# Leaching Behaviour Of Dysprosium-Doped (U,Dy)$O_2$ LVRF Fuel Under CANDU Coolant Conditions

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## ABSTRACT

Experiments were carried out to determine the leaching behaviour of the dysprosium-doped fuels (U,Dy)$O_2$) in chemistry conditions close to that of the coolant in CANDU® reactors. Leaching tests were also carried out with pre-oxidized $UO_2$ and (U,Dy)$O_2$ fuel samples oxidized under conditions selected to oxidize $UO_2$ to $UO_{2.1}$. Leaching tests were also carried out in the presence of coupons made of the pressure tube material to study its effect on fuel leaching. The results of the tests indicate that very little dysprosium is leached out from the dysprosium-doped fuels under the coolant conditions used in the CANDU reactors.

## INTRODUCTION

Atomic Energy of Canada Limited (AECL) has developed dysprosium oxide containing fuel elements to control the neutron flux in CANDU® reactors. This new type of CANDU fuel has reduced coolant void reactivity during postulated accident scenarios such as a large break loss-of-coolant accident [1-2]. The CANFLEX® low void reactivity fuel (LVRF) bundle includes one or more fuel elements with dysprosium (as (U,Dy)$O_2$))[1] as a burnable neutron poison to

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[1] In this paper (U,Dy)$O_2$ is used to represent a fuel prepared by mixing and heat-treating solid powders of $UO_2$ and $Dy_2O_3$

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control the neutron activity. Dysprosium was chosen as the burnable poison because of its burnup characteristics. There is significant literature on CANDU fuel ($UO_2$) leaching and dissolution [3-6 and references therein]. It is necessary to understand the performance of the dysprosium-doped fuel under CANDU operating conditions to demonstrate that there are no performance issues. In particular, it is important to understand the leaching behaviour of dysprosium in LVRF under the conditions expected in CANDU reactors. Therefore, experiments were carried out at AECL to determine the leaching behaviour of dysprosium-doped fuels in chemistry conditions close to that of the coolant in CANDU reactors. The results of the tests give the *solubility* of $(U,Dy)O_2$ fuel samples in stagnant coolant, and chemical leach rates of U and Dy from $(U,Dy)O_2$ fuel samples relative to the leach rate of U from $UO_2$.

Leaching experiments were carried out with $(U,Dy)O_2$ fuel disks of various dysprosium concentrations. Some leaching tests were carried out at 325°C, as this is the highest temperature of the coolant expected in the ACR (Advanced CANDU Reactor) during normal operating conditions [1] and bounds the normal operating conditions for current CANDU reactors. Current CANDU reactors, using LVRF, will have operating coolant temperatures lower than 325°C. Other leaching tests were conducted at 80°C to study the effects of temperature on the leach rates. The temperature of 80°C was selected as representative of typical shutdown temperatures in CANDU reactors.

It is well known that fuel-sheath failure can lead to fuel oxidation [7]. The products formed during the radiolysis of water, by the ionizing radiation associated with the irradiated fuel, can cause fuel oxidation [6]. The fuel leach rate depends upon the oxidation state of uranium in the fuel [3-5]. Therefore, some exploratory leaching tests on pre-oxidized fuel samples were carried out. Leaching tests were also carried out in the presence of pressure tube material coupons to study the effects of the presence of Zr-2.5Nb on the leaching behaviour of the LVRF.

## 2. EXPERIMENTAL

### 2.1 Fuel Samples Used

The fuel samples used in this study were disks of thickness about 4 mm. The disks were obtained by cutting the fuel pellets with a diamond saw. The fuel pellets of $(U,Dy)O_2$ (natural uranium), containing six different concentrations of dysprosium, ranging from 0-15 wt% Dy, were used in this study. Dysprosium concentrations in the fuel are given as wt%, which stands for (mass of Dy/mass of U)×100 [8]. For example, $(U,Dy)O_2$ fuel with 8.5 wt% Dy means that it contains 8.5 g of Dy for 100 g of U. Dysprosium concentrations (wt% Dy) in the fuel samples used in the leaching tests were 0, 1.7, 4.3, 8.5, 11.3 and 15.

The fuel samples (disks) used in this study were free from visible cracks. All disks looked very similar and appeared to have a uniform dark grey colour - the higher Dy concentration disks were slightly darker in colour.

## 2.2 Pre-Oxidized Fuel Samples

Pure $UO_2$ disks and dysprosium-doped fuel disks were subjected to controlled oxidation to prepare pre-oxidized samples for use in the leaching tests. The fuel disks (both $UO_2$ and $(U,Dy)O_2$) were subjected to oxidation conditions selected to oxidize a $UO_2$ sample to a stoichiometry of $UO_{2.1}$, i.e., *O/M* ratio of 2.1. This value of *O/M* ratio was selected, as it was believed to be representative of oxidation that CANDU fuel may experience in a reactor because of a sheath-defect.

The fuel disks were cleaned and polished [9] before oxidation by heating in a Lindeberg high temperature tube furnace under controlled atmosphere and temperature. The oxygen potential was set using the coulometric titration (CT) system [10]. The final oxidation potential at 1250°C was -135 kJ/mol. The extent of the oxidation suffered by the fuel disk was determined using both the CT method and the gravimetric method (weight gain method). The two $UO_2$ disks oxidized using the above procedure (and used in the leaching tests) had *O/M* ratio of $2.094 \pm 0.005$.

Dysprosium doped $(U,Dy)O_2$ (15 wt% Dy) fuel disks were subjected to the same oxidation treatment as the one used to oxidize the $UO_2$ samples to a stoichiometry of $UO_{2.1}$. The extent of oxidation suffered by the $(U,Dy)O_2$ fuel disks were determined using both the CT method and the gravimetric method. The *O/M* ratio in the pre-oxidized $(U,Dy)O_2$ disks was 2.0073, as measured by the gravimetric method, and 2.012 as measured using the CT method. Thus, both techniques indicated that the dysprosium-doped fuel $(U,Dy)O_2$ fuel disks underwent much less oxidation compared to $UO_2$ fuel disks when subjected to the same oxidation treatment.

## 2.3 Apparatus

The 80°C leaching tests were carried out using specially designed 250 mL Pyrex round bottom flasks with ground glass stoppers. The Pyrex flasks containing the fuel disk and solution were heated in an oven equipped with a "heater controller" system.

The 325°C experiments were carried out using 300 mL stainless steel autoclaves. Temperatures of the autoclave were controlled and recorded using a computer.

## 2.4 Method

The solution used for the leaching tests had an initial pH of 10.3 (measured at room temperature). LiOH was used to adjust the pH of the solution as it is used to control the coolant pH in CANDU reactors.

All fuel disks and metal coupons were cleaned to remove any cutting oils and particulates before use in experiments. The disks were polished just prior to use in an experiment to remove any air oxidation products present on the fuel disk surface [9]. The samples were mechanically polished on all sides, including the rim to expose a fresh surface. The samples were washed with water to remove loose particles from the surface. The disk surface area was visibly clean from any residues. After the polishing process was completed, the diameter, thickness and weight of each disk were measured.

### *2.4.1 80°C Tests*

Approximately 150 mL of pH 10.3 LiOH solution was added to a cleaned and weighed Pyrex flask, and the flask was weighed. Then the fuel disk was added to the flask and the flask was re-weighed. The flask was purged with nitrogen or argon before closing. The flask was placed in a sand bath that had been preheated to 80°C in an oven. At the end of the test, the flask was removed from the oven and allowed to cool to room temperature and weighed. Samples of solution were removed for Dy, U and pH analysis. The disk was removed from the flask, allowed to dry and examined.

Uranium and dysprosium concentrations in the leached solution were determined using inductively coupled plasma-mass spectroscopy (ICP-MS).

### *2.4.2 325°C Tests*

A measured amount of pH 10.3 LiOH solution (about 150 mL) was added to the cleaned autoclave. The fuel disk was placed in the autoclave and the autoclave was purged with nitrogen or argon before closing. After closing the autoclave, the heater was turned on to reach a temperature of 325°C. At the end of the test, the heater was turned off and the autoclave was allowed to cool to room temperature. Samples of solution were removed to determine the concentrations of the metal ions in the solution. The pH of the solution in the autoclave was measured. The fuel disk was removed from the autoclave, allowed to dry and examined.

### *2.4.3 Tests in the Presence of Pressure Tube Coupons*

Two leaching tests, at 325°C, with dysprosium-doped fuel samples (15 wt% Dy) were carried out in the presence of the Zr-2.5Nb coupons. The coupon was placed on a specially designed stainless steel coupon holder. The holders were designed to hold the metal coupon above the fuel disk without touching the fuel disk. The top surface of the coupon was completely exposed to the solution while the holder supported the edges of the bottom surface. At the start of the experiment the holder (with the coupons in place) was placed in the autoclave after the fuel disk and before the purging of the solution. At the end of the experiment, the holder (with the coupon) was removed from the autoclave before the disk was removed. The coupon was removed from the stand and allowed to dry. The top surface of the coupon was left undisturbed, so it could be analysed by XPS (X-ray Photoelectron Spectroscopy). The solution and fuel disk in these tests were handled in the same manner as in the experiments without a coupon.

### *2.4.4 Tests* with Pre-Oxidized Fuel Samples

Leaching tests were also carried out with pre-oxidized fuel samples of $UO_2$ and 15 wt%Dy $(U,Dy)O_2$ at 325°C to determine the effects of slight oxidation on the LVRF leach rates. The fuel samples used in these tests are described in Section 2.2. The tests with pre-oxidized samples were carried out in the presence of pressure tube metal coupons. The procedure used for the tests with pre-oxidized fuel samples was the same as described above for non-oxidized samples.

## 3. RESULTS AND DISCUSSION

### 3.1.1 Results

The fuel disks were found to be intact after all the tests and there were no apparent changes in the geometric areas of the disks during the tests.

Nominal leaching rates of dysprosium and uranium from the $(U,Dy)O_2$ fuel pellets were calculated from the uranium and dysprosium concentrations observed in the leached solutions after the tests using a procedure described by Sunder and Miller [11,12].

### *3.1.1 80°C Tests*

Leaching tests at 80°C were carried out with fuels of different dysprosium concentrations. There was a small drop in the pH of the solution in all tests. For tests carried out at 80°C, the pH changed from an initial value of 10.3 to about 9 at the end of the test.

Solutions of the leaching tests were analysed to determine the concentrations of uranium and dysprosium. Leaching rates of dysprosium and uranium were calculated from their measured concentrations in the solution at the end of the test. The dysprosium leach rates were much lower (by about two orders of magnitude) than uranium leach rates in these tests.

### *3.1.2 325°C Tests*

Leaching tests at 325°C tests were carried out with LVRF samples of high dysprosium concentrations (11.3 and 15 wt% Dy) and with pure $UO_2$. In these tests, the solution pH dropped by about 3-4 units at the end of the tests from its initial value of 10.3 at the beginning of the test.

Solutions of the leaching tests were analysed using ICP-MS to determine the concentrations of Ni, Fe and Cr (elements present in steel - the construction material of the pressure vessel of the autoclave) in addition to those of Dy and U. Small but measurable amounts of Ni, Fe and Cr were seen in the leached solutions.

The dysprosium leach rates were much lower (by about two orders of magnitude) than the uranium leach rates in these tests. The uranium leach rates were, generally, lower in 325°C tests than those observed in 80°C tests.

### *3.1.3 Tests in the Presence of Pressure Tube coupons*

Two tests with dysprosium doped fuel samples (15 wt% Dy) were carried out in the presence of the Zr-2.5Nb coupons. The aim of these tests was to study the effects of the presence of zircaloy on the leaching behaviour of dysprosium-doped fuel and the deposition of the leached dysprosium on the pressure tube materials.

Solutions at the end of the tests were analysed to measure the concentrations of the elements present in the steel and Zr-2.5Nb in addition to uranium and dysprosium. Small but measurable amounts of Ni, Fe and Cr were seen in the leached solutions. Zr and Nb were essentially absent in the leached solutions.

Dysprosium leach rates were much lower than uranium leach rates in these tests. The uranium and dysprosium leach rates were essentially similar to those observed in the leaching tests at 325°C, without a pressure tube coupon.

The dysprosium peaks were was absent in the XPS (x-ray photoelectron spectroscopy) [13] spectra of the pressure tube coupons used in the leaching tests.

### *3.1.4 Tests with Pre-Oxidized Fuel Samples*

Leaching tests were also carried out with pre-oxidized fuel samples. The pre-oxidized fuel samples used in these tests were oxidized under conditions selected to oxidize $UO_2$ to $UO_{2.1}$. The fuel disks used in the leaching test had an *O/M* ratio of ~2.094 for the pure uranium oxide samples and an *O/M* ratio of

~2.01 for the dysprosium-doped fuel ($(U,Dy)O_2$) samples (15 Wt% Dy) (see Section 2.2). Leaching tests with pre-oxidized fuel samples were carried out at 325°C in the presence of pressure tube coupons. The concentrations of uranium and dysprosium in the leached solutions of the tests carried out with the pre-oxidized fuel samples were similar to those observed in the solutions of the tests carried out with the un-oxidized samples.

XPS analyses of the pressure tube coupons, used in these tests, did not show any dysprosium deposition on the coupons.

### 3.2. Discussion

The solubility of uranium dioxide fuel is a function of not only the temperature and pH of solution, but also of its $O_2$ and $CO_2$ contents and the nature of the solid sample [4-5]. For $UO_{2.00}$, under anaerobic conditions and with no $CO_2$ or any other complexing moiety in the water, the solubility in water at about 80°C and pH ~10 is expected to be between $1 \times 10^{-9}$ and $1 \times 10^{-8}$ mol/L [4,5,14 and references therein]. The uranium concentrations observed in the leached solutions in these tests were slightly higher than these values. This was probably due to the fact that the leaching conditions were not completely anaerobic during the tests, particularly in the tests carried out at 80°C in glass flasks. Lower uranium concentrations seen in the tests at 325°C than in 80°C tests suggest that the conditions were less oxidizing in the 325°C tests than in 80°C tests. The atmospheric oxygen (from air) is more likely to ingress into a glass flask sealed using a ground-glass stopper, than into an autoclave sealed using a bolted, gas-tight lid.

The dysprosium concentrations in the leached solutions in these tests were very low. In fact, the observed values of the dysprosium concentrations in the leached solutions were close to the estimated errors in dysprosium concentration measurements. This suggests that dysprosium in the LVRF ($(U,Dy)O_2$) fuel is essentially insoluble under the CANDU coolant conditions. This result is consistent with the very low solubility of dysprosium oxide ($Dy_2O_3$) in water at pH = 10.3 recently reported by Sunder *et al*. [15]. These authors measured concentrations of the *dissolved* dysprosium as a function of the solvent pH. Their results show that the concentration of the dissolved dysprosium, in solutions *in equilibrium* with excess solid $Dy_2O_3$, was lowest in the solvent of initial pH around 10.3. The concentration of the dysprosium observed *in the solution phase*, in solvents of initial pH ~ 10.3, was about $10^{-8}$ to $10^{-9}$ mol/L [15].

There were no obvious systematic differences in the final solution concentrations of Dy (or U) regardless of the reaction time or the concentration of dysprosium in the 0-15 wt% Dy concentration – the Dy concentrations in the fuel samples used in these tests. This suggests that the dysprosium solubility in water under the conditions of the experiments is very low and the solution reached a near “saturation concentration”, with respect to dysprosium, even at the end of the shortest time period used in these tests (i.e., about 6 d).

A comparison of the uranium leach rates in different tests showed no significant effect of the presence of dysprosium on uranium leach rates.

Dysprosium and uranium leach rates observed for the pre-oxidized $(U,Dy)O_2$ and $UO_2$ samples were similar to those observed for the corresponding un-oxidized fuel samples. This result is not surprising as it has been shown that the mechanism of dissolution of uranium dioxide fuel, in near neutral or basic solutions, does not change until it has undergone oxidation beyond the $UO_{2.33}$ state, i.e., the fuel has an O/M ratio of higher than 2.33 [3-5]. The oxidation of the fuel in the pre-oxidized fuel samples used in the leaching tests was very low, i.e., *O/M ratio* of about 2.01 for the dysprosium-doped fuel and *O/M ratio* of about 2.1 for the pure uranium oxide fuel. Such low oxidation of the fuel is not expected to significantly affect the leaching rates of the fuel in neutral or slightly basic solutions, i.e., the conditions of the CANDU coolant. Note, dysprosium in the fuel is not expected to undergo any oxidation as +3 oxidation state of dysprosium in the fuel is its main oxidation state [16]. Hence, any change in the leaching rate of the fuel caused by oxidation is expected from a change in the oxidation state of uranium in the fuel.

## 4. SUMMARY AND CONCLUSIONS

Leaching tests were carried out to determine the leaching behaviour of dysprosium-doped fuels in chemistry conditions close to that of the coolant in CANDU reactors. Leaching tests were carried out at 80°C and 325°C with $(U,Dy)O_2$ fuel disks of various dysprosium concentrations.

Presence of dysprosium in $UO_2$, up-to a concentration 15 wt% Dy, does not affect the leaching behaviour and integrity of the fuel under CANDU coolant conditions. The results of the tests indicate that very little dysprosium is leached out from the $(U,Dy)O_2$ fuel under the coolant conditions used in the CANDU reactors. The nominal dysprosium leach rates were more than two orders of magnitude lower than uranium leach rates in the leaching tests described here.

Dysprosium-doped, $(U,Dy)O_2$, is more resistant to oxidation than the conventional CANDU fuel ($UO_2$).

The slight oxidation of the pre-oxidized dysprosium-doped $(U,Dy)O_2$ fuel (15 wt% Dy, and O/M =2.01) did not affect the leach rates of the LVRF fuel under CANDU coolant conditions.

The presence of pressure tube material did not affect the leaching behaviour of the dysprosium-doped fuel.

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