DOE/OR/22459--T2

Monsanto

Lasagna™

November 1997

Development of an Integrated *in-situ* Remediation Technology

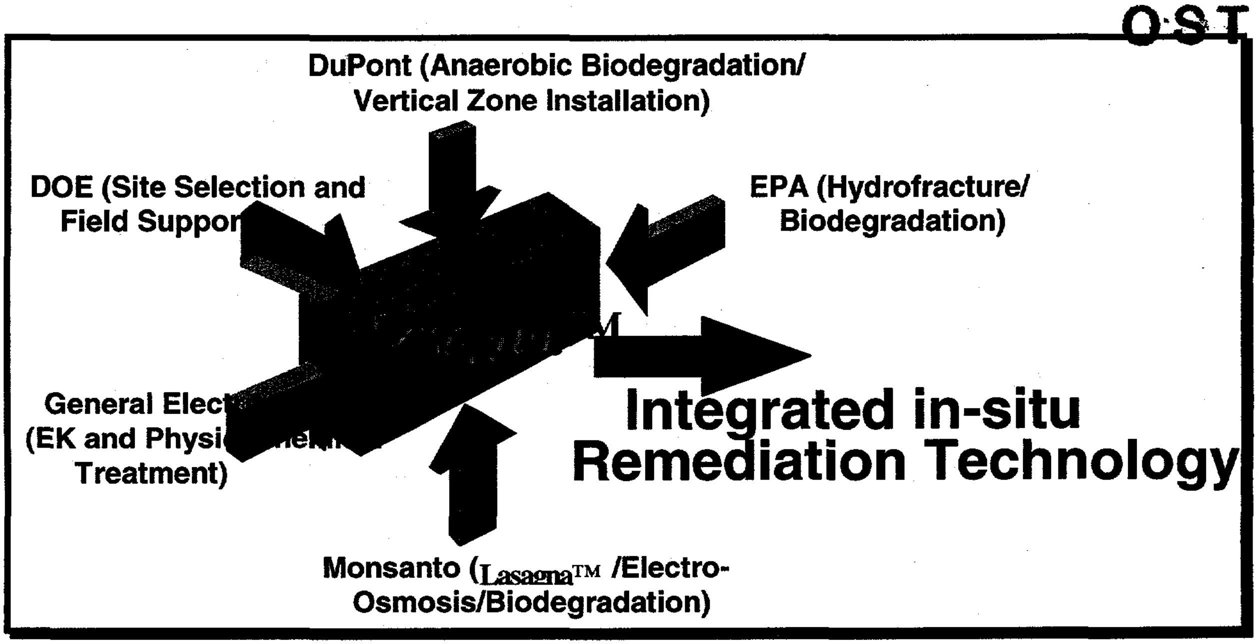
Draft Topical Report for Task #3.3 entitled, "Iron Dechlorination Studies" (September 26, 1994 - August 31, 1997)

Robert Orth, Taiwo Dauda and David E. McKenzie

Monsanto Company

RECEIVED
JUL 14 1998
OSTI

DOE Contract Number: DE-AC05-96OR22459



Submitted to:
U. S. Department of Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

Submitted by:
Monsanto Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63167

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

TM- A Trademark of Monsanto Company

DISCLAIMER

Development of an Integrated *in-situ* Remediation Technology

DOE Contract Number: DE-AC05-96OR22459

Draft Topical Report for Task # 3.3 - "Iron Dechlorination Studies" (January 18, 1996 - August 31, 1997)

Submitted by:

Robert Orth, Taiwo Dauda, and David E. McKenzie
Monsanto Company
800 N. Lindbergh Boulevard, St. Louis, MO

Abstract

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 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 utilized to move the contaminants back and forth through those zones until the treatment is completed. The present Topical Report for Task #3.3 summarizes the iron dechlorination research conducted by Monsanto Company.

B. Acronyms and Abbreviations

DCE	Dichloroethylene
DNAPL	Dense Non-Aqueous Phase Liquid
DOE	Department of Energy
DuPont	E. I. du Pont de Nemours & Co., Inc.
EPA	Environmental Protection Agency
GC	gas chromatography
GE	General Electric Company
LMES	Lockheed Martin Energy Systems
ROD	Record of Decision
RREL	Risk Reduction Engineering Laboratory
SWMU	Solid Waste Management Unit
TCE	trichloroethylene
VC	vinyl chloride

C. Units

C, °C	Celsius, degrees Celsius
cm	centimeters
d, D	days
deg	degrees
F, °F	Fahrenheit, degrees Fahrenheit
f, ft	feet
g	grams
gal, GAL	gallons
h, hr	hours
in	inches
k, K	thousand
kg	kilograms
l, L	liters
lb, lbs	pound(s)
m	meter
mg	milligrams
min	minutes
ml, mL	milliliters
mm	millimeters
ppb	parts per billion
ppm, ppmw	parts per million (by weight)
psi	pounds per square inch
µg	micrograms
µl, µL	microliters
"	inches
'	feet
#	pounds

D. Table of Contents

List of Figures

E. 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 in 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, utilizing very low power consumption, in moving water uniformly through low-permeability soils.

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 figure on the cover page shows a schematic diagram of the various technologies which the government/industry consortium has integrated for the development of an *in-situ* remediation technology.

Project History

To date, this project has been conducted in two parts: Phase I and Phase IIa. A Management Plan was originally prepared for Phase I of this project by Monsanto and submitted on November 30, 1994. That plan summarized the work plan which was developed in conjunction with DuPont, GE, EPA's Risk Reduction Engineering Laboratory (RREL), Lockheed Martin Energy Systems (LMES), and the Department of Energy. The DOE Gaseous Diffusion Plant in Paducah, Kentucky, was chosen as the site for the initial field tests. The specific contamination site selected at the Plant was Solid Waste Management Unit (SWMU) 91. For Phase I, the plot selected to demonstrate the process measured 10 feet by 15 feet by 15 feet deep.

CDM Federal Programs Corporation was chosen to provide the on-site support of the field tests which 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. Technology development was carried out under the present contract in Phases I and IIa by Monsanto, DuPont, and GE. These studies evaluated various degradation processes and their integration into the overall treatment scheme at bench and pilot scales.

Phase IIa was approved on January 18, 1996. For this phase, a significantly larger plot was selected, measuring 21 feet by 30 feet by 45 feet deep, and significant design changes were also implemented in the materials used to construct the electrodes and treatment zones. While Phase I was conducted to demonstrate the movement of TCE from the soil into the treatment zones, Phase IIa was conducted to demonstrate the full scale remediation of the SWMU 91 site. This latter phase included the use of zero-valent iron metal which degrades TCE to light hydrocarbons and chloride ions. In August of 1997, DOE advised that, based upon the performance of the *Lasagna*™ process during Phases I and IIa, *Lasagna*™ would be the preferred remedy given in the proposed Record of Decision (ROD). If signed, this ROD will be the first example of the use of *Lasagna*™ for the full scale remediation of a TCE-contaminated clay site. ROD approval is expected in calendar-year 1998.

Technical Deliverables

Table E-1 summarizes the four topical reports which have been written to describe the results obtained from the Phase IIa research. This table also shows which organization is primarily responsible for the tasks and for preparing the topical reports. The present topical report summarizes Task #3.3.

Table E-1. List of Topical Reports and Responsible Company

Topical Report	Company
Task #3.1 - Emplacement Technology	DuPont
Tasks #3.2 - Modeling and Iron Dechlorination Studies	GE
Task #3.3 - *Lasagna*™ and Iron Dechlorination	Monsanto
Task #7.2 - Field Scale Test	Monsanto/DuPont/GE

F. Iron Dechlorination Studies

Abstract

The reduction of trichloroethylene (TCE) by metallic iron was studied under conditions in which the trichloroethylene would exist as a separate phase in a water/iron system. The products of the reaction were determined over time using gas chromatography and mass spectrometry. The kinetics of the loss of TCE and the formation of chloride were determined to follow zero-order kinetics under these conditions with zero-order rate constants of 4.8×10^{-3} mg TCE hour^{-1} g^{-1} iron and 3.8×10^{-3} mg Cl^- hour^{-1} g^{-1} iron. The -order rate was observed to depend on the mass of iron present. The reaction was carried out in deuterium oxide to compare the reaction pathways suggested in the literature for solution reduction of TCE. It was observed that the major product was acetylene with minor components of ethane and ethene. The deuterium oxide showed that the ethene and ethane were composed of a 68% totally deuterated ethene and 32% ethene containing only one hydrogen. No deuterium was evident when acetylene formed in the deuterium oxide system, indicating that all the hydrogen in the Dense Nonaqueous Phase Liquid (DNAPL) arises from TCE. The result of this study indicates that metallic iron can dechlorinate DNAPL TCE.

Introduction

The new Lasagna™ *in-situ* soil remediation technology combines electrokinetics, treatment zones, and a strategy which allows for the control of liquid flow (electro-osmosis) to remove contaminants from low-permeability soils[1, 2, 3, 4]. The Lasagna™ process operates through the use of planar electrodes which are implanted on the outside boundaries of a contaminated zone. The electrodes are supplemented by several planar treatment zones implanted between the electrodes. When power is applied to the electrodes, electrokinetic flow is induced and water is moved through the soil electro-osmotically. Contaminants which are soluble in the water are moved through the treatment zones toward the cathode. The treatment zones can either capture the contaminant or chemically react with the contaminant and thus remove the contamination from the soil. Recently a larger scale field study was completed in a TCE-containing clay at DOE's gaseous diffusion plant in Paducah, Kentucky, where the treatment zones contained metallic Fe zones to destroy the TCE[5]. Metallic iron was used as a result of extensive evaluations undertaken

---

[1] United States Patent No. 5,398,756, March 21, 1995.

[2] United States Patent No. 5,476,992, December 19, 1995.

[3] Christopher Athmer, Sa V. Ho, B. Mason Hughes, Wayne P. Sheridan, P. H. Brodsky, "Large Scale Field Test of the *Lasagna*™ Process (September 26, 1994 - May 25, 1996) DOE document number DOE/METC/31185-5390De97002156.

[4] S. V. Ho, P. W. Sheridan, C. J. Athmer, M. A. Heitkamp, J. M. Brackin, D. Weber, and P. H. Brodsky, 1995, *Environ. Sci. Technol.*, 29, 2528.

and reported in laboratory and field studies[6, 7, 8, 9, 10, 11, 12, 13]. Field tests using iron zones as a reactive barrier for the in-situ treatment of ground water contaminated with chlorinated hydrocarbons[6, 7, 8, 9] have demonstrated success in dechlorinating the contamination .

In the characterization of the study site, it was found that some areas of the contaminated zone contained DNAPL TCE. This finding raised an important question as to the effectiveness of zero-valent iron in reductively dechlorinating TCE under conditions in which the iron would be interacting with DNAPL TCE as opposed to TCE dissolved in water. Also, questions arose concerning possible by-products and whether these by-products would be different from those observed in past studies of TCE dissolved in water. These questions are important in potential applications using zero-valent iron to treat source contamination directly. The experimental results from this study should provide helpful answers to these questions.

Laboratory studies on the reaction pathways and the rates of reactions for TCE and other chlorinated ethylenes have been studied by many groups. The mechanism of the dechlorination process is thought to be a surface reaction and to depend on the surface area. This surface dependence shows the type of results that would be expected for site-limited reaction kinetics[10, 11, 12]. As concentration increases to high levels, the kinetics would be expected to become zero order.

---

[5] C. J. Athmer, S. V. Ho, and B. M. Hughes, 1997. "Results of the *Lasagna*™ Phase II Field Experiment," Paper 94 presented at *Emerging Technologies in Hazardous Waste Management IX*, American Chemical Society, Pittsburgh, Pennsylvania, September 15-17.

[6] R. W. Gillham and S. F. O'Hannesin, 1994. *Ground Water* 32, 958-967.

[7] R. E. Gillham, 1995. "Resurgence of Research Concerning Organic Transformations Enhanced by Zero Valent Metals and Potential Application in Remediation of Contaminated Ground Water," Natl. Meet Amer. Chem. Soc., Div. Envorin. Chem. 35, 691-694.

[8] R. W. Puls, R. M. Powell, and C. J. Paul, (1995). "In Situ Remediation of Ground Water Contaminated with Chromate qnd Chlorinated Solvents Using Zero-Valent Iron: A Field Study," Natl. Meet Amer. Chem. Soc., Div. Envorin. Chem. 35, 788-791.

[9] C. L. Yamane, J. D. Gallinatti, F. S. Szerdy, T. A. Delfino, D. A. Hankins, and J. L. Vogan, 1995. "Installation of a Subsurface Groundwater Treatment Wall Composed of Granula Zero-Valent Iron" Natl. Meet Amer. Chem. Soc., Div. Envorin. Chem. 35, 792-795.

[10] M. M. Scherer and P. G. Tratnyek, 1995. "Dechlorination of Carbon Tetrachloride by Iron Metal: Effect of Reactant Concentration," 209th National Meeting, Anaheim, Ca, *American Chemical Society*, Vol. 35, No1. pp 805-806.

[11] T. L. Johnson, M. M. Scherer, and P. G. Tratnyek, 1996. "Kinetics of Halogenated Organic Compound Degradation by Iron Metal," Environ. Sci. Technol. 30(8): 2634-2640.

[12] D. R. Burris, T. J. Campbell, and V. S. Manoranjan, 1995. "Sorption of Trichloroehtylene and Tetrachloroethylene in a Batch Reactive Iron Water System.," Environ. Sci. Technol. 29(11): 2850-2855.

[13] L. J. Matheson, and P. G. Tratnyek, 1994. "Reductive Dehalogenation of Chlroinated Methanes by Iron Metal," *Environ. Sci. Technol. 28*(12), 2045-2053.

Studies on carbon tetrachloride dechlorination showed formation of chloroform and methylene chloride sequentially[13]. The mechanism was suggested to be a direct electron transfer from the iron. The process is considered by Matheson[13] to be a corrosion process with the Fe forming Fe (II). Roberts et al[14] and Campbell et al[15] have put forth reaction pathways for the formation of the observed volatile hydrocarbons from dechlorination of TCE and PCE which combine β elimination and hydrogenolysis. The pathways are supported by the observed products and calculations. It has been observed by many researchers [15, 16, 17] that the observed products are ethylene, ethane, and acetylene,with minor amounts of higher C_3 to C_6 hydrocarbons. Along with these hydrocarbons, minor amounts of vinyl chloride and isomers of dichloroethylenes have been observed. The carbon mass balance has varied ranging from 30% to 76%, whereas the chloride balance is generally in the 90 to 100% range.

In the results reported here, the reduction of TCE at levels equivalent to 5,880 ppm were studied in batch reactors. This level of TCE is approximately five times its solubility in water, thus insuring that there is an organic-phase TCE present in the batch reactor. The batch reactor was chosen so that the loss of volatile products would be minimized. The volatile compounds were determined by headspace analysis using gas chromatography with mass spectrometry (GC/MS), and the chloride concentration was determined using a chloride selective electrode. The total loss of TCE was determined by a total extraction of the reaction media with hexane. No attempt was made in this study to carry out a carbon mass balance. However, the mass balance for the loss of TCE and the production of chloride was determined. A set of reductive dechlorination experiments was carried out in deuterium oxide, because of the interest in comparing the volatile products of this reaction with those reported in the literature and the suggested reaction pathways. Since TCE has one hydrogen, then incorporation of deuterium into products such as ethylene, ethane and acetylene should give insight into the reaction pathways suggested by Campbell[15] and Roberts[14].

Experimental Section

Reagent grade trichloroethylene was obtained from Fisher Scientific. Analysis by GC/MS showed trace levels of *cis-* and *trans-*dichloroethylene (DCE) at levels less than one part in 10,000. The iron used in the study was Peerless iron with a mesh size of 8 to 50. The iron was prepared by washing with deionized water several times to remove iron oxide fines. If not

---

[14] A. L. Roberts, A. Totten, W. A. Arnold, D. R. Burris, and T. J. Campbell, 1996. "Reductive Elimination of Chlorinated Ethylenes by Zero Valent Metals," *Environ. Sci. Technol. 30*(8), 2654-2659.

[15] T. J. Campbell, D. R. Burris, A. L. Roberts, and J. R. Wells, 1997. "Trichloroethylene and Tetratchlorethylene Reduction in Metallic Iron-Water-Vapor Batch System," *Environ. Toxicol. Chem. 16*(4), 625-630.

[16] T. Senzaki, and Y. Kumagai, 1989. "Removal of Chlorinated Organic Compounds from Wastewater by Reduction Process: II. Treatment of Trichloroethylene with Powder. *Kogyo Yosui. 369,* 19-25.

[17] W. S. Orth, and R. W. Gillham, 1996. "Dechlorination of Trichloroethene in Aqueous Solution Using Fe°," Environ. Sci. Technol, 30:60-71.

immediately used, the iron was then dried under a stream of nitrogen and stored under nitrogen. The surface area of the Peerless was found to range from 1.2 to 1.6 m2/g as determined by BET analysis using N2. The Peerless was found to have as high as 3% carbon content. Calibration gases were obtained from Scott Specialty Gasses. Several different mixtures were used containing acetylene, ethane, ethene, propane, propene, butane, and butene in nitrogen. Deuterium oxide was obtained from Cambridge Isotope Laboratories, Inc. with a purity of 99.9%.

The batch experiment used 15 mL borosilicate bottles which were capped with Teflon miniert valves so that headspace samples could be taken periodically. The mininert valve allowed the samples to be exposed to the silicone septum only during sampling. It was found that the piercing of a Teflon lined septum would allow the TCE to migrate into the silicone backing. The experiment consisted of 10 bottles which contained TCE and Milli-Q water. The total volume was 10 mL leaving 5 mL headspace. A second set of 10 bottles was prepared which contained 7.2 grams of Peerless iron and Milli-Q water with a total displacement of 10 mL, leaving 5 mL headspace. TCE was added to these bottles after capping so that the amount of TCE would be equivalent to 5,880 ppm. No attempt was made to control pH during the experiment, since in many reactive barriers installed in the field there has been no attempt to control pH in reactive zones. All the bottles were prepared in an anaerobic chamber flushed with nitrogen. The bottles were placed on a wheel which rotated at 15 revolutions per minute (rpm) inside the anaerobic chamber. A control and a sample containing 14 g were prepared in the same manner as the aforementioned samples. These were analyzed after 96 hours for TCE loss and chloride production. This was done to obtain information as to the effect of surface area on the reaction rate.

A batch reactor was set up to test the extreme case where iron would be in contact with liquid phase TCE with small amounts of water dissolved in the TCE. This reactor was prepared by adding one gram of Peerless to a 10 ml borosilicate bottle. Two mL TCE was added to the iron, and the bottle was capped with Teflon miniert valve. 20 µL water was added through the mininert value. This bottle was rotated at 15 rpm for 96 hours and the headspace sampled for volatile hydrocarbons.

At set intervals headspace samples were taken with a gas-tight syringe and analyzed on a GSQ column or on an Al2O3/KCl column using a Hewlett-Packard 5890 gas chromatograph. Both columns had dimensions of 30 meters by 530 micron inside diameter (id). It was found that the hydrocarbons ethane, ethene, acetylene, propane, and propene and chlorinated products DCE and vinyl chloride could be separated on these columns. The samples were injected in splitless mode at an injector temperature of 200°C. The initial temperature of the GC oven was 50°C, which was maintained for 2 minutes and then programmed to 200°C at 10°C/minute. The detector was a Hewlett-Packard mass selective detector (model 5971). The detector was scanned over the mass range of m/z 20 to 200 amu.

The chloride concentration was determined by diluting 0.5 or 1 mL to 10 or 20 mL, respectively, and using a chloride selective electrode and the standards addition method.

Total TCE in each vial was obtained by injecting 3 mL of hexane into each bottle. After shaking, the vial was opened and the contents placed in a separatory funnel. This included the iron metal which was transferred by washing with several aliquots of hexane. The total volume of hexane was 100 mL. The funnel was capped and shaken. The aqueous phase was removed and placed in a second funnel with 50 mL of hexane. The hexane was removed from the first funnel and 100 mL of hexane was added to the iron remaining in the funnel. This mixture was shaken again and the hexane combined with the first 100 mL. This was repeated again to yield a total volume of 300 mL of hexane. The separatory funnel containing the water was washed with 50 mL hexane. The hexane was removed and set aside too determine residual TCE that had not been extracted in the first wash. It was found that the TCE residual was small compared to the overall TCE volume in each of the bottles when sampled. This was repeated with the controls to determine recoveries. It was found that 95% to 102 % recoveries were obtained with a precision in the 5 to 10% range. This suggests that the first samples taken involved a high degree of uncertainty. The total number of moles of TCE was determined for each bottle and compared to the total number of moles of chloride found in the aqueous phase.

For the deuterium oxide studies, only headspace analysis was undertaken to determine the deuterium labeling on each of the volatile products formed during the reaction. The same model GC and the same column were used in the headspace analysis. However, a high resolution ZAB-E mass spectrometer was used so that the m/z from nitrogen in the air could be distinguished from the m/z 28 which arises from ethene and ethane. In the case where deuterium atoms may be present, separation of m/z 32 due to background of oxygen was also necessary. By methods of isotopic dilution, the number of deuteriums could easily be determined for the volatile hydrocarbons. The high resolution instrument was operated in EI mode with a resolution of 5,000. As part of the headspace analysis, the composition of the hydrogen gas was determined by GC/MS using a molecular sieve column. The mass spectrometer detector was the ZAB-E. A control containing iron and D_2O was also analyzed so that results could be compared to the iron/TCE/D_2O experiment.

Results and Discussion

Figure F-1 shows the results for the production of chloride and the loss of TCE over the course of the study. The uncertainties in the TCE loss early in the study were expected, since the determination involved measuring small changes in a large signal. A kinetic model for the loss would be

$$\frac{-d[TCE]}{dt} = k$$

where k is the zero-order rate constant. The integrated form of this equation gives a linear loss of TCE with time and is independent of the TCE concentration. As can be seen in Figure F-1, the loss of TCE is linear with time. The zero-order rate constant based on the slope of the line was $4.8\text{x}10^{-3}$ mg TCE hour^{-1} g^{-1} of Peerless iron. A better approach to reporting this zero-order rate constant would be to express it in terms of the surface area of the Peerless iron. This would allow the value to be compared to other iron source rates which may have different surface areas. The surface normalized zero-order rate constant using the high value of 1.6 m^2/ g Peerless is $3.0\ \text{x}10^{-3}$ mg TCE hour^{-1} m^{-2} of Peerless iron. As the TCE concentration was reduced to less than 2,000 ppm, the data no longer showed a linear response. This indicates that the mechanism changes as the solubility limit of TCE is approached. However, there was insufficient data collected in the range below 2,000 ppm TCE to determined the exact mechanism.

The chloride production values increased over time in a linear fashion. As with the TCE reduction curve, as the concentration of chloride reached the point where the TCE concentration approached <2,000 ppm the curve was no longer linear. This indicates that the chloride production mechanism changes and follows the same change as was observed for TCE. The plot of the chloride mass indicates that the production of chloride follows zero-order kinetics. A linear fit of the production of chloride indicates that the zero-order rate constant is 3.8×10^{-3} mg Cl^{-1} $hour^{-1}$ g^{-1} of Peerless iron (2.4×10^{-3} mg Cl^{-} $hour^{-1}$ m^{-2} of iron). This is lower than the value obtained for TCE loss; however, considering the uncertainty in the values for TCE loss, this agreement is considered good.

The zero-order rate constant for TCE loss can be used to calculate the time it would take a reactive zone of Peerless iron to degrade DNAPL TCE to a level near the solubility limit of TCE. The calculation would be a best case situation where the iron would be mixed homogeneously with the DNAPL TCE . The loss in this zone would depend on the zero-order rate constant and the surface area of the iron per pore volume in the mixed zone. Under conditions of pure iron zones using Peerless iron, this ratio could be as high as 3.5 m^2 / mL. Using this surface-area-to-pore-volume ratio and the zero-order rate constant for loss of TCE normalized to surface area, a contaminated site with a DNAPL TCE concentration of 5,880 would require 19.4 days to reach 1,100??? ppm, or the approximate??? solubility of TCE in water. This would include the assumption that the flow of the DNAPL away from the iron is slow compared to the degradation. These assumptions in this simple model are not meant to reflect reality; indeed, this calculation is meant to demonstrate that the *in-situ* treatment of DNAPL would occur within a manageable time frame.

The chloride mass recoveries as compared to the loss of TCE over the course of the experiment was found to give a mole ratio of 2.9±0.2 chloride to 1 mole of TCE lost. The ratio was obtained by using the individual values from Figure F-1. The uncertainty is the standard deviation of the mean of the 8 ratios. For total removal of chlorine from TCE this value should be 3. Within experimental uncertainties, all the chlorine is being removed from TCE as chloride.

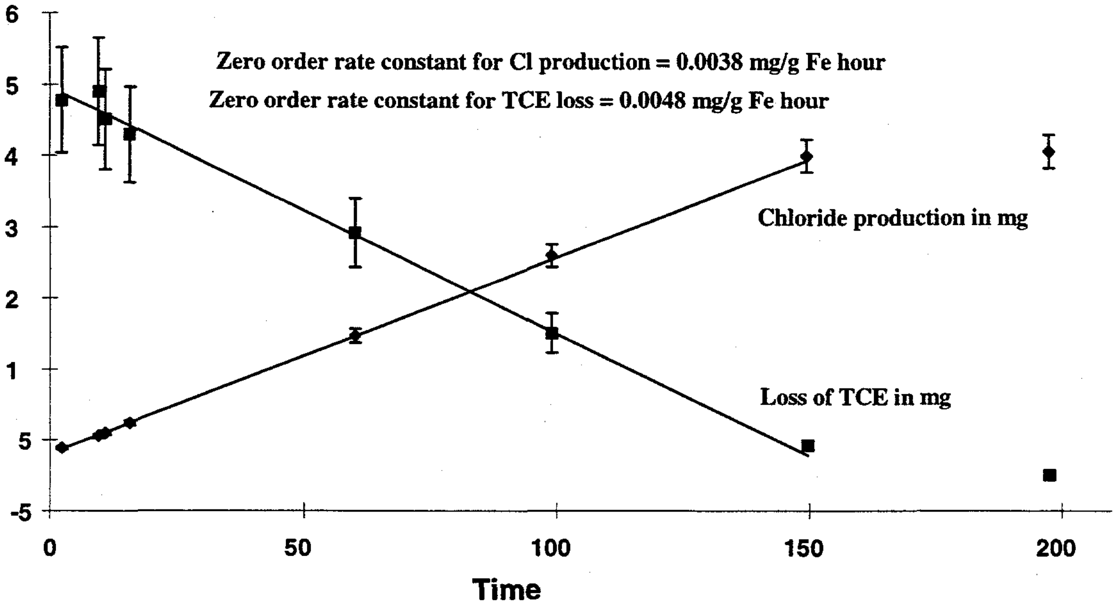


Figure F-1. The Loss of DNAPL Trichloroethylene and the Production of Chloride from an Peerless Iron Water Mixture.

(The lines are least squares fit to the data.)

These results demonstrate that reductive dechlorination does depend on surface coverage as suggested by many reports in the literature[10, 11]. Burris et. al.[12] has shown that a substantial amount of TCE adsorbs to the surface of iron. In the same study, it was shown that much of the adsorbed TCE does not react, indicating that only a portion of the surface is active. Thus, at the high level of TCE used in this study, the active sites will be totally covered. An experiment was conducted over a duration of 96 hours in which the amount of iron was doubled to 14g. The amount of TCE lost after 96 hours was 1.8 times that at the 7.2 gram level, which supports further the surface effect of the iron in this reaction.

Figures F-2A and F-2B show the results of the gas chromatography/mass spectrometry analysis after 96 hours and 1,976 hours. The major product observed in Figure F-2A is the large amount of acetylene as compared to ethene and ethane. Results reported in the literature for degradation products of TCE dissolved in water shows ethene as the major product with ethane about one third of the value for ethene[15, 16]. Due to the kinetics, this ratio may change somewhat depending on when the comparison is made. Acetylene in all studies reported was a minor product[15, 16]; however, inthe results shown in Figure F-2A, acetylene is greater than 7 times the amount of ethene and >20 times the amount of ethane. The observation that acetylene has become the major product would indicate that a change in the reaction pathway has taken place as compared to that observed with TCE dissolved in water. Roberts, et al has suggested that a path to acetylene could be through β elimination. This would be followed by hydrogenolysis. This reaction path, which is summarized below, would go through an intermediate of chloroacetylene. The chloroacetylene has been observed by several research groups[13, 14], but no chloroacetylene was detected in these experiments.

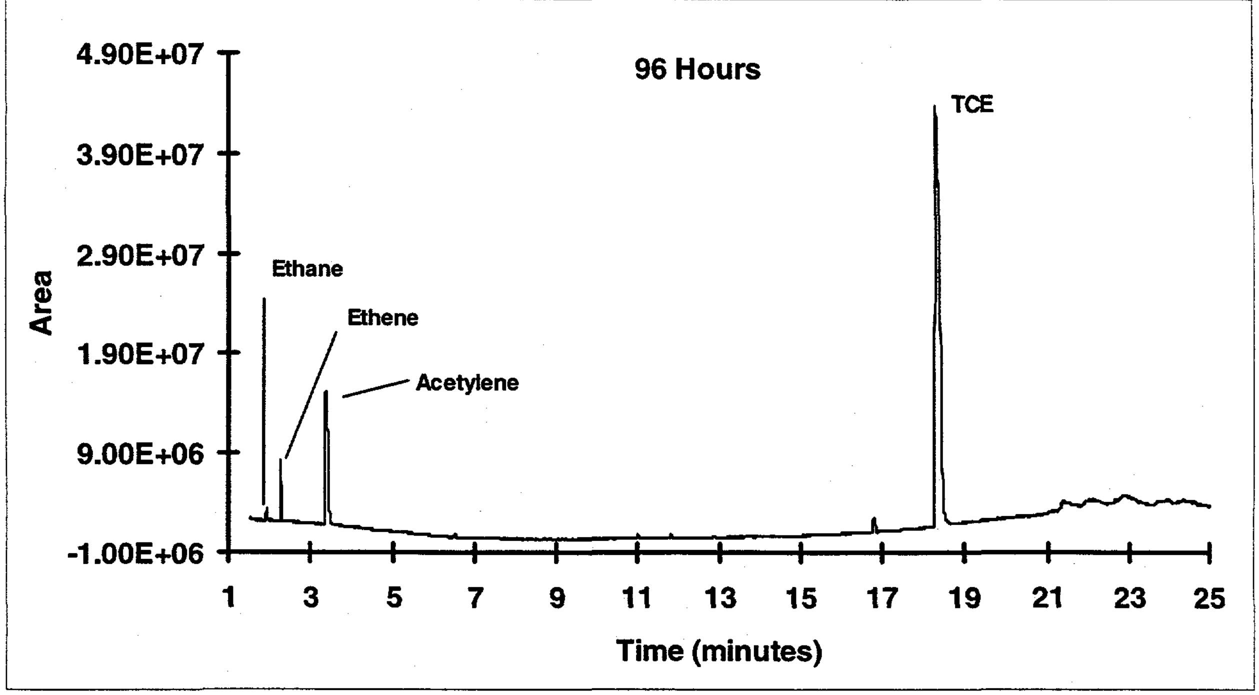


Figure F-2A. Total Ion Gas Chromatograph for DNAPL TCE/Fe/H_2O After 96 Hours.

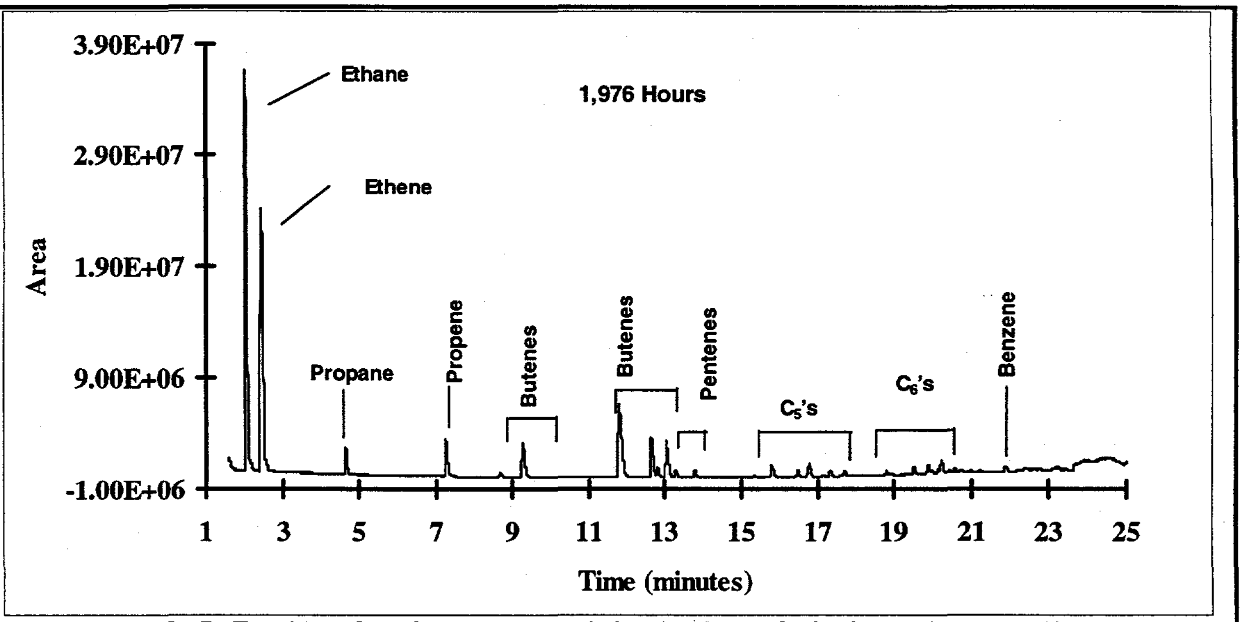


Figure F-2B. Total Ion Gas Chromatograph for DNAPL TCE/Fe/H_2O After 1976 Hours.

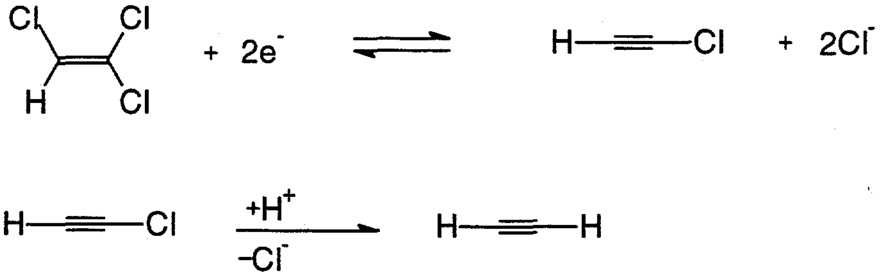


Figure F-2B shows the gas chromatography/mass spectrometry results after 1,976 hours. Note that the major products are now ethane and ethene. In a closed system the acetylene could react on the iron surface to form these products[15]. The chromatogram also shows many higher hydrocarbons that are formed over time. They include hydrocarbons containing up to six carbons. Both unsaturated and saturated hydrocarbons are present based on the mass spectrum. There was a trace level of benzene detected in this sample as well. This could arise from the acetylene reaction on the iron surface. The levels produced from a DNAPL system could be important in terms of using metallic iron in treating sources of TCE contamination in the ground. Since this was a closed system, the products observed after the length of time this experiment was run may not be the same as those observed in column or field studies. The batch reactor is a closed system, whereas in the field and column experiments, migration of acetylene from the iron may change the observedproduct distribution.

The equivalent concentration of 5,880 ppm is not the extreme that could be encountered in a DNAPL TCE zone. The zone could contain pure phase TCE. The TCE phase could be surrounded by water which would assure that the TCE would be saturated in water. The solubility limit of water in TCE is near 4%. With this in mind a limited experiment was undertaken which used pure TCE with about 0.6% water. This was run for a 96-hour period, and the headspace was then analyzed for the presence of volatile hydrocarbons. The surface area of the iron to 1 mL of TCE was 1.6 m^2 . The headspace results indicated that acetylene was being produced along with ethene. Acetylene was the major product with ethene approximately five times lower than the acetylene concentration in the headspace. The Henry's law constants for ethene and acetylene were not determined for TCE, so caution should be used in comparing the ratio of acetylene to ethene. The main point of this single experiment is that it appears that dechorination continues even under conditions where TCE has only 0.6% water present. This result neither indicates whether the reaction continues for long periods of time nor does it indicate the exact reaction mechanism.

In the commercial use of chloroalkenes and alkanes as solvents for cleaning metals, the reactivity of these compounds with metal surfaces has been known and studied[18, 19]. Vigorous

---

[18] W. L. Archer and E. L. Simpson, 1977. "Comparison of Chlorinated, Aliphatic, Aromatic, and Oxygenated Hydrocarbons as Solvents," *Ind. Eng. Chem. Prod. Res.* Dev. 16(4): 319-325.

[19] Archer, W.L., Simpson, E.L. (1977). Chemical Profile of Polychloroethanes and Polychloroalkenes, *Ind. Eng. Chem. Prod. Res.* Dev. 16(2): 158-162.

reactions with aluminum results in the reaction producing metal chlorides and pentachloro-1,2 butene. Reactions with iron were observed as well, yielding the same products. Dry systems of chloronated alkenes showed only marginal reactions. The commercial uses of the chlorinated alkenes and alkanes for metal degreasing required that organic inhibitors be added to stabilize the solvents when in contact with metals. Corrosion of metals in contact with wet TCE can be very high[20]. The presence of water appears to be necessary to solubilize the metal chloride formed[18]. The observation of the formation of acetylene in this study would indicate TCE lost all of the chlorines and the formation of the dimer is not the only organic product formed.

The large amount of acetylene observed early in the 5,880 ppm experiment suggests that the reaction path leading to this product is favored under DNAPL conditions. Since chloroacetylene was not observed, the use of deuterium oxide in place of water was one method of determining the reaction path to form acetylene. Figure F-3 shows the mass spectrum for the observed acetylene. If the acetylene were totally deuterated, the mass spectrum would have an observed molecular m/z of 28 with fragments of 26 and 24 amu. If the acetylene contained one deuterium atom, the mass spectrum would have an observed molecular m/z at 27 amu with fragments of 26, 25, and 24 amu. If no deuterium were present, then the mass spectrum would consist of molecular m/z 26 amu with fragments of 25 and 24 amu. If there is a mixture of these deuterated acetylenes, then the observed spectrum would be made up of a combination of these three possibilities. The mass spectrum in Figure F-3 is that expected for acetylene with no deuterium incorporation. Since the only source of hydrogen in this experiment is TCE, then the hydrogen on the acetylene must arise from TCE. This raises some interesting points about the reaction path suggested above for forming acetylene. In the case where the β elimination step is followed by a hydrogenolysis step and the proton arises from water, the deuterium oxide would give monodeuterated acetylene according to the following reaction:

---

[20] Demo, J.J.,Jr. 1968. Effect of Inorganic Contaminants on the Corrosion of Metals in Chlorinated Solvents. *Corrosion* (1968), 24(5), 139-49.

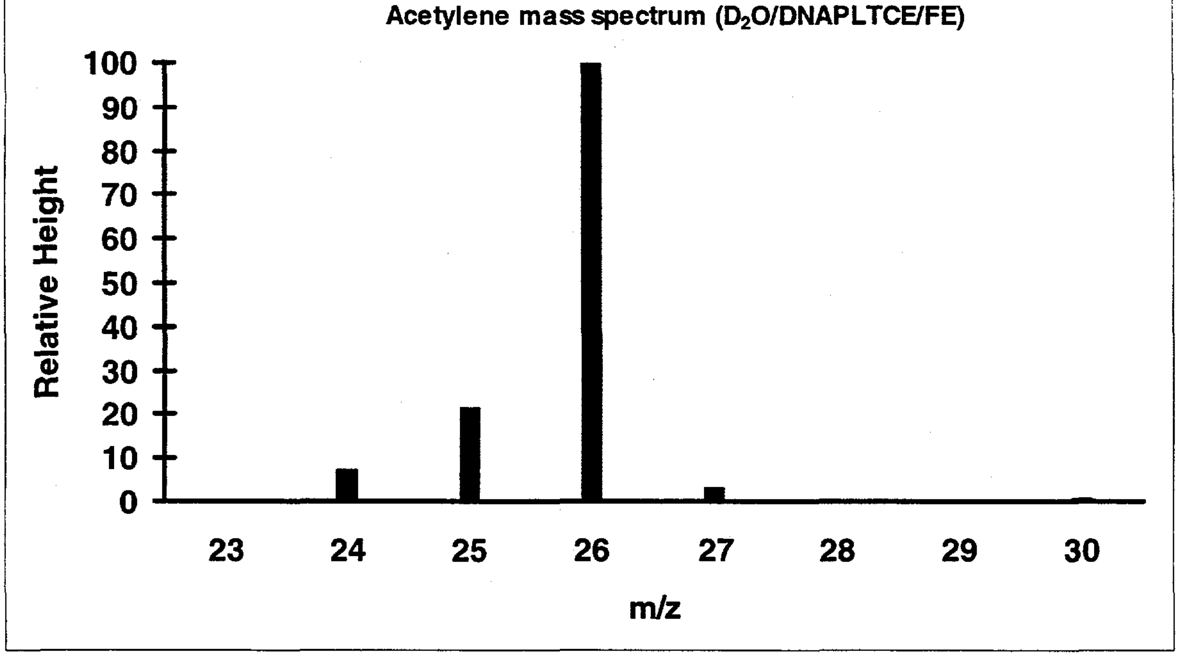
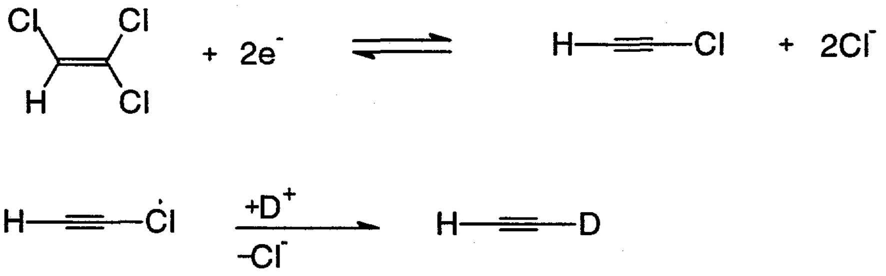


Figure F-3. The Mass Spectrum for Acetylene Produced in DNAPL TCE/Fe/D$_2$0 After 48 Hours.



There is no trace of such a species in the mass spectrum. This does not discount the reaction path, however, since chloroacetylene still could be formed. The hydrogenolysis step would obtain its hydrogen by TCE losing a hydrogen atom to the surface of the iron. The concentration of TCE on the surface of the iron may be so high that this is the major source of hydrogen. This observation suggests that there may be an added pathway by which TCE can give up a hydrogen atom to the surface. If TCE does lose hydrogen, then in the observed hydrocarbon byproducts there should be some totally deuterated hydrocarbons present.

The mass spectra for ethene and ethane are shown in Figure F-4 and Figure F-5 respectively. If all possible combinations of deuterated and non deuterated ethene and ethane are present, the observed mass spectrum would consist of a combination. For example, if a combination of totally deuterated ethene (tetratdeuterated) and trideuterate ethene were present, the resulting mass spectrum would be a mixture of the two. The observed spectrum would have a molecular ion of m/z 32 amu with a very small contribution from the trideutrated molecule. The trideutrated spectrum would have a molecular ion of m/z 31 amu with very little of the tetradeutrated ethene fragment at m/z 30 contributing to m/z 31. Using the known mass spectrum for all the deuterium labeled ethenes and ethanes, the contribution of each to the fragment patterns in Figure F-4 was obtained from an isotopic dilution calculation. The second bar in the mass spectrum represents the calculated fragment pattern based on the contribution of 32% trideuteroethene and 68% tetradeuteroethene. Within experimental uncertainties, no other species were observed. The corresponding distribution is shown for the ethane mass spectrum that was based on 36% pentadeuteroethane and 64% hexadeuteroethane. The 68% tetradeuteroethene indicates that the TCE does lose the hydrogen atom or exchange it for a deuterium atomon the surface of iron. This could occur through a stabilized vinyl carboanion on the metal surface[14]. The reaction pathways of β elimination and hydrogenolysis are supported by the observation of the trideutoethene. The lack of a dideuteroethene or ethane indicates that early in the reaction these compounds do not arise from acetylene directly. Unlike solution dechlorination of TCE, the further hydrogenation of acetylene to ethene and ethane appears to be slow. This allows the acetylene to become the major product. The hydrogenation of the acetylene takes place on the surface of the iron. If the surface is coated with TCE DNAPL, the acetylene could be displaced preventing hydrogenation from occurring. The TCE coating could also limit the access of D_2O to the surface, thus limiting the production of deuterium on the surface. After enough of the TCE has been degraded, the acetylene and water would have access to the surface, and thus the acetylene would produce ethene and ethane. This mechanism is a possible explanation of the observation that after 1,976 hours, acetylene was nondetectable in the headspace.

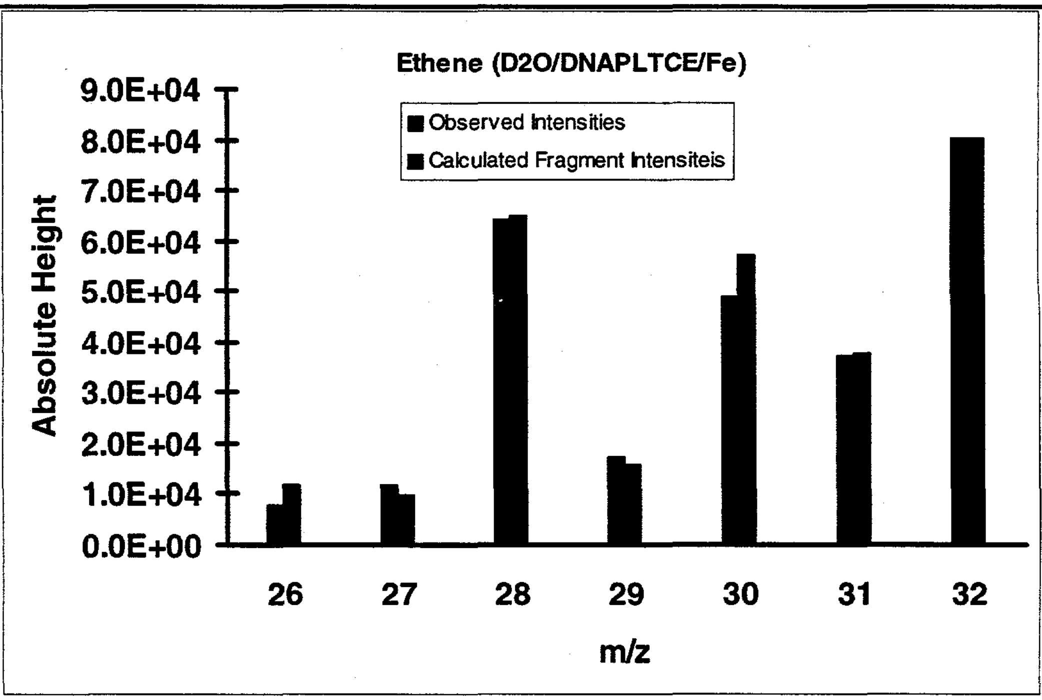


Figure F-4. The Mass Spectrum for Ethene Produced in DNAPL TCE/Fe/$D_2$0 After 48 Hours. (The hashed bar shows the calculated mass spectrum based on a mixture of 32% trideuteroethene and 68% tetradeuteroethene.)

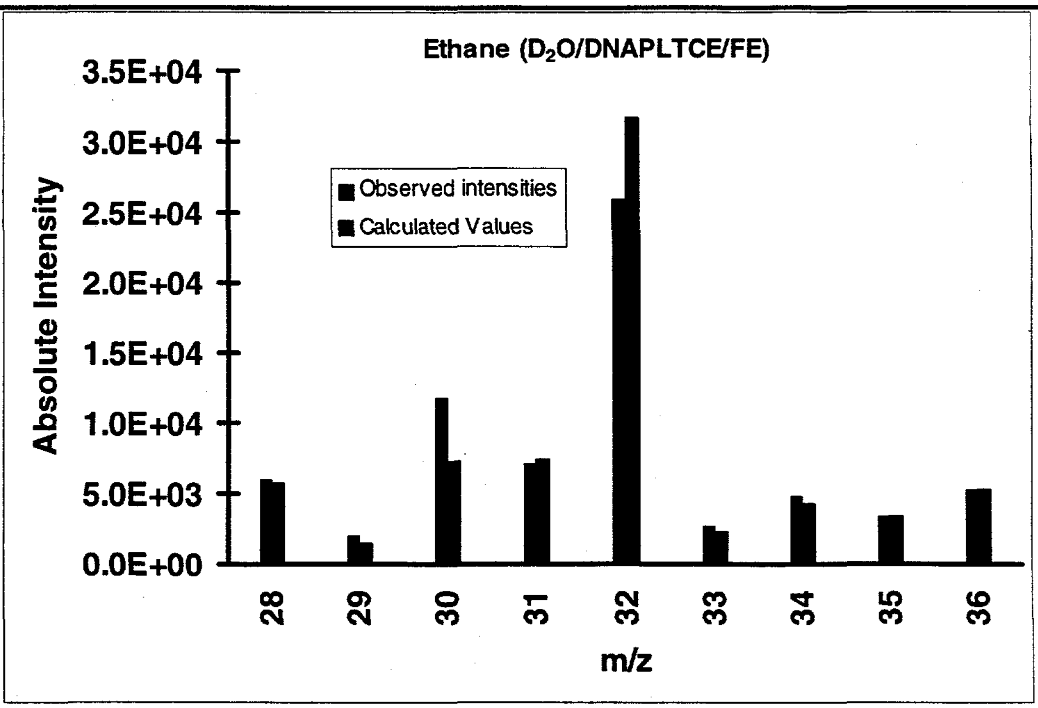


Figure F-5. The Mass Spectrum for Ethane Produced in DNAPL TCE/Fe/D20 aAter 48 Hours. (The hashed bar shows the calculated mass spectrum based on a mixture of 36% trideuteroethene and 64% tetradeuteroethene.)

Trans and *cis*-DCE were observed in the chromatograms. The predominate form of *cis*-DCE contained no deuterium atoms; however, since the control TCE contained *cis*-DCE as an impurity, the presence of non deuterated *cis*-DCE may have no connection to the mechanism of this reaction. Monodeutrated *cis*-DCE was observed, which definitely is an intermediate in the reaction paths for reduction. The monodeutrated *trans*-DCE was less intense on a relative scale compared to the monodeutrated *cis*-DCE. Mondeuterated *trans*-DCE was the predominated form of the *trans*-DCE. A small amount of non deuterated *trans*-DCE was observed. Again because of the small amount in the TCE used, no conclusions can be drawn in terms of the reaction path. The mondeuterated DCE indicates that hydrogenolysis is a likely path to these compounds. The small amount of *trans* observed relative to the *cis* would indicate that the rate of loss of the *trans* is faster than the rate of loss of the *cis*-DCE.

Two controls were also run. The first was a control of TCE in D_2O, which contained no iron and showed no deuterium exchange with the hydrogen of TCE, nor did the small amount of *cis* and *trans* DCE show any hydrogen exchange with D_2O. This exchange has been reported but under very basic conditions with 6N NaOD in D_2O at elevated temperatures[21]. The second control was with iron and D_2O. The results of this control showed no detectable level of hydrocarbons under the same analysis conditions as that for the TCE and iron samples. The

---

[21] Thomas J. Houser, Richard B. Bernstein, Richard J. Miekka, and John C. Angus, 1955. "Deuterium Exchange between Trichloroethylene and Water." Infrared Spectral Data For Trichloroethylen-d. J. Amer. Chem. Soc. 77, 6201-6203.

analysis of the hydrogen gas showed that only D_2 was present. The analysis of the headspace of the TCE/iron/ D2O showed that the majority was D_2 with 5% HD present. The only source of the H, again, is the TCE.

The results of the deuterium oxide experiment suggest that, when DNAPL TCE is present, the predominate reaction pathway changes for reductive dechlorination of TCE by iron. The observation of large amounts of acetylene suggests that a field sample of the water phase or a gas phase sample in an iron reactive zone containing DNAPL TCE should contain acetylene. During the Lasagna™ phase II study at Paducah, Kentucky, this was indeed the case. Analysis of water samples and gas samples from a test well near a reactive iron zone containing DNAPL showed that acetylene was present[5]. Samples farther removed from the treatment zone showed no acetylene.

Reductive dechlorination of DNAPL TCE can occur under conditions in which the major hydrocarbon byproduct of dechlorination is acetylene. The kinetics of the loss of TCE and the production of chloride indicated that the reaction kinetics are zero order. This would suggest that metallic iron could be used to degrade soil contaminated with DNAPL TCE provided the DNAPL could be moved to a treatment zone, or the iron could be injected into the DNAPL zone. The time period required for degradation as calculated from this rate data would be sufficient for *in situ* treatment of DNAPL TCE. Further work needs to be undertaken on the carbon mass balance to determine that the products formed are not of environmental concern. The observations of benzene in particular suggest that column or pilot studies should be done to determine if this compound is formed under conditions that might be found in the field and at what concentration. The results of the deuterium oxide study support mechanisms suggested in the literature previously but also indicate that a route not previously suggested is occurring which causes the loss of hydrogen from the TCE carbon skeleton.

Acknowledgments

The authors would like to thank B. Mason Hughes for his helpful discussions in the mechanism of the formation of acetylene and for his review of this report.

G. Determination of Adsorption Isotherms

Abstract

The partition of trichloroethylene to clay soil from the Puducah test site was studied so the movement of TCE through the soil could be predicted. In addition, adsorption/desorption experiments were conducted on coke to determine the capacity of the coke for adsorption of TCE. This was undertaken because the coke was to be used in the construction of the electrodes for the Lasagna™ phase II study.

The results of these adsorption/desorption studies indicated that the clay had a low capacity for adsorption of TCE and that as the concentration went to very low levels. The transport of TCE through the clay may be affected due to the slow desorption from the clay soil. Two soil samples were examined: the first was collected from outside the site and the second was from the test site. The experiment showed no difference between the two.

The coke results showed that the capacity of the coke for adsorption of TCE was much lower on a weight basis than observed for activated carbon. This indicated that sequestering of large amounts of TCE in the electrode would not be a concern in the remediation.

Introduction

In the Phase IIa study for the remediation of trichloroethylene-contaminated soil, some knowledge of the adsorption/desorption characteristics of the TCE in this clay soil was required. If the adsorption isotherm indicates a strong adsorption, then this would be a factor in determining the time required to remediate the site using the Lasagna™ technology. To determine the isotherm, the soil partitioning experiments were conducted using a batch equilibrium approach [22, 23, 24]. In this approach, the equilibrium partitioning between water and soil is obtained. The total amount of soil and TCE used is varied and the concentration in the clay soil is plotted against the concentration in water. The desorption is determined by removing part of the water phase and replacing it with water containing no TCE. After equilibrium is attained, the water concentration and the soil concentration are determined again.

At the time this study began, it was know that a mixture of iron and coke was to be used in the construction of the electrode zones for Phase IIa.. In the Phase I study, activated carbon had been used in treatment zones to trap TCE by adsorption, and it was determined that activated carbon

---

[22] S. W. Karickhoff, D. S. Brown, T. A. Scott, 1979. "Sorption of Hydrophobic Pollutants on Natural Sediments," *Water Res.* 13: 241-248.

[23] R. P. Schwarzenbach and J. C. Westall, 1981. "Transport of Nonpolar Organic Compounds from Surface to Groundwater, Laboratory Sorption Studies. *Environ. Sci. Technol.*, 15:1360-1367.

[24] C. A. I. Goring and J. W. Hamaker, 1972. "Organic Chemicals in Soil Environment," Vol. 1. *Marcel Dekker*, New York, NY.

had a very high capacity for TCE. It was also observed that the release of TCE from the carbon was very slow. Since coke was to be used in constructing the electrodes in Phase IIa, a question was raised as to the capacity of the coke to sequester TCE. A second question was how much time would be required for the TCE to be released from the coke and then to be degraded by the iron. It was believed that the adsorption isotherms would help answer these questions. The coke would be expected to be different from the activated carbon because of many factors, including differences in surface area. The isotherm for the coke was measured in the same fashion as the isotherms for the clay soil.

Experimental

A modified ASTM batch equilibrium method was followed to determine the partitioning of TCE with the clay soil and with the coke[25, 26]. Where possible carbon-14 labeled TCE was used. This was obtained from Sigma Chemical and the radiolabeled purity was >95%. For the partitioning studies that used the C-14 TCE, a mixture of the nonlabeled TCE and the labeled was used. This isotopic dilution approach allowed for a high concentration of TCE (1 ppm to 800 ppm) to be used while keeping the activity of the radioactive material in the approximate range of 1000 dpms (disintegrations per minute)/ mL. The nonlabeled TCE was obtained from Fisher Scientific. All isotherms were obtained at a temperature of 25 °C.

The clay test solutions were prepared in 30 mL Oak Ridge centrifuge tubes. The tests were carried out with zero headspace. The mass of clay soil used was approximately 6 grams. The remaining volume was made up of water with 0.1 M $CaCl_2$ and TCE. The concentration of TCE varied from 2 ug/ml to 29.3 ug/mL. Two controls were run with each batch so that any loss of TCE from the water solutions could be determined. The first tube that was prepared was the control containing no soil and the last tube prepared was the second control which also contained no soil. Three replicates were carried out for each concentration. The tubes were sampled only once. Total extraction was carried out by extracting with hexane. The tubes were sealed with a Teflon sealing cap assembly. They were rotated at 15 revolutions per minute (rpm) for 2 hours. This duration was determined by testing a set of samples at the 2 ug/mL level and 29.3 ug/mL level and rotating for 2 hours, 4 hours, and 20 hours. The concentration of TCE was determined at each of these times and found to be identical. Thus, 2 hours was chosen as the equilibrium condition for this batch experiment, and samples were taken anytime after 2 hours.

The tubes were centrifuged at 10,000 rotations per minute for 20 minutes to separate the clay from the water. Each tube was punctured to provide a small 0.4 micron opening, and 1 mL of water was removed. The 1 mL water sample was added to 9 to 10 mL of liquid scintillation cocktail (Packard Insta-Gel XF). The amount of TCE was determined by counting the samples in a liquid scintillation counter. The quenching never exceeded 8% and the counting efficiency for

---

[25] *American Society For Testing and Materials,* 1988. Standard Test Method for Determining Sorption Constant for Organic Chemicals in Soils and Sediments. E 1195-8. In *Annual Book of ASTM Standards,* Vol 11.04. Philadelphia, Pa, pp 763-769.

[26] *American Society For Testing and Materials.* 1988. Standard Method for Distribution Ratios by Short Term Batch Method, D4319-83. In *Annual Book of ASTM Standards*, Vol. 4.08. Philadelphia, Pa, pp 693-698.

all sets was never below 93%. The water concentration of TCE was determined from the dpm and the specific activity (SA) for each concentration by

$$C_e = \frac{dpm}{SA}$$

The difference between the total TCE still in solution and that lost from the original solution was the amount partitioned to the clay soil. This was verified by taking selected samples and performing a total extraction with hexane. The hexane concentration was determined by adding 1 mL of hexane to 9 mL of counting solution and determining the total mass of TCE. These values were compared to the TCE controls. The recoveries were 98.8% with an uncertainty of ± 2%. The ideal recovery would be loss of 15 to 50 % of TCE from the solution in order to provide a high degree of confidence in the analysis for the partitioning; however, the partitioning to the clay was observed to be very low, keeping the values of loss to the soil from solution in the 10 to 15% range. The proportional mass of soil was increased to 1 gram soil to 1 mL of water. This, however, did not improve the precision of the measurement. Thus, the final data is shown as the average of the three measurements, with the error bars representing one standard deviation of the mean of the three measurements.

Where nonlabeled TCE experiments were carried out, the determination of TCE was done by gas chromatography using a Volcal column. The detector was an ECD detector. The gas chromatograph was a Hewlett Packard 5980. The injector was set for 170°C and the gc oven initial temperature was 50°C and ramped to 200°C at 8 C/min. Besides the controls, a set of standards was run for each batch of samples analyzed.

The Loresco coke was tested in a similar manner. The steady state for the partitioning was 2 hours, and most samples were taken after 24 hours. The partitioning was high enough that nonlabeled TCE was adequate in this portion of the study. The sampling procedure was the same as that described for the clay soil.

Results and Discussion

Figure G-1 shows the results for the adsorption of TCE on the clay soil from the Puducah site. This figure shows the graph of the soil concentration (C_s) as a function of the water concentration of TCE (C_e). Two sets of data are shown in the figure. They represent the data obtained using Carbon 14 TCE. The Δ represents the values for the nonlabled TCE experiments. The error bars on the Carbon 14 data are for one standard deviation of the mean of three measurements. The results introduce a high degree of uncertainty because of the low adsorption of TCE onto the clay soil. For the best precision and accuracy, the loss of TCE from the aqueous phase to the soil phase should be 25 to 50%; however, for these experiments, the loss ranged from only 10 to 20%. Increasing the water-tosoil ratio from approximately 4 to a ratio of 1 did not increase the loss percentage, since the adsorption rate was so low. Although the low loss of TCE from the water phase introduces a high degree of uncertainty in the actual isotherms obtained, the results do show that TCE does not adsorb to a high degree onto the test site clay soil.

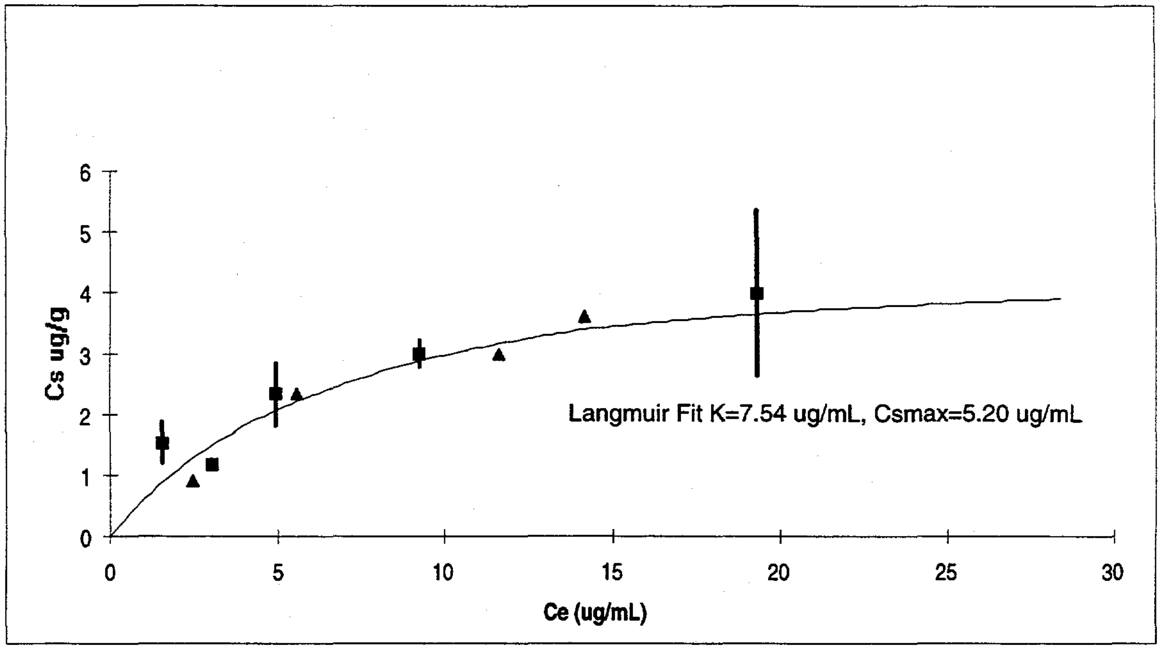


Figure G-1. Adsorption Isotherm for TCE on Paducah Clay

The trend in the data in Figure G-1 indicates that the soil is reaching a maximum capacity for TCE at very low concentrations. The shape indicates that the data follow a Langmuir type of isotherm. The function that describes the Langmuir isotherm is

$$C_s = \frac{C_{s\max} C_e}{K + C_e} \qquad (1)$$

where $C_{s\max}$ represents the maximum concentration of TCE that clay soil can adsorb and K is related to the adsorption coefficient. To find the values for $C_{s\max}$ and K, the equation was rearranged, resulting in the following equation:

$$\frac{C_e}{C_s} = \frac{1}{C_{s\max}} C_e + \frac{K}{C_{s\max}} \qquad (2).$$

Thus a plot of C_e/C_s as a function of C_e would yield a straight line. The slope of this line would be $1/C_{s\max}$ and the intercept would be $K/C_{s\max}$. Figure G-2 shows the plot of the data and the linear least squares fit of the data. The value obtained for $C_{s\max}$ was 5.20 ug/mL and the K value was 7.54 ug/mL. In Figure G-1, the curve through the data points was obtained using these values in equation 1. These values indicate that the TCE exhibits low adsorption to the clay soil and that the process of adsorption/desorption should not slow the transport through the soil matrix. At low levels of TCE, equation (1) becomes

$$C_s = \frac{C_{s\max}}{K} C_e = K_d' C_e \qquad (3).$$

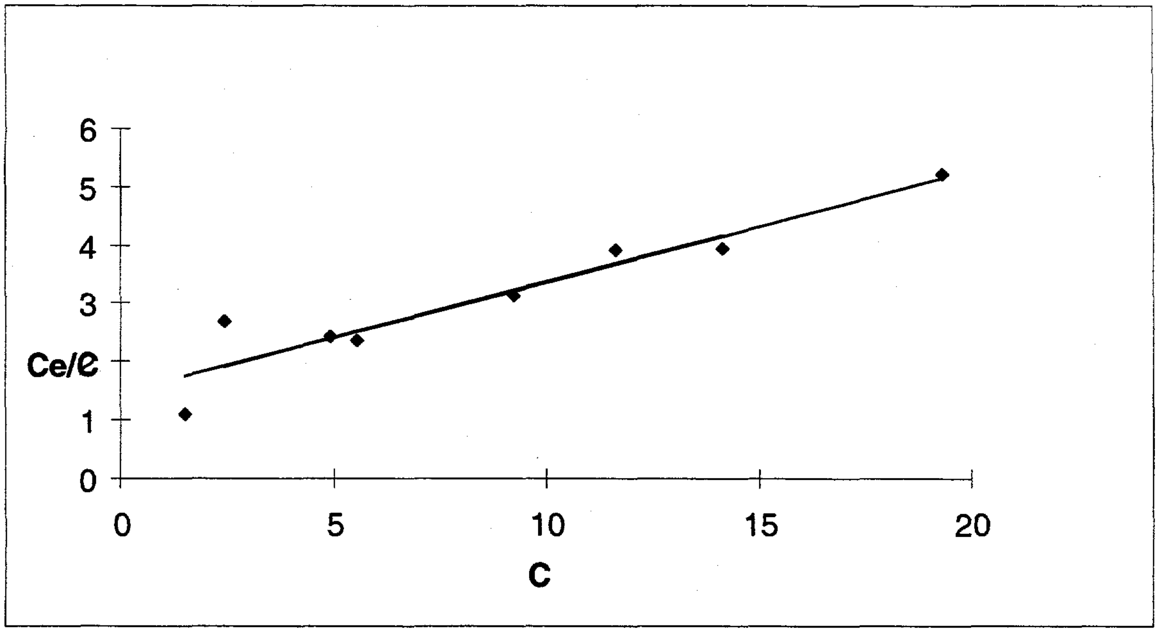


Figure G-2. Linear of Langmuir for Isotherm of TCE on Paducah Clay

$K_d^{'}$ is the adsorption coefficient under these conditions, with a value of 0.69. The levels where this equation holds are < 50 ng/mL. This means that at levels less than 50 ppb TCE in water, as much as 40% of the TCE in the clay matrix will be adsorbed to the clay. This result indicates that, at these levels, transport through the soil will be limited, and cleaning up the last small levels of TCE would require a long treatment period. The time could be reduced at the higher Lasagna™ operating temperature range (50 to 70°C). The isotherms documented in this report were recorded at an operating temperature of 25°C. It is critical also to understand that the above calculation was based on an extrapolation of the data. No data was obtained in this region of the isotherm, which introduces a high degree of uncertainty in the conclusion.

The results of the Loresco coke experiments are shown in Figure G-3. The plot of the concentration on the coke (Cs) versus the concentration in water (Ce) suggests that the isotherm in the region is linear. The linear least squares fit of the data yields a slope of 1.25 mL/g. Since the data follow a straight line, the slope of the equation is the adsorption coefficient where

$$K_d = C_s / C_w \qquad (4).$$

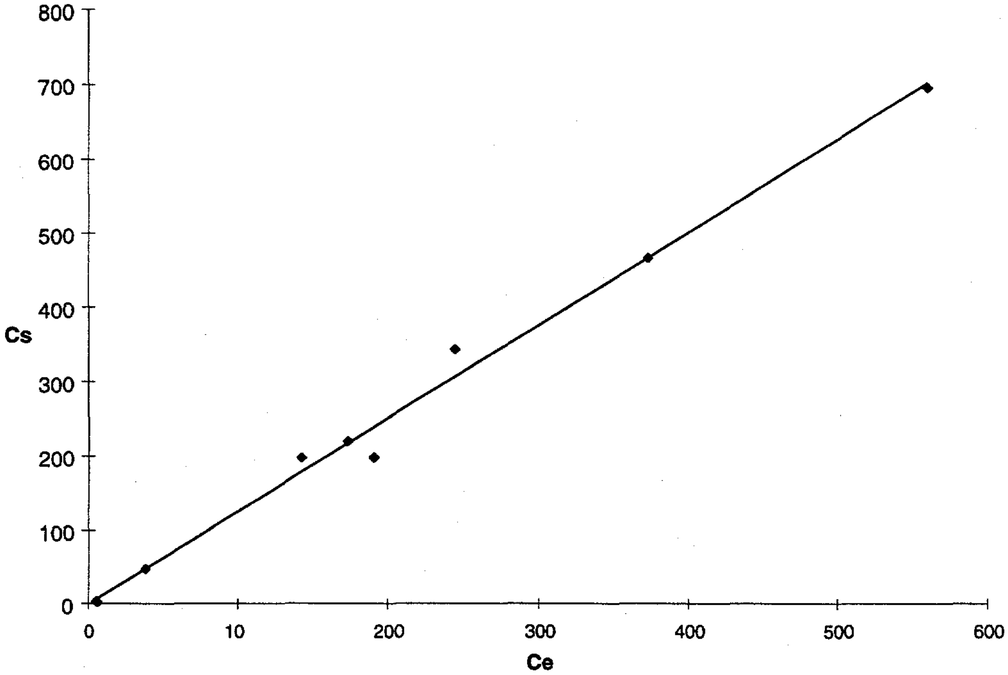


Figure G-3. Loresco Coke Isotherm for Paducah Clay

This value of K_d indicates that the amount of TCE on the coke is 1.25 times that in the water. This value is small compared to that of activated carbon. Notice that the concentration range for this study was within the the solubility range of TCE. The capacity of the coke was not determined, nor was the Langmuir isotherm.

Summary

The adsorption isotherms for TCE on clay and Loresco coke were determined. The data shows that the clay will not adsorb a large amount of TCE in the region of TCE water concentration of 1 ppm or higher. If extrapolation of the isotherm to concentrations of TCE in water of less than 50 ppb holds, then as much as 40% of the TCE in the soil matrix will be adsorbed to the clay. The Loresco coke was found to yield a linear adsorption curve with a K_d of 1.25. This is much less than that of activated carbon.