

Dynamics of celestine precipitation and dissolution in confined spaces: a lab-on-a-chip experiment and complementary pore scale modelling.

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Mineral precipitation and dissolution in porous media and the associated change of transport parameters with respect to fluid movement and solute transport are of major interest in natural environments as well as in engineered systems, such as the barriers in deep geological repositories for radioactive wastes. The implementation of such coupled processes into numerical codes used to evaluate porosity evolution and feedback on transport requires a mechanistic understanding of the relevant precipitation/dissolution processes and validation with quantitative experiments. Recently, there has been a gain in interest to test implementation of process couplings (e.g. between porosity and permeability changes) in reactive transport codes [1, 2, 3]. These experiments have shown the limits of continuum scale models when it comes to changes in the transport properties in porous media due to mineral precipitation, for example in the case of pore clogging. Therefore, pore scale models are versatile tools to investigate processes such as nucleation mechanisms or passivation of surfaces (e.g. Prasianakis et al. [4]). The insight obtained from pore-scale models can be used to introduce corrections into macroscopic (continuum) reactive transport models [5, 6]. The understanding of relevant pore scale phenomena and their description is thus a fundamental requirement for upscaling purposes [7, 8].

In this context, we designed a reproducible and fast to conduct microfluidics experiment to investigate kinetically controlled dissolution/precipitation reactions in confined spaces. Our experimental setup ("lab-on-a-chip") consists of a reaction cell with a size of 77 μm by 60 μm and a height of 1 μm . In the middle of the cell pillars were placed with a distance of 600 nm apart from each other. The chip was fabricated using conventional PDMS (polydimethylsiloxane) on glass technique. Strontium chloride solution and sodium sulphate solutions were allowed to diffuse (constant boundary conditions) across of the cell resulting in the precipitation of celestine in the middle. The growth of the celestine crystals was monitored by optical microscopy. Different saturation indices for strontium sulphate (1.68, 2.04 and 2.48) were tested with regard to the induction time required for nucleation and crystal growth rates. The diffusive transport of the solutes across the cell was calculated to be rather fast ($\sim 10\text{s}$). However, at early stages of the experiments (i.e. up to 7 h), no precipitation of celestine was observed, despite the superstition, indicating metastable conditions (*Figure 1*). This illustrates that the energy barrier for the formation of supercritical nuclei – also referred to as the induction time – has to be reached before first celestine crystals become visible and crystal growth can proceed. Experiments performed at different degrees of celestine

supersaturation revealed that the induction time decreases with increasing saturation index. After a while, a complete clogging at the pillars occurred preventing any further exchange of solutes across the reaction cell. As a consequence, the solutions became undersaturated with respect to celestine, leading to dissolution of the crystals. Celestine precipitation/dissolution rates were estimated from the rate of growth/shrinking of the area occupied by the celestine crystals using image analysis. A macroscopic growth rate equation as function of saturation index was fitted to the data.

For a more accurate determination of these rates the exact conditions (concentrations and fluid velocities) at the fluid-solid growing interface need to be estimated. Even though the global saturation index is known, it is expected that in the region very close to the precipitation front a gradient of concentrations will exist (boundary layer). In addition, the flow itself is in the advective-diffusive regime and the results have to be correlated also with the Peclet and Damkohler numbers. The microfluidic modelling was based on the lattice Boltzmann method and moves along the lines of Prasianakis et al. [4]. This made possible to gain an insight of the underlying processes and to explain for example the growth orientation of the crystals which for this experiment are skewed to the left (See Figure 1).

The combination of microfluidic lab-on-chip experiments with pore scale modelling is considered as a promising tool to provide insight into pore scale phenomena and to parameterize appropriate constitutive equations to describe and simulate coupled processes in porous media.

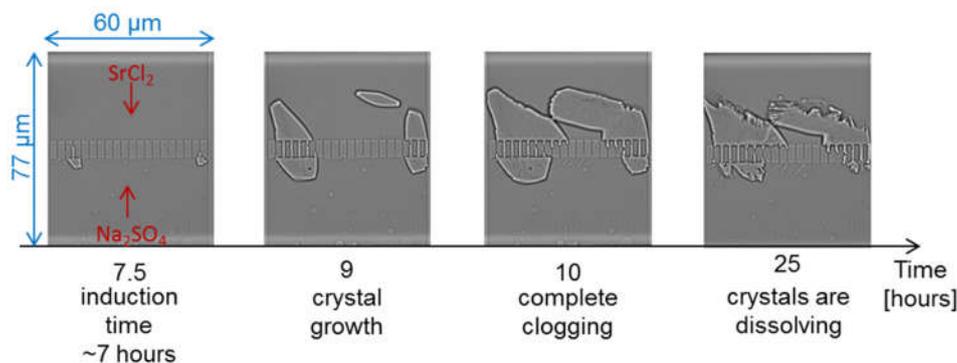


Figure 1: Celestine crystals in the reaction cell at a saturation index of 1.68.

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