



On the fluorination of plutonium dioxide by ammonium hydrogen fluoride



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ABSTRACT

A method for synthesis of PuF₃ from PuO₂ by fluorination using NH₄HF₂ was investigated. The text comprises the literature study on the published methods for PuF₃ syntheses, principles of the applied NH₄HF₂ fluorination, the developed experimental apparatus, the procedure of the synthesis and analysis of the product. The results showed that the proposed method is well suited for the PuF₃ preparation in a sufficient purity and with a good reaction yield.

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1. Introduction

The Molten Salt Fast Reactor (MSFR) is an innovative concept of molten salt reactor (MSR) based on a fast neutron spectrum, studied within the Generation IV International Forum since 2002 [1]. This reactor was derived from the original MSR developed in the 1960's in the U.S. within Molten Salt Reactor Experiment (MSRE) and Molten Salt Breeder Reactor (MSBR) programmes [2]. It takes the advantages of using a liquid fuel composed of actinides dissolved in a molten fluoride carrier salt, which allows, e.g., online reactor core control, flexibility in the fuel cycle and continuous fuel reprocessing [3,4]. This reactor has also many unique safety features, such as negative temperature coefficient of reactivity, i.e., passive temperature regulation, low operating pressure, smaller fissile inventory compared to LWRs and easy in-service inspection [5,6]. Compared to the MSRE, the MSFR concept does not contain graphite blocks (short lifetime) and BeF₂.

To support the safety assessment of the MSFR, physico-chemical properties and basic thermodynamic data of pure actinide fluorides and their mixtures are needed, e.g., viscosity, density, heat capacity and many others. Since the actinides are typically not available in a form of fluorides, a method for synthesis of PuF₃ from PuO₂ by fluorination using NH₄HF₂ was investigated.

In order to produce PuF₃ at a gram scale, fluorination gases such as HF [7,8], F₂ [9–12], NF₃ [13] or ClF₃ [9,10], followed by H₂ reduction [8], can be used. However, except NF₃, these gases

present safety issues for storage and use. Another way is the use of a compound, stable at room temperature, which dissociates into HF (and if possible H₂) upon heating. One of these substances is NH₄HF₂, which melts at 126 °C and dissociates into HF, H₂ and N₂ above 239.5 °C [14].

Tolley [15] reported the results of CeO₂ and PuO₂ fluorination by NH₄HF₂. In Ar atmosphere, he mixed CeO₂ or PuO₂ with NH₄HF₂ (33% excess for forming CeF₄ and 40% excess for PuF₄) and heated up for “several hours” at “low temperatures” (50–250 °C). The ammonium fluoride cerium/plutonium salt was then decomposed at temperatures up to 500 °C. When decomposition was made at 300 °C, it appeared incomplete as further calcliothermic reduction gave higher pressures than expected. This did not happen when the salt was decomposed at 450–500 °C. Tolley observed that Ce(IV) was reduced to Ce(III) but the F:Pu ratio in plutonium fluoride was ranging from 3.2 to 3.9, which shows partial reduction into PuF₃. By this method, Tolley obtained 90% conversion of PuO₂ into PuF₃–PuF₄ mixtures.

Benz et al. [16] studied the formation of xNH₄F–UF_y or xNH₄F–PuF_y salts from heating UF₄/PuF₄ with NH₄F at various temperatures below 300 °C in Ar atmosphere and in vacuum. They observed the slow decomposition of these compounds into UF₄ and PuF₄ at temperatures of 300–330 °C. They calculated and observed the X-ray diffraction patterns of these products. Without exactly identifying the final reduction product, authors suggested that above 400 °C PuF₄ could be reduced by NH₄F into PuF₃.

Wani et al. [17] prepared UF₄, UO₂F₂ and ThF₄ mixed compounds by mixing, at room temperature, NH₄HF₂ and NH₄F with UO₂, U₃O₈ and ThO₂ respectively. They confirmed Benz et al. data on XRD spectra of these compounds and the formation of

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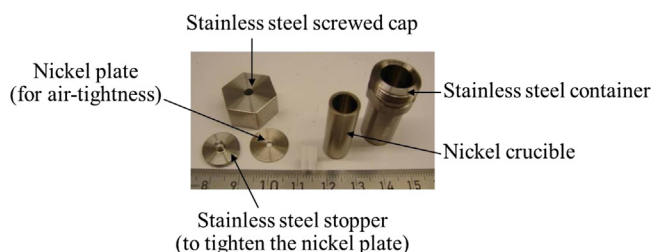


Fig. 1. Picture of the various parts used for the container in which fluorination was carried out.

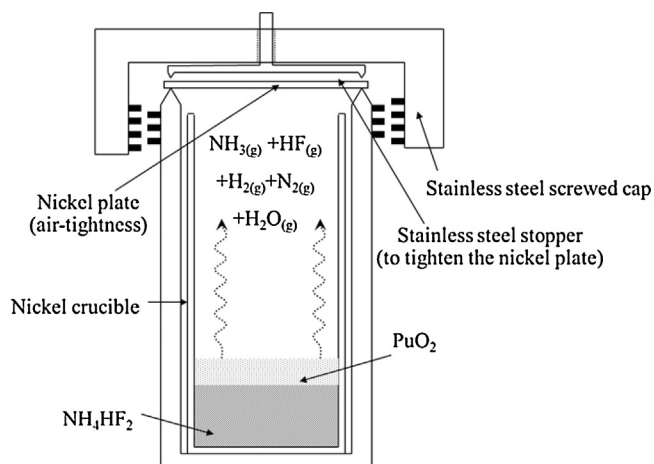
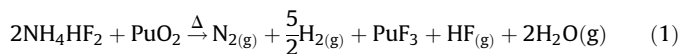


Fig. 2. Sketch of the stainless steel fluorination container for PuF₃ synthesis using NH₄HF₂.

UF₄/ThF₄ at temperatures above 400 °C when starting with the binary oxides. These results were further confirmed by other authors forming mixed lanthanide-NH₄F compounds as intermediate species [18–20].

According to Benz et al. and Wani et al., NH₄HF₂ dissociates into NH₃ and HF above 200 °C [16], and into N₂, H₂ and HF above 400 °C [21]. According to the thermodynamic equilibrium calculation, at 1 bar NH₄HF₂ fully dissociates into NH₃, HF, N₂ and H₂ above 193 °C. HF acts as a fluorination agent to transform PuO₂ into PuF₄. When the reaction is done in a closed environment, as in this study (see Section 2.1), NH₄HF₂ is not fully dissociated due to the increased pressure and some remains liquid. Also, due to the closed environment, H₂ serves as a reductant and keeps the redox potential of the atmosphere such as PuF₄ can be reduced into PuF₃. Upon heating, NH₃ further dissociates in N₂ and H₂ giving a more reductive atmosphere which could explain the formation of PuF₃ only at higher temperatures seen by Benz et al.

In a closed environment, PuO₂ should thus be fully transformed into PuF₃ according to the reaction (1). The Gibbs energy, enthalpy and entropy of the reaction at a temperature of 350 °C corresponding to the experimental conditions were calculated using the FactSage software to be $\Delta G = -107.012$ kJ/mol, $\Delta H = 130.647$ kJ/mol and $\Delta S = 381.5$ J/K/mol.



2. Results and discussion

2.1. Experimental

The experiment was carried out with PuO₂ prepared by calcination of Pu(IV) oxalate from ITU stock. 199.3 mg of PuO₂ powder was added over 328.9 mg of NH₄HF₂ (Sigma–Aldrich, 99.999%), which represents molar ratio of approximately 1:3, respectively, into a Ni crucible (25.5 mm high, 9.5 mm outer diameter and 1 mm thickness). This represents 4 times the amount needed for theoretical complete conversion into PuF₃. The Ni crucible was put into an airtight stainless steel container (30.9 mm high, 13 mm outer diameter and 1.5 mm thickness). The gas-tightness was provided by a nickel plate sealing. Fig. 1 shows all the parts of the container used during the experiment. Fig. 2 presents a sketch of the experiment and the scheme of the container. This container was firstly designed as a DSC (differential scanning calorimetry) crucible as published in [22].

The stainless steel container was put into a quartz cylindrical reactor continuously flushed with argon gas. The off gas was led into traps and bubbling solutions installed to neutralise any HF which would leak from the stainless steel vessel by reaction with 4 and 8 M KOH solutions. The quartz reactor was inserted into a vertical furnace placed in a N₂ filled glove box, where also all experimental work was carried out.

2.2. Fluorination procedure

The furnace was heated up to 350 °C within 3 h and left at this temperature for 17 h before a 5 h cooling ramp to room temperature was initiated. At temperatures higher than 300 °C, a white deposit started to appear on the cold parts of the quartz reactor making it opaque. Indeed, it was found that the stainless steel container was not airtight at such high pressures as reached inside the container (above 300 bars as calculated with respect to the container volume and initial weight of the sample). This led to leakage of the gaseous decomposition products from the reactants, but as confirmed by the analysis of the material, which leaked out from the container, without any Pu losses.

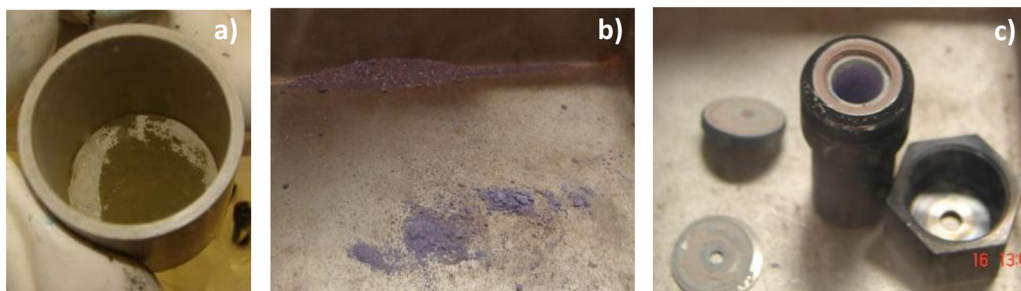


Fig. 3. (a) PuO₂ starting material; (b) product recovered after fluorination step; (c) vessel used for fluorination showing the extent of the corrosion. (For interpretation of the references to color in the text, the reader is referred to the web version of this article.)

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