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Reductive Dechlorination of Tetrachloroethylene in Soils by Fe(II)-Based Degradative Solidification/Stabilization

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Fe(II)-based degradative solidification/stabilization (DS/S) is a modification of conventional solidification/stabilization (S/S) that uses Fe(II) as a reducing agent for chlorinated organics while immobilizing inorganic contaminants. Feasibility of the Fe(II)-based DS/S technology in treating soils contaminated with tetrachloroethylene (PCE) was tested in this study. The results of the PCE degradation experiments conducted in the presence of a humic acid suggest that natural organic matter would not significantly interfere with the degradative reaction by the Fe(II)-containing reactive species in DS/S systems. Solid-phase degradation experiments showed that the DS/S technology could effectively treat PCE in soils without substantial production of chlorinated intermediates. A pseudo-first-order rate law reasonably described degradation kinetics. The half-lives of PCE ranged from 13 to 335 days, which are within time spans allowable for typical in-situ DS/S application. Trichloroethylene (TCE) was the only chlorinated product observed in the solid-phase experiments, and its presence was generally transitory with the amount being less than 7% of the initial amount of PCE on a molar basis. A surface reaction appears to control observed PCE degradation kinetics rather than mass transfer to the reactive surface.

Introduction

Degradative solidification/stabilization (DS/S) is a novel remediation technology that strikes a balance between the low cost of containment alternatives and the environmental attractiveness of destruction alternatives. DS/S is a modification of conventional solidification/stabilization (S/S) (*1, 2*) that combines degradative processes for organic contaminants with immobilization processes for organic and inorganic contaminants. Immobilization of inorganic contaminants can be achieved at high pH by using conventional binders such as Portland cement (cement hereafter), lime, fly ash, or other pozzolanic materials. Immobilization of organic contaminants can be accomplished by physical methods such as permeability reduction. Degradative reactions are promoted by adding degradative reagents to mixtures of reagents used in conventional S/S systems. DS/S could be applied ex-situ to contaminated wastes, soils, and sludges. It could also be applied in-situ, particularly at source areas contaminated by nonaqueous phase liquids (NAPL). In this application, containment would be promoted by the reduction of permeability brought about by the process. Groundwater would not pass through the treated zone while degradation occurs.

A recent study conducted by the authors (*3*) found that Fe(II) could be used as an electron donor to reductively dechlorinate chlorinated organics in slurries containing reagents used in DS/S systems. The study demonstrated that Fe(II) can completely dechlorinate tetrachloroethylene (PCE) in 10% cement slurries to produce only nonchlorinated products. Some component(s) of cement appear to combine with Fe(II) to form a reactive species responsible for dechlorination, because the presence of cement is essential for producing highly reactive systems. A potential reactive species in the Fe(II)-based DS/S system is chloride-containing green rust ($Fe^{II}_3Fe^{III}(OH)_8Cl$, GR1($Cl^-$)) (*4*) or an Fe(II)−Fe(III) (hydr)oxide similar to GR1(Cl^-). Results from the slurry experiments support development of Fe(II)-based DS/S technology for treatment of contaminated soils.

Cement has been employed as a main binder in commercial soil S/S processes (*5*). Cement mainly consists of ∼50% of tricalcium silicate ($(CaO)_3SiO_2$), ∼25% of dicalcium silicate ($(CaO)_2SiO_2$), ∼10% of tricalcium aluminate ($(CaO)_3Al_2O_3$), and ∼10% of tetracalcium aluminoferrite ($(CaO)_4Al_2O_3Fe_2O_3$) (*6*). In-situ S/S is appropriate for volatile chlorinated organics such as PCE because it can minimize disturbances to the site, so that volatilization of the contaminants can be minimized. Natural organic matter (NOM) in soils is important because it can accelerate rates of reductive reactions by acting as an electron mediator (*7, 8*). NOM can, however, interfere with cement hydration reactions by consuming hydroxide ions and by coating calcium silicate hydrate ($CaO-SiO_2-H_2O$) (*6*), which is a primary hydration product of cement.

The objective of this research was to test the feasibility of the Fe(II)-based DS/S technology in treating soils contaminated with chlorinated organics. PCE was used as a model chlorinated organic compound, as was done in the previous study. First, the effect of NOM on reduction reactions of PCE was investigated by using cement slurry reactors. A humic acid was used as a surrogate for NOM. This task tests the hypothesis that NOM can affect degradative reactions in DS/S systems by promoting electron transfer by acting as an electron-transfer mediator or by inhibiting degradative reactions by hindering formation of active reductants. Second, the sorption of PCE by a soil was characterized. It is important to investigate the extent of sorption of target organics by soils in DS/S systems because the partitioning of substrates into the solid phase retards degradation kinetics in the aqueous phase. Sorption of PCE by the cement was found negligible (*3*). Finally, PCE degradation experiments were performed with the soil using a solid-phase reactor system. This system was constructed so that the contaminated soil was solidified, which provides conditions that are more like those in a full-scale DS/S application than those in a slurry reactor.

Materials and Methods

Materials. The chemicals (chlorinated ethylenes, solvents, ferrous chloride, cement) used for this study are the same as those described previously (*3*). PCE was the primary target organic in this study, and its characteristics are shown in Table 1. The soil used for degradation experiments was collected from the first ∼20 cm to ∼40 cm of the surface at a site in College Station, TX. The soil was classified as Silawa loamy sand (*12*). Before being used for the experiments, the soil samples were air-dried, screened to particle sizes below 0.425 mm (no. 40 mesh), and analyzed for physical and

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TABLE 1. Chemical Characteristics of PCE

CAS registry no.	MW	dimensionless Henry's law constant[a]	log K_{ow}[b]	aqueous solubility[c] (mg/L)
127-18-4	165.83	0.525	2.60	149

[a] Reference *9*. [b] Reference *10*. [c] Reference *11*.

TABLE 2. Physical and Chemical Characteristics of the Silawa Soil

specific surface area[a] (m^2/g)	organic C[b] (%)	Fe(II)[c] mg/g)	Fe(III)[c] (mg/g)	pH[d]
13.0	0.69	0.498	5.757	6.1

[a] Determined by EGME (ethylene glycol monoethyl ether) method (*13*). [b] Determined by dry combustion method (*14*). [c] Determined by 1,10-phenanthroline method (*15, 16*) after acid extraction. [d] The soil was equilibrated with water with a soil:water ratio of 1:1 (*14*).

chemical characteristics, which are presented in Table 2. The sand, silt, and clay fractions of the soil were 81.1%, 12.2%, and 6.7%, respectively.

Aqueous stock solutions of Fe(II), ($FeCl_2$), and humic acid (sodium salt, Aldrich) were prepared using the deoxygenated deionized water in an anaerobic chamber containing 95% N_2/5% H_2 (Coy Laboratory Products). The deoxygenated deionized water (water hereafter) was prepared by sparging deionized water with the chamber atmosphere for at least 12 h. The stock solution of the humic acid was prepared by adding 60 g of the humic acid in 1 L of the water, which yielded a TOC concentration of 23 500 mg /L. Aldrich humic acid is reported to contain 7.5% of ash (*17*). Stock solutions of PCE were prepared in methanol daily.

Slurry Degradation Experiments with Humic Acid. Clear borosilicate glass vials (24.2 ± 0.10 mL) with the triple-seals (*3*) were used as batch slurry reactors. Samples were prepared in the anaerobic chamber as described below. Triplicate samples were prepared for reactive experiments and duplicates for controls. Controls contained PCE and water. The mass ratio of cement:solution was 0.1. Slurry samples were prepared by filling the vials with appropriate aliquots of the water and stock solutions of humic acid and/or Fe(II). The dose of Fe(II) was 39.2 mM and that of humic acid 500 mg TOC/L. Headspace volumes of the vials were minimized (0.3−0.6 mL), which would allow less than 1.6% of PCE partitioning into the gas phase assuming no sorption and a dimensionless Henry's law constant of 0.525 (*9*) which is appropriate for the temperature (19.3 ± 0.7 °C) at which experiments were conducted. pH values of slurries were maintained at 12.6 ± 0.05. To control the pH of slurries without cement, an aliquot of deoxygenated 5.3 N KOH solution was added to the slurries when they were prepared. Reactions were initiated by rapidly introducing 10 μL PCE stock solution into the slurries, and the vials were capped immediately. The initial concentration of PCE was 40.6 mg/L. The vials were then mounted on a tumbler that provided end-over-end rotation at 7 rpm. To rule out photochemical effects, the vial containers were covered with aluminum foil.

Duplicate or triplicate samples were sacrificed at every sampling time for the analysis of PCE and its daughter products. The vials were retrieved from the tumbler and were centrifuged at 582 g for 2 min. Then ~5 mL of aqueous samples were withdrawn from the vials and were then extracted with 5 mL of a pentane extractant containing toluene as an internal standard in 20-mL glass vials.

PCE Sorption Experiments. For sorption experiments, the same reactor system used for the slurry degradation experiments was used, and the sample preparation procedures were also similar to those of the slurry experiments. Samples were prepared in triplicate in the anaerobic chamber. To remove oxygen sorbed on the soil surfaces, the vials containing the soil were incubated in the chamber for 2 days. The mass ratio of soil:solution was 1.29. An aliquot of 0.5 N KOH solution was added to slurries to maintain pH of the samples at 12.1, which was selected as a target pH in the solid-phase experiments because PCE degradation reactions were optimal at pH near 12.1 in the previous study (*3*). The headspace volume of the reactor was approximately 0.78 mL, which would render the partitioning of ~2.7% of PCE into the gas phase assuming no sorption. In the sorption kinetic experiment, the initial aqueous phase concentration of PCE was 60 mg/L. In the isotherm experiment, samples with seven different initial PCE concentrations (6.25, 12.5, 25, 52.5, 105, 168, 210 mg/L) were prepared. The equilibration time for the isotherm experiments was 7 days, which was based on results of a kinetic experiment that showed little change in PCE concentration after 1 day and as long as 12 days. This is consistent with reports that sorption of PCE and TCE to aquifer sandstones was completed within 1 day (*18*). After PCE spiking, the vials were placed on the tumbler described above. At each sampling time, the vials were centrifuged at 873 g for 30 min, and an aliquot of the aqueous phase was extracted for PCE as described previously.

Solid-Phase Degradation Experiments. Solid-phase samples were also prepared in the anaerobic chamber by using the same glass vials used for the slurry experiments. All reactive samples were prepared in triplicate and controls in duplicate. The vials containing solids (cement, soil) and two stainless steel balls of 79 mm diameter were incubated in the chamber for 2 days and were then filled with appropriate amounts of the water, Fe(II) stock solution, and the 5.3 N KOH or 5 N HCl solution, if needed. The mass ratio of soil:cement:solution was 62.5:7.5:30, which produced a moderately soft solid that was needed to facilitate crushing, and extraction of the target compounds. The acid or base solution was added to maintain pH of the porewater of solid-phase samples near 12.1. The solid mixtures were then blended with a stainless steel spatula. Reactions were started by spiking 10 μL of methanolic stock solutions of PCE into solid mixtures to yield a PCE concentration of 100 mg/kg soil. After PCE spiking, samples were placed on the tumbler for 2 days. The stainless steel balls in the vials facilitated initial homogenization of the samples when the vials were rotated by the tumbler. The samples were then taken from the tumbler and were cured at the room temperature (19.3 ± 0.7 °C).

At each sampling time, samples were extracted for PCE and its degradation products in 250-mL high density polyethylene bottles with fluorinated surface (Nalgene). While extracted, the sample vials were firmly held onto the bottom of the bottles by using a cement base. To extract the target organics, the closures of the vials were removed rapidly, and the solid-phase samples were crushed with a hammer drill under layers of water (100 mL) and pentane (40 mL). The time required to crush the samples did not exceed 1 min. The bottles were then capped and shaken for 6 h at 250 rpm. Then pentane layers were analyzed for PCE and its degradation products. pH of the porewater of the solid-phase samples was measured when the samples underwent approximately 25, 50, and 75% of PCE degradation reactions. A porewater expression device (*19*) was used to extract the porewater from the samples.

Analytical Methods. PCE and its chlorinated degradation products, TCE, 1,1-DCE (dichloroethylene), c-DCE, t-DCE, vinyl chloride, dichloroacetylene, and chloroacetylene were analyzed by a Hewlett-Packard G1800A GCD. The analytical methods were identical to those described in the previous paper (*3*). Concentration of the humic acid was determined by a total organic carbon (TOC) analyzer equipped with an autosampler (low-temperature combustion type, Shimadzu Model 5050).

Evaluation of Data. The sorbed-phase concentration of PCE on soil (q) was calculated using eq 1, which accounts for the partitioning of PCE into the gas phase (headspace) and the reactor surfaces

$$q = \frac{M_{pce} - C_{eq}(V_l + HV_g + K_s V_l)}{M_{soil}} \tag{1}$$

where q denotes the sorbed-phase concentration of PCE on the soil (mg/kg), M_{pce} is the mass of PCE spiked (mg), C_{eq} is the equilibrium PCE concentration in the solution (mg/L), H is the dimensionless Henry's law constant for PCE (0.525), K_s is the solid-phase partition coefficient (ratio of mass of PCE in the solid phase to mass of PCE in the aqueous phase; 0.12 (*3*)), V_g is the headspace volume (L), V_l is the aqueous phase volume (L), and M_{soil} is the soil dose (kg).

A pseudo-first-order rate law was used to describe kinetics of PCE degradation. The following equation describes changes of PCE concentration in the aqueous phase while considering partitioning of PCE into the gas and solid phases (*3*)

$$\frac{dC_l}{dt} = -\frac{k}{\left(1 + H\frac{V_g}{V_l} + K_s\right)} C_l = -\frac{k}{P} C_l = -k_{app} C_l \tag{2}$$

where C_l denotes the PCE concentration in the aqueous phase, k is the corrected pseudo-first-order rate constant, H is the dimensionless Henry's law constant for PCE (0.525), V_g and V_l are the volumes of the gas and aqueous phases, K_s is the solid-phase partition coefficient of PCE, P is the partitioning factor $= 1 + HV_g/V_l + K_s$, and k_{app} is the apparent pseudo-first-order rate constant. Corrected pseudo-first-order rate constants (k) can be obtained by multiplying the partitioning factor (P) times the apparent pseudo-first-order rate constants (k_{app}). Values of k_{app} were obtained by conducting nonlinear regression of aqueous phase PCE concentrations in the slurry experiments or PCE recoveries in the solid-phase experiments. The nonlinear regression was performed using the SAS System for Windows (Release 6.12, SAS Institute Inc.).

In the case of the solid-phase experiments, PCE recoveries in the controls that contained the water, soil, and PCE decreased substantially over time. To obtain pseudo-first-order rate constants that were exclusively due to Fe(II) treatment of the solid-phase systems, the pseudo-first-order rate constant for the PCE decay in the control was subtracted from the rate constants for the reactive experiments as follows

$$k_{app,corr} = k_{app} - k_{app,con} \tag{3}$$

where $k_{app,corr}$ represents the apparent pseudo-first-order rate constant corrected for the PCE decay in the control, k_{app} is the apparent pseudo-first-order rate constant for the reactive experiments, and $k_{app,con}$ is the apparent pseudo-first-order rate constant for the control. Therefore, the corrected pseudo-first-order rate constant for the solid-phase experiments (k_{so}) can be expressed as the following:

$$k_{so} = Pk_{app,corr} = \left(1 + H\frac{V_g}{V_l} + K_s\right)k_{app,corr} \tag{4}$$

When obtaining values for k_{so}, the term, HV_g/V_l, in eq 4 was neglected because the gas-phase partitioning of PCE was found minimal in the solid-phase experiments.

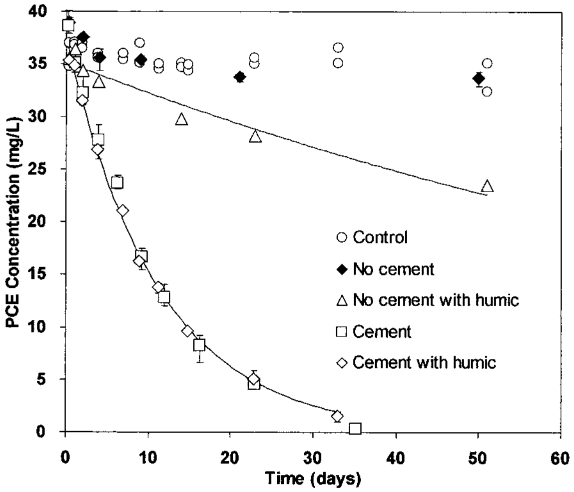

FIGURE 1. Effect of humic acid on PCE degradation by Fe(II) in cement slurries ([PCE]$_0$ = 40.6 mg/L; [Fe(II)]$_0$ = 39.2 mM). Error bars are ranges of measured PCE concentrations. Some error bars are smaller than the symbols. Lines indicate pseudo-first-order fits.

TABLE 3. Pseudo-First-Order Rate Constants for PCE in the Slurry Experiments (Fe(II) Dose = 39.2 mM)

experiment	k^a (day^{-1})	n^b
no cement^c	0.0027 (±51%)	18
10% cement^c	0.10 (±8.3%)	26
500 mg TOC/L humic acid with no cement	0.0098 (±13%)	27
500 mg TOC/L humic acid with 10% cement	0.10 (±3.2%)	30

[a] Uncertainties represent 95% confidence limits expressed in percent relative to estimates for *k*. ±((asymptotic standard error) × *t*(*n* − 2, 0.025)/estimate for *k*) × 100), where *t*(*n*−2, 0.025) is the student's *t* statistic for *n*-2 degrees of freedom and alpha/2 = 0.025. [b] Number of samples used in the nonlinear regression. [c] Reference *3*.

The value for P used for the slurry experiments (1.13) was obtained in the previous study (*3*). In the solid-phase experiments, the partitioning of PCE into the reactor surfaces was found insignificant compared to that into the soil. Thus, the value for K_s in the solid-phase experiment can be calculated using the sorption isotherm data as follows

$$K_s = \frac{C_{so}}{C_l} = \frac{q\,D}{C_l} = K_p\,D \tag{5}$$

where C_{so} is the mass of PCE in the solid phase per unit volume of the aqueous phase (mg/L), C_l is the aqueous phase concentration of PCE (mg/L), q is the amount of PCE sorbed per unit mass of the soil (mg/kg), D is the soil dose (kg/L), and K_p is the linear partition coefficient of PCE on the soil (L/kg).

Results and Discussion

Effect of Humic Acid on PCE Degradation in Fe(II)/Cement Systems. The effect of humic acid on PCE degradation was investigated by adding 500 mg of TOC/L of a humic acid in slurries containing Fe(II) with or without cement. At the pH (12.6 ± 0.05) of these experiments, most of the humic acid added would have been present in a dissolved form, and this level of soluble organic carbon would be at least an order of magnitude higher than those typically observed in subsurface environments (*7, 20*). The results are illustrated in Figure 1, and the corrected pseudo-first-order rate constants are presented in Table 3. When the cement was not present, the addition of the humic acid increased the reaction rate by a factor of about 4. This enhancement is consistent with what was observed in the reductive degradation reactions of organic contaminants by Fe(II) or sulfide in the presence of humic acid or NOM (*7, 8, 21*), suggesting that the humic acid acted as an electron mediator in noncement systems. However, in the presence of the cement, the addition of the humic acid did not change the rate constant substantially. The rate constant for the experiment with the humic acid is not statistically different from that for the experiment without the humic acid at a significance level of 5%. This discrepancy in the role of an electron mediator may support the hypothesis proposed in the previous study (*3*) that the reaction mechanism in cement systems is different than that of noncement systems, i.e., reactive iron species formed in the former systems is different than that formed in the latter. These results also imply that for systems with cement, the rate of the electron-transfer reaction between the reactive iron species and PCE in the absence of humic acid was similar to that in the presence of humic acid.

The humic acid could have limited the availability of ferric iron (Fe(III)), which originated from the cement and appeared to be an essential component of the reactive iron species in cement systems (*3*), by forming organic−metal complexes with Fe(III) or by coating surfaces of hydration products of the cement (*5*). However, the observation suggests that the presence of the humic acid did not interfere with the formation of a reactive Fe(II)−Fe(III) (hydr)oxide. The humic acid used in this study differs from soil organic matter and there is great variation in characteristics of soil organic matter in different locations. Therefore, extrapolation of these results with humic acid to any particular soil must be made with caution. However, the data suggest that NOM is unlikely to substantially enhance or inhibit PCE reduction reactions. NOM in the solid phase may reduce observed PCE degradation rates by removing it from solution.

Sorption of PCE by the Silawa Soil at High pH. A linear partition coefficient (K_p) of 0.622 ± 0.013 L/kg was obtained by linear regression with $r^2 = 0.996$. When the sorption coefficient was normalized by the organic carbon content (f_{oc}) of the soil, a K_{oc} (K_p/f_{oc}) value of 90.1 was obtained. This value is about a factor of 2−4 lower than experimentally determined K_{oc} values of PCE for nine different natural solids (aquifer materials, marls, upper horizons of soils) in the study of Mouvet et al. (*18*). The lower sorption capacity of the Silawa soil observed in this experiment compared to those of other solids might be due to the high pH (12.1) condition of the experiment. In the study of Mouvet et al. (*18*), the sorption experiments were conducted at neutral pH condition (6.8 ± 0.1). Humic materials are known to dissolve in water at high pH conditions (*22, 23*). Therefore, in the current sorption experiments, it is possible that some NOM in the soil could have dissolved in the solution, which could have resulted in losses of the sites in the soil available for sorption of PCE. Different surface charge characteristics of the soil at the high pH condition probably did not directly affect the extent of PCE sorption by the soil because PCE is a neutral organic, but it could have affected it indirectly by changing the structure of the NOM.

Degradation of PCE in a Soil by Fe(II)/Cement Treatment. Figure 2 presents the results of the PCE degradation experiments conducted using the solid-phase reactor system. PCE recoveries in controls decreased slightly over time but were higher than 90% for most of the sampling period. The controls contained the soil, cement, and water with the same mass ratio that was used for the reactive samples. Thus it can be postulated that lower PCE recoveries in the samples containing Fe(II) are mostly due to degradative reactions rather than sorption, volatilization, etc. There are two potential explanations for the decrease in PCE recoveries in the controls over time. First, the decline in the PCE recoveries can result from reduced PCE extraction efficiency in later sampling times, because the solid samples become more hardened and PCE may bind to solids more strongly in the later stage. Second, the decrease in the PCE recoveries can be due to an intrinsic capacity of the soil to reduce PCE, because the soil has a substantial amount of Fe(II). The Fe(II) content of the soil, which is presented in Table 2, is equivalent to 1.8 times the stoichiometric amount to completely reduce all of the PCE initially present in the solid-phase system to ethylene. The apparent pseudo-first-order rate constant for PCE decay in the control was 0.00095 (±29%) day^{-1}.

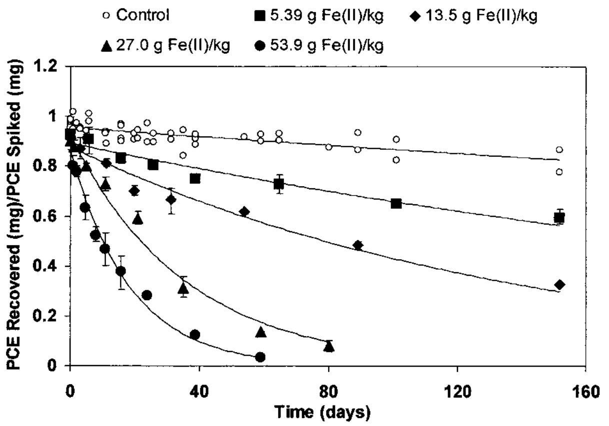

FIGURE 2. Kinetics of PCE reduction by Fe(II) in the solid-phase systems. Error bars are ranges of PCE recoveries. Some error bars are smaller than the symbols. Solid lines represent first-order fits. PCE$_i$ = 100 mg/kg soil.

The pH values of the porewater in the solid-phase systems were initially set to near 12.1, which is the pH at which a maximum PCE degradation rate was observed in the slurry characterization experiments. As the reactions progressed, pH decreased slightly in all experiments. Final pH values of the four reactive experiments were 12.0, 11.9, 11.8, and 12.0, in the order of increasing Fe(II) dose.

TCE was the only chlorinated intermediate product observed in these experiments. In the three higher Fe(II) dose experiments (13.5, 27.0, 53.9 g Fe(II)/kg), TCE disappeared within the first 11 days and its concentration did not exceed 7% of the initial concentration of PCE on a molar basis. However, in the 5.39 g Fe(II)/kg experiment, TCE appeared after 26 days and persisted throughout the experiment. In this experiment, TCE concentration reached a maximum (5% of the initial concentration of PCE on a molar basis) on about 65th day and was approximately constant thereafter. The extent of PCE degradation in this experiment after 65 days also appears to be minimal because the decrement in PCE recoveries after 65 days is almost equivalent to that of the control. Thus it is suspected that the system consumed most of its capacity to reduce PCE and TCE after about 65 days. Considering lower hydrophobicities of dichloroethylenes (DCEs), chloroacetylenes, and vinyl chloride (VC) than PCE or TCE, the extraction technique should have recovered those intermediates from the solid samples, if they had existed. The absence of these less chlorinated products in the solid-phase experiments implies that the Fe(II)-based DS/S technology may completely dechlorinate PCE in soils without production of hazardous intermediates as was observed in the previous slurry study (*3*).

Figure 2 shows that the pseudo-first-order model describes kinetics of PCE degradation in the solid-phase systems reasonably well. The apparent and corrected pseudo-first-order rate constants for the solid-phase experiments are presented in Table 4. Uncertainties in the rate constants for the lower Fe(II) dose experiments (5.39 g, 13.5 g Fe(II)/kg)

TABLE 4. Pseudo-First-Order Rate Constants for PCE in the Solid-Phase Experiments[a]

Fe(II) dose (g/kg)	Fe(II) dose (mM)	$k_{app,corr}$[b] (day^{-1})	$t_{1/2,app}$ (days)	k[c] (day^{-1})	n[d]
5.39	201	0.0021 (±37%)	335	0.0069 (±37%)	24
13.5	503	0.0062 (±24%)	113	0.016 (±24%)	18
27.0	1006	0.027 (±12%)	26	0.064 (±12%)	22
53.9	2012	0.053 (±13%)	13	0.13 (±13%)	28

[a] Uncertainties of the rate constants represent 95% confidence limits expressed in percent relative to estimates for the rate constants. [b] Apparent pseudo-first-order rate constant corrected for the control decay. [c] Corrected pseudo-first-order rate constant $= (1 + K_s)\,k_{app,corr} = 2.29\,k_{app,corr}$; $K_s = K_pD = 0.622$ (L/kg) $\times$ 2.08 (kg/L) $= 1.29$. [d] Number of data points.

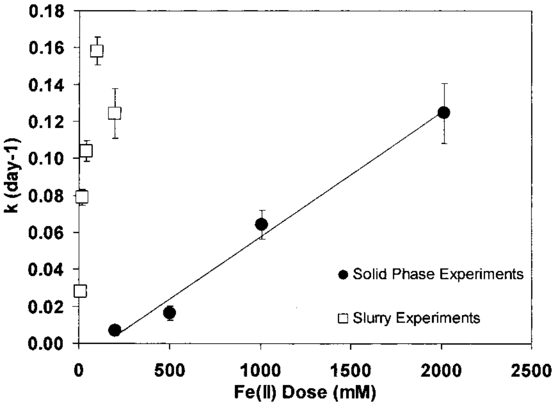

FIGURE 3. Dependence of pseudo-first-order rate constants on Fe(II) dose in the solid-phase experiments. Error bars are 95% confidence intervals. The solid line represents the linear regression equation ($y = (6.7\text{E-}5)x - 0.0098$; $r^2 = 0.987$).

are relatively large due to propagation of the uncertainty of the rate constant for the control. If the rate constants for these experiments were not corrected for the control effect, the uncertainty for both experiments would be 16%. A leach model predicts that degradation reaction with half-lives of 1 year or less would be fast enough to result in no more than 5% release of contaminants to the environment, if the solidified waste form has reasonably large size (*24*). Therefore, it can be argued that half-lives of PCE in the solid-phase experiments are within time frames acceptable for DS/S technology. Furthermore, Fe(II) doses used in this study are practical in that they do not exceed 6% of the soil mass. Addition of Fe(II) from $FeSO_4$ at a dose of 27 g/kg would increase typical S/S costs of $30 to $300/ton (*1, 25*) by only $1/ton, assuming a price of $40/ton Fe(II) (*26*). Half-lives of PCE even shorter than those observed in the present study might be obtained by simply adding Fe(III) and/or an appropriate anion such as sulfate in addition to Fe(II). Such additions were found to increase reaction rates in slurry experiments, possibly by promoting the formation of larger amounts of the reactive iron species (*3*).

Pseudo-first-order rate constants are plotted against Fe(II) dose per unit solution volume in Figure 3. For comparison purposes, the rate constants obtained for various Fe(II) doses in the 10% cement slurry experiments (*3*) are also presented in Figure 3. The experimental procedures used for these slurry experiments are basically the same as those of the slurry experiments in this paper. Within the range of Fe(II) doses studied, a linear relationship between rate constant and Fe(II) dose is observed in the solid-phase experiments, and this linearity continues over much a wider range of Fe(II) dose in the current study than in the previous slurry experiments. However, the slope of the linear region of the slurry data is ~57 times steeper than that of the regression curve for the solid-phase data. This means that much more Fe(II) is required in the solid-phase systems to bring about a certain change in the reaction rate than in the slurry systems.

It was suspected that the slower kinetics in the solid-phase experiments might be due to slower mass transfer of PCE to the reactive iron species. Unlike in the slurry experiments, agitation was not provided for the solid-phase reactors during most of the incubation time. This might have resulted in substantially slower mass transfer kinetics in the solid-phase systems than in the slurry systems. An analysis was carried out to evaluate the significance of the mass transfer kinetics compared to the surface reaction kinetics in the solid-phase experiments. It was assumed that transport of PCE within the pores of solidified matrices could be explained by Fickian diffusion and that the reactive surface was provided by a chloride-containing green rust ($GR1(Cl^-)$). From the material balance equation describing mass transfer and surface degradation of PCE, an expression was derived for the second Damköhler number ($D_{a,II}$), which is the ratio of the diffusion and reaction times scales (*27*). Values for $D_{a,II}$ below 1 indicate that mass transfer does not control the observed rate. Estimates for $D_{a,II}$ were below 10^{-5}, so it is very unlikely that mass transfer controlled the observed PCE degradation kinetics in the solid-phase systems. Detailed procedures for this analysis are available in the Supporting Information.

The complexity of the solid-phase systems compared to slurry systems probably affected the degradation kinetics. Factors or processes that would potentially slow PCE degradation kinetics in solid-phase systems include the following: (1) Oxidation of Fe(II) by soils. Oxidants in anaerobic soils such as MnO_2, SO_4^{2-}, NO_3^-, NO_2^-, and N_2O (*22*) may oxidize Fe(II) added to soil systems. (2) Interference of soils in the formation of reactive iron species. Crystallization of iron oxides is reported to be inhibited by soil components such as citrate, phosphate, and silicate (*28*). Furthermore, a substantial portion of cement components could react with soils to form solidified matrices and would not be available to react with Fe(II) to form the reactive agent. (3) Attachment of the reactive iron species to soils. This attachment would decrease the surface area available for PCE reduction reactions.

The observed rate of PCE degradation in a full-scale application of DS/S could also be reduced by slow desorption of PCE from soils that have been in contact with PCE for a long period of time. The extent of reduction would depend on the contact time and type of soil as well as the rate of degradation of soluble PCE. However, slow desorption rates would also reduce the rate at which PCE would leach from a soil treated by DS/S. Therefore, slow desorption would not affect the ability of DS/S to reduce risk to human health and the environment by degrading contaminants before they can leach from the treated material.

Full-scale applications of Fe(II)-based DS/S could also be adversely affected by oxygen, if sufficient Fe(II) were not added to react with oxygen present in the soil or that could diffuse in after treatment. However, treatment by DS/S should reduce the rate of transport of oxygen by solidifying the soil. Although more research is needed under conditions more like those in a full-scale application, the laboratory results support the feasibility of applying the Fe(II)-based DS/S process to treating materials contaminated with chlorinated organics such as PCE.

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Supporting Information Available

An analysis to evaluate the relative importance of mass transport and surface reaction on the observed kinetics. This material is available free of charge via the Internet at http://pubs.acs.org.

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