



Experiment title: Study of uranium environment of CRMP process precursors at different steps of their synthesis – *the initial proposal did not have this title, topic was changed with the agreement of the local contact and the beamline head*

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CH 4211

Beamline:
BM20

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Shifts:
9

Local contact(s):
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1. Introduction

Americium isotopes represent the main contribution to long-term radiotoxicity and heat load of spent nuclear fuel. In order to limit this contribution, americium (Am) could be transmuted in fast neutron reactors, notably through the heterogeneous mode, consisting of the use of $U_{1-x}Am_xO_{2+\delta}$ compounds placed in the core periphery. In this context, several processes were developed in order to synthesize such compounds, mainly based on powder metallurgy. These processes proved to be reliable at the laboratory scale [1–3], but have a major drawback regarding the high radiotoxicity of Am isotopes, which makes americium-containing powders thus highly contaminant. At an industrial scale, the use of americium-based compounds should therefore be avoided. In this context, new processes are being developed. One of them, called CRMP ((calcined resin microsphere pelletization) process is based on the use of mixed uranium-amerium oxide microspheres obtained through the thermal conversion of ion exchange resin loaded with uranium (U) and americium cations [6,7]. The microspheres obtained can be used for pelletizing and sintering, thus avoiding the use of any americium-bearing powder. To be able to describe the entire route, it is necessary to understand each step of CRMP process, beginning by the work on ion exchange resin and their loading in aqueous solution. Indeed, it is of prime interest to understand how uranium does fix inside the resin and to which chemical complex it can correspond. Moreover, studying the structure of the oxide taken after calcination is also interesting, as hypothesis can be made on the carbon skeleton release step, knowing the initial and final structure. In this aim, EXAFS analysis is well appropriate to investigate the structure of the CRMP precursors at different steps of the synthesis.

2. Experimental

For this experiment, Am was replaced by surrogates such as cerium (Ce) and neodymium (Nd). The first batch of three samples was composed of resin loaded with: 1) pure U under uranyl cation form, 2) 20% Ce cations and 80% uranyl cations, and 3) 20% Nd cations and 80% uranyl cations. Two chemical references were also brought, whose structure and oxidation degree are close to the resin one: U acetate and carbonate. Considering the thermal conversion, second batch of three samples was composed of microspheres obtained after the first calcination under air. Microspheres obtained from above-mentioned samples after thermal conversion were brought: pure U_3O_8 microspheres, mixed oxide with U_3O_8 and Ce, mixed oxide with U_3O_8 and Nd. Reference of pure UO_3 and U_3O_8 powder was brought to compare with the obtained synthesized oxides.

XAS measurements were performed in transmissions and fluorescence modes at 15 K using the cryostat of the BM20 beamline. XANES and EXAFS spectra were recorded at U L_{III} edge.

3. Results

The report presents the results of U-Nd compounds. XANES of the resin is presented and compared to its reference. Figure 1 shows valence of uranium in the resin. It is completely hexavalent, as forecasted with fixation of pure uranyl on the resin. EXAFS of the loaded resin and of the intermediate oxide are presented at the UL_{III} edge. Lanthanide edges are missing today, but will be interesting to acquire in the future, to implement these data.

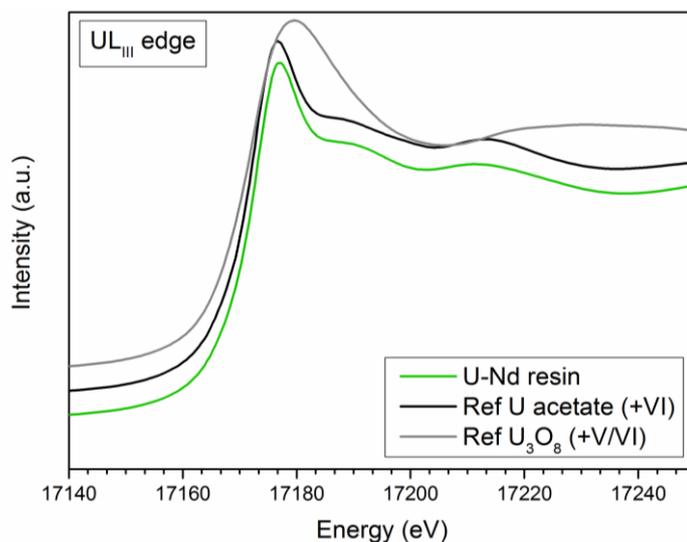


Figure 1. XANES spectra of the loaded U-Nd resin recorded at UL_{III} edge – in black the +VI reference and in grey +V/VI reference.

The local structure of the resin was determined by fitting the data with acetate structure. Comparison between data and fit are presented in Figure 2, in k and R respectively. It finally appears that uranyl ion is surrounded by three carbons: two bi-dentate and a single mono-dentate. One additional water molecule, linked to uranium, was also fitted but did not positively improve the fit, so EXAFS can not settle on the presence of structural water surrounding uranium.

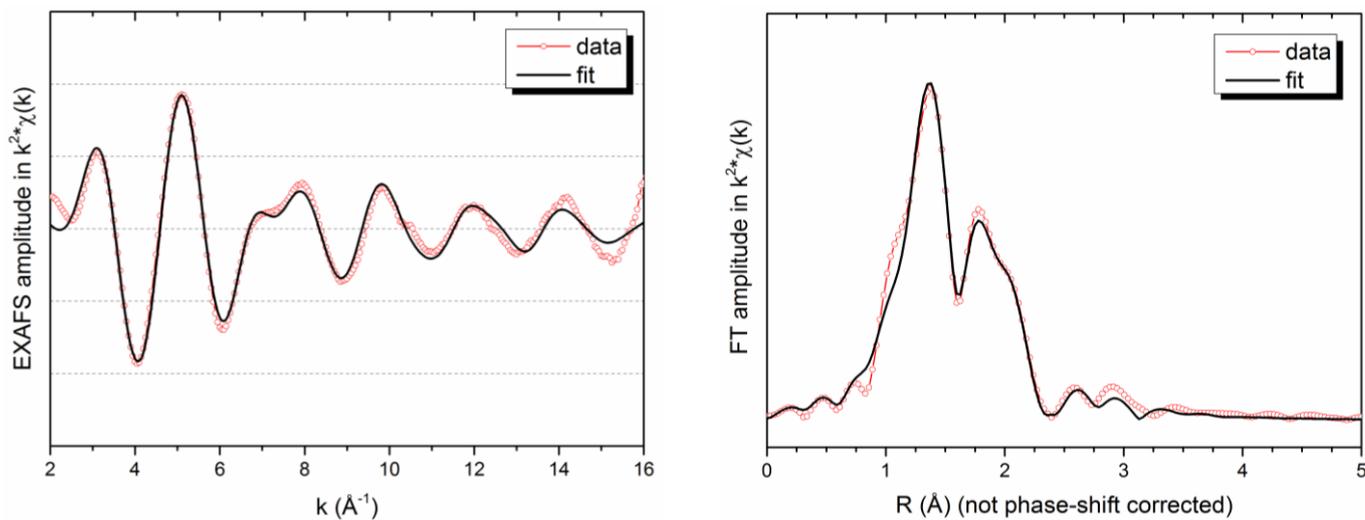


Figure 2. EXAFS spectra of the loaded U-Nd resin, plotted in k and in R , on left and right respectively.

Concerning the oxide, it is obtained after thermal conversion under air. XRD analysis reveals that it has crystallized under an M_3O_8 structure where Nd seems to be included in U_3O_8 structure. Nd has a trivalent valence in the structure, while U is +V/VI, inducing stresses due to important charge compensation. Making EXAFS at U edge helps to understand the structural consequence of such a substitution, from U point of

view. Its local structure was determined by fitting the data with the P-62m structure, which is the crystallographic structure identified by XRD. First refinements are presented below in Figure 3.

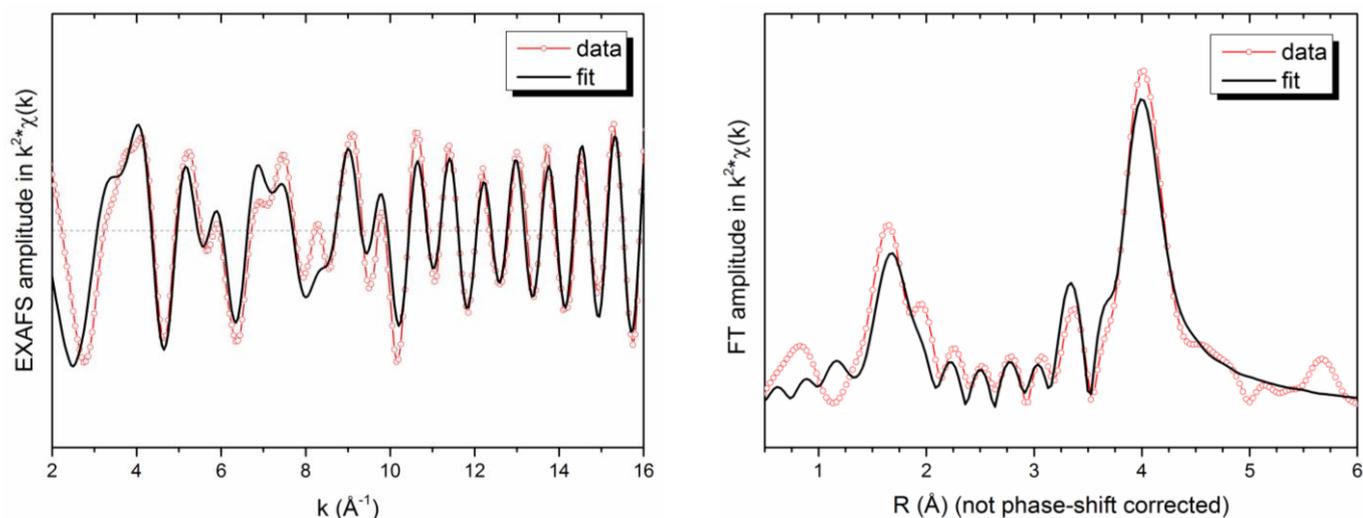


Figure 3. EXAFS spectra of the loaded U_3O_8 -Nd oxide, plotted in k and in R , on left and right respectively

First results show the reduction of the planar U-U bond and of axial U-O bond, the latter becoming closing to uranyl axial U-O distance. It suggests that a suroxydation of the U structure could help Nd substitution through the compensation of +III valence with O^{2-} excess. This needs to be confirmed by further experiences such as Infra-red spectroscopy and neutron diffraction, but remains a first step in this structure understanding.

4. Conclusion

The first results on the structure taken by U in the different steps of CRMP microsphere synthesis was studied through the surrogate system U-Nd. For the moment, only U edge was recorded, giving information on U environment. Results for pure U resin and U-Ce resin are also in progress. Lanthanide edges will be investigated in a further experiment in order to complete present structure information. In the future, these experiments could be corroborated to U-Am system.

5. References

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