Successful Implementation of the In Situ Gaseous Reduction Approach for Vadose Zone Remediation

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Abstract: Laboratory investigations indicate that chemical reduction by reactive gaseous mixtures should be an effective approach to treat and immobilize hexavalent chromium in contaminated soil. To evaluate this innovative remediation approach, a field demonstration was completed at a waste site that involved the injection of a mixture of 200 ppm hydrogen sulfide diluted in air. The gas mixture was drawn through the site soil by a vacuum applied to extraction boreholes located at the site boundary, and residual hydrogen sulfide was removed prior to release of the air back to the atmosphere. The injection test lasted 76 days with no detectable releases of hydrogen sulfide to the site atmosphere. Comparison of hexavalent chromium analyses of soil samples taken before and after the test indicated that 70% of the hexavalent chromium originally present at the site was reduced and thereby immobilized by in situ gaseous reduction. Treatment was generally better in zones of higher permeability sand containing less silt and clay, indicating that geologic heterogeneity is a limitation to treatment effectiveness. However, maximum concentrations of hexavalent chromium were reduced from 85 mg/kg to less than the EPA Region 9 cleanup criteria of 30 mg/kg as a result of in situ gaseous reduction.

Chemical treatment of metal and radionuclide-contaminated soils by reactive gas mixtures may be a viable and cost effective vadose zone remediation approach. In particular, a number of laboratory tests were completed by the U.S. Department of Energy (DOE) involving treatment of hexavalent chromium contaminated soil samples with diluted hydrogen sulfide gas mixtures. The results of these tests indicate that 90 percent or more of the hexavalent chromium present was reduced and immobilized (Thornton and Jackson 1994; Thornton and Amonette 1999). This treatment approach involves the reduction of hexavalent chromium, Cr(VI), to Cr(III) as illustrated by the following generalized reactions:

$$8CrO_4^{2-} + 3H_2S + 10H^+ + 4H_2O \rightarrow 8Cr(OH)_3 + 3SO_4^{2-}$$

and

$$2CrO_4^{2-} + 3H_2S + 4H^+ \rightarrow 2Cr(OH)_3 + 3S^o + 2H_2O$$

Note that the products of these reactions include minor amounts of sulfate or elemental sulfur, which are generally not regarded as contaminants, and Cr(III) hydroxide, a nontoxic and naturally occurring solid.

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Based on the promising experimental findings, a search for a field test site was initiated. A chromate-contaminated waste site located at the U.S. Department of Defense's (DOD's) White Sands Missile Range was eventually identified and a joint DOE and DOD collaboration in support of a field demonstration was established (Thornton et al. 1999). The objectives of this demonstration were to provide information to evaluate the effectiveness of the in situ gaseous reduction (ISGR) approach, to verify that it can be applied in a safe and environmentally acceptable manner, and to collect cost data needed to support a cost analysis. Prior to initiation of the test, a detailed safety plan was prepared, including monitoring and emergency response procedures. During the test, Pacific Northwest National Laboratory (PNNL) and Sandia National Laboratory (SNL) performed all field activities, aided by DOD staff at White Sands Missile Range. Regulatory interface activities and public review was coordinated through the New Mexico Environment Department.

Results of previous investigations by DOD and more recent DOE characterization efforts indicated that chromate contamination of the soil extended to a depth of about 18 feet in gypsum sand. Below this is a dense brownish clay layer. Analytical results indicated that the contamination was confined to the sand and did not extend into the clay.

Application of the ISGR approach involves the injection of the treatment gas mixture into a waste site soil through a central borehole and withdrawal by a vacuum applied through boreholes at the edge of the flowcell (Figure 1). The central borehole was located at the center of the test waste site chromate plume based on the characterization information collected. The six extraction wells were placed beyond the outer limits of contamination at a radial distance of 15 feet from the injection borehole.

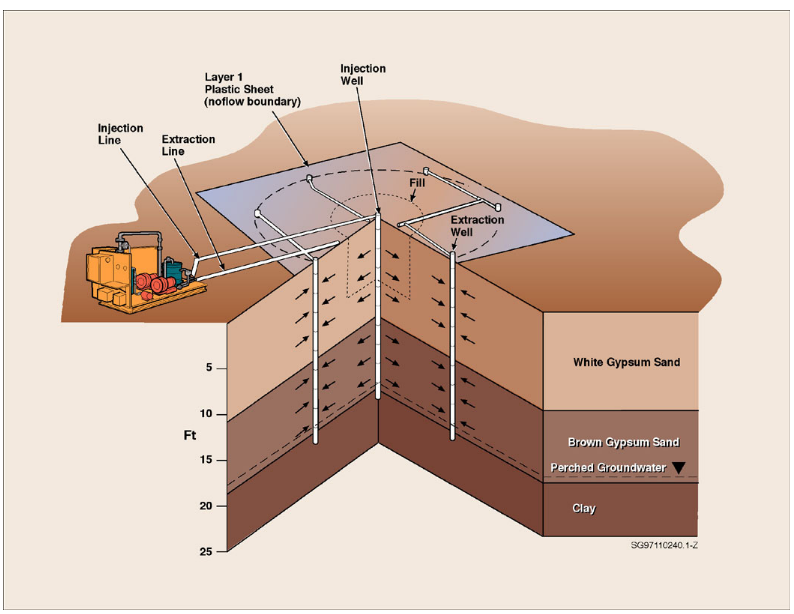

Figure 1. Cross Section of the In Situ Gaseous Reduction Well-Field Network.

The gas treatment test was conducted over a period of 76 days. During the test, a 200 ppm_v mixture of hydrogen sulfide in air was injected into the site soil at flow rates ranging from 20 to 50 cfm (Thornton et al. 1999). Treatment of the flow cell was monitored by measuring the breakthrough of hydrogen sulfide in the extracted air stream. Residual hydrogen sulfide was removed from the extracted air stream by a gas scrubber before release of the clean air back to the atmosphere. All systems performed in a satisfactory manner during the field demonstration, with no significant releases of hydrogen sulfide to the site atmosphere.

Collection and analysis of post-treatment soil samples and comparison with pre-test sampling data was undertaken. This comparison provided a basis to prepare a performance assessment of the ISGR technology (Thornton et al. 1999). Approximately 70% of the mass of hexavalent chromium originally present at the site was reduced. Geologic heterogeneity was found to limit treatment effectiveness, however. In particular, higher levels of treatment appeared to be associated with zones of higher permeability sands, suggesting preferential gas flow through these zones. Treatment results were good overall, however, and hexavalent chromium concentrations of all post-test soil samples were well below the EPA Region 9 cleanup criteria of 30 mg/kg (versus a maximum pre-test concentration of 85 mg/kg). Additional gas treatment of the lower levels of contamination in the less permeable zones could be undertaken, if necessary, by selective injection of hydrogen sulfide into those zones.

Results of the demonstration indicate that the technology should be cost effective. In particular, the ISGR approach is likely to cost less than excavation when hexavalent chromium contamination exists at depths of greater than 15 feet.

As indicated above, no significant releases of hydrogen sulfide occurred during the demonstration, indicating that the ISGR technology can be applied in a safe and environmentally acceptable manner. The safety plan developed in support of the demonstration provides a guide to establish monitoring operations and response actions when applying gas treatment remediation to other sites.

References

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