The effect of molar ratio and flow velocity on the surface area required for pertraction of a Zr/Hf mixture

D Malan¹, DJ van der Westhuizen¹*, HWJP Neomagus², and HM Krieg¹

¹ Chemical Resource Beneficiation (CRB), Membrane Technology Group, North-West University, Potchefstroom Campus, Private Bag X6001, Potchefstroom, 2520, South Africa

² School of Chemical and Minerals Engineering, North-West University, Potchefstroom Campus, Private Bag X6001, Potchefstroom, 2520, South Africa

*Derik.VanDerWesthuizen@nwu.ac.za

Abstract. Zirconium (Zr) and hafnium (Hf) need to be separated before being used in nuclear applications. Equilibria data have shown that Hf can be selectively extracted over Zr from a sulphate medium using organophosphorus extractants. This study investigated a modification of Zr and Hf solvent extraction whereby a hollow-fibre membrane contactor was used to separate the aqueous and organic phases, termed pertraction (PX). The aim of the study was to investigate the effects of the molar D2EHPA:Hf ratio and the volumetric flow rate on the estimated surface area required for an industrial PX extraction unit. Equilibrium experiments showed that the maximum separation factor (8.8) was found at D2EHPA:Hf ratio of 350:1. Mass transfer coefficients and kinetic selectivities of hafnium and zirconium were determined using a hollow fibre PX set-up. Variables investigated were: i) D2EHPA concentration, and ii) volumetric flow rate at a constant organic to aqueous ratio. The mass transfer coefficients of hafnium and zirconium and the separation ratio increased at higher flow rates. The best experimental conditions estimate that an industrial extraction unit capable of producing 500 ton per annum nuclear grade zirconium would require approximately 3 200 m² membrane surface area, at a volumetric flow rate of 1.7 m³.h⁻¹ when operated under similar conditions to those in this study.

1. Introduction

The industrial separation of zirconium (Zr) and hafnium (Hf) is most commonly achieved by means of either the methyl isobutyl ketone (MIBK) or tributyl phosphate (TBP) processes [1,2]. These two processes are hydrometallurgical solvent extraction (SX) processes in which one component is selectively extracted into the organic phase using an extractant as carrier. Most commonly these processes utilize mixer-settler units which have a number of drawbacks such as large chemical inventories, product lockup and flooding at high flow rates [3]. In this study, a novel adaptation to traditional SX of Hf and Zr was investigated by means of introducing a porous membrane to separate the phases as follow-up work on the patent by Van der Westhuizen et al. [4]. Membrane based solvent extraction, also termed pertraction (PX), counters the drawbacks of traditional mixer-settler units due to two major changes. First, the separated state of the phases negates the need for large settling tanks, reducing chemical inventory and product lockup. Second, the hydraulic conditions of each phase can be adjusted independently, allowing significantly varying phase ratios to be used without flooding or unloading [3]. Flow conditions have a significant impact on the performance of the process and the separate phases can be manipulated individually to suit a particular application. The membrane offers a large, fixed surface area through which mass transfer can occur.

This study aimed to estimate the membrane surface area of an industrial PX extraction unit to selectively extract Hf from a mixed Zr/Hf feed stream. The variables investigated were the molar D2EHPA:Hf ratio and the volumetric flow rate of the fluid phases inside a membrane contactor column.
2. Design Considerations

Previous work has shown that organophosphorus extractants can selectively extract Hf over Zr from a sulphate medium. Wang & Lee have published a number of articles on this [2,5,6] and proposed a chemical reaction for Hf extraction using D2EHPA from H2SO4 media [5]:

\[
Hf^{4+} + 3(HA)_{2\text{org}} \rightleftharpoons HfA_4(HA)_{2\text{org}} + 4H^+ \tag{1}
\]

In a PX process, separation is achieved by a difference in the distribution coefficients and the rates of mass transfer of the components in the system. Allahyari et al. describes the mass flux of a PX process by way of a mass balance over the shell side of a membrane contactor [7]. Equation 1 describes the overall mass transfer coefficient.

\[
k_{\text{exp}} = \frac{F \Delta C_{\text{aq}}}{\Delta C_{\text{lm}} A_{\text{eff}}} \tag{2}
\]

where \( k_{\text{exp}} \) is the experimental overall mass transfer coefficient (m.s\(^{-1}\)), \( F \) is the volumetric flow rate (m\(^3\).s\(^{-1}\)), \( \Delta C_{\text{aq}} \) (kg.m\(^{-3}\)) is the concentration difference between the shell side inlet and outlet, \( A_{\text{eff}} \) (m\(^2\)) is the effective membrane area available for mass transfer, and \( \Delta C_{\text{lm}} \) is the log mean concentration difference between the aqueous and organic phases (kg.m\(^{-3}\)).

3. Materials and Methods

3.1. Reagents

The chemicals used in this study along with the purity and supplier are listed in Table 1. All chemicals were used without further purification.

| Reagent         | Purity | Supplier                      |
|-----------------|--------|--------------------------------|
| Zr(Hf)SO\(_4\)·4H\(_2\)O | 98% (2.3wt% Hf)  | Hangzhou Dayangchem Co., Ltd. |
| H\(_2\)SO\(_4\) | 98     | Labchem (Pty) Ltd.            |
| Shellsol 2325   | N/A    | Chemquest (Pty) Ltd.          |
| D2EHPA          | 98%    | Sigma Aldrich                 |
| 1-Octanol       | 95%    | Sigma Aldrich                 |
| Oxalic Acid     | 96%    | Labchem (Pty) Ltd.            |

The aqueous feed solutions were prepared by dissolving the required amounts of Zr(Hf)SO\(_4\)·4H\(_2\)O salt in deionized water (Evoqua Labostar), the acidity was adjusted using sulphuric acid. The aqueous feed conditions were kept constant throughout all the experiments with [Zr] = 15 g/L, [Hf] = 0.34 g/L, and [H\(_2\)SO\(_4\)] = 1.0 M. Fresh feed solutions were prepared for every experiment.

The organic phase was prepared by mixing the required amounts of D2EHPA and 1-octanol with Shellsol 2325 as diluent. Pandey et al. reported that oxalic acid was found to be a very effective and non-selective stripping agent [8]. Between experiments, the organic phase was stripped and regenerated by contacting overnight with 1.0 M oxalic acid at an O/A ratio of 1.

3.2. Batch shake-out procedure

Baudot et al. reported that the overall mass transfer of a species in a PX process is strongly influenced by the distribution coefficient \((HfA_4(HA)_{2\text{org}}/Hf^{4+})_{\text{aq}}\) in Equation 1) of the species [9]. They reported that species with high distribution coefficients exhibit increased mass transfer coefficients. To maximize the distribution coefficient, shake-out experiments were conducted in which the D2EHPA:Hf ratio was varied from 10 to 500 by changing the D2EHPA concentration of the organic phase. Equal volumes (25ml) of the aqueous and organic phases were contacted for 60 minutes at 350 revolutions per minute (Labcon 3081U mechanical agitator). The temperature was kept constant at 25°C. After 60 minutes the phases were allowed to separate and the aqueous phase was sampled for analysis by ICPOES (inductively coupled plasma optical emission spectrometry, Agilent 5110, Chemetrix (Pty) Ltd).
3.3. Pertraction extraction procedure

PX experiments were conducted using the experimental set-up shown in Figure 1. The membrane column consisted of two 3M (Liqui-Cell) 1.7x8.75 mini-modules connected in series and operated under counter-current flow conditions. The specifications for the modules and membrane contained within are listed in Table 2. To regulate the aqueous flow through the shell side of the membrane column a gear pump (Cole-Parmer Instrument Company, LLC.) was used in combination with a return valve to regulate the return flow to the reservoir. Due to the hydrophobic nature of the membrane, organic breakthrough may occur at low aqueous pressures. To prevent this, a 1.8m stand pipe was used to create a minimum pressure head inside the module. A peristaltic pump was used to move the organic phase through the membrane lumen. Chemical incompatibility between the organic phase and the polycarbonate shell material prevented experiments with the organic phase in the shell.

![Figure 1. Pertraction column experimental set-up.](image)

### Table 2. 3M (Liqui-Cell) 1.7x8.75 mini-module specifications [10,11].

| Parameter                  | Value  | Unit | Parameter                  | Value  | Units |
|----------------------------|--------|------|----------------------------|--------|-------|
| Shell OD                   | 42.5   | mm   | Membrane Material          | Polypropylene |
| Shell ID                   | 36.5   | mm   | Wetting phase              | Organic |
| Overall length             | 260    | mm   | Fiber OD                   | 0.3    | mm    |
| Membrane length            | 198    | mm   | Fiber thickness            | 40     | μm    |
| Shell total volume         | 270    | ml   | Pore size                  | 0.04   | μm    |
| Shell flow volume          | 190    | ml   | Porosity                   | 40     | %     |
| Lumen flow volume          | 45     | ml   | Approx. fiber count        | 6500   | N/A   |
| Surface Area               | 0.9    | m²   | Membrane volume            | 50     | ml    |

*Approximated value

Before each experiment the flow rates were calibrated using fluids with similar viscosity and density characteristics to the experimental solutions. The aqueous loop was calibrated first and left running to ensure sufficient pressure head inside the column to avoid organic breakthrough. Once both flow rates had been calibrated the column was drained and the calibration fluids replaced by the experimental solutions. To start the experiment the aqueous phase was pumped until fluid exited the top of the column, point A in Figure 1, at which point the organic pump was switched on. The experimental time
was started when the organic reached the column inlet, point B in Figure 1. In-line samples of the aqueous phase were taken at fixed intervals for analysis by ICP-OES.

4. Results

4.1. Benchmark

Wang & Lee reported liquid-liquid equilibria data that found a D2EHPA:Hf ratio of 62.5 and 1.0 M H2SO4 feed solution resulted in a separation factor of 8.8 [6]. These conditions were tested to determine a benchmark for the rate of mass transfer of a PX system. The aqueous and organic phases were prepared as described in Section 3.1, with a D2EHPA concentration of 40.1 g/L in the organic phase. The flow rates of both phases were set to 1.1x10⁻⁶ m³.s⁻¹. Using Equation 2, the overall mass transfer coefficients were found to be 8.9x10⁻⁸ m.s⁻¹ and 8.3x10⁻⁸ m.s⁻¹ for Hf and Zr, respectively. The separation ratio (kHf/kZr) of 1.07 resulted in nearly equal extraction of Hf and Zr and very poor separation.

4.2. Distribution enhancement

The shake-out results shown in Figure 2 indicate that the higher D2EHPA:Hf ratio resulted in increased distribution coefficients of both Hf and Zr. Increasing the D2EHPA:Hf ratio from 10 to 350 resulted in the separation factor (DHf/DZr) increasing from 1.5 to 7.6 as the extraction is more selective towards Hf. Above a D2EHPA:Hf ratio of 350 a marked decrease in separation was found. This was due to near complete extraction of Hf extraction leaving the excess D2EHPA to co-extract Zr, as seen at a ratio of 500:1.

The D2EHPA:Hf ratio of 350:1 was found to be the best operating point for the purification as the separation factor was at a maximum while high distribution coefficients would facilitate higher mass transfer rates compared to that of the benchmark.

4.3. Mass transfer

To determine the effect of the volumetric flow rate on the overall rate of mass transfer the flow rate was varied between 0.17x10⁻⁶ m³.s⁻¹ (10 mL.min⁻¹) and 8.3x10⁻⁶ m³.s⁻¹ (500 mL.min⁻¹). The linear velocities of the aqueous and organic phases varied between 0.03 cm.s⁻¹ and 1.5 cm.s⁻¹ and 0.07 and 3.4 cm.s⁻¹ respectively. Reynolds numbers for the shell and lumen were determined to be 170 and 4.1 respectively at 8.3x10⁻⁶ m³.s⁻¹, indicating laminar flow (Re < 2100) conditions for both phases during all the experiments conducted. The overall mass transfer coefficients of Hf and Zr were determined using Equation 2 and are reported in Figure 3. From Figure 3 it can be seen that the separation ratio and mass transfer coefficients of both Hf and Zr increased with flow rate. Higher flow rates reduced the boundary layer thickness through which species need to diffuse in order to react (aqueous-membrane interface) or move toward the bulk organic solution (membrane to bulk organic). Since Hf and Zr are known for
their chemical similarity their diffusion rates are expected to be similar as well. The increased separation ratio at higher flow rates indicates that the extraction of Hf is kinetically favoured over that of Zr.

![Figure 3. Overall mass transfer coefficient and separation factor as function of volumetric flow rate. \([\text{Zr}]=15 \text{ g/L}, [\text{Hf}]=0.34 \text{ g/L}, [\text{H}_2\text{SO}_4]=1.0 \text{ M}, [\text{D2EHPA}]=0.95 \text{ M}, [1-\text{C8OH}]=5 \text{ vol% diluent = Shellsol 2325.}]

A summary of the increase in overall mass transfer coefficients relative to the benchmark experiment is provided in Table 3. Increasing the molar D2EHPA:Hf ratio from 62.5:1 to 350:1 resulted in significant improvements to the mass transfer rates of Hf and Zr. The overall mass transfer coefficients of Hf and Zr increased by factors of 3.9 and 2.6 respectively. Additionally the separation ratio also showed an increase from 1.07 to 1.6. At the highest flow rate tested, Hf transferred almost six times faster compared to the benchmark while the rate for Zr doubled. This significantly improved the separation ratio from 1.6 to 3.0, as reported in Figure 3 and Table 3.

### Table 3. Relative mass transfer rates and separation ratio compared to the benchmark experiment:

| D2EHPA:Hf (mol:mol) | Vol. flow rate \((m^3.s^{-1})\) x10^6 | Linear velocity \((cm.s^{-1})\) | Relative overall mass transfer factor | Separation ratio \(k_{\text{Hf}}/k_{\text{Zr}}\) |
|---------------------|-------------------------------------|---------------------------------|-------------------------------------|---------------------|
| 62.5:1 (Benchmark)  | 1.1                                 | Shell U\(_S\) 0.2 Lumen U\(_L\) 0.4 | Hf 1.0 Zr 1.0                       | 1.1                 |
| 350:1               | 0.17                                | 0.03                             | 0.1                                 | 1.9 1.5 1.3         |
| 350:1               | 1.1                                 | 0.2                              | 0.4                                 | 3.9 2.6 1.6         |
| 350:1               | 1.7                                 | 0.3                              | 0.7                                 | 4.1 2.6 1.7         |
| 350:1               | 4.2                                 | 0.7                              | 1.7                                 | 3.0 1.2 2.7         |
| 350:1               | 8.3                                 | 1.5                              | 3.4                                 | 5.8 2.1 3.0         |

4.4. Industrial estimation

The industrial estimation was constrained by the Zr production rate of 500 tpa, and the product purity of less than 100 ppm Hf. Since the raffinate purity is a function of both the Hf and Zr extraction, both have to be included in the estimation. In order to estimate the required membrane surface area and required volumetric flow rate a steady state mass balance was created for each species.

### Table 4. Industrial plant estimation

| Shell linear velocity \(U_S\) \((cm.s^{-1})\) | Lumen linear velocity \(U_L\) \((cm.s^{-1})\) | Mass Flux \(\text{Hf}\cdot10^6\) | Mass Flux \(\text{Zr}\cdot10^6\) | Flow rate \((m^3.h^{-1})\) | Industrial Area \((m^2)\) |
|-------------------------------------------|-------------------------------------------|---------------------------------|---------------------------------|---------------------|---------------------|
| 0.2 (Benchmark)                          | 0.4                                       | 2.9                             | 1.2                             | 20.1                | 214 000            |
| 0.03                                      | 0.1                                       | 2.9                             | 1.2                             | 9.3                 | 100 500            |
| 0.2                                       | 0.4                                       | 9.0                             | 2.7                             | 3.5                 | 12 000             |
| 0.3                                       | 0.7                                       | 11                              | 3.2                             | 3                   | 8 000              |
| 0.7                                       | 1.7                                       | 8.5                             | 1.4                             | 1.8                 | 6 700              |
| 1.5                                       | 3.4                                       | 17                              | 2.6                             | 1.7                 | 3 200              |
It was assumed that the mass flux of each species, listed in Table 4, were constant throughout the length of the membrane column. These were substituted into the relevant mass balances and the membrane area and volumetric flow rate were solved. The results are listed in Table 4. It was further assumed that the mass flux behaviour inside the membrane column would be similar to that of the experimental if the linear velocities of the phases were similar as the hydraulic conditions would be expected to be similar. Constant linear velocities inside the column are maintained by increasing the cross sectional area of the shell and lumen at higher volumetric flow rates.

5. Conclusions and Recommendations
This study estimated the membrane surface area that would be required by an industrial PX extraction unit to selectively extract Hf from a mixed Zr/Hf feed stream. The equilibrium distribution coefficients and separation factor were optimised as a function of D2EHPA:Hf molar ratio. The effect of volumetric flow rate on the overall mass transfer coefficients were investigated using the optimised conditions and compared to a benchmark based on literature conditions.

It was found that a D2EHPA:Hf ratio of 350:1 provided a balance between increased distribution coefficients and a high separation factor. The mass transfer investigation showed that higher the D2EHPA:Hf ratio and volumetric flow rate both improved the rate of mass transfer for Hf and Zr as well as the selectivity toward Hf. The highest tested flow rate of 8.3x10^{-6} m^3.s^{-1} (500 mL.min^{-1}) showed the highest rates of mass transfer for both Hf and Zr as well as the greatest separation ratio. Compared to the required membrane surface area and flow rate of the benchmark case the above conditions resulted in the required membrane area and flow rates being reduced by factors of 67 and 12 respectively. The reduction of both surface area and flow rate would have significant cost savings associated as the size of the required equipment is reduced significantly. It is suspected that the membrane modules will comprise a significant portion of capital expenditures. Reduced pumping costs related to the decreased flow rate will impact the operational costs as well.

It is clear that the rate of mass transfer and separation ratio are vital to the performance of a PX extraction unit. As the extraction of Hf seems to be kinetically favoured it is recommended that ongoing work should focus on the effect of the hydraulic conditions of the aqueous and organic phases, which each contribute to the resistance to mass transfer in a PX process. Other work includes the investigation of scrubbing and stripping of the organic phase for the purpose of recycling back to the extraction unit.

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