Sulfidation as a Sustainable Method to Engineer the Surface of ZVI for Enhanced Degradation of Chlorinated Ethenes

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Background/Objectives. Abiotic reduction of TCE and PCE by reduced iron materials has received increasing interest among researchers and remediation practitioners due to its potential to transform chlorinated ethenes without significant accumulation of recalcitrant and toxic intermediates. Two broad categories of iron materials have been evaluated, including naturally abundant Fe(II)-containing minerals (e.g., iron sulfides and green rust) and artificially amended zero-valent iron (ZVI). Although ZVI has higher intrinsic reactivity for the reduction of chlorinated ethenes than indigenous minerals, it suffers major drawbacks including unproductive loss of its reductive capacity to reactions with water and other reducible background solutes and spontaneous surface passivation. It has been shown recently that treating ZVI with aqueous sulfide or dithionite leads to significantly increased rates of PCE and TCE degradation, however, the fundamental role of sulfur in improving the surface reactivity of iron has not been clearly defined. Lacking this insight has hindered the application of sulfidation as a general method for enhancing or reinstating the reactivity of iron used for in situ groundwater remediation.

Approach/Activities. This study examined the mechanistic role of sulfur in modulating the reactivity and selectivity of ZVI materials towards chlorinated ethenes. Using nanoscale iron as a model ZVI material due to its well-studied surface chemistry and its ability to accommodate different sulfidation procedures during the particle synthesis, we studied systematically the effects of sulfur precursors, sulfur loading, and sulfidation protocols on the reactivity of the resultant particles. Subsequently, sulfidation of several commercially available and widely applied ZVI products was investigated to assess whether sulfur treatment can be applied as a general surface modification method to various types of ZVI products including bulk iron particles and ZVI prepared via methods other than the chemical (borohydride) reduction route. Using laboratory nZVI as a benchmark, the performance of the original and sulfur-modified commercial ZVI for PCE and TCE dechlorination was assessed.

Results/Lessons Learned. It was shown that sulfidation has a fairly broad process window, and the particle reactivity towards TCE and PCE is largely unaffected by the type of sulfur precursors used (viz., sulfide, dithionite, and thiosulfate). Nonetheless, S/Fe ratio was found to exert a strong impact on TCE reduction rates, with up to 60 folds increases in the rate constant at an S/Fe ratio as low as 0.025. At a higher S/Fe ratio, however, reactivity became saturated, suggesting optimal sulfidation requires only a small amount of sulfur reagents in ZVI suspensions. Although the effect of sulfur in heightening the reactivity of iron has been attributed to catalytic or electrochemical causes in previous studies, we demonstrate that the role of sulfur resides in its ability to inhibit recombination of surface H adatoms, thereby making them more accessible to TCE or PCE reduction. This action of sulfidation on iron surface chemistry not only distinguishes itself from conventional methods of improving iron reactivity that rely on the use of expensive or toxic catalysts, but also offers a mechanism to increase the selectivity of iron surface for target contaminants against nonproductive loss of electron source to water reduction and H2 evolution. This new insight on iron surface chemistry suggests sulfidation can be extended to other types of ZVI to enhance their performance in chlorinated ethene degradation, and this notion has been positively confirmed using two commercial ZVI products.