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Solvent Extraction of Zirconium and Hafnium with 1 and 2-octanol: a Comparative Study

John Mpinga Kabangu*, Simon J. Lubbe, Philip L. Crouse

Department of Chemical Engineering, University of Pretoria, Lynnwood Road. Pretoria 0002. South Africa.
johnmpingaka@gmail.com

Comparative solvent extraction studies of Zr and Hf were carried out from acidic chloride and potassium fluoride solutions with 1 or 2-octanol as extractants. The extraction process was experimentally investigated as a function of contact time, hydrochloric acid concentration, sulfuric acid concentration, hydrofluoric acid concentration, nitric acid concentration, amount of potassium fluoride added and organic-to-aqueous phase ratio. The results show that zirconium is preferentially extracted into the organic phase. Under the optimal operating conditions of 10 % HCl, 1.5 M KF, 15 minutes and an organic-to-aqueous phase ratio of 2:1, the extraction percentage of zirconium and hafnium is 94.3 % of Zr and 64.3 % of Hf and a separation factor of 9.2 for 2-octanol and 93.1 of Zr and 60.9 % of Hf and a separation factor of 8.7 %. 2-octanol shows a slightly higher extraction percentage and separation factor over 1-octonal.

1. Introduction

Zircon ($ZrSiO_4$) and baddeleyite, a natural form of zirconium oxide (ZrO_2), are the major sources of zirconium. Zirconium (Zr) and hafnium (Hf) co-exist in these ores. Zircon is the primary source for all Hf, containing around 62.3 wt % of Zr and 1.2 wt % of Hf (Bedinger, 2015). The chemical and physical properties of Zr and Hf are almost similar. They have nearly identical atomic and ionic radius, similar valence electron configurations but the thermal neutron capture cross section of Zr is higher than that of Hf. Zr and Hf have many applications but 90 % of the total world Zr and Hf production are consumed in the nuclear industry (Kozak et al., 2006). Therefore, production of pure Zr and Hf for the use in nuclear industry is essential. The use of Zr in nuclear industry requires a very low concentration, of less than 100 ppm of Hf (Xu et al., 2015). Therefore, the separation of Zr and Hf is of critical importance to the nuclear industry, and is difficult due to the similarity of their chemical properties, such as atomic radius, ionic radius and electronegativity (Smolik et al., 2009). On the other hand, Hf is also used in the nuclear industry as a control rod material in reactors due to its high neutron absorption capacity. Several methods have been used to separate these two elements. These methods include fractional crystallisation (Vinarov, 1967; Zelikam et al., 1966), fractional precipitation, ion exchange (Hurst, 1983, Smolik et al., 2009), solvent extraction (El-Ammouri et al., 1996; Reddy et al., 2004) and molten salt distillation (Megy et al., 1979). Currently solvent extraction is the separation method of choice. It is a prominent effective method for determining the quantities of metal in aqueous and organic solution. The important aim of liquid-liquid extraction is to recover the metal from its solution using a suitable extractant (Jaykishon et al., 2018). Different solvents or extractants have been investigated for the production of pure Zr and Hf but only three commercially available extractants are used, viz. Methyl-isobutyl ketone (MIBK), tri-butyl phosphate (TBP), and high molecular-weight tertiary alkyl amines. Extractant mixtures have been also employed to improve the separation efficiency between Zr and Hf (Yadollahi et al., 2018; Wang et al., 2016). Currently, the manufacture of nuclear-grade Zr relies on solvent extraction with MIBK. This process entails several technological disadvantages and environmental problems. The waste stream contains a high concentration of ammonium cyanides and other organic by-products that lead to environment concerns. The solvent itself is volatile and slightly soluble in water, leading to significant losses by evaporation. Thus extra care is needed in handling and recycling the organic stream and discarding the effluent (Snyder et al., 1990). The often dangerous and unsuitable extractants used in conventional technologies have necessitated the

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search for new alternatives. As an alternative extractant for safer and more effective technology, 1 and 2 octanol were used in this investigation. The choice of octanol was based on the previous work by Kabangu and Crouse, 2012; Agulyansky, 2004; Mayorov and Nikolaev, 2002 and He et al., 1998 in which they demonstrated that the efficiency of extraction and separation of tantalum (Ta) and niobium (Nb) with octanol was comparable with MIBK commonly used in the industrial technology of Ta and Nb (Babkin et al., 1998). These extractants present some advantages compared to the conventional materials, such as low solubility in water, sufficiently low volatility and reduced danger due to their higher flash point (81 °C). In addition octanol has low viscosity and is cheaper compare to MIBK and TBP. Therefore the aim of this investigation is to compare the effectiveness of extraction and separation of zirconium from hafnium between 1 and 2-octanol. Despite these advantages the separation of zirconium and hafnium has not been reported previously to the best of our knowledge.

2. Materials and Methods

2.1 Materials

Zirconium basic carbonate (ZBC) which contained approximately 40 % ZrO_2 and 1–2 % HfO_2 by mass was purchased from Sigma Aldrich and was used for all extraction and separation experiment studies. 2-octanol purchased from ACE (Associated Chemical Enterprises, SA) with a purity of 97 % and 1-octanol with purity of ≥ 99.0 % was purchased from Merck were used as extractants in all the extraction experiments. Potassium fluoride (KF) with a minimum purity of 95, 5 % purchased from Merck was used to prepare the aqueous solutions that were used for all the extraction and separation experiment. Hydrochloric acid (HCl) with a purity of 32 % by mass, purchased from Sigma Aldrich, sulfuric acid (H_2SO_4) with a purity of 98 % by mass purchased from Sigma Aldrich, hydrofluoric acid (HF) purchased from Sigma Aldrich with a purity of 40 % by mass and nitric acid (HNO_3) from Merck with a purity of 70 % by mass were used for the decomposition of ZBC. Deionized water was used in all aqueous preparations. All chemical were of analytical grade and used without further purification. ICP-OES calibration standards were obtained from Monitoring and Control Laboratories, SA. The elemental analyses of the aqueous solution were performed with a Spectro Arcos model inductively-coupled plasma optical-emission spectrometer (ICP-OES).

2.2 Methods

The experiments were conducted at ambient temperature (20–25 ℃) batch wise. Different acids such as HCl, H_2SO_4, HF and HNO_3 of different concentrations were used to leach or decompose zirconium basic carbonate (ZBC). KF of different concentrations was contacted with the leach solution. The extraction experiments were carried out by shaking vigorously the aqueous and organic phase at different ratio and times. After equilibration, the solutions were separated using a separation funnel. The concentrations of Zr and Hf in the aqueous phase were determined by ICP-OES whereas the concentrations in the organic phase were inferred from mass balance analysis. The distribution coefficient (*D*), the extraction percentage (*% E*) and the separation factor (*β*) were calculated according to the equation 1, 2, 3 and 4 below respectively.

$$D= \frac{C_i - C_f}{C_f} \tag{1}$$

$$\% E_{zr}= \frac{D_{Zr} \text{ x } 100}{\left(\frac{V_{aq}}{V_{org}}+ D_{Zr}\right)} \tag{2}$$

$$\% E_{Hf}= \frac{D_{Hf} \text{ x } 100}{\left(\frac{V_{aq}}{V_{org}}+ D_{Hf}\right)} \tag{3}$$

$$\beta= \frac{D_{Zr}}{D_{Hf}} \tag{4}$$

Here C_i is the initial metal ion concentration in the aqueous phase before extraction and C_f is the final metal ion concentration in the aqueous phase after extraction. V_{aq} and V_{org} are the volumes of aqueous and organic phase respectively. D_{zr} and D_{Hf} are zirconium and hafnium distribution coefficient respectively. The reported results are mean values of at least three samples at each set of experimental condition. The error associated with the process is ± 4 %.

3. Results and discussions

3.1 Effect of contact time

To make a valid interpretation of the effect of different experiment parameters, it must be ensured that equilibrium between the phases is reached in all the experiments. It is therefore necessary to determine the minimum time required to establish equilibrium. This investigation was done by shaking vigorously 50 mL of organic solvent (either 1-octanol or 2-octanol) with 50 mL aqueous solution containing 3573.5 mg/L of Zr and 64.0 mg/L of Hf, kept almost constant during all the experiment, before analysis. The times investigated were varied between 5 and 20 minutes. The percentage metal extraction of Zr and Hf as function of time is shown in Figure 1 for 1-octanol. Extraction increases rapidly at first, then levels off above roughly ten minutes. A period of 15 minutes was selected for all subsequent experiments. For both 1-octanol and 2-octanol there is no formation of a third phase that would require the addition of a modifier.

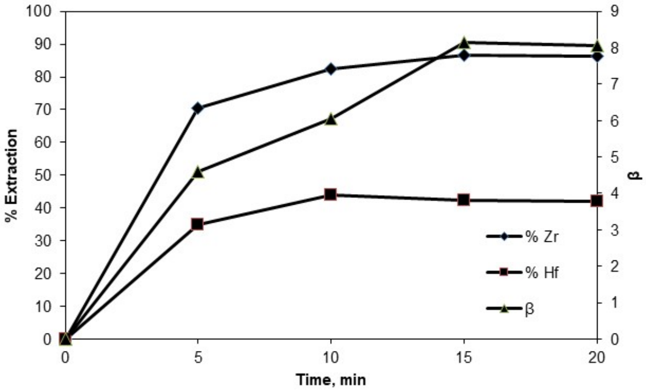

Figure 1: Effect of contact time on extraction of Zr and Hf. Experimental conditions: organic phase: 100% 1-octanol, [HCl] 10 %, KF = 1.5 M, A/O ratio = 1:1.

3.2 Effect of HCl concentration on extraction

The influence of HCl acid concentration was investigated on the extraction and separation of Zr and Hf. ZBC was dissolved in HCl acid at various concentrations from 5 % to 20 %. After dissolution a predetermined concentration of KF was added to the solution. The solution obtained was then contacted either with 1-octanol or 2-octanol. The tests were carried out at an A/O ratio of 1:1 and constant time of 15 minutes. The results in Figure 2 and Figure 3 indicate that the extraction of both Zr and Hf increase rapidly up to 10 % for 1-octanol and 2-octanol respectively, behind which it flattens.

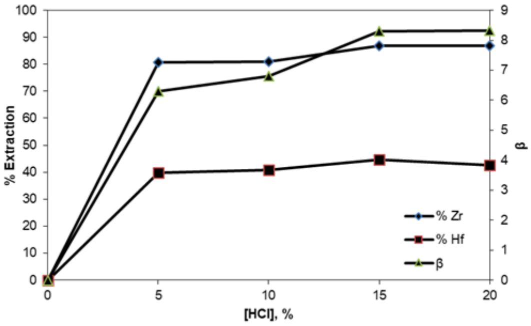

Figure 2: Effect of HCl concentration on extractionof Zr and Hf with 1-octanol. Experiment conditions100 % 1-octanol, [HCl] = 5 to 20 %, KF =1.5 M, O/A=1:1

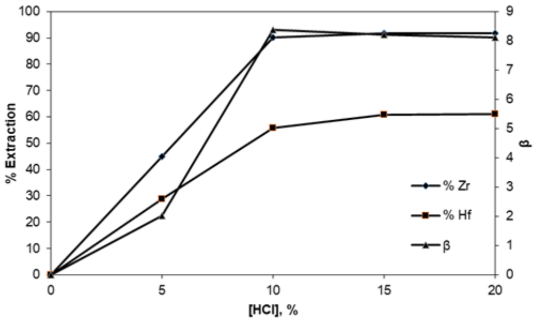

Figure 3: Effect of HCl concentration on extraction of Zr and Hf with 2-octanol. Experiment conditions: 100 % 2-octanol, [HCl] = 5 to 20 %, KF = 1.5 M, O/A =1:1

These results are consistent with the expectation that both Zr and Hf are extracted as a chloride complex through a solvation reaction. The high chloride ion and high hydrogen ion contents are respectively necessary to promote the formation of extractable Zr and Hf complexes and to supress hydrolysis and polymerization. The increase in hydrochloric acid concentration promotes depolymerisation, while, simultaneously, hydroxide ions attached to Zr or Hf are displaced by chloride ions to form inner-sphere complexes (Johnson & Krous, 1956 ; El-Ammouri & Distin, 1996), with M = Zr or Hf according to the following chemical reaction

$$[M(OH)n](4-n) + iCl- + nH^+ \rightleftharpoons [MCli](4-i) + nH_2O$$

The highest extraction was 60.8 % of Hf and 91.8 % of Zr and 44.7 % of Hf and 86.8 % of Zr for 2-octanol and 1-octanol respectively.

3.3 Effect of KF concentration

After dissolution of ZBC in 10 % HCl, KF was added to achieve concentration range of 1 M to 2 M in order to find the optimum values for extraction and separation of Zr and Hf. The results shown in Table 1 and Table 2 indicate that increasing KF concentration increases the extraction and separation of both Zr and Hf, with the highest separation efficacy obtained at 1.5 M KF in solution. The extraction of both depends strongly upon the concentration of KF in the aqueous phase. This peculiar behaviour is probably connected with the change in the nature of complexes formed. It is postulated that a (Zr, Hf) F_4.2KF compound is formed in aqueous solution. At lower KF concentration, the hexafluoride $[(Zr,Hf)F_6]^{-2}$ is formed and has a lower affinity for both extractants. At higher KF concentration, it is possible that there is formation of heptafluoride complex $[(Zr,Hf)F_7]^{-3}$ which is probably the reason for the significant extraction and separation observed. In depth molecular species studies is required to investigate this issue. The separation increases from 6.0 to 8.3 for 1-octanol. Table 2 shows also that the separation of Zr and Hf increases from 3.7 to 8.5 for 2-octanol at A/O ratio of 1:1.

Table 1: Effect of KF concentration on extraction of Zr and Hf. Experiment conditions: 100% 1-octanol, [HCl] 10 %, O/A ratio 1:1, [KF] = 1 to 2 M.

[KF], M	***D_{Zr}***	***D_{Hf}***	***% E_{Zr}***	***% E_{Hf}***	***β***
1.0	4.0	0.82	79.87	39.66	6.0
1.5	6.3	0.77	86.40	43.40	8.3
2.0	6.2	0.77	86.10	43.60	8.0

Table 2: Effect of KF on the extraction and separation of Zr and Hf. Experimental conditions: 100 % 2-octanol, [HCl] 10 %, A/O ratio 1:1, [KF], 1 to 2 M.

[KF], M	***D_{Zr}***	***D_{Hf}***	***% E_{Zr}***	***% E_{Hf}***	***β***
1.0	2.3	0.62	69.70	38.30	3.7
1.5	9.3	1.1	90.30	55.80	8.4
2.0	11.2	1.3	91.80	56.50	8.6

3.4 Effluence of HF, H_2SO_4 and HNO_3

The experiments were conducted by dissolving ZBC in different acids, viz. HF, H_2SO_4 and HNO_3 between a concentration of 5 and 20 % at a constant 1.5 M KF. The experiment conducted without the addition of KF shows that no extraction took place for all acid and concentration investigated. The results obtained when 1.5 M KF was added to the feed solution indicate that the extraction of both Zr and Hf increases drastically with the increasing of acidity for all acids investigated; but the effect is more profound for HCl. In the case of HNO_3 the extraction increases from 38.5 % to 63.6 % Zr and from 20.0 to 45.8 % Hf for 2-octanol and from 30.3 to 44.4 % and from 12.9 to 32.6 % Hf for 1-octanol. This behaviour can be explained by the fact that at a lower nitric acid concentration, the lower acid concentration in octanol cannot complete with the metal for the extractant, but at higher acid concentration, complex formation between the acid and the extractant becomes appreciable which affect the percentage of both metals from the nitric acid medium. The results also indicate that increasing nitric acid concentration decreases the value of the separation factor. Raymond (1954), Beyer and Peterson (1951) reported also a similar trend when extracting Zr and Hf in nitric acid solution with diluted or undiluted TBP. In the case of H_2SO_4, the extraction of Zr and Hf increases from 40.4 to 79.4 % for Zr and from 22.6 to 64.2 % for Hf for 2-octanol and from 34.3 to 65.7 % Zr and from 14.8 to 48.3 % Hf for 1-octanol. The extraction of Zr was higher than that of Hf in the range investigated. However octanol displays extraction ability for both metals, and it is not efficient in separating Zr from Hf. The low extraction percentage of metal ions from sulfuric acid compare to HCl may be attributed to the influence of hydrolysis on the complex formation of each metals ion. Increasing the concentration of HF increases the extraction of Zr and Hf but separation decreases. The highest extraction and separation obtained for 2-octanol were 66.8 % and 49.2 % Zr and Hf respectively at 20 % HF, and 3.5 as separation factor.

3.5 Effect of phase ratio on the extraction of Zr and Hf

A set of experiment was carried out to examine the effect of organic-to-aqueous phase ratio (O/A). The experimental conditions were kept constant, as mentioned, at 1.5 M KF, 10 % HCl and a contact time of 15 minutes, while varying A/O from 1:1 to 1:5. Under the given set of experimental conditions, the results in

Figure 4 and Figure 5 indicated that the preferred A/O ratio in this investigation is 1:2 or even higher. It also shows that the percentage extraction of Zr and Hf increases with an increase in the volume ratio of organic to aqueous phase. However the percentage extraction of both metals increases at different rate, which resulted in the increase of the separation factor. The separation factor between Zr and Hf also increases from 5.2 to 8.6 for 1-octanol and from 8.5 to 9.2 for 2-octanol. This result is consistent with the theory of extraction described by the Equation 2 which can be interpreted as in order to increase the amount of substance extracted, the volume of the extracting solvent can be increased. Sadigzadeh and Chehrenama (2009) also found a similar trend when extracting zirconium from nitric-hydrochloric acid solutions using TBP.

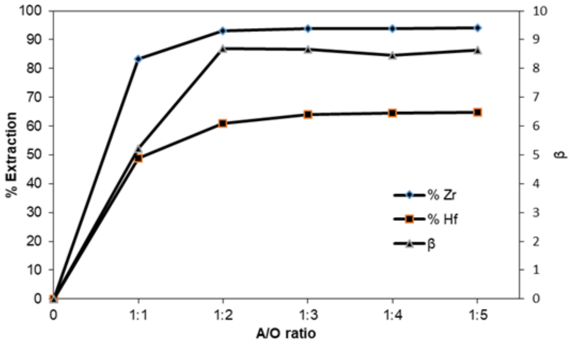

Figure 4: Effect of phase ratio on the extraction of Zr and Hf. Experimental conditions: 100 % 1-octanol,[KF], = 1.5 M, A/O = 1:1 to 1:5

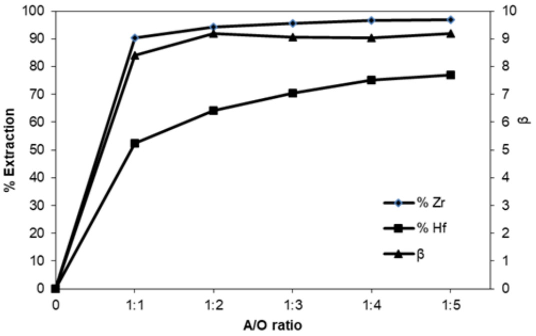

Figure 5: Effect of phase ratio on the extraction of Zr and Hf. Experimental conditions: 100 % 2-octaonl, [KF]= 1.5 M, A/O = 1:1 to 1:5, [HCl] 10 %

4. Conclusions

Separation of zirconium from hafnium using different acids and potassium fluoride was investigated. Hydrochloric acid was found to give good results compared to the other mineral acids like HNO_3, HF and H_2SO_4. Potassium fluoride was found to be crucial to the process. Increasing hydrochloric acid and potassium fluoride concentration increase the extraction percentage and separation factor of both metals using both extractants. Both extractants (1-octanol and 2-octanol) show a greater selectivity for zirconium over hafnium. The values of separation factor are 9.2 and 8.7 for 2-octanol and 1-octanol respectively. Thus 2-octanol gives slightly better results compared to 1-octanol in terms of extraction percentage and separation factor. This investigation shows that octanol can be used as alternative extractant to the conventional for the extraction and separation of zirconium and hafnium. It presents advantages such as lower cost of the process and it circumvents the use of ammonium cyanide and its concomitant environmental concerns.

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