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Longevity of Granular Iron in Groundwater Treatment Processes: Solution Composition Effects on Reduction of Organohalides and Nitroaromatic Compounds

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Although granular iron permeable reactive barriers (PRBs) are increasingly employed to contain subsurface contaminants, information pertaining to system longevity is sparse. The present investigation redresses this situation by examining the long-term effects of carbonate, silica, chloride, and natural organic matter (NOM) on reactivity of Master Builders iron toward organohalides and nitroaromatic contaminants. Six columns were operated for 1100 days (~4500 pore volumes) and five others for 407 days (~1800 pore volumes). Nine were continuously exposed to mixtures of contaminant species, while the other two were only intermittently exposed in order to differentiate deactivation induced by water (and inorganic cosolutes) from that resulting from contaminant reduction. Contaminants investigated were trichloroethylene, 1,2,3-trichloropropane, 1,1-dichloroethane, 2-nitrotoluene, 4-nitroacetophenone, and 4-nitroanisole. Column reactivity declined substantially over the first 300 days and was dependent on the feed solution chemistry. High carbonate concentrations enhanced reactivity slightly within the first 90 days but produced poorer performance over the long term. Both silica and NOM adversely affected reactivity, while chloride evinced a somewhat mixed effect. Observed contrasts in relative reactivities suggest that trichloroethylene, 1,2,3-trichloropropane, and nitroaromatic compounds all react at different types of reactive sites. Our results indicate that differences in groundwater chemistry should be considered in the PRB design process.

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Introduction

The use of granular iron (Fe⁰) permeable reactive barriers (PRBs) for containing contaminants in groundwater has gained widespread acceptance in recent years within the environmental remediation and regulatory communities. Considerable progress has been made toward understanding the interfacial chemistry of granular iron and the mechanisms through which contaminants degrade (1–7), although factors governing changes in iron reactivity over time or in response to differences in groundwater chemistry have received less attention. As a result, the design life of PRB installations is relatively uncertain.

Column studies by Sivavec and co-workers (8–10) and by Farrell et al. (11) have identified some of the factors associated with barrier longevity. Sivavec (8–10) demonstrated that granular iron reactivity toward trichloroethylene (TCE) decreased upon exposure of the iron to 420 pore volumes of carbonate-buffered water. Because experiments were generally conducted at flow velocities (~810 cm/d) considerably higher than those observed in the field, the high pH values characteristic of field installations of granular iron PRBs may not have prevailed within the columns. This could have repercussions on surface speciation (and hence reactivity) as well as on mineral precipitation (and thus contaminant residence time). Such factors complicate extrapolation of their results to field conditions.

Farrell et al. (11) also noted a significant decline in reactivity of iron toward TCE over the course of 667 days (~700 pore volumes) in column studies conducted at a flow velocity (50 cm/d) more representative of field conditions. Rate coefficients for TCE degradation were found to be a function of its concentration as well as of the cosolute composition and column age. This suggests that site-specific differences in groundwater chemistry may affect PRB longevity. Nevertheless, because these researchers used sulfate, chloride, or nitrate as inorganic matrices, the results may not relate to the carbonate systems more commonly encountered in groundwater. Moreover, it is difficult to assess the extent to which alterations in average flow velocity, resulting from precipitate formation, may have contributed to the deterioration in treatment efficiency reported by Farrell et al.

Prior studies of iron corrosion and passivation indicate that reactivity may be a complex function of the inorganic and organic composition of the groundwater. Not only could contaminant type and concentration affect longevity, but the types and amounts of cosolutes present could also play a role. To investigate such issues, we initiated column studies in which the effects of carbonate, silica, chloride, and natural organic matter (NOM) on the reactivity of granular iron toward chlorinated hydrocarbons (CHCs) and nitroaromatic compounds (NACs) were examined over extended periods of time. These solutes could deactivate the interfacial region by altering the local electronic environment of the reductants, by limiting access to reactive sites, or by competing with contaminants for reactive sites. Alternatively, some solutes could assist in maintaining reactivity within the PRB, either by facilitating breakdown of passivating Fe(III) (hydr)oxide coatings or by enabling the formation of new reactive phases. Other solutes could promote precipitate formation, thereby altering flow velocities. Individual solutes may concurrently serve different roles, and the net effect could vary with concentration.

Carbonate, depending on its concentration, can either serve to enhance or inhibit iron corrosion (12–16). Its

presence leads to precipitation of mineral phases such as carbonate green rust (17), siderite (FeCO_3 ; see refs 14 and 18), calcite (CaCO_3 ; see ref 19), or aragonite (CaCO_3 ; see refs 18 and 20). These precipitates may reduce the porosity of the permeable media (10, 20, 21); they could inhibit contaminant access to the iron surface (12, 14); and in the case of carbonate green rust, they could provide a redox-active phase (22).

Chloride acts as a corrosion promoter, and its presence could thus enhance granular iron reactivity. Chloride destabilizes the passive film present on the iron surface, and this can induce corrosion pit formation (23, 24). Such effects have been hypothesized to produce the rate enhancements observed for reduction of TCE (24) and CCl_4 (25). Using an input–output column, we have previously shown that addition of chloride initially led to increased reactivity toward 2-nitrotoluene (2-NT) reduction by Master Builders iron (26). Reactivity nonetheless declined as the column aged, indicating that the rate-enhancing effect may be relatively short-lived.

Silica is a known corrosion inhibitor (27) that may compromise PRB longevity through the formation of surface complexes at the particle–water interface. Typical concentrations in groundwater are in the range of 120–750 μM (7–45 mg/L as SiO_2 ; see ref 28), and field measurements have shown that dissolved silica concentrations decrease precipitously within a granular iron PRB (29). Although the effect of silica adsorption on contaminant degradation within full-scale column reactors has not been previously addressed, preliminary results have indicated a strong detrimental effect on the reactivity of granular iron toward both TCE (30) and NACs (26).

Despite the ubiquity of natural organic matter (NOM), little is known about its effects on PRB efficacy. Results from a column study suggest, however, that high total organic carbon (TOC) concentrations (>500 mg/L) can adversely affect tetrachloroethylene degradation rates (31). Tratnyek et al. (32) observed slight declines in reactivity toward CCl_4 in the presence of three isolated humic acids; in contrast, the four fulvic acids tested did not significantly influence CCl_4 reduction rates.

To gain further insight into such cosolute effects, we undertook long-term studies in which alterations in the reactivity of the interfacial region were decoupled from changes in the hydraulic residence time (HRT) that result from mineral precipitate and H_2 gas pocket formation within the porous media. Three sets of columns, filled with granular iron and continually fed solutions containing various organic and inorganic solutes, were operated concurrently for up to 1100 days. Two sets were housed at Johns Hopkins (columns A–F, run for 1100 days; columns G–J, run for 475 days), and the third was maintained at the Air Force Research Laboratory (K–O, run for 407 days). The results described herein pertain to columns A–F and K–O. At an average flow rate of 0.5 mL/min (~ 220 cm/d), these operation times correspond to up to 4500 pore volumes. We believe these granular iron column experiments to be the longest of any reported to date.

The main objective of this paper is to demonstrate the effect of the type and concentration of various cosolutes (carbonate, chloride, silica, and NOM) on the long-term reactivity of Master Builders iron toward selected CHCs and NACs. Our study of temporal changes in mean hydraulic residence time (33) has allowed us to decouple these effects from the reactivity changes reported here. In addition, more subtle changes in transport properties, such as the formation of “dead-end” or “immobile” porosity and increased dispersivity in the remaining mobile water were discussed. As suggested in that work (33), such transport-related effects may be minor contributions to the observed alterations in

overall column performance that are attributed to the direct changes in surface reactivity described herein.

Experimental Section

Chemicals. Sodium bicarbonate (NaHCO_3 ; Fisher), sodium hydroxide (NaOH ; Fisher), sodium chloride (NaCl ; J. T. Baker Inc.), sodium metasilicate (Na_2SiO_3 ; Sigma), trichloroethylene (TCE; Aldrich), 1,1-dichloroethane (1,1-DCA; stabilized with 0.1% CH_3NO_2 ; TCI America), 1,2,3-trichloropropane (1,2,3-TCP; Fluka), 2-nitrotoluene (2-NT; Fluka), 2-aminotoluene (2-AT; Aldrich), 4-nitroanisole (4-NA; Fluka), 4-aminoanisole (4-AA; Aldrich), 4-nitroacetophenone (4-NAP; Aldrich), and 4-aminoacetophenone (4-AAP) were of the highest purity available and were used as received. All experiments were conducted using deionized water produced by a Milli-Q reagent-grade water system (Millipore Corp.).

Aldrich humic acid (AHA) was pretreated to remove residual fulvic acids and heavy metals and to decrease the ash content (34). In brief, the AHA was dissolved in 10 mM NaOH , was treated with HF-HCl , and was then saturated with sodium using Na-Chelex 100 (Bio-Rad Laboratories). Suwannee River humic acid (SRHA) was obtained from the International Humic Substances Society (IHSS) and was used as received. Great Dismal Swamp water (GDS NOM) containing 39 mg/L NOM (as organic carbon) was collected in the field and was stored at 4 °C until use.

Column Setup and Operation. As described in detail elsewhere (33), Plexiglas columns (39 cm \times 3.1 cm I.D.) were fitted with stainless steel sampling ports and were filled with Master Builders Inc. (Cleveland, OH) GX-27 iron filings. Deoxygenated feeds were withdrawn from 9 L glass reservoirs using a peristaltic pump set at approximately 0.5 mL/min. Organic contaminants in methanol–water (50:50; v:v) were fed at 2.7 $\mu\text{L}/\text{min}$ using a syringe pump and were combined with the deoxygenated feed using stainless steel T-connectors. The corresponding average linear flow velocity (v), as determined by $^3\text{H}_2\text{O}$ tracer tests (33), was 221 ± 5.20 cm/d through columns A–F. This value represents the upper end of pore-water velocities (6–220 cm/d) reported so far for PRBs in the field (18, 35).

Initial results in columns A–F yielded irregular input concentrations. This was corrected by introducing 37-mL mixing chambers ahead of the columns (see Supporting Information Figure S1 for a schematic) after the first 100 days of operation. Experiments with all other columns were initiated with the mixing chambers in place. Three-way valves in front of the peristaltic pump enabled replenishment of the reservoir feed without introducing O_2 to the system. Although the eluent composition varied from column to column, the influent pH for all columns was set to 9.3 ± 0.3 . This pH is representative of that encountered in the interior of many field PRB installations (19, 35, 36) and remained constant within the columns. Details pertaining to solution composition for columns A–F and K–O are provided in Table 1. Other experimental details are reported elsewhere (33).

Various mixtures of CHCs were continuously introduced to most of the columns at a nominal concentration of 100 μM each. TCE was fed to columns C–E and K–O throughout this study. 1,1-DCA was fed only to columns C–E and was eliminated from the feed after 197 days because it was not significantly transformed. 1,2,3-TCP was fed to columns C–E throughout most of their operation, and it was also fed initially to columns K–O. This solute was omitted from columns K–O after 148 days, leaving TCE as the sole contaminant.

Column F was primarily fed a mixture of two NACs throughout the duration of this study. The NAC feed contained 2-NT and either 4-NA or 4-NAP, each at a nominal concentration of 100 μM . The switch from 4-NA to 4-NAP after 301 days of operation was made to examine if the large difference in one-electron reduction potential between 4-NA

TABLE 1. Composition of Feedwater for Columns A–F (Operated for 1100 Days at Johns Hopkins) and K–O (Operated for 407 Days at AFRL)

cosolutes ^d	A	B	C	D	E	F	K	L	M	N	O
2 mM NaHCO ₃	1–1100	1–1100	1–1100	1–1100		1–1100	1–290	1–290	1–290	1–290	1–290
20 mM NaHCO ₃					1–1100						
10 mM NaCl		1–1100		313–409							
500 μM Na ₂ SiO ₃		925–1100	409–538			183–309					
5 mL concentrated HCl					407						
20 mg/L AHA								1–240			
2 mg/L AHA									1–240		
2 mg/L SRHA										1–240	
2 mg/L GDS NOM											1–240
pH 12 NaOH							345–346	345–346	345–346	345–346	345–346
organic contaminants ^{a,d}	A	B	C	D	E	F	K	L	M	N	O
TCE	134–158 264–291 446–513 789–848 918–1100	134–158 264–291 446–513 789–848 918–1100	1–1085	1–1085	1–508 624–1100	134–158 264–291 401–446 509–623 789–848	1–345 346–407	1–345 346–407	1–345 346–407	1–345 346–407	1–345 346–407
1,2,3-TCP			1–1100 ^b	1–1100 ^b	1–508 ^b 624–1100 ^b		1–148	1–148	1–148	1–148	1–148
1,1-DCA			1–197	1–197	1–197						
2-NT					509–623	1–1100 ^c					
4-NA						1–301 ^c					
4-NAP					509–623	301–1100 ^c					

^a Nominal concentration for all compounds 100 μM. ^b During periods when TCE probe experiments were conducted (days 134–158, 264–291, 429–513, 789–848) the TCP feed was suspended. ^c During periods when TCE was fed, the NACs were omitted from the feed. ^d Shown are the times (in days) during which the feed was added.

and 4-NAP would result in substantial differences in the relative reactivity of these compounds (37, 38).

TCE (~100 μM) was fed as the sole contaminant to columns A–F for short periods on an intermittent basis. These periodic “TCE probe” experiments were conducted to provide a consistent metric of column reactivity over time. They enabled reactivity comparisons between columns not normally fed TCE (A, B, and F) with those that were continually fed a mixture of CHCs (C–E, K–O), and they also provided information pertaining to the effect of the co-contaminants, 1,2,3-TCP and 1,1-DCA, on rates of TCE degradation in columns C–E.

We note that strict aseptic techniques were not employed during preparation of the feedwater solutions, and it is therefore conceivable that microbial consortia could have developed within the column reactors. If such consortia did develop, it is unlikely that they played a significant role in contaminant reduction because essential nutrients were not present within the feedwater. Scanning electron microscope (SEM) examination of iron grains extracted from columns A–J at column shutdown did not reveal any evidence of microbial growth.

Column Sampling. At selected intervals, headspace-free aqueous samples were withdrawn from the columns using glass syringes connected to the sampling ports with a PEEK adapter (Upchurch). Samples were collected at rates not exceeding that of column flow, beginning at the distal end of each column. This sampling procedure maximized the probability that the sample composition was representative of pore fluids at that point.

Analytical Techniques. *Gas Chromatography (GC).* For columns A–F, chlorinated hydrocarbons and their daughter products were quantified via a static headspace GC method with flame-ionization detection (39). For columns K–O, 0.40 mL aqueous samples were added to 1.2 mL of acetonitrile (containing *o*-dichlorobenzene as an internal standard) and were analyzed by GC with electron capture detection.

High-Pressure Liquid Chromatography (HPLC). Analyses of nitroaromatic compounds and their aniline reduction

products were performed using an isocratic Waters HPLC system (515 Pump, 717 plus autosampler, 486 UV detector). Chromatographic separation was achieved with an RP-18 reversed-phase column (125 mm × 4 mm I.D.) and precolumn (4 mm × 4 mm I.D.; both LiChroCART stainless steel cartridge, 5 μm spheres; Merck AG, Darmstadt, Germany). The mobile phase was 5 mM sodium phosphate in methanol–water (55:45) at pH 7. The flow rate was set to 0.9 mL/min. The detector wavelength was set to 230 nm (0–4 min) and to 280 nm (4–10 min). External standards were used for quantification.

Other Analyses. Total organic carbon concentrations were determined with a Shimadzu TOC 5000 instrument (40). Silica concentrations were determined either by the heteropoly blue method (40) or via inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Calculation of Rate Coefficients. Spatially averaged rate coefficients and estimates of initial concentration $C_{0,\text{est}}$ in each column were determined by fitting a pseudo-first-order expression to the concentration profiles (C vs residence time, $\tau_x(t)$)

$$\frac{d[C]}{d\tau_x(t)} = -k_{\text{obs}} [C] \quad (1)$$

where k_{obs} (h^{-1}) is a pseudo-first-order kinetic coefficient, C refers to the concentration of a given contaminant (i.e., TCE, 2-NT, 4-NAP, 4-NA), and t denotes the column operation time (i.e., age). Uncertainties in k_{obs} values were computed to reflect 95% confidence intervals; their magnitudes indicate the extent to which the profiles adhered to a pseudo-first-order model. Measured influent concentrations, $C_{0,\text{exp}}$, were included in evaluating concentration profiles except in the rare case where they represented obvious outliers. For the TCE profiles that exhibited a lack of reactivity within the proximal regions, the data obtained within the inactive zones (defined as $C/C_0 > 0.9$ for three or more consecutive samples) were neglected in order to obtain k_{obs} values characteristic of the active portions of the columns.

Values of local residence time, $\tau_x(t)$, for each sample port (at distance x along a column of length L) were calculated using the mean hydraulic residence time, $\tau(t)$, for the entire column:

$$\tau_x(t) = \tau(t) \times \frac{x}{L} \quad (2)$$

The $\tau(t)$ values for columns A–F were calculated using $\tau_{\text{tracer}}(t)$ values interpolated from tracer tests periodically conducted using a near-Dirac pulse of $^3\text{H}_2\text{O}$ and a flow rate of 0.500 mL/min established with an Isco syringe pump. To correct for variations in the flow caused by the peristaltic pump normally used with the columns, the interpolated $\tau(t)$ values were adjusted using the actual volumetric flow rate measured on any given day. Details concerning the determination of $\tau_{\text{tracer}}(t)$ and its variation over time are given elsewhere (33). The $\tau(t)$ values for columns K–O were calculated on the basis of periodic volumetric flow measurements only.

A pseudo-first-order expression has often been used in previous studies of iron-mediated reduction of CHCs and NACs (14, 26, 38, 41). For these experiments it was adopted as a means of quantifying reactivity trends after first exploring a Langmuir–Hinshelwood–Hougen–Watson (LHHW) approach similar to that previously used in our laboratory (1, 42) and elsewhere (25, 43–46). It was found that the LHHW model did not provide any significantly improved fit to the contaminant profiles relative to a simpler pseudo-first-order expression.

Mass Transfer Considerations. As discussed in the Supporting Information, the pseudo-first-order rate coefficients measured for TCE were several orders of magnitude smaller than the value of the rate coefficient (k_{max}) estimated for external mass transfer. Rate coefficients measured for TCE can thus be interpreted to reflect intrinsic surface reaction limitations. Rate coefficients initially measured for NAC reduction were also smaller (see Supporting Information Figure S2) but were within an order of magnitude of k_{max} values; we cannot, therefore, rule out the possibility that initial k_{obs} values for NACs could be partially mass transfer controlled.

Results

Reduction of TCE. Examples of concentration profiles as well as model fits obtained for TCE in columns C, E, and N are shown in Figure 1. Similar results were obtained for other columns to which these contaminants were continuously introduced. TCE was efficiently reduced at early times, although degradation rates decreased markedly as the columns aged. This attenuation in reactivity reflects progressive deactivation of the iron surface. At the proximal ends of the columns, which had experienced considerably greater contaminant and cosolute fluxes than the distal ends, apparently unreactive zones grew over time. The rate at which these zones developed appears to depend on solution composition, with the waters containing 20 mM HCO_3^- (column E) and NOM (columns L–O) exhibiting the most pronounced effects. In fact, by day 1013 the unreactive zone for column E occupied ~40% of the column.

Figures 2 and 3 show the results for columns C–E and K–O, respectively, when TCE was present in a mixture of CHCs. Figure 4 shows the results for columns A–F during “TCE probe” experiments. In each case, k_{obs} values for TCE decrease over time.

Reduction of Chlorinated Alkanes. 1,2,3-TCP (Supporting Information Figure S3) and 1,1-DCA (data not shown) were considerably less reactive than TCE. Because 1,1-DCA was only minimally transformed, it was omitted from the feed to columns C–E after 197 days (and was never introduced to

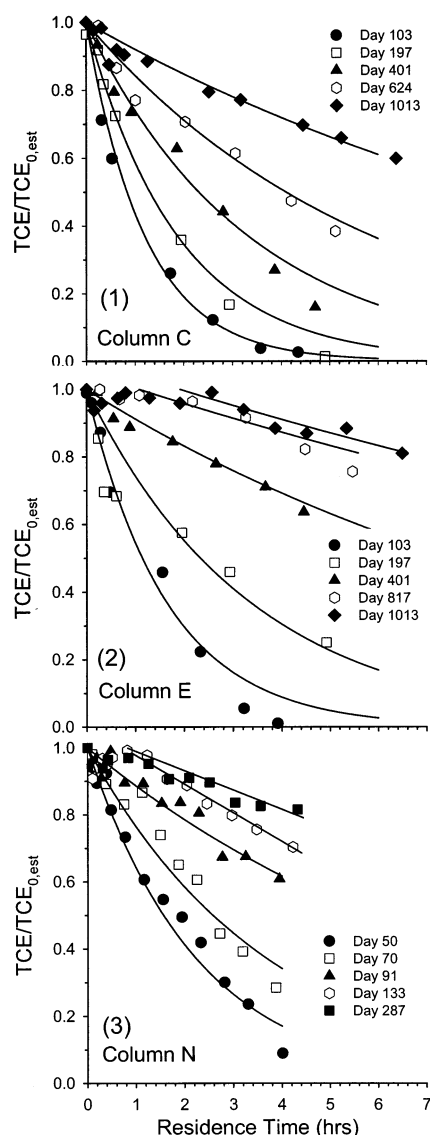


FIGURE 1. TCE profiles for (1) column C, (2) column E, and (3) column N. Curves represent fits to a pseudo-first-order model. For column E and column N, the later time model fits were only applied to data downgradient from the unreactive zone (see text for details). $\text{TCE}_{0,\text{est}}$ was determined as part of the first-order fitting exercise.

the remaining columns). Interestingly, 1,2,3-TCP and 1,1-DCA degraded only within the initial 10% (~4 cm) of each column, remaining at essentially constant concentrations thereafter. This pattern persisted for 1,2,3-TCP throughout this study and was apparent even as the total amount of 1,2,3-TCP degraded decreased from ~20% at day 103 to ~10% by day 1013. Other column studies (47) have shown the dechlorination of 1,2,3-TCP to be a relatively slow process; nevertheless, we are unaware of previous work that demonstrates removal only within the proximal end of a column. To examine whether TCE or one of its degradation products was inhibiting 1,2,3-TCP reduction, the TCE feed to columns C–E was halted on day 1085, with no discernible effect on subsequent 1,2,3-TCP profiles. This suggests that 1,2,3-TCP reduction was unaffected by competition for reactive sites from either TCE or its reduction products.

Products of CHC Degradation. Ethane and ethylene were the primary products of TCE degradation, with acetylene as a transient intermediate (data not shown). Small quantities of 1,1-DCE, *cis*-DCE, and C_4 coupling products (i.e., 1-butene, *cis*-butene, *trans*-butene, *n*-butane) were also typically observed. Trace quantities (<0.25 μM) of *trans*-DCE and vinyl

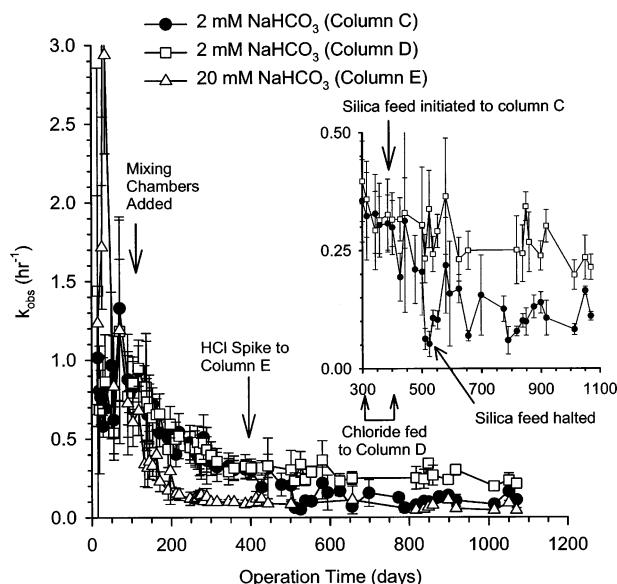


FIGURE 2. Pseudo-first-order kinetic coefficients for TCE reduction in columns C–E. The inset depicts the effect of silica on TCE degradation in column C. These columns were continually exposed to a mixture of CHCs for 1100 days.

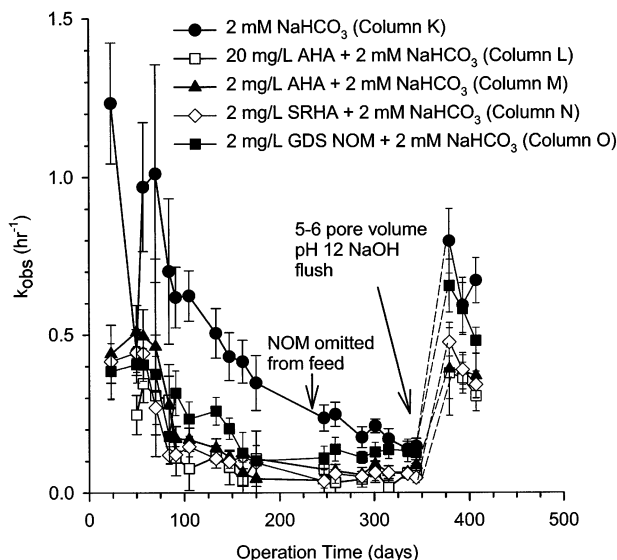


FIGURE 3. Pseudo-first-order kinetic coefficients for TCE reduction in columns K–O continually exposed to a mixture of CHCs. Varying concentrations of NOM were fed to these columns for 240 days. On day 240 the NOM was omitted from the feed to columns L–O, on day 290 the 2 mM bicarbonate buffer was omitted (not shown), and on day 345 a 5–6 pore volume alkaline (pH 12) flush was initiated to each column.

chloride were only occasionally detected. The TCE products are consistent with β -elimination as the predominant reduction pathway (5) and corroborate product distributions previously reported for TCE reduction by Master Builders iron (11). Propane, propylene, and trace amounts of 1-chloro-2-propene were the only 1,2,3-TCP reduction products identified.

Reduction of Nitroaromatic Compounds. The earliest concentration profiles (<30 days) obtained from column F indicated that 2-NT and 4-NA disappeared too quickly to be detectable at the first sampling port (~1 cm from column inlet; Figure 5A). Nevertheless, the concurrent near-stoichiometric appearance of 2-aminotoluene (2-AT) and 4-aminoanisole (4-AA) demonstrated that the NACs were reduced by the granular iron with essentially 100% efficiency.

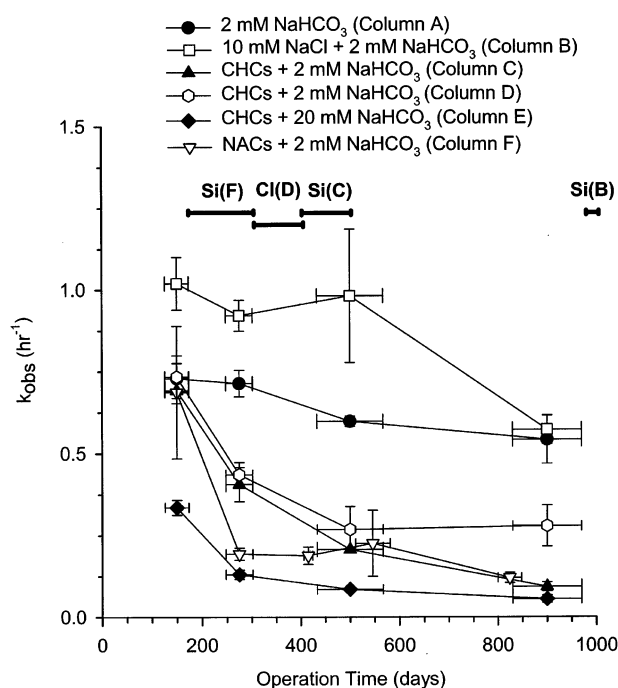


FIGURE 4. Pseudo-first-order kinetic coefficients obtained during the TCE probe tests for columns A–F. Each point represents the average coefficient obtained from 2 to 4 individual profiles (with the exception of column E during the period of 425–575 days, for which only one profile is shown). As discussed within the text, these averaged coefficients only consider the k_{obs} values acquired under quasi-steady-state conditions. Vertical error bars reflect the 95% confidence interval for kinetic coefficients averaged over the operation period indicated by the width of the horizontal error bars. The legend refers to the normal feed to each column. The bars at the top of the figure indicate periods when the normal feed to each column was augmented with either silica (in column F for days 183–300; in column C for days 409–538; and in column B for days 925–1100) or with chloride (in column D for days 313–409). Not shown within the figure is the 5 mL concentrated HCl spike introduced to column E on day 400.

Substantial declines in the 2-AT and 4-NA concentrations toward the distal end of the column within the first month of operation indicated sorption of these anilines to the granular iron, consistent with earlier work (45, 48). Once quasi-steady-state conditions were attained after approximately 49 days, aniline concentrations remained constant at all ports where the NACs were below detection limits.

By day 114, reactivity toward 2-NT and 4-NA had decreased slightly such that both compounds were detected at the second port (2.0 cm from inlet, Figure 5A). Meanwhile, the NAC concentrations observed at the first sampling port continued to increase, indicating deactivation of the proximal end of the column. The NAC concentrations observed at the second port remained low and relatively constant until 500 μ M silica was introduced to the column influent on day 183. Silica addition depressed reactivity of iron toward both 2-NT and 4-NA (Figures 5A,B and S2). On day 300, silica was eliminated from the feed solution, and 4-NA was replaced with 4-NAP. Following these changes, reactivity toward 2-NT rebounded substantially as indicated by lower NAC concentrations at all ports. Note that the rebound in reactivity resulted from omission of the silica from the column feed; it is unlikely to have been caused by the switch from 4-NA to 4-NAP. As with 4-NA, 4-NAP was readily reduced to the corresponding aniline (4-aminoacetophenone, 4-AAP), and the close correspondence between the 2-NT and either the 4-NA or the 4-NAP concentration profiles persisted.

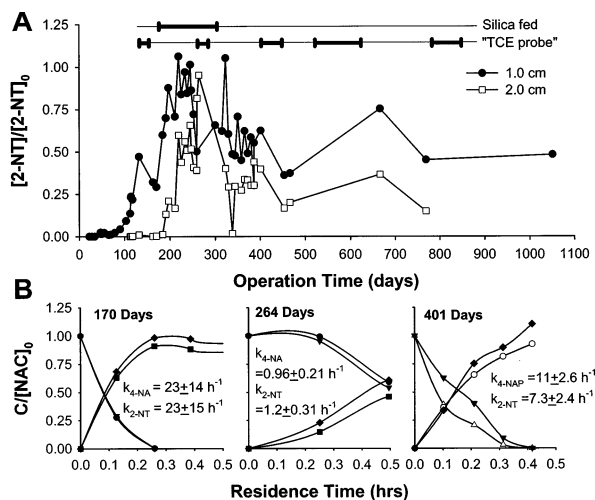


FIGURE 5. (A) 2-NT concentrations at selected ports of column F. For all curves, data points prior to the first point given were all below the method detection limit ($<0.1 \mu\text{M}$) and are not shown. During the addition of silica to the feed (day 183–300), breakthrough of 2-NT was observed up to about 8 cm into the column. After silica was omitted from the feed, concentrations of 2-NT at all ports dropped for a short period of time but stabilized at elevated levels throughout the remainder of the study. (B) Nitroaromatic compound (NAC) profiles for column F for 170, 264, and 401 days, (i.e., prior to and during addition of silica to the feed, and after its elimination). Concentrations of individual NACs (2-NT, \blacktriangledown ; 4-NA, \bullet ; 4-NAP, \triangle) and their corresponding reduction products (2-AT, \blacklozenge ; 4-AA, \blacksquare ; 4-AAP, \circ) are normalized to the initial NAC concentrations. Curves are depicted to show trends and are not representative of model fits. Kinetic coefficients for parent compound reduction were determined using eq 1.

Discussion

Comparison of Replicate Columns. Columns C and D were operated at Johns Hopkins University, while column K was operated at the Air Force Research Laboratory. These columns were run under almost identical conditions during the first 300 days with a constant 2 mM bicarbonate and CHC feed. The decrease in reactivity toward TCE observed for these columns was qualitatively very similar (Figures 2 and Supporting Information Figure S4), with an average variability in k_{obs} of around 15–25%. This level of variability in part may be attributable to the fact that the $\tau_x(t)$ values for the AFRL columns were inferred from periodic flow measurements only and were not computed from the more accurate $^3\text{H}_2\text{O}$ tracer approach employed for columns A–F. Because the water-filled porosity within each column varies with time (33), the $\tau_x(t)$ values calculated using flow measurements may differ by as much as 10–20% from the true values. Nevertheless, this comparison suggests that any observed deviations between k_{obs} values for any two columns that are greater than 15–25% are meaningful and reflect effects other than the normal experimental error associated with replicate columns.

Effect of Continuous vs Intermittent CHC Exposure. The quasi-steady-state k_{obs} values obtained in columns C–E during the TCE-probe experiments (i.e., the periods during which TCE alone was fed; Figure 4) were very similar to those obtained either immediately before or after such an experiment in the presence of a mixture of organohalides (Figure 2). This indicates that reactivity toward TCE was not influenced by the presence of the other CHCs in the feed. In other words, no competitive effect of 1,2,3-TCP or 1,1-DCA on TCE reduction was evident.

Interestingly, the apparent initial k_{obs} values acquired during a “TCE-probe” experiment but prior to the attainment

of quasi-steady-state conditions (k_{obs} varying by less than 15% for replicate profiles) were consistently larger than those obtained once steady state was reached (Figure S5 in the Supporting Information). Because the influent TCE concentration did not change between the mixed CHC feed and the TCE-probe feed, this short-lived apparent enhancement may signify losses incurred through TCE sorption to unreactive sites previously occupied by 1,2,3-TCP. Once these unreactive sites were fully occupied by TCE, the TCE rate coefficient would return to that obtained prior to the onset of a TCE probe test. As previously noted (49), such transient sorptive losses illustrate the need to attain quasi-steady-state conditions for proper evaluation of rates of contaminant reaction with granular iron materials that contain appreciable quantities of unreactive yet sorptive sites.

Although reactivity toward TCE did not appear to be influenced by the presence of 1,2,3-TCP or 1,1-DCA, there did appear to be an “aging” effect that stemmed from total exposure to CHCs. As with columns C–E, rate coefficients obtained during the TCE probe tests for column A progressively decreased but were considerably larger in column A than in columns C and D at corresponding times (Figure 4). The principal difference between these columns is that CHCs (typically 1,2,3-TCP and TCE) were only intermittently included in the feed to column A but were continuously introduced to the feed of columns C and D. The additional deterioration in the performance of columns C and D (beyond that resulting from reactions involving the iron, water, and inorganic cosolutes) can therefore be attributed at least in part to their continuous exposure to CHCs. This suggests that the contaminants undergoing treatment can act so as to reduce the useful lifetime of granular iron.

Effect of Cosolutes on Granular Iron Reactivity. *Influence of Bicarbonate.* Column E, which was exposed to 20 mM bicarbonate, appeared to exhibit slightly greater reactivity during the first 90 days of operation than either columns C or D, which were exposed to only 2 mM bicarbonate (Figure 2); nevertheless, this higher level of reactivity was not sustained indefinitely. Rate coefficients for column E declined rapidly to the point where after 3 months, k_{obs} values were substantially lower than for either column C or D. The initial reactivity enhancement observed for column E is consistent with the corrosion-promoting ability of carbonate (12–16). It has been suggested that carbonate forms the aqueous species FeHCO_3^+ and $\text{Fe}(\text{HCO}_3)_2^0$ by complexing the $\text{Fe}(\text{II})$ generated during iron corrosion (50), thereby destabilizing the passive layer and enhancing the corrosion process.

The longer-term declines in reactivity observed for columns C–E can be attributed to the gradual deactivation of the interfacial region. Occlusion of reactive sites by precipitation of siderite (FeCO_3) has previously been hypothesized (14, 16) to reduce reactivity of iron. Our columns did evince a change in color from an initial dark gray/black to a lighter gray. These color changes were not instantaneous but instead progressed slowly from the column inlet toward the distal end and were initially more pronounced in column E. Estimates of precipitate mass (33) and the more rapid changes in the color of column E suggest more extensive precipitation of mineral phases in this column relative to other columns. X-ray diffraction, transmission electron microscopy with selected area electron diffraction (TEM-SAED), and micro-Raman spectroscopic analyses of iron grains extracted from our columns did not, however, reveal the presence of siderite. Instead, magnetite, iron carbonate hydroxide, and carbonate green rust were the predominant mineral phases identified.

Influence of a Hydrochloric Acid Pulse. To evaluate whether dissolution of an iron (hydr)oxide/iron carbonate passive film would restore reactivity, a 5-mL pulse of concentrated hydrochloric acid was applied to column E on day 407. This

pulse resulted in vigorous gas evolution, the release of ~ 1.7 g of soluble iron, and a drop in effluent pH from 9.3 to 4.8 within the first 7 h. This pH drop was short-lived, and the effluent pH rebounded to 9.3 within 32 h. The release of soluble iron is consistent with the acid-catalyzed dissolution of iron (hydr)oxides (51) and iron carbonates (52) and provides evidence that the passive film on the granular iron surface was at least partially dissolved, although we note that acid addition could also have led to enhanced dissolution of the granular iron itself. The value of k_{obs} increased slightly for a short while following acid addition (Figure 2), although the acid pulse did not result in any long-term reactivity enhancement. Presumably the pulse did not dissolve enough of the passive film to be of lasting benefit.

Influence of Chloride. The influence of chloride on TCE degradation was evaluated in two separate experiments. In the first, 10 mM chloride was continually fed to column B, whose reactivity was periodically examined via intermittent TCE-probe experiments. The results indicate that through the third probe test, the presence of chloride enhanced the reactivity of column B (relative to column A) toward TCE (Figure 4). By the fourth probe test (days 789–848, immediately prior to introduction of silica to column B), however, the reactivities of columns A and B were statistically indistinguishable (at the 95% confidence level). These longer-term results suggest that the corrosion-promoting ability of chloride decreased over time, similar to our prior observations with 2-nitrotoluene (26).

In the second experiment, 10 mM NaCl was added to the feed to column D for days 313–409 (Figure 2). Despite the activating effect of chloride on column B, a comparison of the k_{obs} values obtained for columns C and D during this period reveals that chloride addition had little if any effect on the TCE reduction rate.

The apparent disparity between these observations could be due to differences in the interfacial composition of the granular iron surfaces within each column. If high chloride concentrations are present while a passive film is being formed (as was the case with column B), the film may have a composition that differs from that which develops in the presence of the low chloride concentrations ($< 300 \mu\text{M}$) that result from CHC degradation (i.e., for column D). Previous studies have suggested that the passive film formed in chloride-containing bicarbonate solutions more readily undergoes localized attack by chloride than the passive film formed in bicarbonate solution alone (23, 53). The implication of these observations is that chloride may not be a very effective corrosion promoter for passive films formed in the absence of chloride. It is possible, however, that the chloride amendment to column D was of insufficient duration or magnitude to produce any discernible outcome.

Influence of Silica. To examine the effect of silica on granular iron reactivity, 500 μM sodium metasilicate (Na_2SiO_3) was added to the feed to columns F (days 183–300), C (days 409–538), and B (days 925–1100). In all cases, silica was retained by the granular iron, leading to decreasing silica porewater concentrations between the influent and effluent ends of the column (Figure S6 in the Supporting Information) and its slow breakthrough.

Silica addition resulted in a pronounced loss of reactivity toward the NACs (Figure 5) and to a lesser extent toward TCE (Figures 2 and 4). Reactivity losses were most pronounced near the influent end, where silica retention predominately occurred but were nonetheless manifested throughout each column. After silica was omitted from the feed to column F, dissolved silica concentrations measured at the column outlet decreased slowly, and the reactivity toward the NACs recovered partially (Figure 5). Although aging of the iron by the NACs could contribute to the declining k_{obs} values observed for TCE in column F, this is not likely

to be the sole explanation. Even with silica present, the NACs were fully reduced to their respective anilines within the first 8 cm (20% of the length) of the column; any “aging” effect of NACs would therefore be anticipated to be restricted to this region. Diminished reactivity of the iron toward TCE was not restricted to the initial 8 cm but occurred throughout the entire column. This suggests that silica retained within the distal portion of the column, rather than reaction with NACs, was at least partially responsible for deactivation of the iron for TCE. For column C, the discontinuation of the silica feed led to an initial rebound in reactivity toward TCE (Figure 2), although it never recovered to the level displayed by the otherwise identical column D. For column B, the silica feed also led to significant deterioration in reactivity toward TCE (Figure S7 in the Supporting Information).

Based on mass-balance calculations and dissolved silica profiles, we hypothesize that silica precipitates or adsorbs to the interfacial region at sufficiently high concentrations so as to block reactive sites. Silica most likely initially forms monomeric surface complexes ($> \text{FeH}_3\text{SiO}_4$, $> \text{FeH}_2\text{SiO}_4^-$, and $> \text{FeHSiO}_4^{2-}$) (54–57) that polymerize over time (55). Eventually, a silica film or gel is formed on the iron surface that hinders contaminant access to active sites and may alter the electronic environment of reactive sites (58). Additional detailed studies of silica effects on reactivity of granular iron toward organohalides are currently under way in our laboratory.

Influence of NOM. The columns fed NOM were substantially less reactive toward TCE than “NOM-free” columns (Figures 2 and 3). In fact, by day 100 the k_{obs} values in the presence of NOM were roughly half those for comparable columns not fed NOM (columns C, D, and K). Although the performance of all columns deteriorated over time, rate coefficients for TCE reached low levels ($\sim 0.1 \text{ h}^{-1}$) at early times (~ 150 days) in columns fed NOM, whereas they reached that level only after ~ 400 days in columns C, D, and K.

NOM is known to readily sorb to iron (hydr)oxides (59, 60), and many (hydr)oxide phases are typically present on the granular iron surface (61). NOM sorption to iron surfaces is dictated by nonspecific surface interactions, free energy changes associated with NOM solvation, electrostatic interactions between the oxide surface and the NOM molecule, and the specific interactions that occur between functional groups in the NOM molecules and the oxide surface (60, 62–64). Under the alkaline pH range typically observed in PRBs, specific interactions should dominate NOM sorption because both the NOM molecules and the iron hydr(oxides)/carbonates present in the interfacial region are negatively charged. As a result of the stronger NOM–iron interactions, species such as TCE that are expected to form weakly bonded surface complexes (1, 25) may be competitively excluded from the surface. In addition to this predominantly steric effect, adsorption of NOM to the particle surface is expected to alter the reduction potential of neighboring Fe(II) surface sites, making them poorer reductants. Observed declines in the rate of reduction of CCl_4 (25, 32), TCE (32), and nitrobenzenes (65, 66) in the presence of simple organic ligands (e.g., catechol, ascorbate, EDTA, acetate) or NOM isolates that would be expected to form complexes on iron oxides or on granular iron surfaces are consistent with either explanation.

Of the three types of NOM studied in this work, GDS NOM exhibited the least inhibitory effect on TCE degradation. After 100 days, with the exception of two data points, reaction rates determined for this column were consistently higher than those obtained in columns fed with either AHA or SRHA. This may reflect differences in the character of the NOM. Whereas AHA and SRHA are both humic acids, GDS NOM is predominantly composed of fulvic acids (67). It is well established that humic acids sorb to iron (hydr)oxide surfaces

TABLE 2. Organic Carbon Extracted using 5–6 Pore Volumes of pH 12 NaOH

column	description	mass organic carbon recovered (mg) ^a	% of organic carbon added (minus control)
K	2 mM NaHCO ₃	3	n/a
L	2 mM NaHCO ₃ + 20 mg/L AHA	134	3.6
M	2 mM NaHCO ₃ + 2 mg/L AHA	28	6.9
N	2 mM NaHCO ₃ + 2 mg/L SRHA	44	11
O	2 mM NaHCO ₃ + 2 mg/L GDSW NOM	69	18

^a Corrected for extractable background organic carbon present within Master Builders iron (4 mg).

more strongly than fulvic acids (68), and this enhanced sorption may have led to the earlier declines in reactivity observed for AHA and SRHA relative to GDS NOM.

NOM was omitted from the influent to columns L–O after day 240. Nevertheless, reactivity toward TCE did not rebound (Figure 3), suggesting that the inhibitory effect of NOM did not stem from reversible competition between NOM and TCE for reactive sites. Once NOM sorbs to an iron (hydr)-oxide surface, it is known to be very difficult to remove unless the pH is increased (62, 64). In an attempt to restore column reactivity, an alkaline flush of 5–6 pore volumes of a TCE-free pH 12 NaOH solution was introduced on day 345 to columns K–O. This alkaline flush resulted in mobilization of adsorbed organic carbon, and appreciable quantities of dissolved NOM were measured in the column effluent (Table 2). For columns L–O, the mass of organic carbon eluted as a result of the alkaline flush (28–134 mg; Table 2) was substantially larger than that eluted from column K (3 mg). The organic carbon extracted from column K, the nominally “NOM-free” control, apparently results from sorption of trace quantities of NOM present in the influent water. For columns L–O, the recovered masses range from 3.6% to 18% of the total organic carbon fed to each column.

Following the pH 12 flush, it was observed that reactivity rebounded substantially for all columns. Interestingly, column K (the “NOM-free” control) rebounded the most, followed by the columns to which NOM had been added. The reason for the strong rebound of the control column is not apparent at this time.

NAC Reduction. Despite substantial differences in their one-electron reduction potentials (E_h^r ; –0.590 V for 2-NT and –0.360 V for 4-NAP; see ref 69) or half-wave potential ($E_{1/2}$; –0.53 V for 4-NA, see ref 70), k_{obs} values for each of the NACs were virtually indistinguishable. Previous studies (14, 38) observing a similar lack of correlation between E_h^r (or $E_{1/2}$) and the kinetics of NAC reduction by granular iron have suggested that electron transfer is not the rate-determining process. These investigators have hypothesized that other potential rate-controlling steps (e.g., precursor complex formation, successor complex breakdown, mass transport limitations) may govern observed reaction rates. Scherer et al. (71) have recently demonstrated using a rotating disk electrode that nitroaromatic compounds can be subject to mixed mass transfer and surface kinetic control. Such mixed rate control is also possible in our column system.

External (boundary layer) mass transfer coefficients were estimated using established correlations for flow through porous media, as explained in the Supporting Information. In this regard, the first measurable k_{obs} values for the NACs (~20–35 h^{–1}; Figure S2) are within an order of magnitude of calculated k_{max} values for a reaction limited by external mass transfer limitations (120 h^{–1}). Therefore, we cannot rule out the possibility that external mass transfer effects

could influence reaction rates. Observed declines in the NAC reduction rate during the first months of operation and during periods of silica addition (Figures S2 and 5) suggest, however, that reactions were under at least *partial* reaction control, certainly by about day 183. This conclusion is further supported by the fact that decreased porosity and concomitant increases in interstitial water velocity during early operation (33) should have caused k_{max} to increase slightly over this same period. Other types of mass transfer effects, such as diffusion limitations associated with “immobile water” porosity, could also vary over time and thus alter k_{max} . Our prior transport studies and associated calculations with these same columns suggest, however, that such immobile water effects did not cause a dramatic reduction in overall column performance (33). It is therefore likely that the major portion of the observed decline in NAC reduction rates over time is the result of changes in the interfacial reactivity of the iron.

Comparison of the Reactivity of CHCs to NACs. Of the six organic contaminants examined in this study, the three NACs were significantly more reactive than the three CHCs. In the absence of silica, 2-NT, 4-NA, and 4-NAP were completely reduced to the corresponding aniline within the first ~4 cm of the column. In contrast, the reactivity of TCE was approximately 1 order of magnitude lower, while 1,1-DCA and 1,2,3-TCP only degraded partially within the first ~4 cm of the column (Supporting Information Figure S3).

Our results suggest that TCE, 1,2,3-TCP, and the NAC pairs (either 2-NT/4-NA or 2-NT/4-NAP) all react at different sites on the iron surface. This conclusion is supported by several lines of evidence: (1) Silica introduction to columns B, C, and F resulted in substantial losses in reactivity toward both TCE and the NACs. When silica was eliminated from the influent to columns C and F, the reactivity toward the NACs rebounded (Figure 5), whereas that toward TCE remained low (inset Figure 2). A sustained reduction in reactivity toward TCE was also observed in column F, as shown by the TCE-probe test conducted from days 401–446 (i.e., after the period during which silica was fed to the column; Figure 4). (2) Although its reactivity toward TCE had diminished substantially, column E readily degraded the NACs fed to it from day 509–623 (data not shown). In fact, throughout this period, all of the NACs were reduced to their respective anilines by the second port of the column (~2 cm from the inlet). (3) The proximal ends of columns C–E and G–O displayed at least some reactivity toward 1,2,3-TCP, even under conditions for which TCE underwent little to no reduction. Others (72, 73) have previously suggested that nitroaromatic compounds and chlorinated hydrocarbons degrade at different types of sites; our results would appear to corroborate this.

Reactivity Losses at the Proximal End. The TCE and NAC concentration profiles observed in this study exhibited a progressive loss in reactivity over time. This is the anticipated result of a gradual loss of reactive sites within the porous media. Diminished reactivity was particularly pronounced at the influent ends of the columns, to the point that an essentially unreactive zone was evident in some columns. Larger contaminant and cosolute fluxes were encountered near the influent ends, and this may have preferentially deactivated the proximal region, giving rise to a passivation front. It is, however, also possible that this zone only appeared deactivated as an indirect result of mineral precipitation. As the porosity decreases under constant discharge conditions, local flow velocities increase. This effect could be particularly pronounced if minerals predominantly precipitate near the influent end of a column. Although such spatial variations in flow velocity were not specifically examined for the columns in question in the present study, ³H₂O tracer studies for columns G–J indicate that spatial variations in flow

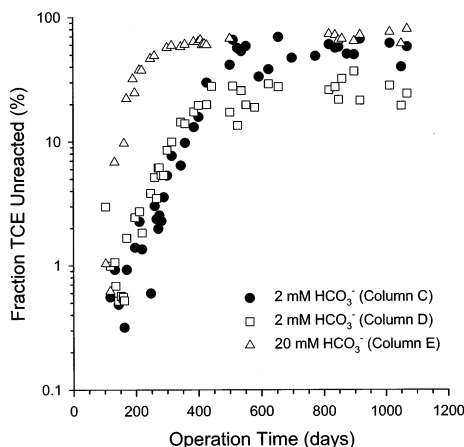


FIGURE 6. Variation in TCE removal over time as a result of surface deactivation and the formation of an apparent unreactive zone near the column inlets. Fraction of TCE unreacted = $(\text{TCE}_{\text{effluent}}/\text{TCE}_{\text{influent}}) \times 100\%$. $\text{TCE}_{\text{effluent}}$ is the TCE concentration measured at the column outlet, $\text{TCE}_{\text{influent}}$ is the estimated influent TCE concentration determined via nonlinear regression of eq 1 and was used in place of the measured influent concentration ($\text{TCE}_{\text{influent}}$) to minimize the effects of sampling errors on the analysis. On day 409 the feed to column C was augmented with $100 \mu\text{M}$ silica, and this resulted in the observed decline in column reactivity relative to column D.

velocity are relatively minor compared to the changes in the reactivity of the iron surface.

Implications for Barrier Design

Our results indicate that the design of a PRB should not only consider the level of treatment needed for organic contaminants and the potential for intraspecies competitive effects (42) but also the influence of cosolutes present in the site groundwater. To adequately account for the diverse array of possible interactions it is critical that bench scale column studies be conducted using site groundwater, with contaminants introduced at concentrations comparable to levels occurring at the site in question. Because the effects of many cosolutes may not manifest themselves immediately, these studies would ideally be of sufficient duration that long-term declines in reactivity are fully evident.

Unfortunately, the length of time required for bench-scale studies to provide reliable long-term results may prove prohibitive. As illustrated in Figure 6, the fraction of TCE that passed unreacted through three of our columns increased dramatically during the early months of column operation, only leveling off after ~300–400 days for columns E and D, respectively, depending on the bicarbonate concentration. (Although it might appear that column C required an even longer period to produce a consistent level of TCE removal, this likely stems from the addition of silica from day 409 to day 538.) At the flow rates employed herein, columns E and D required ~1200 to ~1600 pore volumes to reach quasi-steady-state TCE removal rates, considerably more than the 30–40 pore volumes typically employed in bench scale feasibility testing for TCE treatment (Arun Gavaskar, personal communication).

An alternative to long-term bench-scale testing would be to incorporate a safety factor to account for anticipated declines in reactivity. Such a safety factor must be selected judiciously in order to provide for the requisite longevity and to properly assess the cost-effectiveness of PRBs relative to other treatment or containment techniques. Unfortunately, the dependence of long-term reactivity on feedwater composition makes it impossible to recommend a “generic” safety factor to account for an attenuation of reactivity. Our results indicate that certain solutes, such as silica, NOM, and

relatively high concentrations of bicarbonate, can have a particularly deleterious effect on long-term reactivity. Differences between reactivity in columns continuously exposed to organohalides, and those only intermittently exposed, suggest that contaminant concentration also plays a role in granular iron deactivation and thus should be considered in engineering assessments of an appropriate safety factor. Although high concentrations of chloride initially enhanced reactivity, this effect was relatively short-lived; it might therefore be prudent to apply a somewhat greater safety factor than normal if site groundwater contains appreciable chloride.

Fortunately, although relatively minor variations in k_{obs} can result in large differences in the fraction of a contaminant that passes through a PRB undegraded, the design width of a PRB (and hence, the magnitude of the appropriate safety factor) is less dependent on uncertainties in reaction rate as evident in the following expression (74)

$$W_d = -v \times \text{CF}_D \times \ln \left(\frac{C_{\text{design}}}{C_{\text{influent}}} \right) \times \frac{\text{FS}_w}{k_{\text{obs}}} \quad (3)$$

where W_d is the requisite PRB width, v is the groundwater seepage velocity, CF_D is a correction factor for dispersion, C_{design} is the target effluent concentration of the contaminant requiring treatment, C_{influent} is the influent concentration, and FS_w is a safety factor for barrier width. This expression can be applied if the parent compound, rather than a daughter product, dictates PRB design. A 2-fold decrease in k_{obs} translates quite simply to a doubling of W_d . In this context, it is worth noting that our results with the columns fed 2 mM bicarbonate (C, D, and K) indicate that granular iron reactivity toward TCE decreased approximately 4-fold between day 50 and day 300 of column operation. Similar declines in reactivity have been reported (Arun Gavaskar, personal communication) for other granular iron materials in column tests of somewhat shorter duration (~1500 pore volumes) conducted with site groundwater and either Master Builders iron (4-fold decrease in reaction rate) or Peerless iron (2-fold decrease in reaction rate). Although more work will be required to ascertain the relative importance of iron type versus groundwater composition in dictating longevity, our results suggest that safety factors on the order of 4 may suffice to account for declines in reactivity toward TCE such as those we observed over a 3-year period on exposure of Master Builders iron to bicarbonate (in the absence of NOM or silica). Commensurately larger safety factors may be needed to account for uncertainties in hydraulic parameters (e.g., natural variability in groundwater seepage velocities; alterations in seepage velocity resulting from progressive alterations in PRB permeability; changes in hydraulic residence time distributions resulting from development of zones of “immobile water”). We stress, moreover, that the requisite safety factor may be quite different for contaminants whose mode of attenuation differs substantively from that of TCE. Additional studies examining long-term changes in removal efficiencies would undoubtedly be necessary in such cases.

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Supporting Information Available

Additional figures of the experimental apparatus; figures showing the pseudo-first-order degradation coefficients for the NACs over time; profiles of 1,2,3-TCP at various times; comparisons of the experimental results for columns D (at JHU) and K (at AFRL); illustrations of the initial variation in k_{obs} during a TCE-probe test; changes in silica porewater concentration over time; and effects of silica on the reactivity of column B toward TCE; and a discussion of mass transfer considerations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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