BENCHMARK
ENVIRONMENTAL
ENGINEERING &
SCIENCE, PLLC

November 2, 2012

Eugene W. Melnyk, P.E.
Remediation Engineer
New York State Department of Environmental Conservation
Division of Environmental Remediation, Region 9
270 Michigan Avenue
Buffalo, New York 14203-2999

Re: 275 Franklin Street Site – BCP Site No. C915208
Buffalo, New York
Additional Interim Remedial Measures for Deep Groundwater Work Plan

Dear Mr. Melnyk:

On behalf of our client, Buffalo Development Corporation (BDC), Benchmark Environmental Engineering & Science, PLLC (Benchmark), has prepared this Additional Interim Remedial Measures (IRM) for Deep Groundwater Work Plan to outline the additional remedial work to address the residual chlorinated volatile organic compounds (cVOCs) in deep groundwater at the 275 Franklin Street Brownfield Cleanup Program (BCP) Site.

The NYSDEC previously approved the Additional IRM Work Plan dated September 30, 2011 (with certain modifications), which outlined the scope of work to treat dissolved cVOCs in shallow groundwater in the area of MW-5 and the down-gradient property boundary. We are proposing no modifications or deletions of any of those work elements that have previously been agreed.

Benchmark and BDC met with NYSDEC on October 19th, 2012 to discuss potential remedial alternatives to treat residual cVOC contamination in deep groundwater on-Site, including the use of hydrogen injection to further enhance to bioremediation of dissolved cVOCs. As discussed at the meeting, Benchmark maintains that the residual concentrations of cVOCs in on-Site deep groundwater are not considered significant, albeit in excess of groundwater quality standards, and are anticipated to continue to decrease and attenuate over time in conjunction with past and planned IRM measures. Nonethelesss, BDC has agreed to propose this additional deep groundwater IRM in a cooperative effort to secure Department approval of all the IRMs completed and proposed as the final remedy for the Site.

This work plan describes the planned in-situ treatment of deep groundwater employing direct injection of hydrogen gas using the iSOC® gas delivery system, a proprietary product of inVentures Technologies, Inc.

GENERAL TECHNOLOGY DISCUSSION

Hydrogen Addition

In-situ bioremediation using hydrogen has been successfully utilized since the early 1990s for remediation of sites contaminated with cVOCs (refer to "Direct Hydrogen Addition for the In-Situ Biodegradation of Chlorinated Solvents" in Attachment 1).

The in-situ groundwater bioremediation process relies on microorganisms (bacteria) that are stimulated by adding electron donors and changing prevailing redox conditions where necessary, leading to biologically mediated contaminant degradation in groundwater.

Highly oxidized chlorinated aliphatic hydrocarbons such as tetrachloroethene (PCE) are used as electron acceptors in the anaerobic process of biologically-mediated reductive dechlorination. During the anaerobic biological process, hydrogen substitutes for a chlorine ion on the PCE molecule forming trichloroethene (TCE), which can be further reduced to forms of dichloroethene (DCE), vinyl chloride (VC) and ethene.

iSOC® Technology

Delivery of hydrogen with the iSOC® System for enhanced cVOC bioremediation stimulated by the infusion of dissolved hydrogen is an effective technology to reduce dissolved cVOCs in groundwater. The efficient delivery of dissolved hydrogen into ground water is essential to insure that an abundance of hydrogen is available for the bioremediation process.

The iSOC® gas delivery system is based on inVentures Technologies, Inc. patented gas infusion technology - a method of infusing supersaturated levels of dissolved gas into liquids. iSOC® technology utilizes a proprietary structured polymer mass transfer device that is filled with micro-porous hollow fiber material that provides a high surface area for mass transfer - in excess of 7,000 m^2/m^3. It is hydrophobic and therefore excludes water. The system efficiently delivers gas to liquid by mass transfer without sparging.

iSOC® gas infusion units are constructed of high quality stainless steel and a proprietary structured polymer mass transfer device. iSOC® is 1.6 inches in diameter and 12.7 inches long with a compression fitting for 0.25-inch Teflon tubing. The housings for the pressure and flow control unit and the drain plug are made from nylon. iSOC® has a lifting ring for connecting to a suspension line for insertion in 2-inch or larger monitoring wells. The unit is connected to a regulated supply of compressed hydrogen.

In anaerobic bioremediation applications, the iSOC® supersaturates the treatment area with dissolved hydrogen, typically 2.0 to 4.0 milligrams per liter (mg/L) depending on the immersion depth of the iSOC® unit in groundwater. The iSOC® directly distributes hydrogen resulting in dissolved hydrogen-rich water that disperses and diffuses in all directions away from the treatment area and hydrogen is continuously infused into the aquifer over time. Therefore, a large and continuous supply of hydrogen is infused into the groundwater system to provide significant enhanced degradation of target cVOCs. Hydrogen is infused from the iSOC® into the treatment well at a typical rate of 28 standard cubic centimeters/minute.

DEEP GROUNDWATER IRM PROGRAM ELEMENTS

The planned approach is to use inVenture's iSOC® technology to introduce hydrogen into the deep saturated zone to enhance anaerobic reduction and microbial mineralization of residual cVOCs. The components of the system to be used are as follows:

- Installation of iSOC® units in MW-4 and MW-6, which are the wells with the highest residual cVOC concentrations of 126 micrograms per liter (ug/L) and 139 ug/L total cVOCs, respectively;
- Industrial grade hydrogen in cylinders installed within subgrade sumps, including a road box, adjacent to each of the wells;
- Low-flow hydrogen regulators; and,
- Polyurethane tubing connecting the hydrogen cylinders to the iSOC units.

Figure 1 shows the iSOC® hydrogen injection locations as well as the shallow groundwater treatment areas discussed in the September 2011 Additional IRM Work Plan. Figure 2 illustrates the iSOC® system schematic.

MONITORING REQUIREMENTS

Groundwater quality in MW-4 and MW-6 will be monitored at the same frequency and for the same parameters as the shallow groundwater monitoring wells (see Table 1), which includes the following:

- Field Parameters- temperature pH, specific conductance, ORP, and dissolved oxygen to confirm anaerobic subsurface conditions.
- Volatile Organic Compounds – To monitor for a reduction in PCE and to track the formation of PCE breakdown products indicating reducing conditions.
- Dissolved Gases – ethane, ethane and methane, which are end point products of abiotic degradation of cVOCs.

INSTALLATION SCHEDULE

The installation of the iSOC units will take approximately four to five days in the field to implement. The units will be installed following the shallow groundwater treatment program.

Please contact us if you have any questions or require additional information.

Sincerely,
Benchmark Environmental Engineering & Science, PLLC

Michael Lesakowski
Project Manager

Paul H. Werthman
Principal Engineer

Att.

C: Robert E. Knoer – The Knoer Group
File: 0156-001-400

FIGURES

F:\CAD\Benchmark\Buffalo Development Corp\275 Franklin Street Site\Additional IRM Work Plan\Figure 2; In-Situ GW Treatment Approach (rev OCT 30, 2012).dwg

LEGEND:

- BCP SITE
- EXISTING BUILDING
- PARCEL LINE
- FENCE
- PZ-1 — ON-SITE PIEZOMETER
- MW-5 — ON-SITE MONITORING WELL
- MW-21S / MW-21D — OFF-SITE MONITORING WELL
- MW-5 AREA IN-SITU GROUNDWATER TREATMENT
- DOWNGRADIENT IN-SITU GROUNDWATER TREATMENT AREA
- IRM TREATMENT AREA A (SHALLOW GROUNDWATER)
- IRM TREATMENT AREA B (SHALLOW GROUNDWATER)
- IRM TREATMENT AREA C (SHALLOW GROUNDWATER)
- MW-6 — IRM DEEP GROUNDWATER TREATMENT WELLS

DATE: OCTOBER 2012
DRAFTED BY: BCH

BENCHMARK ENVIRONMENTAL ENGINEERING & SCIENCE, PLLC
2558 HAMBURG TURNPIKE
SUITE 300
BUFFALO, NY 14218
(716) 856-0599

JOB NO.: 0156-001-102

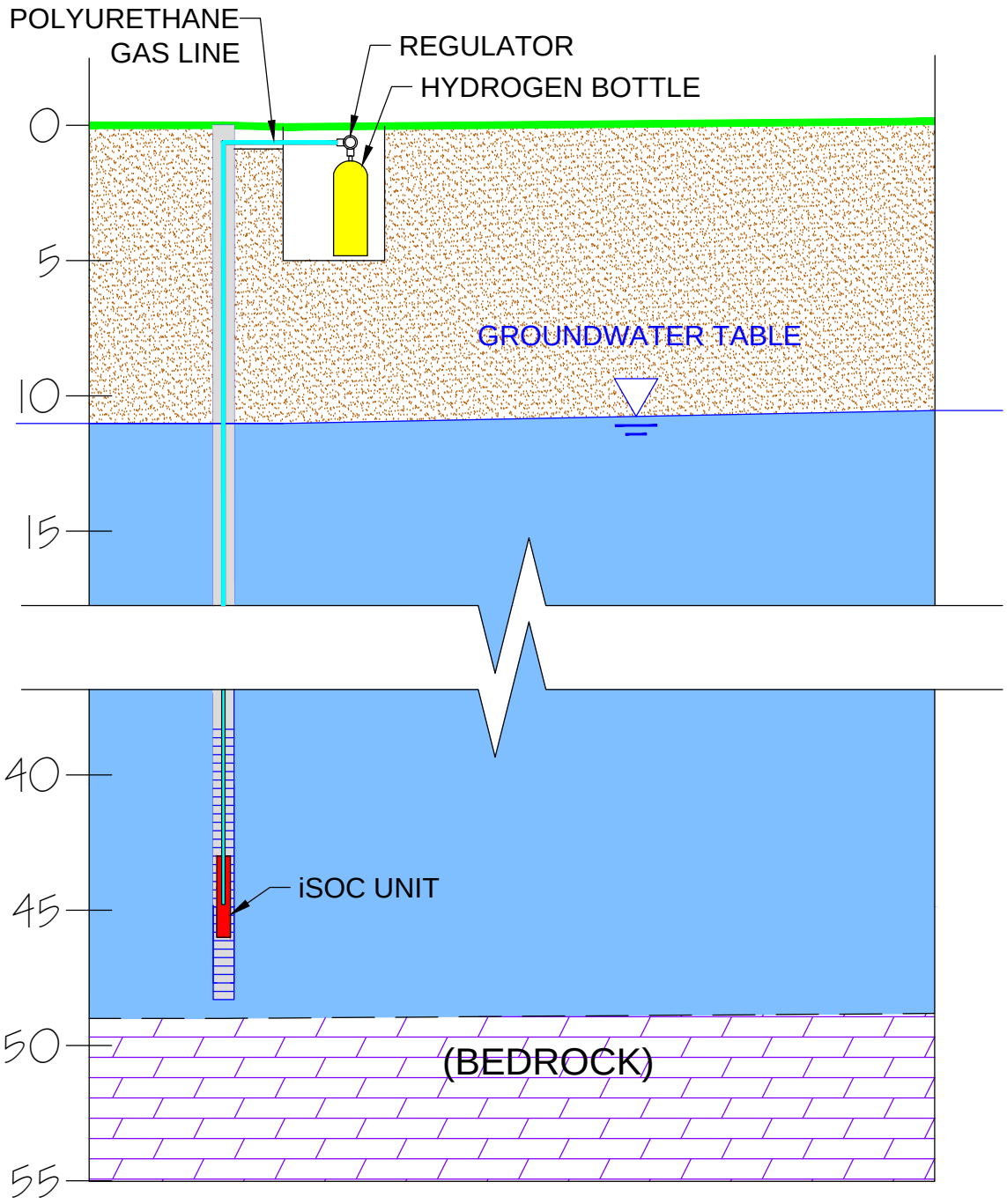
REVISED IN-SITU GROUNDWATER TREATMENT APPROACH

ADDITIONAL IRM FOR DEEP GROUNDWATER WORK PLAN

275 FRANKLIN STREET SITE
BCP NO. C915208
BUFFALO, NEW YORK

PREPARED FOR
BUFFALO DEVELOPMENT CORPORATION

FIGURE 1



NOTE: NOT TO SCALE

BENCHMARK ENVIRONMENTAL ENGINEERING & SCIENCE, PLLC
2558 HAMBURG TURNPIKE
SUITE 300
BUFFALO, NY 14218
(716) 856-0599

PROJECT NO.: 0256-001-102

DATE: OCTOBER 2012

DRAFTED BY: JGT

SYSTEM DESIGN

ADDITIONAL IRM FOR DEEP GROUNDWATER WORK PLAN

275 FRANKLIN STREET SITE
BCP NO. C915208
BUFFALO, NEW YORK

PREPARED FOR

BUFFALO DEVELOPMENT CORPORATION

TABLES

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TABLE 1

GROUNDWATER MONITORING PROGRAM

ADDITIONAL IRM FOR DEEP GROUNDWATER WORK PLAN

275 Franklin Street Site
Buffalo, New York

Sample Location	Field Measurements						CVOCs	Dissolved Gases		
	pH	Temperature	Specific Conductance	Oxidation-Reduction Potential	Dissolved Oxygen	Water Level	TCL VOCs Method 8260B	Ethene	Ethane	Methane
Post-Installation Monitoring										
MW-4	x	x	x	x	x	x	x	x	x	x
MW-6	x	x	x	x	x	x	x	x	x	x

ATTACHMENT 1

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

BENCHMARK

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

Charles J. Newell, Ph.D., P.E.
Groundwater Services, Inc.,
Houston, Texas

R. Todd Fisher, P.E.
Groundwater Services, Inc.,
Houston, Texas

Joseph Hughes, Ph.D.
Dept. of Environmental Science and Engineering
Rice University, Houston, Texas

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.

Presented at the NGWA Petroleum Hydrocarbons Confernce, Houston, Texas, Nov., 1997

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:

$$R\text{-}Cl + H^+ + 2e^- \rightarrow R\text{-}H + Cl^-$$

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.

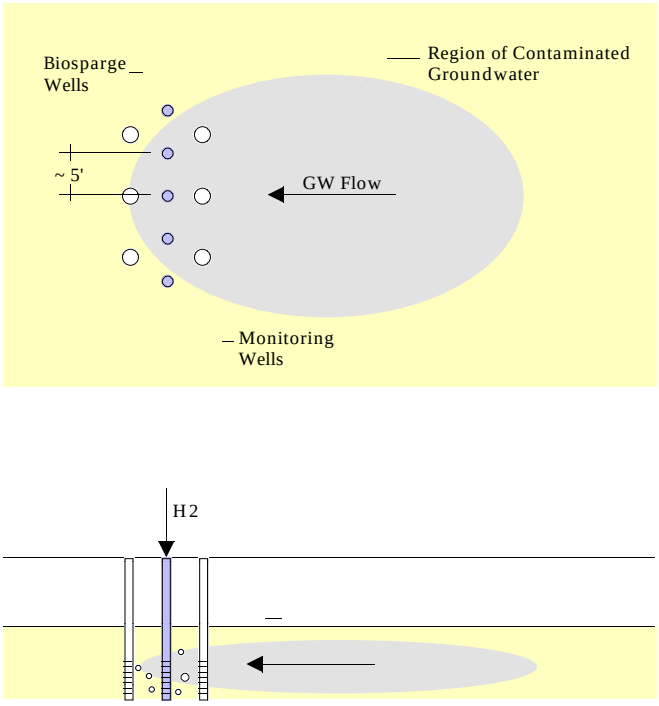

Figure 1. Conceptual Design for Hydrogen Delivery Via Low Pressure Biosparging.

- *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:

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

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:

$$Fe + 2H^{+} \rightarrow Fe^{2+} + H_2$$

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.

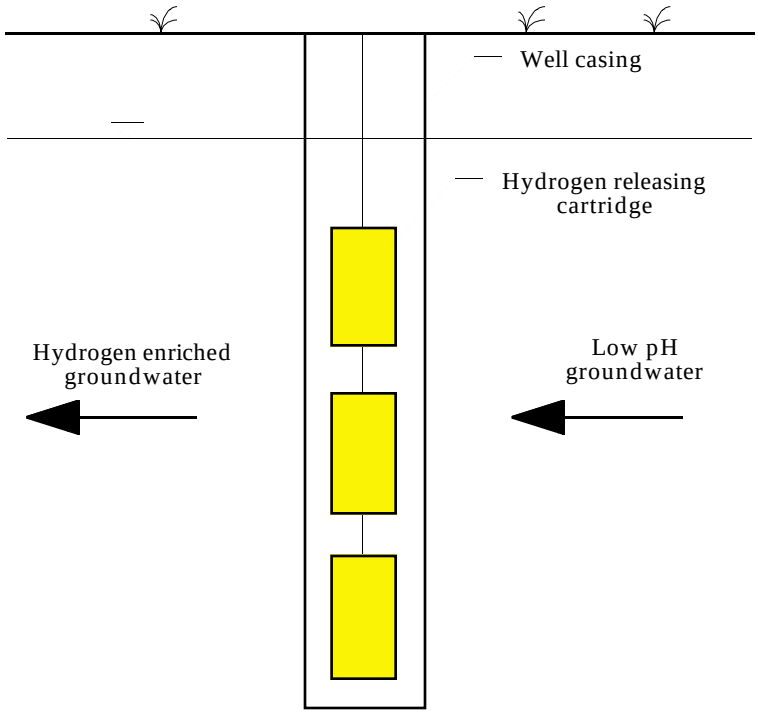

Figure 2. Concept of Hydrogen Releasing Cartridge.

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.

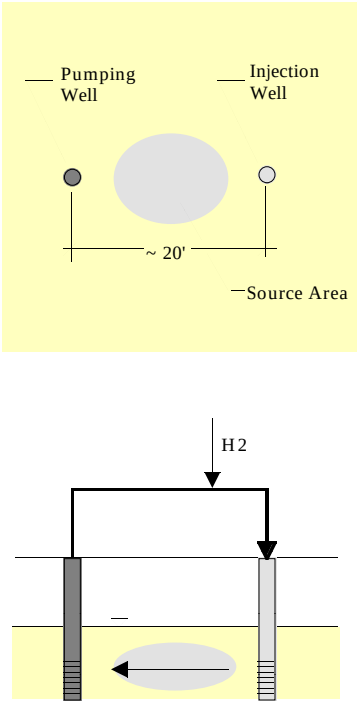

Figure 3. Conceptual Design for Hydrogen Delivery Via Dissolved Hydrogen Injection.

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 (SF_6)) 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

- **Charles J. Newell, Ph.D., P.E.:** Dr. Newell is Vice President and Environmental Engineer with GSI. He received a Ph.D. in Environmental Engineering from Rice University in 1989. Dr. Newell served on the U.S. EPA DNAPL Workshop in 1991 and has authored EPA fact sheets regarding NAPL investigation and remediation strategies. He is currently active in RBCA training and RBCA tool development and is the developer of the Air Force's BIOSCREEN Natural Attenuation Decision Support System. ***Groundwater Services, Inc., 2211 Norfolk, Suite 1000, Houston, Texas 77098 (713) 522-6300 Fax: (713) 522-8010, e-mail: cjnewell@gsi-net.com.***

- **Joseph B. Hughes, Ph.D.:** Dr. Hughes is an Assistant Professor of Environmental Science and Engineering at Rice University. Over the last several years, Dr. Hughes has conducted research on the cometabolic transformation of chlorinated aliphatic mixtures. He is currently investigating chlorinated ethene degradation in methanogenic and nitrifying cultures, and the development of multiple redox bioreactors. Dr. Hughes has successfully developed the first laboratory column in the U.S. for testing the biodegradation of chlorinated compounds in a hydrogen-fed system. *Dept. of Environmental Science and Engineering, Rice University, P.O. Box 1892, Houston, Texas 7725,.* ***(713) 285 5903 Fax: (713) 285 5203, e-mail: Hughes@rice.edu***

- **R. Todd Fisher, P.E.:** Mr. Fisher is an environmental engineer with GSI. He received a B.S. degree in Civil Engineering from the University of Colorado in 1988 and an M.S. degree in Environmental Engineering from Rice University in 1993. He has six years project experience in civil/environmental engineering including hydrogeologic investigations, surface water and groundwater modeling, hydrologic studies, stormwater management, risk-assessments, and the design of environmental remediation and civil infrastructure systems. ***Groundwater Services, Inc., 2211 Norfolk, Suite 1000, Houston, Texas 77098 (713) 522-6300 Fax: (713) 522-8010, e-mail: rtfisher@gsi-net.com.***