Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.35515

Synchrotron-based chemical imaging reveals long-term pore-scale Ni or Zn solid speciation and transport across the $CaCO_3$ clogging interface.

ASHISH RAJYAGURU[1,2], ENZO CURTI[2], DARIO FERREIRA SANCHEZ[2], CHRISTIAN APPEL[2] AND DANIEL GROLIMUND[2]

[1]Paul Scherrer Institute
[2]Paul Scherrer Institut

Mineral-precipitation fronts generate clogging interfaces that modify transport and reactivity in geomaterials, yet their long-term pore-scale evolution remains largely unresolved. In this study, we used an experimental setup consisting of a 300 µm glass microcapillary filled with silica gel to track the formation and chemical evolution of a clogging interface consisting of multiple $CaCO_3$ polymorphs, induced by $CaCl_2$ and Na_2CO_3 counter-diffusion (C/D) over 1-36 months. Three experiments were carried out: (i) with the addition of 1mM $ZnCl_2$, (ii) with the addition of 1mM $NiCl_2$, and (iii) the metal-free system. One month after the start of the C/D experiments, a bromide tracer was introduced in each microcapillary system. Micro X-ray fluorescence maps of the Br signal consistently showed strongly restricted diffusion through the $CaCO_3$ precipitates, indicating the formation of a low-permeability clogging barrier in all three experiments. Subsequently, at predetermined time intervals, multimodal synchrotron imaging (µ-XRF, µ-XRT, µ-XRD, µ-XANES, SAXS, µ-EXAFS) was carried out, and the results were interpreted using geochemical modeling.

Over 36 months, bromide remained below the µ-XRF detection limit across the clogging interface, and no further $CaCO_3$ polymorphs were detected by µ-XRD, demonstrating a stable, low-permeability barrier that suppresses Ca–CO_3 mixing. Yet spectroscopy measurements in the Ni-spiked system revealed the slow accumulation of amorphous $Ni(OH)_2$ nano-aggregates near the clogging interface. Similar precipitation behavior was observed in the Zn-spiked system, where the precipitates formed an octahedral sheet structure analogous to zinc hydroxynitrate ($Zn_3(OH)_4(NO_3)_2$ [1]. In the absence of nitrate in the pore solution, these octahedral sheets were stabilized by the carbonate/bicarbonate species that were released by selective vaterite dissolution in Ca-rich porewater.

Our findings indicate that while $CaCO_3$ precipitation fronts form persistent low-permeability barriers, trace metals exert contrasting controls on interfacial reactivity: Ni drives slow hydroxide-rich solid-solution growth with minimal impact on carbonate stability, whereas Zn destabilizes selected $CaCO_3$ polymorphs by inducing vaterite dissolution and secondary hydroxide formation. These results show that even minor metal fluxes can fundamentally alter reaction pathways at diffusion-limited interfaces, with broad implications for the long-term evolution of clogged porous systems.

References:

[1] Louër, Grandjean & Weigel (1973), Acta Crystallogr., Sect. B, 29, 1703–1706.