# Unlocking the Potential of Phosphogypsum: Leaching of rare earth elements from phosphogypsum derived from sedimentary and magmatic phosphate ore

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**Abstract**

The transition towards renewable energy is becoming increasingly crucial for the sustainability of our planet, and this move is accelerating globally. As the demand for renewable energy sources grows, so does the demand for renewable energy equipment that relies on rare earth elements (REEs). However, the growing importance of these elements in high-tech industries has caused demand to exceed known global supply, sparking a global hunt for new sources. REEs head the list of critical materials: a group of 17 chemical elements widely used in high technology and low-carbon products(Directorate-General for Internal Market, 2023). However, the majority of the EU's supply of REEs is imported from countries outside the EU, notably China, which currently dominates the global market for these elements.

Phosphogypsum (PG), a by-product of the phosphate fertilizer industry, has the potential to be an important source of REEs (Bilal et al., 2023; Cánovas et al., 2018). The large quantities of PG produced contain significant amounts of REEs that are naturally present in processed phosphate ores The annual production of 200 million metric tonnes of PG constitutes almost 95% of the global demand for rare earths (Emsbo et al., 2015). The extraction of REEs from PG could play a vital role in reducing the European Union's (EU) dependence on primary sources and enhancing its self-sufficiency in this critical area. The EU is home to some of PG stacks, located in countries such as Lithuania, Poland, Spain, Greece, Bulgaria, Serbia, and Kosovo, as well as having the capability to import PG from North Africa. By leveraging these resources, the EU can decrease its dependence on external sources and improve its self-sufficiency in this field.

The development of extraction technologies adapted to PG may provide a sustainable and economically viable means of extracting rare earths while minimizing the ecological footprint. In addition, this project aims to examine and compare leaching methodologies applied to two distinct types of PG: magmatic PG (MPG) from the Wizow chemical plant in Poland, and sedimentary PG (SPG) obtained from the OCP group in Morocco. This comparative analysis aims to gain a deeper understanding of the subtleties of the leaching process and to highlight the behavior of MPG and SPG in rare earth extraction techniques.

Prior to commencing leaching, the samples underwent characterization employing ICP-MS/OES, XRD, and MEB techniques to evaluate their elemental composition, mineralogical phases, and morphology, respectively. Subsequently, leaching experiments were conducted to examine the release of REEs and impurities from the processed material. These experiments were carried out within a controlled reactor environment at a consistent temperature of 25±1°C. Three different mineral acids, namely $HNO_3$, HCl, and $H_2SO_4$, were employed, with particular attention to the cost-effectiveness of $H_2SO_4$. Moreover, oxidizing agents such as $H_2O_2$ and $NaClO_3$, as well as reducing agents like Zn and Fe powders, were introduced to augment the leaching process and enhance its efficiency.

The characterization analysis indicates that MPG contains a REE concentration of 4697 mg/kg (0.47% w/w), while SPG exhibits a lower content of 337 mg/kg (0.03% w/w). In terms of mineralogical composition, both PG types are primarily composed of calcium sulfate dihydrate $CaSO_4 \cdot 2H_2O$ as the main phase, accompanied by minor impurities such as Quartz and Chukrovite. Additionally, MPG is characterized by the presence of Celestine as an additional phase.

Our investigation into REEs leaching using acid solutions revealed significant results. Specifically, when examining MPG, we found that a 2 M $HNO_3$ solution demonstrated remarkable efficiency, achieving an 88% recovery of total REEs, while a 1.5 M HCl solution exhibited a robust recovery rate of 87%. Additionally, the utilization of a 2M $H_2SO_4$ solution resulted in a substantial 85% recovery rate, with less than 8% of the gypsum being dissolved. The incorporation of oxidizing and reducing agents alongside the acidic solutions did not notably impact the leaching efficiency of rare earth elements. Notably, the use of $H_2SO_4$ for leaching rare earths from MPG proved highly effective, preserving the residue's structure and rendering it suitable for the plaster industry. This sets it apart from nitric and hydrochloric acids, which tend to dissolve gypsum and induce structural changes.

Furthermore, sulfuric acid offers outstanding cost-effectiveness and controllability in industrial applications. Consequently, our research focused on optimizing the sulfuric acid leaching process, identifying specific conditions for optimum performance: a concentration of 5% $H_2SO_4$, a temperature of 25°C, a solid/liquid (S/L) ratio of 1/8, and a leaching time of 2 hours.

Regarding the leaching process of SPG, we have employed the optimal leaching conditions determined recently by Ait Hak et al. (2023). In this study, we investigated the impact of incorporating oxidizing and reducing agents, as well as their combination, on the leaching efficiency. Our findings revealed that when leaching REEs from SPG using only 2M of $H_2SO_4$, the recovery rate was 34%. Introducing an oxidizing agent increased the recovery to 43%, while the addition of a reducing agent further enhanced the recovery to 48%. Interestingly, employing both oxidizing and reducing agents simultaneously resulted in a slightly lower recovery rate of 47%. These results suggest significant potential for optimizing the leaching process through strategic utilization of oxidizing and reducing agents. Still, the use of oxidizing and reducing agents effectively enhanced recovery rates suggesting differences in the occurrence of rare earth elements between sedimentary and magmatic PG. These findings hold promise for enhancing recovery techniques worldwide, aligning with circular economy objectives.

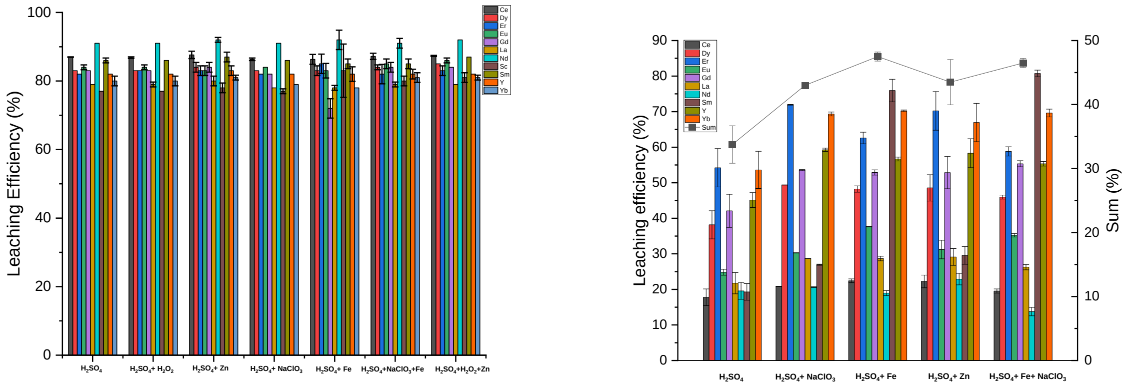


**Figure 1**: Comparative analysis of REE leaching from MPG (left) and SPG (right) with varied oxidizing and reducing agents, and their combinations

**Keywords:** Rare Earth Elements, Critical Raw Materials, Secondary sources, Phosphogypsum, Acid leaching process

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