

## Article

# Sulfuric Acid Leaching Recovery of Rare Earth Elements from Wizów's Phosphogypsum in Poland

Linda Maina <sup>1</sup>, Katarzyna Kiegiel <sup>1,\*</sup>, Zbigniew Samczyński <sup>1</sup>, Nils Haneklaus <sup>2,3</sup>  
and Grażyna Zakrzewska-Kołodziej <sup>1</sup>

- <sup>1</sup> Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland; l.main@ichtj.waw.pl (L.M.); z.samczynski@ichtj.waw.pl (Z.S.); g.zakrzewska@ichtj.waw.pl (G.Z.-K.)  
<sup>2</sup> Td-Lab Sustainable Mineral Resources, University for Continuing Education Krems, Dr.-Karl-Dorrek-Straße 30, 3500 Krems an der Donau, Austria; nils.haneklaus@donau-uni.ac.at  
<sup>3</sup> Unit for Energy and Technology Systems—Nuclear Engineering, North-West University, 11 Hoffman Street, Potchefstroom 2520, South Africa  
 \* Correspondence: k.kiegiel@ichtj.waw.pl

**Abstract:** Rare earth elements (REEs) are considered vital raw materials for the economy and are on the European Union's list of critical raw materials (CRMs). Europe is mainly dependent on REE imports. This dependence could be reduced if locally available primary or secondary resources would be processed. In Poland, there are, for instance, over 5 million metric tons of phosphogypsum (PG), a fine powdery byproduct from the fertilizer industry, available near the former Wizów Chemical Plant near Bolesławiec. This material that is considered a waste in Poland contains significant amounts of REEs that could theoretically be recovered and contribute to Europe's economy. This work is the first systematic analysis of REE leaching studies with sulfuric acid and PG from Wizów. Process parameters such as temperature, particle size, concentration of the leaching solution, and the addition of oxidant and reductant agents were tested to determine the most efficient process. Ultimately, a leaching efficiency of 99% was obtained. Lanthanum exhibited the highest leaching efficiency at almost 100%, followed by Yttrium, Neodymium, Terbium, and Dysprosium. The results of the laboratory experiments are promising and suggest that larger pilot or commercial experiments can be performed next.

**Keywords:** rare earth elements; apatite; phosphogypsum; waste; sulfuric acid; leaching



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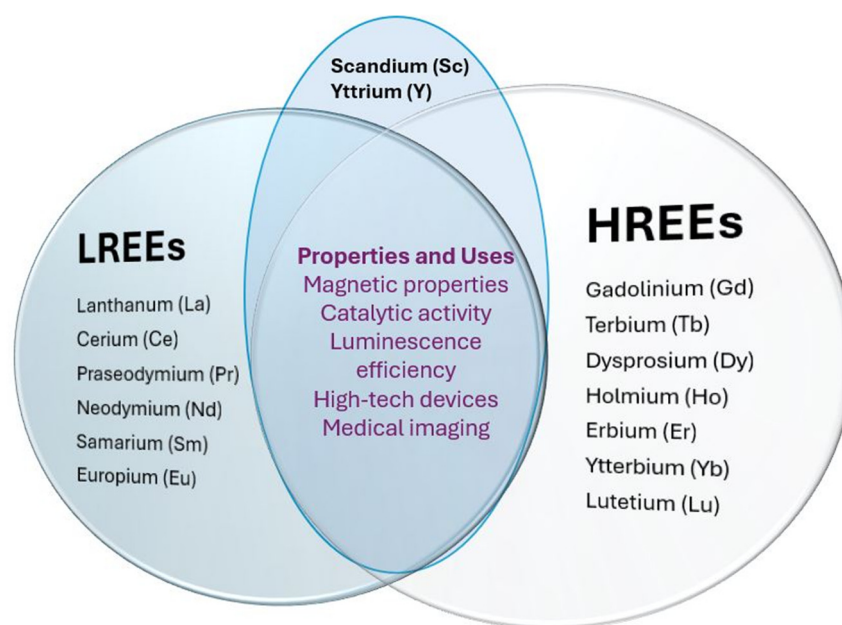
## 1. Introduction

Phosphogypsum (PG) is a byproduct generated in large quantities during wet phosphoric acid (WPA) production. This process involves the reaction of phosphate rock with sulfuric acid, forming phosphoric acid and calcium sulfate dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), known as PG [1]. For every ton of WPA produced, approximately 4.5 to 5 tons of PG are generated, posing significant environmental challenges [2–4]. Global PG production is estimated to be in the order of 300 million tons annually, with major producers including China, Morocco, the USA, and Russia [5–7].

PG contains various impurities, such as soluble phosphorus, fluorine compounds, heavy metals, and even radioactive elements [8]. Despite its potential as a resource, only a small percentage of about 15% is currently recycled, while the majority is either stockpiled or discharged in open waters, exacerbating environmental contamination [4,9]. The utilization of PG remains limited, and its management remains a significant challenge for the fertilizer industry worldwide [2].

Despite the earlier-mentioned impurities, PG can also contain rare earth elements (REEs) in elevated concentrations. REEs constitute a group of 17 elements that can be divided into light and heavy REEs crucial for various advanced technologies, including electronics, communication, and the energy sector [6,10]. Due to their unique magnetic,

luminescent, and electrochemical properties, REEs are essential for advanced technologies. They are used in electronics, renewable energy, and the defense industry at large. The leaching processing of heavy rare earth elements (HREEs) and light rare earth elements (LREEs), as shown in Figure 1 from PG, reveals significant differences in their solubility. Studies by Zhao et al. [11] and Smith et al. [12] indicate that HREEs generally exhibit lower solubility than LREEs when using acid solvents like sulfuric or hydrochloric acid. Additionally, Chen et al. [13] found that the extraction efficiency highly depends on the acid concentration and the specific type of acid used. These differences are crucial for optimizing extraction processes to maximize HREEs and LREEs recovery rates from PG sources, with scandium and yttrium often forming a separate group (Figure 1) since their chemical properties cannot be classified as either LREEs or HREEs.



**Figure 1.** A Venn diagram showing the classification, properties, and applications of rare earth elements (REEs) and scandium.

The solubility of REEs during leaching with acid solvents varies significantly with different types of PG samples. According to Li et al. [14], dried PG tends to have a higher solubility for REEs due to reduced moisture content that can enhance acid interaction. Undried samples, as noted by Wang et al. [15] contain residual moisture that dilutes the acid, subsequently reducing the leaching efficiency. Calcinated PG, studied by Kim et al. [16], showed improved solubility due to structural changes and impurity removal during calcination, facilitating better acid penetration and REE extraction. These differences underscore the importance of sample preparation in optimizing REE recovery from PG.

The REEs, including lanthanides, scandium, and yttrium, are considered vital raw materials for economic growth and are termed critical raw materials (CRMs) in the European Union (EU) [17]. REEs are found in low concentrations within mineable ore deposits, making their extraction and recovery technically complex and economically demanding. These challenges arise due to the need for extensive processing and refinement to isolate the REEs from surrounding materials. The intricate processes involved in the recovery contribute to the high costs and relatively large environmental footprint, further complicating the economic viability of REE production [18]. As global demand for REEs rises, efficient extraction technologies from secondary sources, such as fly ash, are increasingly pursued [19]. Fly ash, a byproduct of coal combustion, contains REEs that can be recovered through advanced processing techniques [20]. Although REEs are often only found in relatively low concentrations of several hundred parts per million (ppm), the overall quantities that could theoretically be recovered are nonetheless relevant since the overall

production volumes are significant. For instance, Hakkar et al. [21] estimated that REEs from phosphate rock production in Morocco alone could cover between 7 and 15% of the annual global REE demand if they could be fully recovered. The concentrations of REEs in phosphate rocks are typically in the order of 300–600 mg/kg [22], with exceptions like the Catalão Minerochemical Complex in Brazil, which reports concentrations of up to 16,650 mg/kg [23].

During phosphate rock processing to WPA, most REEs (approximately 80%) transfer from the phosphate rock to the PG byproduct, with the remaining fraction transferring to the liquid WPA. Igneous phosphate rock is known to contain higher REE concentrations, including the igneous phosphate rock from the Kola Peninsula that was processed at the former Wizów Chemical Plant near Bolesławiec in Poland. Fertilizer production ended at the facility, but there are still over 5 million tons of PG stored that are accessible for potential processing [6]. The REEs in the Wizów's PG pile present a significant secondary REE resource close to production centers in the heart of Europe. Specifically, earlier studies [8,19] reported rare earth oxide (REO) concentrations of 0.6% that would theoretically result in a total REO quantity of approximately 21,000 tons.

REEs have been successfully leached from different PG sources in lab- and even pilot-scale experiments before. However, such work was never conducted for Wizów's PG, which shows relatively high REE concentrations if compared with other PG sources.

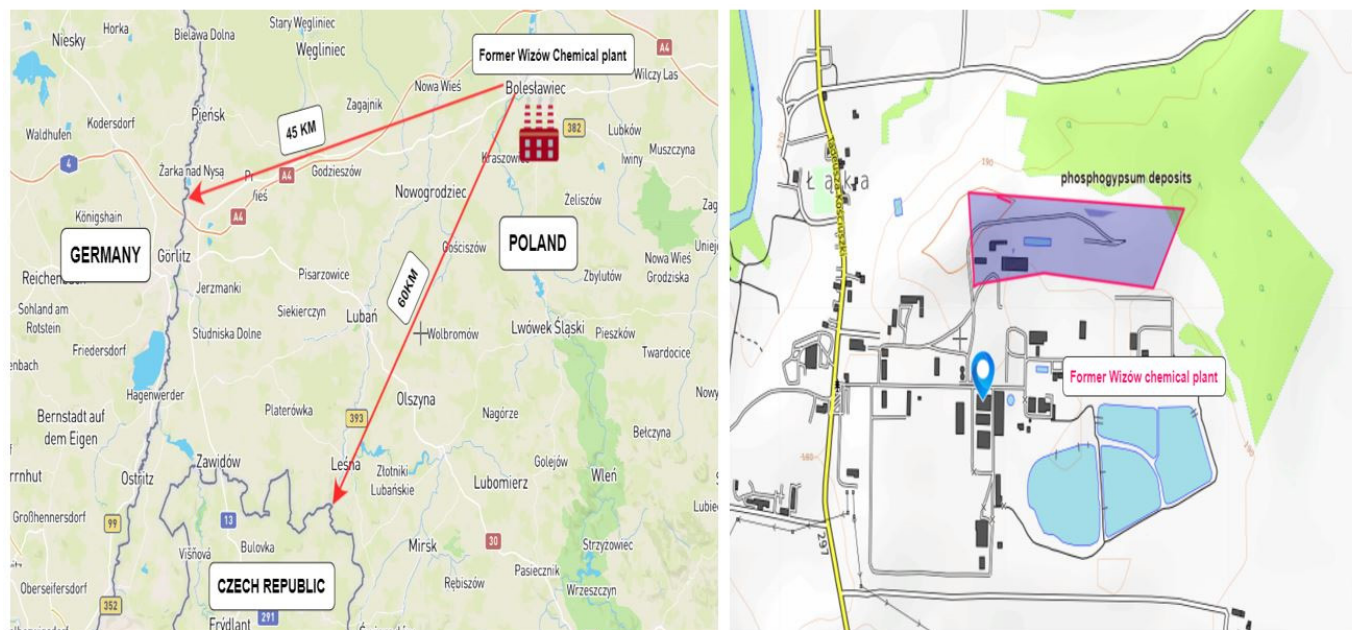
This work aims to systematically investigate the REE leaching behavior from Wizów's PG with sulfuric acid to better understand this approach's technical feasibility. Sulfuric acid has been successfully used in different concentrations and with varying pretreatments of PG for REE leaching from PG. In Florida, the leaching efficiency increased rapidly with sulfuric acid concentrations from 0 to 10% and temperatures between 20 and 70 °C, reaching a maximum of about 43% at 5% sulfuric acid and 50 °C, before gradually decreasing as conditions changed [24,25]. The Philippines PG leaching experiments were conducted to optimize acid concentration (1–10%), leaching temperature (40–80 °C), leaching time (5–120 min), and solid-to-liquid ratio (1:10–1:2) to maximize REE leaching efficiency. The optimum combination for maximum REE leaching from phosphogypsum is 10% H<sub>2</sub>SO<sub>4</sub>, 80 °C, 30–45 min, and a 1:10 solid-to-liquid ratio. A total % REE leaching efficiency of 71% was achieved, including La 75%, Ce 72%, Nd 71%, and Y 63% [26]. In Russia, the leaching conditions for extracting rare earth elements from phosphogypsum involve using 1–10% sulfuric acid at temperatures between 40 and 80 °C, with leaching times ranging from 5 to 120 min and solid-to-liquid ratios of 1:10 to 1:2. These conditions can achieve leaching efficiencies of up to 71% [27,28], and for Brazil, leaching efficiency values for the total rare earth elements reached 89.7% using 3 mol L<sup>−1</sup> sulfuric acid, a solid-to-liquid ratio of 1:20 g/mL, and a temperature of 80 °C [29]. To the best of our knowledge, this is the first study that systematically investigates REE leaching from Wizów's PG in Poland.

## 2. Materials and Methods

### 2.1. Study Area

The studies were conducted on PG sampled from the Wizów plant, which is located approximately 4 km north of the city of Bolesławiec, about 45 km from the German border and 60 km from the Czech border in the southwestern part of Poland, as shown in Figure 2. The PG stacks cover an area of approximately 10 ha, subdivided into three distinct sub-areas based on stack characteristics such as size and volume of stacks, age of stacks, and geographical distribution. To capture variability of the area, ten sampling points were chosen from different locations within the stack (center and edges) to account for horizontal differences. The samples were collected from a depth of about 5 m sampling. Sample collection focused on areas with potential for heterogeneity, using a combination of random and stratified sampling to ensure representative results. The site's history traces back to the company's establishment in 1948, initially producing sulfuric acid and later expanding into phosphoric acid and phosphoric salts production between 1969 and 1979. In the scope

of the research, ten samples were collected from the three distinct areas of the stack, each weighing approximately 15 kg and stored at room temperature.



**Figure 2.** The location of the former Wizów Chemical Plant.

### 2.2. Preparation of PG Samples for Chemical Analysis

The quartering method was employed to obtain a 2 kg laboratory representative PG sample from an initial 15 kg field sample. Portions of approximately 120 mg were taken from the pre-treated sub-samples for chemical analysis. Dissolution was carried out with a mixture of concentrated  $\text{HNO}_3$  (6 mL) and HF (2 mL) using a microwave digestion system for about 2 h. The obtained solutions were then evaporated to dryness. The residue was afterwards dissolved in 12 mL of 4%  $\text{H}_3\text{BO}_3$  acid to complex the excess of fluorides. In mineralization methodology,  $\text{HNO}_3$  oxidizes organic material and solubilizes metals, while HF dissolves silicate minerals by breaking down silicon compounds.  $\text{H}_3\text{BO}_3$  is added after digestion to complex excess fluoride ions from HF, preventing precipitation of metal fluorides and ensuring accurate elemental analysis in the final solution. After cooling, the solution was diluted with distilled water to a volume of 50 mL.

### 2.3. Physical Characteristic Analysis

The color of PG was determined using the RAL color standard chart, and the texture state was determined through surface finger feel and observing whether the PG forms clumps or aggregates. The samples were further subjected to sieving methods to determine the particle size distribution. Dried PG (in a desiccator for 72 h) was passed through a stack of sieves with progressively smaller openings, with the final fraction passing through the 0.02 mm sieve. The sample was dried in an oven at a specific temperature (usually around  $110 \pm 5^\circ\text{C}$ ) until a constant weight was achieved (Method standard—ASTM D2216-19) [30].

### 2.4. Pre-Wash Treatment of Wizów's PG

The pre-wash treatment of the PG sample involved mixing the sample with 15 mL of a 20%  $\text{Na}_2\text{SO}_4$  solution for 5 min. This mixture was then placed in a water bath maintained at  $70^\circ\text{C}$ . After heating, the mixture was filtered to separate the liquid from the solid residue. Pre-treatment with  $\text{Na}_2\text{SO}_4$  was used to increase sulfate ions, remove/reduce soluble impurities (organic, phosphates, and fluoride compounds), stabilize pH, improve leaching kinetics for rare earth elements, and ultimately enhance the efficiency and purity of the

leaching process. The solid residue obtained from this process was then proceeded to the leaching stage [31].

### 2.5. Leaching Process

Sulphuric acid ( $\text{H}_2\text{SO}_4$ ) was used as the leaching agent at different concentrations. The experiments were conducted at 25 °C and 60 °C for various particle sizes. Some samples had reducing (Zinc) and oxidizing agents ( $\text{H}_2\text{O}_2$ ) added during the leaching process, while others were leached without these additional agents. Other conditions were constant, such as a solid-to-liquid ratio of 1:8, agitation speed of 600 rpm and a contact time of 4 h. The leaching solution was filtered and diluted with distilled water to a volume of 50 mL. In this study, reproducibility and repeatability were evaluated through leaching experiments conducted in sextuplicate across various time intervals. ICP-MS (Inductively Coupled Plasma Mass Spectrometry) analytical technique was used to determine the metal content in the solution after leaching and in the initial raw sample, which was prepared as described above. In this analytical technique, the mass concentration of metals can be measured directly in the obtained solutions without requiring chemical separation. The percentage leaching recovery of the REEs was determined according to Equation (1):

$$\% \text{Leaching Recovery of REE} = \left( \frac{\text{mREEs leachate (g)}}{\text{mREEs concentrate (g)}} \right) \times 100 \quad (1)$$

where mREE leachate is the final concentration after the leaching process, and mREE concentrate is the initial concentration of the raw sample.

For each REE, the concentrations were summed across all samples, then divided by the number of samples to get the average REE.

$$\% \text{Average concentration of element} = \frac{\sum \text{concentration of element in each sample}}{\text{Number of samples}} \quad (2)$$

For Total Average REE concentration, the averages of all individual REEs were summed, as shown in Equation (3):

$$\text{Total average REEs} = \frac{\sum \text{concentration of all REEs in each sample}}{\text{Number of samples}} \quad (3)$$

The ICP-MS measurement was based on the following isotopes:  $^{45}\text{Sc}$ ,  $^{89}\text{Y}$ ,  $^{139}\text{La}$ ,  $^{140}\text{Ce}$ ,  $^{141}\text{Pr}$ ,  $^{142}\text{Nd}$ ,  $^{152}\text{Sm}$ ,  $^{153}\text{Eu}$ ,  $^{158}\text{Gd}$ ,  $^{159}\text{Tb}$ ,  $^{164}\text{Dy}$ ,  $^{165}\text{Ho}$ ,  $^{166}\text{Er}$ ,  $^{169}\text{Tm}$ ,  $^{174}\text{Yb}$ ,  $^{175}\text{Lu}$ ,  $^{60}\text{Ni}$ ,  $^{57}\text{Fe}$ ,  $^{98}\text{Mo}$ ,  $^{51}\text{V}$ ,  $^{55}\text{Mn}$ ,  $^{63}\text{Cu}$ , and  $^{59}\text{Co}$ . Indium was applied as an internal standard with a five ng/mL concentration. The applied instrument operation parameters were as follows: RF power 1050 W, lens voltage 5.75 V, and a crossflow nebulizer with Scott double-pass spray chamber and Ni cones were employed.

## 3. Results and Discussion

### 3.1. Physico-Chemical Characterization of the Investigated Material

Wizów's PG is characterized by its grey-white color, dampness, and powdery form. The PG contains 50–75% of particles finer than 0.08 mm, as shown in Table 1, with a moisture content of approximately 11%.

An analysis of the PG sample taken from Wizów stacks yielded a range of elemental concentrations in parts per million (ppm), as shown in Table 2. Chemical analysis by ICP-MS showed that all the REEs that were present, and Ba, Ce, La, Nd, Pr, and Sm, were found to have relatively high concentrations. The content of Total REEs (TREEs) was around 200 mg/kg (0.02 wt%) [32].

**Table 1.** The distribution of particle sizes in different size fractions.

| Sieve Fractions       |                            |           |                             |
|-----------------------|----------------------------|-----------|-----------------------------|
| Sieve Size Range (μM) | Nominal Aperture Size (μM) | Wt (g)    | Percentage of Particles (%) |
| 800–630               | 630                        | 50–250    | 1–5                         |
| 630–400               | 400                        | 250–500   | 5–10                        |
| 400–200               | 200                        | 500–1250  | 10–25                       |
| ≤200                  |                            | 2500–3750 | 50–75                       |
| Total                 |                            | 5000      |                             |

**Table 2.** Typical element concentration ranges (mg/kg) of different elements in Wizów’s PG.

| Heavy Rare Earth Elements (HREEs) [mg/kg] |                   |                   |                   |                   |                  |                   |                 |
|-------------------------------------------|-------------------|-------------------|-------------------|-------------------|------------------|-------------------|-----------------|
| Dy<br>41.92–45.9                          | Tb<br>10.23–11.23 | Er<br>15.45–16.95 | Tm<br>1.21–1.32   | Yb<br>5.46–5.99   | Ho<br>6.26–6.87  | Gd<br>117.2–128.6 | Lu<br>0.54–0.61 |
| Light Rare Earth Elements (LREEs) [mg/kg] |                   |                   |                   |                   |                  |                   |                 |
| La<br>1408–1545                           | Ce<br>2036–2234   | Pr<br>220.0–220.5 | Nd<br>685.9–752.5 | Eu<br>26.98–29.58 | Sm<br>97.4–106.8 | Pm<br>n.d.        |                 |
| Scandium and Yttrium [mg/kg]              |                   |                   |                   |                   |                  |                   |                 |
|                                           | Sc<br>n.d.        |                   |                   |                   | Y<br>n.d.        |                   |                 |
| Other Elements [mg/kg]                    |                   |                   |                   |                   |                  |                   |                 |
| Ag<br>0.16–0.67                           | As<br>4.76–5.23   | Ba<br>476.3–522.5 | Be<br>0.27–0.31   | Cd<br>0.06–0.08   | Co<br>3.35–3.69  |                   |                 |
| Cu<br>19.77–21.69                         | Fe<br>1024–1124   | Mn<br>22.96–25.18 | Mo<br>2.14–2.36   | Ni<br>12.54–13.75 | Pb<br>3.36–3.72  |                   |                 |
| Sb<br>0.12–0.15                           | Se<br>6.46–7.10   | Th<br>9.92–10.88  | Tl<br>0.01–0.02   | U<br>0.67–0.72    | V<br>12.27–13.46 | Zn<br>14.57–15.99 |                 |

Note: n.d. = not detected.

Table 3 presents the chemical composition of phosphogypsum (PG) from Wizów, Poland, the findings in Grabas’ research [19]. The sample analysis reveals key components like P (0.42 mg P kg<sup>−1</sup> total, 0.17 mg P kg<sup>−1</sup> available), K (0.041%), Na (0.101%), and F (0.34%). Major constituents include CaO (29.1%) and SO<sub>3</sub> (42.11%). Additionally, trace elements like Sr (1.45%) and Cu (61.05 mg kg<sup>−1</sup>) are detected, alongside rare earth elements (REEs) such as La (0.1247%) and Ce (0.1890%). These results were derived from methodologies including AAS, ICP-AES, ICP-OES, ICP-MS, and X-ray fluorescence, based on PS 2001 procedures.

**Table 3.** The composition of apatite PG samples from Wizów.

| Component                      | Unit                   | Raw PG |
|--------------------------------|------------------------|--------|
| P total                        | mg P kg <sup>−1</sup>  | 0.42   |
| P available                    | mg P kg <sup>−1</sup>  | 0.17   |
| K                              | mass%                  | 0.041  |
| Na                             | mass%                  | 0.101  |
| F                              | mass%                  | 0.34   |
| CaO                            | mass%                  | 29.1   |
| SO <sub>3</sub>                | mass%                  | 42.11  |
| Al <sub>2</sub> O <sub>3</sub> | mass%                  | 0.21   |
| Fe <sub>2</sub> O <sub>3</sub> | mass%                  | 0.093  |
| SiO <sub>2</sub>               | mass%                  | 0.5    |
| Sr                             | mass%                  | 1.450  |
| Cu                             | mg Cu kg <sup>−1</sup> | 61.05  |
| Zn                             | mg Zn kg <sup>−1</sup> | 9.4    |
| Ni                             | mg Ni kg <sup>−1</sup> | 1.5    |

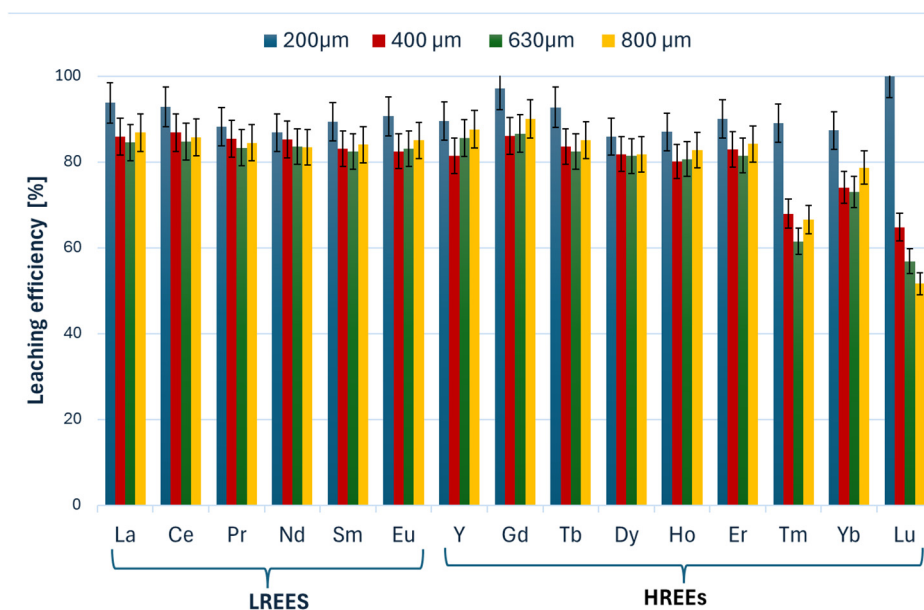
Table 3. Cont.

| Component | Unit     | Raw PG |
|-----------|----------|--------|
| Ba        | mass%    | 0.0    |
| REE       | mass% Ln | 0.4398 |
| La        | mass%    | 0.1247 |
| Ce        | mass%    | 0.1890 |
| Pr        | mass%    | 0.0324 |
| Nd        | mass%    | 0.0595 |
| Y         | mass%    | 0.0192 |
| Sm        | mass%    | 0.0051 |
| Gd        | mass%    | 0.0048 |
| Dy        | mass%    | 0.0022 |
| Eu        | mass%    | 0.0023 |
| Er        | mass%    | 0.0004 |

### 3.2. Effects of Experimental Conditions on REEs Recovery

#### 3.2.1. Effect of Particle Size

Figure 3 shows the leaching efficiencies of different elements using 2 M H<sub>2</sub>SO<sub>4</sub>, indicating that the TREEs leaching efficiencies slightly decreased with increasing particle sizes. Notably, the highest average leaching efficiency of 91% was observed for REEs with a particle size of  $\leq 200$   $\mu\text{m}$ . In the other experiments, the leaching efficiency tends to decrease, with values of 81% for particles sizes of 201–400  $\mu\text{m}$ , 80% for 401–630  $\mu\text{m}$  and 81% for 631–800  $\mu\text{m}$ , respectively.

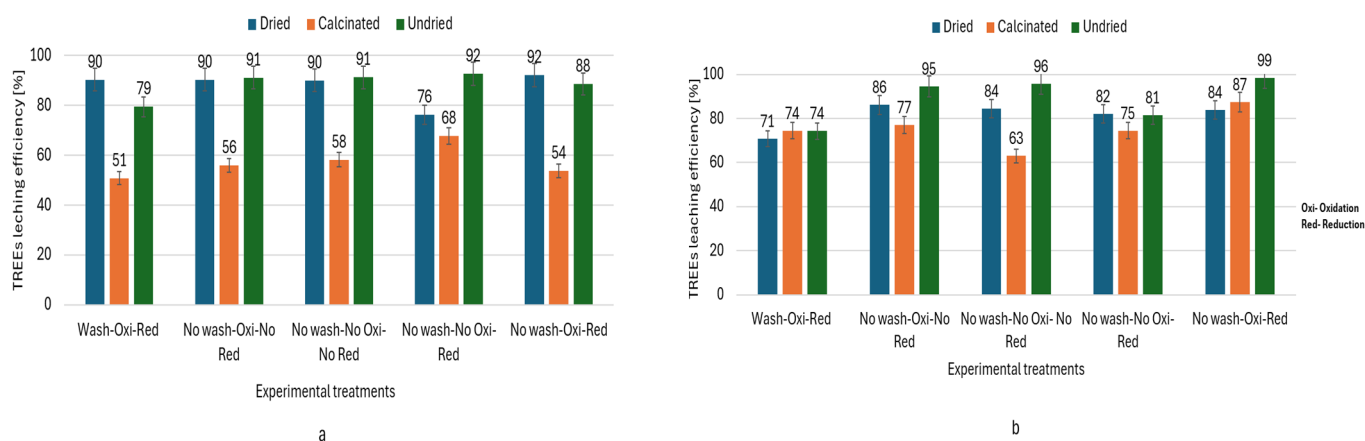


**Figure 3.** The REE recovery from undried PG leaching of different particle sizes 200  $\mu\text{m}$ , 201–400  $\mu\text{m}$ , 401–630  $\mu\text{m}$ , and 631–800  $\mu\text{m}$  using 2 M H<sub>2</sub>SO<sub>4</sub> at 25 °C (stirring rate: 600 rpm, contact time: 4 h, solid/liquid ratio: 1:8).

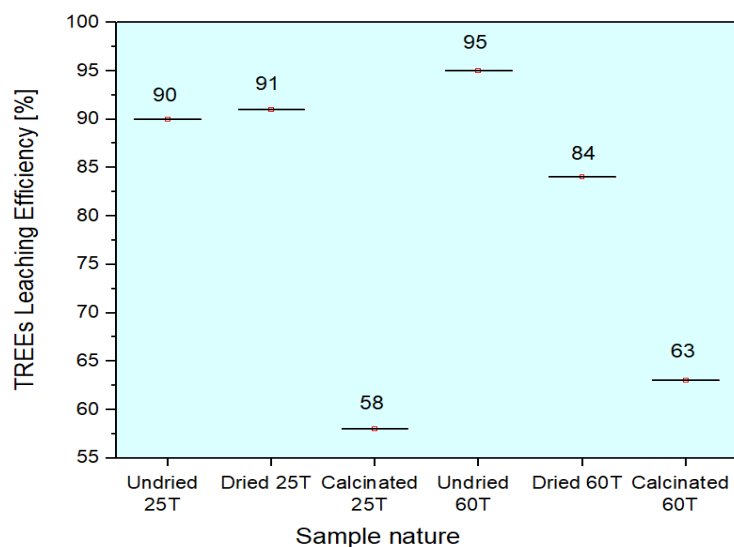
Comparing specific REEs, there are variations in leaching efficiencies across different particle sizes. For instance, for Yb, the leaching efficiency decreases from 87% for particles of  $\geq 200$   $\mu\text{m}$  to 74% for particles of 201–400  $\mu\text{m}$ , 73% for 401–630  $\mu\text{m}$ , and 79% for 630–800  $\mu\text{m}$ . Similarly, Lu shows a significant decrease in leaching efficiency as particle size increases, with values dropping from 100% for particles of  $\geq 200$   $\mu\text{m}$  to 65% for particles of 201–400  $\mu\text{m}$ , 57% for 401–630  $\mu\text{m}$ , and 52% for 631–800  $\mu\text{m}$ . When the PG is finely ground to less than 200  $\mu\text{m}$  particle size, it improves the average leaching efficiency by more than 10%.

### 3.2.2. Effects of Temperature

The effect of temperature on the leaching efficiencies of TREEs from Wizów's PG was investigated across 25 °C as well as 60 °C and is shown in Figure 4. The leaching efficiency results under various treatment conditions, including washing and adding oxidant or reductant reagent, are shown in Figure 5. The leaching efficiency was slightly higher at 60 °C with an average of 82% compared to 25 °C with an average of 78% in different pre-treatment conditions. The increase in temperature enhances REE dissolution efficiency by accelerating chemical reaction rates, improving mass transfer, and enhancing the interaction between the leaching agent and the sample, leading to higher leaching efficiency. This difference suggests that higher temperatures slightly promote leaching efficiency. Higher temperatures do not, however, significantly enhance the solubility of the target elements.



**Figure 4.** The effect of temperature (a) 25 °C and (b) 60 °C on TREEs recovery from PG (solid/liquid: 1:8, stirring at 600 rpm, particle size:  $\leq 200 \mu\text{m}$ ; stirring: 600 rpm, contact time: 4 h, 2 M  $\text{H}_2\text{SO}_4$ ).



**Figure 5.** The influence of PG pre-processing (not drying, drying, calcination) on the leaching efficiency at 25 °C (25 T) and 60 °C (60 T), solid/liquid: 1:8, stirring rate: 600 rpm, particle size:  $\leq 200 \mu\text{m}$ , contact time: 4 h, 2 M  $\text{H}_2\text{SO}_4$ .

### 3.2.3. Influence of Sample Drying

The pre-processing of the PG (drying, not drying, or calcination) influences the leaching efficiencies. Figure 5 indicates that pre-drying the sample slightly promotes the leaching of TREEs. The leaching efficiency of undried PG at 60 °C was 11% higher than the leaching efficiency of the dried PG sample, which reached an average leaching efficiency of 95% at the same temperature. The calcinated PG sample achieved leaching efficiencies of 58%

and 63% at 25 °C and 60 °C, respectively (Figure 5). The values are significantly lower compared to dried and undried samples. The results demonstrate that calcination hinders the leaching of REEs. The process probably induces chemical changes in the PG, potentially altering its composition and structure, especially at high temperatures, which may have reduced the accessibility of target elements for leaching agents.

### 3.2.4. Effects of Oxidant and Reductant Agents

The leaching efficiency of PG under different conditions of temperature (25 °C and 60 °C) and experimental treatments (oxidation, reduction, washing) has a slight influence on the leaching efficiencies of Wizów's PG (Figure 5). At 25 °C, dried samples exhibit consistent efficiencies across treatments, with the highest leaching efficiency with the addition of both oxidant and reductant without the pre-washing process (92%). Calcined samples show lower and more variable efficiencies (51–68%), while undried samples perform well across experimental treatments (79–92%). At 60 °C, dried samples demonstrate increased efficiency, particularly in no wash and with oxidant and reductant treatments having the overall highest leaching efficiency of 97%, indicating temperature sensitivity. Calcined samples show mixed results (up to 87%), while undried samples consistently perform strongly (up to 97%). Oxidation and reduction enhance leaching, notably without washing, which tends to decrease efficiencies across temperatures. The experiments show that the leaching efficiency of undried sample treatments in comparison with the sample with experiment treatments has a slightly higher leaching efficiency of 2%. Adding an oxidation agent to the reaction mixture may have facilitated the dissolution of targeted elements, slightly improving leaching efficiencies; however, there's no relevant significance in using treatments at elevated temperatures. Therefore, the inclusion of oxidizing and reducing agents in leaching processes has a low impact on leaching REEs recovery from Wizów's PG.

### 3.2.5. Impact of Washing Process Step

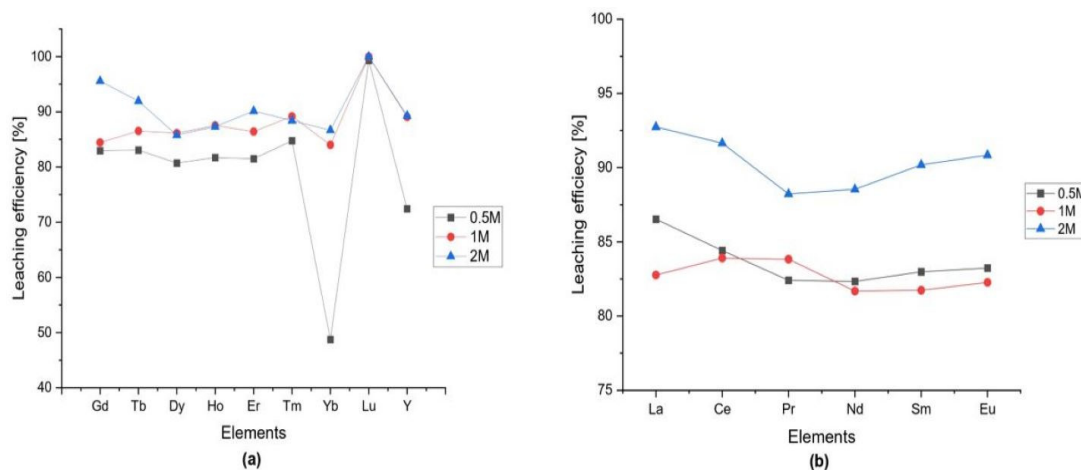
The washing process step with 20% Na<sub>2</sub>SO<sub>4</sub> caused a decrease in leaching efficiency to 73%, as indicated in Figure 5. Sodium sulfate in the washing solution could precipitate onto the sample surface, forming a barrier that hindered the interaction between the leaching solution and target elements. Additionally, sodium and sulfate ions from Na<sub>2</sub>SO<sub>4</sub> competed with target elements for binding sites, reducing their dissolution. pH alterations caused by Na<sub>2</sub>SO<sub>4</sub> could further reduce solubility, while residual salt residues may have obstructed leaching solution access to target elements. These combined effects decreased leaching efficiency compared to leaching without pre-washing PG.

### 3.3. Effect of H<sub>2</sub>SO<sub>4</sub> Concentration on REEs Recovery

The leaching efficiency results of both HREEs and LREEs from Wizów's PG using sulfuric acid solutions of varying concentrations (0.5 M, 1 M, and 2 M) are shown graphically in Figure 6. The figure illustrates the effect of the sulfuric acid concentration on the leaching efficiency for each REE. A concentration of 2 M reached the highest leaching efficiency of 90%, with 86% and 81% for 1 M and 0.5 M H<sub>2</sub>SO<sub>4</sub>, respectively. Results revealed that increasing concentrations of sulfuric acid led to slightly improved leaching efficiency of both HREEs and LREEs.

As Figure 6 shows, the leaching efficiencies of HREEs and LREEs slightly increased with increases in the concentration of sulfuric acid: 79%, 88%, 90%, and 84%, 83%, 91% at 0.5 M, 1 M and 2 M, respectively. The lower dissolving efficiency of some LREEs (La, Nd, Sm, Eu) at 1 M H<sub>2</sub>SO<sub>4</sub> compared to 0.5 M can be due to oversaturation and the common-ion effect. Pr likely had higher leaching efficiency in 1 M H<sub>2</sub>SO<sub>4</sub> than other light rare earth elements (LREEs) due to its greater solubility under slightly stronger acidic conditions, and other LREEs may experience decreased solubility due to stronger complexation or precipitation reducing the solubility of LREE–sulfate complexes, thus limiting further leaching. The higher dissolving efficiency of Nd, Sm, Eu, and La in 2 M H<sub>2</sub>SO<sub>4</sub> compared to 1 M can be explained by the increased proton activity at higher acid concentrations. In 2 M

H<sub>2</sub>SO<sub>4</sub>, the enhanced acidity breaks down the phosphogypsum structure more effectively, overcoming the common-ion effect and gypsum precipitation seen at 1 M. The high increase in LREEs leaching efficiency from lower concentrations to higher concentrations can be attributed to the high solubility of LREEs(OH)<sub>3</sub> in strong acids [33]. For HREEs, the increase in leaching efficiency became less significant at higher acid concentrations. Ytterbium (Yb) likely had lower leaching efficiency due to its specific chemical behavior or complexation in the phosphogypsum matrix, making it less reactive with sulfuric acid compared to other heavy rare earth elements (HREEs), even at higher acid concentrations.



**Figure 6.** An illustration of the effect of sulphuric acid concentration on leaching efficiency for (a) HREE and (b) LREE from examined PG (Temperature: 25 °C, solid/liquid: 1:8, stirring rate: 600 rpm, particle size: ≤200 µm, contact time: 4 h).

### 3.4. Statistical Overview of Leaching Efficiency

Statistical analyses were performed to assess leaching efficiency, including mean, standard deviation (SD), and margin of error (CI), which was approximately 2.65–3.11% and 2.80%, resulting in 95% confidence intervals (CI). The arithmetic mean was initially calculated by summing all five measurements and dividing by the total number, providing a central value for each dataset. Following this, the standard deviation was determined to assess the variability of the measurements around the mean, involving the calculation of squared differences from the mean, their summation, division by the number of measurements minus one, and finally, taking the square root. The relative standard deviation (RSD) was calculated to evaluate precision as a percentage of the mean. Outlier detection methods were employed to identify measurements that deviated significantly from the mean, ensuring data integrity. Replicate tests ensured reproducibility, while ANOVA evaluated differences between sample treatments. Additionally, correlation coefficients validated relationships among variables, assuring accuracy and reliability in the results obtained from the leaching experiments.

### 3.5. Overall Assessment of the Potential of Wizów's PG as a Source of REE

Kulczycka et al. [8] presented the assessment of the economic and environmental aspects of the implementation of REE recovery technology from Wizów's PG compared to the continuation of landfilling the phosphogypsum in an unchanged state performed using the Life Cycle Assessment (LCA) method. The result showed that the storage of PG has much less of an impact on the environment than processing technology for the recovery of REE. Despite that, the technology implementation can be cost-effective but demands high investment and can also be risky because it was not tested earlier. The current cost of energy has a significant impact on the assessment of the proposed technology. Currently, we can observe intensive studies of new industrial energy sources, e.g., Small Modular Reactors (SMRs) [34], which are expected to decrease energy prices in the future. Additionally, the model did not consider the additional advantages such as gradual reduction and, finally,

the elimination of the heaps. The next step can result in the no-waste process of phosphoric acid production, which is fully included in the assumptions of the circular economy.

Moreover, it is necessary to note that the development of electronic and electric industries causes continuously increasing demands for REEs. The recovery of REE from PG could be found much more profitable in the future. Wizów's PG is characterized by quite a high concentration of REEs if compared to other PG examined worldwide. This material is very easy to process, which is what we showed in our experiments. It was demonstrated that even 0.5 M sulfuric acid allows for the recovery of more than 80% of lanthanides, which is a slightly higher yield than the one assumed to the LCA assessment: 50% recovery of lanthanides with leaching with 1.8 M sulfuric acid. In the study by Yongrui Wang et al., PG can be repurposed as a critical ingredient in geopolymers, offering a sustainable alternative to traditional Portland cement. With this research, PG residue, when properly treated, can effectively be reused in geopolymers, reducing environmental waste while providing a robust construction material [35].

#### 4. Conclusions

This study determined the optimal experimental conditions of the leaching method for extracting rare earth elements (REEs) with sulfuric acid from PG sourced from the former Wizów Chemical Plant in Poland. The research investigated various leaching parameters and sample conditions. The results showed the most effective conditions: employing 2 M  $\text{H}_2\text{SO}_4$ , utilizing undried, finely ground particles ( $\leq 200 \mu\text{m}$ ), and maintaining a temperature of 60 °C. The leaching efficiencies reached 92%. It is worth noting that drying or calcinating the Wizów PG sample or introducing oxidant and reductant agents marginally enhances REE leaching recovery.

The use of oxidant and reductant agents did not significantly increase the leaching efficiency. Moreover, decreasing the temperature to 25 °C causes a decrease in the yield of recovery of REE only by about 5%. The benefits of higher REE recovery are of minimal economic importance compared to the additional costs incurred as a result of these steps. Notably, a one-step leaching approach with  $\text{H}_2\text{SO}_4$  demonstrates commendable REE leaching efficiency.

However, the acid consumption is typically high. To enhance its economic viability, 1 M or 0.5 M  $\text{H}_2\text{SO}_4$  is recommended. The efficiencies of leaching were 86% and 81%, respectively. The PG from the former Wizów Chemical Plant in Poland contains significant amounts of REEs and is easily leachable. It can be considered a potential source of these valuable and important metals for the EU economy. The studies focused on solid–liquid extraction, and as a result, a mixture of various REE and other metals present in PG was obtained. Further research will be necessary to explore the separation of individual metals, one of the biggest challenges in hydrometallurgy. More research approaches should be conducted on recovering REEs from the pregnant leach solution (PLS).

This research holds significant importance in environmental management strategies concerning PG. By improving efficient REE extraction methods from this byproduct, the study contributes to mitigating environmental risks associated with PG disposal while simultaneously tapping into its potential as a valuable REE resource.

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