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XAS characterization of U, AM oxides obtained using co-conversion and CRMP processes

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U1-xAmxO2±δ compounds (known as AmBB: americium-bearing blankets) are considered promising materials for americium transmutation in fast neutron reactors.1 The fabrication of these mixed-oxide pellets generally follows a powder metallurgy route that generates significant amounts of highly contaminant fine particles. Dustless processes which can avoid the dispersion of such fine powder in the fabrication line are thus recommended due to the high radiotoxicity of americium. In this aim, the development of innovative concepts has been initiated and two new routes are currently studied. The first one is based on the co-conversion of oxalates precursors.2 It enables obtaining an oxalate complex with a chosen U/Am ratio that can be mineralized to form a solid solution without additional milling or pelletizing step. Green pellets can then directly be pressed from the obtained oxide powder. The second one is Calcined Resin Microsphere Pelletizing (CRMP) process; its general approach consists of elaborating mixed-oxide microsphere precursors through an adaptation of the weak acid resin (WAR) process. The synthesis is based on the fixation of americium and uranium cations into ion exchange resin microspheres. As-loaded amorphous microspheres are then mineralized during a dedicated thermal treatment leading to the formation of porous oxide microspheres employed as pelletizing precursors.3,4

In the present work, samples at different steps of these innovative processes are studied through XANES and EXAFS measurements performed at ULIII, ULII and AmLIII edges on ROBL beamline at the ESRF, coupled with XRD. Concerning the oxalate route, XAS measurements were recorded after co-conversion of oxalates under argon and pellet sintering. For CRMP process, oxide microspheres obtained from loaded resin with uranium and americium were characterized. More precisely, spectra were collected on AmBB-type samples after the first thermal treatment under air, the second thermal treatment under a reducing atmosphere and pellet sintering. Regarding XRD, result interpretation remains however difficult as oxides obtained from starting materials are both low-ordered, preventing structural signal for the first steps. XANES results showed that after mineralization uranium is oxidized compared to U(+IV) and is then reduced during the thermal treatments under a reducing atmosphere (Ar-H2) to a mixture of U(+V) and U(+IV). In the meantime, americium is only present as Am(+III), whatever the thermal treatment conditions. Previous XAS studies on uranium-americium mixed oxides prepared by solid state reaction revealed a similar cationic charge distribution with the presence of reduced Am(+III) but partially oxidized uranium(+IV/+V).5,6 The present results indicate electronic charge transfer between uranium and americium in the compounds and thus their chemical homogeneity.

The presentation will give an emphasis on the influence of the synthesis process on the cationic charge distribution and the local structure of these compounds through the presentation of correlated results from XAS, and XRD.

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