

In Situ Biogeochemical Transformation as a Polishing Step after ISCO: A Field Test

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Background/Objectives. Chlorinated ethenes are amongst the most abundant pollutants of soil and groundwater due to their frequent use in industrial applications. In situ chemical oxidation (ISCO) using activated sodium persulfate is a widely used remedial technology for treating source zones of this type of contamination. High concentrations of sulfate (and iron when used as an activator) in groundwater after treatment may be a drawback of this remedial technology in sensitive areas. Engineered in situ biogeochemical transformation (ISBGT) of these compounds to reactive minerals (e.g., iron sulfide, pyrite) that catalyse abiotic degradation of chlorinated ethenes and thus act as a subsequent polishing technology, may be a viable solution. The objective of this study is to assess this suggested approach at a pilot site using hydrochemical, molecular tools and geochemical modelling.

Approach/Activities. The technology was tested at the pilot site after treatment of the chlorinated ethenes source zone by activated sodium persulfate, which resulted in a high redox potential (~800 mV), low pH (~3) and high sulfate concentrations (9,070 to 12,600 mg/L). Based on qPCR biomarkers, the environment was unfavourable for iron-reducers, sulphate-reducers or dechlorinating bacteria. In the first step, groundwater was neutralized with NaOH and bioaugmented with groundwater from an adjacent contaminant plume. After this step, a mixture of micro-scale magnetite (95 kg) and starch (45 kg) was applied. Based on the monitoring results and geochemical modelling, a mixture of μFe (60 kg) and starch (40 kg) was then injected in order to create sufficiently reducing thermodynamic conditions, favourable for precipitation of iron sulphides. The achieved thermodynamic conditions were further maintained by periodical application of a biodegradable substrate (cheese whey).

Results/Lessons Learned. After the neutralization and bioaugmentation step, favourable conditions for iron reducers and sulfate reducers were created and based on qPCR their relative abundance increased by four orders of magnitude. On the contrary, the abundance of dechlorinating bacteria (*Dehalococcoides mccartyi*, *Dehalobacter* sp. and *Desulfitobacterium* spp.) remained low. After application of the magnetite + starch and μFe + starch mixtures, the activities of the iron-reducers and sulfate -reducers were further stimulated and resulted in an increase in ferrous iron concentrations (from <LOQ to 337 mg/l), a decrease in sulfate concentrations by 74 - 95% and production of hydrogen sulfide (from <LOQ to 25.9 mg/L). At the same time, a gradual recovery of dechlorinating bacteria and an increase in concentrations of non-chlorinated ethene were observed. The chlorine number decreased from ~3.5 to 3.8 to 2.0 to 3.0, which indicates that the removal processes also included sequential biological reductive dechlorination. The maximum decrease in the total concentration of chlorinated ethenes was 98%; however, they persisted in some of the wells, probably due to the presence of residual DNAPL in their surroundings (the pilot test is ongoing). The study and methods used brought an insight into biogeochemical processes that, when properly engineered, could provide a cost efficient and sustainable polishing step after ISCO treatment.