SEPARATION OF ZIRCONIUM FROM HAFNIUM BY ION EXCHANGE

Elaine C. B. Felipe¹, Hugo G. Palhares¹ and Ana Claudia Q. Ladeira¹

1 Centro de Desenvolvimento da Tecnologia Nuclear (CDTN/CNEN - MG)
Av. Presidente Antônio Carlos, 6.627
31270-901 Belo Horizonte, MG
elainecfelipe@yahoo.com.br, hugopalhares@gmail.com, ana.ladeira@cdtn.br

ABSTRACT

Zirconium and hafnium are two of the most important metals for the nuclear industry. Hafnium occurs in all zirconium ores usually in the range 2 - 3%. However, for the most nuclear industry applications, it is necessary to use a zirconium of extremely pure level. The current work consists in the separation of zirconium and hafnium by the ion exchange method in order to obtain a zirconium concentrate of high purity. The zirconium and hafnium liquors were produced from the leaching of the Zr(OH)₄ and Hf(OH)₄ with nitric acid for 24 hours. From these two liquors it was prepared one solution containing 7.5 x 10⁻² mol L⁻¹ of Zr and 5.8 x 10⁻³ mol L⁻¹ of Hf with acidity of 1 M. Ion exchange experiments were carried out in batch with the resins Dowex 50WX4, Dowex 50WX8 100, Dowex 50WX8 50, Amberlite IR-120 and Marathon C at constant temperature 28 ºC. Other variables such as, acidity and agitation were kept constant. The data were adjusted to Langmuir equation in order to calculate the maximum loading capacity (qₘₐₓ) of the resins, the distribution coefficient (Kₕ) for Zr and Hf and the separation factor (αₗ₃₄). The results of maximum loading capacity (qₘₐₓ) for Zr and Hf, in mmol g⁻¹, showed that the most suitable resins for columns experiments are: Dowex 50WX4 50 (qₘₐₓ Zr = 2.21, Hf = 0.18), Dowex 50WX8 50 (qₘₐₓ Zr = 1.89, Hf = 0.13) and Amberlite (qₘₐₓ Zr = 1.64, Hf = 0.12). However, separations factors, αₗ₃₄, showed that the resins are not selective.

Keywords: Zirconium, hafnium, ion exchange.

1. INTRODUCTION

The Zirconium is a metal of great value for the nuclear industry. Its alloys stand out as coating materials for fuel pellets and nuclear reactors. In the chemical industry zirconium is used in alloys with nickel to obtain materials resistant to corrosion. The impure zirconium oxide is utilized to manufacture bricks for aluminum furnaces in the ceramics industry. In the electronics industry zirconium is used in plates and filaments. Moreover, the alloys of zirconium and niobium may be used in the manufacture of superconducting magnets due to their superconductivity at low temperatures [2].

Hafnium occurs in all zirconium ores in the range 2 - 3%, but the use of zirconium in the nuclear industry requires concentrations less than 100 mg.kg⁻¹ of hafnium (nuclear purity). The separation of the pair Zr/Hf is difficult due to the similarity of their chemical properties such as atomic radius, ionic radius and electronegativity [1]. Hafnium, on the other hand, is also used in the nuclear industry as a constituent of control rods in nuclear reactors due to its high capacity of absorbing neutrons. However, the main application of hafnium is in nickel-based superalloys (1 to 2%) for the fabrication of the turbine blades of aircrafts [2].
The salts of zirconium and hafnium may have valences of 4+, 3+, 2+ or 1+, but in aqueous solution the most common oxidation state is 4+. However, other anionic or cationic species can be formed depending on the acidity of the medium [2-6]. Connick and McVey [7] report that the zirconium and hafnium in very acidic solutions do not suffer hydrolysis, being mainly in the tetravalent form.

Several methods have been used to separate this ionic pair. Such methods include fractional crystallization, ion exchange, fractional distillation, thermal diffusion, solvent extraction and electrochemical separation [1, 2, 5, 8]. The application of the ion exchange in the separation processes of Zr and Hf offers many advantages, since it allows the recovery of ions in very dilute solutions and the capacity to handle large volumes of solutions where operations of precipitation or solvent extraction would be unfavorable.

The current work consists in the separation of zirconium and hafnium by the ion-exchange method in order to obtain a pure zirconium concentrate, suitable to be used in the production the zirconium sponge.

2. METHODOLOGY

2.1. Samples:

Samples of zirconium and hafnium hydroxides for the production of the liquors were provided by the Centro Tecnológico da Marinha em São Paulo (CTMSP). The contents of Zr and Hf in the samples of Zr(OH)₄ and Hf(OH)₄, after characterization by fluorescence spectrometry X-ray energy dispersive (EDX Shimadzu Model 720) are shown in table 1.

<table>
<thead>
<tr>
<th>Hydroxides</th>
<th>Zirconium(%)</th>
<th>Hafnium(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(OH)₄</td>
<td>76.26</td>
<td>0.08</td>
</tr>
<tr>
<td>Hf(OH)₄</td>
<td>11.20</td>
<td>57.30</td>
</tr>
</tbody>
</table>

2.2. Feed solution:

The feed solution containing 7.5 x 10⁻² mol L⁻¹ of zirconium and 5.8 x 10⁻³ mol L⁻¹ of hafnium with acidity of 1M HNO₃ was prepared from liquors obtained from the solubilization of zirconium and hafnium hydroxides.

2.3. Resins:

All resins used were strong cationic in the H⁺ form, functional group -SO₃H (sulfonic acid). Resins, Dowex 50WX4 50-100, Dowex 50WX8 100-200, Dowex 50WX8 50-100, Amberlite IR-120 and Marathon C, were selected conform to the literature [3, 4] and a manufacturers’ guidance according with the affinity for Zr and Hf.
The resins were pre-treated by contact (three times) with 5% hydrochloric acid and washed with distilled water to remove the acid excess. Then the air-dried resins were stored in stoppered glass bottles. [4, 6].

2.4. Ion exchange isotherms:

Ion exchange isotherms were performed with aliquots of 100 mL of the feed solution and the mass of resin ranging from 0.5 to 6.5 g. The suspensions were agitated at 140 min⁻¹ on a horizontal shaker (Marconi-model MA830) with the temperature kept at 28 °C for 24 hours. After agitation, the suspensions were filtered and sent for analysis of metals by fluorescence spectrometry X-ray energy dispersive (EDX Shimadzu Model 720). The amount of Zr and Hf adsorbed by the resins was determined using equation (1).

$$Q_{eq} = (C_i - C_{eq}) \cdot \frac{V}{m}$$  \hspace{1cm} (1)

Where, $Q_{eq}$ is the ion concentration in the solid phase at equilibrium (mmol g⁻¹), $C_i$ is the initial ion concentration in the liquid phase (mmol L⁻¹), $C_{eq}$ is the ion concentration in the liquid phase at equilibrium (mmol L⁻¹), $V$ is the volume of the solution (L) and $m$ is the mass of the exchanger (g). The maximum quantity ($q_{max}$ in mmol g⁻¹) of zirconium and hafnium removed by the different resins was calculated by fitting the data to equation (2) Langmuir [9].

$$Q_{eq} = \frac{q_{max} \cdot b \cdot C_{eq}}{1 + b \cdot C_{eq}}$$  \hspace{1cm} (2)

Where $q_{max}$ is the maximum capacity of the resin (mmol g⁻¹), and $b$ is the Langmuir constant.

The distribution coefficients $K_d$ (mL g⁻¹) are calculated from the isotherms data using Equation (3) cited in Poriel et al. [6],

$$K_d = \left( \frac{C_i - C_{eq}}{C_{eq}} \right) \cdot \frac{V}{m}$$  \hspace{1cm} (3)

The separation factor was calculated using equation (4) which is the ratio of the concentration indices of Zr and Hf in the resin ($\bar{C}_{Zr}, \bar{C}_{Hf}$) and in the liquid phase ($C_{Zr}, C_{Hf}$). If the Zr is preferred for the ion exchange the value of $\alpha_{Zr}^{Hf}$ is >1. The opposite, i.e., $\alpha_{Hf}^{Zr}$<1 means that Hf is preferred [10].

$$\alpha_{Zr}^{Hf} = \frac{\bar{C}_{Zr} \cdot C_{Hf}}{\bar{C}_{Hf} \cdot C_{Zr}}$$  \hspace{1cm} (4)
3. RESULTS AND DISCUSSION

3.1. Ion exchange isotherms:

Ion exchange isotherm was used in the present work to describe the relationship between the amount of zirconium and hafnium adsorbed on the resin and the equilibrium concentration of such metals in the liquid phase at a given temperature. Several authors reported that the use of the Langmuir isotherm in studies of ion exchange involving ions Hf$^{4+}$ and Zr$^{4+}$ has been satisfactory [5,11,12]. The equilibrium data were adjusted to the Langmuir equation (2) in order to determine the $q_{\text{max}}$ (maximum loading capacity) of the resins.

Figure 1 shows the isotherms for each resin and the maximum loading capacity for zirconium ($q_{\text{maxZr}}$) in mmol g$^{-1}$.

![Ion exchange isotherm for Zr](image)

**Figure 1:** Ion exchange isotherm for Zr. [Zr]$_{\text{initial}} = 7.2 \times 10^{-2}$ mol L$^{-1}$ and [Hf]$_{\text{initial}} = 5.6 \times 10^{-3}$ mol L$^{-1}$ for the resin Marathon C and [Zr]$_{\text{initial}} = 7.4 \times 10^{-2}$ mol L$^{-1}$ and [Hf]$_{\text{initial}} = 5.5 \times 10^{-3}$ mol L$^{-1}$ for the other resins, acidity 1 M HNO$_3$.

According to Figure 1, it is observed that the best loadings for zirconium ($q_{\text{maxZr}}$) were presented by the resin Dowex 50WX8 100-200 (2.24 mmol g$^{-1}$), followed by Dowex 50WX4 50-100 (2.21 mmol g$^{-1}$) and Dowex 50WX8 50-100 (1.89 mmol g$^{-1}$). Although Dowex 50WX8 100-200 has shown the highest loading capacity, it was not used in experiments of column with fixed bed, since its low granular size is not recommended to industrial scales.
Figure 2 shows the isotherms for each resin and the maximum loading capacity for hafnium ($q_{\text{max}}$) in mmol g$^{-1}$.

As shown in Figure 2, the resins which showed better ion exchange for hafnium were Dowex 50WX4 50-100, Dowex 50WX8 100-200 and 50WX8 50-100, followed by resins Amberlite IR 120 and Marathon C. The values determined for $q_{\text{max}}$ ranged from 0.12 to 0.18 mmol g$^{-1}$.

The behavior of all the sorption isotherms is considered as extremely favorable, in which it is observed an affinity to the ion and the exchanger along with the reduction of the available sites for ion exchange as the concentration of the ion in the aqueous phase increases [9].

Table 2 shows the values of maximum loading for zirconium and hafnium ($q_{\text{max}}$ in mmol g$^{-1}$) as shown in figures 1 and 2 as well as the distribution coefficient ($K_d$) and separation factor ($\alpha_{\text{Hf}}$) of the resins used.
Table 2: Maximum loading capacity ($q_{\text{max}}$) for Zr and Hf, distribution coefficient ($K_d$) and separation factor ($\alpha_{\text{Zr/Hf}}$) for the resins

<table>
<thead>
<tr>
<th>Resins</th>
<th>$q_{\text{maxZr}}$</th>
<th>$q_{\text{maxHf}}$</th>
<th>$K_d\text{Zr}$</th>
<th>$K_d\text{Hf}$</th>
<th>$\alpha_{\text{Zr/Hf}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dowex 50WX4 50</td>
<td>2.21</td>
<td>0.18</td>
<td>98.61</td>
<td>106.0</td>
<td>0.93</td>
</tr>
<tr>
<td>Dowex 50WX8 100</td>
<td>2.24</td>
<td>0.15</td>
<td>67.52</td>
<td>69.32</td>
<td>0.98</td>
</tr>
<tr>
<td>Dowex 50WX8 50</td>
<td>1.89</td>
<td>0.13</td>
<td>49.75</td>
<td>52.83</td>
<td>0.98</td>
</tr>
<tr>
<td>Marathon C</td>
<td>1.49</td>
<td>0.12</td>
<td>57.39</td>
<td>67.79</td>
<td>0.84</td>
</tr>
<tr>
<td>Amberlite IR 120</td>
<td>1.64</td>
<td>0.12</td>
<td>64.40</td>
<td>68.61</td>
<td>0.98</td>
</tr>
</tbody>
</table>

In general, the resins presented the highest values of $q_{\text{max}}$, (mmol g$^{-1}$) for zirconium. It is assumed that these values are due to the greater availability of this species in the solution, since the concentration of zirconium is much higher than the concentration of hafnium. Xu et al. [12] reported a greater ion exchange capacity for Zr ($q_{\text{max}} = 5.19$ mmol g$^{-1}$) compared to Hf ($q_{\text{max}} = 8 \times 10^{-2}$ mmol g$^{-1}$) when studying Zr / Hf separation using in the resin MIBK (methyl isobutyl ketone). Another study carried out by Donia et al. [11] proposes the use of a chelating magnetic cationic resin to investigate the separation of zirconium and hafnium by using a solution of $2.2 \times 10^{-3}$ mol L$^{-1}$ Zr and $6.1 \times 10^{-3}$ mol L$^{-1}$ Hf and pH 2.5. The results for maximum loading capacity, according to the Langmuir model, were: 0.96 mmol g$^{-1}$ Zr and 0.01 mmol g$^{-1}$ Hf. However, the initial concentrations used in the present work, i.e., $[\text{Zr}] = 7 \times 10^{-2}$ mol L$^{-1}$ and $[\text{Hf}] = 5.8 \times 10^{-3}$ mol L$^{-1}$, are much higher than those investigated by the previous authors and favor a more elevated $q_{\text{max}}$, as verified.

Faghihian and Kabiri-Tadi [13] studied the removal of zirconium by the use of zeolites in the form Na$^+$, K$^+$, Ca$^+$ and also in its natural form through adsorption experiments using solution of $[\text{Zr}] = 10^{-2}$ mol L$^{-1}$, temperature 40° C and pH 1.85. The fit of the data to the Langmuir model presented a maximum loading of zirconium of $9.1 \times 10^{-2}$ mol L$^{-1}$ natural zeolite and $6.7 \times 10^{-2}$ mol L$^{-1}$ zeolite Na$^+$.

The high acidity of the medium may also change the $q_{\text{max}}$ of the metal. According to Xu et al. [12] the ion exchange of Zr and Hf decreases with the increase in acidity of the medium (> 2.5 M) due to the competition of H$^+$ for the resin sites. Therefore, all ion exchange experiments of the present work were carried out in acidity of 1 M favoring a higher loading of Zr and Hf.

The distribution of Zr and Hf in the resin was determined according to their respective distribution coefficients ($K_d$). The values of $K_d$, indicated in Table II show that hafnium distribute slightly better than zirconium in all resins, confirming that they have a higher affinity to Hf compared to Zr. Conversely, Poriel et al. [6] obtained a $K_{d\text{Zr}} = 90.4$ and $K_{d\text{Hf}} = 8.7$ in studies of separation of Zr / Hf using anionic resins in solution of $[\text{Zr}] = 2.1 \times 10^{-2}$ mol L$^{-1}$, $[\text{Hf}] = 8.7 \times 10^{-3}$ mol L$^{-1}$ and acidity of 9.5 M HCl.

The preference of the ion exchanger for one of the ions present in the solution can also be expressed by the separation factor $\alpha_{\text{Zr/Hf}}$. If the Zr ion is preferred by the ion exchanger the value of $\alpha_{\text{Zr/Hf}}$ should be $> 1$, otherwise $\alpha_{\text{Zr/Hf}} <1$. However, despite the high concentration of Zr in solution, the resins do not correspond to the expectation of a
greater selectivity for Zr in relation to Hf. This fact can be verified by values close to 1 for the separation factors ($\alpha_{\text{Hf}}^{\text{Zr}}$). Despite being close to 1, all the values of $\alpha_{\text{Hf}}^{\text{Zr}}$ are <1, which means the resins present a higher tendency to be more selective for hafnium. Based on table II it may be affirmed that the resin which best separated hafnium was the Marathon C $\alpha_{\text{Hf}}^{\text{Zr}}=0.84$. The other resins, although have presented $\alpha_{\text{Hf}}^{\text{Zr}}$<1, do not exhibit a great performance since the separation factor is very close to 1.

The literature presents few data about separation factors regarding the pair Zr and Hf. Studies of Donia et al. [11] with a synthetic solution of $[\text{Zr}] = 2 \times 10^{-3}$ mol L$^{-1}$ and $[\text{Hf}] = 6 \times 10^{-5}$ mol L$^{-1}$ and an industrial solution of $[\text{Zr}] = 4.8 \times 10^{-3}$ mol L$^{-1}$ and $[\text{Hf}] = 3 \times 10^{-4}$ mol L$^{-1}$ at pH = 2.5 show that the magnetic cationic resin is more selective for Zr than to Hf, since the separation factors are $\alpha_{\text{Hf}}^{\text{Zr}} = 5$ and $\alpha_{\text{Hf}}^{\text{Zr}} = 6$, respectively.

The selectivity of the resin increases with the increasing of the ion valence, since this ion is strongly attracted to the fixed ions of the resin. The atomic number also favors the selectivity of the resin, i.e., the higher the atomic number, the greater the preference of the resin for this ion [7]. Zirconium and hafnium exhibit valence 4+, so there would be no preference for the ions, but the hafnium has atomic number ($Z = 72$) greater than the Zr ($Z = 40$), making it the preferable ion for the resins, confirming values of $\alpha_{\text{Hf}}^{\text{Zr}}$<1 for the resins assessed. The increase in crosslinking also increases the selectivity of the resins. Large counter ions may be sterically excluded from the narrow pores of the exchanger [14]. All resins have about 8% of divinylbenzene (DVB) crosslinking, except Dowex 50WX4 (4% DVB) [10]. However, analyzing the $\alpha_{\text{Hf}}^{\text{Zr}}$ the latter did not present less selective as expected.

4. CONCLUSION

The results of the maximum loading capacity determined by Langmuir isotherms showed that the resins presented higher loadings for Zr. However, all the resins show a slightly greater selectivity for hafnium. This fact is supported by the values of $\alpha_{\text{Hf}}^{\text{Zr}}$<1, mainly for the resin Marathon C whose value of $\alpha_{\text{Hf}}^{\text{Zr}}$ is 0.84; the lowest one. The resins Dowex 50WX4, 50WX8 100, and 50WX8 50 did not present a good performance, although they are commercial resins recommended for the separation of the pair Zr / Hf by chromatography. Column experiments are in progress, which will assess the selective elution of Zr and Hf as to enable the use of these resins to separate ion pair studied. Thus, the next step should determine the optimum operational parameters such as type of eluate, flow rate, residence time, bed height, among others.

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