

DIRECT HYDROGEN ADDITION FOR THE IN-SITU BIODEGRADATION OF CHLORINATED SOLVENTS

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Abstract

As a result of their widespread use as solvents, degreasers, and dry cleaning agents, chlorinated aliphatic hydrocarbons (PCE, TCE, DCE, etc.) represent one of the most common and most persistent groups of contaminants found in groundwater. Characteristically, these compounds exist in the form of DNAPLs in the subsurface making efforts at remediation particularly difficult.

In-situ bioremediation via *direct hydrogen addition* has the potential to become a simple and low-cost treatment approach for sites contaminated with chlorinated solvent compounds (PCE, TCE, etc.). Based on the results of recent research, the role of hydrogen as an electron donor is now widely recognized as the key factor governing the dechlorination of chlorinated compounds (Holliger et al., 1993; DiStefano et al., 1992; Maymo-Gatell et al., 1995; Gossett and Zinder, 1996; Smatlak et al., 1996; Hughes, Newell, and Fisher, 1997). Because of hydrogen's low cost, its ability to be delivered safely and inexpensively in a variety of ways, and its ability to promote rapid dechlorination, direct hydrogen addition represents a potentially superior approach for managing and remediating chlorinated solvent plumes.

Recent laboratory column studies sponsored by Groundwater Services, Inc. (GSI) and conducted by Dr. Joseph Hughes at Rice University show the potential for directly adding hydrogen, as an electron donor, to aid in the microbially mediated reduction of chlorinated compounds. In Hughes' laboratory system, hydrogen has been shown to support the transformation of PCE to reduced end products. This work has led to the development of a patent for the process of in-situ biodegradation of chlorinated aliphatic hydrocarbons by subsurface hydrogen injection (U.S. Patent No. 5602296; Hughes, Newell, and Fisher, 1997). This process involves the subsurface delivery of dissolved hydrogen using: i) low-flowrate sparge wells, ii) introduction of hydrogen releasing compounds, iii) operation of closed-cycle circulation cells, iv) placing hydrogen-generating electrodes in the subsurface, or v) a number of other methods.

Introduction

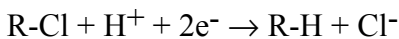
As a result of their widespread use as solvents, degreasers, and dry cleaning agents, chlorinated aliphatic hydrocarbons (PCE, TCE, DCE, etc.) represent one of the most common and most persistent groups of contaminants found in groundwater. While generally regarded as recalcitrant, chlorinated hydrocarbons are known to undergo natural dechlorination in the field (Gossett and Zinder, 1996; Wiedemeier et al., in press). Typically, the rate of natural dechlorination is severely limited by the lack of adequate electron donor quantities. At sites where natural dechlorination is occurring, organic substrates such as aromatic hydrocarbons (BTEX), landfill leachate, or other non-chlorinated organics undergo slow fermentation and produce dissolved hydrogen. The hydrogen is then rapidly utilized as an electron donor by naturally-occurring bacteria to achieve reductive dechlorination of chlorinated compounds in the subsurface. In-situ bioremediation via direct hydrogen addition represents an extension of these naturally-occurring processes. Direct hydrogen addition simply eliminates the rate-limiting step (i.e., slow fermentation) and provides the naturally-occurring dechlorinating bacteria with substantive quantities of the key growth substrate: hydrogen.

The advantages of the hydrogen delivery process are summarized below:

- *Direct hydrogen addition is an extension of naturally-occurring processes occurring at thousands of chlorinated solvent sites across the county (Wilson, 1997). This greatly increases the likelihood of success.*
- *Hydrogen addition provides highly favorable stoichiometry and can tolerate process inefficiencies.*
- *Hydrogen addition will lead to an increase in the efficiency of dechlorination over time.*
- *Hydrogen is a very inexpensive method of chlorinated solvent remediation.*
- *Hydrogen is a commonly used industrial gas and can be used safely for remediation.*
- *Hydrogen does not leave any environmentally harmful residue in the subsurface and does not require any surface treatment system.*
- *Direct hydrogen addition is a much simpler and more flexible process than other treatment approaches for chlorinated solvents (e.g., pump-and-treat, surfactant addition, etc.).*

Biodegradation of Chlorinated Organic Compounds

Generally, organic compounds represent potential *electron donors* to support microbial metabolism (e.g., the oxidation of BTEX compounds). However, halogenated compounds such as chlorinated solvents can act as *electron acceptors* and thus become reduced in the reductive dehalogenation process. Specifically, dehalogenation by reduction is the replacement of a halogen such as chloride, bromide, or fluoride on an organic molecule by hydrogen as described by the following half-reaction:



Reductive dechlorination requires a source of reducing equivalents to drive the reaction, but many contaminated sites are deficient in suitable electron donors (e.g., hydrogen). In anaerobic cultures, individual microbial species are often capable of growth on only one or two primary electron donors. Therefore, the selection of a primary electron donor should be based on the growth requirements of bacteria best suited for chlorinated aliphatic degradation. Most laboratory research concerning the anaerobic degradation of chlorinated aliphatic compounds has focused on methanogenic systems. Such systems typically involve the introduction of an electron donor such as acetate, lactate, methanol, ethanol, or even a co-contaminant such as toluene, to stimulate methane producing bacteria. While chlorinated aliphatic compounds have been observed to be degraded in a variety of such laboratory systems (Bouwer and McCarty, 1983; Vogel and McCarty, 1985; Bouwer and Wright, 1988; Freedman and Gossett, 1989; Sewell and Gibson, 1991), more recent work indicates that the methanol and other substrates used in these systems merely serve as precursors for the formation of an intermediate hydrogen pool through fermentation, and that it is hydrogen that serves as the electron donor for dechlorination (DiStefano et al., 1992; deBruin et al., 1992; Holliger et al., 1993; Hughes, 1994).

Based on the work of these and other researchers (Maymo-Gatell et al., 1995; Gossett and Zinder, 1996; Smatlak et al., 1996; Hughes and Schmidt, in press), the role of hydrogen as an electron donor is now widely recognized as the key factor governing the biologically mediated dechlorination of chlorinated compounds in anaerobic systems.

Biological Competition for Hydrogen

Because hydrogen is an ideal electron donor for anaerobic bacteria, dechlorinating microorganisms compete for dissolved hydrogen with other bacteria in the subsurface (e.g., methanogens, sulfate reducers, nitrate reducers). However, both laboratory studies and kinetic models (Fennell et al., 1997; Hughes and Schmidt, in press; Ji et al., 1997) substantiate the belief that the populations of dechlorinating microorganisms in natural systems will be successful at competing for hydrogen in a hydrogen-rich environment (i.e., concentrations above nano-molar concentrations observed in natural plumes, where hydrogen is being generated only by fermentation). This result can be attributed to the dechlorinators having: i) a higher maximum utilization rate (the ability to use high concentrations of hydrogen); and ii) a higher yield (the ability to reproduce from a given amount of hydrogen). This means that in a hydrogen-rich environment, the population of dechlorinators will increase over time, making bioremediation more efficient over time.

Furthermore, because hydrogen can also be utilized as an electron donor by aerobic bacteria, hydrogen addition can be used to initiate dechlorination at sites which are not currently undergoing natural dechlorination due to the existence of aerobic conditions (i.e.,

1 mg hydrogen can effectively consume 8 mg oxygen, turning aerobic sites anaerobic and allowing dechlorinating microorganisms to grow).

Note that hydrogen-enhanced dechlorination is stoichiometrically favorable toward the use of hydrogen as a remediation agent. For every 1 mg of hydrogen utilized by dechlorinating bacteria, 21 mg of perchloroethene (PCE) are completely converted to ethene. (Comparatively, the aerobic degradation of benzene requires 3 mg of oxygen to biodegrade just 1 mg of benzene.) Based on this stoichiometry, a dissolved groundwater plume with 2 mg/L PCE can be completely degraded through the utilization of only 0.1 mg/L hydrogen, a concentration much lower than the solubility limit for hydrogen (~1.6 mg/L). This means that the hydrogen delivery system does not have to be 100% efficient at bringing the dissolved hydrogen concentration up to solubility, and the loss of some hydrogen to non-dechlorinating bacteria (e.g., methanogens) will not cause the technology to fail.

The hydrogen kinetic model, initially developed by the authors and extended by Ji and Rifai (Ji et al., 1997) includes reaction terms for dechlorination, denitrification, sulfate reduction, and methanogenesis using Monod kinetics, and biomass growth using yield expressions. Preliminary modeling results indicate that the dechlorinators are able to outcompete the sulfate reducers and methanogens at high hydrogen concentrations (i.e., > 0.1 mg/L). However, at very high nitrate concentrations, nitrate reducers will outcompete the dechlorinators and consume most of the hydrogen as long as nitrate is present. Consequently, at sites having high nitrate background nitrate concentrations, additional hydrogen will have to be delivered to the subsurface (e.g., more pore volumes for a water delivery system or more sparging points; see the discussion on delivery systems below) to satisfy the hydrogen demand of the nitrate reducers and reduce nitrate concentrations to a level where dechlorinators may successfully compete.

Delivery Methods

Two approaches have been identified for potential application of hydrogen based bioremediation to chlorinated solvents in the subsurface: 1) dissolved plume management and 2) reduction of NAPL source zones. Respective hydrogen delivery systems appropriate to these two approaches are described below.

Dissolved Plume Management

- *Low Pressure Biosparging.* Sparging is a remediation method wherein air (or other gas) is forced into a wellbore under sufficient pressure to form branching air channels in the groundwater. In a conventional air sparging system, air channels spread through the aquifer to: 1) strip volatile compounds from the dissolved phase and any NAPLs present along the path of the channels and 2) add oxygen to the groundwater to spur in-situ biodegradation processes. Unlike a typical air sparging

process, however, a hydrogen sparging system would not seek to volatilize constituents, but only to saturate the groundwater in the treatment zone with dissolved hydrogen to stimulate biodegradation (Figure 1). Accordingly, to minimize volatilization of constituents and the accumulation of hydrogen gas in the unsaturated zone, the gas pressures and delivery rates normally used in an air sparging system would be reduced.

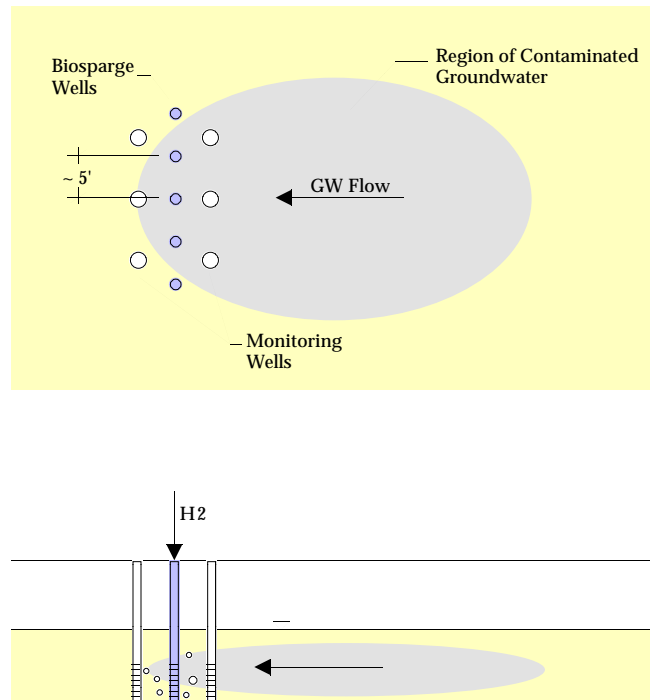
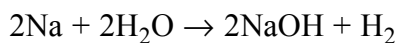
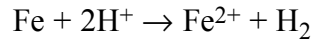


Figure 1. Conceptual Design for Hydrogen Delivery Via Low Pressure Biosparging.

- *In-Situ Controlled Release Reaction.* This method is based on the fact that some substances (such as metals or cations with positive standard potentials: sodium, potassium, lithium, calcium, magnesium, zinc, and iron) are capable of being oxidized in solution to release hydrogen. For example, sodium reacts as follows:



Only the most electropositive metals can release hydrogen directly from water at room temperature where the proton concentration is low. For less reactive metals such as iron or zinc, hot water or acidic solution is required to make the hydrogen generation reactions significant:



Conceptually, hydrogen delivery via an in-situ controlled release reaction would involve the placement of a hydrogen releasing cartridge within a well or borehole that would operate in a passive mode (Figure 2). When using metals, the cartridge would consist of metal filings mixed with a carrier matrix (e.g., sand) and contained within a permeable sack. Groundwater passing through the well would then contact the cartridge, causing the release of hydrogen. The rate of hydrogen release would be controlled by the pH of the groundwater in contact with the cartridge. This, in turn, could be controlled by the release of an acid solution within the same, or upgradient wells. When the ability of the cartridge to release hydrogen has been depleted, the cartridges may be removed and replaced with fresh units.

As an alternate method, any type of hydrogen releasing material could be mixed with sand or gravel and placed directly within a trench or excavation to intercept moving groundwater in a funnel-and-gate type application.

These types of delivery systems are best suited to plume management applications where the goal is to create a barrier to the growth of dissolved constituent plumes, but could also be applied to source reduction. The primary advantage of these types of systems is that they do not require the pumping or handling of groundwater.

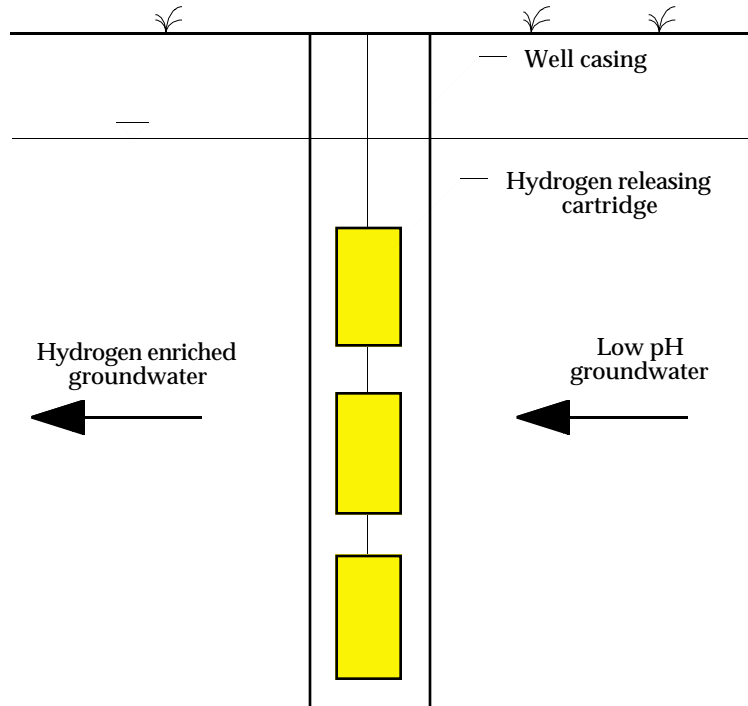


Figure 2. Concept of Hydrogen Releasing Cartridge.

Source Reduction

- *Dissolved Hydrogen Injection.* In this treatment method, groundwater is pumped from a location downgradient of the area to be treated and passed through an above-ground gas diffusion column where hydrogen is introduced into the flow stream. The hydrogen enriched groundwater is then reinjected into the subsurface at a location upgradient of the treatment region (Figure 3). A circular flow system is thus created wherein groundwater containing dissolved hydrogen is moved through the treatment zone stimulating biological activity throughout the zone. This type of delivery system is best suited to application at the source zone where the goal is to achieve source reduction through enhanced dissolution.

A dissolved hydrogen injection system could be configured as: 1) separate pumping and injection wells as described above, 2) a single well operated in an alternating push-pull mode, or 3) a dual zone well with continuous pumping and injection from separate zones in the same well for the purpose of creating a vertical circulation pattern.

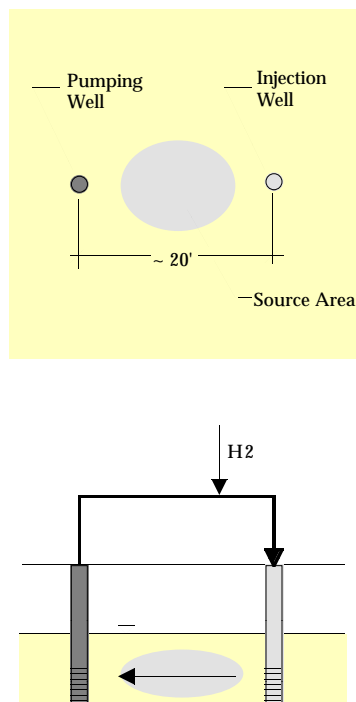


Figure 3. Conceptual Design for Hydrogen Delivery Via Dissolved Hydrogen Injection.

Current Work

A field test program to develop and evaluate the hydrogen addition technology is currently being funded by the Air Force Center for Environmental Excellence (Patrick Haas, Project Officer). The test program consists of short-term (2 day) treatability tests to be conducted at five sites and long term (1 year) pilot tests to be conducted at two sites. The tests will be conducted at Air Force installations in Florida, Georgia, and California.

The treatability tests are designed as site screening tests, and will evaluate hydrogen utilization by indigenous microorganisms via a field test method known as “push-pull.” This type of test has been described by Istok et al. (1997) for use in determining microbial activities related to degradation of petroleum hydrocarbons. The method, as adapted for the measurement of hydrogen utilization and dechlorination, consists of the following steps:

- 1) *Initial Groundwater Extraction:* Extraction of a known quantity of groundwater (e.g., 1000 L) from within the test area through an existing monitoring well.
- 2) *Amendment Addition:* Addition of known quantities of hydrogen and various volatile and non-volatile tracers (e.g., bromide, helium, sulfur-hexafluoride (SF₆)) to the extracted groundwater, followed by thorough mixing to create a homogeneous test solution.
- 3) *Initial Sampling:* Collection of a representative test solution sample which is analyzed for chlorinated organic compounds, hydrogen, tracers, and other constituents of interest (e.g., oxygen, nitrate, sulfate, etc.).
- 4) *Re-Injection of Groundwater Test Solution:* Pulse injection (“push”) of amended groundwater into the saturated zone through the same monitoring well used for groundwater extraction.
- 5) *Final Groundwater Extraction:* Extraction (“pull”) of the test solution/groundwater mixture from the test well following a contact/reaction period (typically 12 to 36 hr).
- 6) *Final Sampling:* Collection of a final representative test solution sample which is again analyzed for chlorinated organic compounds, hydrogen, tracers, and other constituents of interest.

During the injection phase, the test solution enters the test zone through the screened area of the monitoring well. Within the test zone, biologically reactive components of the test

solution (e.g., hydrogen and chlorinated organics) are utilized by the indigenous microorganisms. During the final extraction phase, the test solution is recovered and solute concentrations are measured to determine the quantities of reactants used (e.g., hydrogen, PCE, TCE) and/or products formed (e.g., DCE, chloroethane, vinyl chloride, ethene, ethane). The tracers are used to evaluate abiotic losses of reactants during the test process.

The year-long pilot tests, scheduled to begin in mid-1998, will consist of a two-well extraction/injection system similar to the dissolved hydrogen injection system described above. Hydrogen will be introduced into the groundwater flow stream in the form of micro-bubbles through stainless steel "frits." Hydrogen saturated groundwater will then be passed through the treatment zone by means of the injection well. Sampling will be conducted at periodic intervals to evaluate hydrogen utilization and dechlorinating activity.

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Biographical Information

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