ESRF	**Experiment title:** Study of the solubility and local structure of water−diluted uranium oxide in supercritical conditions	**Experiment number**: CH−1089
Beamline: BM32	**Date of experiment**: from:25/04/01 to:02/05/01	**Date of report**: 14/03/02
Shifts:20	**Local contact(s)**: Dr Olivier Proux	*Received at ESRF:*

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Report:

Experimental:

Dissolution of U3O8 in supercritical water has been studied by XAFS spectroscopy on BM 32 beamline. Our goals were to measure the solubility of that oxide as well as the local structure of dissolved Uranium. The experimental conditions were a constant pressure of 270 bars and temperature ranging from ambient up to 500°C (100°C steps and 50°C around the critical point). Uranyl nitrate solutions have been studied in the same conditions. We used our experimental cell in both transmission and fluorescence modes. The spectra were taken at the Uranium L3 edge (17166 eV). The EXAFS treatment was carried out with FEFF8.

Dissolution of U3O8 in supercritical water:

As explained in reference [1], the absorption edge jump is exploited to calculate the molality of Uranium in the aqueous solution. Figure 1 shows that molality at 270 bars from ambient temperature up to 500°C. That plot stresses a strong dissolution of U3O8 in supercritical conditions. First, the highest absolute value of the molality is high (about 0.2 mole/kg at 500°C) and two orders of magnitude higher than the lowest value (30°C). Then, the increase is not homogeneous (slow in ambient and subcritical conditions, and steep around the critical point (375°C).

Local structure of dissolved Uranium:

Figure 2 represents the experimental spectra obtained. In figure 2 a), the spectra are that of uranyl nitrate solutions in transmission mode at 250 bars from 30°C up to 355°C. They are useful to get the local structure of uranyl ion in supercritical conditions. In figure 2 b), one can observe the fluorescence spectra of dissolved U3O8. Some qualitative comments can be made. First, for each one, an evolution with the temperature is observed (local changes of frequency pointed by the dotted lines) that may correspond to a

change in the U−O distance for the uranyl ion. Then, qualitative comparison of both spectra reveals a strong difference in the environments. As a consequence, it is stated that the uranyl ion is not present (or in a very small quantity) in the aqueous solution resulting from the dissolution of U3O8. That is corroborated by the value of the edge energies (lower in the U3O8 case than in several uranyl references). That is a paradoxical conclusion. Indeed, the Uranium hexavalent form is known for its high solubility as the uranyl ion [2], but in our case, despite the high molality observed in supercritical conditions, no U (VI) form was detected.

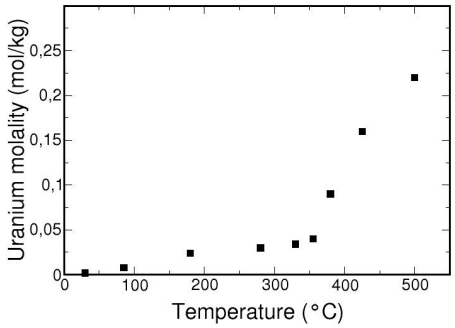

Figure 1: molality of Uranium in dissolved U3O8 aqueous solution.

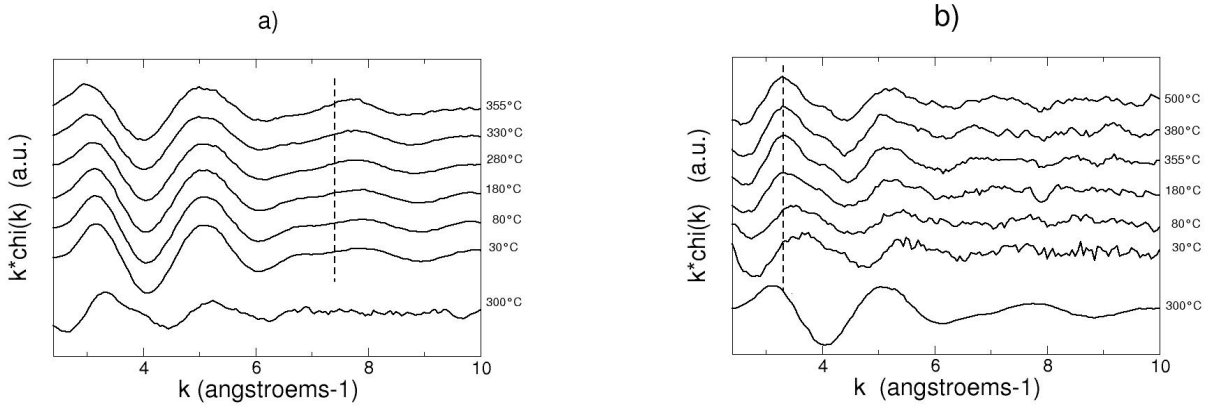

Figure 2: a) k*chi(k) transmission spectra of a solution of uranyl nitrate at 250 bar and different temperatures. The spectrum of dissolved U3O8 at 300°C, 270 bar has been drawn as an element of comparison at the bottom of the graph. **b)** k*chi(k) fluorescence spectra of dissolved U3O8 aqueous solutions at 270 bar and different temperatures. The spectrum of uranyl nitrate at 300°C, 250 bar has been drawn as an element of comparison at the bottom of the graph.

Conclusions and perspectives:

First, this experiment gives evidence of the high sensitivity of our fluorescence experimental set−up: even if the XAS spectra quality is not high, they can be exploited despite the few 10 ppm of the solution. Then, the results concerning the dissolved Uranium in supercritical water are promising. XAFS fitting of the fluorescence spectra need to be conducted in order to get an insight on the precise structure and valence of Uranium in such conditions. Finally, the local change in the structure of the uranyl ion in supercritical conditions has to be studied more carefully.

References:

1 V. SIMONET and al, J Chem. Phys., 116, **2002**, p.2997.
2 P. BURNS and R. FINCH, Reviews in Mineralogy, 38, **1999**, p.220.