EFFECT OF GROUNDWATER INORGANICS ON THE REDUCTIVE DECHLORINATION OF TCE BY ZERO-VALENT IRON

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Abstract. Although permeable reactive barriers (PRB) technology appears to be a very suitable and cost effective option, the extent to which remediation results will be realized, greatly depends on the long-term integrity of the system. The formation of mineral precipitates is possibly a major factor in the long-term performance of PRB. Precipitates may passivate reactive surfaces by blocking electron-transfer sites, and thereby reduce the long-term reactivity of the granular iron to degrade groundwater contaminants. To evaluate the potential passivation impacts of inorganic groundwater chemistry, column experiments containing zero-valent iron (Fe^0) were performed under anoxic conditions to treat two contrasting Danish groundwater types spiked with trichloroethylene (TCE). For most of the experiments using Danish groundwater types, a soft low alkalinity groundwater produced slightly higher TCE dechlorination rate than did a hard high alkalinity groundwater. Compared to a soft low alkalinity baseline groundwater, it was also found the dechlorination of TCE in the column was enhanced in the presence of 1 mM $CaCO_3$ and 1 mM $NaHCO_3$. The dechlorination of TCE in the presence of 1 mM KNO_3 and 1 mM Na_2SiO_3 was found to decrease considerably compared with the baseline solution. The results suggest that the composition of field groundwater is likely to strongly affect the ability of Fe^0 barriers to degrade TCE.

Keywords: groundwater remediation, longevity, permeable reactive barriers, zero-valent iron

Introduction

Traditionally, the field of groundwater remediation has focused extensively on the pump-and-treat approach, but this on the whole has proven to be expensive (USEPA, 1998) and unsuccessful in fully capturing contaminant plumes (Gillham, 1996). As a consequence, over the last decade permeable reactive barrier (PRB) technology has emerged and there has been significant interest in the use of zero-valent iron (Fe^0) as a low cost reactive material for passive remediation of groundwater plumes contaminated by chlorinated organic compounds. The capital costs for the construction of a PRB containing Fe^0 are comparable to those of pump-and-treat options, and therefore the proposed cost advantage of PRB is gained primarily through reductions in operation and maintenance costs (Gillham *et al.*, 2000).

Of the 29 most commonly encountered contaminants in groundwater at hazardous waste sites, 13 are chlorinated organics in which trichloroethylene (TCE)

is the most commonly found organic (Scherer *et al.*, 2000). The widespread distribution of TCE is a result of its extensive industrial uses as dry-cleaning fluids, metal degreasing agents and solvents (Gillham, 1996). In addition to its widespread occurrence, TCE is also a significant groundwater contaminant because the relatively high toxicity of TCE and its intermediate degradation products. Epoxidation of TCE by liver oxidation enzymes produces carcinogenic compounds (Gotpagar *et al.*, 1997) and therefore drinking water limits are generally in the order of a few micrograms per liter (Gillham, 1996). Effective remediation strategies are therefore required to treat TCE.

The available evidence indicates that in the presence of Fe^0, TCE degrades with pseudo-first order kinetics with respect to both contaminant concentration (Equation (1)) and to the quantity of Fe^0 surface area (Equation (2)) (USEPA, 1998; Su and Puls, 1999):

$$\ln C = \ln C_0 - k_{obs} t \tag{1}$$

$$\ln C = \ln C_0 - k_{sa} \lambda_s t \tag{2}$$

where C is the TCE concentration (mg L^{-1}), C_0 the initial TCE concentration (mg L^{-1}), k_{obs} the observed dechlorination rate constant (h^{-1}), k_{sa} the normalized reaction rate constant (mL h^{-1} m^{-2}), λ_s the surface area concentration of Fe^0 (m^2 mL^{-1} of solution), and t the time (h) (Su and Puls, 1999).

Gillham (1996) and Farrell *et al.* (2000) have also reported that the dechlorination rate constant is relatively insensitive to the initial hydrocarbon concentration and therefore first-order kinetics in reactant concentration should be adequate over the range of chlorinated solvent concentrations commonly found in groundwater. On the other hand, Tratnyek *et al.* (1997) have stated that a more complex kinetic model may be necessary to accommodate highly contaminated water.

From Equation (2), it is apparent that the observed rate constant, k_{obs} (h^{-1}) can be determined by plotting $\ln (C/C_0)$ versus time. The time can be easily calculated when the seepage velocity, v, through the reactive zone is known (i.e. $t = x/v$, where x is the distance from the inlet to a sampling port). Equation (2) also reveals that the normalized rate constant, k_{sa} (mL h^{-1} m^{-2}) can be calculated via Equation (3):

$$k_{sa} = \frac{k_{obs}}{\lambda_s} \tag{3}$$

The normalized rate constant is widely used since studies of published dechlorination rate data for individual halogenated hydrocarbons have shown that transformation rates are proportional to iron surface area concentration (USEPA, 1998). Representative values of k_{sa} for TCE studies are typically between 0.1 and 1 mL h^{-1} m^{-2}.

Extensive research has been conducted demonstrating that Fe^0 in the form of iron filings or chips can promote and be very effective in the dechlorination of TCE

into simpler organic compounds (Reynolds *et al.*, 1990; Gillham and O'Hannesin, 1992; Sivavec and Horney, 1995; Mackenzie *et al.*, 1995). While PRB technology appears to be a very suitable and cost effective option, the extent to which these savings and remediation results will be realized greatly depends on the long-term integrity of the PRB. Therefore, the long-term performance of granular iron is a topic of noteworthy practical importance.

The main question regarding the long-term performance of PRBs in treating chlorinated organics is concerned with whether the rates of dechlorination at the time of installation can be maintained over the lifetime of the barrier. The longest field-site operation record available in 2001 covered no more than five years, and this fell short by an order of magnitude of the estimated required remediation period for many contaminated sites (Klausen *et al.*, 2001). Uncertainties that have been identified include the persistence of the iron, the activity of the iron surfaces, and passivation or pore clogging as a consequence of mineral precipitation (Gillham *et al.*, 2000). For these reasons there is a need for a better understanding of the processes and major factors that might affect the long-term performance of Fe^0 reactive barriers.

This study investigates the reductive dechlorination of TCE using flow-through columns packed with Fe^0 under anoxic conditions. The study comprised two phases: phase 1 focused on TCE dechlorination for two Danish groundwater types and phase 2 investigated the effect of spiking field groundwater with four inorganic compounds to quantify the effect of groundwater geochemistry on the TCE dechlorination rate. Therefore, the primary objective of this research is to confirm whether the presence of certain groundwater ions in the field is likely to affect the use of PRB technology as a remediation option at contaminated sites.

Experimental Materials and Methods

Prior to the column experiments, batch tests using two types of commercial iron material, Gotthart Maier and Connelly-GPM were used to select the material for column testing. The results from the initial batch tests showed that Gotthart Maier Fe^0 possessed a k_{sa} of TCE which is approximately 3.5 times higher than that of Connelly Fe^0 (not shown in this paper) and as a consequence Gotthart Maier Fe^0 was chosen as the most suitable reactive material for this study. Table I lists a number of properties for the Gotthart Maier Fe^0 that was used during the column experiments.

One-dimensional laboratory column experiments were run to simulate saturated, anaerobic TCE contaminated groundwater zones. The main criterion for selecting groundwater for these experiments was that it should be representative of geological conditions in Denmark. *Geological Survey of Denmark and Greenland* (GEUS) has classified Danish groundwaters into two main categories: western sandy and lime-depleted groundwater, and eastern clayey and lime-rich groundwater. Groundwater type A predominates in the western sandy part of Denmark, while groundwater

TABLE I

Commercial Gotthart Maier Fe^0 properties

Supplier (abbreviation)	Gotthart Maier (GM)
Origin	Rheinfelden, Germany
Specific surface area ($m^2 g^{-1}$)	0.5[a]
Porosity	0.59[a]
Bulk density (kg L^{-1})	2.1[a]
Carbon content (%)	3.2–3.6[b]
Size (mm)	0.8–3[c]
Cost	$ 550 DM/metric ton[c]

[a]Kjeldsen *et al.* (2002).
[b]Dr. Hermann Schad (I.M.E.S. GmbH) (personal communication).
[c]Environmental Technologies Inc., Iron Supplies Sheet.

type C is found in the more clayey region of eastern Denmark. Both types of groundwater are typical found from the shallow aquifer and most suitable for use as an influent solution. Type A groundwater, classified as soft water with low ion content, was obtained from a well serving the Arnborg water works in Arnborg, Denmark, whereas type C groundwater, classified as hard water with high ion content, was from the Nybrovejens water works in Slangerup, Denmark. The physical and chemical properties of these two Danish groundwaters are listed in Table II.

Nine column experiments were run using varying inlet groundwater solutions. Table III outlines the key characteristics and operating conditions of each column

TABLE II

Physical and chemical properties of groundwater types A and C

Date	pH	°C	O_2	Cl^-	HCO_3^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Fe_T	Na^+	K^+	SiO_2	S^{2-}
Groundwater type A: Arnborg Vandværk in mg L^{-1} (except pH and temperature)														
2000-1-20	6.4	8.1	nd	17	22	0.5	7.9	5.5	1.6	2.5	9.3	0.9	nd	0.2
1993-9-01	6.2	nd	1.5	17	19	0.05	7.9	5.5	1.4	2.4	9.2	1.1	nd	nd
1993-1-26	5.3	nd	0.8	16	19	0.02	9.5	5.5	1.4	2.4	9	1.1	nd	nd
1989-6-14	6.6	nd	nd	15	20	0.01	8.9	5.6	1.3	2.6	10	1.1	23.4	nd
Groundwater type C: Nybrovejens water work in mg L^{-1} (except pH and temperature)														
2000-7-04	7.35	9.5	0.1	39	325	0.9	81	135	6.7	2.5	17	2.2	nd	nd
1997-7-03	7.45	9.5	0.1	37	319	nd	72	130	9	2.5	11	1.9	nd	nd
1994-6-24	7.4	9.5	0.1	36	325	nd	72	127	7.2	2.2	20	2.2	nd	nd
1990-6-29	nd	9.5	0.1	37	365	0.05	110	151	11	0.4	17	3.8	14	nd

Source. GEUS water quality database.
nd, not determined.
Fe_T, total Fe.

TABLE III
Experimental setup and operating conditions

Column experiments	Control		Phase I				Phase II		
	I	II	III	IV	V	VI	VII	VIII	IX
Groundwater solution	Nybrovejen	Arnborg	Nybrovejen	Arnborg	Arnborg	Arnborg + CaCO$_3$	Arnborg + Na$_2$SiO$_3$	Arnborg + KNO$_3$	Arnborg + NaHCO$_3$
PV for iron zone (mL)	nr	nr	275.3	255.4	273.4	229.0	266.9	277.0	274.4
Fe^0 used (g)	0	0	952.6	940.8	950.5	909.2	936.2	960.8	902.9
Fe^0 surface area concentration (m^2 mL^{-1})	nr	nr	1.74	1.82	1.74	1.99	1.75	1.73	1.65
Sand used (g)	nd	nd	161.3	179.2	183.2	177.1	166.8	163.1	191.5
Operating conditions									
Pump flowrate (mL h^{-1})	129	129	129	129	71	71	71	71	71
Seepage velocity (m per day)	2.3	2.3	2.3	2.3	1.3	1.4	1.3	1.3	1.3
Prepared TCE (mg L^{-1}) (measured inlet TCE)	11 (10–11.2)	11 (8.9–11)	11 (8.5–11)	11 (6.3–12)	8.75 (6–9.6)	8.75 (6.1–8.3)	8.75 (6.2–7.5)	8.75 (7.2–9.2)	8.75 (6–8.8)
Inlet pH	7.5–7.7	6.5–6.7	7.5–7.7	6.5–6.7	6.31–7.05	7.79–8.04	8.15–8.38	6.61–7.51	7.34–8.02

Note. PV, pore volume; nd, not determined, water lost during test due to leaking from column sampling port; nr, not relevant.

experiment. For phase I experimentation, groundwater was spiked with TCE. The TCE concentration of 11 mg L^{-1} was prepared by equilibrating 40 μL pure solvent in 5.3 L of type A or type C groundwater for 1 h in a well-stirred, 5.5 L glass solution bottle. For phase II experimentation, type A groundwater was used as the influent solution for columns V–IX. This groundwater was initially tested with TCE only and served as the baseline/control groundwater solution (column V). The other four column experiments were then individually spiked with groundwater containing TCE of 8.75 mg L^{-1} and other inorganic compounds [1 mM calcium carbonate ($CaCO_3$), 1 mM silicate (Na_2SiO_3), 1 mM nitrate (KNO_3), and 1 mM sodium bicarbonate ($NaHCO_3$)]. It should be noted that the inlet pH, when spiked with certain inorganic compounds, rose by between 0.5 and 1.5 units above the 'baseline' type A groundwater. The TCE concentration of 8.75 mg L^{-1} was prepared by equilibrating 30 μL pure solvent in 5 L of groundwater and mixed for 1 h.

The column experiments were designed to simulate field conditions as closely as practicable. Since the field-PRBs are more likely to experience a continuous supply of contaminant, the column experiments were fed a continuous supply of TCE. The seepage velocities used for the column experiments were also similar to velocities commonly found at field sites where funnel-and-gate PRBs are installed. Anaerobic conditions were also maintained throughout the experiments, which was important because of the very low dissolved oxygen field concentrations for the two groundwater types.

The columns used in this study were plexiglass columns with an internal diameter and length of 55 and 245 mm, respectively (see Figure 1a). Sample ports covered with Teflon-faced septa were placed along the lengths of the columns and liquid samples could be extracted through the septa using a syringe and needle. The columns containing Gotthart Maier Fe^0 were packed with 35 mm of sand at the inlet (bottom) of each column. Following the addition of sand, a layer of Fe^0 filings 195 mm thick was added, and an additional 20 mm of sand added at the column outlet (top). Quartz sand was used as the influent filter layer in order to obtain a one-dimensional flow distribution for the iron treatment zone. The function of the sand layer was to help spread the water throughout the highly permeable Fe^0 material so as to ensure that most of the column would be reactive.

The columns were fed with a groundwater-solution from a 5.5 L glass-container, which received compensation gas from two preceding units (see Figure 1b) and which contained the same TCE water concentration as the influent container. This arrangement facilitated equilibration of the gas with the TCE in solution and so minimized TCE volatilization from the container feeding the column, leading to a constant influent TCE concentration. The three containers were also connected via glass headers using stainless steel-wire as tubing. The combination of glass headers on the inlet containers and stainless steel-wire tubing prevented compound losses and oxygen intrusion. The last solution container was similarly connected by steel-wire tubing to a tedlar-bag (12 L) containing nitrogen gas to help maintain
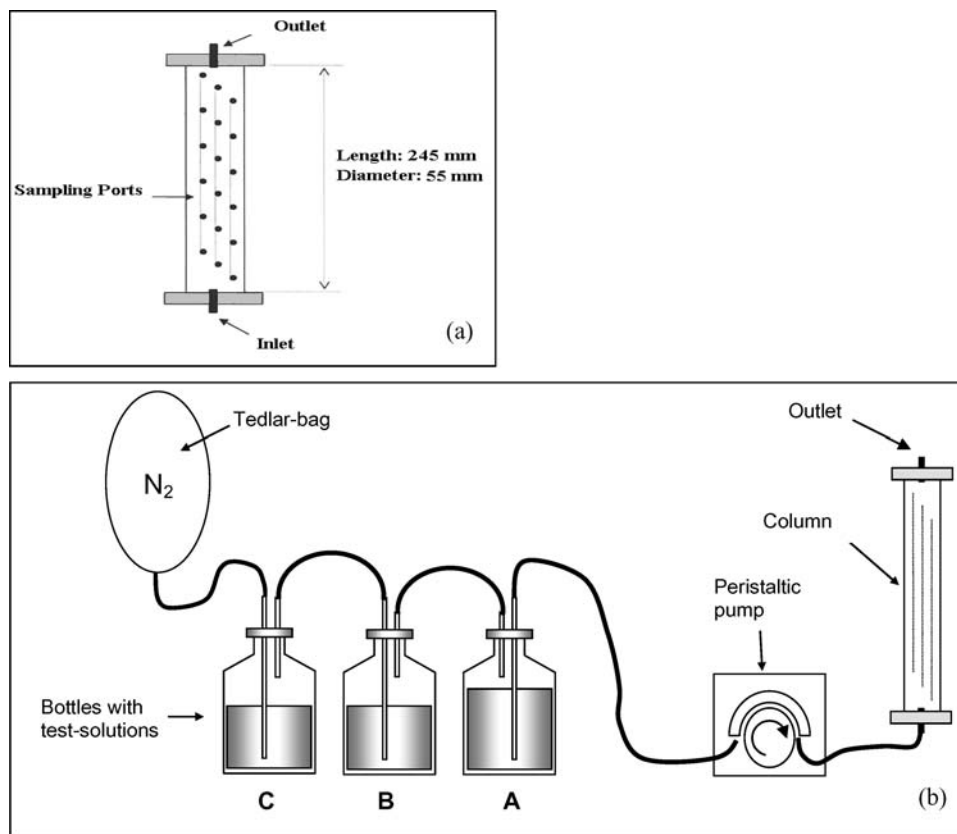
Figure 1. Experimental setup for column test (a) dimension and (b) column fed with groundwater spiked with TCE.

anaerobic groundwater conditions. Furthermore, the columns were run using an up-flow approach whereby constant flow was maintained by a multi-channel precision peristaltic pump. The flow rate at the beginning of each phase of experiments was determined volumetrically.

Sampling and Chemical Analysis

Contaminant and ionic profiles were periodically obtained using five sampling ports vertically spaced along the columns. Groundwater was sampled from the centre-axis of the column by inserting a 5 mL glass syringe with a 27 mm long needle into a sampling port. Water samples were taken from the column in a top down manner in order to avoid disturbing the water level of lower sampling ports and filtered through 0.45 μm membrane filters to prevent reactions with any particle phases.

The types of sampling events that were required during the running of the experiments included:

- TCE and pH sampling and analysis;
- sampling and analysis for chloride, nitrate and sulfate;
- sampling and analysis for calcium, magnesium and total iron; and
- inlet and outlet sampling and analysis for total alkalinity.

For TCE, a 5 mL sample was collected at each sampling port and transferred to a 12 mL glass-vial that was then immediately sealed with aluminum crimp caps fitted with Teflon-lined septa. An additional 2 mL was used for immediate analysis of pH and then stored for future chloride, nitrate and sulfate analysis. A Radiometer Analytical PHM 210 Standard pH Meter was used.

The glass vials containing TCE were then shaken for 30 min at 420 rpm min^{-1} so that equilibrium was reached between the volatile TCE component of the liquid sample and the surrounding gas phase in the sealed vial. Aliquots of the gas phase (1 or 10 μL) were injected for analysis into a gas chromatograph (Carlo Erba Model HRGC 5300 Mega Series) which was equipped with a Carlo Erba Instruments ECD-400 ECD detector and a J& W Scientific column (catalogue number 123-5032, 30 m, 0.32 mm internal diameter). Such an analytical process is referred to as headspace gas chromatography (HSGC) and according to this procedure, the sample containing volatile components is placed in a sealed vial and conditioned until the volatile components partition into the vapor space above the sample and reach equilibrium. When this is done, the volatile components in the vapor phase become a function of the concentration in the original water sample.

Ion chromatography (Dionex DX-120 IC using conductivity detection) was used to analyze the anions (i.e. chloride, nitrate and sulfate). Atomic Absorption Spectrophotometry (AAS) (Perkin Elmer 5000 installed with a Perkin Elmer Burner Control) was employed to measure cation concentrations (i.e. calcium, magnesium and total iron). Many different sample volumes were extracted for cation analysis that varied with the concentration differences between the two groundwaters and also because of the effect of spiking one of the groundwater solutions with calcium carbonate. It was therefore critical to use a dilution factor when analyzing with the AAS that would be appropriate to the concentrations of the prepared standards. The dilution solution that was used for calcium and magnesium samples contained 50 mL LaN_3O_9, 25 mL concentrated HNO_3 and 2500 mL distilled water. The total iron dilution solution consisted of 25 mL concentrated HNO_3 and 2500 mL distilled water. The cation samples were preserved immediately after sampling with the above solutions. Total alkalinity was also sampled at the inlet and outlet to each column. The sample was titrated with sulfuric acid with an added indicator with a color change at pH 4.5.

Results and Discussion

CONTROL EXPERIMENTS

Two control columns containing solely quartz sand were fed with the two types of Danish groundwater spiked with TCE to see whether TCE dechlorination occurred in the absence of Fe^0. The TCE spiked groundwater from Nybrovejens water works was used as influent for column I and sampled along the sampling ports for TCE on three occasions. As shown in Figure 2a, the TCE concentrations through the column were relatively constant and TCE dechlorination was not observed. Similarly, the TCE spiked with Arnborg water works groundwater was used as influent for column II and sampled along the vertical column ports for TCE on three occasions. Although the TCE concentration reduced slightly at the 15.5 cm sample port for 10.7 pore volumes (PV), the results for further pore volumes showed minor TCE changes compared to the inlet concentration and therefore dechlorination did not occur in this column (Figure 2b).
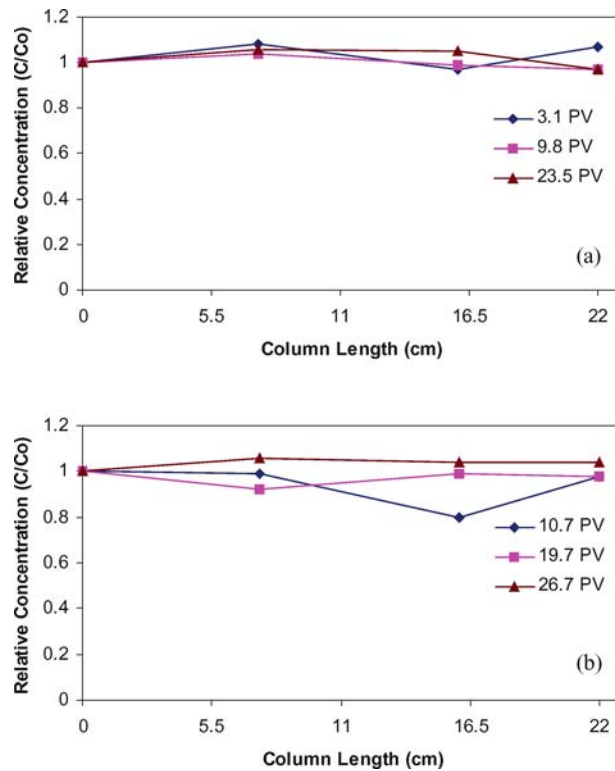

Figure 2. Variation of TCE relative concentration for the control experiment (a) column I and (b) column II.

PHASE I EXPERIMENTS

The objective of the phase I experiments was to investigate Danish groundwater of two distinct types (one was characterized by high hardness/alkalinity and the other by very low hardness/alkalinity) in order to ascertain the degree of change in TCE dechlorination. Figures 3a and 3b evince the variations of TCE relative concentration along the column length for both columns III and IV, respectively. At the first 10 pore volume, over 70% of TCE can be removed from column III and 100% of TCE dechlorination can be reached in column IV. Even over 100 pore volumes, about 40% of TCE removal can also be achieved at the end of both columns. Besides, a high consistence between the raw data and their first order fitted curves shown in Figures 3a and 3b as well as high correlation (R^2 value) for the k_{obs} or k_{sa} values for columns III–IV highlighted in Table IV suggesting that a first-order dechlorination process satisfactorily explains the TCE removal through the columns. In addition, the k_{sa} is found decreasing during the experiment. The k_{sa} varies in the range of 0.390 mL h^{-1} m^{-2} for column III. Tratnyek *et al.* (1997) also compiled results from Fe^0 columns treating TCE and found most k_{sa} values to be between 0.1 and
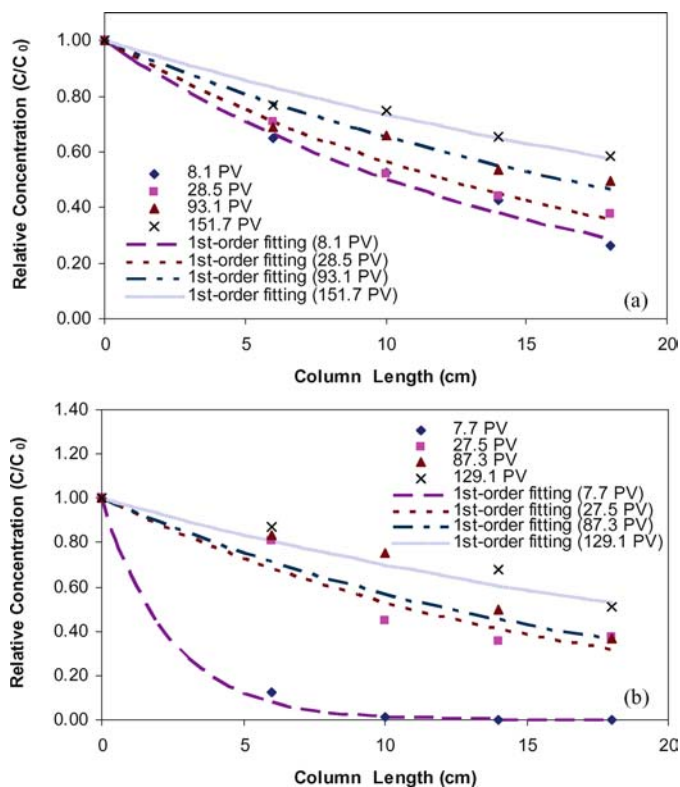

Figure 3. Variation of TCE relative concentration for (a) column III and (b) column IV.

TABLE IV

TCE removal and dechlorination rate constants at different pore volumes

Pore volume	TCE removal (%)	k_{obs} (h^{-1})	$T_{1/2}$ (h)[a]	k_{sa} (mL h^{-1} m^{-2})	$T_{1/2,N}$ (h m^2 mL^{-1})[b]	R^2
Column III (hard water)						
8.1	74	0.68	1.0	0.39	1.8	0.95
28.5	62	0.47	1.5	0.27	2.6	0.97
93.1	50	0.27	2.5	0.16	4.4	0.94
151.7	42	0.22	3.2	0.13	5.5	0.94
Column IV (soft water)						
7.7	100	5.1	0.14	2.8	0.25	–[c]
27.5	64	0.67	1.0	0.37	1.9	0.96
87.3	63	0.58	1.2	0.32	2.2	0.76
129.1	49	0.39	1.8	0.22	3.2	0.95
Column V (soft water baseline)						
9.9	91	0.84	0.83	0.48	1.4	0.97
30.8	73	0.46	1.5	0.26	2.6	0.90
54.6	44	0.20	3.5	0.11	6.1	0.93
Column VI (soft water + CaCO$_3$)						
18.0	97	1.5	0.46	0.75	0.92	0.99
50.4	84	0.77	0.90	0.39	1.8	0.99
62.1	82	0.69	1.0	0.35	2.0	0.99
Column VII (soft water + Na$_2$SiO$_3$)						
16.0	72	0.48	1.5	0.27	2.6	0.94
26.0	44	0.19	3.7	0.11	6.4	0.91
63.7	17	0.04	16	0.024	28	0.71
Column VIII (soft water + KNO$_3$)						
15.4	74	0.38	1.8	0.22	3.2	0.86
30.2	47	0.25	2.8	0.14	4.9	0.98
61.8	30	0.090	7.7	0.052	13	0.99
Column IX (soft water + NaHCO$_3$)						
13.3	94	0.90	0.77	0.55	1.3	0.95
33.3	91	0.81	0.85	0.50	1.4	1.0
62.4	76	0.42	1.6	0.26	2.7	0.92

The seepage velocity used for columns III and IV was 2.3 m per day, while for columns V–IX was 1.3 m per day.

[a] $T_{1/2} = \ln 2 / k_{obs}$.

[b] $T_{1/2,N} = \ln 2 / k_{sa}$.

[c] The R^2 value is not relevant for the first sampling event because there was 100% TCE removal in the column by a depth of 14 cm. Therefore, only two points were used to plot k_{obs} in this case.

1 mL h^{-1} m^{-2}, with a representative value for TCE of 0.39 mL h^{-1} m^{-2}. By comparing it with the results in Table IV, it is noted that the representative k_{sa} found by Tratnyek *et al.* (1997) is equal to that calculated for 8.1 PV. The value, though, at the end of the experiment is at the lower end of the reported range.

In Table IV, the R^2 value is not relevant for the first sampling event of column IV because there was 100% TCE removal in the column by a depth of 14 cm and therefore only two points were used to plot k_{obs} in this case. The results in Table IV also show the k_{sa} value to decrease slightly over the life of the experiment after 7.7 PV. A k_{sa} of 2.814 mL h^{-1} m^{-2} was calculated for 7.7 PV, which reduced quickly to 0.366 mL h^{-1} m^{-2} at 27.5 PV. The decrease in k_{sa} was more gradual from that time on and finished at 0.215 mL h^{-1} m^{-2}. The reason for the sudden drop was not known from 7.7 to 27.5 PV. Although the k_{sa} value for column IV is about seven times higher at the beginning of the experiment than for column III, it is only 1.3–1.7 times greater between 30 and 130 PV. The reduction of discrimination of TCE dechlorination rate constant between columns III and IV at high pore volume manifests that as time goes by, there is curtailing of influences of alkalinity and hardness on the TCE dechlorination.

In column III, decreases in the levels of calcium concentration and total alkalinity were particularly noticeable. The inorganic profiles showed gradual loss of calcium throughout the entire column (Figure 4a), suggesting that precipitation was probably occurring over its entire length. The decrease in calcium and total alkalinity is shown in Table V. It suggests that over half of the total loss of alkalinity through the column can be attributed to calcium carbonate precipitation and that the remainder must come from other precipitates. The magnesium concentration along the column is found to be constant and so magnesite ($MgCO_3$) or dolomite ($CaMg(CO_3)_2$) do not account for the total alkalinity deficit. Since a green layer of rust noticed at the inlet 2–3 cm of the column which continued until reaching a depth of 15 cm, siderite ($FeCO_3$) might reasonably be inferred to account for the bulk of the total alkalinity difference. This was confirmed by the literature review that found siderite to be the dominant precipitate in high alkalinity waters (Köber *et al.*, 2002; Hirnyi, 2001). A balance for total iron and total alkalinity to see whether siderite is the dominant precipitate, as performed for calcium above, is also extremely difficult because iron, unlike calcium, is involved in reactions releasing Fe^{2+} in solution. Considering the near-neutral pH throughout the column (Figure 4a), HCO_3^- will be the dominant carbonate species allowing one to conclude that calcite and siderite are likely to precipitate via the following reactions:

$$Fe^{2+} + HCO_{3(aq)}^- \rightarrow FeCO_{3(s)} + H^+ \tag{4}$$

$$Ca^{2+} + HCO_{3(aq)}^- \rightarrow CaCO_{3(s)} + H^+ \tag{5}$$

The siderite and carbonate corrosion products on iron surfaces have been shown to be an important product in the formation of protective layers against corrosion
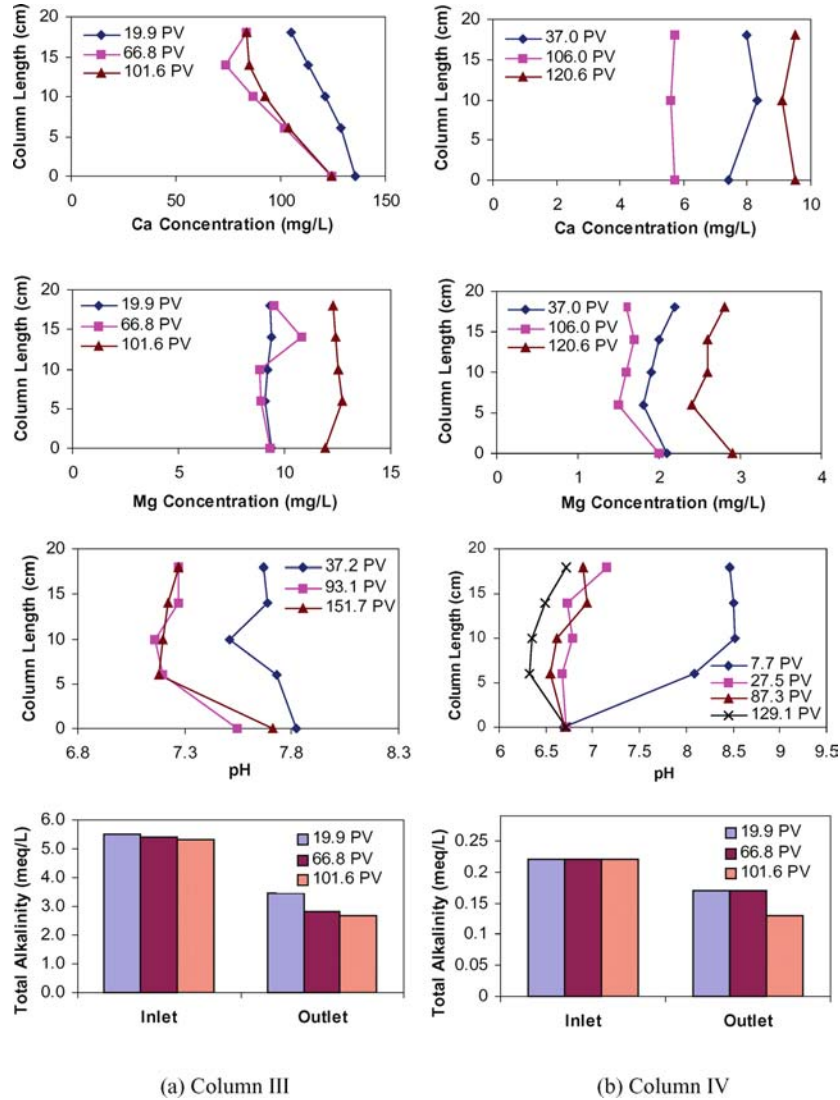
Figure 4. Aqueous inorganic profile for (a) column III and (b) column IV.

(Köber *et al.*, 2002; Hirnyi, 2001). These precipitates might therefore explain the passivating effect for TCE dechlorination and hence the decrease in k_{sa}.

In column IV, it is found that calcium did not decrease in concentration along the flow path and therefore calcite probably did not precipitate within the column. However, a small loss in total alkalinity and a slight reduction in magnesium concentration within the first 6 cm of the column were observed (Figure 4b). Similar findings reported by Lo *et al.* (2003) that no change in Ca concentration and a constant 50% reduction of Mg after 200 PV were found for their columns permeated

TABLE V

The change in inlet and outlet groundwater geochemistry

Column experiments	Phase I				Phase II		
	III	IV	V	VI	VII	VIII	IX
Groundwater solution	Nybrovejen	Arnborg	Arnborg	Arnborg + CaCO$_3$	Arnborg + Na$_2$SiO$_3$	Arnborg + KNO$_3$	Arnborg + NaHCO$_3$
Calcium	124	9.5	4.5	20	5.8	4.7	6.3
	84	9.5	4.7	18	4.1	4.3	6.9
Magnesium	12	2.9	1.7	1.6	1.2	1.8	1.9
	12	2.8	1.7	1.7	0.59	1.9	2.4
Total iron	4.6	20	22	11	5.6	15	11
	7.1	105	15	5.6	5.6	15	27
Chloride	60	23	27	14	16	24	28
	61	29	33	19	16	26	29
Nitrate	–	–	–	–	–	14	–
						11	
Sulfate	32	4.3	9.4	2.6	2.7	8.6	7.7
	36	2.5	9.8	2.8	3.0	8.0	8.1
Total alkalinity	5.4	0.22	0.19	0.73	0.90	0.19	1.5
	2.8	0.13	0.15	0.45	0.69	0.41	1.5
pH	7.7	6.7	6.7	7.8	8.3	6.9	7.5
	7.3	6.7	6.3	8.1	8.5	9.1	7.9

Note. All the units are expressed in mg L^{-1}, except total alkalinity in meq L^{-1} and pH in dimensionless. The upper figure shown in a box indicates the inlet concentration and the lower figure indicates the outlet concentration at the end of the column experiment.

with Cr contaminated groundwater with a hardness level of 200 mg L^{-1} as CaCO$_3$. In addition, the work of Lo and Lai (2001) found MgO to be a dominant precipitate in their column studies and therefore, the slight reduction in magnesium concentration as mentioned earlier, might be caused by precipitation of magnesium oxide (MgO). The outlet pH at 18 cm column depths for the 7.7 PV samples was increased from its inlet pH of 6.5–8.5 (Figure 4b), suggesting that the rapid forming Fe(OH)$_2$ could have precipitated early in the experiment. Beyond 7.7 PV, the aforementioned precipitate is not expected to form as the pH dropped to the near-neutral range for the remainder of the experiment. However, morphology study of the Fe^0 surfaces should be performed to check the validity of the above claims.

PHASE II EXPERIMENTS

The main purpose for conducting the phase II experiments was to study the effect of column performance of TCE dechlorination under different inlet groundwater chemistry conditions. Arnborg groundwater (type A) spiked with TCE only was fed to a baseline column (i.e., column V) to be used as a basis on which future TCE dechlorination performances could be compared. In addition, the other four column experiments (i.e., columns VI–IX) were conducted with type A inlet groundwater solution, which was spiked with TCE and an individual inorganic compound. The operating conditions were a replicate of those followed for phase I experiments, except that a slower seepage velocity of approximately 1.3 m per day was used (Table IV).

Columns V, VI and IX
Table IV shows that the addition of inorganic constituents to the soft/low alkalinity groundwater increased pH at the inlet. This might be expected to increase passivation for column experiments. Columns VI and IX were not considered to be affected by the increase in pH, since the TCE dechlorination rate constants are larger for the addition of CaCO$_3$ and NaHCO$_3$ than those for the baseline groundwater (column V).

In comparison to the baseline column V, the columns that were added with CaCO$_3$ and NaHCO$_3$ (columns VI and IX) were more efficient in percentage TCE removal and furthermore, showed only a gradual decrease in removal efficiencies over the course of their respective experiments. This is in stark contrast to columns V, VII and VIII where drastic declines in removal performance over the greater part of their experimental times were observed.

Considering that the same groundwater source was used as influent to columns IV and V, it is hardly unexpected to find only marginal differences between the two sets of aqueous inorganic profiles. The difference in TCE dechlorination rates for column V compared to column IV might be due to the difference in seepage velocity. As listed in Table III, column IV was operated at 2.3 m per day of seepage velocity while it is 1.3 m per day in column V. Since the mass transport of TCE from

the bulk solution to the surface of Fe^0 can be a limiting step in TCE dechlorination (Scherer *et al.*, 2000), high seepage velocity can accelerate the movement of TCE to the Fe^0 surface and thereby can enhance the rate of dechlorination (Lai *et al.*, 2002). On the other hand, the difference of degree of green rusts formation between columns IV and V may also contribute the discrimination of TCE dechlorination rate. To date, however, no explanation is forthcoming in the literature to explain the presence of a layer of green rusts in column IV whereas only a patchy coating of rust was observed for column V.

For column VI, the inorganic profiles also show the concentrations of calcium and magnesium to be fairly constant (Table V). Therefore, calcite and magnesite are not expected to precipitate anywhere in the column. The formation of siderite in the column might be best explained by assessing the change in total iron and total alkalinity. Similarly, for column IX, apart from the variation of total iron concentrations found in the column, concentrations remained reasonably constant for the remaining aqueous inorganic profiles. The total iron concentrations, however, show a slight decrease near the centre of the column and then a rapid increase at the outlet (not shown in this paper). The TCE dechlorination curves also highlight a passivation effect just before the middle of the column for the 33.3 and 62.4 PV which might be due to siderite formation.

Column VII
The increase in inlet pH, however, may be responsible for the poor performance of column VII considering that the addition of silicate produced the lowest TCE removal for all of the columns. Armstrong *et al.* (1994) claimed that in soft waters the level of silicate protection of iron is because of the increase in pH. Their work, however, did add the qualification that the reduction of the corrosion rate in the pH range 9.6–11.6 could not be entirely accounted for by the change in pH caused by the addition of sodium silicate. Since the inlet pH for column VII was well below this range found by Armstrong *et al.* (1994), the cause of the decreased efficiency of TCE removal is predominantly because of the silicate ion. The influence of pH, in the range 7–8.6, on the inhibitive effect of sodium silicate is known to enhance inhibition when the pH was decreased from 8.6 to 7 (Lahodny-Sarc and Kastelan, 1981). Osterhus (2001) stated that the ability for silicate to react with Fe^{2+} and to form iron-silicate films is well known, and that the silicate adsorbs to the surface, polymerises and gradually forms gel capable of converting to Fe-silicates, which might be able to coat the Fe^0 surfaces and block electron transfer. Therefore, the deactivation of column VII by the silicate ion rather than by pH is thought to be the main cause for the poor removal of TCE.

Even though the inhibitory mechanism for silicate remains unexplained, the study of its effect on TCE dechlorination rates is very important since, in a practical sense, quartz and/or silica sand is often used when installing field PRB. For example, sand is often placed immediately in front of the reactive zone to improve the flow dynamics for the system. This means that, for an aquifer with a high background

pH, a passivation front might develop at the start of the barrier because of quartz dissolution.

Column VIII

The increasing problem of nitrate pollution in groundwater is a significant factor that must be taken into account when assessing the appropriateness of PRB technology for treating chlorinated solvents. The concentration of nitrate spiked in this study is commonly found in polluted groundwater (Appelo and Postma, 1996) and therefore the results from column VIII might have some relevance for remediation under field conditions.

The inhibition of TCE dechlorination by nitrate was evident in work conducted for this study and was thought due to the competition for available electrons. Schlicker *et al.* (2000) also conducted column experiments that investigated the effect on dechlorination for inlet waters containing nitrate and TCE. At the front section of their columns, they found that nitrate reduction was the dominant process and that the dechlorination process was delayed. In contrast, the column experiments conducted in this study showed that TCE dechlorination could occur at the beginning of the column and this was especially evident for the 15.4 PV (Figure 5). The results from this column experiment point to simultaneous reduction of TCE and nitrate during the front/middle sections of the column and this effect was unexpected. As a result, the need for depletion of one compound before the removal of another could start was not evident in this experiment in contrast to the findings of Schlicker *et al.* (2000).

The pH, total iron, nitrate, sulfate and profiles along the column depth are plotted against pore volumes, as shown in Figure 6. The pH profile for this column was the first to confirm a consistent release of OH^- ions into solution because of the anaerobic dissociation of water by Fe^0. A possible reason for the constant increase in pH for the first half of the column is that that only minimal buffering from carbonate
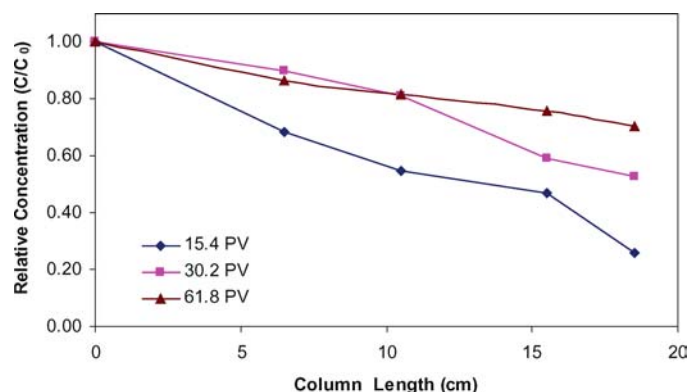

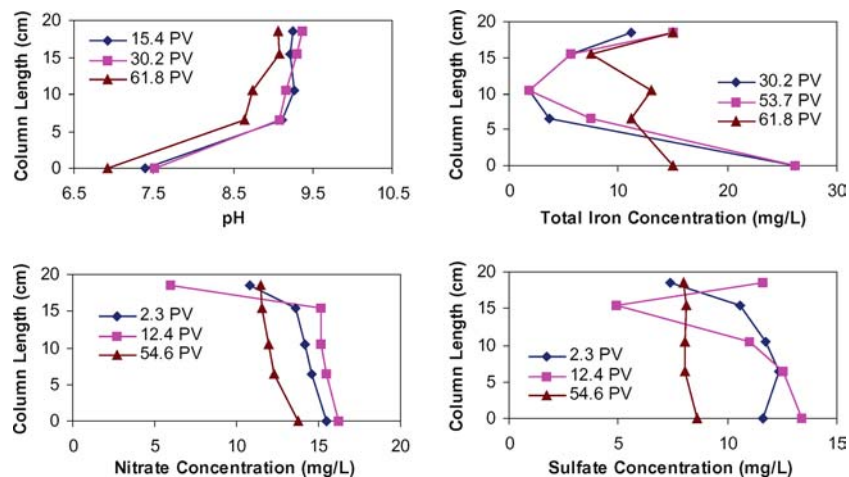*Figure 5*. Variation of TCE relative concentration for column VIII.

Figure 6. Variations in pH, total iron, nitrate, and sulfate for column VIII.

precipitate formation took place. The near-constant pH 9 values throughout the back half of the column suggest that the OH^- was being consumed by the formation of ferrous hydroxide ($Fe(OH)_2$) which is known to dominate around this pH (Gillham, 1996).

The behavior of the nitrate and sulfate profiles is worth discussing for the reason that reductions in concentration are strongly in evidence along the flowpaths. For the 2.3 and 12.4 PV, the nitrate and sulfate concentrations gradually decrease up to the 15.5 cm-mark and then rapidly decrease until the column outlet. For 2.3 PV, it is difficult to ascertain the effect of the sudden decrease in nitrate and sulfate concentrations on TCE dechlorination since most of the TCE had already been removed from the column. The 30.2 PV profile for TCE (Figure 5), however, shows that the slope decreases between 15.5 and 18.5 cm, suggesting that nitrate might out compete TCE for the available electrons.

Conclusions

This study investigates the degree of TCE dechlorination for Fe^0 column experiments under varying inorganic groundwater chemistry conditions. Column experiments were conducted to investigate the reductive dechlorination of TCE under anaerobic conditions and consisted of two phases: phase 1 focusing on TCE dechlorination for two Danish groundwater types and phase 2 investigating the effect of spiking field groundwater with four inorganic compounds.

For the two Danish groundwater types tested, TCE dechlorination was slightly higher for the soft low alkalinity groundwater than for the hard high alkalinity groundwater. The phase 2 experiments found that, compared with the baseline

solution, the addition of 1 mM $CaCO_3$ and 1 mM $NaHCO_3$ stimulated the TCE dechlorination process and led to higher dechlorination rate constants. The presence of green rusts for the 'carbonate/bicarbonate' experiments might be one explanation for the enhanced TCE dechlorination rates caused by the re-activation of previously passivated surfaces. The spiking of 1 mM KNO_3 and 1 mM Na_2SiO_3 decreased TCE dechlorination compared with the baseline solution and led to considerably lower dechlorination rate constants. These findings have important implications for the design of field PRBs. Emplaced reactive zones should avoid mixing Fe^0 and quartz/silica sand because this practice can potentially inhibit the dechlorination process. The findings of this research also confirm that nitrate is, in fact, responsible for reducing the reactivity of Fe^0 to degrade TCE, and that the implementation of PRB technology at TCE and nitrate contaminated sites will be likely to suffer accordingly.

Acknowledgments

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