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## XPS study of external $\alpha$ -radiolytic oxidation of UO<sub>2</sub> in the presence of argon or hydrogen



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#### ABSTRACT

 $\rm UO_2$  pellets exposed to 1.85 MBq and 3.30 MBq Am-241 sources with a 30  $\mu m$  separation in solution were studied under Ar and H<sub>2</sub> atmospheres. The 1.85 MBq Am-241 source was shown to have a too low radiolytic production to cause any measurable change in UO<sub>2</sub> surface oxidation state. However, a significant oxidation was observed after exposure to the 3.30 MBq source under Ar atmosphere through the production of U(V), as seen from the  $U4f_{7/2}$ -peak deconvolution and valence band peak analysis. The  $H_2$  atmosphere was shown to suppress the oxidation of the  $UO_2$  pellet surface as well as the dissolution in both Milli-Q and NaHCO<sub>3</sub> solutions. The dissolved uranium concentration was reduced by a factor 10 under H<sub>2</sub> atmosphere as compared to the Ar atmosphere experiments.

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#### 1. Introduction

The release of radiotoxic species from a final geological nuclear waste repository is governed by the oxidative dissolution of the UO<sub>2</sub>-matrix in the case of a canister failure. At the depths of a final geological repository (~500 m), the conditions are oxygen free and reducing [1]. In repositories built in granitic bedrock, as in the designs planned in Sweden, Canada and Finland, anoxic conditions are further ensured by the redox chemistry of the copper canister as well as with the surrounding biotite, magnetite and organic matter [2,3]. The UO<sub>2</sub> fuel matrix is highly insoluble in the U(IV) state, and the dissolution rate is therefore negligible under these conditions [4]. The main mechanism of dissolution is therefore through formation of locally oxidizing conditions near the fuel surface through water radiolysis. Even though water radiolysis produces both reducing and oxidizing species which are both radicals  $(H\bullet, e^{-}_{aq}, HO_{2}\bullet, O_{2}\bullet, \bullet OH)$  as well as molecular products  $(H_2, H_2O_2)$ [5], the redox conditions due to radiolysis are generally oxidizing at the immediate surface. This is due to the inertness of H<sub>2</sub> at temperatures close to room temperature [6]. The dominant oxidant of the  $UO_2$  matrix under these conditions is  $H_2O_2$  [7]. The oxidation and subsequent dissolution of the UO<sub>2</sub> matrix consequently leads to release of radiotoxic fission products and actinides, which are

to a large extent (>95%) contained in the  $UO_2$ -matrix [8]. In the anoxic corrosion of the large iron inserts in the canister that occurs in contact with water, H<sub>2</sub> is produced. H<sub>2</sub> has been shown in several studies to protect the UO2-surface of used fuel from oxidation, although the mechanism is not fully understood [9].

The kinetic activation of hydrogen can either occur at metallic  $\varepsilon$ -particles (Mo, Pd, Ru, Rh and Tc) or at surface-active UO<sub>2+x</sub> sites. Several studies indicate that the activation occurs on  $UO_{2+x}$  sites through heterogeneous catalysis. In the work of King and Shoesmith, the activation of hydrogen on the pre-reduced electrode surface was delayed until oxidized U(IV)-U(V) sites were formed [9]. This was seen by an initial increase in the corrosion potential followed by a significant decrease, resulting in a corrosion potential ~200 mV below the potential under Ar atmosphere. The decrease in corrosion potential indicates reduction of the oxidized U(IV)-U(V) sites back to U(IV).

Sunder et. al. studied the effect of alpha radiolysis on UO<sub>2</sub>surfaces using <sup>241</sup>Am-sources in water at 100°C [10]. The  $\alpha$ -sources irradiated a 30  $\mu$ m thin water layer between the  $\alpha$ -source and the  $UO_2$ -surface, achieved by placing Pyrex glass fibers (d=30  $\mu$ m) in between. The experiments were conducted for 100 h under N<sub>2</sub> or H<sub>2</sub> atmospheres with Am-241 source strengths up to 14.8 MBq. The oxidation state of the surface was studied through X-ray photoelectron spectroscopy (XPS) measurements. The ratio U(VI)/U(IV) was determined through peak deconvolution of the U4f7/2-peak into its U(VI) and U(IV) components [10]. It was shown that hydro-

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gen suppressed the oxidation of the UO<sub>2</sub>-surface at 100°C. It was also noted that the surface became more reduced under hydrogen as the source strength was increased. However, the concentrations of dissolved uranium showed no discernable trend. This might be due to the large uncertainties in their Bromo-PADAP measurement of uranium concentrations. It was suggested by the authors that uranium colloids are a potential source of error, which combined with the large uncertainties in their concentration measurements could explain that no trend was observed in the evolution of uranium concentrations. Under N<sub>2</sub> atmosphere, the UO<sub>2</sub>-surface oxidation state increased with increasing  $\alpha$ -source strength.

The positions of the U(IV) and U(VI) components of the XPSspectra have been reported by a number of authors as approximately 380 and 382 eV respectively [11-14]. Therefore, the 1.3 eV separation between the U(IV) and U(VI) components used by Sunder et. al. in their peak deconvolution in combination with a U(IV) position of ~380 eV would result in an overall higher oxidation state. As there was previously neither a pure U(V) reference compound nor conclusive studies that U(V) was a component in an oxidized UO2-surface layer, U(V) was not included in the U4f7/2-peak deconvolution process in many earlier studies [10,15,16]. In the more recent works of Kvashnina et. al. and Leinders et. al. the oxidation states in uranium oxide compounds was studied using high energy resolution fluorescence detection X-ray absorption nearedge structure spectroscopy (HERFD-XANES), showing that U(V) is a component in uranium oxides between  $UO_2$  and  $UO_3$ , namely:  $U_4O_9$ ,  $U_3O_7$  and  $U_3O_8$  [17,18]. The U(V)-component is therefore a crucial inclusion in the XPS analysis and U4f7/2-peak deconvolution of any oxidized UO<sub>2</sub> surface. The inclusion of the U(V) component into the U4f7/2-peak deconvolution process in the work of Sunder et. al. would have yielded a lower oxidation state. This is due to the close position of U(V) relative to the U(VI)-component, resulting from a rather low energy of the U(VI)-component in their work. The U(V) component would therefore occupy a significant fraction of the U(VI)-component envelope. This contributes to the rather large uncertainties in their UO<sub>2</sub> surface oxidation state measurements.

In this study, 1.85 and 3.30 MBq <sup>241</sup>Am-sources were used to expose a 30 µm layer of water between the sources and UO<sub>2</sub>surfaces to  $\alpha$ -radiolysis at room temperature. The experiments were performed in both NaHCO<sub>3</sub> solution and Milli-Q water (18.2 MΩ•cm) to study the effect of NaHCO<sub>3</sub> on dissolution of oxidized UO<sub>2+x</sub>. In the absence of NaHCO<sub>3</sub>, the oxidized uranium is retained on the surface to a greater extent, and the degree of surface oxidation can be analyzed. The UO<sub>2</sub>-samples exposed to the <sup>241</sup>Amsources in Milli-Q water were subsequently analyzed using XPS, through which the C1s, U4f, O1s and valence regions were analyzed. The uranium oxidation state was determined by deconvolution of the U4f<sub>7/2</sub>-peak into its U(IV), U(V) and U(VI) components as well as through analysis of the positions of the U4f<sub>7/2</sub> and U4f<sub>5/2</sub> peaks and their corresponding satellites [11]. Further analysis of the valence band region was also performed.

#### 2. Materials and methods

#### 2.1. UO<sub>2</sub> pellets and AmO<sub>2</sub> sources

Slightly enriched UO<sub>2</sub> pellets consisting of 98.0% <sup>238</sup>U and 2.0% <sup>235</sup>U were used in the experiments. Am-241 sources in the americium-oxide chemical form (Eckert & Ziegler) with  $\alpha$ -activities 1.85 and 3.30 MBq respectively were used. The sources are covered by a 2 µm layer of pure gold to fix the radionuclide in the Aumatrix and prevent leakage. The dimensions of the AmO<sub>2</sub>-powder compartment are Ø 15.5 × 0.4 mm. The sources are encapsulated in a SS AISI 304 frame exposing a cross-section Ø 11.5 mm.

#### 2.2. Experimental setup

The surfaces of the pellets were polished using 600 & 2400 grit SiC grinding paper prior to the experiments. The pellets were subsequently cleaned in four washing steps consisting of 80 mL solutions with 50 mM NaHCO<sub>3</sub> (99.99+% Aldrich) in the first washing step, 10 mM NaHCO<sub>3</sub> in the second and third steps and 0 NaHCO<sub>3</sub> mM in the last step for 24 h in each washing step. Experiments were performed in Milli-Q water (18.2 MQ•cm) and carbonate solutions. All experiments were conducted under room temperature (~298.15 K). The carbonate solution experiments were conducted in glass beakers with ~150 mL 10 mM NaHCO<sub>3</sub> solutions for 45 days and the Milli-Q experiments were conducted in plastic tubes with ~45 mL water for 11 days. An additional experiment was conducted with ~150 mL Milli-Q water for 45 days. The experimental setup for the experiments can be seen in Fig. 1. The beakers and tubes were placed inside stainless-steel autoclaves with a total internal volume of 450 mL (Parr Instruments Co., USA). In the NaHCO<sub>3</sub>experiments, a stainless-steel dip-tube was connected to the autoclave lid which allowed for sample outtakes using the overpressure inside the autoclave. The original autoclave designs were modified prior to the experiments by replacing the NPT connections by VCR ones to make the autoclaves more leak tight, minimizing the hydrogen leakage during the experiments. This was further achieved by using graphite gaskets, which deform as the autoclave is closed. The pellet washes and the experiments were conducted in an Inert Technology Glovebox with  $p_{02} \le 1$  ppm. The pellets were transferred to the XPS using a transfer vessel which is compatible with the introduction chamber of the instrument.

#### 2.3. Sample analysis

The dissolved uranium concentration was measured by inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Scientific iCAP Q). ICP-MS samples were prepared using 0.5 M HNO<sub>3</sub> prepared from Merck suprapur 65% HNO<sub>3</sub> and the ICP-MS calibration was performed using  $^{238}$ U standard in the range 0-50 ppb using 10 ppb  $^{232}$ Th as internal standard. The detection limit is approximately 0.1 ppb for the analyzed elements.

#### 2.4. XPS analysis

A PHI5000 VersaProbe III Microprobe XPS instrument was used in the surface measurements. The instrument is equipped with a monochromatic Al K- $\alpha$  x-ray source with energy 1486.6 eV [19], as well as with a dual charge compensation utilizing an electron neutralizer and an ion gun with negative and positive charge compensations respectively. To avoid surface contamination and/or chemical alteration after the carbonate wash or radiation exposure, the treated pellets were mounted to the sample plate and placed in a vacuum transfer vessel while in the glove box before transferred to XPS. The transfer vessel atmosphere is therefore the same as the glovebox, Ar with  $p_{02} \le 1$  ppm. The binding energy scale was calibrated using the Au4 $f_{7/2}$ , Ag3 $d_{5/2}$  and Cu2 $p_{3/2}$  positions at 83.96±0.05, 368.21±0.05 and 932.63±0.05 eV respectively from argon ion sputtered gold, silver and copper pieces [20]. Surface composition was evaluated by a survey scan in the binding energy range between 0 and 1400 eV with an energy step size of 1.0 eV. The chemical states of uranium and oxygen, as well as the electronic structure, were studied in the narrow scan spectrum of the U4f (375-405 eV), O1s (525-540 eV) and valence band (-5-12 eV) regions with a step size of 0.1 eV. The spectrum was aligned with respect to the C1s signal at 284.8 eV stemming from adventitious carbon on the sample surfaces. The fitting routine of the peaks was performed using a 70% Gaussian-Lorentzian with a



Fig. 1. The UO<sub>2</sub>-pellet placed on top of the <sup>241</sup>AmO<sub>2</sub> source with a separation of 30 µm achieved from Pyrex glass fibres.

#### Table 1 Characteristic features of the U(IV), U(V), U(VI) states and associated $U4f_{5/2}$ -satellite positions.

| Uranium oxidation state | U4f <sub>7/2</sub> position (eV) [11,22,23] | U4f <sub>7/2</sub> -FWHM (eV) [23,24] | U4f <sub>5/2</sub> -satellite shift (eV) [11,23-25] |
|-------------------------|---|---------------------------------------|---|
| U(IV)                   | 380.0±0.2                                   | $1.8\pm0.3$                           | 6.9±0.2   |
| U(V)                    | 380.8±0.3                                   | $1.8\pm0.3$                           | 8.5±0.3   |
| U(VI)                   | 382.0±0.3                                   | $1.8\pm0.3$                           | 3.9±0.3, 9.8±0.3                                    |

Shirley background. A UO<sub>2</sub>-sample was sputtered for 1 minute using a 2.0 kV Ar<sup>+</sup> beam with current density of 0.222  $\mu$ A/mm<sup>2</sup> to remove surface oxidation and was used to define characteristics of a pure U(IV) state for the subsequent analyses. This made it possible to identify the FWHM of the pure U(IV) component as well as to verify the Gaussian-Lorentzian distribution in the fitting procedure. Literature values of the positions of the U(IV), U(V) and U(VI) U4f<sub>7/2</sub>-peak components as well as the U4f<sub>5/2</sub>-satellite can be seen in Table 1. It should be noted that binding energy position analysis should be used with caution and always be combined with other methods of spectrum analysis. This is due to the fact that the binding energy scale is dependent on the charge correction, Fermi level position and work function, the latter which is quite substrate dependent [21].

#### 3. Results and discussion

#### 3.1. NaHCO<sub>3</sub> dissolution experiments

Two UO<sub>2</sub>-pellets were exposed to the 3.30 MBq Am-241 source in a 10 mM NaHCO<sub>3</sub>-solution under Ar and H<sub>2</sub> atmospheres respectively for ~45 days. The measured uranium concentrations as a function of time can be seen in Fig. 2. The solubility of U(IV)(am) is from the review of Neck and Kim [26] (accepted in the review of Ekberg and Brown [27]). The dissolved uranium concentration was quite stagnant during the first 15-day period, after which it increased quite rapidly under Ar atmosphere. The Ar atmosphere samples were ultracentrifuged and showed no evidence of colloids being present in the comparison with the non-ultracentrifuged samples. In the later stages of the experiment there were significantly lower amounts of uranium released under H<sub>2</sub> atmosphere, showing that H<sub>2</sub> had an inhibiting effect on the oxidative dissolution of uranium in the presence of carbonate. The solution volumes, duration and measured uranium concentrations at the end of the carbonate and Milli-Q experiments are shown in Table 2.



**Fig. 2.** Uranium concentrations in a 10 mM NaHCO<sub>3</sub> solution as a function of time in the 3.30 MBq Am-241 source exposure experiments under Ar and  $H_2$  atmospheres. The solubility of U(IV)(am) is from the review of Neck and Kim [26].

#### 3.2. ICP-MS results

Duplicate 11-days experiments under both 10 bar Ar and  $H_2$  atmospheres in Milli-Q water using the 1.85 and 3.30 MBq Am-241 sources were conducted. The ICP-MS data from all experiments, including those in carbonate solutions discussed in the previous section are shown in Table 2. The UO<sub>2</sub>-pellets that were exposed to the 1.85 MBq Am-241 source for 11 days under  $H_2$  atmosphere gave dissolved uranium concentrations in the Milli-Q water below the detection limit of the ICP-MS measurement. The same was true for one of the two experiments of UO<sub>2</sub>-pellets exposed to the 1.85

| Table 2         |         |     |       |      |         |          |             |              |
|-----------------|---------|-----|-------|------|---------|----------|-------------|--------------|
| Concentrations, | volumes | and | times | of a | all the | external | irradiation | experiments. |

| A <sub>Am-241</sub> [MBq] | Atmosphere                | Volume [mL] | NaHCO <sub>3</sub> [M] | Time [d] | U-238 concentration [M] |
|---------------------------|---------------------------|-------------|------------------------|----------|-------------------------|
| 1.85                      | H <sub>2</sub> , 10 bar 1 | 45.09       | 0                      | 11       | _ †                     |
| 1.85                      | H <sub>2</sub> , 10 bar 2 | 44.06       | 0                      | 11       | _ †                     |
| 1.85                      | Ar, 10 bar 1              | 45.15       | 0                      | 11       | _ †                     |
| 1.85                      | Ar, 10 bar 2              | 42.73       | 0                      | 11       | 5.09•10 <sup>-8</sup>   |
| 3.30                      | H <sub>2</sub> , 10 bar 1 | 44.43       | 0                      | 11       | 1.84•10 <sup>-8</sup>   |
| 3.30                      | H <sub>2</sub> , 10 bar 2 | 43.34       | 0                      | 11       | 3.53•10 <sup>-8</sup>   |
| 3.30                      | Ar, 10 bar 1              | 43.45       | 0                      | 11       | $2.29 \cdot 10^{-7}$    |
| 3.30                      | Ar. 10 bar 2              | 43.64       | 0                      | 11       | 3.19•10 <sup>-7</sup>   |
| 3.30                      | Ar, 10 bar                | 153.01      | 0                      | 45       | 1.26•10 <sup>-7</sup>   |
| 3.30                      | H <sub>2</sub> , 10 bar   | 154.54      | 10•10 <sup>-3</sup>    | 47       | 3.42•10 <sup>-8</sup>   |
| 3.30                      | Ar, 10 bar                | 153.93      | 10•10 <sup>-3</sup>    | 44       | 2.33•10 <sup>-7</sup>   |

<sup>†</sup> Below detection limit of the ICP-MS measurement.

MBq Am-241 source for 11 days under Ar atmosphere, while the other pellet gave a dissolved concentration of 5.1.10<sup>-8</sup> M. The 11days Milli-Q experiments using the 3.30 MBq Am-241 source gave uranium concentrations that were higher than the corresponding concentrations in the carbonate experiments after roughly the same time period under both Ar and H<sub>2</sub> atmospheres (samples were taken at 13 & 14 days respectively, as shown in Fig. 2). This might be due to the significantly different solution volumes which affect the dissolution kinetics. However, this is somewhat unexpected, as the HCO3<sup>-</sup> ion forms a strong soluble complex with U(VI) [28]. Additionally, by dissolving the oxidized uranium the oxidation product cannot block further oxidation of the surface [7]. On the other hand, the inclusion of HCO3- would buffer the solution at pH ~8.34 (between pKa1=6.35 and pKa2=10.33) even at low concentrations. This buffering would prevent local acidification at the UO<sub>2</sub>-surface due to the anodic dissolution reaction and could thereby possibly inhibit dissolution [29]. The same influence of HCO3- was observed in the work of de Pablo et. al., where the dissolution rate of UO<sub>2</sub> was initially slower in the presence of  $HCO_3^-$  as compared to that in Milli-Q water [30]. This was suggested to be due to radical scavenging by the HCO<sub>3</sub><sup>-</sup> ion, thus reducing the radiolytic production of H<sub>2</sub>O<sub>2</sub>. This effect can however be hard to evaluate as HCO<sub>3</sub>• is also a strong oxidant. Nevertheless, in the later stages of the experiments in the work of de Pablo et. al., the dissolved uranium concentration was higher in HCO<sub>3</sub><sup>-</sup> solution, which corresponds well with the results found in this work [30].

The inclusion of NaHCO<sub>3</sub> increased the final dissolved uranium concentration by a factor two in the 45-days Ar atmosphere experiments. Additionally, comparing the 45-days Milli-Q Ar atmosphere experiment to the 11-days experiment, the total dissolved uranium content was a factor two higher at the end of the long experiment. At the end of the 45-days Milli-Q Ar atmosphere experiment, a 10 mL sample of the autoclave solution was taken out of the glove box and measured using a pH-electrode under air atmosphere. The measured pH was  $6.9\pm0.5$ . The ionic strength of the sample was titrated with low concentration HNO<sub>3</sub> and showed no buffer capacity, indicating that there was no carbonate content present in the sample solution due to the washing procedure.

The experiments performed by Sunder et. al. were considerably shorter (100 h) than the ones performed in this work and were also performed under 100°C [10]. This makes their results somewhat difficult to compare to the ones in this work. The uncertainties in the Bromo-PADAP concentration measurements of Sunder et. al. are considerable, but some trends can be discerned. Under N<sub>2</sub> atmosphere, the uranium concentrations increased with increasing source strength. However, no significant difference in dissolved uranium concentrations under N<sub>2</sub> and H<sub>2</sub> atmospheres could be seen. In this work, the H<sub>2</sub> atmosphere significantly influ-



**Fig. 3.** Modelled  $\alpha$ -dose-rate from the 3.30 MBq Am-241 source as a function of water depth perpendicular to the surface of the source.

enced the dissolved uranium concentrations as compared to the Ar atmosphere experiments by an order of magnitude, roughly  $10^{-8}$  M under H<sub>2</sub>, as compared to  $10^{-7}$  M under Ar. The same was true in both Milli-Q and NaHCO<sub>3</sub>-solutions. The dissolved uranium concentrations in this work are in the same order of magnitude under H<sub>2</sub> atmosphere as the ones obtained by Sunder et. al. at 100°C after an exposure time of 100 h. However, the dissolved amounts under Ar atmosphere in this work are significantly higher, by an order of magnitude.

#### 3.3. Radiolytic oxidant production

Due to the lack of stopping power data for AmO<sub>2</sub>, as well as in the uncertainty of the density of the AmO<sub>2</sub>-powder in the source, UO<sub>2</sub> with 95% theoretical density is used as an approximation of the material. The ASTAR database combined with the CSDA approach and a geometric calculation model was used, as described in a previous work by our group [31]. The dose rate in solution perpendicular to the Am-241 source was calculated, where the attenuation in the 2 µm gold layer was taken into account. The gold layer had quite a large influence on the escape energy of the  $\alpha$ -particles. As can be seen from Fig. 3, few  $\alpha$ -particles have a range longer than 30 µm, and the UO<sub>2</sub>-surface therefore receives a very small fraction of the total dose. The Pyrex glass threads are assumed to absorb less than 1% of the total dose and were not considered in the model.

The irradiated volume between the Am-241 source and the UO<sub>2</sub>-surface is  $V_{irr} = (11.5 \text{ mm}/2)^2 \cdot \pi \cdot 0.03 \text{ mm} = 3.12 \text{ mm}^3$ . Over



Fig. 4. The U4f spectrum of a washed UO<sub>2</sub> pellet after 1-minute argon ion sputtering.

an 11-day period, the total  $H_2O_2$  production in  $V_{irr}$  exposed to the 3.30 MBq Am-241 source is  $3.12 \cdot 10^{-5}$  mol/L. The total H<sub>2</sub>O<sub>2</sub> production is modelled to find an approximate theoretical maximum dissolution assuming that all  $H_2O_2$  causes oxidative dissolution of UO<sub>2</sub>. A significant fraction of H<sub>2</sub>O<sub>2</sub> will undergo decomposition on the  $UO_2$  surface and will therefore not oxidize the surface [32], meaning that the theoretical maximum serves as a rough estimation of the total dissolved uranium concentration and is not a realistic one. If an appreciable fraction of the the locally produced  $H_2O_2$  causes oxidation of the UO<sub>2</sub>-matrix, the oxidative dissolution of the UO2-matrix could produce locally more acidic conditions, enhancing the dissolution rate [29]. However, as the irradiation volume is considerably smaller than the total solution volume, diffusion will have a substantial effect on the chemical conditions close to the UO<sub>2</sub>-surface. The modelling shows that the total dissolved uranium amount is higher than the radiolytic production of H<sub>2</sub>O<sub>2</sub>, indicating that the dissolution behaviour is influenced by dissolved oxygen or the presence of a pre-oxidized layer.

#### 3.4. XPS-analysis

#### 3.4.1. Ion-sputtered U(IV) state

A UO<sub>2</sub>-pellet with low surface oxidation state was sputtered for 1 minute with the Ar+-beam to remove the surface contamination and native oxide layer (see section 2.4 for further details). The U4f spectrum of the sputtered UO<sub>2</sub>-surface can be seen in Fig. 4. Both the U4f<sub>5/2</sub>- and U4f<sub>7/2</sub>-peak positions after shifting the spectra with respect to the C1s-peak position at 284.8 eV are significantly lower than literature values by approximately 0.5 eV [11,22]. The spin orbit splitting of 10.9 eV between the two peaks however agrees very well with literature values [11,33]. This indicates a shift of the spectrum by 0.5 eV. The different U4f<sub>7/2</sub>-peak position relative to the C1s-peak might be due to the dual charge compensation mechanism of the VersaProbe III instrument which differs from the compensation mechanisms of earlier models as well from that of other instruments. A very similar systematic peak shift can be seen in the work of Van den Berge et. al. which was also believed to be due to charging correction procedures [25]. The very distinct U4f<sub>5/2</sub>- and U4f<sub>7/2</sub>-satellites with a separation  $\Delta$ =6.9 eV from their main peaks are indicative of a pure  $U(\ensuremath{\text{IV}})$  oxidation state. The pure U(IV) signal in the U4f<sub>7/2</sub>-envelope on the sputtered surface could be fitted well with a 70% Gaussian-Lorentzian, 1.7 eV FWHM peak at a binding energy of 379.5 eV. This corresponds well with FWHM literature values [24]. The value is however somewhat on the lower end, indicating a good resolution in the measurement [34]. The same parameters and systematic shift of the spectrum are used in the fitting procedure of the peak deconvolution process throughout this work.



Fig. 5. U4f-spectra of the  $UO_2$ -pellets after the carbonate washing procedure, before exposure to the 1.85 (a) and 3.30 MBq (b) Am-241 sources under Ar atmosphere.

#### 3.4.2. 11-days exposure under Ar atmosphere

The UO<sub>2</sub>-pellets were measured by XPS after the initial washing process and were then subsequently exposed to the Am-241 sources. This allowed for a direct measurement of the change in oxidation state over the experiment. The initial U4f-spectra after the washing processes of the UO<sub>2</sub>-pellets before exposure to the 1.85 and 3.30 MBq Am-241 sources are shown in Fig. 5a and Fig. 5b respectively. The U4f7/2-peak positions are higher in energy than the sputtered UO<sub>2</sub> pellet, indicating a remaining contribution of oxidized uranium in the form of U(V) and/or U(VI) in the U4f7/2peak envelope after the washing procedure, despite the rather long washing durations. The satellite peak positions marked in the figures are approximate as their positions are affected by the contributions of U(IV), U(V) and U(VI) respectively. The more oxidation states existing in the main peak, the more spread out the satellite becomes. De Pablo et. al. studied the surface oxidation state of an initially oxidized UO2-powder as it was exposed to 10 mM carbon-



Fig. 6. U4f-spectra of the  $UO_2$ -pellets after 11-days exposure to the 1.85 (a) and 3.30 MBq (b) Am-241 sources under Ar atmosphere. Second experiment.

ate solutions and found that after a 400-day exposure, the surface oxidation state was changed from UO<sub>2.4</sub> to UO<sub>2.05</sub>. This shows that the oxidation above the UO<sub>2.33</sub>-state, which would correspond to a surface with a U(VI)-component, is not required for the removal of oxidized uranium from the surface through carbonate complexation and dissolution of oxidized uranium [35]. It also shows that the complete dissolution of oxidized U(V) and U(VI) from a  $UO_{2+x}$ surface using carbonate washes is a very slow process. The rather high energy of the U4f7/2 peak positions might therefore be due to insufficient washing times or conditions in the glove box that were too oxidizing ( $p_{02}$  up to 1 ppm). It should be noted that carbonate does not act as a redox agent in the washing process and the apparent reducing effect of the surface is purely due to complexation and dissolution of oxidized uranium. As the transfer vessel was equipped with an O-ring and is tailor made for the sample inlet, the pellet surface is unlikely to have been oxidized during transfer to the XPS-instrument.

After exposing the pellets to the 1.85 and 3.30 MBq sources for 11 days in Milli-Q water under Ar atmosphere, the surfaces were analyzed again, and the final U4f-spectra are shown in Fig. 6. The pellet exposed to the 1.85 MBq Am-241 source has a significantly lower U4f<sub>7/2</sub>-peak position than in the initial state, a shift of 0.6 eV. This indicates that the 1.85 MBq Am-241 source is too weak to compete with the dissolution of the pre-oxidized layer, resulting in almost a pure U(IV) signal at the end of the exposure period. However, the U4f<sub>5/2</sub>- and U4f<sub>7/2</sub>-satellites are not as distinct as on the surface of the sputtered sample, indicating some influence of the U(V) oxidation state. The U4f<sub>7/2</sub>-peak deconvolution process into its U(IV), U(V) and U(VI) components as shown in Fig. 7a yields an equivalent oxidation state equal to U0<sub>2.07</sub>.



**Fig. 7.** Deconvolution of the  $U4f_{7/2}$ -peaks on the surface of the  $UO_2$ -pellets exposed to the (a) 1.85 and (b) 3.30 MBq Am-241 sources under Ar atmosphere for 11 days.

The U4f-spectrum of the pellet exposed to the 3.30 MBg Am-241 source (Fig. 6a) has a significant positive shift of the U4f<sub>7/2</sub>peak position. The peak deconvolution process shown in Fig. 7b yields an equivalent oxidation state of UO<sub>2.44</sub>. The equivalent oxidation state is not believed to correspond to a single phase, but rather to an oxidized  $\text{UO}_{2+x}$  surface layer with a composition that probably varies with depth. The satellite positions in the spectrum of the UO<sub>2</sub> pellet exposed to the 3.30 MBq Am-241 source shown in Fig. 6b are somewhat approximate as the  $U4f_{7/2}$ -satellite is close to the tail of the  $\rm U4f_{5/2}\mbox{-}peak$  and the  $\rm U4f_{5/2}\mbox{-}satellite$  is rather broad. However, the satellites are within the 7.8-8.3 eV interval which is reported for the U(V) compounds in the review of Ilton & Bagus [11] and in the work of Gouder et. al. [23]. The corresponding O1s peaks of the Ar atmosphere experiments have not had a significant binding energy shift nor peak shape change in terms of FWHM. This is in agreement with the results of Santos et. al. where the lower applied potentials (up to -200 mV) resulted in an almost negligible O1s peak change [24].

# 3.4.3. 45 days 3.30 MBq Am-241 source exposure under Ar atmosphere

The 45-days exposure time under Ar atmosphere in Milli-Q water using the 3.30 MBq source resulted in a discernable shift of the  $U4f_{7/2}$ -peak position, shown in Fig. 8, as compared to the initial state samples. The position of the  $U4f_{7/2}$ -peak indicates a slightly lower extent of oxidation on the surface as compared to the 11-day experiment. The  $U4f_{5/2}$ -satellite is apparent, showing a position in good agreement with U(V).

The peak deconvolution of the  $U4f_{7/2}$ -peak of the 45-days Ar experiment can be seen in Fig. 9 below. The deconvolution yields a U(V)/U(IV) ratio of 1.88 which is equivalent with  $UO_{2.33}$ . This represents a lower oxidation state than for the 11-days experiment. The lower oxidation state is unexpected as the longer exposure time should allow for more radiolytic oxidation to occur. However, the solution volume is roughly a factor 3 larger as compared to the 11-days experiment (Table 2). The amount of  $H_2O_2$  causing oxidative dissolution as compared to that undergoing decomposition is a function of solution volume, carbonate concentration as well as surface oxidation state composition [36].  $H_2O_2$  decomposition occurs at the  $UO_2$  surface as well as in bulk solution, meaning that a larger solution volume would lead to a larger fraction  $H_2O_2$  decomposing as compared to causing surface oxidation. The work of



Fig. 8. The U4f-spectrum of a  $UO_2$ -pellet after 45-days exposure to the 3.30 MBq Am-241 source under Ar atmosphere.



Fig. 9. Deconvolution of the  $U4f_{7/2}$ -peak from a  $UO_2$ -pellet after 45 days exposure to the 3.30 MBq Am-241 source under Ar atmosphere.

Zhu et. al. show that a mixed  $U(IV)/U(V) UO_2$  surface is efficient at causing decomposition of  $H_2O_2$ , suggesting that a reversible U(IV)-U(V) redox reaction has a catalyzing effect on the surface decomposition reaction [36]. Taking the volume into account, the total dissolved amount of uranium at the end of the 45-days experiment was twice as high as in the 11-days experiment suggesting that the longer exposure times caused an overall higher oxidative dissolution of the  $UO_2$  surface.

#### 3.4.4. 11-days exposure under H<sub>2</sub> atmosphere

The UO<sub>2</sub>-pellets were measured directly after the initial washing process as well as after being exposed to the Am-241 sources under  $H_2$  atmosphere for 11-days. The initial U4f-spectrum after the washing process of the UO<sub>2</sub>-pellets is shown in Fig. 10. Both initial U4f states correspond quite well with the previous reference states. Both the peak positions and their corresponding satellites indicate an almost pure U(IV) state. However, the slightly less clear satellite peaks as compared to the sputtered sample indicate an influence of U(V).

The measured U4f-spectrum after exposure can be seen in Fig. 11. The spectrum is almost unchanged with respect to the ini-



Fig. 10. U4f-spectra of the  $UO_2$ -pellets after the carbonate washing procedure, before exposure to the 1.85 (a) and 3.30 MBq (b) Am-241 sources under  $H_2$  atmosphere.

tial state, with a small decrease in U4f<sub>7/2</sub>-peak energy position of the pellet exposed to the 1.85 MBq Am-241 source. The results were replicated in a second experimental run with highly consistent results. It is likely that the long leaching periods allows for some of the initially oxidized U(V) & U(VI) to be released into solution up to levels close to or below the detection limit, as indicated by the ICP-MS measurements. The absence of change for both U4f7/2-peak and satellite position in the 3.30 MBq exposure indicate that the H<sub>2</sub> atmosphere has a suppressing effect on the radiolytic oxidation of the UO<sub>2</sub> surface. This is supported by the reduction in dissolved uranium concentration by an order of magnitude at the end of the H<sub>2</sub> atmosphere experiment of  $3.5 \cdot 10^{-8}$  M as compared to  $3.2 \cdot 10^{-7}$  M under Ar atmosphere.

In a study by Carbol et. al. where 10 wt% U-233 doped UO<sub>2</sub> was studied under H<sub>2</sub> atmosphere, a uranium concentration of ~9•10<sup>-12</sup> M were found at the end of the 328 days experiment [37]. This indicates a significant protective effect of the H<sub>2</sub> atmosphere, suppressing any radiolytic oxidation. This shows a much stronger protective effect than the one observed in this work, where there were several orders of magnitude higher dissolved uranium concentrations.

#### 3.4.5. Valence band region

The valence band region of the UO<sub>2</sub> pellets before and after exposure to the 1.85 & 3.30 MBq sources for 11 days under Ar and H<sub>2</sub> atmospheres can be seen in Fig. 12 and Figure 13 respectively. The area ratio between the  $O2p_{3/2}$  and U5f states in the initial state is approximately ~1.0, as shown in Table 3. All reported  $O2p_{3/2}$  and U5f state area ratio values are after the Shirley background

U5f and  $O2p_{3/2}$  peak positions and FWHMs from the XPS-measurements.

| Condition U5f posi        | tion [eV] | FWHM U5f [eV] | $O2p_{3/2}$ position [eV] | Area ratio (O2p <sub>3/2</sub> /U5f) |
|---------------------------|-----------|---------------|---------------------------|--------------------------------------|
| Ion-sputtered             | 0.8       | 1.45          | 4.1                       | 1.0                                  |
| Chemical washed           | 0.8       | 1.30          | 4.1                       | 0.9                                  |
| Ar atmosphere             |           |               |                           |                                      |
| 1.85 MBq – 11 days        | 0.7       | 1.35          | 4.0                       | 1.1                                  |
| 3.30 MBq – 11 days        | 0.9       | 1.13          | 4.4                       | 1.9                                  |
| 3.30 MBq – 45 days        | 0.9       | 1.11          | 3.4                       | 1.9                                  |
| H <sub>2</sub> atmosphere |           |               |                           |                                      |
| 1.85 MBq – 11 days        | 0.5       | 1.45          | 3.9                       | 1.0                                  |
| 3.30 MBq – 11 days        | 0.8       | 1.40          | 4.5                       | 0.8                                  |



Fig. 11. U4f-spectra of the  $UO_2\mbox{-pellets}$  after 11-days exposure to the 1.85 (a) and 3.30 MBq (b) Am-241 sources under  $H_2$  atmosphere. Second experiment.

subtraction. In the final state under Ar atmosphere, the  $O2p_{3/2}$  to U5f state area ratios are 1.1 and 1.9 after exposure to the 1.85 and 3.30 MBq sources respectively. This indicates an almost negligible change in the  $O2p_{3/2}$  and U5f electron structure after exposure to the 1.85 MBq source and a significant change in the electron distribution after exposure to the strong source. The more oxidized U0<sub>2</sub> pellet therefore has less electrons in the U5f-orbital and/or more electrons in the O2p-orbital. The U5f-FWHM of the pellet exposed to the 3.30 MBq source for 11 days under Ar atmosphere goes from an initial value of 1.28 eV to a final one of 1.13 eV. This agrees quite well with the U5f-FWHM of pure U<sub>2</sub>O<sub>5</sub> (i.e. pure U(V)) in the work of Gouder et. al. of 1.19 eV [23], supporting the notion of a significant U(V) component on the surface. The U5f-FWHM at the end of the 45-days experiment is very similar of 1.11 eV.

In the exposure under  $H_2$  atmosphere, the area ratios of O2p to U5f-states are quite consistent over the experiment as shown in Fig. 13, of about ~1.0. This indicates a negligible change in surface oxidation state. This is supported by the consistent FWHM of the



**Fig. 12.** Valence band region of the pellets before and after exposure to the 1.85 and 3.30 MBq Am-241 sources under Ar atmosphere.



Fig. 13. Valence band region of the pellets exposed to the 1.85 and 3.30 MBq Am-241 sources under  $\rm H_2$  atmosphere for 11 days.

U5f-peaks in the initial and final states which are approximately ~1.4 eV. This is close to the FWHM of the U5f-peak on the sputtered sample, of 1.45 eV. These values are in good agreement with the FWHM of the pure U(IV) 5f-peak in the work of Gouder et. al. of 1.46 eV [23]. The researchers state that the pure U(V) component has a smaller U5f-FWHM and intensity than a mixture of

U(IV) and U(VI). The results in their work indicate that the oxidation mechanism of UO<sub>2</sub> goes via a U(V) component and not directly to the formation of U(VI). This has been reported in several other studies, however, these studies are primarily of SIMFUEL, which contains RE(III), affecting the redox reactivity of the UO<sub>2</sub> matrix [24,36,38]. The oxidation from U(IV) to U(V) is supported by the results in this work as a substantial U(V) component was found in the U4f<sub>7/2</sub>-peak deconvolution process of the final state on the UO<sub>2</sub>-pellets exposed to the 3.30 MBq source for 11 and 45 days under Ar atmosphere (Fig. 7 & Fig. 9). These states also had significantly smaller U5f-FWHM and reduced intensities. The ratio between the U5f state and the O2p valence band for all the oxidized surfaces are ~1.9, while in the initial state the ratio is close to 1. The summarized O2p and U5f state results from all experiments are shown in Table 3.

#### 4. Conclusion

The H<sub>2</sub> atmosphere had a significant impact on the surface oxidation of a  $UO_2$ -pellet after exposing a 30  $\mu m$  water layer adjacent to the pellet surface to a 3.30 MBq Am-241 source. The H<sub>2</sub> atmosphere also suppressed the oxidative dissolution of uranium, giving an order of magnitude lower measured uranium concentrations at the end of the 11- and 45-days experiments in Milli-Q and NaHCO<sub>3</sub>-solutions as compared to under Ar atmosphere. Exposing the UO<sub>2</sub>-pellets to the 1.85 MBq Am-241 source caused no observable surface oxidation under neither atmosphere as compared to the initial states. The exposure to this source gave a somewhat lower U4f<sub>7/2</sub>-peak position as compared to the initial states, suggesting a more significant effect of dissolution of pre-oxidized uranium. However, the amount of dissolved uranium at the end of the 1.85 MBq source exposures is very low, or even below the detection limit of the ICP-MS measurement (Table 2), suggesting that very little surface oxidation occurs. The 3.30 MBq source resulted in a significant oxidation under Ar atmosphere in the form of a substantial U(V) component. This was also shown by the small FWHM of the U5f-peak, indicative of a minor U(IV) and U(VI) contribution. The results support the claim that UO<sub>2</sub> does not oxidize directly from U(IV) to U(VI), but through the formation of U(V), without having a simultaneous mixed U(IV) and U(VI) oxidation state.

The results of this work indicate that the much stronger influence of hydrogen atmosphere on the pellet surface reduction noted in the work of Sunder et al. is partially due to thermally activated hydrogen, contributing to chemical reduction of U(VI) to U(IV) at 100°C [10]. Ekeroth et al. reported a slow reduction of U(VI) by dissolved hydrogen at 74-100°C [39], while no reduction in bulk solution was observed in another work carried out at 70°C [40]. In this work, carried out at room temperature, i.e. when dissolved hydrogen is expected to be chemically inert, the effect of dissolved hydrogen on preventing surface oxidation by alpha radiolysis is apparently a result of the interaction of ionizing radiation with water adsorbed on the surface of actinide oxides, the exact mechanism of which requires dedicated interfacial radiolysis studies. In this case, in addition to standard radiolytic processes, energy, charge or matter can be transferred through the interface, while catalytic or steric effects can alter the decomposition or reactivity of adsorbed molecules. Similar studies claiming recombination of alpha radiolysis products have been reported in the literature. The results of a radiolytic gas generation study on NpO<sub>2</sub>(s) doped with 0.7 % <sup>244</sup>Cm in the presence of moisture (up to 8 wt% water), show that the gas generation quickly reaches a steady state plateau at relatively low total pressures [41]. The plateau is interpreted by the authors as clear evidence of a significant back reaction (i.e. the recombination of the radiolytic products O<sub>2</sub> and H<sub>2</sub> to water), where the forward reaction (radiolytic decomposition of water) is equal to the

back reaction; a behaviour noticed by the authors also in other actinide systems. Haschke et al. observed a pressure decrease in a 2:1  $(D_2 + O_2)$  gas mixture over <sup>239</sup>PuO<sub>2</sub>(s) at 25 °C, which was interpreted as being caused by the catalytic formation of water on the surface of PuO<sub>2</sub>(s) [42]. The role of  $\alpha$ -radiation in the interfacial processes involved in both these studies has not been discussed in the original publications, but its influence cannot be excluded [43]. It is difficult from our tests to draw any conclusions about the mechanism of the recombination reactions between radiolytic oxidants and hydrogen that we observe as absence of surface oxidation at room temperature, but it cannot be excluded that surface mediated processes contribute to the obtained results.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### **CRediT** authorship contribution statement

**N.L. Hansson:** Conceptualization, Methodology, Software, Formal analysis, Investigation, Writing – original draft, Visualization. **P.L. Tam:** Formal analysis, Investigation, Resources, Writing – review & editing. **C. Ekberg:** Writing – review & editing, Supervision. **K. Spahiu:** Conceptualization, Writing – review & editing, Supervision.

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