or oxalates (Chung, Dong-Yong; Kim, Eung-Ho; Lee, Eil-Hee; Yoo 1998). For instance, researchers (MacIngova and Luptakova 2012) have achieved removals >99% of Cu, Zn, Fe, Al and Mn through staged precipitation, which involved pH adjustment and chemical

reagents. Regarding the recovery of REEs, due to the relatively low contents (mg/L to  $\mu\text{g/L}$ ), the use of IX as selective extraction and post-concentration stage is a promising option.

This study focuses on the fractionation of REEs into Heavy REEs (HREEs) and Light REEs (LREEs) by using two commercial IX resins, one impregnated resin with bis-(2,4,4-trimethylpentyl-) phosphinic acid (TP272) and a chelating one containing iminodiacetic functional groups (S930). For that, a pre-treatment for the removal of the major elements (Fe, Al) and recovery of the valuable elements (Zn, Cu, Co, Ni) present in the AMW was performed. Followed by an optimization of the elution process of the resins. To conclude the work, a crystallization process was performed to recover REEs as oxalates.

## Methods

The AMW used came from the Aznalcóllar open-pit in Seville, Spain and was provided by the company *Minera Los Frailes*. The AMW was characterized by an acidic pH (2.7-2.8) and a high content of Mg (1628.5 mg/L), S (3653.8 mg/L), Al (215.7 mg/L), Fe (47.1 mg/L), Zn (547.5 mg/L), and REEs (18.5 mg/L). The content of REEs, separated in LREEs and HREEs can be seen in Table 1.

To avoid interferences during the IX process, and to maximize the resin capacity towards REEs, Fe, Al and Zn were removed (see Fig. 1). For the removal of Fe and Al the process consisted of the addition of  $\text{H}_2\text{O}_2$  (4 ml/L AMW) to oxidise Fe(II) to Fe(III), followed by an increase of pH (up to 4.5) using NaOH 5 mol/L. Selection of NaOH instead

of CaO(s), a cheapest and widely alkali was done to reduce the content of Ca(II) in the treated AMW as it could cause the reduction of the IX resins' capacity. For the removal of Zn, a dosage of 66.6 mmol/L of NaHS was added to the solution at constant pH of 2. The reaction was carried out for at least 10 min or until no variations of the oxidation-reduction potential were noticed. In both processes, after the precipitation, solutions were filtered through a Mixed Cellulose Esters (MCE) filter with 0.45  $\mu\text{m}$  of porous size to remove suspended solids.

For the selective recovery of REEs, two commercially available resins were selected to fractionate REEs into HREEs and LREEs. These were the Lewatit TP272 from *Lanxess*, presenting high selectivity towards HREEs, and the S930 from *Purolite*, used to focus on the retention of LREEs. The experimental set-up consisted of two columns with the same dimensions (2.16 cm of diameter and 11.3 cm of height) allocated in an in-series configuration. The first column contained 15 g of the Lewatit TP272 and the second column contained 16 g of the Purolite S930. Moreover, the inlet of the columns was connected to a peristaltic pump (Miniplus 3 from *Gilson*) and the outlet to a fraction collector (Fraction Collector 204 from *Gilson*). Continuous tests were performed using the AMW depleted of Fe, Al and Zn at a flow-rate of 3 PV/h. Afterwards, the resins were regenerated with a  $\text{H}_2\text{SO}_4$  solution at 1 PV/h. The chosen concentration for the regeneration of each resin (0.4 mol/L for the TP272 and 0.15 mol/L for the S930) was due to an optimization process. In there,

*Table 1 REEs content in the Aznalcóllar open-pit (Seville, Spain) water (mg/L), average of 5 samples collected along one year.*

LREEs				HREEs			
<b>La</b>	2.3	±	0.1	<b>Y</b>	2.5	±	0.2
<b>Ce</b>	6.3	±	0.3	<b>Tb</b>	0.12	±	0.01
<b>Pr</b>	0.89	±	0.04	<b>Dy</b>	0.54	±	0.04
<b>Nd</b>	3.5	±	0.3	<b>Ho</b>	0.09	±	0.01
<b>Sm</b>	0.76	±	0.04	<b>Er</b>	0.20	±	0.02
<b>Eu</b>	0.12	±	0.01	<b>Tm</b>	0.020	±	0.002
<b>Gd</b>	0.93	±	0.07	<b>Yb</b>	0.12	±	0.01
				<b>Lu</b>	0.020	±	0.001

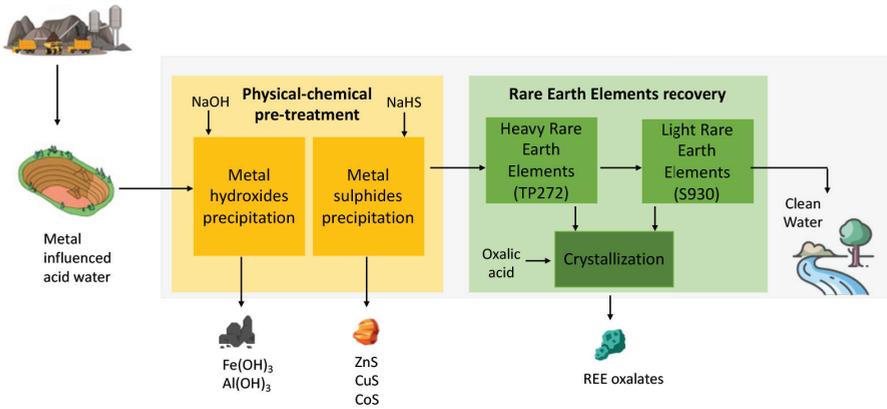


Figure 1 Followed experimental procedure for the selective recovery of REEs from AMWs.

the focus was to balance the concentration factors achieved during the elution step and the minimization of the excess of acid to reduce the cost of the alkali solution in the crystallization process. More information could be found in Roa *et al.* (Roa *et al.* 2024a)

The crystallization process focused on the selective recovery of REEs from the eluate as oxalates. For that, after the regeneration of the resins, the samples with higher content of REEs were mixed and an excess of 100% of oxalic acid was added to ensure the complete precipitation. After the addition of oxalic acid, the pH was corrected to 1 using NH<sub>3</sub> instead of NaOH to avoid the precipitation of sodium oxalates (e.g. NaHC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O(s)) and to not compromise the purity of the resulting solid. When the precipitation was completed, the solution was filtered through a 0.22 μm

MCE filter and the solids were dried at 70 °C for 24 h. More details are provided in Roa *et al.* (Roa *et al.* 2024b)

**Results**

The removal percentages attained during the selective precipitation of Fe, Al and Zn can be seen in Fig. 2, where the blue sections are the metal removals as hydroxides and hydroxy-sulfates at pH 4.5 and the green ones are as sulfides at pH 2. From there, it can be observed that Al, Fe, and Si were mainly removed as hydroxides. The selected pH of operation was a compromise between removing the maximum amount of Fe(III) and Al(III) and minimizing the losses of valuable elements such as Ce. On the other hand, Cu, Zn, Cd, Ni, Co, and Ce were removed as sulfides. Overall, after those two steps of pre-treatment

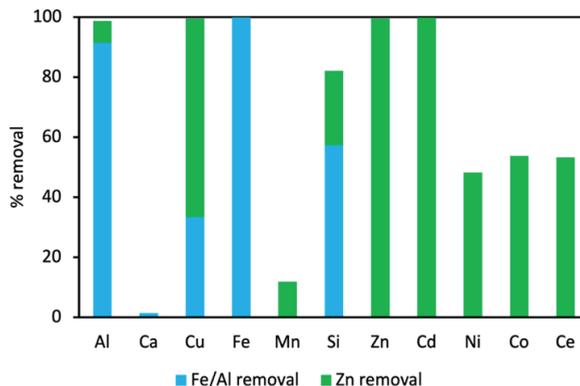


Figure 2 Removal % for the selective precipitation of Fe and Al at pH 4.5 using NaOH 5 mol/L and removal of Zn at pH 2 using 66.6 mmol/L of NaHS.

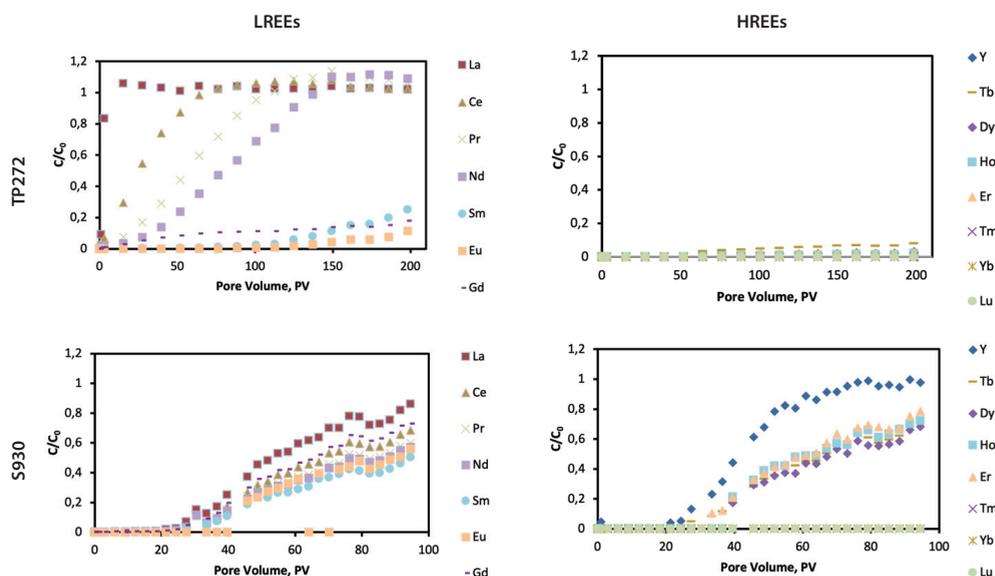


Figure 3 Breakthrough curves of HREEs and LREEs for TP272 and S930 resins when treating pre-treated AMW depleted of Fe, Al, and Zn.

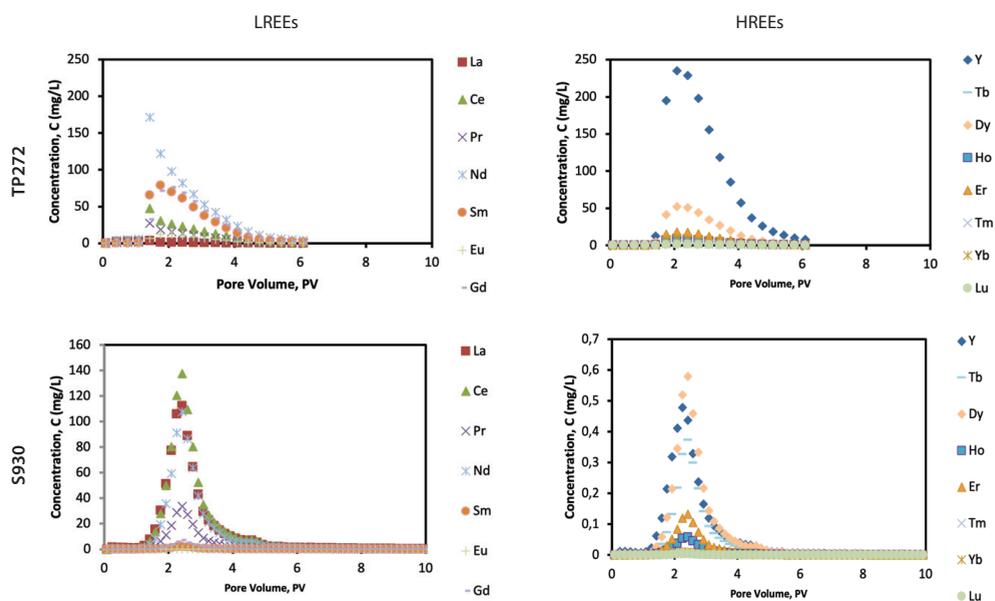
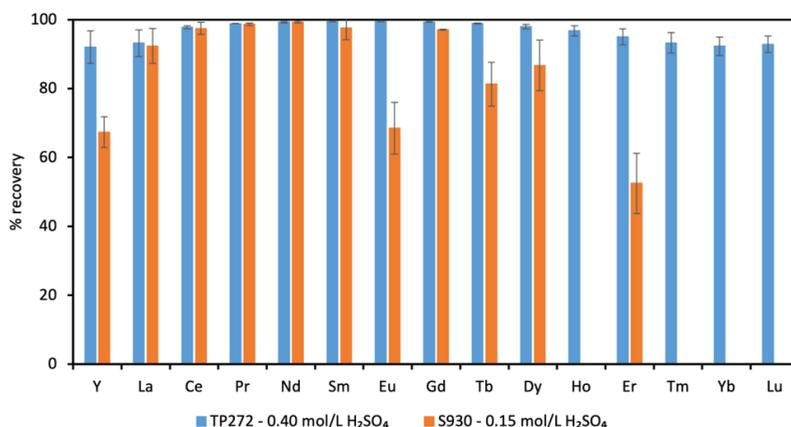


Figure 4 Elution curves of TP272 with 0.4 mol/L and S930 with 0.15 mol/L of  $H_2SO_4$ .

the removals attained were >99% for Fe, Cu, Zn and Cd, >95% for Al and >40% for Ni, Si, Co, and Ce. However, as reported before the losses of certain REEs were expected during this step by sorption and co-precipitation phenomena (Ayora *et al.* 2016; Lozano *et al.*

2020). No significant losses were observed for the remaining REEs (<2%).

For the fractionation of the REEs into HREEs and LREEs, after bibliography research (Page *et al.* 2017; Hermassi *et al.* 2021), it was decided to test the columns in



**Figure 5** Recovery percentage of REEs as oxalates from TP272 and S930 when using 0.4 mol/L and 0.15 mol/L of H<sub>2</sub>SO<sub>4</sub>, respectively in the elution process.

series, where the first resin was the TP272 to extract the HREEs, while the S930 was able to extract the remaining LREEs. It was decided to operate the first resin until reaching 200 PV ( $C/C_0 = 0.1$ ), as seen in Fig. 3, to maximize its uptake of HREEs. If the resin was left until saturation, some of the HREEs would have passed to the second column containing the S930, reducing the uptake of LREEs of this one.

After the breakthrough, the regeneration of the TP272 and S930 was done with 0.4 mol/L and 0.15 mol/L of H<sub>2</sub>SO<sub>4</sub>, respectively (see Fig. 4). In the case of the TP272 the regeneration was completed after 6 PV. In the case of the S930 it was regenerated after 4 PV, which is in accordance with the bibliography (Page *et al.* 2017). In both cases, the curves were quite narrow and uniform, and from them, the selectivity of the TP272 towards the HREEs can be clearly seen. After the regeneration the maximum concentration of Y recovered was near 250 mg/L whereas for the S930 did not reach 1 mg/L.

The recovery percentage REEs as oxalates at the optimum elution conditions for both resins can be seen in Fig. 5. From the samples originated from the TP272 impregnated resin, recoveries higher than 90% were achieved for all the REEs. However, an almost complete recovery for Ce, Pr, Nd, Sm, Eu, Gd, and Tb was obtained. Regarding the S930 chelating resin, recoveries higher than 80%

were attained for La, Ce, Pr, Nd, Sm, Gd, Tb, and Dy. Moreover, recoveries between 50% and 60% were achieved for Y, Eu, and Er. Nonetheless, it is worth mentioning the fact that, even though REEs such as Ho, Tm, Yb, and Lu were in low concentration in the initial AMW (<0.15 mg/L), they were completely retained by the TP272 resin. Hence, at that concentration the S930 is not able to extract them from the treated AMW.

After the solution was filtered and dried, the solid was analysed and it was observed that for both resins, the solid was a mixture of REEs oxalates. However, the proportion of LREEs or HREEs was different depending if the solid came from the TP272 resin or the S930, showcasing the affinities of each one. With the AMW depleted of Fe, Al, Zn and REEs, a post-treatment, focusing on the reclamation of water would be the following step. In addition, a techno-economical analysis must be performed in order to ensure the feasibility of the proposed treatment train.

## Conclusions

This study shows the possibility of implementing a method to valorise AMW based on the integration of selective precipitation and IX processes to selectively recover REEs.

During the pre-treatment, removals of 90% and 99% of Fe and Al, respectively, as hydroxides were attained. In addition, the removal of Zn and other transition metals as

sulfides was carried out, obtaining removals higher than 99% for Zn and Cd and higher than 40% for Ni, Co, and Ce.

Regarding the IX process, it was observed that the resin TP272 presented a high selectivity towards the HREEs, whereas the S930 could concentrate both HREEs and LREEs. Therefore, by integrating both resins in series, REEs could be fractionated into HREEs and LREEs. Afterwards, they were recovered as oxalates by the addition of oxalic acid, achieving recoveries higher than 90% and solids that were a mixture of them.

This work demonstrated the technical viability of recovering REEs (considered critical elements in USA, Canada, Australia and the EU, among others) from secondary sources associated to mining wastes.

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