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Procedia Chemistry 21 (2016) 231 – 238

Procedia Chemistry

5th International ATALANTE Conference on Nuclear Chemistry for Sustainable Fuel Cycles

Dissolution Performance of Plutonium Nitride Based Fuel Materials

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Abstract

Nitride fuels have been regarded as one viable fuel option for Generation IV reactors due to their positive features compared to oxides. To be able to close the fuel cycle and follow the Generation IV concept, nitrides must, however, demonstrate their ability to be reprocessed. This means that the dissolution performance of actinide based nitrides has to be thoroughly investigated and assessed. As the zirconium stabilized nitrides show even better potential as fuel material than does the pure actinide containing nitrides, investigations on the dissolution behavior of both PuN and (Pu,Zr)N has been undertaken. If possible it is desirable to perform the fuel dissolutions using nitric acid. This, as most reprocessing strategies using solvent-solvent extraction are based on a nitride containing aqueous matrix.

(Pu,Zr)N/C microspheres were produced using internal gelation. The spheres dissolution performance was investigated using nitric acid with and without additions of HF and Ag(II). In addition PuN fuel pellets were produced from powder and their dissolution performance were also assessed in a nitric acid based setting.

Peer-review under responsibility of the organizing committee of ATALANTE 2016

Keywords: "Dissolution; Plutonium nitride; Nitric acid; PuN; (Pu,Zr)N"

1. Introduction

Nitride based nuclear fuel has been identified as a viable option for the Generation IV reactor concept. This due to improved properties of the actual fuel, such as better compatibility to liquid metal coolants, higher thermal conductivity and higher fissile material density compared to oxides[1,2] but also due to a better dissolution

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Peer-review under responsibility of the organizing committee of ATALANTE 2016
doi:10.1016/j.proche.2016.10.033

behavior.[1,3,4] Fuel dissolution is an important feature for the possibility of reprocessing, which in turn is a prerequisite for the Generation IV concept.[5]

Possible nitride fuels to be used in Generation IV reactors and in accelerator driven systems could be pure actinide nitrides or be fabricated in solid solution with ZrN. The introduction of ZrN would reduce operating temperatures and improve high temperature stability.[1] Few literature sources are available on the dissolution performance of pure plutonium nitride,[6,7] as well as for mixed uranium plutonium nitrides, (U,Pu)N and pure uranium nitride.[3,4] Even less available data exist for the dissolution of zirconium based actinide nitrides, such as (Pu,Zr)N and (U,Zr)N.[2]

To be able to close the fuel cycle and follow the Generation IV concept, the dissolved fuel has to be subjected to separation processes before being converted and used as raw material for new fuel, Figure 1. Solvent extraction is the method of choice for aqueous separation of the actinides from the rest of the used fuel components and the separation processes developed to this date are almost exclusively based on a nitric acid media.[8] In this work the dissolution performance of (Pu,Zr)N and pure PuN fuel materials has hence been investigated, in nitric acid based settings.

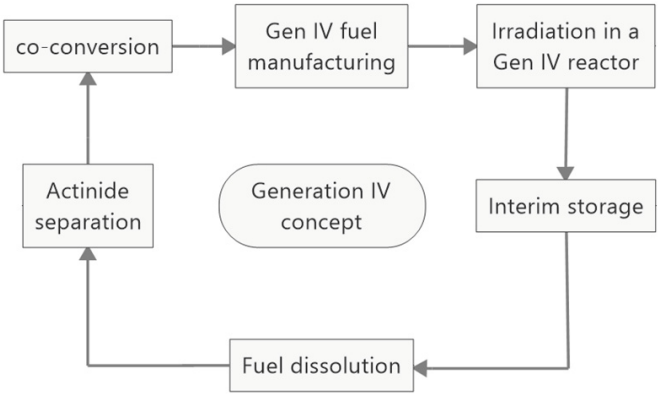


Fig. 1. Schematic overview of the Generation IV concept

2. Methods and Materials

In all cases the stockpile composition of plutonium used was: ^{242}Pu 0.34, ^{241}Pu 0.73, ^{240}Pu, 14.45, ^{239}Pu 84.02 and ^{238}Pu 0.13 atom percent in 1992-10-20. For the mixed plutonium-zirconium material, the plutonium nitrate solution was purified from present americium-241 by solvent extraction prior to use.

2.1 PuN material

PuN pellets have been produced by powder synthesis, mixing PuO_2 powder with carbon powder in a 2.3 C/Pu molar ratio. Carbothermal reduction was performed for 4 hours at 1400 °C in N_2 + 5% H_2 atmosphere followed by decarburization in N_2 + 5% H_2 at 1600-1700 °C for 2 hours. The produced powder was analyzed by XRD to be PuN with a carbide content below 7% and without any detectable residual PuO_2 phase. Pellets were produced by dry pressing before sintering in N_2 + 5% H_2. Two pellets were used for dissolution experiments, A and B, of which A split horizontally upon removal from the pressing tool, rendering pellet fragment A1 and A2. Pellet A (m(A1)= 201.9 mg and m(A2)= 80.4 mg) was compacted using a pressure of 1.8 GPa and sintered at a 1800 °C for 4 hours while B (m(B)= 166.1 mg) was pressed to 1.2 GPa and sintered at 1700 °C for 4 hours, rendering a higher density of A compared to B (*circa* 78% and 63% respectively of the theoretical density). The density was estimated by weighing and measuring the dimensions of the actual pellet (B) and another pellet produced under the same conditions (A).

2.2 (Pu,Zr)N/C material

(Pu,Zr)N based microspheres (diameter=747 ± 31 µm, mass=1.16 ± 0.06 mg, as an average of 16 spheres) with a high carbon content was used for dissolution. The spheres were produced via the internal gelation process[9,10] by adding carbon black powder (Cabot Corporation) to a plutonium and zirconium (40% Pu, 60% Zr) nitrate solution. The oxide spheres were then reduced to carbonitride (roughly 50% nitride) via carbothermic reduction at 1400 °C for 4 hours (5% H_2 in N_2) followed by decarburization at 1650 °C for 4 hours. Pellet sintering was performed in argon (5h at 1700°C). The resulting material was a partly inhomogeneous mixture with one zirconium rich phase and one plutonium rich phase, investigated using SEM-mapping of a cross-section of a sphere.

2.3 Dissolution

All dissolutions were performed inside a glovebox with inert atmosphere (nitrogen) using a 25 ml two-necked round bottomed flask equipped with a swan neck thermometer adapter and a dry condenser (Findenser®) connected to a sodium carbonate buffer scrub. In all cases the nitric acid used was Supra Pure and upon each sample removal for ICP-MS analyses (Thermo Scientific Thermo ICAP-Q), triplicate samples of 10 µl were removed. ICP-MS measurements were performed in 0.5 M nitric acid using a Zr and/or U calibration curve with Bi as internal standard. In no cases were off-gases considered in the mass balances, as no method for quantification is available.

3. Results and Discussion

2.1. Dissolution of PuN pellet material

Dissolution of the A1 pellet fragment was conducted with an increasing nitric acid concentration in order to determine possible mild dissolution conditions for the intact pellet B. Using 6.0 M (V_{tot}=0.97 ml) and 8.0 M (V_{tot}=1.254 ml) HNO_3 no reaction could be seen (by bubbles, NOx formation or color change of the dissolution liquor) after 35 minutes under each condition. When increasing to 9.6 M (V_{tot}=1.61 ml) bubbles instantly started to form on the surface of the pellet and within 35 minutes brown NOx gas had begun to form in the dissolution vessel. ICP-MS analysis of removed samples confirms the ocular results. After 35 minutes in the 6 and 8 M acid, only 0.1-0.2 % of the plutonium had dissolved, while after 35 minutes in the 9.6 M acid *circa* 2.7% had dissolved. The dissolution in 9.6 M nitric acid was then monitored for an additional 23 hours, after which the solution became very dark green and *circa* 59% of the available plutonium had dissolved. Samples for analyses removed from the dark green solution turned brownish pink/orange when diluted at lower nitrate concentrations, as expected.[11] These color changes depending on the nitrate concentration were further elaborated to provide an experimental reference, Figure 2. After the 23 hours the dissolution liquor was removed revealing a dark slurry in the bottom of the reaction vessel. An attempt was made to dissolve the dark residue using 14.4 M HNO_3(V=0.5 ml) This resulted in a dark green plutonium containing solution but solid material still remained after 22 hours of the second dissolution attempt. The residue was therefore washed and dried before being analysed by XRD. The material was found to have a NaCl-fcc structure, which together with peak fitting rendered the conclusion that it most likely consist of undissolved PuN but with a strong ingrowth of PuO and possibly PuO_2-x (Figure 3). The presence of plutonium oxide could be due to PuN oxidation both by oxygen or moisture in the glovebox atmosphere prior to dissolution or during the dissolution experiment.

In order to try and facilitate a complete dissolution, pellet fragment A2 was dissolved in 5 ml 65% (14.4 M) HNO_3 with 0.05 M HF. There was an immediate frothing and evolution of NO_X when introducing the pellet and the dissolution liquor turned dark green within minutes (Figure 4, left).

Samples were removed after different periods of time during up to 30 hours. ICP-MS analyses suggest that no more, or little, dissolution occurred after 13 minutes reaction time. Despite this, visible black fragments in the dissolution liquor could be seen throughout the entire experiment. When analysing one of the fragments with SEM (Figure 4, right), it was clear that the solid consisted of elemental carbon, with a very small presence of active material (white spots). This explains why the final plutonium concentration in the dissolution liquor corresponds to 103 ± 6 % of the starting material despite the presence of solid particles.

Fig. 2. The same amount of Plutonium (IV) diluted to obtain final nitric acid concentrations from left to right of: 1.4, 5.8, 7.9, 10.0 and 14.4 M.

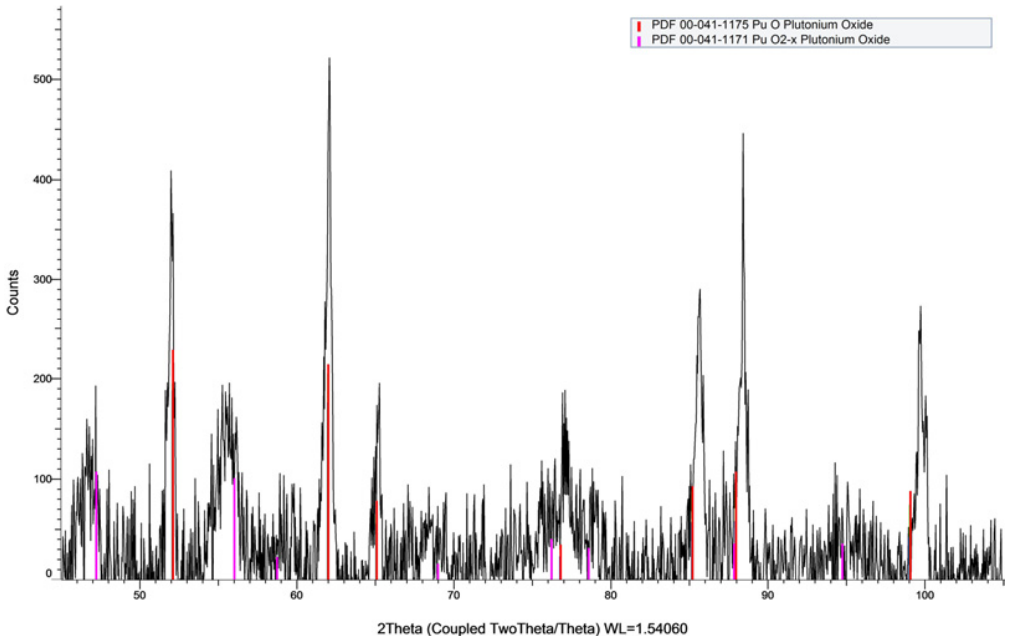


Fig. 3 XRD measurements of dissolution residues after dissolution of a PuN pellet fragment. Red peak fit: PuO, Pink peak fit: PuO2-x

PuN pellet B was now subjected to a dissolution experiment in 5 ml 10 M HNO_3. ICP-MS analyses show that the dissolution seemingly follows an S-curve fit (Figure 5) according to equation 1, compared to the more expected equation 2. The induction time could possibly be explained by the presence of an oxide layer on the surface of the pellet. As is obvious, the dissolution also levels out at around 30% of the theoretical maximum concentration (0.1 M). This could be due to an oxidation of the plutonium nitride to plutonium oxide both before and partly during the dissolution. Complete dissolution could, however, be facilitated within 3 hours by adding HF to a final concentration of 0.05 M to the dissolution liquor.

Samples from the different dissolutions were also analyzed with HPGe in order to detect any possible difference in dissolution kinetics between americium and plutonium. This, as the starting material was not purified before production and hence contained rather large amounts of americium-241. No difference in dissolution kinetics could be observed.

$$C(t) = \frac{C_{max}}{1+e^{-k(t-t_m)}} \quad (1)$$

$$C(t) = C_{max} \times (1 - e^{-kt}) \quad (2)$$

where C is the concentration of solute in the solution, t is time, t_m is the time at the maximum slope of the curve and k is a constant.

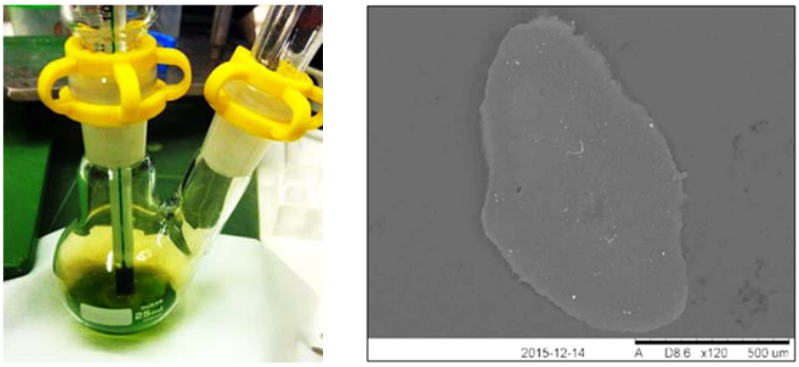


Fig. 4. Dissolution of PuN pellet fragment A2 in 5 ml 65% (14.44 M) HNO_3 + 0.05 M HF. Left: ongoing dissolution. Right: SEM picture of black particle remaining after dissolution.

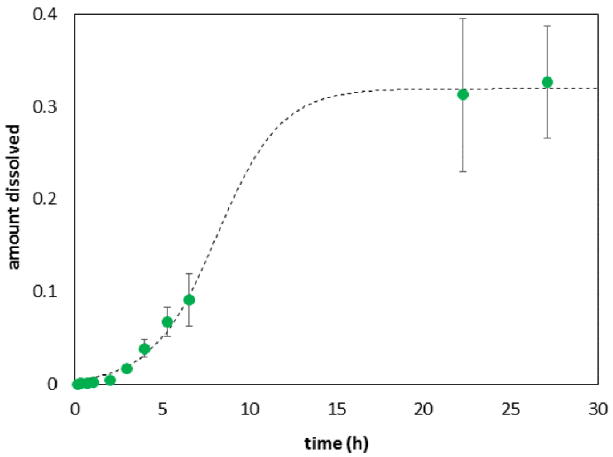


Fig. 5. ICP-MS data from the dissolution of a PuN pellet (m= 166.1 mg) in 5 ml 65% (14.44 M) HNO_3 at room temperature

3.2 Dissolution of (Pu,Zr)N/C microspheres

A (Pu,Zr)N/C microsphere was attempted to be dissolved in 65% (14.4 M) nitric acid at room temperature. ICP-MS analyses confirmed ocular inspection results that the microsphere was unaffected during the entire duration of the experiment (> 48 h). By increasing the temperature to reflux (120°C), dissolution took place but after > 27 h a black solid residue still remained. Existing data on the dissolution of pure ZrN materials in hot nitric acid are ambiguous,[1,2] but as concentrations of the solutes throughout the experiment was *circa* 80% Zr and 20% Pu, this indicates that the residue instead was plutonium rich. Since the previous results in this work suggests that pure PuN should be dissolved under milder conditions than those applied here, the undissolved material could be believed to be formed solid solution of (Pu,Zr)N. Due to acid leakage (in vapor form) from the equipment upon continuation of

the experiment, a fictive end point from the following HF-dissolutions (presented below) was used to retrieve the kinetics data presented in Figure 6. Also, as the leakage caused a decrease in acid volume, the last time point most likely show a slightly high dissolution value. Despite this, it is obvious that both solutes in this case display the same dissolution kinetics, fitted with dissolution equation 2.

Dissolution of microspheres were also performed with the addition of HF (0,05 and 0.01 M) to the dissolution liquor (Figure 7). In both cases complete dissolution of the spheres were achieved. However, contrary to when pure nitric acid and elevated temperature was used for dissolution, the kinetics of the dissolution differed between the two solutes (Pu and Zr). This could possibly be attributed to a slower dissolution of an actual (Pu,Zr)N solid solution. The amount of HF added also affects the dissolution kinetics despite that it in both cases widely exceeds the final dissolved amount of plutonium. There is a possibility that formed plutonium silicates (from etching of the borosilicate glass by the presence of HF) are the reason for the difference in dissolution kinetics between the two solutes. However, this would most likely render a more pronounced difference at higher HF concentrations and in Figure 7 the opposite situation can be seen.

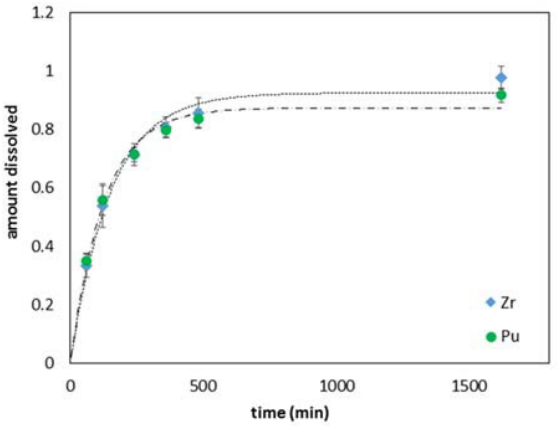


Fig. 6. ICP-MS data from the dissolution of one (Pu,Zr)N/C microsphere in 5 ml 65% (14.44 M) HNO_3 at reflux

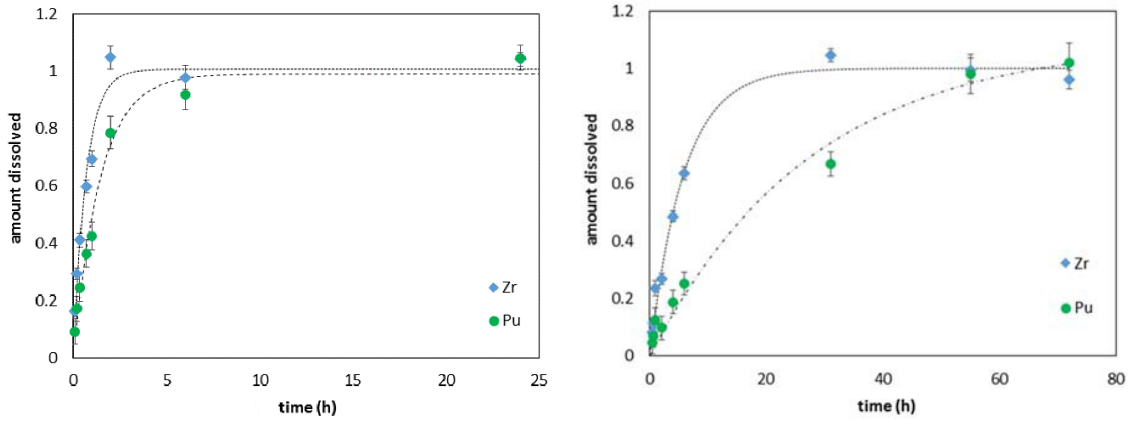
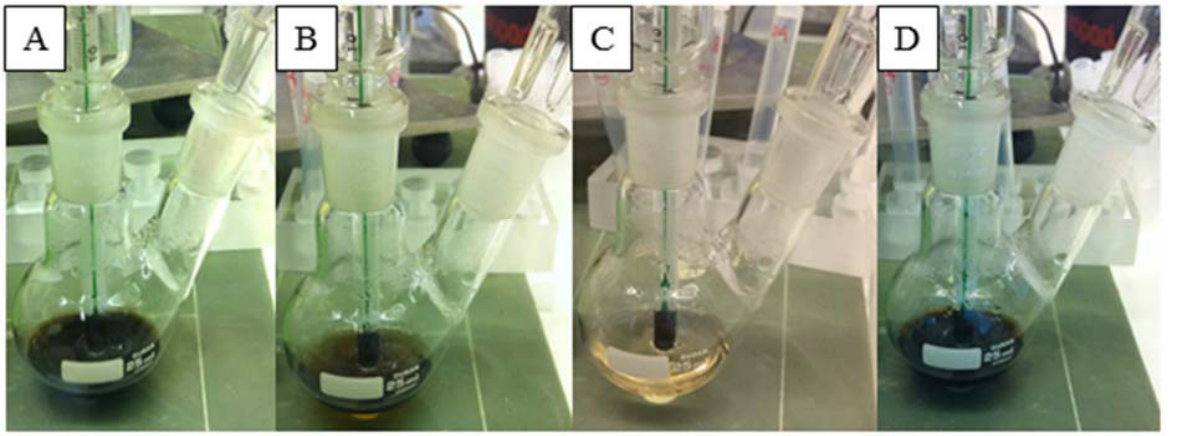


Fig. 7. ICP-MS data from the dissolution of one (Pu,Zr)N/C microsphere in 5 ml 65% (14.44 M) HNO_3 + 0.05 M HF (Left) and in 5 ml 65% (14.44 M) HNO_3 + 0.01 M HF (Right).

Two different dissolutions of microspheres were also performed using additions of Ag(II) (in the form of freshly purchased $AgO_{(s)}$) instead of HF to cold nitric acid, in order to investigate if milder conditions could facilitate

dissolution of the material. Upon addition of Ag(II), the dissolution liquor turns instantly opaque black. The colour then gradually fades with time until the solution once again is transparent and colourless (Figure 8, panel A-C).

In the first dissolution, Ag(II) was continuously added and the solution was maintained at a dark colour as in Figure 8 panel A and B, to ensure a constant presence of excess Ag(II). Dissolution under these conditions was successful and the results are presented in Figure 9. Equation 2 can describe the overall dissolution behaviour fairly well (Figure 9, left) but it does not fit the earlier time-points (< 5 hours) very well. By applying an exponential dissolution model, plotting the dissolution against the added amount of Ag(II), the time points up to circa 80 hours can be well described (Figure 8, right). This suggests that there is a combined dissolution dependence both on time and on availability of oxidant.



dition of Ag(II) in the form of $AgO_{(s)}$ to concentrated nitric acid for dissolution of (Pu, Zr)N/C microspheres

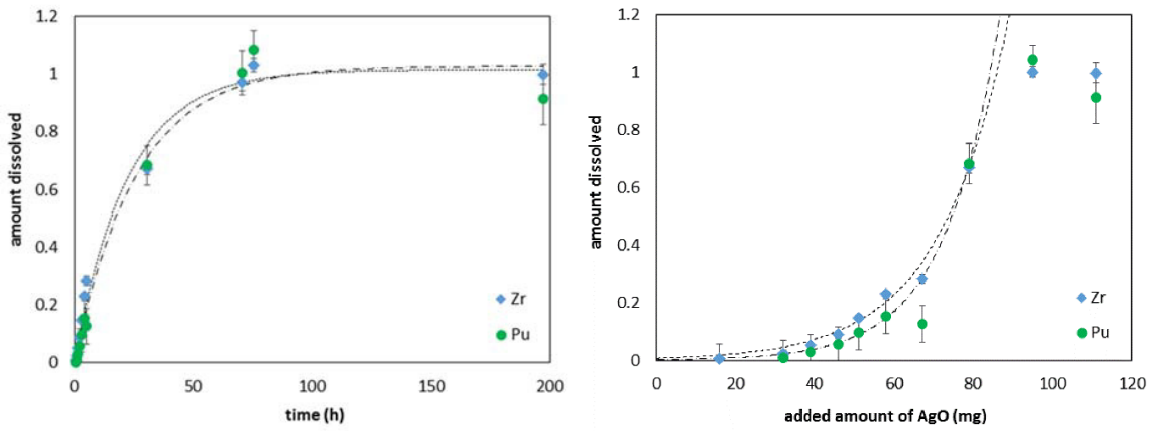


Fig. 9. ICP-MS data from the dissolution of one (Pu,Zr)N/C microsphere in 5 ml 65% (14.44 M) HNO_3 with continuous addition of Ag(II) in the form of $AgO_{(s)}$ Left: amount dissolved plotted against time. Right: amount dissolved plotted against added amount of oxidant.

In the second dissolution, AgO was added to the dissolution liquor and then the colour was allowed to completely disappear before another addition was made, according to Figure 8, panel A-D. Also in this case complete dissolution was accomplished but after a longer time period, due to the nature of the experiment (Figure 10, left). The dissolution could now be described with equation 1 with a combined effect of added amount of Ag(II) and time, as visualized in Figure 10, right. For both dissolutions using Ag(II) the behaviour of the two solutes are similar.

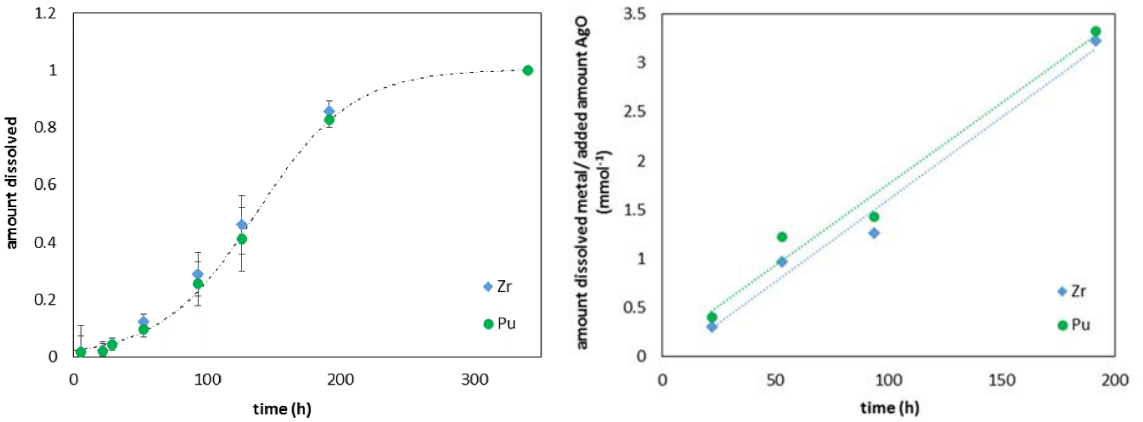


Fig. 10. ICP-MS data from the dissolution of one (Pu,Zr)N/C microsphere in 5 ml 65% (14.44 M) HNO_3 with addition of Ag(II) in the form of $AgO_{(s)}$ Left: amount dissolved plotted against time. Right: amount dissolved per added amount Ag(II) plotted against time.

3. Conclusions

Both PuN and (Pu,Zr)N/C fuel material can be completely dissolved in nitric acid of high concentration with the use of catalytic amounts of HF. The amount of HF added strongly affects dissolution kinetics of (Pu,Zr)N and the presence of HF affects the two solutes differently, possibly due to inhomogeneity of the starting material. Large additions of Ag(II) can also be used to facilitate the dissolution of (Pu,Zr)N in nitric acid. PuN can be dissolved by pure nitric acid of high concentration at room temperature while (Pu,Zr)N is unaffected under similar conditions. At elevated temperature (reflux), (Pu,Zr)N can, however, also be dissolved by concentrated pure nitric acid. Both fuel types could be dissolved for reprocessing to fulfil the requirements of the generation IV concept, however, harsh conditions are required and more studies are necessary in order to optimize dissolution settings.

Acknowledgements

The EU FP7 Project ASGARD (grant agreement n°295825) is acknowledged for the funding of this work.

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