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Liquid–liquid separation of zirconium and hafnium from nitric liquor in order to obtain nuclear zirconium oxide using TBP as extractant

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ABSTRACT

A specific process to obtain nuclear grade zirconium oxide from a nitric acid liquor is described in this work. The liquor was obtained after alkali fusion and water leaching of a zircon concentrate. The production of nuclear zirconium oxide is possible when tributyl phosphate (TBP) is used as extractant with a high acidity nitric liquor. This study comprises steps: (i) batch experiments in order to select the best conditions for the process and (ii) continuous experiments carried out in counter current mixer-settler circuits. The batch experiments indicated that an increase in nitrate concentration did not correspond to a rise in the separation factor among Zr and Hf. Acidity has a significant influence on the Zr/Hf separation. For the organic phase containing 2.5 mol L^{-1} of TBP and an aqueous/organic ratio of the 1/1, 94% of the Zr was extracted and a separation factor of the 13.8 was obtained in one contact of the aqueous and organic phase. In the optimized continuous circuit, a product containing 99% of Zr and 0.03% of Hf (200 mg kg^{-1}), which meets the nuclear zirconium specifications, was obtained.

KEYWORDS

Continuous experiments;
Hafnium; Solvent extraction;
Tributyl phosphate;
Zirconium; Zirconium/
Hafnium separation

Introduction

Due to the high chemical similarity between zirconium and hafnium, higher than for any other pair of elements in the periodic table, their separation requires an elaborate process. Among the known commercial processes to separate zirconium and hafnium, there are four industrially used, namely fractional crystallization, solvent extraction, chloride distillation, and ion exchange (Xu et al. 2015; Amaral and Morais 2016; Pandey et al. 2016). Among these processes, the solvent extraction is an operation used in industry for purification, separation, or concentration of several species. Through this technique, it is possible to obtain products with high purity and to separate several metals.

The production of zirconium and hafnium for nuclear processes is subject to strict industry specifications. For example, we can cite the fact that the zirconium sponge for nuclear use should not have hafnium contents higher than 100 mg kg^{-1} , and in the

zirconium oxide for nuclear use, the hafnium limit should be 200 mg kg^{-1} (ASTM International 2015, 2016).

Although solvent extraction is applied in the separation and concentration of the zirconium, the separation of zirconium and hafnium is still very difficult and of great value. Several studies in the literature have reported the use of the solvent extraction with different extractants and in several media for the separation of the pair Zr/Hf, as shown in Table 1. Various extracts have been evaluated in the Zr and Hf separation presenting good separation factors between these elements. However, it should be noted that in some cases shown in Table 1, the concentrations of these elements in the liquors studied is very small, between 0.045 and 0.1 g L^{-1} of Zr and 0.005 and 0.2 g L^{-1} of Hf, which does not correspond to concentrations used in industrial processes. In this study, concentrations of approximately 20 g L^{-1} of Zr and 0.4 g L^{-1} of Hf were used in the batch experiments, while in the

Table 1. Separation factors of zirconium and hafnium for different media with different types of extractants.

Medium	Concentration (mol L ⁻¹)	Zr and Hf (g L ⁻¹)	Extractant	SF Zr/Hf	Reference
Hydrochloric	8.0 HCl	0.2 and 0.2	ALAMINE 336	91.7	Banda, Lee, and Lee, 2012
Hydrochloric	4.0 HCl and 1.0 HCl	0.2 and 0.2	CYANEX 272 TOPO/CYANEX 272	8.7 6.3	Wang, Lee, and Lee, 2013
Hydrochloric	4.0 HCl	20.5 and 0.4	TBP/CYANEX 923	14.5	Amaral and Morais, 2016
Nitric and hydrochloric	2.0 HNO ₃ and HCl	0.045 and 0.005	CYANEX 272	8.16	Taghizadeh et al., 2008
Nitric	3.0 HNO ₃	26 and 0.5	TBP/CYANEX 923	12.3	Taghizadeh et al., 2011
Nitric	2.0 HNO ₃	1.0 and 0.2	LIX 63	186	Wang and Lee, 2014
Nitric	2.0 HNO ₃	0.2 and 0.2	PC88 and LIX63	46	Wang et al., 2015
Nitric	4.0 HNO ₃	20.5 and 0.4	TBP/CYANEX 923	9.0	Amaral and Morais, 2016
Nitric	7.0 HNO ₃	20.5 and 0.4	TBP	16.1	Amaral and Morais, 2016
Sulfuric	0.5 H ₂ SO ₄	0.2 and 0.2	ALAMINE 308	12.4	Wang and Lee, 2015

continuous experiments, a concentration of 58 g L⁻¹ of Zr and 1.6 g L⁻¹ of Hf was used.

As shown in Table 1, for concentrations of Zr and Hf that can correspond to an industrial process, the best results were obtained using tributyl phosphate (TBP) or a mixture of TBP and CYANEX 923. As demonstrated by Amaral and Morais (2016), the stripping of the metals from TBP/CYANEX 923 mixture is very difficult.

TBP is one of the most known and widely used extractant in nuclear materials processing. However, equations for metal extraction systems are not well-defined. These systems are quite complex, with few of the species formed well-defined and with few similarities among different systems.

In this work, the study of the Zr and Hf separation was carried out with TBP in nitric media through the analysis of discontinuous and continuous experiments and of the possible chemical reactions involved in this process.

Experimental part

Reagents and solutions

The feed solution used in this work was generated by alkaline digestion and subsequent nitric leaching of the zircon. The zircon used in this study was supplied by Indústrias Nucleares do Brasil (INB). The liquor containing Zr and Hf was produced by zircon fusion with sodium hydroxide (NaOH). Prior to the dissolution processes, the silica was removed from the liquor by water leaching. After the washing, the product of the zircon fusion was dissolved in nitric acid (HNO₃) (Amaral and Morais, 2016). Table 2 presents the chemical composition of the leach liquors used in the discontinuous experiments and continuous experiments, respectively. The

pH of the solution was adjusted by adding nitric acid and the nitrate concentration was adjusted by adding sodium nitrate (NaNO₃), according to the medium and acidity of each experiment (Amaral 2015; Amaral and Morais, 2016).

All aqueous solutions used in this work were prepared with distilled water and the reagents used were of analytical grade. In all the stages of the experiments, the concentrations of zirconium, hafnium, nitrates, as well as the acidity were determined by energy dispersive X-ray fluorescence spectrometry-EDXRF (Shimadzu EDX 720), molecular absorption spectrophotometry in the ultraviolet region (302 nm) using a UV-visible spectrophotometer (Varian Cary 50) and potentiometry using a pH-meter (Digimed DM 22) (Amaral and Morais, 2016). The relative standard deviation (RSD) for the analysis of the zirconium and hafnium from EDX and ICP-OES were 2.5 and 5%, respectively.

Discontinuous experiments

The discontinuous experiments were carried out in 150 mL beakers under mechanical agitation (330–350 rpm) using IKA agitators, model RW20, at 25 °C (±2) and with contact time between phases of 15 min. Subsequently, the aqueous phase and organic phase were separated with a separation funnel and then analyzed for Zr and Hf contents. The volumetric ratio between the aqueous and the organic phases was equal to 1, except when specified in the test (Amaral and Morais, 2016).

Continuous experiments

A continuous counter-current extraction and stripping experiment was also carried out. This

Table 2. Chemical composition of the liquors used in the discontinuous and continuous experiments.

Liquor	Species						
	Zr ⁴⁺ g L ⁻¹	Hf ⁴⁺ g L ⁻¹	NO ₃ ⁻ mol L ⁻¹	H ⁺ mol L ⁻¹	Fe ³⁺ g L ⁻¹	Na ⁺ g L ⁻¹	Si ⁴⁺ g L ⁻¹
Discontinuous experiments	20.5	0.4	^a	^a	0.6	22	2.8
Continuous experiments	58.6	1.6	9.8	7.9	3.0	0.20	0.19

^aIon concentration was varied according to the experimental plan.

was done in a sequence of mixer-settler stages at CDTN (Nuclear Technology Development Center), with 70 mL in the mixers and 260 mL in the settlers. About 2.5 mol L⁻¹ of TBP was used as extractant agent. In the experiment, six extraction stages, 10 washing stages and 6 stripping stages were used. In the extraction steps of the continuous experiment, the acidity of the aqueous solution decreases along the process. Therefore, in the fourth stage of the extraction step, nitric acid was added in order to keep the acidity at 7.9 mol L⁻¹. This acidity is the optimal condition to promote the separation of zirconium and hafnium. The system stability was controlled through the determination of the zirconium and hafnium contents, every hour, in the outputs. Figure 1 shows schematically, in a simplified way, the steps used in continuous process, with their respective inputs and outputs.

Theoretical aspects

During the solvent extraction experiments, some parameters were used for the evaluation of the system characteristics. These parameters are extraction percentage (%E), distribution ratio (D), and separation factor (SF). The extraction percentage (%E) was calculated from the relation (Equation (1)).

$$\% E = \frac{M_{ia} - M_{fa}}{M_{ia}} \times 100 \quad (1)$$

where M_{ia} (initial aqueous metal) is the metal ion concentration in aqueous feed before extraction and M_{fa} (final aqueous metal) is the metal ion concentration in the aqueous phase after extraction. The distribution ratio (D) was calculated from the relation (Equation (2)).

$$D = \frac{M_{ia} - M_{fa}}{M_{fa}} = \frac{M_o}{M_{fa}} \quad (2)$$

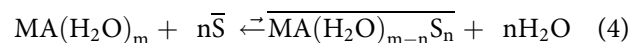
where M_o is the metal ion concentration in the organic phase after extraction. For the separation

factor (SF) the following relation was used (Equation (3)).

$$SF = \frac{D_x}{D_y} \quad (3)$$

where D_x is the distribution factor of the metallic species X (Zr) and D_y is the distribution factor of the metallic species Y (Hf).

Metal extraction by solvating extractants depends on the capacity of the metallic ions to create neutral species or complexes in the aqueous phase; these species are then extracted through a mechanism of solvation of the formed complexes or inorganic molecules according to Equation (4). These species are more soluble in the organic phase. In nitric medium, zirconium is extracted preferentially by TBP, while hafnium is less likely to be extracted by this extractant (Wang and Lee 2014).



where MA is the metallic ionic pair; \bar{S} is the extractant in organic phase and $\overline{MA(H_2O)_{m-n}S_n}$ is the complex in organic phase.

In aqueous systems, zirconium and hafnium may be present in either their M^{4+} or MO^{2+} forms. Studies presented in the literature indicate the absence of the zirconyl ion (ZrO^{2+}) in aqueous solution with high acidity and in solids. The results of these studies show that, even in monoclinic zirconium oxide, the Zr-O-Zr are present instead of the double bond Zr=O [Nuclear Energy Agency (NEA) 2005]. Zirconium and hafnium ions have a tendency to hydrolyze in aqueous solutions due to their high charge and small radius (0.74 Å for Zr⁴⁺ and 0.75 Å for Hf⁴⁺) (Elinson and Petrov 1969). Simple salts of zirconium such as halides and nitrates, react violently with water to form strongly acidic solutions. The nature of ions in the zirconium solutions depend on the hydrogen concentration, and Equation (5) shows the equilibrium established in the aqueous

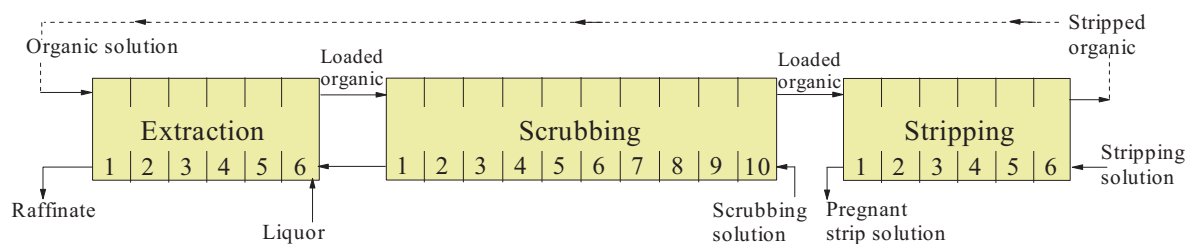
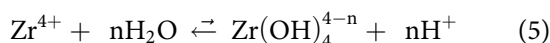
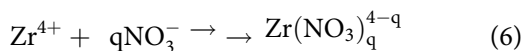


Figure 1. Schematic Diagram of the steps carried out in the continuous process.

solution (NEA 2005). According to Equation (5), the number of hydroxyl groups increases with low acidity, while at high acidity, the quadrivalent zirconium ions (Zr^{4+}) are the predominant species.



The study of the ratio between the hydrolysis and the formation of complexes of zirconium and hafnium in mineral acids solutions is of considerable interest. The hydrolysis of zirconium and hafnium in solution is directly linked to the formation of polymeric compounds. These polymeric compounds have a strong influence on the state and behavior of the zirconium and hafnium ions in the solutions. The polymerization process may explain specific chemical characteristics of aqueous solutions of zirconium and hafnium compounds. Zr^{4+} and Hf^{4+} have a high tendency for the formation of complexes, due to their high charge, small ionic radius and relatively low ionization potential. Therefore, Zr^{4+} and Hf^{4+} ions may form complexes with NO_3^- in acidic solutions, according to Equation (6) (NEA 2005; Taghizadeh et al. 2008).



Results and discussion

Extraction step

Influence of the acidity

According to the literature, at acidities from 6 to 12 mol L^{-1} , zirconium can be found in the form of neutral compounds (Wang et al. 2013). It is known that solvating extractants such as TBP show preferential extraction of these species. Thus, the behavior of TBP in separating Zr/Hf was evaluated using 3.0 mol L^{-1} of TBP while the acidity was varied from 1.0 to 10 mol L^{-1} . Figure

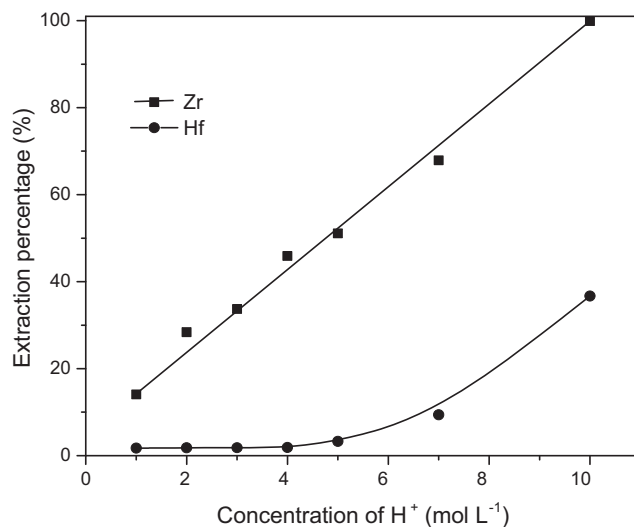


Figure 2. Influence of the acidity on the extraction of zirconium and hafnium. [TBP] = 3.0 mol L^{-1} . Aqueous phase: 15.0 g L^{-1} of Zr, 0.3 g L^{-1} of Hf, $[H^+] = 1.0\text{--}7.0$ mol L^{-1} , 25 °C (± 2).

Table 3. Influence of the acidity on the separation factor of Zr/Hf.

H^+ (mol L^{-1})	1.0	2.0	3.0	4.0	5.0	7.0	10
Separation factor (SF)	0.71	1.63	3.60	10.2	13.4	16	51

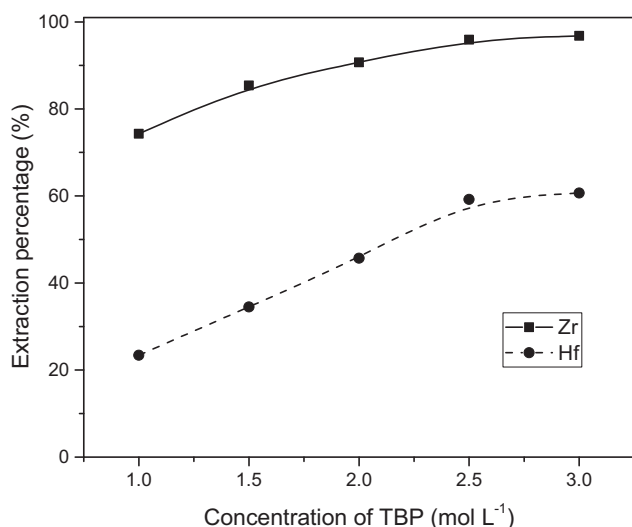
[TBP] = 3.0 mol L^{-1} . Aqueous phase: 15.0 g L^{-1} of Zr, 0.3 g L^{-1} of Hf, $[H^+] = 1.0\text{--}7.0$ mol L^{-1} , 25 °C (± 2).

2 shows the results of zirconium and hafnium extraction and Table 3 shows the separation factor for this pair of elements. It was observed that both the extraction percentage and the separation factor increased with acidity. When TBP was used in an acidity of 7.0 mol L^{-1} , the zirconium extraction percentage increased significantly, while the separation factor remained constant (Table 3). Although Hf extraction in 10 mol L^{-1} of acid was high, reaching 40%, this fact is not relevant, since the objective of this work is the separation of Zr and Hf. The results indicated that the best separation factors occurred when acidities greater than 7.0 mol L^{-1} were used; however, an optimal separation factor and best

Table 4. Stability constants for zirconium and hafnium complex formation in nitric acid medium.

	Ionic strength	Stability constants (K)
$\text{Hf}(\text{NO}_3)_q^{4-q}$	2	$K_1=0.458, K_2=1, K_3=5.26, K_4=33.3$
	4	$K_1=0.12, K_2=3.6 \times 10^{-2}, K_3=1.3 \times 10^{-2}, K_4=8.4 \times 10^{-3}, K_5=8.3 \times 10^{-3}, K_6=1.6 \times 10^{-2}$
$\text{Zr}(\text{NO}_3)_q^{4-q}$	2	$K_1=1.09, K_2=2$
	4	$K_1=0.45, K_2=1.71, K_3=2.36, K_4=3.66$

CALETKA, 1964 cited by Taghizadeh et al. (2008), 118.

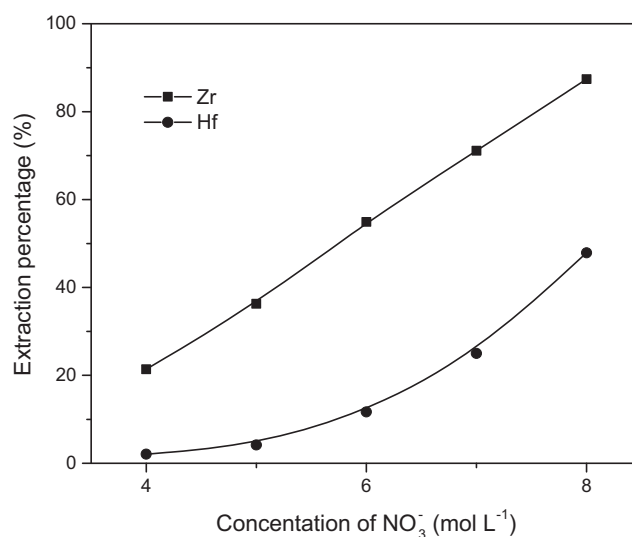
**Figure 3.** Influence of the TBP concentration on the extraction of zirconium and hafnium. [TBP] = 1.0–3.0 mol L⁻¹. Aqueous solution: 20.5 g L⁻¹ of Zr, 0.4 g L⁻¹ of Hf, [H⁺] = 7.9 mol L⁻¹, [NO₃⁻] = 9.8 mol L⁻¹, 25 °C (±2).**Table 5.** Influence of the TBP concentration on the separation factor of Zr/Hf.

[TBP] (mol L ⁻¹)	1.0	1.5	2.0	2.5	3.0
Separation factor (SF)	9.4	11	13	16	20

[TBP] = 1.0–3.0 mol L⁻¹. Aqueous phase: 20.5 g L⁻¹ of Zr, 0.4 g L⁻¹ of Hf, [H⁺] = 7.9 mol L⁻¹, [NO₃⁻] = 9.8 mol L⁻¹, 25 °C (±2).

performance in the zirconium extraction was obtained in an acidity of 7.0 mol L⁻¹. Therefore, this condition was chosen for conducting the stripping experiments.

According to Taghizadeh et al. (2008) zirconium stability constants (Table 4) show that in systems presenting high ionic strength ($\mu=4$), zirconium tends to form neutral complexes [Zr(NO₃)₄], which are preferably extracted by solvating extractants such as TBP. In the case of hafnium, in the system with high ionic strength ($\mu=4$), their stability constants do not favor the formation of neutral species, making it difficult

**Figure 4.** Influence of the nitrate concentration on the extraction of zirconium and hafnium. Aqueous solution: 11.52 g L⁻¹ of Zr, 0.240 g L⁻¹ of Hf, 4.0 mol L⁻¹ of H⁺, [NO₃⁻] = 4.0–8.0 mol L⁻¹. Organic solution: 2.5 mol L⁻¹ TBP; 25 °C (±2).

to extract this element with TBP, when compared to zirconium. This fact justifies the increase in separation factor when TBP was used and when the acidity of the medium, and consequently its ionic strength, was increased.

Influence of the TBP concentration

The effect of the TBP concentration was investigated in the 1.0–3.0 mol L⁻¹ interval. Results of the extraction percentage are shown in Figure 3 and separation factors are presented in Table 5. In these experiments, the concentration of H⁺ was 7.9 mol L⁻¹, nitrate concentration was 9.8 mol L⁻¹ and zirconium and hafnium concentration were 20.5 g L⁻¹ and 0.4 g L⁻¹, respectively. It was observed that extraction of Zr is greater than extraction of Hf for all TBP concentrations evaluated. According to the literature, when organophosphorus extractants are used to extract metals with the same charge, extraction is inversely proportional to the ion radius, that is, for smaller ions the extraction is more effective (Souza Junior et al. 2012). Another factor to be considered is that when Zr is extracted by TBP in media with high acidity and ionic strength, it tends to form neutral species which can be more easily extracted than the species formed by hafnium, as detailed in Table 4. However, during the experiments using solutions with TBP

concentration of 1.0 and 2.0 mol L⁻¹, the formation of a third phase was observed, but not when TBP at 2.5 and 3.0 mol L⁻¹ was used. The good experimental results obtained for the TBP in a concentration of 2.5 mol L⁻¹ led to the continuation of the work using TBP as extractant at this concentration.

Influence of the nitrate concentration

The influence of the nitrate concentration in the separation of Zr and Hf was evaluated in the interval from 4.0 to 8.0 mol L⁻¹ of NO₃⁻. Other variables were kept constant. The concentration of the elements in the aqueous solution were 11.52 g L⁻¹ for Zr, 0.240 g L⁻¹ for Hf, and 4.0 mol L⁻¹ for H⁺, TBP concentration in the organic phase was 2.5 mol L⁻¹. The adjustment of the nitrate concentration in the aqueous phase was carried out by the addition of sodium nitrate (NaNO₃). In order to adjust the nitrate concentration, the aqueous phase was diluted; therefore, the concentration of the metals Zr and Hf, and of H⁺ were smaller than in others experiments. Figure 4 shows the percentage of zirconium and hafnium extraction as a function of nitrate concentration in the aqueous phase, and in Table 6, the respective separation factors are presented. It can be observed that the extraction yields for both metals increased with the increase in the nitrate concentration. The extraction percentage increased from 21.4 to 87.4% (zirconium) and 2.08 to 47.9% (hafnium), when the nitrate concentration was investigated in the range from 4 to 8 mol L⁻¹. The results presented in Table 6 show that an increase in nitrate concentration did not correspond to an increase in the separation factor. Therefore, it does not influence the separation of zirconium and hafnium.

These results are in concordance with a study carried out by Taghizadeh et al. (2011), which evaluated the influence of the nitrate concentration in Zr/Hf separation by using a mixture of TBP and CYANEX 923. The data obtained by the authors show that the increase in the nitrate concentration increased both zirconium and hafnium extraction, and the optimal separation factor was obtained with 3.5 mol L⁻¹ of NO₃⁻. In the

Table 6. Influence of the nitrate concentrate on the zirconium and hafnium separation.

[NO ₃ ⁻] (mol L ⁻¹)	4.0	5.0	6.0	7.0	8.0
Separation factor (SF)	12.8	12.6	7.80	7.36	7.53

Aqueous solution: 11.52 g L⁻¹ of Zr, 0.240 g L⁻¹ of Hf, 4.0 mol L⁻¹ of H⁺, [NO₃⁻] = 4.0–8.0 mol L⁻¹. Organic solution: 2.5 mol L⁻¹ of TBP; 25 °C (±2).

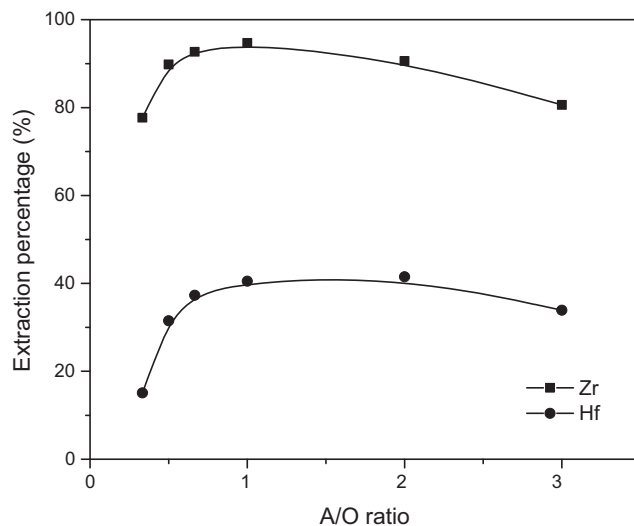


Figure 5. Influence of the A/O ratio on the zirconium and hafnium extraction. Aqueous solution: 22.5 g L⁻¹ of Zr, 0.4 g L⁻¹ of Hf, 7.9 mol L⁻¹ [H⁺], 9.8 mol L⁻¹ [NO₃⁻]. Organic solution: 2.5 mol L⁻¹ of TBP, 25 °C (±2).

Table 7. Influence of the A/O ratio on the zirconium and hafnium separation.

A/O	1/3	1/2	1/1.5	1/1	2/1	3/1
Separation factor (SF)	19.6	19.2	21.3	13.8	10.4	8.1

Aqueous solution: 22.5 g L⁻¹ of Zr, 0.4 g L⁻¹ of Hf, 7.9 mol L⁻¹ [H⁺], 9.8 mol L⁻¹ [NO₃⁻]. Organic solution: 2.5 mol L⁻¹ of TBP, 25 °C (±2).

present work, the best condition was obtained with between 4.0 and 5.0 mol L⁻¹ of nitrate.

Influence of the aqueous/organic ratio

Extraction experiments were carried out by varying the aqueous/organic phase ratio (A/O) from 1/3 to 1/2, 1/1.5, 1/1, 2/1, and 3/1. In these experiments, TBP was used in concentration of 2.5 mol L⁻¹, the acidity remained 7.9 mol L⁻¹ and the nitrate concentration remained 9.8 mol L⁻¹, the concentration of Zr and Hf were 20.5 g L⁻¹ and 0.4 mol L⁻¹, respectively. The results are shown in Figure 5 and Table 7. When A/O ratios of 2/1 and 3/1 were used, a third phase formed, and separation was difficult. This occurred due to the saturation of the organic phase, and it may also have caused a decrease in

Table 8. Stripping of the Zr and Hf with water and H₂SO₄ from TBP loaded with 10.79 g L⁻¹ of Zr and 0.18 g L⁻¹ of Hf, 25 °C (±2).

Stripping solution	Concentration (mol L ⁻¹)	Stripping (%)		
		Zr	Hf	FS
H ₂ O	–	90.19	59.82	6.20
H ₂ SO ₄	0.1	89.73	33.92	17.0
H ₂ SO ₄	0.5	93.48	45.17	17.1
H ₂ SO ₄	1.0	91.92	42.22	17.2
H ₂ SO ₄	2.0	92.99	42.22	17.6
H ₂ SO ₄	4.0	99.22	45.00	22.2

the separation factor. Figure 5 shows that when A/O ratio was increased, the extraction of Zr and Hf also increased. At A/O ratio of 1/1, about 94% Zr and 56% Hf were obtained. When TBP concentration remains constant, an increase in the initial metal concentration decreases its distribution in the organic phase. This was observed that when the A/O ratio was increased from 1/1 to 3/1, as show in the Figure 5. According to NEA (2005) an increase in the zirconium concentration favors polymerization of this metal, it forms species which are more stable in the aqueous phase than in the organic phase, making the distribution of metal in the organic phase difficult.

Stripping step

Stripping experiments were carried out from the organic phase generated in the extraction step. These experiments had the purpose of evaluating the recovery of the metals from this medium. The stripping test was performed using distilled water (H₂O) and sulfuric acid (H₂SO₄) at concentrations ranging from 0.1 to 4 mol L⁻¹ and. Organic solutions used in the stripping experiments were generated in experiments with 3.0 mol L⁻¹ of TBP and feed acidity of 10 mol L⁻¹. Sulfuric acid solutions were used in the stripping experiments to accomplish the complexation of the zirconium, favoring the return of this metal to the aqueous phase. Complexes formed with sulfates are more stable in aqueous solution than nitrate complexes, according to Equations (7) to (11) (NEA 2005). Distilled water was also used, since it is widely used in the stripping of solvating extractants. The sulfuric acid was used at the concentrations 0.1, 0.5, 1.0, 2.0, and 4.0 mol L⁻¹.

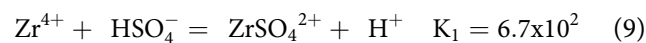
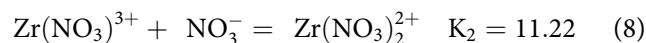
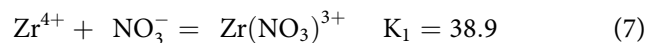


Table 8 shows the extraction percentages from the loaded organic phase for zirconium and hafnium. The organic phase was loaded with 10.79 g L⁻¹ of zirconium and 0.18 g L⁻¹ of hafnium. It can be observed that for every condition evaluated, the extraction yield of Zr was high (89.73–99.22%), even when water was used as stripping solution. The best separation factors were obtained when sulfuric acid was used for every condition evaluated; however, the objective is the separation of these metals in the extraction step. It was preferred to use water in the stripping step; however, due to technical problems during the continuous experiments, sulfuric acid was selected to be evaluated as the stripping solution in the continuous process.

Equilibrium curve: extraction and stripping

In the next step of the study, an extraction isotherm (equilibrium curve) was constructed and a McCabe–Thiele diagram was drawn to determine the number of theoretical stages and the volumetric feeding ratio of the liquor and type of solvent for continuous experiments. The equilibrium curve was constructed according to the successive contacts technique for organic phase loading and aqueous phase depletion. The TBP concentration in the solvent was 2.5 mol L⁻¹. The zirconium extraction isotherm and McCabe–Thiele diagram are shown in Figure 6(a). As shown in Figure 6(a), for a volumetric feeding liquor/solvent ratio of 2.0, to obtain a raffinate containing 0.08 g L⁻¹ of Zr, four mixer-settler stages are required. Under such condition, it would be possible to obtain a loaded solvent containing 32 g L⁻¹ of Zr.

Based on laboratory experimental results, the stripping isotherm (equilibrium curve) was constructed and a McCabe–Thiele diagram was drawn to determine the theoretical number of stages and the volumetric feed ratio of the

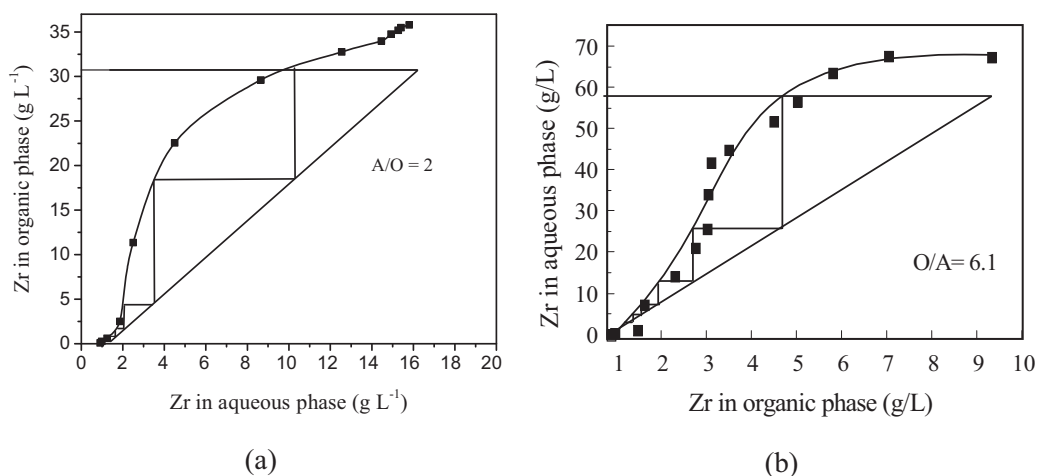


Figure 6. Extraction (a) and stripping (b) isotherm of the zirconium/McCabe–Thiele diagram. (a) 2.5 mol L⁻¹ of TBP. Aqueous phase: 15.7 g L⁻¹ of Zr; 0.32 g L⁻¹ of Hf; 7.0 mol L⁻¹ of H⁺; 9.8 mol L⁻¹ of NO₃⁻ and 25 °C (±2). (b) Aqueous phase: sulfuric acid 3.0 mol L⁻¹. Organic phase: 2.5 mol L⁻¹ of TBP loaded with 10.3 g L⁻¹ of Zr at 25 °C (±2).

liquor and solvent for the continuous experiments. The equilibrium curve was constructed according to the successive contacts technique using phase ratio of 1/1. Sulfuric acid at 3.0 mol L⁻¹ was used as stripping agent. The McCabe–Thiele diagram is shown in Figure 6(b). For a volumetric organic/aqueous ratio of 6.1 in the feed, obtaining a Zr-free organic phase requires at least six mixer-settler stages. Under such conditions, it would be possible to obtain a stripping solution containing 67.3 g L⁻¹ of Zr. According to Ritcey and Ashbrook (1984), for the type of isotherm presented in Figure 6, it is apparent that the raffinate from such a system will always have a high concentration of metals. Thus, in this case, a high number of extraction stages is required in order to obtain a raffinate free of zirconium.

Continuous experiment

A continuous experiment was used to optimize the separation of Zr and Hf. This was carried out using TBP as extractant, in a counter-current system using a sequence of mixer-settler units, with mixers of 70 mL and settlers of 260 mL. In the continuous experiment the variables studied were: number of stages in the extraction and stripping steps; and organic/aqueous ratio in all steps. The experimental

Table 9. Condition used in the continuous experiment.

Step	Reagent		Flow (mL/min)		Number of stages
	Type	Conc.	Aqueous	Organic	
Extraction	TBP	2.5 mol L ⁻¹	2.0	7.0	6
Washing	HNO ₃	5.5 mol L ⁻¹	2.0	7.0	10
Stripping	H ₂ SO ₄	2.5 mol L ⁻¹	1.0	7.0	6

set-up comprised three steps: extraction, scrubbing, and stripping (Figure 1). Variables were progressively adjusted. Table 2 shows the chemical composition of the zircon liquor, and Table 9 shows the conditions of the continuous experiment.

The experiment was carried out in six extraction stages, ten washing stages and six stripping stages for 105 h. The contact time was 7.78 min in the mixer for the extraction stages, 7.78 min for the washing stages, and 8.75 min for the stripping stages. The concentration profiles of the metals in the aqueous and organic phase are shown in Figure 7(a,b). The aqueous/organic ratio was 1/3.5 in the extraction step, 1/3.5 in the washing step, and 1/7 in the stripping step. In the extraction step, zirconium and hafnium concentrations in the organic phase were 18.64 g L⁻¹ and 1.05 g L⁻¹, respectively, whereas in the raffinate, they were 0.15 g L⁻¹ of Zr and 0.35 g L⁻¹ of Hf. In the washing step, the concentrations in the loaded organic were 13.7 g L⁻¹ of Zr and <0.01 g L⁻¹ of Hf, indicating that a part of Zr was removed in this step. The concentration of the metals in the pregnant strip solution was 56 g L⁻¹ for Zr and <0.01 g L⁻¹ for Hf. Therefore,

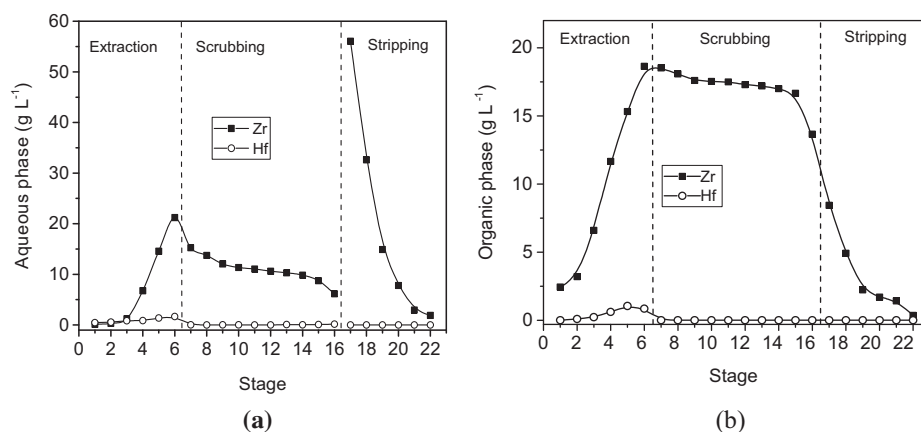


Figure 7. Profile of the zirconium and hafnium concentration in the aqueous (a) and organic (b) phase from continuous experiment.

Table 10. Composition of the oxide obtained from continuous experiment.

Component	Oxide (%)	Individual element in total ZrO ₂ (%)	Concentration mg kg ⁻¹ powder obtained	Maximum concentration limit (mg kg ⁻¹ powder) ^a
Zr	99	–	–	–
Hf	0.03	0.02	200	200
Si	0.4	0.19	1900	2000
Fe	0.1	0.07	700	1000
Al	<0.01	<0.005	<50	1500
Ti	<0.01	<0.006	<60	100
Ca	0.18	0.12	1200	3000

^aASTM International, 2015.

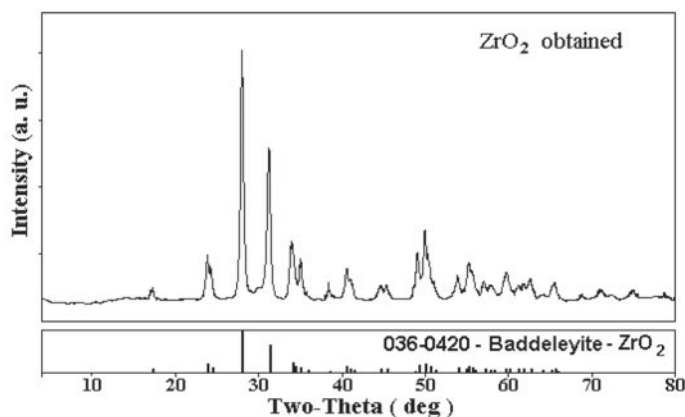


Figure 8. X-ray diffraction of the zirconium oxide obtained from continuous experiment.

it was possible to obtain zirconium oxide from of pregnant strip solution generated in this system.

The chemical analysis of this oxide obtained showed contents of 99% of Zr and 0.03% of Hf as shown in Table 10. The X-ray diffraction analysis of the zirconium oxide obtained from continuous experiment is shown in Figure 8. As it can be noted in Table 10 and Figure 9, the ratio between Zr and Hf was 3300, this value is higher than value required (Zr/Hf = 1000) to obtain a good zirconium and hafnium separation (ASTM

International 2016). The concentration of hafnium in the powder oxide obtained was 200 mg kg⁻¹. This value is in accordance with the ASTM (2015) specification, which defines a maximum hafnium concentration of 200 mg kg⁻¹. According to Table 10, it is noted that the contents of the total impurities is below 0.5 wt%, value recommended by ASTM (2015). However, it was observed that the continuous experiment still needs to be improved in order to adjust the extraction circuit and the parameters used.

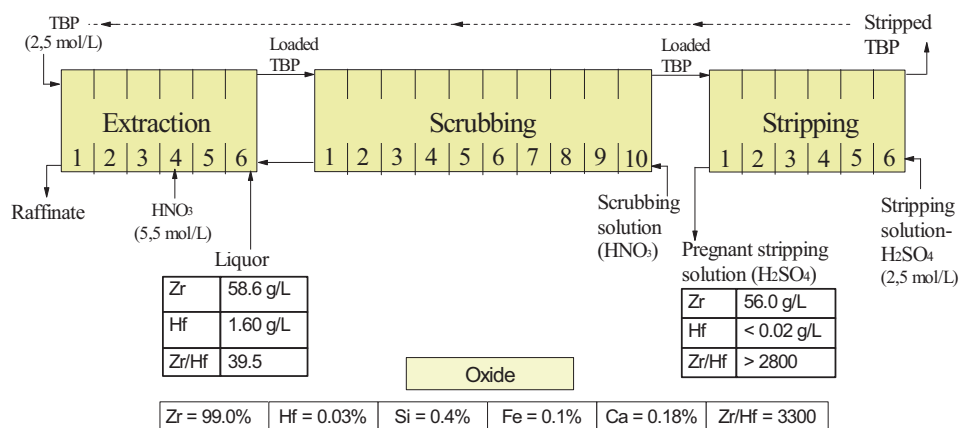


Figure 9. Flow sheet of the solvent extraction circuit for the separation of Zr and Hf, with the composition of the liquor, loaded solvent and of the zirconium oxide obtained in process.

Conclusion

The optimal results were obtained when the liquor used had an acid concentration of 7.0 mol L^{-1} and a nitrate concentration of 9.2 mol L^{-1} , and with 2.5 mol L^{-1} of TBP. Under these conditions, 91.6% of Zr and 12.1% of Hf were extracted; and a separation factor for Zr/Hf of 16 was observed in the discontinuous experiments. The stripping was carried out with sulfuric acid and water. In a continuous experiment, the pregnant strip solution was obtained with Zr/Hf ratio higher than 2800. The oxide obtained by precipitation of the solution generated in the continuous experiments presented a Zr/Hf ratio equal to 3300, and contained 99.0% of zirconium and 200 mg kg^{-1} of hafnium, considered to be of nuclear grade.

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Disclosure statement

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