



Extraction behaviors of rare-earths in the mixed sulfur-phosphorus acid leaching solutions of scheelite



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ABSTRACT

Leaching of scheelite by adopting the sulfur-phosphorus mixed acid allowed the accompanied rare-earth elements to enter a leaching solution. The leaching solution contained ions that could be coordinated with rare-earth ions, such as phosphotungstic acid anions, sulfate anions and phosphate anions, among others. To efficiently extract rare earths from the leachate, the extraction behavior of rare-earth ions in the solution was examined. Experimental results indicated that when the solution pH was lower than 1, phosphotungstic acid existed in the form of Keggin-type (1:12) $[PW_{12}O_{40}]^{3-}$, which exhibited a relatively poor complexing ability. Thus, secondary carbon primary-amine (N1923) could only extract phosphotungstic acid anions without extracting rare earths. As pH increased, a number of WO groups were dropped from the $[PW_{12}O_{40}]^{3-}$ ion to form unsaturated phosphotungstic acid. Unsaturated phosphotungstic acid anions with rare-earth ions exhibited a complexing ability stronger than that with SO_4^{2-} . Rare-earth ions were mainly complex with unsaturated phosphotungstic acid to form stable anions in the solution and could be extracted completely by the anionic extractant N1923. Meanwhile, the cationic extractant P204 could hardly extract rare earths. As the pH rose and exceeded 2.75, the concentration of PO_4^{3-} increased, rendering the complexation between the rare-earth ions and PO_4^{3-} dominant. Hence, rare-earth ions were precipitated.

1. Introduction

Owing to their distinct physical and chemical properties, rare-earth elements are widely used in economic industries and national defense. (Xu, 1995). In addition to independent ores, such as monazite and bastnaesite, rare earths are widely accompanied by other mineral resources. Geological data show that scheelite, fluorite, phosphate ores, and other minerals contain a specific amount of rare-earth elements (Ghaderi et al., 1999; Liu et al., 2007; Yan et al., 2015).

China ranks first in tungsten reserves and production worldwide (Li et al., 2011). Plasma spectral quantitative analysis of the rare-earth content of several well-known quartz vein-type and porphyry type-tungsten minerals was conducted by the Chinese Academy of Sciences in the southern part of China. The content of rare-earth elements in the porphyry-type tungsten minerals reportedly varied from 1049.7 ppm to 3034.59 ppm (in RE_2O_3), and the average content of rare-earth elements in the quartz vein-type tungsten minerals reached 334.88 ppm (Zhang et al., 1990). Other studies indicated that different types of tungsten minerals contain a certain amount of rare earths in different regions (Peng et al., 2005; Yang et al., 2013; Zhang et al., 2012; Zhu

and Xu, 1989). The presence of vast scheelite reserves in China implies substantial accompanied rare earths.

Traditionally, scheelite concentrates are mainly treated by alkaline autoclaving (Zhao and Li, 2008). This process involves transforming tungsten into sodium tungstate in the leaching solution. However, the accompanied rare-earth elements remain in the residue in the form of hydroxide. To recover the rare-earth elements from the residue, acid leaching has to be adopted (Xu et al., 1997). Alkali residue mainly consists of calcium hydroxide or iron oxide and manganese oxide. Acid consumption is considerably large. Therefore, recycling involves high costs, even exceeding the value of accompanied rare earths.

We devised a method of decomposing scheelite by using sulfur-phosphorus mixed acid (Zhao and Li, 2014). The method takes advantage of the properties that allow tungsten to easily combine with P to generate heteropoly acids with high solubility in acidic environments. By leaching at a lower reaction temperature ($< 100\text{ }^\circ\text{C}$) and atmospheric pressure, the WO_3 leaching ratio can exceed 99%. In this process, the acid solution can be reused to solve the problem of large amount of harmful salt wastewater emission. Calcium in scheelite can be combined with sulfate to form gypsum precipitates, which can be

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used as building materials to address the problem of waste residue. Further research shows that accompanied rare-earth elements also enter the leaching solution. Thus, the accompanied rare earths of scheelite may be recovered efficiently by sulfur-phosphorus mixed acid leaching.

In the acid leaching system, sulfate and phosphate anions and phosphotungstic acid anions can react with rare-earth ions generating complexation ions. The properties that rare earths are coordinated with sulfate and phosphate anions are often applied to extract the accompanied rare earths of phosphorus concentrate during the wet-process of phosphoric acid production (Long et al., 2009; Wang et al., 2008). However, local and international studies determine that the main problem is caused by the enrichment of rare-earth elements in phosphogypsum, which results in an unsatisfactory leaching ratio of rare earths. Numerous studies are currently devoted to improving the proportion of rare earths entering the phosphoric acid solution. A study was also conducted on the dihydrate process of leaching accompanied rare earths phosphorus concentrate (Lu, 2007). > 40% of the rare-earth elements were lost in gypsum. Thus, the optimal leaching ratio was only 57.7%. To solve this problem, surfactants were added to control the crystallization rate and crystal growth rate of calcium phosphate, thereby reducing eutectic adsorption of rare earths phosphate and calcium sulfate. The process prompted a 75% increase in the proportion of accompanied rare-earth elements entering the phosphoric acid solution (Wang et al., 2008). However, no studies have been reported on the complexation of rare-earth elements with sulfuric acid and phosphoric acid in the scheelite leaching solution. Tungsten heteropoly acid can also coordinate with rare earths. Tungsten heteropoly acid, regardless of its intact or absent morphology, is distributed to a large number of terminal oxygen atoms on the outer layer. Lanthanide metal ions exhibit strong oxygen-related properties. It is easy to form a complex with the oxygen-rich surface and strong coordination ability of tungsten heteropoly acid (Pope, 1984).

However, in the present study, the solution system is more complex. The system not only contains tungsten, phosphorus, sulfur and rare-earth elements, but also the existence morphology of phosphotungstic acid changes with the nature of the solution. The extraction behavior between different morphologies of phosphotungstic acid and rare-earth ions may change accordingly. Therefore, it is necessary to explore the extraction behavior of rare earth ions in the scheelite leaching solution, which is obtained by adopting sulfur-phosphorus mixed acid. In the actual leachate, if the concentration of rare earths is low, we only extract the tungsten without extracting the rare earths. The raffinate containing rare-earth elements will enter to the next leaching. When the concentration of rare-earth elements are up to 1 g/L with the cycle of leaching, We will extract rare-earth elements from the leachate. The real leaching solution composition was listed in Table 1. In the present study, lanthanum is used to examine the extraction behavior of rare-earth ions in the leachate.

2. Experiment

2.1. Materials

Two extractants, secondary carbon primary amine (N1923) (Shanghai Laiyashi Chemical Co., Ltd.) and D2EHPA (P204) (Shanghai Aladdin Reagent Co., Ltd.), were used for the study. These organic reagents were used without further purification. Kerosene as the diluent was prepared by 2-stage sulfonation of commercial kerosene.

Table 1

The main compositions of scheelite leaching solution with the 4 cycles of leaching.

WO ₃	H ₂ SO ₄	H ₃ PO ₄	La ₂ O ₃	CeO ₂	Nd ₂ O ₃
102 g/L	100 g/L	100 g/L	0.04 g/L	0.089 g/L	0.023 g/L

Table 2

The compositions of 6 synthetic solutions.

Synthetic solutions	Elements in feed solution		
Rare earths-phosphotungstic acid solution	La 1 g/L		WO ₃ 35 g/L
Rare earths-sulfuric acid solution	La 1 g/L	S 32 g/L	
Rare earths-sulfuric acid-phosphotungstic acid solution	La 1 g/L	S 32 g/L	WO ₃ 35 g/L
Rare earths-phosphoric acid solution	La 1 g/L	P 31 g/L	
Rare earths-phosphoric acid-sulfuric acid solution	La 1 g/L	P 31 g/L	S 32 g/L
rare earths-phosphoric acid-phosphotungstic acid solution	La 1 g/L	P 31 g/L	WO ₃ 35 g/L

Phosphotungstic acid (H₃PW₁₂O₄₀·xH₂O, A.R., Hebei Laishui County Yannan Fine Chemicals Co., Ltd.), nitric acid (A.R., Xilong Chemical Co., Ltd.), sulfuric acid (A.R., Chengdu Kelong Chemical Reagent Factory), and phosphoric acid (A.R., Xilong Chemical Co., Ltd.), and lanthanum oxide (A.R., Xilong Chemical Co., Ltd.) were used for the preparation of synthetic solutions.

2.2. Experimental procedures

The study involved 6 different synthetic solutions, and the compositions were shown in Table 2. The synthetic solution containing phosphoric acid was placed in a 200 mL beaker and then adjusted to preset pH. The solution was left to stand for 30 min. The content of each element in the solution was then assayed.

The synthetic solution containing no phosphoric acid was placed in a 200 mL beaker and then adjusted to preset pH for the extraction experiments. N1923 was protonated with 1 mol/L nitric acid prior to the extraction experiments. The extraction experiments were carried out by shaking two phases in a 125 mL separating funnel with a water bath oscillator. After phase separation, the content of each remaining element in the raffinate was analyzed by ICP-OES (Thermo Scientific iCAP 7200 Radial, Thermo Fisher Scientific, USA). The extraction ratios can be calculated according to Eq. (1).

$$E = \frac{C_F V_F - C_R V_R}{C_F V_F} \quad (1)$$

where E represents the extraction ratios, C_F and C_R denote the substance contents in the aqueous phase before and after extraction, V_F and V_R are the volumes of the aqueous phase before and after extraction.

3. Results and discussion

3.1. Extraction behavior of rare-earth ions in the rare earths-phosphotungstic acid solution system

To intuitively explore the extraction behavior between rare-earth ions and phosphotungstic acid in a leaching solution under different conditions, lanthanum oxide solid and phosphotungstic acid solid were added into the aqueous solution. Nitric acid was added dropwise until lanthanum oxide was completely dissolved. The solution was recorded as the rare earths-phosphotungstic acid solution system. As illustrated in Fig. 1, lanthanum were not extracted by the nitric acid-protonated N1923 at pH = 0. With increasing pH, the extraction ratio of lanthanum increased rapidly. The solution pH rose to 3, and a satisfactory extraction ratio of ~99% was obtained. As the pH continued to rise, superior extraction efficiencies of lanthanum were consistently obtained, whereas complete extraction of WO₃ could be readily achieved with N1923 at any pH tested. However, rare earths extracted by P204 obtained poor results. Moreover, with increasing pH, lanthanum extraction remained basically unchanged, that is, consistently lower than 6%.

When the solution pH was 0, [PW₁₂O₄₀]³⁻ underwent no

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