

*Unstable amorphous cerium oxalate precipitation in concentrated HNO<sub>3</sub> media*

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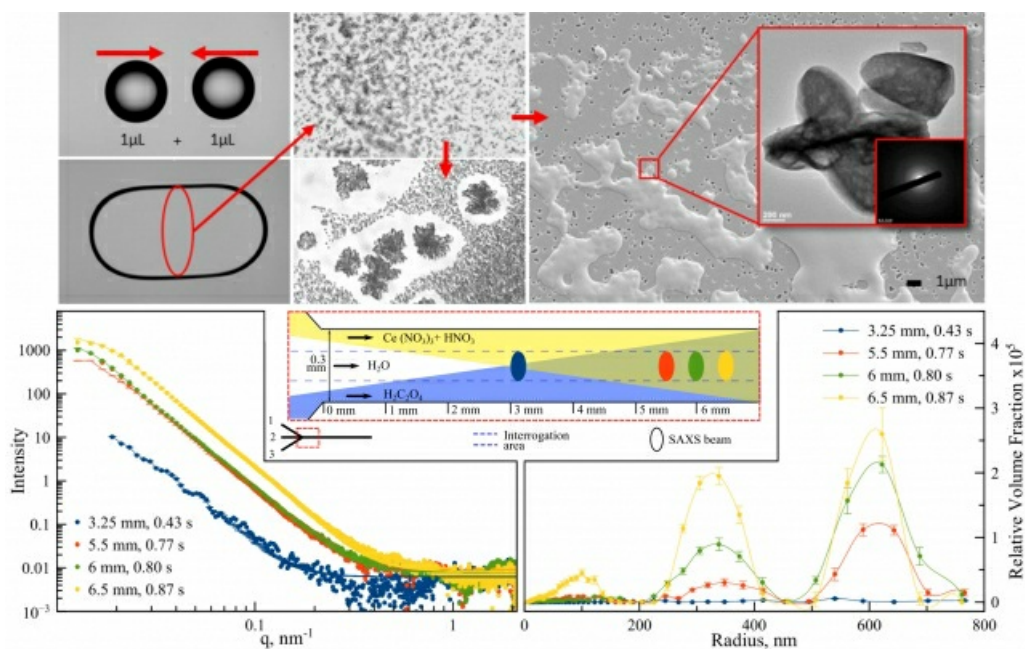
Rare earths precipitation using oxalic acid is broadly used in the industry of nuclear wastes reprocessing. The selective recovery of actinides from highly concentrated solutions is performed by oxalate salts precipitation in nitric acid media, in the range of 1-7 mol L<sup>-1</sup>[1]. As lanthanides and actinides in solution display close thermodynamic properties, the first ones are widely used as models for the understanding and development of new processes involving actinides of interest thus avoiding tedious manipulation of radioactive species. Hence, in the abovementioned framework, Ce (III) cations are frequently used in order to minimize the amount of radioactive materials involved in R&D studies. It is known that the precipitation reaction of Ce in HNO<sub>3</sub> media leads to the formation of Ce<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·10H<sub>2</sub>O at equilibrium. Nevertheless, very little has been investigated regarding the system out-of-equilibrium evolution during the initial stages of reaction, and the understanding of the mechanisms involved in cerium oxalate (CeOX) precipitation/nucleation are still poorly understood.

With a view to elucidate these mechanisms, CeOX precipitation experiments have been performed at room temperature in small volumes using two different experimental setups, both allowing in-situ monitoring of precipitation mechanisms: a Hele-Shaw cell under optical microscopy for micro-droplet batch precipitation, and an hybrid kapton-OSTEMER microfluidic platform, coupled to small angle X-ray scattering (SAXS), for continuous reaction, using a layer of water as a buffer between reagents to achieve diffusion-driven precipitation. Due to the stochastic nature of nucleation, the use of small volumes allowed us to locate the nucleation events in space, facilitating their observation [2]. The new experimental results presented here are questioning regarding CeOX precipitation mechanisms: SAXS experiments complemented by Monte Carlo simulations [3] highlighted the appearance of disperse spherical particles, of initial size close to 5 nm, which rapidly grow up to larger objects, observable by optical microscopy during the first second of reaction. Complementary characterization using HRSEM and TEM revealed the instantaneous primary precipitation of an initially liquid-like amorphous precipitate, which subsequently undergoes a solvent-mediated phase transition to a more stable crystalline phase.

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