EMULSION LIQUID MEMBRANE EXTRACTION OF Zr AND Hf IN ACID NITRIC USING EXTRACTANT TOPO

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ABSTRAK

EKSTRAKSI EMULSI MEMBRANE CAIR Zr dan Hf DALAM LARUTAN ASAM NITRAT DENGAN EKSTRAKTAN TOPO. Telah dilakukan ekstraksi larutan Zr yang mengandung Hf menggunakan extraktan TOPO. Sebagai fasa air digunakan larutan campuran $ZrO(NO_3)_2$ dan $HfO(NO_3)_2$ yang mengandung Zr 10 gr/L dan Hf 500 mg/L, sedangkan ekstraktan atau fasa organik adalah TOPO dengan variasi konsentrasi yang diencerkan dengan kerosen. Emulgator Span-80 digunakan untuk membuat larutan membrane emulsi.Fasa internal yang digunakan adalah asam nitrat 3M dan fasa eksternal yang digunakan adalah asam fosfat 5M. Parameter yang diteliti yaitu konsentrasi ekstraktan, kecepatan pengadukan, waktu pengadukan, dan perbandingan fasa internal serta fasa eksternal. Untuk analisis Zr dan Hf digunakan metode X-Ray Fluorescence (XRF). Dari hasil optimasi proses ekstraksi Zr dan Hf dengan membran emulsi menggunakan ekstraktan TOPO diperoleh kesimpulan sebagai berikut: waktu pembuatan fasa membran adalah dengan kecepatan pengadukan 8000 rpm, konsentrasi TOPO 5% dalam kerosen, konsentrasi internal asam nitrat 3M, konsentrasi asam fosfat 5M, waktu ekstraksi pengadukan 10 menit dengan kecepatan pengadukan tetap 500 rpm , dan perbandingan fasa membran dan fasa eksternal 1 : 1. Pada kondisi ini diperoleh faktor pisah (FP) Zr-Hf = 17,39.

Kata kunci: ekstraksi, TOPO, zirkonium, hafnium, kerosen, XRF, membrane emulsi.

ABSTRACT

EMULSION LIQUID MEMBRANE EXTRACTION OF Zr AND Hf IN ACID NITRIC USING EXTRACTANT TOPO. Extraction solution of Zr that containing Hf using TOPO extraktant has been done. As the liquid phase, mixed solution of $ZrO(NO_3)_2$ and $HfO(NO_3)_2$ containing Zr 10 g/L and Hf 500 mg/L was used, whereas extractant or organic phase was TOPO with a variation of the concentration, that was diluted with kerosene. Emulsifier Span-80 was used to make emulsion of membrane liquid. Internal phase of membrane solution used was 3M nitric acid and the external phase used was phosphoric acid 5M. The studied parameters were extractant concentration, stirring speed, stirring time, and the ratio of internal and external phase. For the analysis of Zr and Hf, the X-Ray Fluorescence (XRF) was used. From the optimation results of the extraction process of Zr and Hf with emulsion membran using TOPO extractants obtained the following conclusions: the manufacture of membrane phase used the stirring speed of 8000 rpm, the concentration of TOPO 5% in kerosene, internal concentration of 3M nitric acid, phosphoric acid concentration 5M , the extraction time stirring 10 minutes with fixed stirring speed 500 rpm, and the ratio of membrane and external phase was 1:1. This conditions acquired a separating factor (SF) Zr-Hf = 17.39.

Keywords: extraction, TOPO, zirconium, hafnium, kerosene, XRF, Membrane Emulsion.

1. INTRODUCTION

Purification of zirconium (Zr) from impurities is necessary because reactor structural material requires Zr with a very high purity (nuclear degrees). One of the impurities that must be removed is hafnium (Hf), which has neutron absorption (102 barns) which absorbs neutrons that should be used to hold a chain nuclear reaction (1). As the material structure of the reactor, Zr metal has some superior characteristics, which are corrosion resistant against water and moisture, high melting teller, strong structure and look of the low absorption of neutrons (barn 0.2) (2,3).

Zirconium and hafnium are elements located in group IV of the periodic table. These elements have chemical properties similar to the ability to form a compound or complex ions are also almost the same. This causes difficulty in separation. Nevertheless there is little difference that the "ionic volume" that play a role in the stability of the shape complexity. Zirconium has a larger volume atoms (Zr = 13.97 cubic Angstroms, Hf = 13.42 cubic Angstroms) but Hf has a volume larger ions (radius of Zr^{+4} = 0.74 Angstroms and fingers Hf^{+4} = 0.75 Angstroms). Zr tendency to combine with other ions is greater than Hf, so complex compound Zr is more stable than the complex compound Hf.(1).

For the separation of Zr of Hf is used in various ways, each using tools, solvents and different systems. Some of the methods used for the separation of Zr and Hf, include fractional crystallization (4), solvent extraction (5-9), ion exchange (10-13),

extractive distillation in molten salts (14), chromatography (15) and sublimation (16-18). Liquid-liquid extraction using a solvent can be used methyl iso-butyl ketone (MIBK) and tri-butyl phosphate (TBP), tri-octyl phosphine oxide (TOPO).

Separation of zirconium and hafnium in a liquid-liquid extraction process can be done by changing the metals into complex compounds soluble in the organic phase. The organic phase has a ligand group that can react selectively to one or more of the metallic elements present in the water phase. Separation of metal elements is due to differences in reactivity and the diffusivity of each metal element to the organic phase.

According to the Nernst distribution law, if the two are not mutually mixed solvents included solute that can be dissolved in the second solvent, there will be a division of solubility. Both solvents are generally organic solvents and water. In the mix, solute will be distributed by itself into the two solvents, after stirring, and then left there will be two separate phases. Comparison of solute concentration in the second solvent remains and is a constant at a constant temperature.

The constant is known as constant coefficients distribution. The distribution coefficient (DC) is expressed by the following formula (18):
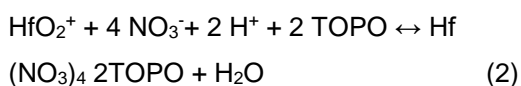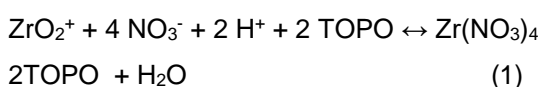
$$DC = C_2/C_1 \text{ or } DC = C_o/C_a$$

with:
C_1 or C_a is the concentration of solute in the first solvent or aqueous solvent.
C_2 or C_o is the concentration of solute in a second solvent or an organic solvent.

This research aimed to study the extraction of Zr-Hf using a mixture of TOPO extractant and diluent kerosene with membrane emulsion method. Kerosene was chosen because it can improve the efficiency of the separation of Zr and enlarge the ability of the extractant in forming a complex with Zr. Reaction extraction separation of Zr-Hf written as follows (9):

$$ZrO_2^+ + 4\ NO_3^- + 2\ H^+ + 2\ TOPO \leftrightarrow Zr(NO_3)_4\ 2TOPO + H_2O \quad (1)$$

$$HfO_2^+ + 4\ NO_3^- + 2\ H^+ + 2\ TOPO \leftrightarrow Hf(NO_3)_4\ 2TOPO + H_2O \quad (2)$$

Membrane processes for separation of chemical species from a mixture are gaining in importance and are emerging as a viable alternative to conventional separation processes. The emulsion liquid membrane (ELM) technique was regarded as an emerging separation technology and was extensively examined for potential applications in such fields as hydrometallurgy, environmental engineering, biochemical engineering, pharmaceutical engineering, and food technology (19-21). Due to large throughput, fast reaction, and easy phase separation, the major method used in the rare earth element separation industry is solvent extraction with mixer settler. However, this traditional equipment has many drawbacks, such as: large equipment area occupation, high energy consumption, and large solvent holdup (22). To solve the problems, many types of methods and equipment are devised, such

as hollow fiber contactor (23), impregnated polymer beads and resin (22-24), ionic liquid (25,26), magnetic absorption[27], and polymer sorbent (28), etc. Emulsion liquid membranes (ELM) separation technique (19,28) has been regarded as an emerging technology with considerable potential for a variety of applications such as recovery and concentration of metal ions and biochemical products and the removal of pollutants from waste waters. ELMs exhibit several attractive features in comparison with solvent extraction. These include a large specific surface area for extraction, simultaneous extraction and re-extraction in a single stage, and the requirement only small quantities of an expensive carrier (30-32). In view of all these advantages, the separation of metals by the ELM techniques has drawn considerable attention (29).

In the present work, Emulsion liquid membrane is investigated to select the suitable conditions for extraction of Zr-Hf ions from acidic nitric solutions using TOPO as extractant. The effects of extractant and surfactant concentrations, mixing speed, concentration and type of stripping solution, phase ratio, treatment ratio, and nature of diluent on the extraction rate were studied. Under the optimum conditions, extraction of Zr-Hf ions has been also studied for different feed mixture solution. Solvent extraction and stripping of Zr-Hf ions were carried out in order to study the influence of the concentration of the aqueous solution, the concentration of TOPO, the equilibrium time on the extraction percent of Zr-Hf ions and stripping percent of this metal ions from

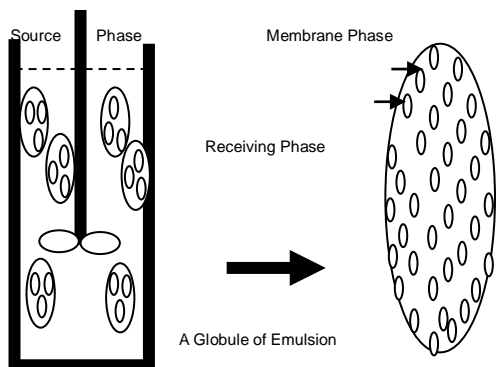loaded organic phase by hydrochloric acid solut

Figure 1: Configurations for Emulsion Unsupported (Kris Tri Basuki et al, Jurnal Urania, Vol 22 No 3 2016, 133-202)

Figure 1 shows possible configurations emulsion (unsupported), the configuration supported liquid membranes system.Globules is a granular of organic phase in the emulsion solution.

In General, liquid membranes can be held in porous structure or bounded on either side by two thin polymeric films. Emulsion (unsupported) liquid membranes are usually in the form of double emulsion drop. In a Water/Oil/Water (W/O/W) system, immiscible is the oil phase, separating the two aqueouse phases, while in an O/W/O system, the liquid membrane is the immiscible water phase which separates the wo oil phases (19).

Figure 2 showed a sequence of even in the preparation and operation for an W/O/W emulsion liquid membrane system. The emulsion system are usually prepared by forming an emulsion from two immiscible phase by vigorously stirring at 2000 – 10000

rpm. Then emulsion disperse in continuous phase (external phase) by low speed agitation. The liquid membrane phase which is separates the encapsulated droplets in the emulsion form the external continuous phase. In general, the internal phase droplets are very small, having diameter of 1 – 10 μm, whereas the emulsion globules are usually about 0,1 – 2 mm in diameter. Surfactant and additives are normally included in the membrane. At the end of an extraction run, the emulsion and external phases can be separated, and reacted internal reagent phase can be recovered, if desired, by breaking the emulsion (19).
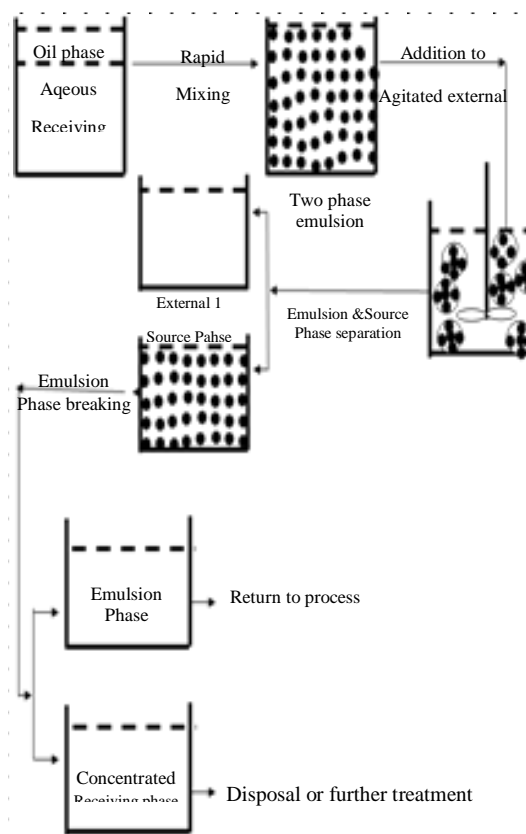

Figure 2 : A Sequence of Events for an (W/O/W) Emulsion Liquid Membrane System(Kris Tri Basuki et al, Jurnal Urania, Vol 22 No 3 2016, 133-202)

The metals are present in the external aqueous phase to be extracted by the extractors that exist in the organic phase by forming complex compounds. Complex compounds is further decomposed by internal water phase, therefore the extraction and re-extraction or stripping occurs simultaneously (19) (Figure 2).

To determine the success of the process can be seen from the efficiency of extraction, stripping efficiency, and total efficiency.
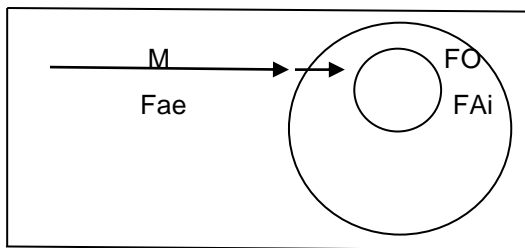

Figure 3 : Metal transfer on the extraction of membrane emulsion (Kris Tri Basuki et al, Jurnal Urania, Vol 22 No 3 2016, 133-202)

M   = Metal
FAe   = External phase aqueous
FAi   = Internal phase aqueous
FO   = Organic phase

Efficiency calculation formula according to the following equation (19):

$$Extraction\ Efficiency = \frac{(VFAeo.CFAeo)-(VFAe.CFAe)}{(FAeo\ CFAeo)} \times 100\%$$

(4)

$$Total\ Efficiency = \frac{(VFAi.CFAi)}{(VFAeo.CFAeo)} \times 100\%$$

(5)

$$Stripping\ Efficiency = \frac{(VFAi.CFAeo)}{(VFAeo.CFAeo)-(VFAe.CFAe)} \times 100\%$$

(6)

Where:

VFAeo   = The volume of the external aqueous phase before extraction (initial).

VFAe   = The volume of the external aqueous phase after extraction

VFAio   = The volume of the internal aqueous phase before extraction (initial)

VFAi   = The volume of the internal aqueous phase after extraction

CFAeo   = The concentration of the internal aqueous phase before extraction (initial)

CFAe   = The concentration of the external aqueous phase after extraction

CFAio   = The concentration of the internal aqueous phase before extraction (initial)

CFAi   = The concentration of the internal aqueous phase after extraction.

2. EXPERIMENTAL

2.1 Material :

ZrO(NO_3)_2, HfO(NO_3)_2 from Merck, HNO_3, TOPO, Kerosene, Span-80.

2.2 Tools :

Heating and magnetic stirrer, stirrer ultra Turax, appliance glass and XRF.

2.3 Ways of working :

2.3.1 Making the emulsion membrane (FM) and internal water phase (Fai)

10 mL of 5 % surfactant Span-80 were dissolved in 10 mL (5 % -Kerosene TOPO) as the organic phase plus 10 mL

H_3PO_4 3M as an internal phase (FAi). Ultra Turax was stirred for 15 minutes with a stirring speed varies from 2000 - 10000 rpm. The emulsion is formed as membrane phase (FM) is used for extraction of 20 ml the feed solution. The feed or external aqueous phase is Zr 10 g/L and Hf 0,5 gr/L in a solution of nitric acid was mixed with 20 mL FM for 10 minutes with stirring extraction at 500 rpm.

2.3.2 The process of extracting and Stripping

UNH feed solution concentration (FAe) 1000 ppm by volume of 10 mL plus FM = 10 mL stirred for 10 minutes with a speed 500 rpm. The mixture was silenced for a moment and then separated with a separating funnel. FAe volume was measured. FM heated briefly, the emulsion will break into FO and FAi. FO and FAi separated and measured its volume. FAe and FAi then analyzed by XRF. This work was repeated to study the effects of % TOPO-kerosene, and then repeated for influence of variations of the internal water phase molarity (M HNO_3), the feed molarity (M H_3PO_4), and the stirring time. Based on the experimental results analysis data calculation is then used to calculate the efficiency of extraction and stripping efficiency Zr and Hf.

3. RESULT AND DISCUSSION

Initial studies were done to study the effect of stirring speed tool wear Ultra Turax on stability of the manufacture of

membranes using 5 % Span-80. The results can be shown in Table 1.

Table 1. Effect of stirring speed on the membrane stability

Speed (rpm)	Time early rupture (hours) in normal Temperature	Time early rupture with heating (minute) in 60-70ºC
2000	25	12
4000	146	11
6000	160	11
8000	210	8
10000	195	15

In the manufacture of emulsion membrane selected stirring speed of 8000 rpm, because the membrane was relatively stable and recovered energy efficiency.

3.1 Influence of percentage of TOPO-kerosene (Ratio FM : FAe = 10 ml : 10 ml = 1 : 1; FAi = 3M H_3PO_4; Fae = 1 M HNO_3; Stirring speed = 500 rpm; time of extraction : 15 minutes)

The membrane emulsion type was water-in-oil emulsion, ie H_3PO_4 in TOPO-kerosene. This emulsion can be formed due to existing of span-80. The previous studies have investigated the parameters that form the emulsion becomes stable. Relatively stable emulsion in the use of Span-80 as much as 5% by volume of the emulsion. Emulsion stability can be measured by the

amount of creaming figures expressed in the following equation:

$$\frac{\Delta VFAe}{\Delta VFAeo} \text{ and } \frac{\Delta VFAi}{\Delta VFAio} \approx 0 \qquad (7)$$

$$\Delta VFAe = (VFAe - VFAeo) \qquad (8)$$

$$\Delta VFAi = (VFAi - VFAio) \qquad (9)$$

Determination of % TOPO is important in the mechanism of metal transfer in the internal water phase (FAi), because with increasing % TOPO, then CFAi of Zr and Hf will be growing and the reaction with TOPO metal will be better. To determine the effect of the displacement of Zr and Hf to the organic phase can be seen in the binding ability TOPO Zr and Hf. At first, the uranium is at FAe in complex form solvated with water and nitrates. Due to the TOPO ligand H_2O through the extraction process will be replaced by TOPO and form a neutral complex in the organic phase. The greater the concentration of TOPO, then the extraction efficiency will be even greater. This suggests that, the more Zr and Hf is extracted and form a neutral complex with TOPO on the membrane phase. Zr and Hf is extracted, indicating more easily form a complex with TOPO. This can be shown in Tabel 2.

In Table 2 it can be seen that the concentration of TOPO affect the efficiency of Zr and Hf. The higher the concentration of TOPO will be increased efficiency. On the use of above 4 % to 5 % relative efficiency TOPO has been steady, due to the greater number of complex compounds of Zr and Hf

with increasing TOPO, while a limited number of H_3PO_4 stripping efficiency of Zr

slightly decreased. H_3PO_4 ability to react is still quite strong, so the stripping efficiency is relatively small. The effectiveness of the whole process of extraction method of emulsion liquid membrane can be known by looking at Distribution of Coefficient and Separation Factor of Zr and Hf.

Table 2. Correlation of % TOPO Kerosen and extraction efficiency

Extraction Efficiency (%)	Extraction Efficiency (EE), Distribution Coefficien (DC), and Separation Factor (SF)		
	Ziconium	Hafnium	SF
1	EE = 50 and DC = 1.00	EE = 25 and DC = 0.33	3.03
2	EE = 55 and DC = 1.22	EE = 24 and DC = 0.32	3.80
3	EE = 65 and DC = 1.86	EE = 30 and DC = 0.43	4.33
4	EE = 94 and DC = 15.67	EE = 32 and DC = 0.47	33.34
5	EE = 95 and DC = 19.00	EE = 32 and DC= 0.47	40.42

Table 3.Correlation of % TOPO Kerosen and stripping efficiency

Stipping Efficiency (%)	Stripping Efficiency (SE), Distribution Coefficien (DC), and Separation Factor (SF)		
	Ziconium	Hafnium	SF
1	SE = 50 and DC = 1.00	SE = 46 and DC = 0.85	1.18
2	SE = 52 and DC = 1.08	SE = 47 and DC = 0.89	1.22
3	SE = 55 and DC = 1.22	SE = 48 and DC = 0.92	1.33
4	SE = 58 and DC = 1.38	SE = 48 and DC = 0.89	1.55
5	SE = 60 and DC = 1.50	SE = 47 and DC = 0.89	1.69

To obtain good extraction efficiency is measured by the value of the total uranium.

From Tabel 3 it can be seen that the relatively good results in the use of 5% TOPO.

3.2 Effect of FAi (HNO$_3$) molarity (Ratio FM : FAe = 10 ml : 10 ml = 1 : 1, TOPO-Kerosene = 5 %, FAe = HNO$_3$, Stirring Speed = 500 rpm, Time of Extraction = 15 minute)

To find out how much Zr-Hf transfer to the organic phase it can be seen in Table 4, FAi molarity relationship with the extraction efficiency, it appears that the extraction efficiency will increase with the increase of phosphoric acid to reach a round 2-3 M HNO$_3$, but thereafter declined. The factors that influence are the chemical reactions and changes negative volume emulsion membrane systems. Increasing concentration of HNO$_3$, causes higher osmotic pressure on FAi, so more water coming into the FAi.

Effect of acidity FAi needs to be done to determine the most optimum acidity, to elaborate on the complex uranium into uranium that was concentration in FAi with ion complexes HNO$_3$.TOPO. Table4. Showed that the extraction efficiency rise with increasing of acidity FAi using nitric acid 3 M.

Stripping efficiency grows with increasing of rice FAi acidity and relatively steady after molarity above of 3 M. With increasing of HNO$_3$ metal-TOPO decomposition reaction will be more perfect,

and causing higher osmotic pressure on FAi causing water to pour into FAi. Basically complex compounds Zr(NO$_3$)$_4$. 2TOPO and Hf(NO$_3$)$_4$. 2TOPO are very strong.

Table 4. Correlation of the volume of internal aqueous phase after extraction and extraction efficiency

Extraction Efficiency (%)	Extraction Efficiency (EE), Distribution Coefficien (DC), and Separation Factor (SF)		
	Ziconium	Hafnium	SF
1	EE = 60 and DC = 1.50	EE = 46 and DC = 0.85	1.76
2	EE = 80 and DC = 4.00	EE = 57 and DC =1.33	1.33
3	EE = 96 and DC = 24.00	EE = 58 and DC = 1.38	17.39
4	EE = 90 and DC = 9.00	EE = 58 and DC = 1.38	6.52
5	EE = 89 and DC = 8.09	EE = 57 and DC = 1.33	6.08

Table 5. Correlation of the volume of internal aqueous phase after extraction and stripping efficiency

Stripping Efficiency (%)	Stripping Efficiency (SE), Distribution Coefficien (DC), and Separation Factor (SF)		
	Ziconium	Hafnium	SF
1	SE = 46 and DC = 0.85	SE = 36 and DC = 0.56	1.52
2	SE = 47and DC = 0.89	SE = 37 and DC = 0.59	1.51
3	SE = 47 and DC = 0.89	SE = 38 and DC = 0.61	1.45
4	SE = 48 and DC = 0.92	SE = 38 and DC = 0.61	1.51
5	SE = 47 and DC = 0.89	SE = 36 and DC = 0.56	1.59

Therefore, when reacted with HNO3.TOPO difficult to unravel. Thus resulting that the stripping of Zr-Hf is not too large.

Effect of molarity FAi against stripping efficiency can be seen in Table 5, the complex TOPO-HNO3 getting weaker so with the addition of HNO3 molarity. Because the difference is not so great for the efficiency stripping of the process taken in 3 M H3PO4. Merging both extraction efficiency and stripping efficiency will be obtained (Table 4 and Table 5).

3.3 Effect of FAe (H₃PO₄) Molarity (Ratio FM : FAe = 10 ml : ml = 1 : 1, TOPO-Kerosene = 5 %, FAi = 3 M HNO₃, stirring speed = 500 rpm, Time of Extraction = 15 Minute).

To find out how much metal transfer to the organic phase it can be seen in Table 6, the relationship with the FAe acidity extraction efficiency. At first the uranium is at FAe in complex form solvated by water and nitrate. Due to the TOPO through the extraction process, H₂O ligands will be replaced by TOPO and form a neutral complex in the organic phase.

In Table 6 it appears that at the time the acidity of 3 M, the efficiency of extraction started rising and reached a maximum of 1 M, but thereafter declined. Affecting factors are chemical reactions and changes negative volume emulsion membrane systems.

Effect of molarity or acidity greatly to the extraction of Zr/Hf. The increase in the acidity of the extraction system is solvation, especially for extractant TOPO, causing TOPO will react with the acid solvent in this case H₃PO₄.

The fall in the efficiency of the extraction on the acidity after 1 M, as a result of the reaction between TOPO with H3PO4 as a solvent feed. The factors that cause TOPO at high acidity are not able to extract the maximum Zr-Hf.

Metal extraction in the extraction system is influenced also by solvation of anions in the water phase. With the increase in acidity is an increase H3PO4 or ion PO4--3 excess in the solution.

Table 6. Correlation of the volume of external aqueous phase after extraction and extraction efficiency

Extraction Efficiency (%)	Extraction Efficiency (EE), Distribution Coefficien (DC), and Separation Factor (SF)		
	Ziconium	Hafnium	SF
1	EE = 60 and DC = 1.50	EE = 46 and DC = 0.85	1.76
2	EE = 80 and DC = 4.00	EE = 57 and DC =1.33	1.33
3	EE = 87 and DC = 6.69	EE = 58 and DC = 1.38	4.85
4	EE = 90 and DC = 9.00	EE = 58 and DC = 1.38	6.52
5	EE = 92 and DC = 11.50	EE = 57 and DC = 1.33	8.65

Table 7. Correlation of the volume of external aqueous phase after extraction and stripping efficiency

Stripping Efficiency (%)	Stripping Efficiency (SE), Distribution Coefficien (DC), and Separation Factor (SF)		
	Ziconium	Hafnium	SF
1	SE = 46 and DC = 0.85	SE = 36 and DC = 0.56	1.52
2	SE = 47 and DC = 0.89	SE = 37 and DC = 0.59	1.51
3	SE = 47 and DC = 0.89	SE = 38 and DC = 0.61	1.45
4	SE = 47 and DC = 0.89	SE = 38 and DC = 0.61	1.45
5	SE = 48 and DC = 0.92	SE = 36 and DC = 0.56	1.64

The formation of complex compounds Zr(NO3)4. 2TOPO and Hf(NO3)4. 2TOPO, cause is not readily biodegradable at the

time of stripping, so the value could not be higher stripping efficiency. Uranium metal complex that forms in greater number, while the Zr/Hf-TOPO reduced, so that the efficiency of stripping decrease (Table 7).

3.4 Effect of Extraction Time (Ratio FM : FAe = 10 mL : 10 mL = 1 : 1, TOPO-Kerosene = 5 %, FAi = 3 M HNO_3, stirring speed = 500 rpm, FAe = 5 M H_3PO_4).

The extraction time is required to allow contact during the process of extraction and stripping lasts until it reaches equilibrium. The extraction process takes place between the reaction of Zr/Hf with TOPO. Stirring or extraction will form a new emulsion to emulsion membrane of a different size. Because there will be increase or decrease between the two phases of water, namely FAe and FAi.

With the entry FAe into FAi accompanied by the transfer of uranium metal into TOPO as FO and forwarded FAi. U-TOPO extraction process and form a complex compound neutral Metal-TOPO pass through the membrane and decomposed by a stripping agent into the FAi. Decomposition for their ion exchange reaction with H3PO4 where the complex will release reacting Zr(NO3)4. 2TOPO and Hf(NO3)4. 2TOPO.

The longer time of extraction, the extracted metals to form metal complex-TOPO will be more and more. Table 8 and

Table 9 are shown the relationship between the extraction efficiency, and eextraction efficiency increases with the length of time of extraction, the optimum condition is

achieved in 10 minutes, because of its efficiency relatively steady, the complex Zr(NO3)4. 2TOPO and Hf(NO3)4. 2TOPO..

Table 8. Correlation of Extraction Time and aqueous phase and Extraction efficiency

Extraction Time (Minute)	Extraction Efficiency (EE), Distribution Coefficien (DC), and Separation Factor (SF)		
	Ziconium	Hafnium	SF
10	EE = 94and DC = 15.67	EE = 56 and DC = 1.27	12.34
20	EE = 95and DC = 19.00	EE = 57 and DC =1.33	14.29
30	EE = 94 and DC = 15.67	EE = 58 and DC = 1.38	11.56
40	EE = 94 and DC = 15.67	EE = 58 and DC = 1.38	11.56
50	EE = 94 and DC = 15.67	EE = 57 and DC = 1.33	11.78

Table 9. Correlation of Extraction Time and the aqueous phase Stripping efficiency

Stripping Time (Minute)	Stripping Efficiency (SE), Distribution Coefficien (DC) and Separation Factor (SF)		
	Ziconium	Hafnium	SF
10	SE = 47 and DC = 0.89	SE = 38 and DC = 0.61	1.46
20	SE = 47 and DC = 0.89	SE = 37 and DC = 0.59	1.51
30	SE = 46 and DC = 0.85	SE = 36 and DC = 0.56	1.52
40	SE = 47 and DC = 0,89	SE = 38 and DC = 0.61	1.45
50	SE = 48 and DC= 0.92	SE = 36 and DC = 0.56	1.64

In Table 8 and Table 9 are shown that efficiency has been steadily after 10 minutes, because during that time already reached saturation point or achieve equilibrium.

The combined efficiency of extraction and stripping efficiency will generate total efficiency. In total efficiency, obtained by the graph in Figure 15. The total efficiency reaches a maximum at 10 minutes and after that relatively constant. It showed that in 10 minutes 5 % TOPO capabilities have reached a saturation point in extraction of Zr/Hf clicking, so although the extraction time plus efficiency will not increase. Relative a good of extraction time at 10 minutes, which means that during time the uranium at feeds extraction by TOPO formed a neutral complex. In that interval H_3PO_4 who are at FAi able to download all the decomposition of metal-ligand complexes TOPO formed on the membrane phase during the extraction process. So as much as the amount of H_3PO_4 complex Zr/Hf-TOPO

4. CONCLUSION

The relative good result of this research is the extraction volume of 10 ml feed solution in an atmosphere of 5 M H_3PO_4, membrane extraction with 10 ml of 5 % TOPO-kerosene and HNO_3 3 M for 10 minutes with a stirring speed at the time of extraction of 500 rpm, speed manufacture of membranes 8000 rpm and the use of span-80 equal the 5 %. In this state obtained Separation Factor (SF) of Zr-Hf Is 17.39.

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