Issue VIII, 22 November 2025
e-ISSN 2707-9481 Institute of Metallurgy and Ore Beneficiation JSC, Satbayev University, Almaty, Kazakhstan
ISBN978-601-323-547-9 https://doi.org/10.31643/2025.12

Azamat Yessengaziyev
Institute of Metallurgy and Ore Beneficiation JSC,
Satbayev University
050010, Shevchenko str., 29/133, Almaty, Kazakhstan.
E-mail: a.yessengaziyev@satbayev.university
ORCID ID: https://orcid.org/0000-0002-4989-4119

Bauyrzhan Orynbayev
Laboratory of Metallurgical Processing of Materials,
Aktobe Regional University Named After K. Zhubanov,
Aktobe 030000, Kazakhstan.
E-mail: Bauyrzhan.Orynbayev@stud.satbayev.university
ORCID ID: https://orcid.org/0000-0002-7730-9060

Zaure Karshyga
Institute of Metallurgy and Ore Beneficiation JSC,
Satbayev University
050010, Shevchenko str., 29/133, Almaty, Kazakhstan.
E-mail: z.karshyga@satbayev.university
ORCID ID: https://orcid.org/0000-0002-3025-7363

Aisha Tastanova
Institute of Metallurgy and Ore Beneficiation JSC,
Satbayev University
050010, Shevchenko str., 29/133, Almaty, Kazakhstan.
E-mail: aisha.tastanova@stud.satbayev.university
ORCID ID: https://orcid.org/0000-0003-1953-8938

Talgat Arynbayev
Institute of Metallurgy and Ore Beneficiation JSC,
Satbayev University
050010, Shevchenko str., 29/133, Almaty, Kazakhstan
E-mail: arynbayev.talgat@mail.ru
ORCID ID: https://orcid.org/0009-0006-5895-6779

Enhancing the Efficiency of Rare Earth Element Recovery from Phosphogypsum by Counter-Current Hydrochloric Acid Leaching

Abstract. This paper examines a three-stage countercurrent hydrochloric acid leaching of phosphogypsum to enhance the recovery of rare earth elements while simultaneously producing a technologically valuable gypsum product. The phosphogypsum under study has a ΣREE content of 340.53 g/t and consists primarily of $CaSO_4 \cdot 2H_2O$ dihydrate with minor silicate and phosphate impurities. The countercurrent leaching process is shown to ensure efficient reagent distribution and profound destruction of the gypsum matrix. At a solid: liquid ratio of 1:10, the overall recovery of rare earth elements reaches 88%, while at a solid: liquid ratio of 1:4, it is 82.4%, accompanied by a threefold increase in the ΣREE concentration in the productive solutions. X-ray phase analysis of the residue confirmed that complete removal of calcium sulfate from the solid phase is achieved at a solid-liquid ratio of 1:10, while at a solid-liquid ratio of 1:4, some sulfate phases are retained. The precipitate that forms during cooling of the solution is represented by $CaSO_4 \cdot 2H_2O$ and is successfully converted by heat treatment (165°C, 4 h) into the hemihydrate form $CaSO_4 \cdot 0.5H_2O$. The strength of the obtained material (5.1 MPa) corresponds to that of G5 gypsum binder. The obtained results demonstrate the effectiveness of three-stage countercurrent leaching and confirm the possibility of comprehensive processing of phosphogypsum, which ensures the production of productive solutions suitable for further sorption or extraction enrichment of rare earth elements, as well as a gypsum residue that meets the requirements of the construction industry.

Keywords: phosphogypsum, rare earth elements, hydrochloric acid leaching, extraction, gypsum binder, phase composition, solution.

Introduction

Rare earth elements (REEs) are critical metals that support the development of high-tech industries such as the production of permanent magnets, electric motors, batteries, optoelectronics, laser systems, and catalytic materials. Global demand for neodymium, praseodymium, and heavy lanthanides has been increasing annually in recent years, increasing the need to develop a sustainable mineral resource base. Given the limited availability of traditional deposits, interest in man-made sources of rare earth metals is growing, with phosphogypsum considered one of the largest and most promising sources for processing (Cuadros-Muñoz et al., 2024; Leal Filho et al., 2023).

Globally, the annual production volume of phosphogypsum exceeds 200–300 million tons, and total man-made accumulations reach 7–9 billion tons (Mukaba et al., 2021; Mashifana, 2019; Yang et al., 2024). No more than 10–15% of the material is processed, while the bulk is stored in waste dumps, forming environmentally hazardous man-made waste containing fluorine, sulfates, residual phosphates, heavy metals, and natural radionuclides (Maina et al., 2025; Men et al., 2022).

The formation of phosphogypsum occurs during the decomposition of apatite raw materials with sulfuric acid at a temperature of about 80 °C. The chemical processing of $Ca_5(PO_4)_3F$ using H_2SO_4 is known as the extraction method for the production of phosphoric acid and is described by the equation:

$$\begin{gathered}Ca_5(PO_4)_3F \text{ (solid, 100\% REE)} + 5H_2SO_4 \text{ (aq)} + nH_2O \text{ (aq)} \rightarrow \\ H_3PO_4 \text{ (aq, 20–30\% REE)} + CaSO_4\cdot nH_2O \text{ (solid, 70–80\% REE)} + HF \text{ (aq)}\end{gathered} \tag{1}$$

During the production of wet-process phosphoric acid, a by-product is calcium sulfate dihydrate ($CaSO_4\cdot 2H_2O$). Depending on the process conditions – temperature, sulfuric acid concentration, solid-to-liquid ratio, and holding time – other modifications of calcium sulfate may also form: hemihydrate ($CaSO_4\cdot 0.5H_2O$) or anhydrite ($CaSO_4$). The majority of the rare earth elements contained in the original phosphate raw material accumulate in the resulting solid phases – approximately 70–80%. The remaining 20–30% are converted into wet-process phosphoric acid, being distributed between the liquid and solid phases depending on their chemical forms and solubility (Hammas-Nasri et al., 2016). Gaseous fluorine is also released, which is captured and converted into fluorine-containing products. Technologically, the processing of 1 ton of phosphate raw material requires approximately 0.6 tons of concentrated sulfuric acid, which leads to the formation of approximately 1.2 tons of phosphogypsum (van Selst et al., 1997; Bilal et al., 2023). It is this stoichiometric balance that determines the colossal volumes of annual accumulation of phosphogypsum and its dominant contribution to the global flow of man-made mineral waste.

Typical ΣREE contents in phosphogypsum vary from 200–500 mg/kg for phosphate raw materials to 1500–2500 mg/kg for apatite phosphogypsum (Cánovas et al., 2019; Kurkinen et al., 2021). REE are present both in an isomorphously included state in the crystal lattice of $CaSO_4\cdot 2H_2O/0.5H_2O$ and in the form of microdispersed phosphate and fluorine-containing phases. The complex phase nature of the inclusions significantly complicates the extraction of REE and requires the use of hydrometallurgical processes aimed at the destruction or rearrangement of the $CaSO_4$ structure and the selective transfer of lanthanides into solution (Kirillov et al., 2021).

Existing studies show that phosphogypsum processing can be carried out using various methods, the most common of which are acid, alkaline and conversion leaching. The processes of phosphogypsum dissolution using HCl, HNO_3, and H_2SO_4, which ensure the destruction of phosphate-fluoride microphases and the transfer of rare earth elements into solution, have been studied in most detail (Lütke et al., 2022; Dong et al., 2025; Guan et al., 2022). In addition to acid methods, alkaline and conversion approaches occupy an important place, where, for example, Na_2CO_3 is used for the preliminary decomposition of $CaSO_4$ and the transfer of the system to a more reactive state, which subsequently increases the efficiency of acidic dissolution (Gasser et al., 2022). Conversion methods based on the conversion of $CaSO_4$ to CaS with subsequent extraction of REE are discussed in detail in Nsaka Ntumba et al., 2023.

The issue of phosphogypsum processing is of particular importance for Kazakhstan. The country's largest man-made phosphogypsum deposits have been created at the Kazphosphate LLC enterprise in the Zhambyl region. According to the state news agency Kazinform (News Agency), in the immediate vicinity of the city of Taraz, there are two operating waste dumps with a total capacity of more than 16 million tons, and the total volume of previously formed deposits exceeds 36 million tons. In addition, a project for the construction of a third waste dump with a capacity of 20 million tons has been approved. The scale of these accumulations is causing serious concern among the population and environmental organizations, since the long-term storage of phosphogypsum negatively affects groundwater, soil, and the sanitary and hygienic condition of the territory, which has been repeatedly noted by the Ministry of Ecology and the deputy corps.

In the face of increasing environmental pressure, issues of managing phosphogypsum accumulations and returning its components to economic circulation are particularly pressing. Large-scale man-made phosphogypsum waste dumps pose environmental risks, but they also represent a potential source of valuable resources. Of particular interest from the perspective of industrial applications and scientific research is the possibility of extracting rare earth elements concentrated in phosphogypsum, as well as using this material in the production of construction and technological products.

The compounds formed during acid processing, such as calcium sulfate dihydrate, have the potential for further use as secondary raw materials in the production of gypsum binders and other materials, which is in line with the principles of resource conservation. The implementation of such projects allows us to simultaneously address environmental issues, improve resource efficiency in production, and create new raw material flows for the metallurgical and construction industries, especially in regions with large technogenic accumulations.

For the practical implementation of phosphogypsum processing approaches, it is important to study its behavior under acidic dissolution conditions, evaluate the release of rare earth elements into solution, and assess changes in the phase composition of the solid phase. The objective of this study is to conduct hydrochloric acid leaching experiments to release rare earth elements into solution and produce a solid product suitable for use in the construction industry.

Materials and methods

Object of Study. The material investigated in this work was phosphogypsum generated as a by-product during the industrial production of wet-process phosphoric acid at the Kazphosphate LLC plant. Figure 1 presents a schematic material balance of the sulfuric acid decomposition of phosphate feedstock, illustrating the formation of wet-process phosphoric acid and phosphogypsum.

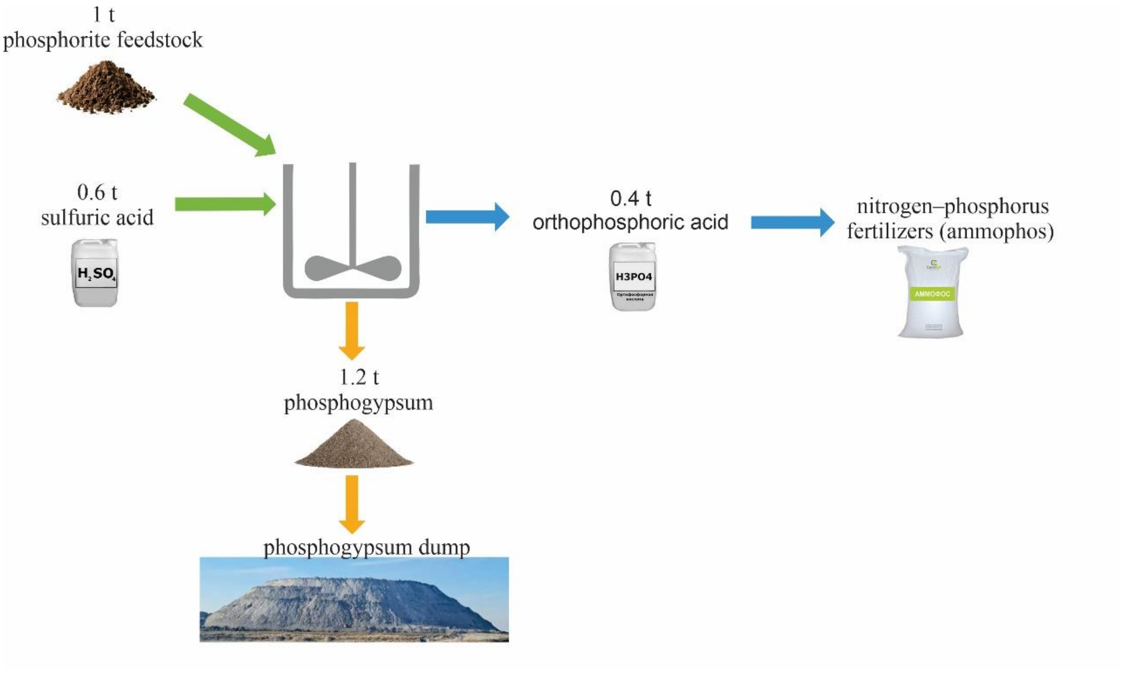


Figure 1. Sulfuric acid decomposition of phosphate feedstock during wet-process phosphoric acid production

Rare earth elements present in phosphogypsum may occur in several forms: (i) as isomorphic substitutions of Ca^{2+} within the crystal lattice of gypsum; (ii) as discrete mineral phases or inclusions such as monazite, xenotime, and residual apatite; and (iii) as ion-adsorbed species represented by secondary precipitates of REE salts (sulfates, carbonates, fluorides) deposited on the surface of gypsum particles (Figure

2). Thus, REEs in phosphogypsum are distributed among the crystal lattice, mineral impurities, and surface-associated formations (Khalil et al., 2025), which collectively determine their behavior during leaching and recovery.

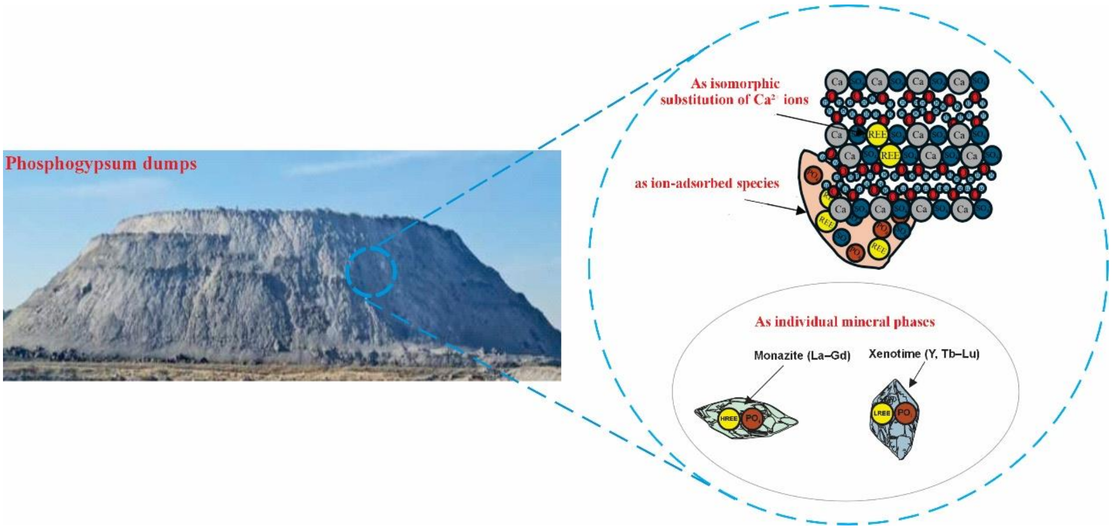


Figure 2. Forms of rare earth element distribution in phosphogypsum

Chemical analysis of the sample showed the following composition (wt.%): Ca – 14.9; Si – 2.9; Al – 0.26; Fe – 0.26; Mg – 0.07; P – 0.5. The total REE concentration is ΣREE = 340.53 g/t, including (g/t): Sc – 0.63; Y – 89; La – 70; Ce – 76; Pr – 12; Nd – 52; Sm – 10.2; Eu – 2.2; Gd – 9.9; Tb – 1.4; Dy – 8.5; Ho – 1.6; Er – 4.4; Tm – 0.5; Yb – 2; Lu – 0.2. Hydrochloric acid of analytical grade ("HCh") was used as the leaching reagent.

Equipment. The laboratory and analytical equipment used in this study included: Pyrex reactor beakers, a VELP Scientifica LS F201A0151 mechanical stirrer, a LOIP LT-100 circulating thermostat, a SNOL 7.2/1300 muffle furnace, a vacuum filtration system, AX1202013 analytical balances, a HANNA HI 2210-02 pH meter, an MIP-25R hydraulic press, a STA 449 F3 Jupiter thermal analyzer, Optima 8300DV ICP-OES and AA-7000 AAS spectrometers, a Bruker D8 ADVANCE XRD diffractometer, and a PANalytical Venus 200 XRF analyzer.

Experimental Procedure. A three-stage counter-current hydrochloric acid leaching scheme was implemented to increase the recovery of REEs and to obtain pregnant solutions with elevated ΣREE concentrations. The process was conducted under optimized conditions: temperature 80 °C, duration of each stage 0.5 h, HCl concentration 10%, sample mass 100 g, and solid-to-liquid ratios S:L = 1:10 and 1:4.

Phosphogypsum batch No. 1 was leached sequentially with three portions of solution, producing residue samples 1/1, 1/2, and 1/3 and their corresponding filtrates. Filtrates 1/2 and 1/3 were subsequently reused as process solutions for leaching phosphogypsum batch No. 2.

Processing of phosphogypsum No. 2 involved three stages: in Stage 1, the material was introduced into the heated filtrate 1/2 to obtain residue 2/1; in Stage 2, residue 2/1 was treated with filtrate 1/3, producing residue 2/2 and solution 2/2, the latter being forwarded to Stage 1 of PG No. 3; in Stage 3, residue 2/2 was leached with fresh acid to obtain residue 2/3 and solution 2/3, which was sent to Stage 2 of PG No. 3.

Phosphogypsum batch No. 3 was processed similarly: residue 3/1 was produced from solution 2/2 at Stage 1; residue 3/2 was formed using solution 2/3 at Stage 2; and the final products – residue 3/3 and filtrate 3/3 – were obtained during Stage 3. All solid and liquid samples from each step were subjected to subsequent chemical analysis.

Since the mass of the solid phase decreased from stage to stage, the S:L ratio was maintained constant by adjusting the solution volume. Despite the multistep configuration, the total acid consumption remained comparable to that of single-stage leaching, while the extraction efficiency increased due to the counter-current mode.

All pregnant leach solutions were cooled, resulting in the precipitation of calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) due to secondary crystallization. The precipitate was filtered, washed with distilled water, and dried at 60–80 °C. For the production of gypsum binders, the material was thermally treated at 145–165 °C for 3–4 h to convert it into the hemihydrate form. Cubic specimens (20x20x20 mm) were then prepared for compressive strength testing and XRD analysis, with results evaluated against the requirements for G4–G5 gypsum binders.

Main results and their discussion

Mineralogical composition of phosphogypsum. X-ray phase analysis revealed that the phosphogypsum sample was predominantly composed of the dihydrate form of gypsum, $CaSO_4 \cdot 2H_2O$. A quantitative assessment revealed a gypsum content of 87.5%, with quartz present as a minor phase at 12.5%. No other crystalline components were detected, confirming the homogeneity of the mineral composition and the predominance of calcium sulfate dihydrate (Figure 3).

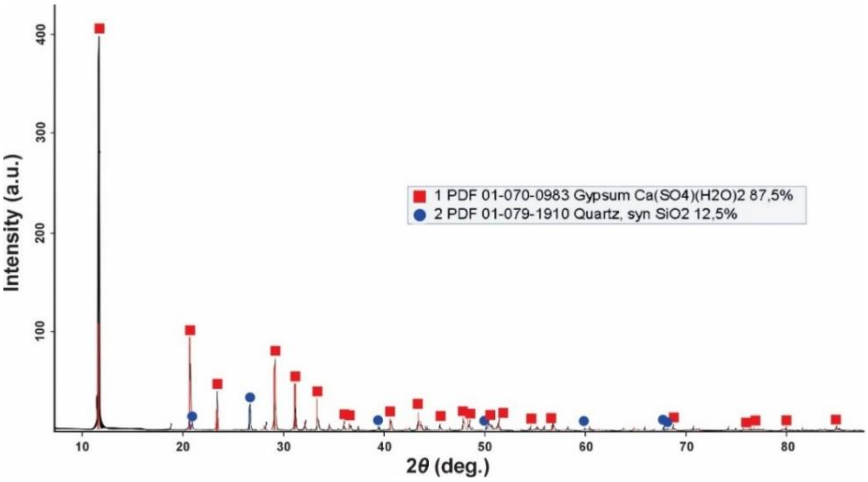


Figure 3. X-ray diffraction pattern of the phosphogypsum sample

Thermal analysis (Figure 4) exhibited transformations characteristic of calcium sulfate dihydrate. Two pronounced endothermic effects were recorded on the DTA curve at 196.1 °C and 225.2 °C, corresponding to the stepwise dehydration of $CaSO_4 \cdot 2H_2O$ with the formation of hemihydrate and anhydrite. The respective peaks on the dDTA curve appear at 165.7 °C and 217.7 °C, while the DTG curve shows mass-loss minima at 166.8 °C and 218.1 °C. An exothermic effect at 457.2 °C indicates structural rearrangement and the formation of insoluble anhydrite. In the high-temperature range, a weak endothermic anomaly near 791–794 °C is associated with minor impurities such as REE-bearing apatite and/or calcite, as well as the polymorphic transition $\beta\text{-}Sr_2P_2O_7 \rightarrow \alpha\text{-}Sr_2P_2O_7$. A faint exothermic peak at ~824.8 °C on the dDTA curve may correspond to the crystallization of a dehydrated phosphate phase of composition $YPO_4 \cdot H_3PO_4 \cdot 2H_2O$, typical for structural rearrangements in REE phosphates following the loss of bound water or phosphoric acid groups. The absence of a low-temperature dehydration peak confirms the low content of surface-bound water and the structural stability of the gypsum matrix.

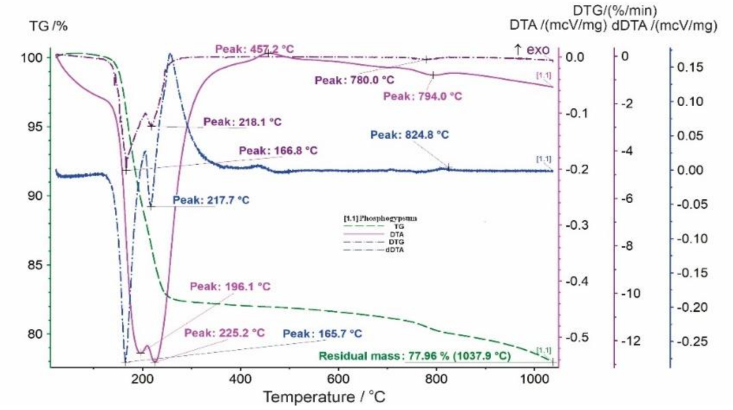
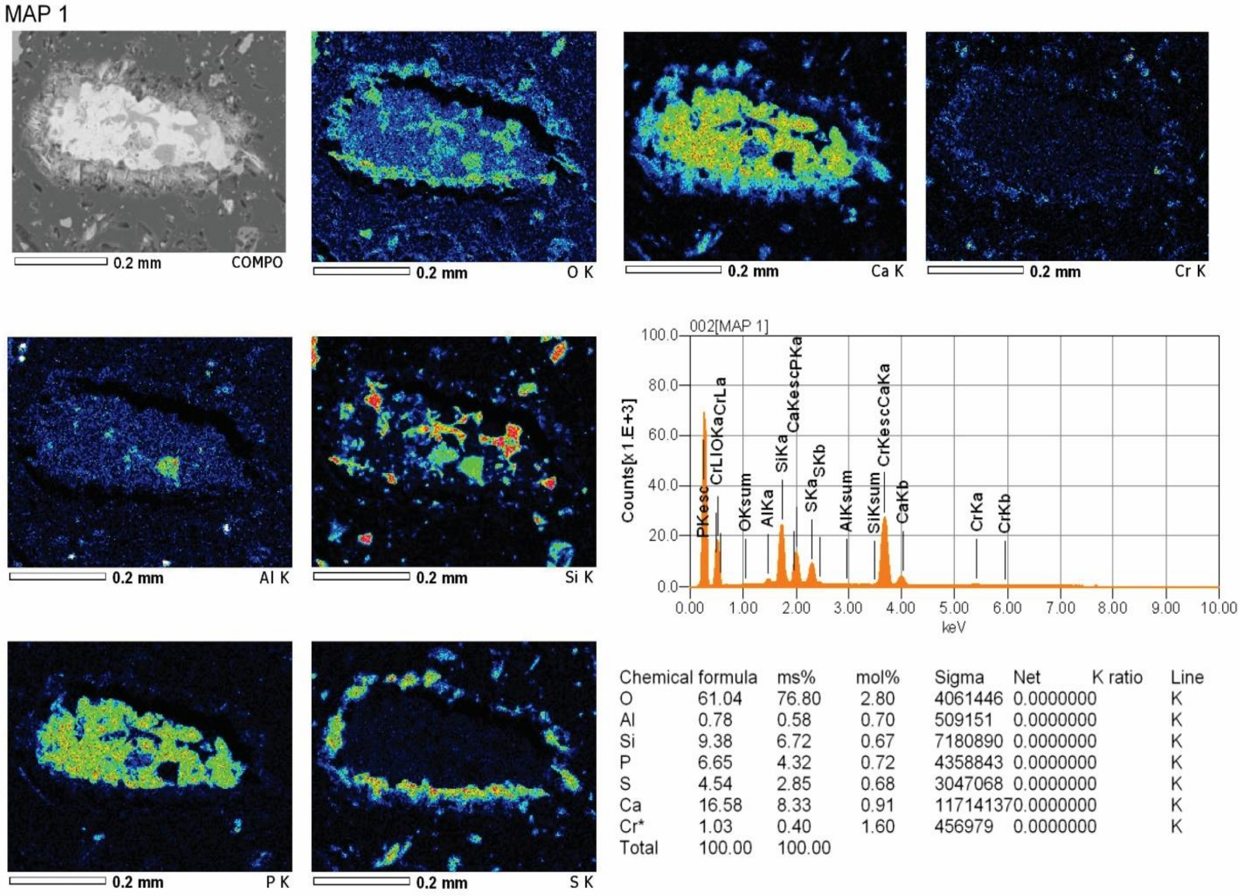


Figure 4. Thermal analysis curve of the phosphogypsum sample

SEM observations demonstrated aggregates of typical platy and needle-like gypsum crystals (Figure 5). Elemental mapping for Ca and S showed uniform distribution of the sulfate phase, while elevated Si and Al signals indicated the presence of silicate and aluminosilicate inclusions. Local enrichment in P is consistent with phosphate impurities. Trace Cr signals reflect minor technogenic inclusions. Semi-quantitative EDS analysis revealed the predominance of O (61.04 wt.%), Ca (16.58 wt.%), Si (9.38 wt.%), P (6.65 wt.%), and S (4.54 wt.%). The Ca/S ratio corresponds to the stoichiometry of $CaSO_4 \cdot 2H_2O$, confirming the results of XRD and thermal analysis.



Chemical formula	ms%	mol%	Sigma	Net	K ratio	Line
O	61.04	76.80	2.80	4061446	0.0000000	K
Al	0.78	0.58	0.70	509151	0.0000000	K
Si	9.38	6.72	0.67	7180890	0.0000000	K
P	6.65	4.32	0.72	4358843	0.0000000	K
S	4.54	2.85	0.68	3047068	0.0000000	K
Ca	16.58	8.33	0.91	11714137	0.0000000	K
Cr*	1.03	0.40	1.60	456979	0.0000000	K
Total	100.00	100.00				

Figure 5. EDS elemental mapping of the examined phosphogypsum sample

Overall, the studied phosphogypsum is mainly represented by $CaSO_4 \cdot 2H_2O$ with silicate and phosphate impurities, consistent with the typical composition of such materials reported in the literature [Lei et al., 2024]. The minor thermal effects observed at 790–825 °C, which are absent in pure gypsum, are characteristic of structural transformations in hydrated REE phosphates (e.g., $YPO_4 \cdot H_3PO_4 \cdot 2H_2O$). The presence of REEs is attributed both to isomorphic substitution within the $CaSO_4$ structure and to microdomains enriched in phosphate phases identified by EDS, where REEs are likely accumulated in their own mineral forms.

Three-Stage Counter-Current Hydrochloric Acid Leaching of Phosphogypsum. Previous studies aimed at determining the optimal conditions for hydrochloric acid leaching have shown that up to 70–75% of REEs can be recovered into solution under single-stage treatment. The three-stage counter-current HCl leaching flowsheet presented in Figure 6 enabled a substantial increase in the extraction efficiency of rare earth elements from phosphogypsum while simultaneously raising the ΣREE concentration in the pregnant leach solutions. The counter-current configuration provides sequential contact of the solid phase with solutions of different stages: fresh phosphogypsum interacts with the most REE-enriched liquor from the second stage, whereas the residues produced in later stages are treated with less concentrated or freshly prepared solutions. This flow arrangement ensures deeper REE dissolution with only minimal additional reagent consumption.

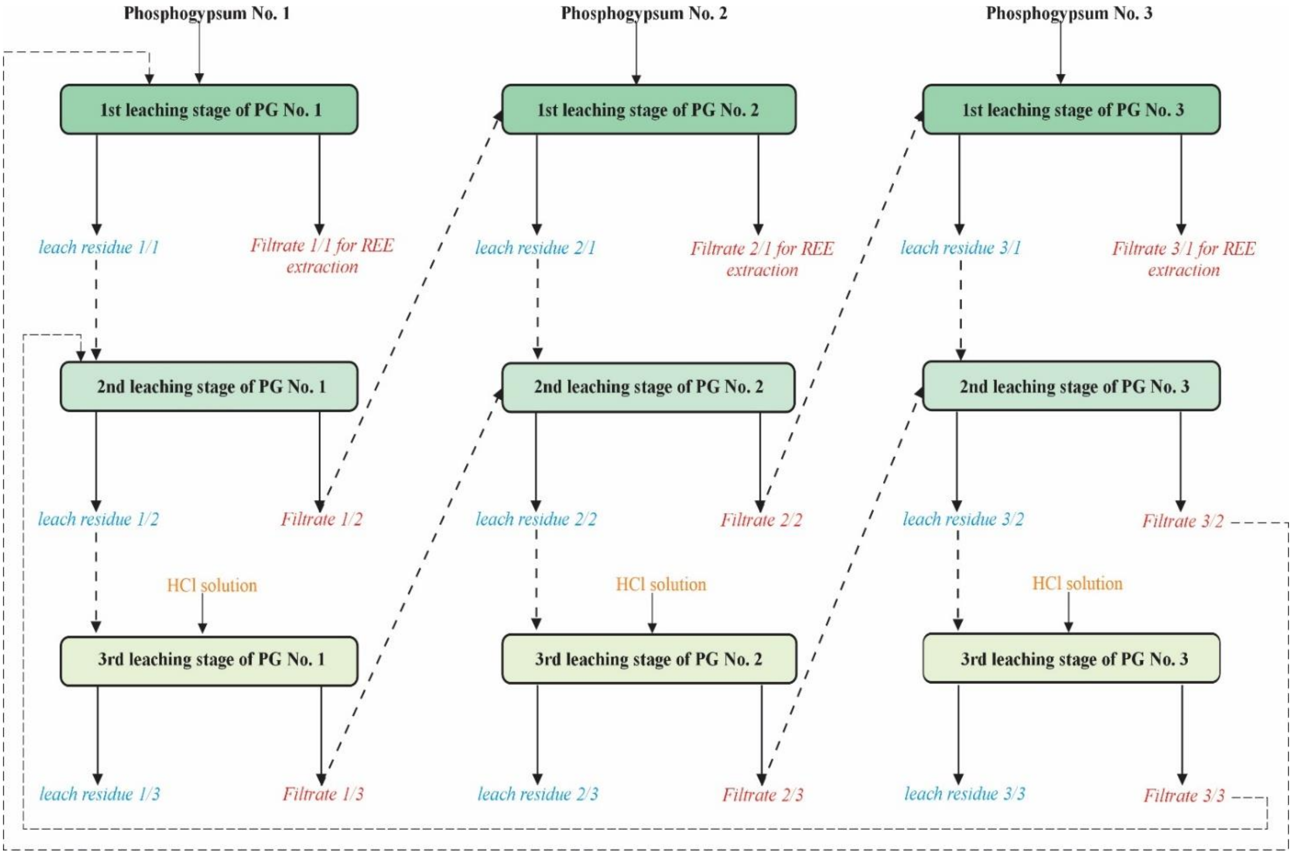


Figure 6. Flow diagram of the three-stage counter-current hydrochloric acid leaching of phosphogypsum

The results of three-stage leaching at a solid:liquid ratio of 1:10 are presented in Table 1. The first stage demonstrates the most intense transfer of rare earth metals into solution – 56.92% ΣREE (Figure 7). This result indicates the high reactivity of some rare earth compounds, which is typical of surface-sorbed and readily soluble forms.

Table 1. Indicators of phosphogypsum leaching with hydrochloric acid according to a three-stage scheme

Name	Concentration in solution, g/dm^3					Extraction, %				
	ΣREE	Ca	Al	Fe	Mg	ΣREE	Ca	Al	Fe	Mg
Filtrate of Stage 1	0.0272	4.66	0.005	0.332	0.072	56.92	16.44	0.68	47.90	56.93
Precipitate	-	-	-	-	-	8.10	-	-	-	-
Filtrate of Stage 2	0.00936	5.04	0	0.237	0.002	13.73	0.73	0	6.03	0
Precipitate	-	-	-	-	-	2.55	-	-	-	-
Filtrate of Stage 3	0.00735	5.49	0.119	0.22	0.018	17.15	23.49	18.31	45.39	14.82
Precipitate	-	-	-	-	-	0.45	-	-	-	-
Residue	-	-	-	-	-	1.1	-	-	-	-

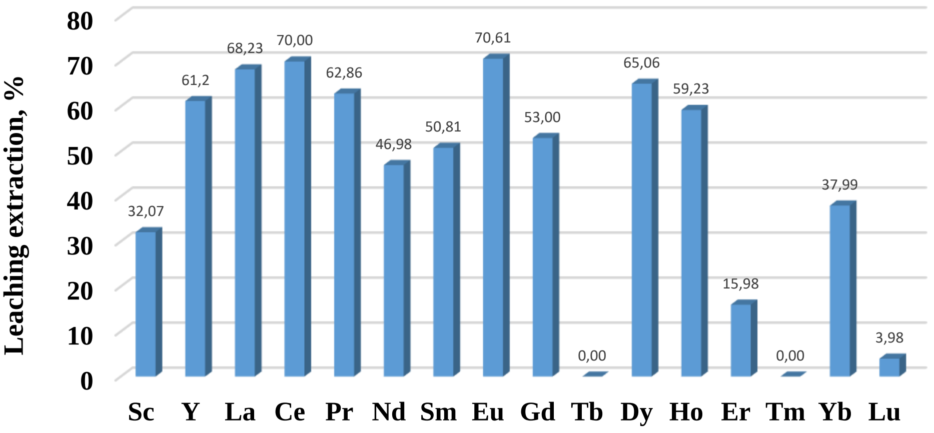


Figure 7. Extraction of REE in the first stage at S:L = 1:10

In the second and third stages, an additional 13.73% and 17.15% of ΣREE are recovered, respectively (Figures 8 and 9), resulting in a total recovery of approximately 88%. This figure significantly exceeds the levels previously achieved with the single-stage process, confirming the effectiveness of the countercurrent approach reflected in the flow chart.

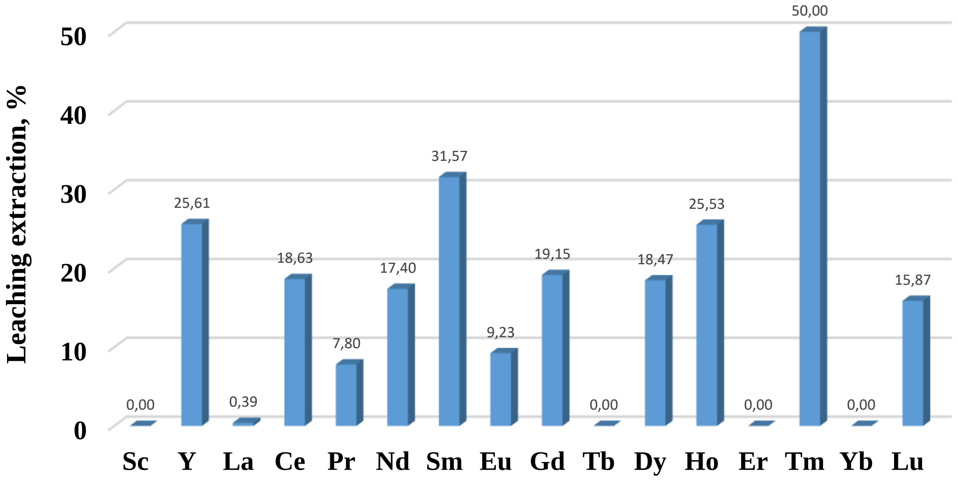


Figure 8. Extraction of REE in the second stage at S:L = 1:10

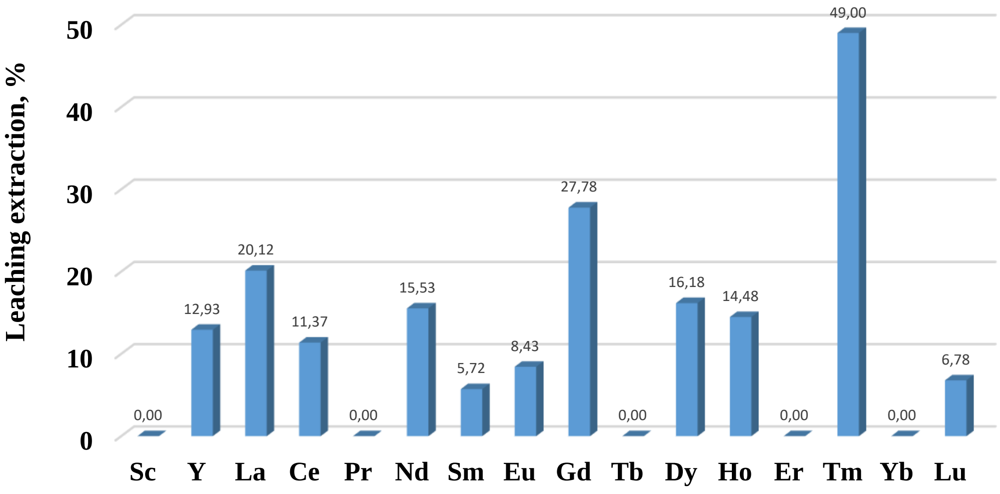


Figure 9. Extraction of REE in the third stage at S:L = 1:10

The behavior of the associated elements is consistent with their chemical nature. Iron and magnesium rapidly dissolve in the first stage. Calcium partially dissolves, simultaneously forming a secondary gypsum precipitate, which accounts for 11.1% of the ΣREE. Only approximately 1.1% of the REE remains in the final residue.

Elemental analysis showed that light REE (La–Nd) are extracted most completely, reaching 60–85%. Among heavy REE, the highest values of dissolution are characteristic of dysprosium, holmium, and thulium, as shown in Figures 7–9. This distribution is due to the higher solubility of the chloride forms of some heavy REE and the lower binding strength within the phosphogypsum microinclusions.

To increase the ΣREE concentration in the solution, three-stage leaching was carried out with a reduced liquid:solid ratio of 1:4. Despite the decrease in the volume of the solution, a significant proportion of 54.28% of ΣREE is extracted at the first stage (Table 2, Figure 10), which indicates the stability of the REE transition kinetics.

Table 2. Extraction of rare earth metals into solution during three-stage hydrochloric acid leaching of phosphogypsum (S:L ratio = 1:4)

Leaching stage	Concentration of ΣREE in solution, g/dm^3	Extraction into solution, %
1	0.0822	54.28
2	0.0403	14.29
3	0.0315	13.83

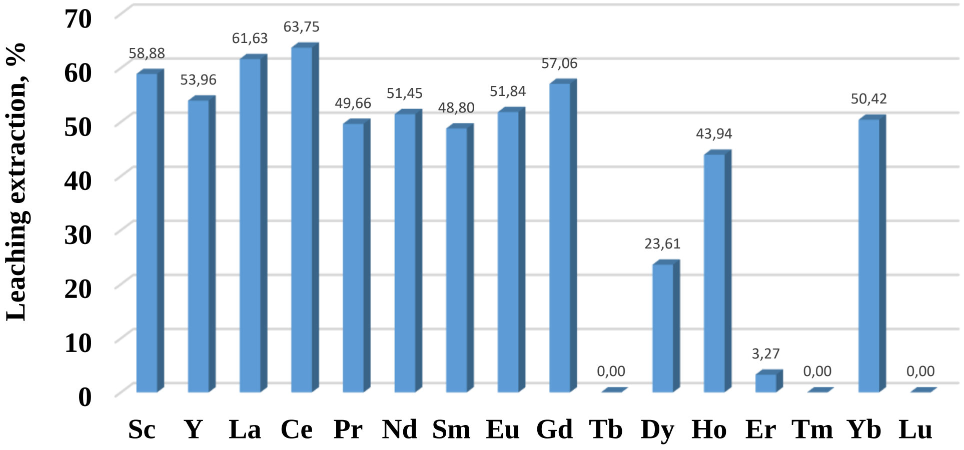


Figure 10. Extraction of REE in the first stage at S:L = 1:4

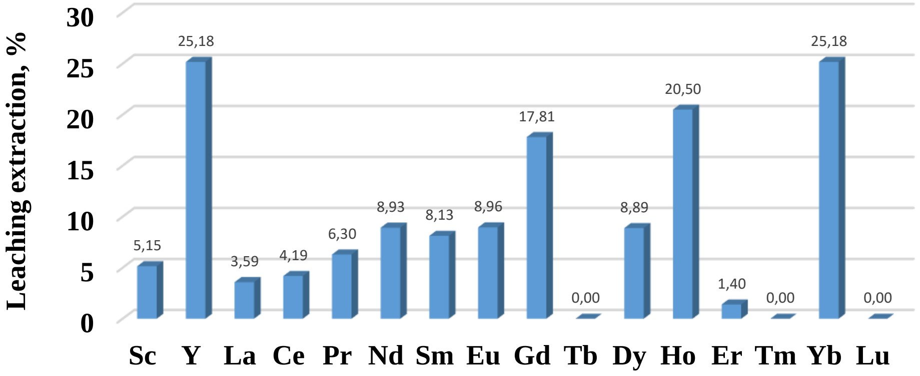


Figure 11. Extraction of REE in the second stage at S:L = 1:4

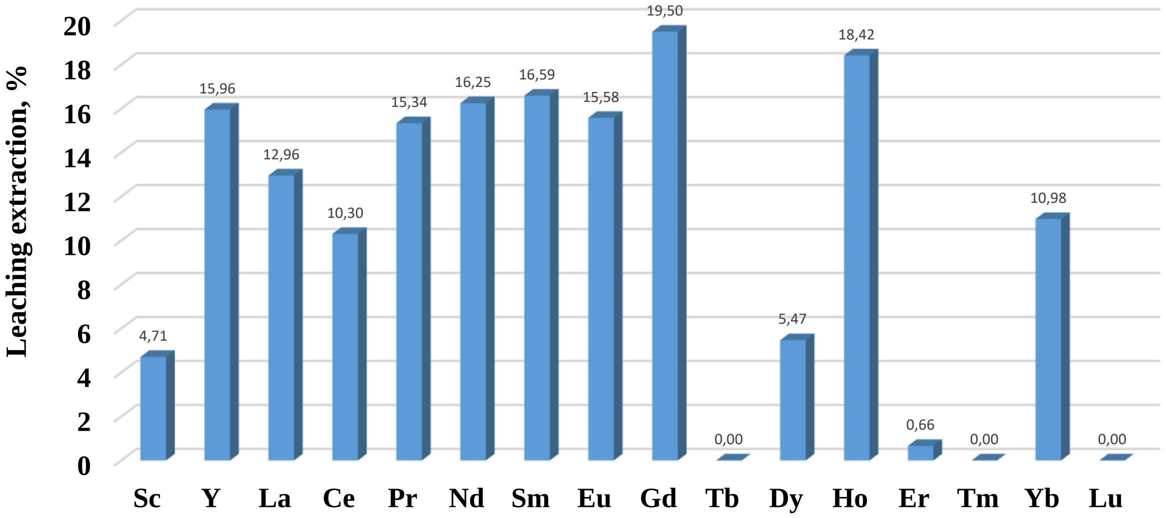


Figure 12. Extraction of REE in the third stage at S:L = 1:4

The second and third stages provide an additional 14.29% and 13.83% of ΣREE (Figures 11 and 12). The total recovery reaches 82.4%, which is slightly lower than the result at a solid: liquid ratio of 1:10. However, the key advantage of the 1:4 mode is a threefold increase in the ΣREE concentration in the solution, which significantly reduces the specific consumption of sorbents or extractants during subsequent processing.

With a decrease in the liquid ratio to S:L = 1:4, the cumulative recovery decreases slightly and amounts to 82.4%, which is due to the partial preservation of calcium sulfate in the solid phase. However, this mode provides a significantly higher concentration of ΣREE in productive solutions. Increasing the concentration by 2.5–3 times is an important technological advantage, since it reduces the consumption of sorbents, extractants, and reagents at subsequent stages of processing, and also reduces the volume of circulating solutions.

X-ray phase analysis of the residue after the third stage of leaching showed that at a ratio of S:L = 1:10, the solid residue is mainly quartz (Figure 13, a), which indicates the almost complete removal of calcium sulfate from the solid phase. When the liquid ratio decreases to S:L = 1:4, in addition to quartz, calcium sulfate semihydrate, and anhydrite are fixed in the residue (Figure 13, b). The preservation of sulfate phases indicates incomplete decomposition of the gypsum matrix at a reduced S:L, which leads to a slight decrease in the degree of REE extraction compared to the optimal mode S:L = 1:10.

A comparative analysis of the two studied leaching modes shows that the ratio of solid and liquid has a significant effect both on the completeness of the transition of rare earth metals into solution and on the phase composition of the resulting solutions and solid products. At S:L = 1:10, the maximum degree of REE extraction into solution is reached, which is about 88%. Under these conditions, the gypsum matrix of phosphogypsum is almost destroyed, which is confirmed by the formation of a residue, represented mainly by quartz. Thus, this mode ensures deep extraction of the target components and effective removal of sulfate phases from intermediate sediments.

A key factor in the high efficiency of the process is the countercurrent stage organization scheme, according to which the most REE-saturated solution is sent to fresh phosphogypsum, while a fresh acid solution is fed to a residue that has undergone two stages of leaching. This flow direction ensures optimal distribution of the reagent, promotes a more complete release of rare earth elements, and eliminates excessive acid consumption. The three-stage scheme demonstrates high technological efficiency, allowing combining deep extraction of REE (82-88%) with the production of concentrated solutions and solid phases of stable mineral composition.

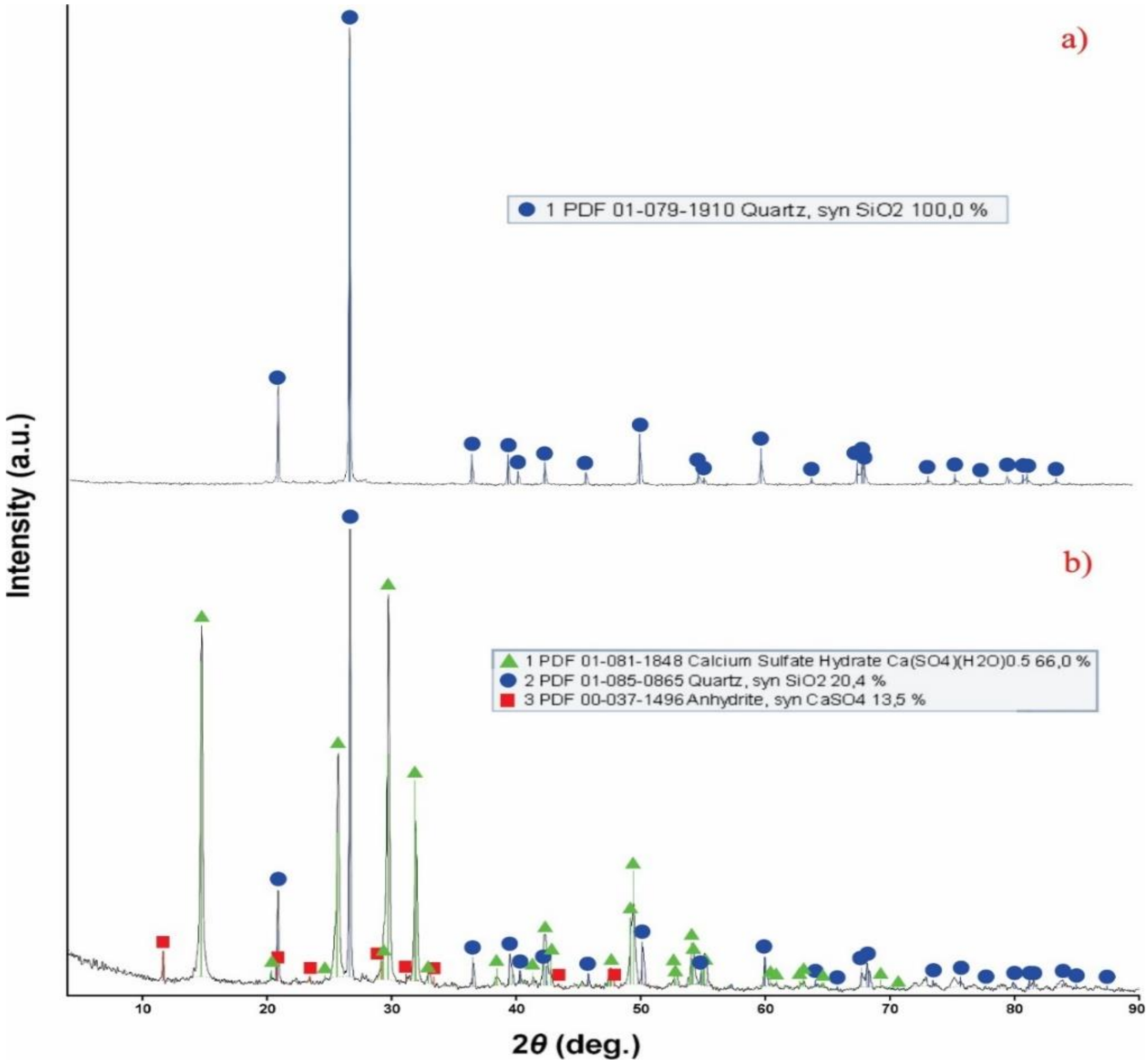


Figure 13. Residue diffractograms after the third stage of phosphogypsum leaching at various ratios S:L: a – 1:10; b – 1:4.

Processing of the Gypsum Precipitate. The properties of the precipitates formed during the cooling of the leached solutions were also studied. According to X-ray fluorescence analysis, the precipitate contains, wt. %: 22.545 Ca; 17.383 S; 52.635 O; 0.011 Si; 0.024 Cl; 0.009 Sr. X-ray phase analysis revealed that the precipitate was predominantly calcium sulfate dihydrate $CaSO_4 \cdot 2H_2O$ (Figure 14, a).

The formation of calcium sulfate from the solution after leaching can be explained by the interaction of calcium chloride with sulfuric acid present in the solution. During the leaching of phosphogypsum with hydrochloric acid, some of the calcium presumably passes into solution via the reaction:

$$CaSO_4 \cdot 2H_2O + 2HCl \leftrightarrow CaCl_2 + H_2SO_4 + 2H_2O \quad (2)$$

After separation of the residue and cooling of the solution below 70°C (Demopoulos et al., 2016), the reaction begins to shift in the opposite direction, which leads to the reprecipitation of calcium sulfate dihydrate.

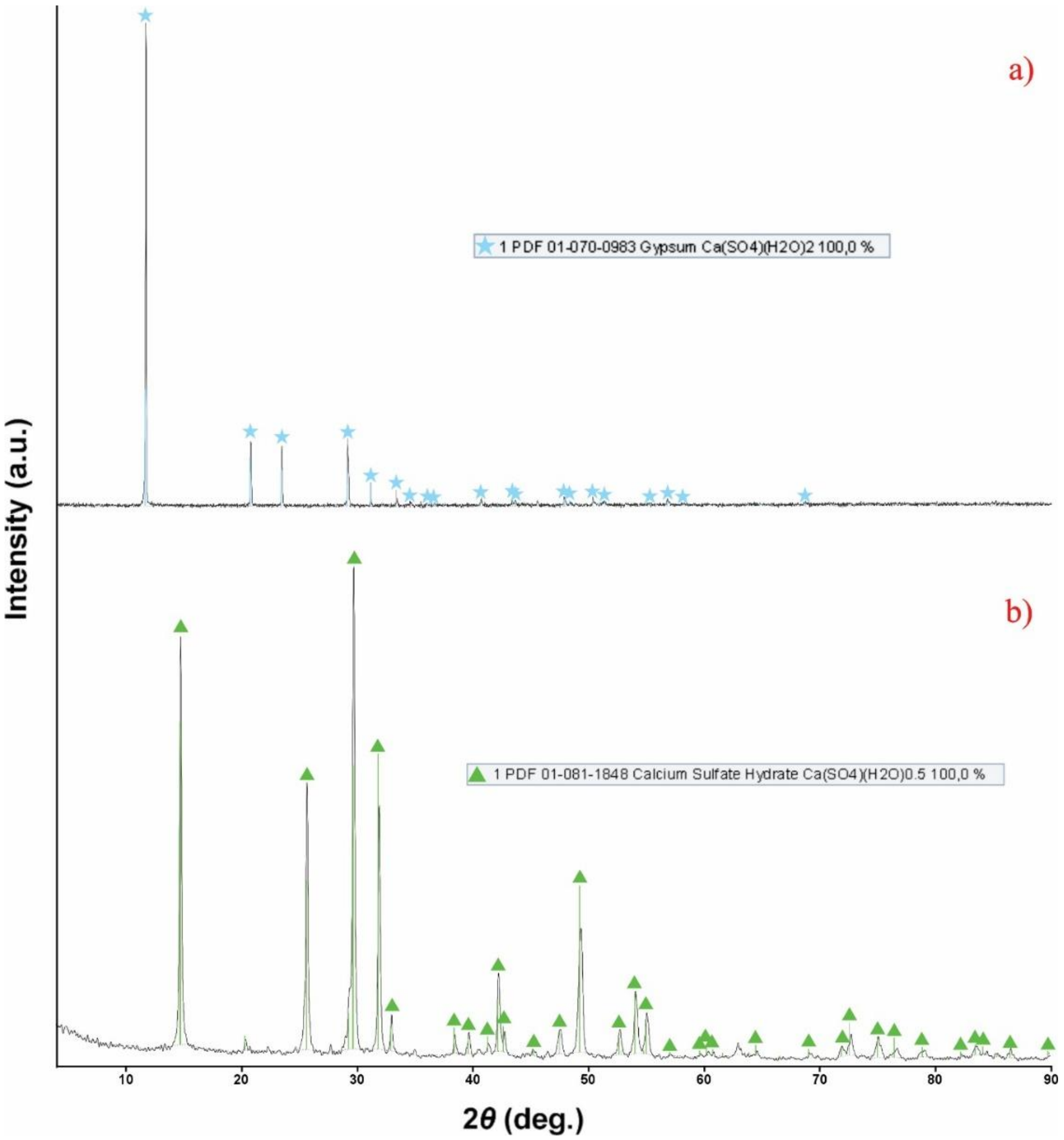


Figure 14. Diffraction patterns of the precipitate before (a) and after calcination (b)

To assess the potential suitability of this material, it was heat-treated to convert the dihydrate gypsum to a hemihydrate form. Calcination at 165°C for 4 hours resulted in the formation of $CaSO_4 \cdot 0.5H_2O$ hemihydrate, as confirmed by the characteristic diffraction pattern (Figure 14, b).

The mechanical properties of the calcined material were evaluated under compression on a mobile MIP-25P press. The ultimate strength of the sample was 5.1 MPa, which corresponds to gypsum binder grade G5. The results obtained show that the precipitate deposited at the stage of cooling the solution can be converted into a semi-hydrate form and meets the requirements for gypsum binders in terms of strength characteristics, at least at the laboratory testing level.

Conclusion

The conducted studies have shown that phosphogypsum, represented mainly by $CaSO_4 \cdot 2H_2O$ dihydrate and containing minor silicate and phosphate compounds, which contain 340.53 g/t of REE, is effectively amenable to three-stage countercurrent hydrochloric acid leaching. The optimal mode is the liquid ratio S:L = 1:10, at which the maximum degree of REE extraction is achieved at 88% and complete removal of calcium sulfate from the solid phase is ensured, whereas at S:L = 1:4, the extraction is 82.4%, but the concentration of REE in solution increases 2.5–3 times. The countercurrent organization of the process ensures a rational distribution of the reagent and a deep destruction of the gypsum matrix, which is confirmed by mineralogical data. The precipitate $CaSO_4 \cdot 2H_2O$ precipitated during cooling of the solutions is successfully converted to the semihydrate form $CaSO_4 \cdot 0.5\ H_2O$ at 165 °C for 4 hours, forming a 5.1 MPa material corresponding to gypsum binder grade G5. Thus, the proposed scheme provides for the complex processing of phosphogypsum to obtain concentrated REE solutions suitable for further sorption or extraction enrichment, and the formation of a gypsum product that meets the requirements of the construction industry.

CRediT author statement: **A.M. Yessengaziyev**: Writing draft preparation, Proof-reading, Software, Data curation, Validation. **Z.B. Karshyga**: Supervision, Methodology, Conceptualisation. **A.E. Orynbayev**: Visualisation. **T. M. Tastanova & T.M. Arynbayev**: Editing.

Cite this article: Yessengaziyev, A. M. Karshyga, Z. B. Orynbayev, B. M. Tastanova, A. E. Arynbayev, T. M. (2025). Enhancing the Efficiency of Rare Earth Element Recovery from Phosphogypsum by Counter-Current Hydrochloric Acid Leaching. Materials of International Scientific-Practical Internet Conference “Challenges of Science”. Issue VIII, pp. 95-108. https://doi.org/10.31643/2025.12

References

Cuadros-Muñoz, J.-R., Jimber-del-Río, J.-A., Sorhegui-Ortega, R., Zea-De la Torre, M., & Vergara-Romero, A. (2024). Contribution of rare earth elements is key to the economy of the future. *Land, 13*(8), Article 1220. https://doi.org/10.3390/land13081220

Leal Filho, W., Kotter, R., Özuyar, P. G., Abubakar, I. R., Eustachio, J. H. P. P., & Matandirotya, N. R. (2023). Understanding rare earth elements as critical raw materials. *Sustainability, 15*(3), Article 1919. https://doi.org/10.3390/su15031919

Mukaba, J.-L., Eze, C. P., Pereao, O., & Petrik, L. F. (2021). Rare earths’ recovery from phosphogypsum: An overview on direct and indirect leaching techniques. *Minerals, 11*(10), Article 1051. https://doi.org/10.3390/min11101051

Mashifana, T. P. (2019). Chemical treatment of phosphogypsum and its potential application for building and construction. *Procedia Manufacturing, 35*, 641–648. https://doi.org/10.1016/j.promfg.2019.06.007

Yang, J., Dong, S., Hu, B., Duan, L., Yan, X., Zhou, G., & Ma, L. (2024). *Review on phosphogypsum high value utilization: Utilization of calcium and oxygen resources* [Preprint]. SSRN. https://doi.org/10.2139/ssrn.4731994

Maina, L., Kiegiel, K., & Zakrzewska-Kołtuniewicz, G. (2025). Challenges and strategies for the sustainable environmental management of phosphogypsum. *Sustainability, 17*(8), Article 3473. https://doi.org/10.3390/su17083473

Men, J., Li, Y., Cheng, P., & Zhang, Z. (2022). Recycling phosphogypsum in road construction materials and associated environmental considerations: A review. *Heliyon, 8*(8), Article e11518. https://doi.org/10.1016/j.heliyon.2022.e11518

Hammas-Nasri, I., Horchani-Naifer, K., Férid, M., & Barca, D. (2016). Rare earths concentration from phosphogypsum waste by two-step leaching method. *International Journal of Mineral Processing, 149*, 78–83. https://doi.org/10.1016/j.minpro.2016.02.011

van Selst, R., Penders, L., & Bos, W. (1997). Processing and application of phosphoric gypsum. In *Studies in Environmental Science* (Vol. 71, pp. 603–615). Elsevier. https://doi.org/10.1016/S0166-1116(97)80244-0

Bilal, E., Bellefqih, H., Bourgier, V., Mazouz, H., Dumitras, D.-G., Bard, F., Laborde, M., Caspar, J. P., Guilhot, B., Iatan, E.-L., Bounakhla, M., Iancu, M. A., Marincea, Ș., Essakhraoui, M., Li, B., Diwa, R. R., Ramirez, J. D., Chernysh, Y., Chubur, V., Roubík, H., Schmidt, H., Beniazza, R., Ruiz Canovas, C., Nieto, J. M., & Haneklaus, N. (2023). Phosphogypsum circular economy considerations: A critical review from more than 65 storage sites worldwide. *Journal of Cleaner Production, 414*, Article 137561. https://doi.org/10.1016/j.jclepro.2023.137561

Cánovas, C. R., Chapron, S., Arrachart, G., & Pellet-Rostaing, S. (2019). Leaching of rare earth elements (REEs) and impurities from phosphogypsum: A preliminary insight for further recovery of critical raw materials. *Journal of Cleaner Production, 219*, 225–235. https://doi.org/10.1016/j.jclepro.2019.02.104

Kurkinen, S., Virolainen, S., & Sainio, T. (2021). Recovery of rare earth elements from phosphogypsum waste in resin-in-leach process by eluting with biodegradable complexing agents. *Hydrometallurgy, 201*, Article 105569. https://doi.org/10.1016/j.hydromet.2021.105569

Kirillov, S. V. (2021). *Physico-chemical foundations for intensifying the extraction of rare earth metals from phosphogypsum* (Candidate of Technical Sciences dissertation). Ural Federal University named after the First President of Russia B. N. Yeltsin. (In Russian)

Lütke, S. F., Oliveira, M. L. S., Waechter, S. R., Silva, L. F. O., Cadaval Jr., T. R. S., Duarte, F. A., & Dotto, G. L. (2022). Leaching of rare earth elements from phosphogypsum. *Chemosphere, 301*, Article 134661. https://doi.org/10.1016/j.chemosphere.2022.134661

Dong, W., Deng, X., Chai, L., Zhang, Y., Chen, H., Wu, H., & Chi, R. (2025). Leaching characteristics and mechanisms of fluorine and phosphorus from phosphogypsum. *Molecules, 30*(1), Article 5. https://doi.org/10.3390/molecules30010005

Guan, Q., Sui, Y., Liu, C., Wang, Y., Zeng, C., Yu, W., Gao, Z., Zang, Z., & Chi, R.-A. (2022). Characterization and leaching kinetics of rare earth elements from phosphogypsum in hydrochloric acid. *Minerals, 12*(6), Article 703. https://doi.org/10.3390/min12060703

Gasser, M. S., Ismail, Z. H., Abu Elgoud, E. M., Abdel Hai, F., Othman, I., & Aly, H. F. (2022). Alkali treatment–acid leaching of rare earth elements from phosphogypsum fertilizer: Insight for additional resource of valuable components. *BMC Chemistry, 16*(1), Article 45. https://doi.org/10.1186/s13065-022-00845-7

Nsaka Ntumba, C., McCrindle, R., Maree, J., & Ngole-Jeme, V. (2023). The behaviour of selected rare-earth elements during the conversion of phosphogypsum to calcium sulphide and residue. *Journal of Material Cycles and Waste Management, 25*, 1658–1671. https://doi.org/10.1007/s10163-023-01640-9

Kazinform News Agency. (2024, November 25). *36 million tons of phosphogypsum dumps pose an environmental threat to residents of Taraz*. https://www.inform.kz/ru/36-mln-tonn-otvalov-fosfogipsa-yavlyayutsya-ekologicheskoy-ugrozoy-dlya-zhiteley-taraza-50bbdf

Khalil, F., Pagnanelli, F., & Moscardini, E. (2025). Phosphogypsum as the secondary source of rare earth elements. *Sustainability, 17*(19), Article 8828. https://doi.org/10.3390/su17198828

Lei, Y., Gong, Y.-J., He, M., Li, L., Qin, J., & Liu, Y. (2024). High-efficiency purification and morphology regulation of $CaSO_4 \cdot 2H_2O$ crystals from phosphogypsum. *Molecules, 29*(16), Article 3910. https://doi.org/10.3390/molecules29163910

Demopoulos, G., Peethamparan, S., & Neil, S. R. L. (2017). *Production of high strength hydrochloric acid from calcium chloride feed streams by crystallization* (Canadian Patent No. CA2926356A1). Canadian Intellectual Property Office.