



# Selective recovery and separation of Zr and Hf from sulfuric acid leach solution using anion exchange resin

Yiqian Ma, Srečko Stopić\*, Zizhao Huang, Bernd Friedrich

Institute of Process Metallurgy and Metal Recycling (IME), RWTH Aachen University, Intzestraße 3, 52056 Aachen, Germany



## ARTICLE INFO

### Keywords:

Zirconium  
Hafnium  
Separation  
Ion exchange  
Eudialyte

## ABSTRACT

Apart from zircon and baddeleyite, some other minerals also contain amounts of Zr and Hf, and  $\text{H}_2\text{SO}_4$  can be the best candidate leachate for their recovery. The subsequent step in the process would be the recovery and separation of Hf and Zr from the resulting leach solution together with impurities. This reported study focused on the recovery process following the leaching of Zr and Hf from a eudialyte residue after REEs extraction. The chemistry of the solution was studied to determine the feasibility of different methods, and based on the results, an anion exchange resin was chosen to selectively recover Zr and Hf from the acidic sulfate solution. Batch and continuous ion exchange experiments using a strong anionic resin (MP600) were performed to develop the ion exchange process. The experimental results showed that Zr and Hf can be selectively recovered over other impurities. In the process of the adsorption of Zr and Hf, the bed volume reached 6 using the feed solution at a pH 0.94 at 25 °C with a contact time of 2 h. Pure Zr sulfate solution was used to scrub the load resin, after which the loaded resin was easily eluted using 10%  $\text{NH}_4\text{HCO}_3$  + 1 mol/L  $\text{NH}_4\text{OH}$  solution. This produced 21.23 g/L Zr, 0.03 g/L Hf, 0.01 g/L Fe, 0.01 g/L Al, 0.02 g/L Nb and < 0.001 g/L Ca in the eluate. The impurity removal from the leachate and the enrichment of Zr were achieved by the process.

## 1. Introduction

Zirconium is widely used in the fields of atomic energy, metallurgy, military, petrochemical, aerospace and new materials science (Nielsen et al., 2000; Zirconium in Steels, 2018). In nature, zircon ( $\text{ZrSiO}_4$ ) and baddeleyite ( $\text{ZrO}_2$ ) are the main sources for commercial production of zirconium, but they are highly stable, thus requiring extreme, drastic conditions to be decomposed (Biswas et al., 2010). In addition, if hydrometallurgical technology is applied to recover Zr from zircon, silica removal from the recovery solution significantly complicates the process. Other relatively common zirconium-bearing minerals include: eudialyte, catapleiite, gittinsite, sabinaite, weloganite, tazheranite, zirconolite, kimzeyite, wadeite, and calzirtite (Wu et al., 2010). These minerals can contain other valuable metals or they may be associated with other valuable minerals. For example, eudialyte is a complex Na-Ca-zirconosilicate mineral that is generally rich in Fe, Al, Mn, Ti, K, Nb and contains attractive quantities of rare earth elements (REE) (Johnsen et al., 2003). On the other hand, some REE-bearing ores like monazite and xenotime can also contain a small amount of zirconium. The zirconium extraction, either from these initial minerals or the residues after metals extraction, would constitute part of the comprehensive recycling of these mineral resources.

Eudialyte can be a potential commercial source of zirconium. The typical empirical chemical formula of eudialyte is  $\text{Na}_4(\text{Ca}, \text{Ce}, \text{Fe})_2\text{ZrSi}_6\text{O}_{17}(\text{OH}, \text{Cl})_2$ , but it can be present in a wide range of chemical compositions (Lebedev, 2003). The content of Zr (5–10%) in eudialyte is much lower than in zircon, but it can be easily decomposed by acid in comparison to zircon (Lebedev, 2003; Davris et al., 2017; Voßenkaul et al., 2016). Another issue to be considered is that REE extraction from eudialyte sometimes takes priority as these materials have a higher value (Goodenough et al., 2016; Ma et al., 2019). The residual Zr after REE extraction of eudialyte should not be overlooked.  $\text{H}_2\text{SO}_4$  is considered to be the best candidate for Zr leaching from the eudialyte or eudialyte residue. After obtaining the pregnant leachate, an efficient impurity removal method to recover zirconium should be considered.

There are no natural minerals that contain Hf exclusively, it is usually present in trace quantities in minerals that contain Zr because its chemistry is very similar to Zr (Kozak and Mountford, 2006). The Hf concentration in eudialyte is about 0.2% and it will be leached with Zr during the treatment of eudialyte (Ma et al., 2019). When Zr is contaminated with Hf, Zr will reflect thermal neutrons in the cladding materials in nuclear reactors (Wang and Lee, 2016). Therefore, it is paramount to remove Hf from Zr for the use in the nuclear industry, and this issue has been widely studied over the last few decades. Various

\* Corresponding author.

E-mail address: [sstopic@ime-aachen.de](mailto:sstopic@ime-aachen.de) (S. Stopić).

<https://doi.org/10.1016/j.hydromet.2019.105143>

Received 19 June 2019; Received in revised form 15 August 2019; Accepted 25 August 2019

Available online 26 August 2019

0304-386X/ © 2019 Elsevier B.V. All rights reserved.

methods have been developed to achieve this separation, including ion exchange (Alfonso et al., 2016; Felipe and Ladeira, 2018; Smolik et al., 2009), fractional crystallization (Niemand and Crouse, 2015), and solvent extraction (Conradie et al., 2018; Wu et al., 2019; Wang and Lee, 2015). These methods have relied on synthetic solutions for the process feed containing pure chemicals, such as HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>.

The objective of this reported study was to employ sulfuric acid to leach Hf and Zr from a eudialyte residue following the extraction of REE from the eudialyte concentrate. There are many other impurities such as sodium, iron and aluminium in the leach solution (Ma et al., 2018). Data concerning the recovery of Zr and Hf and their separation from sulfate media containing these impurities is sparse in the general literature. Precipitation methods have proven to be inefficient in thoroughly removing impurities (Lebedev, 2003). Ion exchange is more effective, and different anion and cation ion exchangers can be employed for the selective adsorption of Zr and Hf (Smolik et al., 2009; Alfonso et al., 2016; Poriol et al., 2006; Machlan and Hague, 1962). In general, it is difficult to achieve separation by selective adsorption of Zr and Hf from hydrochloric acid and sulfuric acid solutions due to their nearly identical chemical properties (Smolik et al., 2014; Hurst, 1983). One possible approach to do this is to elute Zr and Hf from loaded exchangers in a step by step fashion (Begovich and Sisson, 1983). Another is to introduce other ions such as F<sup>−</sup> and SCN<sup>−</sup> to affect the selectivity of resins, because Zr and Hf can form various coordination complexes with different ligands, and the subsequent complexes have different charges and properties (Monroy-Guzman et al., 2002; Jakóbk-Kolon et al., 2013). However, these additives may add further difficulties in the treatment of the process waste water.

In order to recover Zr and Hf from the acidic sulfate solution, this study investigated the chemistry of the solution to better understand the feasibility of the different methods, and based on the results, an anion exchange resin was chosen to selectively recover Zr and Hf from the sulfuric acid leach solution. Chemical separation of Zr and Hf was also attempted.

## 2. Experimental

### 2.1. Materials and analysis

In EURARE project, as a resource for REE, eudialyte ore has been mined in South Greenland. After beneficiation, HCl was then used to leach REE from the eudialyte concentrate. It was found that about 30% Zr and Hf were also leached from the mineral using the HCl. The leached Zr and Hf were then treated like impurities similar to Fe and Al by neutralization using CaCO<sub>3</sub>. The mixture of the eudialyte leach residue together with the impurity precipitation from the pilot-scale test was the material (eudialyte residue) for Zr and Hf recovery. The eudialyte residue used in this study contained 6.26 wt% Zr, 0.22% wt% Hf, 0.53% wt% Nb, 4.98 wt% Al, 3.21 wt% Fe and 25.52% wt% Si. The composition of the sulfuric acid leach solution of the eudialyte residue is listed in Table 1. The detailed leaching process using H<sub>2</sub>SO<sub>4</sub> has been reported by our group (Ma et al., 2018). As can be seen from the data in Table 1, the concentration of SO<sub>4</sub><sup>2−</sup> in the leach solution was high and the main impurities in the leach solution were found to be Al and Fe. The H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, NH<sub>3</sub>·H<sub>2</sub>O, NH<sub>4</sub>HCO<sub>3</sub> used in this study were of analytical grade, and all aqueous solutions were prepared using distilled

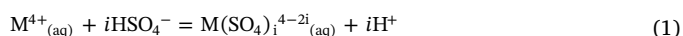
water. The elemental content of the solution was determined by inductively-coupled plasma emission spectroscopy (ICP) with a PS-6 PLASMA SPECTROVAC, BAIRD (Waltham, MA, USA). Lewatit® Mono-Plus MP 600, a strongly basic anion exchange resin was used in this work and was supplied by Lanxess Co., Ltd. (Cologne, Germany). The functional group of the resin was a quaternary ammonium compound and its capacity for Cl<sup>−</sup> was 1.1 mmol/g.

### 2.2. Aqueous chemistry analysis

In aqueous solution, Zr<sup>4+</sup> and Hf<sup>4+</sup> ions tend to form complex compounds with organic and inorganic acids, because they have high coordination numbers. The chemical stability of the complexes formed by zirconium and hafnium with inorganic ligands decreases in the order of OH<sup>−</sup> > F<sup>−</sup> > SO<sub>4</sub><sup>2−</sup> > Cl<sup>−</sup> ≥ NO<sub>3</sub><sup>−</sup> (Solovkin and Tsvetkova, 1962). Hydroxide complexes Zr<sup>4+</sup> and Hf<sup>4+</sup> have a great affinity for hydroxyl ions. The complexation of Zr<sup>4+</sup> with OH<sup>−</sup> depends on the solution pH, and the resulting complexes can be stable even in very acidic solutions (Wang and Lee, 2016). On the other hand, for the solution in this study, the use of SO<sub>4</sub><sup>2−</sup> results in competition between SO<sub>4</sub><sup>2−</sup> and OH<sup>−</sup> ions for the formation of inner-sphere complexes with the metal ion. Thus, a complex reaction with SO<sub>4</sub><sup>2−</sup> inhibits the hydrolysis of Zr<sup>4+</sup> and Hf<sup>4+</sup>. The complex reaction of Zr<sup>4+</sup> and Hf<sup>4+</sup> in the acidic sulfate solution can be represented by Eq. (1) and the corresponding stability constants (β<sub>i</sub>) are listed in Table 2 (Ryabchikov et al., 1964). Fig. 1 shows the fraction of ions of Zr and Hf in the aqueous solution at different pH values. As can be seen, in the absence of SO<sub>4</sub><sup>2−</sup>, the hydrolysis of Zr<sup>4+</sup> and Hf<sup>4+</sup> can begin even at strong acidity, and precipitation of hydroxide can be obtained when the pH is higher than 2.0. However, in a sulfate solution, the predominant forms of Zr and Hf in the acidic sulfate solution are Zr(SO<sub>4</sub>)<sub>3</sub><sup>2−</sup> and Hf(SO<sub>4</sub>)<sub>3</sub><sup>2−</sup> and the pH range for hydrolysis has increased, and is closer to the pH those of hydrolysis of Al(III) and Fe(III).

Fig. 1 also shows the predicted fraction diagrams of dissolved Fe (III), Al(III), Nb(V), Ca(II) in acidic sulfate solution. As can be seen, all these cations exist as several species that have different hydrolysis rates. The anionic forms include NbO(SO<sub>4</sub>)<sub>2</sub><sup>−</sup>, Fe(SO<sub>4</sub>)<sub>2</sub><sup>−</sup> and Al(SO<sub>4</sub>)<sub>2</sub><sup>−</sup>. The Nb(V) in the solution is readily hydrolyzed at low pH.

Taking into account of the predominant forms of the complex in the acidic sulfate solution, anion exchange could be used to recover Zr and Hf. The binding force of the complex ions and the charges of the ions illustrated above would affect the selectivity of their adsorption.



$$\beta_i = \frac{[M(SO_4)_{i-2i}^{4-2i}]}{[M^{4+}][SO_4^{2-}]^i} \quad (2)$$

### 2.3. Batch adsorption and column adsorption experiments

Batch adsorption experiments were conducted using the leach solution with various adsorption conditions, including contact time and solution pH values. A 50 mL feed solution and 10 mL of wet resin were added to a beaker on a magnetic stirrer agitated at 150 rpm at room temperature (25 ± 1 °C). After a period of adsorption, the solution was subjected to elemental analysis, which provided elemental adsorption data for these conditions. From these results, the distribution coefficient

**Table 1**  
Chemical composition of experimental solutions, g/L.

Element	Zr	Hf	Fe	Al	Nb	Si	Ca	SO <sub>4</sub> <sup>2−</sup>	pH
Acid leach solution	10.95	0.26	2.44	10.55	0.48	< 0.001	0.7	117.50	0.57
Feed solution	10.83	0.26	2.44	10.55	0.10	< 0.001	0.6	116.12	0.94
Zr sulfate solution	10.80	–	–	–	–	–	–	118.00	0.98
Zr peak solution	21.23	0.03	0.01	0.01	0.02	< 0.001	< 0.001	–	–

**Table 2**  
Stability constants of sulphate complexes of zirconium and hafnium.

Stability constant	Zr	Hf
$\beta_1$	466	130
$\beta_2$	$3.48 \times 10^3$	$2.1 \times 10^3$
$\beta_3$	$3.92 \times 10^6$	$3.02 \times 10^6$

(D) was calculated to be the ratio of the equilibrium concentrations of the metals in the resin to that in the aqueous solution:

$$D = \frac{(c_0 - c_e)}{c_e} \quad (3)$$

Separation factor of Zr from other metals ( $\beta_{Zr/Me}$ ) can be written as:

$$\beta_{Zr/Me} = D_{Zr}/D_{Me} \quad (4)$$

Adsorption percentage (E) and equilibrium adsorption capacity ( $Q_e$ , mg/g) were calculated using Eqs. (5), (6).

$$E(\%) = \frac{c_e}{c_0} \quad (5)$$

$$Q_e = \frac{V(c_0 - c_e)}{m} \quad (6)$$

where V (L) is the volume of the solution; m (g) is the mass of resin;  $c_0$  (g/L) is the initial concentration;  $c_e$  (g/L) is the equilibrium concentration.

Column adsorption experiments were conducted using the sulfuric acid leach solution at room temperature ( $25 \pm 1^\circ\text{C}$ ) using a resin-filled  $\emptyset 3.0 \times 50$  cm glass column. The resin was pretreated with HCl to convert it to a chlorine type. 100 mL of the resin were wet-packed into the glass column. The operation was performed with the flow rate of 50 mL/h. The column effluent was analyzed periodically to determine the elemental composition of the effluent.

After adjusting the pH of the leach solution, the first step was to recover Zr and Hf from the feed solution in the presence of other impurities. Zr and Hf had been adsorbed first by anion exchange resin prior to other elements. The feed solution (Table 1) was added to the pre-treated resin by downstream flow. When  $< 1$  g/L Zr was detected in the effluent, the feed liquor was replaced with pure Zr sulfate solution as listed in Table 1, which scrubbed Hf and few other impurities from the resin column. The Zr sulfate solution was prepared using analytical  $\text{Zr}(\text{SO}_4)_2$ ,  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ . When the concentration of Hf in the effluent decreased to  $< 0.01$  g/L, the column test was ended. The effluent of the feed solution could be re-used in leaching process, and the effluent of the feed Zr sulfate which contained few impurities was used as the next feed liquor for Zr recovery.

The Zr loaded on the resin column was then eluted using 10%  $\text{NH}_4\text{HCO}_3$  + 1 mol/L  $\text{NH}_4\text{OH}$  with a contact time of 60 min at room temperature. After elution, the resin was regenerated using HCl and used for the next adsorption.

## 2.4. Equilibrium studies

Langmuir and Freundlich isotherms are commonly used to assess the adsorption characteristics of a resin. The Langmuir adsorption model assumes monolayer adsorption onto a surface with a finite number of identical and energetically equivalent adsorption sites, and the adsorbent surface is homogeneous in character. The Freundlich adsorption isotherm is an empirical relation between the concentration of the solute on the adsorbent surface and the concentration of the solute in the liquid with which it is in contact. The linear forms of these two isotherms can be expressed as follows (Godea and Pehlivan, 2006; Bilgili, 2006):

$$\frac{C_e}{Q_e} = \frac{1}{K \times Q_m} + \frac{C_e}{Q_m} \quad (7)$$

$$\log Q_e = \log k_f + \frac{1}{n} \log C_e \quad (8)$$

where  $Q_{max}$  and K are Langmuir constants relating maximal adsorption capacity (mg/g) and the energy adsorption (L/mg), respectively;  $k_f$  (mg/g) and n are Freundlich constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of adsorption.

Batch adsorption experiments were conducted to study the adsorption isotherms of Zr and Hf by comparing experimental data to the linear mathematical expressions. In the experiments, 50 mL of a Zr, Hf-bearing leach solution at the optimum pH was mixed with different volumes of MP600 resin. The volumes of the wet resin were 2 mL, 4 mL, 6 mL, 8 mL, 10 mL, 12 mL. The samples were equilibrated at room temperature for 12 h. The resin was then separated, and the concentrations of Zr and Hf in solution were determined by ICP-OES.  $Q_e$  (mg/g) was calculated based on the metal balance.

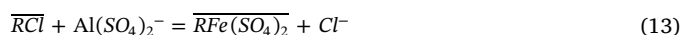
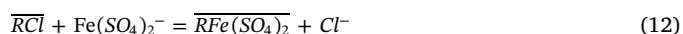
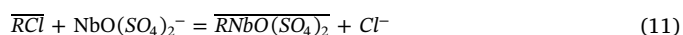
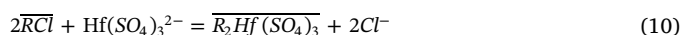
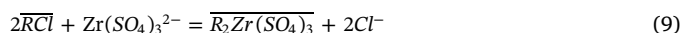
## 3. Results and discussion

### 3.1. Batch adsorption experiments

#### 3.1.1. pH adjustment and selectivity

The sulfuric acid leach solution contained several metals (Table 1) and the behavior of these elements when adjusting the pH was different because of ion transformation and distribution at different pHs (Fig. 1). Fig. 2 shows the effect of pH on the precipitation of the main elements. Based on the aqueous solution chemistry analysis and the precipitation behavior, Nb, Zr, Hf, Al, Fe were precipitated by hydrolysis at a suitable pH. The quantity of dissolved  $\text{Ca}^{2+}$  in the sulfate solution was very low and it also partially precipitated in the form of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  when the pH was increased. Zr and Hf precipitated until the pH was increased to 3.5, but Fe and Al would precipitate simultaneously, so that it was not feasible to selectively recover Zr and Hf via the standard precipitation method from the sulfuric acid leach solution.

Fig. 3 shows the effect of pH on the batch adsorption of the various metals, and the corresponding separation factors of Zr from other elements are listed in Table 3. A solution with pH  $> 0.56$  was obtained after precipitation and filtration, and the data were ignored if there was significant precipitation of the metals during pH adjustment. Based on the aqueous solution analysis, the reactions that occurred during the adsorption can be expressed as follows:



As can be seen from Fig. 3, the adsorption yields of Zr and Hf increased with an increase in pH from 0.1 to 1.0, which was in agreement with the increase in the fraction percentage of  $\text{Zr}(\text{SO}_4)_3^{2-}$  and  $\text{Hf}(\text{SO}_4)_3^{2-}$  in this pH range (Fig. 1), but the yields both decreased as the solution pH was further increased. The adsorption yields of Fe and Al remained at low values at pH from 0 to 2.0. This was probably because the complex anions ( $\text{Fe}(\text{SO}_4)_2^-$  and  $\text{Al}(\text{SO}_4)_2^-$ ) accounted for relatively low proportions in sulfate media, and their charges were less than those of  $\text{Zr}(\text{SO}_4)_3^{2-}$  and  $\text{Hf}(\text{SO}_4)_3^{2-}$ . The separation factors,  $\beta_{Zr/Ca}$ ,  $\beta_{Zr/Al}$  and  $\beta_{Zr/Fe}$  were all relatively high and reached their highest at a pH of around 1.0. However  $\beta_{Zr/Hf}$  remained low and was unsatisfactory for selective adsorption. The value of  $\beta_{Zr/Nb}$  indicated that Nb was adsorbed in preference to Zr when the pH was lower than 0.6. Also, most

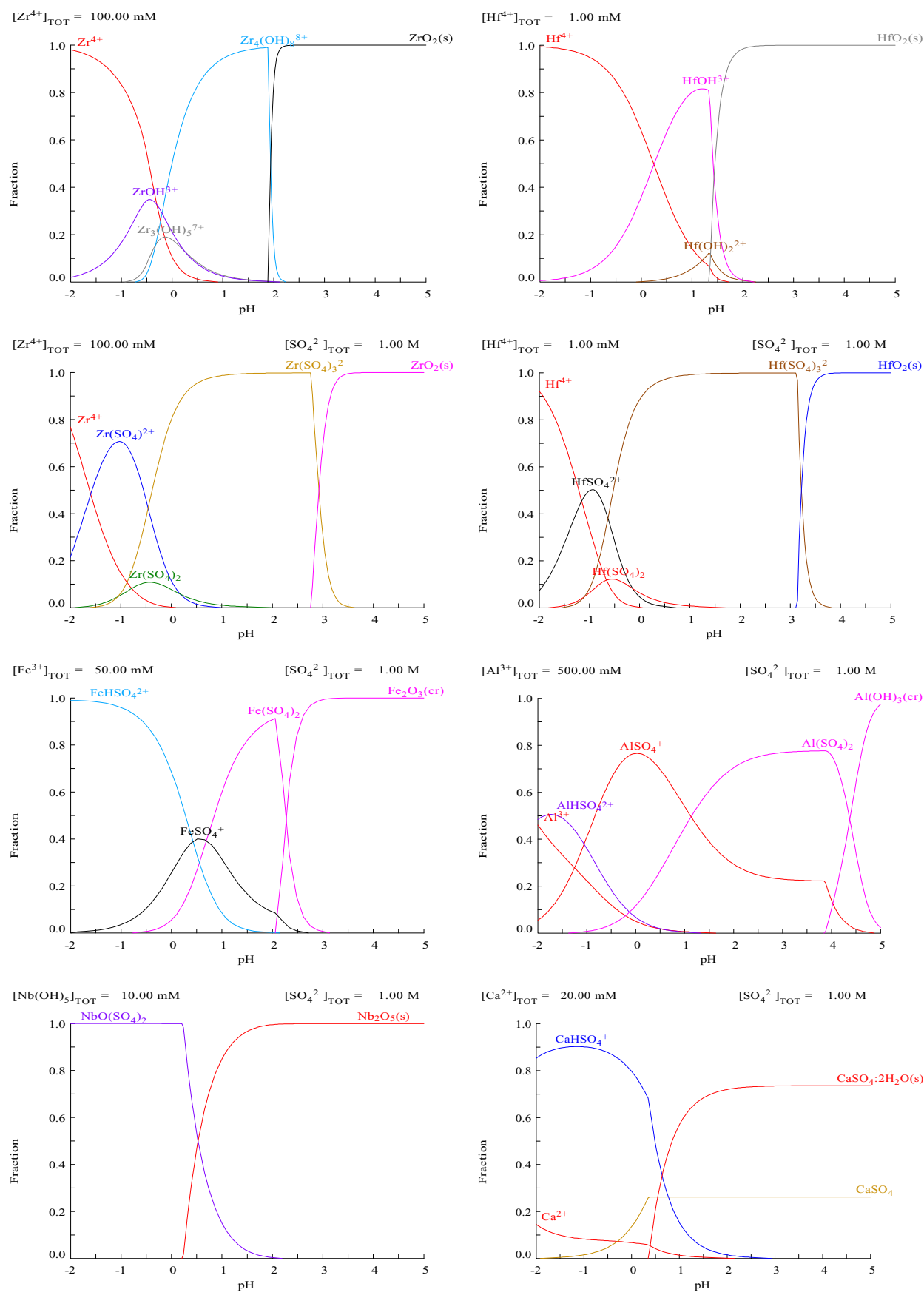


Fig. 1. Predicted fraction diagrams of Zr, Hf, Fe, Al, Nb, Ca in aqueous solutions using MEDUSA software.

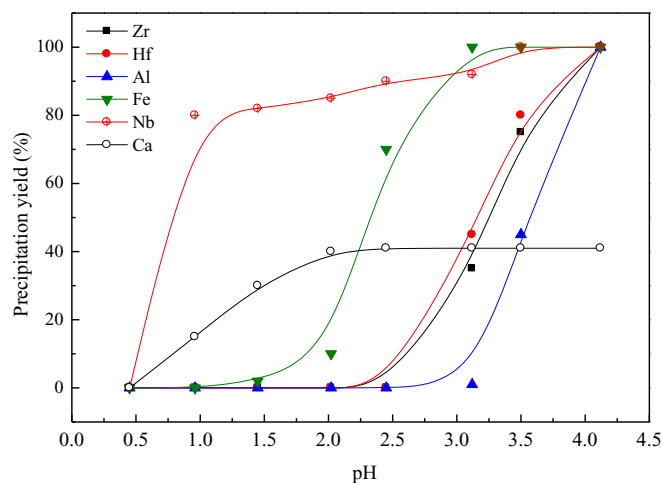


Fig. 2. Effect of pH on the precipitation of elements in the leach solution.

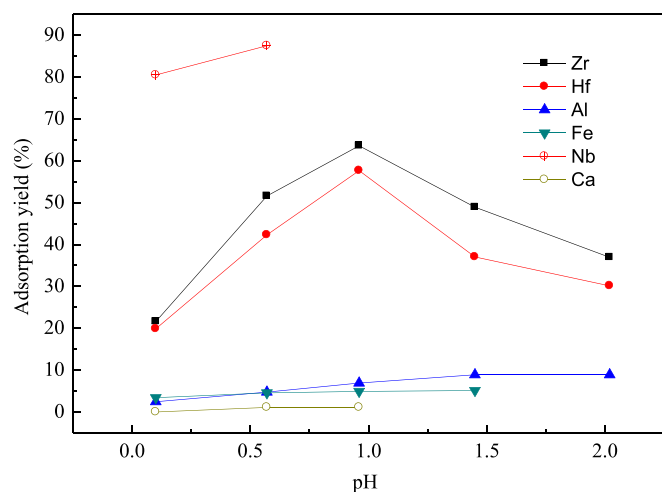


Fig. 3. Effect of pH on the adsorption of elements.

**Table 3**  
Relationship between pH and the separation factors.

pH	0.10	0.57	0.96	1.45	2.02
$\beta_{Zr/Nb}$	0.07	0.15	–	–	–
$\beta_{Zr/Ca}$	68.56	95.82	157.02	–	–
$\beta_{Zr/Al}$	10.91	21.42	23.53	9.81	6.01
$\beta_{Zr/Fe}$	7.78	22.31	33.75	17.75	–
$\beta_{Zr/Hf}$	1.11	1.45	1.28	1.62	1.35

of the Nb selective precipitated over Zr and Hf when the pH was adjusted to 1.0–1.5 (Fig. 2). Thus, it appeared that a pH of around 1.0 was best in the ion exchange process for optimum Zr and Hf recovery, because  $\beta_{Zr/Ca}$ ,  $\beta_{Zr/Al}$ ,  $\beta_{Zr/Fe}$  at pH = 0.96 were very high, and Nb had been removed after adjusting the pH. In addition, a pH lower than 1.5 appeared to prevent the hydrolysis of Zr and Hf, keeping the solution stable during the ion exchange.

### 3.1.2. Relationship between contact time and adsorption of Zr and Hf

The relationship of contact time and the adsorptions of Zr and Hf is shown in Fig. 4. As seen, the adsorption yields of Zr and Hf both increased with the increase of contact time and reached equilibrium after 6 h and 5 h, respectively. This also revealed their high similarity. The equilibrium adsorption capacities were 87.97 mg/g for Zr and 1.89 mg/g for Hf, respectively. Considering the very low separation factor of Zr

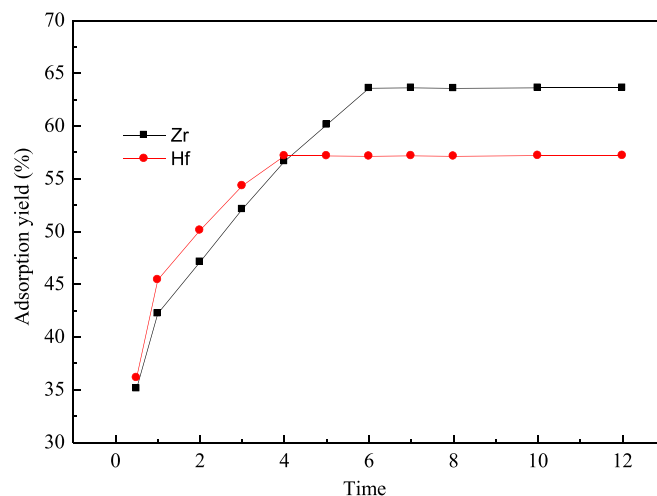


Fig. 4. Relationship between contact time and the adsorptions of Zr and Hf.

from Hf and the closed equilibrium times, it is hard to separate Zr and Hf by selective adsorption.

### 3.2. Column adsorption experiments

#### 3.2.1. Adsorption of Zr and Hf and scrubbing by pure Zr sulfate solution

Fig. 5 shows the adsorption of Zr, Hf and other metals with the contact time of 2 h. The flow rate was 0.5 bed volumes per hour (BV/h). As can be seen, the main impurities (Fe, Al, Ca) in the effluent quickly attained their original concentrations in the feed solution (at 1 BV), because the adsorption capacities of Fe, Al and Ca were low and the adsorption of Zr and Hf took priority. Both Zr and Hf were adsorbed by the resin, but the Hf eluted earlier than Zr. This showed that the adsorption affinity of Hf on the resin was a bit less than Zr, so separation of Zr over Hf was not feasible via column adsorption of the acidic sulfate solution. An alternative method to accomplish this was to use pure Zr sulfate solution to scrub the loaded resin after the simultaneous adsorptions of Zr and Hf, because the amount of Hf in the loaded resin was much lower than Zr, and the Zr adsorption on the resin was a bit higher than Hf. The concentration of Zr was lower than 1 g/L until 6 BV, and the average concentration of Zr in the collected effluent was lower than 0.2 g/L. The pure Zr sulfate solution was used as the feed liquor after 6 BV, so the  $C/C_0$  increased to 1.2 at 6.5 BV and then decreased. The concentration of Hf decreased to < 0.01 g/L in the effluent

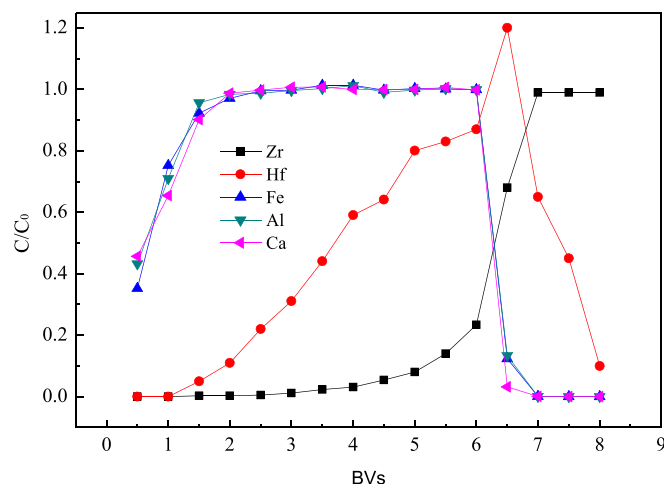


Fig. 5. Adsorption curves of metals on MP600 resin (flow rate 0.5 BV/h, changed to pure Zr sulfate solution after 6 BV).

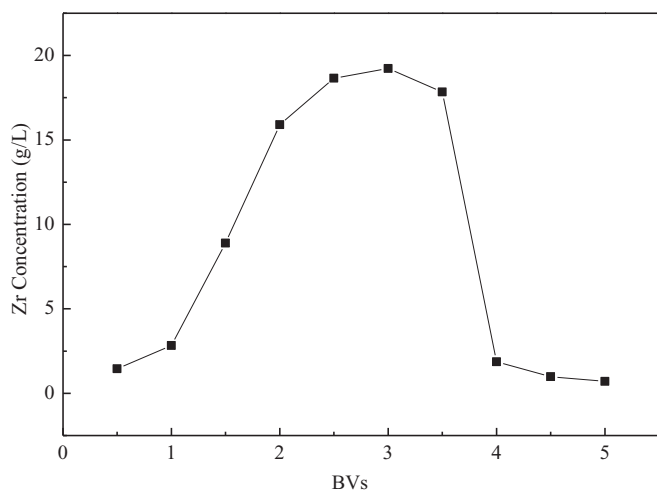
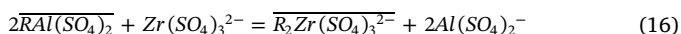
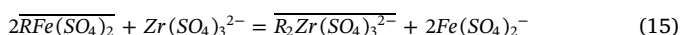
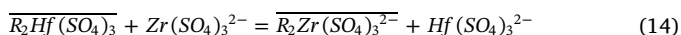


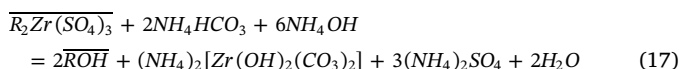
Fig. 6. Desorption curve of Zr loaded resin.

at 8 BV. This demonstrated that Hf could be scrubbed by Zr sulfate solution from the loaded resin. Similarly, the small amounts of Fe, Al, Ca on the loaded resin were also eluted by the Zr sulfate solution. These reactions can be expressed as follows:



### 3.2.2. Elution

After adsorption, the Zr loaded on the resin was eluted with 10%  $NH_4HCO_3$  + 1 mol/L  $NH_4OH$ , and Fig. 6 shows the desorption curve. The product of this elution was  $(NH_4)_2[Zr(OH)_2(CO_3)_2]$ , which was soluble in the eluant, and the desorption reaction can be expressed as follows:



As shown, the peak value of the Zr concentration in the effluent appeared at 3 BV, and the concentration of Zr decreased to lower than

0.1 g/L when the effluent/resin volume ratio was above 5. The elution of Zr reached 99.0% after 5 BV. The composition of the Zr peak solution is listed in Table 1, which shows that impurities were significantly removed by ion exchange and a Zr enriched solution with a very low content of impurities was obtained. As a product  $ZrO_2$  was obtained from the eluate with a purity of 99.5% using precipitation and calcination. It can be used as refractory material, ceramic insulation material and raw materials for Zr metal and its compounds.

### 3.2.3. FT-IR studies

The FT-IR spectra of the MP600 resin before and after metal adsorption are shown in Fig. 7. As can be seen, the presence of  $SO_4^{2-}$  on the resin was confirmed by the absorbance bands at  $660\text{ cm}^{-1}$  and  $1148\text{ cm}^{-1}$ , which corresponded to  $SO_4^{2-}$  stretching vibrations (Long, 2004). Therefore, based on the results for the adsorption of Zr and the presence of  $SO_4^{2-}$  on the loaded resin, it can be concluded that Zr and Hf were absorbed in the form of  $Zr(SO_4)_3^{2-}$  and  $Hf(SO_4)_3^{2-}$  by the MP600 resin in the sulfuric acidic solution.

### 3.3. Adsorption modeling of Zr and Hf

Experiments were conducted using the feed solution at optimum pH to study the adsorption isotherms of Zr and Hf. Evaluation of Zr and Hf adsorption behavior was affected by fitting the experimental data to the isotherm equations. As can be seen from Fig. 8, Langmuir isotherm equation fit the adsorption data better than the Freundlich isotherm equation. Table 4 gives the parameters of Langmuir and Freundlich isotherm equations, which were derived from the slope and intercept of the linear plots. So, it appeared that the adsorption process was Langmuir in nature.

### 3.4. Proposed flowchart and the metal balance

Fig. 9 shows the proposed flowchart for the selective recovery and separation of Zr and Hf from the sulfuric acid leach solution, and it also reveals the directions of the different metals. As shown, firstly, the pH of the leach solution was adjusted to its optimum for ion exchange, and most of the Nb was hydrolyzed and precipitated out of the solution during this pH adjustment. Next, the ion exchange was carried out where Zr and Hf in the feed solution were selectively adsorbed by the MP600 resin over the impurities (Fe, Al, Ca). Attempting to obtain pure Zr product, with little Hf, Fe, Al, the loaded resin was scrubbed using the synthetic Zr sulfate solution, because Zr was preferentially adsorbed

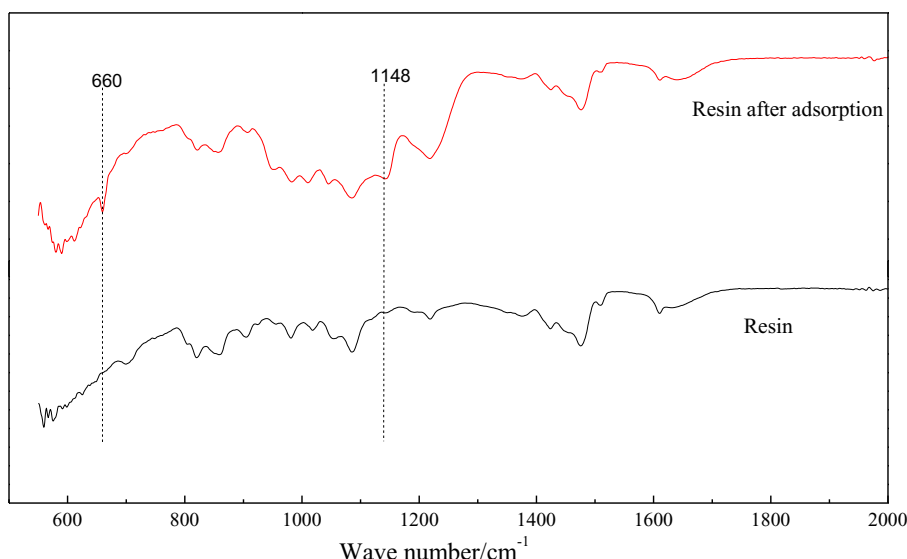


Fig. 7. IR spectra of MP 600 resin before and after adsorption: (a) Activated with HCl; (b) After Zr and Hf adsorption from the acidic sulfate solution.



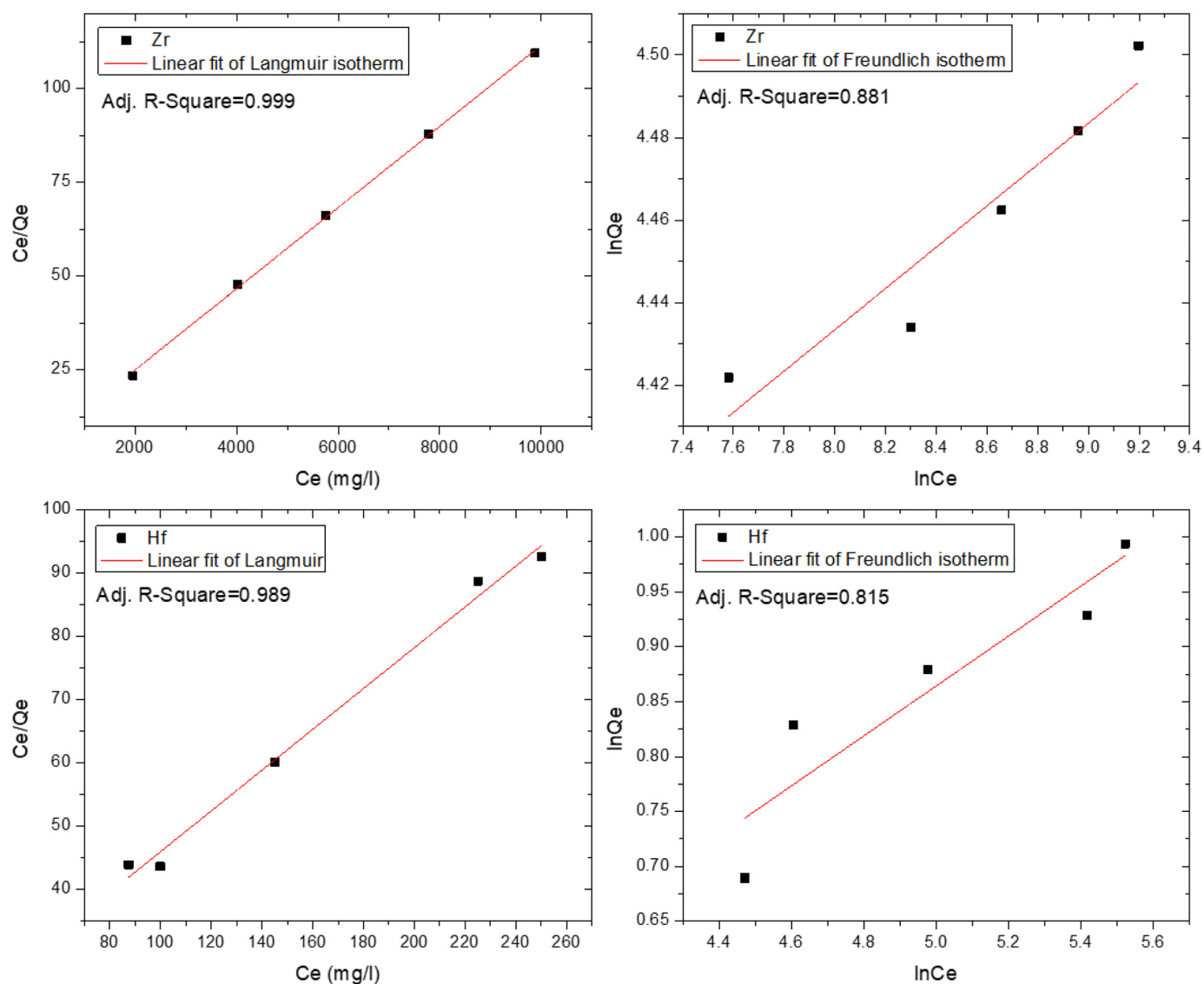


Fig. 8. Adsorption isotherms for Zr and Hf adsorption on MP600 resin.

Table 4

Langmuir and Freundlich parameters for Zr and Hf adsorption on MP600 resin.

	Langmuir			Freundlich		
	$Q_{max}(\text{mg/g})$	$K(\text{L/mg})$	Adj. R-square	$k_f(\text{mg/g})$	$n$	Adj. R-square
Zr	92.34	$3.2 \times 10^{-3}$	0.999	56.436	20	0.881
Hf	3.10	$23.4 \times 10^{-3}$	0.989	0.760	4.39	0.815

and the Zr content in the synthetic solution was much higher. As a result, the scrubbing solution containing Hf, Fe, Al was used in the next feed liquor for Zr and Hf recovery. In the final step, a solution of 10%  $\text{NH}_4\text{HCO}_3 + 1 \text{ mol/L } \text{NH}_4\text{OH}$  was applied to the resin to elute the Zr from the loaded resin. The effluent of the eluant could be used to produce the highly pure Zr product, but it could also be used to prepare the Zr sulfate solution for scrubbing process. The recovery of Zr and Hf from the sulfuric acid leach solution using this flowchart would be more effective than the ordinary precipitation methods. In addition, compared to other ion exchange processes used to separate Zr and Hf, this proposed process avoids addition of other reagents which adds more impurities to the process. Based on the capacity of MP600 for Zr and Hf adsorption, this resin appeared to be suitable for use in an acidic sulfate

solution with a low concentration of Zr and Hf.

Up to now, no extraction processes for eudialyte are known on an industrial scale, and research on the recovery of Zr is not enough or less reported. EURARE project studied some pilot-scale tests (Ma et al., 2019) and resulted a Zr-bearing residue. The recovery of Zr and the separation of Zr and the small amount of Hf would increase the economic benefits of the project.

#### 4. Conclusions

The strongly basic anion exchange resin MP600 was used in this reported study to selectively adsorb Zr and Hf from a sulfuric acid leach solution. The optimum pH for adsorption was around 1.0, and the Nb in the solution was removed via precipitation before the ion exchange process. Zr and Hf were adsorbed by the resin over Fe, Al and Ca in the acidic sulfate solution. The adsorption of Zr and Hf on the resin followed the Langmuir isotherm equation.

Most of the impurities were removed during the column test using MP600 resin. A pure Zr-bearing eluate was obtained after using pure Zr sulfate solution to scrub the loaded resin bed and elution. The concentration of Zr in the eluate (21.23 g/L) was approximately double that in the feed solution (10.83 g/L), achieving the enrichment of Zr.

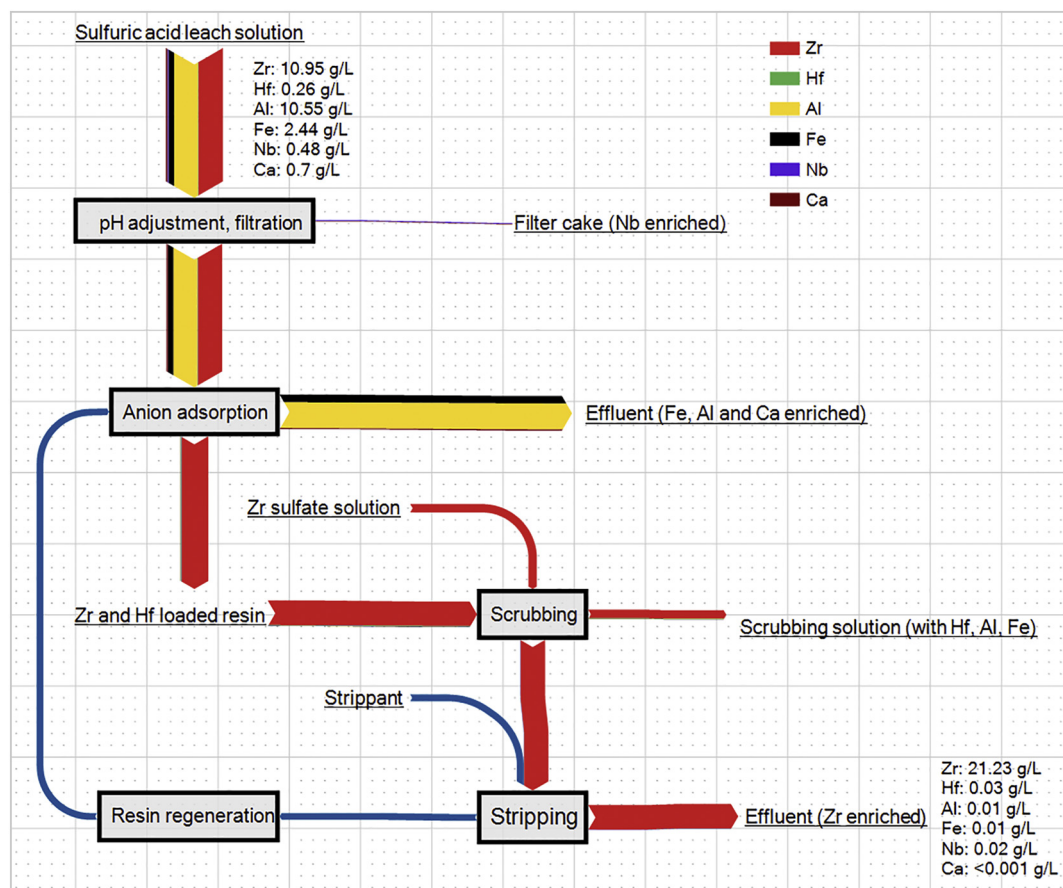


Fig. 9. Proposed flowchart for the selective recovery and separation of Zr and Hf from the sulfuric acid leach solution.

High quality product of  $\text{ZrO}_2$  can be obtained from the eluate. The present study showed a promising process to recover and separate Zr and Hf from sulfuric acid leach solution using anion exchange resin.

## Acknowledgments

Authors are thankful to EURARE project for providing the initial material. One of the authors (Yiqian Ma) is grateful to the Chinese Government for providing a scholarship.

## References

- Alfonso, M.C., Bennett, M.E., Folden III, C.M., 2016. Extraction chromatography of the Rf homologs, Zr and Hf, using TEVA and UTEVA resins in HCl,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$  media. *J. Radioanal. Nucl. Chem.* 307, 1529–1536.
- Begovich, J.M., Sisson, W.G., 1983. Continuous ion exchange separation of zirconium and hafnium by using an annular chromatograph. *Hydrometallurgy* 10 (1), 11–20.
- Bilgili, M.S., 2006. Adsorption of 4-chlorophenol from aqueous solutions by xad-4 resin: isotherm, kinetic, and thermodynamic analysis. *J. Hazard. Mater.* 137 (1), 157–164.
- Biswas, R.K., Habib, M.A., Karmakar, A.K., Islam, M.R., 2010. A novel method for processing of Bangladeshi zircon: part I: baking, and fusion with NaOH. *Hydrometallurgy* 10, 124–129.
- Conradie, E.W., Van Der Westhuizen, D.J., Nel, J.T., Krieg, H.M., 2018. The hafnium-selective extraction from a zirconium(hafnium) heptafluoride ammonium solution using organophosphorus-based extractants. *Solvent Extr. Ion Exch.* 36, 1–17.
- Davis, P., Stopic, S., Balomenos, E., Papias, D., Paspaliaris, I., Friedrich, B., 2017. Leaching of rare earth elements from Eudialyte concentrate by suppressing silicon dissolution. *Miner. Eng.* 108, 115–122.
- Felipe, E.C.B., Ladeira, A.C.Q., 2018. Separation of zirconium from hafnium by ion exchange. *Sep. Sci. Technol.* 53 (2), 330–336.
- Godea, F., Pehlivan, E., 2006. Removal of chromium(III) from aqueous solutions using Lewatit S 100: the effect of pH, time, metal concentration and temperature. *J. Hazard. Mater.* 136 (2), 330–337.
- Goodenough, K.M., Schilling, J., Jonsson, E., Kalvig, P., Charles, N., et al., 2016. Europe's rare earth element resource potential: an overview of REE metallogenetic provinces and their geodynamic setting. *Ore Geol. Rev.* 72, 8384–8856.
- Hurst, F.J., 1983. Separation of hafnium from zirconium in sulfuric acid solutions using pressurized ion exchange. *Hydrometallurgy* 10 (1), 1–10.
- Jakóbk-Kolon, A., Smolik, M., Jaroszek, H., 2013. The influence of the treatment of Zr (IV) and Hf(IV) sulfate solution on the ion-exchange purifying of zirconium from hafnium on Diphonix® resin. *Hydrometallurgy* 140, 77–81.
- Johnsen, O., Ferraris, G., Gault, R.A., Grice, J.D., Kampf, A.R., Pekov, I.V., 2003. The nomenclature of eudialyte-group minerals. *Can. Mineral.* 4, 794–7854.
- Kozak, C.M., Mountford, P., 2006. *Encyclopedia of Inorganic Chemistry, Zirconium & Hafnium: Inorganic & Coordination Chemistry*. John Wiley & Sons, Oxford.
- Lebedev, V.N., 2003. Sulfuric acid technology for processing of eudialyte concentrate. *Russ. J. Appl. Chem.* 76, 1559–1563.
- Long, D.A., 2004. Infrared and Raman characteristic group frequencies. In: *Tables and Charts George Socrates*, 3rd edition. vol. 35(10). John Wiley and Sons, Ltd, Chichester, pp. 905–2001. *J. Raman Spectrosc.*
- Ma, Y., Stopic, S., Gronen, L., Friedrich, B., 2018. Recovery of Zr, Hf, Nb from eudialyte residue by sulfuric acid dry digestion and water leaching with  $\text{H}_2\text{O}_2$  as a promoter. *Hydrometallurgy* 181, 206–214.
- Ma, Y., Stopic, S., Friedrich, B., 2019. Hydrometallurgical treatment of a Eudialyte concentrate for preparation of rare earth carbonate. *Johnson Matthey Tech.* 63, 2–13.
- Machlan, L.A., Hague, J.L., 1962. Separation of hafnium from zirconium and their determination: separation by anion-exchange. *J. Res. Natl. Bur. Stand.* 66 (6), 517–520.
- Monroy-Guzman, F., Trubert, D., Le Naour, C., 2002. Adsorption behavior of Zr, Hf, Nb, Ta and Pa on macroporous anion exchange resin in  $\text{NH}_4\text{SCN}/\text{HClO}_4$  and  $\text{NH}_4\text{SCN}/\text{HF}$  media. *J. Radioanal. Nucl. Chem.* 254 (3), 431–437.
- Nielsen, R.H., Schlewitz, J.H., Nielsen, H., 2000. Zirconium and zirconium compounds. In: Kirk-Othmer (Ed.), *Kirk-Othmer Encyclopedia of Chemical Technology*. vol. 1. John Wiley & Sons, Inc.: Wiley online Library, pp. 1–46.
- Niemand, H.F., Crouse, P.L., 2015. A theoretical approach to the sublimation separation of zirconium and hafnium in the tetrafluoride form. *J. South. Afr. Inst. Min. Metall.* 115, 961–965.
- Poriol, L., Pellet-Rostaing, S., Lamotte, V., Lemaire, M., Favre-Reguillon, A., 2006. Zirconium and hafnium separation, part 2. solid/liquid extraction in hydrochloric acid aqueous solution with anion exchange resins. *Sep. Sci. Technol.* 41, 2711–2722.
- Ryabchikov, D.I., Marov, I.N., Ermakov, A.N., Belyaeva, V.K., 1964. Stability of some inorganic and organic complex compound of zirconium and hafnium. *J. Inorg. Nucl. Chem.* 26, 965–980.
- Smolik, M., Jakóbk-Kolon, A., Porański, M., 2009. Separation of zirconium and hafnium using diphonix® chelating ion-exchange resin. *Hydrometallurgy* 95, 350–353.
- Smolik, M., Siepietowski, L., Jakóbk-Kolon, A., 2014. The effects of concentrations of zirconium(IV) sulphate and sulphuric acid on sorption of zirconium(IV) and hafnium(IV) on Purolite S-957 resin. *Adsorption isotherms of zirconium(IV) and hafnium(IV)*



- ions. *Solvent Extr. Ion Exch.* 32, 437–446.
- Solovkin, A.S., Tsvetkova, Z.N., 1962. The chemistry of aqueous solutions of zirconium salts (does the zirconyl ion exist?). *Russ. Chem. Rev.* 31, 655.
- Voßenkaul, D., Birich, A., Müller, N., Stoltz, N., Friedrich, B., 2016. Hydrometallurgical processing of eudialyte bearing concentrates to recover rare earth elements via low-temperature dry digestion to prevent the silica gel formation. *J. Sustainable. Met.* 1–11.
- Wang, L.Y., Lee, M.S., 2015. Solvent extraction reaction of hafnium(IV) from strong sulfuric acid solutions with D2EHPA and PC 88A. *Sep. Sci. Technol.* 51, 759–766.
- Wang, L.Y., Lee, M.S., 2016. A review on the aqueous chemistry of Zr(IV) and Hf(IV) and their separation by solvent extraction. *J. Ind. Eng. Chem.* 39, 1–9.
- Wu, F., Yang, Y., Mitchell, R.H., Bellatreccia, F., Li, Q., Zhao, Z., 2010. In situ U–Pb and Nd–Hf–(Sr) isotopic investigations of zirconolite and calzirtite. *Chem. Geol.* 277, 178–195.
- Wu, M., He, H., Xu, F., Xu, Z., Zhang, W., He, Z., Qu, J., Chi, R., Huang, L., 2019. High-efficient and selective extraction of Hf over Zr with DIBK-P350 synergistic extraction system. *Sep. Purif. Technol.* 212, 255–261.
- Zirconium in Steels, <http://ispatguru.com/zirconium-in-steels/>, Accessed on 5 March 2018.