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Reduction of Hf Concentration by using Continuous Annular Chromatography (CAC)

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Abstract: Reduction Of Hf Concentration By Using Continuous Annular Chromatography (CAC). Concentration of Hf in Zr to be used in the control rods in nuclear reactors was less than 100 ppm. Various methods for obtaining Hf concentration as small as possible have been carried out, one of them was CAC. The purpose of this research was to find the optimum conditions of rotation speed, concentration and processing time of elution using H₂SO₄ in order to obtain the minimum concentration of Hf in Zr. The apparatus used for the reduction of Hf concentration was CAC equipped with data acquisition control. The size of the annular length is 50 cm, outer diameter of annular pipe is 19.5 cm, inner diameter is annular pipe is 18 cm. Feed of Zr-sulfate obtained from the processing product of zircon sand having concentration of 100 g/l containing 5032.745 ppm or 0.532% Hf. One liter of feed was flown at a feed nozzle from the top of the annulus with speed of (3-5) ml/min and at the same time the elution solution was flown at a flowrate of 3 ml/minutes for 4 hours. Elution was carried out stepwisely with $2M H_2SO_4$ then subsequently followed by a higher concentration of 4M H_2SO_4 for 4 hours. Analysis of the elution results of Zr was done titrimetrically whereas Hf by Neutron Activation Analysis (NAA). The results obtained indicate the rotation speed of 20 rpm, elution by using $4MH_2SO_4$ at the fourth hour producing concentration of Hf/Zr less than 500 ppm.

Keywords: anion of Zr/Hf, continuous annular chromatography (CAC), Dowex1-X8, NAA.

1. Introduction

At PSTA (Center for Accelerator Science and Technology) Yogyakarta, in 2009 the experimental investigation on the separation method of Zr-Hf was carried out¹. Continuous annular cromatography (CAC) was the most prospective molecule separation apparatus, because it can separate and purify Zr-Hf simultaneously even to separate Zr isotope that has lower thermal neutron capture cross section and Hf with its higher level thermal neutron capture cross section in a single operation and yield Zr with Hf purity <50 ppm^{2,3}. In the year of 2010-2011, the separation of Zr-Hf was carried out in a vertical column by using Zr-sulphate. Zr-Sulphate was used as the feed because it has a separation factor equal to 7, while Zr-chloride as the feed giving a separating factor of 1.3³. In 2012, the simulation of Zr-Hf separation using CAC was carried out. In 2013 with funding from List of Budget Implementation (DIPA) and Ministry of Research and Technology (SINAS) design and engineering of CAC apparatus equipped was completed with data acquisition control which basically consists of three main parts: the upper, middle and lower. The upper part consists of one feed channel and 17 elution channels. Middle section consists of two annular tube made of acrylic tube with annular length of 50 cm, the diameter of the outer pipe of 19.5 cm, diameter of the inner pipe of 18 cm. In the annulus (space between the two tubes) filled with anion resin (Dowx 1-X8) 1.5 cm thick along approximately 40 cm. At the end of the annulus, there are 18 channels that can be set with a dripping faucet for elution solution and at

the bottom there are 18 boxes of collecting fraction as shown in Figure 1. In the feed nozle, the feed flows continuously from the top to the middle (resin) and at the same time the elution flows in 17 channels. If zero degrees point was taken as the feed entrance and the bottom part is divided into 18 fractions then there will be 360 degrees divided by 18 fraction boxes means in each fraction fraction shifted 20 degrees. The middle part can rotate concentrically at 10-100 rpm rotational speed.

Zirconium complex can be absorbed by anion exchange resin Figure 1 when the complex was negatively charged while desorption process occurs when the complex was either positively charged or neutral. There are several forms of complex compounds of zirconium sulfate, the negatively charged Zr-sulfate complexes are $ZrO(SO_4)_2^{-2}$ and $Zr(SO_4)_3^{-2}$, the neutral ones are $Zr(SO_4)_2$ and $ZrOSO_4$ while the positive ones are $Zr(SO_4)^{+2}$, Zr^{+4} and ZrO^{+2} . The forms of these complexes in dilute aqueous solution is $1x10^{-3}$ M can be positively or negatively charged.

	1×10 ⁻² M SO ₄ ⁻²	5×10 ⁻¹ M SO ₄ ⁻²				
pН	The charge of Zr (IV)	pН	The charge of Zr (IV)			
1.0	+ or –	0.1	+ or-			
2.0	-	0.3	+ or-			
3.2	-	1.5	-			
4,2	-	4.0	-			
5.9	-	6.0	-			
6.7	-	8.1	-			
7.8	-	10.1	-			
9.4	-					

Table 1. is the charge of Zr (IV) in 1×10^{-2} M solution of SO₄⁻² [4].

Reference ^{5,6} stated if it is considered that there are only anions mixture of $Zr(SO_4)_3^{-2}$ and $Hf(SO_4)_3^{-2}$ in 1-2M H₂SO₄ acidity in the CAC, $Zr(SO_4)_3^{-2}$ anion has a great affinity to be bound to the anion resin (Dowex 1-X8) then $Hf(SO_4)_3^{-2}$ will move to the bottom of the column while $Zr(SO_4)_3^{-2}$ will move horizontally with the resin at the same direction of the column rotation. Finally $Zr(SO_4)_3^{-2}$ moves more slowly than that of $Hf(SO_4)_3^{-2}$ so it will form a groove band slantingly downward movement.

In reference⁷, it was used Zr/Hf–sulphate was used in the acid condition of 1-2M H₂SO₄, because in the sulfuric acid condition the complex anion of $Zr/Hf(SO_4)_3^{-2}$ was formed. In addition, 2M H₂SO₄ is the condition of solubility limit of Zr namely the concentration of 100 g Zr/L. The reactions between complex Zr/Hf (SO₄)₃⁻² with anion resin are

 $2R-CH_2N^{+}(CH_3)_3OH^{-}+Zr(SO_4)_3^{-2} \longleftrightarrow [R-CH_2N^{+}(CH_3)_3]_2Zr(SO_4)_3^{-2} + 2OH^{-}$ (1) $2R-CH_2N^{+}(CH_3)_3OH^{-}+Hf(SO_4)_3^{-2} \longleftrightarrow [R-CH_2N^{+}(CH_3)_3]_2Zr(SO_4)_3^{-2} + 2OH^{-}$ (2)

Zirconium (Zr) adsorbed-desorpted on the CAC is influenced by the eluates, the feed flow rate and elution as well as rotation speed.

Dowex 1-X8 resin is a strong base resin which has an active group of a polystyrene-based with matrix of $R-CH_2N^+(CH_3)_3$ (resin of alkyl or benzyl trimethyl ammonium type 1) which is in spherical form. This resin has a bulk density of 0.70 kg/L, the maximum operating temperature of 60-80°C and pH range during operation of 0-14. Dowex 1-X8 resin means it is made in DOW CHEMICAL COMPANY chemical plant with code 1-X8, which means a strong base anion exchange resin containing divinylbenzena as much as 8%. In addition to Dowex 1-X8 resin can also be used Amberlite IRA anion exchanger resin series of ROHM and HAAS COMPANY.

This experimental investigation was a continuation of previous ones⁸⁻¹⁰, using a simple system of annular chromatography whereas what has been done was a trial test of CAC apparatus that has been engineeringly designed and will be used for mini-pilot plant of Zr-Hf continuous separation processes. The purpose of this investigation was to obtain the optimum conditions of rotational speed, concentration and elution time with H_2SO_4 to obtain the minimum concentration of Hf in Zr. Such data can be used to determine the next step in the separation of Zr and Hf with CAC mainly the optimization of process conditions that is the residence time or speeds of dripping feed and elution .

2. Materials and methods

2.1. Materials

Materials used are Resin Dowex 1-X8 anion exchanger in the form of Cl⁻ 100-200 mesh, 97 % concentrated H_2SO_4 , H_2SO_4 1, 2, 3 and 4 M, ZrOCl₂.8H₂O from MERCK and Zr(SO₄)₂ .4H₂O as the processing product of zircon sand with Hf concentration of 0.532 %. Bismuth Nitrate, 0.05 M EDTA, NaOH Titrisol, Ammonium tartrate (2:1), Theourea, Hf 10.000 ppm standard solutions of Hf Cl₄, deionized water (ABM).

2.2. Equipments

The equipments used are A unit CAC apparatus equipped with data acquisition control, analytical balance, pipette, volume-pipette volume, micro-pipette, flask, graduate cylinder, watch glass, magnetic stirrer, sample bottles, burette, pH meter, Neutron Activation Analysis (NAA).

2.3. Preparation of the anion resin

Preparation of the anion resin was done by weighing as much as 1700 g of the resin, dried in an oven temperature of approximately 90° C to open the pores of the resin and to remove water attached between the resins, then was stored in excicator. Furthermore, the resins soaked with water and put in an annulus tube while occasionally rotated so that no air was trapped.

2.4 . Activation of anion resin

Activation of anion resin was conducted with 1N NaOH solution in 1 L discharged from the elution channel into the annular tube that contains the anion resin and rotated so evenly distributed. After a certain time (approximately 1 hour) the pH at the bottom of each fraction was equal to the initial pH of 1N NaOH solution. Then, deionized water was flown to neutralize the resin, by measuring the pH of the solution in each fraction equal to the initial pH of the deionized water.

2.5. Conditioning of resin

Conditioning of the resin was done by measuring the pH of the 2M H_2SO_4 that will be used as a solution condition, then flow the solution into the CAC by using a dosing pump, then turn CAC at rotating speed of 20 rpm in order to spread 2M H_2SO_4 onto the resin evenly. The pH of H_2SO_4 2M exiting from faucets was measure at the bottom of CAC until the same as the initial pH.

2.6. Preparation of elution solution

Preparation of elution solution was done by the following sequences: dilute solution of concentrated H_2SO_4 into 1,2,3 and 4 M H_2SO_4 respectively of 5 L. The solution was put into an elution container at the bottom connected with the pump that can flow the elution solution at the desired flow rate.

2.7. Preparation of CAC apparatus

Preparation CAC apparatus was done by at first, preparing Erlenmeyer in the total amount of 18 pieces that will be used as a container for the fraction products. Then glass wool was put at the bottom of a resin between the cylinder tube annulus so that the resin did not come out. The resins filling was immersed into deionized water so it will be easily decanted and the resin did not swell that can break the cylindrical tube. The unit of continuous annular chromatography (CAC) can be seen in Figure 1.

2.8. Calibration of the feed flowrate and elution

Feed flow rate calibration was done by regulating valves in the feed part at the feed flow rate of 5 ml/min and collected them in a graduating cylinder and measuring the time with a stop watch so did for the elution flow was 3 ml/min. Furthermore, in order to obtain the balance of fluids in and out of the annulus so the flow calibration was then carried out by maintaining the solution at the height of solution inside the annulus tube remained stable.

2.9. The preparation of zirconium sulfate feed of 100 grams/liter

The feed making was carried out by weighing as much as 389 grams of $Zr(SO_4)_2.4H_2O$ as the product of zircon sand processing which was diluted to 1 liter with deionized water. Furthermore, the solution was analyzed titrimetrically by using a solution of bismuth (III) nitrate which was then made into 100 g Zr/L concentration.





Figure 1. Schematic and CAC apparatus equiped with the acquisition of data control

2.10. Working Step of CAC

Working step in reducing concentration of Hf in Zr was done by stepwise elution referring to previous researcher¹⁰, namely for the preliminary separation experimental of copper, nickel and cobalt as well as the separation of Zr-Hf with CAC. Description of the working steps as shown in Figure 2.

This working steps were done by preparing all glassware such as graduating cylinder, sample bottles, dripping pipettes and a stop watch. Flowing the feed solution by pressing the feed pump button. Flowing the elution solution by pressing the elution button of 2 M H_2SO_4 and after a certain time with 4 M H_2SO_4 of 3 L respectively into the annular tube. Pressing the motor button for rotating speed of 20 rpm, then accumulating the eluate in each fraction numbers for any given time for 4 hours. Pipette of 10 mL eluate fractions in each number and put in a vial and covered by millar (plastic) to analyze the levels of Zr titrimetrically and Hf with NAA. Rotation speeds were varied by 20, 25 and 30 rpm, and so did the variation of elution time.



Figure 2. Diagram of the CAC working steps for reducing the concentration of Hf in Zr.

2.11. Analysis of zirconium content titrimetrically

Analysis of Zr titrimetrically was done by means of pipetting 1 ml of sample by using measuring pipette, adding 10 ml of 0.05 M EDTA, 10 ml of a mixture of ammonium-tatrat 2 : 1 and stirred for 5 minutes, then adjust the acidity to pH 1.8 by using 5 M HNO₃. After that the solution was boiled up to its boiling point for 5 minutes so that the reaction was perfectly occurred. Then the temperature of the solution was drecreased down to the room temperature, its acidity was readjusted at pH of 1.8. Add 5 ml thiourea indicator of 2.5 %. Excess of EDTA was titrated with a solution of 0.05 M Bi (III) to the end point of titration was that the color changes from colorless to yellow pale.

2.12. Analysis of Hf content using NAA

Analysis of Hf content was done by the first method which was sample preparation namely by measuring the pH of the sample, then the pH of sample was neutralized by adding NaOH. Preparing a vial or container for neutron activation analysis by means of immersing the vial for 12 hours in deionized water and concentrated HNO₃ in the ratio of 3 : 1. Then washing the vial with deionized water untill its pH was neutral. Puting the vial into the oven at temperature of 80 ° C until dry. Putting the amount of 0.5 mL samples into the vials which was then be analyzed. The second was irradiation process: irradiation process begins by putting vials filled with samples into the plastic. Putting the samples into the ampoules, every 3 samples contains one standard (HfCl₄), and in one ampoule consists of 6 samples and 2 standards. Putting the ampoules into the cladding, then irradiated them for 12 hours. The third: Analysis of Hf content by using gamma spectrometry by means of taking the activated samples and let them coolingdown for 3 weeks. Counting the samples by gamma spectrometry, with a counting time of 4 minutes. Calculating the concentration of its hafnium.

3. Results and Discussion

3.1. The preparation of 100 grams/liter zirconium sulfate feed

Feed of digesting process products was used from zircon sand, leached it with water, then leached it with HCl followed by manufacturing of zirconium-based Sulfate (ZBS) and conversing it into $Zr(SO_4)_2 x.H_2O$. The products obtained from titrimetrically analysis results was Zr with its concentration of 100 g/L with Hf content of 503.2745 ppm, so that the concentration of Hf in Zr was 5032.745 ppm.

3.2. Effect of rotation speed on the concentration of Zr and Hf.

It was used $Zr(SO_4)_3^{-2}$ as anion of Zr with concentration of 100 g/L containing 5032.745 ppm Hf in the amount 1L, at the same time elution with 2M H₂SO₄ in the amount of 3L was carried out with the feed rate of (3-5) ml/min and elution speed of 3 ml/min. Rotation was adjusted at a speed of 30.25 and 20 rpm for 1-2 hours. Analysis of Zr and Hf were carried out by taking samples at the end of the period to the fraction number of 18th, then the results of the analysis of the concentration of Zr and Hf in the fraction number of 18th – were averaged.



Figure 3. The concentration of Zr and Hf to the rotation speed (rpm) at the first hour.

Figure 3 shows the data that the higher the rotational speed the greater driving force toward the radial direction so Zr and Hf exist inside the resins has a longer path to reach the bottom of the column. Long trajectory traversed by Zr and Hf anions resulting the output Zr and Hf concentrations decreases¹¹. However, in this investigation showed that the higher the rotational speed the greater the concentration of Zr and Hf obtained. This may be due to friction or shaking of the resins existing inside the tube of CAC. The lower the rotational speed the lesser the friction exist, if the rotational speed was very low and approaching to stop the

CAC phenomenon similar to the phenomenon in the vertical column. In the previous investigation by using vertical column (with no rotation), introduced anions feed of Zr and Hf in acidic conditions of 2 M at an interval time its Zr and Hf was analyzed. Subsequently, it was eluted with $4M H_2SO_4$ and at an interval time its Zr and Hf was obtained the results of Hf peak located on the left side of Zr peak but they were almost overlay¹².

Figure 4 shows the data of the concentration of Zr and Hf to the rotation speed at the second hour. The results show the higher the rotational speed the greater the concentration of Zr and Hf. This may be due to the friction inspite of shaking inside resins and also because of no adsorption-desoption occured between the anion resin and Zr and Hf anions so that the greater the output concentrations. In order to obtain the greater products as the higher rotational speed the lesser concentration of Zr and Hf exit, hence the rotational speed shuld be varied < 20 rpm, the speed at which the adsorption and desorption will occur completely along the trajectory because there is no friction and shaking.



Figure 4. The concentration of Zr and Hf to the speed (rpm) at the second hour.

The operation of the CAC was continously selected in the rotational speed of 20 rpm because of which rotational speed of 20 rpm there was relatively no friction and the CAC can only be operated at the lowest speed of 20 rpm. But it is expected in future investigation that rotational speed used is less than that of 20 rpm by providing it with a reducing gear .

3.3 . Effect of elution of H_2SO_4 on the concentration of Zr and Hf

In this investigation, the CAC was operated at 20 rpm rotation speed, feed together with the elution of $2M H_2SO_4$ were introduced into CAC for operating time of 2 hours.



Figure 5. The concentration of Zr (g/L) and Hf (ppm) to fraction number of the first hour.

In Figure 5, Zr concentration (g/L) and Hf (ppm) to the fraction number of the first hour for the elution of 2 M H_2SO_4 , were fluctuating in each fraction number. Elution with 2M H_2SO_4 , anion of Zr will bind more tightly than the anion of Hf so Hf will come out first or Hf peak was on the left side peak of Zr. In this investigation produced no peaks of Zr and Hf but products obtained at fraction number of 18th were fluctuating. The results of the calculation of average at the fractions number of 18th were Zr of 22.42 g/L and Hf of 29.51 ppm respectively. This evident proved that much of Hf adsorbed onto the resin.

In 2M H_2SO_4 the anion of Zr had a greater affinity for the resin that it will bind more tightly to the resin while Hf will come out together with 2M H_2SO_4 . Chemical properties of Zr and Hf are the similar, in this matter the differences will be owing to its affinity for the anion exchange resin. The affinity of an anion in the anion resin depends on the degree of polarization of the anion with that of resin. The geater degree of

polarization will stick more strongly on the resin and its affinity will be greater. Degree of polarization increasing with the increase of its negative charge and decrease with the reducing size of the anion. Generally, polyvalent anion has a greater affinity than that of the monovalent anion and for anions with the same charge of which having the same affinity. The sequence of anions affinity¹³ is

$$F < HCO_3^- < CI < HSO_3^- < CN < Br < NO_3 < I << SO_4^-$$

The elution was carried out with the reverse order of sequences from the latest affinity.

Anions feed of Zr and Hf entered together with the eluent of 2M H_2SO_4 , in this condition in order Hf anion exits from the resin, the anion resin of Hf should have less affinity than the affinity anion of Zr. This may occur if the complex of Hf is not negatively charged (anionic) but positively charged (cationic) or neutral as $Hf(SO_4)_2$, $Hf(SO_4)^{+2}$, Hf^{+4} or $HfO(SO_4)$.



Figure 6. The concentration of Zr (g/L) and Hf (ppm) to the fraction number at second hour.

In this investigation the eluent of $2M H_2SO_4$ solution had not been able to remove anions of Hf, therefore in future investigation, the variation of elution with acidity less than $2M H_2SO_4$ should be carried out.

In Figure 6, the concentration of Zr (g/L) and Hf (ppm) to the fraction number at the second hour elution of 2 M H_2SO_4 were fluctuating in each fraction number. The results of the calculation of average for all 18 fraction numbers were Zr of 28.90 g/L and Hf of 31.07 ppm respectively. Comparison of the results of average concentration for all 18 fraction numbers at the first hour and second hour were both Zr and Hf trend to increase. It is estimated that the longer the elution time Zr and Hf concentrations obtained will initially increase and then decrease. It was expected that in future investigation, variation in elution time will be extent so the location of Hf peak obtained will be on the left side peak of Zr.



Figure 7. Concentration of Zr (g/L) and Hf (ppm) to the fraction number at third hour.

In the acidity of 2M H₂SO₄, the anion of Zr will be bonded stronger than that of Hf so after entering the feed together with elution for 2 hours then Zr anion will accumulate in the resin. The acumulated Zr anion in the resin will immediately be removed by means of stepwise elution with higher acidity that is 4M H₂SO₄. In the acidity of 4M H₂SO₄, anion of Zr having smaller degree of polarisasion so it was not to be bonded to the resin, this happen if the negatively charged anions of Zr smaller or positively charged or neutral ie as $Zr(SO_4)^{+2}$, Zr^{+4} , $Zr(SO_4)_2$ atau $ZrO(SO_4)$.

In Figure 7, the concentration of Zr (g/L) and Hf (ppm) to the fraction number at the third hour for elution of 4 M H_2SO_4 are fluctuating in each fraction number. The results of the calculation of average for all 18 fraction numbers are Zr of 33.84 g/L and Hf of 36.77 ppm respectively. The anion of Hf come out of the elution of 4M H_2SO_4 , this proved that the Hf anions should not be adsorbed but in fact that it was adsorbed onto the

resin in the elution of $2M H_2SO_4$ at the first hour and the second hour. Those was then followed by elution at the fourth hour which can be seen in Figure 8.



Figure 8. The concentration of Zr (g/L) and Hf (ppm) to the fraction number at fourth hour.

In Figure 8, the results show the average calculation for 18th fraction numbers were Zr of 29.81 g/L and Hf of 10.72 ppm. Comparison of the results of the average concentration for all 18 fraction numbers at the third hour can be seen in Figure 7 and at the fourth hour can be seen in Figure 8, both of Zr and Hf trend to decrease respectively. This proved that the properties of anions Zr and Hf were the same therefore they were always altogether even their condition had already been made differently namely the conditions of complex species with the different in charges dan polarisasion condition.

Elution of 4M H_2SO_4 aims to take Zr anion, the concentration results of elution at the third hour was greater than that of the second, this showed that the 4M H_2SO_4 was able to take anion of Zr. The concentration of elution results for Hf anion at the third was lesser than that of the fourth hour, it showed that the 4M H_2SO_4 was not for taking Hf anion, but because of the properties of Zr was the same as that of Hf so in this matter the anion Hf will be uptaken along with Zr in the small amounts.

Concentration of Hf anion in the elution of $4M H_2SO_4$ which was small as estimated from the rotation mechanism for four hours at CAC. Rotation speed of 20 rpm was able to make a long trajectory and competition of anions of Zr and Hf were happened so the anion of Zr will move slower than that of Hf anion. The existence of that trajectory which distinguished between the most recent investigation by using CAC and previous investigation by using the vertical column (not rotating). In the vertical column chromatogram expressed as the concentration of the volume fraction whereas in the CAC was the concentration of the fraction number or angle velocity (degrees). At the CAC rotated at a certain rotation speed, there were 18 fraction boxes so there were 360 degrees divided by 18 boxes which means any number of fraction equal to 20 degrees.

Anion of Zr accumulated in the anion resin was behind the Hf anion so at the elution time with $4M H_2SO_4$ both of those anions exiting together though the Hf concentration was much smaller, because the affinity of Hf anion was greater than that of Zr anion at the time of elution.

The data on the calculation of the Zr to Hf concentration in the feed and the results of elution with 4 M H_2SO_4 at various fraction numbers were shown in Table 2.

Fraction	1	2	3	4	5	6	7	8	9
numbers									
Hf/Zr(ppm)	1164	1069	1196	1523	1365	1349	644	847	872
third hour									
Hf/Zr(ppm)	387	290	350	363	368	296	390	378	429
fourth hour									
Fraction	10	11	12	13	14	15	16	17	18
numbers									
Hf/Zr(ppm)	2115	1503	1539	678	704	697	764	756	944
third hour									
Hf/Zr(ppm)	502	435	342	453	371	260	297	248	367
fourth hour									

Table 2. Results of the calculation of the concentration of Hf in Zr in the various fractions numbers.

From Table 2. The results obtained of Hf/Zr concentration in the elution at the hour of 4 in average was < 500 ppm.

Conclusion

The rotation speed of 20 rpm did relatively not make any shaking occured in between the resins, the higher the rotation speed the higher the concentration of Zr coming out of the column. The concentrations of Hf and Zr to the fraction number of 18th in the variation of rotation speed, time and acidity were fluctuative. In the rotation speed of 20 rpm and elution with 2M H₂SO₄, Hf anion which should come out along with 2M H₂SO₄ but it was adsorbed by the resin together with Zr anion. By way of a step-wise elution, elution of 4M H₂SO₄ able to uptake Zr anion which was bonded strongly than that of Hf anion. Elution 4M H₂SO₄ unable to take Hf anions, because the affinity of Hf anions was greater than that of Zr anion so the decrease of Hf concentration taking place. The decrease of Hf concentration was predicted from the rotation mechanism for 4 hours at CAC. Rotation speed of 20 rpm was able to make a long trajectory and the occurence of competition between Zr anion and Hf anion so Zr anion will move slower than that of Hf anion. The anion of Zr anion accumulated onto the resin was behind the Hf anion so that in the elution time with 4M H₂SO₄ both of those anions will exit together, but the Hf concentration was much smaller because the affinity of Hf anion was greater than that of Zr anion at the time of elution with 4M H₂SO₄. In the elution of 4M H₂SO₄ at the fourth hour, Hf/Zr concentration obtained was less than 500 ppm. The next plan is to provide the motor with a reducing gear by which the rotation speed could be adjusted at a lower rotation speed. Then CAC will be operated with the acidity less than $2M H_2SO_4$, longer variation time and the feed flow rate and elution velocity less than 3 ml/min.

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