

Biogeochemically-Enhanced Treatment of Chlorinated Organics and Metals

Dan Leigh (daniel.leigh@evonik.com) (Evonik Corporation, Walnut Creek, CA, USA)
Alan Seech (alan.seech@evonik.com) (Evonik Corporation, Corona Del Mar, CA, USA)

Background/Objectives. For over two decades, biotic (enhanced reductive dechlorination [ERD]) and abiotic (in situ chemical reduction [ISCR]) processes have been applied to degrade chlorinated volatile organic compounds (CVOCs) in situ. Recently, biogeochemical reduction (BGCR), a process which combines biological and chemical processes, has been combined with ERD and ISCR to provide an additional mechanism to more aggressively degrade CVOCs and to sequester toxic metals. These processes recently have been applied for treatment of CVOCs at sites in California and for treatment of arsenic at a site in Florida.

Approach/Activities. During ERD and ISCR, highly reducing conditions are established which are favorable to the reduction of ferric iron (Fe[III]) to ferrous (Fe[II]) and sulfate (SO_4) to sulfide (HS^-) which are highly soluble. Ferrous and sulfide in solution rapidly combine to produce iron-sulfide minerals such as mackinawite (FeS), and pyrite (FeS_2). These biologically generated minerals have been demonstrated to abiotically degrade CVOCs on contact by the β elimination pathway. This additional biogeochemical degradation pathway minimizes the generation of toxic degradation products such as vinyl chloride, thereby substantially reducing the clean-up time.

In addition to degrading CVOCs, iron and sulfide remove toxic metals from solution as iron-sulfide minerals such as arsenopyrite (FeAsS_2), or as sulfides such as sphalerite (ZnS). These minerals have very low solubility in water and have been demonstrated to be very stable following formation. In addition to forming reactive minerals, the generated sulfide will precipitate on zero valent iron (ZVI) if present. This sulfidation of zero valent iron (ZVI) has been demonstrated to substantially enhance reactivity and reduce passivation of the ZVI.

Bench tests, and full-scale treatment were conducted at multiple sites affected by CVOCs and metals to evaluate the effectiveness a BGCR enhancing reagent (Geoform[®] Extended Release; Geoform ER) for in situ remediation of CVOCs and metals. At two sites in California, groundwater was affected by very high concentrations of chlorinated ethenes. Groundwater at a separate site was affected by mixed chlorinated -ethenes, -ethanes and -methanes. Separately, bench tests and full-scale treatment were conducted to sequester elevated concentrations of arsenic in groundwater at a site in Florida. At each site, full-scale treatment was conducted by distribution of Geoform[®] ER into the affected aquifer by high-pressure injection. Groundwater monitoring was conducted to confirm and quantify treatment.

Results/Lessons Learned. The bench tests at the California sites demonstrated that BGCR significantly increased the reactivity of the ZVI containing ISCR reagents for treatment of CVOCs. The field tests demonstrated that the application of Geoform[™] ER established highly reducing conditions and enhanced the biological reduction of the supplied sulfate to sulfide. Simultaneously, the CVOCs in the mixed CVOC plume were rapidly degraded by both biotic and abiotic processes to below regulatory goals resulting in a no further action determination within 30 months of the start of treatment. Bench tests for the Florida site demonstrated that arsenic was rapidly removed from solution using Geoform[™] ER and a clear dose response for treatment was observed. A description of the BGCR processes applied, and the methods and results of the bench tests and full-scale application of biogeochemical reduction for treatment of CVOCs at the California sites; and for sequestration of arsenic at the Florida site will be presented.