

## Reactivity of Fe(II)/cement systems in dechlorinating chlorinated ethylenes

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### Abstract

Ferrous iron (Fe(II)) in combination with Portland cement is effective in reductively dechlorinating chlorinated organics and can be used to achieve immobilization and degradation of contaminants simultaneously. Reactivities of chlorinated ethylenes (perchloroethylene (PCE), trichloroethylene (TCE), 1,1-dichloroethylene (1,1-DCE), vinyl chloride (VC)) in Fe(II)/cement systems were characterized using batch slurry reactors. Reduction kinetics of the chlorinated ethylenes were sufficiently fast to be utilized for the proposed treatment scheme, and were described by a pseudo-first-order rate law. The order of reactivity of the chlorinated ethylenes was TCE > 1,1-DCE > PCE > VC. Reduction of TCE and PCE mainly yielded acetylene, implying that the transformation of the two compounds occurred principally via reductive  $\beta$ -elimination pathways. Transformation of 1,1-DCE and VC gave rise to primarily ethylene, implying that major degradation pathways were a reductive  $\alpha$ -elimination for the former and a hydrogenolysis for the latter. The reactivity of the Fe(II)/cement systems in dechlorinating TCE was proportional to Fe(II) dose when the Fe(II)/cement mass ratio varied between 5.6 and 22.3%. The Fe(II)/cement systems with a higher Fe(II) loading were less extensively affected by pH in reductive reactions for TCE than in the previous experiments with PCE or chlorinated methanes. Amendment of Fe(II)/cement systems with Fe(III) addition was found effective in increasing the reactivity in the previous study, but the current findings indicated that the extent to which the reaction rate increased by the amendment might be dependent on the source of the cement and/or the compounds tested.

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### 1. Introduction

Environmental hazards of chlorinated ethylenes are well documented in the literature [1–3]. In 2001, for the first time as chlorinated solvents, trichloroethylene (TCE) and perchloroethylene (PCE) were listed as the contaminants regulated by the Soil Environment Preservation Act of Korea [4]. They were frequently found at the groundwater monitoring wells managed by the Korean Ministry of Environment. Substantial amounts of TCE or PCE were detected in 47% of the groundwater samples where some contaminants were found above the groundwater standards, as of 2002 [5]. On

this basis, need for development of remediation technologies for chlorinated solvents has been further increased in Korea recently.

In many cases, remediation of the sites contaminated with chlorinated solvents such as TCE and PCE requires source control. Degradative solidification/stabilization (DS/S) was proposed as an innovative source control technology for chlorinated solvents [6,7]. DS/S combines degradative processes for organic contaminants with immobilization processes for organic/inorganic contaminants. In laboratory experiments, DS/S proved effective in treating soils contaminated with PCE by using Portland cement as an immobilizing agent and ferrous iron as a reductant (degradative agent) [7]. Other potential applications of DS/S include treatment of liquid wastes containing chlorinated solvents and heavy metals, and treat-

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ment of the area contaminated with NAPL (Non Aqueous Phase Liquids) form of chlorinated organics by injection of Fe(II)/cement slurry.

Reductive dechlorination was utilized as a degradative process in the earlier works for DS/S. When Fe(II) in a soluble form is added to cement slurries, it forms a solid-phase iron that can dechlorinate PCE [6], chlorinated methanes [8], and hexachlorobiphenyl [9]. It was hypothesized that Fe(II) sorbed on iron oxides in cement hydrates or an Fe(II) precipitate acted as a reactive reductant for chlorinated organics. Recent studies on solid-phase Fe(II) supports this hypothesis. Ferrous iron bound on iron oxides acted as effective reductants for halogenated methanes [10] and nitroaromatic compounds [11]. Interfacial electron transfer from Fe(II) bound on iron oxides appeared to result in formation of stable Fe(II) mineral phases [12], which then could act as reductants.

It has not been possible to elucidate the structure and composition of the reactive reductant in Fe(II)/cement systems due to a complex nature of the cement and due to difficulties in separating the reductant from cement hydrates [9,13]. However, the experimental evidence [6,9,13] implies that the reactive reductant is a mixed-valent Fe(II)–Fe(III) mineral, which may be similar to green rust [14,15], and that it may be associated with elements such as aluminum and  $\text{SO}_4^{2-}$ .

The objectives of this study were to characterize reduction kinetics of chlorinated ethylenes in Fe(II)/cement systems and to optimize dechlorination reactions in Fe(II)-based DS/S. Kinetics and products of PCE, TCE, 1,1-DCE, and vinyl chloride reductions in Fe(II)/cement systems were investigated to understand mechanisms and pathways through which PCE and its reduction products react with the reactive reductant species in Fe(II)/cement systems. Influences on reactivities of Fe(II)/cement systems of major system parameters such as Fe(II) dose, pH, Fe(III) concentration, cement source, and substrate concentration were evaluated to optimize degradation processes.

## 2. Materials and methods

### 2.1. Materials

The chemicals used were: TCE (99.5%, Aldrich Chemical), 1,1-dichloroethylene (1,1-DCE, 99%, Aldrich Chemical), *cis*-dichloroethylene (*cis*-DCE, 97%, Aldrich Chemical), *trans*-dichloroethylene (*trans*-DCE, 98%, Aldrich Chemical), vinyl chloride (VC, 2.0 mg/mL in methanol, Ac-

cuStandard), 1% acetylene in nitrogen (Matheson Tri-Gas), 1000 ppm ethylene in helium (Matheson Tri-Gas), 1000 ppm ethane in helium (Matheson Tri-Gas), 1,2-dibromopropane (99%, Acros Organics), methanol (99.9%, HPLC grade, Fisher Scientific), hexane (99.9%, HPLC grade, Fisher Scientific), ferrous sulfate (99.5%, heptahydrate, Acros Organics), ferric sulfate (97%, Aldrich Chemical), and cement (type I, Ssangyong cement & Capitol cement). Ssangyong cement that is widely available in Korea was mainly used for kinetic experiments, unless otherwise specified. For selected experiments, Capitol cement that was employed in the earlier studies for Fe(II)/cement systems [6–8] was used for comparison purposes. Table 1 reports chemical composition of the cement from the two different sources. Stock solutions of Fe(II) and Fe(III) were prepared daily by dissolving appropriate salts in deionized water. Methanolic stock solutions of chlorinated ethylenes were also prepared daily. The acid solution of 3.6N  $\text{H}_2\text{SO}_4$  and the base solution of 2.5N KOH were used to control pH values in selected experiments.

### 2.2. Experimental methods

Procedures for batch slurry experiments that were designed to study transformation of volatile chlorinated organics in Fe(II)/cement systems were detailed in the earlier works [6,18]. All experiments were carried out in clear borosilicate glass vials ( $23.4 \pm 0.13$  mL) with triple seals. All samples were prepared in the atmospheric environment at room temperature ( $22 \pm 0.5$  °C). Duplicate samples were prepared for controls and triplicate samples for reactive experiments. Controls contained the deionized water and appropriate chlorinated ethylenes. The mass ratio of the cement to solution was 0.1. The vials were almost completely filled with aqueous solutions to minimize gas phase partitioning of the chlorinated ethylenes. Two types of the cement used in this study were able to buffer the pH of the slurries containing Fe(II) at  $12.8 \pm 0.2$ . To investigate the effect of pH, aliquots of the base or acid solution were added to the slurries when they were prepared.

Reactions were started by introducing 10  $\mu\text{L}$  of methanolic stock solutions of the chlorinated ethylenes to slurry reactors. Initial concentration of PCE, TCE, and 1,1-DCE was 0.25 mM and that of VC was 0.15 mM. After the chlorinated ethylenes were spiked, the slurry reactors were rapidly capped with the closures and were placed in a rotator that provided end-over-end rotation at 8 rpm. At specified intervals, duplicate or triplicate sample vials were retrieved from the rotator and were centrifuged at  $112 \times g$  for 3 min to separate

Table 1  
Chemical composition of the Portland cement from the two different sources [16,17]

	Oxide						Loss on ignition
	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	
Ssangyong cement (wt.%)	61.6	21.7	5.7	3.2	2.8	2.2	1.3
Capitol cement (wt.%)	64.9	20.3	5.5	2.5	1.3	3.2	1.7

aqueous and solid phases. For TCE and DCEs analysis, a 50- $\mu\text{L}$  aliquot was extracted with 1000  $\mu\text{L}$  of a hexane extractant containing 1,2-dibromopropane as an internal standard. For VC and gas (ethylene, acetylene, ethane) analysis, approximately 10 mL of aqueous samples were rapidly transferred to 20 mL glass vials and were equilibrated with the gas phase of the vials to be prepared for headspace analysis.

### 2.3. Analytical methods

PCE, TCE, 1,1-DCE, *cis*-DCE, and *trans*-DCE were analyzed on a Shimadzu GC-17A equipped with an electron capture detector (ECD) and a DB-5 column (30 m  $\times$  0.53 mm i.d.  $\times$  3  $\mu\text{m}$  film thickness; Alltech). Hexane extractants were injected in a split mode (25:1) using an autosampler at 260  $^{\circ}\text{C}$ . Helium was used as a carrier gas at a flow rate of 3 mL/min. Oven temperature was isothermal at 70  $^{\circ}\text{C}$  for 1 min then ramped to 140  $^{\circ}\text{C}$  at a rate of 10  $^{\circ}\text{C}/\text{min}$ . The temperature of the detector was 280  $^{\circ}\text{C}$ .

Vinyl chloride, acetylene, ethylene, and ethane were analyzed on a Younglin M600D GC equipped with a flame ionization detector (FID) and a GS-Alumina column (50 m  $\times$  0.53 mm i.d.; J&W Scientific). Headspace samples were injected manually with a split ratio of 10:1 using a 100  $\mu\text{L}$  gas-tight syringe. The oven temperature was held at 80  $^{\circ}\text{C}$  for 1 min, ramped to 100  $^{\circ}\text{C}$  at a rate of 5  $^{\circ}\text{C}/\text{min}$ , and held for 2 min. The injector and detector temperatures were 250 and 320  $^{\circ}\text{C}$ , respectively. Nitrogen was used as a carrier gas at a flow rate of 2.7 mL/min. Standards curves for VC were generated by using calibration standards prepared by equilibrating aqueous solutions containing specific amounts of VC with gas phase of glass vials. Non-chlorinated gas products were calibrated using the gas standards mentioned above (Matheson Tri-Gas).

### 2.4. Treatment of kinetic data

Degradation kinetics of the chlorinated ethylenes generally followed a pseudo-first-order rate law. Corrected pseudo-first-order rate constants that accounted for partitioning of the substrates into gas and solid phases were obtained using the following equation introduced in the previous work [6]:

$$\frac{dC_1}{dt} = - \frac{k}{\left(1 + H \frac{V_g}{V_l} + K_s\right)} C_1 = - \frac{k}{P} C_1 = -k_{\text{app}} C_1 \quad (1)$$

where  $C_1$  is the concentration of the target chlorinated ethylene in the aqueous phase,  $k$  the corrected pseudo-first-order rate constant for the target chlorinated ethylene,  $H$  the dimensionless Henry's law constant for the target chlorinated ethylene,  $V_g$  and  $V_l$  are volumes of the gas and aqueous phases, respectively,  $K_s$  the solid phase partition coefficient of the target chlorinated ethylene (ratio of mass of the target compound in the solid phase to mass of the target compound in the aqueous phase),  $P$  the partitioning factor for the target chlorinated ethylene =  $1 + HV_g/V_l + K_s$ , and  $k_{\text{app}}$  is the appar-

ent pseudo-first-order rate constant. The kinetic data for the chlorinated ethylenes were fit to Eq. (1) by conducting non-linear regression using the SAS<sup>®</sup> System for Windows<sup>™</sup> (Release 8.2, SAS Institute Inc.) and the values for apparent pseudo-first-order rate constants ( $k_{\text{app}}$ ) were obtained. Corrected pseudo-first-order rate constants ( $k$ ) (pseudo-first-order rate constants hereafter) were calculated by multiplying relevant partitioning factors ( $P$ ) times apparent pseudo-first-order rate constants ( $k_{\text{app}}$ ).

## 3. Results and discussion

### 3.1. Reduction kinetics of chlorinated ethylenes by Fe(II)/cement systems

Fig. 1 shows the reduction kinetics of the target chlorinated ethylenes in cement slurries containing 100 mM Fe(II) at pH  $12.8 \pm 0.25$ . The kinetic data for PCE that were obtained under the virtually identical experimental conditions as the current study [6] are also depicted in Fig. 1. Slurry samples for the PCE experiment were prepared inside an anaerobic chamber using the cement from a source different from the current experiments. As will be discussed later, however, reduction kinetics are not markedly affected by initial presence of oxygen in Fe(II)/cement slurries or a difference in cement source. Therefore, the PCE data can reasonably be incorporated into present discussions on the chlorinated ethylenes. Table 2 presents the pseudo-first-order rate constants which were estimated by fitting aqueous phase concentrations of the target chlorinated ethylenes to the pseudo-first-order kinetic model (Eq. (1)). Uncertainties of the rate constants suggest that the pseudo-first-order model reasonably describes the

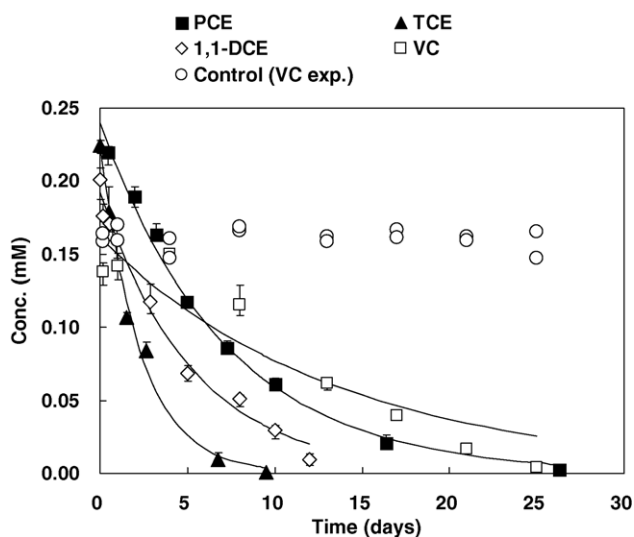


Fig. 1. Reductive dechlorination of chlorinated ethylenes in Fe(II)/cement systems. Controls represent those for VC experiments ( $[\text{VC}]_0 = 0.15 \text{ mM}$ ). The error bars represent ranges of measured concentrations of the chlorinated ethylenes. Curves depict pseudo-first-order fits.  $[\text{Fe(II)}]_0 = 100 \text{ mM}$ .

Table 2

Pseudo-first-order rate constants, final total carbon recoveries, and final products distributions for reductive dechlorination of chlorinated ethylenes in Fe(II)/cement systems<sup>a</sup>

Exp.	Target chlorinated ethylene <sup>b</sup>	$k$ (day <sup>-1</sup> ) <sup>bc</sup>	Total carbon recovery (%)	Final products distribution (%)			$n^d$
				Acetylene	Ethylene	Ethane	
1	PCE	0.16 (±6.5%) <sup>e</sup>	98.0 <sup>f</sup>	82.8 <sup>f</sup>	16.9 <sup>f</sup>	0.3 <sup>f</sup>	23
2	TCE	0.47 (±4.4%)	89.3	79.9	16.3	3.7	18
3	1,1-DCE	0.20 (±11.1%)	70.8	–	88.3	11.7	24
4	VC	0.079 (±23.8%)	93.0	–	100	–	24

<sup>a</sup> Initial concentration of the chlorinated ethylenes was 0.25 mM, except for VC experiment where the concentration was 0.15 mM.

<sup>b</sup> Uncertainties represent 95% confidence limits expressed in % relative to estimates for rate constants:  $\pm \frac{(\text{asymptotic standard error}) \times t(n-2, 0.025)}{\text{estimate for } k} \times 100$ , where  $t(n-2, 0.025)$  is the Student's  $t$ -statistic for  $n-2$  degree of freedom and  $\alpha/2=0.025$ .

<sup>c</sup> Partitioning factors ( $P$ ): PCE (1.13), TCE (1.10), 1,1-DCE (1.06), VC (1.07).

<sup>d</sup> Number of data used to obtain rate constants by conducting nonlinear regression.

<sup>e</sup> Pseudo-first-order rate constant obtained from the previous study [6].

<sup>f</sup> Products information was obtained from the previous study when pH = 12.1 and [Fe(II)]<sub>0</sub> = 39.2 mM [6].

kinetics of the reduction of the chlorinated ethylenes. In the case of VC, however, a zero-order rate law represents the kinetics better than the pseudo-first-order law. By conducting nonlinear regression analysis, a zero-order rate constant of 0.0062 mM/day can be estimated with an uncertainty of ±10.3%.

Half-lives of the chlorinated ethylenes ranged from 1.5 to 8.8 days, indicating that the chlorinated ethylenes could well be treated within reaction times allowable in DS/S scheme. A leach model predicts that organic degradation reactions with half-lives of several months to years would still be effective in DS/S systems [18]. Thus, the results suggest that Fe(II)/cement systems can be extended to treating the less chlorinated ethylenes. In particular, the reduction rate for VC, which is considered a recalcitrant compound, is comparable with those obtained by zero-valent iron systems. A half-life of 6.6 days was observed in a metallic iron system with an iron loading of 333 g/L (5970 mM Fe) [19], whereas the half-life of VC in this study was 8.8 days with a much lower Fe(II) dose (100 mM).

From a thermodynamic perspective, it may be expected that reaction rates increase with increased chlorination of chlorinated compounds [20]. This behavior was documented by numerous research groups on zero-valent iron [21–24]. The order of reactivity observed in the current experiments was TCE > 1,1-DCE > VC. Therefore, the trend is consistent with the thermodynamics and the above-mentioned cases for zero-valent iron. However, the opposite trend of the reaction rate increasing with decreasing level of chlorination has also been reported in several studies on reductive dechlorination [25–28]. Thus, it appears that the order of reactivity for chlorinated ethylenes in reductive reactions cannot be generalized at this point.

When the rate constant for PCE (exp. 1) is considered, the order of reactivity becomes complicated (TCE > 1,1-DCE > PCE > VC). Similar irregular behavior was also observed, when chlorinated ethylenes reacted with a green rust [29]. Green rust is a mixed-valent hydroxide of Fe(II) and Fe(III) that is suspected as a reactive reductant that forms in

Fe(II)/cement systems. The order of reactivity in the green rust study was PCE > VC > TCE > *c*-DCE. In this case, the reactivity of VC is not compatible with the trend seen in Fe(II)/cement systems. Therefore, it may be presumed that irregular behaviors in reacting with chlorinated ethylenes are characteristics of the systems containing mixed-valent Fe(II)–Fe(III) minerals.

### 3.2. Degradation products from reduction of chlorinated ethylenes

Degradation products were monitored during the courses of reduction of the chlorinated ethylenes. Chlorinated products monitored were *cis*-DCE, *trans*-DCE, 1,1-DCE, and VC. Non-chlorinated products monitored include acetylene, ethylene, and ethane. Table 2 reports total carbon recoveries and products distributions at the final sampling times. The chlorinated products were found below the detection limits during the reduction processes. The detection limits for were *cis*-DCE, *trans*-DCE, 1,1-DCE, and VC, were 0.012, 0.012, 0.008, and 0.007 mM, respectively. Table 2 reports that the reduction of TCE produced non-chlorinated products in nearly stoichiometric amounts. This suggests that the reaction proceeded probably via highly reactive chloroacetylenes [27,30] rather than via DCEs and VC. The reduction rates for chloroacetylenes are reported to be high enough not to be detected during the reactions [31]. Reduction of TCE produced acetylene as a major product, which accounted for 80% of the final products, and ethylene and ethane as minor products. A similar distribution of final products was observed in the earlier work with PCE [6]. Predominance of acetylene was also observed in the TCE reduction experiments with green rust [29] and iron sulfide [25]. Preferential formation of acetylene and no detection of chlorinated intermediates are consistent with a reductive β-elimination pathway initially proposed for a zero-valent iron system [27].

Reduction of 1,1-DCE appeared to proceed without formation of vinyl chloride, because the latter was not detected during the sampling. Ethylene was a predominant product.



Thus, a reductive  $\alpha$ -elimination pathway proposed for the zero-valent iron system [27] is also likely to be a preferred pathway for 1,1-DCE reduction in Fe(II)/cement systems. Compared with the system containing TCE, substantially more ethane was observed among the final products in the system with 1,1-DCE. This could be due to the fact that a more stoichiometric amount of electrons was available, i.e., a more reductive capacity was available, in the 1,1-DCE experiment than in the TCE experiment. The total carbon recovery (70.8%) of the system with 1,1-DCE is substantially lower than those of the other systems. Coupling of C2 radicals and subsequent formation of C4 coupling products during the reductive transformation of 1,1-DCE might account for the remaining portion of the carbon balance. However, data on four-carbon compounds are not available in this study.

Vinyl chloride (VC) reacted to ethylene without producing acetylene. This indicates the reaction occurred via a hydrogenolysis pathway, which is generally accepted as a major pathway for VC [19,27,28]. Ethane was not detected in the VC experiment, despite the stoichiometric advantage of the VC experiment (lower initial substrate concentration (0.15 mM) of a less chlorinated compound) over the other experiments with TCE or 1,1-DCE in terms of the amount of electrons available. This appears to be due to the low reactivity of the system to VC, i.e., the conversion of ethylene to ethane was not initiated during the sampling period. Deng et al. [19] also detected ethylene as a major product of VC in their degradation study using zero-valent iron. In the case of highly reactive systems containing electron donors such as Pd/Fe, Pd/Al, and nanoscale iron [26,28,32], ethane was detected as a major product.

### 3.3. Influence of Fe(II) dose and cement source

In the previous PCE study [6], the pseudo-first-order rate constant in 10% cement slurries was directly proportional to Fe(II) dose over a limited range (0–50 mM) and the reaction rate appeared to reach a maximum value at the Fe(II) dose of ~90 mM. Ferrous iron dose was varied more widely (0–400 mM) in this study in order to find an optimum Fe(II) dose for Fe(II)-based DS/S formulation and to better characterize reactivities of the DS/S system with regard to Fe(II)/cement ratio. Fig. 2 illustrates the reduction kinetics of TCE, and Table 3 presents the rate constants from the kinetic experiments (exp. 5 to exp. 9). The pseudo-first-order rate constants for TCE plus the previously obtained constants for PCE are plotted as a function of Fe(II) dose in Fig. 3.

Although the rate constants for TCE versus Fe(II) dose apparently shows a saturation behavior, the range in which the rate constant is proportion to Fe(II) dose is largely expanded in comparison to the former study with PCE (Fig. 3). The reactivity of Fe(II)/cement systems increased until the Fe(II) dose was increased to a value as high as 400 mM. When the rate constants versus Fe(II) dose are fitted to a model equation below, a maximum pseudo-first-order rate constant ( $k_{\max}$ ) of

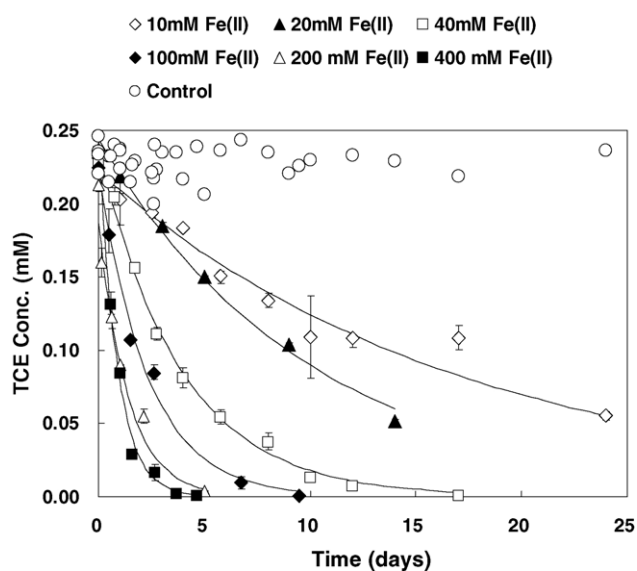


Fig. 2. Kinetics of TCE reduction in Fe(II)/cement systems containing various amounts of Fe(II). The error bars represent ranges of measured concentrations of TCE. Curves represent pseudo-first-order fits.

$2.28 \text{ day}^{-1}$  and a half-saturation constant ( $K_{1/2}$ ) of 367 mM are obtained.

$$k = \frac{k_{\max}[\text{Fe(II)}]_0}{K_{1/2} + [\text{Fe(II)}]_0} \quad (2)$$

where  $k$  is the pseudo-first-order rate constant,  $k_{\max}$  the maximum pseudo-first-order rate constant,  $[\text{Fe(II)}]_0$  the Fe(II) dose, and  $K_{1/2}$  the half-saturation constant. The half-saturation constant for the TCE experiment is 15.2 times larger than that for the PCE experiment. It was suspected that

Table 3

Pseudo-first-order rate constants for TCE in Fe(II)/cement systems as functions of Fe(II) dose, pH, and Fe(III) dose<sup>a</sup>

Exp.	Fe(II) dose (mM)	pH	Fe(III) dose (mM)	$k$ ( $\text{day}^{-1}$ ) <sup>b,c</sup>	$n^d$
5	10	12.8	–	0.064 ( $\pm 15.0\%$ )	24
6	20	12.8	–	0.11 ( $\pm 8.0\%$ )	14
7	40	12.8	–	0.28 ( $\pm 5.4\%$ )	30
2	100	12.8	–	0.47 ( $\pm 4.4\%$ )	18
8	200	12.8	–	0.73 ( $\pm 25.6\%$ )	12
9	400	12.8	–	1.2 ( $\pm 9.1$ )	17
10	100	10	–	0.19 ( $\pm 11.5\%$ )	20
11	100	11	–	0.19 ( $\pm 19.2\%$ )	20
12	100	12	–	0.32 ( $\pm 19.1\%$ )	18
13	100	13.5	–	0.45 ( $\pm 18.2\%$ )	22
14	40	12.8	10	0.28 ( $\pm 10.9\%$ )	24
15	40	12.8	40	0.36 ( $\pm 18.8\%$ )	22
16	40	12.8	100	0.23 ( $\pm 11.8\%$ )	26

<sup>a</sup> Initial concentration of TCE was 0.25 mM.

<sup>b</sup> Uncertainties represent 95% confidence limits expressed in % relative to estimates for rate constants:  $\pm \frac{(\text{asymptotic standard error}) \times t(n-2, 0.025)}{\text{estimate for } k} \times 100$ , where  $t(n-2, 0.025)$  is the Student's  $t$ -statistic for  $n-2$  degree of freedom and  $\alpha/2 = 0.025$ .

<sup>c</sup> Partitioning factor for TCE = 1.10.

<sup>d</sup> Number of data used to obtain rate constants by conducting nonlinear regression.

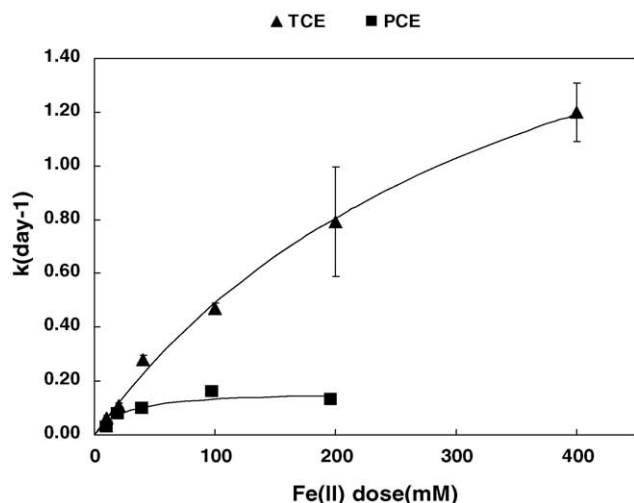


Fig. 3. Pseudo-first-order rate constants for TCE and PCE vs. Fe(II) dose in 10% cement slurries. The rate constants for PCE were abstracted from the previous study [6]. The error bars are 95% confidence intervals. The curves represent fitting by using Eq. (2).

this discrepancy in the Fe(II) dose effects was attributable to the use of the cement from the two different sources (Ssangyong versus Capitol). As presented in Table 1, major compositions of the two different cement appear to be similar, nonetheless, some differences are noticed in the amounts of aluminum, Fe(III), and  $\text{SO}_3$ , which might be correlated with the reactive reductant [13]. Further, the two cements would probably contain different amounts of transition metals that might affect reduction reactions [33,34]. A set of experiments was carried out to test if the difference in the cement source resulted in different performances. The resulting rate constants are reported in Table 4.

By using Capitol cement that had been used in the earlier works [6–8], PCE reduction kinetics observed in the first

Table 4  
Comparison of pseudo-first-order rate constants obtained from two different cement sources<sup>a</sup>

Exp.	Target compound	Cement source	Fe(II) dose (mM)	$k$ (day <sup>-1</sup> ) <sup>bc</sup>	$n^d$
17	PCE	Capitol	40	0.11 ( $\pm 6.2\%$ )	20
18	PCE	Capitol	39.2	0.11 ( $\pm 5.4\%$ ) <sup>e</sup>	29
19	PCE	Ssangyong	40	0.12 ( $\pm 13.0\%$ )	20
20	TCE	Capitol	40	0.37 ( $\pm 9.3\%$ )	16
21	TCE	Capitol	400	1.57 ( $\pm 18.1\%$ )	12
7	TCE	Ssangyong	40	0.28 ( $\pm 5.4\%$ )	30
9	TCE	Ssangyong	400	1.24 ( $\pm 9.1\%$ )	17

<sup>a</sup> Initial concentration of the target compounds was 0.25 mM.

<sup>b</sup> Uncertainties represent 95% confidence limits expressed in % relative to estimates for rate constants:  $\pm \frac{(\text{asymptotic standard error}) \times t(n-2, 0.025)}{\text{estimate for } k} \times 100$ , where  $t(n-2, 0.025)$  is the Student's  $t$ -statistic for  $n-2$  degree of freedom and  $\alpha/2 = 0.025$ .

<sup>c</sup> Partitioning factors ( $P$ ): PCE (1.13), TCE (1.10).

<sup>d</sup> Number of data used to obtain rate constants by conducting nonlinear regression.

<sup>e</sup> Pseudo-first-order rate constant from the previous study when the samples were prepared inside the anaerobic chamber [6].

PCE study [6] were well reproduced in the current experimental conditions (exp. 17 versus exp. 18). This implies that the current method of preparing samples in the atmospheric environment instead of using an anaerobic chamber does not substantially affect the reduction kinetics. In other words, effects of the oxygen initially present in solutions or sorbed on surfaces on the reaction kinetics were negligible. An implication here for field applications of DS/S is that oxidizing conditions of the contaminated soils or wastes can be overcome without difficulty with appropriate doses of Fe(II). Kinetics of PCE reduction by using the cement mainly used for the current study (Ssangyong) were also investigated (exp. 19). Statistical comparison shows that the rate constant obtained from the experiment with Ssangyong cement is identical with that obtained using Capitol cement at a significance level of 5% (exp. 17 versus exp. 19), implying that the source of cement may not affect reduction kinetics of PCE.

Reduction kinetics of TCE obtained from systems containing Ssangyong cement were compared to those obtained from systems with Capitol cement. Table 4 shows that the rate constants obtained for Capitol cement were approximately 1.3 times larger than those for Ssangyong cement (exp. 7 versus exp. 20, exp. 9 versus exp. 21). Statistics also demonstrates that the formers are larger than the latters at a significance level of 5%. Therefore, it can be concluded that the systems with Capitol cement perform slightly better in reducing TCE than those with Ssangyong cement. It has not been possible to draw inferences on basis for this difference due to a lack in the information about the reactive reductant in Fe(II)/cement systems.

The above discussions show that the change of the cement source cannot explain the high reactivities observed in the high Fe(II) dose region of the TCE experiments. This behavior could be due to differences between TCE and PCE in reacting to Fe(II)/cement systems. Higher reactivities of the systems with higher Fe(II) dose would probably be associated with more formation of the reactive reductant. This observation has an implication for the DS/S application to heavily contaminated soils/wastes, because it means that the mass ratio of Fe(II) to cement in DS/S formulation can be increased at least up to 22.3% (equivalent to 400 mM Fe(II) in 10% slurries) when dealing with soils/wastes with very high chlorinated organics loading.

### 3.4. Influence of pH

The reactivity of Fe(II)/cement systems is strongly dependent on pH [6,8]. Besides direct influences on the reactivity caused by changes in hydrogen ion concentrations, pH also appeared to affect the reactivity of Fe(II)/cement systems by determining the amount of the reactive iron reductant formed in the system. To collect more information on the pH dependence, the Fe(II) dose of 10% cement slurries was increased from the previously used value of 39.2–100 mM and TCE reduction kinetics were studied under various pH conditions. The pseudo-first-order rate constants obtained at pH values

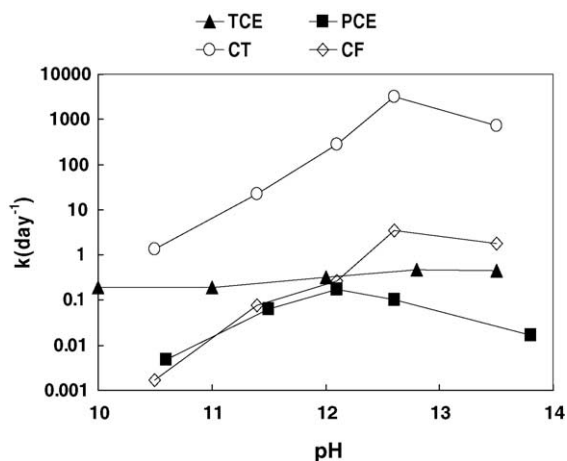


Fig. 4. pH dependence of pseudo-first-order rate constants for the chlorinated ethylenes and chlorinated alkanes. The rate constants for PCE, CT, and CF were abstracted from the previous studies [6,8]. Curves were drawn to guide the eye.

10, 11, 12, 12.8, and 13.5 are presented in Table 3 and are plotted against pH in Fig. 4. For comparison, Fig. 4 also shows the pseudo-first-order rate constants for PCE, carbon tetrachloride (CT), and chloroform (CF) that were obtained at  $\sim 40$  mM Fe(II) dose conditions in the earlier studies [6,8].

The rate constants for TCE were lower in the lower pH conditions and gradually increased with increased pH. An explanation for higher reactivities of iron-based minerals at higher pH conditions is that formation of deprotonated surface groups is promoted as pH increases and that they are more reactive than protonated ones [10,35]. However, changes in the rate constants with regard to pH changes were much less extensive in the current study than in the previous studies. The rate constants for the chlorinated methanes (CT, CF) experiments or for the PCE experiments varied by more than two to three orders of magnitude when pH values were changed between 10.5 and 13.8. However, in the present study, the rate constants were within the same order of magnitude ( $0.19\text{--}0.47\text{ day}^{-1}$ ), indicating that the effect of pH on the reduction kinetics in Fe(II)/cement systems may vary depending on the Fe(II) dose. Assuming this argumentation is valid, the reactivity of Fe(II)/cement systems would be less affected by pH when the systems contain larger amounts of the reactive reductant. The different pH dependencies could also be due to differences in reactions of PCE, chlorinated methanes and TCE.

### 3.5. Influence of Fe(III) amendment

When ferric iron was added to Fe(II)/cement systems in an Fe(III) to Fe(II) molar ratio of 1:3, PCE degradation rates were increased by factors of about 2–3 [6]. From this result, it was hypothesized that the reactive reductant was an Fe(II)–Fe(III) (hydr)oxide and that Fe(III) amendment promoted formation of it. In the present study, the effect of Fe(III) amendment was further characterized by adding vari-

ous amounts of Fe(III) in Fe(II)/cement systems. As reported in Table 3 (exp. 14, 15, 16), the reaction rate increased only when Fe(III) was added in the amount equivalent to Fe(II), and the increment was small (28%) compared to the enhancement observed previously [6]. Amendment of Fe(III) in an amount exceeding the Fe(II) dose resulted in a decrease in the system reactivity (exp. 16). This is probably due to an increase of redox potential of the system originating from the presence of an excessive amount of Fe(III) and/or due to more formation of an Fe(III) oxide mineral, which is inactive. When Fe(II) to Fe(III) ratio is low, the system tends to be dominated by Fe(III) oxide minerals [36,37]. The results of the experiments on Fe(III) amendment are generally not consistent with the previous results with PCE. The difference in the compounds tested and/or in the source of the cement used could have caused the discrepancy in the behavior. More investigation needs to be conducted on the role of Fe(III) in reductive reactions of Fe(II)/cement systems.

### 3.6. Influence of initial substrate concentration

In the kinetic study on the chlorinated methanes, a slight saturation behavior was observed when initial reduction rates were plotted against initial substrate (chloroform) concentrations [8]. Data on initial rates were collected over a wider range of a substrate concentration in this study. The effect of initial TCE concentration on the reduction kinetics was investigated by varying initial TCE concentration from 0.05 to 2 mM in the 10% cement slurries containing 40 mM Fe(II). Fig. 5 represents the results. As shown in Fig. 5, the initial rate increased almost linearly with initial TCE concentration until a value of 0.5 mM and reached a limiting value at the initial TCE concentration of 1.0 mM. This suggests transition from a first-order kinetics to a zero-order kinetics at the initial TCE concentration of 1.0 mM. Such transition to the zero-order kinetics can be interpreted as evidence for saturation of reactive surfaces. Therefore, the current data clearly demonstrate that surface-mediated reactions control the re-

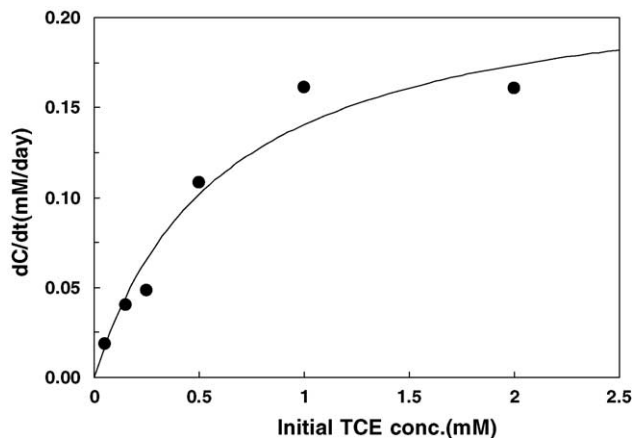


Fig. 5. Initial degradation rates vs. initial TCE concentration. The curve represents a simple saturation model.

action kinetics in Fe(II)/cement systems. The data were fitted to a simple saturation model:

$$R_0 = \frac{v_{\max}[\text{TCE}]_0}{(K_m + [\text{TCE}]_0)} \quad (3)$$

where  $R_0$  is the initial degradation rate,  $v_m$  the maximum degradation rate, and  $K_m$  the half-saturation constant. A non-linear regression analysis was conducted using the data and the values estimated for  $v_m$  and  $K_m$  were 0.227 mM/day and 0.614 mM, respectively. The half-saturation constant ( $K_m$ ) represents the affinity of reactive surface sites for the substrate and is expected to be independent of surface area concentration in the system. Thus, the half-saturation constant can be utilized as a parameter that can interpret characteristics of the reactive reductant produced in Fe(II)/cement systems.

#### 4. Conclusions

Half-lives of the chlorinated ethylenes in Fe(II)/cement systems ranged from 1.5 to 8.8 days, which were within life spans allowable in DS/S applications. The order of reactivity of the chlorinated ethylenes in the Fe(II)/cement systems was as follows: TCE > 1,1-DCE > PCE > VC. The chlorinated ethylenes were mostly converted to non-chlorinated compounds that could easily be attenuated in the environment. The distributions of the reduction products indicate that the major reduction pathways for PCE/TCE, 1,1-DCE, and VC are a reductive  $\beta$ -elimination, a reductive  $\alpha$ -elimination, and a hydrogenolysis, respectively.

The reactivity of the Fe(II)/cement systems in dechlorinating TCE was proportional to Fe(II) dose when the Fe(II)/cement mass ratio varied between 5.6 and 22.3%. The pH dependence of the reductive reactions of TCE was much less pronounced than those observed in reactions of PCE and chlorinated methanes in the previous experiments with a lower Fe(II) loading. Systems containing the cement from the two different sources but with apparently similar compositions generally showed similar reactivities, but differed in reacting to Fe(III) amendment. The initial rate experiments demonstrate that surface-mediated reactions control the dechlorination kinetics in Fe(II)/cement systems.

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