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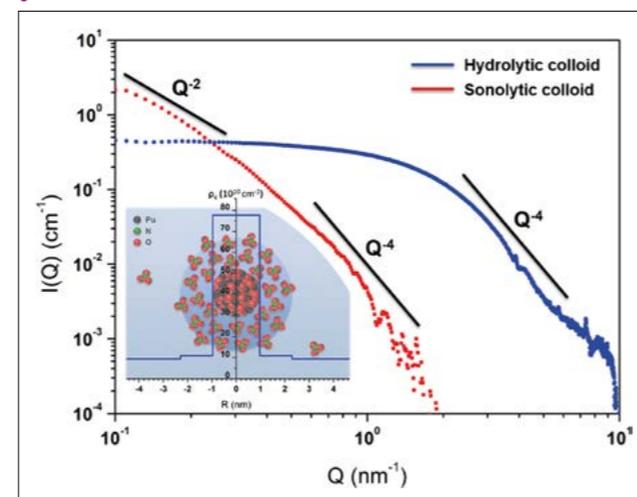
Probing the multi-scale properties of Pu(IV) intrinsic colloids by synchrotron SAXS/XAS techniques

Predicting the behavior and reactivity of radioactive “hot” particles in the geosphere requires their thorough characterization, if possible in their native environment. Research progress on Pu(IV) colloids is particularly challenging because of the complex chemistry of the element Pu and the high radioactivity of all of its isotopes. Within this framework, researchers from Marcoule Institute for Separation Chemistry (ICSM), CEA/DMRC and SOLEIL/MARS beamline, have combined synchrotron SAXS (Small Angle X-ray Scattering) and XAS (X-ray Absorption Spectroscopy) techniques to decipher the multi-scale structural properties of Pu(IV) intrinsic colloids prepared by hydrolysis or sonolysis.

Anthropogenic activities including nuclear weapon rotation, space conquest or industrial accidents have released substantial amounts of actinides into the environment. The element plutonium, which was thought to be highly immobile regarding its very low solubility in aquatic systems and high sorption ability onto minerals, has been proved to possibly move on the scale of kilometers. Both pseudo and intrinsic Pu colloids have been reported as potential vectors for the environmental migration of actinides, thus strengthening the need for their better description and characterization.[1] Pseudo-colloids refer to natural colloids on which Pu has been incorporated or adsorbed, whereas intrinsic ones rely on the ability of Pu to precipitate and form its own colloid. X ray-based scattering and absorption techniques are very useful to probe directly in the native medium, the nanoparticle (NP) properties including their local structure, oxidation state, size and morphology without any specific sample preparation. Two intrinsic Pu(IV) colloidal forms prepared by hydrolysis of Pu(IV) in water (presence of nitrates from the mother Pu solution) or 20 kHz sonication of PuO₂ powder in pure water under Ar/(10 %)CO atmosphere were investigated.[2]

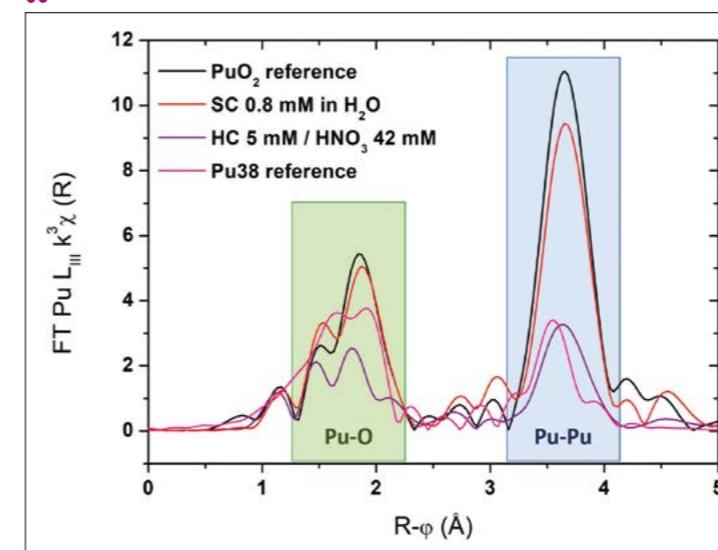
PARTICLE SIZE, MORPHOLOGY AND AGGREGATION PROPERTIES

The normalized scattering curves provided in Fig. 1 in absolute unit evidence strong differences for both hydrolytic (HC) and sonolytic (SC) colloids. The HC displays a Q⁰ for low wave vectors and tends towards Q⁻⁴ at higher wave vectors evidencing a sharp interface typical for 3D objects and compact particles. The SC exhibits a closer Q⁻² at low wave vectors ending with a Q⁻⁴ at larger wave vectors which features are typical from 2D elongated objects. Best fit for the SC was obtained with elongated disk particles of 5.7 nm thickness and more than 30 nm size. HC was rather explained using a spherical core-shell model constituted by a core matching with an ideal PuO₂ fluorite-type Fm-3m oxide structure surrounded by a disordered Pu-O shell solvated with nitrate counter-ions. Whereas HC size agreed with previous high-resolution transmission electron microscopy (HR-TEM) experiments, the bigger size of the SC (7 nm by HR-TEM) was explained by the aggregation of the NPs in the absence of stabilizing or capping agents.[2]



LOCAL STRUCTURE AND NANOSCALE PROPERTIES

The Pu L₃ edge XANES spectra acquired for a selection of HC and SC samples evidenced the strong predominance of the (+IV) oxidation state for the Pu. Their EXAFS spectra were compared with “bulk” PuO₂ and a cluster of Pu(IV) used as references. Besides the observation of two main peaks located at R-φ= 1.84 and 3.68 Å agreeing with the k³-weighted FT spectra of bulk PuO₂, EXAFS analyses reveal two distinctive features for both colloid samples: i) a reduced amplitude for both Pu-O and Pu-Pu coordination shells, and ii) a strong asymmetry and distortion of the Pu-O coordination sphere (Fig. 2). Both effects appear correlated to the NP size shrinking probed by SAXS as evidenced by their spectra observed to be framed with the references. Data fitting demonstrates the dependency of the local structural disorder with the NP size for the Pu-O shell fitting. Such phenomenon is explained by a surface effect resulting from the increasing proportion of Pu atoms standing at the surface of a NP when shrinking.[3,4] The distortion of the Pu-O sphere can be explained by the contribution of other surface moieties (ex: μ₁-Pu-OH, μ₃-Pu-O, Pu-H₂O) which hypothesis is confirmed by the EXAFS simulation of Pu38 cluster (Fig. 2).[5]



MEETING SAXS VS. XAS RESULTS

The results obtained by both SAXS and XAS approaches converge in the description of the highly debated Pu(IV) intrinsic colloids as core-shell NPs made up of a PuO₂ core covered with a size-dependent disordered Pu-O shell. The strong influence of the preparation method on the multi-scale properties of Pu(IV) intrinsic colloids is demonstrated. The local structure of both coordination spheres (XAS) appears correlated with the NP shrinking (SAXS) rather from the contribution of unusual features. The stabilization of the HC particles is further suggested with SAXS simulation to result from the interaction with counter-ions from the medium. The new insights reached about the local structure, size, morphology and interfacial properties of intrinsic Pu(IV) colloids could help in a better understanding of Pu migration mechanism in the environment and pave the way for original investigations with radioactive materials.

MARS BEAMLINE

Associated publication

Relevance of formation conditions on the size, morphology and local structure of intrinsic Plutonium colloids.

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Environmental Science: Nano., 7, 2252 (2020).

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Captions

• SAXS diagrams acquired on SC and HC intrinsic colloids. Black lines indicate the slope power laws. The inset shows the X-Ray scattering length density profile of HC obtained from the simulations of the core-shell model.

•• Fourier transforms (FT) of the k³-weighted 2.5-15 Å⁻¹ interval for a selection of HC and SC compared with bulk PuO₂ and simulated Pu38 cluster used as references.