

A Geochemical Modeling Approach to Understanding Arsenic Treatment by Zero-Valent Iron in a Permeable Reactive Barrier: A Case Study

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Leaching of arsenic from historic smelter slag used as road base at a former log yard has resulted in groundwater contamination that threatens surface water. Unique redox geochemistry characteristics dominate the site groundwater due to iron reducing conditions as a result of ongoing decomposition of wood waste and natural organic matter, which lead to high dissolved iron concentrations in groundwater. As a result, arsenic fate and transport is controlled by precipitation of iron arsenate minerals, co-precipitation of arsenic iron oxide and oxyhydroxide minerals, and adsorption-desorption reactions on the surface of soil minerals, particularly iron oxyhydroxide minerals. Near the surface water where arsenic concentrations are relatively low, adsorption-desorption is the predominant process. The proposed groundwater remedy consists of reducing leaching of arsenic in the source area through capping and installation of a zero-valent iron (ZVI) permeable reactive barrier (PRB) to remove arsenic from groundwater before it discharges to surface water.

Geochemical modeling is performed to assess the efficacy of PRB treatment by evaluating the impact of mineral precipitation on hydraulic performance and reactivity of the PRB as well as downgradient groundwater quality in response to flushing by PRB effluent. Using the chemical results of site-specific column tests, speciation modeling is performed using the Geochemist's Workbench® to evaluate the types and quantity of potential mineral precipitates. One-dimensional reactive transport modeling is performed to evaluate potential mobilization of arsenic from soil downgradient of the proposed PRB alignment and to assess the timeframe for achieving compliance. Preliminary results of the speciation modeling and Eh-pH diagrams indicate that Fe-oxyhydroxides (e.g., goethite, ferrihydrite) and some carbonates (e.g., siderite) could be supersaturated in site groundwater. Some predicted carbonate minerals do not co-precipitate arsenic and could reduce hydraulic performance/reactivity of the PRB over time. Preliminary mineral precipitation rate calculations suggest total precipitation on the order of 0.1 cm³/L H₂O. The simulated mineral precipitation rate will be used to evaluate porosity and hence permeability loss over the PRB's decadal lifespan. X-ray diffraction analysis will be performed on soil/ZVI mixture from the column tests to verify the geochemical modeling results.