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Article in *Chemical Engineering Transactions* · January 2019

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## Separation of Zirconium and Hafnium by Extraction with 2-Octanol

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Zirconium and hafnium are shown to be separable using 2-octanol ( $C_8H_{18}O$ ) as an extractant. Zirconium basic carbonate was dissolved using hydrochloric acids at concentrations ranging from 5 % to 20 %. Potassium fluoride was found to be crucial to the process. Its effect was investigated in the concentration range of 1 M to 3 M. The optimum conditions obtained for extraction were 10 wt % HCl in a 1.5 M KF solution, a contact time of 15 minutes, and 100 % 2-octanol. Under these conditions, the separation factor of zirconium and hafnium is 9.2 with a maximum extraction percentage of 96.58 % of zirconium. The optimum conditions for stripping of zirconium were found to be 3 M  $H_2SO_4$  as stripping agent, an A/O ratio of 1:1 and 40 minutes contact time. The McCabe-Thiele diagrams constructed from the experimental data indicate that four and five equilibrium stages are sufficient for the extraction and stripping of zirconium respectively. A recovery of 97.25 % of hafnium was obtained using a mixture of oxalic acid and nitric acid as a stripping agent. A study of chemical speciation in the two phases would be important for the improvement of the process.

### 1. Introduction

The predominant commercial source of zircon is beach deposits which are recovered from heavy-mineral bearing sand. These deposits are found in Australia, Brazil, South Africa, Ceylon, India, Madagascar, USA, and Egypt (Saberyan et al., 2010). Australia is the major world producer and exporter of zircon sand (Hoddinott, 1995). Zirconium (Zr) metal production is based almost exclusively on the treatment of two ore minerals. Zirconium silicate (zircon,  $ZrSiO_4$ ), which generally contains 49 % Zr and 0.4 to 1.5 % hafnium (Hf), is the principal industrial mineral, while baddeleyite ( $ZrO_2$ ), an impure zirconium oxide, is a commercially important but less abundant, and contains as much as 75 % Zr and 0.4 to 1.7 % Hf (Suriyachat, 1992). Zr has many industrial applications, e.g., as ceramics, enamels, refractory materials, glazes, foundry molds abrasive grits, dye pigments, and catalysts in organic reactions (Rejmane et al., 2006). The major use of Zr metal is in the nuclear industry, as structural material due to its excellent corrosion resistance, high melting point, and low neutron-capture cross section (Banda et al., 2013). It is also used extensively for fuel rods assemblies in the nuclear reactors. On the other hand, Hf has a high neutron-capture cross section and is used as a control material in water-cooled nuclear reactors and rectifiers. The efficiency of the reactor core and generation of power depend directly on the concentration of Hf in Zr. For use in nuclear reactors, Zr should have a very low Hf concentration, of less than 100 ppm. The separation of Hf from Zr is thus extremely important in nuclear science and technology (Da Silva et al., 1998).

Different methods have been used to separate Hf from Zr. These include fractional crystallization, fractional precipitation, ion exchange, solvent extraction, molten salt distillation, and selective reduction. However, only two methods, viz., solvent extraction and molten salt distillation (the CEZUS process developed by Compagnie Europeene du Zirconium, Paris, France) have been used industrially. Solvent extraction is one of the most important technologies for Zr-Hf separation in nuclear industry. A large number of researchers have demonstrated that the extraction and separation of Zr and Hf is possible using different extractants. For example, Jaykishon et al. (2018) reported the extraction of Zr(IV) from sulfuric acid medium using tri-n-octyl amine in kerosene. Yadollahi et al. (2018) reported on solvent extraction separation of Zr and Hf from nitric acid solutions using mixture of cyanex-272 and TBP. Taghizadeh et al. (2009) reported the extraction and

Paper Received: 14 June 2018; Revised: 18 October 2018; Accepted: 29 December 2018

Please cite this article as: Kabangu J.M., Lubbe S., Crouse P.L., 2019, Separation of Zirconium and Hafnium by Extraction with 2-octanol., Chemical Engineering Transactions, 75, 631-636 DOI:10.3303/CET1975106

separation of Zr and Hf using bis-(2, 4, 4-trimethylpentyl) phosphonic acid (Cyanex 272) as extractant in a nitric acid medium. The separation factor of this process was improved by the addition of water soluble  $\alpha$ -hydroxycarboxylic acid. Banda et al. (2013) developed a process to separate Zr and Hf by solvent extraction with tri-2-ethylhexyl amine (TEHA). El-Yamani et al. (1978) investigated the extraction and separation of Zr and Hf using Primene JMT (a long-chain primary amine) in sulfuric acid. Van der Westhuizen et al. (2007) demonstrated that it possible to extract and separate Zr and Hf using acid pre-treated Alamine 336 in a hydrochloric acid medium. Saberyan et al. (2008) conducted a study on a liquid-liquid extraction to separate Hf from Zr, using Cyanex 301 in kerosene. Ling et al. (2016) developed a separation process for the selective extraction of Hf (IV) over Zr (IV) from moderate sulfuric acid solutions using di-2ethylhexylphosphic acid (D2EHPA). De Beer et al. (2016) investigated the possibility of selective extraction and separation of Hf over Zr using Ionquest 801. Xu et al. (2012) developed a process for the separation of Hf from thiocyanic acid medium using mixture of diisobutyl ketone (DIBK) and tributyl phosphate (TBP) as the extractant. Ling et al. (2013) performed a solvent extraction process of Zr and Hf from hydrochloric acid solution by using acidic organophosphorus extractants and their mixtures with TOPO. Navy et al. (2009) carried out a solvent extraction study to extract and separate Zr and Hf from nitrate medium using phosphine oxide extractants (Cyanex 921, Cyanex 923 and Cyanex 925) in kerosene. Da Silva et al. (2000) demonstrated that Cyanex 925 is an efficient selective extractant for getting maximum separation factor of about 37 between Zr and Hf in hydrochloric acid. Poriel et al. (2006) studied the extraction of Zr and Hf from aqueous HCl solutions with Aliquat 336 in organic diluents.

Different solvents have been studied as extractants as shown above but only three commercially available extractants are used in the production of nuclear grade Zr and Hf metals, viz., methyl-iso-butyl ketone (MIBK), tri-butyl phosphate (TBP) and the high molecular weight tertiary alkyl amine. These processes present several technological disadvantages and environmental problems.

In the TBP process, the disadvantages are: low metal concentration in the aqueous and organic phases because of the formation a third phase; large consumption of chemicals; low Zr/Hf separation factor; and the inability to produce high grade Hf for use as control rods (Da Silva et al., 1998). For MIBK the disadvantages are: waste stream contains high concentrations of ammonium cyanides and other organic by-products that lead to environmental concerns; the solvent itself is volatile and is slightly soluble in water leading to significant losses by evaporation, requiring extra care in handling and recycling the organic stream and in discarding the effluent (Synder et al., 1990). High cost due to consumption of expensive chemicals by decomposition; low flash point of thiocyanates and thiocyanic acid in the presence of HCl (Da Silva et al., 1998). In the Toyo zirconium process, many equilibrium stages are required which is time consuming and the starting complex must be produced prior to the extraction process. The CEZUS process requires highly corrosion-resistant alloys and sophisticated technologies to pump and handle the vapour streams, and to avoid any air moisture contamination (Da Silva et al., 1998). The disadvantages of these processes could be largely avoided by using more benign extractants.

This has necessitated the search for new alternative extractants.

Octanol was used in the present investigation as alternative extractant based on its main advantages which include low solubility in water, sufficiently low volatility, and a higher flash point (81 °C). In addition octanol has a lower viscosity, and is cheaper than TBP and MIBK.

The choice of 2-octanol was based on the similar crystal-chemical properties of Zr, Hf, Ta and Nb, i.e., high charge and ionic radii. The high field strength elements (HFSE: Ti, Zr, Hf, Nb and Ta) are considered to behave as a coherent group of substituents in rock-forming silicates minerals (Sun et al., 1989). It was also based on the work by Kabangu et al. (2012) where the separation of niobium (Nb) and tantalum (Ta) from Mozambican tantalite using octanol as extractant was demonstrated. In previous work by He et al. (1998) and Agulyansky (2004), the efficiency of octanol was shown to be comparable with MIBK commonly used in the industrial technology of Ta and Nb (Agulyansky, 2004; Mayorov et al., 2002). Despite the fact that Mayorov et al. (2002) demonstrated the efficiency of extraction and separation of Ta from Nb with octanol to be comparable with MIBK, octanol has not been used in the extraction and separation of Zr from Hf. 1-octanol was used as a modifier to eliminate the formation of emulsions by Van der Westhuizen et al. (2007) and by El-Yamani et al. (1978). The main advantages of 2-octanol compared with MIBK as extractant, are: very low solubility in water; lower volatility; and a higher flash point.

In view of the numerous advantages of solvent extraction, it was the process of choice for this study. In our recently reported work Kabangu et al. (2019) it was discovered that 2-octanol yielded better extraction and separation than 1-octanol. A further study was then done in order to recover Hf from the loaded organic solution and also determine the number of stages required to extract and strip Zr. Then the objective of this investigation is to evaluate the potential of using 2-octanol as an alternative extractant for the extraction and separation of Zr from Hf in order to obtain a more economical and friendly process. To achieve this, the effects

of different parameters, including the initial feed concentration, concentration of KF and HCl in the aqueous phase, contact time, phase ratio, the stripping agent were investigated.

## 2. Materials and Methods

### 2.1. Materials

All chemicals used were of analytical grade. Zirconium basic carbonate (ZBC) which contained approximately 40 %  $ZrO_2$ , and 1-2 %  $HfO_2$  by mass was purchased from Sigma Aldrich and was used for all extraction and separation experiment studies without further purification. 2-octanol ( $C_8H_{18}O$ ) purchased from ACE (Associated Chemical Enterprises, SA) with a purity of 97 % was used as an extractant in all the extraction experiments. Potassium fluoride (KF) with a minimum purity of 98.5 % purchased from Merck and hydrochloric acid (HCl) with a purity of 32 % by mass, purchased from Sigma Aldrich were used to prepare the aqueous solutions that were used for all the extraction and separation experiments. Ammonium sulfate  $[(NH_4)_2SO_4]$  with a purity of  $\geq 99.0$  %, sulfuric acid ( $H_2SO_4$ ) with a purity of 98 % by mass purchased from Sigma Aldrich, nitric acid ( $HNO_3$ ) from Merck with a purity of 70 % by mass, and oxalic acid ( $C_2H_2O_4$ ) with a purity of 99 % was purchased from Merck were used for the stripping of Zr and Hf. Deionized water was used in all aqueous preparations. ICP-OES calibration standards were obtained from Monitoring and Control Laboratories SA. A Spectro Arcos model inductively-coupled plasma optical-emission spectrometer (ICP-OES) was used for the elemental analysis of the aqueous solution.

### 2.2. Methods

All experiments were conducted batch wise in a 200 mL beaker at ambient temperature (20 – 25 °C). (Initial experiments, up to 65 °C, indicated very little temperature dependence and only the ambient results are presented here.) Zirconium basic carbonate (ZBC) containing 40 %  $ZrO_2$  and 2 %  $HfO_2$  was leached or decomposed using HCl acid concentrations between 5 to 20 %. The solution was then contacted with a solution of potassium fluoride (KF) from 1M to 3M in solution. The extraction experiments were carried out by shaking vigorously equal volumes (50 mL) of the aqueous and organic phases at different ratios for 15 minutes. After equilibration, the contents were allowed to disengage. A separation funnel was employed to separate the aqueous from the organic phase. Analyses of the aqueous phase were carried out to determine the concentration of Zr and Hf using an ICP-OES. The metal concentrations of the Zr and Hf in the organic solution were inferred from a mass balance analysis. The distribution ratio ( $D$ ) and the separation factor ( $\beta$ ) were calculated as the ratio between the concentrations of metal at equilibrium in the organic phase to that in the aqueous phase and as the quotient of the distribution ratios respectively. The results reported are mean values of at least three samples at each set of experimental condition for each process parameter variables. The errors associated with the extraction, separation and stripping percentage were  $\pm 4$  %.

## 3. Results and discussions

### 3.1 Effect of HCl and KF concentration on extraction

In order to make a valid interpretation of the effect of different parameters, it must be ensure that equilibrium between the aqueous and organic phase is reached. The initial solution contain 3573.46 mg/L of Zr and 63.96 mg/L of Hf which was kept constant throughout the entire experiment was then contacted with 2-octanol. The effluence of HCl and KF concentration investigated shows that increasing the concentration of these two chemicals increases the extraction and separation of Zr from Hf. The highest extraction and separation obtained were 60.80% of Hf, 92.56 % Zr and a separation factor of 8.38 at an optimum experimental condition of 10 % HCl, 1.5 M KF, an O/A ratio of 1:1 and contact time 15 minutes. It was also established by Kabangu et al. (2019) that the extraction percentage of Zr and Hf increases with time then remains constant at 15 minutes.

### 3.2 McCabe-Thiele diagram: extraction

A set of experiment was carried out to examine the effect of organic phase to aqueous phase ratio (A/O) from 1:1 to 1:5. The results indicate that increasing the phase ratio increase the extraction and separation of both Zr and Hf with the highest separation factor of 9.2 obtained at a ratio of 1:2. This result was also found by Kabangu et al. (2019). McCabe-Thiele diagrams were constructed to determine the number of stages needed to reach the desired separation of Zr from Hf. In this study, the equilibrium data were obtained at a constant ion concentration and different A/O volume ratio using optimum extraction condition as determined above. From the McCabe Thiele diagram Fig.1 for Zr, four equilibrium stages are required for almost 96.58 % Zr extraction.

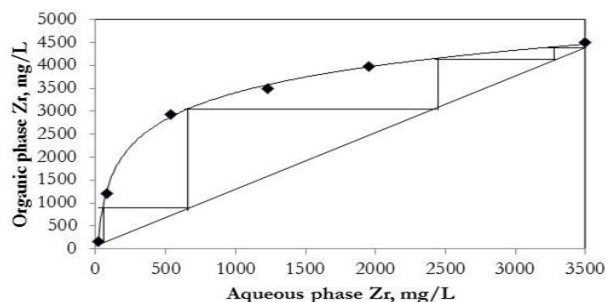


Figure 1. McCabe-Thiele diagram of Zr extraction (experimental conditions 100% 2-octanol, 15 minutes contact time, 10% HCl and 1.5 M KF in solution).

### 3.3 Effect of stripping agent

The effect of stripping agents was studied using different stripping agents (distilled H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and HCl), with the concentration of the stripping agent and other factors kept constant. The best stripping agent for Zr was found to be H<sub>2</sub>SO<sub>4</sub>. The effect of H<sub>2</sub>SO<sub>4</sub> acid concentration was studied in the range of 1 – 5 M. Fig 2 shows that the stripping efficiency increases with increasing acid concentration from 1 M to 3 M (S % 44.48 to 81.20 %) and then decreases. The decreasing stripping efficiency at higher H<sub>2</sub>SO<sub>4</sub> concentration could be due to the successive formation of highly charged anionic species of Zr complexes in aqueous solutions (Pershina et al., 2002).

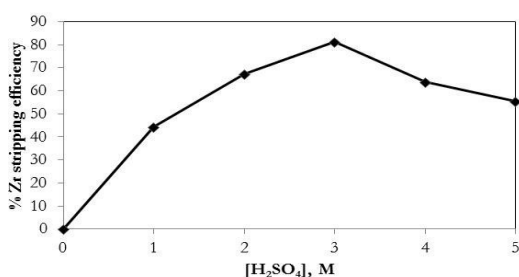


Figure 2. Effect of H<sub>2</sub>SO<sub>4</sub> concentration on the stripping of zirconium from loaded 2-octanol, contact time 15 minutes, A/O 1:1, H<sub>2</sub>SO<sub>4</sub> = 1- 5M.

### 3.4 McCabe Thiele diagram: stripping

The data for the construction of McCabe-Thiele diagram were obtained by shaking different volume of Zr loaded solvent with a fixed volume of H<sub>2</sub>SO<sub>4</sub> acid (3M) until equilibrium was obtained. From this McCabe-Thiele diagram, represented in Fig 3, it is clear that five stages are sufficient for stripping around 98.52 % of Zr from loaded 2-octanol.

### 3.5 Recovery of Hf

After stripping Zr from the loaded organic solvent, the solution was scrubbed with 3 M H<sub>2</sub>SO<sub>4</sub> in order to remove the Zr. Then Hf was recovered by stripping the remaining loaded Hf organic solution with a mixture of oxalic acid and nitric acid. The results obtained show that mixture of oxalic and nitric acid can be considered as a good stripping agent of Hf as it could lead to a good separation of Hf from the remaining Zr. Therefore, stripping with different concentration of a mixture of oxalic acid and HNO<sub>3</sub> acid was investigated. The results obtained are shown in Table 1. A concentration of 0.5 M oxalic acid and concentrated HNO<sub>3</sub> acid was chosen as a good stripping agent. It gave 50.68 % Hf and 23.83 % Zr, after one stripping stage. After two stages, the stripping percentage increased to 73 % Hf and 28, 68 % Zr, and after three stages 97.25 % Hf and 31.92% Zr where stripped, which lead to a good separation of the two metals ions.

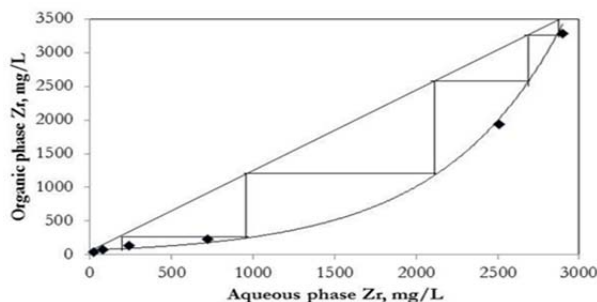


Figure 3. McCabe-Thiele diagram for the stripping of zirconium from loaded 2-octanol.

Table 1. Stripping of Hf and Zr with mixture of oxalic acid and nitric acid.

Oxalic acid, %	HNO <sub>3</sub> , M	Hf, %	Zr, %
0.5	1	2.48	0.86
0.5	3	6.91	2.55
0.5	6	14.74	8.74
0.5	9	18.15	10.62
0.5	11	26.38	18.64
0.5	15.7	50.68	23.83

The process indicates that it is imperative to increase the concentration of HCl, KF and the phase ratio between the aqueous phase and organic phase in order to improve the extraction and separation of Zr from Hf. The effect of stripping is very important in order to strip the hafnium from the loaded organic solution. The performance of the 2-octanol compares well with MIBK and TBP in terms of their separation factor. This process has a slightly higher separation compared to the MIBK which is around 7 (Fisher et al., 1947) and somewhat lower than the TBP which is around 10 (Hure et al., 1956). However, the lack of the third-phase formation makes favourable compared to TBP.

#### 4. Conclusions

The results obtained from this investigation show that Zr ions are preferentially extracted over Hf by 2-octanol from a moderate concentration solution of 10 % HCl and 1.5 M KF. A separation factor of 9.20 between Zr and Hf was obtained using 2-octanol at a ratio of aqueous-to-organic of 1:2. The McCabe Thiele diagrams show that four equilibrium stages are required for 96.58 % zirconium extraction. The McCabe-Thiele diagram for stripping using the optimum parameters, indicate that five theoretical stripping stages are sufficient to strip around 98.52 % of zirconium from the loaded organic solvent. Hafnium was recovered from the loaded solution using a mixture of oxalic acid and HNO<sub>3</sub> acid. The use of octanol as alternative extractant presents both a direct advantage by reducing the cost of the process because of the low price of the latter compared to either MIBK or TBP, and KF is also cheaper compared to ammonium thiocyanate. An indirect advantage by the avoidance of environmental problems such as the use of ammonium cyanide that leads to an environmental concerns.

#### Acknowledgements

The authors would like to thank the University of Pretoria, the South African Research Foundation (NRF) and the Advanced Metals Initiative of the Department of Science and Technology, for financial support.

#### References

- Agulyansky, A., 2004. The Chemistry of Tantalum and Niobium Fluorine compounds. Elsevier, Amsterdam.
- Babkin, A.G., Mayorov, V.G., Nikolaev, A.I., 1998. The extraction of niobium, tantalum and other element from fluorine solutions. L: Nauka. 204 pp.
- Banda, R., Lee, H.Y., Lee, M.S., 2013. Separation of Zr and Hf from strong hydrochloric acid solution by solvent extraction with TEHA. 295, 1537 – 1543.
- Beer, L., van der Westhuizen, D.J., Krieg, H.M., 2016. Solvent extraction and separation of hafnium from zirconium using Ionquest 801. Journal of the Southern African Institute of Mining and Metallurgy. 116, 93 – 99.

- Da Silva, A.B.V., and Distin, P.A., 1998. Zirconium and hafnium separation without waste generation. CIM bulletin: technical paper. 91, 221-224.
- Da Silva, A., El-Ammouri, E., Distin, P.A., 2000. Hafnium/zirconium separation using Cyanex 925. Can. Metall. Q. 39, 37-42.
- El-Yamani, I.S., Farah, M.Y., and Abd El-Aleim, F.A., 1978. Co-extraction and separation of zirconium and hafnium by long-chain amines from sulfate media. Talanta. 25, 523-525.
- Fischer, W., Chalybaeus, W., 1947. Die preparative gewinnung reiner hafniumverbindungen durch verteilung. Zeitschrift for anorganische und allgemeine chemie 255, 277 – 286.
- He, C., Liu, Z and Zhang, H., 1998. Treatment of fluorine-containing waste gas from hydrometallurgy of tantalum and niobium ore. Nonferrous Metals. 4, 141 – 142.
- Hoddinott, P.J., 1995. "Energy Minerals". In Metals & Minerals. Annual Review; Mining Journal Ltd.: London, England. 68-70.
- Hure, J., Saint-James, R., Process for separation of zirconium and hafnium, Proceedings of the International conference on peaceful atomic energy, United Nations, vol. 8, 551 – 555.
- Jaykishon, S., Amit, S., Bhikari, C.B., 2018. Liquid-liquid extraction of Zr(IV) from sulphuric acid medium using tri-n-octyl amine in kerosene. European Journal of Chemistry, 9(3), 222 – 227.
- Kabangu, M.J., Lubbe, S.J., Crouse, P.L., 2019. Solvent extraction of zirconium and hafnium with 1 and 2-octanol: a comparative study. Chemical Engineering Transactions, accepted for publication May 2019.
- Kabangu, M.J., Crouse, P.L., 2012. Separation of niobium and tantalum from Mozambican tantalite by ammonium bifluoride digestion and octanol solvent extraction. Hydrometallurgy. 129-130, 151 – 155.
- Ling, Y.W., Man, S.L., 2016. Development of a separation process for the selective extraction of hafnium (IV) over zirconium (IV) from sulfuric acid solutions by using D2EHPA. Hydrometallurgy. 160, 12 – 17.
- Ling, Y.W., Hwa, Y.L., Man, S.L., 2013. Solvent extraction of zirconium and hafnium from hydrochloric acid solutions using acidic organophosphorus extractants and their mixtures with TOPO. Materials Transactions. 54, 8, 1460 – 1466.
- Mayorov, V.G., Nikolaev, A.I., 2002. Tantalum (V) and niobium (V) extraction by octanol. Hydrometallurgy. 66, 77-83.
- Nayl, A.A., El-Nadi, Y.A., Daoud, J.A., 2009. Extraction and separation of Zr(IV) and Hf(IV) from nitrate medium by some Cyanex extractants. Separation Science and Technology. 44, 2956-2970.
- Poriel, L., Favre-Reguillon, A., Pellet-Rostaing, S., Lemaire, M., 2006. Zirconium and hafnium separation. Part 1. Liquid/liquid extraction in hydrochloric acid aqueous solution with Aliquat 336. Sep. Sci. Technol. 41, 1927-1940.
- Pershina, V., Polakova, D. and Omtveldt, J.P., 2002. Theoretical predictions of complexes formation of group-4 elements Zr, Hf and Rf in H<sub>2</sub>SO<sub>4</sub> solutions. Radiochimica Acta. 94, 407 – 414.
- Rejmane, M. M., Sargar, B.M.; Mahamuni, S. V., and Anuse, M. A., 2006. Solvent extraction and separation of zirconium (IV) from succinate media with N-n-octylamine. J. Serb. Chem.Soc. 71(3), 223-234.
- Saberyan, K., Vahedian-Donyaparast, P., Noparast, M., Zolfonoun, E., Nemati, A., 2010. Solvent extractions of zirconium from zircon leach liquor using triphenylphosphine oxide. Minerals & metallurgical Processing. 27(3), 129-132.
- Saberyan, K., Meysami, A.H., Rashchi, F., Zolfonoun, E., 2008. Proposal of a new Hf(IV)/Zr(IV) separation system by the solvent extraction method. Chinese Journal of Chemistry. 26, 2067 – 2072.
- Sun, S.S., McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and process. In: Saunders, A.D & Narry. M.J. (eds) Magnetism in the Ocean Basins, Geological Society, London Special Publication. 42, 313-345.
- Snyder, T.S., Lee, E.D., 1990. Zirconium-hafnium production in zero liquid discharge process. US Patent No. 5112493.
- Suriyachat, D., 1992. Zirconium solvent extraction using organophosphorous compounds. Master's thesis, McGill University, Montreal, Quebec, Canada.
- Taghizadeh, M., Ghasemzadeh, R., Ashrafizadeh, S.N., Saberyan, K., and Marabeh, M.G., 2009. Determination of optimum process conditions for the extraction and separation of zirconium and hafnium by solvent extraction. Hydrometallurgy. 90, 115-120.
- Van der Westhuizen, D.J.; Lachmann, G.; and Bruinsma, O.S.L., 2007. Separation of zirconium and hafnium via solvent-extraction. The International Mineral Processing Conference (MinProc), Cape Town, South Africa
- Xu, Z., Wang, L., Wu, Y., Chi, R., Zhang, L., Wu, M., 2012. Solvent extraction of hafnium from thiocyanic acid medium in DIBK-TBP mixed system. Trans. Nonferrous Met. Soc. China. 22, 1760-1765.
- Yadollahi, A., Saberyan, K., Meisan, T.M., Amir, C., Mohammad, R.Z., 2018, Solvent extraction separation of Zr and Hf from nitric acid solutions using mixture of cyanex-272 and TBP.