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Impacts of the Non-classical Nucleation Mechanism of Cerium Oxalate

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ABSTRACT

Crystal precipitation in solution is a common process in industry which remains ill-understood. In the last decades, many efforts were made to design precipitation reactors using numerical simulations[1] in order to avoid using trial and error methods, especially for the precipitation of radioactive compounds like the plutonium oxalate. But all the process models are built on the classical view of crystallization, where thermal fluctuations of the reactive solution lead to the formation of some “clusters” of monomers with the same symmetry as the crystal[2]. In other words, the classical nucleation theories (CNT) overlook by construction any possible amorphous intermediate between the ions in solution and the final crystals.

This strong hypothesis of the CNT is more and more questioned. For many systems, including cerium oxalate[3], the nucleation occurs through amorphous states which are currently ignored by the CNT and which lead in some cases to a misestimation of the nucleation rate up to 400 orders of magnitude[4]. The strong mismatch between experimental observations and the CNT potentially impacts deeply the process models; but the implications have not been assessed yet. Progress is hampered by the lack of structural data on the elusive intermediate states, because of their short formation time ($\ll s$) and their characteristic sizes ranging from the Angstrom scale to the micron scale.

Here, we tackle this challenge by studying the nucleation of cerium oxalate using a new “plug and play” apparatus which allow the analysis by SAXS from 250ms to 5min. We show crystallization of cerium oxalate involves transient disordered states which increase the induction time of at least one order of magnitude in comparison with the one measured with the classical view of nucleation. This finding implies that the industrial process models misestimate strongly the driving force of nucleation (supersaturation), because they overlook a pseudo-equilibria between the transient disordered states, the solution and/or the crystal.

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