

Article

Comparative Analysis of Acid Leaching for the Efficient Recovery of Lanthanum and Cerium from Phosphate

Rinat Abdulvaliyev , Almagul Ultarakova , Arailym Mukangaliyeva * , Nina Lokhova and Kaisar Kassymzhanov

The Institute of Metallurgy and Ore Beneficiation, Satbayev University, Almaty 050013, Kazakhstan; rin-abd@mail.ru (R.A.); a.ultarakova@satbayev.university (A.U.); n.lokhova@satbayev.university (N.L.); k.kassymzhanov@satbayev.university (K.K.)

* Correspondence: 000316650668-d@stud.satbayev.university; Tel.: +7-777-3934621

Abstract: The extraction of rare earth elements (REEs) from mineral resources is of significant global importance due to their critical role in modern technologies. This study focuses on the leaching behavior of artificial cerium and lanthanum phosphates using nitric, sulfuric, and hydrochloric acids under varying conditions of acid concentration and temperature. Our experiments demonstrated that the maximum extraction efficiency of lanthanum and cerium was achieved with nitric acid solutions at concentrations of 12.5 mol/dm³, with 85.0% and 79.1% extraction efficiency, respectively. The leaching mechanism involved the protonation of phosphate anions, which disrupted the phosphate matrix, facilitating the dissolution of lanthanum and cerium into solution. Sulfuric acid, although less effective at room temperature, proved to be the most thermodynamically favorable leaching agent at higher temperatures due to the formation of stable sulfate complexes. Additionally, hydrochloric acid displayed high selectivity for cerium extraction, although its applicability is limited by complexation and environmental concerns. This study offers new insights into optimizing REE recovery from phosphates, demonstrating the advantages of sulfuric acid for industrial-scale leaching processes due to its economic and thermodynamic benefits. The novelty of this work lies in its systematic comparison of the three acids' effects on REE extraction, providing a comprehensive framework for selecting optimal leaching agents based on specific operational conditions.

Keywords: lanthanum; cerium; rare earth elements; leaching; dissolution kinetics; phosphates; sulfuric acid; nitric acid; hydrochloric acid; rare-earth sulfate complexes



Citation: Abdulvaliyev, R.; Ultarakova, A.; Mukangaliyeva, A.; Lokhova, N.; Kassymzhanov, K. Comparative Analysis of Acid Leaching for the Efficient Recovery of Lanthanum and Cerium from Phosphate. *Separations* **2024**, *11*, 288. <https://doi.org/10.3390/separations11100288>

Academic Editor: Guoquan Zhang

Received: 7 September 2024

Revised: 29 September 2024

Accepted: 5 October 2024

Published: 10 October 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The current global reserves of rare earth elements (REEs) are estimated at approximately 120 million tons, with significant contributions from various countries, including Cambodia [1,2]. The British Geological Survey indicates that the overall concentration of REEs in the Earth's crust is around 9.2 parts per thousand [3].

China continues to dominate global REE production, responsible for over 60% of total output, primarily from carbonatite-associated deposits. These carbonatite deposits, categorized into primary magmatic, hydrothermal, and weathered carbonatite crusts, also contain valuable elements such as Nb, Th, and Sc [4]. The main REE-bearing minerals in these deposits include silico-carbonatite, magnesio-carbonatite, ferro-carbonatite, and calcio-carbonatite, which are often concentrated using flotation with acid-based collectors [5].

Studies have shown that the enrichment of REEs within these mineral species is driven by the fractional crystallization of calcite, which is incompatible with REEs and often associated with barite and alkaline silicates [6]. From an economic standpoint, the primary sources of REEs are minerals such as bastnaesite, monazite, xenotime, fergusonite, loparite, apatite, and kaolinite [7]. Bastnaesite, in particular, is the world's most concentrated source

of light rare-earth elements (Ce, La, Nd, and Pr), with the Bayan Obo REE-Nb-Fe mine in China being a prime example of a significant global deposit [8–11]. However, other less conventional sources such as belovite, florencite, and brockite have gained attention as potential alternative REE-bearing minerals. The exploration of these minerals is crucial for diversifying REE supply and mitigating the risk of supply chain disruptions, particularly in light of China's export restrictions that have historically caused volatility in the global REE market (Figure 1).

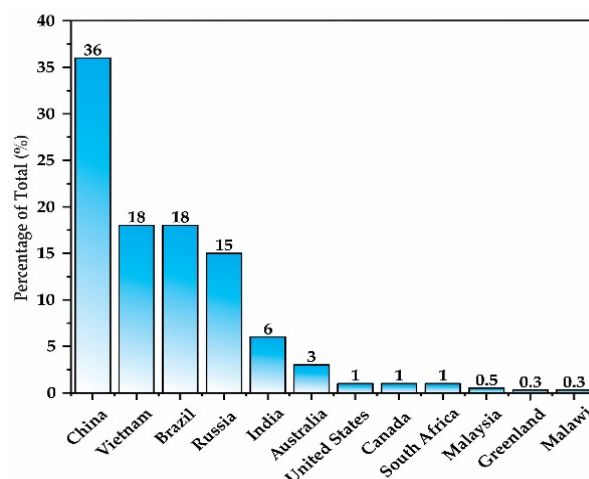


Figure 1. Global REE reserves (modified from Cambogia).

The strategic importance of REEs stems from their unique properties, which drive technological advancements across various industries. Often referred to as the “vitamins of modern industry”, REEs are irreplaceable in a wide range of technological applications [12,13]. China's dominance in the global REE market, accounting for over 90% of global production, was highlighted in 2011 when the country imposed export restrictions, causing prices to surge and revealing the vulnerability of global REE supplies [14–16]. As a result, there has been an increasing emphasis on securing alternative REE supplies and refining extraction technologies to ensure sustainable access to these critical elements [17].

Given the growing demand for rare earth elements in high-tech industries, analysts predict a long-term deficit in REE supplies. This shortage will have significant implications for technological development and innovation. ALCONIX Corporation (Japan) projects that the global demand for REEs will continue to rise, driven by the increasing need for these elements in modern technologies, amidst the ongoing production shortfall [18].

REEs pose unique challenges due to their chemical similarity, making them difficult to separate using conventional methods. Hydrometallurgical processes are currently the most widely used methods for REE extraction [19]. The efficiency of the leaching process—a crucial part of hydrometallurgical extraction—depends on several factors, including the mineralogical composition of the ore, the type of acid used, its concentration, reaction time, temperature, and the presence of impurities. Among the commonly used acids for ore decomposition are sulfuric acid (H_2SO_4) [20,21], nitric acid (HNO_3) [22], and hydrochloric acid (HCl) [23].

Previous laboratory studies have demonstrated the successful extraction of lanthanum and cerium from Indian red mud using sulfuric acid. The process involved the acid leaching of red mud pulp followed by the liquid–liquid extraction of the leached metals using various organic extractants, highlighting the technical feasibility of extracting and separating these metals simultaneously [24,25]. Similarly, [26] valuated the effectiveness of lanthanum and cerium extraction using hydrochloric, sulfuric, and nitric acids. Their results showed that hydrochloric acid was the most effective leaching agent at room temperature and atmospheric pressure, achieving extraction efficiencies of 92% and 94% for lanthanum and cerium, respectively [27,28].

Further advances in selective leaching have focused on improving the efficiency of REE recovery, particularly from minerals such as bastnaesite. In investigated the selective leaching of trivalent REEs from bastnaesite, allowing for the separation of trivalent and tetravalent species [29]. Their work highlighted the importance of refining extraction techniques and demonstrated the selective leaching efficiencies of over 90% for RE(III) without the use of organic solvents [30,31].

Based on the analysis of the available literature, sulfuric acid remains the preferred leaching agent for REEs due to its high efficiency and cost-effectiveness. Although nitric acid is more chemically reactive, its higher cost limits its industrial use compared to sulfuric acid [30]. The interaction of rare-earth-element phosphates, particularly cerium and lanthanum phosphates, with inorganic acids is a critical focus for improving extraction technologies. Optimizing the leaching process could improve recovery rates for lanthanoids, which currently range between 20 and 70% [32,33].

The ongoing research on rare-earth-element extraction from Kazakhstani materials aims to develop a competitive product for the global market, with a focus on identifying accessible sources of rare earth metals, particularly lanthanides [34,35]. The growing demand for REEs in modern technologies underscores the need to refine extraction techniques for REEs from both ores and technogenic materials, as well as to explore new sources of REEs for innovative technologies [36,37].

The novelty of this work lies in its systematic investigation of the leaching behavior of REE phosphates under varying acid conditions, providing new insights into the optimization of extraction processes. Moreover, the findings presented here could contribute to the development of more sustainable and economically viable extraction technologies, reducing the environmental impact and resource consumption typically associated with traditional mining and processing techniques.

2. Materials and Methods

2.1. Materials

The materials: For the experiments, hexahydrate nitrates of cerium and lanthanum classified as “chemically pure” (Almaty, Kazakhstan) and reagent-grade phosphoric acid (Almaty, Kazakhstan) were utilized.

2.2. Analysis Methods

X-ray structural analysis was performed using a D8 ADVANCE “BRUKER AXS GmbH” diffractometer (Bruker, Ettlingen, Germany) with Cu-K α radiation, accessing the PDF-2 database from the International Centre for Diffraction Data (ICDD, Swarthmore, PA, USA). For X-ray fluorescence analysis, we utilized a PANalytical Venus 200 spectrometer (PANalytical B.V., Almelo, The Netherlands). Chemical analyses were conducted with an Optima 8300 DV optical emission spectrometer with inductively coupled plasma (PerkinElmer Inc., Waltham, MA, USA). The samples were dried in a SNOL 7.2/1300 muffle furnace (Almaty, Kazakhstan) and processed using a LOIP LT-100 liquid circulation thermostat, a C931P pH meter (Greifensee, Switzerland), an RW 16 basic stirrer (Almaty, Kazakhstan), and a LOIP LS-110 shaker (Greifensee, Switzerland). The Pourbaix diagrams for the Ce-P-S-N-Cl, La-P-N-Cl, and La-P-S systems at 25.00 °C were meticulously constructed using HSC Chemistry 8, a specialized software product developed by Outokumpu Technology Engineering Research (Pori, Finland).

2.3. Experimental Procedure

For the experiments, hexahydrate nitrates of cerium and lanthanum, classified as “chemically pure”, and reagent-grade phosphoric acid were used.

In Figure 2, the red diffractogram represents the X-ray diffraction (XRD) pattern for lanthanum phosphate ($\text{LaPO}_4 \cdot 0.5\text{H}_2\text{O}$), while the blue diffractogram corresponds to cerium phosphate (CePO_4). Both materials were precipitated from hot nitrate solutions using a

0.1 mol/dm³ phosphoric acid solution and subsequently calcined at 900 °C for an hour, which ensured the formation of crystalline structures.

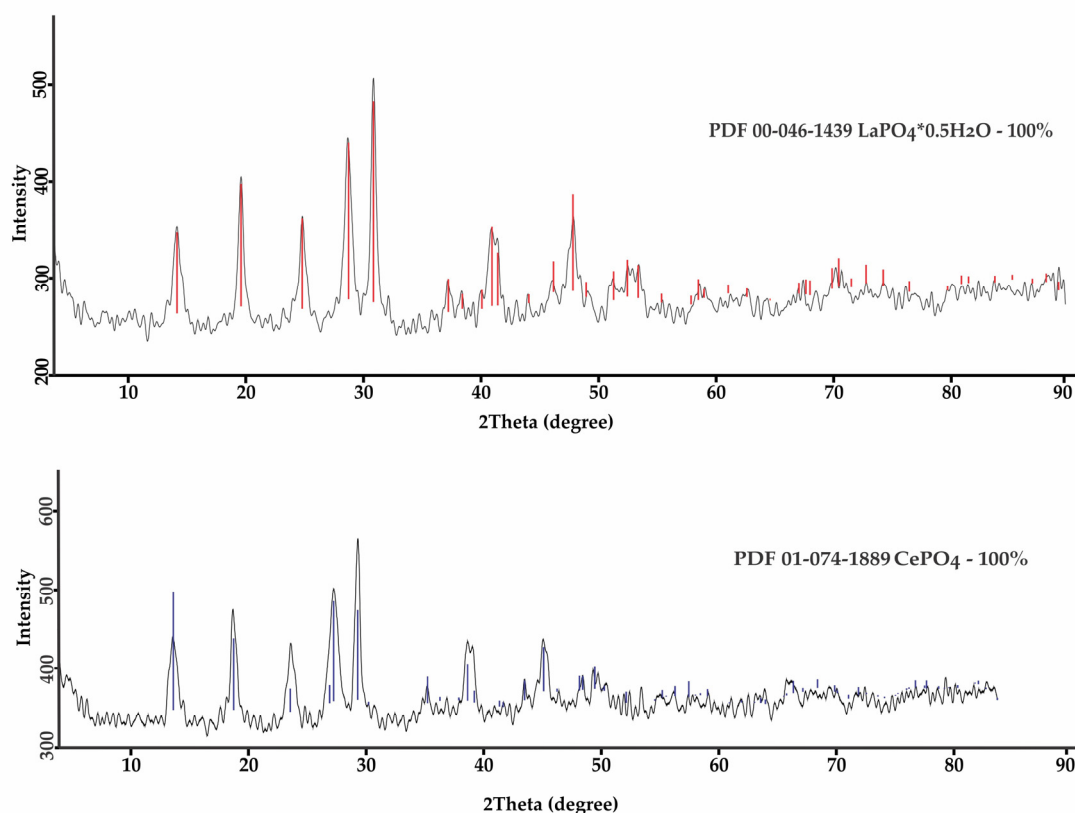


Figure 2. Diffractogram of lanthanum and cerium phosphate.

The XRD patterns reveal that both lanthanum and cerium phosphates crystallize in the rhabdophane structure, as evidenced by the characteristic diffraction peaks present in the diffractograms. The distinct color representation helps differentiate between the two materials and illustrates the similarities in their crystal structures, despite slight variations in peak intensities or positions, which are due to differences in their atomic compositions. The red pattern for lanthanum phosphate shows slightly shifted peaks compared to the blue pattern for cerium phosphate, indicating minor structural differences between the two.

To accurately reflect the composition of lanthanum and cerium phosphates, X-ray diffraction (XRD) analysis was performed on the samples.

The lanthanum phosphate sample (Figure 3) displayed absorption bands corresponding to valence $\nu(\text{OH})$ vibrations at 3456 cm⁻¹ and deformation δHOH vibrations of water at 1632 cm⁻¹ [38].

Phosphate ions $[\text{PO}_4]^{3-}$ showed absorption bands at 1051, 965, 615, 570, and 543 cm⁻¹ [38,39]. Additionally, calcite CaCO_3 exhibited absorption at 1793, 1458, 874, and 712 cm⁻¹ [38–41].

Considering the detailed spectral similarity of anhydrous cerium and lanthanum phosphates [39], and by comparing the spectra obtained from the samples, it is possible to identify the compound under study: lanthanum phosphate (III) monohydrate $\text{LaPO}_4 \cdot \text{H}_2\text{O}$, with absorption bands at 3510, 3456, 1632, 1051, 965, 615, 570, and 543 cm⁻¹.

The cerium phosphate sample (Figure 4) shows absorption bands for $\nu(\text{OH})$ valence vibrations at 3461 cm⁻¹ and δHOH deformation vibrations of water at 1629 cm⁻¹ [38].

Phosphate ion $[\text{PO}_4]^{3-}$ bands appear at 1050, 969, 615, 570, and 543 cm⁻¹, and the $[\text{CO}_3]^{2-}$ group bands appear at 1437 and 878 cm⁻¹ [38–41].

Cerium (III) phosphate, monohydrate $\text{CePO}_4 \cdot \text{H}_2\text{O}$, is characterized by absorption bands at 3510, 3461, 1629, 1050, 969, 615, 570, and 543 cm⁻¹ [39].

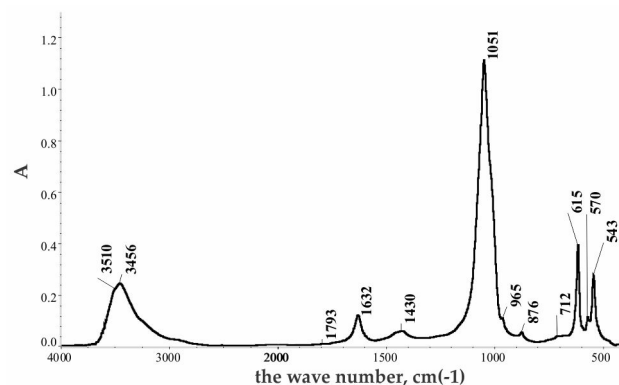


Figure 3. Infrared spectrum of lanthanum phosphate.

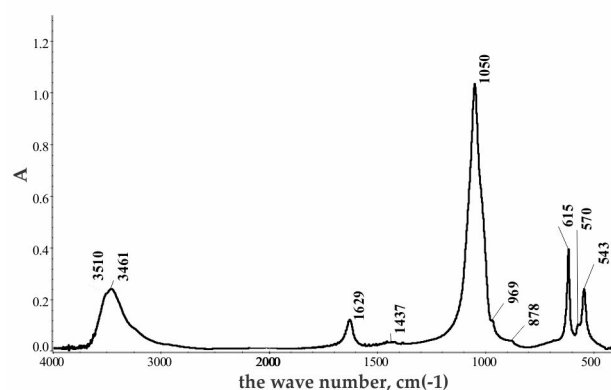
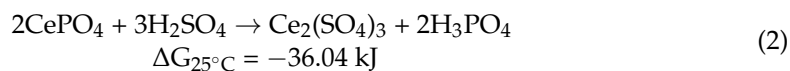
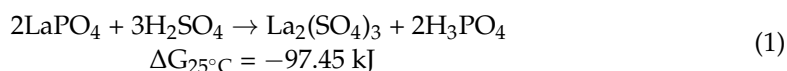


Figure 4. Infrared spectrum of cerium phosphate.

3. Results and Discussion

The primary reactions of rare earth elements with sulfuric acid and hydrochloric acid during the leaching process are presented below (the reaction data and Gibbs free energy values were calculated using HSC Software 8) For simplification, the chemical compounds are considered as individual components, separate from the mineral matrix of apatite or monazite.



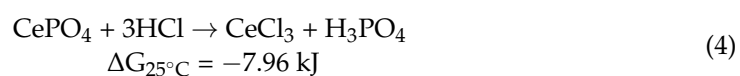
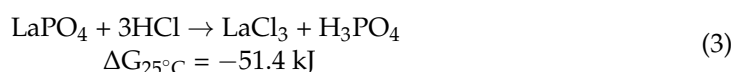
In these reactions, lanthanum phosphate reacts with sulfuric acid, which acts as a strong proton donor, breaking the phosphate bonds in LaPO_4 and leading to the formation of phosphoric acid (H_3PO_4). Simultaneously, lanthanum is oxidized and dissolves in solution as lanthanum sulfate ($\text{La}_2(\text{SO}_4)_3$). This reaction occurs spontaneously, as indicated by the negative Gibbs free energy value ($\Delta G = -97.45 \text{ kJ}$), confirming its thermodynamic feasibility. The solubility product constant (K_{sp}) for $\text{La}_2(\text{SO}_4)_3$, based on the provided Gibbs free energy, is 1.18×10^{17} .

Similarly, cerium phosphate reacts with sulfuric acid, with H_2SO_4 disrupting the phosphate bonds, resulting in the formation of phosphoric acid. Cerium is oxidized and dissolves as cerium sulfate ($\text{Ce}_2(\text{SO}_4)_3$). However, the Gibbs free energy for this reaction is less negative ($\Delta G = -36.04 \text{ kJ}$), indicating that the reaction is thermodynamically less favorable than the lanthanum system. The solubility product constant (K_{sp}) for $\text{Ce}_2(\text{SO}_4)_3$, based on the provided Gibbs free energy, is approximately 2.06×10^6 .

The calculated values of K_{sp} and Gibbs free energy clearly demonstrate the superiority of sulfuric acid as the preferred leaching agent for rare earth elements, particularly lanthanum and cerium, from phosphate minerals. Due to its unique physicochemical

properties, sulfuric acid exhibits high solubility for rare earth sulfates, as evidenced by the significantly larger K_{sp} value for $\text{La}_2(\text{SO}_4)_3$ compared to $\text{Ce}_2(\text{SO}_4)_3$. This indicates that lanthanum-containing compounds more readily dissolve in sulfate form, simplifying their subsequent extraction and making the process both more economically and energetically advantageous.

The Gibbs free energy values (ΔG) calculated for the interactions with sulfuric acid show that reactions involving lanthanum are more thermodynamically favorable than similar reactions for cerium, further underscoring the advantage of sulfuric acid under these conditions. The lower ΔG values for sulfuric acid reactions compared to hydrochloric acid reactions clearly indicate that processes involving H_2SO_4 require less energy to proceed, enhancing the overall efficiency of the technological cycle [1,2].



Based on the provided Gibbs free energy, the solubility product constant (K_{sp}) for LaCl_3 is approximately 1.01×10^9 , and for CeCl_3 , the K_{sp} is 24.8. Moreover, the significantly higher K_{sp} value for LaCl_3 compared to CeCl_3 indicates that lanthanum chloride has greater solubility in hydrochloric acid solutions, also supporting its preferential use in certain technological applications. However, despite this, sulfuric acid remains the most suitable choice for hydrometallurgical processes, as its application leads to higher thermodynamic efficiency and easier control over the solubility of the final products.

Thus, the obtained data serve as compelling evidence that sulfuric acid is the optimal reagent for leaching rare earth elements, and the calculated values of K_{sp} and Gibbs free energy clearly demonstrate its superiority under these conditions.

To determine which types of acids are most effective in selecting optimal conditions for rare-earth-element extraction, Pourbaix diagrams were generated using the HSC Chemistry 8 software. These diagrams are essential for understanding the stability of various ionic species under different pH and oxidation potential conditions, thus providing critical insights into the chemical behavior of elements during leaching processes.

We used an La-P-N-Cl System at 25.00°C . The Pourbaix diagram demonstrates that LaCl_2 and LaNO_3 are the primary species in acidic to neutral pH ranges, with LaCl_2 being more stable at lower pH levels. This stability supports the use of hydrochloric acid in processes where chloride complexation is preferred, ensuring lanthanum remains in solution for further processing (Figure 5).

The selection of nitric acid is corroborated by the diagram's indication that LaNO_3 is stable across a broader range of pH values, making it an ideal choice for environments where the goal is to maintain lanthanum in a nitrate complex. This is particularly relevant in high-purity extraction processes where nitrate complexes are preferred.

The diagram for the La-P-S System at 25°C shows that LaSO_4 and $\text{La}_2(\text{SO}_4)_3$ dominate the stability regions in acidic conditions, with $\text{La}_2(\text{SO}_4)_3$ remaining stable over a wide pH range. This finding directly influences the choice of sulfuric acid for processes aiming to dissolve lanthanum into stable sulfate complexes (Figure 6).

Theoretical Implications: Sulfuric acid is theoretically proven to be the most effective acid for leaching processes where lanthanum sulfate complexes are targeted. The Pourbaix diagram provides a clear rationale for this choice, as it aligns with the goal of maintaining lanthanum in a stable and soluble sulfate form, optimizing the leaching efficiency.

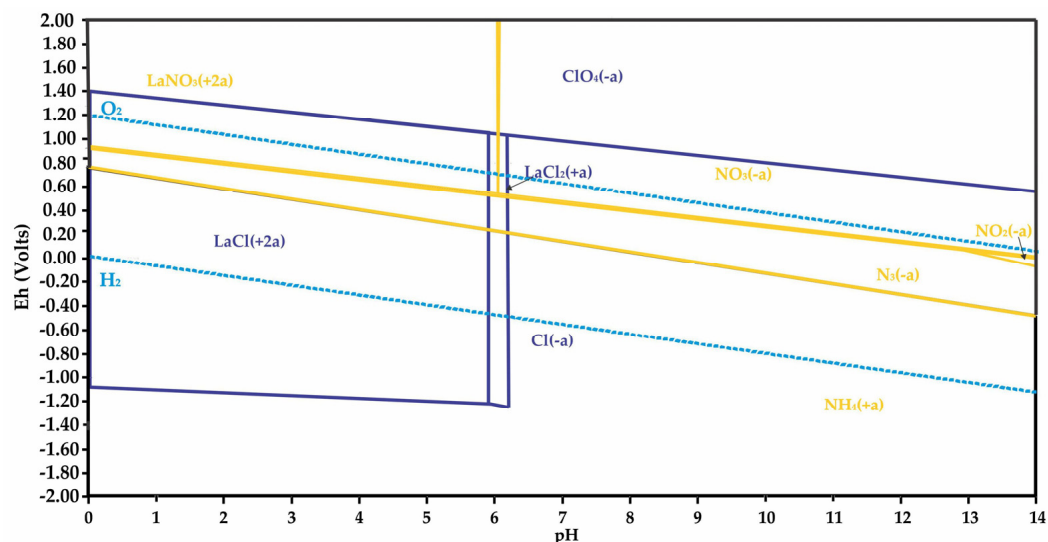


Figure 5. ϕ -pH diagram for La-P-N-Cl system at 25 °C ($a_{\text{Men}+} = 0.01$, 25 °C, 1.0 bar).

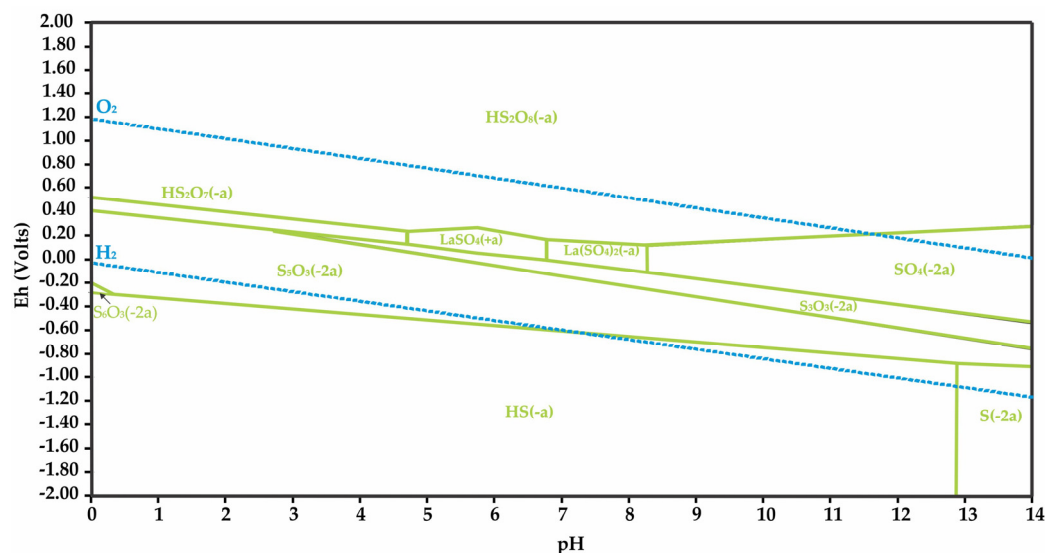


Figure 6. ϕ -pH diagram for La-P-S system at 25 °C ($a_{\text{Men}+} = 0.01$, 25 °C, 1.0 bar).

The Pourbaix diagram for the Ce-P-S-N-Cl system at 25 °C reveals that cerium forms stable chloride and sulfate complexes under specific pH conditions. CeCl_2 is stable in moderately acidic environments, while $\text{Ce}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ becomes predominant in the presence of sulfate ions. This information guided the choice of hydrochloric acid for environments where CeCl_2 is the desired phase and sulfuric acid where $\text{Ce}(\text{SO}_4)_2$ is more stable (Figure 7).

Theoretical Implications: The diagram supports the theoretical preference for hydrochloric acid when targeting the formation of soluble chloride complexes, enhancing cerium's leachability. On the other hand, sulfuric acid's efficacy is theoretically justified by the stability of sulfate complexes in acidic conditions, which facilitates the leaching process by maintaining cerium in solution.

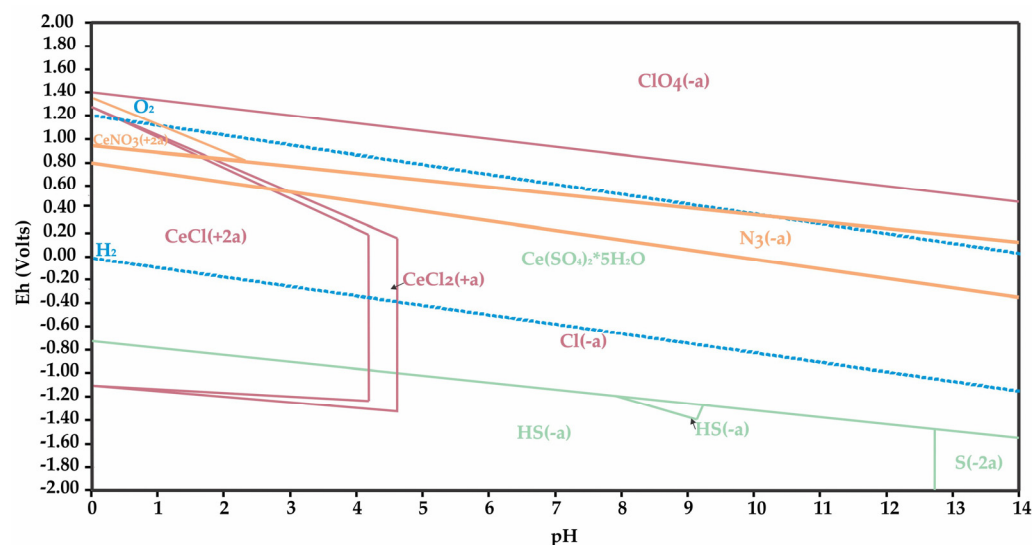


Figure 7. ϕ -pH diagram for Ce-P-S-N-Cl system at 25 °C ($a_{\text{Men}^+} = 0.01$, 25 °C, 1.0 bar).

3.1. The Effect of Nitric Acid on the Leaching of Lanthanum and Cerium from Phosphates

The solubility of lanthanum and cerium phosphates was studied using isothermal methods [42]. The effect of nitric acid concentration on the solubility of these phosphates was examined within a range of 2.38–9.4 g-mol/dm³ at temperatures of 25 and 60 °C. The findings are presented in Table 1.

Table 1. Solubility of lanthanum and cerium phosphates in nitric acid solutions, g-ion/dm³ · 10^{−3}.

Concentration of HNO ₃ , g-mol/dm ³	Temperature, °C			
	25		60	
	La	Ce	La	Ce
2.28	1.11	0.93	9.03	7.40
2.55	1.31	1.11	12.63	10.48
2.96	1.59	1.32	19.62	16.88
3.31	2.19	1.82	28.81	24.49
4.37	3.48	2.89	56.07	48.78
4.97	4.93	4.04	73.32	63.05
5.84	7.06	6.07	100.51	88.45
7.45	17.12	14.38	142.19	118.02
8.42	34.89	29.65	166.83	140.14
9.41	78.63	72.24	198.24	172.69

In order to achieve a more profound understanding of the kinetics governing the interaction between lanthanum and cerium phosphates, the following equations have been meticulously analyzed [43–45].

The fundamental equation for determining the temperature dependence of the reaction-rate constant:

$$k = A \cdot e^{-\frac{E_a}{RT}} \quad (5)$$

where k is the reaction-rate constant; A is the pre-exponential factor (or frequency factor), dependent on the nature of the reactants and their orientation during collision; E_a is the activation energy of the reaction (kJ/mol); R is the universal gas constant ($R = 8.314 \text{ J/mol}$); and T is the absolute temperature in Kelvin (K).

For the calculation of the activation energy and pre-exponential factor using experimental data, the Arrhenius equation can be rearranged into a linear form:

$$\text{Ln}k = \text{Ln}A - \frac{E_a}{RT} \quad (6)$$

This equation allows for the construction of a graph of $\text{Ln}k$ versus $1/T$, where the slope of the line is $\frac{E_a}{RT}$ and the y-intercept provides the value of $\text{Ln}A$.

The solubility study of lanthanum and cerium phosphates shows that at 60 °C, their solubility significantly exceeds that at 25 °C, particularly in the lower nitric acid concentration range of 2.28–3.31 mol/L. As the concentration of nitric acid increases from 3.31 to 9.41 mol/L, solubility continues to rise monotonically, with both lanthanum and cerium reaching much higher solubility values at elevated temperatures. These results suggest that increasing both temperature and nitric acid concentration can greatly enhance the dissolution of these phosphates, offering valuable insights for optimizing rare-earth-metal extraction processes in industrial applications.

The activation energy can also be calculated using the Eyring equation, based on transition state theory:

$$k = \frac{k_B T}{h} \cdot e^{-\frac{\Delta G^\ddagger}{RT}} \quad (7)$$

where k_B is the Boltzmann constant (1.3806×10^{-23} J); h is Planck's constant (6.6261×10^{-34} J); and $\Delta G^\ddagger$ is the Gibbs free energy of activation (kJ/mol). The remaining variables are analogous to the Arrhenius equation.

This equation accounts for both the enthalpic (activation energy) and entropic contributions associated with the orientation and structure of the transition state.

For the reaction between lanthanum/cerium phosphates and acids, a general kinetic equation demonstrating the dependence of the reaction rate on the reactant concentrations can be expressed as

$$\vartheta = k \cdot [\text{LaPO}_4]^m \cdot [\text{H}^+]^n \quad (8)$$

where ϑ is the reaction rate; $[\text{LaPO}_4]$ is the concentration of lanthanum (or cerium) phosphate; $[\text{H}^+]$ is the concentration of hydrogen ions (acid); and m and n are the reaction orders with respect to each reactant (determined experimentally).

As indicated by the data, temperature significantly impacts the equilibrium achievement in the interaction between nitric acid and lanthanum phosphate: equilibrium is reached at 25 °C within 12–14 h, whereas at 60 °C, it takes 8–10 h.

As illustrated in Figures 8 and 9, the kinetic curves show a steady increase in the concentration of La and Ce in solution over time, with no evidence of inhibitory phenomena such as surface passivation or product buildup. This linear progression suggests that the dissolution kinetics are controlled primarily by the acid concentration and the availability of reactive surface area, without significant diffusion limitations. The calculated apparent activation energies further support this interpretation, with values of 413.7 kJ/mol for the temperature range of 298–323 K and 71.3 kJ/mol for 323–343 K, indicating a possible shift in the reaction mechanism at higher temperatures.

Table 2 and Figure 10 demonstrate a strong correlation between nitric acid concentration and both the reaction rates and extraction efficiency of La and Ce. As the nitric acid concentration increases from 3.0 to 12.5 mol/dm³, the reaction rates for La rise from 2.5×10^{-5} mol/L·s to 4.4×10^{-4} mol/L·s, while Ce exhibits a similar but slightly lower increase from 1.7×10^{-5} mol/L·s to 8.9×10^{-5} mol/L·s. The rate constants follow the same trend, with La showing consistently higher values than Ce, indicating a more favorable dissolution process for La under the same conditions.

In terms of extraction efficiency (Figure 10), the results show a monotonic increase as the concentration of nitric acid rises. At the highest concentration of 12.5 g·mol/dm³, La achieves an extraction efficiency of 85%, while Ce reaches 79%. This suggests that higher nitric acid concentrations are beneficial for maximizing the dissolution and recovery of rare earth elements, particularly lanthanum, from phosphate minerals. The results are consistent with the solubility findings, which demonstrate that elevated acid concentrations lead to the enhanced dissolution of the phosphates, corroborating the kinetic data.

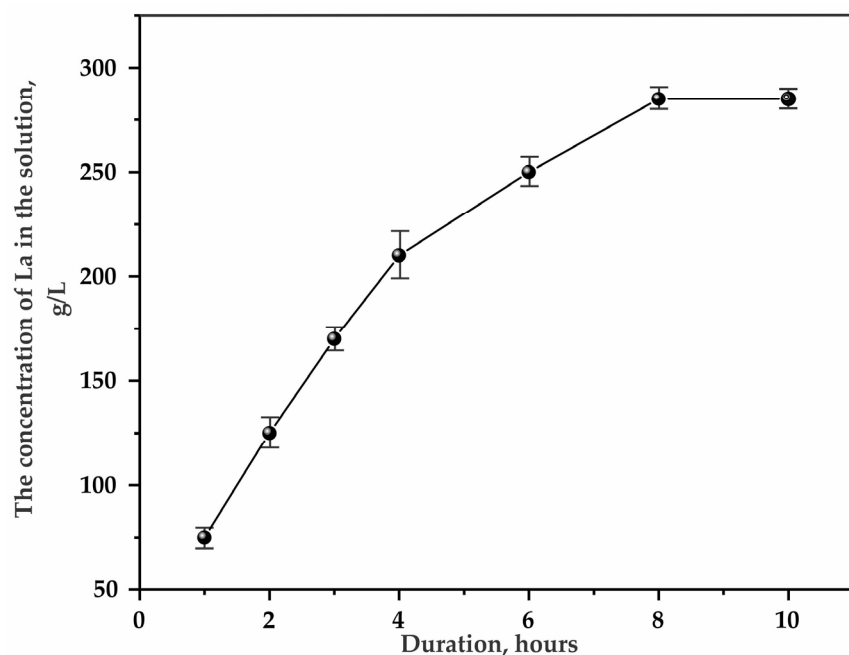


Figure 8. Dependence of lanthanum concentration in solution on the duration of interaction of lanthanum phosphate with a 9.41 g-mol/dm³ nitric acid solution at 60 °C.

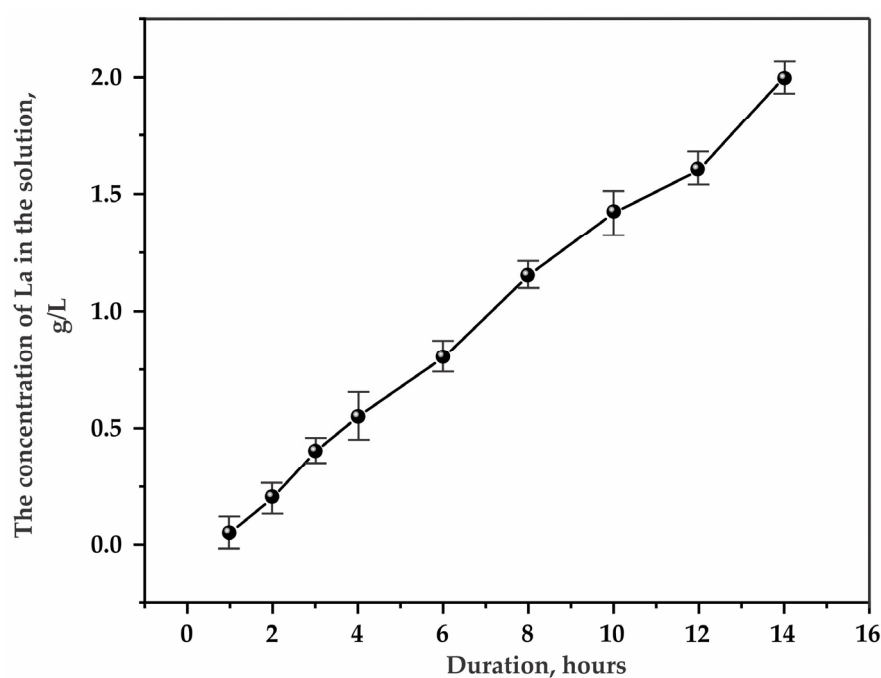


Figure 9. Dependence of lanthanum concentration in solution on the duration of interaction of lanthanum phosphate with a 9.41 g-mol/dm³ nitric acid solution at 25 °C.

The data presented in this study provide valuable insights for optimizing leaching processes in industrial settings. The linear kinetic behavior observed in the dissolution curves indicates that the reaction rate is governed by the acid concentration, suggesting that increasing the nitric acid concentration can significantly enhance the extraction of La and Ce from phosphate ores. The absence of inhibitory effects further supports the robustness of this approach, making it suitable for large-scale applications. Additionally, the pronounced effect of temperature on reaction kinetics, particularly the shift in activation energy, suggests that operating at higher temperatures can further improve the efficiency of the process, especially for lanthanum.

Table 2. Values of rate constant and activation energy for the reaction of lanthanum and cerium phosphates with nitric acid solutions.

The Concentration of Nitric Acid, mol/dm ³	Temperature, °C			
	Reaction Rate, mol/L·s		Rate Constant of the Reaction, mol/L·s	
	La	Ce	La	Ce
3.0	2.5×10^{-5}	1.7×10^{-5}	2.22×10^{-2}	1.03×10^{-2}
6.0	1.0×10^{-4}	7.2×10^{-5}	1.87×10^{-1}	5.42×10^{-2}
8.5	1.0×10^{-4}	2.8×10^{-4}	1.96×10^{-1}	1.43×10^{-1}
10.0	1.2×10^{-4}	7.2×10^{-5}	3.89×10^{-2}	1.35×10^{-1}
12.5	4.4×10^{-4}	8.9×10^{-5}	6.67×10^{-2}	3.68×10^{-2}

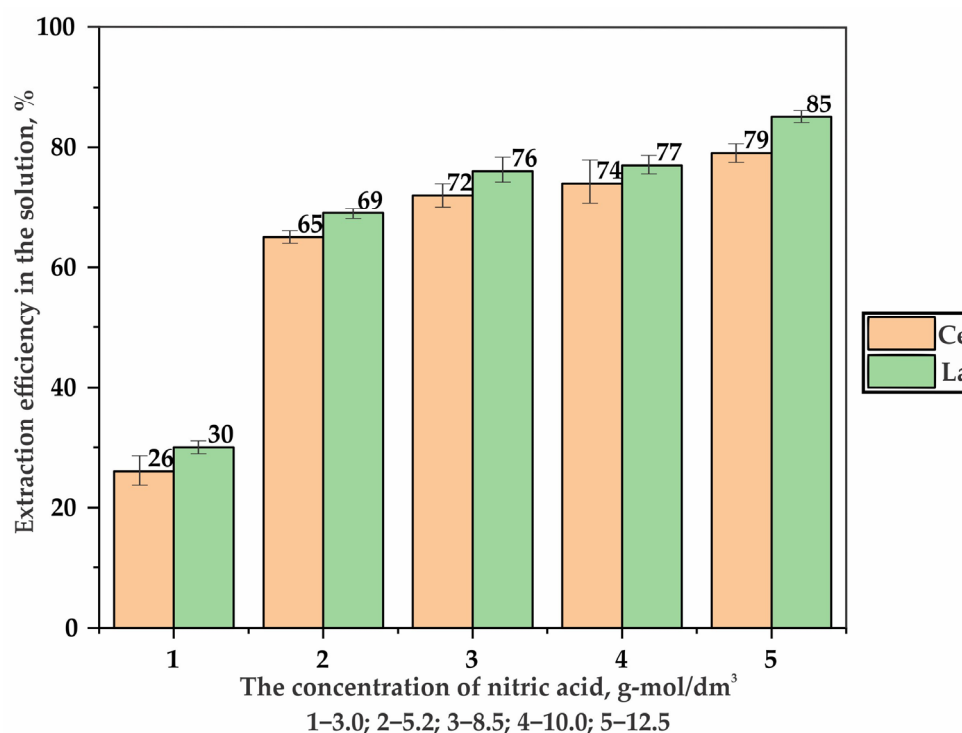


Figure 10. The effect of nitric acid concentration on the extraction efficiency of lanthanum and cerium into solution.

When leaching lanthanum and cerium from phosphates using nitric acid solutions, the maximum extraction efficiency is achieved at an acid concentration of 12.5 g-mol/dm³, reaching 85.0% for lanthanum and 79.1% for cerium.

Dissolving minerals with relatively monodisperse particles in an excess of solvent falls under second-order reactions [46,47].

The results indicate that the rate constant changes with the concentration of nitric acid and the nature of the rare earth element.

The findings in Table 2 mirror those from studies on leaching these elements from phosphates with nitric acid solutions.

The table shows the relationship between the nitric acid concentration (mol/dm³) and the reaction rates, as well as the rate constants for the dissolution of lanthanum (La) and cerium (Ce) at a specified temperature. As the concentration of nitric acid increases from 3.0 to 12.5 mol/dm³, the reaction rates for both La and Ce rise significantly, with La reaching a maximum rate of $4.4 \cdot 10^{-4}$ mol/L·s and Ce reaching $8.9 \cdot 10^{-5}$ mol/L·s. Correspondingly, the rate constants also increase, with La showing a more pronounced rise from $2.22 \cdot 10^{-2}$ mol/L·s to $6.67 \cdot 10^{-2}$ mol/L·s and Ce increasing from $1.03 \cdot 10^{-2}$ mol/L·s to $3.68 \cdot 10^{-2}$ mol/L·s. This indicates that both the reaction rate and rate constant are highly

dependent on the concentration of nitric acid, with lanthanum consistently exhibiting higher values compared to cerium under the same conditions.

3.2. Study of the Influence of Sulfuric Acid on the Leaching of Lanthanum and Cerium from Phosphates

When determining the kinetic parameters of interaction, a mandatory requirement is the use of relatively monodisperse material (−150 + 200 mesh), i.e., the powdered material under study must consist of grains of uniform shape and size.

For a more in-depth study of the kinetics of the interaction process between solid substances and oxidizers (solvents), it is necessary to vary the concentration of the solvent over quite wide ranges. This will allow for an assessment of the impact of solvents on the rate of process change.

The determination of the reaction-rate constant was carried out according to the equation of [48]:

$$K = \frac{C_{\sigma}}{C_0^n \cdot \tau S}, \quad (9)$$

In the equation, K is the rate constant of the reaction; C is the amount of metal that has transitioned from the solid phase into solution, expressed in moles per cubic decimeter (mol/dm^3); σ is the stoichiometric coefficient, representing the number of moles of reagent required to dissolve one mole of solid substance; C_0 is the concentration of the dissolving reagent, in moles per cubic decimeter (mol/dm^3); τ is the time of contact between the solid phase and the reagent, in seconds; n is the order of the chemical reaction at the phase boundary; and S is the magnitude of the reacting surface area of the solid substance at time τ . When calculating the specific surface area of the powder, the shape of the particles was assumed to be spherical, and for the studied particles of lanthanum phosphate and cerium phosphate with a size of 0.104 mm, this equates to $0.7 \times 10^{-27} \text{ dm}^2$. In a 20 g sample, the reacting surface area equals $1.8 \times 10^{19} \text{ dm}^2$.

The order of the reaction at the phase boundary was determined by the tangent of the slope of the dependence, $\lg C/t - \lg C_0$, and is equal to 0.99.

Experiments were conducted in a thermostated cell, where a specified mass (20 g) of lanthanum and cerium phosphates with a particle size of 0.104 mm was leached under constant stirring at a speed of 700 rpm, at temperatures ranging from 20 °C to 95 °C, with S:L = 1:10 and concentrations of sulfuric acid ranging from 1.0 to 3.0 mol/dm^3 and hydrochloric acid ranging from 3.0 to 6.0 mol/dm^3 .

All experiments were carried out with a constant volume of solution. The determination of the kinetic characteristics of the interaction between lanthanum and cerium phosphates and sulfuric acid solutions revealed that their decomposition under the influence of the acid, followed by the transition of rare-earth-element cations into the solution, encounters significant difficulties. This is reflected in the values of the rate constants and activation energy (Tables 3 and 4).

Table 3. Effect of temperature and concentration of sulfuric acid on the rate constant of lanthanum and cerium leaching from phosphates.

The Concentration of Sulfuric Acid, mol/dm^3	Rate Constant, $\text{mol}/\text{L} \cdot \text{s}$									
	20 °C		40 °C		60 °C		80 °C		95 °C	
	La	Ce	La	Ce	La	Ce	La	Ce	La	Ce
1.0	1.83×10^{-9}	4.30×10^{-10}	2.59×10^{-9}	6.51×10^{-10}	3.07×10^{-9}	7.03×10^{-10}	3.11×10^{-9}	1.35×10^{-9}	4.08×10^{-9}	1.93×10^{-9}
1.5	1.89×10^{-9}	4.86×10^{-10}	2.44×10^{-9}	7.59×10^{-10}	3.23×10^{-9}	1.06×10^{-9}	3.96×10^{-9}	1.56×10^{-9}	5.43×10^{-9}	2.79×10^{-9}
2.0	2.11×10^{-9}	7.59×10^{-10}	2.60×10^{-9}	1.10×10^{-9}	3.60×10^{-9}	2.12×10^{-9}	4.56×10^{-9}	2.48×10^{-9}	5.51×10^{-9}	3.39×10^{-9}
2.5	1.84×10^{-9}	7.59×10^{-10}	2.44×10^{-9}	1.35×10^{-9}	3.07×10^{-9}	1.81×10^{-9}	4.37×10^{-9}	2.68×10^{-9}	5.89×10^{-9}	3.37×10^{-9}
3.0	2.07×10^{-9}	9.09×10^{-10}	2.67×10^{-9}	1.30×10^{-9}	3.82×10^{-9}	2.00×10^{-9}	5.05×10^{-9}	2.88×10^{-9}	7.26×10^{-9}	4.24×10^{-9}

Table 4. Effect of sulfuric acid concentration on the apparent activation energy of lanthanum and cerium leaching from phosphates.

The Concentration of Sulfuric Acid, mol/dm ³	1.0		1.5		2.0		2.5		3.0	
	La	Ce	La	Ce	La	Ce	La	Ce	La	Ce
Activation energy, kJ/mol	40.0	45.9	31.9	41.8	28.1	40.0	22.3	25.5	15.7	16.0

The effect of process temperature on the rate constant is most noticeable when phosphates interact with more concentrated solutions of sulfuric acid. For instance, an increase in the leaching temperature with a 1.0 mol/dm³ acid solution from 20 to 95 °C resulted in a 55% increase in the rate constant, while using a solution of 3.0 mol/dm³ led to a 75% increase.

Changing the acid concentration from 1.0 to 3.0 mol/dm³ at a constant process temperature has a less significant impact—for example, at 95 °C, the rate constant increased by 44%.

It should be noted that a kinetic parameter such as the apparent activation energy of the interaction of REE-containing minerals under the conditions of the experiments significantly depends on the concentration of sulfuric acid solutions (Table 4).

Increasing the acid concentration from 1.0 to 3.0 mol/dm³, the apparent activation energy of the lanthanum and cerium leaching process decreases, indicating an increase in the reaction rate.

The conducted studies have established that when leaching rare earth elements from phosphates with sulfuric acid solutions, the determined kinetic characteristics reach optimal values at a process temperature of 95 °C and an acid concentration of 3.0 mol/dm³.

3.3. Study of the Effect of Hydrochloric Acid on the Leaching of Lanthanum and Cerium from Phosphates

It is known that chloride ions, at certain concentrations, enhance the solubility of many metals due to the formation of complex anions. The study of the impact of hydrochloric acid on the leaching kinetics of lanthanum and cerium from phosphates is of practical interest.

Figure 11 presents the kinetic dependencies of leaching rare earth elements from phosphates with a 6.0 mol/dm³ (220 g/dm³) concentration of hydrochloric acid solution.

Based on the data from the figure, it can be concluded that the leaching of lanthanides proceeds differently. For instance, the transition of lanthanum into solution, with an increasing temperature and duration of the process, occurs due to an increase in the reaction rate of hydrochloric acid interaction with the phosphate complex with square antiprismatic symmetry [49].

At the same time, the behavior of cerium during leaching exhibits differences. The extraction process duration at a temperature of 20 °C does not significantly impact the degree of cerium extraction into the solution. After just 2 h of hydrochloric acid exposure, the extraction degree changes only from 22.4 to 28.6%.

Increasing the leaching temperature to 60 °C causes a sharp increase in the degree of cerium transition from phosphates into solution. This behavior of cerium may be correlated with the transition from a trivalent to a tetravalent state.

According to [50], tetravalent cerium acts as a complexing agent with chloride ions serving as ligands. This leads to an increased degree of cerium extraction into the solution.

The experimentally found rate constant is a complex characteristic, dependent on many factors; hence, the decrease in the rate constant of hydrochloric acid leaching was a logical consequence of the parallel reactions of the complex formation of lanthanum and cerium with chloride ions (Table 5).

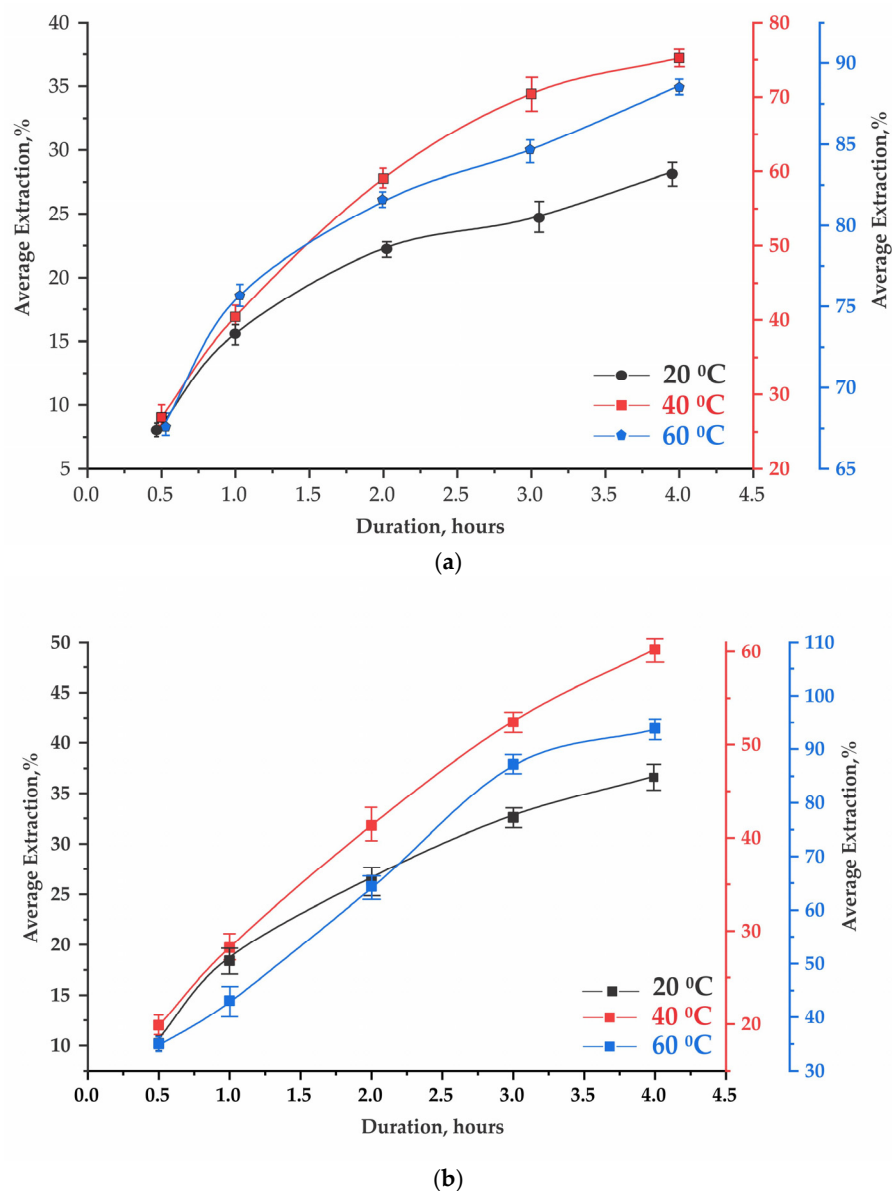


Figure 11. Kinetic dependencies of lanthanum leaching (a) and cerium (b) from phosphates. 1–20 °C; 2–40 °C; 3–60 °C.

Table 5. Rate constant of leaching of lanthanum and cerium and phosphates with hydrochloric acid solution.

Temperature, °C	La		Ce	
	Rate Constant, mol/L·s	Activation Energy, kJ/mol	Rate Constant, mol/L·s	Activation Energy, kJ/mol ^{−1}
20	3.36×10^{-9}	22.2	2.42×10^{-9}	22.8
40	5.04×10^{-9}		4.82×10^{-9}	
60	8.20×10^{-9}		6.32×10^{-9}	

The determination of the kinetic parameters for the leaching of rare earth elements from lanthanum and cerium phosphate demonstrated that under comparable experimental conditions, which include temperature, activation rate, and hydronium concentration H_3O^+ , the rate constants and activation energy for hydrochloric acid opening of salts coincide with those for sulfuric acid.

4. Conclusions

In this study, the leaching process of rare earth elements (REEs) from mineral materials, specifically lanthanum and cerium phosphates, was systematically investigated under varying acid conditions. The research highlights the unique effectiveness of sulfuric acid as a leaching agent, primarily due to its higher efficiency in solubilizing lanthanum and cerium phosphates compared to nitric and hydrochloric acids. The solubility studies demonstrated that, at elevated temperatures (up to 60 °C), the solubility of these phosphates increases significantly in sulfuric acid, providing a more favorable kinetic profile for REE extraction. The kinetic experiments revealed that the apparent activation energy for the dissolution process is lower for sulfuric acid, indicating a more energy-efficient reaction compared to other acids.

While the use of nitric acid can enhance the dissolution of rare earth elements, its cost and higher chemical reactivity limit its industrial application. Hydrochloric acid showed potential for selective leaching, particularly for cerium, but sulfuric acid remains the most effective and economical choice. This study concludes that sulfuric acid not only offers better thermodynamic and kinetic advantages but also simplifies the extraction process, making it highly suitable for large-scale industrial applications. These findings support the continued use of sulfuric acid as the primary leaching agent in the hydrometallurgical extraction of rare earth elements from phosphate minerals.

This research contributes to the ongoing efforts to optimize extraction technologies for REEs, especially from unconventional sources, offering a pathway toward more sustainable and economically viable practices. The use of sulfuric acid, coupled with the insights from the kinetic studies, presents a significant advancement in the efficient recovery of lanthanides from mineral materials, positioning it as the preferred acid for such processes.

Author Contributions: Conceptualization: R.A. and A.U.; Methodology: A.U., A.M. and N.L.; Software: K.K., A.M. and N.L.; Validation: R.A. and A.U.; Formal analysis: A.U.; Investigation: A.U., N.L. and R.A.; Resources: K.K., A.M. and N.L.; Data curation: R.A. and A.U.; Writing—original draft preparation: R.A.; Writing—review and editing: R.A. and A.U.; Visualization: K.K. and A.M.; Supervision: A.U.; Project administration: R.A.; Funding acquisition: R.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research is funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan, Programme Targeted Funding BR21882140.

Data Availability Statement: The data and results presented in this study are available in the article.

Conflicts of Interest: The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

References

1. Dutta, T.; Kim, K.H.; Uchimiya, M.; Kwon, E.E.; Jeon, B.H.; Deep, A.; Yun, S.T. Global demand for rare earth resources and strategies for green mining. *Environ. Res.* **2016**, *150*, 182–190. [\[CrossRef\]](#)
2. Eggert, R.G.; Wadia, C.; Anderson, C.; Bauer, D.; Fields, F.; Meinert, L.; Taylor, P. Rare earths: Market disruption, innovation, and global supply chains. *Annu. Rev. Environ. Resour.* **2016**, *41*, 199–222. [\[CrossRef\]](#)
3. Lafrenière, M.-C.; Lapierre, J.-F.; Ponton, D.E.; Guillemette, F.; Amyot, M. Rare Earth Elements (REEs) Behavior in a Large River across a Geological and Anthropogenic Gradient. *Geochim. Cosmochim. Acta* **2023**, *353*, 129–141. [\[CrossRef\]](#)
4. Wang, Z.-Y.; Fan, H.-R.; Zhou, L.; Yang, K.-F.; She, H.-D. Carbonatite-related REE deposits: An overview. *Minerals* **2020**, *10*, 965. [\[CrossRef\]](#)
5. Tamayo-Soriano, D.A.; Soria-Aguilar, M.d.J.; Picazo-Rodríguez, N.G.; Martínez-Luévanos, A.; Carrillo-Pedroza, F.R.; Figueroa-López, U.; Valenzuela García, J.L. Acid Leaching of La and Ce from Ferrocarbonatite-Related REE Ores. *Minerals* **2024**, *14*, 504. [\[CrossRef\]](#)
6. Yang, J.; Song, W.; Liu, Y.; Zhu, X.; Kynicky, J.; Chen, Q. Mineralogy and Element Geochemistry of the Bayan Obo (China) Carbonatite Dykes: Implications for REE Mineralization. *Ore Geol. Rev.* **2024**, *165*, 105873. [\[CrossRef\]](#)
7. Zhou, F.; Zhang, L.; Wang, Z.; Zhang, Y.; Chi, R. Effect of Surfactant Addition on Leaching Process of Weathered Crust Elution-Deposited Rare Earth Ores with Magnesium Sulfate. *Int. J. Min. Sci. Technol.* **2023**, *33*, 1045–1053. [\[CrossRef\]](#)
8. Yang, B.; He, J. New Insights into Selective Depression Mechanism of Tamarindus indica Kernel Gum in Flotation Separation of Fluorapatite and Calcite. *Sep. Purif. Technol.* **2025**, *354*, 128787. [\[CrossRef\]](#)

9. Yu, A.; Ding, Z.; Yuan, J.; Feng, Q.; Wen, S.; Bai, S. Process Mineralogy Characteristics and Flotation Optimization of a Low-Grade Oxidized Lead and Zinc Ore from Lanping Mine. *Minerals* **2023**, *13*, 1167. [\[CrossRef\]](#)
10. Jha, M.K.; Kumari, A.; Panda, R.; Kumar, J.R.; Yoo, K.; Lee, J.Y. Review on Hydrometallurgical Recovery of Rare Earth Metals. *Hydrometallurgy* **2016**, *165*, 2–26. [\[CrossRef\]](#)
11. Tan, X.; Liu, M.; He, K. Study of Long-Term Determination Accuracy for REEs in Geological Samples by Inductively Coupled Plasma Quadrupole Mass Spectrometry. *Molecules* **2021**, *26*, 290. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Reven, C.G.; Montano, M.; Samaniego, J.O.; Tanciongco, A.R.N.; Quierrez, R.N. Comparative Study on Determination of Selected Rare Earth Elements (REEs) in Ion Adsorption Clays Using Handheld LIBS and ICP-MS. *Philipp. J. Sci.* **2022**, *151*, 1599–1604. [\[CrossRef\]](#)
13. Cai, H.; Guan, B.; Xu, L. Low-cost ferrite PM-assisted synchronous reluctance machine for electric vehicles. *IEEE Trans. Ind. Electron.* **2014**, *61*, 5741–5748. [\[CrossRef\]](#)
14. Takano, M.; Asano, S.; Goto, M. Recovery of Nickel, Cobalt, and Rare-Earth Elements from Spent Nickel–Metal-Hydride Battery: Laboratory Tests and Pilot Trials. *Hydrometallurgy* **2022**, *209*, 105826. [\[CrossRef\]](#)
15. Mazurek, K.; Białowicz, K.; Trypuć, M. Recovery of Vanadium, Potassium, and Iron from a Spent Catalyst Using Urea Solution. *Hydrometallurgy* **2010**, *103*, 19–24. [\[CrossRef\]](#)
16. Yu, G.; Ni, S.; Gao, Y.; Mo, D.; Zeng, Z.; Sun, X. Recovery of Rare Earth Metal Oxides from NdFeB Magnet Leachate by Hydrophobic Deep Eutectic Solvent Extraction, Oxalate Stripping, and Calcination. *Hydrometallurgy* **2024**, *223*, 106209. [\[CrossRef\]](#)
17. Chen, W.; Honghui, H.; Bai, T.; Jiang, S. Geochemistry of Monazite within Carbonatite Related REE Deposits. *Resources* **2017**, *6*, 51. [\[CrossRef\]](#)
18. Brückner, L.; Elwert, T.; Schirmer, T. Extraction of Rare Earth Elements from Phospho-Gypsum: Concentrate Digestion, Leaching, and Purification. *Metals* **2020**, *10*, 131. [\[CrossRef\]](#)
19. Bazin, C.; Boulanger, J.-F. Investigation of the Flotation of an Ore Containing Bastnaesite and Monazite: Kinetic Study and Process Flowsheet Simulation. *Minerals* **2024**, *14*, 906. [\[CrossRef\]](#)
20. ALCONIX. Comprehensive Operations in Non-Ferrous Metals from Distribution and Sales to Manufacturing. Available online: <https://www.alconix.com/en/business/> (accessed on 10 January 2024).
21. Kenzhaliyev, B.; Surkova, T.; Berkinbayeva, A.; Baltabekova, Z.; Smailov, K. Harnessing Microwave Technology for Enhanced Recovery of Zinc from Industrial Clinker. *Metals* **2024**, *14*, 699. [\[CrossRef\]](#)
22. Chen, L.; He, X.; Dang, X.; Wang, X.; Liu, W.; Zhang, D.; Yang, T. Rare earth dissolution from polishing powder waste in H₂O₂–H₂SO₄ system: Condition optimization and leaching mechanism. *Hydrometallurgy* **2024**, *224*, 106248. [\[CrossRef\]](#)
23. Balinski, A.; Atanasova, P.; Wiche, O.; Kelly, N.; Reuter, M.; Scharf, C. Recovery of REEs, Zr(+Hf), Mn and Nb by H₂SO₄ leaching of eudialyte concentrate. *Hydrometallurgy* **2019**, *186*, 176–186. [\[CrossRef\]](#)
24. Tang, M.; Zhou, C.; Pan, J.; Zhang, N.; Liu, C.; Cao, S.; Hu, T.; Ji, W. Study on extraction of rare earth elements from coal fly ash through alkali fusion—Acid leaching. *Miner. Eng.* **2019**, *136*, 36–42. [\[CrossRef\]](#)
25. Chen, X.; Guo, F.; Chen, Q.; Liu, X.; Zhao, Z. Leaching tungsten and rare earth elements from scheelite through H₂SO₄–H₃PO₄ mixed acid decomposition. *Miner. Eng.* **2020**, *156*, 106526. [\[CrossRef\]](#)
26. Kim, K.; Choi, J.S.; Choi, E.; Nieman, C.L.; Joo, J.H.; Lin, F.R.; Gitlin, L.N.; Han, H.-R. Effects of community-based health worker interventions to improve chronic disease management and care among vulnerable populations: A systematic review. *Am. J. Public Health* **2016**, *106*, e3–e28. [\[CrossRef\]](#)
27. Abhilash; Sinha, S.; Sinha, M.K.; Pandey, B.D. Study on the Leaching Conditions of Rare Earth Elements from Uranium Sorption Tails. *Energy Sav. Resour. Sav.* **2014**, *127*, 70–73. [\[CrossRef\]](#)
28. Rao, M.; Xia, H.; Xu, Y.; Jiang, G.; Zhang, Q.; Yuan, Y.; Zhang, L. Study on Ultrasonic Assisted Intensive Leaching of Germanium from Germanium Concentrate Using HCl/NaOCl. *Hydrometallurgy* **2024**, *230*, 106385. [\[CrossRef\]](#)
29. Shen, X.; Finn, E.S.; Scheinost, D.; Rosenberg, M.D.; Chun, M.M.; Papademetris, X.; Constable, R.T. Using connectome-based predictive modeling to predict individual behavior from brain connectivity. *Nat. Protoc.* **2017**, *12*, 506–518. [\[CrossRef\]](#)
30. Akcil, A.; Swami, K.R.; Gardas, R.L.; Hazrati, E.; Dembele, S. Overview on Hydrometallurgical Recovery of Rare-Earth Metals from Red Mud. *Minerals* **2024**, *14*, 587. [\[CrossRef\]](#)
31. He, J.; Tang, H.; Guo, C.; Zhu, L.; Huang, S.; Yang, B. Synergist Enhancement of Effective Desilication of Graphite Ore by Rotary Triboelectric Separation and Surface Modification. *Powder Technol.* **2024**, *444*, 119965. [\[CrossRef\]](#)
32. Zhu, L.; He, J.; Chen, L.; Yang, B. Efficient Extraction of Rare Earth Elements from Coal-Series Kaolin by Combining Alkali Fusion and Sulfamic Acid Leaching. *Process Saf. Environ. Prot.* **2024**, *191*, 122–130. [\[CrossRef\]](#)
33. Ultarakova, A.; Karshyga, Z.; Lokhova, N.; Yessengazyev, A.; Kassymzhanov, K.; Mukangaliyeva, A. Studies on the Processing of Fine Dusts from the Electric Smelting of Ilmenite Concentrates to Obtain Titanium Dioxide. *Materials* **2022**, *15*, 8314. [\[CrossRef\]](#)
34. Zhang, K.; Liu, Z.; Liu, H.; Zhu, W.; Wei, B.; Zhong, X.; Wang, R.; Zeng, Y. Hydrochloric Acid Leaching of Rare Earth Elements from a Novel Source of Deep-Sea Sediments and Advantage of Reduction with H₂O₂. *Hydrometallurgy* **2024**, *230*, 106383. [\[CrossRef\]](#)
35. Ultarakova, A.; Karshigina, Z.B.; Lokhova, N.G.; Yessengazyev, A.M.; Kassymzhanov, K.K.; Tolegenova, S.S. Extraction of amorphous silica from waste dust of electrowinning of ilmenite concentrate. *Metalurgija* **2022**, *61*, 377–380.
36. Xu, D.; Shah, Z.; Cui, Y.; Jin, L.; Peng, X.; Zhang, H.; Sun, G. Recovery of Rare Earths from Nitric Acid Leach Solutions of Phosphate Ores Using Solvent Extraction with a New Amide Extractant (TODGA). *Hydrometallurgy* **2018**, *180*, 132–138. [\[CrossRef\]](#)

37. Dzulqornain, A.M.; Cueva-Sola, A.B.; Chung, K.W.; Lee, J.-Y.; Jyothi, R.K. Strategy for Possible Separation of Light Rare Earth Elements (La, Ce, Pr, Nd) from Synthetic Chloride Solutions by Oxidative Precipitation, Solvent Extraction, and Stripping. *Hydrometallurgy* **2024**, *224*, 106242. [[CrossRef](#)]
38. Ultarakova, A.; Lokhova, N.; Karshyga, Z.; Toishybek, A.; Yessengazyev, A.; Kassymzhanov, K.; Mukangaliyeva, A. Studies of Niobium Sorption from Chloride Solutions with the Use of Anion-Exchange Resins. *Processes* **2023**, *11*, 1288. [[CrossRef](#)]
39. Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Mir: Moscow, Russia, 1966; p. 412.
40. Farmer, V.C. *The Infrared Spectra of Minerals*; Mineralogical Society: London, UK, 1974; p. 539.
41. Pechkovsky, V.V.; Melnikova, R.Y.; Dzyuba, E.D.; Barannikova, T.I.; Nikanovich, M.V. Atlas of Infrared Spectra of Phosphates. In *Orthophosphates*; Nauka: Moscow, Russia, 1981; p. 248.
42. Anosov, V.Y.; Ozerova, M.I.; Fialkov, Y.Y. *Fundamentals of Physical-Chemical Analysis*; Nauka: Moscow, Russia, 1976; p. 503.
43. Moldoveanu, G.A.; Kolliopoulos, G.; Judge, W.D.; Ng, K.L.; Azimi, G.; Papangelakis, V.G. Solubilities of Individual Light Rare Earth Sulfates (Lanthanum to Europium) in Water and H₂SO₄ Solutions (Neodymium Sulfate). *Hydrometallurgy* **2024**, *223*, 106194. [[CrossRef](#)]
44. Ultarakova, A.; Lokhova, N.; Karshyga, Z.; Yessengazyev, A.; Kassymzhanov, K.; Mukangaliyeva, A. Recovery of Niobium Pentaoxide and Ammonium Sulfate from Titanium-Magnesium Production Waste. *J. Ecol. Eng.* **2023**, *24*, 227–235. [[CrossRef](#)]
45. Yatsimirsky, K.B. *Chemistry of Rare Earth Element Complex Compounds*; Institute of General and Inorganic Chemistry: Kiev, Ukraine, 1996; p. 196.
46. Ospanov, K.K. *Thermodynamics and Kinetics of Heterogeneous (Nonequilibrium) Chemical Processes*; Kompleks: Almaty, Kazakhstan, 2006; p. 328.
47. Baigenzhenov, O.S.; Chepushtanova, T.A.; Altmyshbayeva, A.Z.; Temirgali, I.A.; Maldybayev, G.; Sharipov, R.H.; Altaibayev, B.T.; Dagubayeva, A.T. Investigation of thermodynamic and kinetic regularities of asbestos waste leaching processes. *Results Eng.* **2024**, *21*, 102000. [[CrossRef](#)]
48. Dolivo-Dobrovolsky, V.V. Assessment of Selectivity in Dissolution of Mineral Substances. *Ore Benef.* **1964**, *5*, 38–41.
49. Kostromina, N.A. *Complexonates of Rare Earth Elements*; Nauka: Moscow, Russia, 1980; p. 219.
50. Grinberg, A.A. *Introduction to the Chemistry of Complex Compounds*; Chemistry: Leningrad, Russia, 1966; p. 632.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.