

# Separation of Zirconium and Hafnium using Electrical Field

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## Abstract

In this work, a new method of separation of Hafnium and Zirconium is introduced in which, ions movement is facilitated and accelerated via an electric field. Extraction and separation of Hafnium from Zirconium is performed with TBP and D2EHPA extractants. In order to separate the two metals, two cells containing feed solution and recovery solution were utilized. Cells were connected to each other by the organic phase and the electric field acted on them. Transmission of the ions occur through the organic liquid membrane and under the applied electric field. The lower level of organic matter consumption and acceptable separation factor are the benefits of this method.

Results showed that the acceptable separation factor of 8.3 was achieved for Tri-butyl phosphate as the organic extractant.

TBP organic matter was found to be a stronger extractant compared to D2EHPA. Moreover, in addition to its higher extraction, it also revealed a better separation factor with respect to D2EHPA.

**Keywords:** Zirconium; Hafnium; Liquid Membrane; Separation Factor; Electrical Field; Tri-butyl phosphate; D2EHPA

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## 1. Introduction

Zirconium and Hafnium co-exist in the nature, but they have opposite nuclear characteristics. Thus, they have to be separated prior to their transformation into pure metals. Continuous efforts have been made to develop new extractants and new methods for the extraction and possible separation of Zirconium and Hafnium. Conventional solvent extraction technology uses TBP/HNO<sub>3</sub> or MIBK/NaSCN/HNO<sub>3</sub> extractants.

In the process using TBP/HNO<sub>3</sub>, 3 M nitric acid solution containing up to 30 g l<sup>-1</sup> (Zirconium+ Hafnium) and 3.5M sodium nitrate as salting out agent is contacted counter currently with 60% (v/v) TBP in kerosene, under these conditions, the distribution factor for Zirconium was around 1.5 and that of Hafnium around 0.15, therefore separation factor was 10 [1]. The most important disadvantages of this technology are the large consumption of chemicals and low Zirconium/Hafnium separation factor.

In the MIBK/NaSCN/HNO<sub>3</sub> process, thiocyanate complexes of Zirconium and Hafnium are formed in hydrochloric acid (2.0 M). These complexes exhibit a significantly different solubility in methyl iso-butyl ketone (MIBK) [2].

The disadvantages of these processes could be largely avoided if it were feasible to separate Hafnium and Zirconium, using another method. Previous reports have used other extractants but solvent extraction method for Zirconium/Hafnium separation [3-8]. Among them the most successful has been Cyanex 925 which extracted 61% Zirconium and 4% Hafnium giving a separation factor of 37 [6].

Taguchi's method was used to determine the optimum conditions for separation of Zirconium from Hafnium by solvent extraction. The experimental conditions were studied in the range of 0.1 to 2.0 M for three different acids and TBP, D2EHPA or Cyanex 272 as extractant. The optimum extraction of Zirconium was 71% when 2.0 M

nitric acid and Cyanex 272 were used. The optimum Zirconium/Hafnium separation was also achieved using this combination [9].

In this study, extraction behavior of Zirconium and Hafnium has been investigated with D2EHPA or TBP as extractant under an electrical field. Using an extractant liquid layer over the solutions causes very low consumption of organic phase. Also the two steps of extraction and stripping had done in one step using a cell.

## **2. Experimental**

### *2.1. Experimental design*

In order to perform the corresponding tests in this investigation, a series of equipments and materials were used. The whole process was carried out in a special cell designed specifically for this investigation. Two cylindrical parallel chambers were provided within a PTFE polymer bar. The two cylinders were connected from the top side. In order to exert the electrical current from the bottom, two cylindrical electrodes of graphite (99.9% C, 1.5% porosity) and stainless steel (316L) were placed at the bottom of the two hollow spaces. The anode (graphite electrode) was connected to the positive pole of the rectifier and the cathode (stainless steel electrode) was connected to the negative pole. The cathode was accompanied with a multi-meter to measure the current passing through the cell (fig. 1).

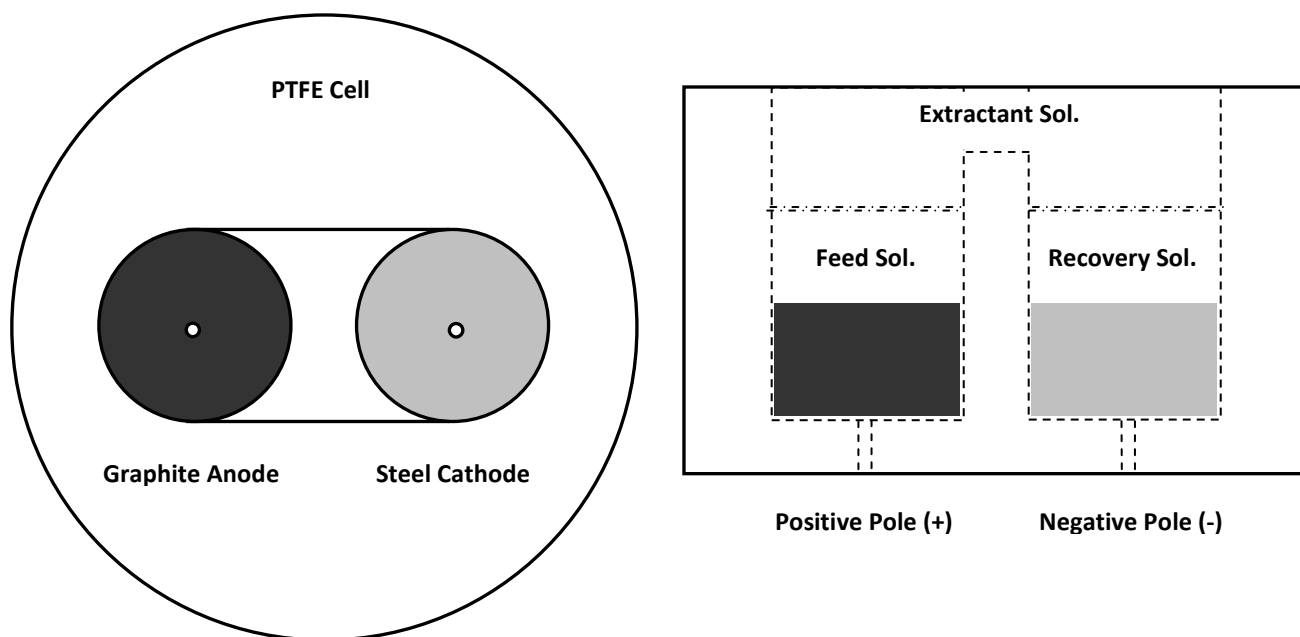


Fig.1. Schematic of the Cell

## 2.2. Reagents

In order to prepare the feed solution,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (Merck 98%) and  $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$  (Aldrich 99%) were used as the source of Zr (IV) and Hf (IV) respectively. D2EHPA and TBP were supplied by Merck (Germany) and kerosene (Fluka) (bp. 200–250 °C) was used as the diluent. All of the other reagents were used at the analytical reagent grade.

## 2.3. Procedure for extraction

The aqueous feed phase was prepared by dissolving amount of Zirconium and Hafnium oxychloride appropriate powder in a solution containing 1 M of nitric acid media or distilled water. Dissolved metal concentrations were  $10 \text{ g.l}^{-1}$  and  $1 \text{ g.l}^{-1}$  for Zirconium and Hafnium respectively.

The necessary concentration of TBP and/or D2EHPA for an acceptable level of Zirconium extraction was determined through the preliminary tests. The selected concentration for D2EHPA and TBP were 50 and 20 vol. %, respectively. The aqueous

recovery phase was prepared by 4 M sulphuric acid. Batch contacts with phase ratio O/A = 0.5 were performed at 25 °C. Because of the difference of the aqueous and organic solutions' densities no mixing would happen in the cell. The contact time was 180 min which was two times larger than the time needed to attain the apparent equilibrium. Solution analyses were made using ICP-OES. A rectifier (GWINSTEK, max. voltage 320V) prepared the electrical DC potential difference. Seven different voltages of 5, 10, 30, 50, 75, 100, 125, 150, 175 and 200V were used in these experiments.

### 3. Results & Discussion

#### 3.1. Effect of the organic extractant solution on the separation factor

In the presence of the distilled water and also nitric acid as feed based solutions, using different potential differences, TBP showed higher separation factor in comparison with other extractants. Under the voltage of 100 V separation factors has achieved 5.86, 3.75 and 1.2 for TBP, TBP-D2EHPA and D2EHPA, respectively. TBP as a neutral solution produces complex with the metal ions during extraction. It seems TBP extracted Zirconium ions with ion pair extraction method more than Hafnium and inclination of Zirconium to make the complex is more than Hafnium. Adding D2EHPA to the extractant solution decreased the effect of TBP in Zirconium extraction. It is because of changing mechanism of extraction. By using D2EHPA as the extractant the mechanism of extraction changed. In this case the reaction for the formation of a transported compound ( $R_nMe$ ) can generally presented as



where  $nRH$  is the number of molecules  $(C_8H_{17}O)_2(OH)PO$  involved in the reaction;  $R_n$  is the number of anions  $(C_8H_{17}O)_2PO_2^-$  entering into the composition

of a compound being formed, and (org) and (aq) are the organic and aqueous phases, respectively.

In this mechanism Hafnium ions could react with D2EHPA like Zirconium ions and it caused more Hafnium extraction and low separation factor.

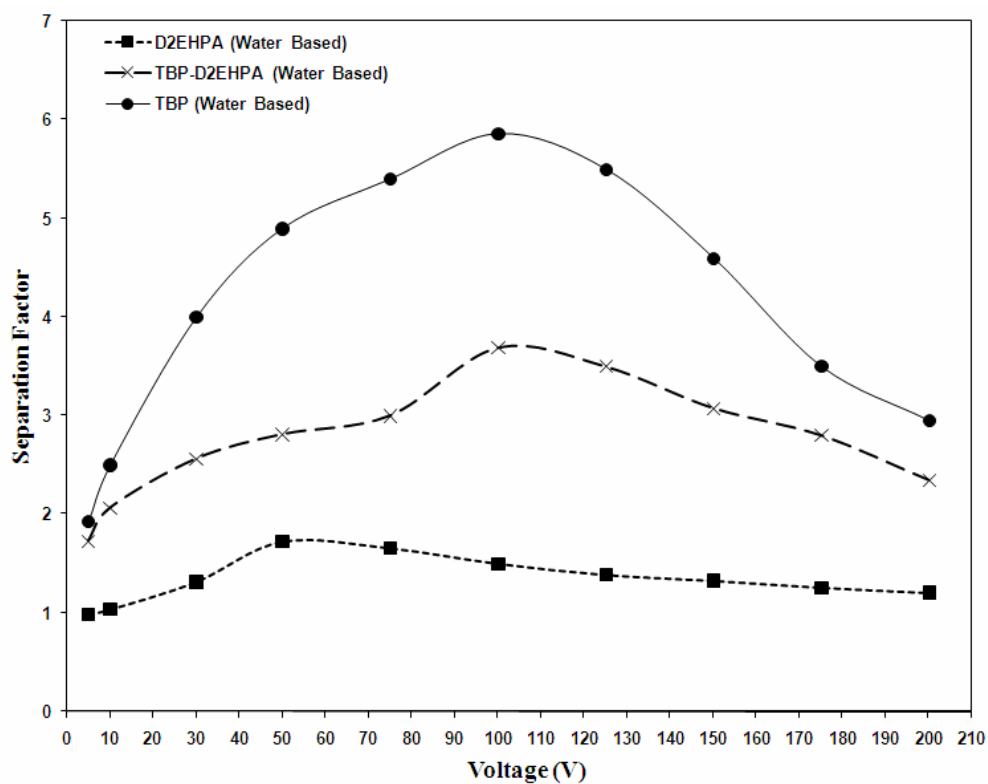


Fig.2. Influence of the organic solution on the separation factor in water-based feed solution

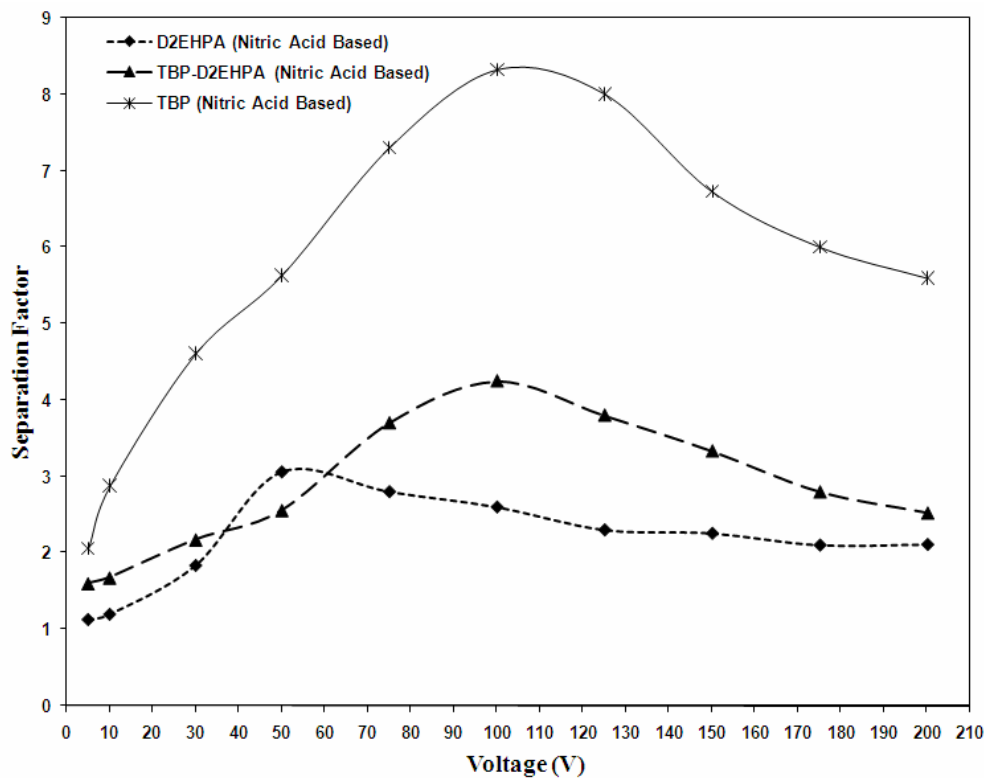
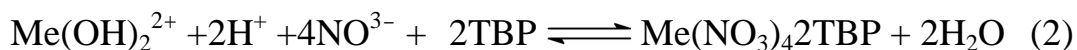


Fig.3. Influence of the organic solution on the separation factor in nitric acid-based feed solution

### 3.2. Effect of the feed solution on the separation factor

Figs. 4 to 7 show the influence of feed solution on the separation factor. The results confirm the absolute superiority of the nitric acid effect on the separation factor. Because of higher atomic weight of Hafnium ions in comparison with Zirconium ions, nitric acid makes stronger complex with the Hafnium ions and it seems that nitric acid media traps Hafnium better than water (hydrochloric media) and helps Zirconium to enter the organic phase from solutions interface. In the presence of TBP as the extractant, and using nitric acid for the feed solution the reaction presented as



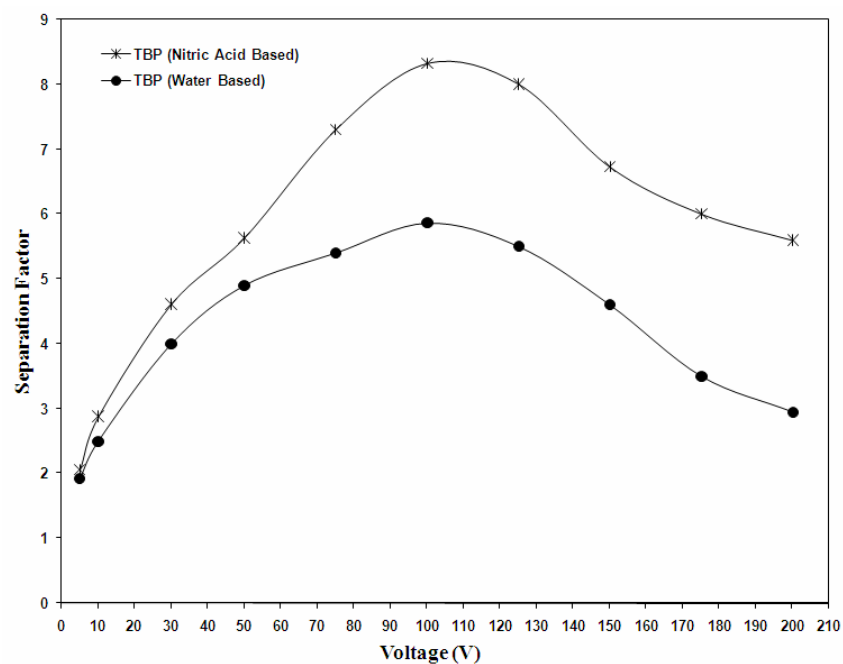


Fig.4. Influence of the feed solution on the separation factor; TBP used

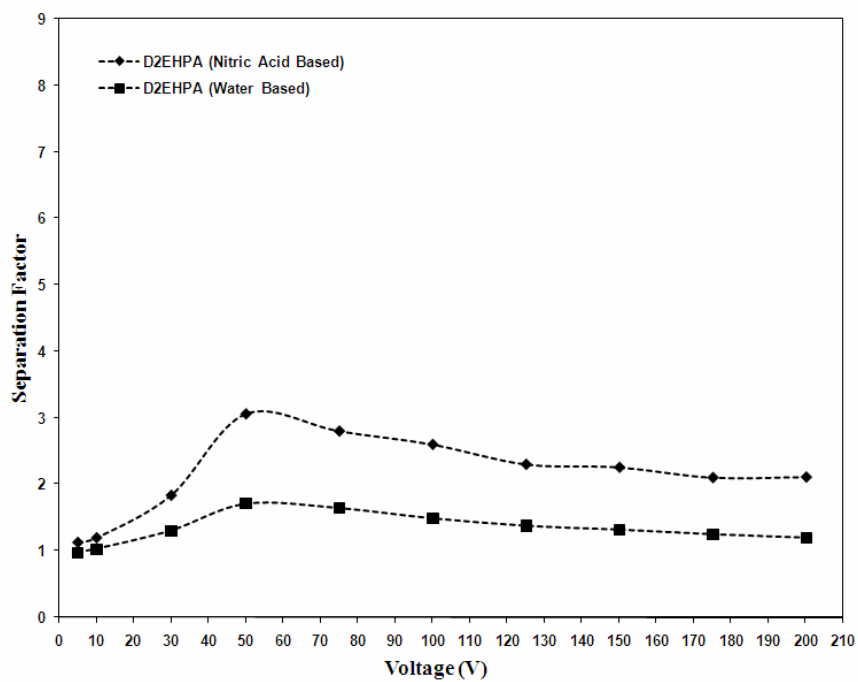


Fig.5. Influence of the feed solution on the separation factor; D2EHPA used



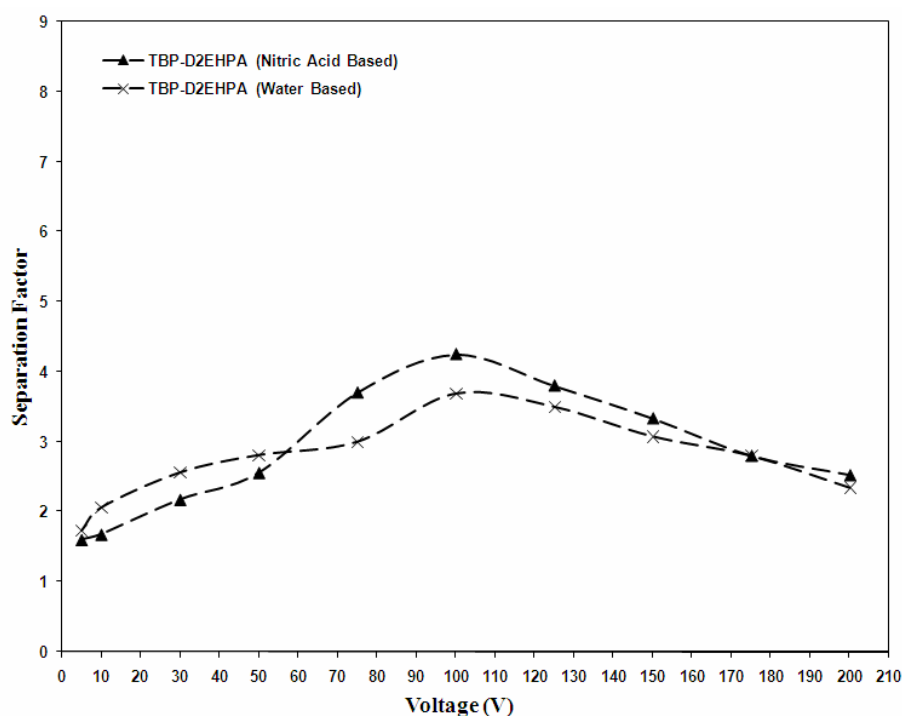


Fig.6. Influence of the feed solution on the separation factor; TBP-D2EHPA mixed used

### 3.3. Effect of the electrical field on the separation factor

Increasing the voltage up to 100 V generally increases the separation factor (fig.7). Above 100 V, the separation factor decreases smoothly.

The reason would be the stronger effect on movement of Zirconium ions in comparison with Hafnium ions. The difference in atomic weight of Zirconium and Hafnium ions, 87.27 gr / mol, caused that the lighter Zirconium ions affected more with the lower electrical field up to 100 V. By increasing voltage, the electrical field power could move the heavier Hafnium ions to the feed/extractant interface and of course more Hafnium would be extracted and the separation factor decreased.

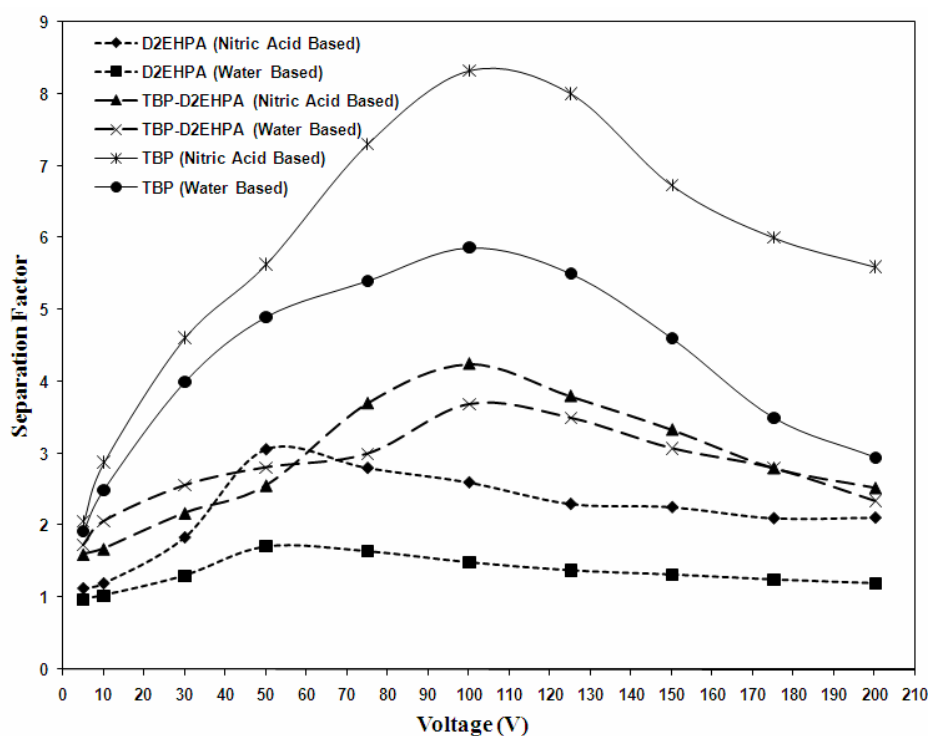


Fig.7. Influence of the electrical field on the separation factor

#### 4. Conclusions

- 1- It seems that exerting the electrical current can affect the separation of the metallic ions. Employing a voltage can accelerate the movement of the positive metallic ions from feed solution towards stripper through the organic solution. Of course, the electrical current is not the only driving force for the movement of the ions and parameters such concentration gradients have also significant effect in this procedure.
- 2- TBP organic material was found to be a stronger extractor which can give rise to a higher separation factor compared with D2EHPA.
- 3- The maximum separation factor of Zirconium and Hafnium in this investigation has been recorded at 100V, from the primary nitric acid base aqueous solution. The transient organic solution was TBP in this condition and the separation factor of 8.32 was achieved.

#### References

- [1] Levitt, E.H., Freund, A., 1956. Solvent extraction of Zirconium withtributyl phosphate. J. Am. Chem. Soc. 78, 1545–1549.
- [2] Voit, O.D., 1980. Equilibrium distribution behavior of zirconyl hafnylthiocyanates between methyl isobutyl keton and aqueous phases.ISEC 80 proceeding, vol. 80.

- [3] El-yamani, I.S., Farrah, M.Y., 1978. Co extraction and separation of Zirconium and Hafnium by long chain amines from sulphate media. *Talanta* 25, 523–525.
- [4] Shults, B.G., Larsen, E.M., 1950. The fractional separation of Zirconium and Hafnium by extraction with trifluoro acetyl acetone. *Am. Chem.Soc.* 72, 3610–3614.
- [5] Kalyanaraman, S., Khopkar, S.M., 1977. Solvent extraction of Hafnium with 4-methyl-3-pentene-2-one. *Talanta separation* 25, 395–397.
- [6] Dasilva, A., El-ammouri, E., Distin, P.A., 2000. Hafnium/Zirconium separation using Cyanex 925. *Can. Metall. Q.* 39, 37–42.
- [7] Dasilva, A., Distin, P.A., 1998. Zirconium and Hafnium separation without waste generation. *CIM bull.* 91, 222–224.
- [8] Poriel, L., Favre-Réguillon, 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.
- [9] Taghizadeh, M., 2008. Determination of optimum process conditions for the extraction and separation of Zirconium and Hafnium by solvent extraction. *Hydrometallurgy.* 90, 115–120.