APPENDIX C

In Situ Bioremediation Using Gaseous Electron Donor Technology (GEDIT)

1.0 Technology Background

Gaseous electron donor injection technology (GEDIT) is an innovative technology for in situ treatment of perchlorate and other contaminants (Evans and Trute, 2006; Evans, 2007). Gases such as hydrogen (the electron donor) are injected into vadose zone soil to promote in situ anaerobic biodegradation of contaminants which serve as electron acceptors by certain bacteria. For example, indigenous autotrophic bacteria such as the Dechloromonas species commonly found in soils use hydrogen as an energy source, and utilize perchlorate as a terminal electron acceptor for respiration (Shrout et al., 2004). In the case of perchlorate, water and the chloride anion are produced via biochemical reduction of perchlorate. In addition to perchlorate, GEDIT is capable of being used for treatment of other oxidized contaminants including chlorate, nitrate, hexavalent chromium, and trichloroethene. As compared to liquids, the high mass-transfer properties of gases in the vadose zone provide an excellent distribution of the electron donor, particularly in fine grained soils with low permeability. The rate of diffusion and distribution of gas is primarily a function of flow rate, moisture, Henry's constant, gas density, and soil permeability (Evans and Trute, 2006). Gaseous electron donors are introduced into the soil through injection wells, which can be used in conjunction with optional soil vapor extraction (SVE) wells. Potential electron donor gases include hydrogen, commercial propane (i.e., liquefied petroleum gas or LPG), and volatile organic compounds such as methanol, ethanol, butanol, acetic acid, ethyl acetate, butyl acetate, and hexene (Nozawa-Inoue et al., 2005; Evans and Trute, 2006; Evans et al., 2009). Electron donor gases can be diluted with nitrogen to improve distribution throughout the vadose zone and promote anaerobic conditions. Alternately, SVE wells may be installed to extract soil vapor within the treatment zone, which is then amended with gaseous electron donor, and injected back into the target treatment zone. In this configuration, the oxygen content in the vadose zone decreases as biodegradation occurs, facilitating development of anoxic conditions and degradation of perchlorate.

The most notable advantage of GEDIT is the improved mass transfer properties of gases as opposed to technologies based on liquid injection. Gaseous electron donors easily advect and diffuse through the vadose zone, improving delivery of the donor and minimizing issues with liquid preferential flow pathways. GEDIT, unlike bioflushing and water flushing, does not require the capture and treatment of mobilized contaminants that otherwise could adversely impact groundwater. In addition to delivery of the gaseous electron donors, oxygen concentrations in the vadose zone must be reduced sufficiently to allow contaminant biodegradation. Too low a soil moisture content can prevent contaminant biodegradation. Other conditions that may limit GEDIT effectiveness include pH extremes and high salinity in soil pore water. Shallow contamination (e.g., < 10 ft) may be remediated in more cost-effectively using alternate technologies potentially including flushing, bioflushing, or ex situ soil biotreatment.

2.0 Technology Implementability

The primary application for GEDIT is treatment of contaminants in deep vadose zone soil for the purpose of groundwater protection. However, successful implementation depends upon distribution of electron donors and reduction of oxygen concentrations for stimulation of anaerobic biodegradation of contaminants including perchlorate. Fulfillment of these conditions is affected by contaminant and co-contaminant concentrations, indigenous organisms present, injection well spacing, remediation system design, and gas flow rates. Additionally, subsurface conditions to consider prior to application of GEDIT include the site geology, heterogeneity of soils, contaminant distribution, soil permeability, and ability to achieve required environmental conditions.

Prior to full-scale implementation of the remedy, a laboratory bench-scale study is warranted to estimate the ability of GEDIT to promote contaminant biodegradation in soil at various moisture contents and to evaluate the optimal gas mixtures. Additionally, pilot-scale tests should be conducted to determine the radius of influence and optimal gas flow rates in site-specific geologic formations.

GEDIT requires installation of gas injection wells, installation of a gas mixing and delivery manifold, monitoring of soil gas concentrations, and collection of soil samples for analysis to assess performance. Health and safety concerns with GEDIT are primarily associated with gas flammability (e.g., hydrogen and liquefied petroleum gas [LPG]). In a field-scale demonstration study at Aerojet in Rancho Cordova, California, this issue was easily managed and did not require extraordinary efforts (Evans et al., 2009). Flammable gaseous electron donors were supplied in cylinders or tanks similar to those used on construction sites or to fuel thermal oxidizers. Flammable gas/no smoking placards were placed near the injection system, similar to how they would be at a gas station facility. No flammable gases were detected above the ground surface, indicating that the release of gases to the atmosphere was not a safety issue. Nevertheless, monitoring of flammable gases should be conducted in a similar manner as would be routine for a gasoline station remediation project.

3.0 Technology Performance

Laboratory microcosm and column studies were conducted to evaluate use of different electron donors, nutrients, and moisture content in soils contaminated with 23 mg/kg perchlorate and 14 mg-N/kg nitrate from a site in Los Angeles, California (Evans and Trute, 2006). The microcosm study ran for 38 days and found that both perchlorate and nitrate were reduced when either hydrogen or ethanol were used as electron donors and the microcosms were supplemented with a target moisture content of 12%. The study found that nutrients native to the soil were sufficient for degradation of perchlorate and nitrate in the presence of an electron donor. Another microcosm experiment lasting 105 days was conducted with varying concentrations of hydrogen or ethanol (200, 300, and 400% of the stoichiometric demand). For microcosms supplemented with hydrogen or ethanol at these concentrations, perchlorate was reduced to less than 0.04 mg/kg and nitrate was reduced to less than 0.5 mg-N/kg.

A bench-scale microcosm study was conducted on soils from the Inactive Rancho Cordova Test Site (IRCTS) Propellant Burn Area in northern California and a series of electron donors were tested including hydrogen, 1-hexene, ethyl acetate, and LPG (Cai et al., 2010). Hydrogen was the most effective electron donor, with first order degradation rate constants ranging from 0.13 to 0.20 day-1. This was not surprising as hydrogen had the highest diffusivity of the other gases tested. Concentrations were reduced in the hydrogen-supplemented bottled from 8.2±1.3 mg/kg to non-detectable levels within 35 to 42 days.

A GEDIT treatability study was also conducted using soil from the former Bermite facility in Santa Clarita, California. This study evaluated various soil moisture contents and various gas compositions. The results demonstrated that GEDIT was capable of promoting perchlorate biodegradation in vadose zone soil and perchlorate concentrations were reduced to non-detectable levels under certain conditions. A pilot-scale test of GEDIT at this site is being planned.

A field scale demonstration of gaseous injection was demonstrated at the Pantex facility northeast of Amarillo, Texas (Rainwater et al., 2002). In this study, pure nitrogen was injected at 5 wells to promote anaerobic respiration of indigenous organisms for degradation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and the 2,4,6- trinitrotoluene (TNT) metabolite 1,3,5-trinitrobenzene (TNB). Soils in the vadose zone above 30 feet below ground surface could not be excavated due to the presence of buried utilities and were the target of the gaseous injection pilot test. Concentrations were initially 70 mg/kg which were above the risk reduction clean-up criteria of 2.6 and 0.51 mg/kg, respectively. The surface of the treatment zone was covered with a 60 mil high-density polyethylene (HDPE) geomembrane to prevent losses of nitrogen and infiltration of water. Nitrogen gas was injected at a flow rate of approximately 10 standard cubic feet per hour (SCFH) through a water column to maintain a relative humidity of 30 percent and prevent dehydration. However, the desired oxygen concentration was not attained in the treatment zone until day 150 due to system leaks, and the majority of the monitoring wells had similar oxygen concentrations as atmospheric air. Approximately one-third of the contaminant mass was destroyed at the completion of the 295-day study. The lower reductions observed in this study were likely attributable to non-attainment of anaerobic conditions.

A field scale demonstration of GEDIT was conducted at the Aerojet site in Sacramento, California and is described further under the case study below (Evans et al. 2009).

4.0 Case Studies

The Department of Defense Environmental Security Technology Certification Program (ESTCP) and Aerojet-General Corporation funded a pilot-scale demonstration of GEDIT at the IRCTS in Rancho Cordova, California (Evans et al., 2009). The primary contaminant treated by this system was perchlorate but nitrate was also present in site soil. Initial perchlorate concentrations in the treatment zone ranged from 2,600 to 75,000 µg/kg and nitrate concentrations ranged from 2.0 to 8.6 mg-N/kg (as nitrate plus nitrite). The treatment zone was 0 to 50 feet below ground surface with a targeted radius of influence (ROI) of 10 feet from the injection well.

The microcosm treatability study was conducted to assess the ability of gaseous electron donors to reduce perchlorate and nitrate in soils from the site. Electron donors tested were hydrogen, 1-hexene, ethyl acetate, and LPG. Two moisture contents were also tested. All electron donors achieved complete or partial perchlorate reduction within 125 to 187 days in the higher moisture bottles (16 percent). No perchlorate reduction was observed in the lower moisture bottles with 7 percent moisture. Hydrogen was the most effective electron donor, with complete perchlorate reduction within 35 to 42 days.

For the full scale demonstration study, concentrations of gases were continuously injected over the period of 5 months were 10 percent hydrogen, 1 percent carbon dioxide, 10 percent LPG, and 79 percent nitrogen. Gases were injected at 18 and 28 feet below ground surface through 6-inch screens at a rate of 50 SCFH each. The treatment objectives for perchlorate and nitrate were to achieve a 90 percent reduction within six months. Perchlorate was removed by approximately 94 percent on average, with final concentrations ranging from less than 13 to 8,800 µg/kg. The actual ROI for perchlorate destruction was conservatively estimated as 10 feet but was more likely 15 feet, and nitrate was approximately 55 feet. Thus the goals of the demonstration were exceeded. Heterogeneity of perchlorate removals complicated the assessments of the reduction rate, but the rate was estimated to be approximately 380±110 µg/kg/d. This is similar to ex situ bioremediation degradation rates where the median rate was about 200 µg/kg/d (Evans et al. 2008). Nitrate was removed by 95 percent on average, with final concentrations ranging from less than 0.054 to 2.9 mg-N/kg. A nitrate reduction rate of 40±11 µg/kg/d was estimated. Five months was required to achieve 94 percent reduction of perchlorate and nitrate, and in some locations three months or less was required.

Hydrogen was able to diffuse into low permeability soils and perchlorate reduction was observed in silty and clayey soils. Because of the buoyancy of hydrogen, it did not penetrate as deep as LPG. LPG is heavier than oxygen and displaces oxygen. The combined use of these gases allowed anaerobic conditions to be maintained above and below the treatment zone, as observed by measured soil gas oxygen concentrations and efficacy of perchlorate reduction. Other important factors affecting performance included the concentration of oxygen present and soil moisture content. Oxygen concentrations of less than approximately 1% and hydrogen concentrations of greater than 0.5% were required for perchlorate removal based on field sampling results. Significant perchlorate reductions were noted in soil with moisture contents between 6.8 to 36%.

This project was recognized by the American Academy for Environmental Engineering with the 2010 Superior Achievement Award and by the International Water Association with a 2010 Honour Award.

5.0 Regulatory Acceptance

The California Regional Water Quality Control Board (RWQCB) approved the ESTCP Technology Demonstration Plan (i.e., Work Plan) for demonstration of GEDIT at the IRCTS (Evans et al. 2009). The California Department of Toxic Substance Control has also approved a Work Plan for pilot testing of GEDIT at the former Bermite site in Santa Clarita, California.

6.0 Costs

The primary cost drivers for GEDIT are gas use and drilling. These factors are site specific. Estimated costs for the IRCTS ranged from $28 to $87 per cubic yard (Evans et al., 2009). These estimates are conservative and are based on the ROI achieved using a single injection point as was used in the demonstration. Multiple injection points yield greater efficiency which in turn will translate to greater ROI and/or less gas use. These factors are being evaluated in collaboration with Lawrence Berkeley National Laboratory using the numerical model TMVOC. Additional cost estimates have indicated that GEDIT costs could be as low as $2 per cubic yard of soil.

7.0 References

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