

In Situ Chemical Precipitation of Cobalt for Long-Term Groundwater Remediation

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Background/Objectives. Shallow groundwater at an industrial facility in Maryland is impacted by cobalt at concentrations above its facility-wide background concentration. The impacted groundwater is limited to a shallow, thin perched saturated zone present above a clay layer that separates impacted groundwater from the regional aquifer. Although no documentation regarding cobalt use at the site was identified, cobalt concentrations in groundwater were greatest near several former septic tank drain fields, suggesting past disposal to septic tank systems. Cobalt concentrations in groundwater as high as 1,080 µg/L have been measured in the past, well above its facility-wide background concentration of 17.7 µg/L. The solubility of cobalt sulfide (CoS), like many metal sulfides, is low, with solubility product values on the order of 2×10^{-21} to 4×10^{-25} . Since recent cobalt concentrations in groundwater are only one to two orders of magnitude above the background value (recent maximum values on the order of 400 µg/L), precipitation of cobalt to less than the facility-wide background value is conceptually feasible if sulfide values as low as 0.1 µg/L in groundwater can be achieved. In situ chemical precipitation (ISCP), if successfully implemented, has significant advantages over other potential alternatives such as monitored natural attenuation and pump and treat. Due to the lack of case studies identified in the technical literature that have demonstrated the effectiveness of this ISCP process for cobalt, a pilot test of this technology was proposed to support the development of a Feasibility Study report.

Approach/Activities. A pilot test of in situ chemical precipitation for cobalt was conducted between July 2015 and July 2016. To induce precipitation of CoS, several reagents were injected into newly installed injection wells near existing monitoring wells that had exhibited the greatest cobalt concentrations in groundwater. Selected reagents included a commercially available emulsified vegetable oil (EVO) to provide a fermentable organic substrate, magnesium sulfate to provide a sulfate source, and sodium carbonate to raise the groundwater pH. After injection of reagents, quarterly groundwater monitoring was conducted in key wells to measure performance indicators, including cobalt and other metals, sulfate, sulfide, total organic carbon (TOC), dissolved iron and manganese, dissolved gases (methane, ethane, and ethene) and standard field parameters.

Results/Lessons Learned. Cobalt concentrations in monitoring wells closest to the pilot test injection zone were reduced from 80% to 97% compared to baseline values. Reagent concentrations and injection methods typically used for stimulating biodegradation of chlorinated solvents were effective in creating desired changes in groundwater geochemistry. Changes in groundwater geochemistry were consistent with those expected from EVO and sulfate injection and included declines in dissolved oxygen, oxidation-reduction potential, cobalt, and sulfate (after an initial increase) and increases in dissolved iron and manganese, alkalinity, methane, and TOC. Time series trends of non-reactive tracer materials suggested that cobalt concentration declines were not caused by dilution from injectate. The overall data indicated that the ISCP process successfully induced CoS precipitation. The potential long term stability of the CoS precipitate was evaluated through a review of Eh-pH diagrams, geochemical data, and a literature review regarding previous evaluations of CoS stability under natural environmental conditions. It was concluded that the ISCP process would likely be successful at

the site as a full-scale remedy and would accelerate the overall time to reach site closure by at least several decades compared to natural attenuation.