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Alpha-radiolysis effects on UO_2 alteration in water

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Abstract

The behaviour of UO_2/water interface under irradiation has been investigated as a function of alpha flux using an alpha beam provided by a cyclotron. The effects of alpha-radiolysis on UO_2 alteration in aerated deionized water were studied by characterizing both the chemistry of irradiated aqueous solutions and the UO_2 surface. Uranium (as uranyl ion UO_2^{2+}) and hydrogen peroxide concentration (H_2O_2) increased whereas pH decreased in the irradiated solutions when alpha-beam flux increased. The formation of hydrated uranium peroxide (metastudtite $UO_4 \cdot 2H_2O$) on UO_2 leached surface was identified by X-ray diffractometry. The production of metastudtite can be considered as a direct effect of water radiolysis due to the production of radiolytic species H_2O_2, since its formation is known to occur out of irradiation via a precipitation reaction between hydrogen peroxide and uranyl ion. From both these observations and literature about hydrated uranium peroxide occurrence, the possibility of metastudtite formation on nuclear spent fuel in storage conditions is discussed. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The environmental assessment of nuclear spent-fuel disposal requires a prediction of the release rates of uranium once contact between spent fuel and groundwater is established. A spent fuel of UOX type is composed of uranium dioxide UO_2 and, depending on its burn-up, typically ~5 wt% of fission products and transuranic elements. The dissolution rate of UO_2 in aqueous solutions depends on the degree of surface oxidation, which is governed by the solution redox conditions [1,2]. Although uranium is sparingly soluble under reducing conditions, its solubility may increase by many orders of magnitude under oxidizing conditions [3]. The oxidation of UO_2 leads to the formation of progressively higher oxidation states of uranium and the formation of an oxidized surface layer. Significant dissolution of uranium is expected to occur once the surface reaches a composition of $UO_{2.33}$ [1,4].

Spent fuel is a gamma, beta and alpha radioactive material with an activity depending on its burn-up and storing age. One important factor affecting spent fuel dissolution may be the production of species by the radiolytic decomposition of water. The radiolysis of water produces both molecular (H_2O_2, H_2) and radical ($^{\cdot}OH$, $O_2^{\cdot-}$, $HO_2^{\cdot}$, e_{aq}^-, $H^{\cdot}$) products, the concentration of which depends on both the nature of the ionizing radiation and the radiation dose deposited in water [5,6]. The production of oxidizing reactants (H_2O_2, $^{\cdot}OH, \ldots$) by radiolysis is accompanied by the production of an equal number of reducing species (H_2, $e_{aq}^-, \ldots$). Consequently, the overall effect of radiolysis depends on

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the relative reactivity of the reactants in the solution. As the reducing molecular product H_2 is relatively inert at temperature below 100°C, the radiolysis effect is expected to cause oxidizing conditions near the fuel surface, even in a disposal vault where groundwater is generally reducing [1].

The strong gamma and beta activity of spent fuel decreases by more than three orders of magnitude in the first few hundred years after disposal. The alpha radiation field, although initially much weaker, persists for a much longer period of time and, consequently, dominates after a few hundred years of storage. Then, after a thousand years of disposal, the composition of water entering in contact with spent fuel can be modified mainly by the radiolytic species produced by the emerging alpha particles. Since the penetration range of an alpha particle emitted by a spent fuel in water is short ($\sim$40 μm for the typical energy of 5.5 MeV), radiolysis leading to oxidative dissolution may occur at the interface spent fuel/water. A significant local production of radiolytic molecular products (e.g. H_2O_2) may also appear in wet pores and cracks in spent fuel.

The leaching experiments of spent fuel involve significant constraints (e.g. hot cells) on the experimental conditions and the characterization techniques that can be used. In addition, the radiation field of spent fuel available today includes gamma and beta radiation. Consequently, its use to study a specific effect as alpha-radiolysis impact on its dissolution rate needs to take into account the specific effects due to gamma and beta activity. Moreover, the use of groundwaters, which contain many ionic species, as leachant increases significantly the complexity of the system. A complementary approach is to use UO_2 pellets as an effective surrogate material and to use deionized water as leachant to study the effect of alpha-radiolysis. Therefore, a first step in the experimental modelling is to investigate a simplified system, constituted by a UO_2/deionized water interface submitted to an alpha-irradiation.

The alpha-radiolysis effects on oxidation and dissolution of UO_2 have been previously investigated by two different methods. The first one consisted of the use of an external alpha-source placed in water to irradiate the UO_2/water interface [1,7–9]. The authors observed the oxidation of UO_2 by the products of water alpha-radiolysis. Oxidation has been measured as a function of strength of the alpha flux and solution pH using electrochemical techniques. The corrosion rate of UO_2 was found to increase with the alpha dose rate. Using X-ray photoelectron spectroscopy, Sunder et al. [8] showed that at a temperature of 100°C, the presence of dissolved H_2 in distilled and deoxygenated water reduced the effect of water radiolysis on oxidation and dissolution of UO_2.

The second method used to study alpha-radiolysis impact consists in investigating the dissolution rate of UO_2 pellets containing alpha emitters (^{238}Pu, ^{239}Pu) [10–12]. The leaching of both undoped and ^{238}Pu, ^{239}Pu-doped UO_2 pellets have been studied in a salt brine at 90°C by Gray [10,11]. Specific activities of a first set of pellets doped mainly with ^{239}Pu were 1.062×10^6 and 1.726×10^8 Bq g^{-1} for a second set doped mainly with ^{238}Pu. The total uranium mass loss rate from Pu-doped UO_2 pellets was about 10 times greater than from undoped pellets. The mass loss rates for the two sets of Pu-doped UO_2 pellets were found about equal, which suggests that alpha activity does not play a role in these experiments. The uranium release from undoped and ^{238}Pu-doped UO_2 pellets have been investigated by Rondinella et al. [12] in demineralized water under anoxic atmosphere at room temperature. The specific alpha-activity of a first type of specimen was of 3.76×10^{10} Bq g^{-1} and 3.76×10^8 Bq g^{-1} for a second type. The released amount of uranium during leaching were 2–3 orders of magnitude higher for alpha-doped UO_2 than for undoped UO_2. Thus, this result indicated a clear alpha-radiolysis effect. However, in spite of the 100-fold difference in the alpha-decay rates of the two types of investigated specimen, no significant differences were observed in the dissolution behaviour of uranium for the two doped materials as in Gray experiments.

Finally, an effect of alpha-radiolysis on spent fuel corrosion may exist, but it was concluded by Sunder and co-workers that it will be transitory and will become minor as alpha dose rates decrease. Consequently, it does not appear that alpha radiolysis effects promote extensive fuel corrosion [9]. Despite these studies, reliable estimates of the uranium release rates due to alpha activity are still lacking. Moreover, up to now, the specific effects of alpha-irradiation both on the alteration and on the microstructural modifications of UO_2 surface in contact with water have been little investigated. The surface alteration with, for example, the formation of secondary uranyl phases is expected to change the dissolution rate of uranium, by controlling the concentration of uranyl ions in solution. Thereby, the type of alteration products formed on the surface in specific leaching conditions and their impact on uranium dissolution rate need to be investigated.

In the present work, a new approach is proposed to investigate how alpha emission from a UO_2 surface may affect both the release of uranium at the UO_2/water interface and the alteration of UO_2 surface. A high-energy beam of $^4He^{2+}$ ions (alpha particles) supplied by a cyclotron is used to pass through a UO_2 disc and emerges into the water in contact with the disc (Fig. 1). This method allows to monitor the energy, stopping power and flux of the alpha beam at the UO_2/water interface. We reported here the first results concerning the alteration of UO_2 surface by the radiolytic species produced by alpha-irradiation.

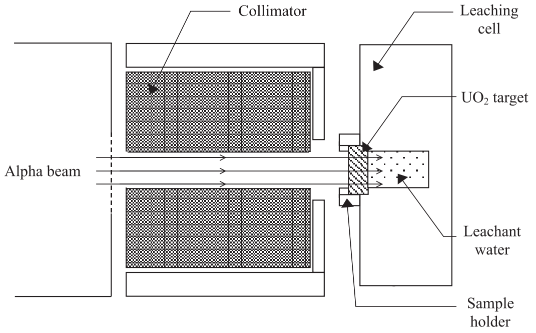

Fig. 1. Schematic diagram of the experimental set up for UO_2 leaching under irradiation with a beam of $^4He^{2+}$ ions (alpha).

2. Experimental procedure

The investigated materials were sintered UO_2 pellets, which were isotopically depleted nuclear fuel (0.2 at.% ^{235}U), with a density of 10.45 g cm^{-3}. The samples were cut into thin discs (8.2 mm diameter) of variable thicknesses (<300 μm). The face of UO_2 discs in contact with water was beforehand mechanically polished. At the end of the polishing, the discs were annealed under a mixture of H_2/Ar gas at 1400 °C to remove polishing damage and adjust the oxygen to metal ratio to the stoichiometric value ($O/U \cong 2$).

The irradiation experiments were performed with the cyclotron at CERI-CNRS, Orléans (France), which delivered a beam of $^4He^{2+}$ ions (alpha particles) with an initial energy of 45 MeV. The beam was collimated so that the irradiated surface of the discs had only a 6 mm diameter. After passing through the UO_2 disc, the beam emerged from UO_2 into water with an energy that depends on the sample thickness (see Fig. 1). In the present work, the thickness of the UO_2 discs was 285 μm, which corresponds to an energy at the UO_2/water interface of ~5 MeV, comparable to the typical energy of alpha particles emitted by a spent fuel. The alpha-range in water at this energy (calculated using TRIM98 code [13]) is equal to about 37 μm.

The UO_2 disc was fixed into a Teflon leaching cell. In this device, the irradiated and the leached surface was the same (0.2827 cm^2). To follow the alteration of the UO_2 surface and the evolution of uranium release as a function of time, sequential batch dissolutions were performed on the UO_2 discs with and without alpha-beam irradiation, without dismounting the specimen from the leaching cell. The leachant was a 10 ml volume of aerated deionized water with a 18 MΩ cm resistivity and pH ≈ 6. For each dissolution test, a fresh leachant (fresh deionized water) was used for each leaching time (usually 1 h). Before irradiation, the surface of UO_2 disc was sequentially leached many times by deionized water to obtain a reference level of uranium release rate. Under alpha-beam irradiation, the leaching experiments consisted of a sequence of dissolutions of 1 h each, where the alpha flux was kept constant. After irradiation, some leaching experiments can be performed again or the UO_2 disc can be removed from the leaching cell to characterize its surface. Leaching-irradiation experiments were performed on different UO_2 discs with two different alpha-flux, 3.3×10^{10} and 3.3×10^{11} α cm^{-2} s^{-1}, respectively. All the tests were carried out at room temperature.

The total uranium concentration in each solutions (leachates) was determined by time resolved laser induced fluorescence (TRLIF). The concentration of hydrogen peroxide in the irradiated solutions was measured by the Ghormley method [14,15].

The microstructure of UO_2 discs surface was characterized by optical microscopy, scanning electron microscopy (SEM) and X-ray diffractometry (XRD) before and after leaching experiments under irradiation. The altered layer of UO_2 surface was also analysed by ion beam techniques, using $^4He^{2+}$ ions of 3.07 MeV at the Aramis facility of the CSNSM in Orsay. The uranium sublattice was studied with standard Rutherford backscattering (RBS), whereas the oxygen sublattice was investigated with the $^{16}O(^4He^{2+}, {}^4He^{2+})^{16}O$ resonant scattering occurring at 3.045 MeV. Optical microscopy and SEM observations were performed at LPS (Pierre Süe Laboratory). XRD patterns were carried out at SEMI. TRLIF measurements were carried out at SESD. All these laboratories are situated in CEA-Saclay.

3. Uranium release, concentration of hydrogen peroxide and pH value in irradiated solutions

Before irradiation, the uranium concentration (as UO_2^{2+}) in the leachates reached a value equal to 0.3 μg l^{-1}. Under alpha-irradiation at a flux of 3.3×10^{11} α cm^{-2} s^{-1}, the uranium concentration increased by nearly four orders of magnitude and reached a constant value of about 2280 ± 230 μg l^{-1} (9.6×10^{-6} mol l^{-1}, Fig. 2, Table 1). The hydrogen peroxide (H_2O_2) concentration in the irradiated solutions was constant for each irradiation and the mean value was equal to $(3.5 \pm 0.3) \times 10^{-3}$ mol l^{-1}. The final pH for each irradiated solution was equal to 3.8 on average. For the lower alpha-flux of 3.3×10^{10} α cm^{-2} s^{-1}, the same behaviour was observed, but the released amount of uranium reached a lower mean value (210 ± 30 μg l^{-1} or 8.8×10^{-7} mol l^{-1}, Fig. 2, Table 1) than for the higher flux. The hydrogen peroxide concentration was also smaller, $(4.8 \pm 0.5) \times 10^{-4}$ mol l^{-1}, than for the higher alpha-flux and pH decreased to a value of 4.9. The results concerning the characterization of irradiated aqueous solutions are summarized in Table 1. The concentrations of chemical species in solution

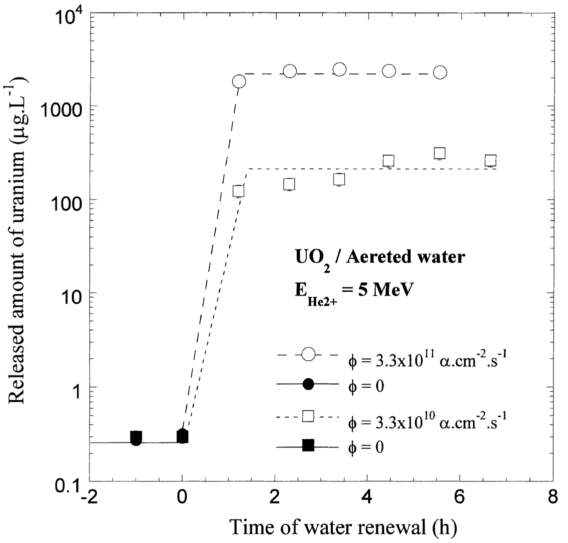

Fig. 2. Released amount of uranium as a function of leaching time under alpha-beam irradiation for a flux of 3.3×10^{10} and of 3.3×10^{11} α cm^{-2} s^{-1}, respectively.

depend on the alpha-flux: the uranyl and hydrogen peroxide concentrations increased and pH decreased when alpha-flux increased.

4. Alteration of UO_2 surface

After dismounting the irradiated UO_2 discs from the leaching cell, the leached surface was coated by a yellow deposit, which was observed by SEM and analysed by X-ray diffraction. Fig. 3 shows a SEM image of a typical polished surface of a UO_2 disc before the leaching test. It is shown as representative of the unleached surface of UO_2. The surface of UO_2 disc after 5 h of leaching under alpha-irradiation to the higher flux is deeply altered (Fig. 4): the alteration product appears as small rod-shaped crystals (Fig. 4(b)). The surface of UO_2 disc irradiated to the lower flux is partially covered by the same fine alteration product, with a significantly lower amount (Fig. 5(a)). It displays also a grain-boundary attack and extensive transgranular boundary corrosion, with the presence of microcracks in some grains of the leached surface (5(b)).

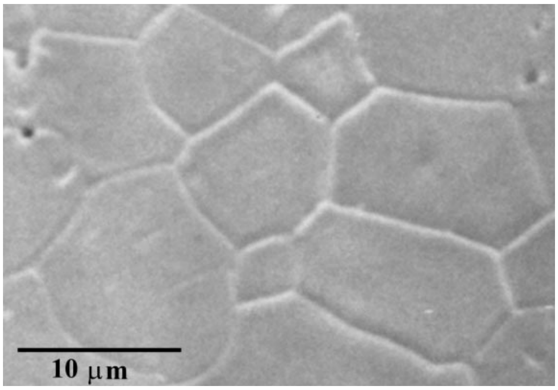

Fig. 3. Scanning electron microscopy (SEM) image of the unleached UO_2 surface.

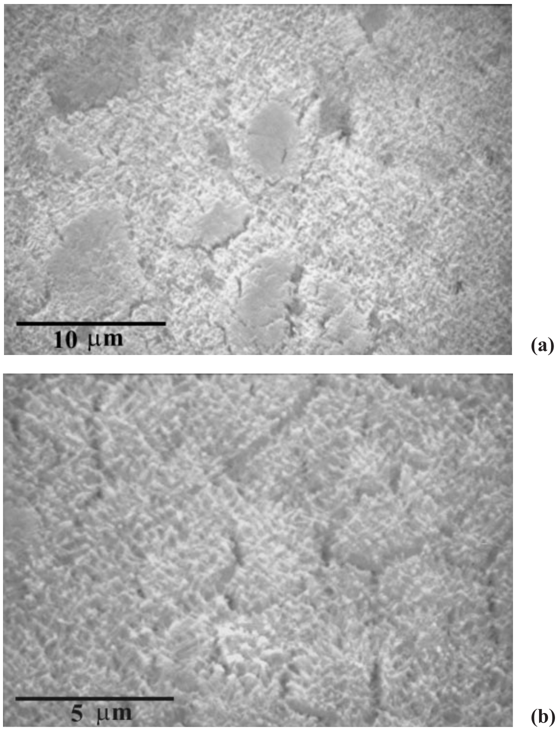

Fig. 4. SEM images of the leached UO_2 surface after 5 × 1 h of alpha-beam irradiation with a flux of 3.3×10^{11} α cm^{-2} s^{-1}.

Table 1
UO_2/water interface under alpha-beam irradiation[a]

Flux (α cm^{-2} s^{-1})	[U] (μg$_U$ l^{-1})	[H_2O_2] (mol l^{-1})	pH
3.3×10^{11}	2280 ± 230	$(3.5 \pm 0.3) \times 10^{-3}$	3.8 ± 0.2
3.3×10^{10}	210 ± 30	$(4.8 \pm 0.5) \times 10^{-4}$	4.9 ± 0.3

[a] Influence of the flux on the uranium release, the radiolytic production of hydrogen peroxide (H_2O_2) and pH in aqueous solutions; the values are averaged on the *n* × 1 h sequential leaching performed under irradiation.

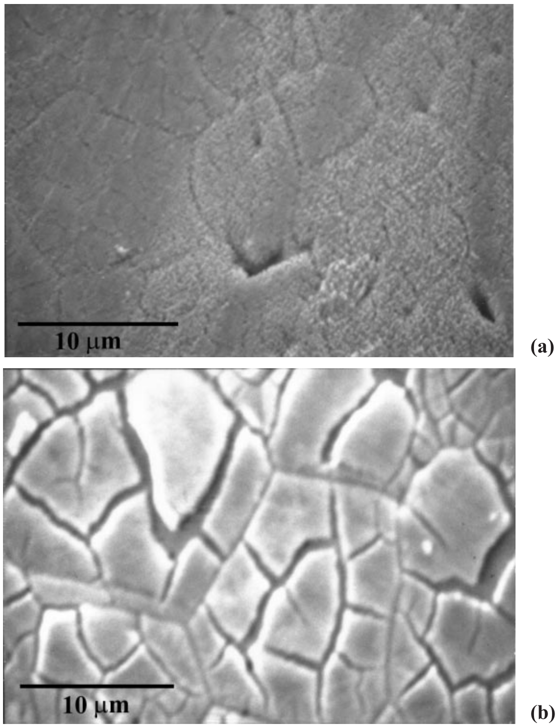

Fig. 5. SEM images of the leached UO_2 surface after 6 × 1 h of alpha-beam irradiation with a flux of 3.3×10^{10} α cm^{-2} s^{-1}.

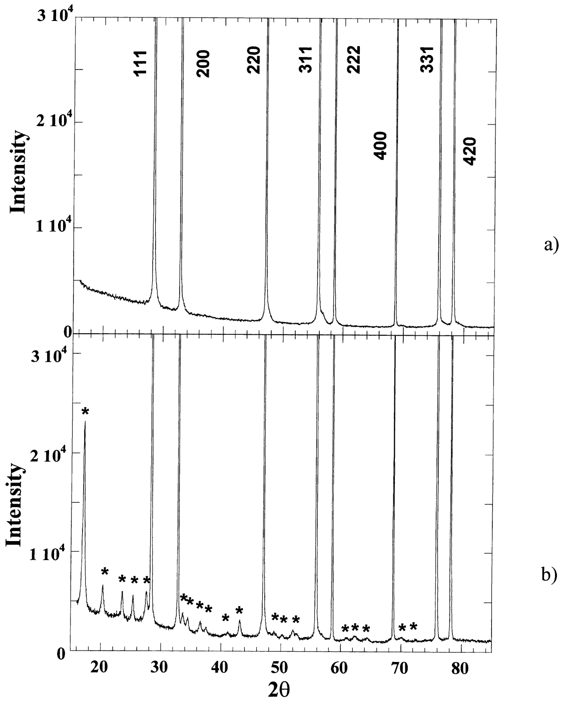

Fig. 6. X-ray diffraction patterns (obtained with the wavelength $\lambda_{CuK_{\alpha1}} = 1.54060$ Å) (a) of an unleached UO_2 sample; (b) of the leached UO_2 disc after 5 × 1 h of alpha-beam irradiation with a flux of 3.3×10^{11} α cm^{-2} s^{-1}.

Fig. 6 shows the X-ray diffraction patterns of an unleached specimen and for the UO_2 disc irradiated to the higher flux, respectively. Extra diffraction peaks (marked with a star) clearly appear in addition to the peaks corresponding to the fluorite structure of UO_2 (6(b)). These extra peaks are related to the presence of the uranium peroxide hydrated $UO_4 \cdot 2H_2O$, called metastudtite (see Table 2). The X-ray diffraction pattern of the surface for the UO_2 disc irradiated to the lower flux presented a lower but significant signal related also to metastudtite.

Fig. 7 displays the experimental RBS spectrum recorded on an alpha-irradiated UO_2 at the higher flux and the simulated spectrum with RUMP code [16] assuming a continuous linear variation of O/U ratio in the altered layer. A good agreement is obtained between experimental and simulated spectra. The small discrepancy between experimental spectrum and RUMP simulation for oxygen resonance peak may be related to the roughness of the UO_2 leached surface. Fit to experimental spectrum provides both the thickness of the oxidized layer during the leaching process and its composition. The thickness of altered layer was 280 ± 20 nm. The O/U ratio at the extreme surface was 5.6 ± 0.1, which is close to the one in $UO_4 \cdot 2H_2O$ (O/U = 6). The ratio O/U varies continuously as a function of depth in the altered layer from 5.6 at the extreme surface to 2 at a thickness of 280 nm, corresponding to the non-altered UO_2.

5. Discussion

5.1. Solution chemistry

The results showed that uranium release and hydrogen peroxide concentration increased whereas pH decreased in the irradiated solutions when the alpha-beam flux increased. We can thereby conclude that, at high flux, the released amount of uranium depends on the radiation dose deposited by the alpha-beam in the aqueous solution. Such an alpha-flux dependence was found neither by Rondinella et al. [12], nor by Gray et al. [10,11] in experiments with alpha-doped UO_2. On the other hand, for studies of the UO_2 leaching experiments using external alpha-sources of various fluxes, at ambient temperatures and in near-neutral solutions, oxidation of UO_2 by the alpha radiolysis of water was reported to be a function of the strength of the alpha-flux [9]. However, the alpha-fluxes used in these experiments were smaller than those of the present investigation.

Table 2
Interplanar spacing d_{hkl} obtained by XRD of yellow deposit on leached UO_2 surface compared to interplanar spacing for metastudtite given in literature[a]

Interplanar spacing and intensity for the unknown compound in the present study			XRD patterns of $UO_4 \cdot 2H_2O$ given in literature					
			Deliens et al. [21] (Natural metastudtite)		Walenta [20] (Metastudtite from heated natural studtite)		Debets [19] (Synthetic metastudtite)	
d_{hkl} (Å)	I (%)	hkl	d_{hkl} (Å)	I (%)	d_{hkl} (Å)	I (%)	d_{hkl} (Å)	I (%)
5.19	100	101	5.22	100	5.24	10	5.23	100
4.38	15	002	4.38	50	4.41	7	4.39	33
3.78	10	011	3.79	50	3.80	7	3.80	33
3.52	5	110	3.538	80	3.54	8	3.53	34
3.24	20	200	3.214	50	3.26	6	3.25	15
–[b]	–	112	2.756	30	2.75	5	2.75	21
2.66	15	103	2.669	20	2.67	5	2.67	21
2.60	5	202	2.61	–	2.61	3	2.61	9
2.46	10	211	2.467	20	2.47	5	2.47	19
2.40	2	013	2.398	20	2.40	4	2.40	15
2.20	2	004	2.191	5	2.19	2	2.19	5
2.09	10	020, 301	2.103	15	2.10	5	2.10	12

[a] XRD patterns given in literature were carried out on powder particles while our results were obtained on a bulk sample. The ratios of X-ray intensities can differ between the two types of patterns due to texture effects for the bulk sample.
[b] Masked by a XRD peak of UO_2.

The radiolytic production of H_2O_2 is directly related to radiation dose deposited in water. The H_2O_2 yields for alpha irradiation of neutral water is G = 0.985 molecules/100 eV [17]. In our experimental conditions, the theoretical H_2O_2 concentration produced by the alpha-beam irradiation for the higher flux in 10 ml of water and calculated from the yields given above would be $\sim 2.8 \times 10^{-3}$ mol l^{-1}, which is smaller by 25% than the experimental value of 3.5×10^{-3} mol l^{-1} measured here after irradiation. The difference may be related to the presence of uranyl ions in solution, which can modify the yields of radiolytic species in water.

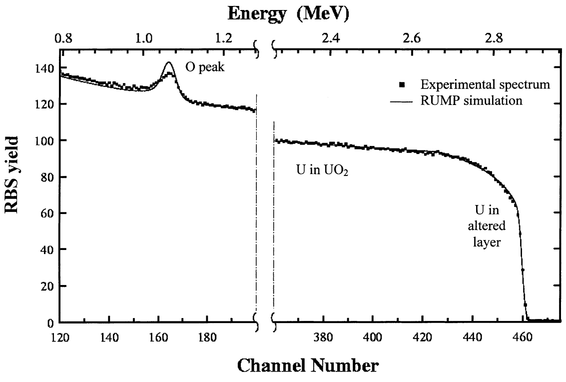

Fig. 7. Rutherford backscattering spectrum for the leached UO_2 specimen after 5×1 h of alpha-beam irradiation with a flux of 3.3×10^{11} α cm^{-2} s^{-1} and comparison with RUMP simulation.

Concerning the pH decrease, the hydrolysis reaction of uranyl in solution:

$$UO_2^{2+} + H_2O \rightarrow UO_2(OH)^+ + H^+ \quad (1)$$

leads to an increase of H^+ concentration, but a calculation shows that it is not enough to reach the low pH value measured after irradiation [18].

5.2. Alteration product: metastudtite

The alteration product formed during our experiments and identified by X-ray diffraction was uranium peroxide dihydrate ($UO_4 \cdot 2H_2O$ or $UO_2(O_2) \cdot 2H_2O$), called metastudtite; its structure is orthorhombic, with cell dimensions of $a = 6.50$ Å, $b = 8.78$ Å and $c = 4.21$ Å, and a density of 4.67 g cm^{-3} [19–21]. A second hydrated uranium peroxide is reported in literature, which has a tetrahydrated form: studtite ($UO_4 \cdot 4H_2O$ or $UO_2(O_2) \cdot 4H_2O$); it has a monoclinic structure and the unit-cell dimensions are $a = 11.85$ Å, $b = 6.78$ Å, $c = 4.25$ Å and $\beta = 93°37'$, with a density of 3.64 g cm^{-3} [19,20]. These compounds contain three different types of oxygen atom and the oxidation degree of uranium is 6 [22–24].

The reaction of uranium peroxide precipitation is usually given by the following equation:

$$UO_2^{2+} + H_2O_2 \rightarrow UO_4 + 2H^+ \qquad (2)$$

In pure solutions, the solubility product ($[UO_2^{2+}][H_2O_2]/[H^+]^2$) was found to be 1.3×10^{-3} at 25–27°C [25]. The reaction (2) produces two H^+ ions, which may partially explain the pH decrease in the irradiated solutions. The hydrogen peroxide H_2O_2 is a product of water radiolysis and is directly involved in the reaction of metastudtite precipitation. Then, our conclusion is that the formation of uranium peroxide results from the radiolytic production of H_2O_2.

We can compare the present results with those given in literature. In oxygenated solutions (in the pH range 5–10), two stages were proposed by Sunder et al. to describe the oxidative dissolution process of UO_2 [1,26,27]. The first stage involves the formation of a surface layer of composition $UO_{2.33}$ (U_3O_7). The second stage consists of the oxidative dissolution of this film (as UO_2^{2+}) accompanied by the formation of uranium secondary phases, probably schoepite ($UO_3 \cdot xH_2O$). In our experiments, the production of the radiolytic species H_2O_2 in the alpha-beam irradiated solutions leads to the formation of hydrated uranium peroxide rather than schoepite as uranium secondary phase on UO_2 surface.

It should be noted that the formation of uranium peroxide was reported in some studies on the specific effect of H_2O_2 on the UO_2 dissolution without irradiation [28–30]. A note in an article by Christensen [28] indicated the formation of $UO_4 \cdot 2H_2O$ for a H_2O_2 concentration of 5×10^{-2} mol l^{-1}. The studtite precipitation has been observed from H_2O_2 concentration superior or equal to 1.5×10^{-2} mol l^{-1}, for a pH range between 4.0 and 6.5 [29]. Wang [30] reported the formation of a deposit identified as a mixture of $UO_4 \cdot 4H_2O$ and $UO_3 \cdot 2H_2O$ phases for oxidation experiments of UO_2 single-crystals by H_2O_2. The formation of uranium secondary phases, which may control the uranium release under oxidizing conditions, are reported in the literature for leaching experiments of UO_2 without irradiation [30–33] and for leaching experiments of spent fuel [34–38]. The mentioned phases are schoepite ($UO_3 \cdot xH_2O$) and related compounds, or secondary uranium phases incorporating cations present in the leachant [32,33,38].

It is the first time that uranium peroxide is mentioned as an alteration product on UO_2 surface for an investigation of radiolysis effects. However, studtite was observed at the surface of Chernobyl 'lava' [39,40]. After the accident of Chernobyl Nuclear Plant, the destruction of reactor cores led to the interaction of heated fuel with structural materials and to the formation of a highly active silicate melt (Chernobyl 'lava') which contained significant amounts of uranium. Despite the building of a 'shelter', the 'lava' is not isolated from surrounding environment: rainwater can come into contact with the lava and yellow products of alteration are forming on its surface. After X-ray diffraction analysis of alteration products, studtite with others secondary minerals of uranium were identified [39,40].

Geologic analogues can provide information on long-term reaction trends. In this way, it seems interesting to point out that uranium peroxides exist in natural state. Studtite and metastudtite occur for instance at the uranium deposit of Shinkolobwe in Shaba, Zaire [21] and at the uranium deposit of Menzenschwand in the Black Forest in Germany [20]. Finch and Ewing [41] explained that the presence of uranium peroxides as natural minerals may be due to the production of highly oxidizing species by the radiolysis of water near the surface of uraninite mineral. Effects of radiolysis in nature have been underlined from investigation of the Oklo natural reactors [42]. As the dose rates from uraninite are much weaker than for a spent fuel for instance, only the very long period of contact (hundred thousands of years) between uraninite and water submitted to radiolysis may explain such a formation of uranium peroxide. In these conditions, which corresponds to low dose rates but very long times of leaching, the local concentration of hydrogen peroxide and uranyl ions can reach locally the threshold values to precipitate uranium peroxide on uraninite surface.

In our experimental conditions of irradiation, which corresponds to high flux of alpha ions or high dose rates, the local concentrations of oxidant radiolytic species like H_2O_2 become rapidly high, since their concentration is directly related to the radiation dose deposited in water. Then, the kinetics of UO_2 oxidation and dissolution may be faster than in lower alpha-flux experiments. The first consequence of this rapid accumulation of oxidant species near the UO_2 surface is a fast grain corrosion, as it can be observed on Fig. 5(b). Then, UO_2^{2+} and H_2O_2 species may accumulate in sufficiently high concentrations near the UO_2 surface to reach locally the conditions of metastudtite formation.

5.3. Implications for spent fuel disposal

Although the experimental conditions in the present work are not representative of those expected in a long-term disposal of spent fuel, they may provide insights into the effects of water radiolysis, like the possibility of uranium peroxide occurrence on spent fuel surface. For lower radiation dose rates than in our experiments, e.g. those for a spent fuel, H_2O_2 production rate is expected to remain sufficiently low to prevent the formation of uranium peroxide for short periods of irradiation. However, the dose rate is not the only factor to take into account. For lower dose rates but for very long times of irradiation, the total dose accumulated in water can become high enough to produce sufficiently high local concentrations of H_2O_2 for uranium peroxide formation.

In the present investigation, the flux of alpha particles supplied by the cyclotron is much higher than the flux of alpha particles emitted by a spent fuel. The irradiation experiments were performed essentially with a low-flux of 3.3×10^{10} α cm^{-2} s^{-1} and a high flux of 3.3×10^{11} α cm^{-2} s^{-1}. The alpha-beam had an energy of ~5 MeV at the UO_2/water interface with a range in water of 37μm: for an irradiated UO_2/water interface of 0.2827 cm^2, the dose deposited by the alpha-beam during one hour in the 37 μm water layer is 2.6×10^7 Gy and 2.6×10^8 Gy for the lower and the higher flux, respectively. These doses can be compared to those for nuclear spent fuel in contact with water. An estimation of the dose (D) for these latter can be calculated from the projected alpha dose rates ($\dot{D}$) in water presented by Sunder [43] in contact with used CANada Deuterium Uranium (CANDU) fuel or with pressured water reactor (PWR) used fuel [9] as a function of cooling time (t_c). The total dose is obtained by an integration of dose rates:

$$D(t) = \int_0^{t_c} \dot{D}(t)\,\mathrm{d}t. \tag{3}$$

For instance, for a PWR spent fuel with a burn-up of 45 MW d $\mathrm{kg}_\mathrm{U}^{-1}$, a cumulated total alpha-dose of 2×10^8 Gy is reached after ~15 years of cooling time. So, in 1 h of irradiation to the highest flux in our experiments, alpha doses equivalent to those obtained for several years of spent fuel storage are accumulated. The use of an alpha beam supplied by an accelerator may strongly increase the radiolysis effects and may enhance the kinetic of oxidation/dissolution or secondary phase precipitation processes which would be too slow to be observable during the leaching experiments at low dose rate. The short-term experiments at high dose rate give however useful information to model the long-term behaviour of spent fuel in contact with water. Thus, the observation of schoepite on spent fuel surface [34–37] rather than uranium peroxides as secondary uranium phase is possibly related to the short time of the leaching experiments conducted on spent fuel: due to the low dose rate, the total radiation dose in water remains too weak to produce sufficiently high concentration of H_2O_2 for uranium peroxide formation in the limited time of the experiments. Thus, assuming that there is no chemical effect related to the spent fuel composition, our conclusion is that hydrated uranium peroxide precipitation may occur on spent fuel surface in presence of deionized water for very long-term leaching experiments.

Finally, the situation of a spent fuel in contact with natural water (e.g. groundwater) is more complex than in presence of deionized water. On the one hand, the groundwaters contain many ionic species leading to the formation of other secondary minerals before uranium peroxide precipitation can occur. On the other hand, complexing anions (e.g. carbonates) present in groundwaters are known to accelerate dissolution by stabilizing the dissolved uranyl ions, and to inhibit then the precipitation reactions. Nevertheless, since hydrated uranium peroxides as natural minerals occur at uranium deposits, their formation on spent fuel in long-term disposal can reasonably be expected depending on the local chemical composition of the groundwater.

Finally, before to convert our results in terms of released uranium in the case of an open aqueous environment, some complementary studies with the alpha-irradiation device used in the present work need to be performed. The effects of temperature (thermal decomposition) and the effects of aqueous solution chemistry (role of complexing agents, deaereted water) on the precipitation of hydrated uranium peroxides on UO_2 surface under irradiation should be studied. Moreover, the precipitation of hydrated uranium peroxides can result in accelerating or inhibiting effects on uranium dissolution rate, depending on the nature of the dissolution process [1]. This phenomenon should be further investigated in our case.

6. Conclusion

In order to investigate the effects of alpha-irradiation on the release of uranium and the alteration of UO_2 in aerated aqueous solutions, a UO_2/deionised water interface was irradiated under high flux with an external alpha beam supplied by a cyclotron. The concentrations of uranyl ions, of the radiolytic species H_2O_2 and pH were measured after irradiation in the aqueous solutions. The surface of UO_2 was characterized by optical microscopy, scanning electron microscopy, X-ray diffraction and Rutherford backscattering. The main conclusions are the following:

(i) The released amount of uranium depends on alpha-flux. It increases by four orders of magnitude in aerated deionized water for the highest alpha-flux (3.3×10^{11} α cm^{-2} s^{-1}). High H_2O_2 concentrations are measured after irradiation and pH decreases in the irradiated solutions;

(ii) The irradiation results in the formation of a secondary phase of hydrated uranium peroxide ($UO_4 \cdot 2H_2O$), called metastudtite, on UO_2 surface. For the highest alpha-flux, the thickness of altered layer is 280 ± 20 nm, with the O/U ratio of extreme surface equal to 5.6 ± 0.1. We attribute the metastudtite formation to the high concentration of uranyl ions and H_2O_2 near the UO_2/water interface and conclude that the occurrence of this alteration product is directly related to the production of the radiolytic species H_2O_2 in water. This work demonstrates that, in aerated deionized water, alpha-radiolysis at high dose leads to a strong alteration of the UO_2 surface by enhancing the oxidation/dissolution processes at the UO_2/water interface.

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