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Solvent extraction behavior of metal ions and selective separation Sc^{3+} in phosphoric acid medium using P204

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ABSTRACT

Acid leaching-solvent extraction is an effective process to extract scandium from scandium-bearing resources. This study was aimed to investigate the extraction behavior of metal ions, including Sc^{3+}, Fe^{3+}, $Al^{3+}$and Ca^{2+}, in phosphoric acid medium using P204. More than 95% of scandium was selectively extracted under the conditions of pH value of 1.5–1.8, aqueous-organic ratio of 3 and oscillation for 15 min. The impurity elements like Fe^{3+}, Al^{3+} and Ca^{2+}, were separated via the solvent extraction process using P204 (e.g., separation coefficient of scandium to iron is 298). In stripping process, the majority of co-extracted metal ions can be removed from the organic phase with hydrochloric acid solution. The scandium-bearing organic phase was stripped with 4 mol/L NaOH, wherein the recovery of scandium attained about 95% while that of the co-extracted iron and aluminum were only 3.1% and 1.2%, respectively. It was also confirmed that both P204 and H_3PO_4 played roles in extraction reaction, and the desirable extraction of scandium in P204 was attributed to the ion exchange between hydrogen ion of $-PO(OH)$ and Sc^{3+} on acidic condition ($pH = 0.4–1.5$). Impurity elements (Fe^{3+} and Al^{3+}) also reacted with phosphate anion to form hydrophilic ions, and in turn result in selective extraction of scandium in phosphoric acid leachate using P204.

1. Introduction

Scandium is one of rare earth elements and has widely application on engineering industrials. Scandium mainly exists in bauxite ores, phosphorite deposits and rare earth ores, which is associated with other metal elements [1]. Bauxite ore accounts for 54% of scandium-bearing ore [2]. After processing bauxite ore in the alumina refineries, scandium and other elements like Fe, Ca and Ti were enriched in bauxite ore residues. Generally, the bauxite ore residues from China, Greece, and India etc., contain 100–200 mg/kg of scandium, which makes these materials exploitable as a scandium-containing resource [3].

Extraction of scandium from scandium-bearing resources can be achieved by directly acid leaching using a variety of lixiviates [4]. From the leachate, scandium is extracted using solvent extraction technology. The major issue is that the concentration of impurities, especially iron, aluminum and calcium in scandium-bearing resources are often much higher than scandium content, exerting adverse effects on the acidic leaching and solvent extraction process of scandium. For the leaching process of hydrochloric acid at concentration of 8 mol/L, majority of metal ions are dissolved into the leaching solution [5]. Metal ions like Fe^{3+}, Al^{3+} and Ca^{2+} would be co-extracted during solvent extraction process. A recent study reported that the rare earth elements (incl. scandium) in rare earth ore can be completely extracted into solutions by roasting with concentrated sulphuric acid at 250–300 °C followed by water leaching [6]. The fractional extractions, seven or even nine stages, are also needed to separate impurity elements from leachate. Kim [7] and Klauber [8] investigated the performance of bauxite residue in sulfuric acid leaching medium. Sulfuric acid concentration of 6 mol/L or even 10 mol/L is needed and it is not suitable for high calcium-bearing resources. Calcium sulfate leads to the formation of emulsion and the third phase during solvent extraction process, resulting in inadequate separation and scandium loss. Hence, it is important to further investigate the extraction behavior of metal ions and selective separation Sc^{3+} in phosphoric acid medium.

Extraction behavior of scandium in acid medium e.g. nitric acid, hydrochloric acid and sulfuric acid was investigated in previous study. Several acidic extractants including P204, P507 and P350 are generally used to extract metal ions in previous study. P204 was used to extract

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scandium in sulfuric acid leachate derived from nickeliferous laterite ore [9]. The extraction ratio of scandium was about 80% after scrubbing process. However, it also needed multi segmentally stripping process to separate other metal ions. Zhu et al. [10] and Chang et al. [11] investigated scandium extraction from red mud by solvent extraction using P507 and P204. The extraction ratio of scandium reached above 90% in hydrochloric acid medium, while the metal ions like Fe^{3+}, Al^{3+} and Ca^{2+} were usually co-extracted. Liu et al. [12] focused on the extraction mechanism by using phosphorodiamidate (TBP and P204) in nitric acid medium. Their results revealed that the coordination reaction occurred between rare earth ions and P═O group.

P204 has strong extraction ability, but it was difficult to separate Sc^{3+} from impurity elements in acid medium [11]. In our previous study [13], P204-H_3PO_4 solvent extraction system is proposed to selectively separate scandium from leachate. In this system, the separation coefficients between scandium and metal ions (e.g. $\boldsymbol{\beta_{Sc/Fe}} = 2703$) in phosphoric acid medium are much higher than other kinds of acid like H_2SO_4, HNO_3 and HCl via solvent extraction process. However, the mechanism of selective separation of metal ions on extraction process was not clear. This study was aimed to systematically investigate the extraction behaviors and mechanisms of metal ions, including Sc^{3+}, Fe^{3+}, Al^{3+} and Ca^{2+}, in phosphoric acid medium using P204. The ion exchange between hydrogen ion of −PO(OH) and metal ions was studied for the selective separation from the phosphoric acid leaching solution of scandium-bearing resources. Finally, a conceptual process flow sheet for separation of metal ions including Sc^{3+}, Fe^{3+}, Al^{3+} and Ca^{2+}, was proposed.

2. Methods

2.1. Experimental procedure

The pH value of acid leachate was adjusted by adding phosphoric acid prior to solvent extraction. Samples of P204 reagent have been mixed with the required volume of kerosene at room temperature. The volumes of both the contacted aqueous and organic phase were filled into separating funnel and oscillated for 15 min. After stratifying, the aqueous phase was withdrawn for analysis, while the loaded organic phase was washed by HCl solution with appropriate concentration. Finally, the scandium-bearing organic phases was stripped with NaOH solution.

The elemental concentration in acid solution was analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES). Furthermore, after solvent extraction, the concentration of the elements in aqueous phase were also analyzed using ICP-AES.

The extraction ratio (η), distribution ratio (D), and separation coefficient (β) were calculated by Eqs. (1)–(3), respectively.

$$\eta = 1 - \frac{C_A \cdot V_A}{C_t \cdot V_t} \times 100\% \tag{1}$$

where η is the extraction ratio; C_A is elements contents of aqueous phase obtained after the solvent extraction, ppm; V_A is the volume of aqueous phase, mL.

$$D = \frac{c_0}{c_A} = \frac{C_t \cdot V_t - C_A \cdot V_A}{C_A \cdot V_O} \tag{2}$$

where D is distribution ratio; c_0 is the concentration of elements in oil phase, ppm; V_O is the volume of oil phase, mL.

$$\beta_{(1/2)} = \frac{D_1}{D_2} \tag{3}$$

where $\beta_{(1/2)}$ is separation coefficient between 1 and 2 partition.

2.2. Instrument techniques

Metal ions content of solution samples were determined by plasma emission spectrometer (ICP-AES, Thermo Fisher Scientific, Icap7400 Radial, USA).

The loaded organic phase was analyzed using Fourier transform infrared spectroscopy (FTIR, Nicolet, NEXUS-670, USA). Infrared absorption spectra of samples were obtained from the KBr pellets by a Fourier transform infrared spectrometer (Nicolet-470, USA).

3. Results and discussion

3.1. Solvent extraction behaviors of metal ions using P204

As described in our previous work [14,15], the scandium-rich material was obtained from bauxite ore residue after reductive roasting followed by H_3PO_4 leaching and NaOH leaching. Iron oxide is changed into metallic iron by reductive roasting, and aluminum silicate is transformed to amorphous silica via H_3PO_4 leaching process. Alumina enriched in acid residue is further leached by sodium hydroxide solution. Along with the stepwise recovery of valuable elements, scandium and titanium are further enriched in the alkaline leaching residue.

The scandium-rich residue was leached by H_3PO_4 with 8 mol/L at 120 °C for 60 min. As TiO^{2+} is the main form in phosphoric acid leachate, before solvent extraction process, it can be removed as metatitanic acid precipitate by adjusting pH value [13]. After adjusting the pH value of solution, the main chemical composition of leachate used for solvent extraction test is shown in Table 1. The content of scandium is enriched to 23.62 mg/L in H_3PO_4 leachate. The solvent extraction behavior and selective separation Sc^{3+} from Fe^{3+}, Al^{3+} and Ca^{2+} was investigated in this study (see Fig. 1).

3.1.1. Effect of P204 concentration

The effect of P204 concentration (the volume ratio of P204/organic phase) on extraction behavior was investigated under the conditions of the phosphoric acid leachate pH value of 0.5, A/O (the volume ratio of aqueous phase/organic phase) of 3, and oscillation time of 15 min. The results are presented in Fig. 2.

The extraction ratio of scandium increased from 45% to 75% with increasing P204 concentration from 1% to 4%, and the extraction of iron and aluminum also increased. The extraction ratio of iron was nearly 30% with 4% P204, whereas it was only 5% with 1% P204. The extraction of aluminum had the similar trend with increasing P204 concentration. As the results shown in Fig. 2(b), the trend of separation coefficient ($\beta_{(Sc/Fe)}$) was similar to that of $\beta_{(Sc/Al)}$, which increased firstly and then decreased. However, the $\beta_{(Sc/Ca)}$ remained stable with P204 concentration increasing. Therefore, the optimal P204 concentration was recommended as 2–3% for extraction of scandium.

3.1.2. Effect of initial solution pH

The effect of solution pH value on extraction behavior was investigated in the aqueous pH value range of 0.1–1.8 under the conditions of 2% (V/V) P204, A/O of 3 and oscillation time of 15 min.

The results in Fig. 3(a) showed that the extraction of scandium increased obviously from 30% to 97% when the initial pH range increased from 0.1 to 1.5, and then remained constant with the further increase of pH value to 1.8. And also, the extraction ratio of iron remarkably decreased from 62% to 18% at the pH range of 0.1–1.5. The extraction ratio of aluminum decreased from 22% to 10% at the pH range of 0.1–1.5. The extraction performance of calcium was similar to scandium, increased from 40% to over 60% with pH value increased. As the results shown in Fig. 3(b), the $\beta_{(Sc/Fe)}$ increased with the increasing

Table 1
The concentration of elements in H_3PO_4 leachate solution.

Element	Sc	Fe	Al	Ca
Content (mg/L)	23.62	1440	825	6639