

Abiotic Dechlorination of Chlorinated Ethene by Naturally-Occurring Ferrous Minerals under Aerobic and Anaerobic Conditions

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Background/Objectives. Persistence of chlorinated solvents such as tetrachloroethene (PCE) and trichloroethene (TCE) in low permeability clayey and silty materials is an ongoing challenge at many sites. Contaminants in these low permeability zones often remain following implementation of in situ remedial approaches such as bioaugmentation or chemical oxidation, and can serve as a long-term source impacting groundwater. Several recent studies have shown that ferrous minerals naturally present in low permeability matrices can serve as an important natural attenuation mechanism, substantially diminishing the adverse impacts associated with these persistent sources. However, methods to efficiently assess such processes have not been fully developed, and the impact of dissolved oxygen on the kinetics of abiotic dechlorination remain largely unexamined.

Approach/Activities. Abiotic dechlorination of PCE and TCE was measured and assessed in natural clayey materials (gamma-irradiated) and minerals using a series of batch systems. Experiments were performed under both aerobic and anaerobic conditions, and at temperatures ranging from 20 to 55 degrees C. Detailed mineralogy of the tested materials also was performed.

Results/Lessons Learned. Abiotic dechlorination products were observed under both anaerobic and aerobic conditions. Under anaerobic conditions, acetylene, ethene, and higher coupling products (e.g., butane) were observed. The distribution of these products varied among the soil types tested. The rate of abiotic dechlorination increased with temperature. The activation energy for abiotic TCE dechlorination via the natural ferrous minerals was determined to be 91 kJ/mol, which is substantially greater than the activation energy observed for zerovalent iron. Under aerobic conditions, interactions between dissolved oxygen and ferrous minerals generated hydroxyl radicals, which subsequently oxidized TCE yielding volatile fatty acids and CO₂. Dechlorination under both aerobic and anaerobic conditions was reasonably described by first order kinetics. Rates of abiotic dechlorination under aerobic conditions were orders of magnitude greater than those under anaerobic conditions.

The first order dechlorination rate constants were reasonably correlated to the ferrous mineral content of the clay, as determined via the 1,10-phenanthroline. No correlation of the derived first order dechlorination rate constants to magnetic susceptibility was observed. XRD results suggest that ferrous minerals such as chlorite and/or riebeckite were likely responsible for the observed abiotic dechlorination. Overall, these results suggest that abiotic dechlorination may be an important component of conceptual site models, playing a key role in the natural attenuation of contaminants in low permeability materials.