

IN SITU OXIDATION BY FRACTURE EMPLACED REACTIVE SOLIDS

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ABSTRACT: In low permeability but naturally fractured media, vertical leaching or volatilization of toxic organic compounds can lead to high exposures and unacceptable human health or environmental risk. A field test was recently completed to evaluate in situ remediation at such sites by using hydraulic fracturing to emplace iron metal (Fe⁰) and permanganate (KMnO₄) solids in the subsurface to chemically treat trichloroethylene (TCE). At an old land treatment site, two test cells were installed in silty clay soils with hydraulic fractures filled with either iron metal or permanganate solids at 1.8, 2.4, and 3.6 m depths. Fracture emplacement was monitored, and soil and ground water conditions were characterized. After 3, 10, and 15 mo of emplacement, continuous cores were collected and morphologic and geochemical data were taken across the fracture zones. Controlled degradation tests were completed using site ground water with TCE concentrations near 53, 144, and 480 mg/L, equivalent to 0.5, 1.2, and 4.1 g TCE per kg media, respectively. The iron-filled fractures formed a discrete reactive seam less than 1 cm thick, wherein the Eh decreased and reductive dechlorination could occur, but effects in the adjacent silty clay soils were negligible. Though the emplaced iron exhibited some surface corrosion after extended emplacement in the subsurface, its reactivity was unaffected. Iron from the fractures degraded TCE at efficiencies of as much as 36% after 24–48 hr of contact, which is consistent with Fe⁰ packed bed degradation half-lives of 1 to 2 hr. The permanganate-filled fractures yielded a diffuse reactive zone that expanded over time, reaching 40 cm in thickness after 10 mo. Throughout this oxidizing zone, the degradation efficiency was >99% after 2 hr of contact for dissolved TCE at 0.5 and 1.2 mg TCE per g of media. When exposed to higher TCE loadings (i.e., 4.1 mg per g), degradation efficiencies after 10 mo dropped to 70% as the TCE load exceeded the oxidant capacity remaining. These efficiencies and rates are consistent with oxidation stoichiometry and previously determined half-lives of <2 min for permanganate oxidation of TCE. In both test cells there were no marked effects on the chemistry or contamination levels in the ground water beneath the cells. Though the results of this research are promising for emplacement of horizontal treatment zones, further work is required to support full-scale application.

INTRODUCTION

Petrochemicals (e.g., benzene) and chlorocarbons (e.g., trichloroethylene, or TCE) are common and problematic contaminants of concern (COCs) at federal facilities and industrial sites across the United States and abroad (Huling and Weaver 1991; U.S. EPA 1992; Siegrist and van Ee 1994; Siegrist et al. 1994; *Petroleum* 1995; DOE 1996). They are often present in source areas near storage tanks and land treatment sites and in associated soil and ground water plumes, where they can exist as vapor, dissolved or sorbed phase constituents, as well as light or dense nonaqueous phase liquids (LNAPLs or DNAPLs). When these COCs are present in low permeability media (LPM) such as silt and clay deposits, there are major challenges with assessment of their behavior and implementation of effective in situ remediation technologies (*Petroleum* 1995; DOE 1996). Despite a low bulk permeability ($K_{rel} < 10^{-5}$ cm/s), these COCs contaminate LPM deposits by moving into and through natural pore and fracture networks, where they partition into multiple phases (Fig. 1). Exposures and unacceptable risk can result from drinking contaminated drinking

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water, ingesting surface soil media, or inhaling vapors that are emitted during showering. In recognition of the need for effective in situ remediation methods, DNAPL compounds in LPM deposits was recently ranked as a top environmental restoration need across the Department of Energy (DOE) Complex (DOE 1996). Similarly, nearly 40% of the underground storage tanks in the world are located on clay soils, and in situ remediation of LNAPL contamination in these settings has been a major challenge for the petroleum industry (*Petroleum* 1995).

In situ remediation by conventional methods such as soil vapor extraction or biodegradation are often ineffective at LPM sites due to poor accessibility to the contaminants and severe mass transfer limitations (*Petroleum* 1995; DOE 1996; Freeze and McKay 1997). Alternative techniques to enhance in situ remediation have been developed based on subsurface disruption by soil mixing (e.g., Siegrist et al. 1995; West et al. 1995; Cline et al. 1997) or the alternative driving forces of electrokinetics (e.g., Probst and Hicks 1993; Shapiro and

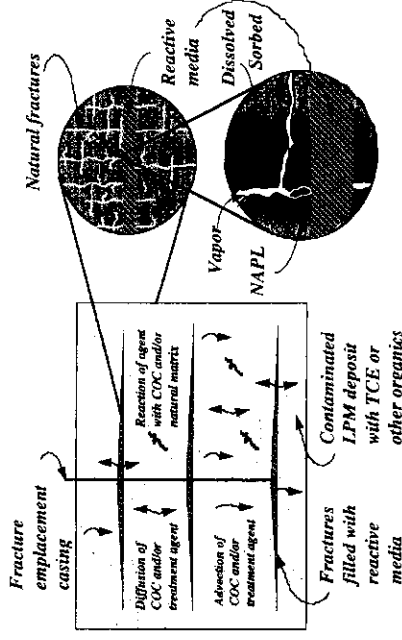


FIG. 1. Illustration of DNAPL Compounds in LPM and Emplacement of DNAPL Compounds to Create Horizontal Treatment Zones

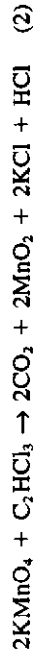
Probst 1993; Ho et al. 1995; Murdoch and Chen 1997). In seeking less intensive methods that could be used over larger areas, multipoint injection and permeation methods have been tested and advanced soil fracturing techniques have been developed (Murdoch et al. 1997a and b; Siegrist et al. 1998a and b).

With soil fracturing, it is feasible to create fractures in LPM deposits by injecting a viscous liquid containing a high content of suspended granular solids (U.S. EPA 1993; Murdoch et al. 1994). The granular solids remain in the fracture after injection, and the properties of the solids can be exploited for in situ remediation. Hydraulic fracturing normally employs sand as a proppant to fill and support the fracture opening and prevent fracture closure during natural healing processes in unconsolidated deposits. Fractures filled with sand can enhance the rate of recovery of fluids from an LPM deposit or aid the delivery of reactive fluids into it. Alternatively, fractures filled with chemically reactive media such as iron metal or permanganate solids can be used to immobilize or degrade organic contaminants in situ (Murdoch et al. 1997a and b).

Zero valent iron metal (Fe^0) as a treatment media has been the subject of intense research and development during the past five years (Gillham and O'Hannesin 1994; Matheson and Tratnyek 1994; Agrawal and Tratnyek 1996; Muflikian et al. 1996; Liang et al. 1997). Based on favorable laboratory results, full-scale applications of permeable iron walls for in situ treatment of contaminated ground water are rapidly increasing (Bavasker et al. 1997; O'Hannesin and Gillham 1998). The reductive dechlorination reaction for TCE to dichloroethene by Fe^0 is shown in (1). The complete dechlorination reaction for TCE to ethene and ethane involves single and multiple electron transfers following pseudo-first order kinetics with half-lives reported to be on the order of 30–60 min as normalized for the solution to solid surface area typical of a packed bed of iron particles (Gavasker et al. 1997; Liang et al. 1997; O'Hannesin and Gillham 1998). The pH of the reacting system tends to rise, but appears to stabilize in the pH 9–10 range due to iron hydroxide precipitation. Key reaction products can include daughter chlorocarbons such as dichloroethenes and vinyl chloride (leading to ethenes and ethanes), hydrogen gas, chlorides, and iron oxide and hydroxide precipitates. Accelerated reaction rates and reduced production of vinyl chloride have been reported with palladized iron metal (Muflikian et al. 1996).



The use of potassium permanganate (KMnO_4) for oxidative degradation of TCE and other organics at contaminated sites has more recently evolved through initial laboratory experimentation with volatile and semivolatile organics in soil and water (Vella and Veronda 1992; Gates et al. 1995; Yan and Schwartz 1996; Case 1997). Recently there have been several field demonstrations including two where recirculation wells have been used to treat TCE DNAPLs in ground water aquifers (Cline et al. 1997; Schnarr et al. 1998; West et al. 1998). The oxidative destruction of TCE by KMnO_4 is given in (2). The reaction can include destruction by direct electron transfer or free radical advanced oxidation. The reaction follows pseudo-first order kinetics and is rapid, with half-lives on the order of 1–2 min. The pH of the reacting system can decline to strongly acidic conditions (e.g., pH 2–3) depending on the buffering capacity of the reaction system. Key reaction products can include intermediate organic acids along with production of manganese oxide solids and chlorides.



While there has been extensive research and development followed by increasing application of vertical treatment zones, particularly with iron metal in permeable aquifer settings (e.g., Gavaskar et al. 1997; O'Hannesin and Gillham 1998; NATO 1998), research and development of horizontal treatment zones, particularly those comprised of permanganate solids and within LPM deposits, has only recently been initiated (e.g., Murdoch et al. 1997b; Siegrist et al. 1998a and b). During the past three years, the writers have been studying in situ treatment zones for degradation of TCE in LPM deposits wherein chemically reactive agents are replaced by permeation lances or fracturing techniques. This paper presents a synopsis of a field test to evaluate hydraulic fracturing with iron metal or permanganate solids to achieve in situ destruction of TCE. Further details regarding this work as well as a description of related work with thermally enhanced mass recovery may be found in Siegrist et al. (1998a). A general discussion of advanced fracturing employing reactive media is given in Murdoch et al. (1997a and b), while information on supporting laboratory experimentation may be found in Case (1997).

MATERIALS AND METHODS

Field Test Cells

In September 1996, two test cells were established at the X231-A land treatment site located at the DOE Portsmouth Gaseous Diffusion plant in central Ohio. The 2.2 ha site was used for disposal of waste oils and solvents during the 1970s until its use was terminated around 1980 and it was capped with a temporary geomembrane. Comprised of unconsolidated Quaternary-age deposits, the site is underlain by 6–8 m of low-permeability clays and silts ($K_{sat} < 10^{-6}$ cm/s) known as the Minford member (Table 1). The Minford has a naturally occurring platy structure and vertically dipping fractures that provide pathways for vertical migration of contaminants released during land treatment of wastes. Underlying the Minford is a moderately permeable sand known as the Gallia member, which consists of pebbles and gravel in a fine-grained, silty-sand matrix that is 1–2.5 m thick. Precipitation percolates through the Minford member to a zone of permanent saturation at about a 4 m depth, and eventually it reaches the Gallia member, where flow is predominantly horizontal. Previous characterization activities at the site revealed total volatile organic compounds (VOCs) in soil (dominantly TCE) ranging to as much as 300 mg/kg, whereas ground water at the site contained variable concentrations of TCE including some DNAPL. To support evaluation and implementation of in situ remediation at the DOE Portsmouth plant, a program of demonstration activities, including several focused on the DNAPL compounds in the Minford LPM deposit, had been ongoing there since 1990. For example, mixed region vapor stripping had been demonstrated at the adjacent X-231B land disposal site (Siegrist et al. 1995).

Within a corner of the X-231A site, two test cells were established for evaluation of reactive fractures as horizontal treatment zones (Fig. 2) (Siegrist et al. 1998a). Each of the test cells comprised five horizontal fractures stacked one over the other within a subsurface region roughly 6 m in diameter and 5 m deep (Fig. 3, Table 2). Sand-filled fractures were propagated at nominal depths of 1.2 and 4.9 m with fractures containing reactive media propagated at depths of 1.8, 2.4, and 3.6 m. In one test cell, iron metal in the form of 0.2 mm diameter Fe^0 particles (Master Builder) was suspended in guar gum gel, and this slurry was used to create three iron-filled fractures. In another test cell, an oxidative particle mixture (OPM) consisting of 0.1–0.3 mm diameter KMnO_4 particles (Carus Chemical) suspended in a mineral-based gel was used to create three permanganate-filled fractures. In each test cell,

TABLE 1. Summary of Test Site Characteristics [after Slegrist et al. (1998a)]

Characteristic (1)	Units (2)	Conditions (3)
Soil type and genesis	—	Minford silty clay deposit of fluvio-lacustrine origin. Typically with 4.6 m thick upper clay unit (CH) transitioning to lower 3.0 m thick silt unit (CL).
Soil particle size distribution	dry wt.%	~0.5
Sand size (0.050–2.000 mm)	dry wt.%	~60–85
Silt size (0.002–0.050 mm)	dry wt.%	~10–35
Clay size (<0.002 mm)	—	
Soil mineralogy	—	In Minford, sand fraction consists of mainly quartz with minor goethite. Silt fraction consists of quartz and minor feldspars but no goethite. Clay fraction is mixture of illite (~33%), quartz (~29%), kaolinite (~26%), and smectite (~12%).
Soil biogeochemical properties	8/cm ³	1.8
Bulk density	wet wt.%	20%
Water content	%	~60
Liquid limit	%	~35
Plastic index	v/v	0.40
Total fractional porosity	% pores	6.0
Water-filled porosity	—	500–1,500
pH (in water)	mg/kg	23,000
Organic carbon	mg/kg	1,350
Iron oxides—free	meq/100g	17.5
Iron oxides—amorphous	org./g	100–10,000
Cation exchange capacity	—	
Total bacteria	—	

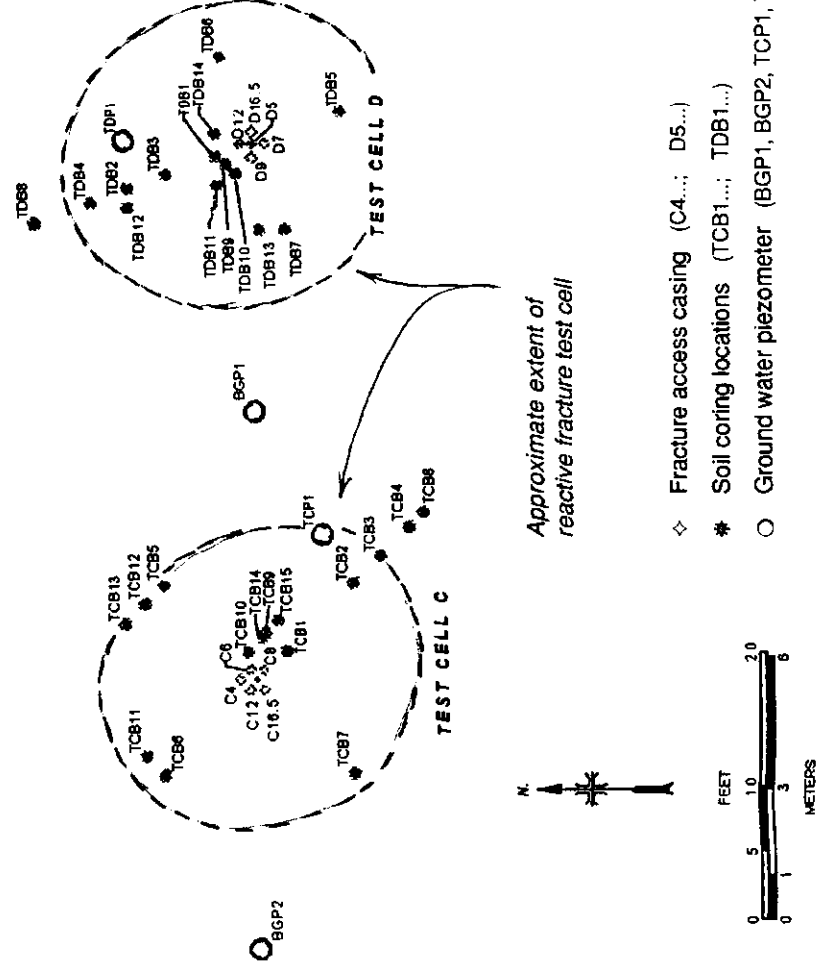


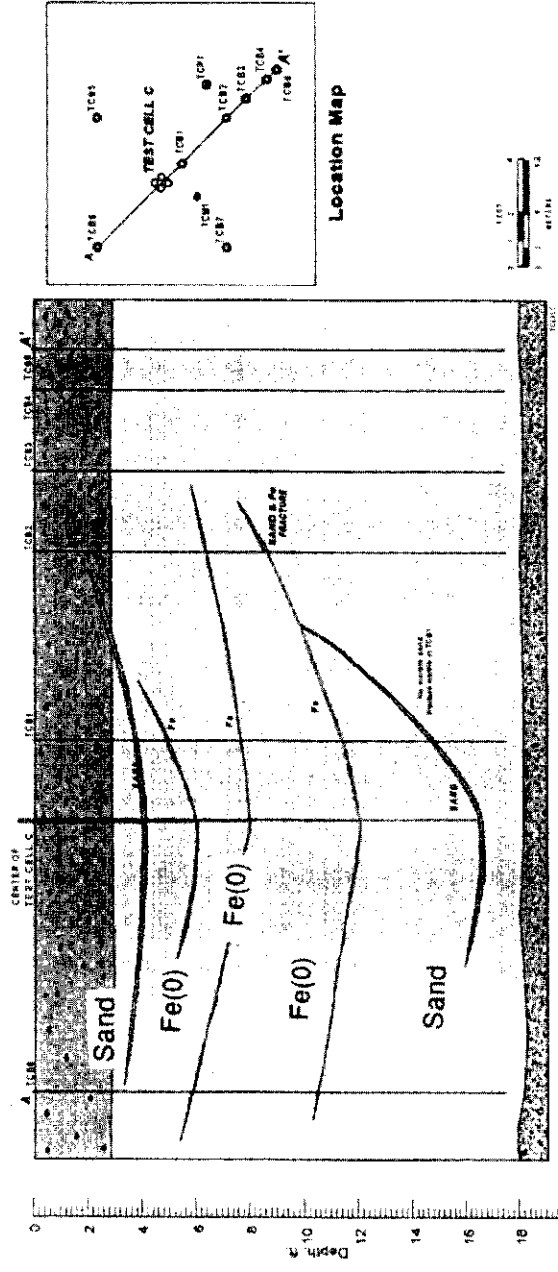
FIG. 2. Plan View of Test Cells Used to Evaluate Horizontal Treatment Zones: Test Cell C with Fe⁰ Metal Filled Hydraulic Fractures; Test Cell D with KMnO₄ OPM Filled Hydraulic Fractures

the shallowest fractures were created first, followed by successively deeper ones. For each fracture, steel casing was driven to depth, used to inject the reactive slurry, and then left in place for future access following procedures similar to those described in Murdoch et al. (1994). Forms of the fractures were estimated by measuring displacements of the ground surface during fracturing as well as by making direct observation via intact cores collected from eight boreholes made within one week of initial fracture emplacement (i.e., TCB1-B8 and TDB1-B8 in Figs. 2 and 3). In general, the fractures are flat-lying around the point of initiation and gradually climb upwards to form a gently bowl-shaped form, in some cases in-

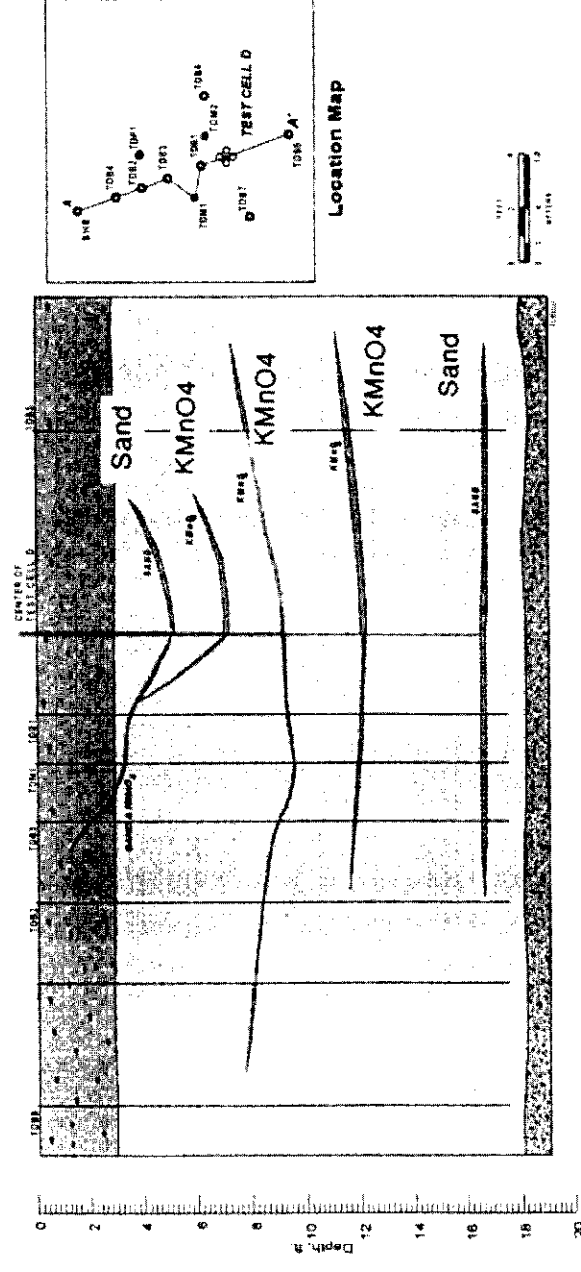
teracting with overlying fractures (Fig. 3). The test cells were established during September 1996 and left in a passive mode of operation for the next 15 mo. Because there was a geomembrane over the site, there was limited infiltration, although minor amounts of moisture did enter through perforations made in the cover for instrumentation and soil coring.

Fracture Zone Morphology and Properties

To enable direct observations and measurements within the fracture zones, intact cores were collected from ground surface to 5 m depth on three occasions. In the iron cell, cores were



(a)



(b)

FIG. 3. Cross Sections of Test Cells Used to Evaluate: (a) Fe⁰ Metal; (b) KMnO₄ OPM Filled Hydraulic Fractures as Horizontal Treatment Zones

TABLE 2. Test Cell Installation Features

Test cell characteristic (1)	Units (2)	Iron-filled fractures for dechlorination (3)	Permanganate-filled fractures for oxidation (4)
Method and time of installation	—	Iron metal and guar gel; 2–3 hr	Permanganate OPM; 2–3 hr
Fracture depth–proppant–amount	—	1.2 m–Sand–0.14 m ³ 1.8 m–Fe ⁰ –1,000 kg 2.4 m–Fe ⁰ –3,000 kg 3.6 m–Fe ⁰ –2,600 kg 5.0 m–Sand–0.57 m ³	1.2 m–Sand–0.14 m ³ 1.8 m–KMnO ₄ –400 kg 2.4 m–KMnO ₄ –600 kg 3.6 m–KMnO ₄ –600 kg 5.0 m–Sand–0.57 m ³
Test cell diameter	m	6	6
Test cell depth	m	5	5
Test cell volume	m ³	148	148
Fracture trend direction	—	SE	NW
Fracture propagation	—	Typical	Typical

collected in December 1996 (+3.5 mo after fracture emplacement from TCB9), in July 1997 (+10.7 mo from TCB10-B13), and in December 1997 (+15.4 mo from TCB14-B15) (Fig. 2). In the permanganate cell, cores were collected in December 1996 (+2.8 mo from TDB9-B10), in July 1997 (+10.0

mo from TDB11-B13), and in December 1997 (+14.6 mo from TDB14) (Fig. 2). All of the soil cores were collected using a truck-mounted hydraulic probe and a 4 cm i.d. thin-tube sampler that was lined with a clear acrylic sleeve. The cores were collected as 1.2 m long contiguous pieces that were

then divided into 30 cm long sections. Upon sectioning, a microring syringe was used to collect 5 g of soil, which was immediately immersed in 5 mL of reagent grade hexane and 5 mL of deionized water. These sample extracts were subsequently analyzed onsite for TCE and related chlorocarbons. Additional subsamples were also collected and analyzed onsite for water content, pH, K⁺, Fe⁺, Mn⁺⁺, MnO₄⁻ and onsite for total organic carbon (TOC).

The micromorphology of the iron particles after extended emplacement in the wet silty clay soils was assessed during July 1997 (+10.7 mo). Iron particles were obtained from a fracture within a core segment collected from the iron test cell (2.1 m depth in TCB13). The characteristics of these iron particles were compared to "fresh iron" particles obtained from a bulk sample of the iron used during the original fracturing operation in September 1996. This bulk sample had been stored in a double zip-closure polyethylene bag that was kept in a laboratory at the Colorado School of Mines (CSM) in the dark under low humidity at 20°C. In July 1997, samples of the fracture-retrieved iron and the fresh iron were placed in glass jars and refrigerated until scanning electron microscopic (SEM) analyses were made at Oak Ridge National Laboratory (ORNL).

During the sampling activities carried out in December 1996 and July 1997, several representative core segments were used for detailed spatial characterization of geochemical properties and also batch tests of TCE degradation. In December 1996, the core segments were from 2.1 to 2.7 m depth in boring TCB9 and 2.4 to 3.0 m depth in boring TDB10; in July 1997, the core segments were from 1.8 to 2.4 m depth in TCB13 and 2.1 to 2.7 m depth in TDB12. These core segments were brought into a field laboratory shortly after collection, where each core was carefully extruded from the acrylic liner onto a fresh aluminum foil covered work surface. Clean stainless steel knives were then used to remove a thin slice of soil along the length of the core. Soil Eh was measured at multiple points above and below the iron- or permanganate-filled fracture by pressing a platinum microelectrode and reference electrode several mm beneath the freshly exposed soil surface. The electrode system was calibrated with Zobell's solution before and after each core was examined. The outer few mm of soil around and along the entire core length were then carved off, and the core was cut into 1 cm thick sections at selected distances from the fracture. Each section was homogenized and 3–8 g subsamples of the soil media were analyzed for pH, water content, TOC, and selected anions.

The potential for degradation of TCE within the fracture zones was evaluated on two occasions using batch tests wherein subsamples from the cores, including the contents of the fracture or soil media in its vicinity, were placed into 4 mL reaction vials containing TCE-contaminated ground water. This approach was used because it allowed a selected range of conditions to be evaluated and because the ambient TCE concentrations in the test cells turned out to be too low to simply rely on changes in ambient TCE levels to assess treatment efficiency. During degradation testing in December 1996, TCE-contaminated ground water (TCE = 143.8 mg/L) was obtained from a nearby monitoring well within 24 hr of the batch test and containerized in 1 L glass jars with Teflon-faced screw tops. Immediately after placement of 5 g of field-moist media (i.e., fracture contents or soil) into a 40 mL glass vial, the vial was filled with the TCE-laden ground water. Based on the ground water to solids ratio in the vial, the mass of TCE to solid media in the vial was 1,200 mg/kg, equivalent to roughly five times the bulk soil media concentration at which the capacity for TCE in the dissolved, sorbed, and vapor phases would be exceeded yielding a DNAPL residual (Siegrist et al. 1998a). The reaction vials were sealed with a Teflon-

faced solid screw cap and continuously rotated on a vertical platter at 20°C during a 24-hr reaction period. Then a 5 mL subsample of the reaction vial contents was taken and immersed in 5 mL of hexane in a 1.5 mL glass vial with a Teflon-faced solid screw cap. These samples were refrigerated until analyses were made onsite for TCE and related VOCs. Subsamples of the reaction vial contents were also taken for post-reaction analyses of pH and chloride ion concentrations.

During the degradation testing completed in July 1997, the same procedures as just described were followed, except that two different ground water TCE concentrations and two reaction periods were used. For the July tests, about 3 L of undiluted ground water (GW1) were collected from a monitoring well at the site and containerized in 1 L bottles. To yield a ground water with a lower TCE concentration, a portion of GW1 was diluted with deionized water (1:10 v/v) to yield GW2. At the beginning of each batch test with iron or permanganate, replicate samples of GW1 and GW2 were analyzed onsite, revealing that TCE was the dominant VOC in the ground water with only minor concentrations (i.e., <500 µg/L) of a few other halocarbons such as perchloroethene (PCE), dichloroethane (DCA), and 1,1,1-trichloroethane (TCA). The initial TCE concentrations for the iron cell tests were: GW1 avg = 477.0 mg/L, n = 6, %R.E. = 7.0; GW2 avg. = 53.7 mg/L, n = 6, %R.E. = 5.0. The initial TCE concentrations for the permanganate cell tests were: GW1 avg. = 490.5 mg/L, n = 5, %R.E. = 3.2; GW2 avg. = 50.5 mg/L, n = 5, %R.E. = 9.7. The reaction periods were: 24 and 48 hr for the iron cell and 2 and 24 hr for the permanganate cell.

During December 1997, limited soil coring and direct examination of the test cells was also accomplished. In the permanganate cell, a single core was collected and analyses were focused on the fracture zone at 2.4–4.0 m depth in boring TDB14. Analyses were made for Eh, pH, MnO₄⁻, and water content, but no degradation tests were made. In the iron cell, three fracture zones within each of two boreholes (TCB14-B15) were analyzed for soil Eh, pH, and water content. To determine the TCE degradation potential of the iron after extended emplacement (15.4 mo), iron particles retrieved from the fractures were used in batch degradation tests. For this purpose, the iron from the shallowest two fractures in borings TCB14-B15 was combined and homogenized and batch degradation tests were then completed with TCE-contaminated ground water from the site (see Siegrist et al. 1998a).

Test Cell Soil and Ground Water Characteristics

The bulk subsurface conditions within the test cells were determined periodically from September 1996 through December 1997. During September 1996 (within a week of fracture emplacement), December 1996, and July 1997, soil samples were collected from the soil cores at 30 or 60 cm intervals from the ground surface to 5.2 m bgs. Analyses were made for water content, pH, extractable K⁺, Fe⁺⁺, and Mn⁺⁺, and VOCs. In addition, ground water monitoring included head level measurements and periodic sampling of the deepest sand-filled fracture and a piezometer placed within each test cell that had a screened interval beneath all of the fractured zones (TCPI or TDPI in Fig. 2). For comparison purposes, ground water characteristics in two nearby background piezometers were also determined (BGP1 and BGP2 in Fig. 2). Ground water samples were collected using micropurging and low-flow sampling methods with dedicated downhole tubing and a peristaltic pump. Analyses were made for temperature, pH, D.O., total dissolved solids, TOC, alkalinity, K⁺, Fe⁺⁺, Mn⁺⁺, and VOCs.

Analytical Procedures

Sample analyses were carried out in a field laboratory at the X-231A site and also in laboratories at CSM and ORNL fol-

Following generally accepted procedures (U.S. EPA 1986; Carter 1993; Siegrist et al. 1998a). Soil and solid media pH was determined by immersing a sample of field-moist media in an equal weight of deionized water and rotating on a vertical platter at 30 rpm for 30 min. The slurry was then centrifuged at 14,000 rpm for 15 min, and a combination pH electrode was immersed into the water phase. At least daily, the pH electrode was calibrated with buffers of known pH. Water content was determined by gravimetric analyses before and after drying for 12–24 hr at 110°C. MnO_4^- was measured on a soil extract (10 g soil and 15 mL deionized water) via absorbency at 525 nm with a spectrophotometer (Hach DR2000) and a five-point calibration curve. Analyses were also made offsite for TOC and chloride. TOC was measured by a CO_2 evolution and titration procedure using the dry samples from the water content analyses. Chloride analyses were made on water samples using ion chromatography (Dionex). Ground water temperature, pH, and conductivity were measured inline during collection with a Hydrolab Multiprobe. D.O. was measured during collection using Hach AccuVac vials and a spectrophotometer (Hach DR2000). Ground water K^+ , Fe^{++} , Mn^{++} , and MnO_4^- were measured directly or after dilution with deionized water using the Hach spectrophotometer. Alkalinity was measured using a Hach digital titrator with 1.6N sulfuric acid to a pH 5.1 endpoint.

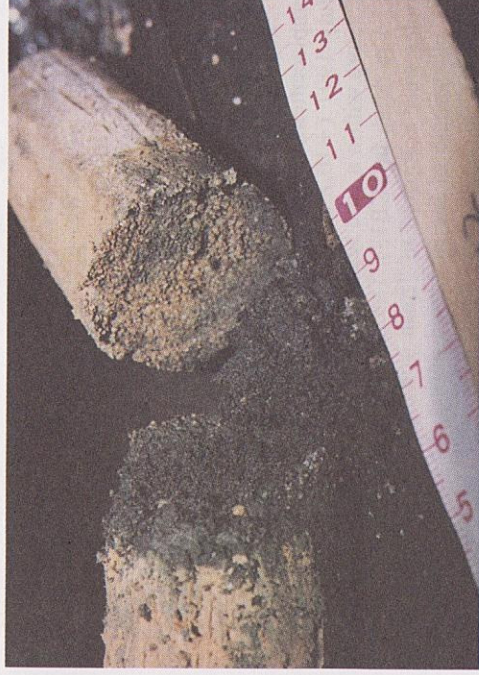
Onsite analyses of VOCs in hexane extracts from soil or water were made using a Hewlett-Packard (HP) 5890 Series II Gas Chromatograph (GC) equipped with a $30 \text{ m} \times 0.53 \text{ mm}$ capillary column (HP-624), a packed injection port, and an electron capture detector. The GC oven was started at 50°C and held for 2 minutes, then ramped at 6°C/min. to 80°C for a total analysis time of 7 min. The GC was calibrated for TCE as well as PCE, TCA, DCA 1,1-dichloroethene (1,1-DCE), cis-1,2-dichloroethene (cis-1,2-DCE), and trans-1,2-dichloroethene (trans-1,2-DCE). A half (0.5) microliter of extractant hexane was injected directly on the column using an HP7673 autosampler. The autosampler and GC were computer controlled using HP's ChemStation software and the TCE and other VOC concentrations were determined by integrating the area under individual peaks. Following initial calibration, a standard was run after every ten samples to check retention times and concentration determination. Every 20th vial contained a blank, consisting of 1 mL of hexane in an autosampler vial, to verify no equipment contamination or sample to sample carryover.

RESULTS AND DISCUSSION

Iron-Filled Fracture Zones

Morphology and Properties of Iron-Filled Fracture Zones

Based on visual inspections (naked eye and hand lens), the iron-filled fractures encountered during soil coring activities exhibited similar macromorphology regardless of location or duration of emplacement. All of the fractures were characterized by a 2–10 mm thick layer of moist black iron metal particles within an otherwise yellow-brown silty clay (Fig. 4). The iron particles were loose and unconsolidated, and the layer of iron readily broke into small granules upon handling (0.5–1 mm in size). There were no visually apparent changes within the soil matrix above and below the iron-filled fracture (e.g., discoloration, interfacial deposits, etc.) as compared with silty clay at a similar depth but in unfractured ground. The micro-morphology of the iron particles retrieved from a fracture after 10 mo indicated some accumulation of iron oxides, presumably due to oxidation of the iron surface (Fig. 5). The oxidized area appeared limited (e.g., <20%), so the effect of surface corrosion on reductive dechlorination would seem to be minimal in these specimens.



(a)



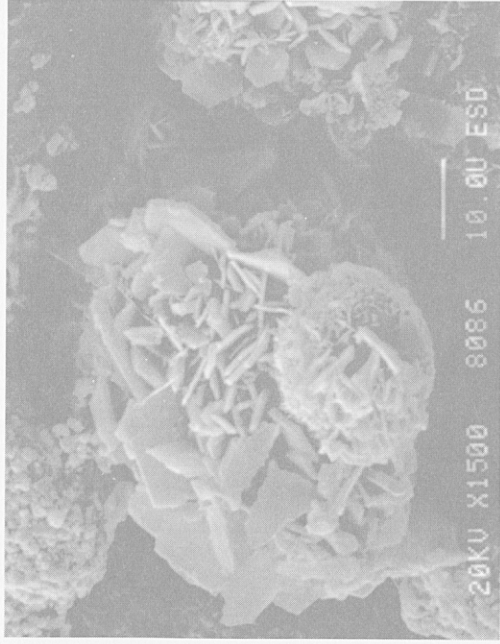
(b)

FIG. 4. Macromorphology of Vicinities of Hydraulic Fractures Filled with: (a) Fe^0 Metal; (b) KMnO_4 , OPM as Observed in December 1996, Approximately 3 mo after Initial Emplacement (Filled Fracture Location is at Center of Each Core where Core is Split Apart)

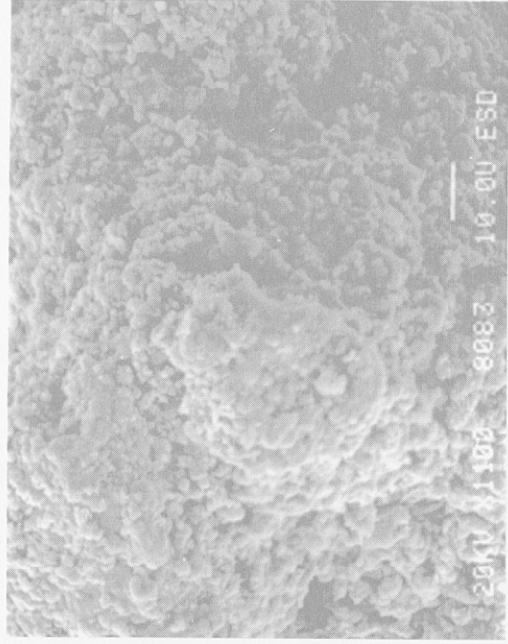
The results of the soil chemical analyses are consistent with the morphologic observations just described in that they demonstrate little geochemical effect on the silty clay soil above and below the iron-filled fracture itself (Fig. 6). For example, within the iron particles, the redox potential was highly reducing (e.g., -400 to -600 mV) and the pH was elevated (e.g., pH 8). However, in the silty clay soil only a cm above and below the fracture, the Eh and pH were typical of natural conditions in the silty clay (e.g., Eh of $+100$ to $+300 \text{ mV}$ and a pH of 5.0 to 6.0). Water content and TOC were also unrelated to proximity to the iron-filled fracture.

TCE Degradation in Iron-Filled Fracture Zones

The results of the batch tests reveal that the iron particles within a hydraulic fracture are capable of degrading TCE, but the soil above and below the fracture is relatively inert (Fig. 6, Table 3). This is as expected given the morphology and chemical data from the fracture zones as discussed above. The degradation of TCE by the iron metal used in this test appeared to be similar to that reported previously by Liang et al. (1997) and O'Hannesin and Gillham (1998). Considering a 24 hr reaction period, with relatively low TCE levels (i.e., 53.7 and



(a)



(b)

FIG. 5. Micromorphology of Iron Metal Particles: (a) 10 mo after Emplacement versus (b) Comparable Fresh Iron

143.8 mg/L), the degradation achieved in the reaction vial was in the range of 28–36%. This degradation occurred using samples of fresh iron, and iron that was exposed in a fracture in the subsurface for 3 or 10 mo (Table 3). With higher concentrations of TCE (477 mg/L), the percent degradation was lower (5–10%), but the mass degraded was similar to that achieved with the lower TCE concentrations. Based on limited data for a 48 hr reaction period (Table 3), the iron exposed in a fracture appeared to perform equal to or better than that of the “fresh iron.” Analyses of the reaction vial contents for chloride ion were difficult to interpret precisely due to background activity in the ground water matrix, but the data are generally consistent with the expected chloride production due to TCE degradation [(1)].

To assess the TCE degradation rate that would occur in an iron-filled fracture, the rates from the batch reaction vial tests must be converted to a flow-through packed-bed situation. This can be approximated using a conversion factor equal to the ratio of the solid:solution ratios of the two situations or more rigorously accomplished by accounting for surface area:solution ratios (Liang et al. 1997; O’Hannesin and Gillham 1998). In the batch tests, 5 g of moist iron were immersed in 40 mL of contaminated ground yielding a solid:solution ratio of 0.12 g/mL, compared with 7.6 g Fe⁰ per mL of pore water in an iron-filled fracture. The degradation rate observed during the batch tests must be divided by a factor of approximately

60 to yield a rate that is equivalent for a flow-through condition. In the batch tests, the half-life of the degradation observed is in the range of 48 hr or more, which yields an estimated half-life of about 0.8 hr for an iron-filled fracture condition. This rate is consistent with previously reported values (e.g., Liang et al. 1997; O’Hannesin and Gillham 1998) including those of Liang et al. (1997), who measured a half-life of 0.7 hr for TCE degradation by iron in a packed bed scenario using ground water from the Portsmouth site. Batch kinetic tests conducted with iron metal retrieved from the fractures in December 1997, 15 mo after initial emplacement, revealed similar results (see Siegrist et al. 1998a).

Soil and Ground Water Characteristics in Iron Cell

Soil water content increased with depth from 12 to 25% (dry wt. basis), and the only apparent change between September 1996 and July 1997 was an increase in water content at the shallowest depths. This is reasonable, because the site was covered by a temporary geomembrane and there were no processes operations with the cell that would have impacted water contents. However, the various core holes did create punctures in the geomembrane that could have increased rainwater infiltration locally. The soil pH ranged from 5.0 to 6.0 during September 1996 with somewhat lower values (about 0.5 pH units) evidenced during July 1997. Acid-extractable levels of soil potassium, iron, and manganese were all low during both sampling periods with values of potassium from 0.5 to 2.5 mg/kg, of iron from 5 to 180 mg/kg, and of manganese from 5 to 150 mg/kg. Of these, soil iron levels appeared elevated by a factor of two or more in all depth intervals as compared with background soil conditions, possibly attributable to migration of dissolved iron generated during corrosion of the Fe⁰ in the emplaced iron-filled fractures [(1)].

Ground water pH observed in the piezometer beneath the iron cell (TCP1) varied mostly within the range of 6.0–7.0, which was somewhat elevated as compared with the background (Table 4). Dissolved iron levels also appeared to increase somewhat over time, and this is consistent with the general increase in extractable iron concentrations within the VOCs in the ground water beneath the test cell were monitored in TC16 and TCP1, and they appear to decrease during the late fall of 1996 and then increase during the fall of 1997. However, this behavior was also exhibited in the background piezometers, BGP1 and BGP2, suggesting that it may be due to regional conditions (e.g., water table fluctuations) as opposed to any effects attributable to test cell emplacement in September 1996.

Permanganate-Filled Fracture Zones

Morphology and Properties of Permanganate-Filled Fracture Zones

The morphology and properties of the reactive fractures containing permanganate OPM solids were markedly different from that of the iron-filled fractures. Rather than a thin discrete layer, the permanganate-filled fracture was enveloped by a zone of silty clay that was stained purple by dissolved permanganate (Fig. 4). This stained zone was 20 cm thick (10 cm above and below the fracture) 3 mo after emplacement, and it increased to 30 cm thick after 10 mo. Careful inspection of several core segments using a hand lens indicated that the staining was uniform from the permanganate fracture to the leading edge of the zone, although staining within preexisting pores and fractures was slightly more intense than elsewhere. The leading edge of the stained zone away from the permanganate-filled fracture was sharp, with the intensity of staining

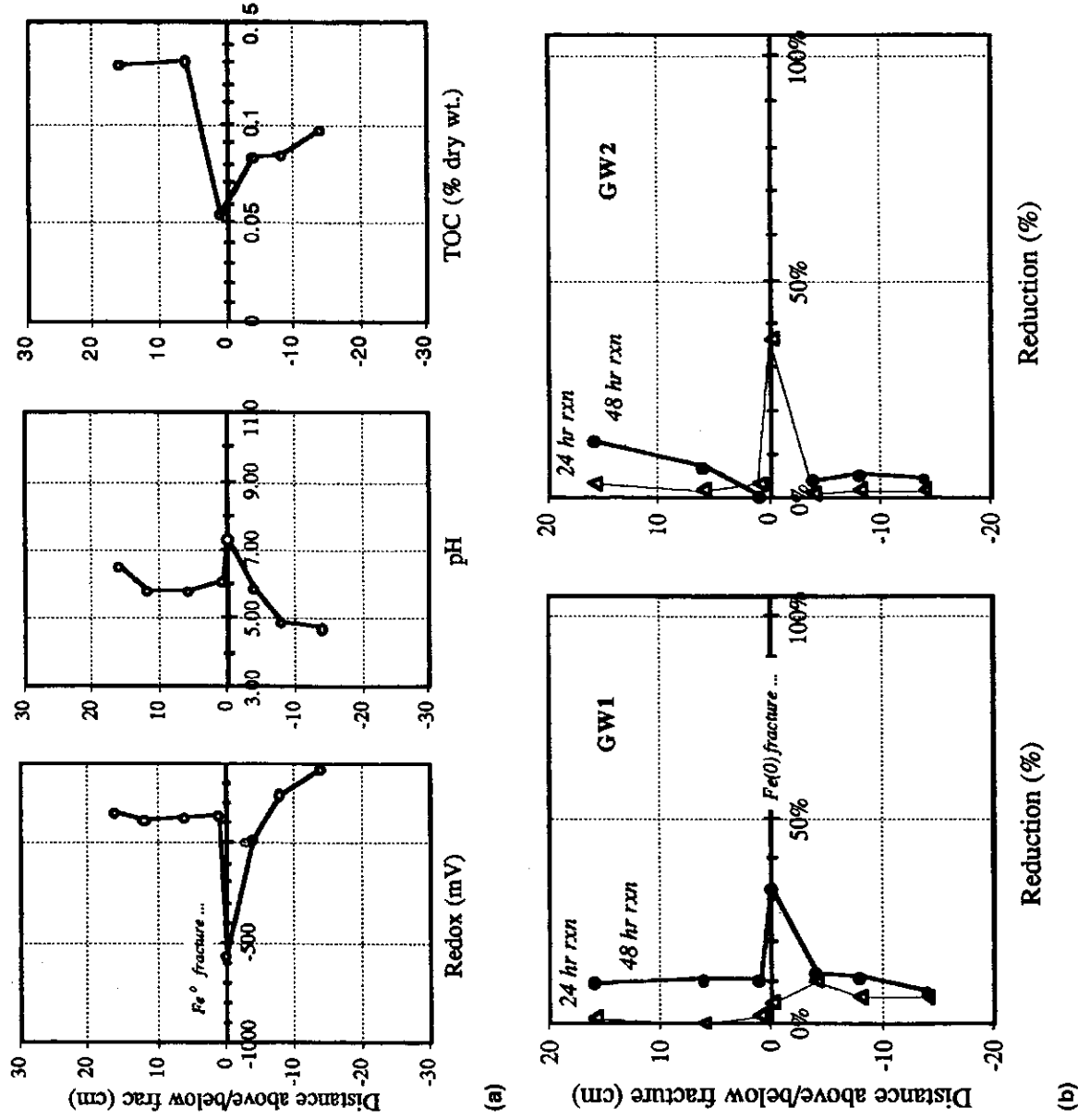


FIG. 6. Geochemical Properties and Degradation Potential of Iron Metal Fracture Zones as Observed 10 mo after Initial Employment in Silty Clay Deposit: (a) Media Redox Potential, pH, and TOC above and below Iron-Filled Fracture; (b) TCE Degradation in Ground Water after 2 and 24 hr Reaction Times versus Distance from Iron-Filled Fracture 10 mo after Initial Employment [TCE Degradation Measured in Batch Tests Using 5 g of Media in 40 mL of GW1 (Initial TCE = 477.0 mg/L) or GW2 (Initial TCE = 53.7 mg/L)]

diminishing from full to negligible values over a few cm. This sharp boundary was nearly planar and horizontal, essentially parallel to the permanganate-filled fracture, which always occurred in the middle of the strained zone. The symmetry of the purple-stained zone about the fracture suggested that diffusion was the dominant transport process for the permanganate, whereas gravity was relatively unimportant.

There were strong spatial trends in Eh, pH, and TOC within a few dm of a permanganate-filled fracture (Fig. 7). In general, the vicinity of the fracture was characterized by soil that is strongly oxidizing, relatively acidic, and depleted in TOC. The elevated Eh as high as +800 mV suggests strongly oxidized conditions throughout the vicinity of the permanganate-filled fracture. The low pH of 4.5 adjacent to the fracture may be due to oxidation of VOCs or natural organic matter. The relatively higher pH in the fracture itself is believed to be due to buffering by the mineral-based gel, which has a pH of about 11.5. The interval that is chemically different from background was <10 cm thick a few days after the fractures were created, but it was 20 cm thick after 3 mo, and 30 cm thick after 10 mo (e.g., Fig. 7). Observations made in the cell 15 mo after emplacement revealed high levels of MnO_4^- in the soil within

a 1 m thick zone (500 to 4,000 mg/L from 2.7 to 3.7 m depth in TDB14). These observations indicate that the growth of the chemically affected zone starts early and continues long after the fracture was filled with permanganate OPM.

TCE Degradation in Permanganate Fracture Zones

TCE was degraded rapidly and thoroughly by both the permanganate material from within a fracture and by the soil around it. Three months after emplacement, samples of soil within 10 cm of a fracture degraded more than 99% of TCE in ground water in 24 hr (Table 5). After 10 mo, the reactive zone was nearly 30 cm thick (Fig. 7), but the soil within it continued to degrade TCE remarkably rapidly. For example, 99% degradation of 50.5 mg/L initial TCE in 2 hr is equivalent to degradation of about 500 mg TCE per kg of media. TCE remained in a batch test during July 1997 only when a relatively high initial concentration of 490.5 mg/L dissolved TCE was used. In this case, 70% of the TCE was degraded in 2 hr, which is consistent with a stoichiometric analysis of the degradation reaction. According to (2), oxidation of TCE consumes 2.5 g $KMnO_4$ to 1.0 g TCE, or to degrade the 490.5

TABLE 3. TCE Degradation during Batch Tests Using Iron Metal Collected from Fracture after Emplacement as Compared with Unused Iron Used to Create Fracture

Emplacement duration (months) (1)	Iron metal source (2)	Initial TCE (mg/L) [g TCE/kg media] (3)	Reduction after 24 hr reaction (%) (4)	Reduction after 48 hr reaction (%) (5)
3	Fracture iron	143.8 [1.2]	28%	no data
10	Fracture iron	53.7 [0.5]	36%	no data
0	"Fresh" iron	53.7 [0.5]	26%	30%
10	Fracture iron	477.0 [4.1]	5-10%	33%
0	"Fresh" iron	477.0 [4.1]	17%	17%

TABLE 4. Ground Water Characteristics Beneath Reactive Fracture Cells as Compared with Nearby Background Locations

Parameter (1)	Units (2)	Iron Cell—TCP1		Permanganate Cell—TDP1		Background—BGP1		Background—BGP2	
		Average	Min-Max	Average	Min-Max	Average	Min-Max	Average	Min-Max
pH	---	(16)	(16)	(16)	(16)	(5)	(5)	(6)	(6)
Alkalinity	mgCaCO ₃ /L	5.53-7.99	146 (14)	5.58-7.90	137 (13)	4.93-6.40	56 (14)	4.67-6.10	63 (14)
TDS	mg/L	50-245	253 (8)	12-238	14-76	14-76	6-146	6-146	6-146
Mn	mg/L	158-299	1.25 (15)	272 (8)	224-306	76-214	144 (8)	91-224	144 (8)
K	mg/L	0.50-4.10	0.50 (14)	1.10-2.20	1.59 (15)	0.49 (15)	0.38 (14)	0.38 (14)	0.38 (14)
Fe	mg/L	0.21-0.76	2.86 (15)	5.29 (13)	3.00-7.25	0.21-0.79	0.1-1.1	0.1-1.1	0.38 (13)
VOCs*	µg/L	0.02-16.10	73 (18)	0.00-1.97	0.17 (15)	0.01-2.48	0.66 (14)	0.03-2.40	0.66 (14)
		5-272	5-196	64 (17)	64 (17)	78 (17)	61 (16)	5-319	5-319

*VOCs are dominantly TCE with minor levels of PCE, 1,1,1-TCA, c-DCE, and t-DCE.

mg/L of TCE in the reaction vial requires about 1,200 mg/L of KMnO₄. However, field samples yielded a maximum solution concentration in the reaction vial of 900 mg/L KMnO₄. This concentration is adequate to degrade all of the TCE in the 50.5 mg/L vial, but only sufficient to degrade about 75% of the TCE in the 490.5 mg/L vial. The chloride ion activity in the reaction vials increased in general agreement with that expected according to (2), confirming that the disappearance of TCE was due to degradation.

Soil and Ground Water Characteristics in Permanganate Cell

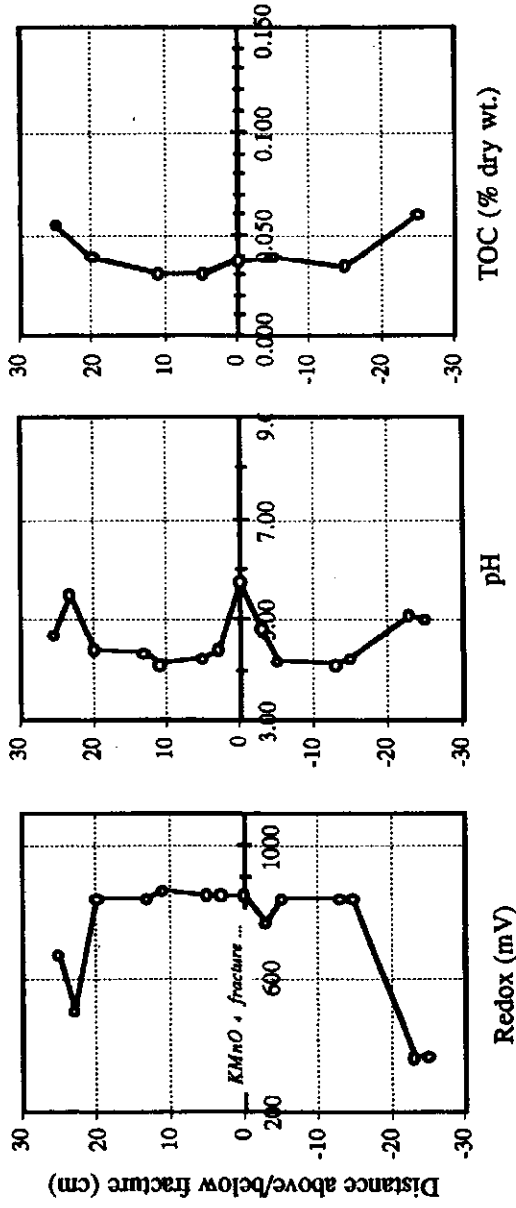
Similar to the iron cell, the soil water content within the permanganate cell increased with depth from about 7 to 22% (dry wt. basis) and there was some increase between September 1996 and July 1997. Again, this is reasonable based on local infiltration through punctures in the geomembrane. During September 1996, the soil pH was in the range of 4.5-5.5 with the lowest values in the 1.5-2.7 m depth zone. This was more acidic than in the iron cell and may have been due to production of H⁺ during permanganate oxidation of natural organic matter or VOCs. The pH appeared to be generally higher at most depths as measured in July 1997, possibly due to buffering reactions within the soil profile following the cessation of active organic matter oxidation. Concentrations of water-extractable K⁺ and Mn⁺⁺ between both measurement periods were comparable, and the range of values observed in the permanganate cell was similarly low and consistent with those observed in the iron cell. Both of these ions would be added to the subsurface as a result of the emplacement of potassium permanganate OPM in the three fractures. The fact that extractable concentrations of K⁺ and Mn⁺⁺ were not elevated within the soil profile suggests that either the ions were relatively immobile or, more likely, the speciation of the ions

was not amenable to the extraction procedure used in the analysis. For example, the Mn⁺⁺ in the permanganate would be reduced during oxidation of organic matter and would likely be present as Mn⁴⁺ in the form of MnO₂ solids, which are insoluble in the weak acid used for extraction.

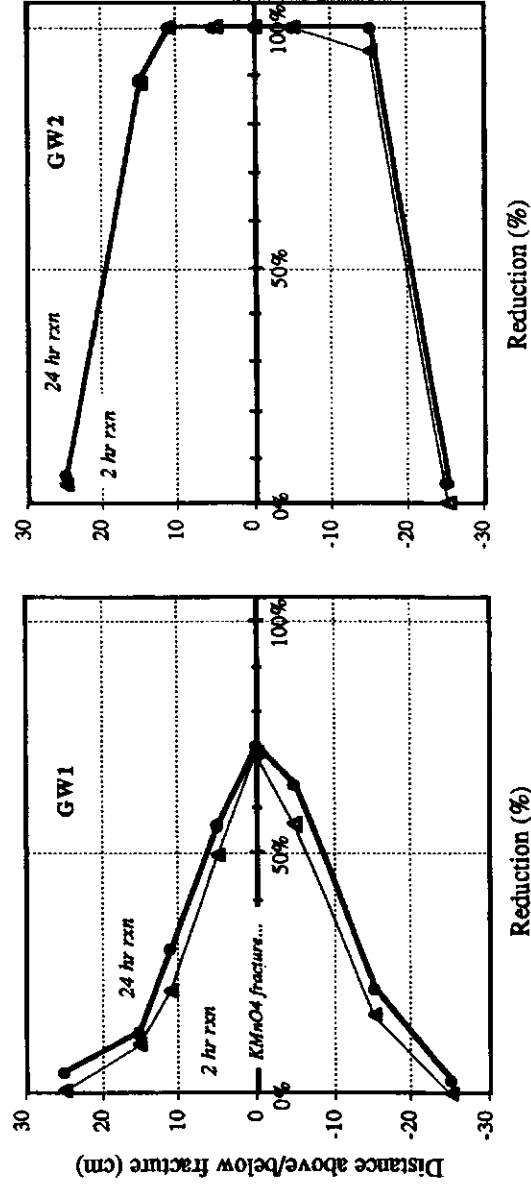
Ground water pH as observed in TDPI varied within the range of 6.0-7.0, which was slightly higher than background (Table 4). Concentrations of K⁺ and Mn⁺⁺ were somewhat elevated beneath the test cell, but ground water concentrations were low, typically in the range of 3-8 mg/L and 1-2 mg/L, respectively. There were no apparent temporal trends in pH or ion concentrations during the 15 mo observation period. Concentrations of TCE in the ground water beneath the test cell were monitored in TD16 and TDP1, and, similar to the results for the iron test cell, the VOC concentrations appeared to decline during the fall of 1996 and into 1997.

Reactive Fractures as Horizontal Treatment Zones

The feasibility of in situ remediation of TCE and other DNAPL compounds at LPM sites using horizontal treatment zones similar to those examined in this study requires consideration of the horizontal continuity, degradation capacity, and longevity of the treatment agents. The results obtained from this field test enable an interesting contrast between reactive fractures created with surface reactive media (i.e., Fe⁰ particles in a guar gel) and those created with reactive media that dissolve and permeate into the surrounding soil to produce a wide reactive zone (i.e., KMnO₄ particles in a mineral gel). Both types of reactive media were handled and emplaced by conventional hydraulic equipment and methods. Handling of the permanganate was more problematic in some respects, but modifications to fracturing equipment or development of encapsulation methods should resolve this. In general, the geometry of the reactive media fractures was similar to that of



(a)



(b)

FIG. 7. Geochemical Properties and Degradation Potential of Permanganate Fracture Zones as Observed 10 mo after Initial Employment in Silty Clay Deposit: (a) Media Redox Potential, pH, and TOC above and below Permanganate-Filled Fracture; (b) TCE Degradation in Ground Water after 2 and 24 hr Reaction Times versus Distance from Permanganate-Filled Fracture 10 mo after Initial Employment [TCE Degradation Measured in Batch Tests Using 5 g of Media in 40 mL of GW1 (Initial TCE = 490.5 mg/L) or GW2 (Initial TCE = 50.5 mg/L)]

TABLE 5. TCE Degradation in Permanganate Fracture and Reactivity of Enveloping Zone

Emplacement duration (months) (1)	Initial TCE (mg/L) (g TCE/kg media) (2)	Approximate reduction at fracture after 2 hr reduction (%) (3)	Approximate reduction at fracture after 24 hr reduction (%) (4)	Reactive zone thickness (cm) (5)	Highly reactive zone thickness (cm) (6)
3	143.8 [1.2]	no data	100	20	10
10	50.5 [0.5]	100	100	45	25
10	490.5 [4.1]	70	70	25	—

Note: Reactive zone is defined by TCE degradation efficiency >20%, and highly reactive zone is defined by TCE degradation efficiency >90%.

conventional sand-filled fractures employed at the same site. Thus, there was no unusual behavior associated with the different fracturing fluids (i.e., iron particles in guar gum gel, permanganate particles in mineral-based gel, or sand in guar gum gel).

Hydraulic fractures may bifurcate to form offset segments, which could produce local areas that are avoided by injected material (Murdoch 1995). This challenges the fracture emplacement to be continuous and uniform horizontally with lim-

ited breaches through it, a requirement that may require overlapping fractures created at several depths. The Fe⁰-filled fractures are discrete layers and appear to have limited effect on the soil deposit beyond the fracture boundaries. Thus, any in situ degradation of TCE or related compounds must rely on contaminants being mobilized to a fracture and then reacting with the Fe⁰ within it. The degradation rates observed in this study were consistent with previous studies suggesting a degradation half-life on the order of 1–2 hr for TCE degradation

in Fe⁰-filled fractures. While slow, this is still rapid enough for high treatment efficiencies to be achieved during a day or less of contact, which is achievable for most LPM deposits. For example, if ground water percolation through the fracture is controlled by the surrounding LPM with a K_{sat} of 10^{-6} cm/s and a hydraulic gradient of unity, then the retention time in an Fe⁰-filled fracture of 5 mm thickness would be on the order of 1–5 days, depending on the effective porosity. As a treatment zone that relies dominantly on diffusive transport of contaminants to the iron, the reactivity of the Fe⁰ surface would need to exist for an extended period (e.g., 2–5 years). Field investigations of iron-filled zones placed in ground water as permeable treatment walls have revealed reactivity for up to five years (O'Hannesin and Gillham 1998). However, such information is lacking for iron metal emplaced in fractures in a vadose zone without high advection through or across the iron surface. Analysis of the micromorphology of iron particles retrieved from the fractures made in this study revealed some corrosion of the iron surface after residing in the subsurface for 10.7 mo. The effect was limited to a fraction of the available iron surface, however, and it had no apparent effect on TCE degradation.

Fractures filled with a KMnO₄ OPM yield MnO₄⁻ ions that migrate away from their original location, dominantly by diffusion in an LPM deposit but possibly aided by advection driven by capillary gradients as well. This behavior will produce a zone at least several dm wide where resident TCE will be rapidly degraded, and it could also provide a barrier that would degrade mobile TCE as well. As a result, the gaps between offset fracture lobes or discontinuities between neighboring fractures might be healed by the migration of permanganate ions. The field results suggest that TCE degradation is fast and extensive, which is consistent with companion laboratory studies carried out with KMnO₄ crystals and OPM. These lab studies revealed nearly 100% destruction of TCE following pseudo first order kinetics with degradation half-lives of <2.4 min for TCE concentrations up to 800 mg/L (Case 1997).

The permanganate degradation of TCE appears to proceed stoichiometrically according to (2), which can be used to roughly estimate the active life of a permanganate-filled fracture. A 5 mm thick permanganate-filled fracture contains about 0.4 g KMnO₄ per cm² of fracture horizontal area. Based on complete oxidation and a stoichiometric TCE demand of 2.5 wt./wt., each cm² of fracture can treat about 0.16 g of TCE. This oxidant loading is sufficient to degrade an initial TCE concentration of 1,000 mg/kg within a zone of LPM that is 90 cm thick. Alternatively, it is sufficient to treat 16 L of percolate with a concentration of 10 mg/L of TCE, which is equivalent to a 50 yr life at a deep percolation flux of 1 cm/d. Realistically, though, it is anticipated that the oxidant demand of natural organic matter or the advective loss of oxidant out of the treatment region could markedly diminish this life. Based on direct observation in this study, the oxidation capacity within and around the permanganate fractures was striking even 15 mo after emplacement.

The cost of remediation using in situ horizontal treatment zones was roughly compared with that of soil vapor extraction (SVE) enhanced by sand-filled fractures. In general, the reactive chemicals are more expensive than sand, and material handling costs are somewhat higher, so the reactive media filled fractures are more expensive to create. The costs for media per fracture amounts to roughly \$1,000 for iron and \$1,500 for permanganate, as compared with \$100 for sand. However, during passive operation, the treatment zones require less resource consumption (e.g., power), less sampling and analysis (e.g., no off-gas), and reduced manpower compared with many SVE systems. As a result, the total estimated costs

of the horizontal treatment zone systems are similar to the costs for SVE systems. For a 2.2 ha site contaminated to 5 m depth, the costs for implementing horizontal treatment zones were estimated to be in the range of \$25–35/m³ for iron and permanganate zones, respectively. This cost was based on 6 m diameter fractured zones with 1 m overlap and fractures installed at depths of 1.7 and 3.5 m. Assuming no bulk media discounts, this yields an estimated materials cost of \$2,700k for the iron metal and \$3,800k for the permanganate. The installation time was estimated at 140 days for a three-person crew and equipment, yielding a labor cost including travel and per diem of \$450k, plus a mobilization/demobilization cost of \$50k.

CONCLUSIONS AND IMPLICATIONS

This work demonstrated two types of horizontal treatment zones for in situ remediation at LPM sites contaminated by TCE. In both cases, hydraulic fracturing equipment and methods were used to emplace reactive zones of Fe⁰ metal or KMnO₄ OPM in horizontally oriented layers within silty clay soils at depths up to 5 m. The Fe⁰-filled fractures produced a reactive seam with limited effect on the surrounding LPM, whereas the KMnO₄-filled fractures yielded a broad zone of reactivity within the LPM. With both types of fracture zones, degradation potential for high levels of TCE was sustained even after 10 mo of emplacement in the subsurface.

Both types of horizontal treatment zones may reduce risks associated with exposure to TCE from a contaminated site. Although the system using iron-filled fractures may leave immobile contaminants in the ground untreated, data from this study suggest that it is capable of degrading mobile TCE and thus may reduce risk by effectively eliminating TCE release from a low permeability unit to the atmosphere or an underlying aquifer. The system using permanganate-filled fractures, where MnO₄⁻ ions are diffusively distributed through a broad region, offers the possibility to both curtail TCE release to the atmosphere or an underlying aquifer as well as destroy TCE throughout a low permeability formation. This approach to remediation using low permeability formations using fracture-emplaced reactive solids is extremely encouraging. Though TCE was the target contaminant in this study, other organic compounds and also redox-sensitive metals might be amenable to such an in situ remediation strategy. While the results to date are promising, this in situ remediation approach is still early in its development, and further work is necessary and appropriate to provide needed design, implementation, and performance data for a range of site and contamination conditions.

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