Critical Biogeochemical Parameters Used for In Situ Bioremediation of Solvents in Fractured Rock

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Two full-scale demonstrations of in situ bioremediation via biosparging/bioventing illustrate the critical biogeochemical parameters for in situ bioremediation of solvents in fractured rock. Both sites were in Virginia, but differed significantly in contaminant composition. One site was dominated by non-chlorinated solvents at high concentrations while the other site had only chlorinated alkenes. Both sites showed rapid responses to sparging and eventually required various other nutrient supplements to maintain high biodegradation rates of the chlorinated solvents.

Effective in-situ aerobic groundwater bioremediation depends upon the successful delivery of oxygen (and other amendments such as nutrients and methane) into the subsurface. While this process is relatively straightforward in granular overburden materials, it can be quite complex in fractured bedrock. Bedrock fractures serve as preferential pathways such that the resultant zone of influence is generally asymmetrical and often unpredictable. Full characterization of the depth, size, orientation, and degree of interconnection of bedrock fractures is prohibitive from a logistical and cost perspective. However, tracer tests and critical inorganic and organic measurements can provide a representative picture of crucial subsurface conditions.

Site 1. Contaminants of concern in bedrock groundwater included chlorinated solvents such as trichloroethylene (TCE); 1,1,1-trichloroethane (TCA); and their breakdown products, as well as acetone and isopropanol. Chemical and microbiological sampling verified that some degree of intrinsic (natural) anaerobic biodegradation was occurring. To optimize and accelerate contaminant breakdown, the natural subsurface conditions were converted to an aerobic state through the injection of air. Injection of gaseous-phase nutrients (triethyl phosphate and nitrous oxide) and methane were also included in the injection system to further stimulate the growth and biodegrading capabilities of native microbial populations.

Bedrock beneath the subject site consists of fractured shales and limestones of the Valley and Ridge physiographic province. The bedrock is overlain by thin, clay-rich overburden, with groundwater generally encountered at the overburden-bedrock interface. Outcrop fracture mapping, drilling and monitoring well installation, borehole geophysical surveys, pumping tests, and packer testing have been utilized to learn more about fracture size, orientation, and water-bearing properties of the subsurface.

In order to delineate the injection system zone of influence, a helium tracer test was conducted. This test produced observable effects in monitoring wells 25 feet or more away. Furthermore, monitored helium concentrations indicated the presence of preferential gaseous phase pathways within the fractured bedrock. This was confirmed by “short-circuiting” air flow observed in monitoring wells near the injection point.
Once air injection was initiated, it became apparent that the air zone of influence was not coextensive with the predicted helium zone, as evidenced by dissolved oxygen measurements in groundwater monitoring wells. This phenomenon may be the result of microbial utilization of oxygen which results in reductions of dissolved oxygen concentrations at the perimeter monitoring wells.

Variations in precipitation during the injection system operation resulted in varying backpressure in the injection well. This in turn limited the rate of air and nutrient injection, reducing the dimensions of the zone of influence during high water table conditions. Conversely, as the groundwater elevation dropped, injection could proceed at higher flow rates, expanding the zone of influence of the injection well. The injection system operation has been dynamically adjusted to correspond with changing subsurface conditions in the fractured bedrock groundwater regime. This enabled the successful conversion to aerobic conditions, with stimulation of native microbial populations, and accelerated contaminant degradation in the zone of influence.

The pilot system features sequential injection of air, gaseous-phase nutrients (nitrous oxide and triethyl phosphate), and methane to evaluate in-situ responses to aerobic microbial stimulation. Groundwater samples have been analyzed for VOCs (including breakdown products), microbial parameters (phospholipid fatty acids and methanotrophs by most probable number counts), nutrients, and groundwater quality parameters such as chlorides, methane, redox potential, and dissolved oxygen. Soil gas has been monitored for methane, carbon dioxide, and oxygen.

Groundwater VOC concentrations in the zone of influence, particularly for acetone, isopropanol, vinyl chloride, and cis-1,2-dichloroethylene, have decreased by one or more orders of magnitude following the air and nutrient injection campaigns. This data is consistent with increases in chlorides, nutrients, and dissolved oxygen, confirming that aerobic degradation processes have become dominant over the former anaerobic conditions.

This is largely attributed to increased microbial activity as evidenced by several orders of magnitude increases in observed biomass (based on phospholipid fatty acid PLFA measurements) in the four months since Interim Measure start-up. Further increases in microbial activity and VOC breakdown are expected to result from the methane injection phase that was initiated in July 1998.

Site 2. The site is in rural Virginia. Depth to groundwater is 8 to 10 ft (2.4 to 3 m), and average groundwater velocity is 1.2 cm/day. The formation consists of approximately 50 ft (15 m) of saprolitic overburden (hydraulic conductivity: 3 - 10^-4 cm/s) above bedrock. The maximum concentration of chlorinated volatile organic compounds (VOCs)—mainly tetrachloroethene (PCE) and TCE—is approximately 2000 μg/L; some hydrocarbon contamination is also present. The contamination is found throughout the saturated saprolite and the upper fractured bedrock. The areal extent of the plume is around 1 acre (0.4 hectare).

The in situ MTT evaluation was operated for 139 days. At the beginning of the test, bubbling and pressure buildup were detected in Well OW-1, possibly due to short-circuiting from the nearby injection well. To prevent stripping of TCE, this well was tightly capped for the rest of the test run.
Chloride was found at concentrations of 20 to 70 mg/L, precluding its use as a proxy for the degradation of approximately 2 mg/L of chlorinated ethenes. Nitrogen (nitrate-nitrite and total Kjeldahl) and phosphorus (orthophosphate and total phosphorus) were well below 1 mg/L, indicating that macronutrients would have to be added. Total organic carbon ranged from 1 to 10 mg/L, dissolved oxygen concentrations ranged from 0.1 to 2.8 mg/L, and pH ranged from 5.4 to 6.6. At the end of the evaluation, total Kjeldahl nitrogen was measured at 0.4 to 4 mg/L, whereas phosphorus (orthophosphate and total phosphorus) was mostly below the detection limit of 0.01 mg/L; the highest values were 0.11 mg/L, in Well MW-7. These low concentrations soon after the addition of the phosphate solution confirm that the subsurface environment is phosphorus-limited. Soil gas was also sampled and analyzed for methane and TCE. Background levels of methane were 2 to 5 ppmV, and no background TCE was detected (detection limit: 0.005 ppmV). On Day 21, and again on Day 48, methane concentrations of up to 4% by volume were found. We assume that disruptions in nutrient delivery limited carbon uptake, which allowed methane to build up in the subsurface. On Day 139, after four weeks of optimal operation, the methane levels had dropped to between 2 and 20 ppmV; 0.95 ppmV of TCE was measured in one vapor sampling well.

Trichloroethene (TCE) levels dropped from 2130 to 150 μg/L in the well initially exhibiting the highest concentration. The radius of influence of the air injection was approximately 30 ft (9 m). Methanotrophic bacteria increased over six orders of magnitude and eventually dominated the subsurface microbiota. The results indicate that, as long as nitrogen and phosphorus were reliably supplied, rapid (two to four weeks) growth of methanotrophs and associated oxidation of TCE followed. This pilot system was expanded to bioremediate the entire plume above bedrock; three additional injection wells were installed, along with observation wells, and a new TEP diffusion system was developed.

**Conclusions.** Fractured rock environments present some unusual obstacles to subsurface biostimulation. Careful control of injection pressure, increased screens, and increasing the number injection points can provide reasonable solutions. Helium tracer tests, respiration tests, pressure analysis over different injection conditions and measurements of microbial activity parameters, electron donors, electron receptors and daughter products help provide monitoring for controlling the bioremediation process in fractured rock.