FABRICATION AND DISSOLUTION OF AMERICIUM PLUTONIUM OXIDE FUELS

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Abstract. As a part of the research on Gen IV oxide fuels the effect of the minor actinides (americium) on the dissolution behaviour of plutonium oxide has been studied. Two compositions of americium plutonium oxide pellets have been fabricated by powder metallurgy in a glovebox specially designed for work with americium. These fresh pellets have been dissolved in hot nitric acid and hot nitric acid with hydrofluoric acid. After a dissolution of 300 minutes, very limited dissolution of just few percent of the starting material was determined, where the dissolution rate of plutonium oxide is about 100 times lower comparing to americium oxide.

1. Introduction

Oxide fuels for Generation IV systems and Inert Matrix Fuels may contain high concentrations of plutonium (up to 50%) and minor actinides (MA). High concentrations of plutonium in oxide fuels strongly limit the solubility in nitric acid. However, the effect of the MA-content (specifically Am) on the dissolution capability is still not very well known. Yet this effect forms a crucial aspect in the design of a reprocessing flow-sheet for oxide fuels for Generation IV systems, as well as for Inert Matrix Fuels. It is the objective to study the basic dissolution properties of oxide fuels with a high concentration of Pu and minor actinides. This enables establishing a relationship between Am-content and dissolution capability, addressing open issues concerning the maximum achievable Minor Actinide content in fuels and targets for transmutation purposes.

The composition of actinides in spent fuel for various Partitioning and Transmutation (P&T) scenarios has been calculated with the SERPENT Monte Carlo code [1]. The calculated fraction of plutonium in the oxide phase of the fuel at end of life (EOL) exceeds 40%, which may constitute an issue for the dissolution performance. Dissolution tests of $(Pu,MA)O_2$ samples with a Pu

fraction of up to 50% therefore should be carried out to assess the solubility limit of this fuel composition.

2. Materials and methods

2.1 Radiation aspects of the pellets fabrication

As Am-241 is an alpha and gamma emitter, the pellet fabrication by powder metallurgy (done manually) is quite challenging in terms of radiation safety. Both the fabrication and the dissolution study have been done in the actinide laboratory equipped with gloveboxes suitable for work with actinides (i.e. alpha emitters). The standard glovebox does not provide sufficient protection against gamma radiation. A Hazard Identification Evaluation has been performed where mainly radiological aspects have been evaluated with conclusion that extra shielding is necessary, this was provided by a glove box shielded by lead glass plates. The highest dose was identified to be obtained on the fingers during the fabrication step, special shielded gloves were used to decrease the finger dose.

The new installed glovebox has been equipped with a standard equipment for the powder metallurgy pellets fabrication, i.e. balance, mixing apparatus (IKA UTTD Ultra-Turrax Tube Drive) and a manual press (YLJ-12T Desk-Top Pressing Machine, MTI Corporation).

2.2 Fabrication of the americium plutonium oxide pellets

Based on the calculated scenarios, two pellets composition were proposed: 50:50 and 70:30 (PuO_2:AmO_2). The pellets have been made by powder metallurgy method. Both PuO_2 and AmO_2 powders were analysed by X-Ray diffraction (XRD, Bruker D2 Phaser) in an air-tight sample holder, this XRD is adjusted to be suitable for placing in a glove box. Both measurements confirmed the composition of the powders.

The AmO_2 powder was agglomerated, the required amount for one batch was weighed, acetone was added, and the mixture was milled using zirconia milling balls to destroy the agglomerates during ball milling. After 30 minutes of mixing a fine powder was obtained. The required amount of PuO_2 was added and mixing continued for the next 30 minutes. When finished, the mixture was put in a Petri dish and left overnight to evaporate the acetone. The dried mixture per batch was divided in four parts. Each part was weighed and put in the pressing dye. The pressing dye with a diameter of 4.5 mm has been used, the height of the pellets was calculated to be 3 mm. The pellets were then pressed by 175 MPa. Zinc stearate was used as demolding agent.

The pellets were sintered in a furnace in a glovebox according to the following sintering regime: 5°C/min to 500 °C air atmosphere, dwell of 1 hour at 500 °C to remove all possible organics, 3 °C/min up to 1600 °C in argon atmosphere; dwell of 6 hours at 1600°C; cool down to room temperature.

2.3 Dissolution experiments

Due to its high plutonium content, this fresh fuel is expected to dissolve slowly poorly in standard nitric acid (PUREX process) with a high amount of residues. Therefore, a series of dissolution experiments with varying conditions were proposed: i) Dissolution in hot concentrated nitric acid, ii) Dissolution in hot concentrated nitric acid with hydrofluoric acid and iii) Oxidation with in-situ chemically generated Ag(II). In this paper the obtained results from the experiments i) and ii) are presented.

The dissolution experiments have been performed in the dedicated glovebox; a simple dissolution setup was used. Each pellet was weighed before being put in the dissolving agent (50 ml), the heating was turned on and the time was measured. The dissolution experiment took 300 minutes. After the experiment was finished, after cooling down, a filtration was done to collect the undissolved residues (see Fig. 1). The residues were subsequently analysed by powder X-Ray diffraction (Bruker D2).

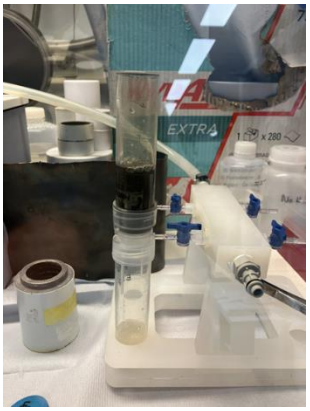

Fig. 1. A filtration setup used for the filtration of the undissolved residues

During the dissolution sub-samples have been taken for subsequent analysis to provide information on the dissolution kinetics. The analysis of americium and plutonium was done by alpha spectrometry. The Pu/Am separation was done by column separation using the TRU and TEVA resins (Triskem), using various acids to eluate the Am and Pu for the analysis. In addition, Am-241 in the solution was determined by gamma spectrometry. The samples for the analysis had to be diluted from range of hundreds of

GBq of starting material to the level of 10Bq/g of the solution to be measured, it means the measurement error is very high and this method is suitable just to make a comparison between the concentration of Am and Pu in the solution.

3. Results

3.1 Fabrication and characterization of americium plutonium oxide pellets

Two types of pellets were fabricated, each batch consisting of 4 pellets. The pellets have been characterized by density measurements (immersion in alcohol) and checked by optical microscopy (see Fig. 2). The green pellets were about 0.45 g each, with diameter of 4.5 mm and 3 mm high, the density after sintering is listed in Table 1.

Table 1. Characteristics of the pellets

	AmO_2 (wt%)	PuO_2 (wt%)	Density (% of TD)
Type I	28.4	71.6	75.1 ±3.2
Type II	52.4	47.6	71.1 ±0.8

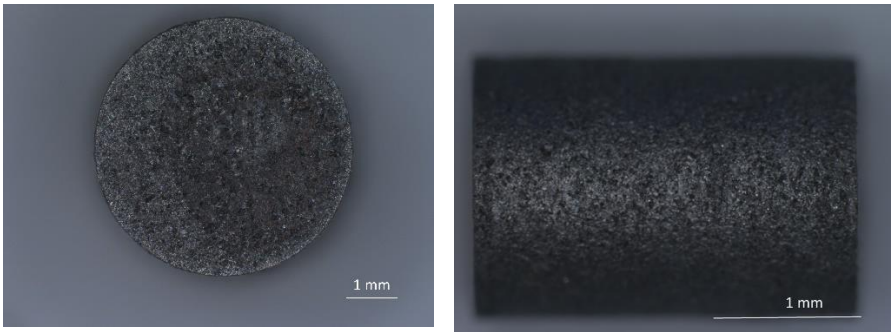

Fig. 2. Optical microscopy pictures of a pellet type II

3.2 Dissolution experiments

3.2.1 Dissolution experiment in hot nitric acid

First experiments have been done in 8M hot nitric acid (50 ml), at a temperature of 90-92°C for a period of 300 minutes. Both pellets types have been tested, in both cases the pellet disintegration took place within 30 minutes (see Fig. 3).

Fig. 3. Pellets dissolution in hot nitric acid, pellet before starting the experiment (left) and disintegration after 30 minutes (right)

3.2.2 Dissolution experiments in hot concentrated nitric acid with hydrofluoric acid

These experiments have been done in a mixture (50 ml) of 8M hot nitric acid with 1 M hydrofluoric acid (HF) at a temperature of 90-92°C for a period of 300 minutes. Both pellets types have been tested, and again in both cases the pellet disintegration took place within 30 minutes (see Fig. 4). The solution is in both cases coloured yellowish, the solids coloured whitish.

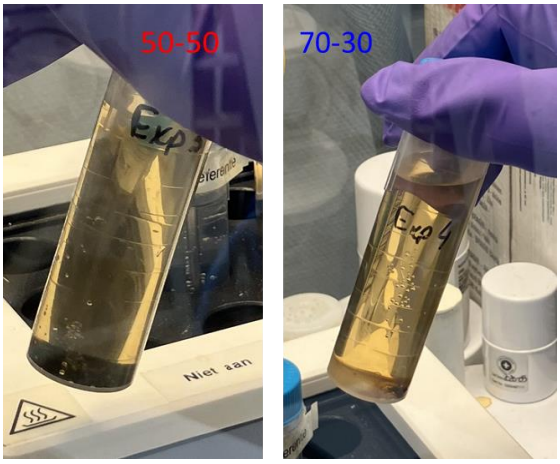

Fig. 4. Pellets dissolution in hot nitric acid with a hydrofluoric acid, experiment 50-50 (left) and experiment 70-30 (right), disintegration took place after 30 minutes

3.3 Analysis of residues

After the filtration, the residues were dried at room temperature, collected and weighed. The pellets before dissolution were about 400 mg and only 10-20 mg materials is determined to be dissolved. Based on that, a very limited dissolution of the pellets was found, just few percent of the starting material is dissolved.

The residues were analysed by XRD, in case of the hot nitric acid peaks of americium and plutonium oxide are determined (see Fig. 5 left). The diffraction patterns for both measured samples were plotted together with the indexes of the PuO_2 and AmO_2 in which the HKL label shown is for both PuO_2 and AmO_2 as both have the same HKL values. The peak shifts are observed and are more pronounced at higher 2θ. The peak shift is commonly correlated with a change in lattice parameters.

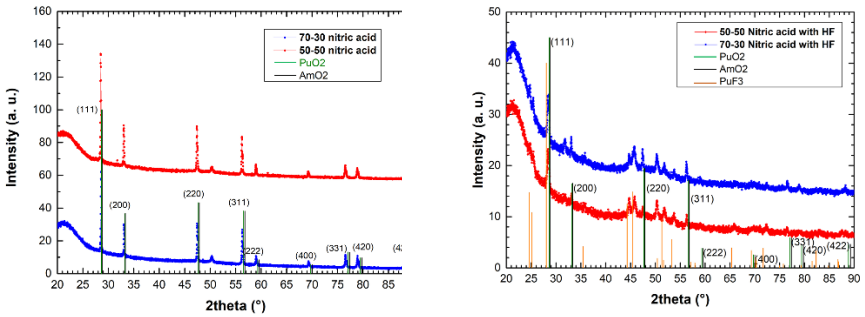

Fig. 5 . XRD analysis of the residues, experiment in hot nitric acid (left) and experiment in hot nitric acid with HF (right)

In case of experiment using the nitric acid with hydrofluoric acid, the analysis of the XRD data is a bit more complicated (see Fig. 5 right). It can be expected that except plutonium and americium oxide which are the starting materials, plutonium and/or americium fluoride should likely form. The XRD analyses confirmed presence of AmO_2 and PuO_2; peaks of plutonium fluoride were identified as well in the analysed samples. No information about americium fluoride diffraction pattern was found in any of the available databases. In comparison to the XRD analysis of the pure nitric acid dissolution tests, the formed peaks of the present oxides show lower intensity and larger width which usually means lower crystallinity of the analysed material.

3.4 Analysis of the aliquots

During the dissolution, aliquots were taken at defined periods to be analysed by suitable analytical methods to provide information on the dissolution

kinetics. The samples taken after 30 minutes, 90 minutes and 300 minutes of the experiment have been analysed.

First Am-241 was analysed by gamma spectrometry, an aliquot was taken and added to a solution of 10 ml nitric acid to get a validated geometry for the gamma spectrometry measurements.

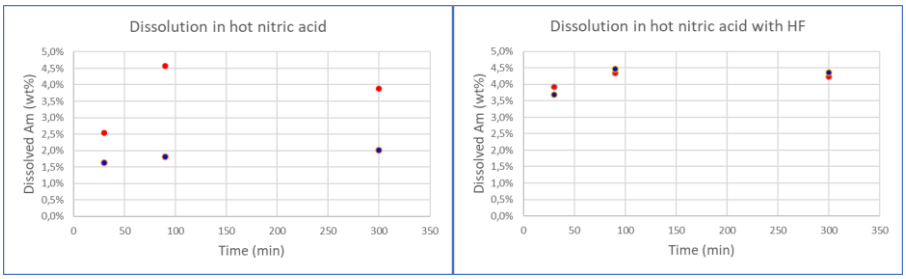

Fig. 6. Gamma spectrometry results for dissolution experiments with hot nitric acid (left) and hot nitric acid with hydrofluoric acid (right); the results are presented as wt.% dissolved Am in solution. The pellets 50/50 are presented in red dots and the pellets 70/30 in blue dots.

These measurements confirmed the results (Fig. 6) obtained after the filtration step, only few percent of the starting material is being dissolved after an experiment of 300 minutes.

Alpha spectrometry was used to determine plutonium and americium in the solution, the samples to be analysed had to be diluted to a concentration of 10 Bq/g sample; the starting material is in the range of tens of GBq. The necessity of this high dilution causes serious uncertainty (measurement error) in the determination of the exact amount of Am and Pu in the solution. Because of that, only the ratio between dissolved Pu/Am is presented. For all experiments, i.e. both hot nitric acid and hot nitric acid with hydrofluoric acid, it was determined that plutonium dissolved about 100 times less than americium. It means that the dissolution of plutonium is determined to be less than 0.1 % of the starting material.

4. Conclusions and outlook

The dissolution experiments on fresh americium plutonium oxide pellets have been performed using hot nitric acid and hot nitric acid with hydrofluoric acid. After a dissolution of 300 minutes, very limited dissolution of just few percent of the starting material was determined, where the dissolution rate of plutonium oxide is 100 times lower comparing to americium oxide. Based on that it can be concluded that dissolution at these conditions does not lead to a sufficient result. In the future the experiments

will continue to examine different dissolution conditions, e.g. higher concentration of the nitric acid and the contact time will be extended.

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References

[1] J. Wallenius: Modelling study on the composition of spent fuel for various P&T scenarios, Asgard project deliverable D 2.2.1 (2013)
[2] J. D. Bruin, E. de Visser-Týnová , F.Q.P. Oud, M.P. Stijkel: Safety aspects of fabrication of Americium-Plutonium Oxide pellets in a glovebox, in proceedings of HOTLAB 2017 conference, 12-17 September 2017, Mito, Japan (2017)
[3] E. de Visser-Týnová: Report on fabrication of (PuxAm1-x)O2 pellets, Asgard project deliverable D 2.2.2 (2016)
[4] C. Ekberg, T. Retegan, E. de Visser – Týnová, M. Sarsfield, J. Wallenius: Fuel fabrication and reprocessing issues: the ASGARD project. EPJ Nuclear Sci. Technol. Volume 6 (2020)
[5] M. Giraud, N. Reynier-Tronche, E. Buravand: Effects of irradiation on the insolubility of sodium fast reactor (U,Pu)O2 mixed oxide with a very high amount of plutonium, J. of Nuclear Materials, Volume 587, 2023.
[6] M.J. Carrott, P.M.A. Cook, O.D. Fox, C.J. Maher, S.L.M. Schroeder: The chemistry of (U,Pu)O2 dissolution in nitric acid, Procedia Chemistry 7 (2012) 92 – 97
[7] H. Ikeuchia, A. Shibata, Y. Sano, T. Koizumi: Dissolution behavior of irradiated mixed-oxide fuels with different plutonium contents, Procedia Chemistry 7 (2012) 77 – 83