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Development of an Integrated, In-Situ Remediation Technology - TCE Degradation Using Non-Biological Methods - Task 9-1

Topical Report

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Development of an Integrated in situ Remediation Technology

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Topical Report for *Task No. 9-Part I*-TCE Degradation Using Nonbiological Methods

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Abstract: *Contamination in low-permeability soils poses a significant technical challenge for in situ remediation efforts. Poor accessibility to the contaminants and difficulty in delivery of treatment reagents have rendered existing in situ treatments such as bioremediation, vapor extraction, pump and treat rather ineffective when applied to low-permeability soils present at many contaminated sites. The technology is an integrated in situ treatment in which established geotechnical methods are used to install degradation zones directly in the contaminated soil and electro-osmosis is used to move the contaminants back and forth through those zones until the treatment is completed. The present Draft Topical Report for Task No. 9 summarizes laboratory investigations into TCE degradation using nonbiological methods. These studies were conducted by the General Electric Company. The report concentrates on zero valent iron as the reducing agent and presents data on TCE and daughter product degradation rates in batch experiments, column studies, and electroosmotic cells. It is shown that zero valent iron effectively degrades TCE in electroosmotic experiments. Daughter product degradation and gas generation are shown to be important factors in designing field scale treatment zones for the Lasagna™ process.*

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Disclaimer

A. Executive Summary

This report summarizes the work conducted in Task 9-Part I-TCE Degradation Using Non-Biological Methods. In addition to work performed under this contract, previous work conducted at General Electric-Corporate Research and Development (GE-CRD) studying the reductive dechlorination of a variety of chlorinated solvents by iron metal filings is reported. This prior work includes several laboratory column systems and one pilot-scale test. One long-term, column treatability study, in particular, addressed the degradation of trichloroethene (TCE) and six other chlorinated solvents in groundwater from DOE's Paducah Gaseous Diffusion Plant site in Paducah, KY.

Two distinct reaction pathways appear to be taken by TCE. The first, hydrogenolysis, accounts for the step-wise transformation of TCE to cis-dichloroethene (cis-DCE) to vinyl chloride (VC) and to ethene. The second, reductive β-elimination, accounts for the production of acetylene. These different reaction pathways, each mediated by the iron metal, merge however, as acetylene may be further reduced to ethene and ethene may be further reduced to ethane.

As a result of modeling work and field measurements made in the Lasagna™ pilot test at Paducah, KY showing that moderately high temperatures (up to 45°C) are achieved between electrodes, a study was undertaken in Task 9-Part I to measure the effect of higher temperatures on TCE reduction within an iron reaction zone. The reduction of TCE by Peerless iron filings was measured in a batch reaction along with the appropriate control reactions. First-order kinetics with respect to TCE are seen in each of the temperature profiles. The TCE degradation half-lives are shown to decrease with temperature: 3.1 h at 25°C, 1 h at 40°C and 0.7 h at 60°C.

Lab-scale electroosmotic flow cells were also used in Task 9-Part I to examine the effects of electrokinetic conditions on iron destruction of TCE and to provide valuable performance data to be used in designing reaction zones in a Lasagna cell in the field. A control cell with no iron and a cell with a 1-cm-thick-iron zone were fed with TCE at a concentration of about 80 ppm. The flow was driven by electro-osmosis. In the cell with the iron zone, only low levels of TCE (1-3 ppm) were detected in the effluent, which indicates a 96% TCE destruction efficiency in the iron zone. Based on the residence time of 6.8 h, the apparent half-life for TCE was between 1.5 and 5.2 h, which is similar to rates measured in packed columns of iron with no applied electric field. These results are also consistent with the final TCE distribution in the pore water of the clay sections. In cell No. 1 with no iron, the TCE concentration is essentially uniform across the sample. In cell No. 2 with the iron zone, the TCE concentration downstream (cathode side) of the iron zone is 4.2% of the upstream (anode side) concentration.

It is important to note that the flow rate gradually decreased after about one pore volume passed through the cell with the iron zone; after about three pore volumes, the flow ceased. The presence of gas pockets in the iron zone was observed while the flow rate in cell No. 2 was decreasing. This gas was determined to be hydrogen formed from the corrosion of iron. After venting the gas, the electroosmotic flow resumed. Methods to prevent gas buildup will be developed in Phase II.

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For this experiment both cis-DCE and vinyl chloride were measured in the effluent on the order of 1% (0.94% and 0.42 %, respectively) of the TCE feed concentration. Previous column experiments conducted at GE-CRD have estimated the dechlorination half-life for cis-DCE and vinyl chloride to be about six times longer than the TCE half-life. If these low concentrations of daughter products are significant, the kinetics of their degradation will govern the sizing of treatment zones in the Lasagna process.

B. Background

Statement of the Problem

Contamination in low-permeability soils poses a significant technical challenge to in situ remediation efforts. Poor accessibility to the contaminants and difficulty in delivery of treatment reagents have rendered existing in situ treatments such as bioremediation, vapor extraction, and pump and treat, rather ineffective when applied to low-permeability soils present at many contaminated sites.

The Solution

The proposed technology combines electro-osmosis with treatment zones that are installed directly into the contaminated soils to form an integrated in situ remedial process. Electro-osmosis is an old civil engineering technique and is well known for its effectiveness in moving water uniformly through low-permeability soils with very low-power consumption.

Conceptually, the integrated technology could treat organic and inorganic contamination, as well as mixed wastes. Once developed, the technology will have tremendous benefits over existing ones in many aspects including environmental impacts, cost effectiveness, waste generation, treatment flexibility, and breadth of applications.

Consortium Description

A consortium has been formed consisting of Monsanto, E.I. du Pont de Nemours & Co., Inc. (DuPont) and General Electric (GE), with participation from the Environmental Protection Agency (EPA) Office of Research and Development and the Department of Energy (DOE) Environmental Management Office of Science and Technology. The five members of this group are leaders in their represented technologies and hold significant patents and intellectual property which, in concert, may form an integrated solution for soil treatment. The Consortium's activities are being facilitated by Clean Sites, Inc., under a Cooperative Agreement with EPA's Technology Innovation Office. A schematic diagram of the government/industry consortium is shown on the front page of this topical report.

Management Plan

A Management Plan for this project was prepared by Monsanto and was submitted on November 30, 1994. This Management Plan summarized the work plan developed in conjunction with DuPont, GE, EPA's Risk Reduction Engineering Laboratory (RREL), Martin Marietta Energy Systems (MMES), and the Department of Energy. The DOE Gaseous Diffusion Plant in Paducah, Kentucky, has been chosen as the site for the initial field tests.

The CDM Federal Programs Corporation was chosen to provide the on-site support of the field tests that were installed at the DOE site in November 1994. This experiment tested the combination of electro-osmosis and in situ sorption in the treatment zones. In 1994 and 1995, technology development was carried out under the present contract by Monsanto, DuPont, and GE. These studies evaluated various degradation processes and their integration into the overall treatment scheme at bench and pilot scales.

Technical Deliverables

Tables 1 and 2 summarize the 13 technical tasks and the 8 topical reports that will be written describing the results obtained in the technical tasks. These two tables show which organization is primarily responsible for the tasks and for preparing the topical reports. The present topical report summarizes Task No. 9-Part I-"TCE Degradation Using Nonbiological Methods."

Table 1. List of Tasks and Responsible Company

Task	Company
Task 1 - Evaluation of Treatment Zone Formation Options (5.1.2)	DuPont
Task 2 - Electrokinetic Model Validation and Improvement (6.5)	GE
Task 3 - Design Guidance for Field Experiments (6.6)	GE/DuPont
Task 4 - Analysis of Electrode Geometry and Soil Heterogeneity (6.7)	GE/DuPont
Task 5 - Cost Analysis (7)	Monsanto/DuPont
Task 6 - Lab-Scale Development of Microbial Degradation Process (8.1.2)	DuPont
Task 7 - Lab-Scale Electrokinetic and Microbial Degradation (8.1.6)	Monsanto
Task 8 - Lab-Scale Tests of Lasagna Process Using DOE Paducah Soil (8.1.7)	Monsanto
Task 9 - TCE Degradation Using Non-Biological Methods (8.2.1, 8.2.2.2, 8.2.3.2)	GE/Monsanto
Task 10 - Bench- and Pilot-Scale Tests (9.3)	Monsanto
Task 11 - Establish Contamination Conditions Before and After Tests (10.1.2)	DuPont/MMES
Task 12 - Design and Fabrication of Large-Scale Lasagna Process (12.1, 12.2)	Monsanto/DuPont/Nilex
Task 13 - Large-Scale Field Test of Lasagna Process (12.3, 12.4)	Monsanto/CDM

Table 2. List of Topical Reports and Responsible Company

Topical Report	Company
Task 1 - Evaluation of Treatment Zone Formation Options	DuPont
Tasks 2 - 4 Electrokinetic Modeling	GE
Task 5 - Cost Analysis	Monsanto
Task 6 - Laboratory-Scale Microbial Degradation	DuPont
Tasks 7, 8, 10 - Bench- and Pilot-Scale Tests of Lasagna Process	Monsanto
Tasks 9 - TCE Degradation Using Non-Biological Methods	GE
Task 11 - Contamination Analysis, Before and After Treatment	Monsanto
Tasks 12 and 13 - Large-Scale Field Test of Lasagna Process	Monsanto

C. Draft Topical Report for Task No. 9-Part I

Task 9-Part I-TCE Degradation Using Nonbiological Methods

Metal corrosion processes in aqueous systems have been studied extensively. When metals are in contact with an aqueous salt solution, an electrochemical corrosion reaction may occur in which electrons are transferred from the anodic region to the cathodic region within the metal. As a result of this electron transfer process, metal cations are produced and oxidized species at the metal surface are reduced. In the presence of added corrosion agents such as chlorinated hydrocarbons, electron transfer to such species at the surface of the metal may occur and could result in its reduction.

Application of this chemistry to water treatment was first reported in the patent literature by Sweeny and Fisher (1972). Later work by Senzaki (1991) focused on the dechlorination of 1,1,2,2-tetrachloroethene and trichloroethene (TCE) by iron metal in batch and column reactors. Gillham and coworkers have since extended the technology to in situ treatment of groundwater using permeable reactive wall design (Gillham and O'Hannesin, 1994). Since 1994, numerous literature reports have appeared that address the reductive dechlorination of chlorinated solvents promoted by zero-valent iron (Matheson and Tratnyek, 1994). The goal of our research has been to develop a fundamental mechanistic understanding of chlorinated solvent/iron reaction chemistry and the factors that affect dechlorination rate and long-term performance in field application.

Zero-valent iron is a well-known reducing agent relative to many redox-reactive species, including oxygen (eq. 1) and water (eq. 2). In the presence of water, alkyl chlorides are

$$2Fe^0 + O_2 + 2H_2O <=> 2Fe^{2+} + 4OH^- \qquad (1)$$

$$Fe^0 + 2H_2O <=> Fe^{2+} + H_2 + 2OH^- \qquad (2)$$

reduced in a thermodynamically favored, two-electron transfer reaction according to eq. 5, the net reaction of redox reactions 3 and 4.

$$Fe^0 -> Fe^{2+} + 2e^- \qquad (3)$$

$$RCl + 2e^- + H^+ -> RH + Cl^- \qquad (4)$$

$$Fe^0 + RCl + H^+ -> Fe^{2+} + RH + Cl^- \qquad (5)$$

Fe(II) complexed to organic ligands and Fe(II) bound to O^{2-} in solid phases or as hydroxo complexes are also stronger reductants relative to Fe(II) itself. Fe(II) complexes and minerals, therefore, may also participate in the reduction of alkyl chlorides as in eqs. 6 and 7.

$$2Fe^{2+}\text{(complex)} + RCl + H^+ -> 2Fe^{3+}\text{(complex)} + RH + Cl^- \qquad (6)$$

$$2Fe^{2+}\text{(solid phase)} + RCl + H^+ -> 2Fe^{3+}\text{(solid phase)} + RH + Cl^- \qquad (7)$$

Recently, we have proposed that the reduction of chlorinated hydrocarbons by iron metal occurs by a reaction of surface-bound Fe(II) at the iron metal-water interface (Sivavec and Horney, 1995). The surface-bound Fe(II) species at the passive oxide-water interface may serve as mediator for the transfer of electrons from Fe^0 to adsorbed chlorinated hydrocarbon. The mediation of redox reactions by Fe(II)/Fe(III) in natural environments is also attributed to the role of this accelerated pathway for electron transfer.

Fast reduction rates for chlorinated hydrocarbons observed in the zero-valent iron system may be attributed to the facile regeneration of reducing surface Fe(II) species caused by the close proximity of the bulk reductant (Fe^0) to the electron carrier, surface-bound Fe(II). A reduction mechanism mediated by Fe(II)/Fe(III) may be considered a refinement of a direct electron-transfer mechanism. It takes into account that iron metal surfaces are protected by a passive film of iron oxide and that the interface between the aqueous alkyl halide and the iron metal surface is this passive oxide. Fe^0 remains the bulk reductant and Fe(II)/Fe(III) serves as the electron transfer mediator.

The passive oxide layer may vary in composition from an inner layer of Fe_3O_4 to an outer layer of γ-Fe_2O_3. Contaminant reduction in the absence of the bulk reductant, i.e., promoted only by iron oxides such as Fe_3O_4, was not observed. Scanning electron microscopy (SEM) of cross sections of iron filings suggests that grain-scale diffusion to reactive sites through this passive oxide may significantly influence mass transport of substrate to a reactive surface.

Depth profile analysis of iron metal surfaces by x-ray photoelectron spectroscopy (XPS) has indicated that commercial iron metals of various forms are similarly protected by a passive film of iron oxide. The presence of Fe^0 was not detected at these native iron surfaces. A linear correlation between the TCE dechlorination rate and the iron specific surface area was determined for a wide variety of commercial iron metals (Fig. 1).

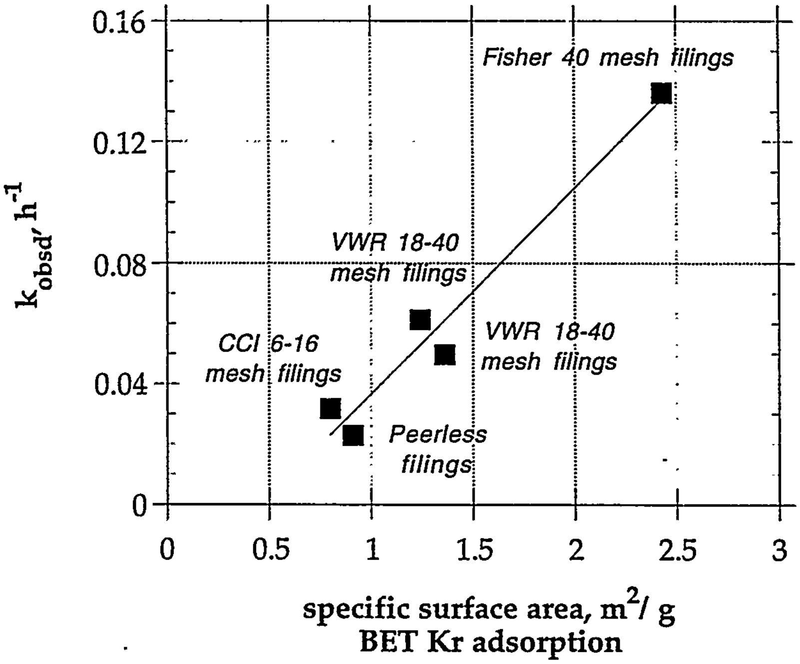


Fig. 1. Linear relationship between iron metal surface area and first-order dechlorination rate for TCE determined in batch reaction.

At the GE Corporate R&D Center (GE-CRD), the reduction of a wide variety of chlorinated solvents including TCE, PCE, DCE isomers, VC, 1,1,1-TCA and 1,1-DCA was studied in batch and column systems. All solvents studied were found to be reduced by zero-valent iron, albeit with different reduction rates. Much of this work has been devoted to the measurement of reduction rates in column systems and to the measurement of products. We have examined many different forms of zero-valent iron from many different sources, but devoted much of the column system work to low-cost iron filings, obtained as a product of cast iron recycling from the automotive industry. Only these materials are available at the cost and volume required for in situ environmental applications.

The requirements used in the selection of commercial iron filings include the following: (1) a high specific surface concentration, typically >1 m^2/g as measured by BET gas adsorption (2) a high proportion of Fe^0 relative to iron oxide in the bulk phase measured by XPS analysis (3) fast dechlorination rates demonstrated in long-term column studies, (4) large particle size that will not impede groundwater flow, and (5) low cost and high availability. Currently, we have worked with three suppliers of cast iron in filing form that meet these requirements: (1) Peerless Metal Powders & Abrasive, Inc., (2) Connelly-GPM, Inc., and (3) Master Builders, Inc. These materials average between $400 and $800 per ton.

We have shown that TCE, for example, is degraded completely to nontoxic endproducts (chloride ion, ethene, ethane, and other minor hydrocarbons) when the chlorinated solvent and its degradation products are contacted with the iron metal surface in a continuous-flow column system. Small concentrations of cis-DCE and VC (less than 10% of the initial TCE) are produced within the treatment zone, but are also degraded completely before exiting the iron zone.

Zero-valent iron is also consumed and precipitates out within the treatment zone as iron carbonate and smaller amounts of iron oxide minerals. These mineral precipitates have been characterized by x-ray photoelectron spectroscopy (XPS), electron microprobe/wavelength dispersive spectroscopy (WDS), and scanning electron microscopy (SEM). Quantification of these precipitates has been accomplished in laboratory and pilot-scale columns using a conservative tracer analysis. Losses of initial porosity of 10% to 25% have been measured after hundreds of pore volumes of site groundwater were introduced into the columns.

In addition to loss of porosity within the iron treatment zone, the issue of pore blockage caused by the oxidation or corrosion of iron metal by dissolved oxygen present in the groundwater has been shown to have significant consequences. On-line dissolved oxygen measurements show a rapid loss of dissolved oxygen in groundwater after it contacts the iron metal. In a column configuration, this plugging at the column inlet results in a significant pressure buildup. In an in situ system, this plugging would result in the diversion of the groundwater away from the treatment zone.

Plugging of the column input is a direct result of the reduction of oxygen, a strong oxidant, with the iron metal (eq. 1). Reduction of water by iron metal (eq. 2), by comparison, is a much slower process. It is possible that the plugging of an iron-filled column or iron reactive zone with precipitates of iron oxide and iron oxyhydroxide may be avoided or at least delayed by diluting the iron with a filler material at the input of the iron zone. In a Lasagna process, the iron may be admixed with clay soil, allowing for the deposition of iron oxide precipitates over a greater distance, rather than at a very narrow input zone.

Laboratory Column Studies

Several laboratory column systems and one pilot-scale test were designed and constructed to study the reductive dechlorination of a variety of chlorinated solvents by iron metal filings. The goals of these column studies include the following: (1) to accurately determine of dechlorination rate for a wide variety of solvents under steady-state conditions that model site hydraulics and site groundwater conditions, (2) to determine the dependence of dechlorination rate on flow velocity, (3) to examine long-term lifetime issues including biofouling and mineral precipitation, and (4) to identify other key performance issues that may not be obvious from batch studies.

Lab-scale electroosmotic flow cells were also used to examine the effects of electrokinetic conditions on iron destruction of TCE and to provide valuable performance data to be used in designing reactions zones in a Lasagna cell in the field. These results are described below.

The results of one long-term laboratory column test using groundwater from the Paducah GCP site spiked with TCE, PCE, cis-DCE, 1,1-DCE, VC, 1,1,1-TCA and 1,1-DCA will be briefly cited to provide information on degradation rates to be expected in a Lasagna process. This column study was performed under Subcontract No. 1CP-GEC43C to GE Corporate R&D by Martin Marietta Energy Systems.

A series of five glass columns connected by 1/8-in.-Teflon tubing was used to contain 5.185-kg-iron filings (100% iron filings with no inert filler). The direction of flow was from bottom to top in each of the columns. A Teflon piston pump (Fluid Metering, Inc., ceramic liner and piston) was used to pump groundwater from a Teflon reservoir bag (125-L capacity, constructed from 0.050-in.-thick Teflon; dimensions 18 in. wide by 24 in. long by 24 ft deep). Weights were placed on top of the Teflon reservoir bag so that no headspace was created above the ground water because an increase in headspace would seriously affect the concentration of VOC in the groundwater.

Pressure transducers were placed before and after every column. Pressure changes could then be monitored very accurately on-line using an Omega digital scanner. A flowthrough dissolved oxygen probe (membrane electrode) was also placed on-line. By placing the flowthrough cell at various points in the column setup, accurate dissolved oxygen measurements could be obtained. Sampling was performed at sample ports directly before every column and at the end of the last column in series. The sample ports were constructed of Teflon and provided a luer-lock fitting to which a gas-tight syringe (5 or 10 cc) could be attached. A schematic drawing of the column setup is shown in Fig. 2.

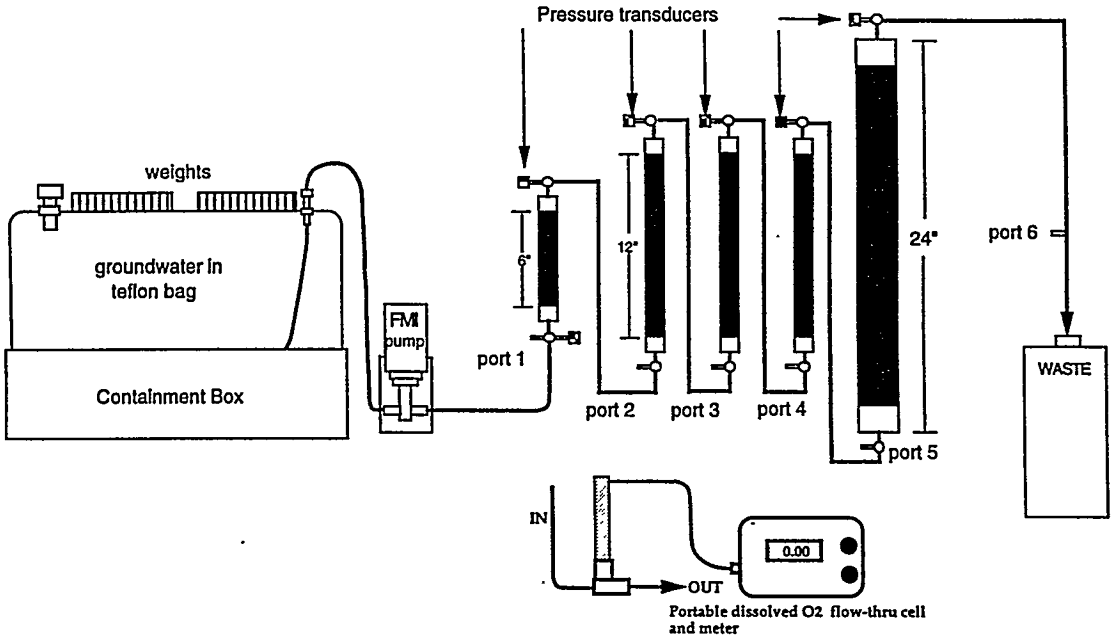


Fig. 2. Laboratory column setup.

Table 3 lists the volume of each of the glass columns, the iron mass that was packed into each of these columns, the void volumes measured in each column, and the measured porosity and iron surface area/volume.

Paducah groundwater spiked with TCE was introduced to the columns set in series initially at an input flow velocity of 2.00 mL/min (phase I). It was then reduced to a flow velocity of 1.00 mL/min with groundwater containing a mixture of the seven chlorinated solvents (phase II). A third phase is currently under way using an input flow velocity of 0.10 mL/min. Approximately 380 L (or 330 pore volumes) of groundwater have been introduced over a 5+ month period. Dissolved oxygen in the groundwater feed was kept at 4 to 5 mg/L to model site conditions.

Table 3. Column Dimensions and Volumes, Volumes of Iron Filings Packed within the Columns and Porosity Measurements

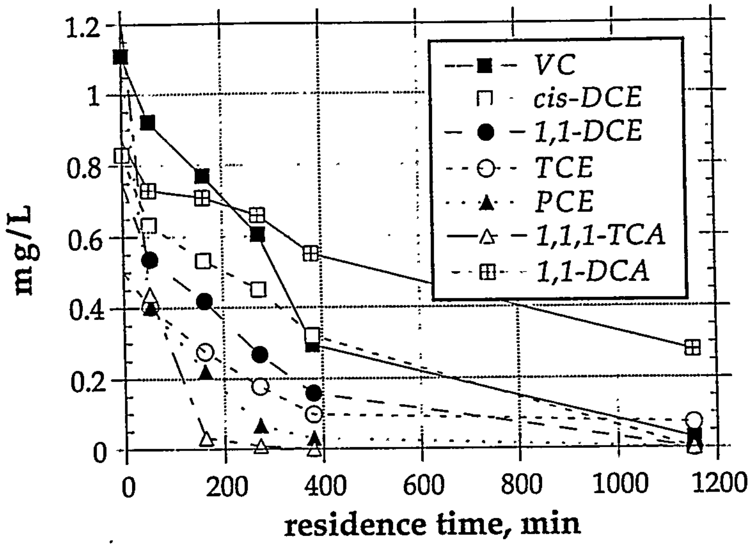
column	column dimensions i.d. × length	column volume, cc	weight of iron filings, g	iron surf. area/vol. m^2/L	volume of voids, cc	porosity, %
1	1 × 6 in	86	241.4	5704	52.47	61.0
2	1 × 12 in	175	477.7	5452	108.65	62.1
3	1 × 12 in	179	489.9	5475	110.96	62.0
4	1 × 12 in	177	488.1	5542	109.21	61.7
5	2 × 24 in	1255	3488	5432	770.56	61.4
cumulative	-	1872	5185	avg. 5544	1151.8	avg. 61.6

Table 4. Summary of Concentration vs Column Residence Time Obtained from Phase II of the Paducah Groundwater Treatability Study; Column Input Flow Velocity: 1.02 ± 0.10 mL/min

column	cumulative residence time, min	TCE mg/L	PCE mg/L	cis-DCE mg/L	1,1-DCE mg/L	VC mg/L	1,1,1-TCA mg/L	1,1-DCA mg/L
input	0	0.59	1.14	0.81	0.77	1.15	1.24	0.88
1	52.6	0.479	0.472	0.730	0.634	0.942	0.414	0.837
2	161.2	0.331	0.164	0.623	0.513	0.813	0.022	0.786
3	272.0	0.197	0.038	0.554	0.352	0.675	0.004	0.741
4	380.6	0.111	0.014	0.421	0.226	0.366	<0.0001	0.628
5	1152.2	0.096	n.d.	n.d.	n.d.	0.037	<0.0001	0.340

n.d.: not detected by purge-and-trap GC-FID. A method detection limit of <1 µg/L for all analytes, except VC (MDL <5 µg/L).

A plot of averaged C/Co vs column residence time for all seven chlorinated solvents is shown in Fig. 3 and 4. Table 5 summarizes pseudo-first-order rate constants, half-lives and fits obtained over the phase II sampling period. All chlorinated solvents demonstrated excellent fits to first-order kinetic models. As was shown in earlier batch experiments, a significantly higher half-life was determined for 1,1-DCA relative to the other seven solvents. However, if only very low concentrations of 1,1-DCA are present at the Paducah site, the daughter products of TCE (cis-DCE and VC) or TCE itself (if at high concentration) may be the determining factor in sizing a treatment column or wall.



[iron surface area] = 5600 m^2/ L
column porosity = 61%
330 pore volumes ground water treated

Fig. 3. Column treatability study: average concentration vs residence time.

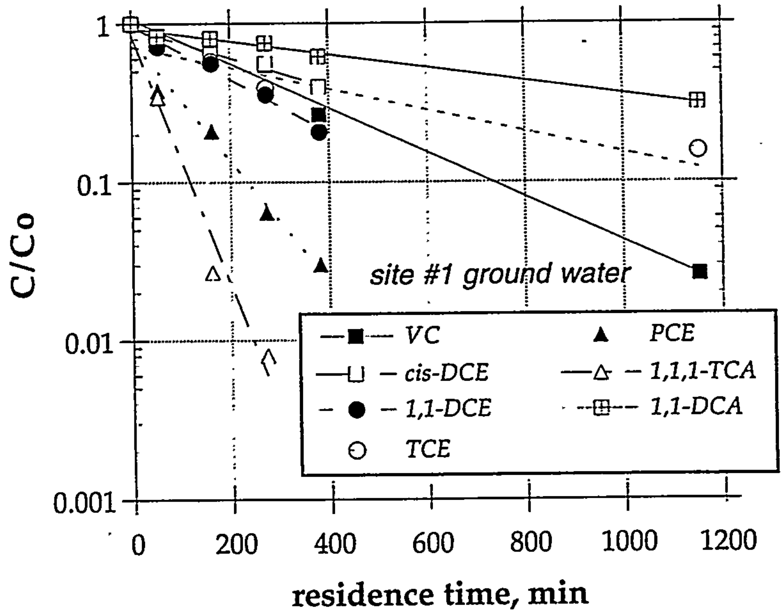


Fig. 4. First-order fits of column rate data.

Table 5. Column Pseudo-First-Order Reductive Dechlorination Rate Constants, Half-Lives and First-Order Fits Measured at an Input Flow Velocity of 1.0 mL/min

chlorinated solvent	first-order rate constant k, min^{-1}	$t_{1/2}$, min	r^2 fit
PCE	0.0147	47	0.996
TCE	0.0037	188	0.974
cis-DCE	0.0016	439	0.987
1,1-DCE	0.0030	235	0.993
VC	0.0025	282	0.986
1,1,1-TCA	0.0223	31	1.0000
1,1-DCA	0.00085	812	0.995

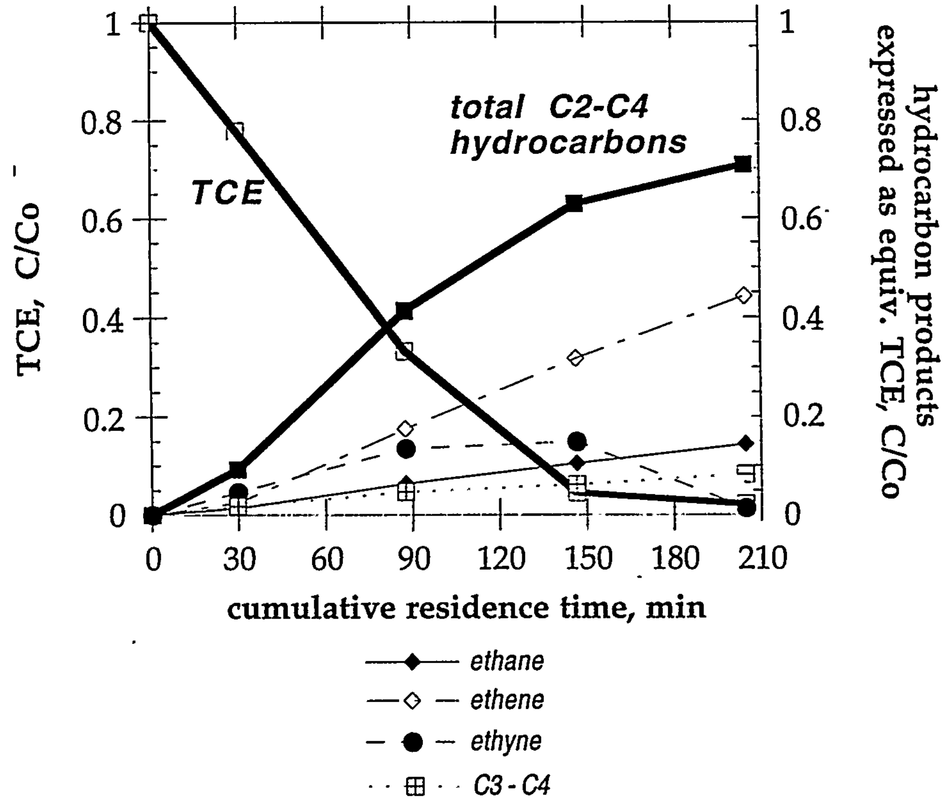


Fig. 5. C2-C4 hydrocarbon product distribution and mass balance measured at 498 pore volumes (Paducah GW column study).

Hydrocarbon product analysis and mass balances are measured using purge-and-trap GC-FID analysis of groundwater sampled directly from the columns. A representive mass balance profile is displayed in Figure 5. Mass balances of approximately 70+ % are commonly measured in column studies. The formation of ethyne (acetylene) is significant at early column residence times. Column experiments at much slower input flow velocities fail to show ethyne formation because they do not afford sufficiently short residence times. Ethyne is rapidly hydrogenated to ethene and ethane at longer residence times.

Two distinct reaction pathways appear to be taken by TCE. The first, hydrogenolysis, accounts for the transformation of TCE to cis-DCE to VC to ethene (Figure 6). The second, reductive β-elimination accounts for the production of acetylene.

Assuming the dechlorination reaction is first order in both iron concentration and in chlorinated solvent concentration, then:

$$d[C]/dt = - k\,[Fe]\,[C] \qquad (8)$$

where [Fe] = concentration of reactive iron surfaces, [C] = concentration of chlorinated solvent and k = rate constant. Since the concentration of reactive iron surfaces is far in excess of the chlorinated solvent concentration, the rate expression may be written as pseudo-first order in chlorinated solvent concentration:

$$d[C]/dt = - k_1\,[C] \qquad (9)$$

where k_1 = pseudo first order rate constant, proportional to [Fe].

Solving Equation 9 gives the standard first order expression:

$$[C] = [C]_0\, e^{-k_1 t} \qquad (10)$$

where, subscript 0 = initial condition. The rate constant is calculated from the slope of ln $[C]/[C]_o$ versus time. Half life ($t_{1/2}$) is defined as:

$$t_{1/2} = 0.693/\, k_1 \qquad (11)$$

Dechlorination rate constants were calculated assuming this pseudo first-order degradation. The first order dependence on iron surface concentration was demonstrated by batch reactions in which the amount of iron was varied. A linear fit of the pseudo first order rate constant versus iron surface concentration was obtained.

The TCE dechlorination rate by these parallel pathways may be expressed as:

$$\text{TCE} \xrightarrow{k_a} \text{cis-DCE} \xrightarrow{k_c} \longrightarrow \text{ethene, ethane}$$

$$\text{TCE} \xrightarrow{k_b} \text{chloroethyne} \longrightarrow \longrightarrow \text{ethene, ethane}$$

Using the pseudo-first order rate expression, the disappearance of TCE may be expressed as:

$$d[C]/dt = - k_a\,[C] - k_b\,[C] \qquad (12)$$

$$= - (k_a + k_b)\,[C] \qquad (13)$$

$$= - k_1\,[C] \qquad (14)$$

with $k_1 = k_a + k_b$.

The consecutive reactions leading to the formation and disappearance of cis-DCE daughter product is expressed as:

$$d[D]/dt = - k_c\,[D] + k_a\,[C] \qquad (15)$$

where [D] = concentration of daughter product. Defining f as the fraction of the TCE going to cis-DCE:

$$f = k_a / (k_a + k_b) = k_a / k_1$$

then Equation 15 may be written:

$$d[D]/dt = - k_c\,[D] + f\,k_1\,[C] \qquad (16)$$

Substituting Equation 10 into Equation 16, yields:

$$d[D]/dt = - k_c\,[D] + f\,k_1\,[C]_0\,e^{-k_1 t} \qquad (17)$$

Equation 17 can be integrated using the integrating factor $e^{k_c t}$ and the initial condition $[D] = [D]_0$ at $t = 0$ to give:

$$[D] = f\,k_1\,[C]_0\,[e^{-k_1 t}/(k_c - k_1) + e^{-k_c t}/(k_1 - k_c)] + [D]_0\,e^{-k_c t} \qquad (18)$$

Equation 18 was entered into a worksheet. For a given column run, $[C]_0$ and $[D]_0$, were known, and k_1 was calculated from the TCE disappearance rate. For the cis--DCE and VC data, "best fit" values of f and k_c for each compound were obtained using the Solver option in Excel.

Rigorously, f represents the fraction of TCE going through the hydrogenolysis pathway. However, not all of the cis-DCE that is formed as an intermediate in this pathway appears as cis-DCE in the aqueous phase. A portion may remained sorbed to the iron surface and react leaving the surface. Since the concentrations measured in the columns reflect only aqueous phase species, f is more correctly interpreted as the fraction of cis-DCE that is formed from TCE dechlorination via hydrogenolysis AND released to the aqueous phase. Equation 18 was used to describe VC formation and degradation also. In this case f represents the fraction of TCE that appears as aqueous phase VC; it is not a rigorous kinetic parameter.

For a typical column experiment with only TCE as the input (Horney, Mackenzie, Salvo and Sivavec, 1995), 9% of the initial TCE appeared as cis-DCE and 4% appeared as VC. Both of these daughter products were subsequently degraded.

To account for the effect of cis-DCE and VC formation from TCE on wall sizing, Equation 18 can be used to size a reaction zone. Table 6 lists the required residence times to degrade TCE, cis-DCE and VC to typical regulatory limits at two initial concentrations of TCE: 100 mg/L and 1 mg/L. The following values were assumed:

$t_{1/2,\,TCE}$ = 3.1 h

$t_{1/2,\,cis\text{-}DCE}$ = 7.3 h

$t_{1/2,\,VC}$ = 4.7 h

f for TCE --> cis-DCE = 5%

f for VC --> = 5%

Table 6. Required Groundwater Residence Times and Iron Treatment Zone Thicknesses (100% Iron Filings) to Meet Regulatory Limits, Assuming Treatment Zone Velocity of 1 cm/day.

initial TCE = 100 mg/L			
solvent	regulatory limit (µg/L)	required residence time (h)	wall thickness (in)
TCE	5	44	0.73
cis-DCE	0.5	103	1.7
VC	0.5	70	1.2
initial TCE = 1 mg/L			
solvent	regulatory limit (µg/L)	required residence time (h)	wall thickness (in)
TCE	5	24	0.40
cis-DCE	0.5	54	0.89
VC	0.5	38	0.63

The calculations in Table 6 assume only advective transport. At these low flow velocities diffusive fluxes may be important and may lead to an increase in the required size of the reactive zone. These calculations are also based on solvent half-lives determined in columns at ambient temperature and do not take into consideration the increase in reaction rate at higher temperatures. This will decrease the required reaction zone thickness.

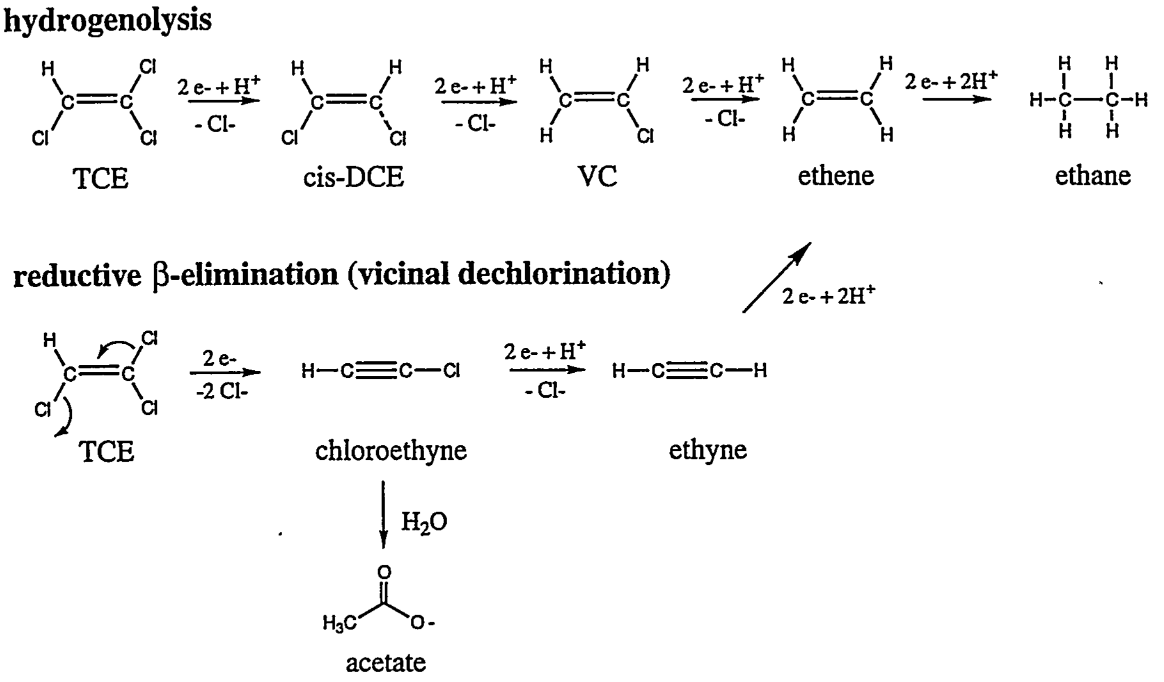


Fig. 6. Mechanism of TCE reductive dechlorination involves two competing pathways.

Temperature Effect Study

As a result of modeling work and field measurements made in the Lasagna pilot test at Paducah, KY showing that moderately high temperatures (up to 45°C) are achieved between electrodes, a study was undertaken to measure the effect of higher temperatures on TCE reduction within an iron reaction zone. Earlier work at GE Corporate R&D showed that temperature may significantly affect reduction rates. In these earlier studies, the temperature was varied from 17°C to 30°C. A second study was initiated to test the reactivity of Peerless iron filings at the following temperatures: 25°C, 40°C, and 60°C.

The reduction of TCE by Peerless iron filings at 200 m^2/L (25.0g iron filings/122 mL aqueous TCE) was measured in a batch reaction along with the appropriate control reactions. These results are displayed in Fig. 7 and 8. Figure 7 shows the loss of TCE (C/Co) relative to time and Fig. 8 displays this same data on a logarithmic scale. First-order kinetics with respect to TCE (eqs. 19 and 20) are seen in each of the temperature profiles. The first-order rate constants k, half-lives and first-order fits are given in Table 7.

$$[TCE] / [TCE]_o = \exp(-kt) \qquad (19)$$

$$\ln([TCE] / [TCE]_o) = -kt \qquad (20)$$

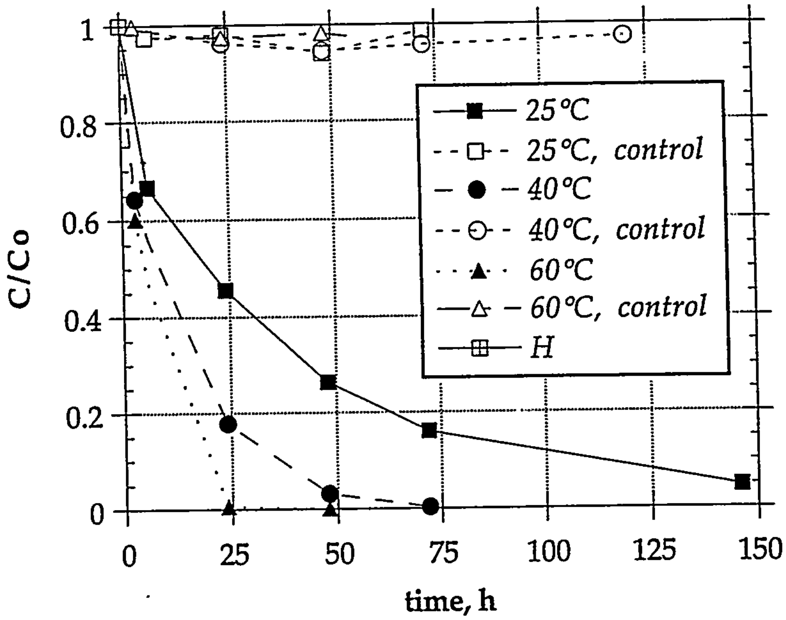


Fig. 7. Dependence of TCE reduction rate on temperature: C/C0 vs time determined in batch reaction with 200 m^2/L Peerless iron filings.

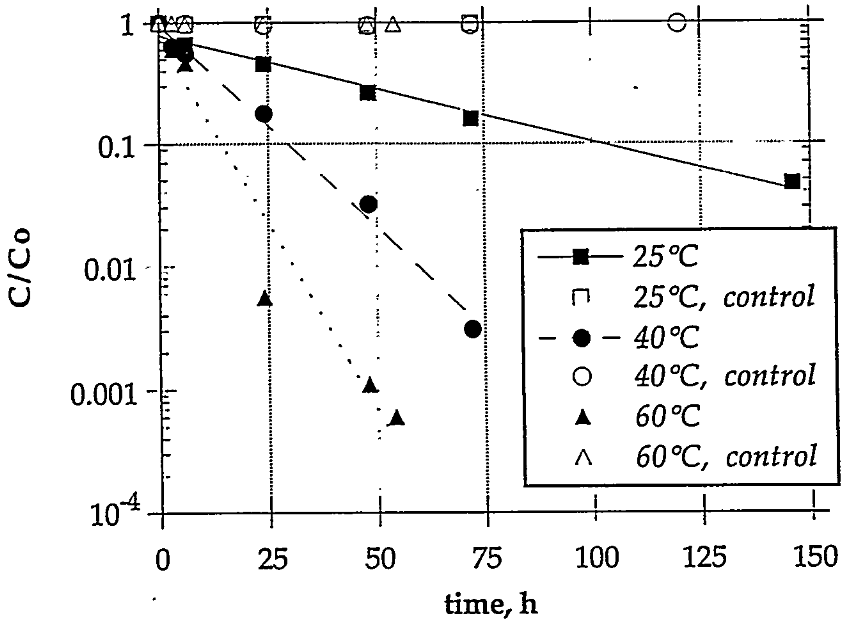


Fig. 8. Dependence of TCE reduction rate on temperature: First order fit of batch reaction data with 200m^2/L Peerless iron filings.

Table 7. Rate Constants, Half-Lives, and First-Order Fits for Batch Reaction of TCE with Peerless Iron Filings (-8 +50 mesh) at 200 m^2/L at Varying Temperatures

temperature	first-order rate constant k, h^{-1}	half-life, h	first-order fit r^2
25°C	0.0316	22.0	0.973
40°C	0.0989	7.0	0.988
60°C	0.1444	4.8	0.997

An Arrhenius plot of the rate data is shown in Fig. 9. From the slope of the curve an activation energy of 8.75 kcal/mol is determined under these experimental conditions (eq. 21 and Table 8).

$$k = A \exp(- E_{act} / RT) \qquad (21)$$

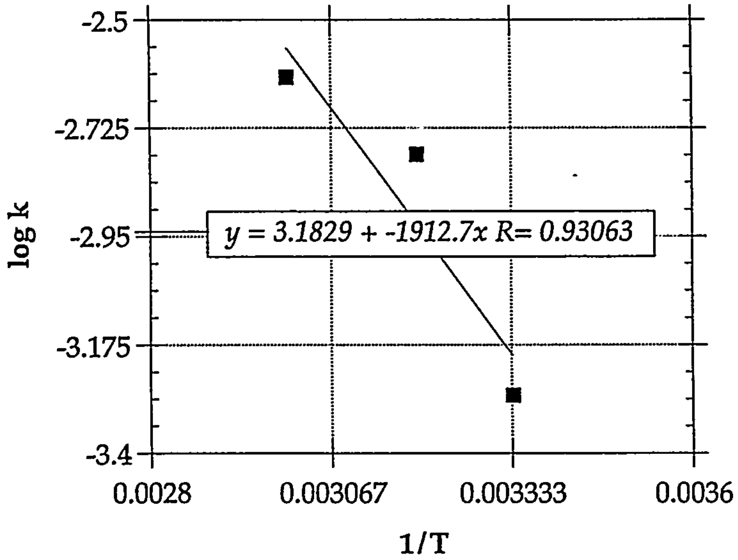


Fig. 9. Arrhenius plot of log k vs 1/T.

Table 8. Arrhenius Equation Data

temp., °C	temp. K	1/T, K^{-1}	rate constant k, h^{-1}	rate constant k, sec^{-1}	logk
25	298.16	3.335×10^{-3}	0.0316	5.258×10^{-4}	-3.28
40	313.16	3.193×10^{-3}	0.0989	1.649×10^{-3}	-2.78
60	333.16	3.002×10^{-3}	0.1441	2.402×10^{-3}	-2.62

In Table 9, extrapolation of the batch rate data to column data is made to more closely approximate the rates expected in an iron-filing treatment zone. Significantly faster degradation rates for TCE are seen in column systems relative to batch based on the much higher loading of iron (weight iron/aqueous solution, g/L) or equivalently, surface area concentration (m^2/L). Using the Peerless iron filings, we have measured a TCE half-life of 3.1 h at 25°C. Extrapolation to 40°C reduces this half-life to 1.0 h and extrapolation to 60°C reduces it further to only 0.7 h. If higher temperatures are indeed achieved in the field, this work indicates that a reduction in the sizing of the iron treatment zones may be taken.

Table 9. Extrapolation of Batch Temperature Data to Column of Iron Treatment Zone Installations batch conditions column or Lasagna
200 m^2/L 5200 m^2/L

temperature	first-order rate constant k, h^{-1}	half-life, h	first-order rate constant k, h^{-1}	half-life, h
25°C	0.0316	**22.0**	0.222	**3.1**
40°C	0.0989	**7.0**	0.695 (extrapolated)	**1.0** (extrapolated)
60°C	0.1444	**4.8**	1.014 (extrapolated)	**0.683** (extrapolated)

Electrokinetic Cell Experiments

Experiments were conducted to test the feasibility of using iron metal for treatment zones in the Lasagna process. The test cells were cylindrical columns (20 cm × 5 cm dia.) shown schematically in Fig. 10. A feed solution containing TCE at a nominal concentration of 100 ppm was fed into a chamber at the anode side of the cell. Electro-osmosis drove some of the feed solution toward the cathode. Enough feed solution was supplied so that some would overflow the chamber to enable nearly constant conditions to be maintained in the chamber. This feed chamber was separated from the anode chamber by a Nafion™ cation exchange membrane. The two reasons for using the membrane were (1) to prevent TCE from being stripped by the oxygen bubbles generated at the electrode and (2) to permit the chloride ions generated in the iron zone, as a result of dechlorination, to be collected with the feed overflow.

™ Nafion is a trademark of the E.I. du Pont de Nemours & Co., Inc

In the experiment with the iron zone, a 1- cm-thick layer of VWR iron filings was placed between two sections of kaolin clay saturated with 0.001 M Na_2SO_4. The liquid content of the packed clay was 32% by weight. The control experiment did not have an iron zone. The TCE concentration of the effluent, feed, and overflow was monitored periodically throughout the experiments. TCE concentrations were determined by hexane extraction followed by gas chromatography/electron capture detection. Periodically, analysis was conducted using purge and trap extraction on 1 and 5 ml aqueous samples followed by gas chromatography/flame ionization detection. The latter method enabled the detection of daughter products of dechlorination, such as cis-DCE, vinyl chloride, ethane, and ethene. Chloride concentration of the overflow was monitored to verify the dechlorination process. The applied current and voltage distribution was also measured through the experiment. At the end of the experiment the pH distribution was measured by inserting an 0.32 cm diameter pH electrode directly into the sample. The clay samples were chilled and then divided and extracted to determine the final TCE distribution.

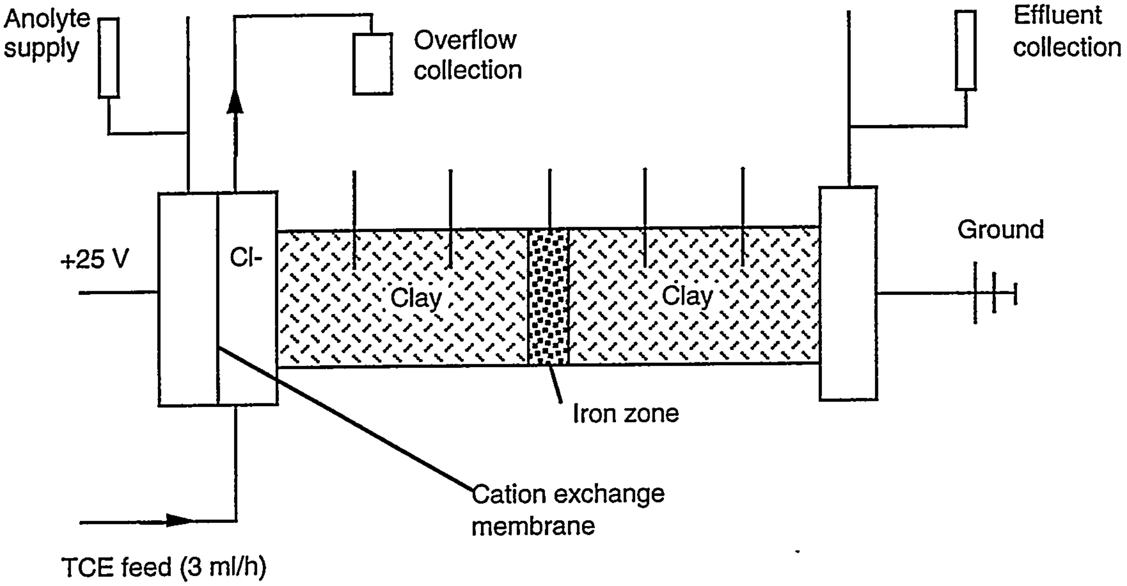


Fig. 10. Schematic of apparatus used in iron zone electrokinetic experiments.

Results and Discussion

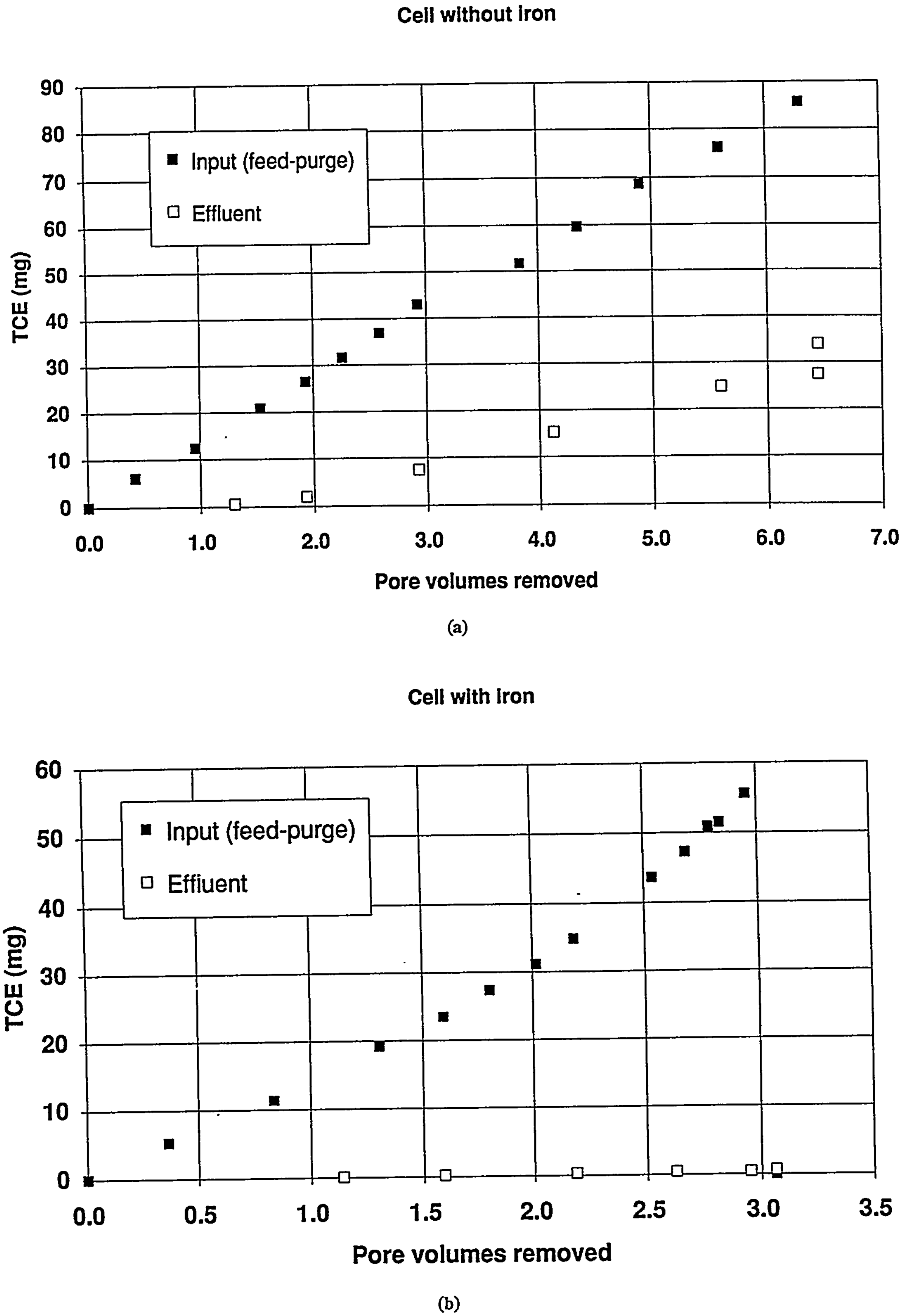
The amount of TCE entering the test cells is compared with that leaving in the effluent in Figs 11a and b. In the control cell (cell No. 1) with no iron zone TCE was fed into the clay section at a rate of about 14 mg per pore volume of liquid (135 ml). After about 1.2 pore volume moved through the cell, TCE was detected in the effluent. The removal rate of TCE was about 6.3 mg per pore volume. Hence about 45% of the TCE entering the clay was accounted for in the effluent. Most of the remaining 55% of the TCE was lost to volatilization in the cathode compartment by hydrogen bubbles generated at the electrode. Some TCE (about 10%) was lost leaking through the cation exchange membrane to the anode compartment. In the cell with the iron zone (cell No. 2), TCE was supplied to the clay section at a rate of about 16 mg per pore volume (142 ml). Only low levels of TCE (1-3 ppm) were detected in the effluent of the cell with the iron zone. About 0.35 mg of TCE per volume was collected in the effluent. Compared to the cell with no iron in which 45% of the input TCE was collected in the effluent, only 2% of the TCE was collected in the effluent of the cell with the iron zone. If losses in cell No. 2 are similar to those in cell No. 1, then about 4% of the TCE input to clay section passed through the iron zone without being dechlorinated. These results are consistent with the final TCE distribution in the pore water of the clay sections shown in Fig. 12. In cell No. 1 with no iron, the TCE concentration is essentially uniform across the sample. In cell No. 2 with the iron zone, the TCE concentration downstream (cathode side) of the iron zone is 4.2% of the upstream (anode side) concentration.

The volume of effluent collected is plotted vs time in Fig. 13. From these data one can calculate a superficial electroosmotic velocity (flow rate/cross-sectional area) of about 3.5 cm day in the control cell, some five-fold higher than the flow rates anticipated in the field. In cell No. 2 the initial flow rate was the same as in the control cell. However, the flow rate gradually decreased after about one pore volume passed through cell No. 2. After about 3 pore volumes, the flow ceased. The presence of gas pockets in the iron zone was observed while the flow rate in cell No. 2 was decreasing. Near the end of the experiment, the gases were released from the iron zone by venting the zone through a voltage probe hole in the cylinder wall. After venting the gases, the flow resumed. Analysis by GC/MS indicated that most of this gas is hydrogen.

The source of the gas is presumably hydrogen resulting from the corrosion of iron by water, or the hydrogen could be produced by electrochemical reactions at the anode end of the iron zone. These reactions could be caused by the bipolar electrode effect. The bipolar electrode effect occurs when electrically conductive solids are placed in conductive solutions in the presence of a sufficiently high electric field. In these experiments, the conductive solid region is the iron zone, and the conductive solution is the pore water in the zone. When the field is high enough, some fraction current will be carried by electrons in the solid and some by the ions in solution. Electrochemical reactions occurring at the anode and cathode side of the solid may generate gases, alter the solution pH, change the dissolution rate of the metal, and change the reduction potential of the metal.

The rate of hydrogen generation is exptected to be similar to those reported by Reardon (1995) which were on the order of 0.5 mmoles/kg iron/day. For a treatment zone 5 cm thick by 15 m deep with 7% (vol/vol) iron, the steady state flux of hydrogen permeating to the surface would be about 4 moles of hydrogen/m^2/day (4.6×10^{-5} mole/m^2/s), assuming all of the hydrogen rises to the top of the treatment zone. Assuming a mass transfer coefficient of 0.5 mole/m^2/s, typical of natural convection, the expected mole fraction of hydrogen at the ground surface would be $4.6 \times 10^{-5} / 0.5 = 9.2 \times 10^{-5}$, or 92 ppm. This hydrogen concentration would be the maximum expected at the surface of the soil, where oxygen is available for combustion. This concentration is well below the explosion limit for hydrogen (18%), and therefore dangers associated with hydrogen combustion are insignificant.

The fact that dechlorination was occurring in cell No. 2 is supported by the measurements of chloride accumulation in the feed overflow liquid. Figure 11 plots the cumulative amounts of TCE entering the clay sample and chloride collected in the overflow liquid. From the slopes of the curves it is apparent that at the end of the experiments more moles of chlorides were collected than TCE supplied to the system. The final rate of TCE entering the system was 0.0076 mmoles/day, and the rate for chloride leaving the system was 0.017 mmoles/day. If all of the TCE were dechlorinated and if all of the chloride were collected in the overflow, the ratio would be 3 moles chloride/ mole TCE. The measured ratio was 2.2 moles chloride/ mole TCE. The missing chloride may have been adsorbed on the clay or may have leaked through the membrane and become oxidized to Cl_2 gas at the anode.


Cell without iron

Cell with iron

Fig. 11. Cumulative TCE input to the system and effluent from the system vs pore volume moved through the cell. (a) control cell with no iron. (b) cell with 1-cm-thick-iron zone in the middle of cell. Clay sections were 12 cm long, 5 cm diameter. Applied voltage was 25 V. Inert electrodes were used.

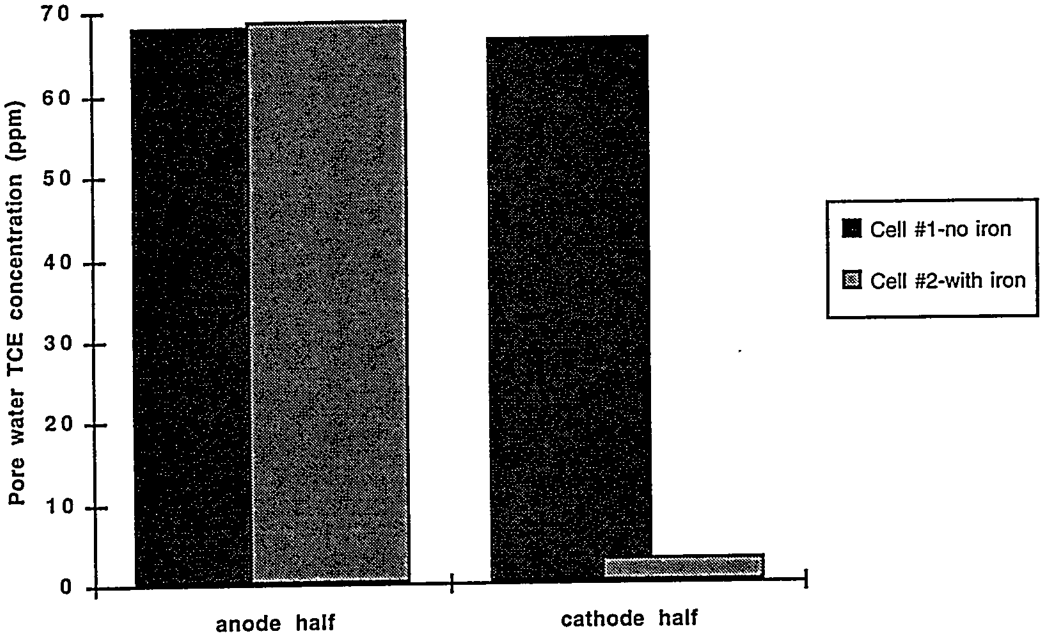


Fig. 12. TCE distribution in pore water at the end of experiment. TCE content determined by hexane extraction with GC/EC analysis.

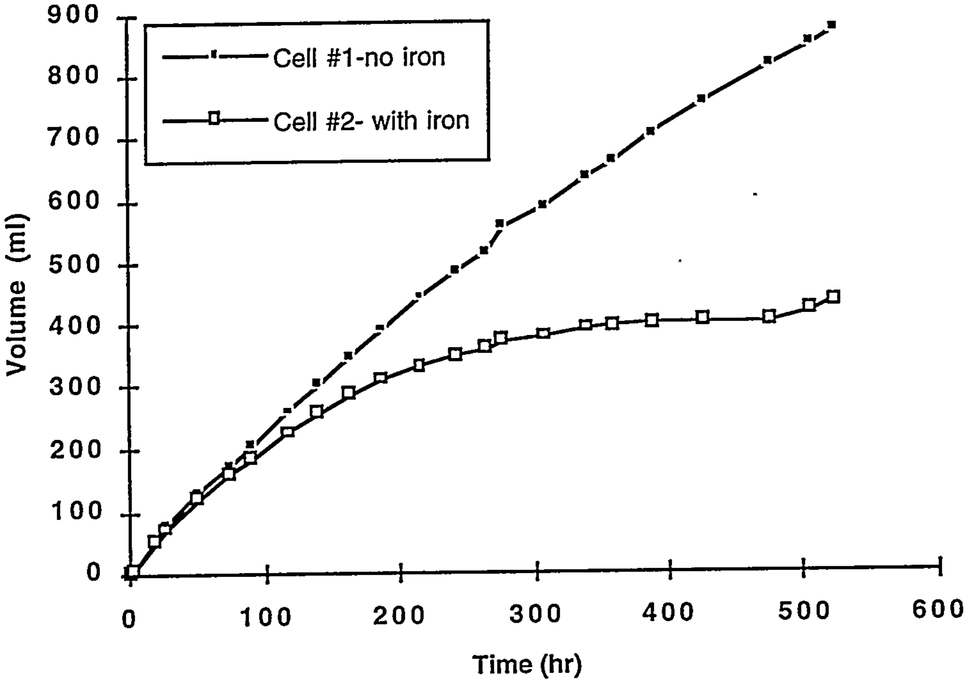


Fig. 13. Effluent volume vs time for experiments with and without iron zone.

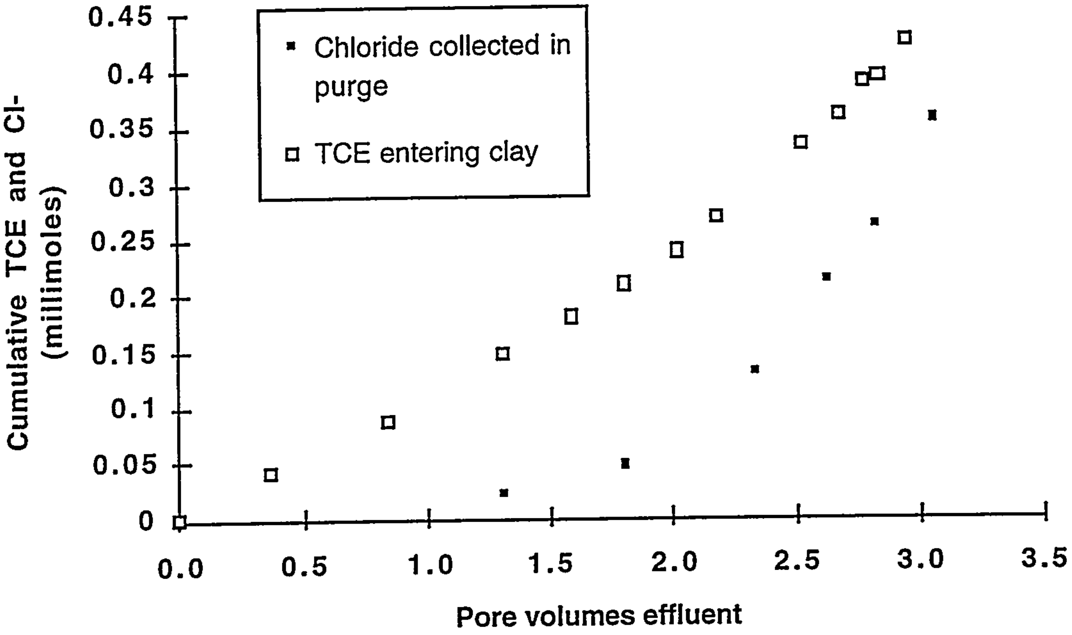


Fig. 14. Cumulative amounts of TCE input to and chloride removed from cell No. 2 .

It is important to determine the rate of dechlorination in cell No. 2, so that full-scale treatment zones can be designed. Column test with pressure driven flow on the VWR iron fillings determines that the half-life of TCE is about 30 min. To estimate the half-life in the electroosmosis cell, one must calculate at residence time. Because the flow rate was not constant in cell No. 2, it is impossible to determine a single residence time. However, the initial superficial velocity of 3.5 cm/day will set lower bound on the residence time. With the iron zone 2.5 cm thick, the lower bound residence time was about 6.8 h. Because the zone is thin, molecular diffusion may reduce then affect residence time. The order of magnitude of the time ittakes a TCE molecule to diffuse a distance of 1 cm is about one day, thus the effect of diffusion early in this experiment should be small. However later in the experiment, when the flow rate ceased, diffusion determined the residence time. Therefore, an upper bound for the residence time may be about 24 h. If we assume first-order kinetics and 4% of the TCE remains after one residence time, then the calculated half-life would be between 1.5 and 5.2 h. From this single experiment it would seem that the rate of dechlorination is somewhat slower under electrokinetic conditions than pressure-driven flow conditions. More experiments are required to verify the reaction half-life.

Another important issue regarding the sizing of the full-scale treatment zones for Lasagna^{TM} field tests is the presence of daughter products. Near the end of the experiment in cell No. 2, the feed and effluent water was sampled for analysis using purge and trap extraction (cryocool) and GC/FID detection. The results of this analysis are shown in Table 10. Given the higher toxicity of vinyl chloride compared to TCE, the treatment zone will have to be designed to achieve acceptable levels of the daughter products. Additional experiments are planned for phase II that will quantify gas production rates and examine long term performance of the treatment zones.

Table 10. Analysis of Dechlorination Daughter Products.

	Feed	Effluent	% of TCE in feed
TCE	78.8 mg/L	1.32 mg/L	1.7
cis-DCE	below d.l.	0.74 mg/L	0.94
Vinyl chloride	below d.l.	0.33 mg/L	0.42
C2 hydrocarbons	below d.l.	11.0 µg/L	
C3 hydrocarbons	below d.l.	0.21 µg/L	
C4 hydrocarbons	below d.l.	1.39 µg/L	

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D. Acronyms and Abbreviations

A563	Ambersorb 563 sorbent (Rohm and Haas)
AS	air stripper or air stripping
BPL	activated carbon (Calgon)
BTC	breakthrough curve
BTEX	benzene, toluene, xylenes
CCl_4	carbon tetrachloride
CH_2Cl_2	methylene chloride, dichloromethane
COD	chemical oxygen demand
CSTR	continuous stirred-tank reactor
CVOC	chlorinated volatile organic compound
D	desorbing gas flow rate
d_p	diameter of particle
D_c	diameter of column
DCM	methylene chloride, dichloromethane
D.O.	dissolved oxygen
DOE	Department of Energy
ΔP	pressure drop
$\Delta P/L$	pressure drop per unit length
EBCT	empty bed contact time
ECD	electron capture detector
EPA	Environmental Protection Agency
EPCM	engineering, procurement and construction management
F	feed flow rate
FBR	fluidized-bed reactor
FID	flame ionization detector
GAC	granular activated carbon
GC	gas chromatography
GE	General Electric Company
GEP	GE Plastics
H	Henry's law constant
HCl	hydrochloric acid
HRT	hydraulic retention time
HW	hazardous waste

HWTSD	hazardous waste toxic substance disposal
ID, I.D.	inside diameter
INEL	Idaho National Engineering Laboratory
K	constant in Freundlich equation (Chapter 3)
K_p	equilibrium constant (aqueous phase - Chapter 8)
K_v	equilibrium constant (vapor phase - Chapter 8)
L_c	length of column, bed height
MC, $MeCl_2$	methylene chloride, dichloromethane
MeOH	methanol
MTZ	mass transfer zone
N_2	nitrogen
n, 1/n	constant in Freundlich equation (Chapter 3)
NA	not available
O&M	operating and maintenance
OD	optical density
PAS	phosphate-ammonium salts
PCE	perchloroethylene, tetrachloroethylene
PVC	polyvinyl chloride
q	sorption capacity ($g_{CVOC}/g_{sorbent}$)
R_2A	a rich agar medium
RD	remedial design
RH	relative humidity
RI/FS	remedial investigation/ feasibility study
ROD	record of decision
SVE	soil vapor extraction
T_m	melting temperature
TCE	trichloroethylene
TSDF	toxic substance disposal facility
TSS	total suspended solids
VOC	volatile organic compound
VSS	volatile suspended solids
WWTP	wastewater treatment plant
XU, XUS	Dow XUS sorbent (Dow Chemical)

E. Units

BTU	British thermal unit
C, ¡C	Celsius, degrees Celsius
cc	cubic centimeters
cfu, CFU	colony-forming units
cm	centimeters
d, D	days
deg	degrees
F, ¡F	Fahrenheit, degrees Fahrenheit
f, ft	feet
g	grams
gal, GAL	gallons
GJ	giga joules (10^9 joules)
gpm, GPM	gallons/minute
h, hr	hours
hp, HP	horsepower
in	inches
in Hg (" Hg)	inches of mercury
k, K	thousand
kcal	kilocalorie
kg	kilograms
kw, KW	kilowatts
kw-hr, KWhr	kilowatt-hour
l, L	liters
lb, lbs	pound(s)
M	molar (moles/liter)
m	meter
mg	milligrams
MGD	million gallons/day
min	minutes
ml, mL	milliliters
mM	millimolar (millimoles/liter)
MM	million
mm	millimeters
mmol, mmole(s)	millimole(s)

mol	mole(s)
mw, MW	molecular weight
N	normal (equivalents/liter)
ppb	parts per billion
ppm, ppmw	parts per million (by weight)
ppmm	parts per million (molar)
ppmv	parts per million (by volume)
psi	pounds per square inch
psia	pounds per square inch -- absolute
psig	pounds per square inch -- gauge
sccm, SCCM	standard cubic centimeters/minute
SCF	standard cubic feet
scfh, SCFH	standard cubic feet/hour
scfm, SCFM	standard cubic feet/minute
sf	square foot
SLPM	standard liters / minute
µg	micrograms
µl, µL	microliters
µm	micrometers
µM	micromolar (micromoles/liter)
µmol, µmole(s)	micromole(s)
yr	year
"	inches
'	feet
#	pounds