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ScienceDirect
Procedia Chemistry 21 (2016) 326 – 333
Procedia Chemistry

5th International ATALANTE Conference on Nuclear Chemistry for Sustainable Fuel Cycles

Irradiation defects in UO_2 leached in oxidizing water: An in-situ Raman study

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Abstract

In this study, the behavior of irradiation induced defects in UO_2 in a specific oxidizing water environment was investigated under alpha irradiation. Raman spectroscopy was used to measure the formation kinetics of irradiation defects in UO_2 when exposed to an aerated medium. The acquired data were then compared with a reference $UO_2/(Ar+H_2)$ system. The results revealed that the presence of either aerated deionized water or reducing environment modifies the formation kinetics of irradiation defects. In addition, the precipitation of the studtite phase is also observed during the leaching experiment and water chemical analysis showed that the dissolution of UO_2 proceeds without the formation of an oxidized UO_{2+x}.layer.

Peer-review under responsibility of the organizing committee of ATALANTE 2016

Keywords: Irradiation defects, Raman spectroscopy, aerated medium, studtite

1. Introduction

The safe handling of spent nuclear fuel remains one of the key issues facing the modern nuclear industry, and a major international effort is currently underway to develop safe management and disposal procedures. In France, the interim storage of unprocessed irradiated fuels in water pools over a few decades remains the reference scenario for the management of MOX fuels before they can be reprocessed and used as fuels in the generation IV fast neutrons

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Peer-review under responsibility of the organizing committee of ATALANTE 2016
doi:10.1016/j.proche.2016.10.046

reactors. During interim storage, the fuel cladding remains the main barrier that will prevent the release of radionuclei in the pools. In this study, we aim to consider an incidental scenario of a defective fuel assembly, i.e., an opening on the cladding material, stored in water pools.

A defective cladding will create a pathway through which water will be allowed to interact with the irradiated fuel matrix. The fuel matrix-water interaction and the physico-chemical conditions of water pools; acidic pH, slightly high temperature (60-90°C) and the irradiation dose from the adjacent fuel assemblies, are more likely to initiate a water radiolysis reaction to produce different radiolytic species[1]. These products play a major role in accelerating the alteration of the irradiated fuel matrix at the defect point through oxidizing dissolution and the precipitation of secondary phases of U(VI) type on the altered layer. The swelling behavior of these secondary phases may further accentuate the defective clad and hence increase the complexity of the reprocessing step of the spent fuels.

The dissolution mechanism of UO_2 pellets has extensively been studied under both aerated and anoxic conditions[2-6]. They were largely devoted on the effect of irradiation on the alteration process focusing on the uranium released rate and the formation of secondary phases. The influence of burn-up has also been studied with the measurement of fission product release[7]. The Raman spectroscopy has been used as a tool for the identification of the secondary phases formed during dissolution experiments[8]. This method has also proven its reliability for the investigation of irradiation defects in nuclear fuels but most of the studies were conducted under dry conditions[9-12] and little is known about the irradiation defects during dissolution experiments. In this study, we aim to provide additional information regarding the irradiation induced defects in UO_2 during a potential fuel matrix-water interaction.

2. Experimental Procedure

2.1. Materials

Sintered UO_2 ceramic (8 mm diameter and 300 µm thickness) was manufactured at CEA Cadarache, France. The disc was heat treated at 1700°C under dry Ar/H_2 and was mirror-polished on one side for subsequent characterization purposes. Before irradiation, the pellet was pre-leached with carbonated water (10^{-4} M) for 2 hours to remove traces of an oxidized layer from the surface.

2.2. Irradiation

The irradiation campaign was conducted using a cyclotron device at the "Conditions Extrêmes et Matériaux: Haute Température & Irradiation" (CEMHTI) laboratory at Orléans. The UO_2 ceramic was irradiated with a 45 MeV He^{2+} beam during 2 hours which corresponds to a final fluence of 2.24×10^{15} He/cm^2. The irradiation was carried out at room temperature to prevent any risk of pellet oxidation.

2.3. Leaching experiment under aerated conditions

The experimental set-up used for this study consisted of an irradiation chamber and a safety room. A schematic of the installation is presented in Figure 1 below.

A newly developed irradiation cell was placed in the irradiation chamber which holds the mirror polished surface of the UO_2 in contact with aerated water while the other side was exposed to the He^{2+} beam. The irradiation cell was filled with 15 mL aerated deionized water and the pH was kept in equilibrium with air, close to the neutral 6.5-7 value. The water chemistry was chosen to be representative of interim storage conditions.

The UO_2 disc was irradiated as specified in Section 2.2. Under such conditions, the He^{2+} ions pass through the pellet and are attenuated in the solution near the UO_2/H_2O interface. The irradiation results in atomistic defects in UO_2 and the attenuation of the ions initiates a water radiolysis reaction to produce several radiolytic products, such as such as radicals, hydrated electrons and hydrogen peroxide (H_2O_2). However during alpha radiolysis, the density of the radical increases in the ionization tracks and the probability for a recombination of short-lived radicals to yield molecular species such as H_2O_2 and H_2 is higher than their diffusion from the spurs in which they are