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A novel synergistic extraction method for recovering vanadium (V) from high-acidity chloride leaching liquor

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ABSTRACT

A selective synergistic extraction process for recovering vanadium (V) from the high-acidity chloride leaching liquor was proposed. Vanadium (V) extraction from the simulated high-acidity leaching liquor with numerous impurities using a mixed extractant consisting of tricaprylmethylammonium chloride (Aliquat 336) and tri-n-butyl phosphate (TBP) was studied while obvious synergism was found. According to synergistic enhancement coefficient and physical property of organic phase, the suitable extractant composition was the volume ratio of Aliquat 336 to TBP 1:4. The vanadium (V) extraction increased sharply as HCl concentration increased from 1.01 mol/L to 4.13 mol/L. Under the optimum extraction conditions (extractant concentration of 50 vol%, 1 min, 25–30 °C, and phase ratio (O/A) of 1:1), the vanadium extraction with three stages was above 90.0%. Almost no other impurity ions, such as Ca, Al, Mg, Cr, Ti, Mn, and Si, were co-extracted. Under the optimum stripping conditions, the vanadium stripping was above 92.0% in a single stage using water as the effective stripping reagent. High-quality V_2O_5 product was obtained after precipitation and calcination. The mechanism of vanadium (V) extraction by Aliquat 336–TBP mixed extractant was discussed based on the analysis of FT-IR and UV–vis spectra.

1. Introduction

Vanadium is a strategic metal that is widely used in many fields, including in alloys, catalysts, batteries, and advanced materials [1,2]. Vanadium is obtained from vanadium-bearing titanomagnetite ores, ferrophosphorus slags, stone coal, spent catalysts, and oil fly ashes [3–5]. Recovery of vanadium is usually obtained by using the acid leaching process. When vanadium enters into the leaching liquor, solvent extraction is an effective method to separate and recover vanadium. The Hongge ores (the biggest vanadium-bearing titanomagnetite deposit in China) cannot be utilized effectively by using traditional blast furnace and direct reduction techniques [6,7]. A novel cleaner process for the treatment of high-chromium vanadium-bearing titanomagnetite concentrates (from the Hongge mineral deposit) was proposed by our laboratory [8]. In this route, the concentrates were partially reduced using pulverized coal, and subsequently grinding and magnetic separation were carried out to produce the iron concentrate and the titanium-bearing tailing. After that the titanium-bearing tailing was leached with hydrochloric acid in order to recover vanadium. After iron (III) has been extracted from the HCl leaching liquor using a mixed extractant [9], it is necessary to develop a solvent extraction system that can separate and recover vanadium from the leaching liquor, which contains approximately 140 g/L HCl and impurities of Ca, Al, Mg, Cr, Ti, Mn and Si ions without neutralisation.

Extraction process has been used to separate vanadium from different media. Vanadium exists in two common valence states, i.e. vanadium (IV) and vanadium (V). Vanadium with the valency of +4 is usually extracted by acidic extractants such as D2EHPA, Cyanex 272, EHEHPA for in general vanadium (IV) exists as cationic species in solution [5,10–13]. In addition, it has been reported that neutral extractants e.g. TOPO, TBP, Cyanex 923 and chelating extractants e.g. LIX 63 could extract vanadium (IV) [14–16]. The extraction of vanadium (IV) is mostly under acidic sulfate or chloride conditions. Various amine extractants have been widely studied to extract vanadium (V) for vanadium (V) usually exists as anionic species in solution. Primary amine e.g. Primene JMT, PRIMENE 81R, N1923, LK-N21, tertiary amine e.g. Alamine 336,

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N235, and quaternary amine salt e.g. Aliquat 336 have been used to extract vanadium (V) [17–27]. Besides, acidic extractants e.g. EHEHPA, D2EHPA, neutral extractants e.g. Cyanex 923, TBP, and chelating extractants e.g. LIX 63, LIX 860-I have been employed for the extraction of vanadium (V) [12,13,16,25,28–34]. Most previous studies have focused on the extraction of vanadium (V) from mildly acidic or mildly alkaline solution within pH range.

Increasing attention has been paid to recover vanadium (V) from high-acidity solutions such as the leaching liquor of spent catalyst, the waste liquor from titanium industry, and the leaching liquor of vanadium-bearing titanomagnetite concentrates [16,22,29,30]. However, studies on the extraction of vanadium (V) from high-acidity liquor are few. Research on the extraction of vanadium (V) from the simulated waste liquor with 3 mol/L HCl was conducted using Cyanex 923, and vanadium was then stripped by 1.5 mol/L HCl [16]. Cyanex 923 has also been used to separate vanadium (V) from the chloride solution (1–4 mol/L HCl) containing many ions [30]. The extraction of vanadium (V) was performed using TBP from multimetal chloride solution, and vanadium was then recovered from the loaded organic phase using 4.0 mol/L HCl [29]. Vanadium (V) extraction from hydrochloric acid media was carried out using Aliquat 336, and the effects of various factors on the extraction and stripping processes were investigated [22]. Cyanex 923 can be used to extract vanadium (V) from high-acidity liquor, nevertheless, it suffers from high price. Previous studies show that Aliquat 336 or TBP exhibits low vanadium (V) extraction efficiency when hydrochloric acid concentration is approximately 140 g/L as in practical solution [22,29]. Mixing amine extractant with neutral extractant has been reported to exhibit synergism and get better extraction ability [35]. Moreover, TBP can inhibit the formation of a third phase while its solvation extraction mechanism contributes to easy stripping [14]. Thus, an Aliquat 336-based synergistic extraction system was employed and TBP was used as a cheaper synergistic extractant in this study. The separation of vanadium (V) using Aliquat 336–TBP synergistic extraction system from chloride liquor with high concentration of hydrochloric acid has not been reported.

In this study, extractant consisting of Aliquat 336 and TBP in kerosene modified with 10 vol% 2-octanol was used to separate vanadium (V) from the chloride liquor with high concentration of hydrochloric acid. The effect of different parameters on the extraction and stripping of vanadium (V) was studied. Synergistic effect was observed and the mechanism of vanadium (V) extraction by the Aliquat 336–TBP mixed extractant was studied.

2. Experimental

2.1. Reagents and apparatus

Aliquat 336 was supplied by Alfa Aesar, and TBP was purchased from Xilong Chemical Co., Ltd. All the extractants were used without further purification. According to previous study [7], feed chloride liquor containing approximately 0.95 g/L vanadium (V) was prepared by dissolving $NaVO_3$ ($\geqslant$99.0%, Aladdin Industrial Corporation) and HCl in distilled water, which was used for vanadium extraction. The other chemicals used were of analytical reagent grade. The concentrations of metals in the aqueous phase were determined using inductively coupled plasma optical emission spectroscopy (Optima 5300DV, Perkin-Elmer). The concentrations of hydrochloric acid in the aqueous phase were measured by acid-base titration. FT-IR measurements were performed using a Spectrum GX spectrometer (Perkin-Elmer). UV–vis measurements were performed using a UV 9100 B spectrophotometer (LabTech). The V_2O_5 product was characterized by X-ray diffractometer (SmartLab, Rigaku Corporation).

2.2. Procedure for extraction and stripping

Extraction experiments were performed in stoppered conical flasks with a mechanical shaker at shaking speed of 150 r/min, and then phase separation was performed using separatory funnels. After phase disengagement within 1 min, the concentrations of metals in raffinate were analyzed by ICP-OES (the wavelength used for determining vanadium was 290.88 nm). The concentrations of metals in loaded organic phase were calculated by mass balance.

The loaded organic phase and stripping agent were mixed in stoppered conical flasks with a mechanical shaker at shaking speed of 150 r/min, and then phase separation was performed using separatory funnels. After phase disengagement within 1 min, the concentrations of metals in stripping solution were analyzed by ICP-OES.

2.3. Data treatment

Extraction (E), distribution ratio (D), synergistic enhancement coefficient (R), and stripping (S) were calculated by the following equations:

$$E = \frac{V_{\mathrm{Org.}} C_{\mathrm{Org.}}}{V_{\mathrm{F}} C_{\mathrm{F}}} \times 100\% = \frac{D}{D + \frac{V_{\mathrm{Aq.}}}{V_{\mathrm{Org.}}}} \times 100\% \tag{1}$$

$$D = \frac{C_{\mathrm{Org.}}}{C_{\mathrm{R}}} \tag{2}$$

$$R = \frac{D_{\mathrm{A+T}}}{D_{\mathrm{A}} + D_{\mathrm{T}}} \tag{3}$$

$$S = \frac{V'_{\mathrm{Aq.}} C'_{\mathrm{Aq.}}}{V_{\mathrm{Org.}} C_{\mathrm{Org.}}} \times 100\% \tag{4}$$

In the above equations, C_F, $C_{Org.}$ and C_R are the concentrations of metal in feed solution, organic phase and raffinate, respectively; V_F, $V_{Org.}$ and $V_{Aq.}$ represent the volumes of feed solution, organic phase and aqueous phase, respectively; D_{A+T} is the distribution ratio of vanadium extraction by Aliquat 336 and TBP mixtures; D_A or D_T represents the distribution ratio of vanadium extraction using single extractant Aliquat 336 or TBP, respectively; $V'_{Aq.}$ is the volume of stripping aqueous phase; $C'_{Aq.}$ is the concentration of metal in stripping solution.

3. Results and discussion

3.1. Solvent extraction of vanadium (V)

3.1.1. Effect of extractant composition on the extraction of vanadium

To determine the extractant composition, experiments were carried out under the following conditions: extractant concentration of 20 vol% in kerosene containing 10 vol% 2-octanol, HCl concentration of 3.75 mol/L, vanadium concentration of 0.96 g/L, contact time of 10 min, temperature of 25 °C, and phase ratio (O/A) of 1:1. The results are shown in Fig. 1. Vanadium extraction increased with increasing volume fraction of Aliquat 336, while the extraction of vanadium was nearly invariant after Aliquat 336 concentration of 60% (v/v). The synergistic enhancement coefficient increased rapidly with Aliquat 336 concentration until 20% (v/v), and then decreased. The maximum synergistic enhancement coefficient of 3.26 was attained at Aliquat 336 concentration of 20% (v/v). Aliquat 336 as ionic liquid has high viscosity, therefore the viscosity of organic phase increased with increasing Aliquat 336 volume fraction, which hindered phase disengagement. Furthermore, the price of TBP was significantly lower than that of Aliquat 336. Hence, the volume ratio of Aliquat 336 to TBP 1:4 was effective for vanadium extraction from this chloride liquor.