

Sulfidized zero-valent iron for trichloroethene reduction: insights on sulfidation treatment and long-term performance

M.C. MANGAYAYAM^{1*}, K. DIDERIKSEN², M. CECCATO³,
H.M. FREEMAN^{4,5}, L.G. BENNING⁴, D.J. TOBLER¹

¹Nano-Science Center, Department of Chemistry, University of Copenhagen, Copenhagen, Denmark
(*mc.marco@chem.ku.dk)

²Geological Survey of Denmark & Greenland (GEUS), Copenhagen, Denmark

³iNANO-Kemi, Aarhus University, Aarhus, Denmark

⁴GFZ German Research Center for Geosciences, Potsdam, Germany

⁵School of Chemical and Process Engineering, University of Leeds, Leeds, United Kingdom

Sulfidized, nanoscale zero-valent iron (S-nZVI) has recently gained much interest for *in-situ* subsurface remediation. This is because the Fe⁰ core - FeS shell structure of S-nZVI particles enables selective reduction of persistent groundwater contaminants, while limiting Fe⁰ oxidation by water. These properties are well assessed based on studies of reaction rates and products. However, much less is known about the intrinsic core-shell structure. This is particularly important in order to understand S-nZVI transformation and performance once injected into contaminated soils and aquifers.

We synthesized two common S-nZVI types. T1: one-pot synthesis using sodium dithionite and T2: two-step synthesis using sodium sulfide. By utilizing a suite of high-resolution microscopic, spectroscopic and diffraction techniques, we unravelled that the shell of T1-S-nZVI was dominated by amorphous Fe(OH)₂, and to a lesser degree by amorphous FeS closely linked to the Fe⁰ core. The T2-S-nZVI instead exhibited a shell entirely made of nano-crystalline FeS. These stark contrasts in shell structure, impacted trichloroethene (TCE) reduction, whereby T2-S-nZVI exhibited 4-fold increase in reduction rate, relative to T1-S-nZVI. In addition, rapid Fe (hydr)oxide formation, concomitant with faster drop in TCE reactivity, was observed in T1-S-nZVI, relative to T2, upon prolonged aging. Overall, our results suggest that for effective contaminant reduction: 1) FeS sites need to be closely associated to Fe⁰ 2) FeS sites need to be accessible by the bulk solution, and 3) the shell must permit Fe⁰ oxidation, i.e., migration of aqueous Fe²⁺.