

DEEP REACTIVE BARRIERS FOR REMEDIATION OF VOCs AND HEAVY METALS

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ABSTRACT: Azimuth controlled vertical hydraulic fracturing technology has constructed full scale in situ iron reactive permeable barriers at moderate to significant depth for remediation of groundwater contaminated with chlorinated hydrocarbons and metals. Zero valent iron reactive permeable barriers have been installed to remediate chlorinated solvent contaminated groundwater by abiotic degradation of the halogenated volatile organic compounds into harmless daughter products. Alternatively iron and other reactive materials have been used for precipitation, sorption or reduction of various groundwater metal contaminants. The azimuth controlled vertical hydraulic fracturing technology has constructed iron reactive barriers up to nine (9) inches in thickness over hundreds of feet in length and down to depths greater than 120 feet. The injection procedure and gel mixture chemistry ensures the barrier is constructed of near uniform thickness, of high permeability and porosity, with minimal impact on groundwater flow regimes, with minimal site disturbance and optimal iron degradation potential.

INTRODUCTION

Zero valent metals abiotically degrade certain compounds; such as, pesticides as described by Sweeny and Fisher (1972), and halogenated compounds as detailed in Gillham and O'Hannesin (1994). The abiotic reduction of trichloroethene (TCE), tetrachloroethene (PCE), vinyl chloride (VC) and isomers of dichloroethene (DCE) by zero valent iron metal is shown on Figure 1, with ethene and ethane being the final carbon containing daughter compounds (Sivavec and Horney, 1995; Orth and Gillham, 1996). The prime degradation pathway of TCE in the presence of iron is via chloroacetylene and acetylene to ethene and ethane, and only a small proportion < 5% (Orth and Gillham, 1996; Sivavec et al, 1997) to the less chlorinated hydrocarbons. The volatile organic compounds (VOCs) degraded by zero valent iron are listed in Table 1. The abiotic degradation of most of these compounds in the presence of iron can be approximated by a first order reduction process.

Certain metals, such as hexavalent chromium are reduced and thus precipitate in the presence of iron; whereas other metals are directly precipitated or absorbed by the iron and thus rendered immobile. Metals that can be removed from the groundwater flow regime in the presence of iron, include Al, Sb, As, Cd, Cu, Cr(VI), Pb, Mg, Hg, Ni, Se, Tc-99, U, V and Zn. A number of workers have constructed iron reactive barriers for the removal of metals, e.g. Gu et al (1998), Morrison (1998), Naftz (1998), Puls (1998), Su and Puls (1998), and in some cases a combination of metals and VOCs, Schlicker et al (1998) and Puls (1998).

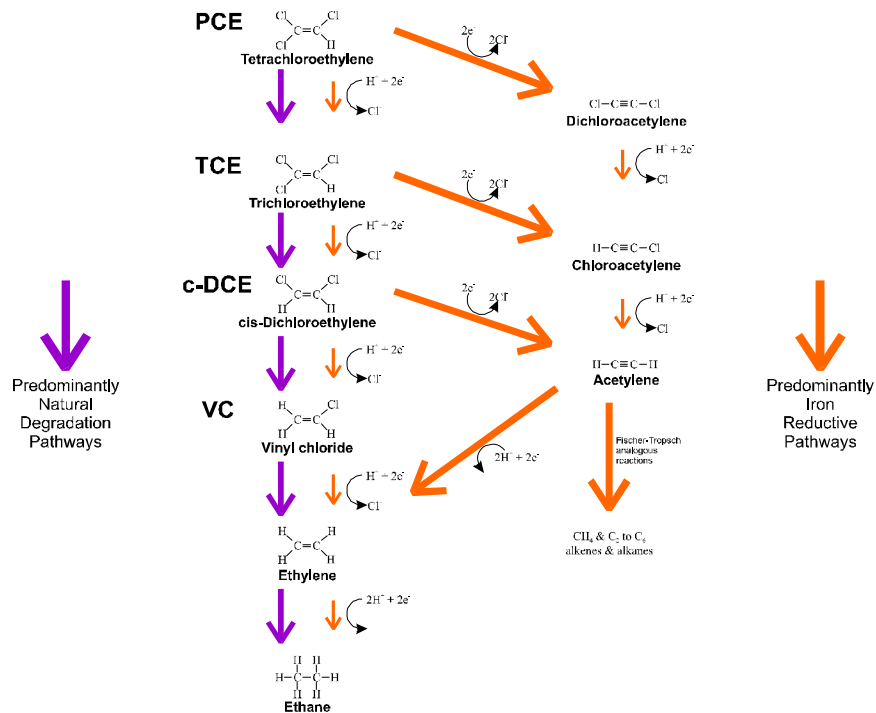


FIGURE 1. Degradation Pathways of Chloroethene Compounds.

TABLE 1. Chlorinated Compounds Abiotically Reduced by Iron.

Common Name	Common Abbreviation	Other Pseudonyms	CAS Number
Methanes			
Tetrachloromethane	CT, PCM	Carbon Tetrachloride	56-23-5
Trichloromethane	TCM	Chloroform	67-66-3
Tribromomethane	TBM	Bromoform	75-25-2
Ethanes			
Hexachloroethane	HCA	Carbon Hexachloride	67-72-1
1,1,1,2-Tetrachloroethane	1,1,1,2-TeCA		630-20-6
1,1,2,2-Tetrachloroethane	1,1,2,2-TeCA	Acetylene Tetrachloride	79-34-5
1,1,1-Trichloroethane	1,1,1-TCA	Methyl Chloroform	71-55-6
1,1,2-Trichloroethane	1,1,2-TCA	Vinyl Trichloride	79-00-5
1,1-Dichloroethane	1,1-DCA		75-34-3
Ethenes			
Tetrachloroethene	PCE	Perchloroethylene	127-18-4
Trichloroethene	TCE	Ethylene Trichloride	79-01-6
cis 1,2-Dichloroethene	cis 1,2-DCE	cis 1,2-Dichloroethylene	540-59-0
trans-1,2-Dichloroethene	trans 1,2-DCE		540-59-0
1,1-Dichloroethene	1,1-DCE	Vinylidene Chloride	75-35-4
Vinyl Chloride	VC	Chloroethene	75-01-4
Propanes			
1,2,3-Trichloropropane	1,2,3-TCP	Allyl Trichloride	96-18-4
1,2-Dichloropropane	1,2-DCP	Propylene Dichloride	78-87-5
Other Chlorinated			
N-Nitrosodimethylamine	NDMA	Dimethylnitrosamine	62-75-9
Dibromochloropropane	DBCP		96-12-8
Lindane		Benzene Hexachloride	58-89-9
1,1,2-Trichlorotrifluoroethane		Freon 113	76-13-1
Trichlorofluoromethane		Freon 11	75-69-4
1,2-Dibromoethane	1,2-EDB	Ethylene Dibromide	106-93-4

CONSTRUCTION METHOD

The azimuth controlled hydraulic fracturing technology can construct in unconsolidated sediments 1) vertical fractures at the required azimuth or bearing, 2) continuous coalesced fractures by injection in multiple well heads, and 3) thick fractures, by a process of tip screen out or multiple fracture initiations. The technology, Hocking et al (1998a & b), involves initiating the fracture at the correct orientation at depth and by controlled injection a continuous reactive barrier is created, see Figure 2. The hydraulic fracture reactive permeable barrier is constructed by injecting through multiple well heads spaced along the barrier alignment. A special down hole tool is inserted into each well and a controlled vertical fracture is initiated at the required azimuth orientation and depth. Upon initiation of the controlled fracture, multiple well heads are then injected with the iron gel mixture to form a continuous permeable iron reactive barrier.

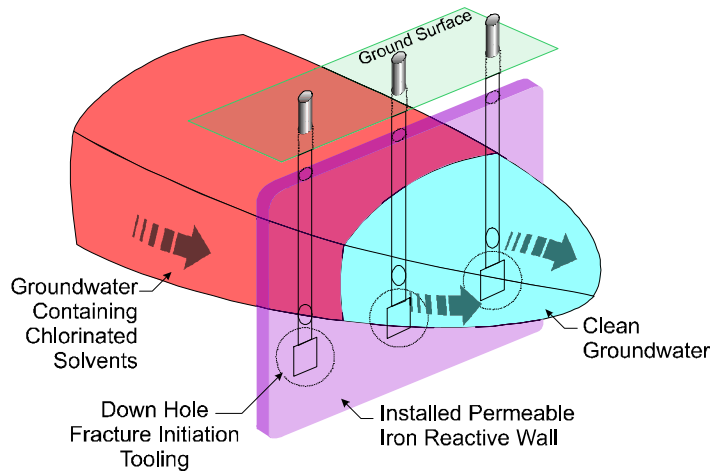


FIGURE 2. Hydraulic Fracture Iron Reactive Permeable Barrier.

The gel is injected into the formation and carries the iron filings to the extremes of the fracture. The gel is a water based cross link gel, hydroxypropylguar (HPG), which is a natural polymer used in the food industry as a thickener. HPG is used in the process because it has minimal impact on the iron's reactivity and upon degradation leaves an extremely low residue. The gel is water soluble in the uncross linked state, and water insoluble in the cross linked state. Cross linked, the gel can be extremely viscous, ensuring the iron filings remain suspended during the installation of the barrier. An enzyme breaker is added during the initial mixing to controllably degrade the viscous cross linked gel down to water and sugars, leaving a permeable iron reactive barrier in place.

With a single initiation and fracture injection, the typical thickness of the reactive barrier constructed by vertical hydraulic fracturing is 3" to 3.5" in dense sand and gravel formations. The ultimate thickness of the fracture is controlled by the formation stiffness and breakout pressure. In soft sediments, 8.5" thick fractures have been constructed in a single injection, see Figure 3. In dense compacted sediments, thick fractures can not be achieved in a single injection;

however, by multiple fracture initiations and injections, thicker fractures up to 9" thick can be constructed as shown on Figure 3.

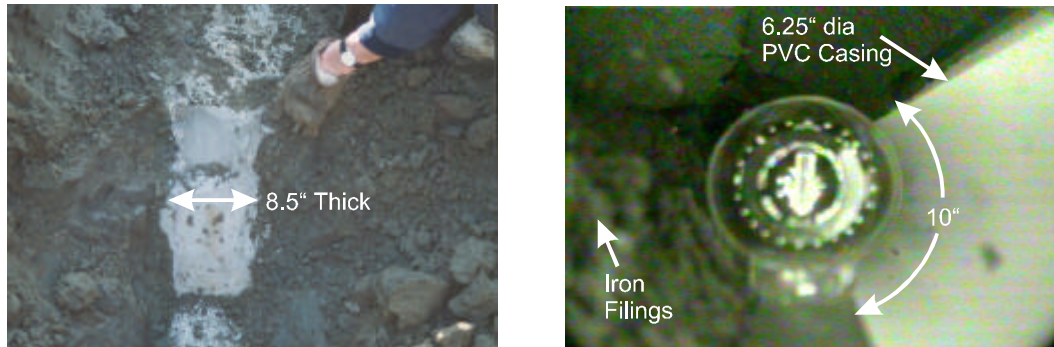


FIGURE 3. Thick Vertical Fractures in Soft and Stiff Sediments.

The iron reactive barrier installation is monitored in real time during injection to determine its geometrical extent and to ensure fracture coalescence or overlap occurs. The quantities of iron reactive mixture injected are continuously monitored to ensure sufficient reactive iron is injected through the individual well heads. During injection, the iron gel mix is electrically energized with a low voltage 100 Hz signal. Down hole resistivity receivers are monitored to record the in phase induced voltage by the propagating fracture, see Figure 4, and utilizing an incremental inverse integral model, the fracture fluid geometry can be quantified during the installation process.

Active resistivity monitoring has the added benefit of determining when the individual fractures coalesce and thus become electrically connected. That is, by energizing each injected well head individually and in unison, the fracture electrical coalescence is clearly recorded. The imaging and inversion of the down hole resistivity data focuses on quantifying the continuity of the reactive barrier. Such monitoring enables construction procedures to be modified if necessary to ensure the barrier is installed as planned.

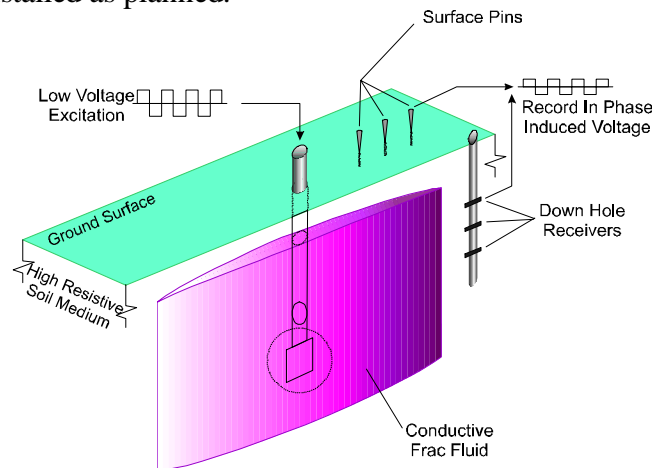


FIGURE 4. Fracture Mapping by Active Resistivity.

IRON REACTIVE BARRIER CONSTRUCTION

A former manufacturing facility in South-Central Iowa was contaminated with trichloroethene (TCE) in the soil and groundwater. Groundwater concentrations of TCE were detected up to levels of 14,000 $\mu\text{g/kg}$. The record of decision (ROD) was modified to an enhanced soil vapor extraction (SVE) system in the vadose zone and an in situ iron reactive permeable barrier for groundwater remediation. The iron reactive permeable barrier was installed by the azimuth controlled vertical fracturing technology. The remnant plume downgradient of the reactive barrier is expected to be in situ bio-remediated by the natural attenuation mechanisms at the site.

The site consists of medium to fine channel sands overlain by an over consolidated stiff to very stiff till. The iron reactive barrier system was constructed perpendicular to the groundwater flow direction and intercepted channel sands characterized as loose flowing sands with a permeability of approximately 1 Darcy. The iron reactive barrier is a source control barrier 240 feet long installed from a depth of 25 feet down to a total depth of 75 feet below ground surface with an average thickness of 3 inches. A plan view of the iron reactive barrier is shown on Figure 5, along with the hydraulic fracturing construction and instrumentation equipment.



FIGURE 5. Plan View of Iron Reactive Permeable Barrier.

The geometry of the reactive barrier was quantified during injection of the barrier by the active resistivity method. Down hole resistivity receiver locations are shown as rectangles in cross-section on Figure 6 and in plan on Figure 6 as RR1 through RR7 and attached to the casings of monitoring wells GW-1 and GW-2. The resistivity receivers consist of copper collars attached to cables that are multiplexed to the instrumentation data acquisition system. The wells F1 through F16, shown on Figure 6 in both plan and section, are the fracture injection wells.

An image of the injection of frac well F16 is shown on Figure 6, with the frac geometry determined by the measured induced voltages at the down hole receivers locations. All of the fracture injections at this site were recorded and their geometries delineated by active resistivity.

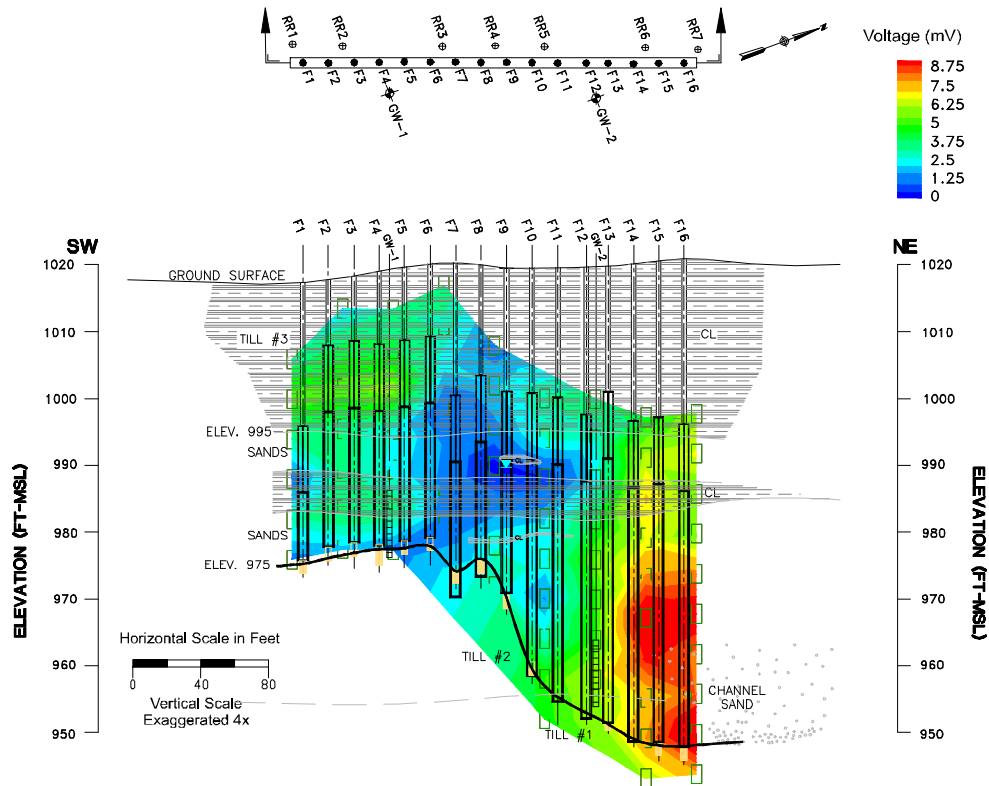


FIGURE 6. Induced Voltages from Propagating Fracture in Well F16.

The cross-section of the constructed iron reactive permeable barrier is shown on Figure 7. The barrier was keyed into the underlying till units #1 and #2 and extended to the lower surface of the upper till unit #3. The total cross-sectional area of the barrier was approximately 7,050 square feet. Due to the low groundwater flow velocity, the in situ reactive barrier has the capacity to degrade extremely high concentrations of TCE to below the MCL level. Of particular importance in selecting the remedy was that the reactive barrier system is complimentary and enhances the natural attenuation mechanisms active at the site. The reactive barrier was completed in October 1999 and recent groundwater down gradient monitoring data shows appreciable decline in TCE concentrations, with no daughter products detected, immediately down gradient of the barrier.

CONCLUSIONS

Permeable reactive barriers are suitable cost effective remedies for contaminated groundwater, both for plume remediation and as source control. Iron permeable reactive barriers have been most efficient in dehalogenating chlorinated

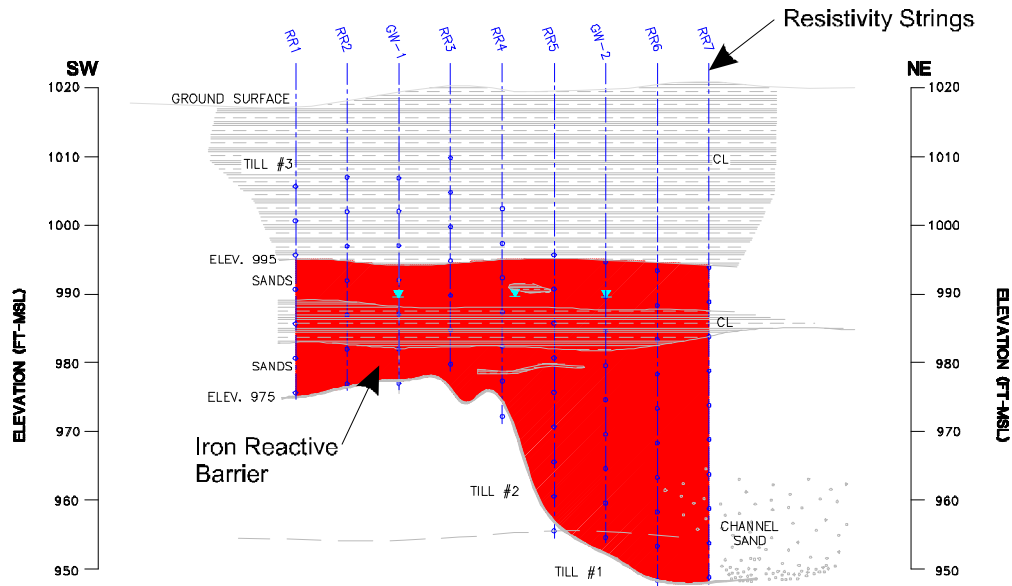


FIGURE 7. Cross-Section of Final Constructed Reactive Barrier.

solvents in groundwater and immobilizing metals and are a viable cost effective alternative to pump and treat. The iron reactive barrier system compliments and enhances natural attenuation mechanisms active at the site. The design, construction and performance monitoring of in situ reactive permeable barriers warrant special attention due to the functional design requirements of the systems and the low piezometric gradients across such systems. Particular attention needs to be paid to skin effects, and construction technique on iron reactivity and barrier permeability and porosity.

Azimuth controlled vertical hydraulic fracturing technology has placed permeable iron reactive barriers of moderate thickness up to 9” in highly permeable sands and gravel down to significant depths. The thicker reactive barriers are constructed by multiple initiations and re-injections, following the breaking of earlier injected gel. The real time monitoring of the injected geometry and materials provide the quality control and assurance required for construction of such systems.

The prime benefits of the fracturing installation method are cost savings over alternate installation techniques, flexibility to accommodate depth and thickness requirements, minimal site disturbance to overlying confining units and groundwater flow regimes, ability to be retrofitted if necessary, minimal waste volumes generated and deep application of the technology

REFERENCES

Gillham, R. W. and S. F. O’Hannesin. 1994. “Enhanced Degradation of Halogenated Aliphatics by Zero-Valent Iron”, *Ground Water*, Vol. 32, No. 6, pp958-967.

Gu, B. D. Watson, W. Goldberg, M. A. Bogle and D. Allred. 1998. "Reactive Barriers for the Retention and Removal of Uranium, Technetium, and Nitrate in Groundwater", RTDF Meeting, Beaverton, OR, April 15-16.

Hocking, G., S. L. Wells, and R. I. Ospina. 1998a. "Field Performance of Vertical Hydraulic Fracture Placed Iron Reactive Permeable Barriers", Emerging Remediation Technologies for Soil and Groundwater Cleanup, Florida Remediation Conf., Orlando, FL, November 10-11.

Hocking, G., S. L. Wells, and R. I. Ospina. 1998b. "Performance of the Iron Reactive Permeable Barrier at Caldwell Superfund Site", RTDF Meeting, Oak Ridge, TN, November 17-18.

Morrison, S. J. 1998. "Status of a Permeable Reactive Barrier Project for Uranium Containment at Monticello, Utah", RTDF Meeting, Beaverton, OR, April 15-16.

Naftz, D. 1998. "Status and Preliminary Results of the Fry Canyon Reactive Chemical Wall Project", RTDF Meeting, Beaverton, OR, April 15-16.

Orth, S. and R. W. Gillham. 1996. "Dehalogenation of Trichlorethene in the Presence of Zero-Valent Iron", *Environ. Sci. Technol.*, Vol. 30, pp66-71.

Puls, R. W. 1998. "Elizabeth City, North Carolina Permeable Reactive Barrier Site Update", RTDF Meeting, Oak Ridge, TN, November 17-19.

Schlicker, O., M. Ebert, R. Kober, W. Wust and A. Dahmke. 1998. "The effect of competing chromate and nitrate reduction on the degradation of TCE with granular iron", RTDF Meeting, Oak Ridge, TN, November 17-19.

Sivavec, T. M. and D. P. Horney. 1995. "Reductive Dechlorination of Chlorinated Ethenes by Iron Metal", Proc. 209th. American Chemical Society National Meeting, Vol. 35, No. 1, pp695-698.

Sivavec, T. M., P. D. Mackenzie, D. P. Horney and S. S. Bagel. 1997. "Redox-active Media Selection for Permeable Reactive Barriers", Int. Containment Conf., St. Petersburg, FL, February 10-12.

Su, C. and R. W. Puls. 1998. "Retention of Arsenic by Elemental Iron and Iron Oxides", RTDF Meeting, Oak Ridge, TN, November 17-19.

Sweeny, K. H. and J. R. Fisher. 1972. "Reductive Degradation of Halogenated Pesticides", U.S. Patent No. 3,640,821.