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Zirconium and Hafnium Separation, Part 2. Solid/Liquid Extraction in Hydrochloric Acid Aqueous Solution with Anion Exchange Resins

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Abstract: Sorption behavior of zirconium and hafnium on different commercial anion exchange resins with different amine functions; ammonium (Amberjet 4200Cl), pyridine (PVP) and pyridinium (HPQ) was investigated in hydrochloric acid by both batch and column methods. Experiments were studied as a function of the concentration of hydrochloric acid. For all resins, zirconium was preferably extracted. The highest separation factors at equilibrium conditions were obtained by poly(vinyl-pyridine) (PVP) with a hydrochloric acid concentration of 9.5 M. It was observed that a single contact of the loaded resins with pure water completely back extracted the metal ions from the resins. On the basis of the significant difference between distribution coefficients of Zr and Hf, the separation was performed on a glass column (25 × 160 mm), packed with the resin. The breakthrough curves

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showed a competitive sorption and desorption process between Zr and Hf for the three resins studied.

Keywords: Zirconium, hafnium, resins, separation

INTRODUCTION

In Part I of this work (1) we examined the aqueous chemistry of Zr(IV) and Hf(IV) and adsorption behavior with liquid anionic exchangers. Adsorption of Zr(IV) and Hf(IV) was shown to occur via the formation of anionic species in a concentrated hydrochloric solution.

Industrial application of ion exchange for the recovery and separation of metal ions is usually carried out on a fixed bed. Extractant-impregnated resin (2) and both cation- and anion-exchange resins have been used for the Zr/Hf separation (3–13) but most of the ion-exchange resins (IXR) are presently used for the trace analysis of geological samples (14–16).

The ion-exchange mechanism is generally described as a result of simple electrostatic interaction, although other factors such as the size and the nature of counterions as well as the nature of functional groups on resin surfaces significantly impact on the thermodynamics and equilibria of the exchange reactions among ions in the feed. Systematic studies of the behavior of Zr and Hf in liquid/liquid extraction from aqueous hydrochloric solution have shown that Zr and Hf form anionic chloro-complexes (1, 17). Thus, we propose to study the Zr/Hf separation with IXR with different amine functions. Ion-exchange reactions and dynamic column flow-through experiments were performed to determine the behavior of these chloro-complexes on commercial anion-exchange resins.

EXPERIMENTAL

Materials and Reagents

$ZrCl_4/HfCl_4$ mixtures with different Zr/Hf molar ratio were kindly supplied by Cezus (Framatome-ANP), France. Zr(IV) and Hf(IV) standard solutions ($1000\ \mu g \cdot mL^{-1}$) were obtained from Alfa Cesar. Analytical grade HCl and NaOH standard solutions were obtained from Merck. Deionized water with a resistivity of $>18\ M\Omega/cm$ (Milli-Q system, Millipore) was used throughout the experiments.

Anion-Exchange Resins

The commercially available resins Amberjet 4200 Cl (Rohm and Haas), Reillex PVP, and Reillex HPQ (Reilly Industries) were purchased from their respective manufacturers (Figure 1).

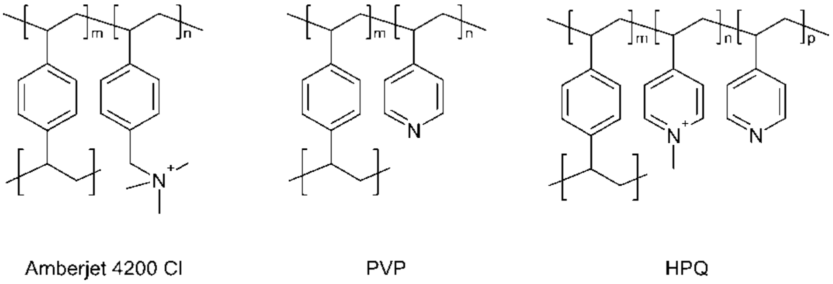

Figure 1. Structure of resins used in this study.

The commercial resins were packed in a column and washed successively (1 L/100 mL of resin) with deionized water, MeOH, deionized water, and 1.0 N NaOH. Then the resins were washed with deionized water until the pH of the eluent was neutral. A 1.0 N HCl solution (1 L/100 mL of resin) was passed through the column and the resins were washed by deionized water until the pH of the eluent was neutral. The resins were then partially dried by filtration through a Büchner funnel. A percent-solid determination was performed on each resin by drying a weighed sample (150–200 mg) of Büchner-dried resin for 12 h at 105°C and reweighing the oven-dried resin. The total anion-exchange capacity (TAEC) for the commercial resins was determined by back titration of NaOH standard solutions and is reported as milli-equivalents per gram of the oven dried resin.

Batch-Equilibrium Sorption Studies

For batch-equilibrium studies, the experiments employed a quantity of Büchner dried resin equivalent to 1 g of oven-dried resin (calculation based on the percent-solid of the particular Büchner-dried sample). The resin samples were accurately weighed into 50 mL glass bottles and first pre-equilibrated with hydrochloric acid solution having the same concentration as the one from which the extraction was to be carried out during 1 h. The pre-equilibration was performed to ensure that Zr and Hf uptake was measured in an environment where the resin was already at equilibrium. At the end of the 1 h treatment, the resin was filtered through a Büchner funnel and put back into a glass bottle. Then 10 mL of the Zr/Hf solution was added to the bottle and then shaken mechanically with a vibrax 100 (Bioblock scientific shaker) for an experimentally determined time needed to reach the extraction equilibrium. Then, the concentration of Zr and Hf in aqueous phase was determined by ICP-AES (Spectro D or Jobin Yvon Ultima 2).

The extraction efficiency, distribution ratio and separation factor were calculated by using the equations (1) to (3), respectively, where C refers to the metal concentration in the aqueous phase, the subscript *i* and *f* refer to initial conditions and final conditions, *V* refers to the volume of the aqueous phase and *m* to the mass of the resin.

$$E = \frac{(C_i - C_f)}{C_i} \times 100 \tag{1}$$

$$D = \frac{(C_i - C_f)}{C_f} \times \frac{V}{m} \tag{2}$$

$$S_{(Zr/Hf)} = \frac{D_{Zr}}{D_{Hf}} \tag{3}$$

Column Breakthrough Experiments

The exchange reactions were further evaluated in column flow-through experiments using an 9.5 mol/L HCl solution containing 2340 mg/L of Zr and 1800 mg/L of Hf. Small glass columns (25 × 160 mm) were used, and resins were wet packed to avoid entrapped air bubbles within the column. A constant flow rate of 80 mL/h (1 BV/h) and linear flow rate (u) of 16 cm/h were applied and the effluent samples were collected over time and analyzed periodically for Zr and Hf concentrations using ICP-AES. The breakthrough data were plotted as the ratio of eluent versus influent concentration (C/C_0) against the number of bed volumes of the input solution that passed through the column.

RESULTS AND DISCUSSION

Based on our preliminary liquid-liquid extraction experiments (1) as well as literature data, it appears that amine-based resins could be exploited to separate Zr and Hf at high HCl concentration (>7 M). The resins listed in Table 1 present the variation of the amine function. Amberjet 4200 Cl is a type I strong-base macroporous resin with a polystyrene backbone and has been used for the separation of Pd(II) from radioactive liquid waste (18).

Table 1. Characteristics of the resins used

Name	Particle size	TAEC
Amberjet 4200 Cl	700 μm	1.7 meq./g ± 0.2
PVP 402	80–250 μm	6.6 meq./g ± 0.2
PVP HPQ	250–600 μm	4.1 meq./g ± 0.2

Reillex PVP 402 is a crosslinked polyvinyl pyridine which has been previously used for selective sorption of V and As (19) or ^{241}Am. (20) Reillex HPQ is a macroporous PVP resin with approximately 70% of its pyridinium sites methylated. HPQ has been used for ^{241}Am separation (21) and ^{229}Th purification (22).

Kinetics of Metal Extraction

Experiments were carried out with a Zr solution containing a high level of Hf ($Zr/(Zr + Hf) = 0.71$) at 9.5 M HCl in order to improve the precision of the analysis of Hf (Fig. 2). The apparent equilibration time is 8 h, but 48 h have subsequently been used to ensure equilibration for various experimental parameters.

Effect of HCl Concentration on Zr and Hf Extraction Sorption by Commercial Resins

To evaluate the adsorption behavior of Zr and Hf onto anion exchangers, the percentage of Zr and Hf extraction (Fig. 3) and distribution ratio (Table 2) for a 48 h equilibration period was studied as a function of the concentration of the hydrochloric acid. No adsorption on the cation exchangers was observed at hydrochloric concentrations below 7 M. As expected, the adsorption of Zr on anion exchange resins increased dramatically with increasing HCl

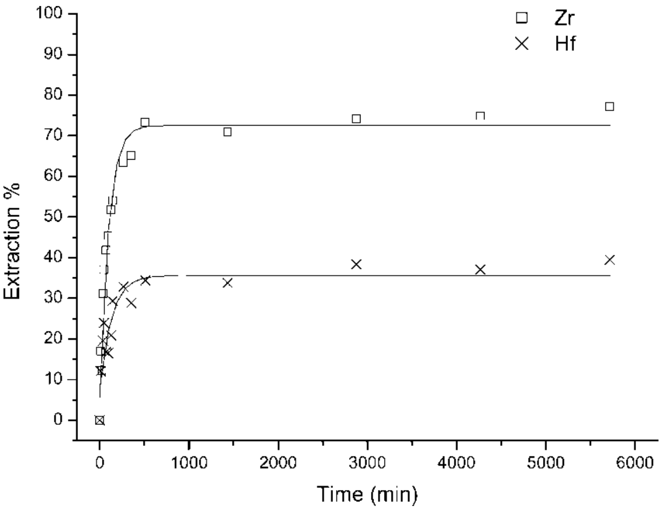

Figure 2. Effect of time on Zr and Hf extraction using Amberjet 4200 Cl, $[HCl] = 9.5$ M at 25°C, Mass resin = 10 g, volume of solution = 100 mL. $Zr/(Zr + Hf) = 0.71$, $[Zr]_i = 2106\ mg \cdot L^{-1}$ and $[Hf]_i = 1654\ mg \cdot L^{-1}$.

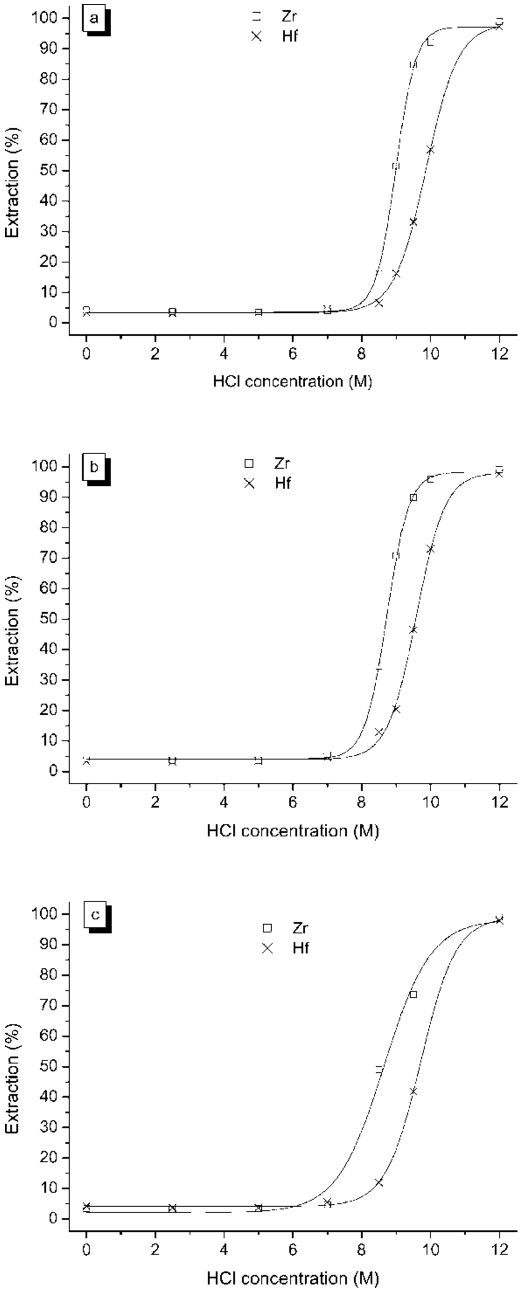

Figure 3. Effect of HCl concentration on Zr and Hf extraction using 1 g of resin and 10 mL of aqueous solution, Zr/(Zr + Hf) = 0.71, $[Zr]_i = 1926\ mg \cdot L^{-1}$ and $[Hf]_i = 1559\ mg \cdot L^{-1}$, 48 hours at 25°C. a) Amberjet 4200 Cl, b) PVP, c) HPQ.

Table 2. Effect of HCl concentration on Zr and Hf distribution ratio and separation factor using 1 g of resin and 10 mL of aqueous solution, $Zr/(Zr + Hf) = 0.71$, $[Zr]_i = 1926\ mg \cdot L^{-1}$ and $[Hf]_i = 1559\ mg \cdot L^{-1}$, 48 hours at 25°C

	Amberjet 4200 Cl			Reillex PVP			Reillex HPQ		
[HCl] conc.	D Zr	D Hf	$S_{Zr/Hf}$	D Zr	D Hf	$S_{Zr/Hf}$	D Zr	D Hf	$S_{Zr/Hf}$
8.5 M	2.2	0.7	3.1	5.3	1.5	3.5	4.6	1.3	3.5
9.0 M	10.6	1.9	5.6	24.2	2.6	9.3	—	—	—
9.5 M	55.7	4.9	11.4	90.4	8.7	10.4	75.9	7.8	9.7
10.0 M	117.7	13.2	8.9	239	27.3	8.7	—	—	—
12.0 M	944	352	2.7	1121	419	2.7	1108	432	2.5

concentration. The adsorption of Hf also showed an increase with HCl concentration but the adsorption occurred at higher HCl concentration.

As shown in Fig. 3, no adsorptions of Zr and Hf were observed below 7 M HCl. The increase in the distribution of Zr and Hf at HCl concentrations higher than 7 M could be explained by the formation of the Zr and Hf chlorocomplexes that could be adsorbed onto the ion-exchange resins. Since Zr shows a higher affinity for Cl^- than Hf ($k_{Zr} > K_{Hf}$ Eqs. (4) and (5)), Zr is therefore preferentially adsorbed. Maximum extraction selectivity was observed around 9.5 M HCl (Table 2).

These results could be rationalized by the Hard-Soft Acid-Base theory (1, 23). Zirconium and hafnium are regarded as hard acids (24), however, values of absolute hardness calculated for Zr and Hf indicate that Hf is softer than Zr (25). The adsorption of Zr and Hf are promoted by the formation of anionic species in hydrochloric solution (Eq. (4)).

$$\left[M(OH)_n\right]^{(4-n)} + iCl^- + nH^+ \leftrightharpoons [MCl_i]^{(4-i)} + nH_2O \tag{4}$$

with $i = 4$ to 6. [1]
For Zr and Hf maximum adsorption is observed in a high chloride concentration based on the adsorption of anionic complexes on anion exchange resins (Eq. (5) with M = Zr or Hf and $i = 4$ to 6).

$$\overline{IXR - N^+Cl^-} + [MCl_i]^{(4-i)} + (i-4)H^+ \leftrightharpoons \overline{IXR - N^+MCl_{i+1}H_{(i-4)}} \tag{5}$$

Since the hard base Cl^- will form inner-sphere complexes with zirconium (i.e. $[ZrCl_i]^{(4-i)}$) the Zr will be selectively adsorbed by IXR.

The resin's selectivity with respect to HCl concentration are listed in Table 2. From this table, it can be noted that the resins showed good Zr selectivity from 9.0–10.0 M HCl. Thus, 9.5 M HCl was chosen as eluent for the column experiments.

Stripping

Previous results on liquid/liquid extraction showed the quantitative stripping of Zr and Hf using an aqueous solution. The use of the same resin/stripping phase (10 mL for 1 g of resin) of water at pH ~5 permits the total recovery of Zr and Hf.

Column Tests

Based on the difference in adsorbance of Zr and Hf in an HCl solution on anion exchange resins from separation experiments for these elements were

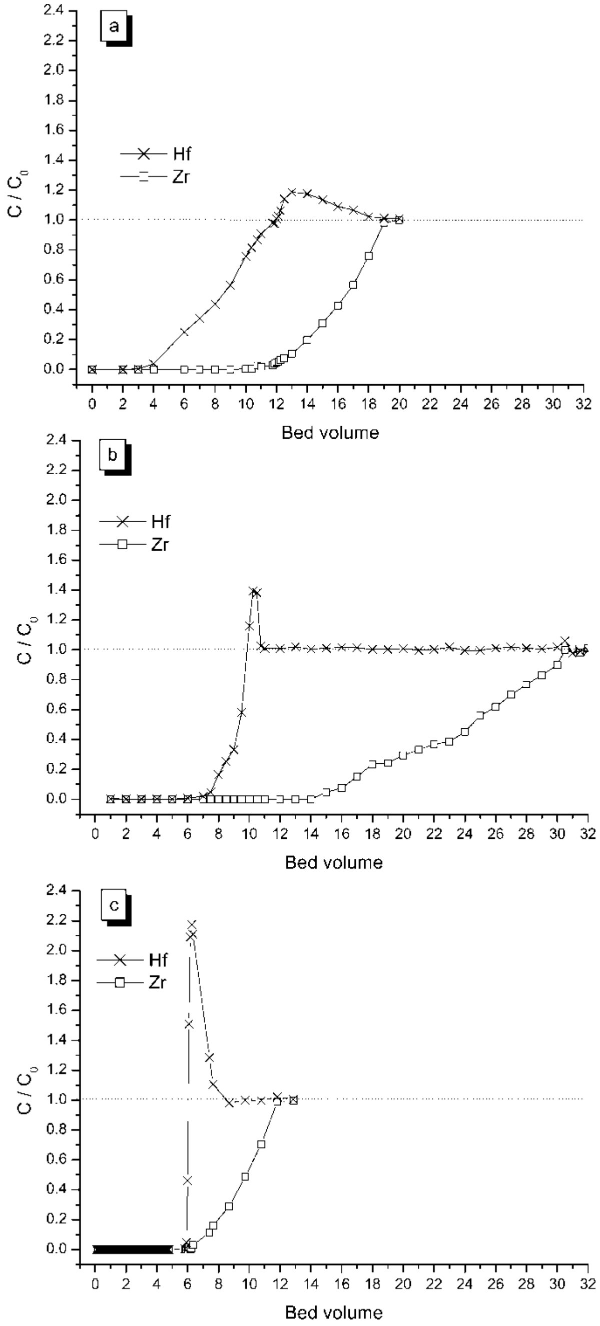

Figure 4. Breakthrough curves for Zr and Hf sorption. Composition of aqueous solution, HCl: 9 mol/L, $[Zr]_{feed} = 2340\ mg \cdot L^{-1}$, $[Hf]_{feed} = 1800\ mg \cdot L^{-1}$, $Zr/(Zr + Hf) = 0.71$, $u = 16$ cm/h @ 25°C. a) Amberjet 4200 Cl, b) PVP, c) HPQ.

carried out by column chromatography. The elution behavior of Zr and Hf was examined by a column adsorption experiment. The results of the loading of the resins by means of an aqueous solution of Zr and Hf in 9.5 M HCl are presented in Fig. 4.

For resin Amberjet 4200 Cl, the initial breakthrough of Hf occurred as early as 3 bed volumes (BVs) because of the relatively low selectivity of Hf for the resin, relative to Zr, when a mixture of Zr and Hf, $Zr/(Zr + Hf) = 0.71$ in a 9.5 M hydrochloric solution was eluted through the resin column (Fig. 4a). After reaching the full breakthrough of 1.0 (C/C_0) at 10 BVs, the Hf concentration became much higher than that in the initial influent solution ($C/C_0 = 1.2$ at 12 BVs). The breakthrough of Zr occurred after 12 BVs of solution had passed through the column and reached a full breakthrough at 20 BVs (Figure 4a). This observation clearly indicates the dynamic competitive sorption and desorption processes as both Hf and Zr are eluted through the Amberjet 4200 Cl resin column. Since the resin was fully loaded with Cl^- as counterions, both Hf and Zr species were adsorbed initially by the resin until the point at which Hf starts to break through (at 3 BVs for the Amberjet 4200 Cl). At this point, the resin continuously adsorbs Zr by competitively displacing previously adsorbed Hf because of the resin's relatively high selectivity for Zr (Fig. 3). This process results in a higher Hf concentration in the effluent than in the influent. This phenomenon is often referred to as the "snowplow" effect (26, 27).

CONCLUSION

Ion exchange and elution characteristics of Zr and Hf in hydrochloric acid by three anion exchangers in both the batch and the column were investigated. The distribution coefficient of Zr and Hf increased significantly with increasing HCl concentration. The adsorption of Zr is considered to result from the formation of anionic chloro-complexes in concentrated hydrochloric acid. The absence of anionic species of Hf, as indicated by its extraction behavior towards anion resins, may be attributed to its electronic configuration, *i.e.* Hf ions are very weakly polarizing. The elution characteristics of Zr and Hf in a packed column with concentrated hydrochloric acid (9.5 M) as eluent showed that those ion-exchange resins could effectively separate Zr and Hf.

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