

Separation and purification of light rare earth elements from chloride media using P204 and Cyanex272 in sulfonated kerosene under non-saponification conditions

Peiqiang Fan ^{1,2}, Wenjie Zhang ^{1,2}, Xiong Tong ^{1,2}, Xian Xie ^{1,2}, Ruiqi Xie ^{1,2}, Qiang Song ^{1,2}, Yunpeng Du ^{1,2}, Yang Cao ³

¹ Faculty of Land Resource Engineering, Kunming University of Science and Technology, Kunming 650093, Yunnan, China

² Yunnan Engineering Research Center for Metal Tailings Resource Utilization, Kunming 650093, Yunnan, China

³ School of Chemistry and Resources Engineering, Honghe University, Mengzi 661199, China

Corresponding author: kgxiongtong@163.com (Xiong Tong)

Abstract: The extraction of light rare earths (Pr and Nd) from chloride medium was investigated using a mixture of di(2-ethylhexyl) phosphoric acid (P204) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) in sulfonated kerosene. The P204+Cyanex272 system exerted a synergistic effect on the separation of light rare earths, and the separation coefficient was higher than when P204 and Cyanex272 were used as extractants alone. The separation coefficient of Pr and Nd in the extraction system reached 1.75 when the pH of the aqueous phase material solution was approximately 2.5, and 1.5 mol/L hydrochloric acid as a stripping agent effectively eluted the rare earth ions in the loaded organic phase. Combining the slope method, infrared spectroscopy, and nuclear magnetic resonance spectroscopy, we explored the mechanism of the extracted Nd and Pr into the organic phase complex, and finally entered the organic phase with $\text{Re}(\text{HA}_2)_2\text{B}$. The P-O-H bond and P=O bond in the extractant P204 and Cyanex272 formed a coordination bond with Re^{3+} . Therefore, this extraction method also provides a reference for a more environmentally friendly and efficient procedure for separation and purification of light rare earth elements Pr and Nd.

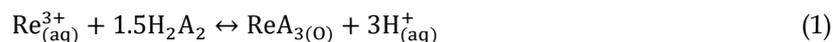
Keywords: P204, Cyanex272, light rare earths, extraction, mechanism

1. Introduction

High-purity single rare earth elements have been used in vital applications in high-end fields such as national defense, new materials, aerospace, and communications. Due to their unique physical and chemical properties, they cannot be replaced by other substances. Because of their extremely high industrial and commercial value, they have been referred to as 'industrial vitamins' (Chen et al., 2021; Chi et al., 2005; Gupta et al., 2021; Sun et al., 2020). Due to the shrinkage of the lanthanide series, the radius and properties of the rare earth elements are very similar, which increases the difficulty of separating a single rare earth element with high purity (Alizadeh et al., 2021; Huang et al., 2015). At present, the methods for separating and purifying rare earths mainly include hierarchical crystallization and precipitation, chemical vapor transmission, ion exchange, extraction resin chromatography, solvent extraction, liquid membrane, and redox methods (He et al., 2015; Inan et al., 2018; Jin et al., 2011; Masmoudi-Soussi et al., 2020). Due to production costs, production efficiency, limitations of separation purity, and other issues, solvent extraction is the most widely used method in industry to produce most of the single high-purity rare earths in the world.

In the process of separating and purifying rare earths, the solvent extraction method selectively separates the rare earth ions in aqueous solution with an organic extractant, and a single rare earth product is obtained (Dashti et al., 2021; Yang et al., 2011; Zhou et al., 2019). Because acidic organic extractants are so inexpensive, it is difficult for other extraction systems to compete. Common acidic

extractants include P204, P507, Cyanex 272, Cyanex 301, Sec-octylphenoxy- substituted acetic acid (CA-12), Bis(2-ethylhexyl) phosphonic acid (P229), and Isopropylphosphonic acid mono(1-hexyl-4-ethyl)octyl ester (PT-2) (Tian et al., 2013; Tong et al., 2009; Wang et al., 2011; Ye et al., 2019). When an acidic extractant extracts rare earth ions in an aqueous solution, the reaction mechanism can be expressed as shown in Eq. 1. The rare earth ion and the organic acidic extractant undergo a cation displacement reaction, and the replaced H^+ enters the aqueous solution, thereby inhibiting the extraction reaction.



To prevent the released H^+ from interfering with the extraction process, the commonly used method in the industry is to use alkaline solution to saponify the acidic extractant prior to use. Although the interference of H^+ can be effectively avoided, the large amount of ammonia nitrogen wastewater generated during the saponification process is harmful to the environment. Every 1 t of rare earth produced will produce 5 t of waste water that must be treated so that it will not harm the environment, which will increase subsequent treatment costs (Scal et al., 2020; Xiao et al., 2013).

In order to achieve the desired end product and not cause environmental problems, researchers have carried out a large number of studies on the extraction and separation of rare earths with non-saponification systems. Among them, the multi-element extraction system has been extensively studied because it can combine the advantages of different extractants (Dashti et al., 2021; Gao et al., 2014; Xiao et al., 2015). The P204+P507 system can effectively extract rare earths under non-saponified conditions. It has a significant synergistic effect on the extraction of Y in sulfuric acid medium. The synergistic extraction coefficient for Y reaches 27.86 when the pH of the aqueous phase is 1.2. The extraction system not only avoids saponification, but it also reduces the degree of emulsification during the extraction process, which is more conducive to industrial production.

As a phosphonic acid extractant, Cyanex272 has a lower charge density than P204. Thus, the hydrogen on the phosphorous hydroxyl group is easier to dissociate. It can be extracted at a higher pH, and back-extraction is facile. However, there are also disadvantages such as small extraction capacity, easy emulsification, and high cost. This process is often used in combination with other extractants (Kashi et al., 2018; Kim et al., 2012; SuiHuang, 2019; Zaheri et al., 2015). The Cyanex272+P507 system has a significant synergistic extraction effect on Y in hydrochloric acid medium under non-saponified conditions, and the Cyanex272+TBP (Tributyl phosphate), Cyanex272+HEHHAP (heptylaminomethyl phosphonic acid 2-ethylhexyl ester), and Cyanex272+ CA-12 systems, and other systems can effectively extract rare earth elements under non-saponified conditions (Chen et al., 2019; Liao et al., 2010; Tong et al., 2009; Wei et al., 2020).

In addition to multiple extraction systems, complexing agents have also been extensively studied in the process of extracting rare earths under non-saponified conditions. Complexing agents are aliphatic carboxylic acids and their substituted derivatives, and common substances are EDTA, lactic acid, citric acid, tartaric acid, and acetate (Nishihama et al., 2003; Zaheri et al., 2015; Zhang et al., 2020). The P507+Cyanex 272 system uses lactic acid as the complexing agent under non-saponification conditions (Gomes et al., 2021). When the lactic acid concentration is 0.5 mol/L and the pH of the aqueous phase is 3.5, the separation coefficients of the extraction system for La and Pr are 13.7 and 12.4, respectively (Scal et al., 2020). Although the application of complexing agents can increase the extraction capacity of acidic extractants under non-saponification conditions, it is difficult for the complexing agents added to the extraction system to be effectively recycled and reused, which increases production costs and restricts the use of complexing agents in the industry.

P204 is the most common extractant used in the industry to separate and purify light rare earths. Although it possesses effective separation capabilities, it also has disadvantages such as low selectivity, large saponification wastewater discharge, and difficulty in stripping. To efficiently separate light rare earths under non-saponified conditions, a new extraction system is necessary. In the current study, an extraction system consisting of P204+Cyanex 272 was used, and its effects on the separation and purification of light rare earths under non-saponification conditions were systematically examined, as well as the extraction mechanism. This work provides a reference for the industrial application of the system.

2. Experiments

2.1. Experimental reagents and equipment

Di-(2-ethylhexyl) phosphoric acid (P204 purity >99%) was provided by Sinopharm Chemical Reagent Company, bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272 purity >99%) was provided by Shanghai Solvay Reagent Co., Ltd., sulfonated kerosene was provided by Guangzhou Xiangyang Fusen Petrochemical Co., Ltd., and rare earth oxides (Pr_2O_3 , Nd_2O_3 ; purity >99.9%) were provided by Sinopharm Chemical Reagent Company. Other reagents are of analytical grade.

A DW-3 digital display mixer was used to fully mix and stir the extraction of the organic phase and water phase material liquid, an ME204E electronic analytical balance (Beijing Rex Instrument Factory) was used to weigh the reagents, a PHS3E desktop pH meter (Shanghai Lei Magnetic Instrument Factory) was used to measure the pH value of the phase material and raffinate, and an LD-UPW water purifier (Shanghai Shuoding Instrument Co., Ltd.) provided deionized water for the experiments.

2.2. Experimental methods

Extraction experimental method: Rare earth oxides (Pr_2O_3 , Nd_2O_3) were dissolved in 3 mol/L hydrochloric acid, diluted with deionized water to the required concentration, and the pH of the aqueous phase was adjusted by dilute ammonia and dilute hydrochloric acid. The organic extractant P204 and Cyanex 272 were mixed uniformly in a certain proportion. The experimental reaction device is shown in Fig. 1. The 20 mL water phase liquid and the organic phase were each transferred to a reaction beaker. The electric stirrer consisted of uniaxial stirring paddles that rapidly rotate so that the organic phase and the water phase are fully mixed and contacted. After the reaction was completed, the liquid was poured into a separatory funnel for layering (Fu et al., 2022; Wang, 2018; Zhang et al., 2014). The quantities of Pr and Nd in the aqueous phase solution and the raffinate aqueous phase were measured and analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES), and then, the quantity of Pr and Nd in the loaded organic phase was calculated by the difference method.

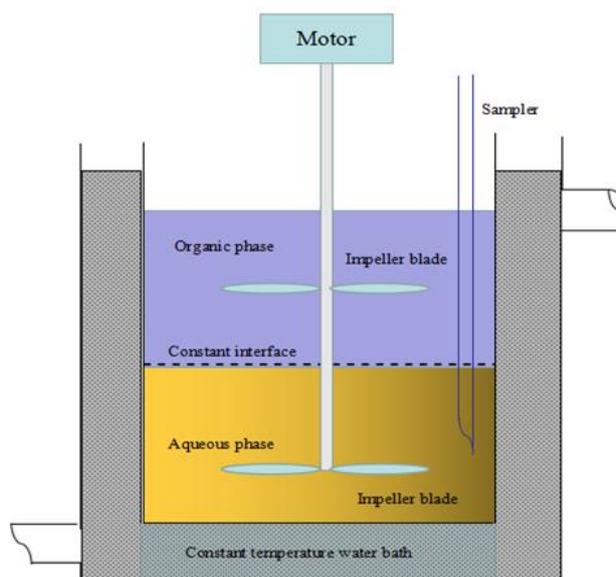


Fig. 1. Schematic diagram of the experimental setup

Back-extraction experimental method: The amount of rare earth in the loaded organic phase was calculated by the difference method, and this was used as the original solution to carry out the back-extraction experiment. Inorganic acids of different concentrations were used as the stripping agent, the loaded organic phase was fully mixed in a certain proportion, and then, the first-stage stripping was performed. After the stripping was completed, a separation funnel was used for liquid separation. Then, ICP-OES was used to determine the amount of Pr and Nd in the stripping solution, and to calculate the stripping rate.

2.3. Data calculation

The extraction percentage (E), distribution ratio (D), separation factor (β), synergy coefficient (R) and stripping rate R_f were calculated according to Eqs. (1)-(5) as follows:

$$E = \frac{n_{Re(o)}}{n_{Re(a)}Re} \quad (1)$$

$$D = \frac{C_{Re(o)}}{C(a)_{Re}Re} \quad (2)$$

$$\beta = \frac{D_a}{D_b} \quad (3)$$

$$R = \frac{D_{P204+Cyanex272}}{D_{P204}+D_{Cyanex272}} \quad (4)$$

$$R_f = \frac{n_{a,Re}}{n_o^1} R \quad (5)$$

where $n_{Re(o)}$ and $n_{Re(a)}$ represent the amount of substance of rare earth ions in the equilibrating organic phase and in the initial aqueous liquid phase, respectively; $C_{Re(o)}$ and $C_{Re(a)}$ represent the concentration of rare earth ions in the organic phase and in the aqueous phase at the time of extraction equilibrium, respectively. D_a and D_b denote the distribution ratios of rare earth ions Re_a and Re_b , respectively; D_{P204} , $D_{Cyanex272}$ and $D_{P204+Cyanex272}$ represent the distribution ratio of single P204, single Cyanex272 and P204+Cyanex272 system for extracting rare earths, respectively; n_a , Re and n_o^1 represent the amount of substance rare earth ions in the back-extraction aqueous phase and loaded organic phase, respectively.

2.4. Characterization of extracted complexes

FT-IR analysis: The extractants, i.e., P204, Cyanex272, mixed P204-Cyanex272 in sulfonated kerosene, the loaded organic phase and organic phase after stripping, the FT-IR spectra of the organic phase and loaded organic phase were recorded in the range of 4000-400 cm^{-1} at room temperature.

NMR analysis: The extractants, i.e., P204, Cyanex272, P204-Cyanex272 and the loaded organic phase, were each diluted with $CDCl_3$. Chemical shifts (δ) of 1H and ^{31}P at room temperature was observed. In addition, tetrasilyl methane (TMS) was used as the reference material for 1HNMR , while 85% phosphoric acid (H_3PO_4) was used as the reference material for ^{31}P NMR.

3. Experimental results and analysis

3.1. Effect of P204 and Cyanex272 concentration on extraction

Using sulfonated kerosene as a diluent, the concentrations of the extractants P204 and Cyanex272 were adjusted to explore the effect of the extractant concentration on the extraction of Pr and Nd. Fig. 2 shows that when P204 and Cyanex272 separately extract Pr and Nd, as the concentration of the extractant increases, the extraction and separation effect of Pr and Nd is more efficient. The most optimal separation coefficients of P204 for Pr and Nd are 1.14 and 1.22, respectively, and the most optimal separation coefficients of Cyanex272 for Pr and Nd are 0.87 and 0.99, respectively.

With the binary extraction system composed of P204 and Cyanex272, the capacity to extract Pr and Nd first increases and then decreases as the mole fraction of P204 increases. When the mole fraction of P204 $XP204=0.8$, the separation coefficients for Pr and Nd were 1.61 and 1.98, respectively, and the extraction effect was significantly stronger than when P204 and Cyanex272 were used as extractants alone. The P204+Cyanex272 binary extraction system had a positive synergistic effect on the extraction of Pr and Nd. When $XP204=0.8$, the synergy coefficient reached the maximum values, which were 1.39 and 1.46, respectively.

3.2. Effect of pH on extraction

P204 and Cyanex272 are organic phosphonic acid extractants. Thus, the extraction effect is achieved by cation replacement during the extraction process, and the released H^+ will affect the extraction. Therefore, the pH of the aqueous phase material liquid has a significant effect on the extraction effect.

Dilute hydrochloric acid and dilute ammonia were used to adjust the pH of the water phase feed solution, and the effect of different pH values on the extraction effect was investigated.

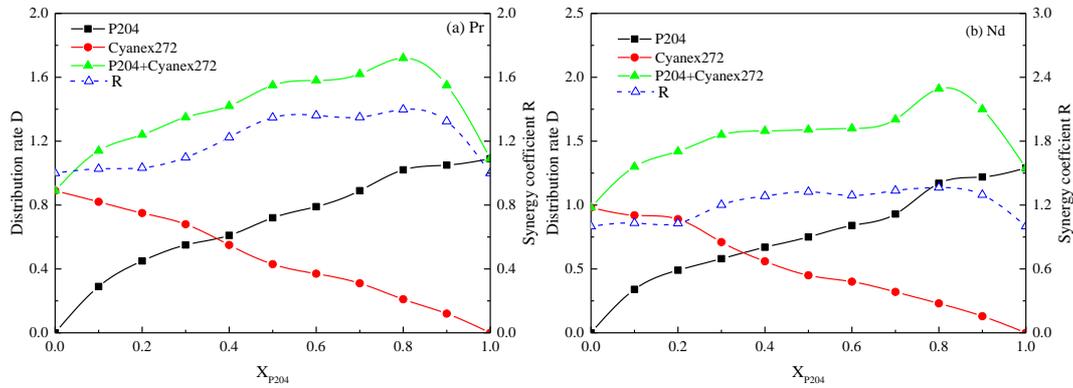


Fig. 2. Synergistic extraction of Pr and Nd by the mixture of P204 and Cyanex272 ($P204+Cyanex272=0.3$ mol/L, $Pr^{3+}=0.1$ mol/L, $Nd^{3+}=0.1$ mol/L, $pH=2.5$, $T=298.15$ k)

Fig. 3 shows that with the increase of the pH of the solution, the rate of extraction of Pr and Nd by P204+Cyanex272 gradually increases. This occurs because the higher the pH of the solution, the greater the buffering effect on the H^+ released during the extraction process. Therefore, it is necessary to reduce the influence of H^+ on the inhibition of the extraction process. When the solution $pH=2.5$, 95.21% and 97.66% extraction was achieved for Pr and Nd, respectively, with the separation coefficient $\beta_{Nd/Pr}=1.75$. As the pH continued to increase, the P204+Cyanex272 system exhibited a small increase in the extraction rate of Pr and Nd, and the precipitation of rare earth elements is prone to occur. Therefore, it was determined that the most efficient reaction will occur when the pH of the aqueous phase is approximately 2.5.

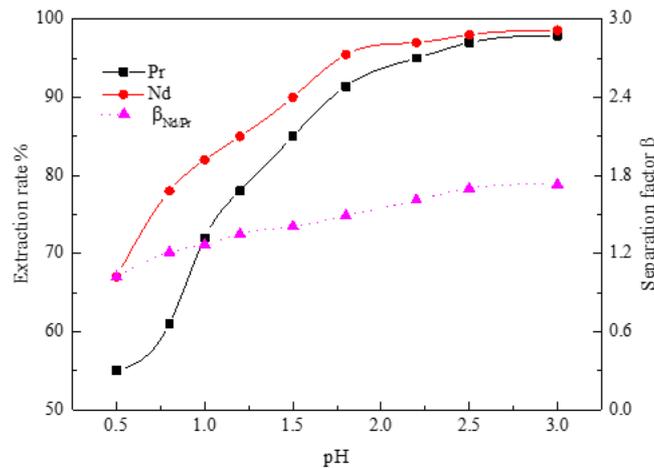


Fig. 3. Effect of the pH of aqueous phase on the synergistic extraction of Pr^{3+} and Nd^{3+} by the mixed P204 and Cyanex272 ($P204+P350=0.3$ mol/L, $x_{P204}=0.8$; $Pr^{3+}=0.1$ mol/L, $Nd^{3+}=0.1$ mol/L, $T=298.15$ k)

3.3. Influence of the aqueous/organic (A/O) ratio on extraction

The concentration of Pr and Nd was maintained in the aqueous solution at 0.1 mol/L, and $pH=2.5$ was unchanged. Then, the ratio of A/O was changed during the extraction process, and the extraction process was simulated with the McCabe-Thiele isothermal extraction equation. The results are shown in Fig. 4, which indicates that when Pr in the aqueous solution is 14.09 g/L, three extractions are required under the condition of A/O=2:1 (blue line) to remove Pr. Under the condition of A/O=1:1 (red line), Pr can be completely removed with 2 extractions. With Nd in the aqueous solution at 14.42 g/L, and when the A/O is 1:1 and 1:2, two extractions will completely remove Nd. Therefore, from the perspective of extraction efficiency and reagent consumption, A/O=1:1 is the most optimal.

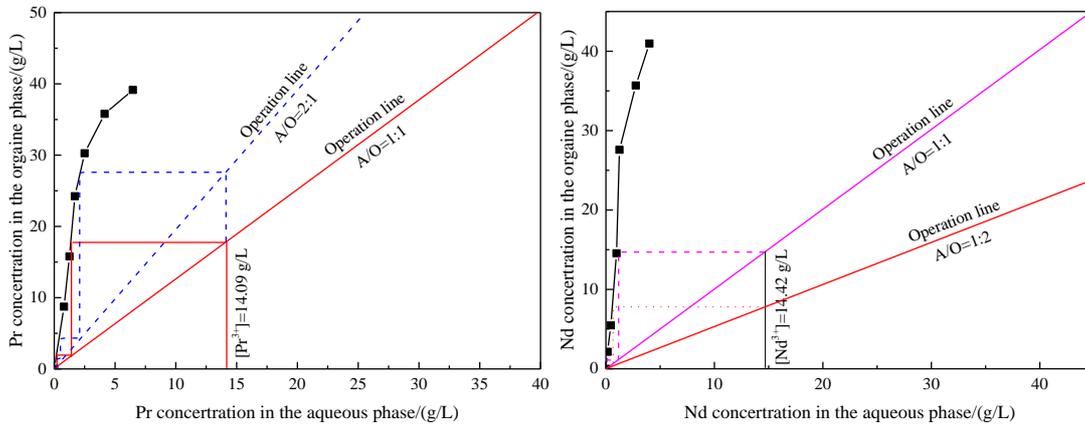
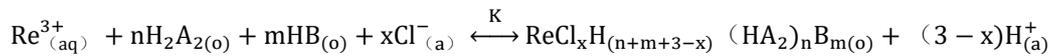


Fig. 4. McCabe-Thiele diagrams for Pr and Nd extraction by P204-Cyanex272 (aqueous phase: $\text{Pr}^{3+} = 0.1 \text{ mol/L}$, $\text{Nd}^{3+} = 0.1 \text{ mol/L}$, $\text{pH}=2.5$; organic phase: P204-Cyanex272=0.3 mol/L, $x_{\text{P204}}=0.8$)

3.4. Extraction mechanism

In the organic phase, P204 mainly exists in the form of dimers, represented by H_2A_2 , and Cyanex272 is represented by HB (Wang et al., 2011). Assuming that the reaction equation of the extraction process is:



Then, the equilibrium constant K of the reaction equation can be expressed as:

$$K = \frac{[\text{ReCl}_x\text{H}_{(n+m+3-x)} (\text{HA}_2)_n\text{B}_{m(\text{o})}] \cdot [\text{H}^{+}_{(\text{a})}]^{3-x}}{[\text{Re}^{3+}_{(\text{aq})}] \cdot [\text{H}_2\text{A}_{2(\text{o})}]^n \cdot [\text{HB}_{(\text{o})}]^m \cdot [\text{Cl}^{-}_{(\text{a})}]^x}$$

When the extraction reaches equilibrium:

$$D = \frac{[\text{ReCl}_x\text{H}_{(n+m+3-x)} (\text{HA}_2)_n\text{B}_{m(\text{o})}]}{[\text{Re}^{3+}_{(\text{aq})}]}$$

It results in:

$$K = \frac{D \cdot [\text{H}^{+}_{(\text{a})}]^{3-x}}{[\text{H}_2\text{A}_{2(\text{o})}]^n \cdot [\text{HB}_{(\text{o})}]^m \cdot [\text{Cl}^{-}_{(\text{a})}]^x}$$

Taking the logarithm of both sides at the same time results in:

$$\begin{aligned} \log K &= \log D + (3-x) \log [\text{H}^{+}_{(\text{a})}] - n \log [\text{H}_2\text{A}_{2(\text{o})}] - m \log [\text{HB}_{(\text{o})}] - x \log [\text{Cl}^{-}_{(\text{a})}] \\ \log D &= \log K + (3-x) \text{pH} + n \log [\text{H}_2\text{A}_{2(\text{o})}] + m \log [\text{HB}_{(\text{o})}] + x \log [\text{Cl}^{-}_{(\text{a})}] \end{aligned}$$

The above formula shows that when the reaction conditions are controlled unchanged, the extraction distribution ratio D has a linear relationship with the reaction equilibrium constant. The slope method is used to determine the composition of the final reaction that will produce the extract compound, keeping other experimental conditions unchanged, only changing a single experimental factor, and determining the coefficients of n , m , and x in the extract compound.

The concentrations of rare earth ions Pr^{3+} and Nd^{3+} are both 0.1 mol/L, the concentration of the extractant P204+Cyanex272 is 0.3 mol/L, maintain the extraction reaction endpoint liquid phase $\text{pH}=2.5$, and sulfonated kerosene is used as the diluent to determine the different concentrations of the P204 and Cyanex272 extracts. The distribution ratio D of Pr and Nd, and plots of $\log \text{P204}-\log D$ and $\log \text{Cyanex272}-\log D$ are shown in the Fig.5. After linear fitting, the slopes of n and m are approximately 2 and 1, respectively.

The concentrations of rare earth ions Pr^{3+} and Nd^{3+} are both 0.1 mol/L, and the concentration of extractant P204+Cyanex272 is 0.3 mol/L ($x_{\text{P204}}=0.8$). The pH value of the initial aqueous phase changes, and the pH value of the raffinate aqueous phase after the reaction reaches equilibrium is then measured. The distribution ratio D is plotted with $\text{pH}-\log D$, and the linear fitting has a slope of 3, that is, $3-x=3$, $x=0$.

The concentrations of rare earth ions Pr^{3+} and Nd^{3+} are both 0.1 mol/L, the concentration of extractant P204+Cyanex272 is 0.3 mol/L ($x_{\text{P204}}=0.8$), the pH of the aqueous solution is 2.5, and the Cl^{-}

in the solution was adjusted with NaCl. P204-Cyanex 272 was measured at different Cl⁻ concentrations to extract the distribution ratio D of Pr and Nd, and pH-logD was plotted with a linear fit to obtain a slope of 0.

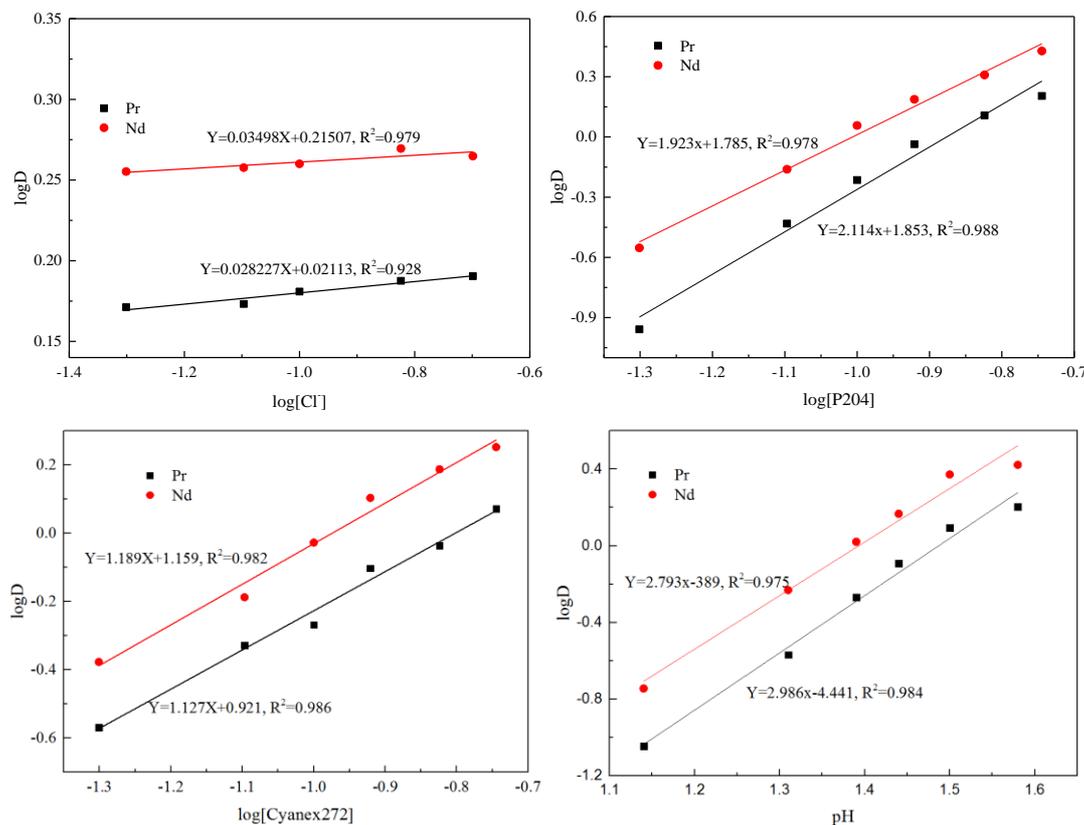
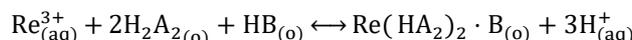


Fig. 5. Effect of the concentration of Cl⁻, P204, Cyanex272 and pH of the aqueous phase in the mixture system and the distribution ratio D

The Cl⁻ had no effect on the extraction process and did not participate in the extraction reaction. In the process of extracting rare earth Re³⁺ in the P204+Cyanex272 system, two P204 and one Cyanex 272 molecules are respectively replaced by cations to release 3 H⁺ into the solution, and the resulting complex entered the organic phase in the form of Re(HA₂)₂B. The extraction reaction equation can be expressed as:



3.5. Infrared spectrum analysis

For organic molecules with different structures, the atoms of different functional groups are constantly vibrating, and their vibrational frequency is similar to that of infrared light. The absorption frequency of different functional groups is different, and functional groups at different positions will appear in the infrared spectrum, thereby deriving the structure of organic molecules. To explore the structure and reaction mechanism of the final extraction compound, the individual extractants P204 and Cyanex272, the mixed extractant P204+Cyanex272 (before and after extraction), and the extractant after back-extraction of the loaded organic phase were analyzed by infrared spectroscopy. The analysis results are shown in the Fig. 6 and Table 1.

It can be seen from Figure (a) that the extractant P204 is a dimer hydrogen bond at 1677 cm⁻¹. After mixing with Cyanex272, the dimer hydrogen bond moves to a low wave number at 1670 cm⁻¹, indicating that hydrogen bonding occurred in the extractant after reorganization via mixing. Figure (b) shows that the hydrogen bond peak strength of the Cyanex272 dimer is weaker, and the hydrogen bond strength is weaker than that of P204. After the extraction agent P204+Cyanex272 combined with the rare earth

ion Nd, the characteristic absorption peak P-O-H disappeared, indicating that P-O-H and Nd³⁺ underwent a cation displacement reaction, which transformed the P-O-H bond into P-O-Nd.

The P=O characteristic peak of the mixed extractant is at 1148 cm⁻¹, which is different from the P=O characteristic peaks of P204 and Cyanex272. This is mainly due to the formation of new dimer hydrogen bonds after the combination of P204 and Cyanex272. The electron cloud density of the P=O group changed, and after extraction, the P=O bond redshifted to 1148 cm⁻¹, indicating that the P=O bond forms a coordination bond with Nd³⁺. The characteristic peak of P-O-C in the extractant P204 changed to a certain extent before and after extraction, and was mainly affected by the coordination bond of adjacent group P-O-Nd. Figure (f) shows that the characteristic absorption peak of the loaded organic phase after HCl stripping is similar to that in Figure (c), and the characteristic peak of the P-O-H bond that disappeared in Figure (d) reappears at 947 cm⁻¹. This indicates that after back-extraction, P-O-H bonds reappear in the extractant, and it also indicates that recycling can be performed with this extraction system.

Table 1. Infrared spectra of the extractants and the extracted complex

Characteristic peaks	Dimer hydrogen bond/(cm ⁻¹)	P=O/(cm ⁻¹)	P-O-C/(cm ⁻¹)	P-O-H/(cm ⁻¹)
P204	1677	1152	1029	962
Cyanex272	1679	1120	-	930
P204+Cyanex272	1670	1148	1033	945
P204+Cyena272+Ce	1671	1162	1033	-
P204+Cyena272+Ce (Stripped)	1673	1149	1032	947

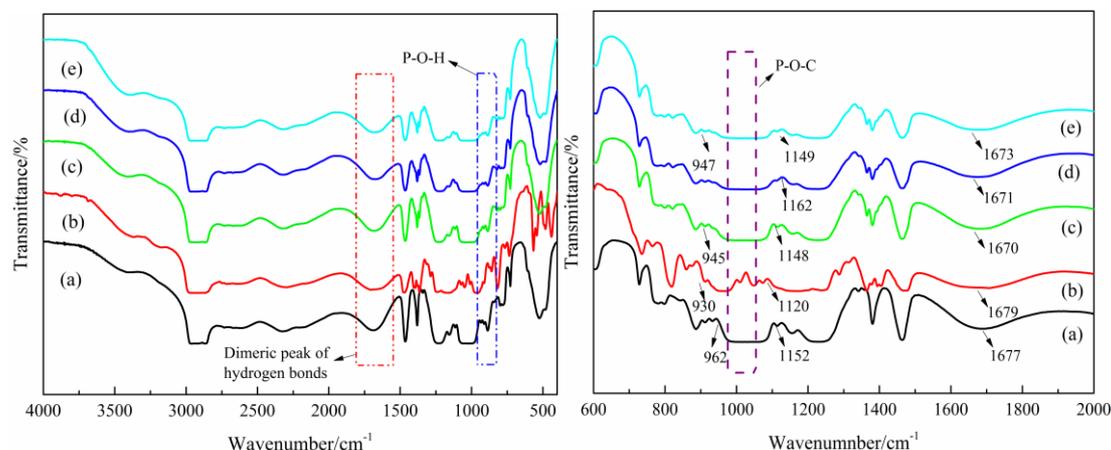


Fig. 6. IR spectra of the extractants and the extracted complex (a: P204; b: Cyanex272; c: P204-Cyanex272; d: P204-Cyanex272+Nd; e: P204-Cyanex272+Nd after stripping)

3.6. ¹H NMR and ³¹P NMR analyses

Nuclear magnetic resonance uses the magnetism of a molecule or nucleus of the substance to be measured, and absorbs electromagnetic waves of a certain energy in a specific external magnetic field. The absorbed characteristic peaks reflect the structural information of the molecule to be measured, thereby providing a basis for the inference of the molecular structure (He et al., 2021). ¹H NMR, ³¹P NMR, and ¹³C NMR were used to further confirm the mechanism used by the P204+Cyanex272 system to extract rare earth elements.

The ¹³C NMR spectrum mainly shows the chemical shift of the P-O-C group in the organic extractant. In Figure (a), the chemical shift of the P-O-C bond in P204 is 69.4 ppm. Because there is no P-O-C bond in the molecular structure of Cyanex272, there is no corresponding chemical shift in Fig. (b). In Figures (c) and (d), the chemical crisis of the P-O-C bond is basically unchanged, indicating that no other new

groups are produced after P204 was mixed with Cyanex272, and it does not participate in the extraction reaction of rare earth ions.

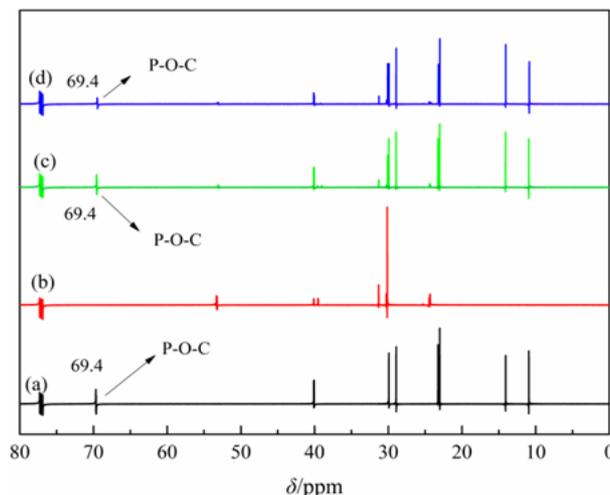


Fig. 7. ^{13}C NMR of the extractant P204, Cyanex272, P204-Cyanex272 and P204-Cyanex272+Nd extracted compounds (extraction conditions: $\text{Nd}^{3+} = 0.1 \text{ mol/L}$, $\text{pH}=2.5$, $\text{P204-Cyanex272}=0.3 \text{ mol/L}$, $x_{\text{P204}}=0.8$)

It can be seen from the Fig. 8 that the chemical shifts of the active hydrogen on the P-O-H group in the extractants P204 and Cyanex272 in Figures (a) and (b) are 11.98 ppm and 10.58 ppm, respectively; the mixture of P204 and Cyanex272 has no effect on the hydrogens on the alkyl group. However, the P-O-H group moves to the high field (Figure (c)), indicating that the hydrogen bonding between the two and the intermolecular steric hindrance enhance the hydroxyl vibration. After the P204+Cyanex272 system is extracted, the chemical vibration of the P-O-H group disappears. This shows that in the extraction reaction, P-O-H combines with Re^{3+} to form a P-O-Re group, and thus, there is no vibration of active hydrogen.

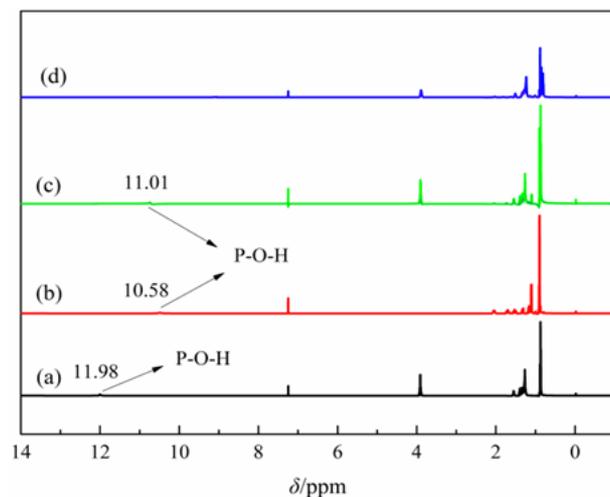


Fig. 8. ^1H NMR of the extractant P204, Cyanex272, P204-Cyanex272 and P204-Cyanex272+Nd extracted compounds (extraction conditions: $\text{Nd}^{3+} = 0.1 \text{ mol/L}$, $\text{pH}=2.5$, $\text{P204-Cyanex272}=0.3 \text{ mol/L}$, $x_{\text{P204}}=0.8$)

The Fig. 9 shows that the chemical shift of P in Cyanex272 appears at 59.84 ppm, and after mixing with P204, it moves to 60.98 ppm, which may be due to the formation of a new dimer hydrogen bond between Cyanax 272 and P204 that changes the electron cloud density of the group connected to P. After the P204+Cyanex 272 extraction reaction, the chemical shift of the P=O group changes, indicating that in the extraction reaction, the group and Re^{3+} form a coordination bond $\text{P}=\text{O}:\text{Re}$, which moves to a high field.

After the slope method, infrared detection, and nuclear magnetic analysis, the P204+Cyanex 272

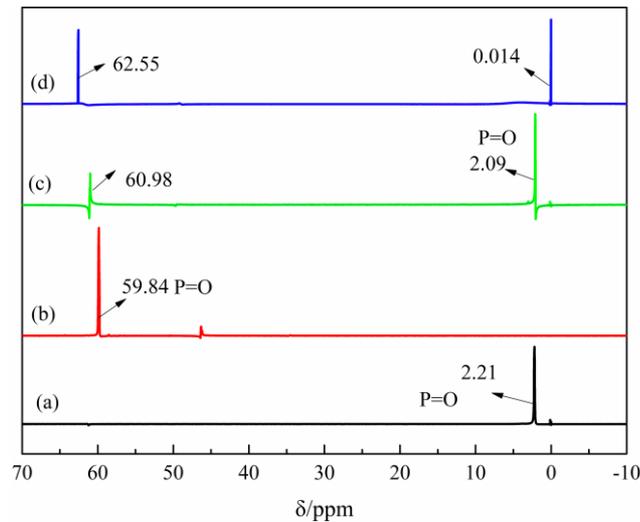


Fig. 9. ^1H NMR of the extractant P204, Cyanex272, P204-Cyanex272 and P204-Cyanex272+Nd extracted compounds (extraction conditions: $\text{Nd}^{3+} = 0.1 \text{ mol/L}$, $\text{pH}=2.5$, $\text{P204-Cyanex272}=0.3 \text{ mol/L}$, $x_{\text{P204}}=0.8$)

system finally enters the organic phase in the form of $\text{Re}(\text{HA}_2)_2\text{B}$ in the process of extracting light rare earths. The P-O-H bond in the extractants P204 and Cyanex272 forms a new chemical bond with the rare earth ion by cation replacement, and releases H^+ into the aqueous solution. At the same time, the P=O bond in the extractant forms a coordination bond with the rare earth ion. The specific extraction mechanism is shown in the Fig. 10.

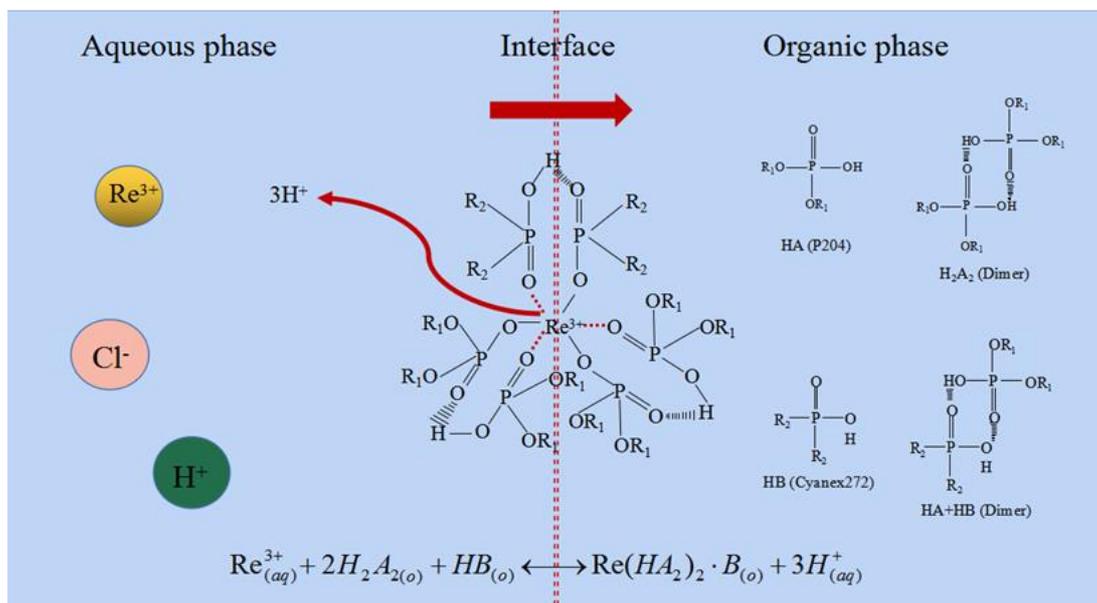


Fig. 10. Schematic diagram of the reaction mechanism of P204-Cyanex272 extraction of Pr and Nd

3.7. Stripping of rare earth ions in the loaded organic phase

The rare earth ions were combined with the extractant in the organic phase, and then washed with the stripping agent to achieve the purpose of separation and purification. Therefore, the quality of the stripping effect is also very important. With different concentrations of inorganic acids HCl , HNO_3 , H_2SO_4 as the stripping agents, the load organic phase with known quantities of rare earth elements was subjected to a primary stripping agent to investigate the respective stripping effects. The experimental results are shown in Fig. 11.

Inorganic acids of different concentrations have a certain ability to back-extract a rare earth element in the loaded organic phase. The back-extraction effect is in the order of $\text{HCl} > \text{HNO}_3 > \text{H}_2\text{SO}_4$. The back-

extraction effect increases with the increase in H^+ concentration, and then slightly decreases. This occurs because when the concentration of the stripping agent is too high, the concentration of the accompanying anions Cl^- , NO_3^- , and SO_4^{2-} in the solution is also higher, causing Re^{3+} to combine with the anions and hinder the exchange reaction with H^+ , so that the stripping rate continues to decrease. HCl exerted the strongest stripping effect on Pr and Nd. At a H^+ concentration of 1.5 mol/L, the stripping rate for Pr and Nd reached the maximum value, 92.47% and 95.21%, respectively. When the concentration of nitric acid was 2 mol/L, the stripping rates for Pr and Nd were 85.31% and 90.52%, respectively. Sulfuric acid has a poor stripping effect on rare earth ions, which may be due to its strong acidity and easy destruction of the structure of the loaded organic phase, which results in a poor back-extraction effect. In the process of extracting Pr and Nd by the P204+Cyanex272 system, when hydrochloric acid with lower acidity was used as the stripping agent, the stripping effect was obvious. Additionally, the use of HCl significantly reduces the acidity required when P204 is used as a single extractant, and this is more conducive to industrial production applications and prevents the equipment from being corroded.

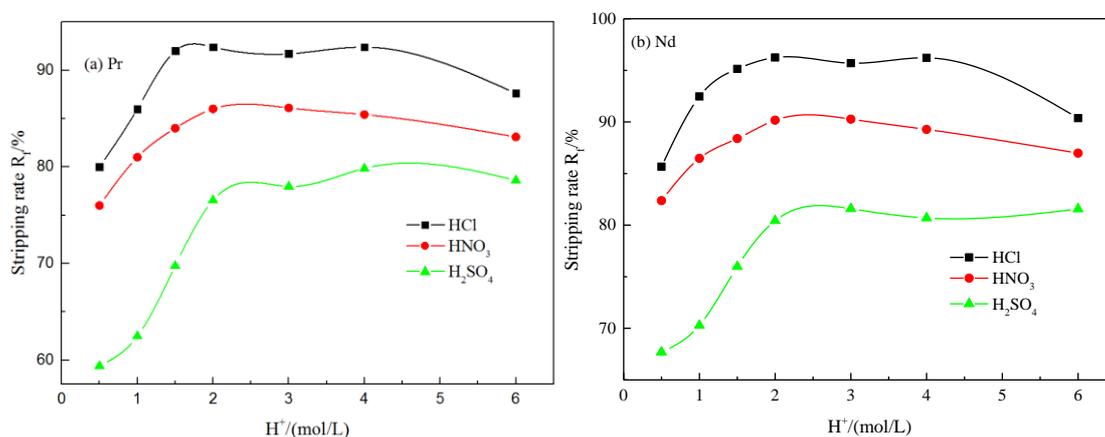


Fig. 11. Stripping of Pr and Nd with HCl, HNO_3 and H_2SO_4 from the loaded organic phase. (O/A=1:1, reaction time=20 min)

4. Conclusion

A mixture of di-(2-ethylhexyl) phosphoric acid (P204) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) in sulfonated kerosene was applied for the extraction and separation of Pr and Nd from chloride solutions. When the molar fraction of P204 was 0.8 ($XP_{204}=0.8$), the synergy coefficient of the P204-Cyanex272 system for Pr and Nd reached the maximum. When the pH of the aqueous solution was 2.5, the separation coefficient $\beta_{Nd/Pr}=1.75$, which is higher than the separation coefficient of P204 for separating Pr and Nd in industrial production. With 1.5 mol/L hydrochloric acid as the stripping agent, 92.47% and 95.21% recovery for Pr and Nd was obtained after single-stage stripping, respectively. In the extraction process, the P-O-H bond and P=O bond in the extractants P204 and Cyanex272 formed coordination bonds with rare earth ions, and finally entered the organic phase as the extract compound $Re(HA_2)_2B$.

Acknowledgments

This work is financially supported by National Natural Science Foundation of China (Nos. U1802252 and 52174252).

References

- ALIZADEH, S., ABDOLLAHY, M., DARBAN, A. K., MOHSENI, M., 2021. Nitrate ions effects on solvent extraction of rare earth elements from aqueous solutions by D2EHPA: Experimental studies and molecular simulations. *J. Mol. Liq.*, 333.

- CHEN, K. H., HE, Y., SRINIVASAKANNAN, C., LI, S. W., YIN, S. H., PENG, J. H., GUO, S. H., ZHANG, L. B., 2019. *Characterization of the interaction of rare earth elements with P507 in a microfluidic extraction system using spectroscopic analysis*. Chem. Eng. J., 356, 453-460.
- CHEN, Y., LIU, S., ZHOU, N., LI, N., ZHOU, H., SUN, L.-D., YAN, C.-H., 2021. *An overview of rare earth coupled lead halide perovskite and its application in photovoltaics and light emitting devices*. Progress in Materials Science, 120.
- CHI, R., LI, Z. J., PENG, C., ZHU, G. C., XU, S. M., 2005. *Partitioning properties of rare earth ores in China*. Rare Metals, 24(3), 205-209.
- DASHTI, S., SADRI, F., SHAKIBANIA, S., RASHCHI, F., GHAHREMAN, A., 2021. *Separation and solvent extraction of rare earth elements (Pr, Nd, Sm, Eu, Tb, and Er) using TBP and Cyanex 572 from a chloride medium*. Minerals Engineering, 161.
- FU, Y. M., HUANG, M. X., ZHOU, Z. L., LI, Z. J., LIAO, W. P., LU, Y. C., 2022. *Separation of trivalent rare earths from nitrate medium using solvent extraction with a novel extractant 2-ethylhexyl ((2-ethylhexylamino) methyl) phosphonic acid**. J. Rare Earths, 40(3).
- GAO, P., LI, Z.-H., HAN, Y.-X., SUN, Y.-S., 2014. *Reaction behavior of associated rare earth minerals during coal-based reduction*. Rare Metals, 33(5), 628-632.
- GOMES, R. D., YOKOYAMA, L., VERA, Y. M., 2021. *Study of lanthanum-didymium separation by solvent extraction from a liquor conditioned with lactic acid*. Minerals Engineering, 170.
- GUPTA, I., SINGH, S., BHAGWAN, S., SINGH, D., 2021. *Rare earth (RE) doped phosphors and their emerging applications: A review*. Ceramics Int., 47(14), 19282-19303.
- HE, H. Y., XU, F., LI, Q. L., DONG, P. F., ZHENG, J., WU, C. J., HE, Z. Y., QU, J., XU, Z. G., CHI, R., WU, M., 2021. *Separation of hafnium from zirconium in HNO₃ solution by solvent extraction with Cyanex572*. Hydrometallurgy, 202.
- HE, J. G., LI, Y., XUE, X. X., RU, H. Q., HUANG, X. W., YANG, H., 2015. *Extraction of Ce(IV) from sulphuric acid solution by emulsion liquid membrane using D2EHPA as carrier*. RSC ADVANCES, 5(91), 74961-74972.
- HUANG, X.-W., LONG, Z.-Q., WANG, L.-S., FENG, Z.-Y., 2015. *Technology development for rare earth cleaner hydrometallurgy in China*. RARE METALS, 34(4), 215-222.
- INAN, S., TEL, H., SERT, S., CETINKAYA, B., SENGUL, S., OZKAN, B., ALTAS, Y., 2018. *Extraction and separation studies of rare earth elements using Cyanex 272 impregnated Amberlite XAD-7 resin*. Hydrometallurgy, 181, 156-163.
- JIN, Y. U., SIQING, D., YU, Z., LI, B. A. I., 2011. *Separation of Neighboring Quaternary Rare Earth Oxides through Chemical Vapor Transport*. Chinese Rare Earths, 32(3), 55-59.
- KASHI, E., HABIBPOUR, R., GORZIN, H., MALEKI, A., 2018. *Solvent extraction and separation of light rare earth elements (La, Pr and Nd) in the presence of lactic acid as a complexing agent by Cyanex 272 in kerosene and the effect of citric acid, acetic acid and Titrplex III as auxiliary agents*. J. Rare Earths, 36(3), 317-323.
- KIM, J. S., KUMAR, B. N., LEE, J. Y., KANTAM, M. L., REDDY, B. R., 2012. *Separation and Recovery of Light Rare-Earths from Chloride Solutions using Organophosphorus based Extractants*. Sep. Sci. Technol, 47(11), 1644-1650.
- LIAO, C. F., JIAO, Y. F., LIANG, Y., JIANG, P. G., NIE, H. P., 2010. *Adsorption-extraction mechanism of heavy rare earth by Cyanex272-P507 impregnated resin*. Transactions of Nonferrous metals of China, 20(8), 1511-1516.
- MASMOUDI-SOUSSI, A., HAMMAS-NASRI, I., HORCHANI-NAIFER, K., FERID, M., 2020. *Rare earths recovery by fractional precipitation from a sulfuric leach liquor obtained after phosphogypsum processing*. Hydrometallurgy, 191.
- NISHIHAMA, S., HIRAI, T., KOMASAWA, I., 2003. *Advanced liquid-liquid extraction systems for the separation of rare earth ions by combination of conversion of the metal species with chemical reaction*. Journal of Solid State Chemistry, 171(1-2), 101-108.
- SCAL, M. L. W., SERUFF, L. A., VERA, Y. M., 2020. *Study of the separation of didymium from lanthanum using liquid-liquid extraction: Comparison between saponification of the extractant and use of lactic acid*. Minerals Engineering, 148.
- SUI, N., HUANG, K., 2019. *Separation of rare earths using solvent extraction consisting of three phases*. Hydrometallurgy, 188, 112-122.
- SUN, X. C., YUAN, K., ZHANG, Y. W., 2020. *Advances and prospects of rare earth metal-organic frameworks in catalytic applications*. Journal of Rare Earths, 38(8), 801-818.
- TIAN, M. M., JIA, Q., LIAO, W. P., 2013. *Studies on synergistic solvent extraction of rare earth elements from nitrate medium by mixtures of 8-hydroxyquinoline with Cyanex 301 or Cyanex 302*. Journal of Rare Earths, 31(6), 604-608.
- TONG, S. S., ZHAO, X. W., SONG, N. Z., JIA, Q., ZHOU, W. H., LIAO, W. P., 2009. *Solvent extraction study of rare earth elements from chloride medium by mixtures of sec-nonylphenoxy acetic acid with Cyanex301 or Cyanex302*. Hydrometallurgy, 100(1-2), 15-19.

- WANG, J., 2018. *Adsorption of aqueous neodymium, europium, gadolinium, terbium, and yttrium ions onto nZVI-montmorillonite: kinetics, thermodynamic mechanism, and the influence of coexisting ions*. *Env. Sci. Pollution Res.*, 25(33), 33521-33537.
- WANG, Y. L., LIAO, W. P., LI, D. Q., 2011. *A solvent extraction process with mixture of CA12 and Cyanex272 for the preparation of high purity yttrium oxide from rare earth ores*. *Separation and Purification Technology*, 82, 197-201.
- WEI, H. Q., LI, Y. L., ZHANG, Z. F., LIAO, W. P., 2020. *Synergistic solvent extraction of heavy rare earths from chloride media using mixture of HEHHAP and Cyanex272*. *Hydrometallurgy*, 191.
- XIAO, Y.-F., FENG, Z.-Y., HU, G.-H., HUANG, L., HUANG, X.-W., CHEN, Y.-Y., LI, M.-L., 2015. *Leaching and mass transfer characteristics of elements from ion-adsorption type rare earth ore*. *Rare Metals*, 34(5), 357-365.
- XIAO, Y. F., LONG, Z. Q., HUANG, X. W., FENG, Z. Y., CUI, D. L., WANG, L. S., 2013. *Study on non-saponification extraction process for rare earth separation*. *J. Rare Earths*, 31(5), 512-516.
- YANG, H. L., WANG, W., CUI, H. M., CHEN, J., 2011. *Extraction Mechanism of Rare Earths with Bifunctional Ionic Liquids [A336][CA-12]/[A336][CA-100] in Nitrate Medium*. *Chinese J. Analytic. Chem.*, 39(10), 1561-1566.
- YE, Q., LI, G. H., DENG, B. N., LUO, J., RAO, M. J., PENG, Z. W., ZHANG, Y. B., JIANG, T., 2019. *Solvent extraction behavior of metal ions and selective separation Sc³⁺ in phosphoric acid medium using P204*. *Separation and Purification Technology*, 209, 175-181.
- ZAHERI, P., ABOLGHASEMI, H., MARAGHE, M. G., MOHAMMADI, T., 2015. *Intensification of Europium extraction through a supported liquid membrane using mixture of D2EHPA and Cyanex272 as carrier*. *Chem. Eng. Process.*, 92, 18-24.
- ZAHERI, P., MOHAMMADI, T., ABOLGHASEMI, H., MARAGHE, M. G., 2015. *Supported liquid membrane incorporated with carbon nanotubes for the extraction of Europium using Cyanex272 as carrier*. *Chem. Eng. Res. Des.*, 100, 81-88.
- ZHANG, F. Y., SUN, X. J., WANG, J., ZHANG, Q., SUN, S. F., 2020. *Extraction enhancement and mechanism of light rare-earth elements (III) in chloride medium through adding complexing agent and synergistic effect*. *Separation and Purification Technology*, 55(18), 3375-3385.
- ZHANG, F. Y., WU, W. Y., BIAN, X., ZENG, W. S., 2014. *Synergistic extraction and separation of lanthanum (III) and cerium (III) using a mixture of 2-ethylhexylphosphonic mono-2-ethylhexyl ester and di-2-ethylhexyl phosphoric acid in the presence of two complexing agents containing lactic acid and citric acid*. *Hydrometallurgy*, 149, 238-243.
- ZHOU, H. Y., DONG, Y. M., WANG, Y. B., ZHAO, Z. Y., XIAO, Y., SUN, X. Q., 2019. *Recovery of Th(IV) from leaching solutions of rare earth residues using a synergistic solvent extraction system consisting of Cyanex 572 and n-octyl diphenyl phosphate (ODP)*. *Hydrometallurgy*, 183, 186-192.