Surface and electrochemical controls on UO₂ dissolution under anoxic conditions

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Abstract

The escape of radionuclides from underground spent nuclear fuel disposal facilities will likely result from anoxic dissolution of spent nuclear fuel by intruding groundwater. Anoxic dissolution of various forms of uranium dioxide (UO$_2$), namely bulk pellet, powder and thin film, has been investigated. Long-duration static batch dissolution experiments were designed to investigate the release of uranium ions in deionized water and any surface chemistry that may occur on the UO$_2$ surface. The dissolved uranium concentration for anoxic dissolution of nearly stoichiometric UO$_2$ was found to be of the order of 10$^{-9}$ mol/l for the three different sample types. Further, clusters (~500 nm) of homogenous uranium-containing precipitates of ~20–100 nm grains were observed in thin film dissolution experiments. Such a low solubility of UO$_2$ across sample types and the observation of secondary phases in deionized water suggest that anoxic UO$_2$ dissolution does not only occur through a U(IV)$_{\text{(solid)}}$ to U(VI)$_{\text{(aqueous)}}$ process. Thus, we propose that dissolution of uranium under anoxic repository conditions may also proceed via U(IV)$_{\text{(solid)}}$ to U(IV)$_{\text{(aqueous)}}$, with subsequent U(IV)$_{\text{(precipitates)}}$ in a less defective form. Quantitative analysis of surface-sensitive EBSD diffractograms was conducted to elucidate lattice-mismatch induced cracks observed in UO$_2$ thin film studies. Variable temperature anoxic dissolution was conducted, and no increased uranium concentration was observed in elevated temperatures.

Keywords: UO$_2$; anoxic dissolution; secondary phases; surface alteration; nucleation; geological disposal
1. Introduction

The relative abundance of uranium as an energy resource, coupled with the high costs of spent nuclear fuel (SNF) reprocessing and the associated risks of nuclear proliferation, make a strong case for direct disposal of SNF in deep underground geological disposal facilities (GDF) [1,2]. The evaluation of such a facility is a multifaceted problem; of which an important consideration is the projected radionuclide release rates from the spent fuel in the case of groundwater intrusion and secondary containment failure [3,4]. Extensive work had been devoted to the analysis of the different aspects of spent nuclear fuel dissolution under geological disposal conditions [2–11]. Depending on burn-up and local position in the rod (the linear power rating), spent fuel is comprised of ~96 at% uranium dioxide (UO₂) matrix with ~3 at% of fission products and ~1 at% of transuranium elements. As such, previous studies have shown that the release of radionuclides (apart from instant release fractions [12,13] of several percent of total inventory for some radionuclides), is mainly dependent on dissolution of the UO₂ matrix under the oxygen-free environment of deep geological facilities [3,4].

However, there has been no consensus on the proposed mechanisms of anoxic UO₂ dissolution in the literature. Ulrich et al. [14] initially suggested that anoxic dissolution of UO₂ proceeds via Eq. 1:

\[ \text{UO}_2(s) + 4H^+ \rightarrow U^{4+} + 2H_2O \] (1)

Based on an XPS analysis of leached UO₂ samples consisting of bulk and surface U(IV), they noted surface oxidation to 7–10% U(VI) and ~20% U(V) under reducing dissolution conditions (5 vol% H₂, 95 vol% N₂ atmosphere) which was explained by a sequential oxidation mechanism of U(IV) to U(V) to U(VI) by water molecules, similar to
that proposed by Shoesmith and Sunder [15] for UO₂ dissolution below the oxidative
treshold potential \((-100 \text{ mV versus saturated calomel electrode on the UO}_2 \text{ surface})\).

\[
\text{UO}_2 + H_2O \rightarrow (U^{V}O_2OH)_{\text{ads}} + H^+ + e_{(\text{aq})}
\]  
\[\text{(2)}\]

\[
(U^{V}O_2OH)_{\text{ads}} + H_2O \rightarrow (U^{VI}O_2(OH)_2)_{\text{ads}} + H^+ + e_{(\text{aq})}
\]  
\[\text{(3)}\]

A caveat to the applicability of these equations is the absence of detectable U(VI) in the
sample solutions with a kinetic phosphorescence analyzer (KPA), although U(VI) is a
few orders of magnitude more soluble than U(IV) [16]. Ulrich et al. concluded that the
anoxic UO₂ dissolution was primarily driven by hydrolysis of U(IV) and not by oxidation
to U(VI) [14]. However, it is possible that, although the sample transfer occurred with
minimal exposure to oxygen in this work, a short exposure was enough to induce
surface oxidation, which led to the observed U(V) and U(VI) at the surface. In addition,
Ollila et al. [5] reported that after anoxic (N₂ atmosphere) dissolution of UO₂ in deionized
water, the uranium oxidation state in the solution was U⁷⁺ as determined by anion
exchange methods in an HCl medium within an inert atmosphere glove box (N₂).
However, there was no information on the characterization of UO₂ samples in contact
with the solution. In view of the above literature, the motivation of this paper is to
investigate the anoxic dissolution mechanism of uranium dioxide with respect to the
anoxic conditions pertaining in a GDF.

Considering the long timeline for SNF storage and disposal, this study focuses on the
long-term surface changes and products due to dissolution of spent nuclear fuel. Three
anoxic experiments with near stoichiometric uranium dioxide were conducted with
different aims. 1) The dissolution of uranium dioxide in solid pellet electrode form to determine electrochemical variation of both solution and surface and subsequent analysis of surface oxidation with Raman spectroscopy, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis techniques. 2) The dissolution of a single crystal uranium dioxide thin film (~100 nm thickness) deposited epitaxially on a (001) silicon substrate, to ascertain uranium dissolution and potential secondary phase precipitation [9,10] on a topographically flat surface with high surface sensitivity. 3) High-surface area UO₂ powder in steel heating vessels with PTFE (polytetrafluoroethylene) liners to analyse differences in dissolved uranium concentrations at different temperatures, simulating decay heat at different disposal ages.

2. Materials and methods

2.1. Anoxic conditions

Anoxic dissolution involves the exclusion of dissolved oxygen in the experiments as far as reasonably possible. All dissolution experiments were conducted in positive pressure gloveboxes with an argon atmosphere with oxygen concentrations controlled to 0.1 ppm O₂ for the thin film and powder experiments and a nitrogen atmosphere of 2.0 ppm O₂ for the solid pellet experiments. In all cases, the dissolution experiments took place in sealed containers containing deoxygenated water. Deionized Milli-Q water (18.2 MΩ/cm), for both dissolution and sample washing, was sparged with 5 vol% H₂ in 95 vol% Ar gas mixture for 6 hours to reduce the amount of dissolved oxygen to a
suitable low level. Post-sparging testing with CHEMetrics® Oxygen CHEMets Kit K-7540 revealed dissolved oxygen content below the detection limit of 2.5 ppb. The dissolved oxygen content was measured at the start and end of each experiment and was found to be low at < 2.5 ppb. Sampling of the solution took place as rapidly as possible and occurred infrequently. During the intervening periods, the vessels were sealed.

2.2. Sample preparation

Efforts have been taken to reduce the amount of U(VI) and U(V) from surface oxidation of the nominal UO₂ samples. Powder and thin film samples were reduced in a 5 vol% H₂, 95 vol% Ar atmosphere and heating to 800°C [17]. Sintered UO₂ pellets were polished with SiC paper under deionized water to remove any oxidized surface layer of UO₂ₓ that arises from exposure to the atmosphere for extended periods of time [18]. Anderson et al. [19] have previously reported that such surface oxidation occurs slowly as a logarithmic function of time due to the chemisorption of oxygen at room temperatures. Pellet and thin film samples were subsequently pre-washed before undertaking dissolution experiments.

A detailed description of the fabrication and initial characterisation of sintered UO₂ pellets has been previously reported by Hiezl et al. [20] with additional characterisation by Popel et al. [10]. In order to make suitable electrodes for use in long-term dissolution experiments, stoichiometric UO₂, disc-shaped slices of sintered pellets (~1 cm diameter and ~1 mm thickness) were mounted onto a threaded brass rod using silver-loaded epoxy. This assembly was then placed in a cylindrically shaped mould and cast in
epoxy resin in order to produce a suitable sealed working electrode. Prior to being
characterised, the working electrodes were polished using 600 and 1200 grit SiC paper
under deionized water (to avoid uranium dust formation). Such a polishing process
reduces differences in electrode surface area between samples and enhances the
reproducibility of triplicate dissolution experiments (see Section 2.5.1). Prior to
dissolution, the polished surfaces were examined by scanning electron microscopy and
Raman spectroscopy (see Section 2.3) before placing them in 10 ml of deoxygenated,
deionized water in a Nalgene® bottle for 21-hours pre-washing under a N₂ atmosphere
with 2.0 ppm O₂. This pre-wash phase again aims to remove any higher oxidation
uranium oxide phases which might have been formed, albeit slowly, in the processing
atmosphere and relies on the higher solubility of surface UO₂⁺ₓ phases vs. bulk UO₂.
Indeed, previous literature studies [21–23] have found that the solubility product at the
standard state, Ksp⁰ of U(VI) is -22.46, significantly higher than that of U(IV), -52.0 with
slight variation dependent on solid form [24].

The thin film of UO₂ was produced by direct current reactive sputtering onto a single
crystal Si substrate with (001) orientation using a Labstation machine at the European
Commission Joint Research Centre (EC-JRC), Karlsruhe. The substrate was cleaned
before the film deposition with ethanol and heated to ~600 °C under pO₂ of 2 × 10⁻⁶
mbar for 40–60 min [25]. A natural uranium metal target was used as a source of
uranium with argon used as the sputtering gas at a pAr set to 5 × 10⁻³ mbar and O₂
used as the reactive gas at a pO₂ set to 7 × 10⁻⁶ mbar. The Si substrate was maintained
at a temperature close to 600 °C. The film was deposited for 30 minutes with deposition
conditions which should give film thickness in the range from 90 to 270 nm. The thin film
sample was then annealed in an anoxic glove box-attached furnace at 800 °C with a reducing mixture of 5 vol% H₂ in 95 vol% Ar for two hours, taking one hour to heat up and three hours to cool down. It was subsequently transferred to another glove box, where the dissolution experiment took place under an argon atmosphere at 0.1 ppm O₂. Finally, pre-wash in 20 ml of sparged deionized water in a plastic bottle for 12 hours was carried out before transfer to a fresh deionized water solution for the dissolution experimental run (see section 2.5.2).

For the powder samples, high surface area, micro-porous UO₂ beads were produced from uranyl nitrate at the EC-JRC by the sol-gel technique [26,27]. About 2.3 g of this powder was weighed and transferred into a 1 ml alumina boat for annealing. In order to achieve stoichiometry, the powder was annealed in a tube furnace attached to a glove box where ingress and egress of the sample into the furnace occurs inside the glovebox with an argon atmosphere (0.1 O₂ ppm). It was annealed at 800 °C for three hours with a reducing gas mixture of 5 vol% H₂ in 95 vol% Ar, after an initial hour of pre-heating to the requisite temperature. There was no pre-wash carried out for this set of experiments.

2.3. Sample characterisation

The solid pellet samples were analysed before and after the dissolution experiment by SEM with EDX as well as a Raman microscopy system. SEM-EDX was carried out at 20 keV using a JSM-6010PLUS (Jeol, Japan). Raman microscopy measurements were taken using a Voyage confocal Raman microscope system (B&WTek, Newark, USA). All Raman spectra were acquired with an excitation wavelength of 785 nm. The sample
was focussed using a 50× objective lens before taking spectra with an integration time
of 40 seconds over a wavenumber range from 190 to 3000 cm⁻¹. Before analysis, the
laser power was adjusted to < 5 mW using neutral density filters in order to avoid any
thermal oxidation of UO₂ to U₃O₆ [28]. In order to account for surface roughness and
surface inhomogeneity, 10 spectra were taken at random locations across the sample
with the highest and lowest outliers removed to produce a sample average.

The thin film sample was analysed before and after the dissolution experiment by
SEM, EDX, X-ray diffraction (XRD) and electron backscatter diffraction (EBSD)
techniques [25]. A FEI Quanta 650F instrument operating at 5 kV with beam spot size 3
under high vacuum was used to acquire SEM images with a Bruker 6130 XFlash EDX
detector. EBSD instrumentation from Bruker with an e-Flash4ID detector associated with
the FEI Quanta 650F SEM was used to obtain EBSD data; the resolution of each
square pixel of 97 nm. The operating voltage was 20 kV and the beam spot size 5.5.
The detector resolution was 320 × 240 pixels, while working distance and sample to
detector distance was 26 mm and 15.5 mm respectively. Analysis of collected EBSD
data from the uranium dioxide thin film was conducted with the computational aid of
MTEX V5.0.3 [29], a freeware toolset for the commercial software package MATLAB™
[30]. The MATLAB™ toolbox MTEX provides a unique way to represent, analyse and
interpret crystallographic preferred orientation, i.e. texture, based on integral (“pole
figure") or individual orientation (“EBSD") measurements.

Due to limitations in examining radioactive uranium oxide powder under vacuum,
capillary XRD was conducted with a Bruker D8 Advance diffractometer (Cu Kα
radiation, λ = 1.541 Å, Ge monochromator and Sol-XE energy dispersive detector).
Measurements were carried out for 12 hours each over an angular range $25^\circ \leq 2\theta \leq 90^\circ$ ($\Delta 2\theta = 0.01^\circ$). Data collection and indexing was performed with Bruker QUANTAX CrystaAlign software [31]. A full Rietveld refinement was carried out of the acquired diffraction patterns. The backgrounds were fitted using linear interpolation and the peak shape was modelled using a pseudo-Voigt function for the micro-porous uranium dioxide powder pre- and post-annealing. Based on the lattice parameter obtained of 5.466 Å, and the equation $a_x = 5.4690 - 0.12x$ [32], a bulk stoichiometric ratio prior to dissolution of UO$_{2.03}$ was found for the UO$_2$ powder. However, in this dissolution study, the bulk stoichiometric ratio may be lower than the surface. As discussed by Sunder [33], the surface is likely to be UO$_{2+x}$ (0 < x < 0.25). This is because XRD is a bulk technique which convolutes the signal from the underlying bulk and surface signals hence typically registering lower values of x than surface sensitive Raman spectroscopy as Raman laser has a lower penetration depth than X-rays.

2.4. Aliquot analyses

For inductively coupled plasma mass spectrometry (ICP-MS), the acquired 1 ml aliquots (see section 2.5) were acidified with another 1 ml of 1 wt% HNO$_3$. All samples were analysed on a Perkin Elmer Nexion 350D ICP-MS instrument. The uranium calibration standards were prepared as an external calibration using serial dilutions of standards (blank, 0.001, 0.01, 0.10, 1.0, 10 ppb, mass basis) prepared from single element high purity standard (CPI, California, USA) in high purity 1 wt % HNO$_3$ (quartz distilled in house). The ICP-MS internal standards were 10 ppb Rh, In and Re and each sample was prepared in 1 wt % HNO$_3$, added online with a t-piece and mixing tube prior to the nebuliser. Two different independently prepared quality control standards (SPS-
SW2, LGC Standards, UK and SCP Science, Canada, ICP-MS Verification Mix) were repeatedly analysed throughout the run to check for calibration accuracy (~5%) with a similar precision. Instrumental drift was less than 10% measured for the raw intensity of the internal standards during the entire analytical run (50 or more solutions per batch). Solutions were analysed using a Micromist FM05 microconcentric nebuliser using a pumped flow rate of 80 μl/min (Glass Expansion, Australia) and a quartz cyclonic baffled spray chamber with nickel sampler and skimmer cones. ICP-MS sensitivity in this configuration was 4.5 × 10^5 cps/ppb In with CeO/Ce ratios = 2.8%. Concentration results were calculated using the Syngistix 1.1 software with a simple linear calibration line and intercept set to zero. The raw intensities were blank subtracted and internal standard normalised before calibration calculations were performed. All results (unknowns and standards) were accurately corrected for dilutions by mass by performing all dilutions with calibrated pipettes on a four place analytical balance.

For the leachate from the uranium dioxide thin film experiment, dynamic light scattering was used to confirm the absence of colloids greater than 5 nm. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) of this leachate found the concentration of dissolved silicon in that experiment to be in the range of 15–25 ppb.

2.5. Dissolution experiment setups

A summary of the dissolution experiments has been tabulated at the end of this section in Table 1.

2.5.1 Solid pellet dissolution
After a 21-hour prewash and drying for 1 hour in the glovebox atmosphere, UO₂ electrodes were immersed in 220 ml of sparged, deionized water in a sealed (screw top) 480 ml Fisherbrand® PTFE dissolution vessel. Dissolution measurements were performed in triplicate, with the setup shown in Fig. 1.

**Fig. 1.** Schematics of the solid UO₂-pellet dissolution experiment set-up to determine the oxidation potential of the UO₂ surface and the solution.

To determine the electrochemical evolution of both the uranium dioxide electrode and the solution potential, open circuit potentiometry was used [34]. Solution potential was
measured using 500 μm Au disk electrodes, polished using 600 and 1200 grit SiC papers and rinsed with deoxygenated, deionized water inside the glovebox prior to immersion. Through the use of a simple switch box, the open circuit potential of both electrodes was measured vs. one reference electrode. In order to avoid chloride contamination, an ammonium nitrate saturated agar double junction was used with an Ag|AgCl reference electrode (RE-5B, BASi, Indiana, USA). All vessels were tightly closed to prevent water evaporation, with gaps around electrodes sealed using parafilm®. One vessel filled with 250 ml of deionized water and an Au electrode only (no UO₂ electrode) was used as a control. During dissolution, batch replenishment tests were conducted, where ~1 ml aliquots of the solution sample were extracted and ~1 ml of the deionized water was replenished at defined time intervals after the start of the experiment, namely 2 hours, 6 hours, 1 day, 5 days, 12 days, 30 days, 61 days and 100 days. The amount of solution in the aliquots was monitored by weighing empty and filled vials on a balance. The dissolution of all samples was performed at an ambient temperature of ~25 °C for 100 days. After completion, the PTFE vessels were acid-washed using 3 M HNO₃. 5 ml of each acid wash was used for ICP-MS analysis in order to determine the presence of any uranium sorption or precipitation on the walls of the leaching vessel.

2.5.2 Thin film dissolution

After the 12-hour prewash and drying for an hour, the UO₂ thin film sample was rinsed with sparged, deionized water and placed into a 60 mL Fisherbrand® PTFE dissolution vessel (shown in Fig. 2) containing 20 ml of the deionized water and two blank Si substrates (to detect any U precipitation/nucleation from the solution) [25].
**Fig. 2.** Schematics of the UO₂ thin film dissolution experiment set up to ascertain uranium dissolution and potential secondary phase precipitation on topographically flat surface with high surface sensitivity.

Static batch replenishment tests were run where ~1 ml aliquots were extracted at various intervals and ~1 ml of the deionized water was replenished. One vessel, filled with 20 ml of the deionized water and two blank Si substrates, was used as a control blank. All vessels were tightly closed to prevent water evaporation. The amount of the solution transferred from the dissolution vessels into the vials was monitored by weighing empty and filled vials. The dissolution experiment was performed at an ambient temperature of ~25 °C for 140 days.

2.5.3 High surface area powder dissolution
After annealing, 100 mg of reduced UO₂ powder was weighed out carefully with a Mettler Toledo XS-104 mass balance and placed into each of twelve stainless steel leaching vessels with a PTFE liner and a Swagelock seal. Upon the addition of 4 ml of sparged, deionized water to each leaching vessel, the leaching vessel was tightly sealed and transferred to another glove box under double containment. The dissolution experiment was performed at 4 different temperatures ambient (~25 °C), 40 °C, 90 °C and 140 °C with deoxygenated water (<2.5 ppb O₂) within an Ar atmosphere glovebox (0.1 O₂ ppm). All vessels were kept in the glove box for the duration of the experiment and tightly sealed. The extraction was carried out on the 390th day with a syringe through a 0.45 µm pore size disposable filter.

Table 1

A summary of the UO₂ dissolution experiments conducted in this study

<table>
<thead>
<tr>
<th></th>
<th>Annealing</th>
<th>Polishing</th>
<th>Prewashing</th>
<th>Oxygen content</th>
<th>Leaching test conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellet</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>2 ppm glovebox</td>
<td>100 days 220 mL deionized water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(SiC paper + deionized water)</td>
<td>(21 hours) – 10 mL</td>
<td>&lt;2.5 ppb dissolved O₂</td>
<td></td>
</tr>
<tr>
<td>Thin film</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>0.1 ppm</td>
<td>140 days 20 mL deionized water</td>
</tr>
<tr>
<td></td>
<td>(5% H₂ in Ar at 800 °C for 2 hours)</td>
<td></td>
<td>(12 hours) – 20 mL</td>
<td>&lt;2.5 ppb dissolved O₂</td>
<td></td>
</tr>
<tr>
<td>Powder</td>
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<td>No</td>
<td>0.1 ppm</td>
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<tr>
<td></td>
<td>(5% H₂ in Ar at 800 °C for 2 hours)</td>
<td></td>
<td></td>
<td>&lt;2.5 ppb dissolved O₂</td>
<td>Filtration 0.45 µm</td>
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3. Results

3.1. Solid pellet dissolution

ICP-MS results, represented in Fig. 13, show a uranium concentration increase from $1 \times 10^{-9}$ mol/l to $\sim 6 \times 10^{-9}$ mol/l being leached from the solid uranium pellet. Such a low level of uranium release is indicative of anoxic dissolution, which has a reduced rate of uranium ion release compared to oxic leaching [35]. This also agrees with the Au-electrode-recorded end solution potential of the uranium containing pots (-56 mV, -52 mV, -52 mV vs. SCE, respectively) and the control pot (-55 mV vs SCE). There is no significantly measurable difference in the solution potential between the leaching and control pots. Such a negligible change in potential is predicted by the Nernst equation, as the dissolved uranium ion release into the solution is so small ($10^{-9}$ mol/l).

![Uranium Concentration vs Time](image)

**Fig. 13.** Uranium concentration in aliquots obtained from three vessels, A, B and C.
containing a uranium pellet each and a control vessel labelled as blank with the same
set up without a uranium pellet.

The concentration of uranium reaches a maximum value of \(6 \times 10^{-9}\) mol/l after 60
days. This may be attributed to the uranium reaching its solubility limit under anoxic
condition, hence there was a decrease in the driving force for further dissolution. Under
such a scenario, reprecipitation can occur, which was confirmed by the detection of
solid uranium precipitates when dissolved uranium was observed in the acid washout
fraction after the experiment. This effect is more pronounced in the uranium
concentration data of the thin film experiment discussed in Fig. 68 under Section 3.2.
ICP-MS of acid washes of the vessels after completion of the dissolution experiment
show a dissolved uranium concentration of \(\sim 3 \times 10^{-9}\) mol/l in 250 cm\(^3\) of 3 mol/l nitric
acid, which is significantly higher than that in the blank pot (\(1 \times 10^{-9}\) mol/l). Such an
observation supports the presence of precipitated uranium phases within the dissolution
vessel.

Fig. 24 shows the recorded open circuit potential of the uranium dioxide electrodes at
the beginning and end of this experiment. These measurements indicate some
evolution [15] of the oxidation state at the uranium dioxide surface. Referencing with a
standard calomel electrode, Shoesmith and Sunder [15] reported potential readings
between -150 to -270 mV for near stoichiometric uranium dioxide in argon-purged
solutions, containing UO\(_{2+x}\). This correlates reasonably well with our data with an
average initial reading of -150 mV shown in Fig. 24. With increased oxidation of the
uranium surface, Shoesmith and Sunder reported that the potential reading would
increase correspondingly, and the region of oxidative dissolution occurs at a threshold
of -50 to -100 mV, where the surface composition approaches a thin layer (2–5 nm) of UO$_2$ as detected from angular-dependent XPS studies [33]. Our experimental reading reaches an average of -70 mV after 100 days of dissolution. We suspect that this might be due to oxidation arising from trace amount of ~2 ppm O$_2$ present in the glovebox atmosphere.

**Fig. 24.** Open circuit potential of the uranium dioxide electrodes recorded at the beginning and end of this leaching experiment. Note values are plotted vs. the standard calomel electrode (SCE) for ease of comparison with data from [15].

Area averaged Raman spectra of a freshly polished UO$_2$ electrode and three UO$_2$ electrodes after 100 days dissolution is shown in Fig. 35, which is a magnification of the Raman shift range 350 to 750 cm$^{-1}$, a region previously reported as being the most important with regards to the degree of oxidation of the UO$_2$ lattice [36,37]. It can be seen that there are two distinct differences between a freshly polished electrode and that leached in deionized water under anoxic conditions. Firstly, there is a decrease in
the large vibration at 440 cm\(^{-1}\), although it should be noted that this intensity difference is only significant for Electrode C after accounting for the measurement’s standard deviation as function of measured area. Secondly, there is a small increase in the broad band from \(\sim 550\) to \(\sim 650\) cm\(^{-1}\).

![Raman spectra](image)

**Fig. 35.** Main: Linear baseline subtracted, area averaged Raman spectra of a freshly polished UO\(_2\) electrode and three UO\(_2\) electrodes after 100 days dissolution over the Raman shift range 350 to 750 cm\(^{-1}\). Inset: Example Lorentzian fit of defect bands at 575 cm\(^{-1}\) and 630 cm\(^{-1}\) from a single measurement point from electrode A after leaching.

Considering the former 440 cm\(^{-1}\) vibration first, group theory predicts that a perfect fluorite structure would be expected to give a triply degenerate Raman active mode (T\(2g\)) [38], typically defined as the fundamental U-O symmetric stretching mode [11,39].
This intense vibration has been reported at \( \sim 445 \text{ cm}^{-1} \) and in the UO\(_2\) pellet samples of Fig. 35 is very close to this value at 440 cm\(^{-1}\). A decrease in the intensity of this peak has been reported as being indicative of deviation from a perfect fluorite lattice structure, caused by either dopant effects or changes in UO\(_2\) stoichiometry [37,39].

Turning now to the broad band from \( \sim 550 \) to \( \sim 650 \text{ cm}^{-1} \), this band has been ascribed to various vibrations that may occur as a result of increasing lattice defectiveness [37]. In the absence of dopants, this region is composed of three overlapping peaks at 550, 575 and 630 cm\(^{-1}\), respectively. The peak at 550 cm\(^{-1}\) has only recently been considered and is tentatively assigned to UO\(_2\) grain boundaries [36,40,41]. The other two peaks are of more interest with regards to the degree of oxidation of the leached samples. The first at 575 cm\(^{-1}\) has been assigned to a longitudinal optical (LO) phonon [37]. Usually, this phonon is forbidden under the selection rule imposed due to lattice symmetry, this peak can appear as a result of changes in translational symmetry at oxygen vacancy sites, leading to lattice disorder and the consequential breakdown in selection rules. These changes in symmetry are caused by either the incorporation of interstitial oxygens or dopant ions. The second peak at 630 cm\(^{-1}\) has been attributed to clustering of interstitial oxygens to form higher oxidation state cuboctahedrons associated with a transition to a defective U\(_4\)O\(_9\) structure [42].

Thus, the ratio of either the 575 cm\(^{-1}\) or 624 cm\(^{-1}\) peak to the 440 cm\(^{-1}\) UO fundamental stretch is indicative of the degree of surface hyperstoichiometry (oxidation) of UO\(_2\) [36]. In order to determine the contributions of each peak to the broad band of Fig. 35, a Lorentzian peak fit was performed for the data of Fig. 35, assuming peak maxima at 440, 575 and 630 cm\(^{-1}\). An example fit for data from electrode A is shown in
Fig. 36 – inset. The results of this peak analysis expressed as a ratio to the 440 cm\(^{-1}\) peak are shown in Fig. 46A for the 575 cm\(^{-1}\) and Fig. 46B for the 630 cm\(^{-1}\) peak.

For both the 575 cm\(^{-1}\) and 630 cm\(^{-1}\) peak, there is a significant increase in surface oxidation heterogeneity as shown by the increase in result standard deviation after electrode leaching in deionized water. However, with the exception of the 575 cm\(^{-1}\) peak for Electrode B, the results show a significant increase in the 575/440 and 630/440 peak ratio after dissolution compared to a freshly polished electrode. This suggests there is an increase in the degree of surface oxidation of the electrodes after leaching for 100 days, corroborating the change in the measured open circuit potentials of the uranium dioxide electrodes discussed above. Finally, despite the observed increase in surface oxidation, no new peaks were observed in the region 800–830 cm\(^{-1}\) [28] in any of the acquired spectra, suggesting that there was no detectable highly-oxidised uranium dioxide (such as U\(_3\)O\(_8\) and above) phases formed during the leaching process.

Scanning electron microscopy and EDX studies of the UO\(_2\) electrode surfaces were carried out pre- (Fig. 57a) and post-dissolution (Fig. 57b) to ascertain the presence of any observable surface morphology changes or secondary phases.
Fig. 46. Lorentzian peak fit results for the data of Fig. 35, assuming peak maxima at 440, 575 and 630 cm$^{-1}$. Results are expressed as a ratio of (A) the 575 cm$^{-1}$ peak and (B) the 630 cm$^{-1}$ peak to the 440 cm$^{-1}$ peak.
Fig 57. SEM at the surface of the (a) pre-leached UO₂ pellet after polishing and (b) the post-leached UO₂ pellet.

Comparison between Figs. 57a and Fig 57b reveals no significant differences before and after the leaching process. Furthermore, the high degree of surface roughness makes the identification of small secondary phases, such as those described for the thin film below, extremely difficult. However, comparison of the area EDX analysis of the electrodes before and after the leaching process reveals a small but measurable increase in oxygen atomic % from 45.71 (±0.23) to 46.44 (±0.35) where the uncertainties arose from the fitting. Again, this agrees with both Raman and open circuit potential measurements (see Figs. 35 and 46) that there is a small oxidation of the surface occurring due to a trace amount of ~2 ppm O₂ present in the glovebox atmosphere.

3.2. Thin film dissolution

A high-quality single-crystalline thin film (~100 nm) of UO₂ deposited on a (001) silicon single crystal substrate has been subjected to an extended anoxic dissolution test in
deoxygenated deionized water under anoxic argon (0.1 O₂ ppm) atmosphere at ambient
temperature (∼25 °C) [25].

The advantages of UO₂ thin film dissolution over pellets or powders is that the flat
morphology of the film facilitates sharper focusing in surface imaging, allowing features
that will have gone unnoticed in samples with rougher surfaces to be made more
apparent.

ICP-MS measurements of both the uranium dissolution vessel and the silicon wafer
only vessel as a function of time are shown in Fig. 68.

![Uranium Concentration vs Time](image)

**Fig. 68.** Dissolved uranium concentrations of extracted aliquots from both the uranium
dioxide thin film dissolution vessel and the silicon wafer only vessel (control),
determined by ICP-MS.

Fig. 68 reveals uranium concentrations in the UO₂ thin film vessel are in the range of
1.2–3.0 × 10⁻⁹ mol/l. This is similar in order of magnitude to the uranium concentration
from the pellet dissolution experiment shown in Fig. 13. The initial increase in uranium
concentrations followed by a decrease and plateau concentration at >10 days
dissolution time is again indicative of a secondary phase precipitation mechanism. The
nature of such deposits is described in more detail in the following sections.

![Micrographs](image)

**Fig. 79.** (a) 30000× magnified secondary electron and (b) backscattered electron
micrographs of the thin film before prewash and heat treatment.

From the pre-leaching SEM micrographs of Fig. 79, the surface is generally smooth with
some trace particulates. Backscattered atomic contrast electron images (not shown)
reveal that the particles are significantly darker than the uranium surface, i.e. they have
a significantly lower atomic number, suggesting they are not uranium dioxide particles.
A likely cause is carbon particles from the carbon tape used in the mounting.

Post-leach SEM images of a UO₂ thin film exposed to anoxic deionized water are
shown in Figs. 849 and 944.
**Fig. 840.** (a) 30000× magnified secondary electron and (b) backscattered electron micrographs of the leached thin film surface after 140 days dissolution.

**Fig. 914.** (a) 200,000× magnification secondary electron and (b) backscattered electron micrographs on the nucelate with clear growth domains ranging between 20-100 nm [25].

From Figs. 840 and 914, there are three main differences that can be seen between pre and post leaching. First, more cracks are observed. These cracks are likely due to the relaxation of the stress between the substrate and thin film during the dissolution process. Both structures are based on the face centred cubic structure with slight differences in the lattice parameters, the uranium dioxide (fluorite type lattice) thin
film and the underlying silicon (diamond type lattice) substrate having lattice parameters
of 5.47 Å [43] and 5.43 Å [44], respectively.

Secondly, high magnification images at 200,000× magnification (Fig. 944) enable the
identification of small pits (20–100 nm) where dissolution has occurred. Based on
previous studies, dissolution is known to initiate at energetically reactive sites [45] such
as point defects, dislocations terminating at the surface and so forth [46–48]. Lastly, Fig.
944 reveal the presence of circular (d = 20–100 nm) secondary phase formations
preferentially nucleated at film cracks. The backscattered electron image in Fig. 944b
shows that the nucleated phases have almost the same contrast as the rest of the film,
which implies similarity in composition. Unfortunately, due to the small size of the
individual grains a reliable EDX analysis could not be carried out to obtain compositional
information on the secondary phase.

SEM imaging was also conducted on the silicon substrates in the same vessel as the
UO₂ thin film, with secondary and backscattered electron images shown in Fig. 102.
**Fig. 102.** Secondary (a) and backscattered electron (b) micrographs of secondary precipitates detected at 30,000× and secondary (c) and backscattered electron (d) micrographs of secondary precipitates detected on blank silicon substrates at 100,000× magnifications.

Fig. 102 shows some precipitates present on the silicon surface. Back-scattered electron image, Fig. 102b and Fig. 102d show that the precipitates contrasted significantly against the silicon substrate suggesting the precipitates have higher atomic numbers. Considering the closed system of deionized water, silicon substrates and uranium thin film, this implies that uranium precipitates are not just a local phenomenon found at the uranium thin film surface. However, the mechanism of precipitation is postulated to be different.
The precipitates formed on the silicon substrates differ significantly from the precipitates formed on the UO₂ thin film in terms of topography and morphology. On the flat silicon substrate, Fig. 102 shows clearly the presence of two types of precipitates, randomly scattered particles and dendritic precipitates at the dissolution trenches and pits, appearing as agglomerates of many grains (~50 nm) with different heights. Both these precipitates have distinctly different morphologies from those formed on the uranium thin film. Spherical UO₂ colloids have previously been reported in oxygen-starved dissolution of uranium dioxide [49]. We believe the scattered particles might be formed from colloidal agglomeration and colloidal precipitation [50] from dissolved uranium in the solution and the dendritic growth are uranium secondary phases formed after interaction with the silicon substrate at dissolution pits/trenches.

Despite the low ionic strength of deionized water contributing to a large kinetic barrier against aggregation [51], the gravitational force on the colloids coupled with the large difference in density between the dense uranium colloids and the surrounding fluid resulted in their precipitation after formation. Neglecting Brownian motion, Fig. 113 shows the relationship of colloidal size to settling time using sedimentation velocity calculation based on the Stokes' equation where sedimentation velocity $\text{\( v \)}$ =

$$
\begin{equation}
\frac{g(\rho_{UO₂} - \rho_f)(d_{UO₂})^2}{18\mu_f}
\end{equation}
$$

where $g$ represents the gravitational acceleration experienced by the colloid, $\rho_{UO₂}$ represents the density of uranium dioxide, $\rho_f$ represents the density of fluid (water), $d_{UO₂}$ represents the diameter of uranium dioxide colloids and $\mu_f$ stands for the dynamic viscosity of water.
**Fig. 13.** Stokes’ equation predicts the relationship between the settling/sedimentation duration against colloidal size for colloidal precipitation in 2 cm deep leaching vessel, similar to our set-up.

For 140 days experiments, colloid precipitation is seen to have a colloidal size limit at 15 nm. Smaller colloids will take a much longer time to settle. The velocity of sedimentation was calculated to be $1.53 \times 10^{-8}$ m s$^{-1}$ for the observed ~50 nm uranium dioxide colloids, achieving sedimentation after 2 cm descent (depth in our experiment) in ~14 days.

To identify the precipitates, EBSD, EDX and XRD were attempted but no signals were detected that allowed differentiation from the underlying UO$_2$ thin film. The lack of elemental analysis opens up possible alternative interpretations for these colloids to be uranium silicates, such as coffinite. Given the high solution concentration of silicon ions (25 ppb or $10^{-6}$ mol/l) from ICP-AES measurement of the solution after the experiment which is close to the $10^{-8}$-mol/l, these colloids are possibly unlikely to be uranium silicate colloids although it is possible that uranium silicate colloids may
have been formed in the near field of the silicon substrate at near neutral pH [52] if there is super saturation of silicon ions of a few orders of magnitude. Our concentrations of silicate to uranium concentration is quite close to that reported in the dissolution of coffinite by S., but this seems unlikely with the low concentration of dissolved silicon ions in the solution.Zenknect et al. [53]. The only caveat to this interpretation is the difficulty in producing coffinite at room temperature in laboratory conditions [6,52,53] where the concentration of silicon is higher than our measured silicon concentrations at 10^{-4} mol/ l. It is however possible that the precipitates might be precursors of coffinite.

The distinct morphology of the dendritic formation implies a different secondary phase from that observed at the uranium thin film. From the sharp contrast from the underlying silicon substrate at Fig. 102d, these grains may be preferential uranium precipitation in the dissolution trenches/pits where super saturation of silicon ions is possible and uranium secondary phases containing silicon, potentially uranium silicates are formed.

X-ray diffraction analysis of the uranium thin film in standard Bragg-Brentano geometry is shown in Fig. 124. Unfortunately, the diffractogram of Fig. 124 does not show any signal from any secondary phases that may be present, most likely due to the low amount of material present versus the bulk UO_{2} film.
**Fig. 124.** XRD diffractogram for the pre-leached and post-leached UO$_2$ thin film sample on a silicon substrate. Only 200, 400, and 600 UO$_2$ reflections corresponding to the (001) crystallographic orientation are present.

Neck and Kim [21] proposed that for actinides in neutral and alkaline solutions, where An(OH)$_4$(aq) are the predominant aqueous species, the solubilities of AnO$_2$(cr) become equal to those of the amorphous solids. Hence, a conclusion was drawn that the crystalline dioxides are covered by amorphous hydroxide layers. Despite this, from X-ray diffraction of the pre and post-leached thin film samples (Fig. 124) and surface sensitive EBSD measurements (Fig. 146), we found that the sample of UO$_2$ did not amorphize during the dissolution duration of 140 days.

Finally, we observe that dissolution of the uranium dioxide thin film led to micro-crack formations seen in Figs. 810 and 941. We postulate this to result from the release of film strain due to lattice-mismatch between the uranium dioxide thin film and the underlying silicon substrate. We investigated carefully the misorientation differences between each
point of the thin film surface with the help of EBSD images. MTEX, a MATLAB toolbox for quantitative texture analysis, was used to quantify the misorientation differences between individual points on the thin film to investigate this dissolution-assisted strain release micro-cracks formation in the compressively stressed thin film. Such crack formation in thin films under tensile stress has been simulated by Zhang et al [54]. These micro-cracks are distinct from previously observed, oxidative cracks [55] as we have no evidence of oxidation of UO₂ to U₃O₇ from our XRD data.

A thresholded EBSD map, Fig. 135, shows that the crystal orientation is constant throughout the grain, with virtually the entire area within 1 degree of misorientation. Next, subgrain boundaries were defined with the fast multiscale clustering (FMC) method [56] with a scaling parameter for grouping and segregating pixels into subgrains, (C_Maha of 4.8). Fig. 135 shows the subgrain features found reflect the crack morphology. By fitting a misorientation profile with a third order polynomial function we calculated a precision error (3sigma) smaller than ± 0.3° (see Electronic Supplementary Information (ESI)).
**Fig. 136.** Thresholded EBSD map showing the misorientation angle of every pixel with respect to the average orientation. The twelve adjacent misorientation profiles delimited by the two red curves were averaged to obtain the averaged misorientation profile of Figure 146.

**Fig. 146.** Averaged misorientation profile (see Fig. 15 as a reference)

The resolution of each square pixel shown in Fig. 135 is 97 nm by 97 nm. Vertical grains with areas of two by ten pixels left and right of each crack were merged and their average misorientation axes were calculated with respect to the immediate adjacent areas to the left. These misorientation axes are plotted in the inverse pole figure shown in Fig 157. Our data show that the misorientation axis looks relatively similar at both flanks of the cracks. With our averaging approach, we have been able to show that the misorientation axes oscillate around <111>, which is the cleavage related direction expected for a cubic fluorite structure [57]. Our interpretation is that due to the lattice mismatch between the UO₂ and the silicon substrate crystal structures, the oxide
structure is distorted along the <111> cleavage directions throughout the entire thin film. This distortion becomes experimentally significant (i.e. larger than 0.3°) at the proximity of the cracks: that is, the crack allows for a larger crystal distortion. Such distortion promotes further propagation of the cracks themselves in a positive feedback loop. This can be seen from Fig. 840 where the cracks are seen at 90° to each other, implying a <111> direction of propagation in this (001) oriented uranium dioxide thin film.

**Fig. 157.** Plot of misorientation axes obtained on either side of the three cracks. They have similar misorientation axis with some statistical variation.

3.3. **Powder samples**

This last experiment aims to determine the effect of temperature on uranium dioxide dissolution. High surface area uranium dioxide powder was leached under varying temperatures to determine the effect of temperature on uranium dioxide dissolution. These high-temperatures, high surface area uranium dioxide powder experiments were designed to maximise the concentration of dissolved uranium ions with the backdrop of low concentration of dissolved uranium dioxide ions observed in both the solid pellet
and thin-film experiments. ICP-MS determined uranium solution concentration values from the UO₂ powder leaching vessels held at different temperatures (ambient temperature (∼25°C), 40 °C, 90 °C and 150 °C) are shown in Fig. 168. It should be noted that the aliquot extraction was done at the ambient glovebox temperature of 25°C.

From Fig. 168, it can be seen that the concentration of dissolved uranium does not vary significantly despite the different temperatures employed. In fact, the mean U concentration appears to decrease from 40 °C to 150 °C. It should be noted that the aliquot extraction was done a few minutes after removing the samples from the autoclave and temperatures may have fallen slightly. This observation indicates that increased temperatures do not increase dissolved uranium concentrations for long duration dissolution. It can again be seen that the final concentrations are ∼10⁻⁹ mol/L consistent with our results on the thin film and bulk dissolution experiments at ambient temperature.
Fig. 168. ICP-MS determined uranium concentration values after 390 days of dissolution at temperatures from 25 to 140 °C.

4. Discussion

4.1. Simulations

Phreeqc 3.4.0-13927 [58] calculates the equilibrium concentration of ions for a given combination of reactants in solution after inputting initial conditions, such as solubility, pH, Eh, concentration of dissolved oxygen and so forth. Using a referenced thermodynamic database, such as Hatches [59], we estimated the equilibrium concentration of dissolved uranium ions by integrating the different speciation of uranium (IV, V, VI) at different concentrations of dissolved oxygen using existing solubility and reaction parameters for UO₂ from the Nuclear Energy Authority (NEA) database.
Fig. 179. Phreeqc simulation of dissolved uranium concentration at equilibrium as a function of oxygen content for UO$_2$ (NEA) dissolution in deionized water at room temperature, where $\log K^0 = 54.5 \pm 1.0$.

Given a starting condition of stoichiometric tetravalent uranium dioxide, oxidation of uranium dioxide, U(IV)O$_2$ to U$^{5+}$ and U$^{6+}$ are dominant in solution at concentrations of dissolved oxygen above 0.1 ppb. Based on the highest dissolved uranium concentration readings in all our experiments (see Fig. 13) of about $6 \times 10^{-5}$ mol/L, we can relate that the upper limit of dissolved oxygen in our system is about 0.1 ppb.

Simulations show constant equilibrium concentration of tetravalent uranium at these low levels of dissolved oxygen indicating that anoxic dissolution of uranium dioxide in its tetravalent form proceeds invariably at a limiting rate due to low associated solubility and such tetravalent dissolution becomes dominant at low levels of dissolved oxygen for stoichiometric uranium dioxide where oxidation of uranium dioxide to higher oxidation
levels is seen to drop off sharply according to these thermodynamic calculations.

4.2. Experimental discussions

There is some variability in reported uranium concentrations for the anoxic dissolution of uranium dioxide, ranging from $10^{-7}$ mol/L to $10^{-10}$ mol/L [21] and these have been noted by NEA [60] to result from a range of solids with different thermodynamic stabilities. The common theme from the results of this series of experiments, with different physical forms of UO$_2$, is that the dissolved uranium concentration is $\sim 10^{-9}$ mol/l and in all cases less than $10^{-8}$ mol/l, for all physical forms when care is taken to control the oxygen content of the water and therefore oxidation potential of the water. Thermodynamic calculations indicate that concentrations in this range represent the solubility limit of uranium in its tetravalent oxidation state.

For the first time, well-defined growth of precipitates at low uranium concentration was observed [25]. This contradicts the notion of an oxidative dissolution mechanism for U with it transforming to hexavalent form prior to dissolution, as U$^{6+}$ has solubility limits ($\sim 10^{-5}$ mol/l) [3] that are 3 orders of magnitude higher than the U concentration values observed ($\sim 10^{-9}$ mol/l). This difference in solubilities is also observed with anoxic dissolution as ICP-MS results from pre-washes are noted to contain a higher concentration of uranium, which we attribute to preferential dissolution of U$^{5+}$ and U$^{6+}$ in slightly oxidized uranium dioxide.

The low concentration of dissolved uranium ions and the high solubility of hexavalent uranium implies that no secondary phase formation should take place at this concentration if dissolution was going through the hexavalent pathway. Hence, the
observation of these uranium precipitates leads us to conclude that anoxic dissolution of uranium must proceed through the tetravalent phase.

We put forward that the anoxic dissolution of stoichiometric uranium over time is made up of two simultaneous and competing processes:

1) A widely-accepted mechanism [3] dissolved oxygen-dependent transformation of $U(IV)_{(solid)}$ to $U(V,Vl)_{(solid)}$ then $U(VI)_{(aqueous)}$.

This will lead to $U(VI)_{(precipitates)}$ at a high concentration of dissolved uranium ions at its solubility limit, as in the case of oxic dissolution.

We observe a small amount of transformation of uranium to higher oxidation states indirectly through the increase in oxygen levels with EDX at the surface of our solid pellet electrode dissolution experiments and from Raman evidence of higher numbers of interstitial oxygens in leached samples, but not a significant increase in the dissolved uranium concentration.

2) A proposed non-oxygen dependent [25] $U(IV)_{(solid)}$ to $U(IV)_{(aqueous)}$ then $U(IV)_{(precipitates)}$

process 2 has been demonstrated to prevail in our sets of anoxic experiments and thus has significance in real-life nuclear repositories which are expected be anoxic [2].

From the solid pellet experiment, it can be concluded that in anoxic dissolution with low levels of oxygen at 2.0 ppm $O_2$, it is still possible to observe surface oxidation indirectly from Raman spectroscopy inferences, open circuit potential and EDX
measurements. Despite this, the dissolved uranium concentration remains low at $6 \times 10^{-9}$ mol/l, which is an indication that mainly tetravalent uranium ions are present in solution with their characteristic low solubility. However, with pellet studies the higher surface roughness inhibits clear observations of any secondary phases that may be formed. Nevertheless, we have observed from ICP-MS results of the acid post-washes of the leaching vessel, an average of $3 \times 10^{-9}$ mol/l of dissolved uranium in 250 cm$^3$ of 3.0 M nitric acid. This highlights the presence of uranium sorption/precipitation on the wall of the PTFE vessels as observed before [10,61].

Considering an accidental container corrosion scenario of 500-1000 years when container will fail to be water tight and groundwater ingresses, the temperature of spent nuclear fuel interacting with groundwater will be higher than the prevailing underground repository temperatures depending on the fuel burn-up and the waste canisters. Thus, temperatures in the vicinity of the spent nuclear fuel will vary from $\sim$45 °C to $\sim$130 °C [62].

High-surface area powder dissolution conducted at elevated temperatures for 390 days showed uranium concentrations falling within a range between $0.1 \times 10^{-9}$ to $2 \times 10^{-9}$ mol/l. We notice a slight decrease in the mean dissolved uranium concentrations at higher temperatures, albeit within the error bars. Although, it should be noted that the aliquot extraction was performed at an ambient glove box temperature of $\sim$25 °C.

Slightly higher concentration of dissolved uranium concentrations in the solid pellet experiment ($6.0 \times 10^{-9}$ mol/l) might be attributed to a thin layer of higher oxidized
uranium on its surface as these samples were not annealed in a reducing environment like the others with values of about $3.0 \times 10^{-9}$ mol/l. Since the uranium concentration values in the contact solutions were essentially of the same order of magnitude ($\sim 10^{-9}$ mol/l) for the pellet, thin film and powder samples, and formation of a uranium containing secondary phase took place, it can be suggested that the equilibrium uranium concentration in the solution is limited by the solubility of the nucleating secondary phase and is independent of the UO$_2$ form (bulk pellet, thin film or powder). Just as schoepite’s solubility [35] forms the upper limit of uranium dissolution in oxic conditions, the limitation of uranium dioxide dissolution in anoxic conditions will be limited by solubility of these uranium (IV) secondary nucleates. Hence, parameters such as specific surface area, density of reactive surface sites, particle sizes and sample crystallinity (amorphous vs. crystalline) should not affect the uranium concentration established in the solution in the long-term and may only affect the kinetic aspects of the process [63].

5. Conclusions

For extended durations up to 390 days, we conclude that the baseline scenario of uranium dioxide dissolution in deionized water will result in dissolved uranium dioxide concentration of the order of $10^{-9}$ mol/l, which is indicative of U$^{4+}$ dissolution. Relatively slight variation in uranium concentrations of less than one order of magnitude is observed between different sets of UO$_2$ samples (pellets, thin film and powder). Variable temperature dissolution was conducted over a duration of 390 days and the concentration of dissolved uranium did not increase with elevated temperatures.
The dissolved uranium concentration of these long-term anoxic uranium dissolution experiments went through a maximum before decreasing to a constant value being indicative of a dissolution and precipitation mechanism, which is verified by the observed uranium containing secondary phases. At such low dissolved uranium concentration, dissolution and precipitation of uranium is hypothesized to proceed through the tetravalent form. This hypothesis is reinforced by clear observations of clusters (~500 nm) of homogenous uranium-containing precipitates of 20–100 nm grains in the thin film dissolution experiment.

From these experiments, we conclude that anoxic uranium dissolution with deionized water proceeds in 2 forms simultaneously at the surface.

1) a dissolved oxygen-dependent step of $\text{U(IV)}_{\text{solid}}$ to $\text{U(V, VI)}_{\text{solid}}$ then $\text{U(VI)}_{\text{aqueous}}$

2) a non oxygen-dependent $\text{U(IV)}_{\text{solid}}$ to $\text{U(IV)}_{\text{aqueous}}$ process to $\text{U(IV)}_{\text{precipitates}}$

We proposed that the equation for process 2 will take the following form:

$$\text{UO}_2(s, \text{defective}) + 2\text{H}_2\text{O}(l) \rightarrow \text{U(OH)}_4(aqueous) \rightarrow \text{UO}_2(s, \text{less defective}) + 2\text{H}_2\text{O}(l), \Delta H < 0 \text{ (5)}$$

Acknowledgements

We would like to acknowledge the Singapore Nuclear Research and Safety Initiative for partial funding. We would also like to acknowledge Thomas Gouder, Rachel Eloirdi, Alice Seibert from the European Commission, Joint Research Centre, Directorate for Nuclear Safety and Security for providing the thin film sample. Lastly, we will also like to
express our thanks for being able to use the UTGARD National Nuclear User Facility (NNUF) for some of our experiments.

Conflicts of interests

There are no conflicts of interests to declare.

Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study. However, additional information on EBSD data processing has been included in the electronic supplementary information.

References


oxides/hydroxides in NaCl systems, solubility products, hydrolysis constants and 
doi:10.1016/j.jct.2017.05.039.


The Oxides, (1949).

characterisation of a UO2-based ceramic for disposal studies on spent AGR fuel, 


doi:10.1021/ic00327a022.


[44] Y. Okada, Y. Tokumaru, Precise determination of lattice parameter and thermal


Highlights

- Extended dissolution of different forms of UO$_2$ was conducted under strict anoxic conditions.
- Dissolved uranium of the same magnitude (10^{-9} \text{ mol/L}) was obtained for all physical forms of UO$_2$.
- Different secondary phases of uranium were observed from dissolution in distilled water.
- These U(IV) secondary phases limit dissolved concentrations of uranium.
Surface and electrochemical controls on UO₂ dissolution under anoxic conditions

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Abstract

The escape of radionuclides from underground spent nuclear fuel disposal facilities will likely result from anoxic dissolution of spent nuclear fuel by intruding groundwater. Anoxic dissolution of various forms of uranium dioxide (UO₂), namely bulk pellet, powder and thin film, has been investigated. Long-duration static batch dissolution experiments were designed to investigate the release of uranium ions in deionized water and any surface chemistry that may occur on the UO₂ surface. The dissolved uranium concentration for anoxic dissolution of nearly stoichiometric UO₂ was found to be of the order of 10⁻⁹ mol/l for the three different sample types. Further, clusters (~500 nm) of homogenous uranium-containing precipitates of ~20–100 nm grains were observed in thin film dissolution experiments. Such a low solubility of UO₂ across sample types and the observation of secondary phases in deionized water suggest that anoxic UO₂ dissolution does not only occur through a U(IV)ₗ(solid) to U(VI)ₗ(aqueous) process. Thus, we propose that dissolution of uranium under anoxic repository conditions may also proceed via U(IV)ₗ(solid) to U(IV)ₗ(aqueous), with subsequent U(IV)ₗ(precipitates) in a less defective form. Quantitative analysis of surface-sensitive EBSD diffractograms was conducted to elucidate lattice-mismatch induced cracks observed in UO₂ thin film studies. Variable temperature anoxic dissolution was conducted, and no increased uranium concentration was observed in elevated temperatures.

Keywords: UO₂; anoxic dissolution; secondary phases; surface alteration; nucleation; geological disposal
1. Introduction

The relative abundance of uranium as an energy resource, coupled with the high costs of spent nuclear fuel (SNF) reprocessing and the associated risks of nuclear proliferation, make a strong case for direct disposal of SNF in deep underground geological disposal facilities (GDF) [1,2]. The evaluation of such a facility is a multifaceted problem; of which an important consideration is the projected radionuclide release rates from the spent fuel in the case of groundwater intrusion and secondary containment failure [3,4]. Extensive work had been devoted to the analysis of the different aspects of spent nuclear fuel dissolution under geological disposal conditions [2–11]. Depending on burn-up and local position in the rod (the linear power rating), spent fuel is comprised of ~96 at% uranium dioxide (UO$_2$) matrix with ~3 at% of fission products and ~1 at% of transuranium elements. As such, previous studies have shown that the release of radionuclides (apart from instant release fractions [12,13] of several percent of total inventory for some radionuclides), is mainly dependent on dissolution of the UO$_2$ matrix under the oxygen-free environment of deep geological facilities [3,4].

However, there has been no consensus on the proposed mechanisms of anoxic UO$_2$ dissolution in the literature. Ulrich et al. [14] initially suggested that anoxic dissolution of UO$_2$ proceeds via Eq. 1:

$$\text{UO}_2(\text{s}) + 4\text{H}^+ \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O}$$

(1)

Based on an XPS analysis of leached UO$_2$ samples consisting of bulk and surface U(IV), they noted surface oxidation to 7–10% U(VI) and ~20% U(V) under reducing dissolution conditions (5 vol% H$_2$, 95 vol% N$_2$ atmosphere) which was explained by a sequential oxidation mechanism of U(IV) to U(V) to U(VI) by water molecules, similar to
that proposed by Shoesmith and Sunder [15] for UO₂ dissolution below the oxidative
treshold potential (−100 mV versus saturated calomel electrode on the UO₂ surface).

\[
\text{UO}_2 + \text{H}_2\text{O} \rightarrow (\text{U}^{\text{V}}\text{O}_2\text{OH})_{\text{ads}} + \text{H}^+ + e_{(\text{aq})} \quad (2),
\]

\[
(\text{U}^{\text{V}}\text{O}_2\text{OH})_{\text{ads}} + \text{H}_2\text{O} \rightarrow (\text{U}^{\text{VI}}\text{O}_2(\text{OH})_2)_{\text{ads}} + \text{H}^+ + e_{(\text{aq})} \quad (3).
\]

A caveat to the applicability of these equations is the absence of detectable U(VI) in the
sample solutions with a kinetic phosphorescence analyzer (KPA), although U(VI) is a
few orders of magnitude more soluble than U(IV) [16]. Ulrich et al. concluded that the
anoxic UO₂ dissolution was primarily driven by hydrolysis of U(IV) and not by oxidation
to U(VI) [14]. However, it is possible that, although the sample transfer occurred with
minimal exposure to oxygen in this work, a short exposure was enough to induce
surface oxidation, which led to the observed U(V) and U(VI) at the surface. In addition,
Ollila et al. [5] reported that after anoxic (N₂ atmosphere) dissolution of UO₂ in deionized
water, the uranium oxidation state in the solution was U⁶⁺ as determined by anion
exchange methods in an HCl medium within an inert atmosphere glove box (N₂).
However, there was no information on the characterization of UO₂ samples in contact
with the solution. In view of the above literature, the motivation of this paper is to
investigate the anoxic dissolution mechanism of uranium dioxide with respect to the
anoxic conditions pertaining in a GDF.

Considering the long timeline for SNF storage and disposal, this study focuses on the
long-term surface changes and products due to dissolution of spent nuclear fuel. Three
anoxic experiments with near stoichiometric uranium dioxide were conducted with
different aims. 1) The dissolution of uranium dioxide in solid pellet electrode form to
determine electrochemical variation of both solution and surface and subsequent
analysis of surface oxidation with Raman spectroscopy, Scanning Electron Microscopy
(SEM) and Energy Dispersive X-ray (EDX) analysis techniques. 2) The dissolution of a
single crystal uranium dioxide thin film (~100 nm thickness) deposited epitaxially on a
(001) silicon substrate, to ascertain uranium dissolution and potential secondary phase
precipitation [9,10] on a topographically flat surface with high surface sensitivity. 3)
High-surface area UO₂ powder in steel heating vessels with PTFE (polytetrafluoroethylene) liners to analyse differences in dissolved uranium
concentrations at different temperatures, simulating decay heat at different disposal
ages.

2. Materials and methods

2.1. Anoxic conditions

Anoxic dissolution involves the exclusion of dissolved oxygen in the experiments as
far as reasonably possible. All dissolution experiments were conducted in positive
pressure gloveboxes with an argon atmosphere with oxygen concentrations controlled
to 0.1 ppm O₂ for the thin film and powder experiments and a nitrogen atmosphere of
2.0 ppm O₂ for the solid pellet experiments. In all cases, the dissolution experiments
took place in sealed containers containing deoxygenated water. Deionized Milli-Q water
(18.2 MΩ/cm), for both dissolution and sample washing, was sparged with 5 vol% H₂ in
95 vol% Ar gas mixture for 6 hours to reduce the amount of dissolved oxygen to a
suitable low level. Post-sparging testing with CHEMetrics® Oxygen CHEMets Kit K-7540 revealed dissolved oxygen content below the detection limit of 2.5 ppb.

2.2. Sample preparation

Efforts have been taken to reduce the amount of U(VI) and U(V) from surface oxidation of the nominal UO₂ samples. Powder and thin film samples were reduced in a 5 vol% H₂, 95 vol% Ar atmosphere and heating to 800° C [17]. Sintered UO₂ pellets were polished with SiC paper under deionized water to remove any oxidized surface layer of UO₂ₓ that arises from exposure to the atmosphere for extended periods of time [18]. Anderson et al. [19] have previously reported that such surface oxidation occurs slowly as a logarithmic function of time due to the chemisorption of oxygen at room temperatures. Pellet and thin film samples were subsequently pre-washed before undertaking dissolution experiments.

A detailed description of the fabrication and initial characterisation of sintered UO₂ pellets has been previously reported by Hiezl et al. [20] with additional characterisation by Popel et al. [10]. In order to make suitable electrodes for use in long-term dissolution experiments, stoichiometric UO₂, disc-shaped slices of sintered pellets (~1 cm diameter and ~1 mm thickness) were mounted onto a threaded brass rod using silver-loaded epoxy. This assembly was then placed in a cylindrically shaped mould and cast in epoxy resin in order to produce a suitable sealed working electrode. Prior to being characterised, the working electrodes were polished using 600 and 1200 grit SiC paper under deionized water (to avoid uranium dust formation). Such a polishing process reduces differences in electrode surface area between samples and enhances the
reproducibility of triplicate dissolution experiments (see Section 2.5.1). Prior to
dissolution, the polished surfaces were examined by scanning electron microscopy and
Raman spectroscopy (see Section 2.3) before placing them in 10 ml of deoxygenated,
dionized water in a Nalgene® bottle for 21-hours pre-washing under a N₂ atmosphere
with 2.0 ppm O₂. This pre-wash phase again aims to remove any higher oxidation
uranium oxide phases which might have been formed, albeit slowly, in the processing
atmosphere and relies on the higher solubility of surface UO₂⁺ phases vs. bulk UO₂.
Indeed, previous literature studies [21–23] have found that the solubility product at the
standard state, Kₚ₀ of U(VI) is -22.46, significantly higher than that of U(IV), -52.0 with
slight variation dependent on solid form [24].

The thin film of UO₂ was produced by direct current reactive sputtering onto a single
crystal Si substrate with (001) orientation using a Labstation machine at the European
Commission Joint Research Centre (EC-JRC), Karlsruhe. The substrate was cleaned
before the film deposition with ethanol and heated to ~600 °C under ρO₂ of 2 × 10⁻⁶
mbar for 40–60 min [25]. A natural uranium metal target was used as a source of
uranium with argon used as the sputtering gas at a ρAr set to 5 × 10⁻³ mbar and O₂
used as the reactive gas at a ρO₂ set to 7 × 10⁻⁶ mbar. The Si substrate was maintained
at a temperature close to 600 °C. The film was deposited for 30 minutes with deposition
conditions which should give film thickness in the range from 90 to 270 nm. The thin film
sample was then annealed in an anoxic glove box-attached furnace at 800 °C with a
reducing mixture of 5 vol% H₂ in 95 vol% Ar for two hours, taking one hour to heat up
and three hours to cool down. It was subsequently transferred to another glove box,
where the dissolution experiment took place under an argon atmosphere at 0.1 ppm O₂.
Finally, pre-wash in 20 ml of sparged deionized water in a plastic bottle for 12 hours was carried out before transfer to a fresh deionized water solution for the dissolution experimental run (see section 2.5.2).

For the powder samples, high surface area, micro-porous UO₂ beads were produced from uranyl nitrate at the EC-JRC by the sol-gel technique [26,27]. About 2.3 g of this powder was weighed and transferred into a 1 ml alumina boat for annealing. In order to achieve stoichiometry, the powder was annealed in a tube furnace attached to a glove box where ingress and egress of the sample into the furnace occurs inside the glovebox with an argon atmosphere (0.1 O₂ ppm). It was annealed at 800 °C for three hours with a reducing gas mixture of 5 vol% H₂ in 95 vol% Ar, after an initial hour of pre-heating to the requisite temperature. There was no pre-wash carried out for this set of experiments.

2.3. Sample characterisation

The solid pellet samples were analysed before and after the dissolution experiment by SEM with EDX as well as a Raman microscopy system. SEM-EDX was carried out at 20 keV using a JSM-6010PLUS (Jeol, Japan). Raman microscopy measurements were taken using a Voyage confocal Raman microscope system (B&WTek, Newark, USA). All Raman spectra were acquired with an excitation wavelength of 785 nm. The sample was focussed using a 50× objective lens before taking spectra with an integration time of 40 seconds over a wavenumber range from 190 to 3000 cm⁻¹. Before analysis, the laser power was adjusted to < 5 mW using neutral density filters in order to avoid any thermal oxidation of UO₂ to U₃O₆ [28]. In order to account for surface roughness and
surface inhomogeneity, 10 spectra were taken at random locations across the sample with the highest and lowest outliers removed to produce a sample average.

The thin film sample was analysed before and after the dissolution experiment by SEM, EDX, X-ray diffraction (XRD) and electron backscatter diffraction (EBSD) techniques [25]. A FEI Quanta 650F instrument operating at 5 kV with beam spot size 3 under high vacuum was used to acquire SEM images with a Bruker 6130 XFlash EDX detector. EBSD instrumentation from Bruker with an e-FlashHD detector associated with the FEI Quanta 650F SEM was used to obtain EBSD data; the resolution of each square pixel of 97 nm. The operating voltage was 20 kV and the beam spot size 5.5. The detector resolution was 320 × 240 pixels, while working distance and sample to detector distance was 26 mm and 15.5 mm respectively. Analysis of collected EBSD data from the uranium dioxide thin film was conducted with the computational aid of MTEX V5.0.3 [29], a freeware toolset for the commercial software package MATLAB™ [30]. The MATLAB™ toolbox MTEX provides a unique way to represent, analyse and interpret crystallographic preferred orientation, i.e. texture, based on integral ("pole figure") or individual orientation ("EBSD") measurements.

Due to limitations in examining radioactive uranium oxide powder under vacuum, capillary XRD was conducted with a Bruker D8 Advance diffractometer (Cu Kα radiation, λ = 1.541 Å, Ge monochromator and Sol-XE energy dispersive detector). Measurements were carried out for 12 hours each over an angular range 25° ≤ 2θ ≤ 90° (Δ2θ = 0.01°). Data collection and indexing was performed with Bruker QUANTAX CrystaAlign software [31]. A full Rietveld refinement was carried out of the acquired diffraction patterns. The backgrounds were fitted using linear interpolation and the peak
shape was modelled using a pseudo-Voigt function for the micro-porous uranium
dioxide powder pre- and post-annealing. Based on 5.466 Å, and the equation $a_x = 5.4690 - 0.12x [32]$, a bulk stoichiometric ratio prior to dissolution of UO$_{2.03}$ was found for the UO$_2$ powder. However, in this dissolution study, the bulk stoichiometric ratio may be lower than the surface. As discussed by Sunder [33], the surface is likely to be UO$_{2+x}$ ($0 < x < 0.25$). This is because XRD is a bulk technique which convolutes the signal from the underlying bulk and surface signals hence typically registering lower values of $x$ than surface sensitive Raman spectroscopy as Raman laser has a lower penetration depth than X-rays.

2.4. Aliquot analyses

For inductively coupled plasma mass spectrometry (ICP-MS), the acquired 1 ml aliquots (see section 2.5) were acidified with another 1 ml of 1 wt% HNO$_3$. All samples were analysed on a Perkin Elmer Nexion 350D ICP-MS instrument. The uranium calibration standards were prepared as an external calibration using serial dilutions of standards (blank, 0.001, 0.01, 0.10, 1.0, 10 ppb, mass basis) prepared from single element high purity standard (CPI, California, USA) in high purity 1 wt % HNO$_3$ (quartz distilled in house). The ICP-MS internal standards were 10 ppb Rh, In and Re and each sample was prepared in 1 wt % HNO$_3$, added online with a t-piece and mixing tube prior to the nebuliser. Two different independently prepared quality control standards (SPS-SW2, LGC Standards, UK and SCP Science, Canada, ICP-MS Verification Mix) were repeatedly analysed throughout the run to check for calibration accuracy (~5%) with a similar precision. Instrumental drift was less than 10% measured for the raw intensity of the internal standards during the entire analytical run (50 or more solutions per batch).
Solutions were analysed using a Micromist FM05 microconcentric nebuliser using a pumped flow rate of 80 μl/min (Glass Expansion, Australia) and a quartz cyclonic baffled spray chamber with nickel sampler and skimmer cones. ICP-MS sensitivity in this configuration was $4.5 \times 10^5$ cps/ppb In with CeO/Ce ratios = 2.8%. Concentration results were calculated using the Syngistix 1.1 software with a simple linear calibration line and intercept set to zero. The raw intensities were blank subtracted and internal standard normalised before calibration calculations were performed. All results (unknowns and standards) were accurately corrected for dilutions by mass by performing all dilutions with calibrated pipettes on a four place analytical balance.

For the leachate from the uranium dioxide thin film experiment, dynamic light scattering was used to confirm the absence of colloids greater than 5 nm. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) of this leachate found the concentration of dissolved silicon in that experiment to be in the range of 15–25 ppb.

2.5. Dissolution experiment setups

A summary of the dissolution experiments has been tabulated at the end of this section in Table 1.

2.5.1 Solid pellet dissolution

After a 21-hour prewash and drying for 1 hour in the glovebox atmosphere, UO₂ electrodes were immersed in 220 ml of sparged, deionized water in a sealed (screw top) 480 ml Fisherbrand® PTFE dissolution vessel. Dissolution measurements were performed in triplicates.
To determine the electrochemical evolution of both the uranium dioxide electrode and the solution potential, open circuit potentiometry was used [34]. Solution potential was measured using 500 μm Au disk electrodes, polished using 600 and 1200 grit SiC papers and rinsed with deoxygenated, deionized water inside the glovebox prior to immersion. Through the use of a simple switch box, the open circuit potential of both electrodes was measured vs. one reference electrode. In order to avoid chloride contamination, an ammonium nitrate saturated agar double junction was used with an Ag|AgCl reference electrode (RE-5B, BASi, Indiana, USA). All vessels were tightly closed to prevent water evaporation, with gaps around electrodes sealed using parafilm®. One vessel filled with 250 ml of deionized water and an Au electrode only (no UO₂ electrode) was used as a control. During dissolution, batch replenishment tests were conducted, where ~1 ml aliquots of the solution sample were extracted and ~1 ml of the deionized water was replenished at defined time intervals after the start of the experiment, namely 2 hours, 6 hours, 1 day, 5 days, 12 days, 30 days, 61 days and 100 days. The amount of solution in the aliquots was monitored by weighing empty and filled vials on a balance. The dissolution of all samples was performed at an ambient temperature of ~25 °C for 100 days. After completion, the PTFE vessels were acid-washed using 3 M HNO₃. 5 ml of each acid wash was used for ICP-MS analysis in order to determine the presence of any uranium sorption or precipitation on the walls of the leaching vessel.

2.5.2 Thin film dissolution

After the 12-hour prewash and drying for an hour, the UO₂ thin film sample was rinsed with sparged, deionized water and placed into a 60 mL Fisherbrand® PTFE
dissolution vessel containing 20 ml of the deionized water and two blank Si substrates (to detect any U precipitation/nucleation from the solution) [25].

Static batch replenishment tests were run where ~1 ml aliquots were extracted at various intervals and ~1 ml of the deionized water was replenished. One vessel, filled with 20 ml of the deionized water and two blank Si substrates, was used as a control blank. All vessels were tightly closed to prevent water evaporation. The amount of the solution transferred from the dissolution vessels into the vials was monitored by weighting empty and filled vials. The dissolution experiment was performed at an ambient temperature of ~25 °C for 140 days.

2.5.3 High surface area powder dissolution

After annealing, 100 mg of reduced UO₂ powder was weighed out carefully with a Mettler Toledo XS-104 mass balance and placed into each of twelve stainless steel leaching vessels with a PTFE liner and a Swagelock seal. Upon the addition of 4 ml of sparged, deionized water to each leaching vessel, the leaching vessel was tightly sealed and transferred to another glove box under double containment. The dissolution experiment was performed at 4 different temperatures ambient (~25 °C), 40 °C, 90 °C and 140 °C with deoxygenated water (<2.5 ppb O₂) within an Ar atmosphere glovebox (0.1 O₂ ppm). All vessels were kept in the glove box for the duration of the experiment and tightly sealed. The extraction was carried out on the 390th day with a syringe through a 0.45 μm pore size disposable filter.

Table 1

A summary of the UO₂ dissolution experiments conducted in this study
<table>
<thead>
<tr>
<th>Pellet</th>
<th>Annealing</th>
<th>Polishing</th>
<th>Prewashing</th>
<th>Oxygen content</th>
<th>Leaching test conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>2 ppm glovebox</td>
<td>100 days 220 mL deionized water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(SiC paper + deionized water)</td>
<td>(21 hours) – 10 mL</td>
<td>&lt;2.5 ppb dissolved O₂</td>
<td></td>
</tr>
<tr>
<td>Thin film</td>
<td>Yes</td>
<td>No.</td>
<td>Yes</td>
<td>0.1 ppm</td>
<td>140 days 20 mL deionized water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(5% H₂ in Ar at 800 °C for 2 hours)</td>
<td>(12 hours) – 20 mL</td>
<td>&lt;2.5 ppb dissolved O₂</td>
<td></td>
</tr>
<tr>
<td>Powder</td>
<td>Yes</td>
<td>Not applicable</td>
<td>No</td>
<td>0.1 ppm</td>
<td>390 days 4 mL deionized water</td>
</tr>
<tr>
<td></td>
<td>(5% H₂ in Ar at 800 °C for 2 hours)</td>
<td></td>
<td></td>
<td>&lt;2.5 ppb dissolved O₂</td>
<td>Filtration 0.45 μm</td>
</tr>
</tbody>
</table>

### 3. Results

#### 3.1. Solid pellet dissolution

ICP-MS results, represented in Fig. 1, show a uranium concentration increase from $1 \times 10^{-9}$ mol/l to $\sim 6 \times 10^{-9}$ mol/l being leached from the solid uranium pellet. Such a low level of uranium release is indicative of anoxic dissolution, which has a reduced rate of uranium ion release compared to oxic leaching [35]. This also agrees with the end solution potential of the uranium containing pots (-56 mV, -52 mV, -52 mV vs. SCE, respectively) and the control pot (-55 mV vs SCE). There is no significantly measurable difference in the solution potential between the leaching and control pots. Such a negligible change in potential is predicted by the Nernst equation, as the dissolved uranium ion release into the solution is so small ($10^{-9}$ mol/l).
Fig. 1. Uranium concentration in aliquots obtained from three vessels, A, B and C containing a uranium pellet each and a control vessel labelled as blank with the same set up without a uranium pellet.

The concentration of uranium reaches a maximum value of $6 \times 10^{-9}$ mol/l after 60 days. This may be attributed to the uranium reaching its solubility limit under anoxic condition, hence there was a decrease in the driving force for further dissolution. Under such a scenario, reprecipitation can occur, which was confirmed by the detection of solid uranium precipitates when dissolved uranium was observed in the acid washout fraction after the experiment. This effect is more pronounced in the uranium concentration data of the thin film experiment discussed in Fig. 6 under Section 3.2. ICP-MS of acid washes of the vessels after completion of the dissolution experiment show a dissolved uranium concentration of $\sim 3 \times 10^{-9}$ mol/l in 250 cm$^3$ of 3 mol/l nitric acid, which is significantly higher than that in the blank pot (1 $\times 10^{-9}$ mol/l). Such an observation supports the presence of precipitated uranium phases within the dissolution
vessel.

Fig. 2 shows the recorded open circuit potential of the uranium dioxide electrodes at
the beginning and end of this experiment. These measurements indicate some
evolution [15] of the oxidation state at the uranium dioxide surface. Referencing with a
standard calomel electrode, Shoesmith and Sunder [15] reported potential readings
between -150 to -270 mV for near stoichiometric uranium dioxide in argon-purged
solutions, containing UO$_{2+x}$. This correlates reasonably well with our data with an
average initial reading of -150 mV shown in Fig. 2. With increased oxidation of the
uranium surface, Shoesmith and Sunder reported that the potential reading would
increase correspondingly, and the region of oxidative dissolution occurs at a threshold
of -50 to -100 mV, where the surface composition approaches a thin layer (2–5 nm) of
UO$_{2.33}$ as detected from angular-dependent XPS studies [33]. Our experimental reading
reaches an average of -70 mV after 100 days of dissolution. We suspect that this might
be due to oxidation arising from trace amount of ~2 ppm O$_2$ present in the glovebox
atmosphere.
Fig. 2. Open circuit potential of the uranium dioxide electrodes recorded at the beginning and end of this leaching experiment. Note values are plotted vs. the standard calomel electrode (SCE) for ease of comparison with data from [15].

Area averaged Raman spectra of a freshly polished UO₂ electrode and three UO₂ electrodes after 100 days dissolution is shown in Fig. 3, which is a magnification of the Raman shift range 350 to 750 cm⁻¹, a region previously reported as being the most important with regards to the degree of oxidation of the UO₂ lattice [36,37]. It can be seen that there are two distinct differences between a freshly polished electrode and that leached in deionized water under anoxic conditions. Firstly, there is a decrease in the large vibration at 440 cm⁻¹, although it should be noted that this intensity difference is only significant for Electrode C after accounting for the measurement’s standard deviation as function of measured area. Secondly, there is a small increase in the broad band from ~550 to ~650 cm⁻¹.
Fig. 3. Main: Linear baseline subtracted, area averaged Raman spectra of a freshly polished UO$_2$ electrode and three UO$_2$ electrodes after 100 days dissolution over the Raman shift range 350 to 750 cm$^{-1}$. Inset: Example Lorentzian fit of defect bands at 575 cm$^{-1}$ and 630 cm$^{-1}$ from a single measurement point from electrode A after leaching.

Considering the former 440 cm$^{-1}$ vibration first, group theory predicts that a perfect fluorite structure would be expected to give a triply degenerate Raman active mode (T2g) [38], typically defined as the fundamental U-O symmetric stretching mode [11,39]. This intense vibration has been reported at ~445 cm$^{-1}$ and in the UO$_2$ pellet samples of Fig. 3 is very close to this value at 440 cm$^{-1}$. A decrease in the intensity of this peak has been reported as being indicative of deviation from a perfect fluorite lattice structure, caused by either dopant effects or changes in UO$_2$ stoichiometry [37,39].
Turning now to the broad band from $\sim 550$ to $\sim 650$ cm$^{-1}$, this band has been ascribed to various vibrations that may occur as a result of increasing lattice defectiveness [37]. In the absence of dopants, this region is composed of three overlapping peaks at 550, 575 and 630 cm$^{-1}$, respectively. The peak at 550 cm$^{-1}$ has only recently been considered and is tentatively assigned to UO$_2$ grain boundaries [36,40,41]. The other two peaks are of more interest with regards to the degree of oxidation of the leached samples. The first at 575 cm$^{-1}$ has been assigned to a longitudinal optical (LO) phonon [37]. Usually, this phonon is forbidden under the selection rule imposed due to lattice symmetry, this peak can appear as a result of changes in translational symmetry at oxygen vacancy sites, leading to lattice disorder and the consequential breakdown in selection rules. These changes in symmetry are caused by either the incorporation of interstitial oxygens or dopant ions. The second peak at 630 cm$^{-1}$ has been attributed to clustering of interstitial oxygens to form higher oxidation state cuboctahedrons associated with a transition to a defective U$_4$O$_9$ structure [42].

Thus, the ratio of either the 575 cm$^{-1}$ or 624 cm$^{-1}$ peak to the 440 cm$^{-1}$ UO fundamental stretch is indicative of the degree of surface hyperstoichiometry (oxidation) of UO$_2$ [36]. In order to determine the contributions of each peak to the broad band of Fig. 3, a Lorentzian peak fit was performed for the data of Fig. 3, assuming peak maxima at 440, 575 and 630 cm$^{-1}$. An example fit for data from electrode A is shown in Fig. 3 – inset. The analysis of this peak expressed as a ratio to the 440 cm$^{-1}$ peak are shown in Fig. 4A for the 575 cm$^{-1}$ and Fig. 4B for the 630 cm$^{-1}$ peak.

For both the 575 cm$^{-1}$ and 630 cm$^{-1}$ peak, there is a significant increase in surface oxidation heterogeneity as shown by the increase in result standard deviation after
electrode leaching in deionized water. However, with the exception of the 575 cm⁻¹ peak for Electrode B, the results show a significant increase in the 575/440 and 630/440 peak ratio after dissolution compared to a freshly polished electrode. This suggests there is an increase in the degree of surface oxidation of the electrodes after leaching for 100 days, corroborating the change in the measured open circuit potentials of the uranium dioxide electrodes discussed above. Finally, despite the observed increase in surface oxidation, no new peaks were observed in the region 800–830 cm⁻¹ [28] in any of the acquired spectra, suggesting that there was no detectable highly-oxidised uranium dioxide (such as U₃O₈ and above) phases formed during the leaching process.

Scanning electron microscopy and EDX studies of the UO₂ electrode surfaces were carried out pre- (Fig. 5a) and post-dissolution (Fig. 5b) to ascertain the presence of any observable surface morphology changes or secondary phases.
Fig. 4. Lorentzian peak fit results for the data of Fig. 3, assuming peak maxima at 440, 575 and 630 cm$^{-1}$. Results are expressed as a ratio of (A) the 575 cm$^{-1}$ peak and (B) the 630 cm$^{-1}$ peak to the 440 cm$^{-1}$ peak.
Fig 5. SEM at the surface of the (a) pre-leached UO\textsubscript{2} pellet after polishing and (b) the post-leached UO\textsubscript{2} pellet.

Comparison between Fig. 5a and Fig 5b reveals no significant differences before and after the leaching process. Furthermore, the high degree of surface roughness makes the identification of small secondary phases, such as those described for the thin film below, extremely difficult. However, comparison of the area EDX analysis of the electrodes before and after the leaching process reveals a small but measurable increase in oxygen atomic % from 45.71 (±0.23) to 46.44 (±0.35) where the uncertainties arose from the fitting. Again, this agrees with both Raman and open circuit potential measurements (see Figs. 3 and 4) that there is a small oxidation of the surface occurring due to a trace amount of ∼2 ppm O\textsubscript{2} present in the glovebox atmosphere.

3.2. Thin film dissolution

A high-quality single-crystalline thin film (∼100 nm) of UO\textsubscript{2} deposited on a (001) silicon single crystal substrate has been subjected to an extended anoxic dissolution test in deoxygenated deionized water under anoxic argon (0.1 O\textsubscript{2} ppm) atmosphere at ambient temperature (∼25 °C) [25].
The advantages of UO₂ thin film dissolution over pellets or powders is that the flat morphology of the film facilitates sharper focusing in surface imaging, allowing features that will have gone unnoticed in samples with rougher surfaces to be made more apparent.

ICP-MS measurements of both the uranium dissolution vessel and the silicon wafer only vessel as a function of time are shown in Fig. 6.

![Graph](image)

Fig. 6. Dissolved uranium concentrations of extracted aliquots from both the uranium dioxide thin film dissolution vessel and the silicon wafer only vessel (control), determined by ICP-MS.

Fig. 6 reveals uranium concentrations in the UO₂ thin film vessel are in the range of 1.2–3.0 × 10⁻⁹ mol/l. This is similar in order of magnitude to the uranium concentration from the pellet dissolution experiment shown in Fig. 1. The initial increase in uranium concentrations followed by a decrease and plateau concentration at >10 days dissolution time is again indicative of a secondary phase precipitation mechanism. The nature of such deposits is described in more detail in the following sections.
Fig. 7. (a) 30000× magnified secondary electron and (b) backscattered electron micrographs of the thin film before prewash and heat treatment.

From the pre-leaching SEM micrographs of Fig. 7, the surface is generally smooth with some trace particulates. Backscattered atomic contrast electron images (not shown) reveal that the particles are significantly darker than the uranium surface, i.e., they have a significantly lower atomic number, suggesting they are not uranium dioxide particles. A likely cause is carbon particles from the carbon tape used in the mounting.

Post-leach SEM images of a UO₂ thin film exposed to anoxic deionized water are shown in Figs. 8 and 9.
Fig. 8. (a) 30000× magnified secondary electron and (b) backscattered electron micrographs of the leached thin film surface after 140 days dissolution.

Fig. 9. (a) 200,000× magnification secondary electron and (b) backscattered electron micrographs on the nucleate with clear growth domains ranging between 20-100 nm [25].

From Figs. 8 and 9, there are three main differences that can be seen between pre and post leaching. First, more cracks are observed. These cracks are likely due to the relaxation of the stress between the substrate and thin film during the dissolution process. Both structures are based on the face centred cubic structure with slight differences in the lattice parameters, the uranium dioxide (fluorite type lattice) thin film and the underlying silicon (diamond type lattice) substrate having lattice parameters of 5.47 Å [43] and 5.43 Å [44], respectively.

Secondly, high magnification images at 200,000× magnification (Fig. 9) enable the identification of small pits (20–100 nm) where dissolution has occurred. Based on previous studies, dissolution is known to initiate at energetically reactive sites [45] such as point defects, dislocations terminating at the surface and so forth [46–48]. Lastly, Fig.
9 reveal the presence of circular ($d = 20\text{–}100$ nm) secondary phase formations preferentially nucleated at film cracks. The backscattered electron image in Fig. 9b shows that the nucleated phases have almost the same contrast as the rest of the film, which implies similarity in composition. Unfortunately, due to the small size of the individual grains a reliable EDX analysis could not be carried out to obtain compositional information on the secondary phase.

SEM imaging was also conducted on the silicon substrates in the same vessel as the UO$_2$ thin film, with secondary and backscattered electron images shown in Fig. 10.

**Fig. 10.** Secondary (a) and backscattered electron (b) micrographs of secondary precipitates detected at 30,000× and secondary (c) and backscattered electron (d)
micrographs of secondary precipitates detected on blank silicon substrates at 100,000×
magnifications.

Fig. 10 shows some precipitates present on the silicon surface. Back-scattered
electron image, Fig. 10b and Fig. 10d show that the precipitates contrasted significantly
against the silicon substrate suggesting the precipitates have higher atomic numbers.
Considering the closed system of deionized water, silicon substrates and uranium thin
film, this implies that uranium precipitates are not just a local phenomenon found at the
uranium thin film surface. However, the mechanism of precipitation is postulated to be
different.

The precipitates formed on the silicon substrates differ significantly from the
precipitates formed on the UO₂ thin film in terms of topography and morphology. On the
flat silicon substrate, Fig. 10 shows clearly the presence of two types of precipitates,
randomly scattered particles and dendritic precipitates at the dissolution trenches and
pits, appearing as agglomerates of many grains (~50 nm) with different heights. Both
these precipitates have distinctly different morphologies from those formed on the
uranium thin film. Spherical UO₂ colloids have previously been reported in oxygen-
starved dissolution of uranium dioxide [49]. We believe the scattered particles might be
formed from colloidal agglomeration and precipitation [50] from dissolved uranium in the
solution and the dendritic growth are uranium secondary phases formed after interaction
with the silicon substrate at dissolution pits/trenches.

Despite the low ionic strength of deionized water contributing to a large kinetic barrier
against aggregation [51], the gravitational force on the colloids coupled with the large
difference in density between the dense uranium colloids and the surrounding fluid resulted in their precipitation after formation. Neglecting Brownian motion, Fig. 11 shows the relationship of colloidal size to settling time using sedimentation velocity calculation based on the Stokes’ equation where sedimentation velocity \( v = \frac{g(\rho_{UO_2} - \rho_f)(d_{UO_2})^2}{18\mu_f} \) (4)

where \( g \) represents the gravitational acceleration experienced by the colloid, \( \rho_{UO_2} \) represents the density of uranium dioxide, \( \rho_f \) represents the density of fluid (water), \( d_{UO_2} \) represents the diameter of uranium dioxide colloids and \( \mu_f \) stands for the dynamic viscosity of water.

**Fig. 11.** Stokes’ equation predicts the relationship between the settling/sedimentation duration against colloidal size for colloidal precipitation in 2 cm deep leaching vessel, similar to our set-up.

For 140 days experiments, colloid precipitation is seen to have a colloidal size limit at 15 nm. Smaller colloids will take a much longer time to settle. The velocity of
sedimentation was calculated to be $1.53 \times 10^{-8}$ ms\(^{-1}\) for the observed ~50 nm uranium dioxide colloids, achieving sedimentation after 2 cm descent (depth in our experiment) in ~14 days.

To identify the precipitates, EBSD, EDX and XRD were attempted but no signals were detected that allowed differentiation from the underlying UO\(_2\) thin film. The lack of elemental analysis opens up possible alternative interpretations for these colloids to be uranium silicates, such as coffinite. Given the high solution concentration of silicon ions (25 ppb or $10^{-6}$ mol/l Si from ICP-AES measurement of the solution after the experiment), these colloids are possibly uranium silicate colloids that have been formed in the near field of the silicon substrate at near neutral pH [52] if there is super saturation of silicon ions of a few orders of magnitude. Our concentrations of silicate to uranium concentration is quite close to that reported in the dissolution of coffinite by Szenknect et al [53]. The only caveat to this interpretation is the difficulty in producing coffinite at room temperature in laboratory conditions [6,52,53] where the concentration of silicon is higher than our measured silicon concentrations at $10^{-4}$ mol/l. It is however possible that the precipitates might be precursors of coffinite.

The distinct morphology of the dendritic formation implies a different secondary phase from that observed at the uranium thin film. From the sharp contrast from the underlying silicon substrate at Fig. 10d, these grains may be preferential uranium precipitation in the dissolution trenches/pits where super saturation of silicon ions is possible and uranium secondary phases containing silicon, potentially uranium silicates are formed.
X-ray diffraction analysis of the uranium thin film in standard Bragg-Brentano geometry is shown in Fig. 12. Unfortunately, the diffractogram of Fig. 12 does not show any signal from any secondary phases that may be present, most likely due to the low amount of material present versus the bulk UO₂ film.

Fig. 12. XRD diffractogram for the pre-leached and post-leached UO₂ thin film sample on a silicon substrate. Only 200, 400, and 600 UO₂ reflections corresponding to the (001) crystallographic orientation are present.

Neck and Kim [21] proposed that for actinides in neutral and alkaline solutions, where An(OH)₄(aq) are the predominant aqueous species, the solubilities of AnO₂(cr) become equal to those of the amorphous solids. Hence, a conclusion was drawn that the crystalline dioxides are covered by amorphous hydroxide layers. Despite this, from X-ray diffraction of the pre and post-leached thin film samples (Fig. 12) and surface sensitive EBSD measurements (Fig. 14), we found that the sample of UO₂ did not amorphize during the dissolution duration of 140 days.
Finally, we observe that dissolution of the uranium dioxide thin film led to micro-crack formations seen in Figs. 8 and 9. We postulate this to result from the release of film strain due to lattice-mismatch between the uranium dioxide thin film and the underlying silicon substrate. We investigated carefully the misorientation differences between each point of the thin film surface with the help of EBSD images. MTEX, a MATLAB toolbox for quantitative texture analysis, was used to quantify the misorientation differences between individual points on the thin film to investigate this dissolution-assisted strain release micro-cracks formation in the compressively stressed thin film. Such crack formation in thin films under tensile stress has been simulated by Zhang et al [54]. These micro-cracks are distinct from previously observed, oxidative cracks [55] as we have no evidence of oxidation of UO$_2$ to U$_3$O$_7$ from our XRD data.

A thresholded EBSD map, Fig. 13, shows that the crystal orientation is constant throughout the grain, with virtually the entire area within 1 degree of misorientation. Next, subgrain boundaries were defined with the fast multiscale clustering (FMC) method [56] with a scaling parameter for grouping and segregating pixels into subgrains, (C_Maha of 4.8). Fig. 13 shows the subgrain features found reflect the crack morphology. By fitting a misorientation profile with a third order polynomial function we calculated a precision error (3sigma) smaller than ± 0.3° (see Electronic Supplementary Information (ESI)).
**Fig. 13.** Thresholded EBSD map showing the misorientation angle of every pixel with respect to the average orientation. The twelve adjacent misorientation profiles delimited by the two red curves were averaged to obtain the averaged misorientation profile of Figure 14.

**Fig. 14.** Averaged misorientation profile (see Fig. 15 as a reference)

The resolution of each square pixel shown in Fig. 13 is 97 nm by 97 nm. Vertical grains with areas of two by ten pixels left and right of each crack were merged and their
average misorientation axes were calculated with respect to the immediate adjacent areas to the left. These misorientation axes are plotted in the inverse pole figure shown in Fig 15. Our data show that the misorientation axis looks relatively similar at both flanks of the cracks. With our averaging approach, we have been able to show that the misorientation axes oscillate around <111>, which is the cleavage related direction expected for a cubic fluorite structure [57]. Our interpretation is that due to the lattice mismatch between the UO₂ and the silicon substrate crystal structures, the oxide structure is distorted along the <111> cleavage directions throughout the entire thin film. This distortion becomes experimentally significant (i.e. larger than 0.3 °) at the proximity of the cracks: that is, the crack allows for a larger crystal distortion. Such distortion promotes further propagation of the cracks themselves in a positive feedback loop. This can be seen from Fig. 8 where the cracks are seen at 90° to each other, implying a <111> direction of propagation in this (001) oriented uranium dioxide thin film.

**Fig. 15.** Plot of misorientation axes obtained on either side of the three cracks. They have similar misorientation axis with some statistical variation.
3.3. *Powder samples*

This last experiment aims to determine the effect of temperature on uranium dioxide dissolution. High surface area uranium dioxide powder was leached under varying temperatures to determine the effect of temperature on uranium dioxide dissolution. ICP-MS determined uranium solution concentration values from the UO$_2$ powder leaching vessels held at different temperatures (ambient temperature (~25°C), 40 °C, 90 °C and 150 °C) are shown in Fig. 16. It should be noted that the aliquot extraction was done at the ambient glovebox temperature of 25°C.

From Fig. 16, it can be seen that the concentration of dissolved uranium does not vary significantly despite the different temperatures employed. In fact, the mean U concentration appears to decrease from 40 °C to 150 °C. It should be noted that the aliquot extraction was done a few minutes after removing the samples from the autoclave and temperatures may have fallen slightly. This observation indicates that increased temperatures do not increase dissolved uranium concentrations for long duration dissolution. It can again be seen that the final concentrations are $\sim 10^{-9}$ mol/l consistent with our results on the thin film and bulk dissolution experiments at ambient temperature.
Fig. 16. ICP-MS determined uranium concentration values after 390 days of dissolution at temperatures from 25 to 140 °C.

4. Discussion

4.1. Simulations

Phreeqc 3.4.0-13927 [58] calculates the equilibrium concentration of ions for a given combination of reactants in solution after inputting initial conditions, such as solubility, pH, Eh, concentration of dissolved oxygen and so forth. Using a referenced thermodynamic database, such as Hatches [59], we estimated the equilibrium concentration of dissolved uranium ions by integrating the different speciation of uranium (IV, V, VI) at different concentrations of dissolved oxygen using existing solubility and reaction parameters for UO₂ from the Nuclear Energy Authority (NEA) database.
Fig. 17. Phreeqc simulation of dissolved uranium concentration at equilibrium as a function of oxygen content for UO₂ (NEA) dissolution in deionized water at room temperature, where log K⁰ of UO₂ = 54.5 ± 1.0.

Given a starting condition of stoichiometric tetravalent uranium dioxide, oxidation of uranium dioxide, U(IV)O₂ to U⁵⁺ and U⁶⁺ are dominant in solution at concentrations of dissolved oxygen above 0.1 ppb. Based on the highest dissolved uranium concentration readings in all our experiments (see Fig. 1) of about 6 × 10⁻⁹ mol/L, we can relate that the upper limit of dissolved oxygen in our system is about 0.1 ppb.

Simulations show constant equilibrium concentration of tetravalent uranium at these low levels of dissolved oxygen indicating that anoxic dissolution of uranium dioxide in its tetravalent form proceeds invariably at a limiting rate due to low associated solubility and such tetravalent dissolution becomes dominant at low levels of dissolved oxygen for
stoichiometric uranium dioxide where oxidation of uranium dioxide to higher oxidation levels is seen to drop off sharply according to these thermodynamic calculations.

4.2. Experimental discussions

There is some variability in reported uranium concentrations for the anoxic dissolution of uranium dioxide, ranging from $10^{-7}$ mol/L to $10^{-10}$ mol/L [21] and these have been noted by NEA [60] to result from a range of solids with different thermodynamic stabilities. The common theme from the results of this series of experiments, with different physical forms of UO$_2$, is that the dissolved uranium concentration is $\sim 10^{-9}$ mol/l and in all cases less than $10^{-8}$ mol/l, for all physical forms when care is taken to control the oxygen content of the water and therefore oxidation potential of the water. Thermodynamic calculations indicate that concentrations in this range represent the solubility limit of uranium in its tetravalent oxidation state.

For the first time, well-defined growth of precipitates at low uranium concentration was observed [25]. This contradicts the notion of an oxidative dissolution mechanism for U with it transforming to hexavalent form prior to dissolution, as U$^{6+}$ has solubility limits ($\sim 10^{-5}$ mol/l) [3] that are 3 orders of magnitude higher than the U concentration values observed ($\sim 10^{-9}$ mol/l). This difference in solubilities is also observed with anoxic dissolution as ICP-MS results from pre-washes are noted to contain a higher concentration of uranium, which we attribute to preferential dissolution of U$^{5+}$ and U$^{6+}$ in slightly oxidized uranium dioxide.

The low concentration of dissolved uranium ions and the high solubility of hexavalent uranium implies that no secondary phase formation should take place at this
concentration if dissolution was going through the hexavalent pathway. Hence, the
observation of these uranium precipitates leads us to conclude that anoxic dissolution of
uranium must proceed through the tetravalent phase.

We put forward that the anoxic dissolution of stoichiometric uranium over time is
made up of two simultaneous and competing processes:

1) A widely-accepted mechanism [3] dissolved oxygen-dependent transformation of
\( \text{U(IV)}_{(\text{solid})} \rightarrow \text{U(VI)}_{(\text{solid})} \rightarrow \text{U(VI)}_{(\text{aqueous})} \),

This will lead to \( \text{U(VI)}_{(\text{precipitates})} \) at a high concentration of dissolved uranium
ions at its solubility limit, as in the case of oxic dissolution.

We observe a small amount of transformation of uranium to higher oxidation
states indirectly through the increase in oxygen levels with EDX at the surface of our
solid pellet electrode dissolution experiments and from Raman evidence of higher
numbers of interstitial oxygens in leached samples, but not a significant increase in
the dissolved uranium concentration.

2) A proposed non-oxygen dependent [25] \( \text{U(IV)}_{(\text{solid})} \rightarrow \text{U(IV)}_{(\text{aqueous})} \) then \( \text{U(IV)}_{(\text{precipitates})} \)
process 2 has been demonstrated to prevail in our sets of anoxic experiments and thus
has significance in real-life nuclear repositories which are expected be anoxic [2].

From the solid pellet experiment, it can be concluded that in anoxic dissolution with
low levels of oxygen at 2.0 ppm \( \text{O}_2 \), it is still possible to observe surface oxidation
indirectly from Raman spectroscopy inferences, open circuit potential and EDX measurements. Despite this, the dissolved uranium concentration remains low at $6 \times 10^{-9}$ mol/l, which is an indication that mainly tetravalent uranium ions are present in solution with their characteristic low solubility. However, with pellet studies the higher surface roughness inhibits clear observations of any secondary phases that may be formed. Nevertheless, we have observed from ICP-MS results of the acid post-washes of the leaching vessel, an average of $3 \times 10^{-9}$ mol/l of dissolved uranium in 250 cm$^3$ of 3.0 M nitric acid. This highlights the presence of uranium sorption/precipitation on the wall of the PTFE vessels as observed before [10,61].

Considering an accidental container corrosion scenario of 500-1000 years when container will fail to be water tight and groundwater ingresses, the temperature of spent nuclear fuel interacting with groundwater will be higher than the prevailing underground repository temperatures depending on the fuel burn-up and the waste canisters. Thus, temperatures in the vicinity of the spent nuclear fuel will vary from $\sim$45 °C to $\sim$130 °C [62].

High-surface area powder dissolution conducted at elevated temperatures for 390 days showed uranium concentrations falling within a range between $0.1 \times 10^{-9}$ to $2 \times 10^{-9}$ mol/l. We notice a slight decrease in the mean dissolved uranium concentrations at higher temperatures, albeit within the error bars. Although, it should be noted that the aliquot extraction was performed at an ambient glove box temperature of $\sim$25 °C.
Slightly higher concentration of dissolved uranium concentrations in the solid pellet experiment (6.0 \times 10^{-9} \text{ mol/l}) might be attributed to a thin layer of higher oxidized uranium on its surface as these samples were not annealed in a reducing environment like the others with values of about 3.0 \times 10^{-9} \text{ mol/l}. Since the uranium concentration values in the contact solutions were essentially of the same order of magnitude (~10^{-9} \text{ mol/l}) for the pellet, thin film and powder samples, and formation of a uranium containing secondary phase took place, it can be suggested that the equilibrium uranium concentration in the solution is limited by the solubility of the nucleating secondary phase and is independent of the \text{UO}_2 form (bulk pellet, thin film or powder).

Just as schoepite’s solubility [35] forms the upper limit of uranium dissolution in oxic conditions, the limitation of uranium dioxide dissolution in anoxic conditions will be limited by solubility of these uranium (IV) secondary nucleates. Hence, parameters such as specific surface area, density of reactive surface sites, particle sizes and sample crystallinity (amorphous vs. crystalline) should not affect the uranium concentration established in the solution in the long-term and may only affect the kinetic aspects of the process [63].

5. Conclusions

For extended durations up to 390 days, we conclude that the baseline scenario of uranium dioxide dissolution in deionized water will result in dissolved uranium dioxide concentration of the order of 10^{-9} \text{ mol/l}, which is indicative of \text{U}^{4+} dissolution. Relatively slight variation in uranium concentrations of less than one order of magnitude is observed between different sets of \text{UO}_2 samples (pellets, thin film and powder).
Variable temperature dissolution was conducted over a duration of 390 days and the concentration of dissolved uranium did not increase with elevated temperatures.

The dissolved uranium concentration of these long-term anoxic uranium dissolution experiments went through a maximum before decreasing to a constant value being indicative of a dissolution and precipitation mechanism, which is verified by the observed uranium containing secondary phases. At such low dissolved uranium concentration, dissolution and precipitation of uranium is hypothesized to proceed through the tetravalent form. This hypothesis is reinforced by clear observations of clusters (~500 nm) of homogenous uranium-containing precipitates of 20–100 nm grains in the thin film dissolution experiment.

From these experiments, we conclude that anoxic uranium dissolution with deionized water proceeds in 2 forms simultaneously at the surface.

1) a dissolved oxygen-dependent step of \( U(IV)_{(solid)} \) to \( U(V, VI)_{(solid)} \) then \( U(VI)_{(aqueous)} \)

2) a non oxygen-dependent \( U(IV)_{(solid)} \) to \( U(IV)_{(aqueous)} \) process to \( U(IV)_{(precipitates)} \)

We proposed that the equation for process 2 will take the following form:

\[
UO_2(s, \text{defective}) + 2H_2O(l) \rightarrow U(OH)_4(aqueous) \rightarrow UO_2(s, \text{less defective}) + 2H_2O(l), \ \Delta H < 0 \ (5)
\]

Acknowledgements
We would like to acknowledge the Singapore Nuclear Research and Safety Initiative for partial funding. We would also like to acknowledge Thomas Gouder, Rachel Eloirdi, Alice Seibert from the European Commission, Joint Research Centre, Directorate for Nuclear Safety and Security for providing the thin film sample. Lastly, we will also like to express our thanks for being able to use the UTGARD National Nuclear User Facility (NUUF) for some of our experiments.

Conflicts of interests
There are no conflicts of interests to declare.

Data Availability
The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study. However, additional information on EBSD data processing has been included in the electronic supplementary information.

References


fuel (UO2) inside a failed nuclear waste container | NWMO TR-2012-09, 2012.


[29] F. Bachmann, R. Hielscher, H. Schaeben, Texture Analysis with MTEX – Free


doi:10.1016/S0022-0728(81)80384-1.


The graph illustrates the uranium concentration over time, with data points indicating the concentration in samples A, B, and C, as well as the weighted average. The concentration is given in units of $10^{-9}$ mol L$^{-1}$.
- Uranium Concentration in sampling vessel
- Uranium Concentration in control vessel

Uranium concentration (x 10^{-9} mol L^{-1}) vs. Time (days)
- Settling duration for colloids

<table>
<thead>
<tr>
<th>Colloidal size / nm</th>
<th>Settling Duration in Days</th>
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The low amount of measured uranium indicates low amount of dissolved oxygen according to this simulation.

This region indicates the detection limits of our oxygen sensors.
**Figure Captions**

**Fig. 1.** Uranium concentration in aliquots obtained from three vessels, A, B and C containing a uranium pellet each and a control vessel labelled as blank with the same set up without a uranium pellet.

**Fig. 2.** Open circuit potential of the uranium dioxide electrodes recorded at the beginning and end of this leaching experiment. Note values are plotted vs. the standard calomel electrode (SCE) for ease of comparison with data from (Shoesmith and Sunder, 1992).

**Fig. 3.** Main: Linear baseline subtracted, area averaged Raman spectra of a freshly polished UO₂ electrode and three UO₂ electrodes after 100 days dissolution over the Raman shift range 350 to 750 cm⁻¹. Inset: Example Lorentzian fit of defect bands at 575 cm⁻¹ and 630 cm⁻¹ from a single measurement point from electrode A after leaching.

**Fig. 4.** Lorentzian peak fit results for the data of Fig. 5, assuming peak maxima at 440, 575 and 630 cm⁻¹. Results are expressed as a ratio of (A) the 575 cm⁻¹ peak and (B) the 630 cm⁻¹ peak to the 440 cm⁻¹ peak.

**Fig 5.** (a) SEM at the surface of the (a) pre-leached UO₂ pellet after polishing and (b) the post-leached UO₂ pellet.

**Fig. 6.** Dissolved uranium concentrations of extracted aliquots from both the uranium dioxide thin film dissolution vessel and the silicon wafer only vessel (control), determined by ICP-MS.

**Fig. 7.** (a) 30000× magnified secondary electron and (b) backscattered electron micrographs of the thin film before prewash and heat treatment.
Fig. 8. (a) 30000× magnified secondary electron and (b) backscattered electron micrographs of the leached thin film surface after 140 days dissolution.

Fig. 9. (a) 200,000× magnification secondary electron and (b) backscattered electron micrographs on the nucleate with clear growth domains ranging between 20-100 nm (Aleksej J. Popel, Beng Thye Tan, Thomas Gouder, Giulio I. Lampronti, Jason Day, Rachel Eloirdi, Alice Seibert, 2019).

Fig. 10. Secondary (a) and backscattered electron (b) micrographs of secondary precipitates detected at 30,000× and secondary (c) and backscattered electron (d) micrographs of secondary precipitates detected on blank silicon substrates at 100,000× magnifications.

Fig. 11. Stokes’ equation predicts the relationship between the settling/sedimentation duration against colloidal size for colloidal precipitation in 2 cm deep leaching vessel, similar to our set-up.

Fig. 12. XRD diffractogram for the pre-leached and post-leached UO₂ thin film sample on a silicon substrate. Only 200, 400, and 600 UO₂ reflections corresponding to the (001) crystallographic orientation are present.

Fig. 13. Thresholded EBSD map showing the misorientation angle of every pixel with respect to the average orientation. The twelve adjacent misorientation profiles delimited by the two red curves were averaged to obtain the averaged misorientation profile of Figure 16.

Fig. 14. Averaged misorientation profile (see Fig. 15 as a reference)
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In the ESI

**Fig. ESI 1.** Thresholded EBSD map showing the misorientation angle of every other pixel with respect to the average orientation. The misorientation profile used for the quantification of the precision error is shown in red.

**Fig. ESI 2.** Distance (in um) versus misorientation angle (in °) fitting plot of the profile shown in Figure 13 (green curve). The red dashed represent the 3rd order polynomial fitting curve plus or minus ± sigma = 0.08°.