



Fluoride volatility experiments on irradiated thoria fuel at Canadian Nuclear Laboratories

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ABSTRACT

Fluoride volatility experiments were completed on irradiated thoria fuel in a hot cell facility at Canadian Nuclear Laboratories (CNL). Uranium was removed from irradiated thoria fuel in significant quantities, with longer fluorination times resulting in greater uranium removal for tests up to 24 h. Some fission products were also removed *via* fluorination; fission products with fluorides having low boiling points (Mo and Ru) were removed in greater quantities than fission products with fluorides having higher boiling points (Zr and Rh).

1. Introduction

The PUREX (plutonium uranium extraction) process is the major reprocessing method used to separate plutonium and uranium in irradiated fuels [1]. THOREX is a similar method developed to separate uranium from thorium fuels that is also an aqueous method [2]. Fluoride volatility (FV) is an alternative approach to aqueous fuel reprocessing [3,4]. The method exploits the differences in volatility of fluorides of fissile and fertile nuclides, minor actinides, and other fission products as a means of separating these fractions in irradiated fuel. For example, the main fractions of irradiated ThO₂ fuel are ThO₂ and UO₂. Upon exposure to F₂ gas, uranium hexafluoride (UF₆) and thorium tetrafluoride (ThF₄) form. UF₆ is volatile above 57 °C and ThF₄ has a much higher boiling point at 1680 °C [5]. Thus, the uranium fraction may be separated from bulk thorium by reaction of the irradiated fuel with F₂ at elevated temperatures. The application of fluoride volatility to unirradiated mixed-oxide Th-fuels was studied by Shimada et al. [6]. Through a series of experiments, they determined:

- 1) High fluorine pressure at high temperature resulted in hard cakes forming on the outer surfaces of particles, preventing further fluorination of the inner portions. Slowly increasing the fluorine pressure with temperature resulted in softer cakes forming and faster volatilization of uranium.
- 2) Rate of uranium removal increased with a temperature increase from 530 °C to 580 °C.
- 3) Uranium removal decreased with increasing particle size. Particle

sizes of < 46 μm resulted in more uranium extraction than particle sizes of approximately 53–63 μm.

At Canadian Nuclear Laboratories (CNL), the feasibility of reprocessing of thoria fuel *via* FV has been investigated. Thoria fuel reprocessing focuses primarily on the extraction of U-233 (the primary fissile material bred during irradiation) rather than other nuclides. A series of FV experiments on unirradiated thoria, 1.5 wt.% UO₂ in ThO₂, and SIMulated irradiated FUEL (SIMFUEL) were conducted with promising results. Through these experiments, the effects of some key parameters were found [2]:

- 1) Uranium removal increased with higher temperatures during fluorination. Temperatures tested included 400 °C, 550 °C, and 700 °C.
- 2) Uranium removal increased with greater exposure times. Exposures of 2 h, 4 h, and 6 h were used with crushing conducted after each 2 h of exposure.
- 3) Uranium removal decreased with increasing particle size. Particle sizes of < 45 μm resulted in more uranium extraction than particle sizes of approximately 3 mm.
- 4) SIMFUEL samples exhibited other extracted species along with U, including Zr and Mo.

Through this research on unirradiated fuel samples, a test plan was developed to study the applicability of FV on irradiated thoria fuel. This paper presents the results of these irradiated fuel FV experiments.

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Fig. 1. Irradiated thoria fuel removed from sheath.

2. Irradiated thoria fuel experiments

The irradiated thoria fuel samples were from experiment DME-221 fuel element BC04 [7]. Element BC04 was a pure thoria element that was irradiated in stages in the NRU reactor at CNL from 2000 August to 2005 February to a chemically-measured burnup of 596 MWh/kgHE. It had a mid-plane maximum sustained linear power of 40 kW/m. The nuclide inventory by mass of the fuel after discharge and storage outside of the reactor was calculated by the WIMS-AECL 3.1.2.1 physics code from the irradiation history [9].

Irradiated thoria fuel samples were cut and removed from the fuel sheath in a hot cell facility at CNL (Fig. 1). The fuel was subsequently crushed and passed through a 45 μm sieve. Crushed samples were loaded into alumina sample boats and inserted into a Monel tube inside a tube furnace. The tube was sealed in a flow-through configuration with process gas supplied from upstream of the Monel tube and off-gas scrubbers downstream containing sodium hydroxide to remove excess fluorine and volatile uranium hexafluoride. A schematic of the once-through gas flow system is shown in Fig. 2.

The samples were heated to 700 $^{\circ}\text{C}$ under an argon gas purge and then exposed to a 4% vol. fluorine in balance argon gas mixture with a flow rate of 30 mL/min for various exposure times before cooling back to ambient temperature under pure argon. Sample masses of approximately 0.5 g were measured before and after fluorination using an

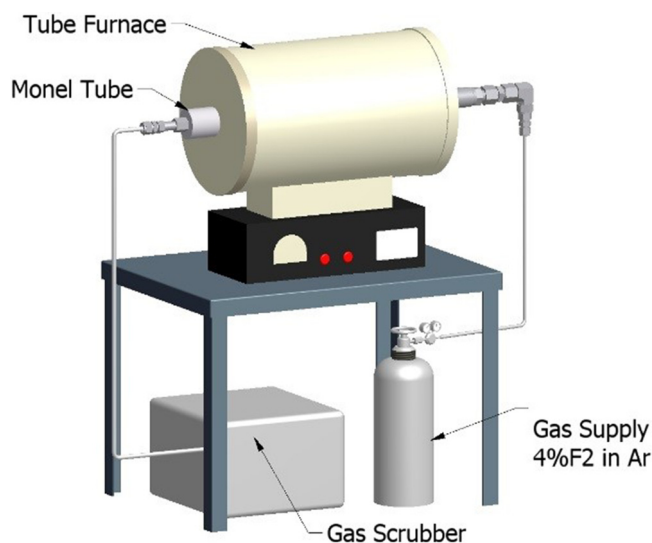


Fig. 2. Schematic of the once-through gas flow system.

Table 1
Summary of irradiated thoria fuel sample fluorination exposure times.

Fuel Sample #	Exposure # and Time					Total Exposure Time
	1	2	3	4	5	
A	2 h	2 h	2 h	2 h	16 h	24 h
B	2 h					2 h
C	2 h	2 h	2 h	5 h		11 h
D	2 h	2 h				4 h
E	2 h					2 h
F	2 h					2 h
G	not fluorinated					0 h
H	not fluorinated					0 h

analytical balance in the hot cell. For samples with multiple fluorination steps, the fluorinated material was removed from the Monel tube and crushed between successive fluorination steps to break up any agglomerates that formed. The samples were once again passed through a 45 μm sieve before they were returned to the tube furnace for further fluorination. A summary of fluorination times is presented in Table 1.

After fluorination, the fluorinated samples were dissolved by reflux in concentrated phosphoric acid. Two samples of unfluorinated irradiated thoria fuel were also dissolved by reflux in concentrated nitric acid with 0.05 M hydrofluoric acid. Dissolution methods were previously developed and benchmarked using SIMFUELS. The dissolved samples were analyzed by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) using a modified version of the ASTM D5673-10 method [8]. The modifications included purchased certified reference materials instead of prepared solutions and variation in standard solution concentration and number of standards.

3. Results and discussion

As a result of the elements analyzed being predominantly fission products and fuel matrix (*i.e.*, not naturally occurring elements of natural isotopic abundances), only a semi-quantitative analysis of the ICP-MS data could be completed, determining isobar mass per fuel mass. There were cases of two or more different nuclides with the same atomic masses (isobars) and mathematical separation of these isobars was not possible (*e.g.*, Sr-90, Zr-90, and Y-90). The WIMS-AECL physics code [9] was used to predict the fuel isotopics at the time of ICP-MS analysis. This facilitated the assignment of a single nuclide to an isobar mass in cases where that nuclide was the only nuclide or the dominant nuclide (*i.e.*, accounted for > 99.99% by mass) with that atomic mass expected in the fuel (*e.g.*, La-139). The only data used in this analysis was where a unique nuclide was assigned to an isobar mass.

All fuel samples gained mass when exposed to 4% F_2 in Ar gas. As thoria remains the dominant component of irradiated thoria fuel, mass gain from fluorination may indicate fluorination of the thoria fuel (from ThO_2 to ThOF_2 or ThF_4) and fission products with non-volatile fluorides. This mass gain from fluorination may have been greater than the mass loss from volatilization of UF_6 and fission products with volatile fluorides (chemical compositions were not verified). The increase in mass of the fuel samples presented a challenge in that the change in concentration of any nuclide of interest could not be directly measured on the basis of nuclide mass per fuel mass. This problem was amplified by other uncertainties in the fuel mass measurements such as the introduction of impurities during fluorination, minor fuel losses during interim crushing between successive fluorination periods, and difficulty in achieving highly accurate mass measurements in a hot cell environment. The use of “normalization nuclides” resolved this issue, as described below.

For the purposes of this article, a normalization nuclide is a nuclide for which the number of atoms in a given fuel sample is assumed to be the same before and after fluorination (*i.e.*, non-volatile elements). The ratio of a nuclide of interest to a normalization nuclide in fluorinated

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