

Effects of Alpha-Decay on Spent Fuel Corrosion Behaviour

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Abstract – An overview of results in the area of spent fuel characterization as nuclear waste is presented. These studies are focused on primary aspects of spent fuel corrosion, by considering different fuel compositions and burn ups, as well as a wide set of environmental conditions. The key parameter is the storage time of the fuel e.g. in view of spent fuel retrieval or in view of its final disposal. To extrapolate data obtainable from a laboratory-acceptable timescale to those expected after storage periods of interest have elapsed (amounting in the extreme case to geological ages) is a tough challenge. Emphasis is put on key aspects of fuel corrosion related to fuel properties at a given age and environmental conditions expected in the repository: e.g. the fuel activity (radiolysis effects), the effects of helium build-up and of groundwater composition. A wide range of techniques, from traditional leaching experiments to advanced electrochemistry, and of materials, including spent fuel with different compositions/burnups and analogues like the so-called alpha-doped UO_2 , are employed for these studies. The results confirm the safety of European underground repository concepts.

INTRODUCTION

One of the most challenging aspects when studying the safe disposal of spent fuel is the extrapolation of the behaviour of the fuel to storage times of interest. Depending on the disposal scenario considered the events of interest may be the retrieval of the fuel (for e.g. reprocessing) or the interaction between fuel and the environment (namely, groundwater) after failure of all the containment barriers present in the repository. The storage time corresponding to these two events could be of the order of up to a few hundred years for the retrieval option [1], or in the range of thousands (at least) or tens of thousand years in the case of final disposal in a geologic repository. The protection of the environment from radiotoxic release is the common goal for all waste management strategies. Therefore, the most important aspects to study in the case of retrieval are related to the conditions (mechanical integrity) of the spent fuel and its containers, in order to ensure safe transport/handling; for the final disposal option. In addition to the fuel conditions, the interaction fuel/groundwater constitutes the principal object of investigation for final disposal, as this directly determines the amount of mobilization of radionuclides from the spent fuel.

The spent nuclear fuel available today is not entirely representative of aged fuel after hundreds or thousands years of storage because it has not experienced the long accumulation of microstructural defects and of He due to α -decay. Moreover, by the time of a hypothetical contact spent fuel-groundwater, α -decays will dominate the radiation field in and around the fuel [2]; today's fuel instead presents dominant γ - and β -decay contributions. Radiolysis products (radicals, molecular species) may induce local oxidation, hence dissolution-enhancing conditions, in spite of the overall reducing conditions of the repository, which would be beneficial to ensure the chemical stability of the UO_2 matrix [3-5]. In particular, water radiolysis caused by α -decay affects a ~ 50 μm thick water film on the surface of the fuel, and yields mainly molecular species like H_2O_2 . Alpha--doped UO_2 , i.e. sintered unirradiated UO_2 containing short-lived α -emitters, can be used to help extrapolating spent fuel properties corresponding to a given amount of integrated α -decay (i.e. after a given storage time). By selecting high loading fraction and/or high specific activity α -emitters, amounts of damage and He corresponding to long storage times can be accumulated within experimentally acceptable time intervals.

Alpha-doped UO_2 is also used in leaching experiments to single out the effects of α -radiolysis on the corrosion behaviour of spent fuel [6-7]. The α -activity of spent fuel at different ages can be reproduced by appropriately tuning the amount and specific activity of the dopant [8].

Radiation damage studies were performed on two sets of α -doped UO_2 samples containing concentrations of ^{238}Pu differing by two orders of magnitude, in order to investigate the build up of α -decay damage (He-ion and ~ 100 keV daughter recoil ion) in the structure. Significant property- (lattice parameter, hardness) and microstructural- (accumulation of He and of dislocation loops) changes were observed, as expected, in the material with the highest α -activity, indicating a relatively rapid build-up of α -decay damage [7-11]. In parallel to the radiation damage studies, leaching experiments under various conditions have been performed. Results of leaching tests performed in deionized water and in groundwater at room temperature under air and under deaerated conditions on monolith [7, 9, 11,12] and crushed [8] samples of undoped and α -doped UO_2 have been described elsewhere. The concentrations of U measured in the leachates for the α -doped materials were in all cases significantly higher than those for undoped UO_2 leached under the same conditions. Moreover, under experimental conditions characterized by high surface to volume (S/V) ratios, the concentrations of U measured in the leachate solutions for the alpha-doped materials showed converging behaviour over four orders of magnitude of α -activity [12]. Experiments in relatively lower S/V [11] and free corrosion potential measurements using electrodes made of alpha-doped UO_2 showed a dependence of the corrosion potential on the activity of the material [13].

STATIC LEACHING EXPERIMENTS ON α -DOPED UO_2

In the following sections, results of the leaching experiments performed on alpha-doped UO_2 are presented.

Experiment and result

Alpha-doped materials were fabricated using a sol-gel technique to ensure an intimate mixing of the alpha-emitters with the UO_2 matrix [14].

Table I summarizes the activity levels of some of the alpha-doped UO_2 pellets.

Before the leaching tests, all the samples were annealed for several hours at 1000°C in Ar/H_2 to reduce the specimens to stoichiometry and to recover alpha-decay damage and mechanical stresses accumulated during the sample preparation.

TABLE I. Summary of some properties of the α -doped materials used in this work.

wt% of added ^{233}U w/o	α -activity $\text{Bq}\cdot\text{g}^{-1}$	surface α -activity $\text{Bq}\cdot\text{cm}^{-2}$	dose rate in water* $\text{Gy}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$
10	$3.1\cdot 10^7$	$1.8\cdot 10^5$	0.019
1.0	$3.1\cdot 10^6$	$1.8\cdot 10^4$	0.002
0	$1.1\cdot 10^4$	80	$8.3\cdot 10^{-6}$

Although some degree of pre-oxidation cannot be excluded, the initial condition after annealing for all the samples was the same. Therefore, possible differences between alpha-doped and un-doped in terms of pre-oxidized surface layer forming before contacting the water must be ascribed to the different alpha-activities of the samples.

The discs used in the experiments were of similar size and the S/V was ~ 2.3 - 2.6 m^{-1} for the ^{233}U -doped samples

All tests were performed at room temperature, using borosilicate (Pyrex) glass vessels, in gloveboxes with N_2 atmosphere under static conditions (no water flow). The leachates were filtered through 450 nm membrane filters. Deionized water (DM) or ~ 1 mM carbonated water (CW) [15] were used for the leaching tests. The volume of leachant used for each test was ~ 35 mL. The leaching time ranged from 0 to ~ 125 days. After each experiment, pH was measured, and the leachate obtained was filtered through a 450-nm membrane filter and acidified with 2M HNO_3 . The solutions were analyzed for the concentration of different uranium isotopes using a high resolution inductively coupled plasma-mass spectroscopy (HR-ICP-MS). Alpha-spectrometry was used for the determination of the alpha-emitters [15].

Fig 1 shows the cumulative release of U as a function of time for alpha-doped and undoped UO_2 . The release from the samples containing 10% ^{233}U is clearly higher than for the other materials. Essentially no difference is observed between the samples containing 1% ^{233}U and undoped UO_2 . Moreover, the release is higher in

presence of carbonate, especially after short leaching times.

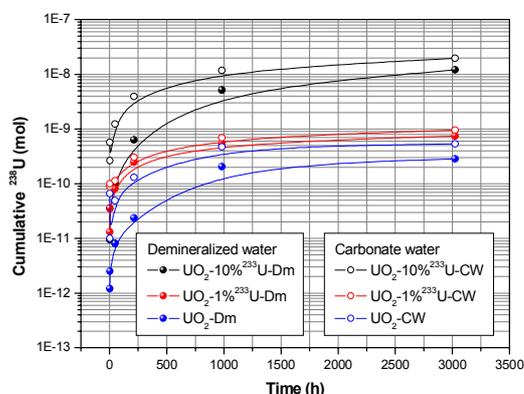


Fig. 1 Cumulative U release vs. time from alpha-doped and undoped UO_2 pellets under un-aerated conditions in carbonated (CW) and demineralized water (DM).

ALTERATION PHASES FORMED ON UO_2 MATERIAL DURING GEOLOGIC PROCESSES

The stability of the fuel matrix material UO_2 is controlled by the dissolution behaviour at the solid-liquid interface. The material that constitutes the topmost layer will control the release. UO_2 was found to develop uranium peroxide (UO_4) layers in contact with water radiolysis products [16]. However in the presence of typical repository water ions like Fe(II) , the behaviour was found to be different.

Experiments and results

UO_2 pellet material was exposed to dilute oxygen-free solutions of the water radiolysis product H_2O_2 (10^{-5} and 10^{-4} mol/l). The solutions were spiked with the reducing ion Fe(II) in two concentrations (10^{-5} and 10^{-4} mol/l). Kinetic profiles of dissolution were measured, and the surface of the UO_2 solids was examined for corrosion and alteration after about 3 weeks.

When both Fe(II) and H_2O_2 were present at 10^{-4} mol/l, surprisingly the UO_2 surface did not show any crystalline or amorphous coverage.

Following our results, equimolar Fe(II) is able to reduce and neutralise the radiolysis product H_2O_2 before it can do significant damage to the UO_2 surface. Excess H_2O_2 , however, is not cleaved quickly enough by solid precipitation products [17] and can therefore attack the surface and form $\text{UO}_4 \cdot x \text{H}_2\text{O}$.

These observations are valid when the reaction partners meet in second-order fashion in the homogeneous bulk liquid. However when the oxidant H_2O_2 is continuously generated at the solid-liquid interface different effect may control the reaction.

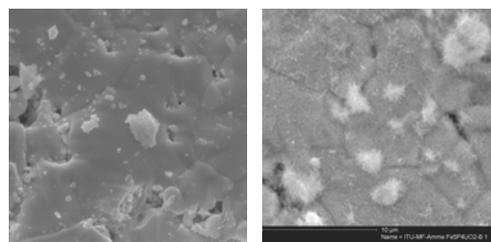


Fig. 2 Secondary phase formation on UO_2 in presence of H_2O_2 and with/without Fe(II) : If H_2O_2 is present in excess, UO_4 is generated (right). If equimolar Fe(II) is present, no coverage is observed (left).

EFFECT OF ALPHA-DAMAGE ON THE LONG TERM BEHAVIOUR OF IRRADIATED FUEL.

The total corrosion rate of spent fuel depends partially on the extent of the surface exposed to the groundwater attack, and, more comprehensively, on the configuration of all possible defects, including those created by fission during reactor irradiation and by radioactive decay during storage. We must, therefore, consider two classes of defects with their mutual interactions:

First, extended defects like grain boundaries, along which chemical etching proceeds more rapidly than into the bulk. In this context, the open intergranular porosity determines the initial specific surface of the fuel exposed to water attack, and also the patterns for further intergranular corrosion. This configuration depends on the fuel irradiation history. More specifically, at increasing burnup the periphery of the fuel pellet is restructured in a porous layer with the original grains being subdivided, the so-called rim-effect.

The second class includes the lattice defects consisting of fission products dissolved or precipitated in the lattice, of vacancies and dislocations, and of dispersed intragranular precipitates and bubbles. The alterations depend both on the accumulation of decay damage during storage and on the corrosion process itself through, *e.g.*, formation of re-precipitated phases, increase of roughness, *etc.*

The structural modifications occurring during very long storage times must be anticipated from the results of laboratory experiments.

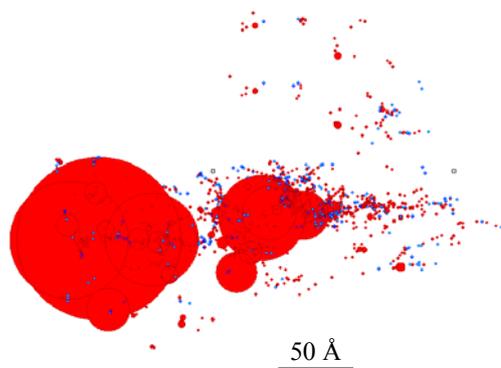


Fig. 3 Recoil cascade in UO_2 from an alpha-decay calculated with SRIM2003 [18]. The blue dots are the uranium atom displaced from their lattice site while the red ones are for the oxygen atoms. The size of the dots is proportional to the elastic energy communicated to knock-on atom.

Recoil cascades (Fig. 3) and subsequent rearrangements of point defects into loops create a permanent stress field in the fuel which may result in a progressive intergranular sliding. This phenomenon might be enhanced by the precipitation at grain boundaries of helium generated over large time scales. The extreme end-effect could be a grain separation process. The negative consequences on an eventual handling of the spent fuel after interim storage are evident as well as the impact on the total surface of the fuel that would be exposed to water in case of the rupture of all the confinement barriers.

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