

Effects of Carbonate Species on the Kinetics of Dechlorination of 1,1,1-Trichloroethane by Zero-Valent Iron

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The effect of precipitates on the reactivity of iron metal (Fe^0) with 1,1,1-trichloroethane (TCA) was studied in batch systems designed to model groundwaters that contain dissolved carbonate species (i.e., C(IV)). At representative concentrations for high- C(IV) groundwaters ($\approx 10^{-2}$ M), the pH in batch reactors containing Fe^0 was effectively buffered until most of the aqueous C(IV) precipitated. The precipitate was mainly FeCO_3 (siderite) but may also have included some carbonate green rust. Exposure of the Fe^0 to dissolved C(IV) accelerated reduction of TCA, and the products formed under these conditions consisted mainly of ethane and ethene, with minor amounts of several butenes. The kinetics of TCA reduction were first-order when C(IV) -enhanced corrosion predominated but showed mixed-order kinetics (zero- and first-order) in experiments performed with passivated Fe^0 (i.e., before the onset of pitting corrosion and after repassivation by precipitation of FeCO_3). All these data were described by fitting a Michaelis–Menten-type kinetic model and approximating the first-order rate constant as the ratio of the maximum reaction rate (V_m) and the concentration of TCA at half of the maximum rate ($K_{1/2}$). The decrease in $V_m/K_{1/2}$ with increasing C(IV) exposure time was fit to a heuristic model assuming proportionality between changes in TCA reduction rate and changes in surface coverage with FeCO_3 .

Introduction

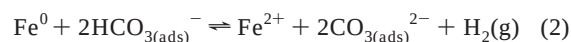
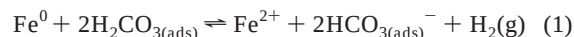
Many studies have reported on the pathways, kinetics, and mechanisms of contaminant degradation by zero-valent iron metal (Fe^0) (e.g., refs 1–5). In addition, a smaller number of studies have focused on incidental processes that indirectly influence contaminant degradation by Fe^0 in groundwater remediation, such as the production of hydrogen gas during anaerobic corrosion (6, 7), possible formation of hydrocar-

bons by the reduction of aqueous C(IV) (8, 9), co-metabolism of partial degradation products (10, 11), and formation of steep chemical gradients in treatment zones containing Fe^0 (12–15). These chemical gradients produce a spatially and temporally variable mixture of precipitates, and it is now widely believed that passivation of the Fe^0 metal surface by these precipitates is one of the most likely limitations to effective long-term performance of permeable reactive barriers (16, 17). Therefore, there is clearly a need for a more in-depth understanding of the relationship between precipitate formation on the Fe^0 surface and contaminant degradation rates under realistic groundwater conditions.

In this study, we focused on the effects of precipitation in systems containing substantial concentrations of dissolved carbonate species (i.e., $\text{CO}_2(\text{aq})$, $\text{H}_2\text{CO}_3(\text{aq})$, HCO_3^- , and CO_3^{2-} ; hereafter referred to simply as C(IV)) because (i) C(IV) -buffered model systems are used for studies of contaminant reduction by Fe^0 (18), (ii) precipitation of FeCO_3 (siderite) has been noted in columns and cores involving treatment zones of granular Fe^0 (13, 19–22), and (iii) moderately high C(IV) concentrations are common in groundwaters where Fe^0 is being considered to remediate contamination. We chose 1,1,1-trichloroethane (TCA) to probe changes in the kinetics and mechanism of contaminant reduction because this alkyl halide complements our previous work using nitrobenzene to probe the effects of carbonate precipitation (18, 23), and the degradation of TCA by Fe^0 has been studied thoroughly in a C(IV) -free batch model system (24). Our results (i) demonstrate that exposure of granular Fe^0 to dissolved C(IV) may stimulate corrosion initially but eventually passivates the surface by precipitation of FeCO_3 , (ii) show that these changes in corrosion regime affect rates of contaminant reduction, and (iii) illustrate the use of “progress curve analysis” to fit contaminant degradation data that exhibit a transition from zero- to first-order kinetics.

Background

Corrosion in the Fe^0 – H_2O – CO_2 System. The effect of aqueous C(IV) on corrosion of Fe^0 has been studied extensively because of the frequent occurrence of slightly acidic, anaerobic, CO_2 -rich deep subsurface formation waters in oil and gas production (25). It is well-established that dissolved C(IV) species can accelerate corrosion of Fe^0 , whereas significant precipitation of FeCO_3 results in passivation. Although the exact mechanism by which C(IV) accelerates corrosion is unclear (26), it is generally accepted that adsorbed H_2CO_3 and HCO_3^- react as oxidants, providing cathodic reactions that help drive metal dissolution (26–28):



In addition, it is known that some ferric oxides, which are abundant in air-formed passive films on Fe^0 , dissolve more readily in the presence of aqueous C(IV) because of the formation of stable aqueous complexes such as FeOHCO_3 and $\text{Fe}(\text{CO}_3)_2^-$ (29).

Figure 1 shows an E_h –pH diagram for the Fe^0 – H_2O – CO_2 system under conditions relevant to groundwater and the experiments performed in this study. Note that FeCO_3 is the thermodynamically stable product of corrosion at pH 6–11 but that $\text{Fe}(\text{OH})_2$ becomes more important at pH > 11. In a traditional equilibrium analysis of corrosion potentials (30), conditions that favor the formation of $\text{FeCO}_3(\text{s})$, $\text{Fe}(\text{OH})_2(\text{s})$,

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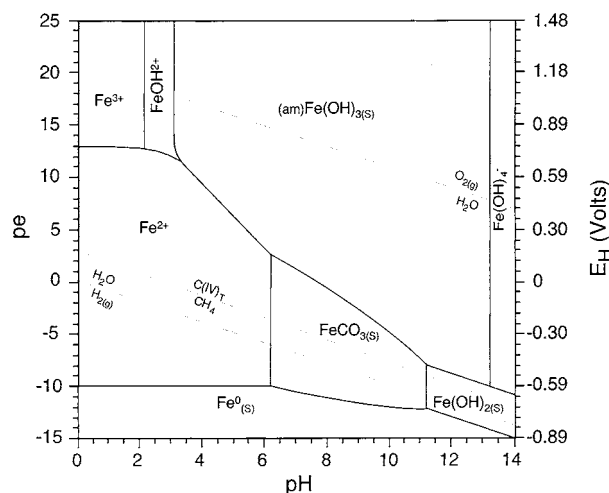


FIGURE 1. E_h -pH diagram for the Fe^0 - H_2O - CO_2 system with 10^{-4} M total dissolved iron and 1.5×10^{-2} M C(IV), neglecting activity corrections (after ref 77). All the E_h -pH lines involving FeCO_3 assume that total C(IV) is constant (i.e., no reduction of C(IV) by the Fe^0). Fe_2O_3 , Fe_3O_4 , and green rusts are not considered in this diagram.

and $\text{Fe}(\text{OH})_3(\text{s})$ should passivate Fe^0 , whereas sustained corrosion is expected only below pH 6 where the oxidation product is aqueous Fe^{2+} . In practice, the situation is complicated by supersaturation with respect to FeCO_3 , which is frequently observed under environmental conditions (31). This phenomenon is a reflection of the slow kinetics of $\text{FeCO}_3(\text{s})$ precipitation (32, 33) and the high stability of various aqueous complexes involving iron and C(IV) (29, 31). Since FeCO_3 is a weaker reductant than Fe^0 (Figure 1), the degree to which FeCO_3 precipitates coat Fe^0 surfaces under environmental conditions will be an important determinant of potential remediation performance.

Figure 1 also shows that it is thermodynamically feasible for Fe^0 to reduce the C(+IV) of carbonate species to the C(-IV) of hydrocarbons. This reaction is well-documented in experiments where large cathodic overpotentials are imposed at metal electrodes (34), and one study has suggested that reduction of C(+IV) to C(-IV) occurs to a measurable degree on Fe^0 surfaces even without an imposed potential (9). However, a follow-up investigation on the latter concluded that the reduction of C(IV) to hydrocarbons by granular Fe^0 is not a significant process (8), so the reduction of C(IV) by Fe^0 apparently is kinetically limited under the conditions relevant to Fe^0 permeable reactive barriers.

Experimental Section

Chemicals and Reagents. All chemical reagents were obtained in high purity and used without further purification. These included 1,1,1-trichloroethane (anhydrous, 99+%, Aldrich), 1,1-dichloroethene (99%, Aldrich), 1,1-dichloroethane (99%, Aldrich), vinyl chloride (0.243%, Air Products), methane (zero grade, Liquid Carbonic), ethane (purity 99.99%, Air Products), ethene (99.99%, Air Products), acetylene (BOC Gases, Murray Hill, NJ), NaHCO_3 (certified ACS, Fisher), CO_2 (99.99%, Liquid Carbonic), and N_2 (Air Products, grade 5). CO_2 and N_2 gases were deoxygenated prior to use by passing through a heated column (275 °C) of reduced copper turnings. Analytical standards of gases were obtained (Scott Specialty Gases, Plumsteadville, PA) in the following certified molar concentrations: propane (1%), propene (1%), 1-butene (1.01%), *cis*-2-butene (1%), *trans*-2-butene (1.01%), and acetylene (1.01%). The iron metal used was Fisher electrolytic powder (Catalog No. I60-3) unsieved and generally not acid-washed (BET surface area, $a_s = 0.61 \text{ m}^2 \text{ g}^{-1}$). For some control experiments, the Fe^0 was acid-washed in 10% HCl for 2–3 min, as in the method described previously (18).

Preparation of Stock Solutions and Standards. Saturated stock solutions of TCA (1309 mg L^{-1} or 9.81 mM at 25 °C; 35) were prepared with deoxygenated, deionized water ($18 \text{ M}\Omega \cdot \text{cm}$ Nanopure, Barnstead). Calibration standards for headspace analysis of TCA, 1,1-dichloroethene, and 1,1-dichloroethane were prepared by adding their respective stock solutions to sealed 160-mL serum bottles (containing 100 mL of DI water and 60 mL of headspace). The absolute accuracy of these standard curves was verified by comparison with certified analytical standards obtained in sealed ampules (ChemService, West Chester, PA). To prepare calibration standards for other gaseous products, volumes of the commercial standards were injected into sealed serum bottles containing 100 mL of DI water and 60 mL of headspace (the same proportion of headspace to solution used in batch reactors for the product appearance studies). The amounts of volatile organic products that were formed in the batch reactors were quantified as total mass per bottle, according to a method previously described (36, 37).

Batch System Design. Experiments to determine the kinetics of TCA degradation were performed in 72-mL glass serum bottles containing 20 g of Fisher iron powder and filled with freshly prepared C(IV) buffer (18). The C(IV) buffer used in TCA degradation studies was prepared by bubbling high-purity, deoxygenated CO_2 through 5 mM NaHCO_3 for roughly 2 h, resulting in a total initial concentration of C(IV) species equal to $3.8 \times 10^{-2} \text{ M}$. Immediately after setup, the pH measured in the bottles was 5.3–5.6. The reactors were then crimp-sealed (without headspace) with Teflon-lined butyl rubber stoppers (Wheaton). The resulting iron surface area concentration in these batch reactors was $169 \text{ m}^2 \text{ L}^{-1}$.

To characterize volatile products of TCA degradation, experiments were performed in similar batch reactors but with headspace. These headspace reactors were prepared in an N_2 -filled glovebox by sealing 160-mL glass serum bottles containing 20 g of Fisher Fe^0 powder in 97 mL of deoxygenated deionized water, leaving 59 mL of headspace. The batch reactors were purged with deoxygenated nitrogen gas for 15 min to remove trace amounts of oxygen. Subsequently, 1 mL of 500 mM NaHCO_3 was added to each bottle, and high-purity, deoxygenated CO_2 was bubbled into the bottle. Thus, immediately after setup of the headspace reactors, the total C(IV) concentration was $3.8 \times 10^{-2} \text{ M}$, and the iron surface area concentration was $126 \text{ m}^2 \text{ L}^{-1}$. The resulting pH values were ~5.5.

Each reactor was equilibrated on an end-over-end rotary shaker (Glas Col) at 40 rpm in the dark at room temperature (23 ± 1 °C). Then, to initiate an experiment, the reactors were injected with an aqueous TCA stock solution (usually, 150–700 μL depending on the desired initial TCA concentration), hand-shaken for 2 min, and placed on the rotator. A rapid mixing rate of 40 rpm was chosen to minimize mass transfer effects (4, 18, 38–41). Aqueous or headspace samples were withdrawn periodically from the reactors and analyzed by gas chromatography (Hewlett-Packard GC 6890 with ECD and FID). Control experiments showed that loss of TCA was negligible in the absence of Fe^0 . Dissolved H_2 was determined from headspace samples using a reduction gas analyzer (model RGA-3, Trace Analytical, Inc., Menlo Park, CA), using a method described previously (42).

Results and Discussion

Solution Chemistry of the Fe^0 - H_2O - CO_2 System. Previously, we have described the development of E_h -pH conditions over time in an Fe^0 - H_2O - CO_2 model system similar to the one used in this study (23). Although the pH remained about 6, the Pt electrode potential decreased rapidly from about 600 mV (vs SHE) to less than 50 mV after 2 h, followed by a gradual decline to around -200 mV after about 6 h. The

decrease in measured potential suggests convergence to the equilibrium potential for the $\text{Fe}^0/\text{Fe}^{2+}$ couple as anaerobic corrosion causes a gradual dissolution of Fe^{2+} (Figure 1). From these results, it is apparent that the solution chemistry of the $\text{Fe}^0\text{--H}_2\text{O--CO}_2$ system can vary considerably over the time period in which typical batch experiments are set up and executed, and this has implications for the interpretation of some of the results presented below.

The formation of molecular hydrogen is a characteristic of anaerobic corrosion, and eqs 1 and 2 suggest that H_2 formation should be enhanced by the presence of aqueous C(IV) species. Enhanced corrosion of granular Fe^0 by aqueous C(IV) has been reported previously in studies performed in batch reactors (6). To verify that this occurred in our model system, we measured the amount of H_2 that accumulated in batch reactors with 0.5 g of Fisher Fe^0 , as a function of time and NaHCO_3 concentration (0, 0.25, 1, and 5 mM). The accumulation of hydrogen generally leveled out after about 300 min, and the rate of accumulation increased markedly with increasing C(IV) concentration (data not shown). These results are consistent with other evidence, presented below, that aqueous C(IV) species accelerate corrosion of Fe^0 initially but passivate Fe^0 after long exposure times because of gradual accumulation of precipitates, mainly FeCO_3 .

It was concluded that precipitates formed gradually over the range of exposure times used in this study because the color of the iron changed from black to gray over the first few hours of exposure to C(IV), and several days of exposure turned the whole bottle cloudy because of suspended light gray to white fine-grained particles. Scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS) was used for a more detailed characterization of the surfaces of Fe^0 grains as a function of exposure time to aqueous solutions of C(IV). We reported previously (23) that precipitation of FeCO_3 completely covered grains of Fluka Fe^0 in less than 1 day, and similar results were obtained with the Fisher Fe^0 used in this study (data not shown). As with the accumulation of iron oxides, extensive accumulation of FeCO_3 on the Fe^0 surface is expected to passivate the metal with respect to further corrosion. However, under a variety of conditions, we also noted that short exposure times (a few hours) of granular Fe^0 to aqueous C(IV) gave features that suggest enhanced pitting or crevice corrosion, with comparatively little precipitation of FeCO_3 . The apparent predominance of C(IV)-enhanced corrosion during the first few hours of exposure is consistent with the well-known strength of H_2CO_3 and HCO_3^- as corrosive species (26–28) and slow kinetics of FeCO_3 precipitation (33).

Qualitative Aspects of TCA Reduction. The products from reduction of TCA by Fe^0 were determined in batch experiments performed after various time periods of exposure to aqueous C(IV). A representative result is shown in Figure 2 for unwashed Fe^0 that was exposed to aqueous C(IV) for 2 h prior to addition of TCA. Ethane is the major product along with lesser but significant amounts of ethene and C4 hydrocarbons (mainly 1-butene and *cis*-1,2-butene). Only very small amounts of C2 chlorinated hydrocarbons were formed (mostly 1,1-dichloroethane). The combination of all the identified products accounted for about 90% of the nominal initial concentration of TCA near the beginning of the experiment and declined to about 70% after 4 h. Qualitatively, the products observed in this study are generally consistent with the scheme for reaction of TCA with Fe^0 that was proposed by Fennelly and Roberts (24). There are, however, some notable differences in the relative amounts of products formed (e.g., we see more ethane than 1,1-dichloroethane, consistent with what Fennelly and Roberts found for Zn^0 but in contrast to what they found for Fe^0). These differences in branching ratios appear to be due, in part, to effects of exposure to aqueous C(IV). However, the

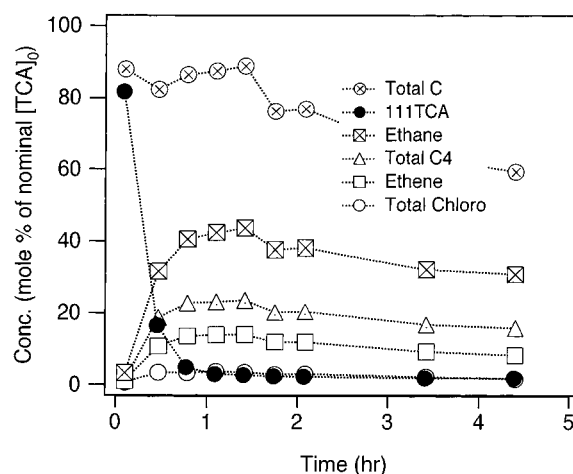


FIGURE 2. Concentration vs time plots showing products of TCA reduction by Fe^0 after 2-h exposure to 3.8×10^{-2} M aqueous C(IV) (initial pH 5.57). The nominal initial concentration of TCA ≈ 0.13 mM, $[\text{Fe}^0] = 126 \text{ m}^2 \text{ L}^{-1}$, mixing by rotation at 40 rpm, and $T = 23 \pm 1^\circ\text{C}$.

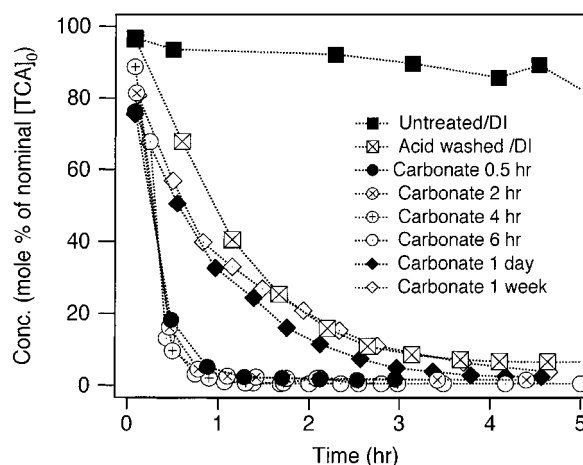


FIGURE 3. Concentration vs time plots showing effects on TCA disappearance of pretreating Fe^0 with acid or 3.8×10^{-2} M aqueous C(IV). The nominal initial concentration of TCA ≈ 0.13 mM, $[\text{Fe}^0] = 126 \text{ m}^2 \text{ L}^{-1}$, mixing by rotation at 40 rpm, and $T = 23 \pm 1^\circ\text{C}$.

effect on product branching ratios was not investigated further in this study.

Our original interest in the effects of aqueous C(IV) on contaminant reduction by Fe^0 arose from unexplained aspects of control experiments that were done in association with an early study on the kinetics of reduction of nitrobenzene (18). The results of an expanded but analogous set of control experiments performed with TCA as the model contaminant are shown in Figure 3. The data for systems based on deionized water (square symbols) show an increase in the rate of reduction when the granular Fe^0 was pretreated by washing in dilute acid, as has been observed in many studies of contaminant reduction in batch model systems. More notably, exposure to aqueous C(IV) caused at least as much increase in the TCA reduction rate as acid washing. Of particular interest is the fact that brief exposures to aqueous C(IV) had the largest effect on TCA reduction rates and that extended periods of exposure to aqueous C(IV) resulted in smaller rate enhancements. To investigate these effects further, we set out to quantify the kinetics of TCA reaction by Fe^0 as a function of time that the Fe^0 was exposed to aqueous C(IV).

Quantitative Kinetics of TCA Reduction. Most of the kinetic data for disappearance of TCA that were obtained in

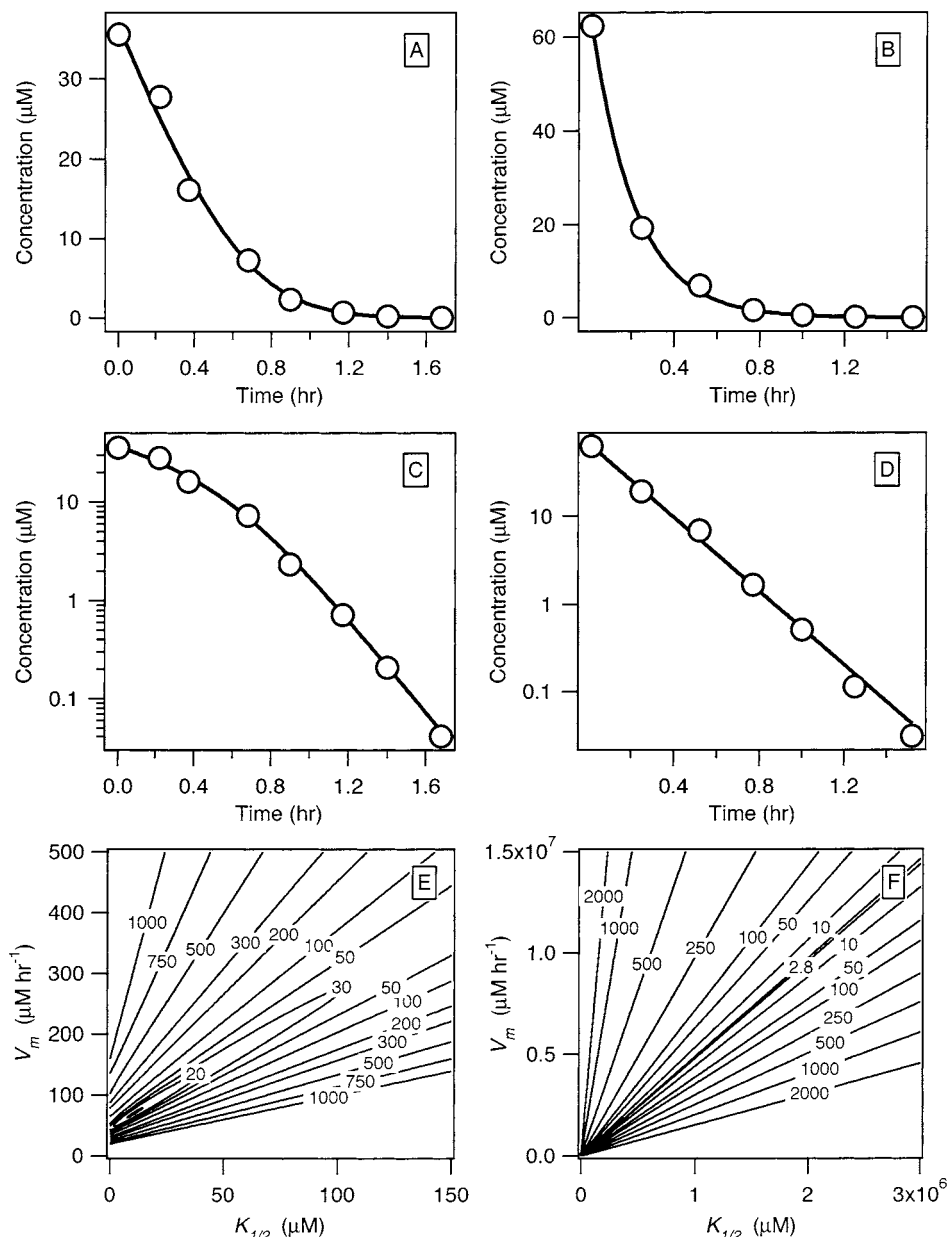


FIGURE 4. Kinetics of TCA reduction in batch model systems containing 169 g L⁻¹ Fisher Fe⁰ in 3.8×10^{-2} M aqueous C(IV): (panels A, C, and E) 1.1-h exposure to buffer at initial pH 5.36; (panels B, D, and F) 4.03-h exposure to aqueous C(IV) at initial pH 5.54. Curves in panels A–D and parameters used to make panels E and F are from fits of the data to eq 4. The contours in panels E and F show the shape of the χ^2 surface that results from the fitting calculation.

this study did not obey a simple first-order rate law. Instead, log concentration vs time plots usually showed curvature that suggest a transition from zero- to first-order kinetics (e.g., Figure 4C), and the corresponding linear concentration vs time plots (e.g., Figure 4A) have the shape often referred to in the enzyme kinetics literature as a “progress curve” (43). Such data can be fit directly to the integrated form of the Michaelis–Menten equation, and this method has certain advantages over the traditional method of obtaining Michaelis–Menten parameters from initial rates of multiple experiments done at different substrate concentrations (44, 45). Although progress curve analysis has sometimes been used to describe biodegradation kinetics (46–49), it apparently is not as well-known in environmental chemistry or engineering, where the approach could be used to analyze the kinetics of surface reactions. For example, Wüst et al. (50) recently reported data for the reduction of TCE by Fe⁰ that gave well-defined progress curves, but they developed their own mixed-order kinetic model to describe the transition from zero- to

first-order kinetics. Many other studies have recognized that initial rates of contaminant reduction by Fe⁰ are dependent on contaminant concentration in a way that is indicative of site saturation kinetics (e.g., refs 1, 4, 51, and 52), but no study prior to Wüst et al. appears to have observed the transition from zero- to first-order kinetics in the data from individual experiments.

For the purposes of this study, we will continue to express our kinetic model for site saturation-limited kinetics in terms that are commonly used for enzyme catalyzed reactions, as we have in several previous publications (4, 51, 53). This model has usually been written as

$$-\frac{dC}{dt} = \frac{V_m C}{K_{1/2} + C} \quad (3)$$

where V_m is the maximum reaction rate and $K_{1/2}$ is the concentration of contaminant (C) where $-dC/dt = V_m/2$.

TABLE 1. Summary of Kinetic Data for TCA Reduction by Fe⁰ ^a

exposure time (h)	initial pH	fitted C ₀ (μM)	K _{1/2} (μM)	V _m (μM h ⁻¹)	V _m /K _{1/2} (h ⁻¹)
1.1	5.36	37 ± 1	15 ± 6	80 ± 15	5 ± 1
1.2	5.36	41 ± 1	15 ± 6	105 ± 19	7 ± 2
2.0	5.57	82 ± 13	(3 ± 35) × 10 ³	(1 ± 17) × 10 ⁴	4.9 ± 0.8
2.05	5.57	48 ± 1	(3 ± 35) × 10 ³	(1 ± 13) × 10 ⁴	3.6 ± 0.5
4.03	5.54	67 ± 1	(9 ± 44) × 10 ³	(5 ± 22) × 10 ⁴	4.9 ± 0.3
4.03	5.54	48 ± 1	(9 ± 44) × 10 ³	(3 ± 16) × 10 ⁴	3.6 ± 0.2
24.1	5.5	38 ± 1	51 ± 11	195 ± 34	4 ± 3
24.05	5.5	27 ± 1	51 ± 11	180 ± 33	3.5 ± 0.3
48.05	5.54	47.6 ± 0.9	51 ± 11	156 ± 24	3.1 ± 0.2
48.07	5.54	50.8 ± 0.9	51 ± 11	171 ± 26	3.3 ± 0.3
95.75	5.5	45 ± 1	51 ± 11	186 ± 30	3.6 ± 0.3
95.75	5.5	48.0 ± 0.9	51 ± 11	162 ± 25	3.2 ± 0.3

^a Standard conditions: total aqueous C(IV) species = 3.8 × 10⁻² M, Fisher electrolytic Fe⁰ (without pretreatment) = 169 m² L⁻¹, mixing by rotation = 40 rpm, and T = 23 ± 1 °C.

Note that V_m is equivalent to the rate constant for the zero-order portion of the progress curve and that V_m/K_{1/2} approximates the rate constant for the first-order portion (represented by k₀ and k₁, respectively, in ref 50). This formulation is simpler than but formally consistent with the more mechanistically explicit models used in some other recent studies (1, 52, 54–56).

Direct integration of eq 3 gives an implicit solution (eq 4) that cannot be solved for C as a simple function of t:

$$K_{1/2} \ln C + C = -V_m t + K_{1/2} \ln C_0 + C_0 \quad (4)$$

Fitting eq 4 to experimental data presents a variety of challenges, many of which have been discussed extensively (e.g., refs 57 and 58). We used the bisection method (59) to solve eq 4 for C as a function of V_m, K_{1/2}, C₀, and t, and the result was fit to experimental data by χ² minimization. The calculations were performed without weighting for uncertainties in the concentration data, so the resulting uncertainties in the fitting coefficients are only adequate for relative comparisons among the results and not for calculating confidence intervals.

We tried fitting each experiment independently (local fitting) and fitting experiments in each of three corrosion regimes (described in the next section) with a common value of K_{1/2} (global fitting). Only the results from the latter were used because the two methods gave similar results and the global method takes advantage of the prior information that K_{1/2} is relatively constant for a particular contaminant reacting on different types of iron with similar surface conditions (51, 55). The parameter estimates obtained for each experiment are given in Table 1.

Figure 4 illustrates how well the model fit the data for two representative cases: an experiment where both zero- and first-order behavior were observed (Figure 4A, C, and E) and an experiment where the data exhibit only first-order behavior (Figure 4 B, D, and F). Although the disappearance plots suggest good fits in both cases, the χ² contours (Figure 4E,F) reveal that the first-order only data give a long, narrow trough in V_m vs K_{1/2} space rather than a well-defined minimum. Therefore, the first-order only data can be used to obtain a reliable estimate of V_m/K_{1/2} (the slope of the line defined by the bottom of the χ² trough in Figure 4F), but they are not sufficient to define independent values of V_m and K_{1/2}. This problem has frequently been encountered in the analysis of progress curves for enzyme kinetics (60) and has been highlighted in recent studies of biodegradation (47, 61) and growth (62) kinetics. It has also been discussed in the broader context of limits to parameter identifiability in studies of microbial growth and substrate utilization kinetics (63).

Since V_m/K_{1/2} is well-defined for all the experiments performed in this study and V_m/K_{1/2} has essentially the same meaning as a first-order rate constant (64), it is an attractive parameter for comparing kinetic data that exhibit variable amounts of zero- and first-order behavior. For this purpose, it is also desirable to estimate uncertainties in this composite parameter from calculations performed to fit V_m and K_{1/2} as independent parameters. The variance in V_m/K_{1/2} can be represented by

$$\sigma_{V/K}^2 \approx \sigma_{V,V}^2 \left(\frac{\partial V/K}{\partial V} \right)^2 + \sigma_{K,K}^2 \left(\frac{\partial V/K}{\partial K} \right)^2 + 2\sigma_{V,K}^2 \left(\frac{\partial V/K}{\partial V} \right) \left(\frac{\partial V/K}{\partial K} \right) \quad (5)$$

where we have neglected terms with derivatives of degree larger than one and dropped the subscripts of V_m and K_{1/2} for convenience. Evaluation of the derivatives in eq 5 gives

$$\sigma_{V/K}^2 \approx \frac{\sigma_{V,V}^2 + \sigma_{K,K}^2 (V/K)^2 - 2\sigma_{V,K}^2 (V/K)}{K^2} \quad (6)$$

which can be evaluated with results found in the covariance matrix for each fit. Recall that the calculations were performed without weighting for uncertainties in the concentration data, so the resulting uncertainties in the fitting coefficients are only adequate for relative comparisons among the results and not for calculating confidence intervals. The results of these calculations are included in Table 1.

Effect of Carbonate Exposure on TCA Reduction Kinetics. Figure 5 shows the effect of exposure time to aqueous C(IV) on the kinetics of TCA reduction. The trends in V_m and K_{1/2} (Figure 5A,B) suggest an increase followed by a decrease resulting in maximum values around 4 h. A similar profile was obtained when initial rates (calculated by linear regression on concentration vs time data for the first few minutes) were plotted against C(IV) exposure time (not shown). In addition, a qualitatively similar effect of C(IV) exposure has recently been reported for reaction of TCE in columns containing Fe⁰ (21). In light of the SEM results discussed above, we hypothesized that these apparent maxima were due to the opposing effects of rapidly induced C(IV)-enhanced corrosion and slow passivation because of precipitation of FeCO₃. The combination of these processes might produce three corrosion regimes: (i) initially inhibited by a passive film of iron oxide, (ii) transiently activated by attack of C(IV) on the passive film, and (iii) ultimately limited by formation of a passive film composed predominantly of FeCO₃. These three regimes might give different kinetics and mechanisms of contaminant degradation.

However, the apparent maxima in V_m and K_{1/2} arise from the only experiments that did not show enough zero-order

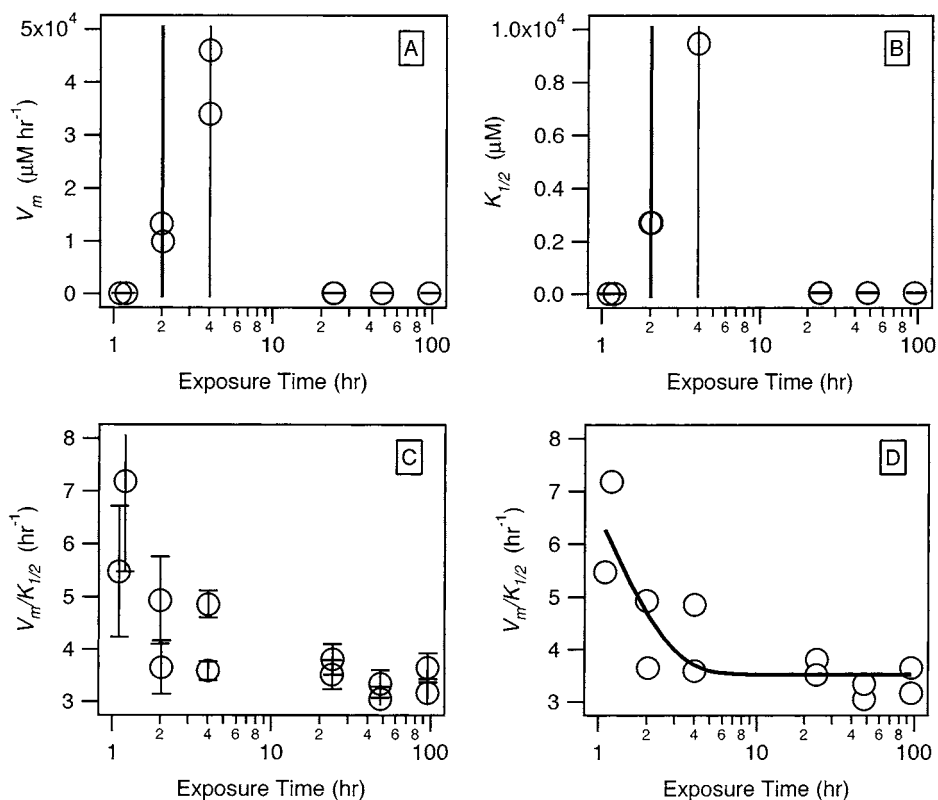


FIGURE 5. Effect of exposure time to 3.8×10^{-2} M aqueous C(IV) on the kinetics of TCA reduction. The curve in panel D is from the fit of data in panel C to the model based on eqs 7 and 8. All time axes have been log-transformed to resolve the effects of short exposures. Error bars in panels A–C are ± 1 SD. Note that some error bars are smaller than the symbols and that a few are off scale.

behavior to give reliable estimates of both parameters (exemplified by Figure 4B–D). These data do define the first-order portion of the progress curve (Figure 4D), so the ratio $V_m/K_{1/2}$ may be well-constrained, as discussed in the previous section. Figure 5C shows that the calculated uncertainties in $V_m/K_{1/2}$ are modest relative to the effect of C(IV) exposure time, so the overall effect is well-defined and appears to be a gradual decline to a limiting value. The apparent inconsistency between the shapes of Figure 5C and Figure 5A,B could be explained if, for example, the peaks in V_m and $K_{1/2}$ are due to conditions where surface sites become more reactive but less abundant (e.g., during pitting corrosion). Even though the peaks in Figures 5A,B reflect transient phenomena that should not effect steady-state systems, they occur in a time period that could influence the results of many laboratory studies done with batch model systems and, therefore, deserve further study.

The profile for $V_m/K_{1/2}$ shown in Figure 5C most likely results from gradual passivation of the Fe^0 as FeCO_3 accumulates on the surface. To explore this hypothesis, it is helpful to consider the following simple, heuristic model. Assuming that the decrease in $V_m/K_{1/2}$ is proportional to the increase in surface coverage by FeCO_3 (x), we can write

$$V_m/K_{1/2} = (V_m/K_{1/2})_0 - \beta x \quad (7)$$

where the subscript 0 indicates the initial condition before exposure to aqueous C(IV) and β is a proportionality constant. Furthermore, if the rate of change in surface coverage with respect to C(IV) exposure time (dx/dt) is determined by a constant driving force for precipitation (A) and a declining supply of dissolved iron due to inhibition of corrosion by accumulation of FeCO_3 (Bx), then we can write the rate law as follows:

$$dx/dt = A - Bx \quad (8)$$

Solving the linear system represented by eqs 7 and 8 yields an expression for $V_m/K_{1/2}$ that decays exponentially (to a nonzero limit) with C(IV) exposure time. Fitting this expression to the data shown in Figure 5C gives the result shown in Figure 5D. It is interesting that the fitted model reinforces the impression that $V_m/K_{1/2}$ reaches a steady value, presumably when the iron surface is fully covered with precipitates, and does not decline further with additional accumulation of precipitate. Possible explanations for sustained reactivity after extensive accumulation of authigenic precipitates are discussed below.

Generalizations on How Precipitates Affect Reductions by Fe^0 . Since contaminant reduction by zero-valent metals occurs predominantly at the metal–water interface, it is not surprising that this reaction is strongly influenced by the formation of precipitates on the metal surface. Even in simple Fe^0 – H_2O systems, the thin film of (oxy)hydroxides that develops on bare Fe^0 soon evolves into a complex layered structure as the result of recrystallization, oxidation, and further precipitation (65). The presence of aqueous C(IV) alters the surface layer through the (co)precipitation of FeCO_3 (66), but a thin film of freshly precipitated FeCO_3 is readily oxidized by O_2 to Fe_2O_3 (67). Therefore, the surface film will contain a population of Fe^{2+} sites only as long as reduction by the underlying Fe^0 is competitive with oxidation to Fe^{3+} (because of reaction with dissolved O_2 or other oxidants) (68). These “structural” Fe^{2+} sites, or Fe^{2+} adsorbed onto the solid phase from solution, might serve as reductants (55) and thereby contribute to the sustained reduction of TCA even in the presence of large amounts of FeCO_3 .

However, since the Fe^{2+} sites associated with FeCO_3 probably are not as readily renewed (by the underlying Fe^0) as those associated with iron oxides (55), passive films dominated by FeCO_3 will be more strongly passivating. This means that transport of TCA through the FeCO_3 layer via pits, pores, crevices, and other defects might be necessary

for the sustained dechlorination of TCA we obtained with Fe^0 that had been exposed to aqueous C(IV) for extended periods. Alternatively, or in addition, the sustained reduction of TCA could be due to small amounts of potentially reactive, mixed valent phases such as green rust, which is likely to coprecipitate with FeCO_3 in the passive film (69–74). All of these scenarios are possible in permeable reactive barriers under field conditions because FeCO_3 apparently accumulates preferentially where groundwater first contacts the Fe^0 , green rust forms in the Fe^0 -bearing zone (12, 75), and iron oxides make up most of the precipitates found downgradient (13, 19, 76).

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