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Separation of Zr and Hf from sulfuric acid solutions with amine-based extractants by solvent extraction

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ABSTRACT

The extraction and separation behavior of Zr and Hf was investigated from sulfuric acid solutions by using amine-based extractants. In the sulfuric acid concentration range of 0.1–3 M, zirconium was selectively extracted over hafnium by using amines. Among the tested amines (Aliquat 336, Alamine 300, Alamine 308, Alamine 336, and TEHA), Alamine 308 led to the highest separation factor of 12.4 at 0.5 M H_2SO_4 solution. The extraction behavior of Zr and Hf in sulfate medium by amines was compared with that by acidic extractants in terms of solvent extraction reaction and complex formation. Quantitative stripping of both metals from the loaded Alamine 308 was achieved by using low concentration of Na_2CO_3 solution.

1. Introduction

Zirconium and hafnium co-exist in natural mineral ores and therefore zirconium compounds always contain a small amount of hafnium [1]. However, they have opposite characteristics in their application to nuclear industry. Zirconium components used in water-cooled nuclear reactors require hafnium-free materials due to the larger cross-section of hafnium for thermal neutron capture than that of zirconium [2]. Zirconium and hafnium are members of group 4 in the periodic table. They have extreme similar chemical properties, exhibit the same valence, and have similar ionic radii (0.074 mm for Zr^{4+}, 0.075 mm for Hf^{4+}). These similarities make their separation difficult. At present, the separation of zirconium and hafnium by multistage counter-current solvent extraction is normally practiced on a commercial scale.

The methyl iso-butyl ketone (MIBK) process proposed by Fischer and Chalybaeus has been used on a commercial scale to separate hafnium from zirconium [3,4]. In this process, thiocyanate complexes of zirconium and hafnium are formed in 2 M hydrochloric acid solution. Due to the different solubility of zirconium and hafnium thiocyanate complexes in MIBK, hafnium is selectively extracted into the organic phase and pure zirconium remains in the aqueous. Nonetheless, this method has some disadvantages, such as possible generation of waste streams containing high concentration of ammonium, cyanides and other organic by-products, high aqueous solubility and low flash point of the solvent (MIBK) [5,6].

In our previous works, separation of Zr and Hf have been performed from various media (chloride, nitrate and sulfate) based on the diverse characteristics of the complex formation behavior of Zr and Hf in each inorganic solution. It has been reported that zirconium is selectively extracted over Hf from chloric or nitric acid solutions by cationic, neutral and amine extractants [7–13]. Meanwhile, selective extraction of Hf over Zr is noticed from strong sulfuric acid solutions by acidic organophosphorous extractants, namely D2EHPA, Cyanex 272 and PC 88A [10]. Although, selective extraction of the minor element (Hf) over Zr is desirable and has some advantages such as the ease of multi-stage operation and process economics, this process has some drawbacks, such as the degradation of extractant in strong acid solution and difficulty in stripping. This promoted us to investigate a solvent extraction process to separate Zr and Hf.

Solvent extraction of Zr from sulfuric acid solutions by amines has been reported [14–17]. It has been reported that Zr could be extracted from moderate sulfuric acid solutions (0.1–1 M) with long-chain aliphatic amines [14]. However, few studies have been reported on the separation of Zr and Hf from sulfuric acid solutions by amine-based extractants. The difference in the stability of Zr and Hf sulfate complexes can be made use of separating these two metals by employing amines. In this work, solvent extraction experiments were carried out from 0.1 to 3 M sulfuric acid solutions to investigate the separation behavior of Zr and Hf by using amines. The operating parameters, such as the nature of extractant,

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effect of acid and extractant concentration, the nature of a stripping agent were studied. The difference between amine-based extractants and acidic extractants in the extraction of Zr and Hf from sulfate medium was discussed.

2. Materials and methods

2.1. Materials

Aliquat 336 (tricaprylmethylammonium chloride, a quaternary ammonium salt), Alamine 308 (tri-isooctyl amine), Alamine 336 (mixture of tri-octyl/decyl amine) and TEHA (tri-2-ethylhexyl amine) were purchased from BASF Chem Co. Ltd. Alamine 300 (tri-n-octyl amine) were supplied by Sam Chun pure Chemical Co., Ltd (Korea). These reagents were used without any further purification. Kerosene (Daejung Chemicals and Metals CO., Ltd., Korea) was used as a diluent and all the other chemicals used were of analytical grade.

Stock solution of Zr and Hf was prepared by dissolving the necessary amount of $ZrOCl_2{\cdot}8H_2O$ and $HfOCl_2{\cdot}8H_2O$ (Alfa Aesar, Johnson Matthey Company, 99.9%) in doubly deionized water. In our experiments, the initial concentration of Zr (IV) and Hf (IV) was kept at 0.2 g/L. Reagent H_2SO_4 was used to adjust the acidity of the solution. Since the composition of Zr and Hf may continuously change owing to hydrolysis and polymerization reaction [18], freshly prepared solutions of Zr and Hf were used in these experiments.

2.2. Methods

The general extraction and stripping experiments were carried out by shaking equal volumes (20 mL) of the aqueous and organic phases for 30 min (previous results on the effect of reaction time suggest that shaking time of 30 min is sufficient to achieve equilibrium [11]) in a 100 mL screwed cap bottle using wrist action shaker (Burrell model 75, USA). After equilibrium, the contents were allowed for phase disengagement. All the extraction experiments were carried out at ambient temperature. The concentration of metal in the aqueous phase was measured by ICP-OES (Spectro arcos). The concentration of metal in the organic phase was obtained by mass balance.

The distribution coefficient (D) was taken as the ratio of the concentration of metal present in the organic phase to that in the aqueous phase at equilibrium. From the D values, the extraction percentage was obtained by using $EX\% = D \times 100/[D + (V_{aq}/V_{org})]$ where V_{aq} and V_{org} are the volume of aqueous and organic phases, respectively. The separation factor (β) ($\beta = D_{Zr}/D_{Hf}$) was calculated from the value of distribution coefficient of each metal.

3. Results and discussion

3.1. Effect of sulfuric acid concentration on the extraction of Zr and Hf with several amine extractants

The initial experiments were performed to choose a suitable amine-based extractant for the separation of Zr and Hf from sulfuric acid solutions. In these experiments, synthetic aqueous solutions with Zr and Hf concentration of 0.2 g/L and with sulfuric acid concentration from 0.1 to 3.0 M were employed to investigate the possibility of separating Zr and Hf by using amine-based extractants. For this purpose, five amines with 0.01 M concentration were employed and the results are shown in Figs. 1 and 4. Fig. 1 indicates that the extraction of both zirconium and hafnium by Aliquat 336 decreased steeply with the increase of the sulfuric acid from 0.1 to 1 M and the extraction of Zr and Hf was nearly zero

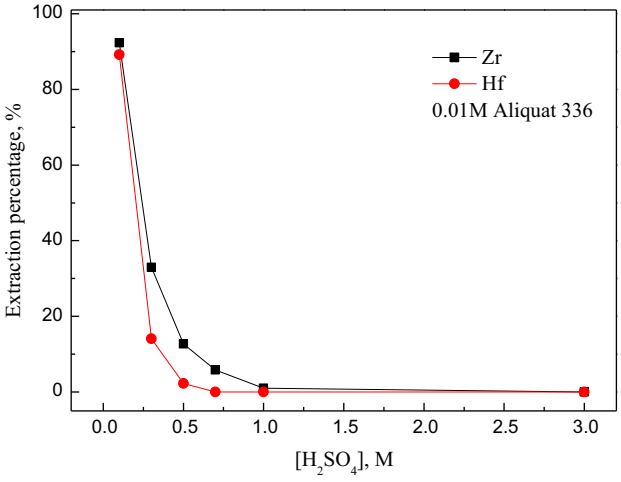

Fig. 1. Extraction of Zr and Hf from H_2SO_4 solutions by 0.01 M Aliquat 336 in kerosene.

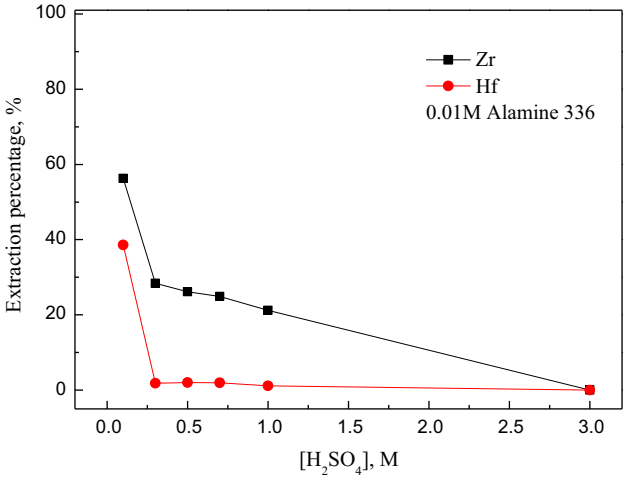

Fig. 2. Extraction of Zr and Hf from H_2SO_4 solutions by 0.01 M Alamine 336 in kerosene.

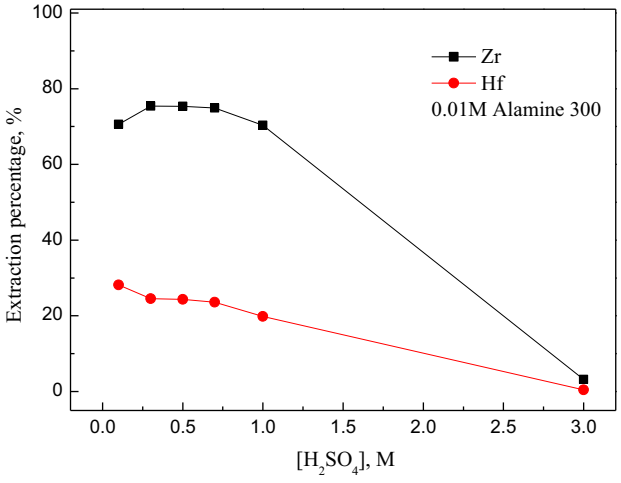

Fig. 3. Extraction of Zr and Hf from H_2SO_4 solutions by 0.01 M Alamine 300 in kerosene.