Influence of Metal Impurities in ZVI Matrix on Reactions with Chlorinated Ethenes

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Background/Objectives. Zero-valent iron is among the most widely applied material for remediation of sites contaminated with chlorinated solvents. Due to the differences in metal source and manufacturing routes, the ZVI products used in remediation applications typically carry varying amounts of impurities such as carbon, sulfur, silicon, and trace metals. Laboratory investigations of ZVI reactions with halogenated contaminants tend to use high-purity ZVI prepared from research grade chemicals under well-controlled conditions. The influence of minor foreign ingredients commonly present in commercially applied ZVI on contaminant degradation is largely overlooked. This study aims to evaluate the effects of common metal impurities on ZVI reactive properties with representative chlorinated ethenes (PCE, TCE and cis-DCE). The findings will provide new understanding on the variations in ZVI performance observed across different products and assist in designing materials for optimal treatment of target contaminants.

Approach/Activities. This study is focused on four metal impurities frequently detected in scrap metals or cast iron that are used to manufacture ZVI. They are manganese, copper, nickel, and chromium. The base material is ZVI produced via borohydride reduction or decomposition of iron pentacarbonyl, which has negligibly low levels of metal impurities. Individual secondary metals were incorporated into the base ZVI either during the synthesis procedures or by reacting with as-formed ZVI in aqueous solutions. The amount of secondary metal was controlled to be below one percent (wt%) of the ZVI matrix, and the actual loading was verified using the acid-digestion method. The ZVI with artificially amended impurities was evaluated in batch experiments with PCE, TCE, and cis-DCE.

Results/Lessons Learned. The presence of small quantities of impurities was found to have a significance effect on the reduction rates of various chlorinated ethenes. Specifically, PCE dechlorination rate was enhanced with the incorporation of copper and nickel to a moderate extent. The rate of TCE reduction was most significantly increased by the presence of Ni. *cis*-DCE, which has the slowest degradation rate of three, was rapidly degraded by copper-laden ZVI, while nickel amendment has no major impact. Manganese in ZVI does not have a significant enhancement or inhibitory effect on any of the chlorinated ethenes assessed, while the effect of chromium is under ongoing investigations. Characterization of the reaction products and H2 production rates shed light on the mechanisms of the metal impurities in changing the reactive behavior of ZVI. The data obtained point to several practical implications. It demonstrates for the first time that the properties of ZVI are affected to a substantial degree by minor elements in the iron matrix. Secondly, the variations in reactivity observed with different metal impurities suggest it is possible to tune or optimize the ZVI materials for the intended applications with considerations of the contaminants involved and the age and history of prior remediation efforts. Lastly, the application of sulfidation, an approach to depassivate or improve ZVI properties, can annihilate some of the enhancement effects caused by the metal impurities.