Transition Plan

1.0 Introduction

This section of the final report considers issues that are relevant in transitioning the membrane technology from the laboratory to the field. This transition plan is intended to define the design and construction approach for installing the first full-scale field application of the passive membrane barrier technology (PMBT). We have defined an "ideal" conceptual site for the initial application. The site parameters were chosen to fall within the range of conditions evaluated in laboratory and initial pilot-scale field work conducted to date. Actual sites will vary from this ideal. The site conditions are as follows.

- A dissolved PCE or TCE plume with concentrations up to 1 mg/L
- A cross-gradient plume width of 50-100 m
- An aquifer thickness of 7-12 m
- A depth to water of 3 m
- A total depth less than 25 m (the practical limit of direct push drilling technology)
- An unconfined aquifer comprised of sand with a hydraulic conductivity between 10^{-3} and 10^{-4} cm/sec, bounded below by an aquitard
- The documented presence of partial anaerobic biological degradation by-products
- A site in a secured area or in an active facility with available electrical service

2.0 Site Evaluation/Preliminary Design

2.1 Site Characterization

The level of detail in a Remedial Investigation conducted under USEPA guidance should provide a sufficient level of detail for evaluating a membrane-based remedial system. The level of site characterization is highly site specific. We expect that the technology would be evaluated in the feasibility study phase of a project along with other applicable technologies.

There are some specific areas of detail that will aid in evaluating and designing a membrane system, shown below.

- Detailed stratigraphy along alignment of system
- Hydraulic conductivity estimates along alignment of system
- Detailed plume concentrations horizontally and vertically along alignment of system
- Characterization of the redox states and active biological populations (*e.g.*, methane concentrations) up-gradient and down-gradient of the system

These data needs should be incorporated into the Remedial Investigation workplan or predesign work plan for a site. These data will aid in evaluating and comparing other permeable reactive barrier technologies as well.

2.2 Test for presence of microorganisms capable of bioremediation

It is first necessary to assess the suitability of H_2 as an electron donor for bioremediation at the site. One appropriate way to do this is to use the methods recommended by the USEPA for evaluating biological degradation as part of natural attenuation at a site (Reference). This method involves developing a numerical score based on the redox state within an aquifer, the level of dissolved oxygen, and the presence of degradation daughter products (*e.g.*, *cis*-DCE and VC). Ideally, the screening should show evidence of dechlorination to confirm that the proper conditions and organisms exist to sustain PCE and TCE degradation if stimulated by the addition of electron donor.

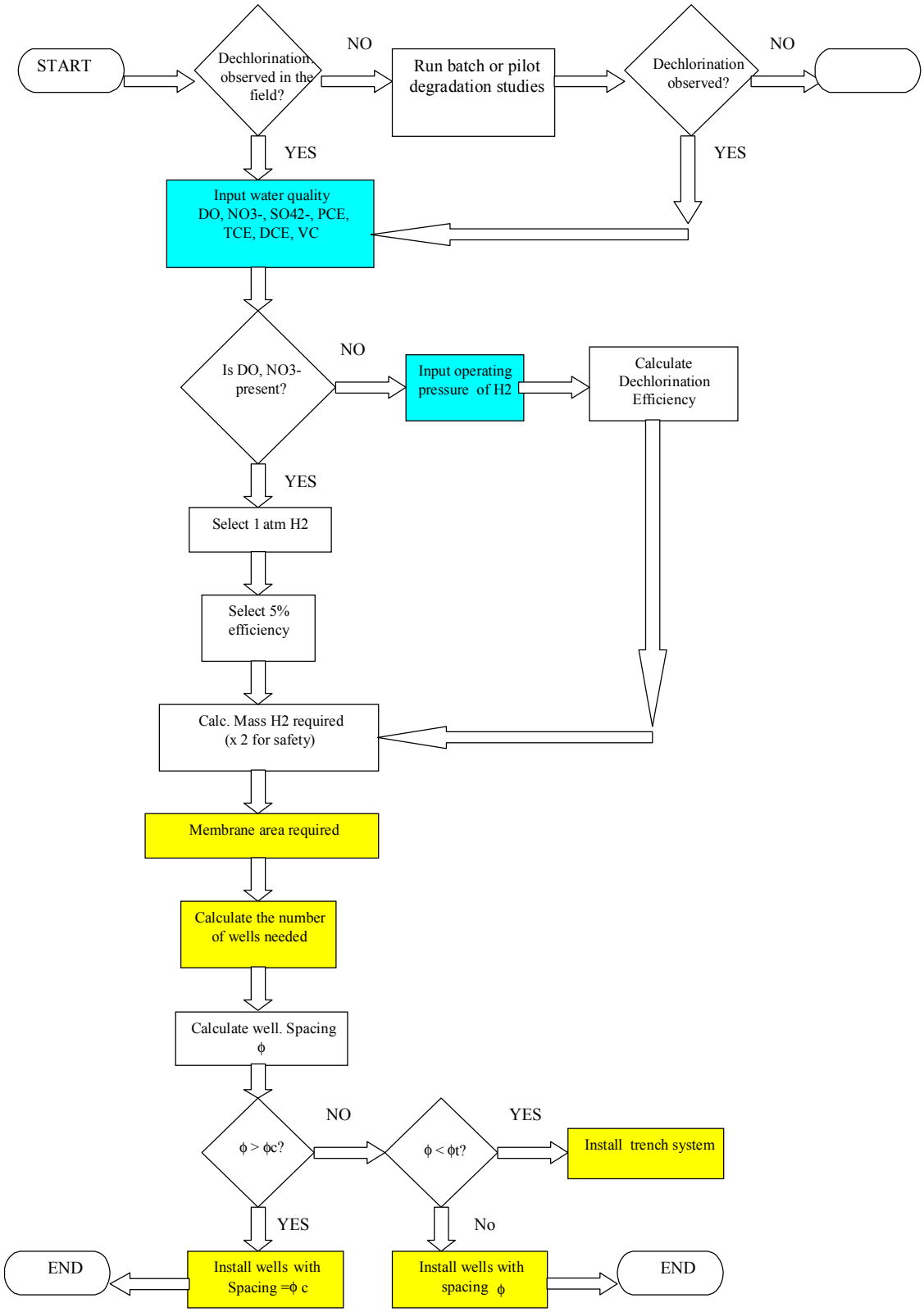
In the absence of this evidence, a laboratory microcosm study can be conducted on samples of the aquifer material to determine if PCE and TCE degradation will occur upon addition of H_2. The microcosm study requires aseptic collection of aquifer material from the site and incubating this material in the presence of contaminated groundwater, also from the site. Anaerobic conditions should be maintained throughout the experiment and microcosms should be prepared in triplicate to permit a statistical analysis of the results. The microcosms will be incubated under a headspace of N_2 (unfed control), 100% H_2, and 1% H_2. The two different H_2 concentrations will be tested because dechlorination has been observed to proceed more rapidly in aquifer material fed with a lower partial pressure of H_2 when the culture is unacclimated to high H_2 partial pressures (Muenzner et al., 2002). The rate and extent of dehalogenation will be determined by measuring the concentration of PCE or TCE and their daughter products as a function of time. If no dehalogenation is observed after a lag period of 4-6 weeks, it suggests that either the conditions at the site are inappropriate for supporting dechlorination or the microorganims required for PCE and TCE dechlorination are not present at the site. In this case, bioaugmentation of the aquifer material with a dehalogenating culture followed by H_2 addition could be tested in another round of experiments. The use of the PMBT technology should only be considered if there is evidence that the addition of H_2 will stimulate dechlorination by indigenous or added dehalogenating microorganisms.

2.3 Estimate Membrane Needs for Site

The total membrane surface area and the well spacing (ϕ) required for adequate treatment may be calculated by using simple an Excel spreadsheet program as illustrated in Exhibit A (Copies of this software are available from the principle investigators). The decision path followed to determine ϕ is illustrated in Figure 1. Inputs are marked in blue and output data are highlighted in yellow. The input parameters (hydraulic properties) should be selected to represent the aquifer at the desired barrier location. The range of input values appropriate to the site should be explored so that the most conservative option may be identified.

The amount of H_2 required for dechlorination is automatically calculated from the electron acceptor concentrations in the groundwater, based on stoichiometry. If oxygen and nitrate are present in high concentrations, they will exert a significant H_2 demand. This will need to be addressed before the H_2 requirements for dechlorination are considered. If oxygen and nitrate are initially present, operation at high H_2 partial pressures will likely be required to ensure sufficient H_2 is dissolved into the groundwater to achieve reducing conditions and contaminant

Figure 1. Flow Chart Showing the Algorithm Used in the Excel Spreadsheet to Calculate the Membrane Area and Installation Type



dehchlorination. If no oxygen and nitrate are present at the site then the system can be operated at a lower H_2 partial pressure to minimize wastage of H_2. The selection of operating pressures is discussed in detail in Clapp et al. (2003) (Appendix D).

Once the H_2 gas pressure is selected, the rate of H_2 dissolution is calculated for each well based upon the dimensionless mass transfer correlations developed by Fang et al. (2002). For a specific membrane module design (known number, length and diameter of membranes in the module), known groundwater temperature and groundwater velocity, the gas dissolution rate at each well can be determined.

The number of wells needed to supply the required mass of H_2 is then estimated in the spreadsheet by dividing the total H_2 requirement by the quantity contributed by each well. Knowing the width of the plume, the required well spacing (ϕ) is thus calculated. In a plume with varying concentrations across its width, separate iterations with the spreadsheet may be made to evaluate the well spacing for each zone of the plume. For example, one may choose to use closer well spacing in the center of a plume and a wider spacing toward the plume margins if PCE or TCE concentrations are higher, and therefore H_2 requirements are higher, along the center line.

Once the spacing between the wells, ϕ, is calculated, it must be compared with a critical spacing, ϕ_c. The critical spacing is estimated on the basis of groundwater flow and dispersivity to ensure that H_2 is delivered across the entire plume. This can be determined for a specific aquifer material using groundwater modeling software as shown by Agarwal et al. (2003). If ϕ is greater than ϕ_c, some of the flow between the wells may not receive H_2, leading to pinstriping of the plume. In this case the well spacing should be set to ϕ_c. If, however, ϕ is less than ϕ_c, the spacing for the wells should be set equal to ϕ. It is possible that for some plumes ϕ will be very small, requiring the installation of a great number of wells; in this case it may be less expensive to install a trench containing membrane fabric. To determine if this is the case, ϕ should be compared with ϕ_t, which is the critical well spacing at which the cost of well installation equals the cost of installing a trench. If the value of ϕ is greater than ϕ_t then the membrane well modules should be installed with a spacing of ϕ; if ϕ is less than ϕ_t, then a trench containing membrane fabric, rather than wells, should be installed.

3.0 System Design

3.1 Component Design

The major components for this technology are commercially available, except for the membrane modules. These components can be competitively bid and are discussed in the following subsections.

3.1.1 Membrane Modules

Most commercial membrane modules designed for gas transfer are designed for use in the industrial and medical markets. Industrial applications include oxygenation, pH control with carbon dioxide, and gas stripping. The principal medical application for membranes is blood oxygenation. These modules are designed for pumped flow and provide a very high specific

surface area for rapid gas transfer. They are not well-suited for application in a passive groundwater treatment application. As such, a fresh approach to membrane module design was required.

Membrane modules for groundwater treatment must satisfy the following objectives.

1. The membranes must be long enough to extend vertically through the depth of the contaminated water column
2. The membrane surface area must be large enough to transfer the desired loading rate of H_2 to the water flowing through the well with H_2
3. The membrane must be contained in a highly porous housing so that it does not impede water flow through the well
4. The membranes must be robust and durable so that they can be easily transported, handled, and installed in the field without being damaged
5. All components used in the membrane design must be corrosion-resistant under the redox conditions at the site
6. A non-rigid module design is desirable so that it can be easily transported and installed in the field regardless of module length
7. Membrane modules must fit within standard well sizes
8. Membrane modules must be equipped with flexible, corrosion-resistant wires that may be used to lower and retrieve the membrane modules from wells
9. Provisions must be made for the removal of condensate or the membrane units will fill with water and fail

There are two modes of operation, flow-through or dead-end. In a flow-through mode the gas flows in at one end of the membrane module and out the other end. A dead-end mode allows no gas to exit the module except for that which dissolves into the passing groundwater. Flow-through and dead-end membrane module designs are illustrated in Figures 2 and 3, respectively. Condensate removal in the dead-end mode of operation requires the installation of a hydrophilic microporous membrane at the base of the membrane module so that it is in communication with the gas phase at the sealed-end of the membranes. This section of membrane will automatically wet and allow condensate to pass out when the gas pressure exceeds the external water pressure. It will not, however, allow the gas to escape from the membrane (Semmens, 1991)
Both modes of operation have benefits. We contrast the merits of these modes of application below.

1. Flow-through mode
    a. The gas composition within the membrane can be controlled by manipulating the gas flow rate
    b. Inlet and exit gas flows must be regulated
    c. With good design, condensate may be blown out of the membrane module periodically
    d. This design can strip dissolved gases, such as N_2, from the well water
    e. More flexible operation than dead-end mode

Figure 2. Flow-Through Membrane Module Design

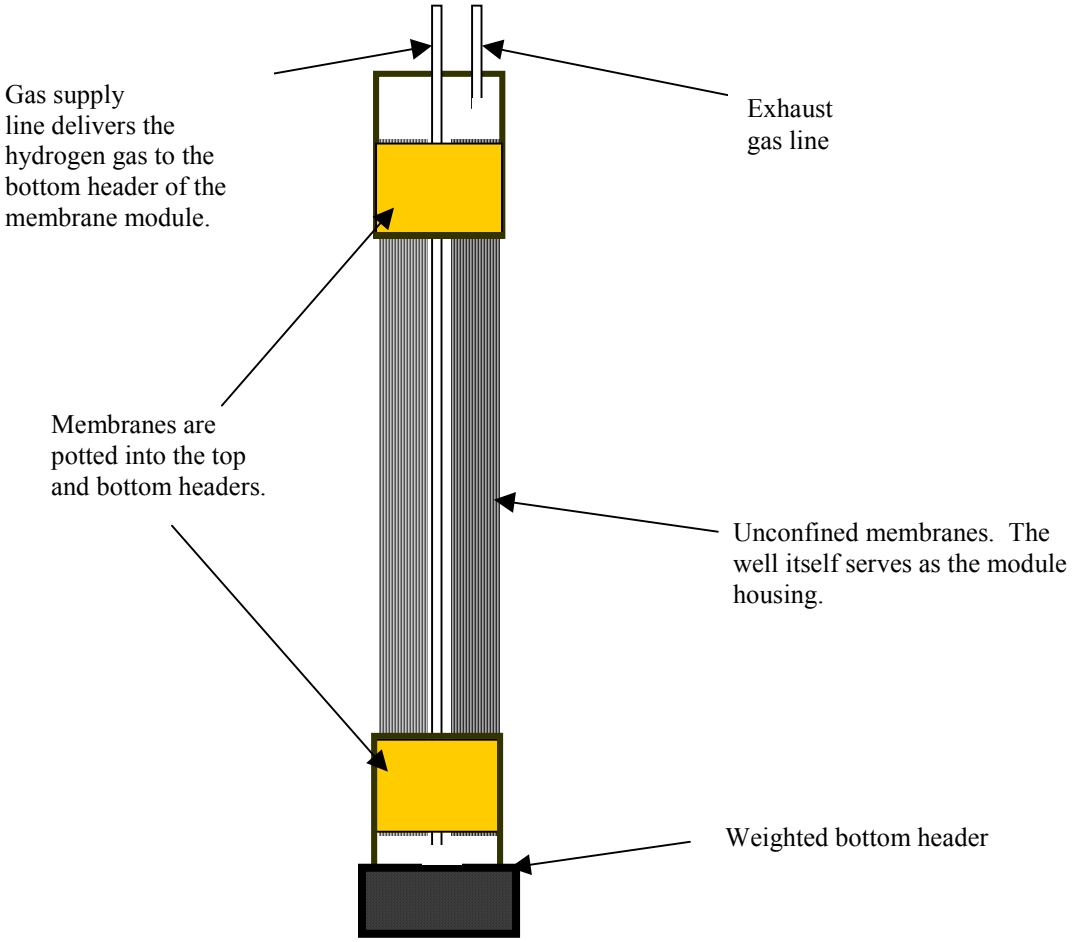
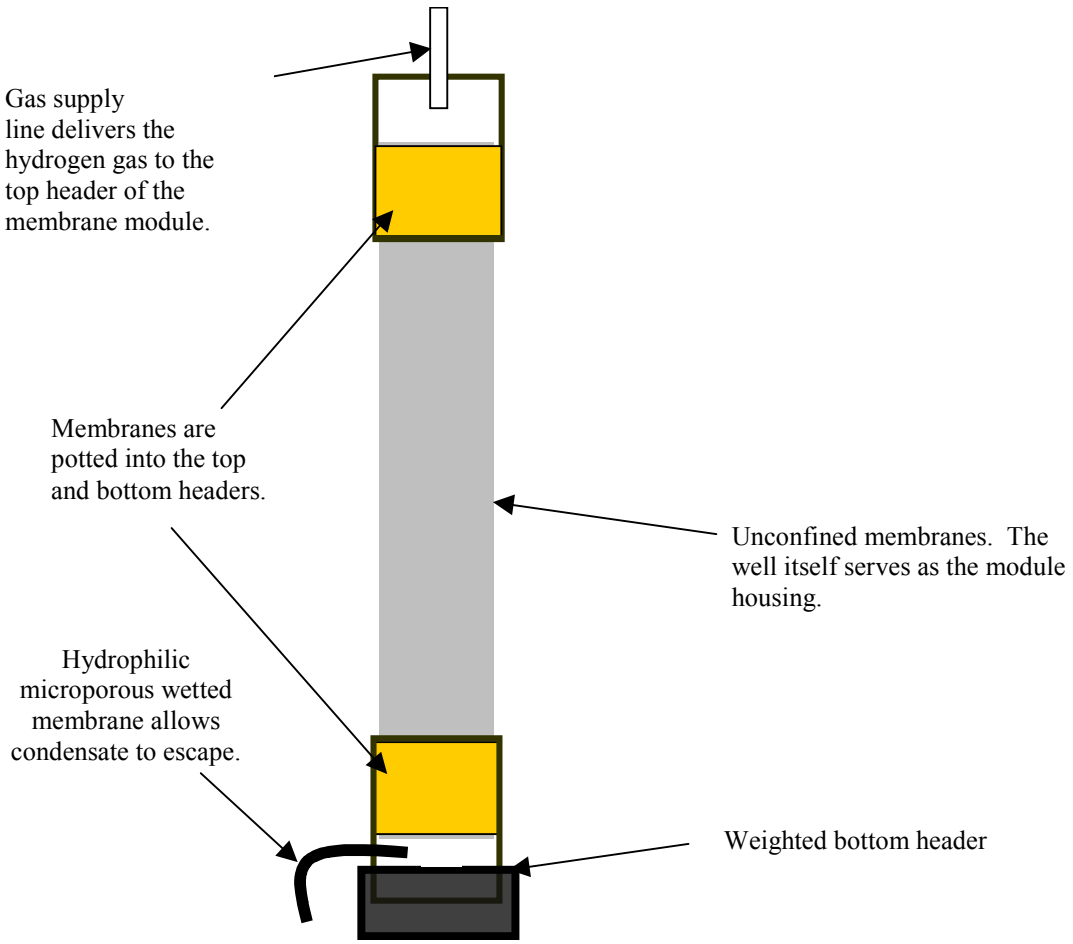


Figure 3. Dead-end Membrane Module Design Equipped with Hydrophilic Membrane to prevent condensate accumulation



2. Dead-end mode
    a. No gas exits the membrane module and any concern about the safety of such exhaust gas is eliminated
    b. 100% of the gas supplied to the module is transferred to the water
    c. The system is simple to operate because only the influent gas pressure must be selected; the influent gas flow rate automatically adjusts to equal the dissolution rate in the well
    d. This mode does not strip other dissolved gases from the water

The membrane modules manufactured in our laboratories for field application have worked well under warm weather conditions. We have experienced failures, however, during cold weather operation. These failures were caused by the freezing of condensate in the membrane fibers of flow-through modules. For this reason we favor the dead-end mode of operation in any climate where freezing is possible.

The membrane module designs and the design correlations we have developed in this study provide a solid basis for commercial module manufacture. Membrane module manufacturers such as Porous Media in St Paul, MN would be able to design and manufacture membrane modules for field applications in the future.

3.1.2 Well Construction

Standard small diameter well construction techniques are appropriate for installing the membrane barrier system. Recent developments in direct-push drilling technology allows for relatively quick and inexpensive installation of 1-inch or 2-inch diameter wells. PVC well screens and casing are appropriate for use in this application. The screen length should span the entire aquifer thickness, or the thickness of the plume in a stratified aquifer. Depending on the pre-existing site characterization data, soil sampling can be conducted at selected locations to confirm the aquifer thickness and to aid in selecting well screen size.

3.1.3 Groundwater Monitoring Wells

Monitoring wells can be installed using the same technology as the membrane module wells. The number and location of monitoring wells is dependent on the pre-existing well network and database. At a minimum, an up-gradient monitoring well and several down-gradient monitoring wells are needed. In a hypothetical case with a 100-m wide plume, monitoring wells placed every 20 m up-gradient and down-gradient of the PMBT would be appropriate for evaluating the system performance.

The membrane module wells can also be used as monitoring wells prior to the installation of the membrane modules. Due to the expected close spacing of the membrane module wells, if used for initial monitoring, a detailed plume cross section can be developed. From this plume cross section, specific locations for additional monitoring wells can be selected to address specific hot spots or other areas of concern. After the membrane modules are installed, the wells can be used for water level monitoring.

3.1.4 Controls

Controlling the H_2 delivery can be accomplished using available technology for handling low volume flammable gases (*e.g.*, control systems for natural gas). Instrument Control Systems Inc. (ICS) of Plymouth Minnesota prepared a discussion of control and instrumentation systems for a membrane-delivered H_2 remediation system. ICS identified configurations for either fixed pressure delivery or flow controlled delivery of the H_2. The architecture for either system is based on a modular programmable logic control (PLC) system. The modular PLC can be scaled up or down according the number of membrane wells needed. The control system and interface panel must be installed in weather-tight enclosures. Heat must be provided in winter conditions. Appropriate enclosures can be provided by the vendor. Power needs are standard 120 volt power with a 20 amp circuit. Exhibit B presents ICS' Proposal for a Control and Instrumentation System. discusses the design of the control systems using off the shelf components and provides a preliminary pricing for such a system.

3.1.5 H_2 Source

H_2 will be provided in standard commercial cylinders. These are readily available, cost effective, compatible with control systems, and can be delivered directly to the site. Handling H_2 cylinders is standard industrial practice and familiar to local fire departments and OSHA inspectors. Other alternatives such as on-site generation may be considered in future applications. The manifolding of tanks and the number of tanks required for a site will be designed to require tank replacement less than once a month.

3.1.6 Safety

The control system will include combustible gas metering at appropriate locations within the system to detect potentially explosive conditions resulting from H_2 leaks. The meters measure explosive gases as a percentage of the lower explosive limit (LEL) and report to the PLC. The system can be programmed to activate an automatic dialer and/or shut down the system when a prescribed percentage of the LEL is detected (typically 10% LEL). Because of the low pressure and volume of H_2 used, there is a low likelihood of explosion hazards developing. Also, because H_2 is less dense than air, H_2 will not collect in low areas such as sumps or subsurface enclosures.

3.2 System Layout

3.2.1 Dead-end Mode Membrane Modules

Passive membrane modules operating in dead-end mode may be supplied with gas from a common header. Headers must be designed to avoid significant headloss, such that all the wells receive gas at the same pressure. A single half-inch gas manifold may be used to supply up to 250 wells or may be used to supply gas over a distance of about 50 ft without a major loss in head. This approach is illustrated in Figure 4.

The gas pressure that should be supplied is determined by considering the back pressure required to prevent condensate accumulation within the membranes themselves. If the depth of the aquifer is H ft, then the pressure (P) required to expel condensate is (H/33*14.7 +1) psig. The gas supply design for this application is illustrated in Figure 5. The gas pressure should be set at P psig; the gas flow to the membrane modules will then adjust automatically to equal the dissolution rate.

Figure 4. Passive Membrane Modules Design Detail; Dead-End Module Array

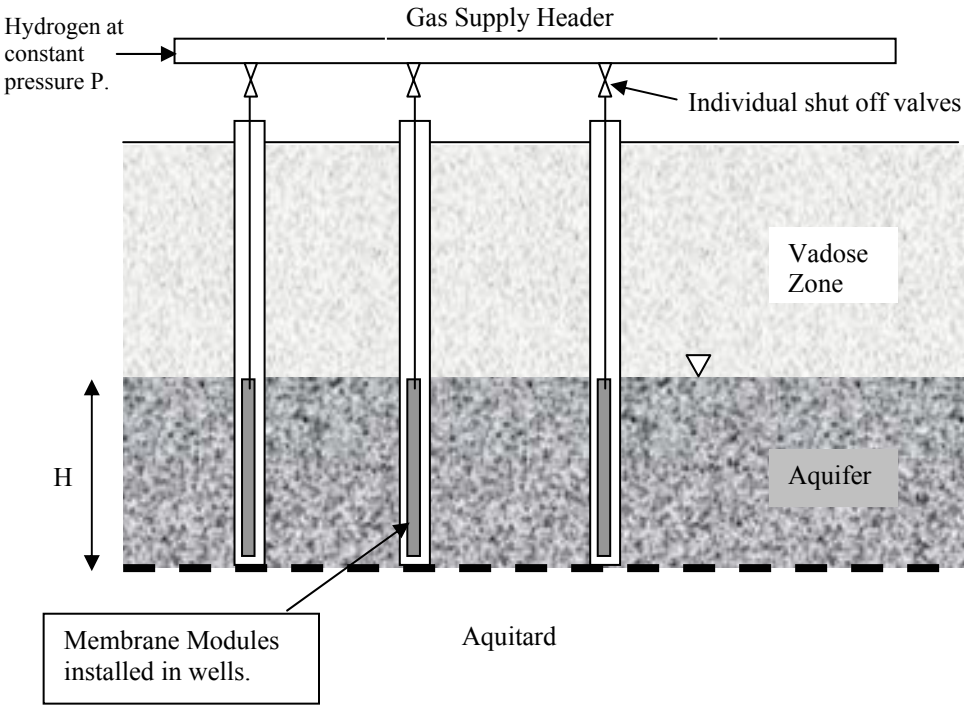
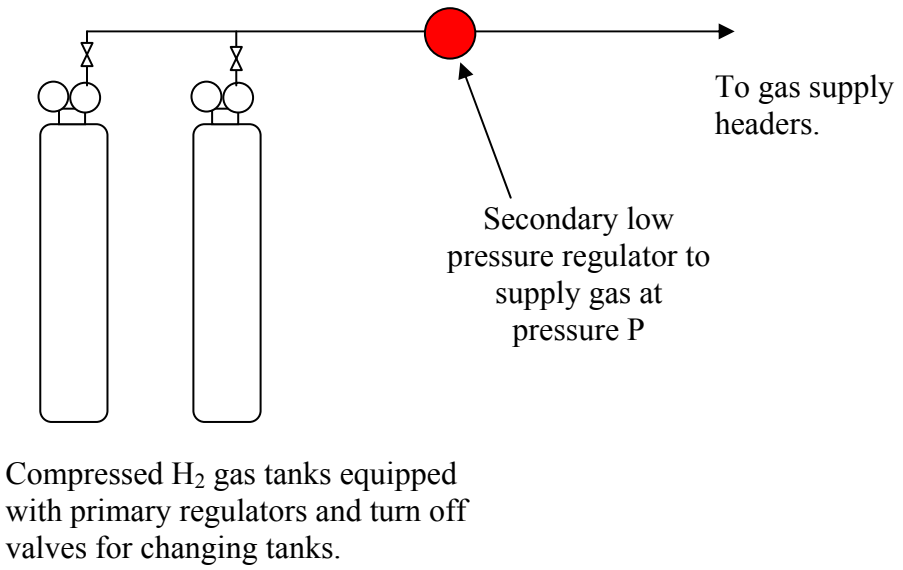


Figure 5. Gas Supply Configuration for Dead-End Mode of Operation; Constant Pressure



3.2.2 Flow-through Mode Membrane Modules

Membrane modules may also be operated in flow-through mode. In this case the flowrate of the gas to the modules must be regulated. A typical gas supply line equipped with flow control is illustrated in Figure 6. This configuration includes a secondary low pressure regulator that may be used in conjunction with a flowmeter to accurately set the gas flow to the membranes. In this case the membranes cannot be operated in parallel since the flow to each membrane cannot be easily controlled in such a configuration. Series operation (Figure 7) is therefore recommended, with the gas flowing from membrane to membrane. Unfortunately, if a large number of membrane modules was operated in series, a problem with any well on the supply line could result in problems throughout the whole line. For this reason we believe that 50 wells or fewer should be operated in series in a single line.

The issue of condensate freezing is extremely important, as mentioned above. It is therefore recommended that if operated in flow-through mode, the gas lines should be buried between wells or warmed (perhaps with heat tape) to prevent freezing in cold weather operation.

Pulsed operation with the flow through configuration is possible. A solenoid valve on the gas supply line can be controlled to turn on and off by a timer to create any desired pulsing strategy.

4.0 Monitoring and Evaluation

A monitoring plan for start up and operation of the system will be prepared in advance. The monitoring plan will address the groundwater monitoring locations, sample frequency, and the chemical parameters to be tested.

At least one round of background sampling is required to establish baseline conditions. Once the system is started, weekly monitoring should be conducted until the H_2 distribution around the PMBT stabilizes. Once the system stabilizes, the monitoring frequency can be reduced to monthly or quarterly.

Monitoring parameters will include:

VOCs (PCE, TCE, *cis*-DCE, VC and ethene)
Dissolved H_2
Dissolved oxygen
pH
The initial sampling should also include a suite of general water quality parameters (sulfate, nitrate, Fe, Mn, hardness, alkalinity, eH, pH). This should be repeated periodically to monitor changes in the water chemistry and redox conditions.

5.0 Cost Estimates

For comparing costs of a H_2 PMBT and competing passive remediation barrier (PRB) technologies we developed three typical PCE plume configurations and a set of initial geochemical conditions. Table 1 presents the three scenarios. Based on these scenarios we developed capital cost estimates for a H_2 PMBT and two competing technologies: a granular iron

Figure 6. Gas Supply Configuration for Flow-through Mode of Operation; Constant or pulsed gas flow to the modules

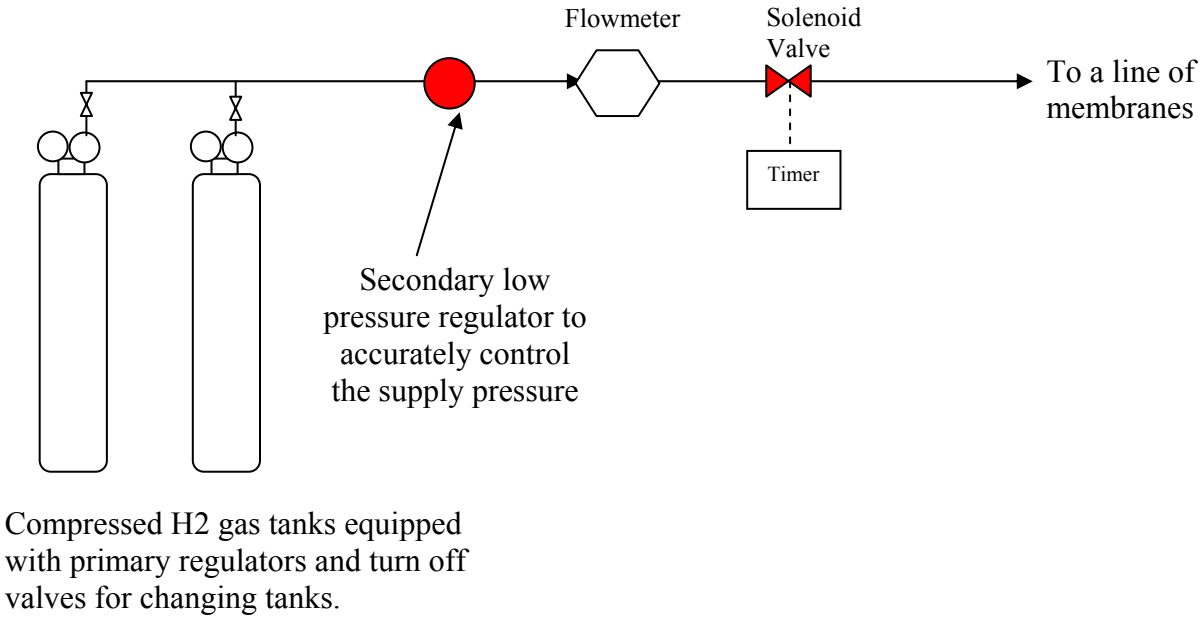
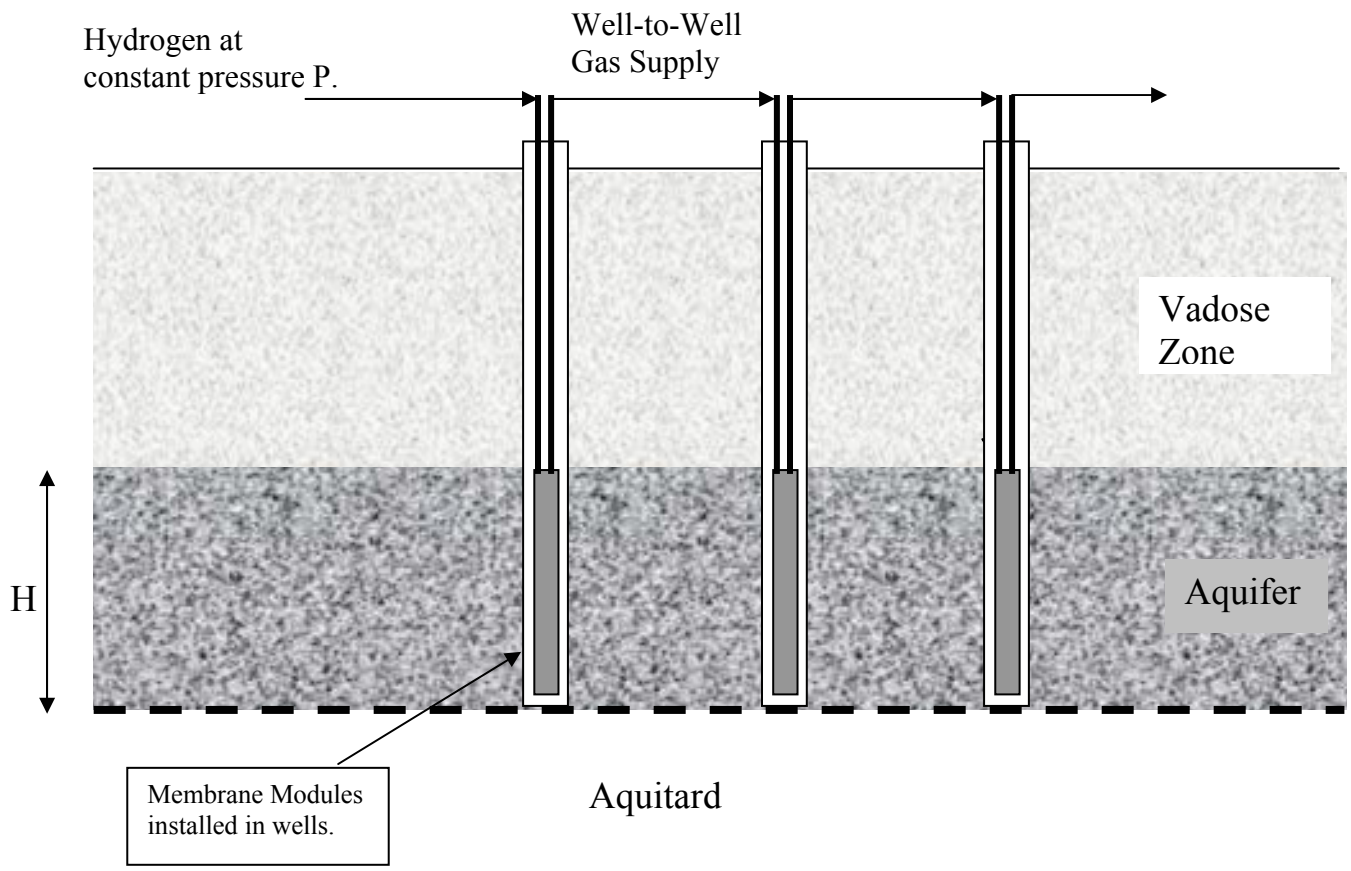


Figure 7. Passive Membrane Modules Design Detail; Flow-Through Module Array



permeable reactive barrier (iron PRB), developed and licensed by Envirometal Technolgies Inc. (www.eti.ca) and Hydrogen Release Compound (HRC), developed and licensed by Regenesis (www.regenesis.com).

These competing technologies are described on their respective company websites. Iron PRBs consist of a subsurface wall of granular iron placed across a contaminated zone, perpendicular to groundwater flow, to create a permeable reactive zone for the chemical dehalogenation of dissolved chlorinated solvents. HRC is a polylactate ester that slowly releases lactic acid when contacted with water. HRC is injected into an aquifer via closely spaced boreholes to create a permeable reactive zone *in situ*. The lactic acid ferments to form H_2, thereby supporting the biological degradation of chlorinated solvents.

To estimate the cost of an iron PRB, the three scenarios (Table 1) were sent to Envirometal Technology Inc. The detailed cost estimates generated by Envirometal Technologies Inc. is shown in Exhibit C

To estimate costs for an HRC PRB, the software provided by Regenesis on its website was used. The software calculates the volume and cost of raw HRC for a set of geochemical conditions and plume size. Installation costs were estimated from experience with direct push drilling and HRC installation at other sites.

The costs for an H_2 PMBT were developed using the Excel spreadsheet and shown in Exhibit A. The cost estimate for the required control systems was provided by ICS and an estimate for well installation was provided by Matrix Technologies Inc. (a drilling contractor). Cost for installing the system components was based on experience with similar systems (*e.g.*, air sparging systems).

Table 2 presents the comparison of capital costs for each system. These costs are budgetary in nature and do not include regulatory costs, consulting fees, or long term monitoring costs. These costs will likely be similar for each technology and will be site specific. The cost comparisons show that for generic scenarios, the capital cost for an H_2 PMBT is competitive with the alternatives.

6.0 Summary and Conclusions

PMBT implementation does not pose significant engineering challenges. Most of the components required for the safe delivery of H_2 gas to an aquifer are standard and commercially available. Furthermore, if a market exists, it should not be difficult to find a membrane company able to construct in-well membrane modules. The studies completed in this SERDP project provide the engineer with all of the information and design correlations needed for field design and installation.

When these design correlations are employed to estimate the costs of PMBT for an ideal site, it compares favorably with other PRB technologies. In addition, it is likely that the PMBT will have extremely low operating costs and the least impact on subsurface water quality. For these reasons we believe that the H_2 PMBT is worthy of field testing.

Table 1
Cost Comparision Scenarios
Ideal Site Characterization

	Depth to Water (m)	Plume Thickness (m)	Plume Width (m)
CASE 1	3	7	50
CASE 2	3	7	100
CASE 3	3	12	100

Site Geochemistry:

Ca	40 mg/L	Alkalinity	2.6 mg/L
Fe	1 mg/L	Diss. O2	0 mg/L
K	2 mg/L	TOC	0.7 mg/L
Mg	14 mg/L	DOC	0.7 mg/L
Mn	0.5 mg/L	TDS	310 mg/L
Na	35 mg/L	pH	8
Si	10 mg/L	Temperature	10 C
Cl	71 mg/L		
SO4	0.1 mg/L	Perchloroethene	1 mg/L
NO3	0 mg/L		

Site Hydrogeology

Hydraulic Conductivity:	0.01 cm/sec
Horizontal Gradient:	0.003
Porosity	0.3
Groundwater velocity	31.5 m/yr
Material	Silty Sand

Table 2
Capital Cost Comparision
Permeable Reactive Barrier (PRB) Technologies

	HRC		PMBT		Fe PRB	
Case 1						
	HRC material	21,432	Wells	69,700	Iron	57,000
	Installation	10,000	Modules	32,800	Construction	131,000
	Annual Total	31,432	Controls	35,000	License	28,000
	Total (x10 Applications)	**314,320**	Installation	50,000	Total	**216,000**
			Total	**187,500**		
Case 2						
	HRC material	42,252	Wells	139,400	Iron	113,000
	Installation	20,000	Modules	65,600	Construction	212,000
	Annual Total	62,252	Controls	40,000	License	49,000
	Total (x10 Applications)	**622,520**	Installation	75,000	Total	**374,000**
			Total	**320,000**		
Case 3						
	HRC material	72,462	Wells	188,600	Iron	197,000
	Installation	25,000	Modules	98,400	Construction	403,000
	Annual Total	97,462	Controls	40,000	License	90,000
	Total (x10 Applications)	**974,620**	Installation	75,000	Total	**690,000**
			Total	**402,000**		

Notes:
Case 1: Plume 50 m wide by 7 m thick
Case 2: Plume 100 m wide by 7 m thick
Case 3: Plume100 m wide by 7 m thick
All cases have the same geochemical conditions and 1 mg\L Perchloroethene
HRC cost based on online software at www.regenesis.com
Fe PRB cost based on estimated provided by Enviromental Technologies Inc.

EXHIBIT A
Estimating Membrane Needs Spreadsheet
Sheet 1 – Well Spacing Required

NOTE: User inputs in blue and developer inputs are in orange
Output data are highlighted in yellow.

Decision path for determining:

1.) whether a membrane-delivered H2 system may be advantageous at your site
2.) what membrane spacing is appropriate in a passive H2-addition system

1.) Do you have evidence of biological PCE and/or TCE degradation at the site (i.e. cis-DCE, VC, or ethene detection)?

YES Continue below.
NO Conduct microcosm studies.

Is dechlorination observed under anaerobic conditions in microcosm studies?

YES Continue below.
NO Use of H2 is inappropriate. Consider other remediation technologies.

2.) Input the following:

O2 concentration:	5	mg/L	Well diameter :	0.0508	m
NO3- concentration:	10	mg/L	radius of membrane fiber:	0.75	mm
SO42- concentration:	20	mg/L	membrane fibers per module:	50	
PCE concentration:	1	mg/L	membrane length:	10	m
TCE concentration:	0.5	mg/L	membrane area per module:	2.356194	m2
			groundwater temperature :	20	Degrees C
groundwater velocity:	0.5	m/day			
plume depth:	10	m			
plume width:	100	m			
average porosity:	0.3	%			
well diameter:	2	in			
Hydrogen pressure:	2	atm			

3.) If only TCE and PCE are present, the hydrogen required is

164.8 mol/day fraction H2 that goes to dechlorination vs. methane production: 0.05

4.) If O2 , NO3- and SO4- are present

276.4 mol/day fraction H2 that goes to dechlorination vs. methane production: 0.5

5.) The amount of hydrogen gas dissolved by each well will be 0.301 mol/day

The number of wells needed for this site is: 547

The required well spacing ϕ is = 0.18 m

EXHIBIT A
Estimating Membrane Needs Spreadsheet
Sheet 2 – Stoichiometric Calculations for Hydrogen Gas Required

Mass of H2 needed if alternative electron acceptors are present:

	mg/L	mol/L	H2 needed mol/L	Total H2 needed mol/L
O2 concentration:	5	1.56E-04	3.91E-04	1.84E-03
NO3- concentration:	10	1.61E-04	4.74E-04	
SO42- concentration:	20	2.08E-04	8.68E-04	
PCE concentration:	1	6.02E-06	3.77E-05	
TCE concentration:	0.5	3.80E-06	1.73E-05	

Note in the above analysis there is no accounting for methane formation.

Mass of H2 needed if no alternative electron acceptors are present:

	mg/L	mol/L	H2 needed mol/L	Total H2 needed mol/L
PCE concentration:	1	6.02E-06	3.77E-05	1.10E-03
TCE concentration:	0.5	3.80E-06	1.73E-05	

Fractional effectiveness of H2 added = 0.050000143

The fractional effectivenss of H2 is an exponential decay.
However, we have fixed the minimum effectiveness at 5% for this analysis.

References

Semmens, M.J., "A Bubbleless Gas Transfer Device and Process." Patent No. 5034164 Issued July 23, 1991