In-Situ Remediation of a Chromium-Contaminated Site Using Calcium Polysulfide

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URS Corporation is using calcium polysulfide (CPS) for in-situ geochemical fixation of hexavalent chromium, Cr(VI), in soil and groundwater in alluvial fan sediments at a former metal plating facility in western Arizona. Concentrations of Cr(VI) in groundwater at the site exceed 200 milligrams per liter (mg/L) compared to the maximum contaminant level of 0.1 mg/L for dissolved chromium in drinking water set by the U.S. Environmental Protection Agency. URS has completed vadose zone and groundwater pilot tests using CPS and has begun full-scale vadose zone application in the source area.

CPS is used extensively as an agricultural soil amendment and for removal of metals in water treatment systems, and has recently been approved for in-situ remediation at several sites in the United States. CPS is more stable and persistent in subsurface environments than other reductants such as



Groundwater samples from an observation well: pretreatment (left) and day 9 of treatment (right).

sodium dithionite, does not form insoluble precipitates such as ferrous sulfate, and is relatively safe to handle in the field. CPS reduces Cr(VI), commonly in the form of chromate, $CrO_4^{2^\circ}$, to the relatively insoluble form of trivalent chromium, Cr(III), which is less toxic and tends to fall out of solution and adhere to soil. One example of the reaction is:

 $2CrO_{4^{-2}}^{2-} + 3CaS_{5} + 10H^{+} \longrightarrow$ $2Cr(OH)_{3}(5) + 15S_{5} + 3Ca^{2+} + 2H_{2}O$

The fixation of Cr(VI) by CPS is considered to be a permanent remediation technique under most groundwater conditions. The reaction is theoretically reversible; however, under natural groundwater conditions the



Vadose zone pilot test infiltration trenches and lysimeters.

equilibrium condition is dominated by the right side of this reaction. Furthermore, the only mechanism identified in the literature for the re-oxidation of Cr(III) under natural groundwater conditions is by a grain surface reaction that occurs when dissolved Cr(III) is exposed to aquifer sediments coated with manganese dioxide (MnO₂). Since Cr(OH)₃ is a solid precipitate, reaction with MnO₂ is limited by the extremely low solubility of this compound.

Prior to vadose zone treatment, Cr(VI) concentrations in the 20 square-foot test zone were as high as 2,190 mg/kg in soil and 3,600 mg/L in the vadose zone pore water. Over a period of about 24 hours, approximately 660 gallons of 29 percent CPS were applied to infiltration trenches, followed by 2,500 gallons of water to disperse the chemical through the test zone. The wetting front was monitored and sampled with soil lysimeters installed in a basement wall (see figure above). Results during the first 30 days indicated that eight of the nine lysimeters used to monitor the test were impacted and demonstrated a 90 percent reduction in Cr(VI) concentrations.

> In the groundwater pilot test area, the aquifer at 165 feet below surface was impacted by Cr(VI) concentrations of 240 mg/L, nitrates exceeding 400 mg/ L, and trichloroethene and other VOCs. Approximately 9,000 gallons of 29 percent CPS were injected through an existing monitor well, followed by 79,000 gallons of water, at an average rate of 31 gallons per minute, to flush the well and push the reductant to an observation well at a distance of 30 feet across the regional

hydraulic gradient. Downhole monitoring was conducted in the observation well using a multiparameter probe and depth-specific sampler. After 35 hours, breakthrough of CPS was indicated by a decrease in oxidation/ reduction potential (ORP) and an increase in pH and total dissolved solids. Concentrations of Cr(VI) in the observation well dropped from 240 mg/L to less than 1 mg/L shortly after ORP became negative. Mobilization of arsenic, iron, and manganese from aquifer solids due to the reducing conditions was not observed. In the observation well at the edge of the injected CPS footprint, rebound of Cr(VI) concentrations occurred after 115 days. In the injection well at the center of the injected reductant, ORP has remained negative and Cr(VI) concentrations were below detection after 419 days. URS is proceeding with full-scale vadose zone application in the source area and plans a fullscale groundwater remediation.

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