

ION EXCHANGE COLUMN PERFORMANCE MODEL FOR SEPARATION OF ZIRCONIUM AND HAFNIUM IN ADSORPTION PROCESS

Moch. Setyadji and Endang Susiantini

Center for Accelerator Science and Technology BATAN
Babarsari Street, Pos Office Box 6101 ykbb Yogyakarta 55281
e-mail: mstyadji@batan.go.id

Received: 21 October 2014

Revised: 1 December 2014

Accepted: 17 December 2014

ABSTRACT

ION EXCHANGE COLUMN PERFORMANCE MODEL FOR SEPARATION OF ZIRCONIUM AND HAFNIUM IN ADSORPTION PROCESS. A mathematical model for the separation of zirconium (IV) and Hafnium (IV) in the fixed bed column containing anion exchange resin Dowex-1X8 have been developed. The purpose of this experiment was to validate the mathematical model that will be used to determine (verify) the effective axial diffusivity, overall mass transfer coefficient and zirconium-hafnium separation factor. The flow in the column was assumed to follow plug flow. Zirconium and hafnium transferred from liquid phase to solid phase. In this experiment, zirconium and hafnium separation was studied using anion exchange resin (Dowex-1X8) in batch and fixed bed column processes. Batch process experiments were carried out to determine the adsorption equilibrium constants, while the continuous process experiments were carried out to determine the effective axial diffusivity coefficient (Dez) and overall mass transfer coefficient ($k_c a$). The values of Dez and $k_c a$ were determined by taking certain values so that the simulation results of zirconium and hafnium concentrations in the solution (C) and in the adsorbent (X) at any time on any element of column compared with concentrations of laboratory data were similar. The results showed that the adsorption equilibrium of complex compounds of zirconium and hafnium sulphate on Dowex-1X8 anion resin approached by Henry's equilibrium model with values, $H_{Zr} = 0.089$ L/g resin dan $H_{Hf} = 0.130$ L/g resin. The separation factor of Zr-Hf (α_{Zr-Hf}) is 2.184 for 10 cm height of resin in the column, and $\alpha_{Zr-Hf} = 1.924$ for 14.7 cm. Mathematical model based on Henry's equilibrium constants to simulate zirconium and hafnium concentrations out of the fixed bed ion exchange column could fit the experimental data very well with maximum average relative error of 17.962%.

Keywords : Ion exchange resin, Adsorption model, Zirconium, Hafnium

ABSTRAK

MODEL KINERJA KOLOM PERTUKARAN ION UNTUK PEMISAHAN ZIRKONIUM DAN HAFNIUM PADA PROSES ADSORPSI. Sebuah model matematika untuk pemisahan zirkonium (IV) dan Hafnium (IV) pada kolom tetap yang berisi resin penukar anion Dowex-1X8 telah dikembangkan. Tujuan dari penelitian ini adalah untuk memvalidasi model matematika yang akan digunakan untuk menentukan (memverifikasi) difusivitas aksial efektif, koefisien perpindahan massa keseluruhan dan faktor pisah zirkonium-hafnium. Aliran dalam kolom diasumsikan mengikuti aliran plug. Zirkonium dan hafnium berpindah dari fase cair ke fase padat. Pada percobaan ini, pemisahan zirkonium dan hafnium dipelajari dengan menggunakan resin penukar anion (Dowex-1X8) proses secara *batch* dan kontinyu dalam kolom *fixed bed*. Percobaan proses secara *batch* dilakukan untuk menentukan konstanta kesetimbangan adsorpsi, sedangkan percobaan proses secara kontinyu dilakukan untuk menentukan koefisien difusivitas aksial efektif (Dez) dan koefisien perpindahan massa keseluruhan ($kc.a$). Nilai-nilai Dez dan $kc.a$ ditentukan dengan mengambil nilai-nilai tertentu sehingga hasil simulasi konsentrasi zirkonium dan hafnium dalam larutan (C) dan dalam adsorben (X) setiap saat pada setiap elemen kolom dibandingkan dengan konsentrasi data laboratorium hampir sama. Hasil penelitian menunjukkan bahwa keseimbangan adsorpsi senyawa kompleks zirkonium dan hafnium sulfat pada Dowex-1X8 resin anion didekati dengan model keseimbangan Henry yang nilainya, $H_{Zr} = 0.089$ L/g resin dan $H_{Hf} = 0.130$ L/g resin. Faktor pisah Zr-Hf, $\alpha_{Zr-Hf} = 2.184$ untuk tinggi resin di dalam kolom 10 cm dan $\alpha_{Zr-Hf} = 1.924$ untuk tinggi resin di dalam kolom 14,7 cm. Model matematika berdasarkan konstanta keseimbangan Henry

untuk mensimulasikan konsentrasi zirkonium dan hafnium keluar dari kolom pertukaran ion sangat sesuai dengan data percobaan dengan kesalahan relatif rerata maksimum 17,962%.

Kata kunci: Resin pertukaran ion, Model adsorpsi, Zirkonium, Hafnium

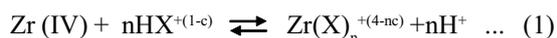
INTRODUCTION

Zirconium (Zr) is a strategic material for both nuclear and non- nuclear industries. In the nuclear industry, Nuclear grade zirconium is used as a fuel cladding materials in nuclear power plants. Zirconium is highly resistant to aqueous corrosion and radiation damage and has good mechanical properties even under intense radiation conditions. Therefore it is a good choice for use in fuel cladding material, e.g. in nuclear power reactors like pressurized water reactors (PWR's) and boiling water reactors (BWR's) [1]. Zirconium in the form of ZrC (Zirconium Carbide) is used as UO₂ kernels coating material for High Temperature Reactor (HTR) fuel. Zirconium Carbide (ZrC) is used as substitution for SiC (Silicon Carbide) on HTR nuclear fuel elements. This is due to ZrC has corrosion resistant properties to nuclear fission. In addition, ZrC has a very high melting point of about 3450°C while SiC decomposes at temperature above 1600°C so the operation at temperature above 1600°C will cause TRISO kernel fuel leakage [2]. HTR with coated particle fuel is a future reactor (generation IV) because it is not only having high efficiency but also release no fission product into the environment. It has a passive safety principles and negative reactivity [2]. In the non-nuclear industry, ZrO₂ has numerous uses, among of which as a colour stabilizer for paint or ink, ceramic coating materials (coating), for fuel cell cathode, refractory, catalysts, construction materials, and electrolyte components [3].

Hafnium (Hf) is very difficult separated from Zr because their chemical properties are similar even could be said to be the twin element of valence IV. However, Zr and Hf have different core cross-sections, Hf has core absorbing thermal neutrons cross-sections of 600 times greater than that of Zr. In producing the nuclear grade Zr, the separation processes of Zr-Hf have been carried out including solvent extraction used various extractants namely Tributyl Phosphate (TBP), Trioctyl Phosphine oxide (TOPO), Tri-n-oktilamine (TNOA), and Methyl isobutyl Ketone (MIBK), but the results are not satisfactory due to the presence of Hf > 100 ppm [1,4-6]. In gaining a high purity zirconium (Hf concentrations < 100 ppm), the separation of Zr-Hf by using ion exchange method is possibly applied. To obtain a mathematical model expected to quantitatively describe the separation process in fixed bed, therefore the preparation of this research on element volume mass balance is needed to be done [7].

Zirconium and Hafnium have the ability to form complexes with several ionic compounds such as hydroxyl ions (OH⁻), chloride ions (Cl⁻), fluoride ion (F⁻),

and sulphate ions(SO₄²⁻). In particular, the formation reaction of Zr complex compounds as follow Equation (1) [7-9]:



With c is the charge of X and X is the ion of OH⁻, Cl⁻, F⁻, or SO₄²⁻. Zirconium and hafnium have a different tendency to form complexes with sulphuric acid, this is due to their differences in atomic radius and atomic volumes. The strength of the resulting complex compounds can be used for separating Zr from Hf. [7-9]

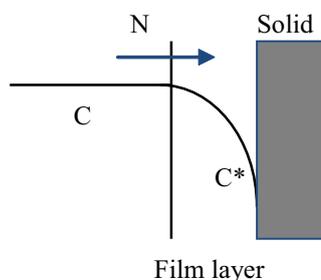


Figure 1. Film layer adsorption process

The adsorption mechanism of Zr-Hf sulfate into Dowex-1X8 resin with a particle size of 0.075 to 0.150 mm (100-200 mesh) through three stages, i.e.mass transfer in the liquid film layer, diffusion in solids and chemical reactions. Diffusion in solid grains occurred in the pores of the solid. Solute will diffuse through the pores into the resin granules, then a chemical reaction occurred. Diffusion in granular solids and chemical reactions take place very quickly so they do not control the overall mass transfer. Resin grains are so small that the adsorption process is controlled by the mass transfer from the liquid to the surface of the grain [8-10].

$$N = k_c \cdot a (C - C^*) \dots \dots \dots (2)$$

$$C^* = H \cdot X \dots \dots \dots (3)$$

Where:

N = mass transfer velocity ~ mass/volume/time

$k_c \cdot a$ = mass transfer coefficient ~ 1/minute

C = solute in liquid ~ mass/volum

X = solute in solid

Mathematical model was obtained by arranging mass balance of solute in the volume element at the adsorption process with assumptions as follow [9,12,13]:

1. The resin bed was homogeneous with uniform porosity
2. The resin particles were spherical and uniform in density, radius and porosity
3. Fluid flow in the resin bed followed the plug flow pattern. To ensure the plug flow so that ratio of height to diameter of the resin column (L/D) e²⁰ and fluid flow in the column should be turbulent with Reynolds number values (Re) e¹
4. Isothermal process
5. Radial diffusion direction was negligible.
6. Adsorption process was controlled by mass transfer in the liquid film layer of the surface of the grain.

Mathematical model in the liquid phase [7,9] :

$$\varepsilon \cdot Dez \left(\frac{d^2C}{dz^2} \right) - v_z \left(\frac{dC}{dz} \right) - kca(C - C^*) = \varepsilon \left(\frac{dC}{dt} \right) \quad \dots (4)$$

Mathematical model in the solid phase [7,9] :

$$(1 - \varepsilon) \left(\frac{dX}{dt} \right) = \frac{kca}{\rho b} (C - C^*) \quad \dots (5)$$

Initial condition [6,8,12] :

$$C(z,t=0) = 0 \text{ and } X(z,t=0) = X_{A0}$$

Boundary condition [6,12]:

$$\text{BC (1) } C(z=0, t) = C_{A0} \text{ and BC (2) } C(z=L, t) = \text{finite or } dC/dz(z=L, t) = 0$$

Equations (4) and (5) were rearranged numerically by explicit finite differences approximation in the z direction (i) [9,14]:

$$\left(\frac{d^2C}{dz^2} \right) = \frac{C_{i+1} - 2C_i + C_{i-1}}{\Delta z^2} \quad \dots (6)$$

$$\left(\frac{dC}{dz} \right) = \frac{C_{i+1} - C_{i-1}}{2\Delta z} \quad \dots (7)$$

Substitution of Equations (6) and (7) to Equation (4)

$$\frac{dC_i}{dt} = (\alpha - \beta)C_{i+1} - (2\alpha + \gamma)C_i + (\alpha + \beta)C_{i-1} + \gamma C_i^* \quad (8)$$

With:

$$\alpha = \frac{Dez}{\Delta z^2} \quad \dots (9)$$

$$\beta = \frac{v_z}{2\Delta z} \quad \dots (10)$$

$$\gamma = \frac{kca}{\varepsilon} \quad \dots (11)$$

Equation (8) used for i = 2 to i = N-1

For i = 1 used BC (1) C₁(t,z=0)=C_{A0}

$$\text{so that } \frac{dC_1}{dt} = 0 \quad \dots (12)$$

For i = N, used BC(2)

$$C(t,z=L)=\text{finite}, \frac{dC}{dz}(t, L) = 0 \quad \dots (13)$$

$$\frac{dC}{dz}(t, L): 0, \left(\frac{dC}{dz} \right) = \frac{C_{i+1} - C_{i-1}}{2\Delta z} = 0, \text{ so that}$$

$$C_{i+1} = C_{i-1} \quad \dots (14)$$

Equation (14) is substituted into equation (8):

$$\frac{dC_i}{dt} = (2\alpha)C_{i-1} - (2\alpha + \gamma)C_i + \gamma C_i^* \quad \dots (15)$$

For partial differential equation on solids:

$$\frac{dX_i}{dt} = \frac{kca}{(1 - \varepsilon)\rho b} (C_i - C_i^*) \quad \dots (16)$$

The resulting equations (3, 9, 10, 11, 12, 15 and 16), which is based on minimizing SSE (Sum of Squares of Errors), was used to estimate the values of *Dez* and *k_ca*. The minimization of SSE was performed using following object function [7,11] :

$$\text{Minimum} = \Sigma(C_{\text{dat}} - C_{\text{sim}})^2 \quad \dots (17)$$

where C_{dat} is the experimental concentration data and C_{sim} is the calculated concentration data.

In The separation factor is defined as follow [7,12]:

$$\alpha_{Zr-Hf} = (k_c a)_{Zr} / (k_c a)_{Hf} [7] \quad \dots (18)$$

$$\alpha_{Zr-Hf} = (Dez_{Zr} / Dez_{Hf})^{0.5} [12] \quad \dots (19)$$

EXPERIMENTAL METHOD

Apparatus

Batchwise experimental investigation was conducted to determine the equilibrium constant by using the proper equipment, including glass beaker, magnetic stirrer, magnetic rods, glassfunnel, Erlenmeyer and sample bottles. While the adsorption process of Zr(IV) and Hf(IV) were continuously carried out in a glass column with a diameter of 5.21 mm to determine the values of *Dez* and *k_ca*. All experiments were performed at constant temperature of 27°C.

Materials and Standards

A mixture of zirconium and hafnium sulphate containing 15-20% (w/w) Zr and about 1.2% (w/w) Hf made from zircon sand processed at the Center for Accelerator Science and Technology, Yogyakarta. Dowex-1X8 anion exchange resin with a mesh size of 100-200 was used as an adsorbent. This resin has the bulk density of 0.5308 g/cm³, particle porosity of 0.4385. The resin was dried in an oven for about 3 hours at

80°C in order to activate particles. Zirconium oxychloride (ZrOCl₂.8H₂O, Merck) was dissolved in sulphuric acid and pure hafnium in chloride matrix solution with a concentration of 1 g/L was used as a standard solution.

Batchwise Adsorption Process

Adsorption process was carried out batchwisely by mixing 10 mL of the feed solution with different concentrations of Zr(IV) and Hf(IV) in 4.2 M sulfuric acid and 0.1 grams of resin. The mixture was stirred with a magnetic stirrer for 1 hour and then allowed to stand for 23 hours to reach a state of equilibrium. The samples were then filtered and Zr(IV) and Hf(IV) content in the filtrate were determined by X-Ray Fluorescence (XRF) and Neutron Activation Analysis (NAA). The experimental equilibrium data of each single component were fitted to determine Henry's constants.

Continous Adsorption Process

Continous adsorption process was performed at room temperature (27 °C) by using a glass column with 0.521 cm diameter and 10 cm height as well as 14,7 cm height. It was filled up with Dowex-1X8 anion exchange resin. The feed solution used was zirconium with concentration of 3.7214 g/L and hafnium content of 0.8821 g/L which was pumped into the column with a superficial velocity of 0.0626 cm/minute. The column effluent was sampled at regular time intervals and was analyzed by XRF and NAA.

RESULTS AND DISCUSSION

Henry's Equilibrium Constants

The experimental equilibrium data (Zr and Hf) are shown in Table 1. Table 1 and Table 2 show the equilibrium data of solute in liquid and solute in solid for zirconium and hafnium. The results of fitting

Table 1. Concentrations of solute in liquid (C*) and solute in solid (X) for zirconium equilibrium

C* data (g/L)	C* calc. (g/L)	X (g/g resin)	Relative errors, SSE (%)
0.6179	0.6450	7.247	0.192
1.114	1.0230	11.494	0.667
16.694	18.8282	211.553	1.634
27.987	26.5524	298.341	0.263
36.0422	35.4087	397.851	0.031

Table 2. Concentrations of solute in liquid (C*) and solute in solid (X) for hafnium equilibrium

C* data (g/l)	C* calc. (g/l)	X (g/g resin)	Relative errors, SSE (%)
0.0852	0.0321	0.0247	38.847
0.1462	0.0873	0.6721	16.202
0.8529	0.6247	4.8055	7.158
2.1515	2.2617	17.398	0.262
3.6746	3.6136	27.797	0.028

the Henry's equilibrium model with experimental data in Table 1 was presented in Figure 2 and Figure 3.

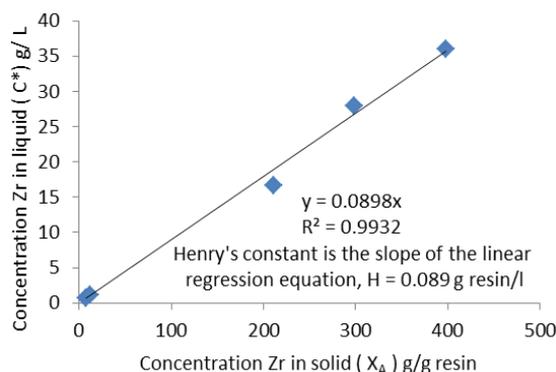


Figure 2. Henry's equilibrium model of zirconium

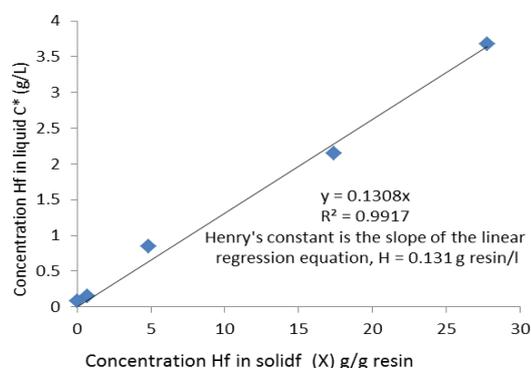


Figure 3. Henry's equilibrium model of hafnium

Effective axial diffusivity, overall mass transfer and Zr-Hf separation factor .

The mathematical models have been used to simulate the concentrations of zirconium and hafnium in the solution (C) out of the column any time, and the results were compared with C experimental data. Comparison of C simulation and C experimental data are presented in Table 3, Table 4, Table 5 and Table 6 or Figure 4 and Figure 5. Data that supports the mathematical model such as bulk density, $\rho_b = 0.5308 \text{ g/cm}^3$; porosity, $\epsilon = 0.4385$; superficial

Table 3. The concentration of zirconium in solution from the column at room temperature, superficial velocity of 0.0626 cm/s and 10 cm high resin

No.	Time (seconds)	C simulation (g/l)	C data (g/l)	Relative error SSE (%)
1	0	0	0	0.000
2	150	0.0804	0	100.000
3	300	0.5059	0.0765	72.043
4	450	1.2856	1.2960	0.007
5	630	2.1399	2.3475	0.941
6	810	2.8232	2.8975	0.069
7	970	3.2238	3.3030	0.060
8	1140	3.4434	3.4270	0.002
9	1300	3.5694	3.5470	0.004
10	2150	3.6646	3.6690	0.000
11	4285	3.7190	3.5000	0.347
SSE average				15.770

Table 4. The concentration of hafnium in solution from the column at room temperature, superficial velocity of 0.0626 cm/s and 10 cm high resin

No.	Time (seconds)	C simulation (g/l)	C data (g/l)	Relative error SSE (%)
1	0	0	0	0.000
2	150	0.0069	0.00043	87.925
3	300	0.0649	0.01835	51.446
4	450	0.2182	0.30565	16.062
5	630	0.4545	0.50805	1.388
6	810	0.6805	0.62875	0.578
7	970	0.8107	0.71955	1.264
8	1140	0.8630	0.72160	2.685
9	1300	0.8799	0.72415	3.133
10	2150	0.8829	0.72475	3.209
11	4285	0.8825	0.79893	0.897
SSE average				15.326

Table 5. The concentration of zirconium in the solution out of column at room temperature, superficial velocity of 0.0626 cm/s and 14.7 cm high resin.

No.	Time (seconds)	C simulation (g/l)	C data (g/l)	Relative error SSE (%)
1	0	0	0	0.000
2	155	0.0137	0	100.000
3	545	0.4670	0.0145	93.887
4	747	1.2787	1.5105	3.286
5	954	1.9944	2.0125	0.008
6	1160	2.5967	2.5120	0.106
7	1567	3.1388	3.2655	0.163
8	1780	3.4904	3.4780	0.001
9	2190	3.6164	3.4970	0.109
10	3016	3.6962	3.7075	0.001
11	5062	3.7197	3.6555	0.030
SSE average				17.962

Table 6. The concentration of hafnium in the solution out of column at room temperature, superficial velocity of 0.0626 cm/s and 14.7 cm high resin.

No.	Time (second)	C simulation (g/l)	C data (g/l)	Relative error SSE (%)
1	0	0	0	0.000
2	155	0.0012	0.00013	79.507
3	545	0.0760	0.00568	85.611
4	747	0.2404	0.32800	13.278
5	954	0.4326	0.46995	0.745
6	1160	0.6155	0.61870	0.003
7	1567	0.7742	0.70005	0.917
8	1780	0.8626	0.74315	1.918
9	2190	0.8824	0.79715	0.933
10	3016	0.8905	0.87085	0.049
11	5062	0.8860	0.8796	0.005
SSE average				16.633

velocity, $v = 0.0626$ cm/s; Henry constant, $H_{Zr} = 0.089$ l/g resin; $H_{Hf} = 0.130$ l/g resin.

By minimizing the different data of experiment and simulation using SSE on the program Matlab were obtained the effective axial diffusivity coefficient (De_z) for Zr of 0.2677 cm²/s and Hf of 0.0737 cm²/s, while the value of the overall mass transfer coefficient ($k_c a$) for Zr of 1.1288 /s and Hf of 0.9386 /s. It is found that average relative errors (SSE) are 15.770% for Zr and 15.326% for Hf. The separation factor of Zr-Hf (α_{Zr-Hf}) is 2.184. This

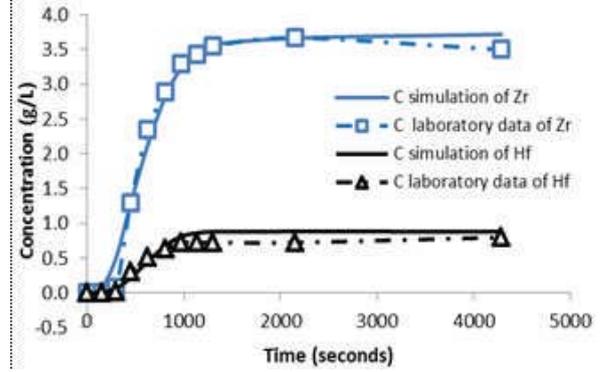


Figure 4. Comparison of concentration for zirconium and hafnium from laboratory data and simulation (at room temperature, superficial linear velocity of 0.0626 cm/s and 10 cm high of anion exchange resin dowex-1X8).

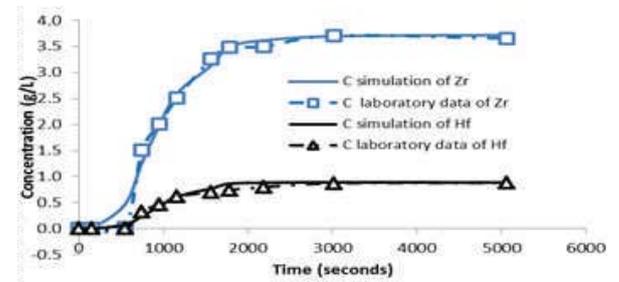


Figure 5. Comparison of concentration for zirconium and hafnium from laboratory data and simulation (at room temperature, superficial linear velocity of 0.0626 cm/s and 14.7 high of anion exchange resin dowex-1X8).

result is better than the results of research by CB Elaine et al [13]. A similar study using the resin of dowex50WX8 100 obtained the separation factor of Zr-Hf (α_{Zr-Hf}) is 0.98. Where separation factor (α_{Zr-Hf}) was defined the ratio of distribution coefficient (D) as follow Equation (20) [13]:

$$\alpha_{Zr-Hf} = D_{Zr} / D_{Hf} \dots\dots\dots (20)$$

By minimizing the different data of experiment and simulation using SSE on the program Matlab were obtained the effective axial diffusivity coefficient (De_z) for Zr of $0,2711$ cm²/s and Hf of $0,0775$ cm²/s, while overall mass transfer coefficient ($k_c a$) for Zr of $1,0361$ /s and Hf of $0,9421$ /s. The separation factor, $\alpha_{Zr-Hf} = 2.184$. It is found that average relative errors (SSE) are 17.962% for Zr and 16.633% for Hf.

Figures 4 and Figure 5 show that high of anion resin dowex-1X8 in the column affects the saturation time of zirconium and hafnium. The higher resin in the column causing the contact time between the adsorbent with solute was longer. Based on Figures 4 and Figure 5, the feed solution with zirconium concentration of 3.7214 g/L and hafnium content of 0.8821 g/L was pumped into the column at room temperature and with a superficial velocity of 0.0626 cm/min, it is known that

hafnium reach saturation faster than zirconium. In the column with 10 cm high of resin, hafnium reached saturation state at 970 seconds while the zirconium reached saturation state at 1300 seconds. As for the resin of 14.7 cm high, hafnium reached saturation at 1567 seconds while the zirconium reached saturation at 2190 seconds. The investigation results show that effective axial diffusivity (D_{ez}) of zirconium is about third larger than the one of hafnium.

Overall mass transfer coefficient ($k_c a$) of zirconium is also larger than that of hafnium. Hafnium molecules diameter has bigger than the one of zirconium that makes zirconium molecules diffuse faster than hafnium molecules. Mathematical model based on Henry equilibrium which proposed to simulate zirconium and hafnium concentrations out of the column in this research could fit the experimental data very well with maximum average relative error (SSE) of 17,962%. The model parameters for each component were 0.089 L/g resin and 0.130 L/g resin for Henry's constant of zirconium and hafnium, respectively. Meanwhile the results of research by Xu zhi-gao et al [14] Freundlich equilibrium is more suitable to the adsorption of both Zr and Hf.

CONCLUSION

Ion exchange column using dowex-1X8 anion resin could be used for zirconium-hafnium separation. The mathematical models have been used to simulate the concentrations of zirconium and hafnium in the solution (C) out of the column any time, and than the results were compared with C experimental data. Mathematical model based on Henry equilibrium which proposed to simulate zirconium and hafnium concentrations out of the column in the research could fit the experimental data very well with maximum average relative error of 17,962%. The model parameters for each component were 0.089 L/g resin and 0.130 L/g resin for Henry's constant of zirconium and hafnium, respectively. In the column with 10 cm height of resin, the effective axial diffusivity coefficient (D_{ez}) for Zr of 0,2711 cm²/s and Hf of 0,0775 cm²/s, the overall mass transfer coefficient (kca) for Zr of 1,0361/s and Hf of 0,9421/s, the separation factor (α_{Zr-Hf}) of 2.184. Meanwhile, in the column with 14.7 cm height of resin, the effective axial diffusivity coefficient (D_{ez}) for Zr of 0,2711 cm²/s and Hf of 0,0775 cm²/s, the overall mass transfer coefficient (kca) for Zr of 1,0361/s and Hf of 0,9421/s, the separation factor (α_{Zr-Hf}) of 1.924.

ACKNOWLEDGMENT

The authors would like to thank to Dora Inda Khaelia who has helped the research and to Center for Accelerator Science and Technology BATAN for financial support.

REFERENCES

- [1] J.T. Nel, J.L. Havenga, M.M. Makhofane and A.A. Jansen "The plasma-assisted manufacture of zirconium metal powder from zirconium tetrachloride." The Journal of The Southern African Institute of Mining and Metallurgy, South Africa, vol. 112, pp. 63-67, 2012.
- [2]. X. Zhou and T. Tang. "Current status and future development of coated fuel particles for high temperature gas-cooled reactors," Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, China, 2010.
- [3]. D.I. Khaelia. "Validation on modeling of the adsorption process for Zr-Hf separation by means of Chromatography Fixed Bed," Undergraduate Thesis, Nuclear Technochemistry Study Programe, STTN BATAN, Yogyakarta, 2011.
- [4]. L.Y.Wang, H.W Lee and M.S. Lee. "Solvent Extraction of Zirconium and Hafnium from Hydrochloric Acid Solutions Using Acidic Organophosphorus Extractants and Their Mixtures with TOPO," Materials Transactions, The Japan Institute of Metals and Materials, vol. 54, no. 8, 2013, pp. 1460-1466.
- [5]. B.S. Janúbia Cristina, R.T.Amaral Laura, Carlos Antônio de Moraes. "Study of the Separation of Zirconium and Hafnium from Nitric Solutions by Solvent Extraction. International Nuclear Atlantic Conference INAC, 2013.
- [6]. B. Raju, L. Hwa, L Man. "Separation of Zr and Hf from Strong Hydrochloric acid Solution by Solvent Extraction with TEHA," Journal of Radioanalytical & Nuclear Chemistry, no.2, vol 295 ,pp. 1537, 2013.
- [7]. M. Setyadji. "Zirconium Migration Model on Dowex-1X8 Anion Resin in its Separation from Hafnium," Senior Researcher Scientific Presentation, PTAPB BATAN Yogyakarta, 2013.
- [8]. E. Susiantini, M. Setyadji. "Separation of Zr-Hf in Sulfuric Acid by Using Anion Exchange Resin, Journal of Nuclear Materials Technology, PTBN-BATAN, vol. 8, pp. 67-78, 2012.
- [9] M. Setyadji. "Mathematics Model on Determination of Mass Transfer Coefficient and Axial Diffusivity of Zirconium in the Adsorption Process of Chromatography Fixed Bed," Proceedings on the 17th Seminar of Technology and Nuclear Power Plant as well as Nuclear Facility Safety, 2011, pp. 622-634.
- [10]. E.C.B. Felipe, A.C.Q. Ladeira. "Separation of Zirconium from Hafnium by Ion Exchange," Holos, no 30, Vol. 3 - Edição Especial - XXV ENTMME / VII MSHNT, 2014.
- [11]. T. Nur, W.G. Shim, P. Loganathan, S. Vigneswaran, J. Kandasamy. "Nitrate removal using Purolite A520E ion exchange resin: batch and fixed-bed

- column adsorption modeling,” *Int. J. Environ. Sci. Technol.* 6DOI 10.1007/s13762-014-0510-6, 2014.
- [12] S. Jain, A.S. Moharir, G. Wozny, “Heuristic design of pressure swing adsorption: a preliminary study,” *Institut für Prozess und Anlagentechnik, Technische Universität Berlin, KWT9, 10623 Berlin, Germany.*
- [13] C. B. Elaine, Felipe, G. Hugo, Palhares, Q. Ana Claudia, Ladeira. “separation of zirconium from hafnium by ion exchange,” *International Nuclear Atlantic Conference - INAC 2013 Recife, PE, Brazil, November 24-29, 2013*
- [14] Xu zhi-gao, Wu yan-ke, Jian-dong, Zhang li, Wang li-jun, “Equilibrium and kinetic data of adsorption and separation for zirconium and hafnium onto MIBK extraction resin,” *Division of Mineral Resources, Metallurgy and Materials, General Research Institute for Nonferrous Metals, Beijing 100088, China, 2010.*