



---

## Separation of Zirconium and Hafnium Tetrachloride from the Nuclear Power Reactors using a Distillation Column with NaCl-KCl Salt Mixtures

Sevil AKÇAĞLAR

Dokuz Eylül University, Engineering Faculty, Mechanical Engineering Department, Kaynaklar Campus, Buca-İzmir, Turkey

**Abstract** In this study, in order to remove the zirconium tetrachloride ( $ZrCl_4$ ) and hafnium tetrachloride ( $HfCl_4$ ) from nuclear power reactors a distillation column with extraction was used at optimum NaCl-KCl salt mixture to built up a suitable vapor-liquid phase in the nuclear reactor. The effects of tetrachloride percentages (10%, 35%, 65%), the effects of NaCl-KCl salt mixture concentrations (1:10, 3:20, 8:30), temperatures (100 °C, 200 °C and 400 °C) and pressures (400 mmHg, 600, 800 and 1200 mmHg) on the removal of zirconium and hafnium were investigated. The bottom stream with high purity  $ZrCl_4$  molten salt was run through a stripper column to collect  $ZrCl_4$  as a solid product and the solvent salt was returned to the feed storage. The  $HfCl_4$  unit to obtain the salt-free  $HfCl_4$ . Under optimized conditions ( $ZrCl_4$  percentage of 60%,  $HfCl_4$  percentage of 76%; NaCl-KCl salt mixture of 5:10, temperature of 200 °C, a pressure of 600 mmHg, pH=4) the maximum Zr and Hf removals were 93% and 89%, respectively, at a flow rate of 50m<sup>3</sup>/day. Approximately 80%  $ZrCl_4$  and  $HfCl_4$  recoveries were observed using a novel distillation column with extraction by a proper molten salt system to separate the Zr and the Hf from nuclear power reactors.

**Keywords** Nuclear waste,  $ZrCl_4$ ,  $HfCl_4$ , Distillation column with extraction, Molten salt

---

### 1. Introduction

Zirconium (Zr) alloy has many useful properties for applications in nuclear facilities, such as low absorption cross-section of thermal electrons, high ductility, good fabricability, hardness, and corrosion resistance [1,2]. In the utilization of Zr for the nuclear reactor applications the existence of hafnium (Hf), found in zirconium ore at 1–3 wt%, should be avoided because of its high thermal neutron cross section. By taken into consideration the physical and chemical properties Hf and Zr are almost identical ionic radii (0.074 nm for  $Zr_4^+$ , 0.075 nm for  $Hf_4^+$ ) therefore the remove a reactor applications. Since the tetrachlorides are the preferred compounds used in the reduction reactions for the production of Zr and Hf in a metallic form,  $HfCl_4$  and  $ZrCl_4$  should be removed. Although extraction is still the most popular and economic way for commercial Zr-Hf removals this method requires relatively expensive, corrosive and environmentally harmful solvent chemicals. Furthermore, it also generates a huge volume of liquid waste, which is difficult to dispose of due to stringent environmental protection laws [3,4]. For example, isobutyl methylketone (MIBK), which is the most popular solvents used for Zr-Hf extraction, requires environmentally harmful cyanogen (CN) chemicals as an additive. Distillation has attracted considerable attention for Zr purification because of its potential for clean separation and many other advantages for a large scale production, such as fewer unit operations and chemical consumption, higher overall yield, and less effluent [3,5]. On the other hand, the boiling points of  $ZrCl_4$  and  $HfCl_4$  limits the distillation applications: a large number of separation stages, high temperatures, pressures and sublime properties of  $ZrCl_4$  and  $HfCl_4$  when heated under normal pressures



limits the utilization of distillation. The extractive distillation technique can be an attractive alternative to overcome these limitations of conventional distillation. A certain mixture of  $\text{HfCl}_4$  and  $\text{ZrCl}_4$  in certain fused salts is potentially useful for this purpose. Fused salts for extractive distillation should have some important properties, such as high solubility for  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  at elevated temperatures, low vapor pressure, low viscosity, and high dissolution for many different materials [6]. In addition, the lowest operating temperature of the column must be higher than the sublimation temperature of  $\text{HfCl}_4$  at atmospheric pressure [6]. The aim of this study was the separation of  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  using molten salt-based extractive distillation column. The effects of tetrachloride percentages, the effects of  $\text{NaCl}:\text{KCl}$  salt mixture ratio percentages, temperatures (100 °C, 200 °C and 400 °C) and pressures (400 mmHg, 600, 800 and 1200 mmHg) on the removal of zirconium and hafnium were investigated

## 2. Materials and methods

### 2.1. Reactor configuration

Schematic configuration of extractive distillation column for separation of  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  using molten salt ( $\text{NaCl}:\text{KCl}$  salt mixture) system is illustrated in Figure 1, [7]. In other words to examine the optimum separation of  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  from the nuclear power reactor applications, an extractive distillation column was carried out for the zirconium and hafnium tetrachlorides and molten salt system consisting of different mixing ratios of  $\text{NaCl}$  and  $\text{KCl}$ . Different ratios of  $\text{ZrCl}_4$ - $\text{HfCl}_4$  and molten salts ( $\text{NaCl}:\text{KCl}$ ) compositions were used to determine the optimum tetrachlorides and molten salts mixtures for the removal of Zr and Hf. [8]. The optimum operational conditions were 200 °C temperature, 600 mmHg pressures and a molten salt mixture of 5:10%.

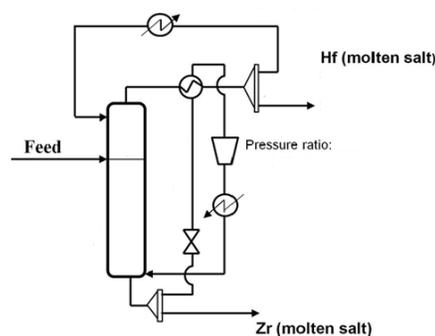


Figure 1: The novel distillation column with extraction mode for separation of  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  from nuclear wastes

### 2.2. Measurements of Zr and Hf

Zr and Hf were measured by x-ray fluorescence spectrometry following the procedure given by [9]. The Ali Quots were added to Teflon bakerevaporated to dryness. Then they were vaporized within 5 min. The residues were dissolved in concentrated  $\text{HfCl}_4$  and  $\text{ZrCl}_4$ . Than  $\text{HCl}$  after the addition of  $\text{HCl}$ , they purified by sub-boiling distillation. Zr and Hf concentrations are calculated were performed from the intensities of the corresponding Zirconium and Hafnium fluorescence X-rays. These analyses were performed in Lawrence Berkeley Laboratory in Canada.

### 2.3. Statistical analyses

The regression analyses between Zr and Hf removals and operational conditions were performed by Microsoft Excel 2012. The ANOVA statistical programme was used to determine the significance of the regressions by using  $\alpha=0.05$ .

## 3. Results and Discussion

### 3.1. Physical properties of zirconium and hafnium tetrachlorides



Distillation utilizes volatility difference of the components associated with vapor-liquid equilibrium, both a narrow region of vapor-liquid phase and close boiling point difference in  $ZrCl_4$  and  $HfCl_4$  are a main obstacle to its application for Zr-Hf separation. Table 1 lists the properties of  $ZrCl_4$  and  $HfCl_4$  [10].  $ZrCl_4$  and  $HfCl_4$  directly sublime at 331 and 317 °C at ambient pressure, respectively. Their vapor pressures are 22.36 and 45.01 bar at the triple points of 437°C and 432°C, respectively, which easily approach to their critical condition as the temperature increases. The temperature range for the existence of vapor-liquid phase, which is essential for the separation of  $ZrCl_4$  and  $HfCl_4$  mixtures through distillation, is relatively narrow.

**Table 1:** Physical properties of zirconium and hafnium tetrachlorides

Properties	$ZrCl_4$	$HfCl_4$
Sublimation temperature °C	331	317
Triple point		
Temperature °C	437	432
Pressure (bar)	22.36	45.01
Critical point		
Temperature °C	506	499
Pressure (bar)	57.66	57.76
Volume (ml/mol)	319	303

The vapor pressure of  $HfCl_4$  was reasonably higher than that of  $ZrCl_4$  as expected. The volatility of  $HfCl_4$  was approximately 1.7 times higher than that of  $ZrCl_4$  in the range of investigated temperatures, which revealed the feasibility of economic separation of  $HfCl_4$  and  $ZrCl_4$  by high pressure distillation. The vapor pressures of pure  $ZrCl_4$  and  $HfCl_4$  were correlated.

### 3.2. Effects of $ZrCl_4$ percentages on the removals of Zr

As the  $ZrCl_4$  percentage was increased from 10% to 45% the Zr yield increased from 23% up to 93% (Figure 2). Further increase in  $ZrCl_4$  percentage to 60% on the Zr yield decreased to 60%. The maximum Zr removal was obtained at a  $ZrCl_4$  percentage of 45% as 93%. A linear regression between Zr yield and  $ZrCl_4$  percentage was obtained for the  $ZrCl_4$  percentage up to 60% ( $R^2 = 0,999$ ). ANOVA test showed a significant correlation between Zr yield and  $ZrCl_4$  percentage up to the aforementioned  $ZrCl_4$  percentage ( $F = 0.003 < \alpha = 0.05$ ).

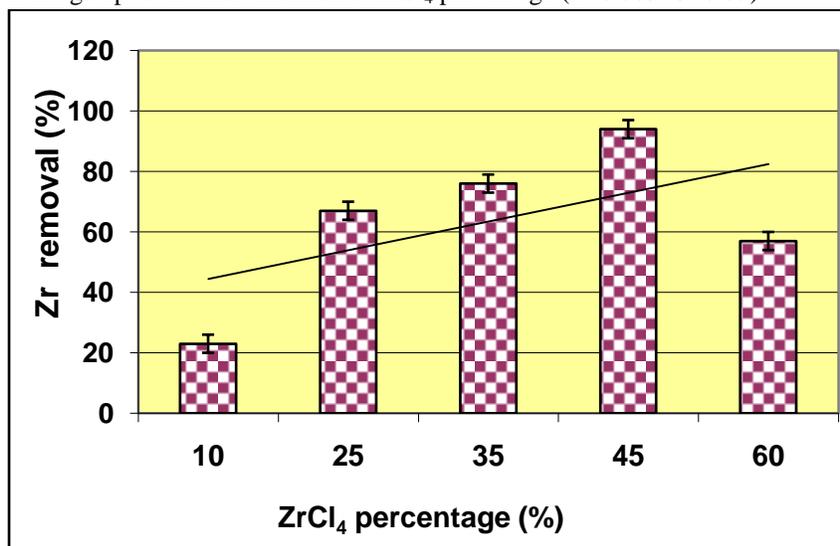


Figure 2: Effect of  $ZrCl_4$  percentages on the removals of Zr under a flow rate of  $50 \text{ m}^3/\text{day}$ ; a temperature of  $185 \text{ }^\circ\text{C}$ , a pH of 4.0 and a pressure of 550 mmHg.



### 3.3. Effects of HfCl<sub>4</sub> percentages on the removals of Hf

As the HfCl<sub>4</sub> percentages were increased from 10% to 76% the Hf removal increased from 10% to 89% (Figure 3). Further increase of HfCl<sub>4</sub> percentage to 90% reduced the Hf yield to 70%. The maximum Hf removal was obtained at a HfCl<sub>4</sub> percentage of 76% as 89%. A linear regression between Hf removal and increasing HfCl<sub>4</sub> percentage was observed ( $R^2=0.99$ ) up to an HfCl<sub>4</sub> percentage of 90%; while the ANOVA test results exhibited a significant correlation between Hf removal and HfCl<sub>4</sub> percentage ( $F=0.006 < \alpha=0.05$ ).

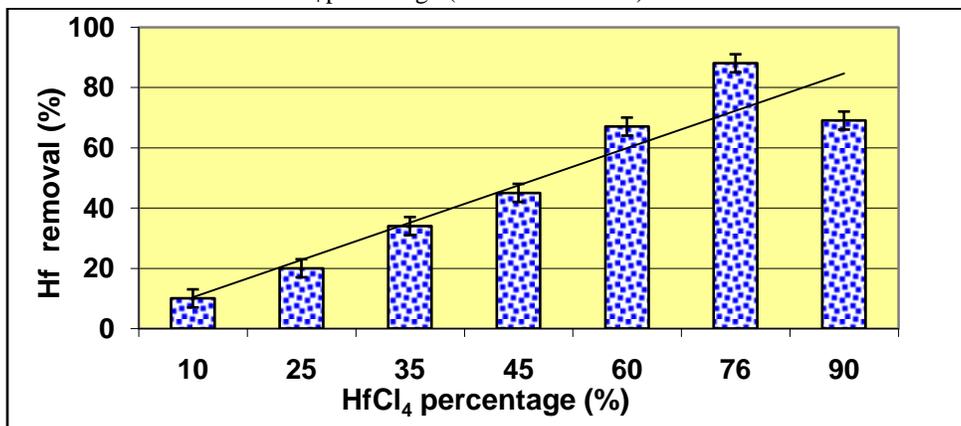


Figure 3: Effect of HfCl<sub>4</sub> percentages on the removals of Hf under a flow rate of 50 m<sup>3</sup>/day; a temperature of 185 °C, a pH of 4.0 and a pressure of 550 mmHg

### 3.4. Effects of molten salt (NaCl:KCl -%) ratios on the removals of Hf and Zr

The optimum ZrCl<sub>4</sub> and HfCl<sub>4</sub> percentages were chosen as 76% and 45%, respectively, according to the studies results given above (Figure 4). As the NaCl: KCl ratio was increased from 1:10% up to 5:10%, the Hf and Zr removals increased from 42% to 88% and from 49% to 96%, respectively, under a flow rate of 50 m<sup>3</sup>/day; a temperature of 185 °C, a pH of 4.0 and a pressure of 550 mmHg. The increasing of NaCl:KCl ratio up to 8:30%, decreased both Hf and Zr removals. Under these conditions, the Zr and Hf yields decreased to 75% and 60%, respectively. For maximum Zr (96%) and Hf (88%) yields the optimum molten salt ratio was found to be 5:10%. A linear regression between Hf and Zr removals and molten salt mixture ratios was obtained ( $R^2= 0.998$ ) up to a molten salt mixture ratio of 8:30%. The ANOVA test statistics showed that a significant correlation between Hf and Zr yields and molten salt mixture ratios was observed ( $F=0.0005 < \alpha=0.05$ ).

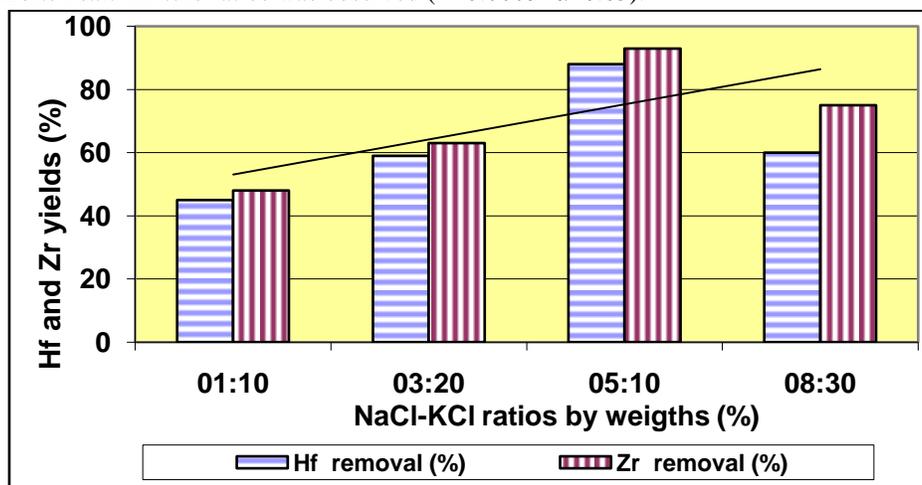


Figure 4: Effect of molten salt ratios on the removals of Hf and Zr under a flow rate of 50 m<sup>3</sup>/day; a temperature of 185 °C, a pH of 4.0 and a pressure of 600 mmHg

### 3.5. Effects of increasing temperature on the removals of Zr and Hf

Based on the studies performed above, in this run of this study, the optimum  $ZrCl_4$  and  $HfCl_4$  percentages, and NaCl:KCl mixture ratios were chosen as 76% and 45%, and 5:10%. As the temperature was increased from 100 °C to 200 °C the Zr and Hf removals reached 93% and 89%, respectively (Figure 5). The increasing of temperature to 400 and 600 °C reduced both yields. For maximum Zr and Hf removals was obtained at 200 °C temperature.

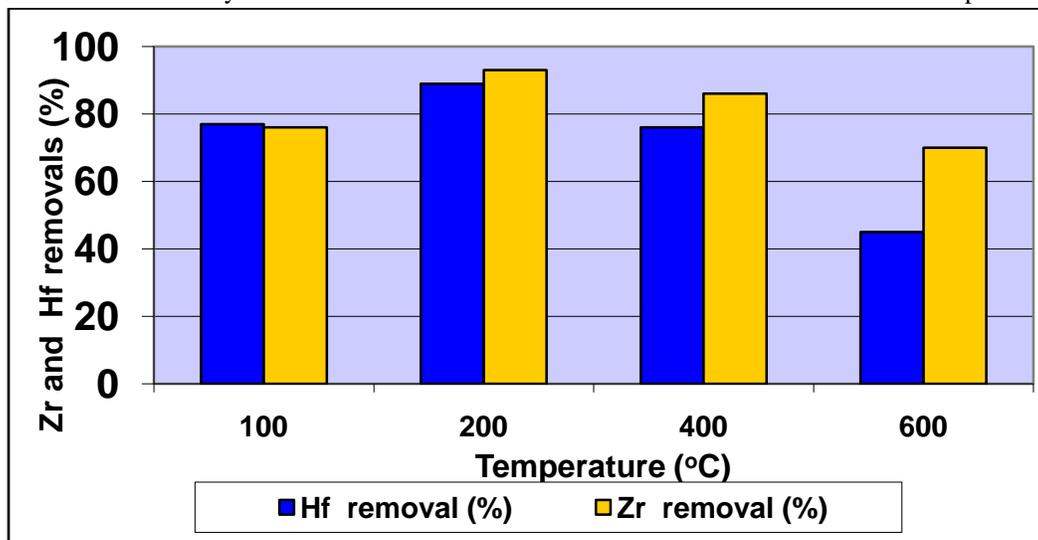


Figure 5: Effects of temperature on the Zr and Hf removals under a flow rate of 50 m<sup>3</sup>/day; a pH of 4.0 and a pressure of 550 mmHg. ( $ZrCl_4$  and  $HfCl_4$  percentages, and NaCl:KCl mixture ratios were 76% and 45%, and 5:10%, respectively)

### 3.6. Effects of pressure on the yields of Zr and Hf

The optimum conditions to determine the effects of increasing pressure on the Zr and Hf removals were 76%  $ZrCl_4$  and 45%  $HfCl_4$  percentages, NaCl:KCl mixture ratios, molten salt mixture ratio 5:10% and 200°C temperature from the above studies results (Figure 6). As the pressure was increased from 400 mmHg to 600 mmHg the Zr and Hf yields were recorded as 94% and 89%, respectively. These are the maximum yields obtained for Zr and Hf. Further increase of pressure to 800 and 1200 mmHg did not increase the yields.

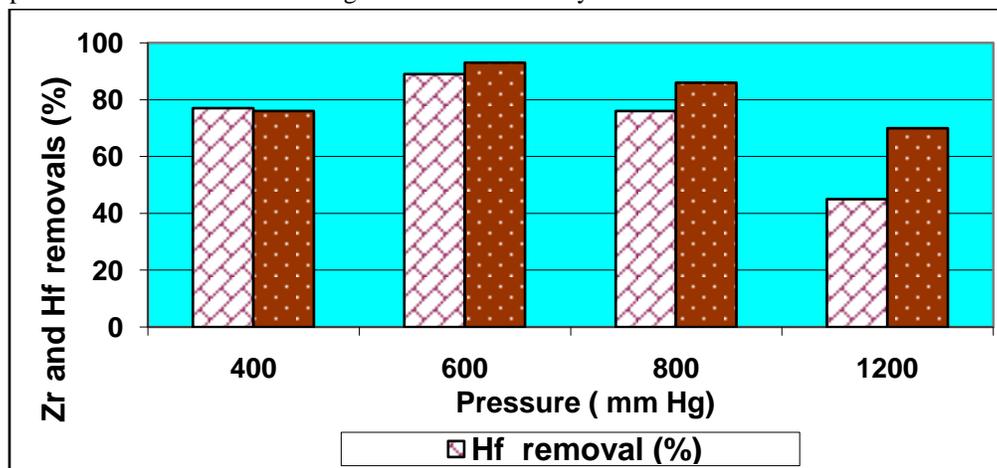


Figure 6: Effects of pressure on the yields of Zr and Hf under a flow rate of 50 m<sup>3</sup>/day; a pH of 4.0 and 200 °C temperature ( $ZrCl_4$  and  $HfCl_4$  percentages, and NaCl : KCl mixture ratios were 76% and 45%, and 5:10%, respectively)



### 3.7. Effects of pH on Zr and Hf yields

Under the optimal operational conditions given above were used to determine the pH effect. The maximum Zr and Hf removals were obtained as 93% and 89% at pH =4 under acidic conditions (Table 2).

**Table 2:** Effect of pH on Hf and Zr Yields under a flow rate of 50 m<sup>3</sup>/day; a pH of 4.0 and 200 °C temperature and 600 mmHg pressure

pH	Hf removal (%)	Zr removal (%)
4	89	93
7	70	79
10	56	62

### 4. Conclusion

Adding a proper molten salt mixture to a new design distillation column with extraction leads to the increase in the relative volatility of ZrCl<sub>4</sub> and HfCl<sub>4</sub>. This also allowed milder pressure and temperature conditions as well as a wider range for vapor–liquid phase existence for distillation applications. The optimal conditions for the extractive distillation column to separate the Zr and Hf were 200 °C temperature, 600 mmHg pressure, ZrCl<sub>4</sub> and HfCl<sub>4</sub> percentages of 76% and 60%, respectively, under molten salt mixture percentages of 5:10% at a pH of 4 and at a flow rate of 50 m<sup>3</sup>/day. Under these conditions the maximum removals of Zr and Hf were found to be 93% and 89%, respectively.

### References

- [1]. L. Moulin, P. Thouvenin, P. Brun, Paperpresented at the 6<sup>th</sup> International Conference on Zirconium in the Nuclear Industry, Van-couver, B.C., Canada (1982). 04-824000-3504-824000-35 ISBN: 9780803102705, 0803102704. <http://www.pricestube.com/book/0803102704>
- [2]. D.J, Branken, M.S. Thesis, North-West University (2009). URI: <http://hdl.handle.net/10394/4978>
- [3]. R.P. Tangri, D.K. Boseand C.K. Gupta, J. Chem. Eng. Data, 40, 823 (1995). doi:10.1021/je00020a019
- [4]. H. Li, H.H. Nersisyan, K.T. Park, J.G. Kim, J.M. Lee and J. H. Lee, J. Nucl. Mater., 413, 107 (2011). doi:10.1016/j.jnucmat.2011.04.008
- [5]. A.A. Palko, A.D. Ryanand D.W. Kuhn, J. Phys. Chem., 62, 319 (1958). doi: 10.1021/j150561a017
- [6]. J. R. Elliotand C.T. Lira, Introductory chemical engineering thermodynamics, Prentice-HallInc., N. J. (1999). ISBN-13: 9780136068549/ISBN10:0136068545
- [7]. Le Quang Minh, Nguyen Van Duc Long, Pham Luu Trung Duong, Youngmi Jung, Alireza Bahadori and Moonyong Lee, Energies 8, 10354 (2015) energies ISSN 1996-1073 [www.mdpi.com/journal/energies](http://www.mdpi.com/journal/energies) doi:10.3390/en80910354
- [8]. Le Quang Minh, Gyeongmin Kim, Jongki Park, and Moonyong Lee, Korean J. Chem. Eng., 32 , 30 (2015) doi: 10.1007/s11814-014-0175-3.
- [9]. E. Ricci, Analytical Chemistry, 52, 1708(1980) doi: 10.1021/ac50061a040
- [10]. N.D. Denisova, E. K. Safronov, A. I. Pustil'nikand O. N. Bystrova, Russ. J. Phys. Chem., 41, 30 (1967). doi: 10.7763/IJCEA.2012.V3.235

