

An experimental study of the fate and reactivity of zero-valent iron nanoparticles during the injection of nanofluids in saturated porous media polluted with chlorinated hydrocarbons

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Nanotechnology has special relevance to the in situ soil and groundwater remediation, due to the combination of nanoparticles properties with fluid characteristics and thus the potential for injecting nano-sized (reactive or adsorptive) particles into contaminated porous media (e.g. soils, sediments, and aquifers). Among the various nano-materials explored for remediation (e.g. zeolites, metal oxides, carbon nanotubes, etc) nanoscale zero-valent iron (nZVI) is currently the most widely used for the in situ remediation of soils from a variety of toxic pollutants (e.g. chlorinated hydrocarbons, nitro-aromatics, Cr^{VI} etc). The nanoparticles are typically injected as slurries (nanofluids) directly into the subsurface to remediate contaminated groundwater plumes or contaminant source zones. A variety of coatings (e.g. polyelectrolytes, surfactants, polymers) and supports (e.g. carbon, silica) may be used to stabilize the nanofluids by increasing their resistance to particle aggregation and facilitating their delivery to target pollutants. There is a need to understand the interacting factors controlling the stability, mobility, and reactivity of nanoparticles when injected in saturated porous media. *In this respect, the current study is breaking new boundaries as no systematic study has previously been made to specify the most suitable agents that ensure the stabilization of reactive nanomaterials and their successful delivery to the target pollutants within contaminated groundwater.*

Aqueous suspensions of nZVI (nanofluids) are prepared by adding NaBH₄ solution under anoxic conditions in an aqueous solution of FeSO₄ · 7H₂O pre-grafted with the following polymers acting as coatings: PAA-Na (sodium polyacrylic acid), CMC-Na (sodium carboxymethyl cellulose), CMC-g-PDMAM (carboxymethyl cellulose-g-polydimethylacryl amide), and PAA-g-PDMAM. The size distribution of nanoparticles (NP) is measured with dynamic light scattering (DLS) and transmission electron microscopy (TEM), whereas their stability is evaluated with sedimentation tests and measuring the ζ-potential. Per-chloroethylene (PCE) is used as model non-aqueous phase liquid (NAPL). To assess the nZVI reactivity with respect to dissolved and bulk NAPL, tests are performed in batch reactors, and mechanistic multi-step reaction models are developed to estimate all pertinent kinetic parameters.

Visualization studies in glass-etched pore networks enable us to identify the nanoparticle flow and reaction mechanisms at pore-scale and quantify the fate of nZVI. The transient NP sticking coefficient associated with the attachment/detachment of NPs is determined as a function of the pore blockage reflected in the “effective” water permeability. The accumulation of NPs in the water/free NAPL/solid contact line may change the interfacial tension and/or wettability and detach NAPL from the solid surface and is studied by using the non-dissolved n-dodecane as model NAPL. The capacity of nanoparticles to dechlorinate the bulk and dissolved PCE under realistic conditions is tested with pulse and step flow tests in the glass micromodel. To evaluate the capacity of NPs to reduce trapped ganglia of PCE (source zone), the residual PCE is created with successive drainage-imbibition displacement cycles at adjustable flow rates. The effluents from the tests are collected, treated adequately (e.g. filtration, centrifuging, solvent extraction), and analyzed to measure the concentration of PCE or any other intermediate reaction product (e.g. TCE) with GC-ECD (Gas Chromatography-Electron Capture Detector) and the concentration of nZVI with UV-Vis and atomic absorption spectroscopy (AAS). Finally, the

various types of nanofluids are classified according to their mobility, longevity and reactivity under realistic conditions.