

Enhanced Degradation of Halogenated Aliphatics by Zero-Valent Iron

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Abstract

Laboratory tests were conducted to examine zero-valent iron as an enhancing agent in the dehalogenation of 14 chlorinated methanes, ethanes, and ethenes. All compounds were tested by batch procedures in which 10 g of 100-mesh electrolytic iron was added to 40 ml hypovials. Aqueous solutions of the respective compounds were added to the hypovials, and the decline in concentration was monitored over time. Substantial rates of degradation were observed for all compounds tested with the exception of dichloromethane. The degradation process appeared to be pseudo first-order with respect to the organic compound, with the rate constant appearing to be directly proportional to the surface area to volume ratio and increasing with increasing degree of chlorination. Column tests showed the process to proceed under flow conditions with degradation rates independent of velocity and consistent with those measured in the batch tests. When normalized to 1 m²/ml, the t₅₀ values ranged from 0.013 to 20 hr, and were about 5 to 15 orders of magnitude lower than values reported for natural rates of abiotic degradation. The results indicate abiotic reductive dechlorination, with iron serving as the source of electrons; the mechanism is, however, uncertain. Based on the rapid rates of degradation, both in situ and aboveground applications for remediation of contaminated ground water are proposed.

Introduction

Over the past decade, the development of improved methods for remediation of ground water contaminated by halogenated organic compounds has emerged as a significant environmental priority. Furthermore, with growing awareness of the limitations of pump-and-treat technologies (Mackay and Cherry, 1989, for example), the priority is shifting to in situ methods.

Of the substantial research effort that is now being focused on remediation technologies, a very large proportion concerns biological processes. Research in this area has been directed primarily toward the development of an understanding of biochemical pathways, developing/isolating effective strains of bacteria and the development of methods for stimulating effective populations of indigenous bacteria. In spite of the significant progress that has been made, in situ bioremediation technologies continue to be frustrated by the requirement of intimate mixing between the contaminated ground water and solutions injected into the subsurface for the purpose of stimulating favorable biological activity.

With the exception of granular activated carbon and advanced oxidation processes (ultraviolet irradiation, for example), neither of which is easily adaptable to in situ applications, relatively little attention has been focused on abiotic degradation processes. This is undoubtedly a consequence of the observed persistence of many chlorinated organic compounds in the subsurface environment and the

very long half-lives that have been reported for these processes (Vogel et al., 1987 and Jeffers et al., 1989). Electrolytic transformations of carbon tetrachloride and 1,1,1-trichloroethane, as reported by Criddle and McCarty (1991), and the transformation of carbon tetrachloride in the presence of sulfide, biotite, and vermiculite, as reported by Kriegman-King and Reinhard (1992), are notable exceptions. In addition, several studies have examined biochemical transformations through the use of organo-metallic complexes including porphyrins and corrinoids. Gantzer and Wackett (1991), for example, reported half-lives of 0.09, 2.4, and 96 hr for tetrachloroethylene (PCE), trichloroethylene (TCE), and cis 1,2-dichloroethylene (cDCE), respectively, in the presence of vitamin B12 and titanium (III) citrate. In these reactions, the reduced metal of the organo-metallic complex is considered to be the source of electrons for the reductive dechlorination process.

In view of the observed rates of transformation in the presence of reduced metals of organo-metallic complexes, and in view of the significant literature related to metal corrosion by organic liquids and the use of zero-valent metals in the processing of organic liquids (as reviewed in Baciocchi, 1983, for example), it is perhaps surprising that environmental applications of zero-valent metals have not received greater attention. To our knowledge, the first environmental application, for removal of chlorinated organic compounds from aqueous solution, was reported in the patent literature (Sweeny and Fischer, 1972) and later in Sweeny (1981a, 1981b). In this case, catalyzed metallic iron powder was shown to degrade a wide range of halogenated organic contaminants. Though the results were promising, it appears that the work of Sweeny was not published in refereed journals, and has been largely overlooked by the research community.

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Received January 1994, revised May 1994, accepted July 1994.

More recently, in the presence of galvanized metal, Reynolds et al. (1990) reported 50% loss of 1,1,1-trichloroethane, hexachloroethane, and tribromomethane, in times of 1.5, 0.25, and 0.75 hr, respectively. Gillham and O'Hannesin (1992) confirmed the results of Reynolds et al. (1990) and extended the work to include other metals. Iron and zinc (galvanized metal) were found to give similar rates of degradation, followed by aluminum, with brass and copper giving substantially lower rates. No degradation in the presence of stainless steel was noted. These authors proposed the use of metals for both in situ and aboveground treatment of ground water contaminated by halocarbons.

Senzaki and Kumagai (1988, 1989) and Senzaki (1991) considered the use of iron powder for removal of 1,1,2,2-tetrachloroethane and trichloroethylene from waste water. Under the conditions of their experiments, the results indicated that the time for 50% removal of tetrachloroethane decreases from about 4 hr to 1 hr as the temperature increases from about 20 to 50°C, the rates of degradation were highly sensitive to the surface area of iron available for degradation, and there appeared to be a significant decline in the degradation rate at pH values in excess of about 8.0.

As a consequence of the limited but highly encouraging results of previous tests, the present study was undertaken to evaluate the rate of degradation of a wide range of halogenated aliphatic compounds in the presence of zero-valent metal. Because it is readily available at low cost and because of the effectiveness demonstrated in previous tests, iron was selected as the metal to be used in the tests. Tests were conducted to confirm the abiotic nature of the reaction and to examine the effect of the surface area to solution volume ratio on the reaction rate. Though not exhaustive, some tests were performed to determine the breakdown products of the degradation process. Most tests were conducted using batch procedures; however, column tests were also performed to evaluate the process under conditions of flow.

Methods

Analytical

Fourteen organic compounds were studied. These included four halogenated methanes, tetrachloromethane (CT), trichloromethane (TCM), dichloromethane (DCM), and tribromomethane (TBM); four chlorinated ethanes, hexachloroethane (HCA), 1,1,2,2- and 1,1,1,2-tetrachloroethane (1,1,2,2-TECA and 1,1,1,2-TECA), and 1,1,1-trichloroethane (1,1,1-TCA); and six chlorinated ethenes, tetrachloroethene (PCE), trichloroethene (TCE), trans 1,2-dichloroethene (tDCE), cis 1,2-dichloroethene (cDCE), 1,1-dichloroethene (DCE), and vinyl chloride (VC). The various compounds were obtained as analytical grade chemicals.

All samples for analyses were collected in aqueous solution; however, because of the number of compounds considered, several analytical procedures were required. Most of the compounds were extracted from the aqueous phase using pentane with an internal standard of 1,2-dibromoethane, at a water to pentane volume ratio of 1:1. The samples were placed on a rotary shaker for 10 minutes to allow equilibration between the water and pentane phases. For analysis, a 0.5-1.0 μ l aliquot of the equilibrated

pentane was removed and injected directly into a Hewlett Packard 5710A gas chromatograph with a Hewlett Packard 3390A integrator. The chromatograph was equipped with a ^{63}Ni electron capture detector (ECD) and a glass column packed with 10% Squalane on Chromasorb P, AW-DMCS (80/100 mesh). The oven temperature was 110°C with a detector temperature of 300°C. The carrier gas was 5% methane and 95% argon, with a flow rate of 20 ml/min. For high aqueous organic concentrations, dilutions were necessary in order to work within the calibrated range of the gas chromatograph. When concentrations were low, the water to pentane ratio was increased to improve analytical sensitivity.

For compounds that are highly volatile, including VC, DCM, and the DCE isomers, a headspace was created within the sample vial with a ratio of 3.75 ml headspace to 11.25 ml solution. The samples were equilibrated for 15 minutes on a rotary shaker. For analysis, a 50 μ l gas sample was injected directly onto a "Photovac," Model 10S50, and/or 10S70, gas chromatograph equipped with a photoionization detector (PID). The Model 10S50 chromatograph was fitted with a TFE packed column with 5% SE-30 on Chromosorb G, AW-DMCS (100/120 mesh). The oven temperature was 30°C and the carrier gas was ultra-zero air with a flow rate of 10 ml/min. The Model 10S70 was fitted with a capillary column CP-Sil5, with an isothermal oven temperature of 30°C and a carrier gas flow rate of 3 ml/min. Detection limits for all compounds studied, as given in Table 1, were determined using the EPA procedure for Method Detection Limit (MDL) (U.S. EPA, 1982).

Redox potential (Eh) was determined using a combination of Ag/AgCl reference electrode with a platinum button and a MarksonTM Model 90 meter. The electrode was standardized with ZoBellTM. Millivolt readings were converted to Eh, using the electrode reading plus the standard potential of Ag/AgCl electrode at a given temperature. The pH measurements were conducted using a combination of pH/reference electrode and a MarksonTM Model 90 meter, standardized with the pH buffer 7 and the appropriate buffer of either 4 or 10.

Batch Tests

In the batch tests, 10 g of 100 mesh (0.15 mm) electrolytic iron powder (obtained from Fisher Scientific Inc., and with no pretreatment) were added to 40 ml glass hypovials. The hypovials were then filled with an aqueous solution containing the organic compound of interest, leaving no headspace, and were sealed immediately with aluminum crimp caps with Teflon[®]-lined septa. BET analysis gave a specific surface area for the iron of 0.287 m²/g. The above procedure gave a surface area-to-solution volume ratio of 0.078 m²/ml. In addition to the organic compound of interest, the solution contained 40 mg/l of calcium carbonate (CaCO₃). The calcium carbonate was added to give inorganic characteristics to the solution (pH and specific conductance) that might be typical of a dilute ground water. Five hypovials were prepared for each sampling time, two blanks containing only solution, and triplicate reactive hypovials containing solution and iron. The hypovials were

filled by gravity flow through tubing connected to a spigot at the bottom of a glass reservoir containing the stock solution. To check for losses by volatilization during the filling process, one blank was filled followed by the three reactive hypovials, then the second blank. The hypovials were placed on a rotating disc (two complete revolutions per minute), allowing for complete mixing without agitation. Sufficient hypovials were prepared to accommodate seven sampling times, over periods as long as 500 hr. At the selected times, a set of five hypovials, triplicate samples, and two controls, were removed from the shaker and subsamples were transferred to vials for extraction. The remaining solution was analyzed for pH and Eh.

Two sets of supplementary tests were performed using adaptations of the above procedure and TCE as the test compound. In the first, two tests were performed in which a bactericide was added to the solution. Formaldehyde was added at a concentration of 250 mg/l, and in the second test, sodium azide was added at a concentration of 1000 mg/l. In the second supplementary test, iron was added in amounts of 1, 5, 10, 20, and 50 g to the hypovials, resulting in surface area to solution ratios of about 0.0076, 0.038, 0.078, 0.15, and 0.45 m²/ml.

Column Procedures

A schematic of the column apparatus is given in Figure 1. The column consisted of acrylic tubing, 50 cm long by 3.8 cm I.D. Tests similar to those reported in Reynolds et al. (1990) showed sorption of organics by acrylic to be measurable but slow (comparable to rigid PVC). Thus, considering the small surface area to volume ratio, sorption onto the acrylic was not expected to have a significant effect on the

results. Four sampling ports were located at 10 cm intervals along the column, and three additional ports were located at distances of 2.5, 5, and 15 cm from the influent end (Figure 1). Each sampling port was constructed using a nylon Swagelok® fitting (0.16 cm O.D.) with a 16G Luer-Lok™ syringe needle 3.8 cm long. The needles were held permanently in place in the fittings with the needle tips located along the longitudinal axis of the column. The reactive column was packed with silica sand containing 10% by weight 100 mesh iron filings. This mixture resulted in a surface area of iron to solution volume ratio of about 0.14 m²/ml. A control column was identical except that no iron was added to the silica sand.

In order to assure complete saturation, the columns were initially flushed with carbon dioxide (CO₂) followed by several pore volumes of organic-free water. Solution containing the organic chemicals of interest was held in a collapsible Teflon® bag and was fed to the inlet end of the column by means of a peristaltic pump. With the exception of short lengths of Viton® tubing that passed through the pump, all tubing in the delivery system was Teflon®. A stainless steel "T" located in the delivery line, immediately before entering the column, was used to collect samples for determining the influent concentrations. Column tests were conducted for CT, TCE, and PCE.

Results and Discussion

Batch Tests

Figure 2 is an example of the results obtained from the batch tests. The organic compound in this case was TCE at an initial concentration of 1600 µg/l. As shown in Figure 2a, the concentration in the control hypovials remained relatively constant, declining by about 100 µg/l over the 100 hr duration of the experiment. The concentration in the reactive hypovials, on the other hand, showed what appeared to be an exponential decline in concentration to about 9.0 µg/l at the conclusion of the experiment. The log of relative concentration versus time, where relative concentration was calculated by dividing the measured concentration by the initial concentration, is included in Figure 2a, along with a least-squares fit of the first-order decay model. The half-life (t_{1/2}) obtained from the model was 13.6 hr, with a coefficient of variation (r²) of 0.99. The high r² value suggests that the reaction is pseudo first order.

Corresponding trends in Eh and pH are included in Figure 2b. Eh declined from an initial value of almost 400 mV to -150 mV within the first 10 hr, then remained relatively constant at about -200 mV until a time of 50 hr. The Eh at the final sampling time, 100 hr, was about -500 mV. While it is clear that highly reducing conditions existed in the hypovials for almost the entire duration of the experiment, there do not appear to be significant changes in the rate of degradation (Figure 2a) corresponding to the changes in Eh. The pH increased from an initial value of 7.2 to 9.2 at a time of 24 hr then remained relatively constant for the duration of the experiment. Though previous studies (Senzaki and Kumagai, 1989) suggest that rates of degradation of TCE decrease at pH values above about 8, this observation is not supported by the results shown in Figure

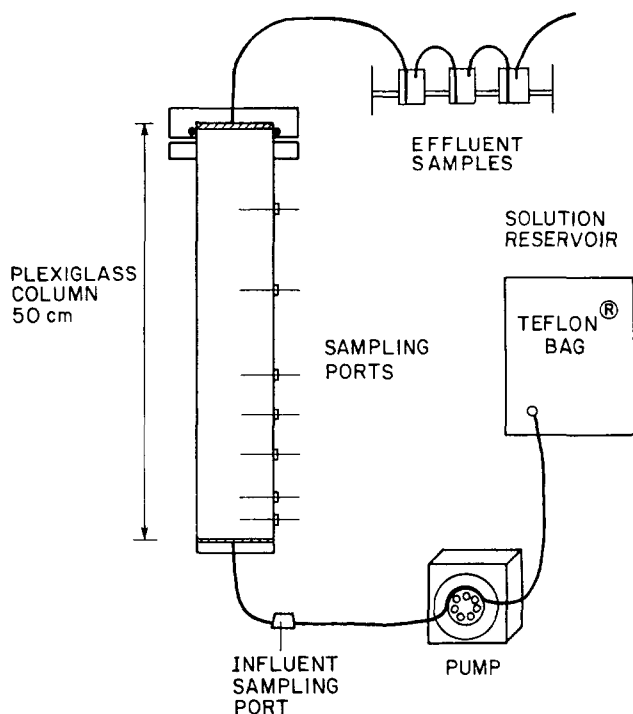


Fig. 1. Schematic of the apparatus used in the column experiments.

Table 1. Table of Compounds Studied Showing the Method Detection Limit (MDL) for the Analytical Procedures, the Calculated Half-Lives ($t_{1/2}$), and the Regression Coefficients (r^2) Determined from Fitting the First-Order Decay Equation to the Experimental Data and Times for 50% Loss (t_{50}) and Normalized t_{50} Values (The Last Column Includes Half-Lives for Abiotic Degradation Taken from the Literature)

Organic compound	MDL ($\mu\text{g/l}$)	Initial concentration ($\mu\text{g/l}$)	$t_{1/2}$ ^a (hr)	r^2	t_{50} ^b (hr)	t_{50-N} ^c (hr)	Half-lives ^d (hr)
Methanes							
CT	3.5	1631	0.25	0.993	0.25	0.020	3.6×10^5
TCM	2.6	2013	33.0	0.918	19.1	1.49	1.6×10^7
TBM	3.6	2120	0.24	0.999	0.52	0.041	6.0×10^6 ^e
DCM	4.2	2751	No decline				1.3×10^4 ^e
Ethanes							
HCA	3.1	3621	0.13	0.999	0.16	0.013	1.6×10^{13}
1122TECA	1.3	2513	19.2	0.887	0.68	0.053	3.5×10^3
1112TECA	1.6	2334	4.4	0.775	0.63	0.049	4.1×10^5
111TCA	2.9	683	5.3	0.920	0.83	0.065	9.6×10^3
Ethenes							
PCE	4.2	2246	17.9	0.860	3.6	0.28	8.7×10^{10}
TCE	4.4	1555	13.6	0.990	8.6	0.67	1.1×10^{10}
11DCE	1.2	2333	40.0	0.972	70.0	5.47	1.1×10^{12}
tDCE	0.8	1774	55.0	0.973	82.0	6.41	3.9×10^{14}
cDCE	1.1	1949	432.0	0.817	252.0	19.70	(both t & c)
VC	0.5	3663	374.0	0.849	160.6	12.55	—

^a Calculated half-lives.

^b Times for 50% loss.

^c Normalized to 1 m²/ml.

^d Jeffers et al., 1989.

^e Vogel et al., 1987.

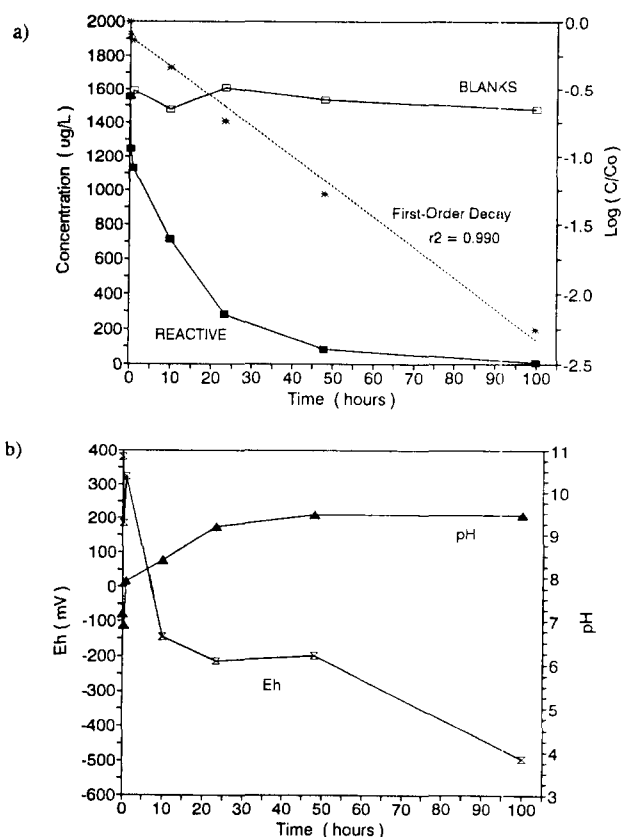


Fig. 2. Results of batch tests conducted using TCE. a) Concentration of TCE versus time; b) Eh and pH versus time.

2. In particular, the rate constant, as reflected in the linear semilog plot, did not appear to change significantly with changes in pH. Though the magnitude of the changes in Eh and pH varied from experiment to experiment, the trends were generally similar to those observed for TCE and therefore will not be discussed further.

Consistent with the observation of others (Senzaki and Kumagai, 1988, 1989) a headspace was observed to develop in the reactive hypovials over time. Though not quantified, consistent with the above references, the major components of the headspace were nitrogen and hydrogen. Other than the possibility of sample contamination, the only apparent source of nitrogen would be from air dissolved in the stock solution.

Table 1 summarizes the results for the 14 compounds tested. Of these, only DCM did not show a measurable decline in concentration. For the remaining 13, half-lives obtained by fitting the first-order decay model ranged from 0.13 hr for HCA to 432 hr for cDCE. The r^2 values varied from 0.999 for HCA to 0.775 for 1,1,1,2-TECA.

The variation in r^2 raises questions concerning the generality of our earlier conclusion based on the TCE results, that the reaction is pseudo first order. From an examination of the graphs (not shown), compounds that degraded slowly tended to reflect a declining rate constant at late time. This appeared as a slowly declining but persistent "tail" in the concentration versus time graphs. Indeed, in spite of the particularly high r^2 value, the distribution of the data points about the regression line of Figure 2a suggests the possibility of a declining rate constant with time. Thus, for compounds that degraded slowly, with an apparent

decline in the rate constant at late time, the half-lives obtained by a least-squares fit of the first-order model are higher than the actual values at early time and lower than the actual values at late time. Fitting of zero- and second-order models, in general, gave poorer representations of the data. It should also be noted that for those compounds that did not reach the detection limit at the conclusion of the tests, because of the "tailing" effect, the reported half-lives and r^2 values would be influenced to some degree by the duration of the tests.

Based on the generally high r^2 values, but the late-time trends in the data for those compounds that degrade slowly, it is proposed that the reaction is indeed pseudo first order with respect to the parent compounds, but that the rate constant declines at late time as a consequence of secondary effects. These may include the accumulation of reaction products, increasing pH, or other unidentified changes in the reaction conditions.

As a second index of reaction rate, the time required for a 50% reduction in the initial concentration (t_{50}) is included in Table 1. Though the trends in the t_{50} and $t_{1/2}$ values are similar, as a consequence of the observed tailing, the t_{50} values are, in most cases, substantially lower than the half-lives, particularly for those compounds that degrade slowly.

Within each group of compounds, the rate of degradation increases with an increase in the degree of chlorination. Further, the only brominated compound that was tested (TBM, $t_{1/2} = 0.24$ hr) degraded much more rapidly than its chlorinated counterpart (TCM, $t_{1/2} = 33$ hr). These trends are consistent with the expectation that, under the reducing conditions of the tests, the more highly oxidized compounds would be the most susceptible to degradation.

Comparing the half-lives measured in this study with those reported in Jeffers et al. (1989) and Vogel et al. (1987), and included in Table 1, the presence of the iron enhanced the degradation rates by about 3 to 13 orders of magnitude.

Abiotic Tests

Figure 3 shows the results in which sodium azide was added to the solution phase. The two blanks (with and without azide) behaved in a similar manner, as did the two sets of reactive samples. At early time, both reactive tests showed a very similar and rapid decline in TCE concentration resulting in a t_{50} value for both tests of 0.5 hr. At later times, the samples containing azide showed a slightly slower rate of decline in TCE concentration, though the difference was small and was not believed to be significant. Bacterial counts confirmed that the azide inhibited both heterotrophic and anaerobic activity over the duration of the test. Though bacterial counts were not performed, the results of the degradation tests using formaldehyde (not shown) were very similar to those obtained for azide. Based on these results, there is little doubt that the degradation process is indeed abiotic.

Surface Area to Solution Volume Ratio

The results of tests to examine the effect of the surface area to solution volume ratio on the degradation rate of TCE are given in Table 2. At values greater than $0.078 \text{ m}^2/\text{ml}$

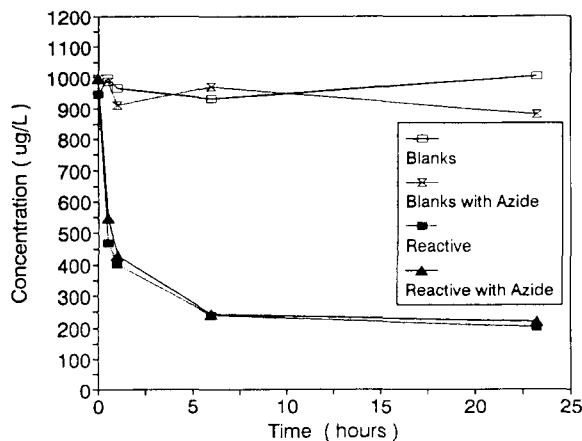


Fig. 3. Graph showing the effect of a bactericide (azide) on the rate of degradation of TCE.

(corresponding to 10 g of iron in a 40 ml hypovial), the t_{50} value appears to be inversely proportional to the surface area to volume ratio (the rate constant is directly proportional). At lower values of the surface area to volume ratio, the t_{50} values were disproportionately high. This is believed to be the result of mass transfer limitations in that on average, with small amounts of iron, a longer period of time would be required in order for the solute to contact an iron surface. It follows from this hypothesis that at area-to-volume ratios greater than about 0.078, the rate of degradation of TCE is limited by the reaction rate rather than by mass transfer rates in the bulk solution. Though similar trends are expected for other compounds, the area-to-volume ratio at which degradation would be limited by the reaction rate would be expected to increase as the reaction rate increases. It also follows that at low area-to-volume ratios, mass transfer would be influenced by the degree of agitation and thus observed rates of degradation could be a function of the shaking procedure. A second hypothesis could be that in the presence of small amounts of iron, a longer period of time is required in order for the necessary solution chemistry to develop. The threshold time for the start of degradation that this model implies was not observed.

Based on the above results, and to provide a convenient basis for comparison, the t_{50} values of Table 1 were normalized to an area-to-volume ratio of $1 \text{ m}^2/\text{ml}$. That is, the values obtained using 10 g of iron in a 40 ml hypovial ($0.078 \text{ m}^2/\text{ml}$) were divided by 12.8. The rationale for using t_{50} values as an index for comparing rates of degradation is further supported by the results of the column tests.

Table 2. Effect of Surface Area to Volume Ratio on t_{50} Values for TCE Degradation

Mass of iron (g)	Surface area/volume (m^2/ml)	t_{50} (hr)
1	0.0076	110.0
5	0.038	1.0
10	0.078	0.24
20	0.15	0.12
50	0.45	0.05

Column Tests

Tests were conducted on two columns, one containing silica sand only (the control column) and the other containing 10% iron and 90% silica sand by weight. The column containing only silica sand gave a TCE breakthrough curve typical of a nonreactive solute. That is, the relative concentration in the effluent was approximately 0.5 after one pore volume had passed through the column, and by two pore volumes, the influent and effluent concentrations were approximately equal.

Distance along the column can be readily converted to residence time, provided the flow rate is known and is steady. Thus, if the reaction is indeed pseudo first order, a steady-state exponential decline in concentration would be expected along the length of the column. Further, a graph of $\log C/C_0$ versus residence time should be a straight line, and if the reaction rate is independent of flow velocity, graphs of $\log C/C_0$ versus residence time should coalesce.

After 10 pore volumes of solution had passed through the column, at a velocity of 242 cm/day, the concentration profile appeared to be stationary and to decline exponentially along the column. As the velocity was reduced in steps to 166, 59, and 38 cm/day, a new steady-state profile developed for each new velocity with, as expected, the profile receding toward the influent end with decreasing velocity.

The results of the column tests are plotted as $\log C/C_0$ versus residence time in Figure 4. The least-squares fit of the first-order decay model to the data is included. The high degree of scatter in the data for $V = 38$ cm/day suggests sampling or analytical error, and thus this data will not be considered further. The high r^2 values and the similarity between the $t_{1/2}$ and t_{50} values suggest that the degradation process within the columns is indeed pseudo first-order. Excluding $V = 38$ cm/day, the graphs for the other three velocities are quite similar with the t_{50} values falling within a narrow range (3.96 to 4.12 hr). Thus, for the fourfold increase in velocity of this experiment, there appears to be little or no velocity dependence in the rate of degradation.

The average t_{50} value for the three column tests was 4.04 hr. Normalizing the area-to-volume ratio in the column ($0.14 \text{ m}^2/\text{ml}$) to $1 \text{ m}^2/\text{ml}$ gives a t_{50} value of 0.57 hr. Normalized t_{50} values were also calculated for the PCE and CT column tests. The results are given in Table 3, along with the corresponding batch test results from Table 1. It should be noted that because of the rapid rate of degradation, even at a velocity of 1,019 cm/day, CT appeared at very low concentrations at the sampling point 2.5 cm from the influent end and was nondetectable at a distance of 5 cm. In the absence of other data, the concentration was assumed to decline linearly to zero at a distance of 2.5 cm, and thus the t_{50} value was taken as the time required to travel a distance of 1.25 cm. Because the degradation process gives an exponential decline, this would overestimate the t_{50} value. Thus, the normalized value of Table 3 is given as < 0.01 hr. Referring to Table 3, and in view of the different procedures and various sources of uncertainty, the normalized t_{50} values obtained from the batch and column tests are remarkably similar.

Based on the small amount of data that is available, it is

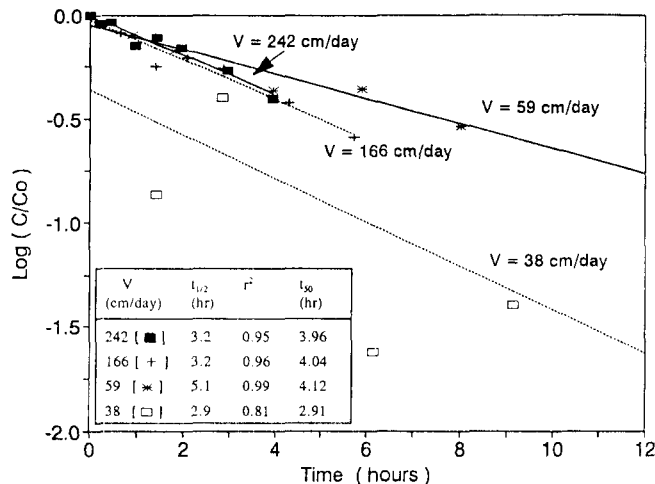


Fig. 4. Results of column tests for TCE conducted at four different pore-water velocities, expressed as $\log C/C_0$ versus residence time.

perhaps not reasonable to draw conclusions regarding relative reaction rates for batch tests and dynamic column tests. One can conclude, however, that the reaction does proceed under conditions of flow, and with no apparent adverse effect on the reaction rate.

It should also be noted that the tailing characteristic discussed previously for late time in the batch tests was not evident in the column tests. While this difference in behavior warrants further investigation, it appears to support the earlier hypothesis that the decline in the rate constant at late time in the batch tests was the result of the accumulation of reaction products. As discussed in a subsequent section of this paper, reaction products could include inorganic precipitates such as calcium carbonate, iron hydroxide, and siderite. Though as yet unconfirmed, accumulation of these products could reduce the reactivity of the iron surfaces.

Degradation Products

An exhaustive study of degradation products has yet to be performed; however, several important observations have been made. Figure 5 shows the results of batch tests in which tetrachloromethane (CT) was the only chlorinated compound present in the initial solution. The CT disappeared, rapidly accompanied by the appearance of trichloromethane (TCM). The peak TCM concentration (about $540 \mu\text{g}/\text{l}$) occurred at a time of about 2 hr, then declined as the TCM itself degraded, though at a slower rate than CT (see Table 1). Accounting for the difference in molecular weight, only about 26% of the original CT appeared as TCM. Though chloromethane (CM) was not detected, trace

Table 3. Comparison of Normalized t_{50} Values for the Batch and Column Tests

	Normalized t_{50} (hr)	
	Batch	Column
TCE	0.67	0.57
PCE	0.28	0.12
CT	0.02	<0.01

concentrations of DCM were evident in the chromatograms.

As shown in the following section, degradation of PCE and/or TCE resulted in accumulations of cDCE and VC. The maximum total accumulation was about 10% of the parent concentration, and the degradation products also degraded over time.

Degradation Using Site Materials

The results reported to this point, using analytical grade organic compounds and laboratory grade electrolytic iron, provide considerable encouragement for the use of zero-valent metals in remediation of contaminated water at industrial sites. Unlike laboratory-grade organic chemicals, industrial chemicals are generally of lower purity, and often have chemicals added as preserving/stabilizing agents. Further, the high-purity iron used in the laboratory tests would not be practical in the large quantities that would normally be required at contaminated sites.

Laboratory tests have now been conducted on contaminated water from several industrial sites, using an iron material that is commercially available in large quantities. The iron is collected as a waste product from machining and foundry operations, and after processing, is marketed primarily as an additive to improve the wear characteristics of concrete. The material used in these tests had a grain between 0.57 and 2.0 mm and a specific surface area (determined by the BET method) of about 1.1 m²/g. The following example is typical of the results that have been obtained.

Water was obtained from a zone of contaminated ground water in the vicinity of an electronics manufacturing facility. Organic contaminants included PCE (4,400 µg/l), TCE (900 µg/l), cDCE (190 µg/l), and 1,1-DCE (2 µg/l). The tests were conducted using the column procedure described previously, with the exception that the column contained only the iron material, giving a surface area-to-solution volume ratio of about 8.8 m²/ml. Steady-state concentration profiles were determined at two flow velocities, 47 and 76 cm/day. Even at the highest velocity, PCE was not detected at a distance greater than 20 cm from the influent end of the column and as expected, with decreasing veloc-

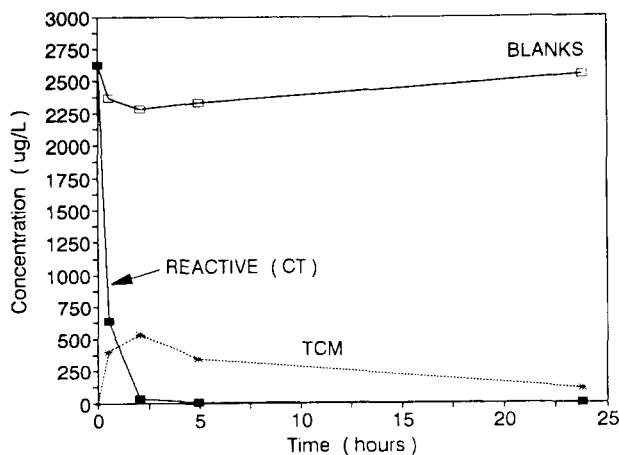


Fig. 5. Graph showing the accumulation and subsequent degradation of TCM during degradation of CT.

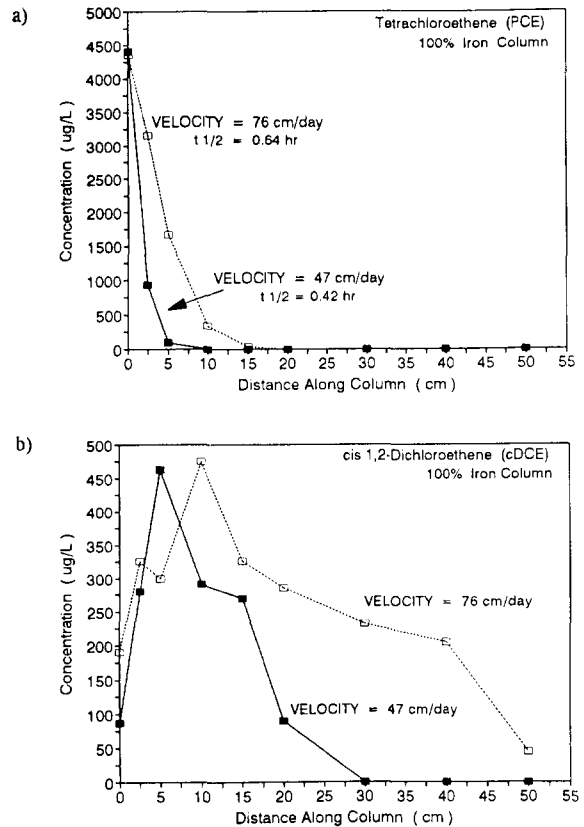


Fig. 6. Results of column tests conducted using commercial grade iron and ground water from a contaminant plume at an industrial site: a) PCE at two velocities; b) cDCE, showing an increase as a consequence of PCE dechlorination and subsequent cDCE degradation.

ity, the profile receded toward the influent end (Figure 6a). Half-lives were 0.64 and 0.42 hr at velocities of 76 and 47 cm/day respectively, and semilog plots (not shown) gave no indication of declining rate constants with residence time, and thus the $t_{1/2}$ and t_{50} values were very similar. The TCE profile (not shown) was very similar, resulting in a half-life of 0.52 hr at a flow velocity of 47 cm/day (r^2 of 0.99). Though small transformations would not have been detected, from the shape of the TCE curve, it was clear that large amounts of TCE were not being generated as a consequence of PCE degradation.

Figure 6b shows cDCE profiles along the column. Considering only the profile measured at a velocity of 76 cm/day, at a distance of 10 cm from the influent end of the column, the concentration had increased from the initial value of 190 µg/l to about 475 µg/l, then declined to a value of 50 µg/l at the effluent end. The profile measured for the lower velocity (47 cm/day) was similar but was displaced toward the influent end of the column. 1,1-DCE (not shown) increased from 2 µg/l to about 6 µg/l, but was not detected beyond a distance of 15 cm from the influent end. Similarly, though no VC was present in the influent, maximum concentrations of about 14 µg/l were detected at travel distances of about 10 to 20 cm. At the lower velocity there was no VC in the effluent, but at a velocity of 76 cm/day the effluent contained about 4 µg/l of VC. No tDCE was detected, and

the increase in cDCE, 1,1-DCE, and VC could account for only 10% of the initial PCE and TCE.

The results clearly show the process to be effective using materials (iron and industrial-grade solvents) of commercial relevance. Normalizing the measured half-lives to 1 m²/ml gives an average value of 4.8 hr for PCE and 4.7 hr for TCE. These are on the order of 10 times greater than the normalized t₅₀ values of Table 1. There are several possible reasons for the lower degradation rates: the commercial iron may be less reactive, the commercial solvents may be less reactive, the rates may be influenced by the different inorganic characteristics of the site water or indeed, the normalization procedure may not be applicable at the very high area-to-volume ratio of this particular test. Further tests are required to evaluate these possibilities. It is noteworthy, that while relatively small proportions of the parent compounds appear as chlorinated products, because of their longer half-lives, the chlorinated products of degradation may be the critical parameters in the design of treatment systems.

Degradation Process

In a review of transformation of organic chemicals, Baciocchi (1983) noted that because of the heterogeneous nature of the reactions, there is relatively little known concerning the mechanisms by which metals enhance organic transformation processes. Though an examination of the degradation process and pathways was not the purpose of the work reported here, several observations of relevance to the process can be made.

It is reasonable to conclude that the degradation process is abiotic and electrochemical in nature, involving oxidation of the iron and reductive dechlorination of the organic compounds. Figure 7 shows the log of the normalized t₅₀ values of Table 1 (excluding DCM) plotted against the relative half-reaction reduction potentials for the respective compounds. Including all three groups of compounds contributes significant scatter to the data and to a relatively low r² (0.72) for the regression line. Nevertheless, there is an

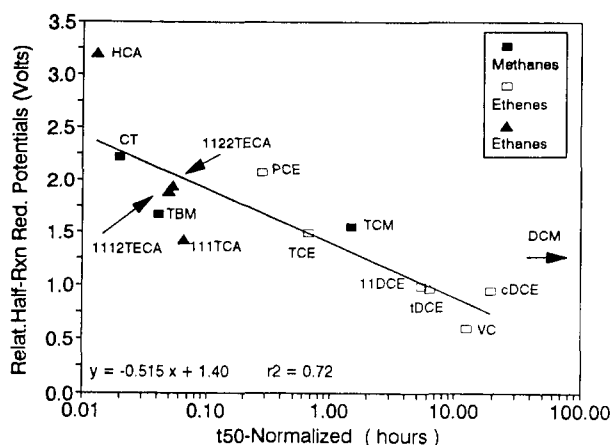
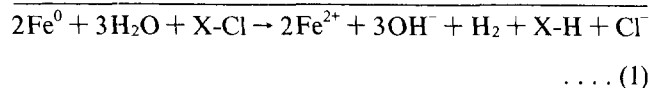
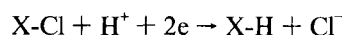
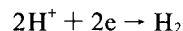
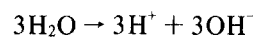
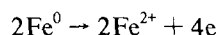


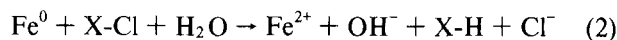
Fig. 7. Log of the normalized t₅₀ values versus the half-reaction reduction potential of the respective compounds (calculated using the expression given in Vogel et al., 1987).

unmistakable trend, as one would expect for reductive dechlorination, toward decreasing rates of degradation (increasing t₅₀ values) with declining reduction potential of the compounds. This is consistent with the observed increase in t₅₀ values with decreasing degrees of chlorination. Based on Figure 7, DCM would be expected to degrade and thus appears to be an exception to the trend.

The formation of hydrogen, along with the increase in pH, is evidence of the dissociation of water. Supplementary tests in which water without organics was added to the iron powder resulted in the formation of a headspace, a decline in Eh and increase in pH, indicating that the dissociation reaction proceeds independently of the degradation reaction. It is, however, uncertain if the dissociation of water is necessary in order for the degradation reaction to proceed. Considering only the presence of water, zero-valent iron and a chlorinated organic compound X-Cl, the following equations are suggested:



In this case, for each mole of Cl⁻ released to the solution phase, 2 moles of Fe²⁺ should also appear in solution. On the other hand, if the dissociation of water is not included, the overall reaction can be written:



In this case, only one mole of Fe²⁺ would be released to the solution phase for each mole of Cl⁻. Thus, the complete dechlorination of 1.0 mg/l of CT would result in a chloride concentration of 0.92 mg/l, and would contribute 2.8 or 1.4 mg/l of iron, based on equation (1) or (2), respectively. Total iron measured in column effluent ranged from nondetectable to about 6 mg/l, and because of the low Eh conditions, Fe²⁺ was considered to be the dominant species. Because corrosion of iron by water proceeds independently of the organic degradation reaction, there was no apparent relationship between iron concentration and organic degradation. Furthermore, under the pH and Eh conditions of the tests, precipitation of ferrous hydroxide [Fe(OH)₂] can be expected (at a pH of about 9.2) and further, with the addition of CaCO₃ to the stock solution, precipitation of siderite (FeCO₃) could also occur. Thus, should secondary mineral phases form during the tests, very low dissolved iron concentrations in the effluent should not be surprising. No attempt has yet been made to identify iron precipitates in the column materials. Further, because of the formation of secondary minerals, stoichiometry is of little value in attempting to verify equations (1) and (2).

In an additional supplementary test, iron was added to water containing only CaCO₃ until an Eh value of about -400 mv was reached. The water was then decanted, and while taking care to exclude oxygen, CT was added to the

solution, which was then sealed in hypovials. Under the highly reducing conditions of these tests, but in the absence of metallic surfaces, no dechlorination was observed. Two additional batch tests were conducted in which ferrous chloride and ferric oxide were added to the initially reduced solution. In both cases, no degradation of CT was observed.

The fact that no degradation products other than less chlorinated forms of the parent compound have been detected suggests the degradation process to be simple reductive dechlorination, with Fe^0 serving as the source of electrons. Further, the fact that only small proportions of the parent compound appear as less chlorinated products suggests a precipitous transfer of electrons. This is likely to occur only through direct contact between the organic molecules and the iron surface. The apparent mass transfer limitation observed in the area-to-volume ratio studies further supports the hypothesis that direct contact between the organic solute and the metal surface is required in order for the degradation process to proceed.

Considering pure-phase degradation of CT in contact with metals, Archer and Simpson (1977) proposed the transfer of a single electron from the metal to a chlorine atom. As a consequence, the chlorine is partially bonded to both the metal and the carbon atom until a second electron is transferred, releasing a chloride ion and a metal ion to the liquid phase. The authors suggest that the mechanism could apply to other chlorinated solvents. Though plausible with respect to the results of the present study, there is no direct supportive evidence. Further research is required to identify the mechanism and indeed, there may be several mechanisms depending upon the compound and test conditions.

Conclusions

The batch tests confirmed that zero-valent iron is highly effective in enhancing the rate of degradation of a wide range of chlorinated aliphatic compounds in aqueous solution. Of the 13 halogenated methanes, ethanes, and ethenes tested, with the exception of DCM, all showed significant rates of degradation. The rates of degradation increased with an increase in the ratio of surface area of iron to volume of solution and though there was significant scatter in the data, there is a strong indication that the rate declines logarithmically as the reduction potential of the compounds declines. This is consistent with the observation that the rate of degradation declined with decreasing degree of chlorination.

The batch experiments suggested that the reactions are pseudo first order with respect to the organic compounds. Though the batch tests tended to show "tailing" at late times, this was not evident in the column tests, and thus it appears that the same rate constant is applicable over the concentration range used in the tests, from a few milligrams per liter to the detection limit (generally a few micrograms per liter). No attempt was made to determine the upper limit of concentration for which the process is applicable.

The reaction appears to be reductive dechlorination with the metallic iron serving as the source of electrons. The fact that only small proportions of the parent compound appear as breakdown products is strong evidence that the

process does not require sequential dechlorination. The organic compound may be attracted to the iron surface until sufficient electrons have been transferred for complete dechlorination or upon contact, there may be a precipitous transfer of electrons. In either case, direct contact between the organic molecule and the metal surface would be required. This is consistent with the apparent proportionality between the rate constant and the surface area-to-volume ratio.

Using the values normalized to 1 m^2 iron/ml of solution, the degradation rates are indeed rapid with t_{50} values ranging from 0.013 to 20 hr for the compounds tested (with the exception of DCM which did not degrade at a measurable rate). These values are about 5 to 15 orders of magnitude lower than half-lives reported for natural abiotic degradation processes. A further increase in the surface area-to-volume ratio, through the use of greater amounts of iron, or iron of finer grain size, should result in even lower t_{50} values.

The measured rates of degradation are highly encouraging for both in situ and aboveground treatment applications. For example, a decrease in concentration from 1.0 mg/l to $1.0 \text{ } \mu\text{g/l}$ requires 10 half-lives. Using the upper and lower limits of the normalized t_{50} values, 10 half-lives would correspond to residence times of 200 to 0.13 hr, respectively. Clearly, the design of both in situ and aboveground treatment systems would be based on the initial concentration of the parent compound and/or the concentration of chlorinated breakdown products, the relevant half-lives, the objective concentration, and the velocity of the contaminated water. However, for normal ground-water velocities, in situ permeable reaction walls, as proposed in Gillham and O'Hannesin (1992) and discussed further in Gillham and Burris (1994), should be applicable for a wide range of ground-water contamination problems. In order to avoid unreasonably large containment structures, aboveground treatment could be limited to those compounds with relatively short half-lives.

The applicability of the metal-enhanced degradation process is further encouraged by the availability and relatively low cost of granular iron, by the fact that the process does not appear to be significantly inhibited through the use of commercial grade iron and organic solvents, and by the fact that once installed, the treatment system should be entirely passive. Further, though the iron is consumed by the reaction, it should nevertheless be very persistent. For example, based only on the electron requirement for reduction of the organic, 1 kg of iron could completely dechlorinate CT in 0.5 million liters of water at an initial concentration of 1 mg/l . Though encouraging, it must be recognized that corrosion of the iron through dissociation of water undoubtedly consumes iron at a greater rate than the dechlorination reaction. Though corrosion rates of iron were not investigated, it is quite reasonable to expect that in situ walls or aboveground canisters could be constructed such that the iron would persist for many years or even decades.

Further investigations of breakdown products are required. In this study, reduction of CT resulted in very low but persistent concentrations of DCM, while reduction of PCE resulted in the production of low concentrations of

DCE isomers and VC. In the latter case, however, the chlorinated products of degradation were not persistent. Degradation products formed as a consequence of dechlorination of the ethanes were not tested for, and no tests were conducted on, the dichloro and monochloro ethanes. Because of the lower degradation rates associated with less chlorinated compounds, the degradation products may be the critical compounds in the design of treatment systems, even though they generally appear at concentrations that are low relative to the parent compound (< 20%).

Further uncertainties in application concern effect on the inorganic chemistry. Though not within the scope of this study, formation of siderite (FeCO_3) and ferrous hydroxide $\text{Fe}(\text{OH})_2$ is anticipated. Further, the observed increase in pH, depending upon the inorganic characteristics of the water, could result in the formation of other solid phases. Should precipitates form within the reactive material they could, over time, fill the pore spaces reducing the permeability. Precipitates may also adhere to the iron surfaces, blocking reaction sites and thus reducing the reactivity of the iron. Further studies of the inorganic consequences of the reactions and means of controlling these consequences are in progress.

Acknowledgments

The authors wish to acknowledge Paul Tratnyek of the Oregon Graduate Institute, Eric Reardon and Jim Warren of the Waterloo Centre for Groundwater Research, and Mark Pritzker of the Chemical Engineering Department, University of Waterloo for their helpful comments at various stages over the course of the study. We also wish to thank Greg Friday for his tireless efforts in conducting many of the laboratory tests. This research was funded by the Waterloo Centre for Groundwater Research, an Ontario Centre of Excellence supported by the Ontario Technology Fund, and by the Ontario Ministry of the Environment through the Environmental Technology Program (ETP). Industrial matching funds for the ETP grant were provided by Beak Consultants Ltd. of Brampton, Ontario.

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