

# Comparison of Reductive Transformations of Chlorinated Hydrocarbons by Chemically-Reduced versus Bio-Reduced Hydrous Ferric Oxide

**Jaya Das** (jaya.das217@gmail.com) and Abinash Agrawal (abinash.agrawal@wright.edu)  
(Wright State University, Dayton, OH, USA)

**Background/Objectives.** Chlorinated hydrocarbons (CHCs) are common groundwater pollutants and pose a significant threat to human health as suspected carcinogens. An inexpensive approach of handling complex site contaminated with CHCs can be by monitored natural attenuation. It is well known that certain chemically precipitated Fe<sup>2+</sup>-containing mineral phases (e.g., magnetite, green rust, iron sulfide, etc.) can facilitate abiotic transformations of highly chlorinated hydrocarbons to less/non chlorinated species. This work investigates abiotic degradation of CHCs by a reduced iron oxide that can contribute to natural attenuation processes in contaminated aquifers. Here, we examined if common hydrous ferric oxide that may get 'reduced' under Fe<sup>3+</sup>-reducing condition, can facilitate natural attenuation of CHC in subsurface zones.

**Approach/Activities.** Bench-scale microcosm studies were conducted with *Shewanella putrefaciens* CN32, a dissimilatory iron reducing bacteria (DIRB), and lactate as electron donor to bioreduce laboratory-synthesized hydrous ferric oxide (HFO) that produced reactive Fe<sup>2+</sup> species. The microcosms containing deoxygenated HFO slurry were incubated with *Shewanella putrefaciens* CN32 and lactate to generate varying amounts of Fe<sup>2+</sup> species in situ. On the other hand, chemically reduced HFO were prepared by amendment with Fe<sup>2+</sup> externally as solid FeSO<sub>4</sub> to the batch reactors containing HFO slurry. The degradation potential of various CAHs such as carbon tetrachloride (CT), 1,1,1,2- tetrachloroethane (1,1,1,2- TeCA), 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA), and trichloroethene (TCE) were investigated with chemically reduced and bioreduced HFO, and the production of daughter products were monitored for 2-3 months. The reaction kinetics of CHC degradation with 10 and 100 mM initial HFO were compared with varying initial Fe<sup>2+</sup>, and with/without an electron shuttle, anthraquinone-2,6-disulfonate (AQDS). The total HCl-extractable Fe(II) and the extent of Fe(III) bioreduction in the microcosms were monitored during the experiments, and analyzed by phenanthroline method.

**Results/Lessons Learned.** The results show that CT, 1,1,1,2-TeCA, 1,1,2,2-TeCA and TCE can degrade by reduced HFO through various pathways. While the CT degradation produced CF as the major byproduct suggesting hydrogenolysis as a dominant reaction pathway, the degradation of 1,1,1,2-TeCA produced 1,1-dichloroethene through dichloroelimination pathway, and 1,1,2,2-TeCA degraded to TCE by dehydrochlorination pathway. Further, on one hand CT, 1,1,1,2-TeCA, and 1,1,2,2-TeCA degraded quickly with a half-life of a few hours, the degradation of TCE was much slower with half-life of several weeks. The increase in reactive Fe<sup>2+</sup> concentration (in reduced HFO) shows a systematic increase in CHC degradation kinetics. The results also showed that the pseudo first-order rate constant of CT degradation with chemically reduced HFO was smaller than with bioreduced iron oxides at similar initial Fe(II) concentration.