

***Exploring the effects of zinc(II) on
CaCO₃ clogging interface formation
and stability through advanced
synchrotron-based μ -XRF, μ -XRT, μ -
XRD, μ -XANES, and SAXS techniques***

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The ubiquitous occurrence of reactive transport processes leads to alterations in the physicochemical properties of various geomaterials. Field-scale evaluation of these processes is challenging due to the complex interplay between porous material properties, permeating pore fluids, and microscopic geometrical features. Consequently, a lab-based approach is required to allow direct (in-situ), spatially resolved probing of pore-scale reactive transport processes at undisturbed conditions. The present study investigates the temporal alterations in the stability of a CaCO₃ precipitates-based clogging interface due to the presence of dissolved zinc ions. Our investigations are based upon a novel microcapillary setup, wherein a silica-gel porous medium is directly prepared within a 300 μ m glass capillary. Two large reservoirs are connected at the ends of the capillary to enable counter-diffusion of CaCl₂ and Na₂CO₃ titrants and the formation of a clogging interface by precipitation of various CaCO₃ polymorphs. The evolution of multiple processes near CaCO₃ clogging interfaces was studied in the absence and presence of 1 mM ZnCl₂.

Synchrotron-based chemical imaging techniques, such as μ -XRF, μ -XRT, μ -XRD, μ -XANES, and SAXS, were employed to characterize the system at specific time intervals (1, 6, 12, 24, and 36 months) in an undisturbed manner. The capillary geometry facilitated direct investigation of critical emerging processes on a microscopic scale (1-10 μ m). Vaterite crystals in a calcium-rich environment remained stable near the clogging interface throughout the experimental duration in the metal-free system. In contrast, the presence of Zn resulted in a temporal dissolution of vaterite crystals in the calcium-rich region of the clogging interface. Notably, over time, instead of reprecipitating CaCO₃ polymorphs, the released carbonate ions promoted the nucleation of amorphous Zn-carbonate nanoflakes with a structure akin to Zn-kerolite-type clay. We present a novel methodology that allowed us to investigate clogging dynamics and the evolution of clogged systems over an extended period under in-situ and undisturbed conditions. Our findings indicate that even small concentrations of Zn²⁺ ions in the pore water significantly influence the precipitation and selective dissolution kinetics of CaCO₃ polymorphs. The results demonstrate the profound impact of trace metals on the formation and stability of carbonate-based clogging interfaces in porous media.