

## **Sulfidation of ZVI for Degradation of Chlorinated Ethenes: A New Approach to In Situ Biogeochemical Transformation**

Syful Islam, Andrew Murray, Kayleigh Millerick, and **Weile Yan** (weile.yan@ttu.edu)  
(Texas Tech University, Lubbock, TX, USA)  
Yanlai Han (U.S. EPA, Athens, GA)

**Background/Objectives.** Abiotic reduction by reactive iron minerals such as iron sulfide and magnetite represents an important pathway for the degradation of chlorinated ethenes in the subsurface environment. Nonetheless, site remediation using in situ biogeochemical processes faces the challenge of controlling the formation of reactive minerals with consistent and predictable characteristics. Zero-valent iron (ZVI) is an engineered material that has been used extensively for the remediation of chlorinated ethene-impacted sites. Several recent studies have demonstrated that controlled dosing of sulfur onto ZVI can significantly improve the reactivity and selectivity of ZVI for hydrodechlorination of TCE to benign end products. This study aims to address three questions related to sulfidation of ZVI: i) what are the critical factors that control the reductive dechlorination efficiency of sulfided ZVI; ii) what is the effect of sulfidation on the reactivity and specificity of ZVI towards different chlorinated ethenes; and iii) can sulfidation of ZVI be achieved via biological sulfate reduction process?

**Approach/Activities.** Four commercial ZVI products and lab synthesized nanosized ZVI (nZVI) were subject to various sulfidation treatments. The reactivity of the sulfided iron was assessed using TCE as a model contaminant in batch reactors. Surface and solid phase analyses were conducted to elucidate the structure and surface chemistry of the resultant solids. Collectively, these data reveal key surface chemistry attributes and important sulfidation parameters that control the performance of the sulfur-treated particles. The feasibility of enhancing the reactivity of ZVI through biogeochemical perturbation was evaluated by exposing iron to microbial sulfate reducing media.

**Results/Lessons Learned.** In general, sulfur treatment in dilute aqueous environment led to major enhancements in TCE reduction rates. The choice of sulfur precursor and the contact time between sulfur precursor and ZVI were found to cast minor impacts on the reactivity of the resultant solids. However, three out of the four commercial ZVI products entailed an acid pre-treatment step to attain optimal reactivity, indicating the presence of a native oxide layer can be a significant barrier for sulfur to anchor to the iron surface. A small dose of sulfur (up to 5 atom% of Fe) was sufficient to attain the optimal rate enhancement for TCE reduction. While sulfur treatment improves TCE and to smaller extent, PCE degradation rates, the performance towards cis-DCE was more nuanced. Surface chemistry investigations reveal that the presence of metal impurities in a subset of ZVI products plays an adventitious catalytic role in cis-DCE conversion. The catalyst was poisoned after sulfur treatment, and as a result, led to decreases in cis-DCE reduction rates. This contaminant-specific effect suggests the potential of precise formulation for treating plumes of different age and history. Finally, ZVI immersed in media of a common sulfate reducer, *Desulfovibrio desulfuricans*, exhibited significantly increased TCE reaction rates. Our on-going effort is examining whether biologically derived sulfur anions can be used to improve or reinstate ZVI reactivity under field-relevant conditions.