

Application of a novel miniaturized counter diffusion cell for deriving time and space-resolved dynamics of CaCO₃ precipitation in silica gel via coupled micro-XRF/XRD and SAXS.

ASHISH RAJYAGURU^{1,2}, ENZO CURTI¹, CHRISTIAN APPEL¹, DARIO FERREIRA SANCHEZ¹, BEAT MEYER¹ AND DANIEL GROLIMUND¹

¹Paul Scherrer Institut

²Paul Scherrer Institute

Presenting Author: ashish.rajyaguru90@gmail.com

Geochemical processes like mineral precipitation and dissolution in confined space continuously modify the natural properties of porous systems such as rocks, aquifers, sediments, or soils. Yet, the small space (nanometer to micrometer) scale in these systems hinders the quantification of critical dynamical processes and features (e.g. phase identity and crystal morphology, nucleation pathways, and ionic mobility through clogging zone). An additional difficulty is the continuous monitoring of such phenomena over the long time scale of their evolution.^{1, 2} Nevertheless, the quantitative experimental derivation of the process parameters is imperative for the validation of pore scale reactive transport models. In this study, we overcome such limitations through the development of a novel miniaturized counter diffusion cell setup consisting of a 300 μm glass capillary filled with silica gel, connected to reservoirs containing CaCl₂ and Na₂CO₃ solutions on the opposite ends. The system was monitored continuously through optical microscopy (Figure 1). At selected time points, XRF/XRD chemical imaging and SAXS measurements were carried out in order to reflect the different precipitation stages and the geometry of clogging zones. Thus, these data allowed the quantification of local growth kinetics of the different CaCO₃ polymorphs formed (vaterite, calcite, aragonite and amorphous CaCO₃) in Silica-gel, and the diffusion behavior of solutes before and after clogging process. Currently, these experimental results are being analyzed in the light of recent developments related to non-classical nucleation theory. Furthermore, these datasets can be used in the development and/or validation of advanced pore scale reactive transport models.



Figure 1. Sequential images from continuous monitoring of CaCO₃ crystal growth within silica gel under diffusion regime over the period of 16 hours. The first image of this series shows a vaterite crystal in the vicinity of amorphous calcium carbonate (ACC) regions. Over time, the nucleation of a new vaterite crystal within the ACC region results in partial dissolution of the amorphous phase.

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