ROBL-CRG	**Experiment title:** **Study of the alumina-uranium interaction under ultrasonic cavitation**	**Experiment number**: **20-01-658**
Beamline: BM 20	**Date of experiment**: from: 12/05/2008 to: 16/05/2008	**Date of report**: 13/11/2008
Shifts: 8	**Local contact(s)**: Andreas Scheinost	*Received at ROBL:*

Names and affiliations of applicants (* indicates experimentalists):

Tony Chave ICSM, Marcoule
Sergey Nikitenko CNAB, CNRS, Gradignan
Andreas Scheinost ROBL ESRF

Report:

I. Context and objectives

A preliminary study carried out on MSU-X type mesoporous alumina has shown the drastic effect of ultrasound on its behavior in aqueous solution at ambient temperature. Thus, it was shown that sonication causes aluminum oxyhydroxyde (boehmite) formation instead of the aluminum hydroxide which is the main phase under stirring conditions [1-2]. The resulting boehmite forms a 2x20 nm fibrils with a significant specific surface area. The dehydration of $Al(OH)_3$ into AlOOH without ultrasound is observed under hydrothermal conditions at temperature about 150-200°C [3-5]. The current project is focused on interaction of uranyl ions with mesoporous alumina as a model matrix for the radionuclide confinement.

II. Materials and methods

Ultrasonic treatment was performed with a 20 KHz generator (Vibra Cell 600) coupled with a 1 cm^2 titanium horn under argon atmosphere in glass reactor thermostated at 37±1°C. The acoustic power absorbed by the media was around 0.6 $W.mL^{-1}$ with an intensity of 30 $W.cm^{-2}$. In each experiment, 300 mg of MSU-X type mesoporous alumina was mixed with a 50 ml total aqueous volume prepared with ultrapure water (18.2 MΩ.cm). Uranyl chloride solution was added to the system under

acoustic cavitation and weakly acidic conditions in order to reach a given uranium mass percentage between 5 and 30%. After a 30 min treatment, solution pH was adjusted to 11, thanks to ammonia addition, and the system was left under power ultrasound for further 30 to 60 min. This procedure was followed in order to optimize the formation of high aspect ratio boehmite and thus to maximize the interaction of alumina and uranium. Finally, powder samples were centrifugated, washed until neutral pH, dried at 70°C and calcinated at 800°C prior to U L_{III} XAFS and TEM analysis.

III. Results and discussion

First of all, it can be seen in Figure 1 that the fibrilar shape of the boehmite, observed in our previous study, remains even after its transformation into δ/θ alumina at 800°C. In the same way, experiment with 5% uranium and 60 min ultrasonic treatment in basic conditions leads to the formation of 5 nm uranium nanoparticles dispersed within the alumina matrix as it can be seen in Figure 2. XAFS analysis reveals the presence in this sample the uranyl species as shown in Figure 4 (U5% 800°C). Both XANES and EXAFS spectra are quite similar to those obtained for uranyl ions adsorbed onto gamma alumina at pH 6.

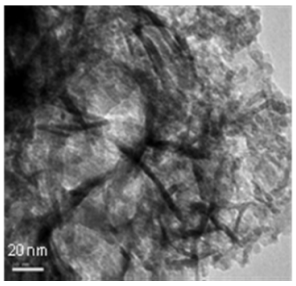

Figure 1: TEM picture of calcinated sample after 30 min pH 4 + 30 min pH 11 ultrasonic treatment with 5% uranium.

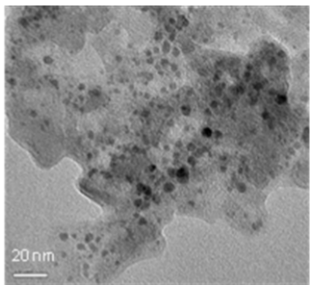

Figure 2: TEM picture of calcinated sample after 30 min pH 4 + 60 min pH 11 ultrasonic treatment with 5% uranium.

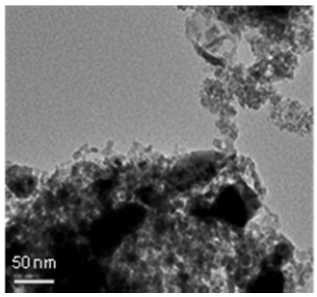

Figure 3: TEM picture of calcinated sample after 30 min pH 4 + 60 min pH 11 ultrasonic treatment with 30% uranium.

On the other hand, increasing the uranium concentration to 30% induces a drastic evolution of the sample after calcination with the occurrence of 50 nm crystals (Fig. 3) which could remind U_3O_8. In contrast to the previous sample, EXAFS spectrum points out in this case a strong U-U interaction at 4 Å (raw value) comparable with that of U_3O_8 reference sample. However, the XANES part of this analysis looks quite different and could not confirm for certain the presence of this formerly expected phase in our system.

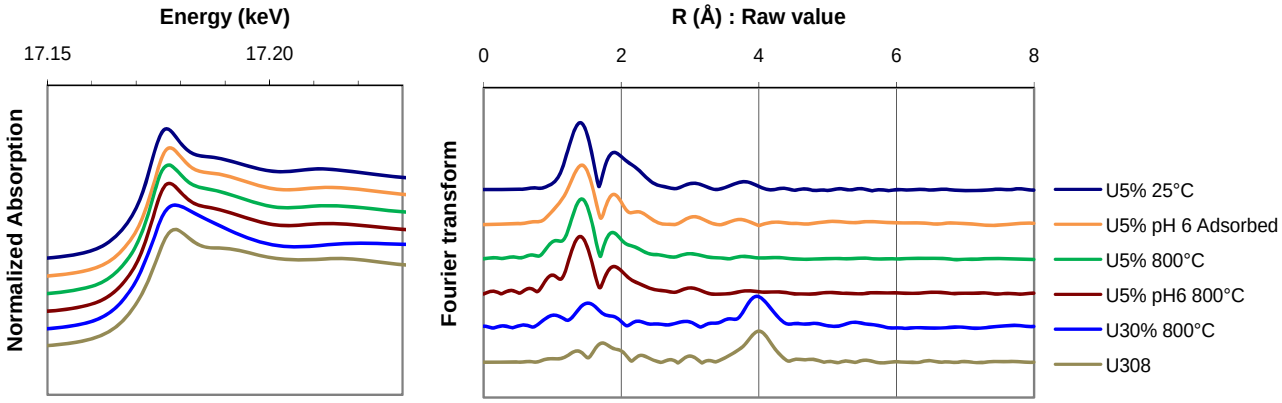

Figure 4: U L_{III} XANES and EXAFS spectra of samples obtained after various treatments. 'U5% 25°C' and 'U5% pH 6 adsorbed' samples were not calcinated and 'U5% pH 6 Adsorbed' was carried out under mechanical stirring.'U5% pH6 800°C' was obtained with the described procedure however the final pH was adjusted to 6 instead of 11 whereas 'U3O8' refers to a reference sample prepared at 800°C.

IV. Conclusions and perspectives:

To conclude these preliminary results, it can be focus on that, depending on the uranium concentration in the system, uranium nanoparticles could be formed and finely dispersed within the alumina matrix. However, further experiments are needed in order to understand the interaction of the uranyl group with the alumina matrix (5% U) and to characterize the large crystals formed with higher uranium concentration (30% U). In order to answer these questions, solid state ^{27}Al NMR and UV/Visible spectroscopy analysis are planned for the low uranium concentration system whereas X-Ray diffraction should enable the identification of the phases formed in the other case.

V. References:

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