EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

ESRF	**Experiment title: Study of the neoformed phases formed during the spent nuclear fuel alteration in groundwater** merged with **Study of the impregnation of microporous ThO_2 powder for new generation of nuclear fuel**	**Experiment number**: MA5319 MA5320
Beamline: ID02	**Date of experiment**: from:21/06/2022 to:23/06/2022	**Date of report**:
Shifts: 6	**Local contact(s)**: Narayanan Theyencheri	*Received at ESRF:*

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Report:

<u>First study</u>: Study of the neoformed phases formed during the spent nuclear fuel alteration in groundwater

In this experiment, 4 capillaries filled with 4 mg of $U_{0.93}Ce_{0.08}O_2$ powder having grain sizes comprised between 500 nm and 3 µm will be prepared in glove box of our laboratory. Three of these capillaries will be filled in glove box with synthetic groundwater prepared as in [1], sealed and altered during 4 months. During the beamtime, measurements were done at 16 keV (below the L3 edge of U) at a distance sample-detector of 1.4 m and 31m.

The initial goal of the experiments was to localize isolated grains presenting reflectivity due to the formation of an alteration layer of few nanometers. With this sample, no reflectivity and / or modification of the grain surfaces were observed.

<u>Second study</u>: Study of the impregnation of microporous ThO_2 powder for new generation of nuclear fuel

In this experiment, spherical particles of UO_2 (instead of ThO_2) were analyzed in order to determine their morphology and porous texture. These particles were prepared using wet chemistry routes aiming to precipitate directly morphology-controlled actinide oxides from mixtures of solutions. Such methods are mostly based on the hydrothermal decomposition of U(IV) carboxylate, followed by the hydrolysis of the cations which leads to the formation of amorphous $U(OH)_4$ samples, finally aging to UO_2.nH2O.

In order to minimize the absorption effect, sample located in katpon capillary has been characterized using synchrotron SAXS on ID02 beamline at the ESRF (Grenoble, France). The operating beam energy was 16 keV with a beam size of 70×90 μm^2 (vertical and horizontal, respectively). The sample to detector distances were 1.4 m, 6 m and 31 m. The scattering patterns were recorded using an Eiger 2 4M detector (Dectris). First, we centered the beam just above the powder/air interface of the capillary in order to probe just one or several isolated grains on the wall of the capillary. The azimuthally averaged 1D and merged SAXS profile obtained on 4 particles is shown on Figure 1. The scattering intensity at low q was fitted using a sphere form factor of having a size ditribution centered on 350 nm of radius. The large bump observed at high q due to the microporosity was treated as in [2]. From this method specific surface area of 26 m²/g, a porosity of 0.05 and a pore form factor of cylinders having 0.4 nm of radius and 0.2 nm of length were obtained.

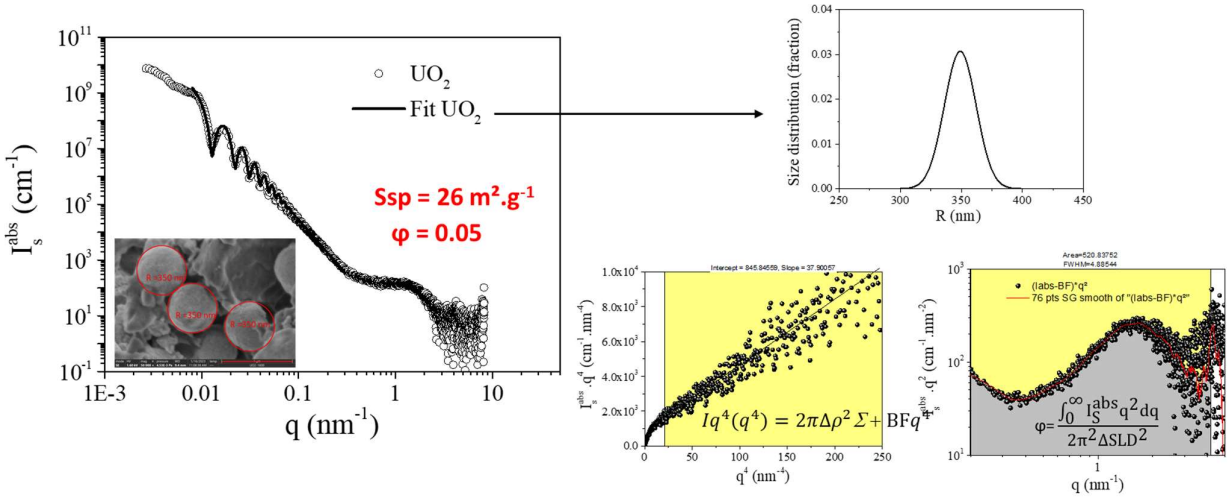

Figure 1: Experimental scattering intensity in absolute scale of 4 spheres, radius distribution of measured spheres obtained from the fit of the data at low q, Porod representation used to calculate the specific surface area and determination of the porosity using the invariant method.
The analyses of the SAXS data of the same samples after various thermal treatments are still ongoing.

References

[1] Michelin A., Burger E., Rebiscoul D., Neff D., Bruguier F., Drouet E., Dillmann P., Gin S., Silicate Glass Alteration Enhanced by Iron: Origin and Long-Term Implications, Environ. Sci. Technol. 47, 2, 750 (2013)
[2] Lu, Z., Rébiscoul, D., Narayanan, T., & Zemb, T. (2022). Specific analysis of highly absorbing nanoporous powder by small-angle X-ray scattering. Journal of Applied Crystallography, 55(5).