Dechlorination by Sulfidated Iron and Iron Oxides

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Background/Objectives. Iron-based materials are involved in remediation of many contaminated groundwater sites by abiotic natural attenuation (with iron oxides) and in situ chemical reduction (with micro- and nano-sized zerovalent iron, ZVI). The increasing reliance on iron-based materials for groundwater remediation has created demand for new and improved materials and methods utilizing these materials. Sulfidation is the newest of the most promising ways of improving the performance of iron-based materials for remediation.
Sulfidation can be accomplished in various ways, most commonly by aqueous-aqueous (i.e., dissolved sulfur and iron species, in the presence of a strong reducing agent) and aqueous-solid (i.e., dissolved sulfur species and solid iron materials) processes. The resulting sulfidated materials can have complex structures, including morphologies that are core-shell and/or multiphase. However, most characterization of these materials has focused on the degradation of organic contaminants, especially chlorinated organics, such as carbon tetrachloride (CT), trichloroethene (TCE), and tetrachloroethylene (PCE). Almost all of this work has focused on the kinetics of dechlorination, with much less work on pathways and products of dechlorination. Furthermore, most claims that sulfidation accelerates dechlorination by iron-based materials are based on comparisons between sulfidated materials and controls under narrow ranges of conditions, so the generality of these conclusions is unclear. One objective of this work is to provide a more comprehensive understanding of the effect of sulfidation dechlorination of organic contaminants, including a wider range of contaminant types and reaction conditions.

Approach/Activities. To accomplish this, we have performed an extensive analysis using all current available data. Recent publications on sulfidation were reviewed, and sulfidation methods were compiled and classified. A novel meta-analysis of kinetic data of reductive dechlorination of chlorinated organics by various iron-based materials (sulfidated and non-sulfidated) was conducted to reveal the improved reactivity via sulfidation. A conceptual model was presented that explains the observed results.

Results/Lessons Learned. Using the extensive dataset presented here, a variety of conclusions can be drawn regarding the reaction pathways in abiotic reductive dechlorination by sulfidated iron-based materials. Sulfidation usually increases dechlorination rates, although the degree of enhancement varies with contaminants. Data available to date shows that the enhancement effect of sulfidation on TCE dechlorination is significantly greater than others. Another benefit of sulfidation is it simultaneously suppresses hydrogen production, reduces water reductions, and improves selectivity of contaminant degradation. Together, these benefits make sulfidation a promising new strategy to improve the utility of iron-based materials in water treatment and remediation.