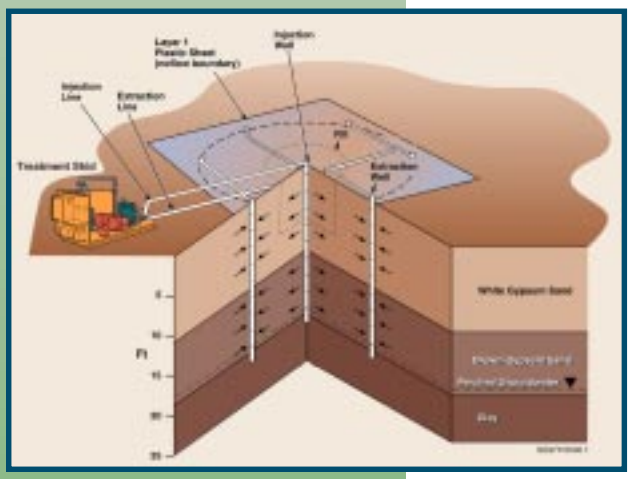
A Technical Resource for Government and Private Industry

Innovations for Vadose Zone Cleanup

In Situ Gaseous Treatment

Over the last several years, scientists at the Pacific Northwest National Laboratory have conducted laboratory and field investigations of In Situ Gaseous Treatment, a remediation technology that immobilizes or destroys contaminants in place within the vadose zone. The gaseous treatment approach uses chemically reactive gas mixtures to *reduce or oxidize* contaminants such as hexavalent chromium and other heavy metals, chlorinated solvents and dense non-aqueous phase liquids (DNAPLs), and explosive agents (e.g., TNT). The technology offers a cost-effective alternative to excavation, particularly for sites with contamination at depths greater than 15 feet.



With gaseous treatment, a gas mixture is injected into the vadose zone through a central borehole. The gas mixture is then drawn through the waste site by vacuum applied at extraction boreholes located along the perimeter of the site. Reactive gas species are monitored in the extraction wells to provide a real-time basis for assessing treatment progress.

In Situ Gaseous Reduction

For the reduction of contaminants, a diluted hydrogen sulfide gas mixture is used. The primary chemical reaction associated with immobilization of hexavalent chromium involves the reduction of Cr(VI) to Cr(III), with subsequent precipitation as a nontoxic solid product as indicated by the following generalized reaction:

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

Reduction of hexavalent chromium proceeds rapidly under laboratory conditions with greater than 90% of the chromium being reduced.

We demonstrated the gaseous reduction technology at the U.S. Army's White Sands Missile Range in New Mexico to remediate hexavalent chromium contamination in the vadose zone. The project involved injection of a 200-ppm hydrogen sulfide gas mixture into the soils, in accordance with standard industrial safety and monitoring practices. The test was concluded in just 80 days when breakthrough of residual hydrogen sulfide was detected in the extraction wells. No releases of hydrogen sulfide were detected during the test, verifying that in situ gas treatment can be accomplished safely.

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Final performance assessments indicate that 70% of the Cr(VI) mass present at the site was reduced to Cr(III) during the field demonstration, with final concentrations meeting EPA cleanup guidelines. The work resulted in the technology being recognized as a presumptive remedy by the State of New Mexico. In addition to the successful technical approach, the project provided an effective safety plan for guiding operations, including emergency response actions, which can be applied to treatment at other sites. It is anticipated that this technology may be useful in the immobilization of other metals besides chromium, including cadmium, mercury, and lead, as well as for radionuclides such as uranium and technetium.

In Situ Gaseous Oxidation

Ozone, a strong oxidizing agent used extensively for purifying water, is a promising gas for in situ treatment of organic contaminants in soils. PNNL is advancing the use of ozone for in situ destruction of explosive agents and chlorinated solvents, including DNAPLs in vadose zone sediments. The technique is similar to In Situ Gaseous Reduction. It provides for controlled delivery of a reactant gas to the subsurface, however, in place of hydrogen sulfide, this technology uses ozone.

Laboratory studies have shown that ozone is effective in destroying trichloroethylene (TCE) and other chlorinated compounds via the Criegee oxidation mechanism. The technique leads to complete mineralization without formation of undesirable reaction byproducts. No chemical reagents are required since ozone can be produced from air or oxygen passed through a commercially available corona discharge-based ozone generator. Since ozone is a gas, it can be injected readily into the vadose zone, and its movement can be controlled by pressure gradients generated by standard regenerative blowers.

Additional PNNL studies have verified the application of oxidation using ozone for destruction of TNT in soils. Tests indicate that TNT destruction occurs quickly, with 80% destruction occurring in 16 hours. Essentially all reacted TNT was replaced by nitrate.

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