Removal of uranium from thorium-uranium SIMFUEL by fluoride volatility

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Abstract

One of the most significant impediments to the implementation of a sustainable thorium-oxid-based fuel cycle is the lack of an industrially viable discharged fuel recycling process. The major difficulty lies in the aggressive nature of the reagents required for the initial fuel dissolution step. The concentrated nitric acid containing a small amount of hydrofluoric acid necessary to dissolve the solid fuel presents material challenges from the corrosion perspective, and process problems from the chemistry perspective. In this work a simple and effective separation of uranium from a solid solution of uranium and thorium oxide will be presented. Separations of >99% have been achieved on thorium-uranium SIMFUEL (SIMulated-irradiated FUEL). The paper will describe the starting material, experimental apparatus, experimental conditions and results. This work is preliminary in nature but the promising results have significant implications and warrant further study and development.

Introduction

It is well known that the utilisation of thorium in a closed nuclear fuel cycle offers a virtually endless energy supply due to its vast global abundance and 100% fertile isotopic nature. The work presented in this paper addresses a technical aspect of the thorium fuel cycle related to reprocessing or recycling of the irradiated fuel. While once-through thorium fuel cycles have been shown to present advantages in some reactor types [1] [2], the best resource utilisation requires recycle of the ^{233}U bred into the fuel during irradiation. A variation of the PUREX wet-chemical process, used for the recycle of uranium-based fuel, called THOREX, has been used on a semi-industrial scale in the past. Difficulties arose due to the need for hydrofluoric acid in addition to the nitric acid to achieve dissolution of the thorium dioxide spent fuel [3]. Recent research into alternative methods of thorium dissolution suggests that this issue is still relevant [4] [5].

In this work we investigate the use of fluoride volatility to separate the uranium from thorium in the initial stage of a recycling process. A laboratory scale apparatus was used to contact small samples of thorium-uranium oxide (ThO_2-UO_2) and thorium-uranium oxide simulated irradiated fuel (SIMFUEL) with fluorine gas at elevated temperatures. The effectiveness of the uranium removal was determined by analysis of the non-volatile residue. Further purification of the volatile and non-volatile fractions is not considered here. It is worth noting that considerable work has been done in the design of a system for the purification of the volatile fraction arising from the application of the fluoride volatility process to uranium dioxide–based fuel and that effort can be utilised for the thorium dioxide system as well [6].

Fabrication and characterisation of thorium-uranium oxide (ThO_2-UO_2) and thorium-uranium oxide SIMFUEL

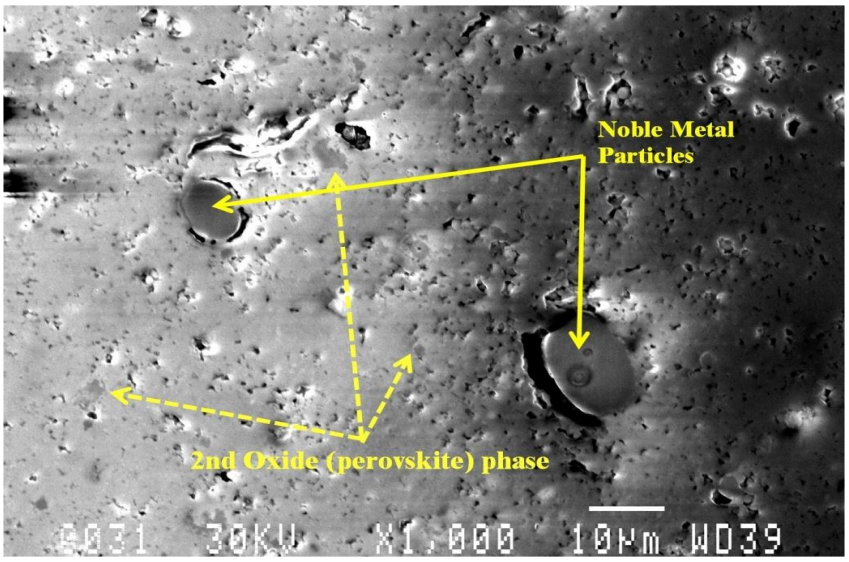
Three types of thorium-uranium oxide pellets were used. Initial experiments to investigate the parameters of temperature, time and particle size were conducted on thorium dioxide samples containing 1.5 wt% UO_2. Optimised conditions were applied to two different SIMFUELs; one based on the irradiation of pure thoria (low burn-up SIMFUEL) and the other on a high burn-up (60 MWd/kgHE) SIMFUEL with a high (13 wt%) initial loading of UO_2. The chemical composition of the irradiated fuel was calculated using the AECL-developed code WIMS-ORIGEN (WOBI). The chemical composition of irradiated fuel is too complex to duplicate exactly. For the fabrication of SIMFUEL, the most abundant fission products, actinides and rare-earths are either represented directly or as a group with non-radioactive elements. The element represented, additive used and target quantity added for the two SIMFUELS in this study are given in Table 1.

All samples were made by combining the starting materials in the appropriate proportions followed by dry powder milling. Powders were directly compacted into pellets and sintered in dry flowing hydrogen at 1750ºC for 6 hours. Pellets were characterised by optical and scanning-electron microscopy (SEM), mensuration, microprobe analysis and X-ray diffraction. All pellets were >95% of theoretical density (note: for the 60 MWd/kgHE SIMFUEL the theoretical density is an estimate). Microscopy and X-ray results confirm that the uranium is in solid solution with the thorium dioxide. Microprobe analysis showed that the SIMFUEL contained microstructural features found in irradiated fuel [7] including metal particles (mostly ruthenium) and a second oxide phase containing barium, strontium, zirconium, and uranium. The concentration of the various components corresponds roughly to the perovskite phase commonly observed in irradiated fuel. A SEM micrograph of the high burn-up SIMFUEL is given in Figure 1.

Table 1: SIMFUEL elements represented, additive used and target quantity added (150 g batch size)

Element in irradiated fuel	Chemical form added	Low-burn-up (pure thoria) SIMFUEL (g)	High burn-up 60 MWd/kgHE SIMFUEL (g)
Ag	Ag	NA	0.044
Ba	$BaCO_3$	0.0744	0.502
Ce/Np	CeO_2	0.1123	0.720
La	La_2O_3	0.0502	0.331
Mo/Nb	MoO_3	0.1520	1.083
Nd/Pr/Pm/Sm/Gd/Tb/Eu/Ho/Er/Dy	Nd_2O_3	0.2312	1.589
Pd	PdO	0.0068	0.649
Rh	Rh_2O_3	0.0092	0.196
Ru/Tc	RuO_2	0.0764	1.119
Sn	SnO_2	NA	0.022
Sr	SrO	0.0559	0.167
Th	ThO_2	145.6023	128.329
U/Pu/Am/Pa/Cm	UO_2	2.3715	14.292
Y	Y_2O_3	0.0723	0.092
Zr	ZrO_2	0.1569	0.864

Figure 1: Scanning electron micrograph of high burn-up thoria SIMFUEL



Apparatus

A horizontal tube furnace containing a 13 mm diameter Monel tube was connected to a 4% fluorine-in-argon gas supply via a 3 mm Monel line. A gas flow of 30 mL/min was used for all experiments discussed here. Gas exiting the furnace tube was carried to gas scrubbers via another 3 mm Monel line. The gas scrubbers consisted of a dry bed of sodium hydroxide beads in the first stage and a sodium hydroxide solution in the second phase. The gas was bubbled through the sodium hydroxide solution. Gas flow was controlled with a needle valve. The apparatus is shown schematically in Figure 2. Alumina (Al_2O_3) boats were used to hold the samples for all experiments. An alumina boat containing a powder sample following a 700°C exposure to fluorine gas is shown in Figure 3.

Figure 2: Fluoride volatility apparatus

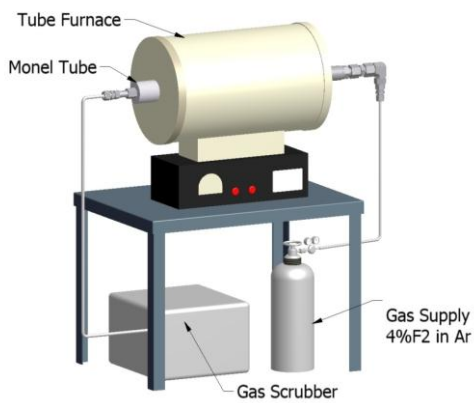
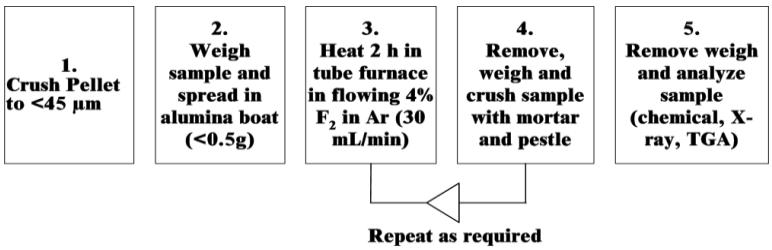


Figure 3: Alumina boat used for all experiments, shown with powder sample following a 700°C exposure to fluorine gas

Experimental procedure

A typical procedure flowchart is given in Figure 4.

Figure 4: Typical experimental procedure



Results

Results are considered as a function of the variable examined. All experiments to investigate experimental variables were conducted using thoria with 1.5 wt% UO_2. For all experiments except the one noted in the sub-section below, the starting particle size of the powder was <45µm (by sieving). SIMFUEL results follow. X-ray diffraction verified the non-volatile residue as ThF_4.

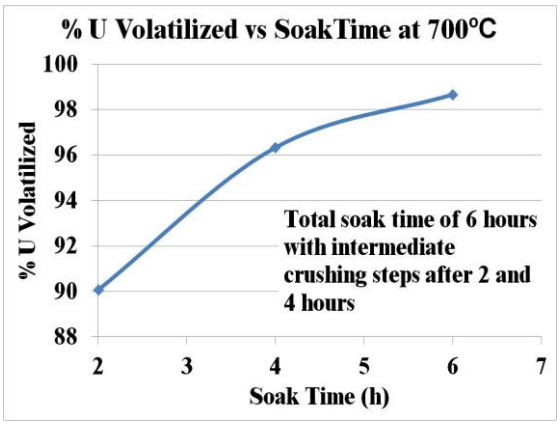
Effect of particle size (surface area)

As expected in a gas-solid reaction, the extent of uranium removal increased as the sample particle size decreased. This is a surface area effect but since the surface area was not known, the results are discussed as a function of particle size. Unfortunately, three experimental samples with different intermediate particle size distributions were deemed not acceptable due to process variations and the experiments have not been repeated to date. One experiment was conducted on samples with a particle size of approximately 3 mm. In this experiment the sample was subjected to 6 hours of fluorine exposure at 700°C. Chemical analysis indicated that 17 wt% of the uranium was released. A sample sieved to <45µm and exposed to the same temperature and flow conditions but for only 2 hours released 90 wt.% of the uranium.

Effect of intermediate sample crushing and increased soak time

Based on the results from previous work [8] it was anticipated that the ThF_4 product of the reaction between ThO_2 and F_2 was impeding the penetration of the F_2 gas and preventing a complete conversion of the ThO_2 to ThF_4 and consequently, preventing the complete release of the uranium (as UF_6). To overcome this, samples were removed following 2 hours of F_2 exposure at maximum temperature and then manually crushed with a mortar and pestle. The crushed powder was then returned for another 2 hours of F_2 exposure at maximum temperature. A third iteration of removal, crushing and F_2 exposure resulted in the best uranium removal of the conditions examined here. Figure 5 presents the results of uranium removal vs. the number of removal, crushing and F_2 exposure iterations (at 700°C).

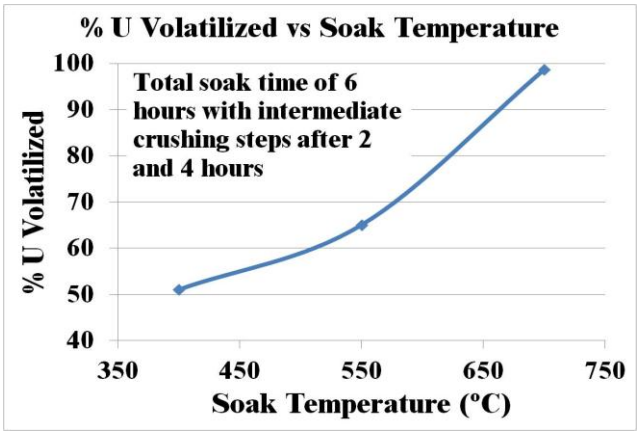
Figure 5: Uranium removal vs. the number of removal, crushing and F_2 exposure iterations (at 700°C)



Effect of maximum soak temperature

Soak temperatures of 400°C, 550°C and 700°C were examined. Experiments were performed with intermediate crushing steps after 2 and 4 hours of F_2 gas exposure at maximum temperature. The results are presented in Figure 6. The maximum uranium removal corresponded with the maximum temperature of 700°C used in these tests.

Figure 6: Uranium removal vs maximum soak temperature



SIMFUEL results

The two SIMFUEL formulations were exposed to the same experimental conditions of a total of 6 hours of F_2 exposure at 700°C with intermediate crushing steps after 2 and 4 hours. The results are presented in Figures 7 and 8. The results demonstrate similar behaviour regarding the volatility of the various additives. Results for ruthenium and rhodium are not included because analysis of the starting material did not produce representative results for these two elements. It is suspected that the dissolution technique used did not dissolve the noble metal particles, resulting in their anomalously low concentration result. The same analytical technique was used on the non-volatile residue following fluoride exposure and so the results from this analysis for ruthenium and rhodium could not be considered valid for the same reason.

Figure 7: Extent of element volatility as a function in low burn-up SIMFUEL

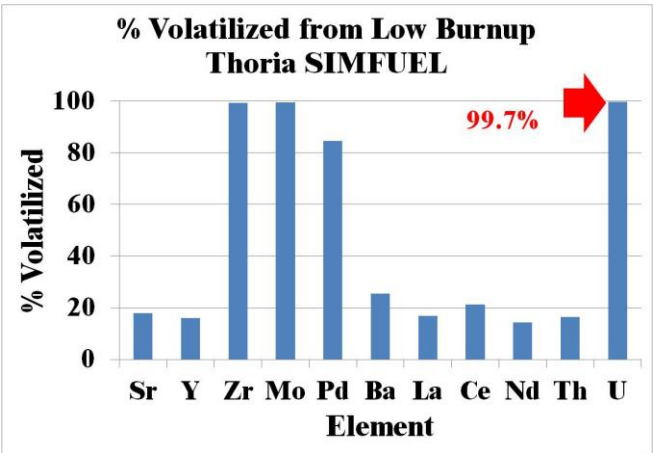
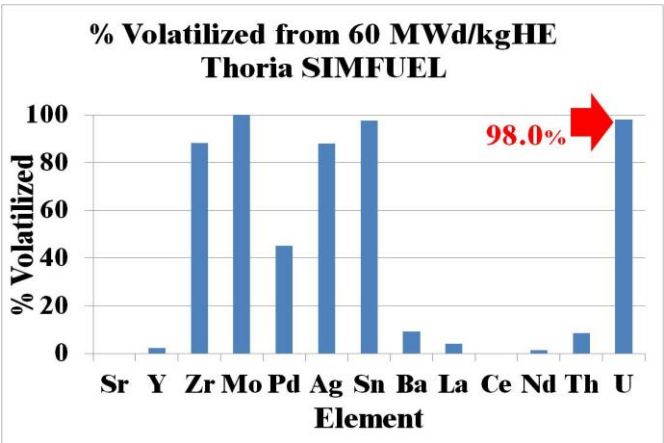


Figure 8: Extent of element volatility as a function in high burn-up SIMFUEL



Discussion and conclusions

The most effective uranium separation was achieved at 700°C, the highest temperature used in this study, suggesting higher temperatures should be investigated. It is expected that the use of higher temperatures will also increase the extent of fluorine reaction with structural material and that the optimum temperature will be one that is a compromise between these opposing effects.

The ThF_4 reaction layer formed at the surface of the oxide particles impedes further reaction. Exposure of fresh oxide surface and re-exposure to fluorine has been shown to allow for uranium removal in excess of 99%. The effect of particle size was investigated but some experimental results could not be used due to process variations. The limited information available suggests that, with a particle size <45 µm, complete uranium removal was not possible at the conditions of 2 hours at 700°C. This, in turn, suggests a smaller particle size is required if complete uranium removal is to be achieved in a single step without comminution of the intermediate product.

These "proof of principle" tests suggest that fluoride volatility can achieve an effective separation of uranium and thorium. It is suggested that an operation that could combine the processes of comminution and fluoride volatility could achieve uranium and thorium separation in a single, dry step.

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