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Oxidation and dissolution of UO_2 in bicarbonate media: Implications for the spent nuclear fuel oxidative dissolution mechanism

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Abstract

The objective of this work is to study the UO_2 oxidation by O_2 and dissolution in bicarbonate media and to extrapolate the results obtained to improve the knowledge of the oxidative dissolution of spent nuclear fuel. The results obtained show that in the studied range the oxygen consumption rate is independent on the bicarbonate concentration while the UO_2 dissolution rate does depend on. Besides, at 10^{-4} mol dm^{-3} bicarbonate concentration, the oxygen consumption rate is almost two orders of magnitude higher than the UO_2 dissolution rate. These results suggest that at low bicarbonate concentration ($<10^{-2}$ mol dm^{-3}) the alteration of the spent nuclear fuel cannot be directly derived from the measured uranium concentrations in solution. On the other hand, the study at low bicarbonate concentrations of the evolution of the UO_2 surface at nanometric scale by means of the SFM technique shows that the difference between oxidation and dissolution rates is not due to the precipitation of a secondary solid phase on UO_2.

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1. Introduction

The stability of the spent nuclear fuel matrix is a key process in the performance assessment of the final nuclear spent fuel disposal in geological formations. In this context, the dissolution of spent fuel as well as its chemical analogues UO_2 (s) and SIMFUEL have been studied as a function of pH, carbonate concentration, temperature and dose of α- and γ-radiolysis under reducing, anoxic and oxidising conditions [1–7].

Some of these studies are based on the determination of the dissolution rate of the spent fuel or unirradiated UO_2 (s) at different conditions by measuring the uranium concentration in the steady state using continuous flow reactors. Gray et al. have carried out an extensive work [5,8] determining dissolution rates of both spent fuel and UO_2 (s) as a function of oxygen partial pressure, carbonate concentration and temperature. The effect of pH and oxygen partial pressure has also been extensively studied by Torrero et al. [7] and de Pablo et al. [9].

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In de Pablo et al. [10] we have proposed an oxidative dissolution mechanism for unirradiated UO_2, according to experimental evidences [11,12] of the evolution of the solid surface. This mechanism has three main steps:

(1) sorption of the oxygen and electron transfer to oxidise part of the surface of the U(IV) solid to U(VI);
(2) surface complexation of the U(VI) with carbonate;
(3) detachment of the surface complex formed.

This mechanism explains most of the overall dissolution rates found in the literature, including some obtained using spent fuel [5] and natural uraninites [13,14].

However, the recent development of models for the stability of the spent fuel matrix based on the production of oxidants by the α-radiolysis of water [15–17] shows the need to separate the contributions in the overall rate of both the oxidation and the dissolution steps. Up to now, the determining step of the overall process has been considered to be the oxidation since the dissolution has been assumed to be very fast in carbonate medium. This assumption has not been experimentally proven for the whole range of bicarbonate concentrations studied.

In order to separate the two processes we have determined, in the present work, both the oxidation rate of unirradiated UO_2 (s) by measuring the oxygen reacting with the UO_2 solid surface, and the dissolution rate by measuring the uranium concentration in solution as a function of time.

In addition, a special attention has been devoted to the evolution of the solid surface composition with time as well as the possibility of uranium secondary phase formation. For this study we have used the Scanning Force Microscopy technique, which has been recently used in studies of UO_2 dissolution in the presence of hydrogen peroxide [18].

2. Experimental

2.1. Leaching experiments

The experiments were carried out in a batch reactor of cylindrical shape, especially designed to avoid any gas phase in the reactor even when the samples are collected (see Fig. 1). 2.6 g of unirradiated synthetic uranium dioxide with a particle size of 10–50 μm were used, this solid was supplied by Empresa Nacional del Uranio S.A. (ENUSA). The specific surface area was determined by the BET method to be $0.098 \pm 0.006\ m^2\ g^{-1}$. The solid was washed prior to the start of the experiments with diluted $HClO_4$ to dissolve oxidised phases on the surface.

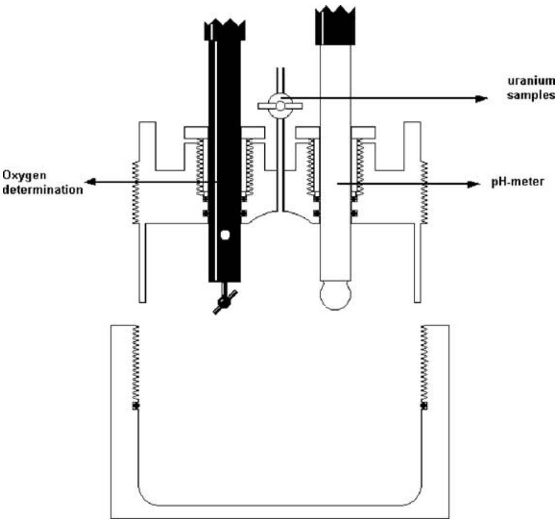

Fig. 1. Reactor used in the experiments.

A constant ionic strength of $0.1\ mol\ dm^{-3}$ was kept in all the experiments by the addition of $NaClO_4$. The bicarbonate concentration in solution was varied between 10^{-4} and $5 \times 10^{-2}\ mol\ dm^{-3}$. The initial oxygen concentration in solution was $2.6 \times 10^{-4}\ mol\ dm^{-3}$, obtained by saturating the solutions with a mixture of 21% of O_2 (g) in N_2 (g) before the start of the experiments. Experiments were carried out at 25 °C.

The uranium concentration in solution was determined using ICP-MS (Perkin–Elmer ELAN 6000). Both oxygen concentration in solution and pH were continuously monitored by using a Dissolved Oxygen Meter (ORION 850) and a combined glass electrode, respectively. A blank experiment was carried out in the absence of uranium dioxide in order to determine the oxygen consumption due to the Dissolved Oxygen Meter.

The percentage of U(IV) and U(VI) on the solid surface was determined by using X-ray photoelectron spectroscopy (XPS, VG Scientific Microlab MK II).

2.2. SFM experiment

We used a disk of unirradiated UO_2 that weighted 0.31 g and was 10 mm in diameter and 0.8 mm thick. The disk was mechanically polished to 1 μm roughness prior to the leaching experiment. The specific surface area of the disk was calculated to be $1.8 \times 10^{-3}\ m^2\ g^{-1}$ based on the surface area of a pellet of the same material [7] and taking into account the ratio between surface area and mass of the two geometries.

Two carbon markings were deposited on the surface of the solid by means of the spot function of a scanning electron microscope (Jeol JSM-840). The deposition of these markings allows more precise results deduced from the topographic profiles [26,27].

The disk was put into a methacrilate cylindrical shaped batch reactor. Before the start of the experiment, the disk was cleaning with $HClO_4$ at pH 3 in order to eliminate the presence of possible oxidised layers on the UO_2.

The experiment was carried out with a batch methodology in a reactor with 200 cm^3 of a 10^{-4} mol dm^{-3} $NaHCO_3$ solution. 0.1 mol dm^{-3} $NaClO_4$ was used as ionic medium. The experiments were carried out at room temperature and open to air. Samples were taken periodically to determine the evolution of the total uranium concentration in solution with time.

Ex situ SFM was used at different times throughout the experiment to observe the evolution of the UO_2 surface in contact with oxygen and bicarbonate. Prior to each observation, the UO_2 disk was removed from the batch reactor and rinsed with ethanol.

Ex situ measurements were conducted at room temperature using an Extended Multimode SFM head with a Nanoscope IIIa electronic controller (Digital Instruments Veeco Metrology Group). Imaging was carried out in tapping mode, an intermittent-contact technique used to reduce lateral and frictional forces.

In addition, because the SFM technique does not allow to know the chemical composition of the surface of the solid, an X-ray diffraction (XRD, Brucker D5005) machine with a Cu Lα radiation source was used to identify any potential secondary solid phase formed on UO_2.

3. Results and discussion

3.1. UO_2 dissolution and oxidation rates

As indicated above, we measured the variation of both oxygen and uranium concentration in solution as a function of time. An example of the data obtained is shown in Fig. 2, where it can be seen that uranium concentration increases linearly with time while oxygen concentration in solution decreases linearly with time. The UO_2 dissolution rate has been calculated from the slope of the uranium concentration variation with time, while oxygen consumption rate has been calculated considering the slope of the oxygen concentration decrease with time.

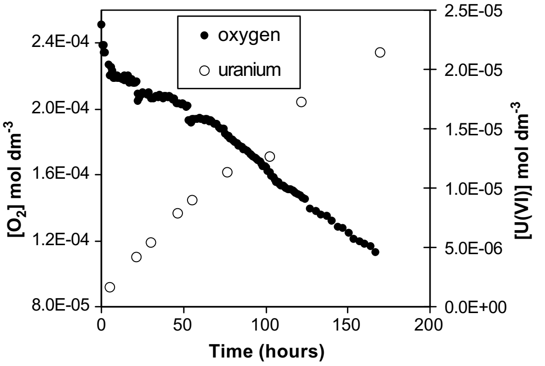

Fig. 2. Typical series of data obtained in the experiments ($[HCO_3^-] = 10^{-2}$ mol dm^{-3}).

The results obtained in terms of UO_2 dissolution rate, as determined from the uranium released to the solution, as a function of bicarbonate concentration are shown in Fig. 3. In this figure, dissolution rates are compared to those obtained by different authors [5,6,10,19–23] with both spent fuel and unirradiated uranium dioxide obtained in flow through reactors.

As it can be seen, a similar trend is obtained in spite of the different experimental approaches used, i.e. batch versus flow through reactors. Consequently, the dependence of both UO_2 and spent fuel dissolution rates on bicarbonate concentration at oxidizing conditions is well established. A more detailed mechanistic explanation deduced from this dependency of the dissolution rate with bicarbonate concentration can be found in de Pablo et al. [10].

On the other hand, the oxidation rates, which can be considered the oxygen consumption rates measured in our experiments, are plotted in Fig. 4 together with dissolution rates determined above. As it can be seen in this figure, the difference between oxidation and dissolution rates increases when bicarbonate concentration decreases indicating that at low bicarbonate concentration it is not possible to consider the dissolution rate equal to the alteration rate of the UO_2, since part of the solid is oxidised at these conditions. From a mass balance study, we have calculated the $U_{released}/U_{oxidised}$ ratio, where

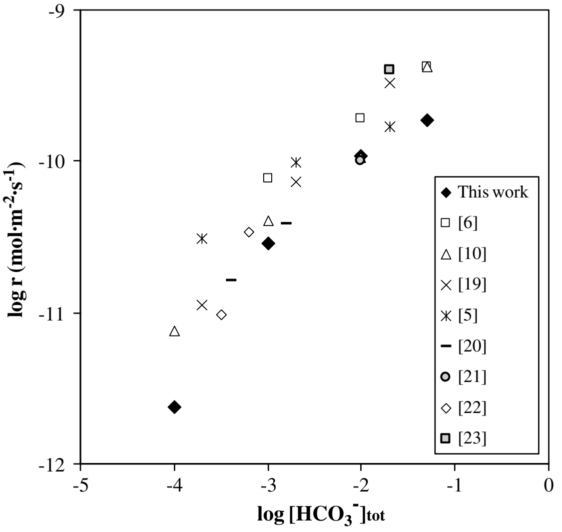

Fig. 3. Comparison of the dissolution rates obtained in this work with other published values.

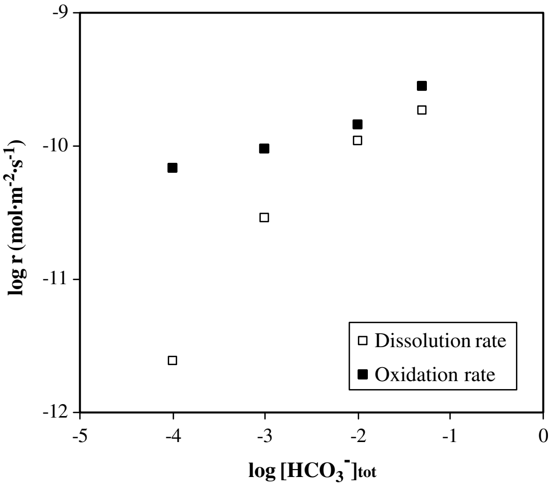

Fig. 4. Dissolution and oxidation rates obtained in this work at different bicarbonate concentrations.

$U_{released}$ accounts for the mols of uranium in the aqueous phase and $U_{oxidised}$ accounts for the mols of uranium that have been oxidised according to the oxygen consumed in the experiments.

The results show that at low bicarbonate concentrations this ratio has values around 0.03 while at higher bicarbonate concentrations the values are near 0.8, which indicates that the higher the bicarbonate concentration in solution the higher the uranium dissolved.

3.2. Solid surface composition

In order to support the results presented above, a XPS study of the final surface of the solids was performed. By deconvolution of the $U_{4f7/2}$ peak [12,24] in the XPS spectra, we determined the percentage of U(VI) in the solid surface at the end of the experiments. As it is shown in Fig. 5, at a relatively high bicarbonate concentration (experiment with 10^{-2} mol dm^{-3}) the surface has a composition of $UO_{2.05}$, whereas in the experiments performed at lower bicarbonate concentrations (10^{-3} and 10^{-4} mol dm^{-3}), the solid surface has a composition of $UO_{2.20}$.

There are two different possibilities to explain the presence of a relatively high percentage of U(VI) on the UO_2 surface at low bicarbonate concentration: (1) oxidation of the solid surface followed by a slow dissolution of U(VI); (2) precipitation of a U(VI) secondary phase.

3.3. SFM study of the UO_2 surface at low bicarbonate concentration

In order to test the precipitation of a secondary solid phase on the UO_2 surface at low bicarbonate concentrations, where dissolution rates are significantly lower than oxidation rates and XPS shows a more oxidised surface, we have performed an experiment using the SFM technique, which allows the study of the processes that occur in a solid surface at a nanometric scale.

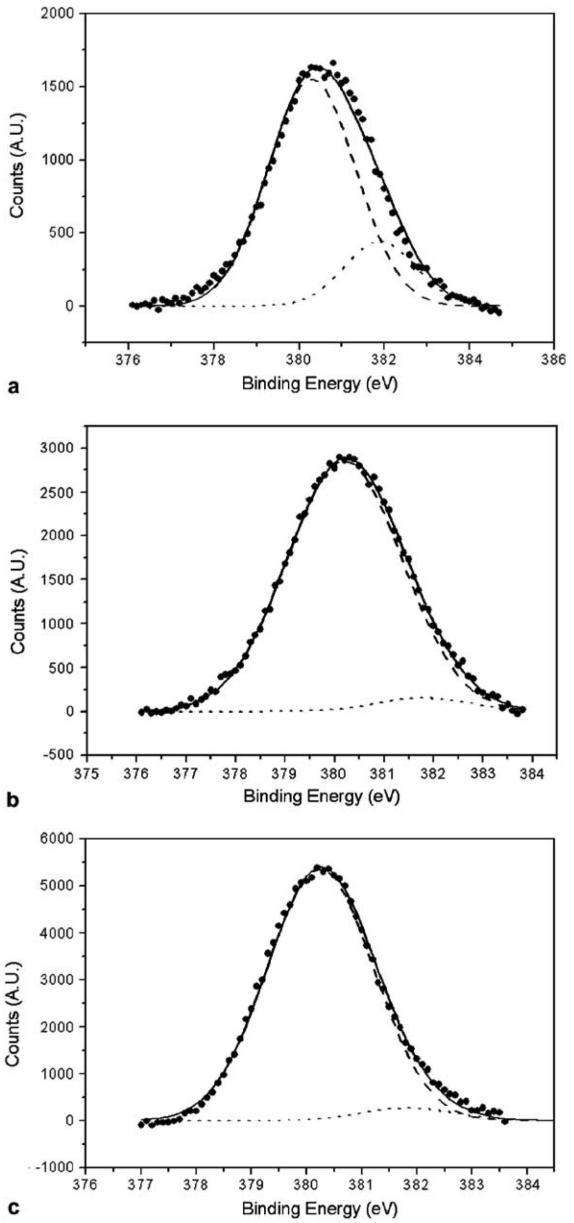

Fig. 5. XPS spectra of the $U_{4f7/2}$ peak of the solids at the end of the experiments at (a) $[HCO_3^-] = 10^{-4}$ mol dm^{-3}, (b) $[HCO_3^-] = 10^{-3}$ mol dm^{-3} and (c) $[HCO_3^-] = 10^{-2}$ mol dm^{-3}. The component at lower energies corresponds to the U(IV) and the component at higher energies to the U(VI).

In this sense, as we said above, a disc of unirradiated UO_2 was introduced in a reactor containing a

10^{-4} mol dm^{-3}HCO_3^- solution. Periodically, the disc was taken off of the reactor to record the SFM images and the uranium concentration in solution was determined by ICP-MS.

The variation of the uranium concentration in solution is shown in Fig. 6. From the slope of this variation during the first 65 days and taking into account the surface of the disk we have calculated a dissolution rate of $(1.12 \pm 0.02) \times 10^{-11}$ mol m^{-2} s^{-1}. This value is similar to the dissolution rates, between 9×10^{-12} and 1×10^{-11} mol m^{-2} s^{-1}, reported by de Pablo et al. [10] at the same bicarbonate concentration in a flow-through reactor.

The SFM images taken during the experiment reflected no significant differences in the aspect of the solid surface and no deposition of a secondary phase could be observed. On the other hand, the XRD spectrum of the solid surface at the end of the experiment did not show other solid phase than UO_2.

In addition, we made an analysis of the topographic profiles, which can be seen in Fig. 7. We calculated in six different points the height difference between the initial solid and the solid after 100 d of contact with the solution. The heights were quantified with reference to unchanged points, the carbon markings (indicated with R1 and R2 in Fig. 7) [25–27]. The variation of the height

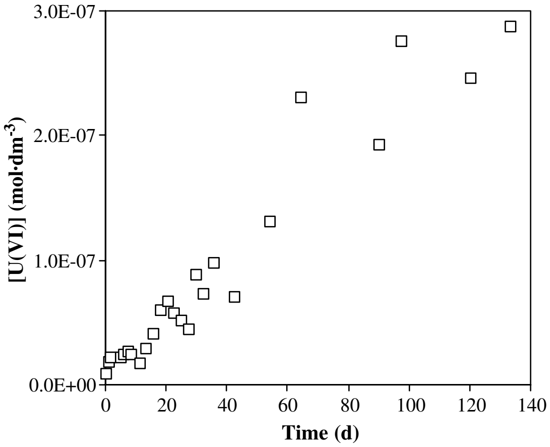

Fig. 6. Variation of the uranium concentration in solution with time in the SFM experiment (with bicarbonate 10^{-4} mol dm^{-3}).

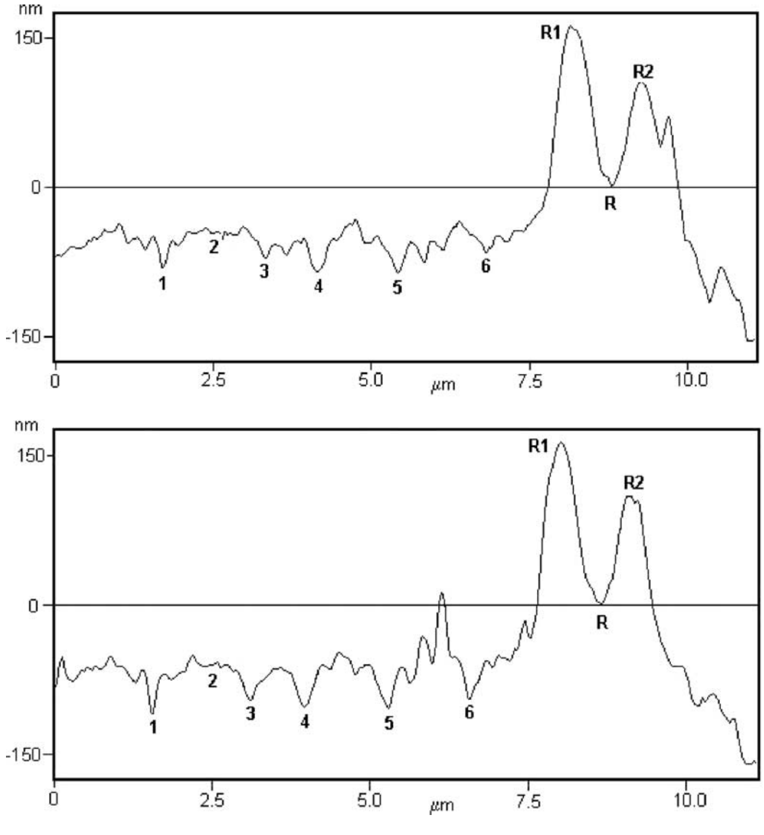

Fig. 7. Topographic profiles illustrating the height variation between the initial UO_2 surface (first picture) and the surface after 97.7 d (second picture) in the experiment with bicarbonate 10^{-4} mol dm^{-3}. The points R1, and R2 are unchanged reference points, corresponding to the carbon markings.

Table 1
Heights (in absolute values) measured in the different points with respect to the reference points

Point	Position of the point (μm)	Initial height (nm)	Height after 97.7 days (nm)
1	7.1	83.05	115.72
2	6.3	47.71	63.38
3	5.5	74.12	97.82
4	4.6	85.44	103.83
5	3.6	87.75	105.64
6	2.0	69.27	98.03

(in absolute values) of the six points can be seen in Table 1. Considering the height variation in all the positions, no deposition of a secondary solid phase is observed.

From the variation of the heights with time it was possible to determine the UO_2 dissolution rate by using the following equation:

$$r_{\text{diss}} = h(\text{m}) \cdot \rho(\text{kg m}^{-3})/P_{\text{A}} \text{ of } \text{U}(\text{kg mol}^{-1}) \cdot t \text{ (s)}$$

where ρ is the UO_2 density (10960 kg m^{-3}), P_A is the atomic weight of uranium, and t is the elapsed time. The value obtained considering the six different height is $(1.2 \pm 0.4) \times 10^{-10}$ mol m^{-2} s^{-1}. This value is higher than the one determined from uranium release, $(1.12 \pm 0.02) \times 10^{-11}$ mol m^{-2} s^{-1}, which is not surprising because it corresponds to the dissolution of the highly reactive sites of the surface and it is not representative of the global dissolution rate, as it has been commented elsewhere [26].

The decrease of the height of the six points together with the observations of the SFM images and the DRX characterization of the surface of the solid reflects the fact that dissolution (and no precipitation of a secondary phase) is the process involved in the UO_2 surface at these conditions.

Thus, the difference between oxidation and dissolution rates observed at low bicarbonate concentration as well as the increase of the percentage of U(VI) in the surface, are due to the oxidation of the UO_2 and a slower release of U(VI) than at higher bicarbonate concentrations. This would indicate that when considering the UO_2 (or spent nuclear fuel) oxidative dissolution mechanism, it should not be assumed that the oxidised layer formed on UO_2 is rapidly dissolved at low bicarbonate concentration.

4. Conclusions

The main conclusions of this work are:

(1) At low bicarbonate concentration ($<10^{-2}$ mol dm^{-3}), the alteration of the spent nuclear fuel cannot be directly derived from the measured uranium concentrations in solution.
(2) The lower dissolution rates (compared to oxidation rates) at low bicarbonate concentrations are not due to the precipitation of a secondary phase.
(3) The mechanisms proposed for the spent nuclear fuel oxidative dissolution should take into account that at relatively low bicarbonate concentrations a fast detachment of the uranium(VI) formed in the surface cannot be assumed.

Acknowledgements

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