

## Environmental fate and impacts of ceria nanomaterials: Distribution, transformation and bioaccumulation within aquatic mesocosms

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Ceria (CeO<sub>2</sub>) NPs are largely used as oxidation catalysts, gas sensor, polishing materials, but also as UV absorber. Their attractiveness comes from the high oxygen storage capacity related to the easy Ce(III)/Ce(IV) redox cycle. The presence of Ce(III) within the structure of CeO<sub>2</sub> NPs enhance reactivity towards living organisms (prokaryotic and eukaryotic cells). Within the ANR-P2N MESONNET project, we determined the behavior of CeO<sub>2</sub>-based nanoparticles (NPs) within aquatic mesocosms simulating a pond environment. Another challenge was to work with NPs contamination representative of concentrations expected in natural aquatic environments. Consequently, NPs were chronically applied to water column (0.1 mg L<sup>-1</sup> per injection). After 4 weeks, we determined the distribution of Ce in water, sediments and biota, speciation with X-ray absorption spectroscopy and oxidative stress in organisms was measured. Over time, NPs tend to hetero-aggregate and accumulate at the surface of sediments. A partial reduction of Ce from oxidized CeO<sub>2</sub> NPs was observed in the sediment. Bioaccumulation of major Ce(III) was also detected in digestive gland of pond organisms (snail, *Planorbarius corneus*) and correlated with a significant oxidative stress. In addition, using two kinds of CeO<sub>2</sub> NPs for experiments (organic-coated CeO<sub>2</sub>-NPs used as paint additives (Nanobyk®), and “bare” CeO<sub>2</sub>-NPs (Rhodia®), we highlighted the influence of CeNPs surface formulation on their fate into mesocosms and their reactivity towards organisms.

## Effect of solution supersaturation and presence/absence of seeding crystals on the precipitation kinetics of celestite and strontianite

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In general, precipitation kinetic experiments allow us to determine parameters such as critical saturation index (SI<sub>crit</sub>), rates of precipitation (R<sub>precip</sub>) and induction time (t<sub>ind</sub>) of nucleation. The objectives of this study follow a two-side approach: First we quantify the precipitation kinetics of the isostructural minerals celestite and strontianite over variable saturation indexes (SI) using the method of mixed flow reactors (MFR) in the presence of homogeneous seed crystals. Building on the findings of precipitation kinetics, we will investigate the sorption/incorporation of trivalent actinides/lanthanides in these Sr-minerals under comparable R<sub>precip</sub> extending the work of [1]. In MFR experiments, equimolar solutions of SrCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> or Na<sub>2</sub>CO<sub>3</sub> in 0.1M NaCl (background electrolyte) were fed through separate inlets in the reactor (v<sub>outflow</sub> = 0.6 ml/min). Solution composition was monitored via ICP-OES and IC. R<sub>precip</sub> of Celestite were calculated using the mass-balance equation to be ranging from 4\*10<sup>-9</sup> to 20\*10<sup>-9</sup> mol/ (m<sup>2</sup>s) for SI's from 0.2 to 1.4, respectively. Plotting R<sub>precip</sub> vs. SI's showed a parabolic trend suggesting a surface controlled precipitation mechanism at low SI and 2-D nucleation at higher SI. The SI<sub>crit</sub> was found to be at 0.5 for SrSO<sub>4</sub>. t<sub>ind</sub> between mixing of solutions and formation of the first cluster/colloid were determined by laser-induced breakdown detection (LIBD) in the absence of seeding material. t<sub>ind</sub> decreased with increasing SI and two linear regressions could be performed with a change of slope at SI ~1.1. This SI is considered as the threshold for the transition between homogeneous and heterogeneous nucleation. The precipitation kinetics of celestite and strontianite will be compared and discussed with respect to nucleation mechanisms and metal uptake.

[1] Holliday, Chagneau, Schmidt, Claret, Schäfer, Stumpf (2012) Dalton Transactions 41, 3642. [2] Delos, Walther, Schäfer, Büchner (2008) J. Colloid Interface Sci. 324, 212.