ROBL-CRG	**Experiment title:** XAS study of the PuO_{2+x} oxides	**Experiment number**: 20 01 607
Beamline: BM 20	**Date of experiment**: from: 20 to: 22 November 2002	**Date of report**: 29 November 2002
Shifts: 6	**Local contact(s)**: Andreas BAUER	*Received at ROBL:*

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Report:

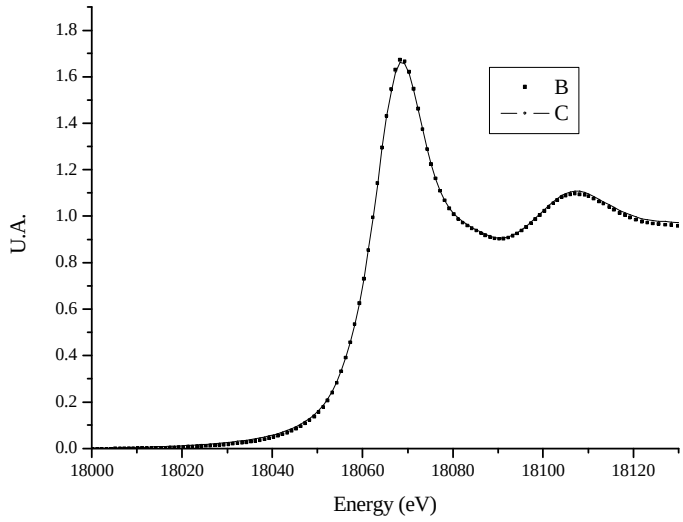
The aim of our measurements is to verify the existence of hyperstoichiometric PuO_2 and to characterise more precisely its structure using X-ray Absorption Spectroscopy. As described by Haschke *et al*[1]., PuO_{2+x} appears under specific conditions by reaction of PuO_2 with adsorbed water following the global scheme:
PuO_2 (s) + x H_2O (ads.) à PuO_{2+x} (s) + x H_2 (g)

Preliminary tests performed at CEA Marcoule, by prolonged action at 340°C of a PuO_2 powder obtained by oxalic conversion, with an inert gas saturated with water, did not reproduce the previous reaction. It seems that very specific physico-chemical conditions are required, in particular the PuO_2 powder surface state. The temperature and pressure conditions of the reaction also has to be precisely reproduced to reach the oxidation kinetics required to obtain a significant hyperstoichiometry and within a period of a few months.

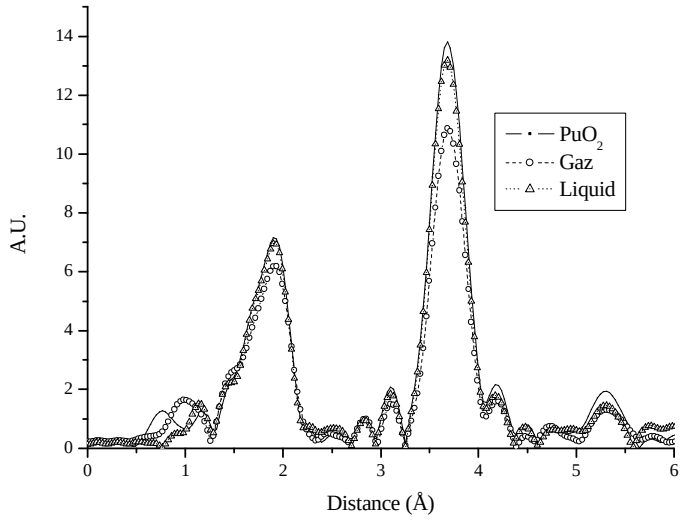
Two new samples were then prepared by total immersion and in water atmosphere during 2800 hours at temperatures between 130 and 180°C. They were conditionned in the Atalante facility at Marcoule in order to respect the standards of

protection against radiation of the BM20 line. They were encapsulated and sent to ESRF by special transportation according to the French regulations.

For each sample, the transmission and fluorescence signals were collected at the plutonium (18.056 keV) L_{III} edges. Energy calibration of the XANES data was achieved using the reference Zr foil (17.998 keV) positioned after the second ionisation chamber. As shown on the following figure, the XANES spectra are always the same, whatever the reaction conditions used.



As observed on the Fourier Transforms, the position of the white line remains the same to the one of a PuO_2.reference compound. The oxidation state of plutonium remains equal to +IV in all our samples.



Further data analysis are conducted to confirm these results.

[1]J. M. Haschke, T. H. Allen, L. A. Morales, Science, 287, 285 (2000).