# EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

## ESRF

# Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF**.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
*https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

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### Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the <u>period of 3 months</u> after the end of the experiment.

### Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, <u>you must submit a report on each of your previous measurement(s)</u>:

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

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### Deadlines for submitting a report supporting a new proposal

- ➤ 1st March Proposal Round - **5th March**
- ➤ 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### Instructions for preparing your Report

- fill in a separate form for <u>each project</u> or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

| | **Experiment title:** Understanding the corrosion mechanism of mixed actinide nitride nuclear fuels | **Experiment number**: A28-1-1358 |
|---|---|---|
| **Beamline**: BM28 – CRG XMaS | **Date of experiment**: from: 17th May 2023 to: 24th May 2023 | **Date of report**: 01/06/2023 |
| **Shifts:** 18 | **Local contact(s):** Didier Wermeille | *Received at ESRF:* |

**Names and affiliations of applicants** (* indicates experimentalists):

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**Report:**

Actinide-based mono- and mixed-nitrides (UN, ThN, $\{U_xTh_{x-1}\}N$), are at the forefront of advanced technology fuel (ATF) research and development. The requirement for an ATF material is to outperform the current $UO_2$ – zirconium alloy fuel-clad system under normal operating conditions, and in the event of an accident, for example, a loss-of-coolant-accident, an event which occurred during the 2011 Fukushima Daiichi Nuclear Power Plant accident. In addition to their use in generation-III light-water reactors (LWRs), the nitride-based actinide fuels are also considered for use in next-generation high-temperature gas reactors as the fuel kernel for the TRISO concept.

The UN and ThN mononitrides, and (U,Th)N composites have gained interest due to their increased fissile density and improved thermal properties compared to $UO_2$, benefiting the overall performance of the nuclear reactor. A thorium-based fuel has further advantages over the uranium fuels due to the production of U-233 when Th-232 undergoes neutron absorption, resulting in a more efficient fission process in the thermal energy regime, as well as the high natural abundance of thorium in the Earth's crust.

If these proposed ATFs are to be implemented into the nuclear fuel cycle, it is vital for the aqueous corrosion behaviour of each phase to be investigated. There is the potential for fuel components to come into contact with aqueous environments *in* and *ex operando*, therefore assessing the structural and chemical evolution of fuel phases within such scenarios is imperative to our knowledge.

The experiments performed at the XMaS beamline aimed to investigate the aqueous corrosion behaviour of mixed-actinide oxide and nitride surfaces. Using the XMaS beamline, it was possible to conduct an *in situ* x-ray diffraction investigation into these corrosion mechanisms, utilising the synchrotron as both a radiation source to

drive radiolytic corrosion and a measurement probe to determine the phases present during and after corrosion, giving a unique insight into this important reaction.

## Experimental Results

During our allocated beamtime, we were able to assess the effect of radiolytic species at the surface of eight mixed-actinide phases with varied stoichiometries. This has allowed us to understand the effect of adding thorium into uranium nitride (UN) and uranium oxide ($UO_2$) systems and how the dissolution behaviour changes as a function of thorium content. From previous studies, conducted by Bright *et al*., [1] it was found that [001]-oriented UN oxidises to form topotactic $U_2N_3$ and $UO_2$. It was therefore a priority to assess the mixed-actinide oxide phases $(ThO_2)_x(UO_2)_{1-x}$, as these systems will be the primary oxidation phase forming at the surface of [001]-UN and [001]-oriented $(ThN)_x(UN)_{1-x}$.

The first set of measurements taken replicated the previous dissolution measurements conducted by Springell *et al*., [2], where the thin film sample is held within a surface tension cell (Fig 1). Once in place, MilliQ water is injected into the cell and, at a grazing incidence angle, incident photons radiolyse the water allowing for dissolution at the surface of the sample.
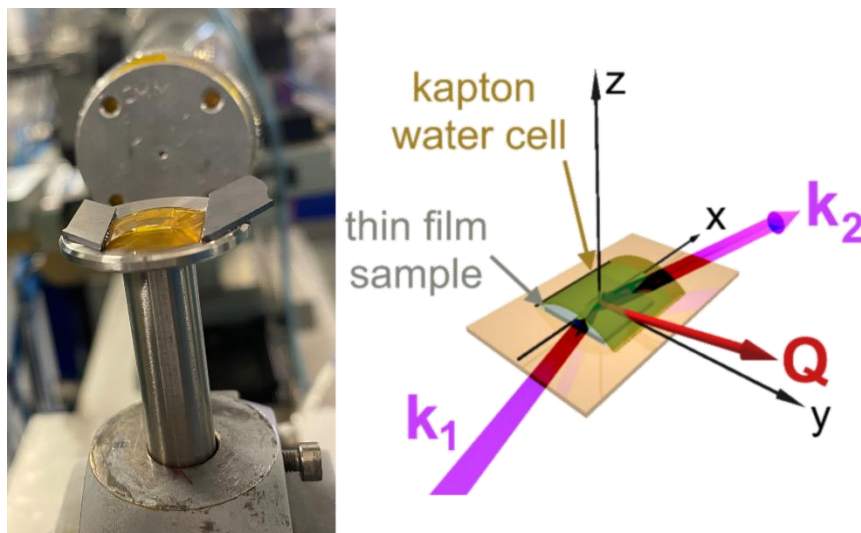


*Figure 1: (Left) Kapton cell set-up at the XMaS beamline. (Right) Schematic of kapton cell for grazing incidence reflection geometry set-up.*

Fig. 2 shows the fitted XRR dissolution data collected from [001]-oriented UN. Here, the XRR data has been offset to allow for an easier visual inspection of how the Keissig fringes evolve as exposure to radiolytic species increases. All raw data points are shown with open black circles, with each fit shown with a solid coloured line. The pristine UN sample is shown with a pink solid line, with the final exposure dataset shown with purple. Minimal changes happen to the fringes situated between $Q = 0.15 - 0.4$, this is because these particular fringes stem from the Nb buffer layer which is the epitaxial matching layer between r-plane $Al_2O_3$ and UN. The extracted layer thicknesses are presented on the right. The total thickness lost from the [001]-UN sample was approximately 38 Å, suggesting a dissolution rate of 0.013 Ås$^{-1}$. This rate is of the same order as the dissolution rate calculated by Bright *et al*., [3] (0.02 Ås$^{-1}$), suggesting a good agreement with literature. What must be stressed here is the data collected by Bright *et al*., [3] was from nano-crystalline thin films, suggesting that any differences in the dissolution rate could be linked to crystallite orientation. A further study into the effect of

radiolytic species on the [110] and [111] surfaces of UN would be beneficial to furthering our understanding of the corrosion behaviour of UN.
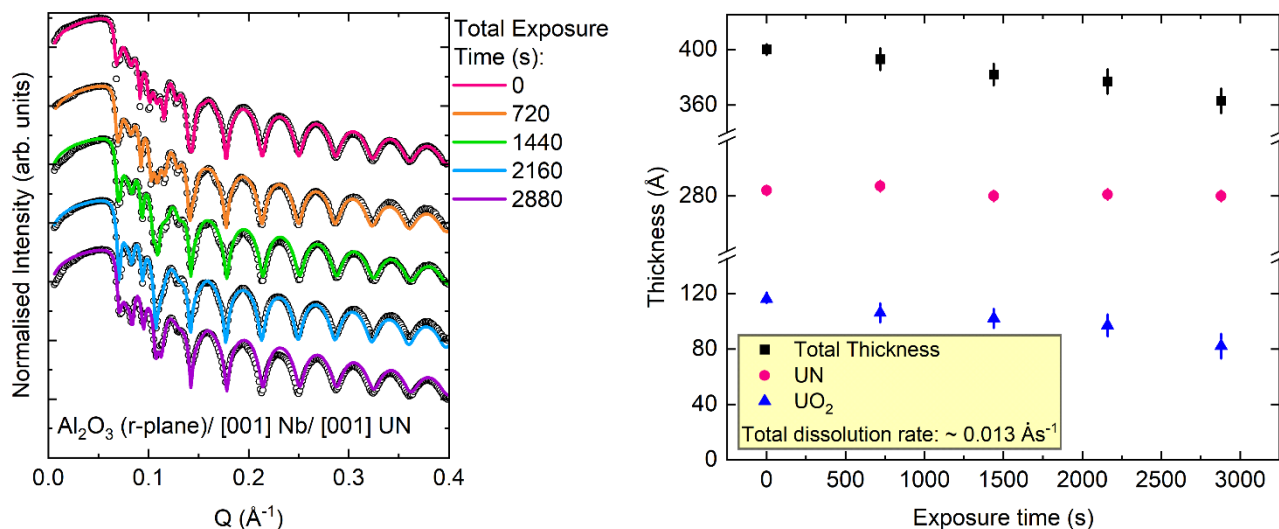


*Figure 2: (Left) XRR dissolution data collected from [001]-UN thin film. Data offset to show changes to Keissig fringes as exposure time to radiolytic species increases. (Right) Thicknesses extracted from XRR data, total (black squares), UN (pink circles), and $UO_2$ (blue triangles). Total dissolution rate calculated to be approximately 0.013 As$^{-1}$.*

The second phase of experiments conducted on XMaS utilised the epitaxial match of $Al_2O_3$ r-plane /[001] Nb/ [001] UN. The samples deposited upon r-plane $Al_2O_3$ has a unique feature of a 2.5° miscut, causing the [010] reflection to lie 2.5° away from the plane of the film surface. The <010> reflections can therefore be measured in a grazing incidence reflection geometry, which is ideal for driving radiolytic corrosion. As the surface $UO_2$ and intermediate $U_2N_3$ layers are shown to form topotatically on UN, all in the [001] orientation [1], these reflections can also be measured using the same geometry. For this experiment, we utilised a 2D detector to measure the relative intensity from the [111] type reflections of UN and $UO_2$. The integrated intensities gathered from the reflections is presented in Fig 3. This part of the experiment allowed for the dissolution of epitaxial UN to be measured *in situ*. From the data collected, it is clear that the relative intensity of the (222) UN reflection decreases as a function of exposure time, whereas the intensity of the (222) $UO_2$ reflection appears to stay almost constant. This could be suggesting that the oxidation products are continuously replenished resulting in the oxidation of UN to $UO_2$.
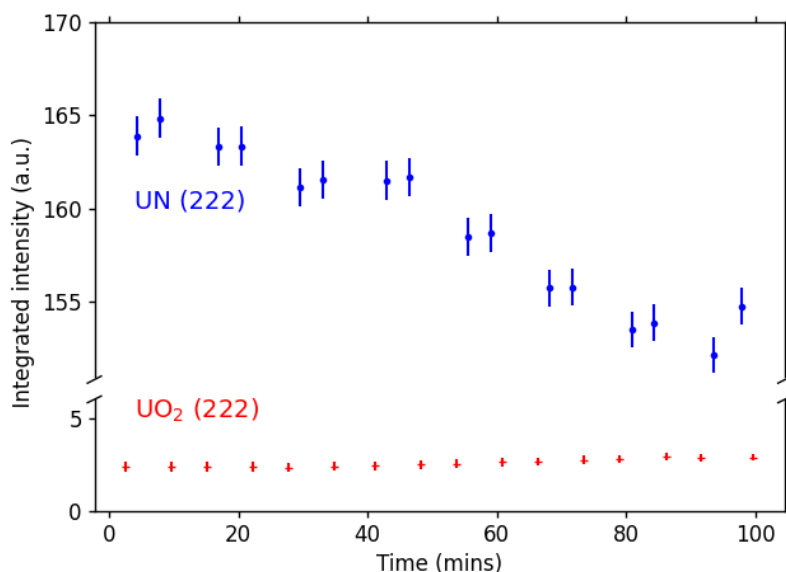


*Figure 3: Dissolution results from grazing incidence experiment. Preliminary analysis showing a clear decrease in the intensity of the (222) reflection from UN, integrated intensity of the (222) of oxide layer, assumed to be UO2, remains constant.*

## Conclusions

In this experiment, the aqueous dissolution of mixed (U,Th) oxides and nitrides was measured using x-ray reflectivity techniques. The advantage of using synchrotron radiation for this experiment, is that the incident photons can be used as a source to radiolyse water and as a probe to measure changes to the sample surface. Data presented in this report indicated the dissolution rate of [001]-oriented UN within a MilliQ water environment is slower when compared to values previously presented, suggesting there is a crystallite orientation dependence on the dissolution of UN. Probing the corrosion behaviours of (U,Th) oxide systems has further benefited our corrosion models for the mixed-nitride systems.

Using the unique epitaxial match of $Al_2O_3$/UN, in-plane Bragg reflections were monitored *in situ* (Fig. 3), allowing for a deeper insight into the corrosion mechanism of UN. The confirmation that this particular method works, has opened up another avenue of work with regards to investigating the corrosion behaviour of epitaxial UN and (Th,U)N systems.

**References:**
[1] Bright, E.L., Darnbrough, J.E., Goddard, D.T., Griffiths, I., Cattelan, M. and Springell, R., 2022. Oxidation and passivation of the uranium nitride (001) surface. Corrosion Science, 209, p.110705.
[2] Springell, R., Rennie, S., Costelle, L., Darnbrough, J., Stitt, C., Cocklin, E., Lucas, C., Burrows, R., Sims, H., Wermeille, D. and Rawle, J., 2015. Water corrosion of spent nuclear fuel: radiolysis driven dissolution at the UO 2/water interface. Faraday Discussions, 180, pp.301-311.
[3] Bright, E.L., Rennie, S., Siberry, A., Samani, K., Clarke, K., Goddard, D.T. and Springell, R., 2019. Comparing the corrosion of uranium nitride and uranium dioxide surfaces with H2O2. Journal of Nuclear Materials, 518, pp.202-207.