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Extraction and Separation of Zr(IV) and Hf(IV) from Nitrate Medium by Some CYANEX Extractants

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Abstract: A solvent extraction study has been carried out to extract and separate zirconium and hafnium from nitrate medium by using some phosphine oxide extractants (CYANEX 921, CYANEX 923, and CYANEX 925) in kerosene. The influence of the different factors affecting the extraction process was studied in detail. Apparently the rate of extraction of Zr(IV) and Hf(IV) in CYANEX 921, CYANEX 923, and CYANEX 925 is reasonably fast. The extraction increases with increasing temperature, suggesting that the reaction is endothermic. The stripping percent of Zr(IV) and Hf(IV) by 0.5 M HNO_3 from the loaded organic phase after two stages reached 97.5% and 10.2%, respectively, which lead to good separation of the two metals. Under the optimum conditions, the extraction of zirconium was about 90, 87.6, and 91.6% and separation factors equal to 17, 21.4, and 40.7 were obtained for CYANEX 921, CYANEX 923, and CYANEX 925, respectively. The results obtained reveal that 2.0 M nitric acid is the optimum acid concentration for the separation of Zr(IV) and Hf(IV) and 0.4 M CYANEX 925 performs more efficient separation compared with other organophosphorus extractants.

Keywords: Extraction, hafnium, organophosphorus extractants, zirconium

INTRODUCTION

Zirconium and hafnium co-exist in nature, but these metals have opposite nuclear characteristics. Zirconium is used in nuclear reactors as structural and container material and hafnium is used as a control material in

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water-cooled nuclear reactors and rectifiers. Thus, Zr and Hf have to be separated prior to their transformation into pure metals (1). These metals have very similar chemical properties and are commonly referred to as "chemical isotopes" (2). Zirconium metal should contain less than 100 ppm hafnium for use in nuclear reactors. Solvent extraction processes are employed currently on a commercial scale to separate hafnium from zirconium. Neutral organopohosphorus reactants such as tributylphosphate (TBP) and trialkylphosphine oxide (TOPO) have been employed in the solvent extraction studies of Zr(IV) and Hf(IV) (3,4). Acidic organophosphorus extractants, namely, di-2-ethylhexyl-phosphoric acid, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester, and dithiophosphinic acids have also been widely employed (5,6). Sato and Watanabe (7) studied the extraction of Zr(IV) from sulphate solutions using di-n-octylamine, tridodecylamine, trioctylamine, and tris (2-ethylhexyl) amine and they reported secondary amines to be more effective than tertiary amines. Suriyachat and Distin (8) studied the extraction of Zr(IV) from acidic chloride solutions using CYANEX 923 and CYANEX 925. It was found that Zr(IV) is extracted more readily by CYANEX 923 than by CYANEX 925. The separation of Zr(IV) and Hf(IV) has been investigated using different extractants (9–11). It was found that the most successful of the extractants has been CYANEX 925 which extracted 61% zirconium and 4% hafnium giving a separation factor of 37 (10). Previous reports have used other extractants for zirconium/hafnium separation mainly from hydrochloric acid medium (12–15). Despite the large number of investigations reported on the extraction and separation of zirconium and hafnium from chloride medium, limited studies are reported on the extraction of the two metal ions from nitrate medium by CYANEX extractants. The investigations recently given by Taghizadeh et al. (1,16) are that of the main investigations on the extraction of Zr and Hf from acidic nitrate solutions using the organophosphorus acidic extractant CYANEX 272 and HDEHP.

In this context, the aim of this work is directed to comparable studies on the extraction and separation of zirconium and hafnium from nitrate media by the neutral organophosphorus extractants CYANEX 921, CYANEX 923, and CYANEX 925. Within this text, parameters affecting the individual extraction efficiency of Zr(IV) and Hf(IV) by each of the investigated extractants such as extraction time, acid concentration, nitrate ion concentration, hydrogen ion concentration, extractant concentration, and temperature are investigated. The equilibrium of each system is performed. The results of the three systems are compared and discussed. Optimum conditions for maximum Zr/Hf stripping and separation is given and a general equation for the separation of the two metals ions by CYANEX 925 is deduced.

EXPERIMENTAL

Reagents

CYANEX 921, CYANEX 923, and CYANEX 925, kindly supplied by Cytec Inc., USA, are trade names for industrial reagents which contain trialkylphosphine oxides as the active substances. CYANEX 921, $(C_8H_{17})_3PO$, is an off-white waxy solid which contains trioctylphosphine oxide as the active substance (93%). It is considered to be more advantageous than pure TOPO due to its relatively higher solubility in common hydrocarbon diluents especially at low temperatures. CYANEX 923 extractant is a colorless liquid which comprises a mixture of four trialkylphosphine oxides, with the general formula R_3PO(14%), $R_2R'PO$(42%), RR'_2PO(31%), and R'_3PO(8%), in which R denotes n-octyl and R′ stands for n-hexyl group (17). Its average molecular weight is 348 g/mol (18). CYANEX 925, bis (2,4,4-trimethylpentyl) octylphosphine oxide of average molecular weight 386 g/mol, is a colorless to light amber liquid claimed as a mixture of trialkylphosphine oxides containing normal and branched octyl groups (19). Alguacil et al. (20) stated that this reagent is a mixture of only two compounds with the formula R_3PO and $R_2R'PO$, where $R = CH_3C(CH_3)_2CH_2CH(CH_3)CH_2$ (2,4,4-trimethylpentyl) and $R' = CH_3(CH_2)_7$ (n-octyl).

The reagents contain very similar active substances which differ only slightly by the length of the alkyl group (hexyl or octyl) and/or the structure of the alkyl group (normal or branched). However, an important difference between these reagents is that CYANEX 921 is a solid while CYANEX 923 and CYANEX 925 as being mixtures of few components are liquids, thus, they can be used alone without any diluent. These reagents were all used as received without further purification. Kerosene was obtained from Misr Petroleum Ltd. Company, Egypt. All the other chemicals used were of analytical reagent grade.

The stock solutions of the metal ions were prepared by dissolving their suitable salts, $(ZrO(NO_3)_2 \cdot 8H_2O$ and $HfO(NO_3)_2 \cdot 8H_2O)$, which were obtained from Fluka, in double-distilled water containing a minimum amount of the corresponding mineral acid. Suitably diluted solutions of the above-mentioned metal ions were used in the extraction and analysis studies.

Analysis

Zirconium and hafnium concentrations were separately determined spectrophotometerically by the Arsenazo-III method (21) using a Shimadzu

160-A double beam spectrophotometer. Confirmatory simultaneous determination of both metals concentrations was carried out using ICPS-7500 Shimadzu Sequential Plasma Spectrometer. A Hanna pH-meter was used for the pH measurements.

Extraction Procedure

For the distribution studies, equal volumes of the aqueous (containing 0.1 g/L of each metal ion) and organic phases were shaken for 5 min (sufficient to attain equilibrium) in glass-stoppered vials using a water thermostated mechanical shaker adjusted at $25 \pm 1°C$ (except when studying the effect of temperature). The two phases were then separated, and a suitable aliquot of the aqueous phase was analyzed. The metal ion concentration in the organic phase was determined by mass balance. The extraction behaviors of the investigated metal ions from nitric acid media were recorded for each individual metal.

The distribution ratio (D) was calculated from the relation:

$$D = (C_o - C)/C \quad (1)$$

Where, C_o is the original metal ion concentration in the aqueous phase before extraction and C is the metal ion concentration in the aqueous phase after extraction.

Stripping experiments were carried out by shaking 10 ml of the organic phase loaded with the extracted metal for 5 min with a known volume of the aqueous acid solution under study. The concentration of the metal ion in the aqueous phase was determined and the stripping percent (S%) was calculated by the following relation:

$$S\% = [C_s/(C_o - C)] \times 100 \quad (2)$$

where, Cs is the metal ion concentration in the aqueous phase after stripping.

RESULTS AND DISCUSSION

The effect of the different parameters affecting the extraction of 0.1 g/L of Zr(IV) or Hf(IV) by CYANEX 921, CYANEX 923, and CYANEX 925 were investigated. These parameters include the HNO_3, nitrate, hydrogen ion, metal ion, and extractant concentrations as well as temperature for the different systems.

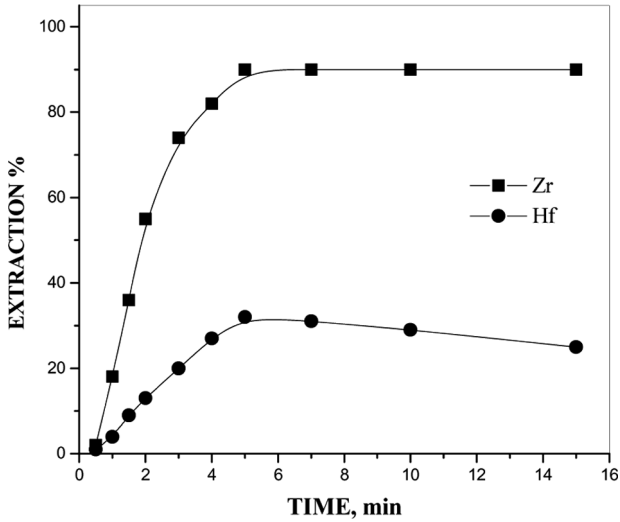

Figure 1. Effect of time on the extraction percent of Zr and Hf from 2 M HNO_3 by 0.1 M CYANEX 921.

Effect of Equilibration Time

The effect of equilibration time on the extraction of Zr(IV) and Hf(IV) was investigated in the range 1–15 min from 2.0 M HNO_3 by 0.1 M CYANEX 921. The results reported in Fig. 1, show that a 5 min contact time is sufficient to achieve the extraction equilibrium (90% Zr(IV) and 32% Hf(IV)). The equilibrium was also reached after 5 min for 0.35 M CYANEX 923 and 0.4 M CYANEX 925 in kerosene, with different extraction percents for both Zr(IV) and Hf(IV). In the different studies, the two phases were shaken for 5 min to ensure complete equilibrium.

Effect of HNO_3 Concentration

The influence of nitric acid concentration on the extraction of Zr(IV) and Hf(IV) was investigated between 0.1 and 3.5 M, keeping the metals concentration constant at 0.1 g/L for both Zr(IV) and Hf(IV) by using 0.1 M CYANEX 921, 0.35 M CYANEX 923, and 0.4 M CYANEX 925 in kerosene. The plots of (D) as a function of nitric acid concentration on a log-log scale show that the extraction of both metals increases with the increase in nitric acid concentration until 2.0 M, Fig. 2. Further increase in the acid concentration decreased the distribution ratio (D) and

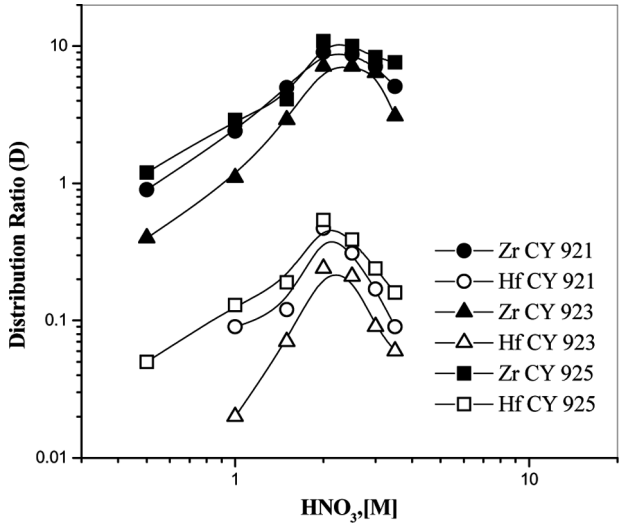

Figure 2. Effect of nitric acid concentration on the extraction of Zr(IV) and Hf(IV) by 0.1 M CYANEX 921, 0.25 M CYANEX 923, and 0.4 M CYANEX 925 in Kerosene.

consequently decreased the extraction percent of both elements, which may be attributed to the extraction of nitric acid by either extractants at high acidity.

Effect of Hydrogen Ion Concentration

The effect of hydrogen ion concentration at 2.0 M $[NO_3]^-$ on the extraction of Zr(IV) and Hf(IV) from nitrate media by 0.1 M CYANEX 921, 0.35 M CYANEX 923, and 0.4 M CYANEX 925 in kerosene was investigated in the range 0.01 M – 0.1 M. The increase in H^+ concentration in the investigated range had almost no effect on the extraction under the used experimental conditions, which shows that hydrogen ion does not participate in the extracted metals species.

Effect of Nitrate Ion Concentration

The change in the nitrate ion concentration from 1.0 M to 2.5 M at fixed hydrogen ion concentration of 2.0 M from mixtures of $HNO_3 + NH_4NO_3$ by using 0.1 M CYANEX 921, 0.35 M CYANEX 923, and 0.4 M

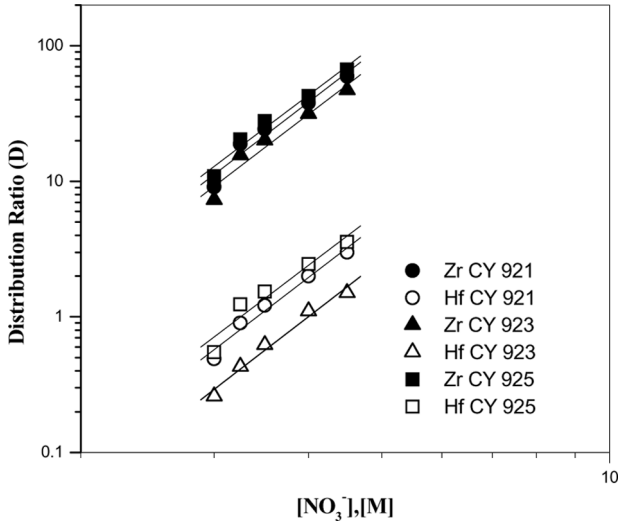

Figure 3. Effect of nitrate concentration on the extraction of Zr(IV) and Hf(IV) by 0.1 M CYANEX 921, 0.25 M CYANEX 923, and 0.4 M CYANEX 925 in kerosene.

CYANEX 925 in kerosene was found to increase the extraction of Zr(IV) and Hf(IV). Plotting the nitrate concentration (M) against the distribution ratio (D) for the different systems as a log-log relation, Fig. 3, gave straight line relations with positive slopes equal to about two indicating the presence of two nitrate ions in the extracted metal species.

Effect of Extractant Concentration

The influence of varying the CYANEX 921, CYANEX 923, and CYANEX 925 concentration in kerosene on the extraction of Zr(IV) and Hf(IV) from 2.0 M nitric acid solution has been studied. The log–log plot between the extractants concentration and distribution ratio for different systems, Fig. 4, gave straight lines relations with a slope of around two for Zr(IV) and Hf(IV) for CYANEX 921 and a slope of about three in the case of CYANEX 923 extractant. In case of CYANEX 925 the slope is similar to case of CYANEX 921 for Zr(IV) but in the case of Hf(IV) the slope decreased to about one. From the slopes of the plots, it is inferred that two molecules may be involved in the extracted Zr(IV) and Hf(IV) species in case of CYANEX 921 and three molecules in case

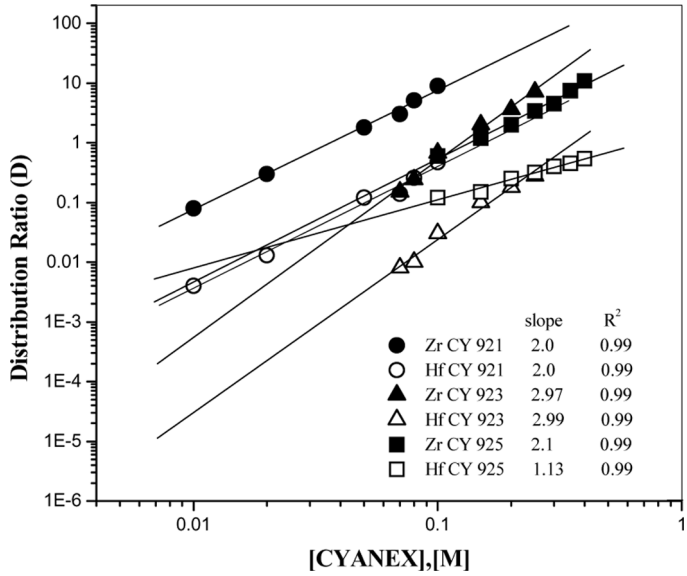

Figure 4. Effect of extractant concentration in kerosene on the extraction of Zr(IV) and Hf(IV) from 2 M HNO_3 solution.

of CYANEX 923. On the other hand, the slopes of the plots in case of CYANEX 925 indicate that two molecules of the extractant are involved in the extracted Zr(IV) and one molecule in the extracted Hf(IV) species.

Extraction Equilibrium

In slightly acidic aqueous solution zirconium and hafnium are mainly present as the oxycations, MO^{2+} and in slightly acidic nitrate medium, formation of $MO(NO_3)_2$ is present as a main species (16). This together with the fact that neutral organophophorus extractants extract neutral metal ions by solvation, the following extraction equilibrium can represent the extraction process for the systems under investigation;

$$MO^{2+}_{(aq)} + 2NO^{-}_{3(aq)} + xL_{(org)} \longrightarrow MO(NO_3)_2 \cdot xL_{(org)} \qquad (3)$$

where, L stands for the extractants (CYANEX 921, CYANEX 923 or CYANEX 925) and x is the number of moles of extractants involved in the extracted Zr(IV) or Hf(IV).

The extraction constant K_{ex} may be given by:

$$K_{ex} = \frac{[MO(NO_3)_2 \cdot xL]_{(org)}}{[MO^{2+}]_{aq}[NO_3^-]_{aq}^2[L]_{org}^x} \quad (4)$$

$$K_{ex} = \frac{D}{[NO_3^-]_{aq}^2[L]_{org}^x} \quad (5)$$

Under the experimental conditions investigated, the slope of the relation given in Fig. 3, supports the presence of two moles of $[NO_3^-]$ with both zirconium and hafnium in the extracted species. Further, the slopes of the relations given in Fig. 4 indicate that in case of Zr(IV) the values of x equal 2,3 and 2, while that of Hf(IV) equal 2,3 and 1 for CYANEX 921, CYANEX 923, and CYANEX 925, respectively.

Therefore, the main extracted species of Zr in the investigated systems are $ZrO(NO_3)_2 \cdot 2$ CYANEX 921, $ZrO(NO_3)_2 \cdot 3$ CYANEX 923 and $ZrO(NO_3)_2 \cdot 2$ CYANEX 925 with respective average extraction constants of 756 ± 1, 457 ± 1 and 53 ± 1. In the case of hafnium, the main extracted species in the different systems are $HfO(NO_3)_2 \cdot$ 2CYANEX 921, $HfO(NO_3)_2 \cdot 3$CYANEX 923 and $HfO(NO_3)_2$. CYANEX 925, with respective extraction constants of 45 ± 1, 21 ± 2 and 1.3 ± 0.1, respectively. These indicate that the main extracted species of Zr and Hf are more or less similar using CYANEX 921 or CYANEX 923 and different when the extractant is CYANEX 925.

Effect of Temperature

The results of the effect of temperature (10–50°C) on the extraction of Zr(IV) and Hf(IV) from 2 M HNO_3 medium by 0.1 M CYANEX 921, 0.35 M CYANEX 923 and 0.4 M CYANEX 925 are shown in Fig. 5. The extraction percent of Zr(IV) and Hf(IV) increased with increasing temperature, in all the investigated systems. Using the following Van't Hoff equation, the enthalpy change (ΔH) associated to the extraction can be calculated.

$$\mathrm{Log}(K_{ex}) = \left(\frac{-\Delta H}{2{:}303R}\right)\left(\frac{1+C}{T}\right) \quad (6)$$

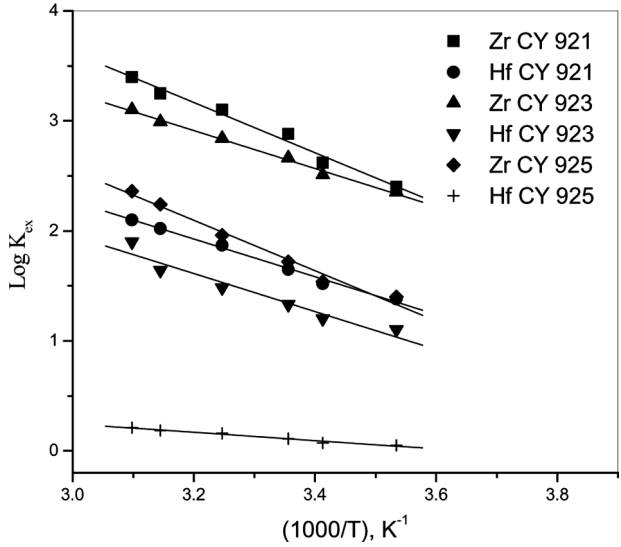

Figure 5. Effect of temperature on the equilibrium constant of extraction of Zr(IV) and Hf(IV) by 0.1 M CYANEX 921, 0.25 M CYANEX 923, and 0.4 M CYANEX 925 in kerosene.

Where, R is the universal gas constant (8.314 $J\,mol^{-1}\,K^{-1}$) and C is a constant. As shown in Fig. 5, log K_{ex} is linearly related to the reciprocal of the temperature (1/T).

The slopes obtained from the figure were used to calculate ΔH. The free energy change (ΔG) and the entropy change (ΔS) were calculated from the following relations:

$$\Delta G = -RT \ln K_{ex} \tag{7}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{8}$$

The data in Table 1 represent the calculated thermodynamic functions for the studied systems. The tabulated data show that the extraction process for Zr(IV) and Hf(IV) in the different CYANEX systems is endothermic as indicated by the positive values of ΔH.

The reactions for both Zr(IV) and Hf(IV) in CYANEX systems are spontaneous in nature as referred to the negative sign of ΔG. The positive values of the entropy changes indicate the disordered nature of the extracted species, and the low values of entropy changes obtained for hafnium shows that its extracted species are more ordered than zirconium species.

Table 1. Thermodynamic functions of the extraction of Zr(IV) and Hf(IV) from 2 M HNO_3 medium by the different CYANEX–kerosene solutions

Thermodynamic functions	CYANEX 921		CYANEX 923		CYANEX 925	
	Zr(IV)	Hf(IV)	Zr(IV)	Hf(IV)	Zr(IV)	Hf(IV)
ΔH, kJ mol^{-1}	43.6 ± 2.8	32.8 ± 1.4	33.0 ± 1.2	33.1 ± 4.1	43.9 ± 2.8	7.3 ± 0.5
ΔG, kJ mol^{-1}	-16.4 ± 0.1	-9.4 ± 0.2	-15.2 ± 0.1	-7.6 ± 0.3	-9.8 ± 0.1	-0.6 ± 0.02
ΔS, J mol^{-1} K^{-1}	202 ± 9	142 ± 5	162 ± 4	136 ± 14	180 ± 9	27 ± 2

Loading Capacity and Stripping Studies

The loading capacity of 0.4 M CYANEX 925 was studied by shaking repeatedly 10 ml of 0.4 M CYANEX 925 (organic phase) with 10 ml of 2.0 M HNO_3 solution (aqueous phase) containing 0.1 g/L of Zr(IV) and 0.1 g/L of Hf(IV). After equilibration, the two phases were separated and analyzed for both zirconium and hafnium content in the aqueous nitrate phase. The amount of Zr(IV) and Hf(IV) transferred into 0.4 M CYANEX 925 in each contact was calculated by difference and the concentration of Zr(IV) and Hf(IV) in the organic phase after each stage of contact was calculated. After eight stages, the loaded extractant was 0.69 g/L Zr(IV) and 0.22 g/L Hf(IV). These quantities remained constant with any further contacts with other Zr(IV) and Hf(IV) aqueous phases solutions.

The effect of stripping agents on the recovery of Zr(IV) and Hf(IV) from a loaded organic solution consisting of 0.4 M CYANEX 925 containing 0.69 g/L Zr(IV) and 0.22 g/L Hf(IV) has been investigated. A single stage experiment with hot distilled water (60°C) and different mineral acids (nitric and hydrochloric acids) on the stripping of Zr(IV) and Hf(IV) was studied and the results obtained are summarized in Table 2. The stripping percent (calculated from Eq. (2)) with hot water is quantitative at O/A phase ratio of 1/1 to 1/2 but at lower phase ratios the stripping was not quantitative (14).

The data obtained show that dilute nitric acid can be considered as a good stripping agent as it could lead to good separation of Zr(IV) from Hf(IV). Therefore, the stripping by different concentrations of HNO_3 was studied in detail and the data obtained are shown in Table 2. Although high stripping percentages of Zr(IV) and Hf(IV) were obtained when using 4.0 M HNO_3 as stripping agent, 0.5 M HNO_3 was chosen as a stripping agent where it gave 82.4% and 7.6% for Zr(IV) and Hf(IV), respectively, after one stage stripping. After two stages, the stripping percent reached 97.5% and 10.2% for Zr(IV) and Hf(IV), respectively, which may lead to good separation of the two metal ions. The concentration of

Table 2. Stripping of Zr(IV) and Hf(IV) with water and different concentrations of mineral acids after extraction with different CYANEX 925 solutions at 25°C

Stripping agent	Stripping % Zr(IV)	Stripping % Hf(IV)
Water (60°C), O/A		
1/1	97.8	97.8
1/2	97.8	97.8
1/4	92.6	95.9
HCl, M		
0.01	89.9	57.9
0.1	91.8	78.9
1.0	98.7	95.8
2.0	99.6	99.5
HNO_3, M		
0.01	38.6	4.8
0.05	39.8	5.1
0.1	42.3	5.8
0.2	52.7	8.7
0.5	82.4	7.6
0.6	84.9	12.7
0.8	86.7	21.7
1.0	88.9	29.8
2.0	91.7	34.8
2.5	94.6	77.8
3.0	99.8	99.1
4.0	>99.9	>99.9

Zr(IV) and Hf(IV) after extraction and stripping were simultaneously measured in the same solution. The extraction percent and the separation factor obtained for Zr(IV) and Hf(IV) by recycled CYANEX 925 were found to be almost the same as previously obtained.

Separation Feasibility

The extraction constants for Zr(IV) and Hf(IV) extraction from nitrate medium by the different systems studied show that the extraction by the investigated extractants is relatively depending on the extractant concentration.

The separation feasibility of Zr(IV) from Hf(IV) can be evaluated in terms of the separation factor ($S_{Zr/Hf}$) between Zr(IV) and Hf(IV),

$$S_{Zr/Hf} = D_{Zr}/D_{Hf} \tag{9}$$

For both CYANEX 921 and CYANEX 923 systems, the separation factor from nitrate medium is obtained from Eqs. (3–5) as follows:

$$S_{Zr/Hf} = D_{Zr}/D_H = \frac{K_{ex(Zr)}[NO_3^-]_{aq}^2\,[L]_{org}}{K_{ex((Hf)}[NO_3^-]_{aq}^2\,[L]_{org}} = \frac{K_{ex(Zr)}}{K_{ex((Hf)}} \qquad (10)$$

Equation (10) shows that the separation factor is dependent on the values of the extraction constant for each cation and independent of the extractant concentration, NO_3^- concentration or pH of the medium.

For CYANEX 925 system, the separation factor from the nitrate medium is obtained from Eqs. (3–5) at 25°C as follows:

$$S_{Zr/Hf} = D_{Zr}/D_H = \frac{K_{ex(Zr)}[NO_3^-]_{aq}^2\,[L]_{org}^2}{K_{ex((Hf)}[NO_3^-]_{aq}^2\,[L]_{org}} = \frac{K_{ex(Zr)}}{K_{ex((Hf)}}[L] \qquad (11)$$

or

$$S_{Zr/Hf} = 101.75[L] \qquad (12)$$

Equation (12) shows that $S_{Zr/Hf}$ is first power dependent on the CYANEX 925 concentration and independent of the $[NO_3^-]$ or $[H^+]$, within the experimental conditions. The variation of the separation factor as function of extractant concentration at constant $[NO_3^-]$ and $[H^+]$ is given in Fig. 6. This figure shows that as the CYANEX 925 concentration increases, the separation of the two cations increases linearly in favor of Zr(IV). In order to verify this relation, the extraction of Zr(IV) and Hf(IV) was carried out from 2.0 M HNO_3 using different CYANEX 925 concentrations in the range 0.07–2.5 M. The results obtained show that the separation factor experimentally found also increases linearly with the increase in CYANEX 925 concentration and are in good agreement with the calculated values up to 1 M extractant concentration after which $S_{Zr/Hf}$ becomes nearly constant and deviation from linearity is observed, Fig. 6. This deviation at high extractant concentration may be attributed to the formation of other species which affect the extraction equilibrium and consequently the value of $S_{Zr/Hf}$.

The above conclusions show that the optimum Zr/Hf separation could be governed in case of CYANEX 925 by increasing the extractant concentration up to 1.0 M. Besides, under similar experimental conditions Zr(IV) is better extracted than Hf(IV) from nitrate medium at CYANEX 925 concentration less than 1.0 M. The separation factor experimentally found under the optimum conditions for CYANEX 921 and CYANEX 923 is 17 and 21.4, respectively, and 40.7 for CYANEX 925.

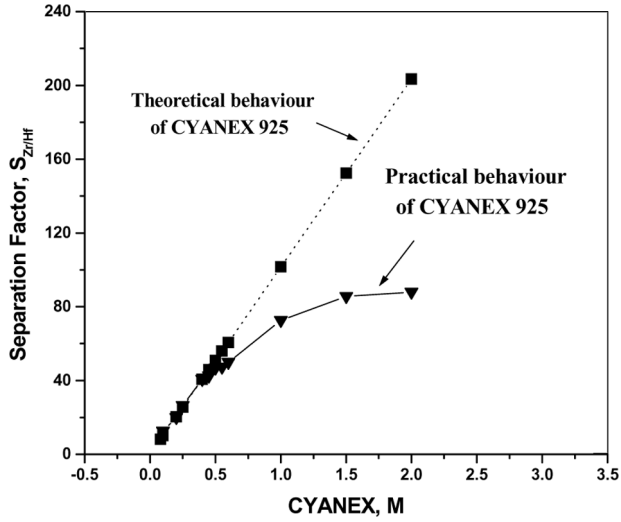

Figure 6. Effect of CYANEX 925 concentration on the separation factor $S_{Zr/HF}(D_{Zr}/D_{Hf})$ from 2 M HNO_3.

According to the results obtained, the selectivity between Zr(IV) and Hf(IV) with the three commercial organophosphorus extractants follows the order.

CYANEX 925 > CYANEX 923 > CYANEX 921.

In conclusion, the results obtained reveal that 2.0 M nitric acid is the optimum acid concentration for the separation of Zr(IV) and Hf(IV) and 0.4 M CYANEX 925 is more efficient than many other organophosphorus extractants. TBP is reported to give a separation factor of 10 (3) and CYANEX 272 reached a separation factor of 34 (1) while with CYANEX 925 under the present experimental conditions the separation factor reaches 40.7. Besides, in the investigated system the extraction of zirconium reaches 91.6% which is also higher than that reported by some recent works (1,10).

REFERENCES

1. Taghizadeh, M.; Ghasemzadeh, R.; Ashrafizadeh, S.N.; Saberyan, K.; Ghanadi Maragheh, M. (2008) Determination of optimum process conditions for the extraction and separation of zirconium and hafnium by solvent extraction. *Hydrometallurgy*, *90*: 115.

2. Pickles, C.A.; Flengas, S.N. (1997) Separation of $HfCl_4$ from $ZrCl_4$ by reaction with solid and liquid alkali chlorides under non-equilibrium conditions. *Can. Metall. Q.*, *36* (2): 131.
3. Levitt, A.E.; Freund, H. (1956) Solvent extraction of zirconium with tributylphosphate. *J. Am. Chem. Soc.*, *78*: 1545.
4. Gupta, B.; Poonma, M.; Niti, M. (2005) Extraction and recovery of zirconium from zircon using Cyanex 923. *Solvent Extr. Ion Exch.*, *23*: 345.
5. Biswas, R.K.; Hayat, M.A. (2002) Solvent extraction of zirconium(IV) from chloride media by D2EHPA in kerosene. *Hydrometallurgy*, *63*: 149.
6. Reddy, B.R.; Rajesh Kumar, J.; Reddy, A.V.; Neela Priya, D. (2004) Solvent extraction of zirconium(IV) from acidic chloride solutions using 2-ethylhexyl phosphonic acid mon-2-ethylhexyl ester. *Hydrometallurgy*, *72*: 303.
7. Sato, T.; Watanabe, H. (1974) The extraction of zirconium(IV) from sulphuric acid solutions by long-chain aliphatic amines. *J. Inorg. Nucl. Chem.*, *36*: 2585.
8. Suriyachat, D.; Distin, P.A. (1993) Zirconium solvent extraction with Cyanex 923. *Solvent Extraction in the Process Industries*, Logsdail, D.H.; Slater, M.J., eds.; Elsevier Applied Science: London, 1: 265.
9. Da Silva, A.B.V.; Distin, P.A. Jr. (1998) Zirconium and hafnium separation without waste generation. *CIM Bulletin*, *91*(1018): 221.
10. Da Silva, A.; El-Ammouri, E.; Distin, P.A. (2000) Hafnium zirconium separation using Cyanex 925. *Can. Metallurg. Q.*, *39*: 37.
11. Lee, H.Y.; Kim, S.G.; Oh, J.K. (2004) Stoichiometric relation for extraction of zirconium and hafnium from acidic chloride solutions with Versatic Acid 10. *Hydrometallurgy*, *73*: 91.
12. El-Yamani, I.S.; Farrah, M.Y. (1978) Co-extraction and separation of zirconium and hafnium by long chain amines from sulphate media. *Talanta*, *25*: 523.
13. Shults, B.G.; Larsen, E.M. (1950) The fractional separation of zirconium and hafnium by extraction with trifluoroacetylacetone. *Am. Chem. Soc.*, *72*: 3610.
14. Poriel, L.; Favre-Réguillon, A.; Pellet-Rostaing, S.; Lemaire, M. (2006) Zirconium and hafnium separation, part 1. Liquid/liquid extraction in hydrochloric acid aqueous solution with aliquat 336. *Sep. Sci. Technol*, *41*: 1927.
15. Kalyanaraman, S.; Khopkar, S.M. (1977) Solvent extraction separation of hafnium with 4-methyl-3-pentene-2-one. *Talanta*, *25*: 395.
16. Taghizadeh, M.; Ghasemzadeh, R.; Ashrafizadeh, S.N.; Ghanna, M. (2009) Stoichiometric relation for extraction of zirconium and hafnium from acidic nitrate solutions with CYANEX 272. *Hydrometallurgy*, *96*: 77.
17. Rickelton, W.A.; Boyle, R.J. (1988) Solvent extraction with organophosphines—commercial & potential applications. *J. Sep. Sci. Technol.*, 23, 12, 1227.
18. American Cyannamid Company, Cyanex 923 Extractant, Wayne, USA, 1991.
19. American Cyannamid Company, Cyanex 925, Wayne, USA, 1991.
20. Alguacil, F.J.; Caravaca, C.; Martinez, S.; Cobo, A. (1994) The phosphine oxides CYANEX 923 and CYANEX 925 as extractants for gold(I) cyanide aqueous solutions. *Hydrometallurgy*, *36*: 369.
21. Marczenko, Z. (1976) *Spectrophotometric Determination of Elements*; Ellis Harwood. Ltd: Poland.