Task 14 - Bubbleless Gas Transfer Technology for the In Situ Remediation of Chlorinated Hydrocarbons

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BUBBLELESS GAS TRANSFER TECHNOLOGY FOR THE IN SITU REMEDIATION OF CHLORINATED HYDROCARBONS

1.0 INTRODUCTION/BACKGROUND

Chlorinated hydrocarbons have been widely distributed in the environment because of their chemical and physical properties and the formerly widespread use of these compounds. In fact, chlorinated hydrocarbons such as trichloroethylene (TCE), tetrachloroethylene (PCE), chloroform (CF), and others are the most common pollutants in groundwater. Moreover, these pollutants represent one of the most important classes of pollutants at Department of Energy and Department of Defense sites. While there are surface-based remediation technologies, such as air stripping and carbon adsorption, that are applicable to these pollutants, these technologies are expensive and do not remediate the subsurface effectively. Subsurface contamination is difficult to address because of the poor solubility of the chlorinated hydrocarbons and the strong tendency of them to sorb to surfaces. In situ remediation technologies operate where the pollution occurs and do not rely on desorption and transport to the surface. Most in situ remediation technologies for the chlorinated hydrocarbons rely on biological destruction, directly or indirectly. Biological methods can be used in virtually any aquifer, but are limited by the ability to supply nutrients, electron donors, electron acceptors, or cosubstrates.

The most recalcitrant groups of chlorinated hydrocarbons are the highly chlorinated aliphatics such as PCE, tetrachloroethylene, and carbon tetrachloride. These compounds are not metabolized by microorganisms that can degrade TCE and other less chlorinated compounds. However, they can be degraded by a process known as reductive dehalogenation. Reductive dehalogenation is mediated by microorganisms or their biomolecules and results in a replacement of a halogen such as chlorine with hydrogen. In essence, the microorganisms use the chlorinated hydrocarbon as an electron acceptor. As such, the appropriate conditions to stimulate reductive dehalogenation are anaerobic conditions with a good supply of electron donors and a paucity of electron acceptors. Reductive dehalogenation can be stimulated by the addition of organic compounds to supply electrons. However, many microorganisms can degrade these organic substrates without affecting the chlorinated hydrocarbons. The addition of hydrogen gas supplies electrons without supplying carbon, resulting in less nonspecific growth and metabolism.

In order to induce active dehalogenation of chlorinated hydrocarbons in a typical aquifer, the zone of contamination must be converted to reducing conditions, and excess electron donors must be supplied. The addition of hydrogen gas can remove oxygen from the aquifer as it is readily metabolized by a variety of common microorganisms. Hydrogenase enzymes that can strip electrons from hydrogen are widespread among anaerobic and many aerobic bacteria. Once the aquifer is reduced by the removal of oxygen, the hydrogen will supply the reducing equivalents necessary for reductive dehalogenation.

To accomplish hydrogen-mediated reductive dehalogenation, efficient mechanisms are needed to add hydrogen to zones of contamination. Bubbleless gas transfer technology allows for the direct dissolution of gases into water through modules containing sealed, hollow, gas-permeable fibers filled with pure gases under pressure. The diameter of the fibers ranges from 200 to 400 microns,

providing a large surface area in the module. The gas diffuses across the fiber walls and dissolves directly into the water surrounding and flowing past the outside surface of the fiber membrane.

The chief advantage of this technology over other gas dissolution technologies is that the gas is dissolved without the generation of bubbles, increasing gas-transfer efficiency and preventing off-site migration of gases and clogging of the aquifer with bubbles. Additionally, in other gas transfer techniques the excess gases supplied to the aquifer will generate offgas that may require treatment.

The factors limiting the amount of gas that can be dissolved into water are Henry's Law constant and the aqueous solubilities of the gases. The mass flux of the gases into the groundwater determines the rate of bioremediation since biological demand for the gas can exceed the water solubility of the gas. Because the amount of water that can be pumped through an aquifer is determined by the hydrogeological characteristics and the number of injection and recovery wells that can economically be placed at a contaminated site, gas dissolution devices that generate high dissolved gas concentrations are desirable.

2.0 OBJECTIVES

The primary objective of this project is to demonstrate the ability of hydrogen to supply reducing equivalents for the reductive dehalogenation of PCE. This objective will be accomplished by two types of activities. First, laboratory experiments will compare the kinetics of hydrogen-mediated dehalogenation with natural routes of loss (hydrolysis and natural attenuation). Secondly, bench-scale column experiments will be performed to demonstrate hydrogen-mediated reductive dehalogenation in aquifer sediments.

3.0 ACCOMPLISHMENTS/WORK PERFORMED

The bench-scale laboratory columns have been constructed and leak tested, and flows have been calibrated. The columns are 1.75 m in length and 15 cm in diameter. They are constructed of heavy-wall borosilicate glass, with Teflon® seals, fittings, and tubing. The pressure gauges are of stainless steel, and the pumps are positive displacement type, constructed of ceramic and Kynar®. One column will be treated with hydrogen while the other will be a control. A separate control is important when working with highly volatile, viscous, and low solubility compounds such as PCE. Losses through even Teflon® are known to exceed 40% in some short-term experiments. Each of the columns is plumbed to pump in a separate continuous loop, with the influent entering from the bottom, exiting at the top, and entering a 2-liter reservoir in between. The columns have been packed with a sandy loam obtained from a glacial delta deposit in the Rader, North Dakota, area. This sediment was dried, sieved, homogenized, and stored at 4°C until use. This sediment had no known exposure to chlorinated hydrocarbons and should be representative of a freshly contaminated aquifer. When packing the columns, a small amount of quartz wool and pea gravel was used to prevent plugging of fittings and damage to the pump. Forty-two kg of sandy loam were wet-packed into each column. Pumping rates were established to provide for the turnover of about one pore volume every two days. This water velocity is similar to natural conditions at many sites and will maintain the low head typical of in situ remediation techniques.

4.0 FUTURE WORK

In the coming months, PCE will be introduced into the columns by adding PCE-saturated water and pumping it through the sediment. When a water concentration of PCE of about 100 mg/L is attained, hydrogen gas will be added to one of the columns. Samples will be collected from the circulating water of each of the columns at intervals and analyzed for PCE and for the degradation products TCE, dichloroethylene, vinyl chloride, and chloride. Rates, stoichiometry, and operating data will be obtained during the operation of the columns. Operation of the columns will end when the concentration of chlorinated hydrocarbons in the circulating water of the test column has declined such that the rates of dehalogenation are nil. At that time, the sediments from the column will be analyzed to determine the remaining type and quantity of sorbed chlorinated hydrocarbons and the number of soil bacteria present compared to the control column. This will show whether the total microorganism population has increased and if the population has adapted to become more proficient at dehalogenation than at the start.

In addition to the column tests, a series of batch experiments will be conducted to determine the kinetics with respect to hydrogen partial pressure and to evaluate the time required to convert the sediments to reducing conditions. These experiments will compare the Rader unexposed sediment with a sediment from a site with previous exposure to chlorinated hydrocarbons to determine whether adaptation of the microbial community is important for this technology.

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