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**EM14 - Bubbleless Gas Transfer Technology for the In Situ
Remediation of Chlorinated Hydrocarbons**

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EM14 – BUBBLELESS GAS TRANSFER TECHNOLOGY FOR THE IN SITU REMEDATION 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 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

3.1 Analytical Methods

3.1.1 Aquifer Simulators

Samples for analysis of chlorinated aliphatic hydrocarbons (CAH) are withdrawn from a septum on each aquifer simulator with a syringe. This aliquot is injected into a small vial containing the internal standard, methyl *tertiary*-butylether (MTBE). The contents of this vial are mixed, and a sample is withdrawn from it using solid-phase microextractors (SPME) and injected into the gas chromatograph. The gas chromatography is performed using an HP 5890 with a 100-m $\times$ 0.25-mm Petrocol DH column (0.5- μ m phase thickness). The carrier gas is hydrogen at 1.0 mL/min, measured at 330°C. Split injections are used, and the detector is flame ionization (FID). The oven temperature was 35°C at the injector; Rate A was 5°C/min to 160°C;

and Rate B was 50°C/min to 300°C. The total run time was 29 minutes. This method has allowed for separation and a determination of the concentrations of PCE, TCE, cis-dichloroethylene (cis-DCE), trans-dichloroethylene (trans-DCE), and vinyl chloride (VC).

3.1.2 Batch Samples

Batch experiments are performed in borosilicate serum bottles sealed with Teflon Miniert® valves. For analysis, an aliquot is withdrawn from the appropriate bottle with a syringe and injected into a 2-mL vial containing the internal standard MTBE. Analysis is done with SPME and gas chromatography, as described above.

3.1.3 Precision and Accuracy

A solution containing 75 mg/L of PCE was prepared and injected into the gas chromatograph five times in the same manner as used for other analysis. The results of this showed a mean PCE concentration to be 73.4 mg/L, with a standard deviation of 3.2 mg/L.

3.2 Sediment Characterization

The sediment selected for these experiments was chosen to represent a high conductivity aquifer. It is a sandy loam from Rader, North Dakota, a pristine aquifer located approximately 20 miles southeast of Grand Forks, North Dakota. This deposit is a deltaic aquifer located at the western edge of the Red River Valley, near the beachline of the former glacial Lake Agassiz. The sediment is a medium, subrounded, well-sorted sand containing a low clay content and low organic matter. There is no evidence for calcareous minerals. Approximately 70% of the sediment is composed of quartz, about 25% a mixture of quartz and feldspar, and the remainder a mixture of shale, hornblende, and miscellaneous minerals.

3.3 Sediment Sorption

Sediment sorption studies were initiated to determine the quantity of PCE that would be sorbed to the sediment in the aquifer simulators. These experiments were conducted in borosilicate glass bottles, sealed with Teflon Miniert® valves. Each 160-mL bottle contained 100 mL of distilled/deionized water containing 125 mg/L of PCE. Rader sediment was added at doses of 0, 5, 10, 15, 20, and 25 g. The mixtures were allowed to mix for 24 hours on stir plates. Then the bottle was centrifuged at 1000 rpm for 4 minutes to pelletize the sediment, then 1 mL was withdrawn and added to a vial containing the internal standard. Analysis of PCE was performed as described above.

Preliminary sorption data are shown in Figure 1. These data show that sorption of PCE to this sediment is low. Additionally, the data do not show the expected increase in sorption of PCE at the higher sediment loads. Further experiments will be performed to verify these data.

Figure 1. Preliminary sorption data.

4.0 FUTURE WORK

The aquifer simulation columns were saturated by pumping the simulated groundwater, distilled/deionized water with 1 g/L of NaHCO_3 , saturated with PCE through the two columns in a once-through mode. After the columns were saturated, they were plumbed into the separate closed loops. The closed loops were maintained and monitored for PCE for about 2 weeks, to allow the contents to be well mixed with respect to PCE. At that time, hydrogen gas was introduced into one of the columns. Hydrogen was added by injecting the gas via syringe into the sampling port through the Teflon-faced septum. The hydrogen would flow into the headspace of the pump reservoir where it would dissolve and circulate through the column sediment. At this time, the PCE concentrations in the two columns are maintaining at around 85 to 90 mg/L. The biota in the columns is presumably adapting to the use of hydrogen. Additional monitoring, along with the batch studies of hydrogen partial pressure, will be needed to show the effects of added hydrogen.