

Field Monitoring of a Permeable Reactive Barrier for Removal of Chlorinated Organics

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Abstract: The application of zero-valent iron (Fe^0) in the funnel-and-gate permeable reactive barrier (PRB) installed at the Vapokon site, Denmark, was conducted in 1999 to remediate the groundwater contaminated by chlorinated aliphatic hydrocarbons (CAHs). Over the past 4 years, except in September 2002 and January 2003, about 92.4–97.5% CAH removal could be achieved with the PRB. Although there was a continuous decrease in total alkalinity (90.3%), calcium (81.7%), and sulfate (69.2%) ions in the groundwater crossing the PRB, probably caused by mineral precipitation and resulting in 0.88% porosity loss per year, no noticeable deterioration of the barrier's performance was observed between March 2000, and August 2003. Instead, climatic variation in the barrier's performance on CAH dechlorination was examined. The dechlorination rates in the cold season (January 2003 and March 2000) were generally smaller than those in the hot season (August 2003, September 2000, and September 2001). Besides, 1,2-dichloroethane and dichloromethane, which were proven to be not treatable by Fe^0 , could also be removed with the PRB, thereby suggesting enhancement from Fe^0 adsorption or microbial degradation.

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Introduction

To date, the pump-and-treat system is a primary technology used in the remediation of chlorinated aliphatic hydrocarbon (CAH) polluted groundwater. However, this conventional system has in the past decade been proven to be expensive and difficult to use in meeting environmental standards (Travis and Doty 1990). As a consequence, the permeable reactive barrier (PRB) technology has emerged recently because of its low operation and maintenance costs. Up until 2002, 31 full-scale PRBs were built (USEPA 2002). In general, a PRB involves the placement of reactive materials in the subsurface environment to intercept a contaminant plume in which toxic contaminants are transformed into innocuous forms (USEPA 1998). Among various reactive materials packed into PRBs, zero-valent iron (Fe^0) is most commonly used (USEPA 2002) because of its low cost and high ability to dechlorinate CAHs over wide concentration ranges (Hardy and Gillham 1996; Lai and Lo 2002).

The mechanisms of dechlorinating CAHs by Fe^0 involve a series of redox reactions. Under both aerobic and anaerobic conditions, the electrons released from the oxidation of Fe^0 provide a thermodynamically favorable condition and electron source for the reduction of CAHs with concomitant release of hydroxide ions (OH^-) and hydrogen gas (USEPA 1998). Besides, the ferrous iron (Fe^{2+}) and hydrogen gas released from the Fe^0 oxidation can thermodynamically provide another electron source for the dechlorination reactions via the oxidation reaction of Fe^{2+} and catalytic hydrogenolysis by hydrogen gas, respectively (Matheson and Tratnyek 1994). As described by Arnold and Roberts (2000), hydrogenolysis and reductive- β -elimination are the main pathways involved in the dechlorination reactions by Fe^0 (USEPA 1999).

Apart from CAHs, the oxygen and hydrogen in groundwater can simultaneously be transformed into lower oxidation states under the chemically reducing condition exerted by Fe^0 . The presence of sulfate-reducing bacteria within Fe^0 PRBs also leads biologically mediated reduction of sulfate (SO_4^{2-}) into sulfide along reactive barriers, thereby highly encouraging formation of metal oxides, hydroxides, and sulfides on Fe^0 surface. Further, the elevated pH in groundwater within iron barriers can decrease the solubility of a number of minerals, resulting in precipitation (Yabusaki et al. 2001). Numerous laboratory and modeling studies of the hydraulic and geochemical performances of Fe^0 PRBs have verified the potential impacts of mineral precipitation, which potentially can passivate Fe^0 and reduce the porosity inside PRBs, thereby adversely influencing barrier's long-term performance (Odziemkowski et al. 1998; Mackenzie et al. 1999; Benner et al. 2001). In addition, climatic variation of groundwater characteristics, such as the high dissolved oxygen (DO) content in groundwater during rainy season and the low groundwater temperature in winter, causes fluctuation in barrier's performance. This is because oxygen in groundwater can compete with CAHs for the

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released electron (Helland et al. 1995) and also dechlorination reactions by Fe^0 are controlled primarily by chemical reaction-limited kinetics (Su and Puls 1999). Recently, beneficial contribution from CAH adsorption by Fe^0 has been reported (Burris et al. 1995) and positive influence of microorganisms on the efficiency of Fe^0 PRBs for CAH dechlorination has also been proposed (Gu et al. 2002).

Since the groundwater chemistry (e.g., pH, redox potential, alkalinity, major cations, and anions) is a critical factor determining the influence of mineral precipitation, microbial activity and Fe^0 adsorption on barrier's performance, variations in groundwater chemistry from site to site may consequently give rise to variations in the long-term performance of a standard implementation of a PRB. Therefore, understanding the impact of the local groundwater chemistry on the performance of PRBs not only provides an opportunity to assess the feasibility of this novel technology but it also allows us to adapt the engineering design to site-specific conditions.

Comprehensive monitoring of the behavior of a funnel-and-gate Fe^0 PRB installed at the Vapokon site in Denmark was conducted on six occasions between March 2000 and August 2003. The objectives of this field study were to (1) examine the variation of the performance of the Fe^0 PRB in dechlorinating CAHs from the calcium-rich groundwater over the past 4 years; (2) investigate the geochemical variations in the Vapokon groundwater along the Fe^0 PRB; and (3) identify the contribution of Fe^0 adsorption and microbial degradation on CAH removal.

Site Description and History

The Vapokon site is located in the northern part of Fuen Island in Denmark. Its geological features are a layer of loam and soil filings extending approximately 1.5 m below the ground surface, which is about 22.22 m above sea level (masl). Just below the vadose zone, there is a water-saturated sandy aquifer approximately 9 m in depth underlain by a relatively impermeable clay layer with a minimum thickness of about 15 m (Lo et al. 2003a,b). The groundwater flows in a southeastern direction at a seepage velocity of 400–500 m/year toward a creek and rain water pond nearby (Lai et al. 2004). Vapokon groundwater is classified as very hard groundwater since it contains high concentrations of calcium ion (Ca^{2+}). Besides, significant amounts of total alkalinity (TAL) and sulfate ion (SO_4^{2-}), certain concentrations of chloride (Cl^-) and magnesium ions (Mg^{2+}), as well as a trace amount of total dissolved iron (Fe_T) can also be detected in samples (Table 1).

From 1976 to 1997, a solvent recycling factory was located at this site to treat used solvent and paint containing CAHs and aromatic hydrocarbons (BTEX). Because of a spill from an underground concrete tank in which the used solvent was reloaded from drums, there has been heavy soil and groundwater contamination with CAHs and BTEX, resulting in a 80×200 m contaminant plume (Lai et al. 2004). As shown in Table 2, tetrachloroethylene (PCE), trichloroethylene (TCE), 1,1,1-trichloroethane (1,1,1-TCA), *cis*-dichloroethylene (*cis*-DCE) and dichloromethane (DCM) were determined to be the major CAHs found in the contaminant plume. These contaminants were accompanied by trace amounts of vinyl chloride (VC), 1,1-dichloroethylene (1,1-DCE), *trans*-dichloroethylene (*trans*-DCE), 1,1-dichloroethane (1,1-DCA), 1,2-dichloroethane (1,2-DCA), and chloroform (TCM). To clean up this contaminated site, 4,600 tons of contaminated soils were first removed

from the hotspot and a funnel-and-gate Fe^0 PRB was then constructed to remediate the CAH contaminated groundwater.

As illustrated in Fig. 1, the funnel-and-gate Fe^0 PRB, which was installed at the Vapokon site in September 1999, was composed of two 110–130 m long sheet pilings (the funnel) and a reactive gate containing 270 tons of Fe^0 (ETI-CC-1004, Connelly-GPM Inc.). The Fe^0 packed in the PRB had a particle density of 6.43 g/mL and a specific surface area of 1.80 m^2/g . In addition, over 94% by weight of the Fe^0 fell in the range of particle diameter 0.30–1.18 mm. For the sake of spreading the contaminated groundwater uniformly across the reactive zone, gravel packs with 1 m in thickness were placed just upgradient and downgradient of the reactive barrier. The reactive gate, 14.5 m wide, 9.0 m deep, and 0.8 m thick, possessed an average hydraulic conductivity of 20.28 m/d (Birkelund and Harrekilde 2003), a porosity of 0.60 as well as a Fe^0 surface area to solution volume ratio (λ_{SA}) of 7.79 m^2/mL . There was also an upgradient groundwater drainage system surrounding the opening of the funnel-and-gate Fe^0 PRB to prevent any uncontaminated groundwater from flowing into the capture zone of the funnel-and-gate system (see Fig. 1), thereby consequently increasing the residence time inside the reactive zone. Results from the natural gradient tracer study of the PRB at the Vapokon site (Lai et al. 2004) showed that the groundwater flow velocity was about 99.5 m/year within the barrier, which was equivalent to the hydraulic retention time or contact time of about 70.4 h in the iron part of the barrier.

Methods and Materials

Installation of Monitoring Network and Groundwater Sampling

Two types of monitoring networks, which are shown in Fig. 1, were installed across the Fe^0 PRB, resulting in six sampling fences located 0.0, 0.1, 0.4, 0.6, 0.7, and 1.1–5.8 m from the upgradient edge of the PRB. The 15 monitoring wells constructed at the time of the PRB installation totally possessed 45 piezometers each ended by 1 m long screen. The 3 piezometers in each well generally screened at depths of 12.52–14.22, 15.62–16.47, and 18.02–19.12 masl. In addition, 20 nylon and 6 copper multilevel samplers with 310 screens distributing at approximately 13.78–20.28 masl were also installed in the central part of the PRB using the Geoprobe technique in September 2002 (Lai et al. 2004). Groundwater samplings were conducted in March 2000, September 2000, September 2001, September 2002, January 2003, and August 2003 in order to obtain long-term monitoring data. A 12 V DC pump (In-Line 991, Whale) connected to a 10 m long nylon tube was used for sampling from the monitoring wells, whereas a sampling manifold with a vacuum pump was used for the simultaneous sampling of six sampling points of the multilevel sampling wells. Prior to storage in 10 mL glass volumetric flasks without headspace, 5–15 L and 50 mL of groundwater were first removed from both the monitoring wells and multilevel samplers, respectively, to remove stagnant water.

Groundwater Sample Analyses

For the measurements of the less volatile CAHs such as PCE, TCE, 1,1,1-TCA, TCM, 1,1-DCA, 1,2-DCA, and DCM, the method of liquid–liquid extraction using pentane (Pestican, LAB-

Table 1. Variations of the Inorganic and Physical Characteristics of the Vapokon Groundwater along the Permeable Reactive Barrier (PRB)

Parameters/date		March 2000	September 2000	September 2001	September 2002	January 2003
Inorganic parameters						
Calcium, Ca ²⁺ (as CaCO ₃)	U	510 (145)	646 (747)	na	338 (157)	299 (152)
	M	160 (147)	133 (129)		136 (112)	96 (86)
	D	146 (161)	81 (44)		54 (36)	48 (39)
Magnesium, Mg ²⁺ (as CaCO ₃)	U	64.9 (14.0)	52.1 (7.3)	na	na	na
	M	37.2 (36.8)	41.2 (18.5)			
	D	21.4 (25.9)	27.7 (22.6)			
Total alkalinity, TAL (as CaCO ₃)	U	372 (93)	323 (81)	na	na	248 (90)
	M	78 (120)	99 (99)			125 (101)
	D	19 (12)	31 (12)			35 (17)
Total dissolved iron, Fe _T	U	13.2 (10.3)	13.2 (10.4)	na	0.18 (0.39)	0.15 (0.27)
	M	8.1 (15.3)	9.8 (16.3)		0.25 (0.33)	0.13 (0.08)
	D	0.4 (0.5)	0.6 (0.7)		0.13 (0.13)	0.38 (0.36)
Sulfate, SO ₄ ²⁻	U	189 (125)	145 (71)	na	27.2 (13.8)	na
	M	73 (67)	48 (30)		3.7 (3.6)	
	D	108 (145)	40 (43)		2.2 (1.6)	
Chloride, Cl ⁻	U	50.3 (12.0)	43.6 (11.1)	na	46.1 (23.9)	43.9 (23.4)
	M	43.1 (14.6)	55.4 (21.8)		65.2 (37.3)	38.9 (15.0)
	D	42.0 (13.5)	47.8 (7.0)		38.0 (22.9)	33.9 (11.9)
Physical parameters						
pH	U	7.03 (0.23)	7.38 (0.22)	7.33 (0.23)	na	7.16 (0.18)
	M	8.98 (1.11)	9.69 (1.24)	9.53 (1.17)		9.44 (0.85)
	D	9.50 (0.39)	10.56 (0.65)	10.62 (0.86)		10.21 (0.96)
Specific conductance (μs/cm)	U	1153 (304)	644 (155)	679 (132)	na	646 (82)
	M	463 (351)	330 (163)	378 (206)		309 (183)
	D	432 (316)	238 (54)	230 (25)		229 (102)
Redox potential (mV)	U	na	na	na	na	105 (25)
	M					-115 (90)
	D					-150 (88)
Dissolved oxygen (mg/L)	U	na	na	na	6.25 (1.59)	0.53 (0.09)
	M				na	0.84 (1.30)
	D				na	0.40 (0.13)
Temperature (°C)	U	na	na	na	13.08 (0.88)	9.55 (0.06)
	M				13.75 (0.60)	8.93 (0.47)
	D				14.30 (0.44)	8.70 (0.26)

Note: The units of the inorganic parameters are in milligrams per liter (mg/L). na=not available. The values shown in the box from the top to bottom represent the average value of the parameters collected from the upgradient location (U), middle (M), and downgradient part (D) of the Fe⁰ PRB, respectively. The bold values represent the original characteristics of the groundwater. The values shown in parentheses indicate the corresponding standard deviation of the data.

SCAN) as a solvent and trichlorofluoromethane (LB05780, SUPELCO) as an internal standard was applied in which water to pentane ratio is 3 to 3 mL (Clesceri et al. 1998). After rotating at 60 rpm for 30 min, a 1 μL aliquot of equilibrated pentane was injected into the gas chromatograph (Model HRGC 5300, Carlo Erba Instruments) equipped with a Ni⁶³ electron capture detector (ECD-400, Carlo Erba Instrument) and a capillary column (DB-5, J & W Scientific) for measurement. For the more volatile compounds including *cis*-DCE, *trans*-DCE, 1,1-DCE, and VC, 2.5 mL water sample was added into 5 mL glass bottle. After rotating at 60 rpm for 30 min, 500 μL gas sample was collected from the headspace of the glass bottle and then injected into gas chromatograph (HP 5890 Series II, Hewlett Packard) equipped

with a HNU photoionization detector and capillary column (Fused Silica, NSW-PLOT) for the analysis (Clesceri et al. 1998; EnviroMetal Technologies Inc. 1998).

Detection of Ca²⁺, Mg²⁺, and Fe_T was through atomic absorption spectrometry (Perkin Elmer 5000, Perkin Elmer, Eden Prairie, Minn.) and detection of Cl⁻ and SO₄²⁻ was through ion chromatography (LC 20 Chromatography, Dionex). Additionally, a titration method using 0.02 N sulfuric acid (UN 1830, General Chemical) as a titrant and 0.1% by weight Bromocresol green (B-0443-100, Exaxol Chemical Corporation) as an indicator was used for TAL measurement (Clesceri et al. 1998). The physical characteristics of the Vapokon groundwater collected along the

Table 2. Maximum Concentrations of Chlorinated Aliphatic Hydrocarbons (CAHs) in the Contaminant Plume between March 2000 and August 2003

Parameters/date	March 2000	September 2000	September 2001	September 2003	January 2003	August 2003
Tetrachloroethylene, PCE	12.00	20.00	19.00	4.81	4.86	7.30
Trichloroethylene, TCE	5.00	34.00	19.00	23.66	17.47	22.00
<i>cis</i> -Dichloroethylene, <i>cis</i> -DCE	5.50	16.00	20.00	29.54	18.13	38.00
Vinyl chloride, VC	0.55	0.10	0.71	na	na	2.40
1,1-Dichloroethylene, 1,1-DCE	0.04	0.31	0.32	na	na	0.61
<i>trans</i> -Dichloroethylene, <i>trans</i> -DCE	0.10	0.02	0.03	nd	nd	0.43
1,1,1-Trichloroethane, 1,1,1-TCA	4.40	37.00	12.00	15.47	15.32	31.00
1,1-Dichloroethane, 1,1-DCA	0.15	0.58	0.52	0.70	0.77	0.66
1,2-Dichloroethane, 1,2-DCA	6.10	na	0.07	nd	nd	0.03
Chloroform, TCM	0.64	0.77	0.69	nd	nd	0.26
Dichloromethane, DCM	2.90	33.00	15.00	1.69	0.94	1.30

Note: The units of the CAH concentrations are in milligrams per liter (mg/L). na represents not available and nd refers to not detectable.

PRB were measured immediately in the field. By using the 12 V DC pump, the groundwater collected from the monitoring wells was first transferred to a flow cell equipped with pH (pH 330 SET-1, WTW), DO (OXI 330-SET, WTW), conductivity (LF330-SET, WTW), and redox potential (Ag/AgCl Model 800-323-4340, Cole-Parmer) probes. Readings were taken when three successive readings were within 10%/min of variation (USEPA 1999).

Batch Test

In order to substantiate the contribution of Fe⁰ adsorption to 1,2-DCA and DCM removal, time series batch experiments were conducted under 10°C with Millipore water containing 1,2-DCA and DCM, with concentrations ranging from 5.7 to 6.1 and from 26.6 to 30.5 mg/L, respectively (Lai and Lo 2002). Two types of Fe⁰ were used in these batch experiments. One was Fe⁰ (the same as the Fe⁰ used in the PRB) without any pretreatment (i.e., fresh Fe⁰), whereas the other was Fe⁰ heavily coated by calcium and iron carbonates (i.e., coated Fe⁰), resulting in two sets of glass bottles (i.e., the control+fresh Fe⁰ bottles and control+coated Fe⁰ bottles). The empty 25 mL glass bottles (control) were filled with the feed solution as were the 25 mL glass bottles containing fresh and coated Fe⁰. They were then crimp-sealed without headspace using rubber septa (Burris et al. 1995) and then continuously

shaken at 420 rpm (SF1, Stuart Scientific). With the application of 5 mL glass syringe and 18G stainless steel syringe needles, water samples were extracted from the glass bottles through one of the syringe needle with concomitant substitution of the volume of the extracted solution with ambient air via another syringe needle. Sampling from different glass bottles was conducted at different time intervals and 1,2-DCA and DCM concentrations were measured through the methods mentioned before.

Data Analysis

Gillham and O'Hannesin (1994) determined that the dechlorination reaction is a pseudo first-order reaction with respect to contaminant concentration, with the dechlorination rate constant (k_{obs}) appearing to be directly proportional to λ_{SA} . Because of sequential dechlorination of major chlorinated organics (MCOs), such as PCE, TCE, 1,1,1-TCA, and TCM into corresponding chlorinated daughter products (CDPs), including *cis*-DCE, 1,1-DCE, VC, 1,1-DCA, and DCM (Vogel and McCarty 1987; Helland et al. 1995; Su and Puls 1999), three sequential dechlorination models (Models 1, 2, and 3), which take account of concurrent production and dechlorination of CAHs, were used in the

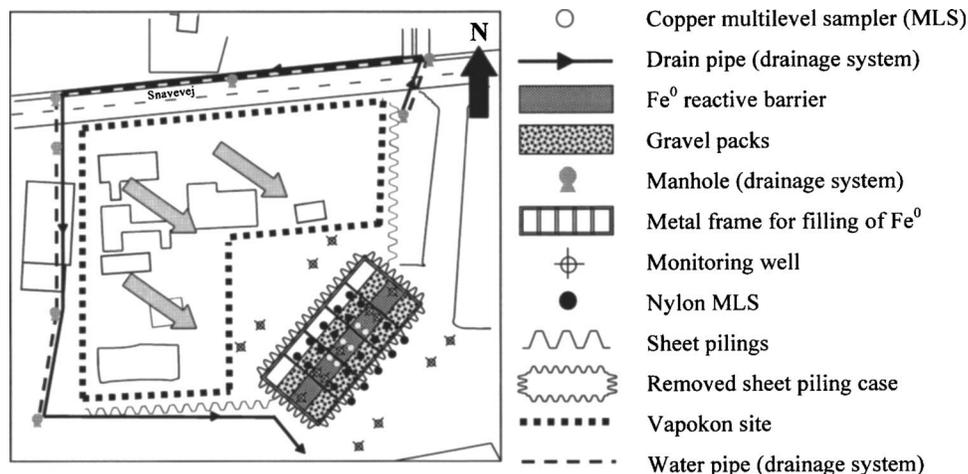


Fig. 1. Plan views of the funnel-and-gate Fe⁰ PRB and drainage system as well as plan distributions of the monitoring wells, nylon and copper multilevel samplers (not in scale)

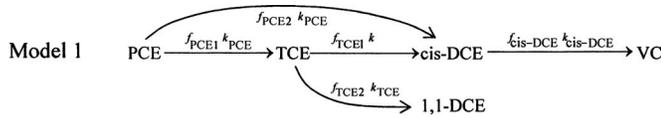
computation of k_{obs} . The highest concentration of CAHs measured in each sampling fence was considered to be the most reliable data indicating the change of CAH concentration of the center of the contaminant plume along the PRB and also the most representative of the concentration distribution through the wall (O'Hannesin and Gillham 1998). Therefore, k_{obs} of different CAHs can be determined by fitting the maximum concentration profile of CAHs along the reactive barrier into the analytical solution

$$\frac{C}{C_0} = \exp\left(\frac{\left(v_y - v_y \sqrt{1 + \frac{4k_{obs}D_y}{v_y^2}}\right)L_y}{2D_y}\right) \quad (1)$$

of one-dimensional advection–dispersion equation with first-order decay (van Genuchten 1981; Bedient et al. 1999)

$$R \frac{\partial C}{\partial t} = D_y \frac{\partial^2 C}{\partial y^2} - v_y \frac{\partial C}{\partial y} - k_{obs}C \quad (2)$$

However, in this study, an assumption of plug flow approximation within the reactive barrier was made and simple first-order equation was finally applied for k_{obs} determination because of the absence of an equation considering both CAH transport or dispersion and sequential dechlorination of CAHs within the reactive barrier. The first-order equations for Models 1, 2, and 3 are given, respectively, in



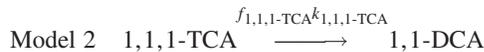
$$\frac{d[\text{PCE}]}{dt} = -k_{PCE}[\text{PCE}] \quad (3)$$

$$\frac{d[\text{TCE}]}{dt} = f_{PCE1} k_{PCE}[\text{PCE}] - k_{TCE}[\text{TCE}] \quad (4)$$

$$\begin{aligned} \frac{d[\text{cis-DCE}]}{dt} &= f_{PCE2} k_{PCE}[\text{PCE}] + f_{TCE1} k_{TCE}[\text{TCE}] \\ &\quad - k_{cis-DCE}[\text{cis-DCE}] \end{aligned} \quad (5)$$

$$\frac{d[\text{VC}]}{dt} = f_{cis-DCE} k_{cis-DCE}[\text{cis-DCE}] - k_{VC}[\text{VC}] \quad (6)$$

$$\frac{d[1,1\text{-DCE}]}{dt} = f_{TCE2} k_{TCE}[\text{TCE}] - k_{1,1\text{-DCE}}[1,1\text{-DCE}] \quad (7)$$



$$\frac{d[1,1,1\text{-TCA}]}{dt} = -k_{1,1,1\text{-TCA}}[1,1,1\text{-TCA}] \quad (8)$$

$$\begin{aligned} \frac{d[1,1\text{-DCA}]}{dt} &= f_{1,1,1\text{-TCA}} k_{1,1,1\text{-TCA}}[1,1,1\text{-TCA}] \\ &\quad - k_{1,1\text{-DCA}}[1,1\text{-DCA}] \end{aligned} \quad (9)$$

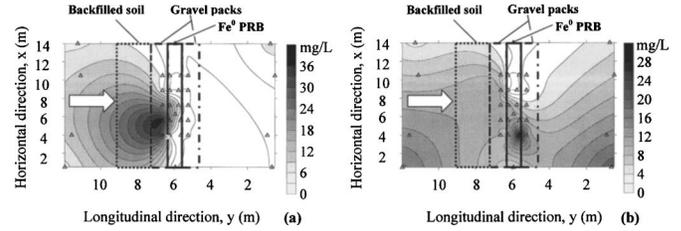


Fig. 2. Plan distributions of the sum of maximum concentration of (a) major chlorinated organics (MCOs) and (b) chlorinated daughter products (CDPs) across the Fe^0 PRB in January 2003. \cdots refers to the region of backfilled soil. \square , \square and \square indicate gravel packs and Fe^0 PRB, respectively. Δ represents the screens of the monitoring wells, nylon, and copper multilevel samplers.

$$\frac{d[\text{TCM}]}{dt} = -k_{\text{TCM}}[\text{TCM}] \quad (10)$$

They were applied to the maximum CAH concentrations measured in the first five sampling fences (i.e., located 0.0, 0.1, 0.4, 0.6, and 0.7 m from the upgradient edge of the reactive barrier). Since sequential transformations of PCE and TCE into *trans*-DCE by Fe^0 have not been proven (Su and Puls 1999), a first-order equation solely considering dechlorination of *trans*-DCE was used to determine $k_{\text{trans-DCE}}$, i.e.,

$$\frac{d[\text{trans-DCE}]}{dt} = -k_{\text{trans-DCE}}[\text{trans-DCE}] \quad (11)$$

Computation of the dechlorination rates of 1,2-DCA and DCM was not considered because these contaminants have been substantiated to be not treatable by Fe^0 (USEPA 1998). With the application of the f_{PCE1} (0.983), f_{PCE2} (0.017), f_{TCE1} (0.014), f_{TCE2} (0.003), $f_{cis-DCE}$ (0.048), and $f_{1,1,1\text{-TCA}}$ (0.441) previously determined by EnviroMetal Technologies Inc. (1998), Eqs. (3)–(11) were used directly in *SCIENTIST* (MicroMath 1995), which can perform integration and thereby calculate the k_{obs} of different CAHs by fitting the integrated solutions to the relevant experimental data using the least squares fitting method.

As mentioned, the k_{obs} was found to be directly proportional to λ_{SA} . Therefore, the dechlorination rate constant normalized to the ratio of the Fe^0 surface area to the solution volume (k_{SA}), which can be obtained from the following equation, is usually reported in the literature for comparison:

$$k_{SA} = \frac{k_{obs}}{\lambda_{SA}} \quad (12)$$

Results and Discussion

Performance of the Funnel-and-Gate Fe^0 PRB on CAH Remediation

Over the past 4 years, rapid dechlorination of MCOs and CDPs occurred across the reactive barrier and it was found that approximately 73–87% of the groundwater samples collected from the downgradient part of the Fe^0 PRB met the regulatory standards for drinking water (USEPA 1996; Masters 1998). Concerning the drinking water standards of TCE, 1,1-DCE, *trans*-DCE, 1,1,1-TCA, and TCM, over 90% of the collected groundwater samples met the regulatory requirements. As shown in Fig. 2(a), in January 2003, the sum of maximum concentration of MCOs in

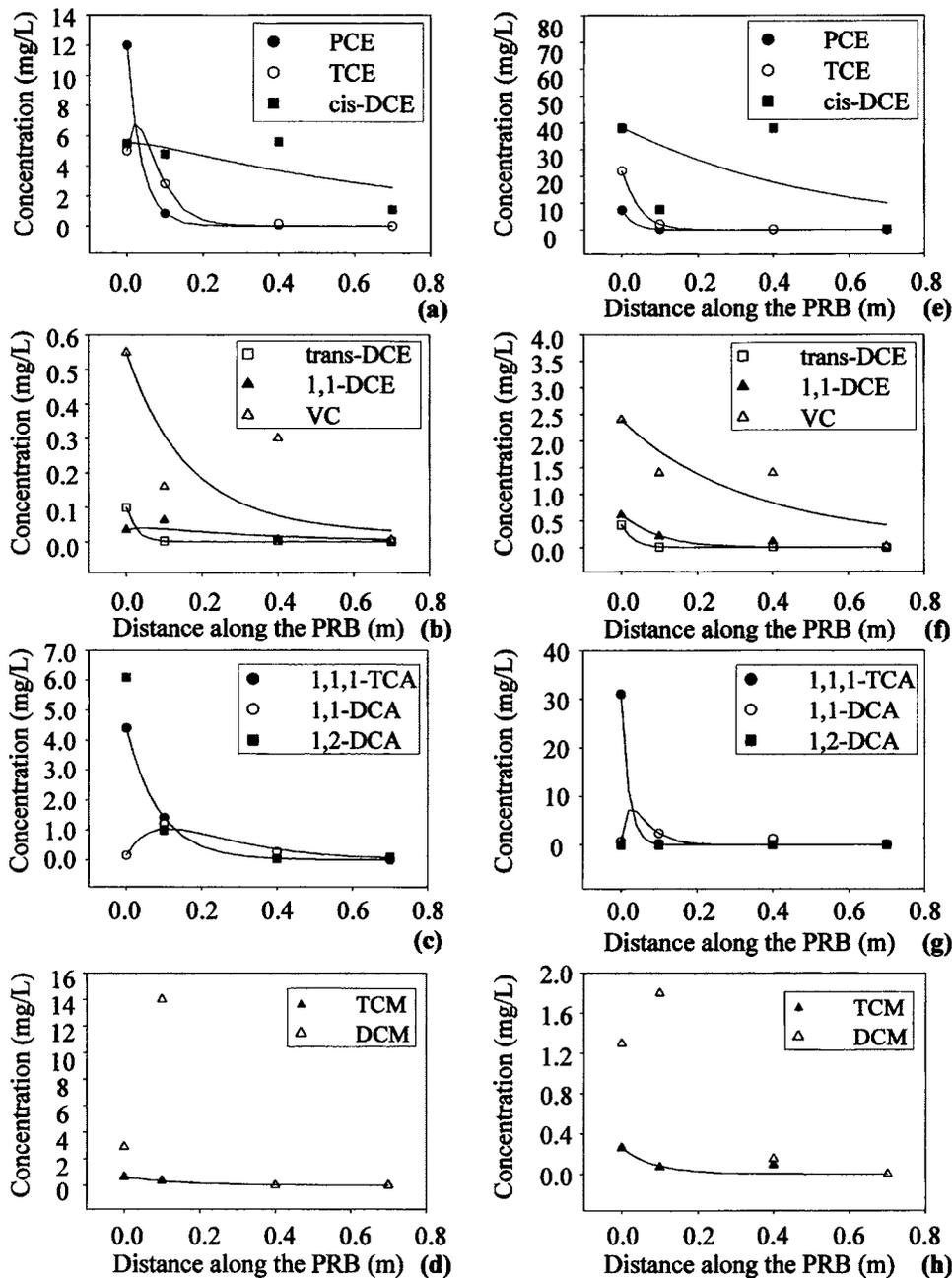


Fig. 3. Maximum concentrations of (a) PCE, TCE, and *cis*-DCE, (b) *trans*-DCE, 1,1-DCE, and VC, (c) 1,1,1-TCA, 1,1-DCA, and 1,2-DCA, as well as (d) TCM and DCM along the Fe^0 PRB in March 2000. Moreover, the highest concentrations of (e) PCE, TCE, and *cis*-DCE, (f) *trans*-DCE, 1,1-DCE, and VC, (g) 1,1,1-TCA, 1,1-DCA, and 1,2-DCA, as well as (h) TCM and DCM along the Fe^0 PRB in August 2003. The lines represent the best fit of the sequential dechlorination model to the data.

the Vapokon groundwater was about 38 mg/L in the immediate vicinity of the front edge of the Fe^0 PRB. Along the reactive barrier, the MCO concentration dropped to less than 0.6 mg/L just downgradient of the Fe^0 PRB. However, because of the high background concentration and the significant spatial variation in the Cl^- concentration in the groundwater, fluctuating between 6.32 and 113 mg/L (Table 1), a concurrent increase in the Cl^- concentration could not be observed. For the sake of understanding the variation of the performance of the Fe^0 PRB on CAH dechlorination, the k_{SA} of different CAHs obtained between March 2000 and August 2003 were compared. Figs. 3(a–h) show the maximum concentration profiles of different CAHs along the reactive barrier measured in March 2000 and August 2003 as well

as the corresponding fitted curves generated by *SCIENTIST* (MicroMath 1995). The CAH concentrations measured in the sampling fence located in the downgradient location of the PRB (i.e., 1.1–5.8 m downgradient from the front edge of the PRB) were omitted from the k_{SA} computation because of the interference from the desorption of CAHs from the native soil, as illustrated in Figs. 2(a–b).

Table 3 shows the k_{SA} of different CAHs obtained between March 2000 and August 2003. As seen, over the past 4 years, no pronounced deterioration in the iron barrier's performance on CAH dechlorination was observed even though there was continuous diminution in dissolved ions in the groundwater along the barrier, probably caused by mineral precipitation (Table 1). In-

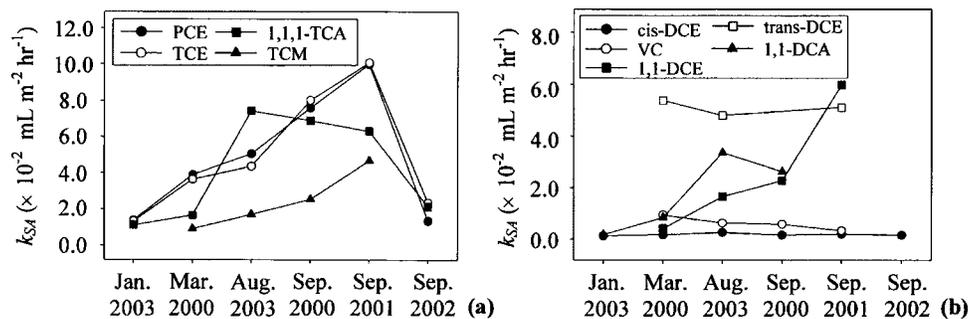


Fig. 4. Climatic variation of the k_{SA} of (a) PCE, TCE, 1,1,1-TCA, and TCM and (b) *cis*-DCE, VC, 1,1-DCE, *trans*-DCE, and 1,1-DCA

stead, fluctuation of the Fe^0 reactivity in CAH dechlorination was examined, particularly for PCE, TCE, and 1,1,1-TCA because their k_{SA} obtained in September 2000, September 2001, and August 2003 were approximately three- to four-fold higher than those obtained in March 2000, September 2002, and January 2003. The k_{SA} of *cis*-DCE and *trans*-DCE, on the contrary, were fairly stable over the past 4 years with standard deviations of about 0.0005 and 0.0029 $mL\ m^{-2}\ h^{-1}$, respectively.

Despite the fact that low Fe^0 reactivity on PCE, TCE, and 1,1,1-TCA dechlorination was recorded in March 2000, September 2002, and January 2003, the removal efficiency of MCOs across the reactive barrier did not exhibit severe deterioration at those times. On average, between March 2000 and August 2003, about 97.5% of MCOs in the groundwater were removed by the PRB although the removal efficiency was comparatively low in September 2002 (91.6%) and January 2003 (96.5%). The insignificance of the influence of the low Fe^0 reactivity on MCO removal is most likely due to most of MCOs being dechlorinated into nondetectable levels in the first half of the reactive barrier [Figs. 3(a, c, e, and g)]. Therefore, even though there was deterioration in the PCE, TCE, and 1,1,1-TCA dechlorination rates in March 2000, September 2002, and January 2003, the downgradient part of the reactive barrier still provided enough residence time for the effective removal of MCOs, thereby maintaining high efficiency in MCO removal throughout the whole study period.

In March 2000, September 2000, September 2001, and August 2003, approximately 92.4% of CDPs in groundwater was dechlorinated into harmless products across the PRB. Because of the sequential dechlorination from the corresponding MCOs, there were intermediate increases in CDP concentrations in the upgradient part of the PRB prior to the significant drop in the concentrations in the downgradient part of the reactive barrier (see Fig. 3). In September 2002 and January 2003, however, poor performance of the Fe^0 PRB on CDP dechlorination was observed. As shown in Fig. 2(b), in January 2003, the peak concentration of the CDPs within the PRB was examined appearing at the end of the PRB rather than the upgradient part of the reactive barrier. Similar phenomenon could also be observed in September 2002. As you can see from Table 2, *cis*-DCE was the dominant CDP in the contaminant plume and its rate of dechlorination between March 2000 and August 2003 was quite stable without a noticeable decrease in k_{SA} in September 2002 and January 2003 (Table 3). Therefore, the appearing of the peak concentration of CDPs or *cis*-DCE at the end of the PRB in September 2002 and January 2003 was not due to the low Fe^0 reactivity in *cis*-DCE dechlorination. In fact, the low rate of dechlorination of PCE and TCE in September 2002 and January 2003 are believed to be one of the underlying reasons for the poor performance of the PRB on CDP removal since PCE and TCE could dechlorinate into *cis*-DCE

within the Fe^0 PRB (EnviroMetal Technologies Inc. 1998). The reduction of PCE and TCE k_{SA} in September 2002 and January 2003 consequently shifted the peak concentration of *cis*-DCE from the upgradient part to the end of the reactive barrier, resulting in an increase in the *cis*-DCE concentration across the PRB.

The low Fe^0 reactivity of PCE and TCE dechlorination in March 2000 did not adversely influence the removal efficiency of CDPs at that time in which about 92.8% of CDPs were removed from the Vapokon groundwater across the barrier. The insignificance of the influence from the low k_{SA} of PCE and TCE on the CDP removal is believed to pertain to the low CAH concentrations in the Vapokon groundwater in March 2000 (Table 2). As described, 4,600 tons of heavy contaminated soil were first excavated from the hotspot prior to the installation of the Fe^0 PRB in September 1999. Most likely owing to the removal of the main source of contamination and the slow rate of desorption of CAHs from the remaining contaminated soil, the CAH concentration in the Vapokon groundwater was relatively low in March 2000 compared with those between September 2000 and August 2003. Low PCE and TCE concentrations in the groundwater consequently led to minor production of *cis*-DCE within the reactive barrier, thereby indicating an insignificant contribution from PCE and TCE dechlorination to the peak concentration of *cis*-DCE within the PRB. As a consequence, no significant detrimental effect on the CDP removal was exerted from the low dechlorination rate of PCE and TCE in March 2000.

Climatic Variation of the Performance of the Fe^0 PRB

Careful examination of Table 3 indicates that, except for September 2002, the k_{SA} of different CAHs obtained in the cold season (i.e., January 2003 and March 2000) were usually smaller than those measured in the hot season (i.e., August 2003, September 2000, and September 2001). As you can see from Figs. 4(a and b), excluding the k_{SA} obtained in September 2002, the k_{SA} generally increased in the following order: January, March, August, and September, thereby indicating climatic variation in the barrier's performance on CAH dechlorination. According to Table 1, the groundwater temperature in cold season (i.e., January 2003) was observed approximately 3.5–5.6°C lower than that in hot season (i.e., September 2002). Probably owing to the low temperature in the groundwater in the cold season, the Fe^0 reactivity in CAH dechlorination was comparatively low in January 2003 and March 2000, since the dechlorination reactions of CAHs by Fe^0 have been substantiated primarily to be reaction-limited kinetics (Su

Table 3. Variations of the Normalized Dechlorination Rate Constant ($k_{SA} \times 10^{-2}$) of Different CAHs between March 2000 and August 2003

Parameters/date		March 2000	September 2000	September 2001	September 2002	January 2003	August 2003
PCE	k_{SA}	3.90	7.59	10.00	1.34	1.39	5.04
	R^2	1.000	0.987	0.989	0.955	0.993	1.000
TCE	k_{SA}	3.64	8.01	10.09	2.36	1.33	4.36
	R^2	0.999	0.984	0.940	0.992	0.998	1.000
<i>cis</i> -DCE	k_{SA}	0.18	0.17	0.21	0.17	0.14	0.28
	R^2	0.930	0.861	0.569	0.835	0.851	0.632
VC	k_{SA}	0.95	0.60	0.34	na	na	0.64
	R^2	0.824	0.741	0.766	na	na	0.933
1,1-DCE	k_{SA}	0.43	2.28	5.98	na	na	1.66
	R^2	0.850	0.965	0.915	na	na	0.975
<i>trans</i> -DCE	k_{SA}	5.38	nc	5.11	nc	nc	4.80
	R^2	0.999	nc	0.760	nc	nc	0.998
1,1,1-TCA	k_{SA}	1.67	6.89	6.30	2.14	1.12	7.43
	R^2	1.000	0.996	0.987	0.694	0.998	0.999
1,1-DCA	k_{SA}	0.85	2.62	nc	nc	0.19	3.36
	R^2	0.975	0.951	nc	nc	0.524	0.786
TCM	k_{SA}	0.91	2.55	4.67	nc	nc	1.71
	R^2	0.993	0.944	0.645	nc	nc	0.899

Note: na represents not available and nc refers to not calculable. The unit of k_{SA} is milliliter per square meter per hour ($\text{mL m}^{-2} \text{h}^{-1}$). R^2 means coefficient of determination. The k_{SA} for every CAH was calculated from their maximum concentration profiles along the Fe^0 PRB.

and Puls 1999). The low temperature in groundwater might consequently lower the rate of oxidation of Fe^0 or the release of the electrons from Fe^0 and thereby adversely affected the rate of dechlorination reactions in the cold season.

The abnormally low rate of dechlorination of CAHs in September 2002, however, is most likely attributed to the high DO content in the groundwater at that time. During the day of groundwater sampling in September 2002, because of recharge from rainfall, the DO content in the groundwater, on average, was about 6.25 mg/L (4.50–9.90 mg/L), which was much higher than the usual DO content measured in the Vapokon groundwater (i.e., about 0.40–0.70 mg/L). The DO in the groundwater did not just compete with CAHs for the electrons released from Fe^0 ; it reduced the availability of the reactive site on the Fe^0 surface for the dechlorination reaction and inhibited the binding rate between the Fe^0 surface and CAHs, thereby slowing the dechlorination kinetics in September 2002 (Helland et al. 1995).

Geochemical Variation in the Vapokon Groundwater along the PRB

The OH^- and electrons emanating from the oxidation of Fe^0 caused an increase of 2.5–3.3 pH units and nearly 300 mV decrease in the redox potential across the reactive barrier. The pH between 9.50 and 10.62 as well as about –150 mV of redox potential within the PRB encouraged the transformation of oxygen and hydrogen in the groundwater into lower oxidation states, reduced the solubility of minerals and enhanced the surface complexation of cations on iron oxide (Yabusaki et al. 2001). In addition, biologically mediated reduction of SO_4^{2-} into sulfide probably by sulfate-reducing bacteria led obvious drop in SO_4^{2-} concentration across the barrier (Gu et al. 2002). As a consequence, across the reactive barrier, on average, there were approximately 81.7% decrease in Ca^{2+} , 57.0% reduction in Mg^{2+} , 90.3% diminution in TAL, as well as 69.2% drop in SO_4^{2-} , result-

ing in 64.1% decrease in specific conductance in the groundwater (Table 1). There was also a small decrease in or insignificant change of the Fe_T concentration along the Fe^0 PRB despite ferrous and ferric irons being released from the oxidation of Fe^0 .

Because carbonate ion (CO_3^{2-}) is predominant in the carbonate system at pH 9.50–10.62 (Freeze and Cherry 1979), these decreases in concentration along the barrier indicate a high likelihood of the formation of carbonate precipitates including calcite (CaCO_3), carbonate-containing green rust $\{[\text{Fe}_4^{2+}\text{Fe}_2^{3+}(\text{OH})_{12}]^{2+}[\text{CO}_3 \cdot 2\text{H}_2\text{O}]^{2-}\}$, dolomite [$\text{CaMg}(\text{CO}_3)_2$], magnesite (MgCO_3) and siderite (FeCO_3) (Mackenzie et al. 1999; USEPA 1999; Bonin et al. 2000). The relatively low quantity of Mg^{2+} removed from the groundwater, which was in a range of 24.4–43.5 mg/L as CaCO_3 , across the reactive barrier compared with the quantities of Ca^{2+} (366 mg/L as CaCO_3) and TAL (286 mg/L as CaCO_3) removed indicates an insignificant precipitation of dolomite and magnesite on the Fe^0 surface. Formation of oxyhydroxide or oxide precipitates such as goethite ($\alpha\text{-FeOOH}$), and magnetite (Fe_3O_4) were also expected with high pH and low redox potential conditions (Bonin et al. 1998; Farrell et al. 2000). As Ca^{2+} , CO_3^{2-} , and SO_4^{2-} were the major dissolved ions precipitated from the Fe^0 PRB (Table 1), it is believed that calcite and mackinawite (FeS) were the precipitates most likely formed inside the PRB (USEPA 2003).

Except for carbonate-containing green rust and magnetite, all the mineral precipitates possibly formed on the surface of Fe^0 have the ability to passivate Fe^0 , thereby preventing Fe^0 corrosion as well as the generation of Fe^{2+} and hydrogen gas (USEPA 1998; Ritter et al. 2002). Since dechlorination of CAHs through hydrogenolysis and reductive- β -elimination pathways involves a direct transfer of electrons from the Fe^0 surface to the contaminants as well as an indirect electron transfer from Fe^{2+} or via catalytic hydrogenolysis by hydrogen gas, the formation of passive precipitates on the Fe^0 surface can potentially prevent both direct and indirect transfers of electrons and thereby adversely affect the Fe^0 reactivity on CAH dechlorination. However, the lack of deterio-

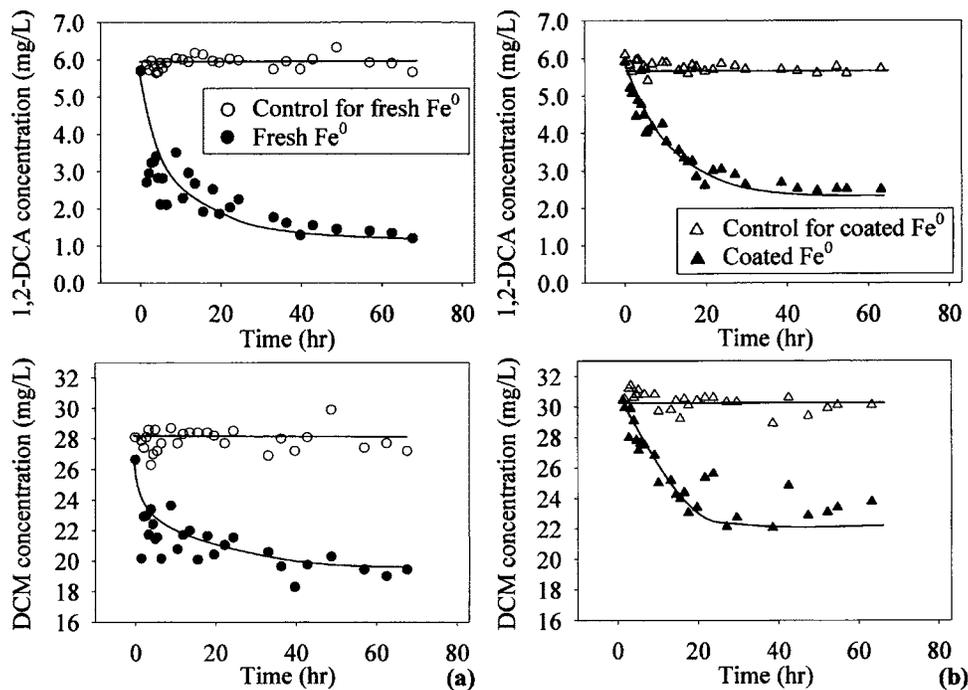


Fig. 5. Adsorption of 1,2-DCA and DCM by (a) fresh Fe^0 (\circ) and (b) coated Fe^0 (\triangle)

ration in the rate of CAH dechlorination by the Fe^0 over the past 4 years indicates the insignificance of the passivated effect from the mineral precipitation, probably due to the precipitation of minerals on the nonreactive site of Fe^0 surface rather than the reactive site for the CAH dechlorination (Deng et al. 2003). Instead, given the results from the natural gradient tracer experiment (Lai et al. 2004), the potential influence of mineral precipitation on the hydraulic performance of the PRB (e.g., the flow pattern of the groundwater, the hydraulic conductivity and the groundwater flow velocity) was rather more significant than that on CAH dechlorination.

By assuming that calcite and mackinawite were the only precipitates formed inside the barrier as well as by selecting the Fe^0 corrosion rate to be 0.4 mmol/kg d (Reardon 1995), it was figured that mineral precipitation caused 2.14 m^3 loss of void volume throughout the whole reactive barrier between March 2000 and August 2003, which corresponded to 3.46% total loss of porosity or 0.88% loss per year. However, the practical rate of percentage loss of porosity in the Fe^0 PRB should be higher than 0.88% per year, because most dissolved ions were precipitated out of the first half of the barrier. Based upon the information listed in Table 1, about 84.7% decrease in Ca^{2+} , 54.2% drop of Mg^{2+} , 72.6% diminution in TAL, and 93.2% reduction in SO_4^{2-} were observed in the first half of the PRB, thereby consequently causing 6.60% total porosity loss or 1.68% loss per year in the front part of the barrier.

Microbial Degradation and Fe^0 Adsorption of Chlorinated Aliphatic Hydrocarbons

Despite the fact that 1,2-DCA and DCM were proven to be not treatable by Fe^0 (USEPA 1998), obvious removal of these contaminants from the Vapokon groundwater occurred during the past 4 years. As shown in Figs. 3(c and d), the concentration of

1,2-DCA dropped from 6.10 to 0.04 mg/L across the PRB in March 2000 whereas the concentration of DCM dropped from 14.00 to 0.01 mg/L within the reactive barrier. More obvious decrease in DCM concentration could also be observed in September 2000 and September 2001 in which across the Fe^0 PRB, the concentration in groundwater reduced from 33.00 and 15.00 mg/L to approximately 0.46 and 0.81 mg/L, respectively. Microbial degradation or adsorption by Fe^0 , or both are believed to be the cause of the removal of 1,2-DCA and DCM (Burris et al. 1995; Mägli et al. 1998; Deng et al. 2003). In fact, Bower and McCarty (1983) reported the possibility of transformation of 1,2-DCA under methanogenic condition. Moreover, biodegradation of DCM has also been mentioned by Freedman and Gossett (1991) and Kohler-Staub et al. (1995). Unfortunately, the contribution of microbial degradation cannot be verified at the moment since further iron core sampling followed by phospholipid fatty acids and DNA analyses of the microorganisms growing on the core sample are required (Gu et al. 2002). However, the adsorption of 1,2-DCA and DCM by Fe^0 were directly substantiated through the time series batch experiments using fresh and coated Fe^0 .

Figs. 5(a and b) illustrate the results of the batch experiments. There were significant drops in the concentrations of 1,2-DCA and DCM in both batch experiments containing fresh and coated Fe^0 . Since the concentrations in the corresponding control experiments were relatively steady, the significant decrease in 1,2-DCA and DCM concentrations conclusively indicate adsorption by Fe^0 . The equilibrium times for 1,2-DCA and DCM adsorption by fresh Fe^0 were nearly 40 h, whereas it took about 25–30 h for them to reach equilibrium with the coated Fe^0 . Although precipitation of calcium and iron carbonates on the Fe^0 surface shortened the equilibrium time for the adsorption, it could adversely affect the amount of adsorbates to be sorbed by the Fe^0 . Each kilogram of fresh Fe^0 adsorbed approximately 2.18 mg of 1,2-DCA and

3.49 mg of DCM, whereas only 1.69 mg of 1,2-DCA and 3.32 mg of DCM was adsorbed per kilogram of coated Fe⁰.

Conclusions

Results from the 4-year monitoring of the performance of the funnel-and-gate Fe⁰ PRB installed at the Vapokon site, Denmark indicated effective removal of CAHs from the groundwater. Over the past 4 years, approximately 97.5% of MCOs were removed from the groundwater across the PRB and approximately 92.4% of CDPs were removed except in September 2002 and January 2003. Moreover, on average, about 73–87% of groundwater samples collected from the downgradient part of the reactive barrier met the environmental standards for drinking water. Even though there was continuous diminution in dissolved ions in the groundwater along the barrier, probably caused by mineral precipitation, no evident deterioration of the iron barrier's performance was observed, thereby indicating the insignificance of the passivated effects exerted from mineral precipitation. Instead, over the past 4 years, climatic variation in the performance of the PRB on CAH dechlorination was indicated. In general, most likely owing to the low groundwater temperature in the cold season, the k_{SA} of CAHs in January 2003 and March 2000 were smaller than those in August 2003, September 2000, and September 2001 (i.e., the hot season) especially for PCE, TCE, and 1,1,1-TCA. The unusually low rate of dechlorination in September 2002 was probably due to the high DO content in the groundwater caused by recharge from rainfall since the oxygen competed with CAHs for the electrons released from Fe⁰.

The high pH and low redox potential conditions within the reactive barrier as well as the possible presence of sulfate-reducing bacteria consequently led to significant decreases in Ca²⁺, Mg²⁺, TAL, and SO₄²⁻ in the groundwater across the PRB. Among various mineral precipitates possibly formed on the Fe⁰ surface, calcite, and mackinawite are expected to be the precipitates most likely formed within the PRB since Ca²⁺, TAL, and SO₄²⁻ were the major dissolved ions being precipitated out, thereby theoretically resulting in 3.46% total loss of porosity or 0.88% loss per year. Based upon the monitoring results over the past 4 years, it is expected that there will be still no significant loss of the reactivity of the Fe⁰ PRB in CAH dechlorination in the next 5–10 years. However, the continuous loss of porosity due to the mineral precipitation will be problematic, which will significantly deteriorate the hydraulic performance of the reactive barrier and may consequently limit the barrier's longevity to only about 10 years.

1,2-DCA and DCM, which are not treatable by Fe⁰, were found to be removed from the groundwater across the PRB, thereby indicating the enhancement of the barrier's performance from microbial degradation or Fe⁰ adsorption. According to the results from the times series batch experiments, adsorption of 1,2-DCA and DCM by Fe⁰ was conclusively substantiated in which 2.18 mg of 1,2-DCA and 3.49 mg of DCM as well as 1.69 mg of 1,2-DCA and 3.32 mg of DCM could be adsorbed per kilogram of fresh and coated Fe⁰, respectively.

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Notation

The following symbols are used in this paper:

- C = CAH concentration at a longitudinal distance L_y (mg L⁻¹);
- C_0 = initial CAH concentration (mg L⁻¹);
- [*cis*-DCE] = *cis*-DCE concentration along the Fe⁰ PRB (mg L⁻¹);
- D_y = longitudinal dispersion coefficient (m² h⁻¹);
- $f_{cis-DCE}$ = molar fraction of *cis*-DCE converting into VC;
- f_{PCE1} = molar fraction of PCE converting into TCE;
- f_{PCE2} = molar fraction of PCE converting into *cis*-DCE;
- f_{TCE1} = molar fraction of TCE converting into *cis*-DCE;
- f_{TCE2} = molar fraction of TCE converting into 1,1-DCE;
- f_{TCM} = molar fraction of TCM converting into DCM;
- $f_{1,1,1-TCA}$ = molar fraction of 1,1,1-TCA converting into 1,1-DCA;
- $k_{cis-DCE}$ = *cis*-DCE k_{obs} (h⁻¹);
- k_{obs} = observed first-order dechlorination rate constant (h⁻¹);
- k_{PCE} = PCE k_{obs} (h⁻¹);
- k_{SA} = dechlorination rate constant normalized to the ratio of Fe⁰ surface; area to solution volume (mL m⁻² h⁻¹);
- k_{TCE} = TCE k_{obs} (h⁻¹);
- k_{TCM} = TCM k_{obs} (h⁻¹);
- $k_{trans-DCE}$ = *trans*-DCE k_{obs} (h⁻¹);
- k_{VC} = VC k_{obs} (h⁻¹);
- $k_{1,1-DCA}$ = 1,1-DCA k_{obs} (h⁻¹);
- $k_{1,1-DCE}$ = 1,1-DCE k_{obs} (h⁻¹);
- $k_{1,1,1-TCA}$ = 1,1,1-TCA k_{obs} (h⁻¹);
- L_y = longitudinal distance of transport along the Fe⁰ PRB (m);
- [PCE] = PCE concentration along the Fe⁰ PRB (mg L⁻¹);
- R = retardation factor;
- [TCE] = TCE concentration along the Fe⁰ PRB (mg L⁻¹);
- [TCM] = TCM concentration along the Fe⁰ PRB (mg L⁻¹);
- [*trans*-DCE] = *trans*-DCE concentration along the Fe⁰ PRB (mg L⁻¹);
- t = time (h);
- [VC] = VC concentration along the Fe⁰ PRB (mg L⁻¹);
- v_y = groundwater velocity in longitudinal direction (m h⁻¹);
- y = longitudinal distance (m);
- [1,1-DCA] = 1,1-DCA concentration along the Fe⁰ PRB (mg L⁻¹);
- [1,1-DCE] = 1,1-DCE concentration along the Fe⁰ PRB (mg L⁻¹);
- [1,1,1-TCA] = 1,1,1-TCA concentration along the Fe⁰ PRB (mg L⁻¹); and

$$\lambda_{SA} = \text{ratio of Fe}^0 \text{ surface area to solution volume} \\ (\text{m}^2 \text{ mL}^{-1}).$$

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