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Development of a Bioassay to Assess Clogging of a Zero-Valent Iron Permeable Reactive Barrier

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Background/Objectives. This study focused on finding a solution to the clogging of a zero-valent iron (ZVI) permeable reactive barrier (PRB) which was designed to treat a plume of chlorinated ethenes in groundwater in the southeastern part of the United States. The permeability of the PRB decreased over time at the up gradient face, likely due to biofouling and precipitate formation. The overall objective was to assess chemical inhibitors and heat treatment to inhibit biofilm activity within the ZVI. To do so, a bioassay was developed based on hydrogen consumption.

Approach/Activities. The hypothesis that biofouling contributes to clogging of the ZVI was based in part on accumulation of iron sulfides, with the sulfides presumably generated by sulfate reducing bacteria (SRBs). ZVI generates hydrogen, which is readily utilized by SRBs. Control of these hydrogenotrophs was evaluated using chemical treatments. Samples from the ZVI PRB were soaked in solutions of sodium hypochlorite, chlorine dioxide, neat ethanol, and a mixture of 95% ethanol and 5% isopropanol (v/v), at varying concentrations, under anaerobic conditions. A four hour contact time was used, to simulate the approximate retention time of groundwater within the PRB. The ZVI was then washed with upgradient groundwater to remove the inhibitors and placed in serum bottles. Hydrogen was added and then monitored over approximately four months of quiescent incubation. Heat treatment of ZVI from the PRB consisted of incubating samples at 60, 80 and 100 °C for 4, 8, 12 and 24 hours, followed by addition of hydrogen and monitoring.

Results/Lessons Learned. The original samples contained acid extractable sulfur levels as high as 36 g/kg ZVI confirming the contribution of sulfate reduction to clogging of the ZVI. Bacterial DNA (determined by qPCR with universal primers) was orders of magnitude higher on samples of ZVI from the PRB in comparison to fresh ZVI. Hydrogen consumption under anaerobic conditions was fastest in samples from the interface of the PRB (pseudo first order rate coefficient up to 0.35 d^{-1}), confirming the presence of hydrogenotrophs. In comparison, hydrogen accumulated in serum bottles containing autoclaved ZVI, due to corrosion of the ZVI and lack of biotic activity. NaOCl and ClO_2 (Purogene®) did not inhibit hydrogen consumption at any of the doses tested, presumably due to preferential reaction of the oxidants with the ZVI rather than the hydrogenotrophs. Ethanol and ethanol/isopropanol mixtures (5 to 100% by volume) inhibited hydrogen consumption, with generally longer lasting inhibition at higher doses. Use of a phosphate buffer to dilute the ethanol enhanced the extent of inhibition. Hydrogen accumulation occurred in some of the ethanol treatments, similar to the autoclaved controls. Heat treatment was also effective in slowing the rate of hydrogen consumption, with generally improved results at higher temperatures and longer exposure times. Heating at 100 °C notably increased hydrogen accumulation.

Based on the lab results, a pilot test is underway in the PRB using ethanol/isopropanol to control any further growth of hydrogenotrophs. Heating will be evaluated in the PRB if chemical inhibition is insufficient.