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Extraction and Separation of Zirconium Using 1-Octanol

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Abstract

A selective extraction and separation of zirconium by solvent extraction with 1-octanol is proposed. The process is based on the dissolution of the metal basic carbonates in hydrochloric acid in the presence of potassium fluoride, using 1-octanol as extractant. The effect of several process parameters, including hydrochloric acid and potassium fluoride concentrations, reaction time, and phase ratio between the aqueous and the organic phase was investigated. Zirconium is enriched in the organic phase. The best extraction and separation results were obtained with the basic carbonate dissolved in 10% hydrochloric acid and 1.5 M potassium fluoride. The optimum reaction time was 15 min with an organic to aqueous phase ratio of 2:1. Based on the selectivity of zirconium over hafnium in the organic phase, a McCabe-Thiele diagram was constructed. A near complete stripping of zirconium from the organic phase was achieved using a 3 M sulphuric acid solution. Additional studies are required in order to determine the reaction mechanism and the chemical speciation of the current investigation.

Keywords Zirconium · Hafnium · Solvent extraction · 1-Octanol · Potassium fluoride

1 Introduction

Zirconium (Zr) ore generally contains 2 to 4% hafnium (Hf). Owing to its low thermal neutron capture cross-section, Zr is used as a structural component for reactor cores and container materials. The neutron absorption capacity for Hf is very high; the latter is used as an excellent control material for reactors [1]. The efficiency of the reactor core and generation of power depend directly on the concentration of Hf in Zr. For use in a nuclear reactor, the Zr should have a very low Hf content not exceeding 100 ppm [2]. Therefore, the separation of Zr from Hf is very important in the applications of the two metals in a nuclear reactor.

Different methods on the extraction and separation of Zr and Hf have been investigated. These include fractional crystallisation [3, 4], fractional precipitation, ion exchange [5, 6], solvent extraction [7, 8], molten salt distillation [9], and selective reduction. However, only two methods, viz. solvent extraction and molten salt distillation (the CEZUS process developed by Compagnie Europeene du Zirconium, Paris, France) have been used industrially. Currently, solvent extraction process is the separation methods of choice. Many solvents have been used to extract and separate Zr from Hf such as tri-n-octyl amine [10] and organophosphorus-based extractant [11]. Extractant mixtures have been also employed to improve the separation efficiency between Zr and Hf [12, 13]. Some information on the extraction and separation of Zr and Hf using different types of extractant is summarized in Table 1 in terms of separation efficiency.

In this article, only two commercially available solvents, namely methyl isobutyl ketone (hexone) (MIBK) and tributyl phosphate (TBP) are discussed.

In the MIBK-thiocyanic process, Zr(Hf)Cl_4 is firstly dissolved in an aqueous solution whereby the tetrachloride is converted to oxychlorides, Zr(Hf)OCl_2. An initial extraction is performed for the removal of the ferrous impurities from the oxychloride solution by extraction. The purified oxychloride solution is then mixed with NH_4SCN and NH_4OH, which causes the formation of zirconyl and hafnyl thiocyanate which forms the feed solution. The feed solution is contacted in a series of countercurrent stages with MIBK as the extractant; the Hf complex is then preferentially extracted into the organic phase (MIBK). The aqueous solution enriched with Zr is treated with sulphuric acid and by adjusting the pH with NH_4OH, pentazirconyl is precipitated. The product is then either calcined to produce zirconia, or mixed with ammonia solution to form a $Zr(OH)_4$ which is filtered, rinsed, and calcined to form the oxide [23, 24, 25, 26].

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Table 1 Extraction and separation of Zr and Hf using different types of extractant

Extractants name	Diluent	Separation efficiency or separation factor	Reference
Di(2-ethylexyl) phosphoric acid D2EHPA	Octane	A maximum separation factor of 4.16 was obtained at 0.5 mol/L HCl using 0.02 mol/L D2EHPA.	[14]
Bis(2-ethylhexyl)-1-(2-ethylexylamino) propyphosphonate (BEAP or B)	n-heptane	A separation factor of 6.8 was found under the optimum conditions of 0.59 mol/L H_2SO_4, a BEAP concentration of 0.05 mol/L and a phase ratio O/A of 1:1	[15]
A mixture of Cyanex-272 and TBP	Kerosene	Separation of Zr and Hf was improved by mixing Cyanex with TBP and a maximum separation factor of 99.7 was achieved in the mixture of 0.5% (*v*/*v*) Cyanex and 20% (*v*/*v*) of TBP.	[12]
Bis(2,4,4-trimethylpentyl phospnonic acid (Cyanex 272)	Kerosene	Separation efficiency between Zr and Hf of around 34 was obtained at 2 M HNO_3	[16]
A mixture of PC 88A and LIX 63		The highest separation efficiency of 46 was obtained from 2 M HNO_3 solution by the mixture of PC 88A and LIX 63.	[17]
Cyanex 301	Kerosene	An optimum separation factor value of 7 was obtained at a pH of 4 in the presence of NaCl as an added salt.	[18]
A mixture of DIBK and P204	–	The separation factor of 10.5 was obtained when a concentration of 3.0 mol/L of sodium chloride was added to the solution. The optimum conditions where 117.1 g/L Zr, 2.89 of Hf, 1.0 mol/L, acidity, 4.0 mol/L NH_4SCN in aqueous phase, and 10% (*v*/*v*) P204 and 90% (*v*/*v*) DIBK in organic phase	[19]
D2EHPA	–	A separation factor of around 30 between Zr and Hf was obtained at 4.0 H_2SO_4 and 0.01 mol/L D2EHPA	[20]
MIBK	–	In this process, the thiocyanic complexes of Zr and Hf are formed at 2.0 HCl. A separation factor of around 7 was obtained.	[21]
TBP	Kerosene	A selective separation factor of 10 between Zr and Hf is achieved with 60% (*v*/*v*) TBP in kerosene, in 3 M HNO_3, and in 3.5 M $NaNO_3$ as a salting out reagent.	[22]

In the TBP-nitric acid process, sodium zirconate ($Na_2ZrO_{.3}$) was used as a feed solution. It is obtained from caustic soda fusion with zircon sand and is dissolved in concentrated nitric acid [27]. The Zr and Hf nitrates were separated by extracting with TBP diluted with 40 vol% of n-heptane to shorten the time required for separation of phases [28]. The zirconium nitrate-TBP complex is preferentially extracted into the organic (TBP) phase [27, 29]. Unlike the MIBK process, the separation of Zr and Hf with TBP as extractant is selective for Zr. Sodium nitrate ($NaNO_3$) is added as a salting agent. Most of the impurities remain in the aqueous phase together with Hf while Zr is stripped into a suitable aqueous solution. Nitric acid is recycled from both metal streams by distillation, and the solution is neutralized to precipitate hydrates. The hydroxides are then calcined to yield the oxide [26].

Currently, the manufacturing of nuclear-grade zirconium 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 [30]. The process is costly due to the consumption of expensive chemicals by decomposition and equipment maintenance required because of the corrosion caused by acids and the organic solvent. Thiocyanates and thiocyanic acid have a low flashpoint in the presence of HCl [31]. The disadvantages of the TBP process are the formation of the third phase which leads to low metal concentration in the aqueous and organic phases, large consumption of chemicals, and the inability to produce nuclear-grade Hf which is used as control rods in nuclear reactors [32].

The constraint of these processes, e.g. the often dangerous and unsuitable extractants used, has necessitated the search for new alternative extractants.

As a safer and more effective alternative method, octanol was used in the present investigation as an extractant based on its main advantages, which include low solubility in water (0.46 kg/m^3), sufficiently low volatility, and the reduced danger because of the higher flashpoint (81 °C). Despite its low extracting ability, octanol has a number of advantages over the conventional extractants TBP and MIBK. Its higher flashpoint than TBP and MIBK make it safer. In addition, 1-octanol has a lower viscosity and is cheaper than TBP and MIBK. Octanol also has a very low solubility in aqueous media and has a particular commercial potential as an alternative extractant for the extraction and separation of zirconium and hafnium.

The aim of this investigation is to find an alternative extractant for the extraction and separation of Zr and Hf to conventional extractants such as MIBK and TBP. The choice of potassium fluoride (KF) was based on the strong complexes that Zr forms with fluoride without forming the Zr-oxy type of complexes. It is also known that K_2ZrF_6 or $2KF.ZrF_4$ crystals can easily be precipitated, but it is not as easier to precipitate Na_2ZrF_6. Preliminary experiments indicate that HCl-KF solutions were viable, with the use of KF presenting an interesting opportunity for exploiting local resources such as CaF_2. The effects of various parameters, including the concentration of the initial feed solution, concentration of HCl and KF in the aqueous phase, contact time, phase ratio (aqueous to organic A/O), and the use of stripping agent, were investigated. The extraction and separation of Zr from Hf using 1-octanol is possible only in the presence of KF.

2 Materials and Methods

2.1 Materials

All chemicals used were of analytical grade. Zirconium basic carbonate (ZBC) was purchased from Sigma-Aldrich, 1-octanol ($C_8H_{18}O$) with a purity of ≥ 99.0% was purchased from Merck, and hydrochloric acid (32% HCl) was obtained from Sigma-Aldrich. Potassium fluoride (KF) with a minimum purity of 98.5% purchased from Merck. Sulphuric acid (98% H_2SO_4), with a purity of 98% by mass, and ammonium sulphate ($(NH_4)_2SO_4$) with a purity of ≥ 99.0% were obtained from Sigma-Aldrich and used without further treatment. Deionized water was used in all aqueous preparations. The ICP-OES calibration standards were obtained from Monitoring and Control Laboratories SA.

2.2 Methods

A Spectro Arcos model inductively coupled plasma-optical emission spectrometer (ICP-OES) was used for the elemental analysis.

Shake-out tests were conducted batchwise in a 200-ml beaker at ambient temperature (20–25 °C) in order to obtain liquid-liquid equilibrium (LLE). Zirconium basic carbonate (ZBC), which contains 40% ZrO_2 and 1–2% HfO_2, was dissolved using HCl at different concentrations. KF at different concentrations was added to this solution in order to obtain the feed for the liquid-liquid extraction experiment. The extractions were carried out by vigorously shaking the aqueous and organic phases at different ratios (A/O) for 15 min. After equilibration, the contents were allowed to separate. A separation funnel was used to separate the aqueous and the organic phases. ICP-OES was used to determine the concentration of Zr and Hf in the aqueous solution. The metal concentrations of Zr and Hf in the organic phase were inferred by mass balance analysis. The distribution coefficient (D) was calculated as the ratio between the concentration in organic phase at equilibrium and the aqueous phase according to Eq. (1), where C_i is the initial metal concentration in the aqueous phase before extraction and C_f is the final metal ion concentration in the aqueous phase after extraction. From the D value, the extraction efficiency (E) and separation factor (β) were calculated using Eqs. (2), (3), and (4), respectively.

$$D = \frac{C_i – C_f}{C_f} \tag{1}$$

$$\%E_{Zr} = \frac{D_{Zr} * 100}{\left[\frac{V_{aq}}{V_{org}} + D_{Zr}\right]} \tag{2}$$

$$\%E\mathrm{Hf} = \frac{D_{Hf} * 100}{\left[\frac{V_{aq}}{V_{org}} + D_{Hf}\right]} \tag{3}$$

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

V_{aq} and V_{org} are the volume of aqueous and organic phases, respectively. D_{Zr} and D_{Hf} are Zr and Hf distribution coefficient, respectively.

Stripping percentage (S %) was calculated by using the following relationship:

$$S\% = \frac{C_s * 100}{(C_i – C_f)} \tag{5}$$

Here, C_i is the original Zr concentration in the aqueous phase before extraction, C_f the Zr concentration in the aqueous phase after extraction, and C_s is the Zr concentration in the aqueous phase after stripping. The results reported are mean values of at least two samples at each set of experiment condition for each process parameter. It must also be noted that the feed solution used during the extraction was freshly prepared for each experiment. The errors associated with the results obtained were ± 4%.

3 Results and Discussion

To optimise the extraction and separation efficiency, the influence of experimental parameters, such as HCl and KF, concentrations in the aqueous phase, the contact time, and concentration of different stripping agents, was examined.

3.1 Effect of Contact Time

To make a valid interpretation of the effect of different experiment parameters, it must be ensured that the equilibrium between the organic and aqueous phase is reached in all experiments. Thus, it is necessary to determine the minimum time required to establish the equilibrium. This was investigated by shaking 50 ml of organic solvent (1-octanol) vigorously with 50 ml aqueous solution containing Zr and Hf for varying times between 5 and 20 min. Percentage metal extraction as a function of time is shown in Fig. 1. The minimum shaking time required to achieve equilibrium between the organic and aqueous phase was found to be 5 min. A maximum value of 15 min was selected for all subsequent experiments because extending this time did not greatly affect the extraction of either the Zr or Hf species.

3.2 Effect of HCl Concentration

The influence of hydrochloric acid concentration on the extraction of Zr and Hf was investigated. Zirconium basic carbonate was dissolved in hydrochoric acid at various concentrations from 5 to 20%. After dissolution, a predetermined concentration of potassium fluoroide was added to the solution. The solution obtained was then contacted with 1-octanol for the extraction and separation of Zr from Hf. The tests were carried out at a ratio of A/O of 1:1 and contact time of 15 min. The results in Fig. 2 indicate that the extraction of both Zr and Hf increases with increasing acid concentration. This can be explained as follows: an 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 [7, 33] Eq. (6) with M = Zr or Hf.

$$\left[\mathrm{M(OH)_n}\right]_{(4-n)} + \mathrm{iCl^-} + \mathrm{nH^+} \rightleftharpoons [\mathrm{MCl_i}]_{(4-i)} + \mathrm{nH_2O} \qquad (6)$$

Thus, at high hydrochloric acid concentration, the extraction of Zr by 1-octanol is improved. The increase in HCl concentration shows a positive effect on the extraction of Zr. Hence, 10% HCl was chosen for the extraction and separation of zirconium from hafnium.

The extraction percentage for Zr increased at different rates with increased HCl concentration. The extraction percentage of Zr increases considerably while Hf exhibits a small increase. This leads to an increase of the separation factor between Zr and Hf. The remarkable difference from the extraction of Zr and Hf in the organic phase is that Hf has a lower tendency than Zr to form anionic complexes, which confirms the findings of Poriel et al. [18]. They stated that Zr and Hf are regarded as hard acids [34], but the absolute values of hardness calculated for Zr and Hf indicate that the hardness of Hf is less than that of Zr [35]. This indicates that in the solvent extraction process using liquid anion extractants, the hard base Cl^- will by preference form inner-sphere anionic complexes with Zr that is extracted to the organic phase by octanol. The increase in the percentage extraction of Zr with increasing HCl concentration may also imply that solvation reactions are responsible for the extraction of both metals by the extractant used.

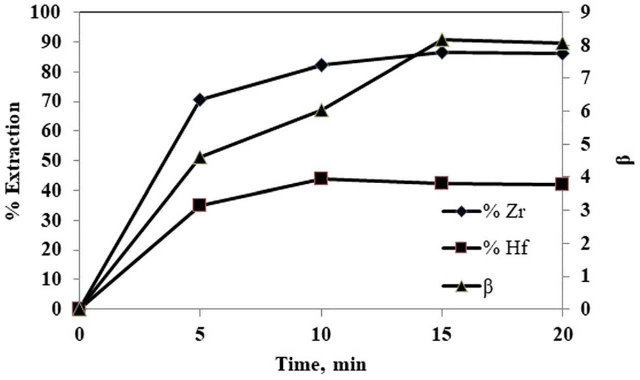

Fig. 1 Effect of contact time on the extraction of Zr and Hf. Experimental conditions: organic phase: 100% 1-octanol, [HCl] 10%, KF = 1.5 M, A/O ratio = 1:1

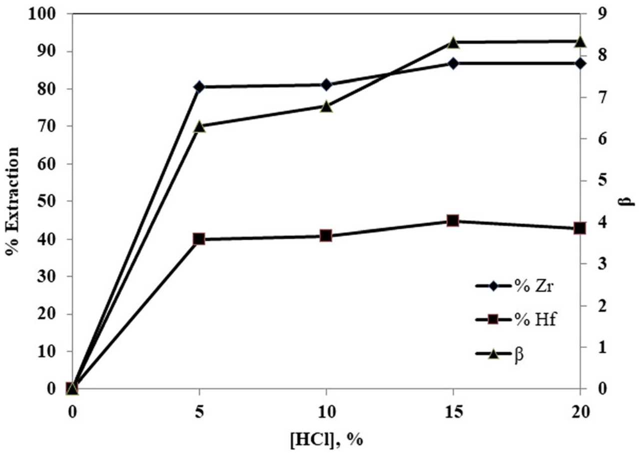

Fig. 2 Effect of HCl concentration on the extraction of Zr and Hf with 1-octanol. Experiment conditions: 100% 1-octanol, [HCl] % = 5 to 20, O/A ratio = 1:1, KF = 1.5 M

The suggested reaction may be expressed by the following chemical expression [36].

$$\mathrm{M^{x+}}_{(aq)} + \mathrm{xCl^-}_{(aq)} + \mathrm{y(HA)}_{(org)} \rightleftharpoons \mathrm{MCl_{x}.\ y(HA)}_{(org)} \qquad (7)$$

where M^{x+} represents cationic species of Zr and Hf in HCl solution. The chloride concentration affects the speciation of the metal complexation, and higher chloride concentration favours the formation of extractable metal chloro-complexes, pushing the equilibrium concentration in Eq. 7 to the right. The extraction behaviour of Zr in the present study is in good agreement with the results reported by Ling et al. [36] which found an increase in HCl concentration promotes the separation of Zr over Hf. Banda et al. [37] also reported that the extraction of Zr was selective over Hf with TOPO from chloride concentration. The extraction and separation also improve with an increase in HCl concentration.

3.3 Effect of KF Concentration

The zirconium basic carbonate was dissolved in 10% HCl. A predetermined potassium fluoride concentration between 1 and 2 M was added in order to find the optimum values for extraction and separation of Zr and Hf. Increasing of KF concentration increases the extraction and separation efficiency of zirconium, with the highest separation efficiency obtained at 1.5 M KF in solution. This shows that the extraction of zirconium strongly depend upon the concentration of KF in the aqueous phase. It is postulated that a (Zr,Hf)F_4.2KF compound is formed in aqueous solution, which has a higher affinity for 1-octanol. However, additional studies are required in order to fully describe the chemical speciation involve in this current investigation. Beyond this value, a small increase was observed. This concentration was regarded as the optimum value. Table 2 shows the effect of KF concentration on the extraction and separation of zirconium and hafnium.

3.4 Effect of Phase Ratio on the Extraction of Zr

The effect of contacting different volume ratios of organic to aqueous phase was investigated. In this study, the volume ratio of organic to aqueous was varied from 5:1 to 1:1. The organic solution was contacted with zirconium basic carbonate dissolved in 10% HCl and 1.5 M KF. Under the given set of experimental conditions, the results in Fig. 3 indicate that the preferred (A/O) ratio in this investigation is 1:2 or even higher. It shows that the percentage extraction of Zr and Hf increases with the increase of the volume ratio of organic to aqueous phase. The separation factor between Zr and Hf also increases from 5.22 up to 8.69 from the ratio 1:1 to 2:1, then remains constant up to the volume ratio of 5:1. El Shafie [38] also reported the same trend when extracting zirconium from nitric acid medium using Cyanex 921.

3.5 McCabe-Thiele Diagrams

McCabe-Thiele diagrams were constructed to determine the number of stages needed to reach the desired separation of Zr from Hf. In this study, the equilibrium data was obtained at different O/A volume ratio, using optimum extraction conditions of 100% 1-octanol, contact time 15 min, 10% HCl, and 1.5 M KF at room temperature by keeping the initial concentration of Zr constant during the experiment. From the McCabe-Thiele diagram in Fig. 4, four equilibrium stages are required for almost 94% Zr extraction.

Table 2 Effect of KF concentration on the 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	3.97	0.82	79.87	39.66	6.04
1.5	6.32	0.77	86.35	43.4	8.25
2	6.18	0.77	86.08	43.58	8.01

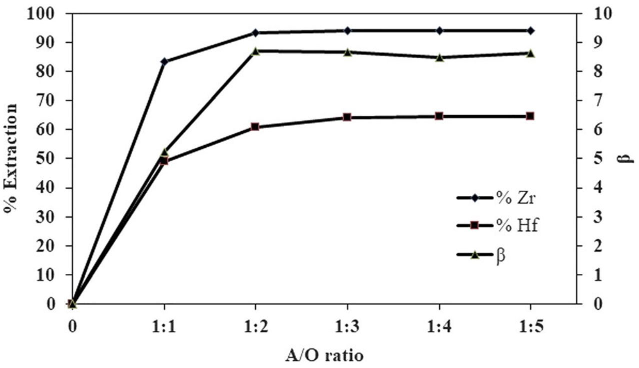

Fig. 3 Effect of phase ratio on the extraction of Zr with 1-octanol. Experimental conditions: 1-octanol, 1.5 M KF, 10% [HCl], O/A = 5:1 to 1:1

3.6 Effect of Stripping Agent

The effect of different stripping agents, such as distilled H_2O, H_2SO_4, $(NH_4)_2SO_4$, and HCl, was studied by using a constant concentration value of 1 M and keeping other factors constant. The results obtained are given in Fig. 5a and show that the stripping efficiency of Zr depend on the stripping agent. The highest stripping percentage of 38.87% was obtained using H_2SO_4 as a stripping agent, and the lowest was 24.38% obtained using HCl as a stripping agent. H_2SO_4 exhibit a higher stripping percentage efficiency this is probably because of the chemical energy bond formed between Zr(IV) and the stripping agent is stronger than that in Zr(IV)-octanol complex.

The effect of contact time on the stripping of Zr from loaded organic solution was studied at different contact times, running from 10 to 60 min, while other parameters were kept constant. The stripping efficiency increased with increasing time. The optimum stripping efficiency was achieved after 30 min. In order to investigate the stripping behaviour of Zr into the loaded extract solution, stripping experiments were conducted. The extract solution obtained from the HCl/KF 1-octanol system was stripped with sulphuric acid at concentrations between 1 and 5 M. The decreasing stripping efficiency

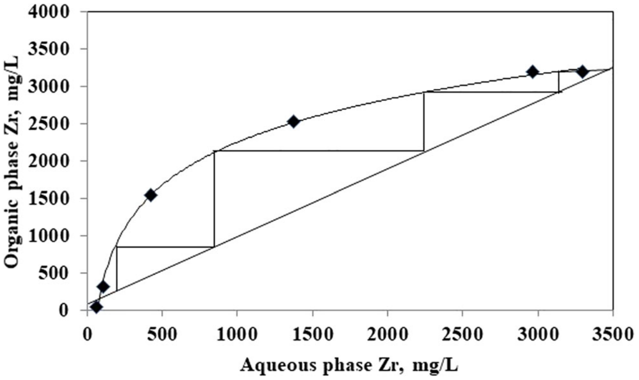

Fig. 4 McCabe-Thiele diagram for Zr extraction. Experimental conditions: A/O ratio from 1:1 to 1:5, 100% 1-octanol, 15 min contact time, 10% HCl, and 1.5 M KF

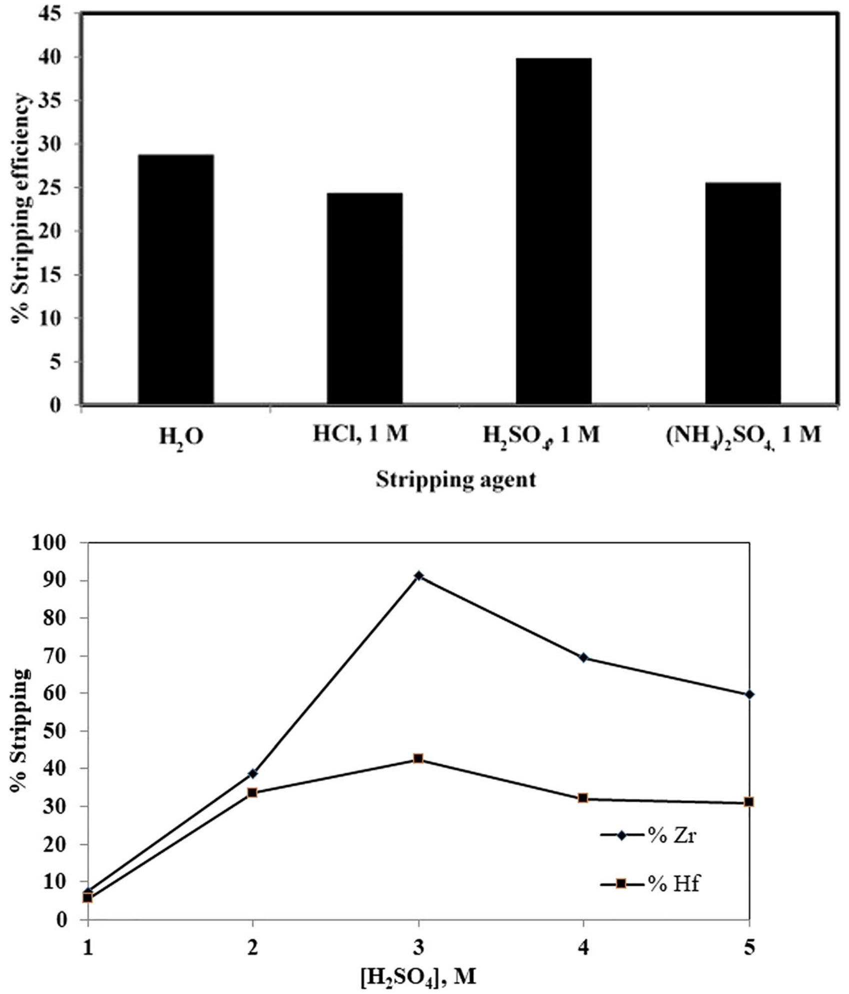

Fig. 5 **a** Effect of stripping agent on the stripping of Zr from loaded 1-octanol. Contact time 15 min, A/O 1:1. **b** Effect of sulphuric acid concentration on the stripping of zirconium from the loaded 1-octanol, A/O: 1:1, $H_2SO_4 = 1$ to 5 M

at higher H_2SO_4 concentration could be due to the successive formation of highly charged anionic species of Zr complexes in aqueous solutions [37]. The results in Fig. 5b indicate that the highest stripping efficiency of Zr was obtained at a sulphuric acid concentration of 3 M. H_2SO_4 was also reported to be a great stripping agent of zirconium by Reddy [8] and El Shafie [38].

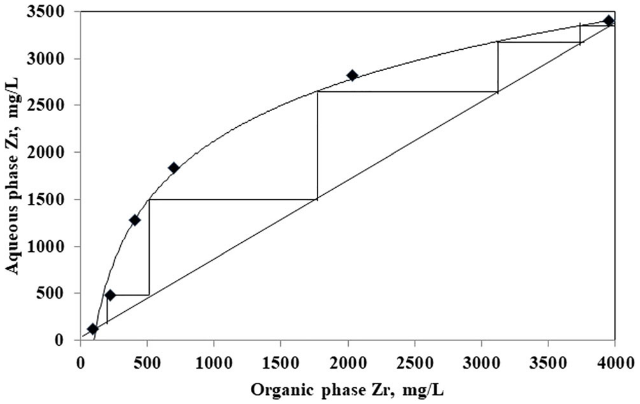

Fig. 6 McCabe-Thiele diagram for Zr stripping from loaded 1-octanol. Experimental conditions: 30 min contact time and 3 M sulphuric acid

3.7 McCabe-Thiele Diagram for Stripping of Zr

In order to determine the number of equilibrium stages required to strip Zr from the loaded extractant, a McCabe-Thiele diagram was constructed. The data was obtained by shaking the loaded organic solution with a fixed volume of 3 M sulphuric acid until equilibrium was obtained. It was found (Fig. 6) that five equilibrium stages will be sufficient for the stripping of Zr from the loaded extract.

4 Conclusion

Selective extraction and separation of zirconium from HCl/KF system using 1-octanol as extractant was investigated. The results show that zirconium ions were preferentially extracted over hafnium with undiluted 1-octanol in 10% HCl and 1.5 M KF at a ratio of aqueous to organic of 1:2. A separation factor of 8.6 was obtained. McCabe-Thiele diagrams indicate that four equilibrium stages are necessary for almost 94% Zr extraction. The McCabe-Thiele diagram for Zr stripping indicates that five theoretical stages are required. The use of octanol as alternative extractant presents both a direct advantage by reducing the cost of the process because of the low price of the latter compared with either MIBK or TBP, and KF is also cheaper compared with ammonium thiocyanate. An indirect advantage by the avoidance of environmental problems such as the use of ammonium cyanide leads to an environmental concern. There is no third phase formation which could lead to the use of expensive chemicals and reduction of the extraction efficiency.

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Compliance with Ethical Standards

Conflict of Interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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