The separation of zirconium and hafnium from $(NH_4)_3Zr(Hf)F_7$ using amine–based extractants

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Synopsis

The suitability of the amine-based extractants Alamine 336, Aliquat 336 and Uniquat 2280 (10 wt%) for the selective extraction of zirconium (Zr) and hafnium (Hf) from a $(NH_4)_3Zr(Hf)F_7$ solution was investigated. The extractant-containing organic phase consisted of cyclohexane and 5 v/v% 1-octanol as phase modifier. The $(NH_4)_3Zr(Hf)F_7$ was dissolved in either hydrochloride acid or sulphuric acid (0.01–8.0 mol/dm^3). The following variables were investigated: (i) the type and concentration of the acid, (ii) the equilibrium time, (iii) the organic/aqueous phase ratio and (iv) the extractant to metal ratio. Subsequently, using the optimized extraction conditions, the stripping of extracted metals from the organic phase was investigated using sodium chloride and sulphuric acid. The metal content in the aqueous phase was determined using ICP-OES before and after extractions.

When using sulphuric acid solutions, extractions of >80% were reached both for Zr and Hf. In all cases equilibrium was achieved in less than 25 minutes of contact between the organic and the aqueous phase. Stripping of metals was achieved with >40% separation and 50% extraction using a sodium chloride (0.7 mol/dm^3) stripping solution.

Keywords

zirconium, hafnium, amine extractants, $(NH_4)_3Zr(Hf)F_7$.

Introduction

Zirconium (Zr) and hafnium (Hf) coexist in nature and have similar chemical properties such as ionic radii (0.074 mm for Zr^{4+} and 0.075 mm for Hf^{4+}) and valence electrons in the outer orbitals. (Xu *et al.*, 2015; Nielsen *et al.*, 2000). Although both elements can be found in group 4 of the periodic table, their properties as regards nuclear application differ, the thermal neutron capture cross-section being much higher for Hf than that for Zr. (Purohit and Devi, 1997; Yang *et al.*, 2002) Zr also has a high corrosion resistance in acid media, which improves the lifetime of cladding materials in nuclear reactors. Hence, for Zr to be used as fuel cladding material and water-cooled components in nuclear reactors, the Hf content must be reduced from the naturally occurring 3% to <100 ppm. (Li *et al.*, 2011)

There are several processes that are currently in use for the extraction and purification of Zr and Hf, such as the methyl isobutyl ketone (MIBK) process proposed by Fischer and Chalybaeus (Overholser *et al.*, 1960). In this process, Zr and Hf form complexes with thiocyanate that have different solubilities, resulting in Hf being preferentially extracted into the organic phase. The disadvantages of this process are the high concentrations of ammonium and cyanides in the waste stream. The formation of cyanides from thiocyanate can occur in various ways, but in the case of the MIBK process the thiocyanate (SCN^-) is converted to OCN^- by the ammonium and to HCN by nitric acid solutions also present in the mixtures (Jenny *et al.*, 2001). The low flashpoint of the solvent is also a disadvantage. Other processes known to the industry are the tributyl phosphate (TBP) and Cyanex 923 processes, in which selective extraction is attained in a nitric acid solution as proposed by Taghizadeh *et al.* (2011). In 1974, Sato and Watanabe investigated the extraction of Zr in a sulphate medium using different types of amine extractants, showing that secondary amines are superior to tertiary amine extractants (Amaral *et al.*, 2013). In 2014, Wang and Lee reported on the preferential extraction of Zr in a sulphate medium using Aliquat 336, Alamine 336, Alamine 300 and Alamine 308 (Wang and Lee, 2015). All of the abovementioned methods and processes use Zr and Hf chloride salts as the starting reagent.

The South African Nuclear Energy Corporation (Necsa) has patented a plasma and fluoride process for the manufacturing of

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The separation of zirconium and hafnium from $(NH_4)_3Zr(Hf)F_7$

zirconium metal starting from the mineral zircon ($ZrSiO_2$) (Nel *et al.*, 2014). According to the patent, plasma-dissociated zircon is reacted with ammonium bifluoride and an $(NH_4)_3Zr(Hf)F_7$ complex is formed and isolated for downstream processing, *i.e.* separation of Zr and Hf. It is the purpose of this research to determine the suitability of amine extractants (Alamine 336, Aliquat 336 and Uniquat 2280) for the separation of Zr and Hf from $(NH_4)_3Zr(Hf)F_7$ (97 ppm Zr and 3 ppm Hf) in hydrochloric and sulphuric acid solutions (0.01–8 mol/dm³). Since the extraction from this salt has not been published previously, limited comparison of the data to literature data was possible. The parameters investigated were the type of acid and acid concentration, the type of extractant, extractant concentration and the effect of the two metals (Zr and Hf) on one another. Subsequently, two stripping agents (sodium chloride and sulphuric acid) were evaluated to regenerate the organic phases and to serve as possible scrubbing liquors.

Materials and methods

Tri-octyl/decyl amine (98% Alamine 336, Cognis Corporation), tricaprylmethylammonium chloride (97% Aliquat 336, Cognis Corporation) and didecyl dimethyl ammonium chloride (Uniquat 2280, 80%, Lonza) were diluted with cyclohexane (98%, Labchem) to 10 wt%. Lastly, 5 v/v% 1-octanol (98%, Sigma Aldrich) was added to the solvent to prevent the formation of a third phase. All chemicals were of analytical grade and used as received.

Fresh stock solutions of sulphuric (9% H_2SO_4, Labchem) or hydrochloric acid (32% HCl, LabChem) were prepared containing $(NH_4)_3ZrF_7$ and $(NH_4)_3HfF_7$ obtained from Necsa. The pure Zr and Hf salts were prepared by simulating the Necsa plasma process (Nel *et al.*, 2014) using a single metal feed of zirconium oxide (99.9% ZrO_2, Sigma-Aldrich) and hafnium oxide 99.9% HfO_2, Sigma-Aldrich). The prepared $(NH_4)_3ZrF_7$ and $(NH_4)_3HfF_7$ were analysed at Necsa to ensure the correctness and purity (97%) of the compounds. Pelindaba Analytical Laboratories (PAL) performed ICP analysis to verify the metal concentrations. Distillation methods were used to obtain the relevant fluoride data and an ion-selective electrode was used to analyse the ammonium content. Acid concentrations varied from 0.001–8 mol/dm³, while the metal concentrations were fixed for single salt extractions at 100 mg/dm³ Zr/Hf and for mixed salts extractions at 97 mg/dm³ and 3 mg/dm³ for Zr and Hf respectively. Aqueous phase dilutions were made with deionized water (Millipore Milli-Q Plus® Q-pack CPMQ004R1).

H_2SO_4 and sodium chloride (98%NaCl, LabChem) were diluted with deionized water to concentrations ranging from 0.001–2 mol/dm³.

The extraction and stripping experiments were done by contacting equal volumes of the organic and aqueous phase (25 mL; A/O = 1) at 25°C for 60 minutes in a rotary shaker and incubator at 310 r/min. Although equilibrium was reached after 25 minutes (data not shown), all samples were shaken for 60 minute to ensure sufficient equilibrium. After achieving equilibrium and separating the phases in standard separation funnels, inductively coupled plasma–optical emission spectrometry (ICP-OES, Thermo Scientific iCAP 6000 SERIES ICP + CETAC ASX- 520 Auto sampler) was used to analyse the metal concentration in the aqueous phase. The concentration of the metal in the organic phases was assumed to be in accordance with the mass balance.

Results and discussion

Extraction

Influence of acid concentration on single salt extraction

The initial experiments were designed to observe the effect and correlation of single- and mixed salt extractions. Both single and binary systems were evaluated using HCl and H_2SO_4 solutions with as wide as possible concentration range for the initial screening (0.1–8 mol/dm³). In subsequent experiments more data points in narrower ranges were selected. Three different amine-based extractants were used. Alamine 336 is a tertiary amine with three carbon chains extended from the nitrogen ($C_{24}H_{51}N$). Both Aliquat 336 and Uniquat 2280 are quaternary ammonium salts with a positively charged nitrogen bonded to a methyl group and three additional carbon chains in the case of Aliquat 336 and two methyl groups and two carbon chains in the case of Uniquat 2280 (Senol, 2001; Tan *et al.*, 2007; Barnabas and Treadway, 2010)

In the single salt experiments, emulsions were observed and hence no analysis was possible when extracting with Uniquat 2280 in 4–8 mol/dm³ H_2SO_4 as well as when using Alamine 336 in 0.1 mol/dm³ H_2SO_4. Banda *et al.* (2012) observed similar emulsions and third phase formations while using Alamine 336 in HCl.

Figure 1 and Figure 2 display data on the single metal extraction of Zr and Hf from HCl and H_2SO_4 respectively using the experimental conditions described. No significant extraction was obtained above 1 mol/dm³ acid, irrespective of the type of acid or extractant used. The highest extraction
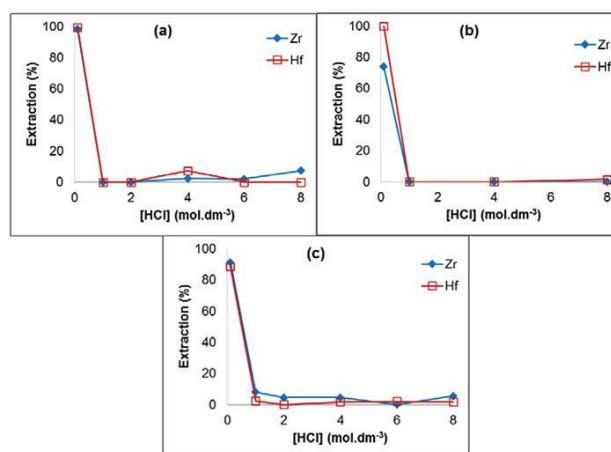

Figure 1—Effect of hydrochloric acid concentration with single salt extraction using (a) Alamine 336, (b) Aliquat 336 and (c) Uniquat 2280. Conditions: 10 wt% extractants, 100 ppm Zr, 100 ppm Hf, A/O = 1, contact time 60 minutes

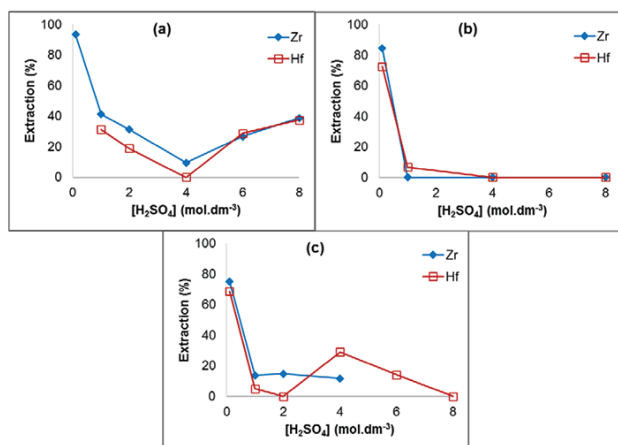# The separation of zirconium and hafnium from $(NH_4)_3Zr(Hf)F_7$

Figure 2—Effect of sulphuric acid concentration with single salt extraction using (a) Alamine 336, (b) Aliquat 336, (c) Uniquat 2280. Conditions: 10 wt% extractants, 100 ppm Zr, 100 ppm Hf, A/O = 1, contact time 60 minutes

values (>85%) were attained at 0.1 mol/dm³, with a slightly higher extraction from a HCl environment. The only noteworthy selectivity at high enough extraction values was obtained using Aliquat 336 (Figure 1b), where a 27% Hf selectivity was observed at 0.1 mol/dm³. The percentage selectivity was calculated by subtracting the lesser extracted metal from the greater extracted metal.

Influence of acid concentration on mixed salt extractions

Using the same parameters that had been used for single salts, mixed salt (97 wt% Zr and 3 wt% Hf) experiments were performed to correlate single- and mixed salt extractions, thereby determining whether the metals affected each other; for example, due to mutual inhabitation during extraction. Mixed salt extractions with the three amine-based extractants and the two acids were evaluated. HCl and H_2SO_4 solutions with a concentration range of 0.01–8 mol/dm³ were used.

Similar to the discussion in the previous section, Figure 3 and Figure 4 illustrate the data on the mixed metals extractions of Zr and Hf from an HCl and H_2SO_4 solution, respectively. When attempting extraction from HCl, no extraction was attained when using Alamine 336 between 0.1–4 mol/dm³ HCl (Figure 3a), increasing to just over 20% extraction at 6 mol/dm³ HCl. With Aliquat 336, 48% extraction was obtained at 0.1 mol/dm³ HCl with a 4% Hf selectivity (Figure 3b). Although Uniquat 2280 (Figure 3c) showed some extraction in the range of 1–8 mol/dm³ HCl, the extraction remained less than 20%. It is known that amine-based extractants can form emulsions when extracting from an HCl environment (Barnabas and Treadway, 2010); this was also observed in the present study when using Alamine 336 combined with H_2SO_4 at 0.1 mol/dm³ and Uniquat 2280 at 6–8 mol/dm³. Emulsions were observed in HCl solutions of 8 mol/ dm³ for Alamine 336 and 0.1 mol/dm³ solution for Uniquat 2280.

Due to the high extraction with Alamine 336, seven extractions were completed with less than 1 mol/dm³ H_2SO_4 (0, 0.01, 0.1, 0.2, 0.4, 0.6, 0.8 mol/dm³) to obtain more comprehensive data. When considering the extraction of the mixed salts from a H_2SO_4 solution (Figure 4), significant extraction for Alamine 336 and Aliquat 336 was observed when extracting from a low acid concentration, while no significant extraction was observed when using Uniquat 2280. Extraction with both Alamine 336 and Aliquat 336 increased at high (>6 mol/dm³) and low (<2 mol/dm³) H_2SO_4 concentrations. For both Alamine 336 and Aliquat 336 the extractions decreased from above 80% to 20–30% between 0.1 and 2 mol/dm³, remained practically constant between 2 and 4 mol/dm³ and then gradually increased again from 4–8 mol/dm³ H_2SO_4. The highest extractions with Alamine 336 and Aliquat 336 were 91% and 78% respectively at
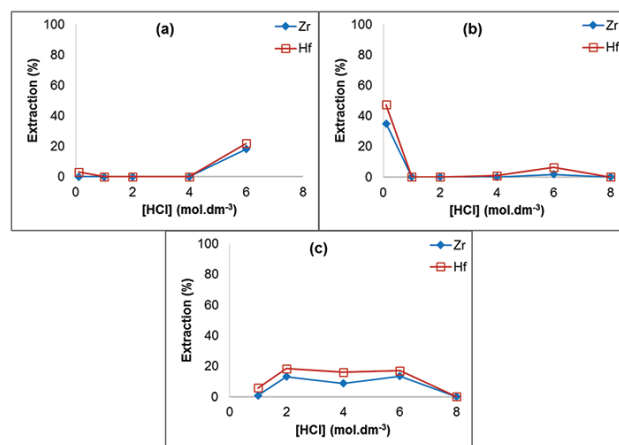

Figure 3—Effect of hydrochloric acid concentration with mixed salts using (a) Alamine 336, (b) Aliquat 336, (c) Uniquat 2280. Conditions: 10 wt% extractants, 97 ppm Zr and 3 ppm Hf, A/O = 1, contact time 60 minutes
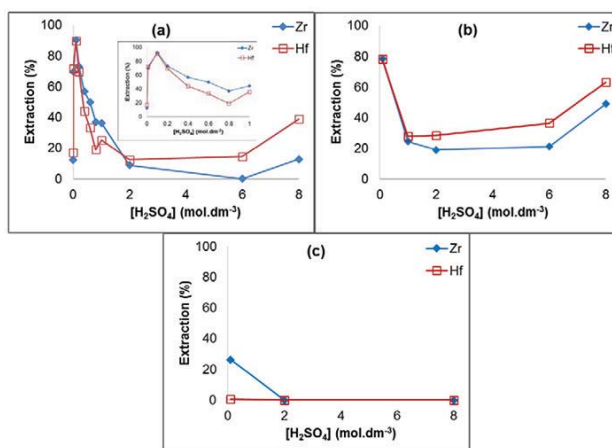

Figure 4—Effect of sulphuric acid concentration with mixed salts using (a) Alamine 336, (b) Aliquat 336, (c) Uniquat 2280. Conditions: 10 wt% extractants, 97 ppm Zr and 3 ppm Hf, A/O = 1, contact time = 60 minutes

The separation of zirconium and hafnium from $(NH_4)_3Zr(Hf)F_7$

0.1 mol/dm³ H_2SO_4. This trend has been observed in previous studies – when increasing HCl above 6 mol/dm³ a similar increase in extraction took place. (Banda *et al.*, 2012; Poriel *et al.*, 2006)

When comparing the single (Figure 1 and Figure 2) and mixed salt (Figure 3 and Figure 4) extractions, both correlations and differences become apparent. In HCl (Figure 1 and Figure 3), the same negligible extraction was observed above 1 mol/dm³ HCl. However, at 0.1 mol/dm³ the extraction with Aliquat 336 was >80% for single salts, which is significantly higher than the 50% attained for mixed salts. No significant extraction was attained when using either Alamine 336 (where emulsion formation was observed above 6 mol/dm³) or Uniquat 2280 when extracting mixed salts compared to the >90% extraction achieved when using single salts. The differences in extractions for the various extractants could be related to the fact that tertiary amines (Alamine 336) have a neutral charge, whereas quaternary amines have a positive charge. The zirconium salt used for extraction $((NH_4)_3Zr(Hf)F_7)$ probably has a negative charge in solution $(Zr(Hf)F_7{}^{3-}$, or possibly $Zr(Hf)F_6{}^{2-})$. In spite of some protonation of the tertiary amine in the acid environment, it can be assumed that this will still be less charged than the quaternary amine where all extractants remain positively charged irrespective of the acid concentration. Assuming the negatively charged Zr salt $(ZrF_6{}^{2-}/ZrF_7{}^{3-}$ anion) in solution, a higher extraction can be expected with the quaternary amine due to its positive charge. This expectation is corroborated in Figure 4 when comparing (a) (tertiary amines) and (b) (quaternary amine). While higher extraction for quaternary amine (Aliquat 336) occurred only above 2 mol/dm³ H_2SO_4, higher extraction was observed with lower acid concentrations (>1 mol/dm³) for Alamine 336. This is preferential in view of the lower amount of acid used, which has both economic as well as environmental advantages

While most data correlates between the single and mixed salts, it is clear that the two salts influence each other's extractions, specifically at low HCl concentrations (<1 mol/dm³). While the competitive behaviour is influenced by the speciation, which due to its complexity falls beyond the scope of this article, the changed extraction behaviour, specifically of Hf in the mixed salt, could be related to the change in the Hf concentration from 100 ppm to 3 ppm from the single to the mixed salts. It was shown that Cl⁻ at higher concentrations in both the single and mixed salts inhibits extraction. Hence, when the Hf concentration was decreased from the single to the mixed salt experiments, the Cl to Hf ratio increased, implying that at 3 ppm Hf the Cl⁻, even at low HCl concentrations, was sufficiently in excess to inhibit the extraction of Hf. It remains, however, unclear why this would also result in such a significant decrease in the Zr extraction.

In H_2SO_4 (Figure 2 and Figure 4) mostly similar tendencies for single and mixed salts were observed irrespective of the acid concentration (0.1–8 mol/dm³), which again confirms the role of the Cl⁻ ion during extraction from an HCl environment. Some differences were observed; for example, the Alamine 336 formed no emulsions during the extractions with mixed salts while emulsions did occur when using single salts. A reason for this is not apparent. In addition, Aliquat 336 yielded 20% higher extraction from 1 mol/dm³ H_2SO_4, which increased gradually with the increase in acid concentration with mixed salts. Uniquat 2280, on the other hand, formed emulsions at 4 and 6 mol/dm³ (Figure 4c). Comparing the data with Figure 2b, where emulsions were formed only in the presence of Zr, it seems that the Zr is responsible for these emulsions (Nielsen *et al.*, 2000).

Influence of extractant to metal$_{Zr+Hf}$ ratio on mixed salts xxtraction

According to the previous section, the best results for mixed salts were attained when extracting from a low H_2SO_4 concentration using Alamine 336 as extractant (Figure 4). Accordingly, the influence of the extractant to metal (E/M) ratio was determined by changing the Alamine 336 concentration between 0.01–10 wt% at 0.01, 0.1 and 0.5 mol/dm³ H_2SO_4.

Figure 5 illustrates the extraction behaviour of Zr and Hf with increasing Alamine 336 concentration at three different H_2SO_4 concentrations. Apart from yielding the best results in the previous section, low concentrations of acids are also more cost-effective and leave a smaller chemical footprint. It is interesting to note that the extraction curve with 0.01 and 0.5 mol/dm³ H_2SO_4 has a near S-shape, while extraction at 0.1 mol/dm³ first increases logarithmically ($R^2 = 0.9082$) before levelling off. This might be related to the change in extraction between 0 and 1 mol/dm³ H_2SO_4 (shown in the insert in Figure 4a) where the 0.01 mol/dm³ data point was to the left of the inclining slope while the 0.5 mol/dm³ data point was to the right of the descending slope with 0.1 mol/dm³ on the peak of the graph. This, however, only confirms that there is a change in the speciation in the vicinity of 0.1 mol/dm³ H_2SO_4, but not what this change might be. Irrespective of the variation in the shape of
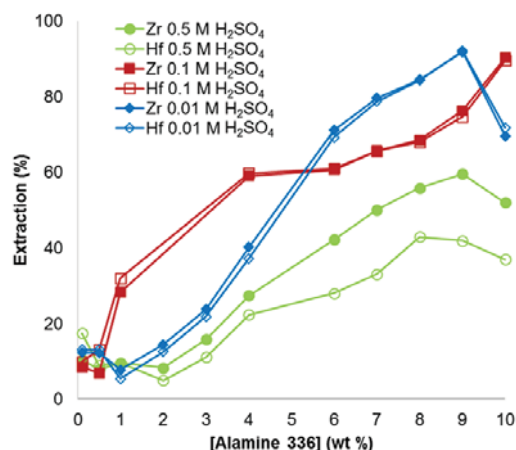

Figure 5—Effect of extractant concentration changes with mixed salts in sulphuric acid using Alamine 336. Conditions: 0.001–10 wt% extractant, [acid]: 0.01, 0.1 and 0.5 mol/dm³, 97 ppm Zr and 3 ppm Hf, A/O = 1, contact time 60 minutes

The separation of zirconium and hafnium from $(NH_4)_3Zr(Hf)F_7$
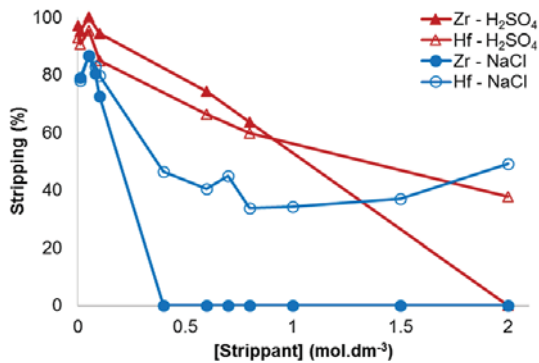

Figure 6—Effect of sodium chloride and sulphuric acid as strippants on loaded Alamine 336. Extraction conditions: 9 wt% Alamine 336, 0.5 mol/dm³ sulphuric acid, 97 ppm Zr and 3 ppm Hf, O/A = 1, contact time 60 minutes. Stripping conditions: 9 wt% Alamine loaded, [strippant] = 0 - 2 mol/dm³, O/A = 1, contact time 60 minutes

thecurves, however, extraction increased in all cases with increasing Alamine 336 concentration from 2 to 9 wt%.

An extraction of 92% was attained at 9 wt% Alamine 336 when extracting from 0.01 mol/dm³ H_2SO_4 and 87% at 10 wt% Alamine 336 when extracting from 0.1 mol/dm³ H_2SO_4. Extraction from 0.5 mol/dm³ H_2SO_4, while also increasing with increasing extractant concentration, had the smallest gradient, resulting in the lowest extraction reaching a maximum of 60% Zr and 41% Hf at 9 wt% Alamine 336. In spite of the lower extraction, the experiment at 0.5 mol/dm³ was the only one that displayed any selectivity between the two metals, in this case favouring the extraction of Zr with a 19% selectivity at 9 wt% Alamine 336.

Stripping

In the work described in the previous sections the extractions were optimized. In order to be able to reuse the extractants for subsequent extraction in a solvent extraction process, the stripping of the metal complexes (Zr and Hf) from the loaded Alamine 336 has to be investigated. While stripping has been demonstrated in the literature with various stripping liquors (Gefvert, 1994), in this study the best results were attained when using NaCl and H_2SO_4 (Banda *et al.*, 2012).

Figure 6 indicates the stripping of a loaded organic phase attained by a 60-minute extraction from a 0.5 mol/dm³ H_2SO_4 solution using 9 wt% Alamine 336. The stripping liquor concentrations were varied from 0–2 mol/dm³ for H_2SO_4 and NaCl. According to Figure 6, both stripping liquors achieved stripping of the Zr and Hf, with decreasing stripping with increasing strippant concentration. However, when using H_2SO_4 as stripping liquor, a 48% Hf selectivity was achieved at 2 mol/dm³. NaCl yielded favourable stripping results at 2 mol/dm³ NaCl with a 46% Hf stripping and 0% Zr stripping. Although 2 mol/dm³ NaCl was not able to strip all the Hf, it did result in a selective removal of Zr leaving pure Hf in the organic phase, which can be stripped in a second stripping step, for example using H_2SO_4.

Proposed extraction, scrubbing and stripping scheme

Using the extraction and stripping data obtained in this study a possible scheme with various stages of extraction and stripping can be proposed (Figure 7), which ultimately could lead to a process for the manufacturing of nuclear-grade Zr, if designed correctly. In the extraction step, the aqueous feed (0.5 mol/dm³ H_2SO_4) and the aqueous scrubbing liquor (2.0 mol/dm³ NaCl) are contacted with the organic solution (Alamine 336, 9 wt%) and the loaded organic solution. During this extraction an excess of Zr is extracted into the organic phase. During the scrubbing of the loaded organic phase most of the remaining extracted Hf is scrubbed to the aqueous phase. Thereafter the Zr is stripped from the organic phase using 0.05 mol/dm³ H_2SO_4. Subsequently, the solvent is regenerated, water being used to remove any residual Zr or Hf from the organic phase. Finally, the depleted solvent is recirculated to the solvent make-up where any lost extractant is replenished, completing the process.
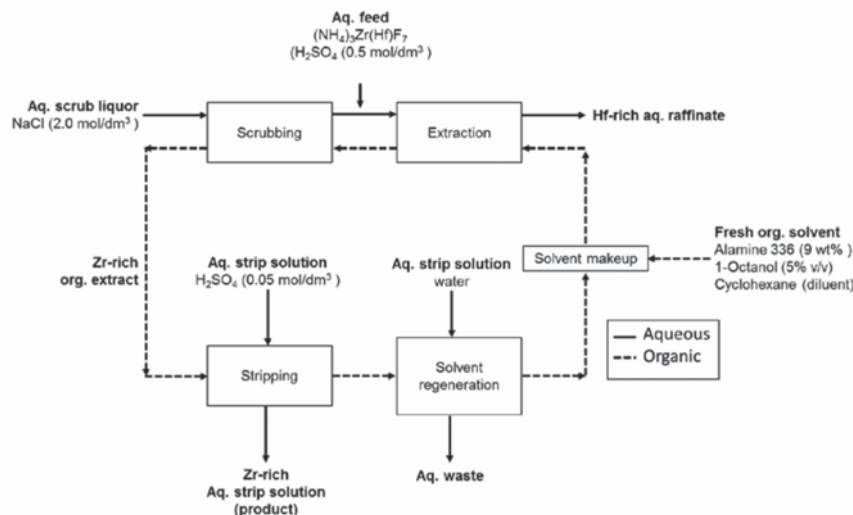

Figure 7—Proposed extraction, scrubbing and stripping scheme for Zr purification

The separation of zirconium and hafnium from $(NH_4)_3Zr(Hf)F_7$

Conclusion

A solvent extraction study was done to determine the extraction and separation of Zr and Hf as $(NH_4)_3Zr(Hf)F_7$ from a HCl and H_2SO_4 environment (0.01–8 mol/dm³) using three amine-based extractants (Alamine 336, Aliquat 336 and Uniquat 2280). While similar extractions were attained for single and mixed salts, both the Zr and Hf extractions were significantly lower when using mixed salts at low HCl concentrations. Of the three amines tested, Alamine 336 exhibited the best extraction and selectivity for the separation of Zr from Hf at both low (86%) and high (39%) H_2SO_4 concentrations. Varying the E/M ratio of Alamine 336 at three low H_2SO_4 concentrations (0.01, 0.1 and 0.5 mol/dm³) led to a 19% selective extraction of Zr over Hf with 9 wt% Alamine 336 in 0.5 mol/dm³ H_2SO_4. Complete stripping of Zr and Hf from loaded Alamine 336 was achieved using 2 mol/dm³ NaCl. A proposed extraction, scrubbing and stripping scheme was presented showing the possibility for the development of a process for the separation of Zr and Hf from $(NH_4)_3Zr(Hf)F_7$ in a H_2SO_4 environment using amine-based extractants such as Alamine 336. With the current data it is possible to purify Zr from 97% to 98.49%. By combining further extraction, scrubbing and stripping steps, it should be possible to reduce the Hf concentration to below 100 ppm as required by the nuclear industry.

Acknowledgements

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