



## Permeable Reactive Subsurface Barriers for the Interception and Remediation of Chlorinated Hydrocarbon and Chromium(VI) Plumes in Ground Water

Office of Research and Development

U.S. EPA REMEDIAL TECHNOLOGY FACT SHEET

### Scope of this fact sheet:

This document concerns the use of permeable reactive subsurface barriers for the remediation of plumes of chlorinated hydrocarbons and Cr(VI) species in ground water, using zero-valent iron ( $\text{Fe}^0$ ) as the reactive substrate. Such systems have undergone thorough laboratory research, pilot-testing, and are now being installed as full-scale remedial technologies at field sites. Although research is progressing for other contaminants and different reactive substrates, these technologies are not as mature and will not be considered in this document.

### Chemistry of TCE and chromate remediation by $\text{Fe}^0$ :

Chlorinated hydrocarbons such as trichloroethylene (TCE) have been widely used as commercial solvents and are commonly found as ground water contaminants. As chlorinated hydrocarbons contact iron metal, they react at the iron surface. Figure 1 illustrates the reductive dechlorination of TCE to ethene and ethane which are easily biodegraded. Electrons are provided by the corrosion (or oxidation) of the iron metal. Two competing pathways, sequential hydrogenolysis (A) and reductive  $\beta$ -elimination (B), each lead to ethene and ethane as final products. A reactive subsurface barrier is designed to provide sufficient contaminant residence time for intermediate products, such as cis-1,2-DCE and vinyl chloride (VC), to fully degrade to ethene and ethane.

Chromium is also a very common contaminant, typically having been released to the environment as a result of plating and other industrial operations. It occurs in the subsurface in either the Cr(VI) or Cr(III) valence states. The higher oxidation-state Cr(VI) forms, e.g. chromate (Figure 2), are far more toxic, carcinogenic, and mobile in the ground water than the reduced Cr(III) species. At typical ground water pH of 6 to 9, Cr(III) tends to precipitate from the ground water as chromium hydroxide,  $\text{Cr}(\text{OH})_3$  (Figure 2). When iron is present, the Cr(III) can precipitate as a mixed chromium-iron hydroxide solid solution, which has a lower solution equilibrium activity than either pure solid-phase hydroxide (2). Hence both the toxicity and mobility of chromium are greatly decreased when it is reduced from Cr(VI) to Cr(III).

Both TCE and chromate (as well as many other chemicals) have been shown to be reduced by  $\text{Fe}^0$ , resulting in the dechlorination of the TCE and the precipitation and immobilization of Cr. The  $\text{Fe}^0$  donates the electrons necessary to reduce the contaminants and becomes oxidized to  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ . A variety of Fe precipitates and other chemical species can occur, dependant upon the system geochemistry.

### Concept and definition of reactive barriers:

Environmental scientists are generally familiar with the concept of barriers for restricting the movement of contaminant plumes in ground water. Such barriers are typically constructed of highly impermeable emplacements of materials such as grouts, slurries, or sheet pilings to form a subsurface *wall*. The goal of such constructions is to eliminate the possibility that a

contaminant plume can move toward and endanger sensitive receptors such as drinking water wells or discharge into surface waters. Permeable reactive barrier walls reverse this concept of subsurface barriers. Rather than serving to constrain plume migration, permeable reactive barriers are designed as preferential conduits for the contaminated ground water flow. When the contaminated water passes through the reactive zone of the barrier, (for example, a zone comprised of granular iron), the contaminants are either immobilized or chemically transformed to a more desirable (e.g., less toxic, more readily biodegradable, etc.) state. A permeable reactive subsurface barrier can be defined as:

*an emplacement of reactive materials in the subsurface designed to intercept a contaminant plume, provide a preferential flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals at points of compliance.*

### Barrier configurations:

Currently, two basic designs are being used in full-scale implementations of reactive barriers: (1) the funnel and gate and (2) the continuous trench. Other designs are being researched and evaluated.

The design of a funnel and gate system is shown in Figure 3a. Basically, an impermeable *funnel*, typically consisting of interlocking sheet pilings or slurry walls, is emplaced to enclose and direct the flow of contaminated water to a *gate* or *gates* containing the permeable zone of reactive Fe metal. The design must prevent the contaminant plume from flowing around the barrier. Due to directing large amounts of water through a much smaller cross-sectional area of the aquifer, ground water velocities within the barrier will be higher than those resulting from the natural gradient. The continuous trench (Figure 3b) is simply a trench that has been excavated and simultaneously backfilled with reactive Fe, allowing the water to pass through the barrier under its natural gradient.

Both configurations require that information on contaminant concentration, contaminant degradation rate in the presence of the reactive substrate, and ground water flow rate through the barrier be known. This allows determination of the required residence time in the zone needed to achieve remedial goals, hence allowing calculation of the required thickness of the reactive zone.

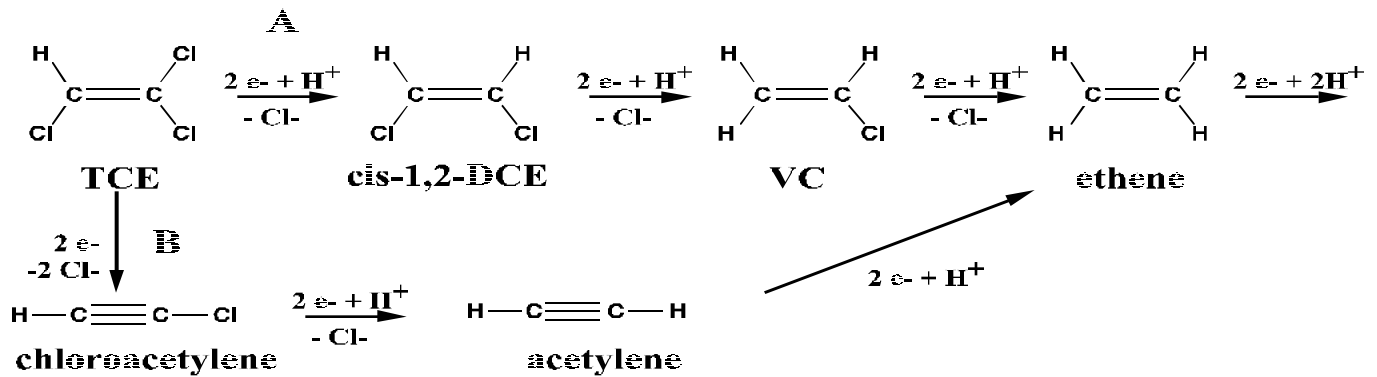


Figure 1. Reductive dechlorination of TCE to ethene and ethane.

**Site characterization:**

A complete site characterization is of critical importance for the successful installation of a reactive barrier. The entire plume must be directed through and remediated within the reactive zone of the barrier. The plume must not be able to pass over, under, or around the barrier and the reactive zone must be capable of reducing the contaminant to concentration goals without rapidly plugging with precipitates or losing its reactivity. To achieve the required performance requires knowledge of:

- plume location
- plume direction
- contaminant concentrations
- hydrologic changes with time
- concentration attenuation over time and distance
- stratigraphic variations in permeability
- confining layers
- fracturing, and
- aqueous geochemistry

The barrier design, location, emplacement methodology, and estimated life expectancy are based on the site characterization information, therefore faulty information could jeopardize the entire remedial scenario. A complete discussion of site characterization is beyond the scope of this document, but guidance documents are in preparation that will contain extensive discussions of characterization requirements.

**Compliance and performance monitoring:**

Monitoring for regulatory compliance and treatment performance are both necessary when using reactive barrier technology. When locating the wells, selecting the screen lengths, and designing other aspects of the monitoring well system, the sampling program objectives and site conditions should be carefully considered.

Compliance monitoring determines whether regulatory contaminant concentration requirements are being met. Typically the compliance monitoring criteria will be set by the State where the site is located. Normal compliance monitoring parameters include:

- the contaminants of interest
- potential contaminant daughter (degradation) products
- general water quality parameters

In general, several monitoring wells should be installed to determine:

- are regulatory goals being achieved?
- does contaminant breakthrough occur (immediately or over time)?
- is the contaminant flowing around the wall?

Typical well locations would include:

- upgradient of the wall
- within the reactive zone of the wall
- immediately downgradient of the reactive zone discharge
- at each end of the wall
- below the wall, and
- above the reactive zone (if possible)

In addition to the contaminants, their products, and the routine water quality parameters listed above, performance monitoring of permeable reactive barriers should include:

- hydrologic parameters (baseline and changes over time)
- precipitates on the iron surfaces (and rate of buildup)
- Eh
- dissolved oxygen, and
- ferrous iron

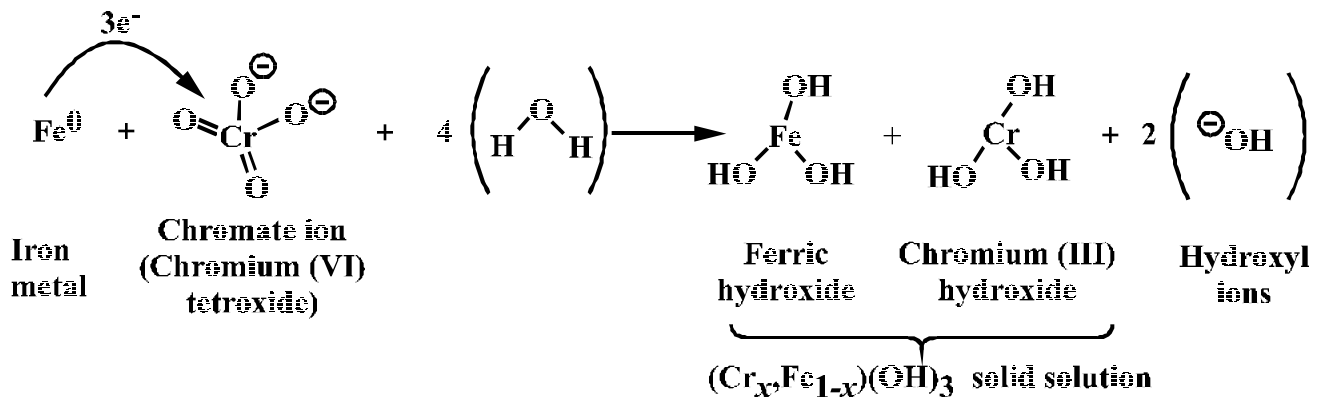
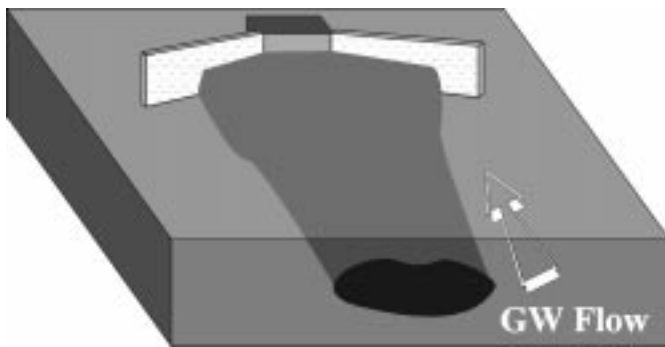


Figure 2. Reduction of Cr(VI) to Cr(III) and precipitation of hydroxide phases.



**Figure 3a.** *Plume capture by a funnel & gate system. Sheet piling funnels direct the plume through the reactive gate.*



**Figure 3b.** *Plume capture by a continuous trench system. The plume moves unimpeded through the reactive gate.*

Knowledge of these parameters helps confirm emplacement as well as address and detect possible:

- loss of reactivity
- decrease in permeability
- decrease in reaction zone residence time
- short circuiting of the reactive zone (i.e., preferential pathways), and
- funnel wall leakage

### **Some advantages and disadvantages of reactive barrier technology:**

#### *Advantages--*

- actual in situ contaminant remediation, rather than simple migration control as with impermeable barriers
- passive remediation, no ongoing energy input and limited maintenance following installation
- no required surface structures other than monitoring wells following installation
- can remediate plumes even when the source term of the plume cannot be located
- should not alter the overall ground water flow pattern as much as high-volume pumping
- contaminants are not brought to the surface; i.e., no potential cross-media contamination
- no disposal requirements or disposal costs for treated wastes
- avoids the mixing of contaminated and uncontaminated waters that occurs with pumping

#### *Disadvantages--*

- currently restricted to shallow plumes, approximately 50 feet or less below ground surface
- plume must be very well characterized and delineated
- limited long-term field testing data is available and field monitoring is in its infancy
- limited field data concerning longevity of wall reactivity or loss of permeability due to precipitation
- currently no field-tested applications to remediation of contaminant source terms

### **Current applications of reactive barriers to contaminant plumes:**

Permeable reactive subsurface barriers are currently being used in full-scale field applications for the treatment of plumes of chlorinated hydrocarbons and chromate. As of this writing, six full-scale reactive barriers have been installed in the field. Information on five of these installations is provided in Table 1.

### **Regulatory acceptance of permeable reactive barriers for subsurface contaminant remediation:**

The U.S. Environmental Protection Agency has supported the development of this innovative in-situ technology through active collaboration on research involving the National Risk Management Research Laboratory and the National Exposure Research Laboratory of U.S. EPA's Office of Research and Development, through the Remediation Technologies Development Forum (RTDF) Permeable Barriers Action Team, and from support provided by U.S. EPA's Technology Innovation Office (TIO). In addition, support has been provided from several regional offices where sites are testing the technology at pilot scale. The U.S. EPA recognizes this technology as having potential to more effectively remediate subsurface contamination at many types of sites at significant cost savings compared to other more traditional approaches. The U.S. EPA is actively involved in the evaluation and monitoring of this new technology to answer questions regarding long-term system performance, and in providing guidance to various stakeholder groups.

As with any remedial technology, adequate site characterization is necessary to demonstrate that the technology is suitable for application at a particular site. There are site characteristics, such as excessive depth to contaminant plume, fractured rock, etc., which would argue against permeable reactive barriers as a remedy selection. These situations are currently topics of research and/or pilot testing. More definitive information regarding the application of the technology will be included in a forthcoming EPA Issue Paper.

The Interstate Technology and Regulatory Cooperation (ITRC) Workgroup (Permeable Barrier Wall Subgroup) is also actively involved in defining the regulatory implications associated with the installation of permeable reactive barriers in the subsurface and in providing guidance on regulatory issues where possible.

### **Additional sources of information on reactive barriers:**

Remedial Technologies Development Forum, Permeable Barriers Work Group

<http://www.rtdf.org>

Ground-Water Remediation Technologies Analysis Center (GWRTAC)

<http://www.gwrtac.org:80/>

EnviroMetal Technologies Inc.

<http://www.beak.com:80/Technologies/ETI/eti.html>

**Table 1.** Specifications for selected permeable reactive barrier installations.

Site	Industrial facility, Mountain View, California	Industrial facility, Belfast, Northern Ireland	Industrial facility, Coffeyville, Kansas	USCG facility, Elizabeth City, North Carolina	Government facility, Lakewood, Colorado
Installation Date	Sept. 1995	Dec. 1995	Jan. 1996	June 1995	Oct. 1996
Contaminant & high conc. Design	2 mg L <sup>-1</sup> cDCE	300 mg L <sup>-1</sup> TCE	400 µg L <sup>-1</sup> TCE	10 mg L <sup>-1</sup> TCE 10 mgL <sup>-1</sup> Cr(VI)	700 µg L <sup>-1</sup> each TCE & DCE 15 µg L <sup>-1</sup> VC
Reactive Wall Type	Excavate & fill	Reaction Vessel	Funnel & Gate	Continuous Trench	Funnel & Multiple Gate
Funnel Material	Not Applicable	Slurry Walls	Soil-Bentonite Slurry	Not Applicable	Sealable Joint Sheet Pileings
Funnel Length	Not Applicable	100 ft + 100 ft	490 ft + 490 ft	Not Applicable	1040 ft total
No. of Gates	Not Applicable	1 Reaction vessel	1	Not Applicable	4
Reactive Material	Fe <sup>0</sup>	Fe <sup>0</sup>	Fe <sup>0</sup>	Fe <sup>0</sup>	Fe <sup>0</sup>
Reactive Zone Height	5 ft	16 ft in vessel	11 ft	Approx. 23 ft	10-15 ft
Reactive Zone Length	44 ft	NA	20 ft	150 ft	40 ft each (4 x 40 = 160)
Reactive Zone Thickness	4.5 ft	16 ft in vessel	3 ft	2 ft	Gates differed, low = 2 ft high = 6 ft
Total Mass of Reactant	90 tons	15 tons	70 tons	450 tons	No Information
Treatment Wall Depth	15 to 20 ft bgs	18 to 40 ft bgs	17 to 28 ft bgs	3 to 26 ft bgs	10-15 to 20-25 ft bgs
Total System Length	44 ft	Approx. 200 ft	1000 ft	150 ft	1200 ft
Special Features & Misc.	HDPE atop Fe to surface upgradient directs H <sub>2</sub> O through Fe	Walls direct H <sub>2</sub> O to vessel inlet, gravity flow to outlet downgradient		Two contam. treated. Chain trencher with immediate Fe placement	Largest of its kind. Gates installed using sheet pile box.
Cost	No Information	\$375 K	\$400 K	\$500 K	No Information

**For more information, contact:**

Dr. Robert W. Puls (RTDF co-chair)  
 U.S. Environmental Protection Agency  
 National Risk Management Research Laboratory  
 P.O. Box 1198  
 Ada, OK 74820  
 Tel: (405) 436-8543  
 Email: puls@epamail.epa.gov

**Authors:**

Robert W. Puls, Subsurface Protection and Remediation Division, NRMRL, ORD, U.S. EPA  
 Robert M. Powell, Powell & Associates Science Services, Las Vegas, NV (under subcontract to ManTech Environmental Research Services Corp.)

**References for the chemical reactions and mechanisms:**

- (1) Roberts, L. A.; Totten, L. A.; Arnold, W. A.; Burris, D. R.; Campbell, T. J. *Environmental Science & Technology* **1996**, 30, 2654-2659.
- (2) Powell, R. M.; Puls, R. W.; Hightower, S. K.; Sabatini, D. A. *Environmental Science & Technology* **1995**, 29, 1913-1922.

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