

In-situ Reduction of Geogenic Hexavalent Chromium by Calcium Polysulfide and Assessment of Chromium Re-oxidation

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Background/Objectives. Groundwater hexavalent chromium Cr(VI) concentrations have reached or exceeded the California Maximum Contaminant Level (MCL) of 50 microgram per liter ($\mu\text{g/L}$) at several locations in the Sacramento Valley, well above the newly established California public health goal of $0.02 \mu\text{g/L}$. One example is a site in the southern Sacramento Valley where two, small landfills were formerly located. Cr(VI) concentrations downgradient of the site are high (historical high of $613 \mu\text{g/L}$), but background concentrations are also high (e.g., $\sim 180 \mu\text{g/L}$, measured in nearby water supply wells). Given that no anthropogenic sources of chromium contamination have ever been detected, the most likely cause of elevated Cr(VI) concentrations downgradient of the landfills is organic and/or nitrogenous matter, either from leachate from the former landfills or infiltrate from animal husbandry operations at the site, that altered the site's geochemistry, causing Cr(VI) to be released from chromium-rich minerals in the serpentinite-derived alluvial deposits at the site.

The overall goal of this work was to determine if in situ chemical reduction with calcium polysulfide (CaS_x) can reduce Cr(VI) concentrations at this site. To achieve this goal, two field pilot tests were conducted, with the following specific objectives: 1) to document the extent of the treatment zones; 2) to evaluate the emergence and persistence of any unwanted secondary effects; and 3) to evaluate Cr(VI) concentrations rebound/re-oxidation over the long-term.

Approach/Activities. Two field pilot tests using CaS_x were performed, in the upper, very low permeability hydrostratigraphic unit (HSU)-1, and the more highly permeable HSU-2. The HSU-1 test used high pressure nitrogen gas to pneumatically fracture the saturated soil, followed by the injection of a CaS_x -bearing aerosol. The second test involved gravity injection of CaS_x solution into a well screened across the upper portion of HSU-2. As part of the monitoring program, depth-discrete monitoring wells were installed downgradient from the injection points, and chromium and other geochemical indicators, including tracer dyes, were monitored over a two year period.

Results/Lessons Learned. CaS_x addition reduced Cr(VI) to less than $50 \mu\text{g/L}$ in HSU-1 within the treatment radius, and below $5 \mu\text{g/L}$ in HSU-2. Arsenic and nickel concentrations increased by more than an order of magnitude for a short period, but then returned to near-baseline concentrations. However, dissolved manganese increased by two or more orders of magnitude and persisted at high concentrations. Freshly dissolved manganese is of concern, because it could promote the re-oxidation of additional Cr(VI) if the aquifer reverts to aerobic conditions, as indicated in microcosm studies previously performed with site sediments (as reported at the 2011 Bioremediation Conference, Abstract # 456). Recently collected data suggest that chromium re-oxidation may already be occurring, as indicated by decreasing manganese concentrations and increasing Cr(VI) concentrations in at least one observation well. The site will be monitored further, to more completely assess the performance of CaS_x addition, and the potential of chromium re-oxidation.