



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://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months 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, you must submit a report on each of your previous measurement(s):

- 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 from 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.

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 each project 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 hydrothermal conversion mechanism of mixed uranium-cerium oxalate into oxide thanks to in situ XANES analysis | Experiment number: CH-6608 |
| Beamline: 30 | Date of experiment: from: 03/05/2023 to: 09/05/23 | Date of report: 20/10/2023 |
| Shifts: 18 | Local contact(s): Jean-Louis Hazemann / Isabelle Kieffer | <i>Received at ESRF:</i> |
| Names and affiliations of applicants (* indicates experimentalists): Sofian Benarib, CEA/ICSM * Maëva Munoz, CEA/ICSM * Nicolas Clavier, CNRS/ICSM * Nicolas Dacheux, University of Montpellier/ICSM * Jean-Louis Hazemann, CNRS/ESRF * | | |

Report:

New generations of nuclear reactors require the development of innovative methods to elaborate nuclear fuels. Within this framework, studies have been devoted to the hydrothermal conversion of An(IV) oxalates (An = Th, U, Np, Pu) which allows the direct and quantitative precipitation of hydrated oxides from solution. In this frame, our group is currently studying the hydrothermal conversion of uranium(IV)-cerium(III) mixed oxalates into oxides, cerium being used as a surrogate for plutonium. These two elements can exist in several oxidation state in solution, thereby inducing a complex redox behaviour during hydrothermal treatment. Monitoring the variation in the degree of oxidation of uranium continuously during hydrothermal conversion using in situ XAS analysis should enable us to understand the mechanisms by which uranyl ions are reduced by oxalates, to obtain kinetic information about this reduction, and also to monitor the speciation of uranium in solution and in the precipitated solid.

In order to explore the redox mechanisms driving the reductive hydrothermal conversion of uranyl ions to UO_{2+x} , *in situ* XANES analyses were carried out on ESRF BM30-FAME beam line. The FAME line is specifically designed for X-ray absorption spectroscopy analyses in the field of materials and the environment. During experiments carried out on this line, it is possible to use internally heated autoclaves developed at the Institut Néel, mainly for in situ XAS studies in hydrothermal fluids at moderate temperature and pressure ($T < 800^{\circ}C$, $P < 2000$ bars). The XANES spectra were acquired at the U-L₃ edge (about 17.166 keV). Also, the inner cell, containing the reaction mixture, can be moved vertically, allowing the beam to interact with different zones during the experiments. The study focused on monitoring the degree of oxidation of uranium in solution and within the precipitate formed rapidly during hydrothermal treatment, as seen in **Figure 1** below.

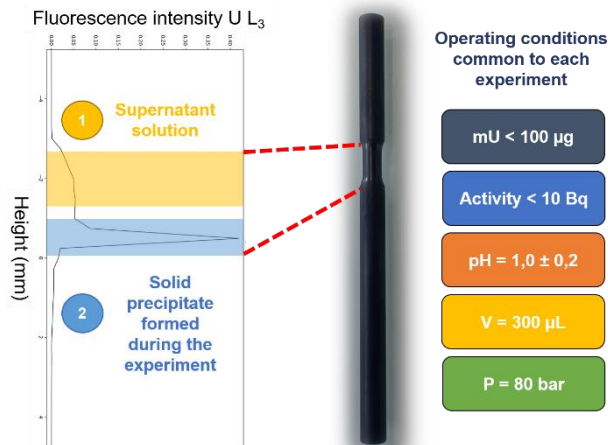
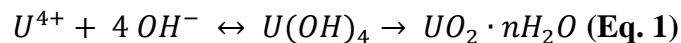


Figure 1: Summary of the experimental conditions common to all the experiments carried out on BM30.

An almost complete reduction of uranium(VI) in solution was observed, as well as a change in its complexation caused by the decomposition of oxalate entities under the combined effect of pressure and temperature. Similarly, the decrease in the fluorescence intensity in solution was correlated with the rapid precipitation of uranium, which followed a first-order kinetic law. In addition, the study of the solid phase showed that uranium(IV), coming from the rapid reduction of uranyl ions in solution, precipitated directly as UO_{2+x} , which provides new insights into the formation mechanisms of tetravalent actinide hydrated oxides. Furthermore, no variation in the degree of oxidation of uranium within the solid was detected under the conditions of the analysis. The white line of the spectra recorded on the solid fraction did not vary with the duration of the hydrothermal treatment and the complexation of uranium remained constant within the precipitate. Thus, no signal corresponding to the $U(OH)_4(s)$ species was observed. In the literature, some authors have questioned the equilibrium to be considered for the formation of hydrated oxide from U^{4+} cation in solution and proposed the following two equilibria:



Our observations show that under the conditions studied, the precipitated phase is directly the hydrated oxide, and that the $U(OH)_4$ species is only a potential reaction intermediate, existing only for a very short time. The equilibrium to be considered should therefore be that of **Equation 2**. Our various observations are summarised in **Figure 2**, which can be seen below.

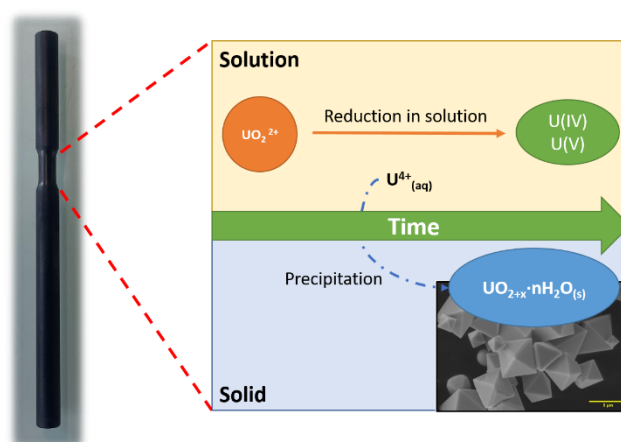


Figure 2: Summary of the hydrothermal conversion of a uranyl solution into hydrated uranium(VI) dioxide.

These results, obtained through a novel experiment using cutting-edge techniques, provide a more accurate reaction scheme for the hydrothermal conversion process. This series of experiments therefore demonstrated that the precipitated solid is directly UO_{2+x} .