

# RARE EARTH ELEMENT SEPARATION FROM PHOSPHOGYPSUM WITH ION EXCHANGE AND BIODEGRADABLE ELUENTS

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## Abstract

Recovery of rare earth elements (REE) from phosphogypsum using resin-in-leach was studied in laboratory scale. The main impurity in the loaded resin is calcium. Selective removal of calcium and elution of REEs from the loaded resin was studied using conventional and biodegradable complexing agents. It was found that Calcium free fractions with high REE concentration (up to 4 – 6 g/L) can be obtained. Calcium/REE separation was done with two-step elution by varying eluent pH.

## Introduction

Many modern technical applications and devices are not possible without certain unique elements. One important group of these elements is rare earth elements, REEs. Rare earth elements consist of lanthanoids, yttrium and cerium. Availability of these precious elements is not necessarily guaranteed especially when the China dominates global REE markets and production. Current situation of REEs availability and its uncertainty in long time period has given rise to other countries to develop their own REE production. The approximate 10 % of global annual production of REEs outside of China is not enough to fulfil the demand.<sup>1</sup> This has led to the situation where countries are searching for secondary sources for REEs. Certain industrial wastes contain REEs as impurities. Two potential wastes are red mud and phosphogypsum. In these wastes the REE is originated from minerals used in these processes (bauxite and apatite). Concentration of REEs in the waste is low. REE ore can contain 3.39 wt.% of REEs.<sup>2</sup> Phosphogypsum is potential source for REEs because its production volumes are huge. The global production of phosphogypsum is estimated 100 – 280 Mt annually.<sup>3</sup> Even with low concentration of 1 – 2 g of REEs per kg the amount is significant.

One method for REE extraction from wastes is ion exchange (IX). Conventional ion exchange is phenomenon between electrolyte solution and IX resin. In resin-in-leach

(RIL, also known as resin-in-pulp) process the IX resin is added to the slurry. RIL simplifies processing by eliminating the dissolution step. Additional separation of resin and leftover solid material is needed after contact. Selectivity of desired species can be achieved during RIL process even in complex sample matrices.<sup>4</sup> RIL can be repeated multiple times to ensure high resin loading.

During RIL the resin uptakes usually multiple different ions and some of them are often unwanted contaminants. Changing the RIL conditions is often difficult to prevent sorption of impurities. During elution it is possible to use more than one step. In each step the composition of eluent is different (pH, concentration, chelating agent etc.) With stepwise elution impurities can be removed from the resin and leave desired ions inside the resin. After successful removal of impurities, the final elution can be complete regeneration of the resin and wanted product is collected from effluent.

## **Ion-exchange in REE separation from phosphogypsum**

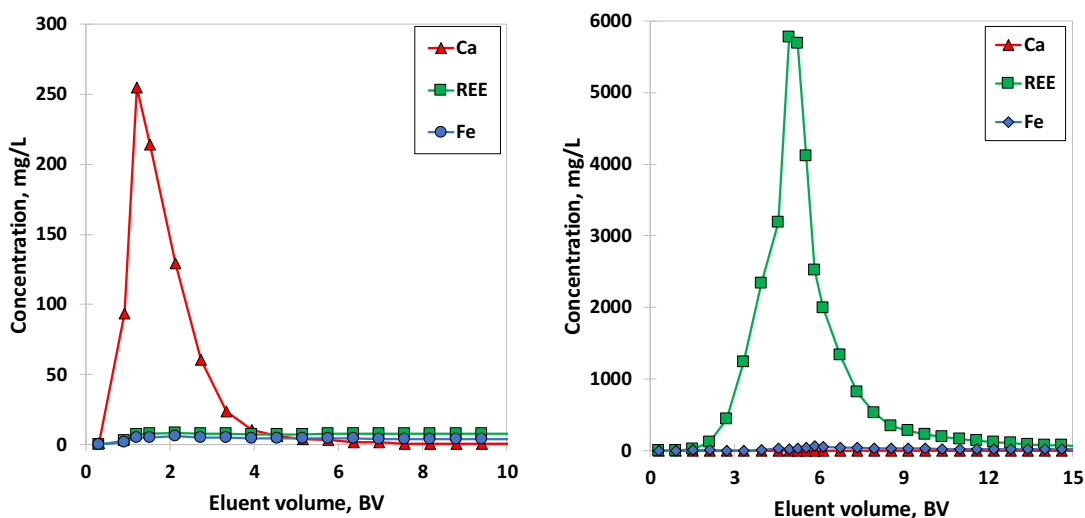
REE\* content of phosphogypsum was 1.74 g/kg (\*Sum of lanthanoids, yttrium and scandium). Other impurities to consider were calcium (41.3 g/kg), iron (0.32 g/kg), strontium (4.05 g/kg). REE separation from high calcium containing matrix is possible with resin-in-leach (RIL) method. RIL is proven to be efficient method for trace level extraction from solution.<sup>5</sup> Resin used in separation was Purolite S940 (Macroporous, chelating). Resin and phosphogypsum were added to the 10 g/L H<sub>2</sub>SO<sub>4</sub>. With multiple loading cycles (up to eight cycles) REE loading of 0.92 equiv./kg (S940 capacity 1.11 equiv./kg, Purolite.com). Calcium loading after eight cycle was 0.03 equiv./kg. For every loading cycle new acid/phosphogypsum slurry was prepared.

Selected eluents for REE removal were readily or partially biodegradable. Complexing agents (IDA, MGDA, GLDA, oxalic acid, citric acid, sodium citrate) were used as eluents. Effect of eluent mixture pH was investigated. 15 g of resin was packed to the column. Operating conditions were held same in all experiments.

### **Elution procedure of resin with two-step elution**

It was shown that first elution with acidic eluent (pH < 3) eluted almost only calcium. Small REE leakage was observed with all eluents during first step. It was shown that nature of chelating agent does not affect calcium removal at low pH. Calcium is simply eluted due to the low pH as protons replace it in the resin. After first elution the calcium is eluted 95 – 100% depending of eluent. During second elution step the chelating agents were introduced to column at high pH (> 10). GLDA and MGDA were

most promising. Elution graph with MGDA is shown in Figure 1. REEs purity during elution was high, up to 99%. Yield of 95% can be collected with 95% purity. Iron was not eluted from the resin with used complexing agents. MGDA and GLDA thus show



promising properties for further studies.

**Figure 1.** Fractionating elution of Purolite S940 (loaded with five resin-in-leach cycles) using MGDA at low pH (left) and high pH (right).

## References

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