In Situ Chemical Reduction of Chlorinated Ethenes and its Effect on a Commingled Molybdenum Plume

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Background/Objectives. Environmental investigations at a former industrial plant revealed the presence of chlorinated ethenes (tetrachloroethene and its reductive dechlorination daughter products) in groundwater at concentrations that indicate a potential vapor intrusion risk. The chlorinated ethene plume is commingled with dissolved-phase molybdenum (Mo) at concentrations that exceed its generic reference standard. The local aquifer, characterized by heterogeneous intercalations of sand and clay layers, has a slightly acidic pH and is generally under sub-oxic conditions, with a redox potential (Eh) around +200 millivolts (mV). Under these conditions, Mo exists as the molybdate oxyanion, MoO₄², which is relatively mobile in the environment. Using an integrated carbon and zero valent iron source, in situ chemical reduction (ISCR) was selected to reduce the chlorinated ethene concentrations to acceptable levels. Under the resulting reducing conditions, Mo is expected to precipitate as MoS₂. Prior to field implementation, geochemical modeling and bench-scale laboratory tests were being used to assess the geochemical reactions that influence dissolved-phase Mo concentrations and mobility under the strongly reducing conditions fostered by the ISCR process.

Approach/Activities. The U.S. Geological Survey (USGS) geochemical code PHREEQC was used to simulate ISCR's reducing effects. Aqueous Mo concentrations and adsorption to the iron hydroxide present in the aquifer matrix were simulated under progressively more reducing conditions and for four different pH scenarios: ambient, 6.0, 6.5, and 7.0. Bench-scale laboratory tests were then conducted using soil and groundwater samples from within the chlorinated ethene and Mo plume. Sacrificial microcosms were used to test a range of pH conditions and ISCR reagent doses. This allows to more accurately estimate pH and redox conditions that maximize chlorinated ethene reduction and minimize dissolved-phase Mo concentrations and mobility in the target treatment zone.

Results/Lessons Learned. The geochemical simulations and the bench test results suggest that maintaining a slightly acidic 6.0 pH will prevent increased dissolved-phase Mo concentrations over a greater range of redox conditions compared to higher pH. The main factors controlling Mo are adsorption to iron hydroxides and precipitation of molybdenite (Mo[IV]) as Mo sulfide. On the other hand, the bench test results show that reduction of chlorinated ethenes was most effective at neutral pH. In short, ISCR presents itself as a promising technique to remediate the chlorinated ethenes while minimizing mobilization of dissolved-phase metals.