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Development of a separation process for the selective extraction of hafnium(IV) over zirconium(IV) from sulfuric acid solutions by using D2EHPA

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ABSTRACT

A new process for the separation of Zr(IV) and Hf(IV) from sulfuric acid solution by selective extraction and stripping was proposed. Firstly, Hf(IV) was preferentially extracted by di-2-ethylhexylphosphoric acid (D2EHPA) from moderate sulfuric acid solutions. From the loaded D2EHA, co-extracted Zr(IV) was selectively stripped by strong sulfuric acid solution with a separation factor of 10, leaving only Hf(IV) in the stripped D2EHPA. Hafnium(IV) was then completely stripped by oxalic acid solution and thus D2EHPA was regenerated. The McCabe–Thiele plots for the extraction and stripping isotherms were constructed and the results were verified by the simulated cross-current extraction and stripping experiments. Zirconium(IV) solutions of high purity were obtained in the extraction raffinate and sulfuric acid stripping solution, while Hf(IV) was present in the oxalic acid stripping solution.

1. Introduction

Hafnium usually accompanies zirconium in natural sources to the extent of 1.5–2%, and has a high neutron capture cross-section of 120 b compared to 0.18 b of zirconium (Marczenko and Balcerzak, 2000; Mukherji, 1970). The thermal neutron capture cross-section of the zirconium metal would be about 1.6 b, in the presence of hafnium, which lessens the merits of zirconium as a raw material for nuclear reactors (Mukherji, 1970). This highlights the need for high purity metals for nuclear industry and the importance of the separation of hafnium(IV) from zirconium(IV).

In aqueous solutions, zirconium(IV) and hafnium(IV) have high coordination numbers, exhibit hydrolysis, and as a consequence exist as metal ion-complexes. The tendency of the anions to form complexes with zirconium(IV) and hafnium(IV) decreases in the following order: $OH^- > F^- > C_2O_4^{2-} > SO_4^{2-} > NO_3^- > Cl^-$ (Solovkin and Tsvetkova, 1962; Ryabchikov et al., 1964). The difference in complex formation behavior of zirconium(IV) and hafnium(IV) with each inorganic anion makes it possible to separate them by solvent extraction. We have investigated the separation and extraction behavior of zirconium(IV) and hafnium(IV) from chloride, nitrate and sulfate aqueous solutions by using cationic, neutral and amine-based extractants (Banda et al., 2012, 2014; Lee et al., 2015; Wang and Lee, 2014, 2015; Wang et al., 2013, 2015).

According to our previous research (Banda et al., 2014; Lee et al., 2015), selective extraction of hafnium(IV) over zirconium(IV) occurs from only sulfuric acid solutions with organophosphorous acid as the extractants. However, the mass of the co-extracted zirconium(IV) is quite considerable in the extraction process, due to the large mass composition ratio of Zr(IV) to Hf(IV) (about 50) in sources. Therefore, separation and recovery of the zirconium(IV) and hafnium(IV) metal ions from the loaded D2EHPA is necessary to improve the purity and recovery percentage of each metal for the overall process. The most suitable sulfuric acid concentration for the separation of hafnium(IV) from zirconium(IV) with D2EHPA in the previous experiments was demonstrated to be 4 M (Banda et al., 2014). When zirconium(IV) and hafnium(IV) metal ions were extracted from 4 M H_2SO_4, the disadvantage of the process lies in the difficulty in the separation of the two metal ions by stripping step or from the liquor. In the sulfuric acid concentration range from 0.5 to 7 M, the extraction percentage of Hf(IV) and Zr(IV) ions from solutions of 0.5-7 M sulfuric acid decreased with the increasing acid concentration. These data indicate that it is possible to strip zirconium(IV) and hafnium(IV) from loaded D2EHPA using strong sulfuric acid once the extraction has been done at a lower concentration of sulfuric acid (Wang and Lee, In press).

In this present work, we developed a process for the efficient separation of zirconium(IV) and hafnium(IV) from sulfuric acid solutions of moderate concentrations (0.05–1 M) by selective extraction and stripping. This process consisted of preferential extraction of hafnium(IV) over zirconium(IV) at moderate sulfuric acid solution by D2EHPA, selective stripping of zirconium(IV) from loaded D2EHPA with strong sulfuric

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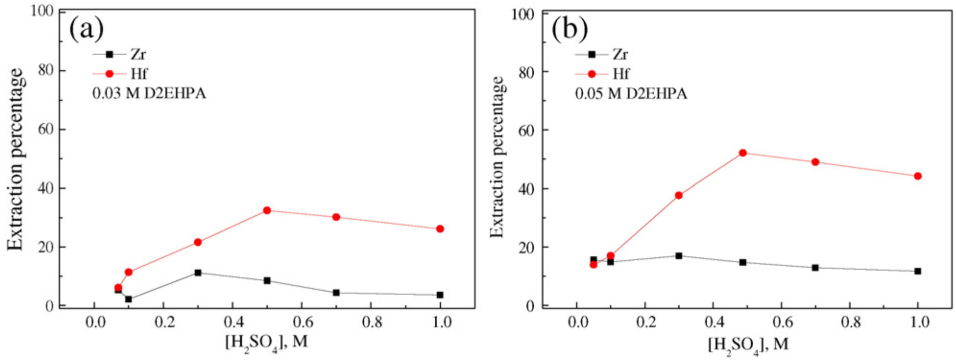

Fig. 1. Effect of H_2SO_4 concentration on the extraction of Zr(IV) and Hf(IV) with (a) 0.03 and (b) 0.05 M D2EHPA. Experimental conditions: $[H_2SO_4] = 0.05–1$ M, [Zr(IV)] = 10 g/L, [Hf(IV)] = 0.2 g/L, [D2EHPA] = 0.03, 0.05 M, diluent = kerosene.

acid solution and complete stripping of hafnium(IV) by oxalic acid. The most suitable conditions for separation using extraction and stripping steps were investigated. Moreover, extraction and stripping isotherms were constructed. The proposed separation process was verified by batch simulation experiments for the cross-current extraction and stripping.

2. Experimental

2.1. Reagents

The extractant D2EHPA was purchased from Cytec Canada Inc. It was used without any further purification. Kerosene (Daejung Chemicals and Metals Co., Ltd., Korea, 95%, Aromatic content <19%) was used as a diluent and all other chemicals used were of analytical grade.

The mixed feed solutions of Zr(IV) and Hf(IV) with various compositions were prepared by dissolving the necessary amount of $Zr(SO_4)_2 \cdot 4H_2O$ (Alfa Aesar, Johnson Matthey Company, 98 + %) and $Hf(SO_4)_2$ (Alfa Aesar, Johnson Matthey Company, 99.9%) in doubly deionized water. Throughout the whole experiments, the concentration of Zr(IV) was kept at 10 g/L, while that of Hf(IV) was 0.2 g/L. Sulfuric acid was used to adjust the acidity of the solution. Since the composition of Zr(IV) and Hf(IV) may continuously change owing to hydrolysis and polymerization reaction (Biswas and Hayat, 2002), freshly prepared solutions of Zr(IV) and Hf(IV) were used in these experiments.

2.2. Solvent extraction and stripping procedure

The general extraction and stripping experiments were carried out by contacting equal volumes (20 mL) of the aqueous and organic phases at a phase ratio of 1:1 for 30 min using wrist action shaker (Burrell model 75 USA). All the experiments were performed at room temperature (25 ± 1 °C). After disengagement of the two phases, the concentration of metal ions in the aqueous phase was measured by ICP-OES (Perkin Elmer Optima 4300 DV model) and the concentration of metal ions in organic phase was determined by mass balance.

The number of extraction and stripping stages in a continuous operation was determined by constructing a McCabe–Thiele diagram. The equilibrium isotherms were determined using shakeout tests with aqueous and organic solutions at different phase volume ratios and mass balance after equilibration.

The cross-current simulation experiments for the selective extraction and stripping were carried out to verify the results obtained from McCabe–Thiele diagrams. During the cross-current simulation of the extraction of Hf(IV) with D2EHPA, the feed solution containing 10 g/L of Zr(IV), 0.2 g/L of Hf(IV) and 0.5 M of H_2SO_4 and 0.05 M D2EHPA in kerosene was employed at an O/A volume ratio of 2. Fresh D2EHPA was fed into each extraction stage and the corresponding extract was obtained. All extract streams were combined together to obtain the overall extraction, while the raffinate was obtained from the last stage.

The extraction percentage (Ex%) and stripping percentage (Strip%) of metal ions were obtained from the following equations:

$$\mathrm{Ex\%} = \frac{M_{\mathrm{initial}} - M_{\mathrm{aq}}}{M_{\mathrm{initial}}} \times 100\% \tag{1}$$

$$\mathrm{Strip\%} = \frac{M_{\mathrm{org}} - M_{\mathrm{stripped}}}{M_{\mathrm{org}}} \times 100\%. \tag{2}$$

The symbols M_{initial} and M_{aq} represent the mass of metal ions in the aqueous phase before and after extraction, respectively. Moreover, M_{org} and M_{stripped} represent the mass of metals ions in the organic before and after stripping, respectively. The distribution ratio (D) was defined as the ratio of the concentration of metal ions present in the organic

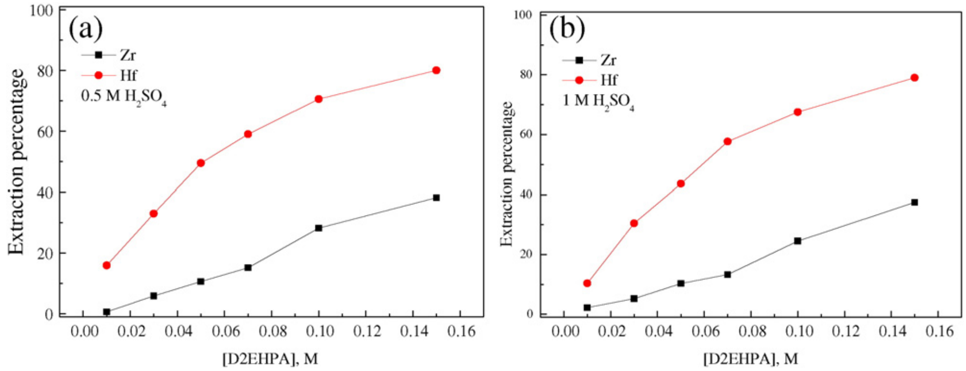

Fig. 2. Effect of D2EHPA concentration on the extraction of Zr(IV) and Hf(IV) from (a) 0.5 and (b) 1 M sulfuric acid solutions. Experimental condition: $[H_2SO_4] = 0.5$, 1 M, [Zr(IV)] = 10 g/L, [Hf(IV)] = 0.2 g/L, [D2EHPA] = 0.01–0.07 M, diluent = kerosene.