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Radiolytic Corrosion of Uranium Dioxide: Role of Molecular Species

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Abstract

In this work, oxidative corrosion of UO₂ particles by molecular species produced by ⁴He²⁺ radiolysis of water (simulated by irradiation with ⁴He²⁺ beam) has been investigated as a function of the absorbed dose under open and closed atmosphere. This work was carried out by coupling for the first time: 1) characterization of the UO₂ surface after oxidation, 2) analysis of H₂ and H₂O₂ produced by water radiolysis and 3) quantification of the uranium species leached into the solution during irradiation. Oxidation of the surface of the UO₂ particles was characterized by Raman spectroscopy. H₂ and H₂O₂ were analyzed by micro gas chromatography and UV-VIS spectrophotometry respectively. Inductively coupled plasma mass spectrometry was used to quantify the soluble uranium species released into the solution. The results showed that when the ultra-pure water above the UO₂ particles was irradiated in open atmosphere, metastudtite was formed on the UO₂ surface indicating its oxidation by the H₂O₂ produced by water radiolysis. This oxidation was accompanied by migration of soluble uranium species (U(VI)) into the irradiated solution. After irradiation in closed atmosphere, oxidation of the UO₂ surface and migration of soluble uranium species were limited due to the presence of H₂. The inhibition does not occur by direct effect of H₂ on H₂O₂ but more probably by adsorption of H₂ molecules on the UO₂ surface.

Keywords: Water Radiolysis, UO₂ Radiolytic Corrosion, Raman Spectroscopy, Soluble Uranium, Chemical Yields.
1. Introduction

Management of nuclear waste as the spent nuclear fuel is one of the major political, social and scientific concerns in the countries using nuclear industry\(^1\). Among various management possibilities, the concept of direct disposal of this high level waste in deep geological vaults (500 to 1000 m of depth) is being seriously considered by several countries\(^2\). In this case, the spent nuclear fuel will be stored within canisters (from steel or copper) and its disposal is planned to be made in presence of a series of natural and artificial barriers whose aim is to protect the biosphere from an eventual radioactive contamination by insulating the waste from the outside environment\(^3\). However the impact of these disposal repositories on the environment over tens or hundreds of thousands of years is still being studied.

In the concept of deep geological disposal, groundwater is assumed to success within geological timescales (\(\geq 300\)-1000 years)\(^4\)\(^5\) to percolate the different barriers and arrive to the nuclear waste package. Considering the scenario of canister failure, groundwater could get then in direct contact with the spent fuel. It is then crucial to study the behavior of the spent fuel in presence of water in real conditions encountered in deep geological sites in order to predict its possible dissolution mechanism, dissolution rate and thus, migration of radioactive elements to the environment. In fact, the spent nuclear fuel matrix is formed mainly by uranium dioxide (\(\text{UO}_2\)) with a small fraction (< 5%) of long-lived highly radiotoxic actinides and other fission products\(^1\). The majority of these radionuclides is trapped in the \(\text{UO}_2\) matrix and the only credible mechanism of their migration into the environment is dissolution and transport by water in contact with the spent fuel. In this case, the releasing rate of these radionuclides is governed by the dissolution rate of the \(\text{UO}_2\) matrix\(^6\).

Groundwater present at the expected depth of deep geological repositories is generally reducing and spent fuel matrix (in its reduced form \(\text{U(IV)}\)) has a very low solubility in these conditions\(^2\). However, the reducing environment near the fuel surface may be altered by water
radiolysis caused by the radiation field associated to the spent fuel. Water radiolysis generates indeed various oxidants (e.g. O₂, H₂O₂, OH·...) near the waste surface (about 30 - 40 µm)². This leads to the oxidation of UO₂ to U(VI), a species more soluble than its reduced form (U(IV))¹⁰ which favors the spent fuel dissolution and consequently the migration of radiotoxic elements from the repository to the biosphere³. On the other hand, it is known that the corrosion process is limited in presence of H₂ produced by water radiolysis due to its reducing properties¹¹-¹². Then, the knowledge of the chemistry of the solid-liquid interface (oxidation, corrosion…) which controls the radionuclide release under the conditions encountered in deep geological repositories is of great importance to ensure secure and safe management of this type of nuclear waste. However, it is not expected that groundwater reaches the spent fuel surface before few thousands of years of storage time¹³. At these geological timescales, short-lived radionuclides emitting principally β and γ rays will have been disappeared due to their radioactivity decay and the radiation field of the spent fuel will be mainly limited to α irradiation²⁻⁴.

In this work, we propose to investigate the effect of molecular species produced by ⁴He²⁺ radiolysis of water on the UO₂ corrosion under controlled irradiation and environmental conditions.

Earlier papers relate that among all the products generated by water radiolysis, H₂O₂ is considered an important¹⁴-¹⁶ and even the major¹⁷,¹⁸-¹⁹ actor in the oxidative dissolution of UO₂ under irradiation. The effect of O₂ on this latter process is considered negligible²⁰. Moreover, some authors¹⁷,¹⁸-¹⁹ considered H₂O₂ as the unique oxidant to retain in UO₂ oxidation and dissolution, whereas others¹⁴,¹⁵ defend the idea that the effect of H₂O₂ is combined to that of radical radiolytic species. In presence of oxidant and in absence of complexing agent in the solution, oxidation of UO₂ starts by the formation of an oxidized phase on its surface²¹,²². Characterization of the oxidized phase by XRD (X Ray Diffraction),
Raman Spectroscopy and XPS (X-ray Photoelectron Spectroscopy) showed that this phase is mainly formed of studtite (or metastudtite when dehydrated) corresponding to UO$_4$ in case of oxidation by H$_2$O$_2$ produced or not by water radiolysis$^{13, 14, 23}$. Later, the oxidized phase undergoes a dissolution reaction in the form of U(VI) which may precipitate at sufficiently high oxidant concentrations on the UO$_2$ surface as secondary phase of schoepite (UO$_3$ xH$_2$O)$^{21, 22}$. In deep geological repositories, this dissolution step leads to the migration of different radionuclides contained in the UO$_2$ matrix with a leaching rate depending on the UO$_2$ dissolution rate. Dissolution rate of UO$_2$ was investigated in the literature by quantifying the oxidized uranium species leached into water based on leaching and electrochemical experiments coupled sometimes to model calculations$^{6, 24-26}$. The UO$_2$ dissolution rate varies widely with the irradiation conditions (irradiation source, irradiation environment, absorbed dose, dose rate…) which make it very difficult to compare the values obtained from different works.

The inhibitory effect of H$_2$ on the UO$_2$ corrosion process was largely investigated in the literature$^{11-12, 1}$. In general, presence of H$_2$ during irradiation leads to diminution and even total inhibition of UO$_2$ dissolution. To explain this inhibition process, some authors$^{27}$ proposed a reduction mechanism based on radical interactions with the oxidized U(VI) released into solution.

Despite the high number of publications about UO$_2$ corrosion by the radiolytic products of water irradiated by $^4$He$^{2+}$ radiation, a distinction between the effect of radicals and molecular oxydants on this process was never realized. To the best of our knowledge, combination of solid corrosion characterization, analysis of H$_2$ and H$_2$O$_2$ produced by water radiolysis and quantification of soluble uranium species leached in to the solution during the oxidative dissolution of UO$_2$ was not reported in the literature. Also, the effect of H$_2$ produced by water
radiolysis has not been sufficiently investigated to have a complete understanding of the involved complicated inhibition mechanism.

The aim of this work was to investigate experimentally the effect of molecular radiolytic species (in particular \(H_2\) and \(H_2O_2\)) produced by localized \(^4\text{He}^{2+}\) radiolysis of water on \(\text{UO}_2\) corrosion under different parameters encountered in deep geological repositories. Water in contact with the \(\text{UO}_2\) particles was then irradiated by \(^4\text{He}^{2+}\) beam at different absorbed doses under open and closed atmospheres in order to evaluate the effect of \(H_2\) on the corrosion process. To fulfill this work, we chose to characterize the surface oxidation of the solid particles by Raman Spectroscopy which is known to be very efficient in surface characterization of solid state materials. It was used in some earlier works to investigate \(\text{UO}_2\) corrosion under irradiation\(^{28, 29}\). Soluble uranium species leached into the solution were analyzed by Inducted Coupled Plasma Mass Spectrometry (ICP-MS) technique. \(H_2O_2\) and \(H_2\) produced by water radiolysis were quantified by UV-VIS Spectrophotometry and Gas Chromatography (\(\mu\)-GC) respectively in order to calculate their radiolytic yields, compare them to those of pure water and clarify the role of these two species in the \(\text{UO}_2\) corrosion process.

2. Materials and Methods

2.1. System studied: \(\text{UO}_2\) Particles and Ultra pure Water

The material studied in this work is \(\text{UO}_2\) TRistuctural-ISOtropic (TRISO) particles which were provided by Professor Fachinger of FZ-Jülich (Forschungszentrum Jülich) and their synthesis is detailed in the work of Brähler et al.\(^{30}\) particularly with a calcination phase performed at 1600\(^\circ\)C for \(\text{UO}_2\) crystallization. \(\text{UO}_2\) TRISO particle constitutes a \(\text{UO}_2\) based kernel (500 \(\mu\)m of diameter) composed by grains and grain boundaries (Figure 1). The grain
size has been measured between 10 and 20 µm. Other details about the characterization of the UO$_2$ TRISO particle sample can be found elsewhere$^{31}$.

Figure 1: SEM picture of an unirradiated UO$_2$ particle surface.

In all the experiments, water used in this work is ultra pure water Millipore Alpha-Q with an electrical conductivity of 18.2 MΩ.

2.2. Experimental Conditions

$^4$He$^{2+}$ irradiation was performed at the ARRONAX cyclotron facility (Saint-Herblain, France). The $^4$He$^{2+}$ beam diameter was around 10 mm. The energy range was 64.5 or 66.5 MeV depending on the irradiation conditions with an average LET of 22.7 keV/µm. The energy of the $^4$He$^{2+}$ particles inside the irradiation cell is systematically evaluated by using the SRIM 2008 simulation code$^{32,33}$. In these calculations, all the obstacles upstream of the cell are taken into account. The intensity of the particles beam, measured on an internal Faraday cup located one meter upstream, was maintained at 70 nA. The uncertainty of the current measurement is about 10 %.

Irradiation was realized in two atmospheric conditions: I) open to air, II) closed with air and III) closed with Ar/H$_2$ atmospheres. The last one is considered as a reference and the main difference between these conditions is that in closed atmosphere, H$_2$ produced by water radiolysis is not evacuated. It can then interact with the UO$_2$ solid surface which is not
possible in open atmosphere due to gas evacuation during irradiation. The irradiation time was 1, 3, 5, 10, 15 and 20 min according to the desired dose.

2.2.1. Experimental Setup

The experimental setup consists of two compartments named Cell 1 and Cell 2. Cell 1 served as a container of the UO$_2$ particles which permitted their irradiation. It is made of Polypropylene (PP) with a removable cover of aluminium perforated in the middle to allow sample irradiation. After introducing the UO$_2$ particles in the Cell 1, the distance between the solid surface and the entrance window of the aluminium cover was 5 mm. It was chosen carefully to avoid direct irradiation of the UO$_2$ particles from one hand and to prevent its interaction with the radical species produced by water radiolysis from the other hand. Indeed this work is devoted to study the effect of the molecular species produced by water radiolysis onto the solid corrosion and not the consequences of direct irradiation of the solid or the effect of the radical species. As mentioned above, the $^4$He$^{2+}$ ions beam was provided by the ARRONAX cyclotron facility with $E = 64.5$ or $66.5$ eV. For these two energies the average length of the $^4$He$^{2+}$ particles, calculated by the SRIM 2008 simulation code $^{32, 33}$, is not expected to exceed 3.5 mm in ultra-pure water used in this investigation. Thus, after filling the experimental setup by ultra-pure water, the direct effects of the $^4$He$^{2+}$ ions irradiation in the cell 1 occur onto the solution and not onto the solid surface (distance between UO$_2$ particles and $^4$He$^{2+}$ beam is 5 mm as described before). In case of irradiation in closed atmosphere, a borosilicate glass disc with a diameter of 25 mm and a thickness of 150 μm was placed between the cover and the PP Cell.

Cell 2 is a glass bottle with two necks: the first one contains a UV-VIS probe for in-situ dose rate determination and the second one is used for atmospheric conditioning of the experimental setup in close atmosphere experiments. In these latter conditions, the second neck of the Cell 2 was closed by a valve after atmospheric conditioning. The second neck can
also be connected to a GC (Gas Chromatography) device for gas analysis. The lower part of the Cell 2 has two outlets for connexion with the cell 1.

The two compartments of the experimental setup were connected by Viton hoses. A peristaltic pump was used for evacuation in closed atmosphere and to circulate the solution in order to ensure its homogenization in the whole system for all the atmospheres.

First of all, 200 particles of UO$_2$ were introduced in the Cell 1. Based on previous experimental tests, this number is sufficient to quantify any soluble uranium species which may be leached into the solution. 28 ml of ultra-pure water were then introduced in the Cell 2. This volume was chosen carefully to cover the optical path of the visible Ultra Violet (UV-VIS) probe and to ensure a sufficient void volume in the system for gas production (in closed atmosphere experiments).

For each experiment, the first step realized after irradiation was molecular hydrogen analysis (this step was absent for experiments realized in open-to-air atmosphere). Then, one UO$_2$ particle was retrieved and a volume of 3 ml of the irradiated solution was collected: 1 ml for H$_2$O$_2$ analysis, 1 ml for soluble uranium species analysis and 1 ml to stock the UO$_2$ particle in order to perform further kinetic solid analysis. 3 ml of ultra-pure water were later added to the system (before the next irradiation) to compensate the volume collected for solution analysis.

2.2.2. Dose Rate Determination

In this investigation, Super Fricke dosimetry$^{34}$ was used to determine the irradiation dose rate. This method is based on the oxidation of Fe$^{2+}$ to Fe$^{3+}$ by the species produced by water radiolysis. These measurements are carried out during irradiation (in situ). Super Fricke solutions are prepared by dissolving the desired quantity of ferrous sulphate (H$_2$SO$_4$, [Fe$^{2+}$] = 10 mmol l$^{-1}$) and sodium chloride (NaCl) (1 mmol l$^{-1}$) in aerated aqueous 0.4 mol l$^{-1}$ sulfuric acid (H$_2$SO$_4$) solutions. All reagents are analytical grade or equivalent. NaCl is added to
suppress any organic impurities. Fricke dose rate was found around 4370 Gy min$^{-1}$ using the ferric ion radiolytic yield from the literature$^{35}$. In our conditions, the ferric ions yield $G(\text{Fe}^{3+})$ was $1.16 \times 10^{-7}$ mol J$^{-1}$.

2.3. Measurement Techniques

2.3.1. UV-VIS Spectrophotometry

In this work, the Fricke dose rate and the concentrations of H$_2$O$_2$ produced by water radiolysis were determined by a CARY4000 (VARIAN) spectrophotometer. For the dose rate calculation, the concentration of ferric ions was monitored by UV-Vis measurements at 304 nm ($\varepsilon = 2197$ l mol$^{-1}$ cm$^{-1}$). Concentrations of H$_2$O$_2$ have been determined after irradiation (about 15 min after the experiment), with the Ghormley triiodide method$^{36}$ using two reagents. One is a mixture of ammonium molybdate (Mo$_7$O$_{24}$(NH$_4$)$_2$H$_2$O, Carlo Erba), potassium iodide (KI, VWR) and sodium hydroxide (NaOH, VWR) and the second is a buffer solution (pH 4–5) of acid potassium phthalate (C$_8$H$_5$KO$_4$, VWR). For a total volume of 2 mL, 0.5 mL of both reagents was mixed with 1 mL of the sample solution. The concentration of H$_2$O$_2$ is obtained indirectly by measurement of I$_3^-$ absorbance. The molar extinction coefficient of I$_3^-$ at the 351 nm wavelength is previously determined at 25300 l mol$^{-1}$ cm$^{-1}$ in the studied solution at 298 K.

2.3.2. Inductively coupled Plasma Mass Spectrometry

After irradiation, the collected solutions were acidified adding 3 ml of pure nitric acid (HNO$_3$) 3 mol l$^{-1}$ at 2% and analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to determine the concentration of the soluble uranium species released into the solution. The detection limit of the apparatus is $10^{-9}$ mol l$^{-1}$ with an uncertainty of 10% and the solvent is pure HNO$_3$ 3 mol l$^{-1}$ at 69%.

2.3.3. Micro Gas Chromatography
In the closed atmosphere experiments, molecular hydrogen produced by water radiolysis was measured by gas chromatography technique. The apparatus is a 490-GC, which is a l-GC model from VARIAN. The carrier gas was ultra-high purity argon (Ar) with a pressure of 150 kPa. The gas sample was introduced using a Swagelok connection and the injection volume is 10 µl. The column is a Molecular Sieve 5A (length = 4 m and diameter = 0.25 mm). The detection was performed using a thermal conductivity detector. Calibration of the detector is performed by injection of different gas mixture of Ar/H₂ with a proportion of H₂ varying from 0.1 to 5 mol l⁻¹. Uncertainty in gas measurements is estimated to be less than 10%.

2.3.4. Raman spectroscopy

Analysis of the solid UO₂ particles by Raman spectroscopy was performed after irradiation (around 20 min after the experiment). A kinetic solid analysis was then started by recording Raman spectra of the corroded particles as a function of time until the spectra remained stable (1 week). For each experiment, spectra were registered each hour at first and then each day.

All the Raman setup is purchased by the HORIBA Jobin–Yvon Company. Raman spectra are recorded with an iHR550 spectrometer equipped with two optical fibers (diameter = 100 µm, length = 20 m). The detector is a charged coupled device (CCD) cooled by Peltier effect (203 K). The samples are excited with a red laser beam at 632.8 nm emitted by a He/Ne Laser. The laser beam is focused on the samples by a near infra-red 100X Mitutoyo lens with a diameter of 24.6 mm and a power of 14 mW for a working distance of 12 mm from the sample and an acquisition time of 1 min. The spectral range studied was between 100 and 1400 cm⁻¹. The region beyond 900 cm⁻¹ presents Raman bands characteristic of defects present in the UO₂ matrix¹³, 3⁷ and the spectrum of water which makes data analysis very difficult in this domain. Therefore this paper will present spectra in the interesting spectral range between 100 and 900 cm⁻¹. The Raman backscattering is collected through the same objective and dispersed by 1200 grooves/mm gratings to reach 5 cm⁻¹ spectral resolution for
Raman stokes spectra excited at 632.8 nm. The wavenumber accuracy has been checked and was better than 0.5 cm⁻¹.

2.3.5. Scanning Electron Microscopy

Before and after irradiation, the UO₂ particles were characterized by SEM (Scanning Electron Microscopy) in order to describe their surface and localize the corroded zones (grains or grain boundaries). The SEM microscope used in this work is a JEOL 5800 SV with a voltage of 15 or 10 kV. The SEM samples were covered by a Pt layer in order to improve electron conduction and increase the picture resolution.

3. Data Treatment

3.1. Calculation of Raman Peak Area Ratios

Raman spectra were imported to Dmfit software 2010 in order to decomposed them in the spectral range between 100 and 900 cm⁻¹. Four Raman peaks were then obtained. For each peak “i”, its area Aᵢ is given by the software to overcome the relative peak intensity variation. Relative areas (named Sᵢ) were calculated as follows:

\[ Sᵢ = \frac{Aᵢ}{A_t} \times 100 \]  

(1)

where \( A_t \) is the total area of the Raman spectrum calculated according to equation (2):

\[ A_t = \sum_{i=1}^{4} Aᵢ + A_{ap} \]  

(2)

where \( A_{ap} \) is the Raman peak area of the adjustment peaks used to adjust the fit to the experimentally obtained Raman spectra.

3.2. Dissolution Rate

The dissolution rate \( r \) (g m⁻² d⁻¹) of the oxidized phase can be defined as

\[ r = \frac{\nu d[u]}{S} \frac{d[U]}{dt} M_{UO₂} \]  

(3)
where \( V \) is the volume of the leaching solution (m\(^3\)), \( S \) is the total surface area of the solid (m\(^2\)), \( M_{UO_2} \) is the molar mass of UO\(_2\) and \( d[U]/dt \) (mol m\(^{-3}\)) is the variation of soluble uranium species as a function of the irradiation time. \( V/S = 0.18 \) m, it was calculated by dividing the volume of the leaching solution on the surface of the 200 UO\(_2\) particles. \( M_{UO_2} = 270 \) g mol\(^{-1}\) and \( d[U]/dt \) can be calculated from the slope of the curve representing the variation of soluble uranium species in the irradiated solution as a function of the irradiation time.

3.3. Chemical Radiolytic Yields

The radiolytic yield is defined as the number of species formed or disappeared per unit of deposited energy. It is expressed in the international system by \( \mu \)mol J\(^{-1}\) and is calculated at a time \( t \) after transition of the ionizing irradiation according to the equation (4):

\[
G_t(X) = \frac{X_t}{\rho D}
\]  

(4)

where \([X]_t\) is the concentration of the species X at the time \( t \) (mol l\(^{-1}\)), \( \rho \) is the density of the irradiated solution (kg l\(^{-1}\)) and \( D \) the absorbed dose (J kg\(^{-1}\)).

4. Results

4.1. UO\(_2\) Surface Characterization

The spectrum of the unirradiated UO\(_2\) is presented in Figure 2.
Figure 2: A) Raman spectra of a non-irradiated UO$_2$ particle (dotted line) and the particles corroded by water radiolysis in open atmosphere (Set I) as a function of the irradiation time. B) Zoom on the spectral region between 800 and 900 cm$^{-1}$ where metastudtite is formed by oxidation of UO$_2$.

It presents two characteristic bands around 445 cm$^{-1}$ and 560 cm$^{-1}$. The former is affected to the triply degenerated Raman active mode (T$_{2g}$) of U-O stretch$^{13,40-41,37}$ whereas the latter characterizes the defects present initially in the UO$_2$ fluorite structure$^{37}$.

To estimate the Raman spectral modifications brought by the radiolytic products of water in the different studied conditions, a comparison was performed between the UO$_2$ spectra before and after irradiation. The results showed that after irradiation in closed atmosphere (with air and with Ar/H$_2$), the spectra of the UO$_2$ particles remained stable as a function of the dose. That’s why these spectra will not be presented in this paper. On the other hand, when water in contact with the UO$_2$ particles was irradiated in open to air atmosphere, no spectral modifications were observed until 21.8 kGy deposited in the solution (Figure 2). From 43.7 kGy, modifications can be seen between 800 and 900 cm$^{-1}$ and appear clearly at the dose of 87.3 kGy. Indeed, two peaks appear at 825 and 860 cm$^{-1}$. Both of these bands characterize
the metastudtite \((\text{UO}_2(\text{O}_2) \cdot 2\text{H}_2\text{O})^{13, 28, 29}\) formed on the \(\text{UO}_2\) surface by oxidation with \(\text{H}_2\text{O}_2\) produced by water radiolysis according to the reaction (i): \(\text{UO}_2 + 2\text{H}_2\text{O}_2 \rightarrow \text{UO}_2(\text{O}_2)(\text{H}_2\text{O})_2\) (i)

After irradiation, kinetic analysis of the solid particles was realized by Raman spectroscopy as detailed previously. The results showed that Raman spectra of the samples irradiated with an irradiation time \(t = 1\) min remained unchanged after two months of the experiment. It seems that in these conditions, \(\text{UO}_2\) oxidation is very low due to low \(\text{H}_2\text{O}_2\) concentration produced. The sensitivity of the Raman apparatus used does not permit to detect it. For \(t \geq 3\) min, Raman spectra of the irradiated particles evolved slightly as a function of time until one week after irradiation and then remained stable. In this paper, we will discuss only the spectra that evolved as a function of time (until 1 week after irradiation). For instance, Figure 3 displays the spectra recorded versus time after irradiation for the particles irradiated for 20 min under open to air atmosphere.

**Figure 3:** A) Evolution as a function of time after irradiation of the \(\text{UO}_2\) Raman spectra for the samples irradiated during 20 min in open to air atmosphere (Set I). B) Zoom on the spectral region between 800 and 900 cm\(^{-1}\) where metastudtite is formed by oxidation of \(\text{UO}_2\).
In order to analyze the temporal evolution of the UO$_2$ Raman spectra after irradiation, area ratios of the characteristic peaks observed at 445, 535, 820 and 865 cm$^{-1}$ were calculated and are discussed below. A similar work was done by He and al. [32] who followed the variations of UO$_2$ Raman peak intensities as a function of matrix doping by fission products. Area ratios of the characteristic peaks at 445, 535, 820 and 865 cm$^{-1}$, designed here by $S_1$, $S_2$, $S_3$ and $S_4$ respectively, were calculated as a function of time as described before. Adjustment peaks area ratios were also calculated to verify that the sum of all the area ratios is equal to 100%.

**Figure 4** shows the variation of the sum $S_3 + S_4$ (area ratios of the peaks at 820 and 865 cm$^{-1}$ characterizing the metastudtite) as a function of the irradiation time until one week after irradiation. Beyond one week, no significant variation of peak intensities was observed.

Regardless the irradiation atmosphere, $S_3 + S_4$ characterizing the metastudtite formed by oxidation of the UO$_2$ surface increased with both the irradiation time and the time after irradiation. However, this increasing is delayed after H$_2$ evacuation in closed atmosphere which confirms that this gas has an inhibition effect on the corrosion process.

4.2. Uranium Solubility and Dissolution Rate
After irradiation, water in contact with the UO\textsubscript{2} particles was collected to quantify the soluble uranium species leached into the solution. Indeed, the metastudtite phase formed on the surface of UO\textsubscript{2} after oxidation by H\textsubscript{2}O\textsubscript{2} produced by water radiolysis underwent later a dissolution step where uranyl ions (UO\textsubscript{2}\textsuperscript{2+}) were leached into the solution. The mechanism of this dissolution reaction in ultra-pure water was rarely discussed in the literature. According to some authors\textsuperscript{23}, the dissolution step occurs according to reaction (ii):

\[
\text{UO}_2^{2+} (s) + \text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})^{+} + \text{H}^{+}
\]  

However, Sattonay et al.\textsuperscript{23} proposed this dissolution mechanism based on a pH decreasing observed in their case after the solution irradiation. But, in our work, measurement of the irradiated solutions acidity after each irradiation showed that pH did not evolve and remained between 6.5 ± 0.5 and 7.5 ± 0.5. This means that the above proposed mechanism (reaction (ii)) does not occur in our case.

**Figure 5** shows the variation of the soluble uranium species concentration leached into the solution after irradiation as a function of the dose and the irradiation time in both open and closed atmosphere.

![Figure 5](image_url)

**Figure 5**: Variation of the concentration of soluble uranium leached to the irradiated solution versus the absorbed dose in open (○) and closed with air (●) atmosphere.
Regardless the irradiation atmosphere, the quantity of soluble uranium species increased with the dose and then remained constant from 43.6 kGy. At this latter dose, concentration of soluble uranium species found in closed atmosphere \( (4.5 \pm 0.5 \times 10^{-7} \text{ mol l}^{-1}) \) is two-fold lower than that observed in open atmosphere \( (11.0 \pm 1.0 \times 10^{-7} \text{ mol l}^{-1}) \) due to the inhibition of the UO\(_2\) oxidation by H\(_2\) produced by water radiolysis. Figure 5 shows too the variation of the [U] with respect to the irradiation time for each set of samples. Two domains can be seen: the first one is for an irradiation time between 0 and 10 min (domain I) with a higher leaching rate, the second one is for an irradiation time beyond 10 min (domain II) with either lower leaching rate or approach to steady state concentration values. The final steady state of [U] values measured in our system are presented in Table 1 for an irradiation time of 10 min together with the normalized leaching rate \( (r) \) obtained from the domain I. Moreover, Table 1 presents also UO\(_2\) solubility values obtained from literature in order to compare it to our data.

**Table 1**: Steady state U concentrations, Dissolution rate and factor \( (r \text{ and } r') \) of UO\(_2\) and experimental conditions used in this study and others found in the literature.

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<th>(^4\text{He}^{2+}) Beam</th>
<th>Dose Rate Gy min(^{-1})</th>
<th>Atm. ([\text{U}] \times 10^{-7} \text{ mol l}^{-1})</th>
<th>Diss. rate (r) mg m(^{-2}) d(^{-1})</th>
<th>Diss. factor (r') (\mu\text{g m}^{-2} \text{ Gy}^{-1})</th>
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<tr>
<td>24</td>
<td>Colloids</td>
<td>External source*</td>
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<td>Red</td>
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<td>0.246</td>
</tr>
<tr>
<td>43</td>
<td>Pellets</td>
<td>Internal**</td>
<td>18</td>
<td>Ox</td>
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</tr>
<tr>
<td>1.8</td>
<td>Ox</td>
<td>0.2</td>
<td>0.076</td>
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</tr>
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</table>

* \(^4\text{He}^{2+}\) Beam produced by cyclotron facility

** Doped UO\(_2\) with Pu
When UO$_2$ particles were irradiated between 10 and 20 min in closed atmosphere, concentration of uranium species remained practically constant (Figure 5). Indeed the obtained values were respectively $4.5 \pm 0.5 \times 10^{-7}$ and $5.2 \pm 0.5 \times 10^{-7}$ mol l$^{-1}$ for the latter mentioned irradiation time. These values are comparable to most solubility data reported in the literature$^{6, 24, 39, 43}$. However, we believe that in our work the thermodynamic equilibrium of the UO$_2$ dissolution was not achieved due to their composition of grains and grain boundaries. We could calculate, in these conditions, the dissolution rate which was equal to $13.5$ g m$^{-2}$ d$^{-1}$. A comparison of our dissolution rates (domain I on Figure 5) with the literature data is given in Table 1. Despite the similarity with [U] reported in the literature, r values obtained in this investigation are at least $10^3$ fold higher. It seems then that with the irradiation conditions used in our work, the UO$_2$ oxidation/dissolution mechanism occurred with a faster kinetic. This is very probably due to the impact of the high doses deposited in this work into the irradiated solution. In order to apprehend the dose impact on the UO$_2$ corrosion, we propose here a new methodology to express the dissolution rate. This methodology consists in calculating the dissolution rate as a function of the dose deposited into the solution and not as a function of the irradiation time. Thus, the new dissolution factor r’ can be defined as follow:

$$r' = \frac{V}{s} \frac{d[U]}{dd} M_{UO_2}$$  \hspace{1cm} (5)$$

where $d[U]/dd$ (mol m$^{-3}$) is the variation of soluble uranium species as a function of the dose deposited into the solution. In our case the r’ values are $2.0$ µg m$^{-2}$ Gy$^{-1}$ for the open atmosphere experiments and $1.1$ µg m$^{-2}$ Gy$^{-1}$ for the closed atmosphere ones. These results confirm that the reducing atmosphere (in presence of H$_2$) has a strong diminishing impact onto the UO$_2$ dissolution rate. Moreover, Table 1 displays the dissolution factor r’ obtained by previous data$^{24, 43}$ in order to compare it to our results. Even after taking into account the effect of the absorbed dose, the values obtained in this work still higher than those reported in
the literature (Table 1). However, in our investigation, we used a very high dose rate (4370 Gy.min\(^{-1}\)) which certainly influences the UO\(_2\) dissolution. It appears clearly then that the dose rate is the main parameter which controls the UO\(_2\) dissolution rate.

4.3. \(\text{H}_2\) and \(\text{H}_2\text{O}\) Chemical Yields

When the ultra-pure water above the UO\(_2\) particles was irradiated in closed air atmosphere, \(\text{H}_2\) produced by water radiolysis was quantified by calculating its radiolytic yield (G) in order to compare it to that of pure water and explain any gas consumption by the inhibition of the UO\(_2\) corrosion process. As described previously, the solution used during irradiation is ultra-pure water (\(\rho = 1 \text{ kg l}^{-1}\)) and the mean \(G(\text{H}_2)\) was \(0.02 \pm 0.002 \mu\text{mol J}^{-1}\). It corresponds to the slope of the curve in Figure 6 representing the variation of \([\text{H}_2]\) measured by \(\mu\)-GC as a function of the dose.

![Figure 6](image)

**Figure 6**: Variation of the concentration of \(\text{H}_2\) produced by water radiolysis in closed with air atmosphere versus the dose.

Crumière et al.\(^{44}\) irradiated ultra-pure water by a cyclotron \(^4\text{He}^{2+}\) beam with an energy of 64.7 MeV and doses up to 800 Gy in Argon saturated atmosphere. \(G(\text{H}_2)\) obtained in their work was \(0.061 \pm 0.006 \mu\text{mol J}^{-1}\) which is three-fold higher than that found in this investigation (\(G(\text{H}_2) = 0.02 \pm 0.002 \mu\text{mol J}^{-1}\)). The irradiation conditions used by Crumière et al.\(^{44}\) are very similar to those used in our work which means that for the system UO\(_2\)/ultra-
pure water, a non negligible part (around 2/3) of the H₂ produced by water radiolysis was consumed certainly by inhibition of the UO₂ oxidation process.

In both open and closed to air atmospheres, concentrations of H₂O₂ produced by water radiolysis was determined by the Ghormley method³⁶, as described into the experimental section, to analyze the effect of the irradiation atmosphere on its consumption by the UO₂ oxidation. Figure 7 presents the variation of [H₂O₂] produced by water radiolysis under open and closed atmospheres as a function of the dose.

Figure 7: Variation of the concentration of H₂O₂ produced by water radiolysis versus the absorbed dose in open (○) and closed to air (●) atmosphere.

It shows that in both open and closed atmospheres, [H₂O₂] produced by water radiolysis increased with the dose and then reached a steady state from 21.8 kGy and 65.5 kGy in open and closed atmosphere respectively. At these latter doses, the value of [H₂O₂] were respectively 1.4 ± 0.2 10⁻⁴ and 5.6 ± 0.6 10⁻⁴ mol l⁻¹ which means that the quantity of H₂O₂ was four-fold higher when the UO₂ particles were irradiated in closed atmosphere. It seems then that in the latter conditions consumption of H₂O₂ and thus oxidation of the UO₂ surface was inhibited by H₂ produced by water radiolysis. Radiolytic yields of H₂O₂ were also calculated and the values obtained were 0.06 ± 0.006 and 0.1 ± 0.01 μmol J⁻¹ in open and closed atmosphere respectively (Figure 7). It appears then that in presence of H₂, G(H₂O₂)
was equal to that found for ultra-pure water $^{45-46}$ (0.102 μmol J$^{-1}$) irradiated by $^4\text{He}^{2+}$ beam. This confirms that in closed atmosphere, H$_2$O$_2$ was not consumed and oxidation of UO$_2$ was limited.

5. Discussion

From a macroscopic point of view, corrosion of UO$_2$ by the radiolysis products of water, in particularly by H$_2$O$_2$, occurs according to a two-step process. It starts by oxidation of the UO$_2$ surface leading to the formation of an oxidized metastudtite phase on the material surface (reaction i). The oxidized phase undergoes later a dissolution step (reaction ii) resulting in migration of uranyl ions into the solution.

Raman spectroscopic analysis realized after irradiation on the UO$_2$ particles confirmed that the oxidized phase formed on the surface was metastudtite (UO$_2$(O$_2$) 2H$_2$O)) which is consistent with the data reported in the literature$^{28}$. In recent works$^{28,29}$ on oxidation of UO$_2$ exposed to water radiolysis, the authors detected by in situ Raman spectroscopy the formation of schoepite beside metastudtite which was not observed in our case. However, in their investigation, the whole system (water + UO$_2$ matrix) was irradiated whereas in our work only water in contact with the UO$_2$ particles was irradiated. The spectroscopic analysis performed in our work also showed that when water in contact with the UO$_2$ particles was irradiated in closed atmospheres, the oxidation step during irradiation was limited due to its inhibition by H$_2$ produced by water radiolysis. Few days after irradiation in these latter conditions, in particular after H$_2$ evacuation, oxidation of the UO$_2$ surface and formation of metastudtite took place again which confirms that this gas has an inhibition effect on the corrosion process. This result is consistent with the analytical characterization of the irradiated solution which showed two-fold lower uranium releasing, four-fold higher quantity of H$_2$O$_2$ and consumption of H$_2$ produced by water radiolysis in closed atmosphere. In this
latter condition, the higher quantity of H$_2$O$_2$ and the consumption of H$_2$ observed let us conclude that the inhibition process did not occur by direct action of H$_2$ on the oxidant but by interaction between the H$_2$ produced by water radiolysis and the UO$_2$ surface. This result can be confirmed by the work of Pastina and Laverne$^{47}$ who studied the effect of H$_2$ on H$_2$O$_2$ production in $^{4}$He$^{2+}$ radiolysis of water. They showed that 800 μM of H$_2$ has no effect on the production of H$_2$O$_2$ which reinforce our hypothesis supposing that H$_2$ did not react directly with H$_2$O$_2$. Besides, some authors$^{48}$ reported that the UO$_2$ surface itself can act as a catalyst of dissolved hydrogen causing the reduction of any oxidized phase (U(VI)) formed by oxidation with H$_2$O$_2$ to its reduced form (U(IV)). This catalytic process cannot be excluded in our case; however, concentration of H$_2$O$_2$ observed in closed atmosphere was four-fold higher than that found in open atmosphere which means that the latter process, if held, was not the principal inhibition path. Another explanation of the absence of oxidation in closed atmosphere may be considered when taking into account possible interactions between the UO$_2$ surface and dissolved H$_2$ molecules (e.g. hydrogen bonds) which may form a sort of barrier preventing H$_2$O$_2$ from arriving to the UO$_2$ surface and oxidize it as presented on Figure 8.

![Figure 8](image)

**Figure 8**: Representation of possible interactions (hydrogen bonds) between dissolved H$_2$ and the UO$_2$ surface preventing the oxidation of this latter by H$_2$O$_2$ produced by water radiolysis.

These interactions may increase the solubility of H$_2$ in water which may explain the low G(H$_2$) value obtained in our work after irradiation in closed atmosphere comparing to G(H$_2$) for pure water (around 1/3). This hypothesis may be reinforced by the fact that the solubility
of H₂ in water \((1.535 \times 10^{-3} \text{ mol l}^{-1} \text{ at } 25^\circ \text{C} \text{ and } 1 \text{ bar})\) is of the order of magnitude of H₂ concentrations produced by water radiolysis in this work.

The data reported in the literature about soluble uranium species leached into the solution by radiolytic corrosion of UO₂ is rare and comparison to our results is very difficult due to the differences in the irradiation conditions. In a recent work, Trummer et al.\textsuperscript{27} studied by simulation the effect of H₂ on the radiation induced dissolution of UO₂-base spent fuel. The concentration of soluble uranium species in the solution was around \(10^{-10} \text{ mol l}^{-1}\) for a dose between 3.2 and 17.1 kGy and a H₂ pressure of 40 bar. This value is lower than that obtained in our work (around \(5.2 \times 10^{-7} \text{ mol l}^{-1}\)) when the UO₂ particles were corroded in closed atmosphere with a dose between 43.7 and 87.3 kGy. However, we should note that the difference in the values may be due to the differences in the experimental conditions between the two works, in particular the dose rate effect which is the main parameter controlling the radiolytic corrosion of UO₂.

Concerning UO₂ dissolution rates, it appears from Table 1 that the dissolution rate of UO₂ depends largely on the irradiation conditions, in particular, the dose rate and the irradiation atmosphere. However, we can consider that the steady state of the uranium concentration obtained in this work is comparable to those reported in the literature despite the differences in the irradiation conditions.

Besides, SEM pictures were realized on the surface particles after irradiation in order to determine the zones most affected by the corrosion process. Regardless the irradiation atmosphere, the grain boundaries are a lot more degraded than the UO₂ grains. For instance, Figure 9 shows the surface of a UO₂ particle irradiated in open atmosphere at a dose of 87.3 kGy.
Figure 9: SEM picture of the surface of UO₂ particles corroded in open atmosphere.

The corrosion did not occur then homogeneously on the entire surface. Some regions of the grains surface are indeed more corroded.

Finally, as mentioned before, it is not actually possible to have a detailed mechanism of the oxidative dissolution of UO₂ particles by the radiolysis products of water. Thus, determining the kinetic constant of the different steps of this mechanism is not neither possible. On the other hand, in order to have a complete understanding of the radiolytic corrosion of UO₂, further studies will be later performed with pulse ⁴He²⁺ beam to determine the effect of the radical species produced by water radiolysis on UO₂ corrosion. Indeed, this type of experiment will permit us to measure the radical species produced during irradiation (e.g. OH⁻) and determine their role in the radiolytic corrosion of UO₂.

6. Conclusion

This work was done to study the effect of the molecular species produced by ⁴He²⁺ beam radiolysis of water on UO₂ corrosion. For that, UO₂ particles were covered by ultra-pure water and the ⁴He²⁺ beam was monitored so that only the liquid was irradiated.
After irradiation, the effect of the molecular species was investigated by characterizing the corroded solid particles, quantifying \( \text{H}_2 \) and \( \text{H}_2\text{O}_2 \) produced by water radiolysis and measuring the soluble uranium species migrated to the solution. The influence of two parameters was investigated: the absorbed dose and the oxidant/reducing character of the irradiation atmosphere. In open atmosphere, corrosion of UO\(_2\) started with an oxidation step by \( \text{H}_2\text{O}_2 \) produced by water radiolysis, which leaded to the formation of a metastudtite phase on the particles surface. The oxidized phase underwent later a dissolution reaction which resulted in migration of soluble uranium into the solution. In closed atmospheres, UO\(_2\) corrosion was limited due to the inhibition effect of \( \text{H}_2 \): metastudtite was not observed, \([\text{H}_2\text{O}_2]\) was four fold higher, \([\text{U}]\) was twofold lower and \(2/3\) of \( \text{H}_2 \) produced by water radiolysis was consumed. \( \text{H}_2 \) did not react then with \( \text{H}_2\text{O}_2 \) but directly interacted with the UO\(_2\) surface. The inhibition process may occur by adsorption of \( \text{H}_2 \) on the material surface which prevents \( \text{H}_2\text{O}_2 \) from oxidizing it.

Dissolution rate of the soluble uranium leached into the irradiated solution were also calculated in this work as a function of the time and the absorbed dose. The dissolution rate values were lower in presence of \( \text{H}_2 \). These values depend on the irradiation conditions, in particular the dose rate which is the main parameter influencing it.

After irradiation, SEM pictures realized on the UO\(_2\) particles showed that the corrosion did not take place homogeneously on the particles surface. The grain boundaries were more corroded than the grains.

Further studies will be later performed with pulse \(^4\text{He}^{2+}\) beam to determine the effect of the radical species produced by water radiolysis on UO\(_2\) corrosion. This will permit us to have a global radiolytic data and a complete understanding of UO\(_2\) corrosion.
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Authors have experimentally and quantitatively evidenced that the radiolytic corrosion of UO₂ is inhibited by the H₂ produced by the water radiolysis.