

Article

Study on the Effect and Mechanism of Impurity Aluminum on the Solvent Extraction of Rare Earth Elements (Nd, Pr, La) by P204-P350 in Chloride Solution

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Abstract: Solvent extraction is the most widely used method for separation and purification of rare earth elements, and organic extractants such as di(2-ethylhexyl) phosphoric acid (P204) and di(1-methyl-heptyl) methyl phosphonate (P350) are most commonly used for industrial applications. However, the presence of impurity ions in the feed liquid during extraction can easily emulsify the extractant and affect the quality of rare earth products. Aluminum ion is the most common impurity ion in the feed liquid, and it is an important cause of emulsification of the extractant. In this study, the influence of aluminum ion was investigated on the extraction of light rare earth elements by the P204-P350 system in hydrochloric acid medium. The results show that Al^{3+} competes with light rare earths in the extraction process, reducing the overall extraction rate. In addition, the Al^{3+} stripping rate is low and there is continuous accumulation of Al^{3+} in the organic phase during the stripping process, affecting the extraction efficiency and even causing emulsification. The slope method and infrared detection were utilized to explore the formation of an extraction compound of Al^{3+} and the extractant P204-P350 that entered the organic phase as $\text{AlCl}[(\text{HA})_2]_2\text{P350}_{(o)}$.

Keywords: Al^{3+} ; light rare earths; P204; P350; impurity



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1. Introduction

Rare earth elements include the lanthanides in the periodic table as well as scandium (Sc) and yttrium (Y) [1,2]. Owing to their excellent physical and chemical properties, rare earth elements are widely used in high-end technology, including the critical fields of new energy, national defense, and aerospace [3–5]. They are also known as the “vitamins” of the modern industry [6,7]. The physical and chemical properties of different REEs (Rare earth elements) are highly similar, and with increasing purity requirements of a single rare earth for industrial applications, the effective separation of REEs becomes crucial [8,9]. Solvent extraction is most widely used in the separation of REEs because it is considered more effective, lower cost and easier to implement than other separation techniques, and the use of selective organic solvents such as di(2-ethylhexyl) phosphoric acid (P204) and 2-Ethylhexylphosphonic acid mono-2-ethylhexyl ester (P507) allows the separation and purification of REEs with similar properties in solution to obtain high purity single rare earth products [10–12].

During the separation and purification of REEs in industrial production using organic extractants, emulsification of the extractant often occurs. This seriously adversely affects the continuous production process, resulting in decreased production efficiency, increased production costs, and fluctuations in the quality of produced products [13–15]. In China, the use of extraction agent P507 to separate rare earths causes nearly 300 tons of damage each year due to emulsification, with a loss of millions of dollars [16]. The economic loss of production shutdown caused by the emulsification of the extractant is even more

serious [17]. Given the serious economic consequences of the emulsification problem, there is a significant need for research into this problem. Years of research by many groups revealed that non-rare earth impurity ions (generally including Fe^{3+} , Al^{3+} , Mg^{2+} , Ca^{2+} , Si^{4+} , etc., which can affect the performance of the extractant during the extraction process) are the primary cause of extractant emulsification during the rare earth extraction process [13,18–20]. The Baotou mixed rare earth mine is the world's largest light rare earth element resource mine, with significant amounts of bastnaesite $((\text{Ce},\text{La})[\text{CO}_3]\text{F})$ and monazite $(\text{CePO}_4 \text{ or } (\text{Ce},\text{La})\text{PO}_4)$. Emulsification problems often occur in solvent extraction. To address this, ammonium bicarbonate solution is typically used to adjust the pH value to remove iron, then BaCl_2 and Na_2S are used to remove lead and zinc, and then trioctyldecyl tertiary amine (N235) is finally used to further extract impurity ions and minimize the content of impurity ions in the extraction solution [21]. Ionic rare earth ore is leached by $(\text{NH}_4)_2\text{SO}_4$, and rare earth ions adsorbed on the clay can react with NH_4^+ ions to enter the leachate. The leaching solution of rare earth ions also contains many impurity ions such as Al^{3+} , Ca^{2+} , Fe^{3+} , and Mg^{2+} , and the presence of these ions significantly impact the subsequent extraction and separation process [22]. In particular, the presence of aluminum ion impurity in this solution can cause different levels of hydrolysis, complexation, flocculation, and precipitation at different pH values, and the aluminum ions can be easily extracted into the organic phase during the extraction process, causing the extractant to emulsify [23,24].

The 209 Geological Brigade of the Nuclear Industry of China's Yunnan Province discovered a massive amount of ionic rare earth ore in southern Yunnan, consisting of La, Ce, Pr, Nd, and Y. In addition to rare earth minerals, the clay in this location also contains a large amount of impurity ions such as Al^{3+} and Ca^{2+} . Leachate prepared at this site would contain a large amount of impurity ions and rare earth ions, which will have a significant impact on the subsequent extraction and separation process. For this newly discovered ionic rare earth ore, studies have focused on the extraction and separation process of the P204-P350 system. The addition of P350 can reduce the extraction capacity of P204 for light rare earths to a certain extent, but significantly reduces the acidity required for stripping. Aluminum ion is the most common impurity ion in this ion-type rare earth ore and it is essential to determine its influence on the extraction of light rare earth by the P204-P350 system for the future efficient utilization of this extensive ion-type rare earth ore. This study systematically examined the effect of Al^{3+} on the P204-P350 system for the extraction and stripping of light rare earths and explored the combination mechanism of P204-P350 and Al^{3+} .

2. Experiment

2.1. Experimental Instruments and Reagents

Di(2-ethylhexyl) phosphoric acid (P204) was supplied by Sinopharm Chemical Reagent Co. Ltd in china. (purity > 99%), di(1-methyl-heptyl) methyl phosphonate (P350) was obtained from Aladdin reagent company (purity > 99%), the sulfonated kerosene for extractant dilution was supplied by Guangzhou Xiangyang Fusen Petrochemical Co., Ltd. in china, rare earth oxide and AlCl_3 were supplied by Sinopharm Chemical Reagent Co. Ltd., (purity > 99.9%), and other reagents were of analytical grade.

DW-3 digital display electric stirrer was used to stir the organic phase and the stock solution, ME204E electronic analytical balance was used to accurately weigh the chemical reagents, FE20 pH meter was used to determine the pH value of the stock solution and raffinate, Optoma8000 inductively coupled plasma spectrometer (ICP-OES) was used to detect the content of rare earth ions and aluminum ions in the solution, and FT-IR spectra were recorded on a Bruker Vertex 70 spectrometer ($500\text{--}4000 \text{ cm}^{-1}$).

2.2. Experimental Methods

The extraction experiments were carried out as follows. Light rare earth ions in aqueous solution were prepared by dissolving rare earth oxide in 3 mol/L hydrochloric

acid, and the Al^{3+} in aqueous solution was prepared by dissolving the AlCl_3 in deionized water to the desired concentration. The organic phase was prepared by fully mixing P204 and P350 in various proportions. Equal volumes (10 mL) of aqueous and organic phases were mixed and stirred in a beaker using a single-shaft stirring paddle for 20 min to achieve complete equilibrium. All experiments were conducted at a temperature of 298 ± 2 K. After the completion of the extraction process, the phases were separated using a funnel, and the concentrations of rare earth ions and Al^{3+} in the aqueous phase and the raffinate aqueous phase were analyzed using ICP-OES. The concentrations of the rare earth ions and Al^{3+} in the organic phase were determined by subtracting the equilibrium aqueous phase concentrations from the initial concentrations.

The back-extraction experiments were carried out as follows. P204 and P350 were mixed in a specific volume ratio, and equal volumes of the aqueous and organic phases were mixed and stirred in a beaker using a single-shaft stirring paddle for 20 min. After phase separation, the concentrations of rare earth ions and Al^{3+} in the loaded organic phase were determined using mass balance. A stripping agent was then used to perform single-stage stripping on the loaded organic phase, and the concentrations of rare earth ions in the stripping solution were then determined.

2.3. Experimental Calculation

The extraction rate (E_{Re}), distribution ratio (D_{Re}), stripping rate (R_f) were calculated according to Equations (1)–(3) as follows:

$$E_{\text{Re}} = \frac{n_{\text{Re}(O)}}{n_{\text{Re}(a)}} \times 100\% \quad (1)$$

$$D_{\text{Re}} = \frac{C_{\text{Re}(O)}}{C_{\text{Re}(a)}} \quad (2)$$

$$R_f = \frac{C_{\text{Re}(a)}^1 V_a}{C_{\text{Re}(o)}^1 V_o} \times 100\% \quad (3)$$

where $n_{\text{Re}(O)}$ and $n_{\text{Re}(a)}$ represent the amount of rare earth ions in the extracted organic and the amount of rare earth ions in the feed solution, respectively; $C_{\text{Re}(O)}$ and $C_{\text{Re}(a)}$ represent the concentration of rare earth ions in the organic phase and in the aqueous phase at the time of extraction equilibrium, respectively. $C_{\text{Re}(O)}^1$ and $C_{\text{Re}(a)}^1$ represent the molar concentration of rare earth ions in the loaded organic phase and the back-extraction aqueous phase, respectively; V_o , V_a represent the volume of the loaded organic phase and the back-extraction aqueous phase, respectively.

3. Results and Discussion

3.1. Form of Aluminum Ion and Lanthanum Ion in Aqueous Solution

The component distribution of 0.1 mol/L aluminum and lanthanum solution at different pH values was calculated by Visual MINTEQ simulation, as shown in Figure 1. When the pH of solution was in the range of <2 , most aluminum ions in the solution are Al^{3+} . With pH value increased to the range of 2–4, the aluminum ions in the solution are mainly $\text{Al}(\text{OH})^{2+}$, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$, AlOH^{2+} , and Al^{3+} . Although there is significantly less Al^{3+} , it remains the main component of the solution. When the pH of solution in the range of >4 , Al^{3+} is basically transformed into polymer ions or hydrated ions through hydrolysis and flocculation, and white flocculent precipitate $\text{Al}(\text{OH})_{3(\text{aq})}$ begins to appear. When precipitation occurs in the solution, it is difficult to separate the phases during the steps of extraction and separation. Compared with aluminum, the solution composition of lanthanum under different pH conditions is much simpler. When the pH of solution is in the range of <9 , most lanthanum ions in the solution are La^{3+} . With pH value increased to the range of 9–14, the lanthanum ions in the solution is mainly LaOH^{2+} . Additionally, the optimal pH range for P204-P350

is about 3 for the extraction of rare earths. Therefore, the pH of the aluminum solution is controlled between 2–4 in the experiment.

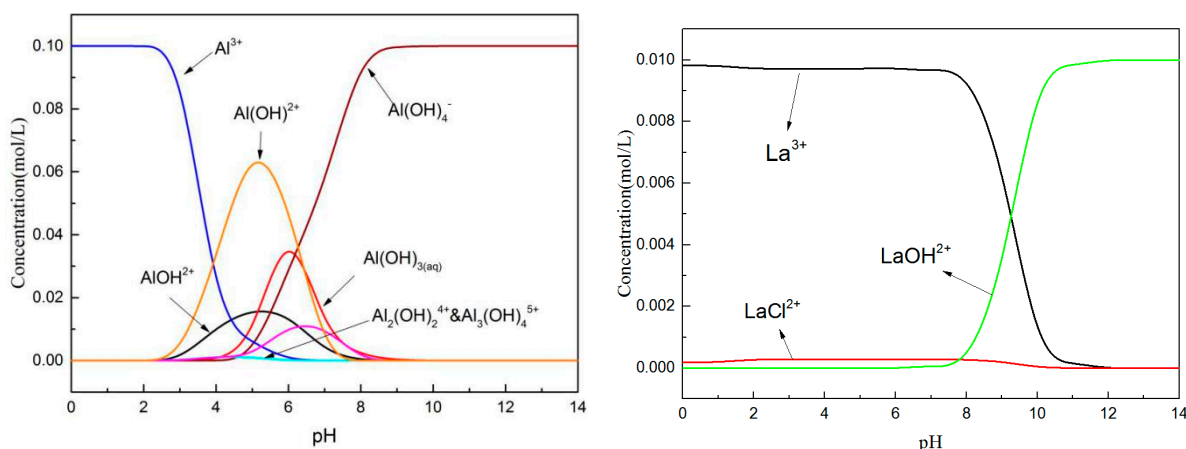


Figure 1. The composition diagram of a solution of 0.1 mol/L Al³⁺ and 0.01 mol/L La³⁺ under different pH conditions.

3.2. Effect of Aluminum Ion Concentration

The influences of pH value and aluminum ion concentration on the extraction of Al(III) from the feed solution were determined. Extraction was performed at a temperature of 298 ± 2 K with a volume ratio of P204 in the organic extractant P204-P350 of 0.9. Extraction was performed for 20 min under the condition of O/A = 1:1. During the extraction process, the pH value of the aqueous solution was adjusted with different gradient concentrations of dilute HCl and ammonia. After completion of extraction, the content of aluminum in the raffinate was determined to assess the influence of pH value on the extraction of Al(III). The experimental results are shown in Figures 2 and 3.

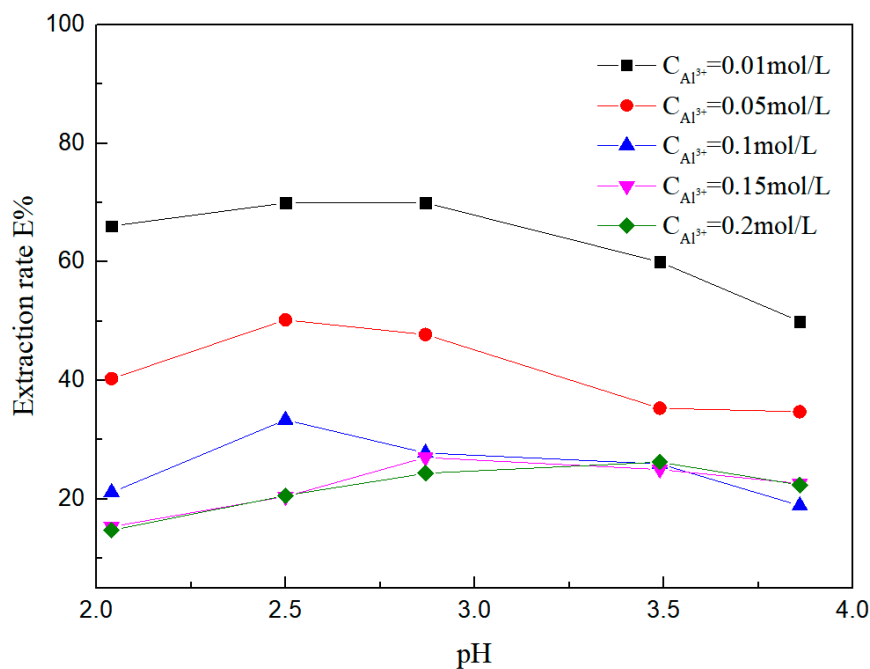


Figure 2. The relationship between concentration of Al³⁺ and extraction rate.

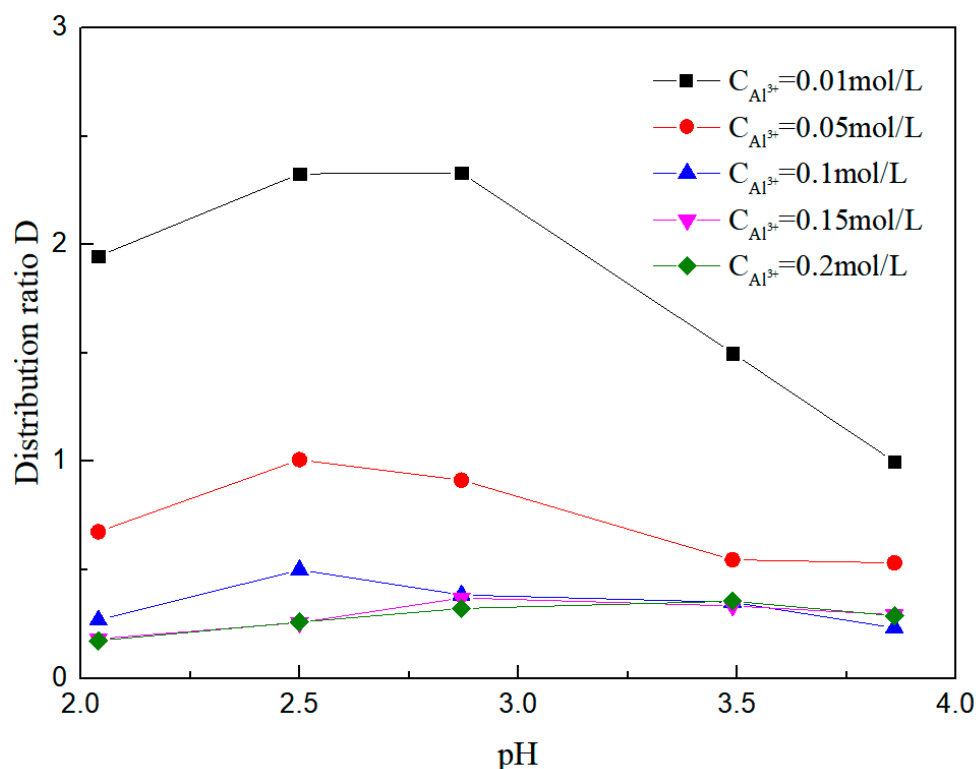


Figure 3. The relationship between concentration of Al^{3+} and distribution ratio.

As shown in the figures, the concentration of Al^{3+} and the concentration of H^+ in the solution affect the extraction. Under the same pH value, the lower the concentration of Al^{3+} in the solution, the higher the extraction rate of Al^{3+} by P204-P350. At a concentration of aluminum ion of 0.01 mol/L, the extraction rate was significantly higher than the rates at other concentrations. At a pH of the aqueous phase of 2.86, the extraction rate and distribution ratio were 71% and 2.37, respectively. For Al^{3+} concentration in the range of >0.1 mol/L, the extraction rate in the solution was lower overall and below 30%. At constant concentration of Al^{3+} in the solution, as the pH of the solution increased, the extraction rate of Al^{3+} first increased and then decreased. The best extraction effect was obtained when the solution pH = 2.5. This may be because the content of Al^{3+} in the solution gradually decreases with the continuous increase in pH value, but the content of polymer ions $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, $AlOH^{2+}$ continues to increase. With almost no cation exchange between the substance and the organic extractant, the extraction rate of aluminum appears to decline. At pH less than 2.5, the H^+ content in the solution is high, which will inhibit the release of H^+ when Al^{3+} is combined with the extractant, thereby hindering the extraction reaction.

3.3. Stripping of Aluminum Ion in the Loaded Organic Phase

Organic phase P204-P350 and 0.1 mol/L aluminum ion solution were mixed under the condition of O:A = 1:1 and fully stirred for 20 min at a temperature of 298 ± 2 K. The aluminum ion content in the raffinate aqueous phase was then determined. To determine the effect of different concentrations of stripping agents on the stripping of aluminum in the loaded organic phase, this process was performed with different concentrations of HCl, HNO_3 , and H_2SO_4 as the stripping agents. The experimental results are shown in Figure 4.

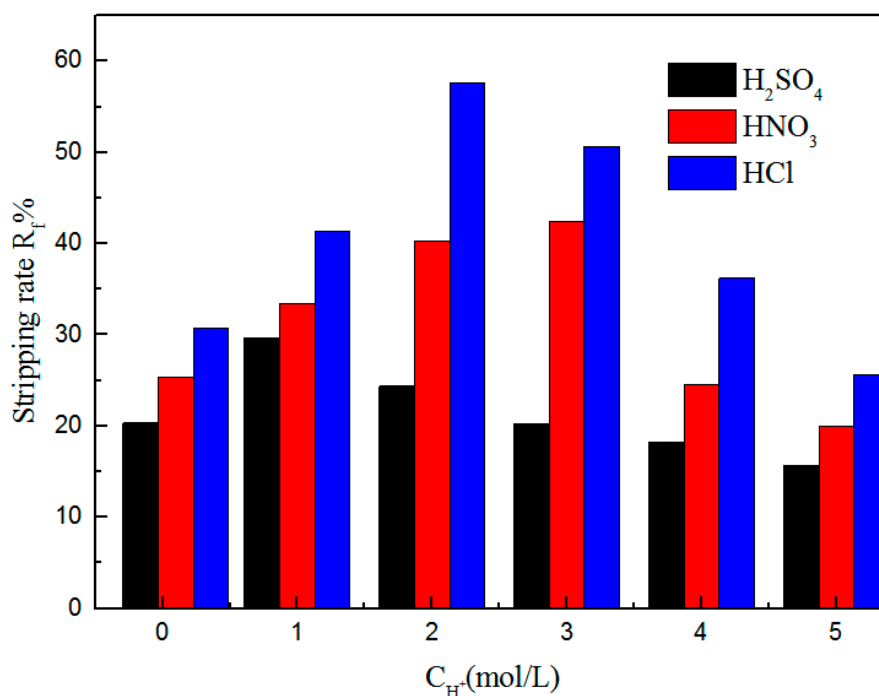


Figure 4. Stripping of Al³⁺ with HCl, HNO₃ and H₂SO₄ from the loaded organic phase.

As shown in Figure 4, the ability of different stripping agents to strip light rare earth ions in the loaded organic phase is in the decreasing order of HCl, HNO₃, and then H₂SO₄. This may be caused by the difference of the acid radical ion radius of different inorganic acids. The order of the radius of Cl⁻, NO₃⁻, SO₄²⁻ is Cl⁻ > NO₃⁻ > SO₄²⁻, which makes it easier for Al³⁺ to combine with Cl⁻. Al³⁺ ions in the loaded organic phase are most easily stripped into the aqueous phase by HCl. At a concentration of H⁺ of 2 mol/L, the stripping rate of Al³⁺ is 58%. With increasing concentration of the stripping agent, the stripping rate of Al³⁺ decreases. When HNO₃ is used as the stripping agent, the stripping rate of Al³⁺ within the range of 2–3 mol/L of H⁺ concentration is 43%. Poor stripping effect was achieved for H₂SO₄ as the stripping agent, with only 31% stripping rate at H⁺ concentration of 0.5 mol/L. During stripping, as the concentration of stripping agent increases, the stripping effect first increases and then decreases. This is mainly because in the stripping process, the H⁺ in the stripping agent is exchanged with Al³⁺ in the loaded organic phase. As the concentration of the stripping agent increases, the H⁺ content in the solution increases for improved exchange capacity with Al³⁺, so the stripping rate becomes higher and higher. However, when the concentration of the stripping agent further increases, the concentration of the corresponding anions in the solution such as Cl⁻, NO₃⁻ and SO₄²⁻ will also increase, causing Al³⁺ to combine with the anions and hinder the exchange reaction with H⁺, resulting in a decrease in the stripping rate.

3.4. Effect of Aluminum Ion on Rare Earth Extraction

The effect of aluminum ion on rare earth extraction was next determined. At a temperature of 298 ± 2 K, solutions were prepared with La³⁺, Pr³⁺, and Nd³⁺ at concentrations of 0.01 mol/L and Al³⁺ at varying concentrations. The organic phase P204-P350 was mixed with the different solutions under the condition of O:A = 1:1 for 20 min. The effect of different concentrations of Al³⁺ on the extraction of rare earth elements was measured, and the experimental results are shown in Figure 5.

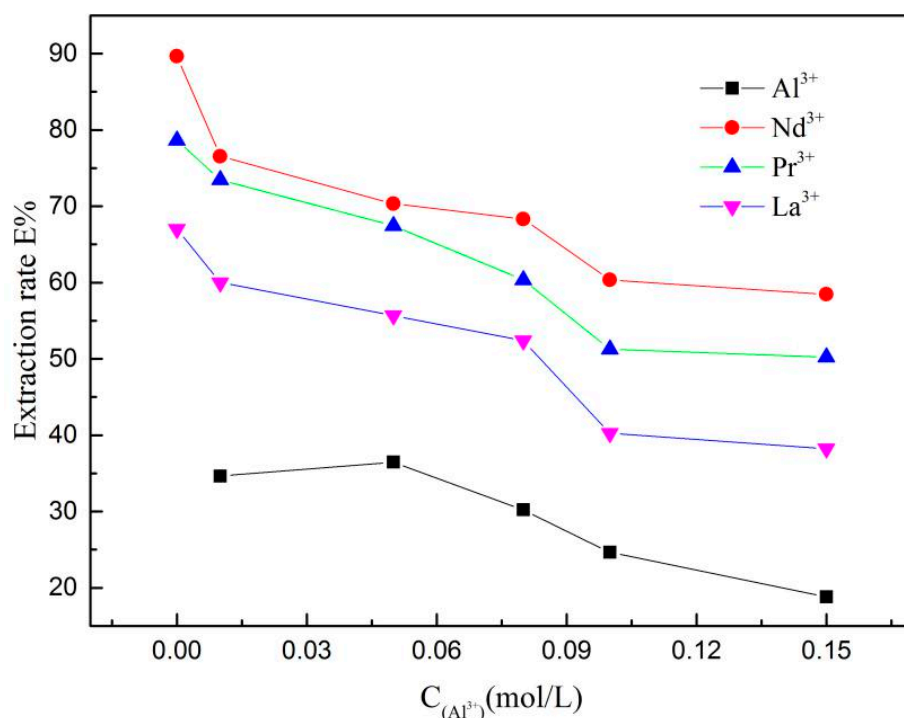


Figure 5. The effect of different concentrations of Al^{3+} on the extraction of light rare earth elements (pH = 2.86).

The presence of Al^{3+} will significantly affect the extraction rate of light rare earth elements in the P204-P350 system. With the increase in Al^{3+} concentration, the extraction rate of light rare earths gradually decreases, indicating that there is a competitive relationship between Al^{3+} and light rare earth elements. Al^{3+} is extracted into the organic phase, which inhibits the extraction effect of rare earth elements and significantly reduces the extraction rate. In the absence of Al^{3+} in the solution, the highest extraction rates of light rare earth elements by P204-P350 were obtained, with $E_{Nd^{3+}} = 89\%$, $E_{Pr^{3+}} = 79\%$, and $E_{La^{3+}} = 65\%$. The presence of Al^{3+} in the range of >0.1 mol/L had basically no effect on the extraction rate of light rare earth elements. This is mainly because when the Al^{3+} concentration is too high, the extraction of Al^{3+} by P204-P350 becomes saturated and no more can be extracted into the organic phase. The results indicate that the presence of Al^{3+} has a significant impact on the extraction rates of light rare earth elements, so its presence can reduce industrial production efficiency and increase production costs.

3.5. Effect of Aluminum Ion on Rare Earth Stripping

The light rare earth ions that are extracted into the organic phase can form complexes with the extractant. These complexes are destroyed by the stripping agent, which allows the rare earth ions to enter the stripping solution. Therefore, the stripping process is critical to the overall extraction and separation process. We next evaluated the effect of aluminum ions on rare earth stripping. To do this, organic phase P204-P350 was mixed with 0.1 mol/L aluminum ion and 0.01 mol/L light rare earth elements under the condition of O:A = 1:1 and fully stirred for 20 min. The amounts of aluminum ions and rare earth ions in the raffinate aqueous phase were then determined. Different concentrations of hydrochloric acid were used as the stripping agent to explore the aluminum ion effect on the stripping of rare earth ions and the experimental results are shown in Figure 6.

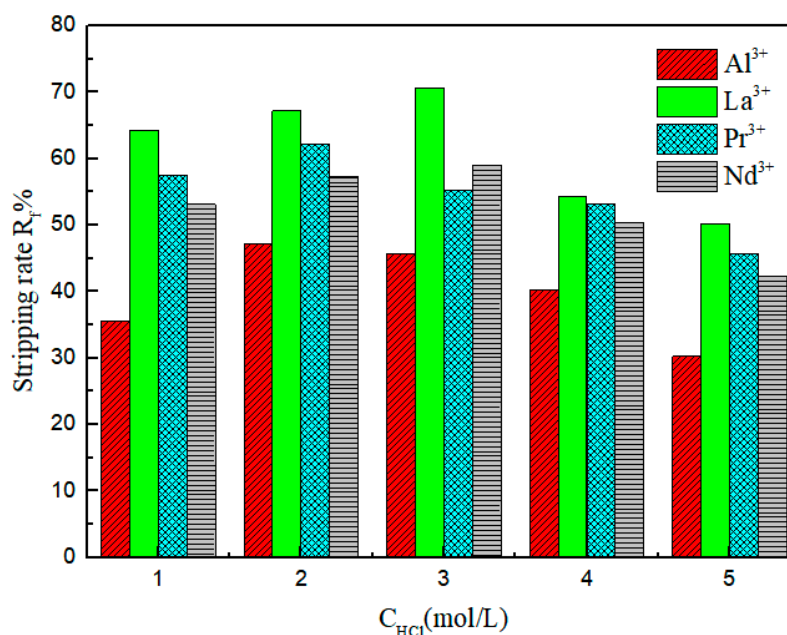
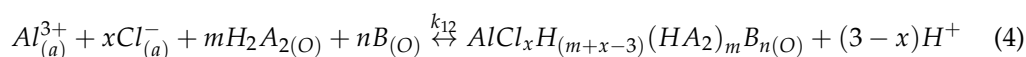


Figure 6. Stripping of Al³⁺ and light rare earth elements from the loaded organic phase using HCl.

When Al³⁺ and light rare earths are back-extracted together, the back-extraction rates are low, indicating that the stripping between Al³⁺ and rare earth ions has mutual influence. The best rare earth ion stripping effects were observed at 3 mol/L hydrochloric acid: Rf_{La³⁺} = 73%, Rf_{Pr³⁺} = 57%, and Rf_{Nd³⁺} = 64%. As the concentration of hydrochloric acid increased, the back-extraction effect of Al³⁺ and rare earth ions decreased. This may be because the excessive acidity can destroy the complex structure formed between the rare earth ions and the extractant, limiting the effective back-extraction of the rare earth ions. Al³⁺ can combine with Cl⁻ to hinder the exchange reaction with H⁺, resulting in an increase in the back-extraction rate. After Al³⁺ is extracted into the organic phase, it is difficult to effectively complete the stripping, as the aluminum ions in the organic phase will affect the recycling of the extractant and increase the subsequent possibility of emulsification of the extractant.

3.6. Aluminum Ion Extraction Mechanism

When the pH of the solution is in the range of 2–4, Al(III) mainly exists in the form of Al_(a)³⁺ and is extracted into the organic phase as Al_(a)³⁺ during the extraction process. Therefore, assuming that P204-P350 extracts Al_(a)³⁺ in hydrochloric acid, the reaction equation can be expressed as [25,26]:



Then the equilibrium constant K_{12} of the reaction can be expressed as:

$$K_{12} = \frac{[AlCl_xH_{(m+x-3)}(HA_2)_mB_{n(O)}]_{(O)} [H^{+}]_{(a)}^{(3-x)}}{[Al^{3+}]_{(O)} [Cl^{-}]_{(a)}^x [H_2A_2]_{(O)}^m [B]_{(O)}^n} \quad (5)$$

The Al³⁺ distribution ratio D_{12} is expressed as:

$$D_{12} = \frac{AlCl_xH_{(m+x-3)}(HA_2)_mB_{n(O)}}{Al_{(a)}^{3+}} = D_3 - D_1 - D_2 \quad (6)$$

Rearranging Equation (6) into its logarithmic form:

$$\lg D_{12} = \lg K_{12} + x \lg [Cl^-] + m \lg [H_2A_2] + n \lg [B] + (3 - x)pH \quad (7)$$

where D_1 and D_2 represent the distribution ratio of P204 and P350 single extraction aluminum, respectively; D_3 represents the distribution ratio of P204-P350 co-extracted aluminum; K_{12} is the extraction equilibrium constant of extracted aluminum; H_2A_2 represents the acidic extractant P204; B represents the neutral extractant P350.

To determine the extraction stoichiometry of aluminum ions in the P204-P350 extraction system, a series of experiments were carried out by varying the pH of the aqueous phase and the concentrations of extractants P204 and P350. The pH value of the initial aqueous phase changes, and the pH value of the raffinate aqueous phase after the reaction reaches equilibrium were measured. These experiments used 0.1 mol/L aluminum ion, an A/O ratio of one, and unchanged concentrations of extractants P204 and P350. The values of $\lg D_{12}$ versus pH are plotted and fitted as shown in Figure 7. The $\lg D_{12}$ increases linearly as the pH increases and the linear relationship between $\lg D_{12}$ and pH is obtained with a slope of two. This means that in the process of extracting Al^{3+} , each Al^{3+} extracted into the organic phase releases two H^+ into the water. This is consistent with the observed significant increase in the H^+ concentration of the raffinate aqueous phase during the extraction process. Similarly, concentrations of the initial aqueous acidity and aluminum ion ($C_{Al^{3+}} = 0.1$ mol/L) were fixed, and sulfonated kerosene was used as the diluent to change the concentrations of extractants P204 and P350. The values of $\lg D_{12}$ versus $\lg[P204]$ and $\lg[P350]$ were plotted and fitted, as shown in Figure 8. The $\lg D_{12}$ increases linearly with the increases in $\lg[P204]$ and $\lg[P350]$. Linear relationship between $\lg D_{12}$ and $\lg[P204]$ is obtained with a slope of two, and linear relationship between $\lg D_{12}$ and $\lg[P350]$ is obtained with a slope of one.

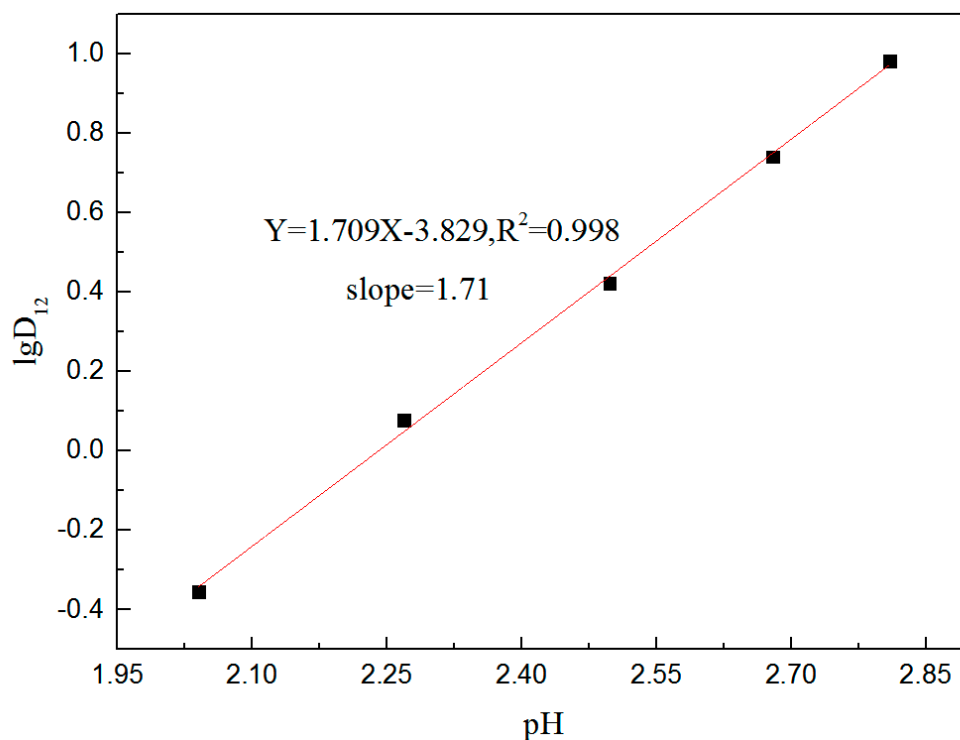


Figure 7. Effect of the concentration of H^+ and the distribution ratio D for Al^{3+} extracted by P204-P350.

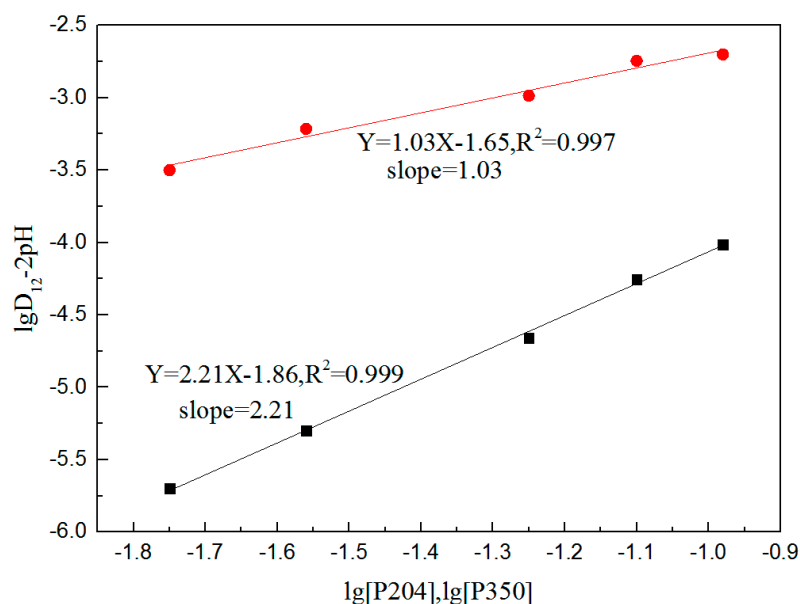


Figure 8. Effect of the concentration of P350 and P350 in the mixed system on the distribution ratio D.

Based on the above results, Equation (4) can be expressed as:



3.7. Infrared Spectrum Analysis

The P-O-H bond in P204 can participate in a substitution reaction with rare earth elements, and the P=O bond in P350 forms a coordination bond with rare earth elements for extraction. Previous research found that the addition of P350 into P204 somewhat weakened the hydrogen bonding ability of P204 and shifted the characteristic absorption peak corresponding to hydrogen bonds, which promotes the back-extraction of rare earths. To further explore the structure of the complex formed by Al^{3+} and the extractant, we detected the infrared spectrum of Al^{3+} and the rare earth ions with the extractant and then inferred the structure of the complex based on the change of the characteristic absorption peaks. The result is shown in Figure 9.

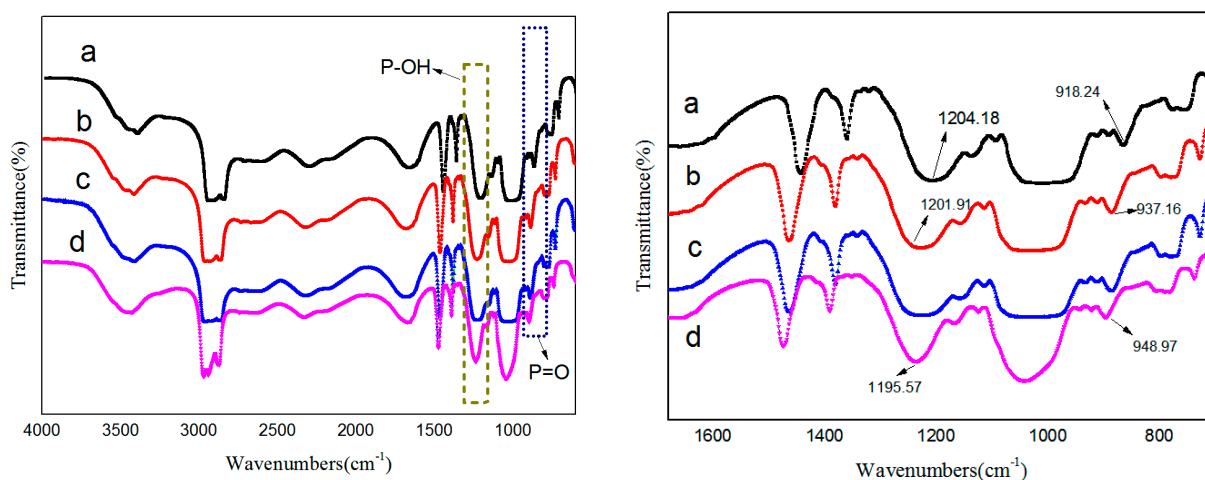


Figure 9. FT-IR spectra of La^{3+} and Al^{3+} extracted by P204-P350 (a P204-P350; b Al^{3+} + P204-P350; c La^{3+} + P204-P350; d Al^{3+} + La^{3+} + P204-P350).

It can be seen from the figure that the FT-IR spectra of Al^{3+} + P204-P350 (b) and La^{3+} + P204-P350 (c) are basically similar, indicating a potentially similar structure of the complex formed by Al^{3+} and rare earth ions with the extractant. Compared with the pattern seen for P204-P350 (a), the characteristic absorption peak of the extractant P-OH shifted from 918.24 cm^{-1} to 937.16 cm^{-1} . This indicates that the P-O-H bond combines with Al^{3+} to form P-O-Al. The special absorption peak of the P=O bond of the extractant is red-shifted from 1204.18 cm^{-1} to 1201.91 cm^{-1} . This indicates that the P=O bond in the extractant forms a coordination bond with Al^{3+} , which reduces the electron cloud density of the P=O double bond and weakens the strength of the bond, causing the vibration frequency to drop. When the extractant P204-P350 extracts Al^{3+} and rare earth elements, the FT-IR spectra are similar with those of Al^{3+} P204-P350 and La^{3+} P204-P350. This is because Al^{3+} has the same binding site as the extractant, and both bind with the extractant, so P-O-H and P=O form a complex. The characteristic absorption peak of the P-O-H bond shifted from 918.24 cm^{-1} to the left to 948.97 cm^{-1} , $\Delta\nu = 30.53\text{ cm}^{-1}$, and the characteristic peak of P=O double bond redshifted from 1204.18 cm^{-1} to 1195.57 cm^{-1} . The Al^{3+} and rare earth ions coordinate with the P=O double bond, causing the P=O dipole moment to change and the characteristic peak to move [27,28].

3.8. Structure Formula of Extraction Compound

The above application of the slope method and spectra analysis allows the proposal of the structure of the final extracted complex. In the extraction process, Al^{3+} and the P-O-H bond in the two P204 molecules undergo a substitution reaction, release 2 H^+ into the solution, and at the same time form a coordination bond with a P=O double bond of P350. The specific structure of the extraction compound is shown in Figure 10.

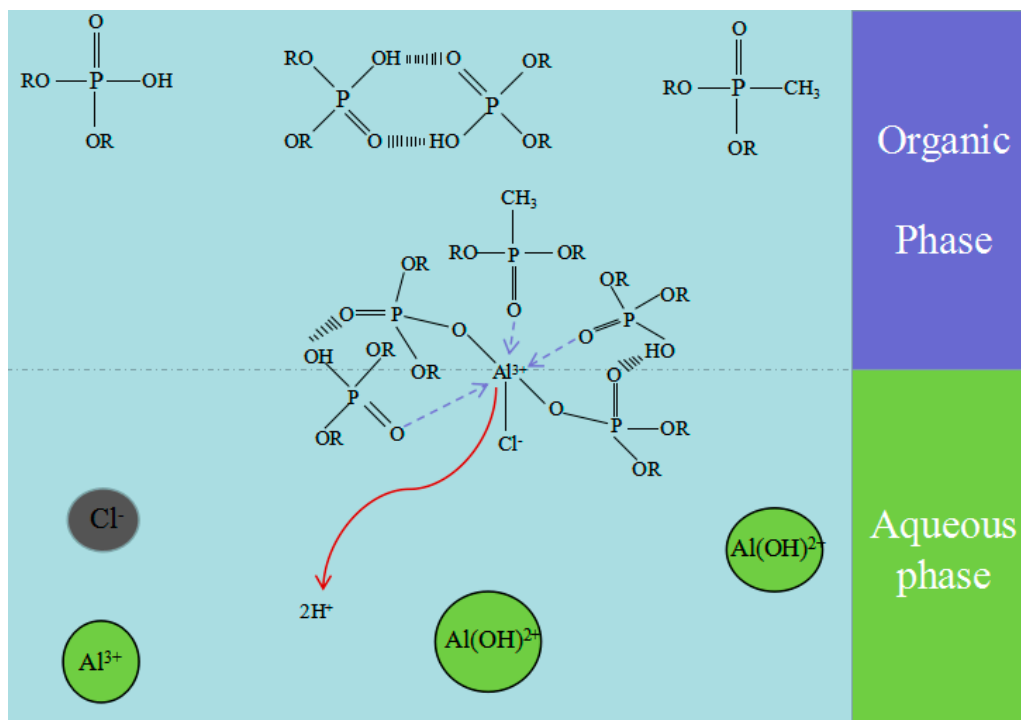


Figure 10. Structure of extracted complex.

4. Conclusions

The influence of the impurity aluminum ion on the extraction of light rare earth elements in hydrochloric acid medium by P204-P350 system was determined. The following conclusions can be drawn:

1. Aluminum ions in the feed liquid will compete with light rare earths, and with the increased concentration of aluminum ions, the greater the inhibition of the rare earth extraction rate.
2. At an aluminum ion concentration in the solution of 0.15 mol/L, the extraction rates of the light rare earths were $E_{Nd}^{3+} = 58\%$, $E_{Pr}^{3+} = 50\%$, and $E_{La}^{3+} = 40\%$.
3. The effect of Al^{3+} in the P204-P350 system on the stripping by HCl, HNO_3 , and H_2SO_4 was also investigated, and the stripping effect was in a decreasing order of HCl, then HNO_3 , followed by H_2SO_4 . At a concentration of hydrochloric acid of 2 mol/L, the back-extraction rate of Al reached the maximum value of 58%. The presence of impurity aluminum also has a significant impact on the back-extraction of light rare earths.
4. Al^{3+} combined with P-O-H in the extractant P204 and P=O in P350 to form a complex, and finally entered the organic phase with the structure of $AlCl[(HA)_2]_2P350_{(o)}$.

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References

1. Linda, O.; Satu, P.; Esa-Matti, T.; Paula, S.; Kati, O.; Riitta, L.K. Recycling and substitution of light rare earth elements, cerium, lanthanum, neodymium, and praseodymium from end-of-life applications-A review. *J. Clean. Prod.* **2018**, *236*, 117573.
2. Jia, S.; Guo, X.G.; Gao, Y.; Wu, S.; Xu, R.G.; Sun, X.Q. Recovery of thorium and rare earths from leachate of ion-absorbed rare earth radioactive residues with N1923 and Cyanex572. *J. Rare Earths* **2020**, *9*, 13.
3. Zhao, H.Y.; Xia, J.L.; Yin, D.D.; Luo, M.; Yan, C.H.; Du, Y.P. Rare earth incorporated electrode materials for advanced energy storage. *Coordin. Chem. Rev.* **2019**, *390*, 32. [[CrossRef](#)]
4. Liu, J.; Wu, X.H.; Huang, K.; Liu, W.Q.; Zhao, Z.M.; Liu, H.Z. Instability behavior of bubble supported organic liquid membrane in extraction of low-concentration rare earths from in-situ leaching solutions of ion-adsorption ores. *Miner. Eng.* **2020**, *159*, 106645. [[CrossRef](#)]
5. Vipin, K.S.; Vinod, K.; Ravinder, S.J. Investigation of rare earth particulate on tribological and mechanical properties of Al-6061 alloy composites for aerospace application. *J. Mater. Res. Technol.* **2019**, *8*, 3504.
6. Ni, S.N.; Chen, Q.W.; Gao, Y.; Guo, X.G.; Sun, X.Q. Recovery of rare earths from industrial wastewater using extraction-precipitation strategy for resource and environmental concerns. *Miner. Eng.* **2020**, *151*, 106315. [[CrossRef](#)]
7. Nagaphani, K.B.; Zheng, L.; Bram, V.; Koen, B. Structural effects of neutral organophosphorus extractants on solvent extraction of rare-earth elements from aqueous and non-aqueous nitrate solutions. *Sep. Purif. Technol.* **2021**, *225*, 117711.
8. Chen, L.; Li, H.L.; Chen, J.; Li, D.Q.; Liu, T.C. Separation of heavy rare earths by di-(2-ethylhexyl) phosphinic acid: From fundamentals to cascade extraction simulation. *Miner. Eng.* **2020**, *149*, 106232. [[CrossRef](#)]
9. He, Y.; Guo, S.H.; Chen, K.H.; Zhang, L.B.; Li, S.W.; Yin, S.H. Application of microchemical technology in mass transfer behavior contrastive research of rare earth extraction. *Microchem. J.* **2019**, *150*, 104180. [[CrossRef](#)]
10. Wei, H.Q.; Li, Y.L.; Zhang, Z.F.; Liao, W.P. Synergistic solvent extraction of heavy rare earths from chloride media using mixture of HEHHAP and Cyanex272. *Hydrometallurgy* **2020**, *191*, 105240. [[CrossRef](#)]
11. Na, S.; Kun, H. Separation of rare earths using solvent extraction consisting of three phases. *Hydrometallurgy* **2019**, *188*, 112.
12. Wei, H.Q.; Li, Y.L.; Kuang, S.T.; Zhang, Z.F.; Liao, W.P. Separation of trivalent rare earths from chloride medium using solvent extraction with heptylaminoethyl phosphonic acid 2-ethylhexyl ester (HEHHAP). *Hydrometallurgy* **2019**, *188*, 14. [[CrossRef](#)]
13. Judgea, W.D.; Azimi, G. Recent progress in impurity removal during rare earth element processing: A review. *Hydrometallurgy* **2020**, *196*, 105435. [[CrossRef](#)]

14. Liu, T.C.; Chen, J.; Li, H.L.; Li, K.; Li, D.Q. Further improvement for separation of heavy rare earths by mixtures of acidic organophosphorus extractants. *Hydrometallurgy* **2019**, *188*, 73. [[CrossRef](#)]
15. Lou, Z.; Xiao, X.; Huang, M.; Wang, Y.; Xing, Z.; Xiong, Y. Acrylic acid functionalized metal-organic frameworks (MOFs) for Sc(III) selective adsorption. *ACS Appl. Mater. Interfaces* **2019**, *11*. [[CrossRef](#)]
16. Wang, Y.; Zhang, Y.M.; Huang, J.; Liu, T.; Li, W.; Zhang, G.B. Cause of Emulsion during Vanadium Extraction with P204 from Stone Coal Acid Leaching Solution. *Nonferr. Metals (Extr. Metall.)* **2013**, *11*, 25.
17. Shinozaki, T.; Ogata, T.; Kakinuma, R.; Narita, H.; Tokoro, C.; Tanaka, M. Preparation of polymeric adsorbents bearing diglycolamic acid ligands for rare earth elements. *Ind. Eng. Chem. Res.* **2018**, *57*, 11424. [[CrossRef](#)]
18. Ye, Q.; Li, G.; Deng, B.; Luo, J.; Rao, M.; Peng, Z.; Zhang, Y.; Jiang, T. Solvent extraction behavior of metal ions and selective separation Sc³⁺ in phosphoric acid medium using P204. *Sep. Purif. Technol.* **2019**, *209*, 175. [[CrossRef](#)]
19. Ruberlan, G.S.; Carlos, A.M.; Leandro, V.T.; Éder, D.O. Selective removal of impurities from rare earth sulphuric liquor using different reagents. *Miner. Eng.* **2018**, *127*, 238.
20. Wang, Y.D.; Li, J.H.; Gao, Y.; Yang, Y.; Xu, Z.F. Removal of aluminum from rare-earth leaching solutions via a complexation-precipitation process. *Hydrometallurgy* **2020**, *191*, 105220. [[CrossRef](#)]
21. Peng, F.Z.; Liu, Z.F.; Zhang, S.L.; Liu, Y.; Chen, S.L.; Li, M.L. Emulsion during Rare Earth Extraction-Separation Process I-Emulsion Caused by Accumulation of Inorganic Impurities. *Chin. J. Rare Metals* **2007**, *4*, 547.
22. Cánovas, C.R.; Chapron, S.; Arrachart, G.; Rostaing, P.S. Leaching of rare earth elements (REEs) and impurities from phosphogypsum: A preliminary insight for further recovery of critical raw materials. *J. Clean. Prod.* **2019**, *219*, 225. [[CrossRef](#)]
23. Qiu, T.S.; Fang, X.H.; Wu, H.Q.; Zeng, Q.H.; Zhu, D.M. Leaching behaviors of iron and aluminum elements of ion-absorbed-rare-earth ore with a new impurity depressant. *Trans. Nonferr. Metals Soc. China* **2014**, *24*, 2986. [[CrossRef](#)]
24. Abhishek, L.; Animesh, J. Selective separation of rare earths and impurities from ilmenite ore by addition of K⁺ and Al³⁺ ions. *Hydrometallurgy* **2009**, *95*, 254.
25. Ning, Y.C. *Structural Identification of Organic Compounds and Organic Spectroscopy*; Science Press: Beijing, China, 2000; pp. 329–332.
26. Maria, K.; Catherine, G.; Catherine, P.R. pH-specific synthesis, isolation, spectroscopic and structural characterization of a new dimeric assembly of binuclear vanadium(V)-citrate-peroxo species from aqueous solution. *Inorg. Chim. Acta* **2007**, *11*, 1–10.
27. Zhou, H.Y.; Wang, Y.L.; Guo, X.G.; Dong, Y.M.; Su, X.; Sun, X.Q. The recovery of rare earth by a novel extraction and precipitation strategy using functional ionic liquids. *J. Mol. Liq.* **2018**, *254*, 414. [[CrossRef](#)]
28. Lahiri, S.; Nayak, D.; Ramaswami, A.; Manohar, S.B. Separation of carrier-free ytterbium and thulium produced in 80 MeV 12C⁶⁺ irradiated gadolinium foil target by liquid–liquid extraction with HDEHP. *Appl. Radiat. Isot.* **2000**, *52*, 797–802. [[CrossRef](#)]