Analysis of dechlorination kinetics of chlorinated aliphatic hydrocarbons by Fe(II) in cement slurries

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Abstract

Degradative solidification/stabilization with ferrous iron (DS/S-Fe(II)) has been found to be effective in degrading a number of chlorinated aliphatic hydrocarbons including 1,1,1-trichloroethane (1,1,1-TCA), 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA), tetrachloroethylene (PCE), trichloroethylene (TCE), 1,1-dichloroethylene (1,1-DCE), vinyl chloride (VC), carbon tetrachloride (CT) and chloroform (CF). Previous studies have characterized degradation kinetics in DS/S-Fe(II) systems as affected by Fe(II) dose, pH and initial target organic concentration. The goal of this study is to investigate the importance of various chemical properties on degradation kinetics of DS/S-Fe(II). This was accomplished by first measuring rate constants for degradation of 1,1,1-TCA, 1,1,2,2-TeCA and 1,2-dichloroethane (1,2-DCA) in individual batch experiments. Rate constants developed in these experiments and those obtained from the literature were related to thermodynamic parameters including one-electron reduction potential, two-electron reduction potential, bond dissociation energy and lowest unoccupied molecular orbital energies. Degradation kinetics by Fe(II) in cement slurries were generally represented by a pseudo-first-order rate law. The results showed that the rate constants for chlorinated methanes (e.g. CT, CF) and chlorinated ethanes (e.g. 1,1,1-TCA) were higher than those for chlorinated ethylenes (e.g. PCE, TCE, 1,1-DCE and VC) under similar experimental conditions. The log of the pseudo-first-order rate constant (k) was found to correlate better with lowest unoccupied molecular orbital energies (E_{LUMO}) ($R^2 = 0.874$) than with other thermodynamic parameter descriptors.
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1. Introduction

Chlorinated aliphatic hydrocarbons (CAHs) are one of the main groups of compounds causing subsurface contamination in the U.S. [1]. One of main mechanisms to treat CAHs under anaerobic environment is a reductive dechlorination. Reductive dechlorination of various CAHs such as tetrachloroethylene (PCE), trichloroethylene (TCE), 1,1,1-trichloroethane (1,1,1-TCA) and carbon tetrachloride (CT) can be achieved by various natural or synthesized reductants including zero-valent iron [2–4], ferrous iron [5], iron-oxides (e.g. goethite, hematite and magnetite) [6–14], iron hydroxides (green rust) [15–18], iron sulfide (FeS) [19–21], pyrite (FeS₂) [9,22] and iron-phyllosilicates [23]. Iron-based degradative solidifica-

tion/stabilization (DS/S-Fe(II)) is a treatment process for media contaminated with CAHs that combines reductive dechlorination with immobilization. Active reductants are formed in DS/S-Fe(II) by reactions between Fe(II) and cement hydration products. The effectiveness of DS/S-Fe(II) to dechlorinate PCE, CT, chloroform (CF), polychlorinated biphenyls (PCBs), TCE, 1,1-dichloroethylene (1,1-DCE) and vinyl chloride (VC) has been reported [24–27]. These investigations characterized the effects of Fe(II) dose, pH and initial target organic concentration on the kinetics of degradation, which was typically described with a pseudo-first-order rate model.

There are two prospective reactions for chlorinated aliphatic hydrocarbons. The first one is a non-reductive process, which does not involve external electron transfer and the other is a reductive process requiring electron transfer. Hydrolysis and dehydrochlorination (or called β-elimination) are non-reductive transformations. In dehydrochlorination, the halide leaves, and a proton is removed from the beta-carbon (the adjacent one)

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to give a double bond. Dehydrochlorination has been seen in the conversion of 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA) to TCE [28], pentachloroethane (PCA) to PCE [29] and 1,1,1-TCA conversion to 1,1-DCE [30]. Three kinds of reductive transformation that require two-electron transfer are as follows [31]: (1) hydrogenolysis, in which a hydrogen atom replaces a chloride substitute, (2) reductive β-elimination, in which two chlorides are removed from different carbons that are next to each other in the molecule and (3) coupling, in which two alkyl groups connect to one another. By hydrogenolsyis, 1,1,1-TCA can be successively converted to 1,1-dichloroethane (1,1-DCA), chloroethane (CA) and ethane. Also, CT will be transformed via stepwise hydrogenolysis to CF, methylene chloride (MC) and chloromethane (CM). Furthermore, PCE will successively transform to TCE, *cis*-dichloroethylene (*c*-DCE) or *trans*-dichloroethylene (*t*-DCE), VC and ethene by hydrogenolysis. PCE and TCE can undergo reductive β-elimination, resulting in dichloroacetylene and chloroacetylene, respectively [32]. *c*-DCE and *t*-DCE could be formed from 1,1,2,2-TeCA by reductive β-elimination. In addition, 1,1,2-TCA and 1,2-DCA can produce VC and ethene, respectively, via reductive β-elimination. In several studies, ethane was simultaneously observed with the formation of 1,1-DCA in the dechlorination of 1,1,1-TCA, which will be followed by reductive α-elimination [33,34]. It is known that reductive α-elimination occurs to the compounds which chlorine is present in only one carbon (e.g. 1,1,1-TCA and 1,1-DCE) [33].

Many studies have developed linear free energy relationships (LFERs) for rate constants describing dechlorination by (nanosized) zero-valent metal or iron sulfide [18,20,32–35]. One-electron reduction potential is commonly used as the independent variable in correlation with the relevant rate constants, which is based on the assumption that the initial reaction forming the radial is the rate-limiting step [36]. Scherer et al. tested correlation of the kinetic data for dechlorination of chlorinated ethanes and ethenes by zero-valent iron with descriptor variables including one-electron and two-electron reduction potential and lowest unoccupied molecular orbital (LUMO) energies [35]. Arnold and Roberts have investigated the kinetics of chlorinated ethanes and ethenes by Zn(0). The regression of surface area-normalized rate constants of chlorinated ethenes with one-electron reduction potential has shown a good correlation ($R^2 = 0.958$) [32]. The dechlorination of nine CAHs by iron sulfide was studied by Butler and Hayes. Linear regression of rate constants for eight CAHs was conducted with the following descriptor variables; the standard one-electron reduction potential (E°_{HAC}), the lowest unoccupied molecular orbital energy (ε_{LUMO}), the free energy of aqueous-phase radical ($\Delta G^{\circ}_{f}(R^{\bullet})_{aq}$), and the gas-phase homolytic bond dissociation enthalpy (D_{R-X}) [20]. However, no attempts have been made to develop LFERs for the rate constants describing dechlorination in mixtures of Fe(II) and cement. Although extensive kinetic data for degradation of a wide range of chlorinated compounds in mixtures of Fe(II) and cement has not been obtained, this study will provide a preliminary analysis of LFERs for rate constants for DS/S-Fe(II).

The objectives of this study are to (1) determine the kinetics of degradation of three chlorinated aliphatic hydrocarbons (CAHs) (1,1,1-trichloroethane (1,1,1-TCA), 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA), 1,2-dichloroethane (1,2-DCA)) by DS/S-Fe(II), (2) examine the effect of chemical structure on reduction kinetics by DS/S-Fe(II) and (3) perform correlation analysis relating pseudo-first-order rate constants with thermodynamic parameters, including one-electron reduction potential, two-electron reduction potential, bond dissociation enthalpies and lowest unoccupied molecular orbital energies.

2. Materials and methods

2.1. Chemicals

Stock solutions of 1,1,1-trichloroethane (99.5%, anhydrous, Aldrich), 1,1,2,2-tetrachloroethane (98%, Aldrich) and 1,2-dichloroethane (99.8%, Aldrich) were prepared in methanol (99.8%, HPLC grade EM). Ferrous chloride (tetrahydrate, 99%, Aldrich) and Portland cement (type I, Capitol Cement) were used as DS/S agents. Prior to analysis by gas chromatography (GC), 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane were extracted from the aqueous solution with hexane (99.9%, HPLC grade, EM) that contained 1,2-dibromopropane (1,2-DBP, 97%, Aldrich Chemical Company Inc.) as an internal standard. Deaerated deionized water (ddw) was prepared by sparging the water purified by the Barnstead Nanopure system for at least 12 h with the atmosphere of an anaerobic chamber (Coy Laboratory Products) containing 95% N_2 and 5% H_2.

2.2. Experimental procedures

The following experimental and analytical procedures have been used in earlier studies [37]. All preparative work was conducted in an anaerobic chamber. Batch kinetic experiments were conducted using 20 mL clear borosilicate glass vials with triple-sealed closures. To protect losses of volatile organic compounds, these closures consist of a Teflon lined silicon septum, lead foil tape (3 M, adhesive backed) and Teflon tape (Norton Performance Plastics Co. non-adhesive, 2 mm thick). Two types of controls were prepared in duplicate. One control contained water and a target organic and the other control contained water, the target organic and cement, in order to evaluate the effect of pH. Experimental reactor vials were prepared in triplicate and contained water, a target organic, cement and Fe(II). The mass ratio of solid (cement) to solution was 0.1. The vials were spiked with 10 µL of the methanolic stock solution of target organics to yield an initial concentration of 0.245 mM and were rapidly sealed. The solution of $FeCl_2$ was added to the reactors to achieve the desired Fe(II) concentrations. After preparation, the vials were placed in a tumbler providing end-over-end rotation at 7 rpm at room temperature. At the specified reaction time, the reaction vials were removed from the tumbler and centrifuged at 2000 rpm (912 g) for 10 min (International Equipment Co. model CS centrifuge). To extract target organics, 50 µL of supernatant was transferred into autosampler vials containing 1 mL hexane with 2.6 mg/L 1,2-DBP. After shaking at 250 rpm for 1 h,

the extractant was injected into the gas chromatograph using an automatic injection system.

2.3. Analytical procedures

Hexane extracts were analyzed for 1,1,1-TCA, 1,1,2,2-TeCA and TCE, with a Hewlett-Packard 6890 series gas chromatograph with a J&W Scientific DB-VRX column (60 m × 0.25 mm i.d. × 1.4 mm film thickness) and an electron capture detector (ECD). A 1 μL volume of the extracts was injected using an autosampler with a split ratio of 20:1. Injector and detector temperatures were 220 and 240 °C, respectively. Oven temperature was kept at 80 °C for 1 min and ramped from 80 to 130 °C at a rate of 5 °C/min and then was isothermal at 130 °C for 1 min. Nitrogen (99.99%) was used as both carrier gas and makeup gas and their flow rates were 4.0 and 60 mL/min, respectively. A headspace sampling procedure was used to analyze 1,2-DCA, and chlorinated products (c-DCE, t-DCE, 1,1-DCE, 1,1-DCA and VC). A 10 mL sample of supernatant was rapidly transferred with a 10 mL gas tight syringe into a 20 mL amber vial. The vial was tightly capped and shaken for 30 min at 250 rpm and then allowed to stand for 5 h at room temperature to equilibrate the gas and liquid phases. Samples of 100 μL were withdrawn from the headspace using a 100 μL gas-tight syringe (Hamilton) and were manually introduced into the injection port of a Trace GC 2000 equipped with a HP-5MS column and a flame ionization detector (FID). The temperatures of the injector and detector were 200 °C. The oven temperature was programmed to be isothermal at 50 °C for 5 min. The column flow rate was 1.5 mL/min and makeup gas was helium at a flow rate of 40 mL/min. The ignition gases were hydrogen and zero air and their flows were 40 and 450 mL/min. Concentrations of all compounds were quantified by comparing peak areas to standard calibration curves.

2.4. Kinetic data and descriptors used in LFERs

The total concentration of target organics in a system with gas, liquid and solid phases can be related to the concentration in the aqueous phase if equilibrium can be assumed among all phases [37].

$$C_{CA,t} = \left(1 + H\frac{V_g}{V_l} + K_s\right)C_{CA,l} = pC_{CA,l} \tag{1}$$

where $C_{CA,t}$ is the total concentration of target organics (mM, total amount in all phases/volume of aqueous phase), $C_{CA,l}$ the concentration of target organics in the aqueous phase (mM), V_g (∼0.3 mL) and V_l (∼23 mL) the volumes of the gas and aqueous phases, respectively, H the dimensionless Henry's constant for target organics ($H_{TCA} = 0.622$ for 1,1,1-TCA, $H_{TeCA} = 0.015$ for 1,1,2,2-TeCA, $H_{DCA} = 0.043$ for 1,2-DCA and $H_{TCE} = 0.419$ for TCE) [20], K_s the solid phase partition coefficient for the target organic (ratio of mass of target organic in the solid phase to mass of target organic in the aqueous phase) and p is the overall partitioning coefficient (total amount in all phases/amount in aqueous phase). The solid phase partition coefficients (K_s) were determined as the average measured in controls without cement ($K_s = 0.067$ for 1,1,1-TCA, $K_s = 0.031$ for TCE). The

loss of target organic compound in controls with only water was shown to be caused by partitioning to the gas phase or to the solid phase, which included the triple-layered septum and the reactor wall [24]. The values of the partitioning factor (p) calculated by Eq. (1) for 1,1,1-TCA and TCE were 1.07 and 1.04, respectively.

A material balance for a batch system with pseudo-first-order degradation rate and phase equilibrium can be expressed as Eq. (2).

$$-\frac{dC_{CA,l}}{dt} = \frac{k}{p}C_{CA,l} = k_{obs}C_{CA,l} \tag{2}$$

where k is the corrected pseudo-first-order rate constant and k_{obs} is the observed pseudo-first-order rate constant. The parameters ($C_{CA,l}^0$, k_{obs}) in Eq. (2) were determined by a non-linear-regression using MATLAB and corrected pseudo-first-order rate constants (k) were obtained by multiplying k_{obs} by p. Corrected pseudo-first-order rate constants by a partitioning factor (k) for CAHs were used to drive the correlations described in this study.

Eberson presented a method for estimating the one-electron reduction potential using Marcus theory that relates the free energy of activation ($\Delta G^{\neq}$) of a single electron transfer reaction to the standard Gibbs free energy ($\Delta rG^{\circ\prime}$) for the reaction [36,38]. This procedure has been applied to calculate reduction potentials of chlorinated hydrocarbons by many researchers [20,31,35,36,39,40]. One-electron reduction potential (E_1°), two electrons reduction potential (E_2°), dissociation bond enthalpy (D_{R-X}), lowest unoccupied molecular orbital energies (E_{LUMO}), aqueous solubility (S_{aq}), free energy of formation of the aqueous-phase radical ($\Delta rG^\circ(R^\bullet)_{(aq)}$) and vertical attachment energies (VAE) have been used as descriptors in correlation analysis by different researchers [20,31,35,36,39–41]. Four different descriptor variables (E_1°, E_2°, D_{R-X} and E_{LUMO}) were used for LFERs development in this work. E_{LUMO} calculated by Scherer et al. using molecular modeling with ab initio methods (Mulliken with 6-31G*) was selected [35].

3. Results and discussion

3.1. Characterization of CAHs in Fe(II)/cement system

This study characterized the degradation kinetics of 1,1,1-TCA, 1,1,2,2-TeCA, TCE* and 1,2-DCA by Fe(II) in cement slurries. Here, the nomenclature "TCE*" is used to designate trichloroethylene that was not an original target compound spiked into a reactor but was produced by degradation of 1,1,2,2-TeCA. Table 1 presents the pseudo-first-order rate constants, products and potential pathways for transformation of 1,1,1-TCA and TCE*. Batch experiments for 1,2-DCA were conducted at two different Fe(II) doses of 39.2 and 196 mM. The concentration of 1,2-DCA was monitored over 14 and 36 days, respectively. The ratio of final concentration to the initial concentration (C/C_0) of 1,2-DCA was reported to be approximately 95% (Fe(II) 196 mM) at the reaction time of 36 days (see Supplementary material). No kinetic data is calculated for 1,2-DCA because it was not degraded. This is consistent with other studies which has shown that 1,2-DCA is not degraded by

Table 1
Pseudo-first-order rate constants and products for degradation of chlorinated ethanes by Fe(II) in cement slurries

Compound	Intermediate major chlorinated products	Minor chlorinated products	Non-chlorinated products	Hypothesized pathway[a]	Fe(II)[b] (mM)	k (h^{-1})	Reaction time	n
1,1,1-TCA	1,1-DCA (>95%)	N/A	Ethane (~6.5%)	Hydrogenolysis/reductive α-elimination	39.2	2.063 (±2.0%)[c]	72 h	13[d]/26[e]
1,1,2,2-TeCA	TCE* (~100%)	cis-DCE, trans-DCE, 1,1-DCE, VC (all negligible)	Acetylene[f]	Dehydrochlorination/reductive β-elimination	39.2	0.0003 (±42%)	123 days	24[d]/55[e]
1,1,2,2-TeCA	TCE* (~100%)	cis-DCE, trans-DCE, 1,1-DCE, VC (all negligible)	Acetylene[f]	Dehydrochlorination /reductive β-elimination	98	0.002 (±20%)	87 days	30[d]/66[e]

The initial concentration of target organics was 0.245 mM. The pH of the solution was not adjusted, reported at around pH 12.5. The distribution of 1,1,1-TCA in the first row was measured at the reaction time of 1440 min. The chlorinated products of 1,1,2,2-TeCA in the second and third row were measured at the last sampling point.

[a] It is a potential pathway to explain the products.
[b] Source of Fe(II) was FeCl$_2$.
[c] Uncertainties represent 95% confidence limits expressed as percent relative to estimate for k.
[d] The number of data points used in non-linear regression.
[e] The number of vials prepared in the degradation experiment, which includes two kinds of controls and reactors with Fe(II).
[f] Acetylene was not measured in this study but it was hypothesized with the production results of chlorinated compounds. More detail was explained in the text.

Table 2
Literature data of dechlorination products and transformation pathway of CAHs in DS/S-Fe(II) process

Parent compound	Intermediate major chlorinated products	Minor chlorinated products	Non-chlorinated products	Hypothesized pathway	Reference
CT[a]	MC (71%)	CM (10%) and CF (3%)	Methane (10%)	Hydrogenolysis	[25]
PCE	N/A	TCE (<1.6%)	Acetylene (82.8%), ethene (16.9%) and ethane (0.3%)	Reductive β-elimination	[24]
TCE	N/A	N/A	Acetylene (79.9%), ethene (16.3%) and ethane (3.7%)	Reductive β-elimination	[26]
1,1-DCE	N/A	N/A	Ethene (88.3%) and ethane (11.7%)	Reductive α-elimination	[26]
VC	N/A	N/A	Ethene (100%)	Hydrogenolysis	[26]

[a] The distribution of CT in the first row was observed at the reaction time of 14 day where the maximum concentration of MC was reported. CF is the first product produced from CT, which will continue to degrade resulting in MC or CM. The distribution of non-chlorinated products for PCE, TCE, 1,1-DCE and VC were obtained at the final reaction time. Total carbon recovery for PCE, TCE, 1,1-DCE and VC are reported as 98.0 [24], 89.3, 70.8 and 93.0% [26], respectively. See the references for more detail conditions.

nanosized Fe(0) [34], by green rust, or by mixtures of green rust and Ag and Cu [18].

The primary product of 1,1,1-TCA degradation was 1,1-DCA, as shown in Table 1. The rapid accumulation of 1,1-DCA indicates that 1,1,1-TCA rapidly undergoes hydrogenolysis, but transformation of 1,1-DCA into other chlorinated products such as CA did not occur over the reaction time period of 1440 min. Small amounts of ethane were observed and other literatures have reported that ethane is probably produced from 1,1,1-TCA via the concerted pathway of reductive α-elimination and hydrogenolysis, not a stepwise hydrogenolysis of 1,1,1-TCA [18,33,42]. 1,1,2,2-TeCA rapidly transformed to TCE* in the control that contained cement and as well as in the reactor with Fe(II) and cement. It has been reported that polychlorinated alkanes undergo dehydrochlorination reactions under basic and neutral pH conditions [31]. TCE* produced from transformation of 1,1,2,2-TeCA by dehydrochlorination will be reduced either by hydrogenolysis or reductive β-elimination. TCE* appears to be degraded by DS/S-Fe(II) through the reductive β-elimination pathway, which leads to acetylene as the final product. Although no attempt was made to measure non-chlorinated products in these experiments, the fact that no significant intermediate chlorinated products (*c*-DCE. *t*-DCE, 1,1-DCE and VC) were detected supports this reaction pathway. Furthermore, acetylene has been reported as the major final product when PCE or TCE was degraded by DS/S-Fe(II) [24,26]. No kinetic data is presented for 1,1,2,2-TeCA because it was not reductively dechlorinated, but rapidly dehydrochlorinated to TCE*. The rate constant for dechlorination of 1,1,2,2-TeCA was replaced with dechlorination rate constant of TCE* in the latter LFERs development.

The ability of Fe(II)-based DS/S process to degrade chlorinated ethylenes, chlorinated ethanes, and chlorinated methanes including PCE, TCE, 1,1-DCE, VC, 1,1,1-TCA, 1,1,2,2-TeCA, 1,2-DCA, CT and CF has been investigated [24–27]. Degradation products and possible pathways of five chlorinated compounds by DS/S-Fe(II) from the literature are summarized in Table 2 (see Supplementary material for kinetic data).

Fig. 1 presents the effects of iron dose and pH on pseudo-first-order rate constants (*k*) for degradation of chlorinated compounds in batch experiments. Data on the kinetics of degradation of 1,1,1-TCA and TCE* were obtained from Jung and Batchelor [28,42] and the data for CT and PCE were obtained by Hwang and Batchelor [24,25]. The rate constants for removal of CT and 1,1,1-TCA were about 2–5 orders of magnitude greater than those for removal of TCE* and PCE. Although the magnitude of the rate constants varied over a wide range, the general effect of iron dose and pH was similar for these four chlorinated compounds. Fig. 1a shows that the pseudo-first-order rate constants increased nearly linearly with Fe(II) dose at low Fe(II) dose and then approached a maximum at high Fe(II) dose. Such behavior is well fitted by a saturation model [42]. Fig. 1b shows that the rate constants increased with pH to a maximum and then decreased at higher pH. The pH where the maximum rate constants were measured varied for the different compounds, but it was generally observed in the range between pH 12.1 and pH 12.6.

Fig. 2 compares values of the pseudo-first-order rate constants (*k*) for eight chlorinated aliphatic hydrocarbons in mixtures of Fe(II) and cement. The rate constants for 1,1,1-TCA and TCE* are shown in Table 1 and those for PCE, TCE, 1,1-DCE, VC, CT and CF* are shown in Supplementary material. Fig. 2 shows that the pseudo-first-order rate constants (*k*) for chlorinated methanes (CT and CF*) and chlorinated ethanes (1,1,1-TCA) are higher than those for chlorinated ethylenes (PCE, TCE, 1,1-DCE and VC) under similar experimental conditions. The reactivity order is as follows: CT > 1,1,1-TCA > CF* > TCE > PCE > TCE* when an Fe(II) dose of about 40 mM was used. The more rapidly degraded chlorinated methanes and ethanes were converted to other chlorinated compounds (CT → CF, 1,1,1-TCA → 1,1-DCA) by hydrogenolysis (Tables 1 and 2). In contrast, the more slowly degraded chlorinated ethylenes (PCE, TCE, 1,1-DCE or VC) were mostly converted to non-chlorinated compounds (acetylene or ethylene) by reductive β-elimination or hydrogenolysis. Many studies have reported that dechlorination of compounds containing a carbon atom that is saturated with chlorine (e.g. CT, 1,1,1-TCA) show more rapid dechlorination rates than those without a saturated carbon (e.g. PCE, TCE, 1,1-DCE), regardless of the type of reductant [20,35,43,44].

The rate constant for TCE* measured in this study was lower than that reported for TCE that was added as a target compound. This might be explained by considering the hydrogen ion (H$^+$) produced in dehydrochlorination. When 1,1,2,2-TeCA is converted to TCE* by dehydrochlorination, H$^+$ and Cl$^-$ are released, which would cause pH to be low in the region near the surface of reactive solids. Released hydrogen ion could affect the surface properties of the active reductants so that its ability to reduce chlorinated compounds can be converted into non-active solid, resulting in decrease of reaction rates.

3.2. Correlation analysis of rate constants

The reactivity of different compounds in electron transfers have been thermodynamically described in terms of linear free energy relationships (LFERs). The values of four descriptors for the organics considered by this research are summarized in Table 3.

Reductive transformation of CAHs shown in Tables 1 and 2 led to various products through the hydrogenolysis or reductive α- or β-elimination pathways. Reductive dechlorination by hydrogenolysis and β-elimination is a two-step process. The first-step is the formation of an alkyl radical by a one-electron transfer (R–X + e$^-$ → R$^{\bullet}$ + X$^-$) and it is known to be the rate-limiting step. For example, the first step for 1,1,1-TCA reduction is a formation of 1,1-dichloroethyl radical (H$_3$C–C·Cl$_2$) [2]. The one-electron reduction potential (E_1°) is often used as a thermodynamic descriptor for dechlorination because the limiting step is the formation of an alkyl radical, which then undergoes another one-electron transfer and protonation. The form of this reaction will determine which pathway is taken (hydrogenolysis, reductive α-elimination, reductive β-elimination and coupling) and that will determine the ultimate product distribution. The two-electron reduction
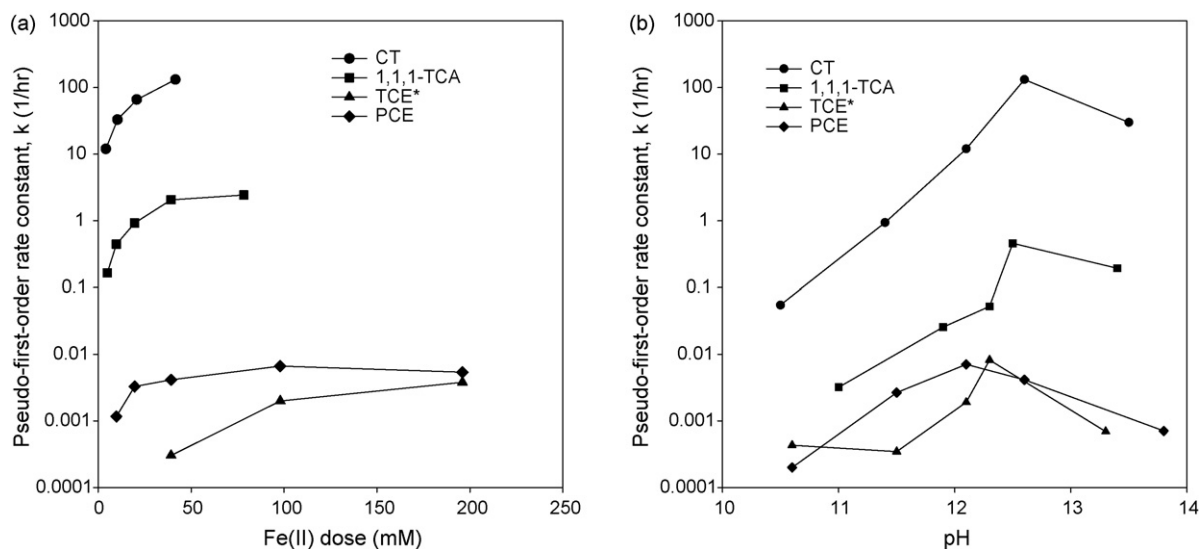
Fig. 1. Effects of different factors on pseudo-first-order rate constants for dechlorination of chlorinated compounds: (a) effect of Fe(II) dose and (b) effect of pH.

potential (E_2°) considers the overall reduction potential for dechlorination whether it occurs by hydrogenolysis (e.g. $CCl_4 + H^+ + 2e^- \rightarrow CHCl_3 + Cl^-$) or reductive β-elimination (e.g. $CCl_3CCl_3 + 2e^- \rightarrow CCl_2CCl_2 + 2Cl^-$). The values of E_2° used in this study were estimated by Vogel et al., and they correspond to reduction by hydrogenolysis [31].

Linear relationships between $\log k$ and E_1°, E_2°, $D_{R–X}$ and E_{LUMO} were assumed as shown in Eq. (3).

$$\log k = a(E_1^\circ, E_2^\circ, D_{R–X} \text{ and } E_{LUMO}) + b \qquad (3)$$

The results of linear regressions between logarithm of pseudo-first-order rate constant ($\log k$) and the four descriptors are shown in Figs. 3–6. These regressions used the kinetic data for the experiments that conducted with Fe(II) doses of about 40 mM and the data for 1,1-DCE and VC were excluded. The regression results for eight compounds including the rate constants of 1,1-DCE and VC, regardless of the experimental conditions (e.g. Fe(II) dose and initial target organic conc.) are presented in Supplementary material. The regression equations calculated in Figs. 3–6 are as follows:
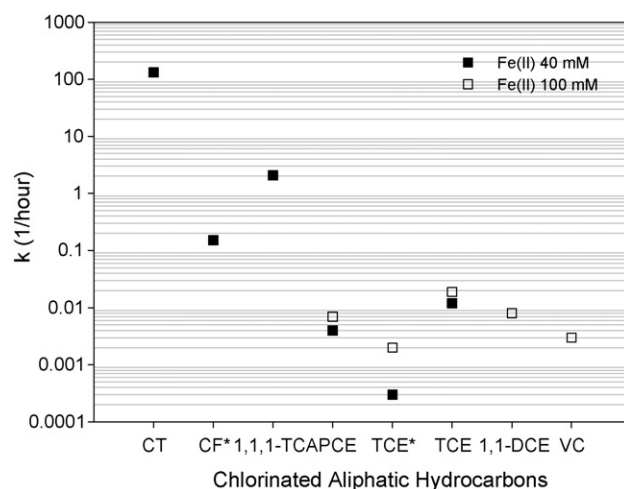

Fig. 2. Pseudo-first-order rate constants for degradation of various chlorinated hydrocarbons by Fe(II) in cement slurries. Experimental conditions are shown in Table 1 and Supplementary material. The solid and open symbols represent rate constants obtained in experiments conducted with Fe(II) doses of 40 and 100 mM, respectively.

Table 3
Thermodynamic descriptors used in LFERs

Parent compound (RX)	Radical[a] (R•)	Hydrogenolysis product[b]	E_1° (V)[c]	E_2° (V)[d]	$D_{R–X}$[e] (kJ/mol)	E_{LUMO}[f] (eV)
CT	Cl_3C•	CF	0.13	0.67	304.1	−3.054
CF[*]	HCl_2C•	MC	−0.23	0.56	322.4[g]	−2.277
1,1,1-TCA	H_3CCl_2C•	1,1-DCA	−0.23	0.57	316.8	−2.160
PCE	Cl_2CClC•	TCE	−0.36	0.58	334.6	−1.689
TCE	Cl_2CHC•	1,1-DCE	−0.91[h]	0.50	357.4	−1.435
1,1-DCE	H_2CClC•	VC	−0.72	0.4		−1.140
VC	H_2CHC•	Ethene	−0.95	0.49		−0.761

[a] Radicals are products of one-electron reduction reaction [36].
[b] Products are those produced by hydrogenolysis pathway, corresponding to E_2° [31].
[c] One-electron reduction potential [35].
[d] Two-electron reduction potential from ref. [31].
[e] Gas-phase bond dissociation enthalpy [20].
[f] Lowest unoccupied molecular orbital(LUMO) energies [35].
[g] Calculated using the data from the ref. [36].
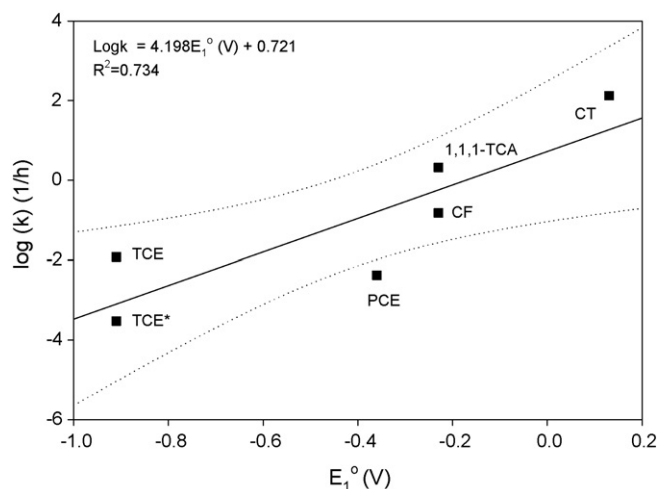[h] One-electron reduction potential [40].

Fig. 3. Correlation between rate constants and one-electron reduction potential (E_1°). The dotted line represents the 95% confidence interval. The equation of linear regression and the R-square value are presented in the corner.
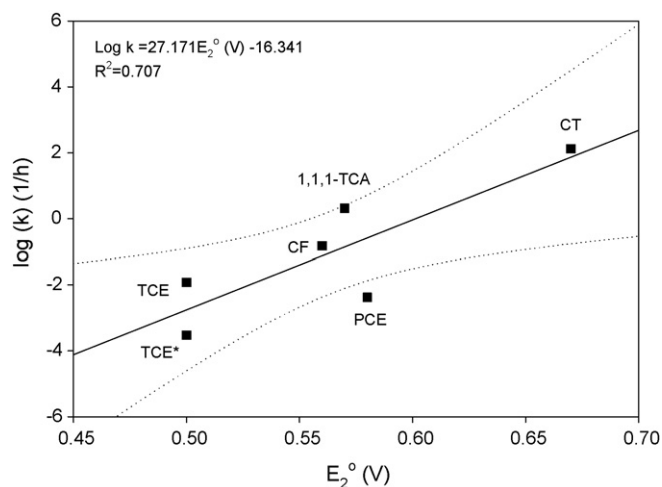

Fig. 4. Correlation between rate constants and two-electron reduction potential (E_2°). The dotted line represents the 95% confidence interval. The equation of linear regression and the R-square value are presented in the corner.
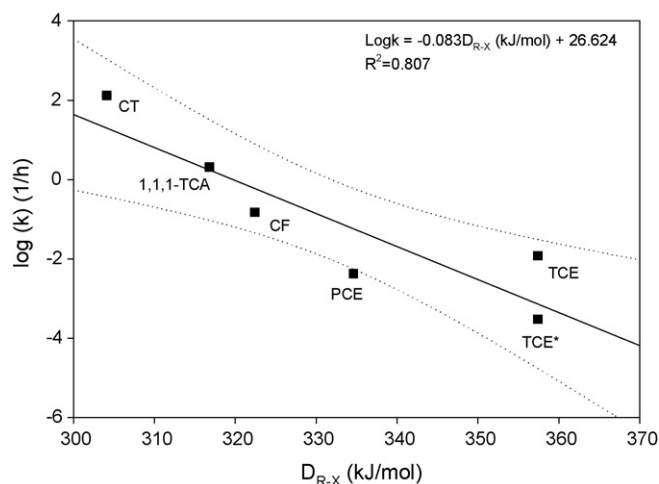

Fig. 5. Correlation between rate constants and gas-phase bond dissociation enthalpy ($D_{R–X}$). The dotted line represents the 95% confidence interval. The equation of linear regression and the R-square value are presented in the corner.
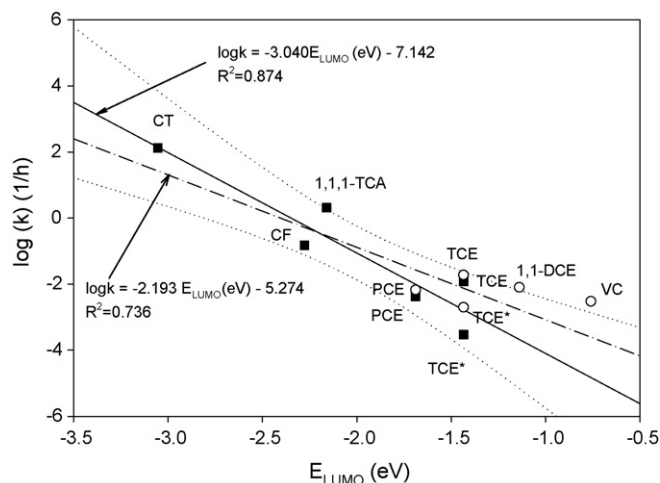

Fig. 6. Correlation between rate constants and lowest unoccupied molecular orbital energies for eight chlorinated compounds. Data represented by a solid square data (■) were obtained from experiments with Fe(II) doses of about 40 mM. Data represented by an open circle (○) were obtained from experiments with Fe(II) doses below 100 mM. The solid regression line fits the data represented by the solid squares (■). The dotted line represents the 95% confidence interval for the solid line. The dash-dotted line is the regression line for all of the data (■ and ○).

$\log k = 4.198E_1^\circ + 0.721$ ($R_2 = 0.734$), $\log k = 27.171E_2^\circ - 16.341$ ($R^2 = 0.707$), $\log k = -0.083D_{R–X} + 26.624$ ($R^2 = 0.807$) and $\log k = -3.040E_{\text{LUMO}} - 7.142$ ($R^2 = 0.874$). Despite the expectation that E_1° would be a good descriptor because of the one-electron transfer to produce an alkyl radical [36], the regression results in this study show that it does not correlate with rate constants better than most of the other descriptors. The molecular properties such as $D_{R–X}$ and E_{LUMO} are fairly well correlated with the rate constants for chlorinated compounds studied here. But these properties are also related to the thermodynamic driving force for one-electron reduction. The correlation coefficient (R) between E_1° and $D_{R–X}$ and between E_1° and E_{LUMO} are 0.924 and 0.986, respectively. $D_{R–X}$ is the enthalpy required for a species R–X to dissociate to $R^\bullet$ and $X^\bullet$ ($D_{R–X} \equiv \Delta H_f(RX)_{(g)} - \Delta H_f(R^\bullet)_{(g)} - \Delta H_f(X^\bullet)_{(g)}$) and reflects the radical stability [36]. $D_{R–X}$ showed the best relationship with the rate constant for dechlorination by iron sulfide reported by Butler and Hayes ($R^2 = 0.82$) [20]. E_2° presented in Table 3 is defined with particular products by hydrogenolysis, but the rate constants for CAHs are not limited to the reaction pathway, hydrogenolysis. Therefore, correlation between rate constants and E_2° was not strong compared to other descriptors. Fig. 4 in Supplementary material shows the linear regression for four compounds (CT, CF*, 1,1,1-TCA and VC), which is known to undergo hydrogenolysis in Tables 1 and 2, and for eight compounds (CT, CF*, 1,1,1-TCA, PCE, TCE, TCE*, 1,1-DCE and VC). The regression result for four and eight compounds with two-electron reduction potential is $\log k = 25.760E_2^\circ - 14.975$ ($R^2 = 0.956$) and $\log k = 16.597E_2^\circ - 10.212$ ($R^2 = 0.533$),   respectively. When the rate constants for the compounds that do not undergo hydrogenolysis were excluded, the R^2 value in correlation with E_2° increased to 0.956. The lowest unoccupied molecular

orbital energy (E_{LUMO}) was the best thermodynamic descriptor ($R^2 = 0.874$) for the rate constants obtained in mixtures of Fe(II) and cement as shown in Fig. 6. Previously, Scherer et al. have reported that the best linear free energy relationships (LFERs) ($R^2 = 0.83$) was shown by the regression between the surface area normalized rate constant (k_{sA}) with E_{LUMO} calculated from ab initio methods [35]. Fig. 6 also shows the importance of using rate constants obtained under identical conditions in LFERs analysis. Fig. 6 shows two sets of data of rate constants for eight chlorinated compounds and their correlations with a descriptor, E_{LUMO}. One data set (■) was obtained from experiments conducted at an Fe(II) dose of 40 mM and its regression line ($\log k = -3.040E_{LUMO} - 7.142$, $R^2 = 0.874$) is shown as a solid line. The other data set (○) was obtained from experiments conducted at an Fe(II) dose of 100 mM. The dash-dot line is the regression line ($\log k = -2.193E_{LUMO} - 5.274$, $R^2 = 0.736$) obtained using both data sets. Although the data for 100 mM was within or near the 95% confidence limits for the regression using the 40 mM data, the R^2 for the combined data ((■) + (○)) was significantly lower than that for the 40 mM data set (■).

4. Conclusion

Previous researches on iron-based degradative solidification/stabilization (DS/S-Fe(II)) have shown that degradation kinetics of chlorinated aliphatic hydrocarbons is determined by Fe(II) dose, pH and initial target organic concentration. Individual batch experiments for 1,1,1-TCA, 1,1,2,2-TeCA and 1,2-DCA were conducted. 1,1,1-TCA was transformed to 1,1-DCA with half-lives of 0.4 h when Fe(II) dose was 39.2 mM. Transformation of 1,1,2,2-TeCA to TCE* was completed within 1 h, even in reactors that contained cement without Fe(II). No transformation of 1,2-DCA was observed, nor 1,1-DCA produced from 1.1.1-TCA during the reaction time investigated. Kinetic data for degradation of 1,1,1-TCA and TCE* determined by this study were combined with kinetic data for degradation of CT, CF*, PCE, TCE, 1,1-DCE and VC by the DS/S-Fe(II) process from literatures. These data were used to investigate the importance of various chemical molecular properties on degradation kinetics. The results showed that the rate constants for chlorinated methanes and chlorinated ethanes were higher than those for chlorinated ethenes under the similar experimental conditions. Rate constants (k) for dechlorination of six compounds (CT, CF*, 1,1,1-TCA, PCE, TCE and TCE*) in mixtures of Fe(II) and cement were correlated with four thermodynamic descriptors (E_1°, E_2°, D_{R-X} and E_{LUMO}). The log of k was found to correlate better with lowest unoccupied molecular orbital energies (E_{LUMO}) ($R^2 = 0.874$) than with other thermodynamic parameter descriptors such as gas-phase bond dissociation enthalpy (D_{R-X}) ($R^2 = 0.807$), one-electron reduction potential (E_1°) ($R^2 = 0.734$) and two-electron reduction potential (E_2°) ($R^2 = 0.707$). However, this conclusion is limited by the limited amount of kinetic data available for the DS/S-Fe(II) process. The purpose of conducting correlation analyses is to develop LFER that are useful predictive models and this requires abundant kinetic data. LFER based on sufficient data would provide

a better perspective on understanding how molecular structure is related to the kinetics of dechlorination in mixtures of Fe(II) and cement.

Supplementary material

The results for 1,2-dichloroethane degradation, kinetic data summarized from the literature and linear regression results for eight chlorinated aliphatic hydrocarbons with one-electron (E_1°) and two-electron reduction potential (E_2°) are available.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2007.06.061.

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