



# Reductive dechlorination of carbon tetrachloride in acidic soil manipulated with iron(II) and bisulfide ion

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## ABSTRACT

Batch and column tests were conducted to investigate the effect of reductant concentration, reductant contact time, and suspension pH on reductive dechlorination of carbon tetrachloride (CT) by soil manipulated with Fe(II) and HS<sup>-</sup>. Kinetic rate constants for the reductive dechlorination increased as the reductant concentrations increased. Fe(II) was more effective reductant than HS<sup>-</sup>, resulting in higher rate constants. The contact time of 1 day for the soil with HS<sup>-</sup> and that of 4 h with Fe(II) showed the highest reaction rates, respectively. The kinetic rate constants increased as the pH of soil suspensions with Fe(II) (5.2–8.0) and HS<sup>-</sup> (8.3–10.3) increased. Soil column with Fe(II) showed larger bed volumes (13.8) to reach a column breakthrough than that with HS<sup>-</sup> (4.0). Fe(II) treatment showed better removal of CT in the soil column with the addition of CaO than HS<sup>-</sup> treatment did. In contrast, HS<sup>-</sup> treatment not producing toxic products could be considered as an environmentally favorable reductant.

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## 1. Introduction

Chlorinated organic compounds are widespread soil and groundwater contaminants which have been widely used as refrigerants, agricultural fumigant, and solvents for metal degreasing and production of semiconductors in industrial processes for several decades [1]. They have been attracted an attention due to their carcinogenic and mutagenic characteristics [2] and persistence in natural environments [3]. They have been steadily observed in common engineered and natural systems. Carbon tetrachloride (CT) is one of the chlorinated organic compounds frequently shown in soil and groundwater at National Priority List Sites of the United States (US) [4]. Under the Safe Drinking Water Act, its maximum contaminant level has been limited to 5 µg L<sup>-1</sup> by US Environmental Protection Agency. CT is a dense non-aqueous phase liquid so that it can sink below water table and form a low-permeable layer [5]. Applying conventional technologies such as pump-and-treat and soil vapor extraction to the sites contaminated with CT has been proved to be ineffective [3].

Natural attenuation has been evaluated as an efficient and cost-effective remedial alternative to degrade chlorinated organic compounds without extensive changes in the contaminated sites. Natural reductants such as iron bearing soil minerals and soil con-

taining the soil minerals under reducing environments can cause reductive degradation of chlorinated compounds [6,7]. Reduced forms of iron and sulfur, i.e. Fe(II) and bisulfide (HS<sup>-</sup>) contained in the soil minerals have been known to play a pivotal role for the reductive dechlorination [6–13]. Reductive capacity of soil can be significantly enhanced by manipulating the soil with Fe(II) and HS<sup>-</sup> and it can be ultimately used to reductively degrade chlorinated compounds during natural attenuation. Several studies have been carried out to facilitate natural attenuation by applying reductants such as Fe(II) and dithionite to soil and groundwater contaminated with chlorinated compounds [14–17]. In practice, the soil has limited intrinsic reductive capacity for the degradation of chlorinated organic compounds [7], thereby adding the reductants to the soil can enhance its capacity and facilitate the degradation during the natural attenuation process. Some researchers have shown that the addition of Fe(II) to soil and soil minerals enhanced the dechlorination kinetics of chlorinated ethylenes [7,10]. Others have identified the effect of sulfur on reductive dechlorination and reported that reduced sulfide can also enhance reductive capacity of soil and soil minerals for chlorinated ethylenes [7,11,18]. Most research showing the enhancement in the reaction kinetics and reductive capacity has been performed under ideal experimental conditions, e.g. pure soil mineral or soil suspensions rather than real soil system. In addition, specific environmental conditions, e.g., acidic soil contaminated by chlorinated compounds, have not been significantly considered for the identification of reductive dechlorination during the modified natural attenuation process. The research to identify the reductive dechlorination in the soil system and to enhance the reduction capacity of soil under such conditions is essential to provide funda-

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mental knowledge to be applied to the development and operation of novel remedial alternatives.

In this study, we conducted batch and column tests to investigate the effect of reductant concentration, reductant contact time, and suspension pH on the reductive dechlorination of CT by real acidic soil and to enhance its reductive capacity by a manipulation with Fe(II) and HS<sup>-</sup>. CT and acidic soil were chosen as representative target compound and soil. CaO was added to acidic soil columns treated with the reductants to increase the pH of the soil and its reductive capacity.

## 2. Experimental

### 2.1. Anaerobic environments

An experimental procedure to obtain anaerobic environments can be easily found in literature [6,16].

### 2.2. Materials

Carbon tetrachloride (CT, 99.5%, Aldrich) and chloroform (CF, 99%, Aldrich) were used as a target compound and a potential by-product, respectively. FeCl<sub>2</sub>·4H<sub>2</sub>O (99%, Aldrich) and NaSH (Aldrich) were used as sources of Fe(II) and HS<sup>-</sup>. Sodium hydroxide (96%, Junsei) was used to adjust and keep the pH of batch samples constant during reaction time. Calcium oxide (98%, Junsei) was used to increase the pH of soil in the column. In addition, sodium bromide (99%, Junsei) was used as a tracer for column experiments and sodium carbonate (99.9%, Merck) was used to make an eluent for ion chromatograph analysis. Stock solutions of CT and CF were prepared by diluting them in methanol (99.9%, Merck). Normal hexane (*n*-hexane, 98.0%, Merck) was used as an extractant and 1,2-dibromopropane (1,2-DBP, 97%, Aldrich) was used as an internal standard for gas chromatograph (GC) analysis.

Soil was taken from the top 10–20 cm on a hill near Korea Institute of Science and Technology. The soil was fully dried in the air for 14 days (d) and screened with a 10 mesh sieve to separate particles less than 2 mm. The soil samples were equilibrated with mixed gases (95% nitrogen and 5% hydrogen) for 2 d in an anaerobic chamber (Coy Laboratory Products Inc., Grass Lake, MI) before use. X-ray diffraction (XRD) analysis (RINT2000 Wide angle goniometer using Cu K $\alpha$  radiation) showed that the soil was mainly composed of quartz (80%) and phyllosilicates (kaolinite and vermiculite, 20%). pH, iron content, and surface area of the soil were 4.0, 2%, and 14.9 m<sup>2</sup> g<sup>-1</sup>, respectively.

### 2.3. Experimental procedures

#### 2.3.1. Batch kinetic experiments

Batch kinetic experiments were conducted by using amber borosilicate glass vials (nominal volume: 20 mL, Kimble) with open-top cap with three layered septum system [6]. The vials were kept in an anaerobic chamber for 2 d to remove oxygen possibly sorbed on the reactor wall and exact amounts of soil (5 g) were transferred to the vials. To manipulate and equilibrate the soil with Fe(II) and HS<sup>-</sup>, the reductant solutions (20 mL of 100 mM Fe(II) and 100 mM of HS<sup>-</sup>, respectively) were transferred to the vials and 8 M and 4 M NaOH solutions were added to adjust suspension pH to 6.3 in Fe(II) system and 9.3 in HS<sup>-</sup> system, respectively. The vials were capped rapidly, taken out of anaerobic chamber, mounted on the tumbler providing an end-over-end rotation at 7 rpm, and mixed for 3 d at room temperature (25 ± 0.5 °C) for complete mixing. Reaction was initiated by spiking 50  $\mu$ L of CT stock solution (240 mM) into the soil suspensions resulting in 0.5 mM of CT. Controls (deaerated deionized water (DDW) + CT, Fe(II) or HS<sup>-</sup> solution + CT, soil + DDW + CT) were prepared to investigate any possible losses of target compound

due to sorption, volatilization, and homogeneous reductive dechlorination in each experiment. The degradation kinetics of CT was determined by sacrificial sampling and monitoring CT concentration in aqueous solution at each sampling point. All samples were prepared in duplicate.

#### 2.3.2. Parametric experiments

Parametric experiments were conducted to investigate the effect of reductant concentration, reductant contact time, and suspension pH on the reductive dechlorination of CT. Firstly, the concentration of Fe(II) or HS<sup>-</sup> in reactors was set to 10, 50, and 100 mM, respectively to identify the reductant concentration effect. The remaining experimental procedures followed the batch kinetic experiments described above, including pH adjustment. Secondly, experiments were conducted to investigate an appropriate contact time to reduce soil by the reductants under different contact times (4 h (h), 9 h, 0.5 d, 1 d, 3 d, and 7 d). The concentrations of Fe(II) and HS<sup>-</sup> were 100 mM, and their suspension pHs were kept constant at 6.3 and 9.3, respectively. Lastly, the experiments were conducted to investigate the effect of pH on the reductive dechlorination. The pHs of soil suspensions treated with Fe(II) were kept constant at 5.2, 6.3, 7.1, and 8.0 by 8 M NaOH solution and those with HS<sup>-</sup> were kept at 8.3, 9.3, and 10.3 by 4 M NaOH solution.

#### 2.3.3. Column experiments

Column experiments were conducted using glass column reactors (2.44 cm inside diameter × 43.8 cm length). The reactors were equilibrated with anaerobic atmosphere for 2 d and packed with the same acidic soil used at batch kinetic experiments resulting in a uniform bulk density of 1.22 ± 0.05 g/cm<sup>3</sup> and total porosity of 0.45 ± 0.05. The column reactors were filled with glass wool, plugged with Teflon adapters at each end, and flushed with nitrogen to remove air pockets. The soil in the columns was then equilibrated with DDW at the flow of 0.07 mL/min for 5 d with a peristaltic pump in the anaerobic chamber. Fe(II) and HS<sup>-</sup> solutions (200 mM) were then introduced into the DDW-saturated soil columns at the same flow rate for four bed volumes, respectively. Control column to check retardation due to sorption of CT was prepared by introducing DDW into column for four additional bed volumes instead of reductants. A non-reactive tracer, standard bromide solution, was prepared for tracer tests to investigate physical characteristics of soil columns. The reductive dechlorination of CT in the soil columns was initiated by introducing standard CT and bromide mixture to the column inlets at the same flow rate under the room temperature. The concentrations of CT and bromide in the reservoir were 1 mM, respectively. A self-collapsible Teflon bag was used as a feeding reservoir to prevent the partitioning of CT to its headspace. The effluents from outlets of control column and soil columns manipulated with Fe(II) and HS<sup>-</sup> were collected at the regular sampling times to monitor the concentrations of target organic compound, transformation products, and tracer. All samples were prepared in duplicate. Reductive capacity of the soil for CT could be limited due to its acidity. In this research, we tried to enhance the reductive capacity by increasing the pH of the soil through the addition of CaO. CaO and soil were mixed at a mass ratio of 1:20 and the mixture was then transferred to the columns.

### 2.4. Analytical methods

Batch reactors at each sampling time were centrifuged at 2535 × g for 20 min and 100  $\mu$ L of supernatant was transferred to an extractant (1.4 mL of *n*-hexane containing 50  $\mu$ M of 1,2-DBP as an internal standard). It was shaken for 30 min using an orbital shaker at 200 rpm. In case of column test, the same preparation was used except the centrifugation. Target compound and products were analyzed by a gas chromatograph with electron capture detector

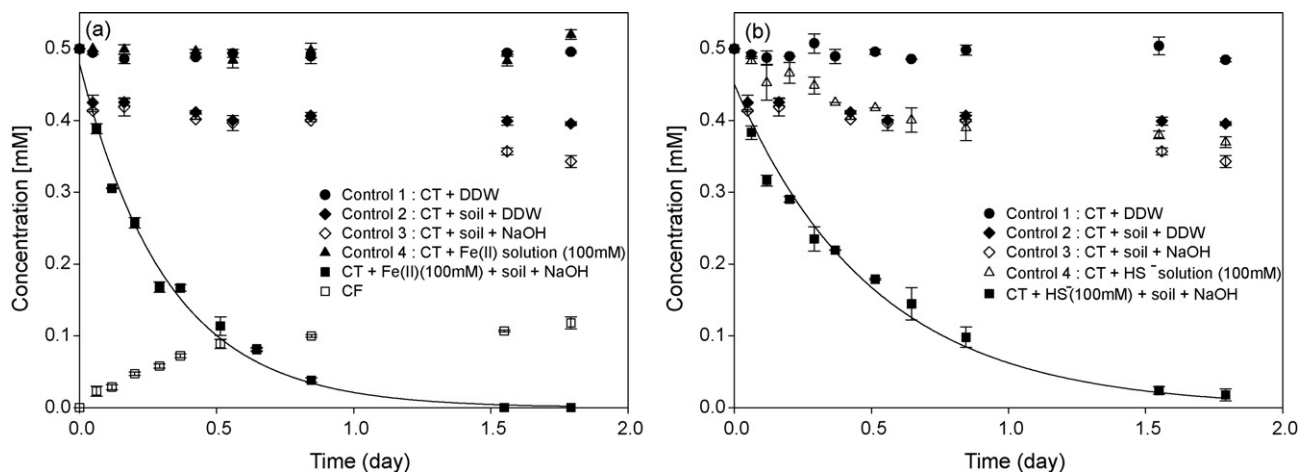


Fig. 1. Reductive dechlorination of CT by soil manipulated with (a) Fe(II) and (b) HS<sup>-</sup>. DDW: deaerated deionized water; CF: chloroform.

(GC/ECD, Hewlett Packard (HP) 5890) equipped with HP-5 column (Agilent Technologies, Inc.: 30 m length, 0.32 mm internal diameter (i.d.), 0.25  $\mu$ m thickness). For the analysis of bromide, an aliquot of outlet sample filtrate by 0.2  $\mu$ m membrane filter (Advantec, Japan) was introduced into the injection port of ion chromatograph (DX-120) equipped with Dionex AS9-HC column (Dionex, Co.: 250 mm  $\times$  4 mm i.d.) and suppressed conductivity detector. To measure the amount of target and transformation products sorbed on soil, septum, and reactor wall, the supernatant was decanted and replaced by 10 mL of extractant. The extractant mixed for 1 h on the orbital shaker at 200 rpm was analyzed as the same way described above.

### 2.5. Data treatment

Reaction kinetics for the reductive dechlorination of CT was described by a pseudo-first-order rate law shown in Eq. (1):

$$\frac{dC_{aq}}{dt} = \frac{-(k \cdot C_{aq})}{(1 + H \cdot (V_g/V_{aq}))} = -\left(\frac{k}{p}\right) \cdot C_{aq} = -k_{app} \cdot C_{aq} \quad (1)$$

where  $C_{aq}$  is the concentration of the target organic compound in aqueous phase,  $k$  is the corrected pseudo-first-order rate constant reported as a rate constant in this study,  $H$  is the dimensionless Henry's law constant for CT (1.20) [19],  $V_g$  and  $V_{aq}$  are volumes of gas and aqueous phases, respectively,  $p$  is the partitioning factor, and  $k_{app}$  is the apparent pseudo-first-order rate constant. The calculated

$p$  for CT in this study was 1.005.  $k_{app}$  was obtained by conducting a nonlinear regression of aqueous phase concentrations of target organic compound using a Gauss–Newton algorithm in MATLAB<sup>®</sup> (MathWorks, Inc.).  $k$  was calculated by multiplying  $p$  and  $k_{app}$  and used to account for the effect of partitioning of CT between the aqueous and gas phases.

The distribution of surface species (complexes/precipitates) during the reductive dechlorination of CT by soil was estimated by an equilibrium model, PHREEQC [20].

## 3. Results and discussion

### 3.1. Reductive dechlorination of CT by soils manipulated with Fe(II) and HS<sup>-</sup>

Fig. 1 shows the reductive dechlorination of CT by soils treated with Fe(II) and HS<sup>-</sup> which was reasonably described by a pseudo-first-order rate law (solid lines). More than 96% of target was reductively degraded in soil suspensions with Fe(II) and HS<sup>-</sup>. The remarkable removal of CT in the soil suspensions with the reductants may be due mainly to the increase of reactive sites on the soil surfaces by forming reactive surface Fe(II) or HS<sup>-</sup> complexes and/or precipitates [6,9,10,18,21,22]. The removal of CT (~20%) in controls 2 and 3 was due to the loss by sorption on the surface of soil. No significant CT removal was observed in control 4 of Fig. 1(a) indicating no reductive degradation of CT in homogeneous Fe(II) solution, while

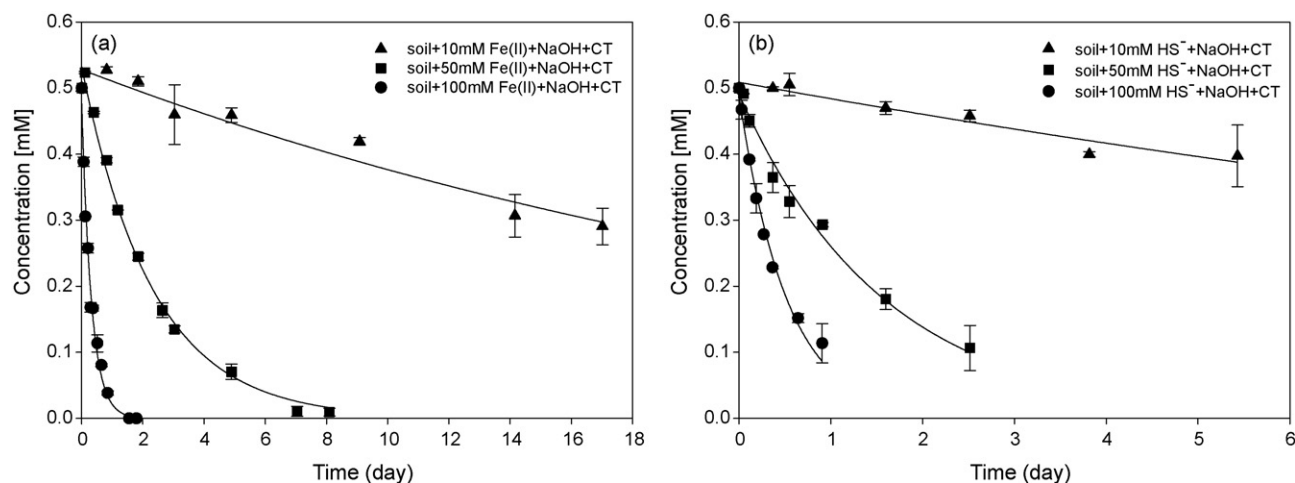


Fig. 2. Reductive dechlorination of CT by soil under different concentrations of (a) Fe(II) and (b) HS<sup>-</sup>.

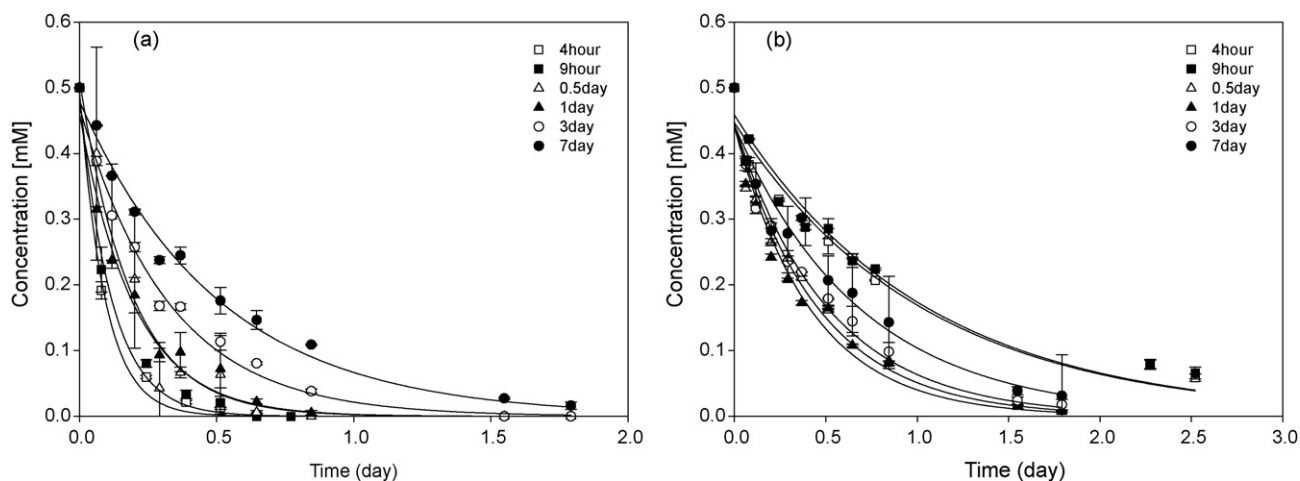


Fig. 3. Reductive dechlorination of CT by soil under different contact times with (a) Fe(II) and (b) HS<sup>-</sup>.

slight CT removal (~25% in 1.8 d) was observed in homogeneous HS<sup>-</sup> solution (Fig. 1(b)). Most chlorinated organic compounds have been known to accompany heterogeneous solid surfaces to trigger reductive dechlorination, however CT can be reductively degraded in bisulfide solution without solid surfaces. The results of previous studies showed that sulfur species can contribute to the reductive dechlorination of CT in aqueous solution [11,23,24], however they did not show better reactivity for the reductive dechlorination of

CT in homogeneous solution than in heterogeneous suspension. The similar trend was also observed at higher HS<sup>-</sup> concentration (>100 mM), indicating that aqueous HS<sup>-</sup> has a limited reactivity for the reductive degradation of CT [11,25]. CF, a transformation product, increased gradually to 0.12 mM in soil suspension with Fe(II) but was not detected above detection limit (0.020 mg/L) in the suspension with HS<sup>-</sup>. Other potential products such as CS<sub>2</sub>, CO<sub>2</sub>, CO, and HCOO<sup>-</sup> [8,11,12] could form in the suspension with HS<sup>-</sup>

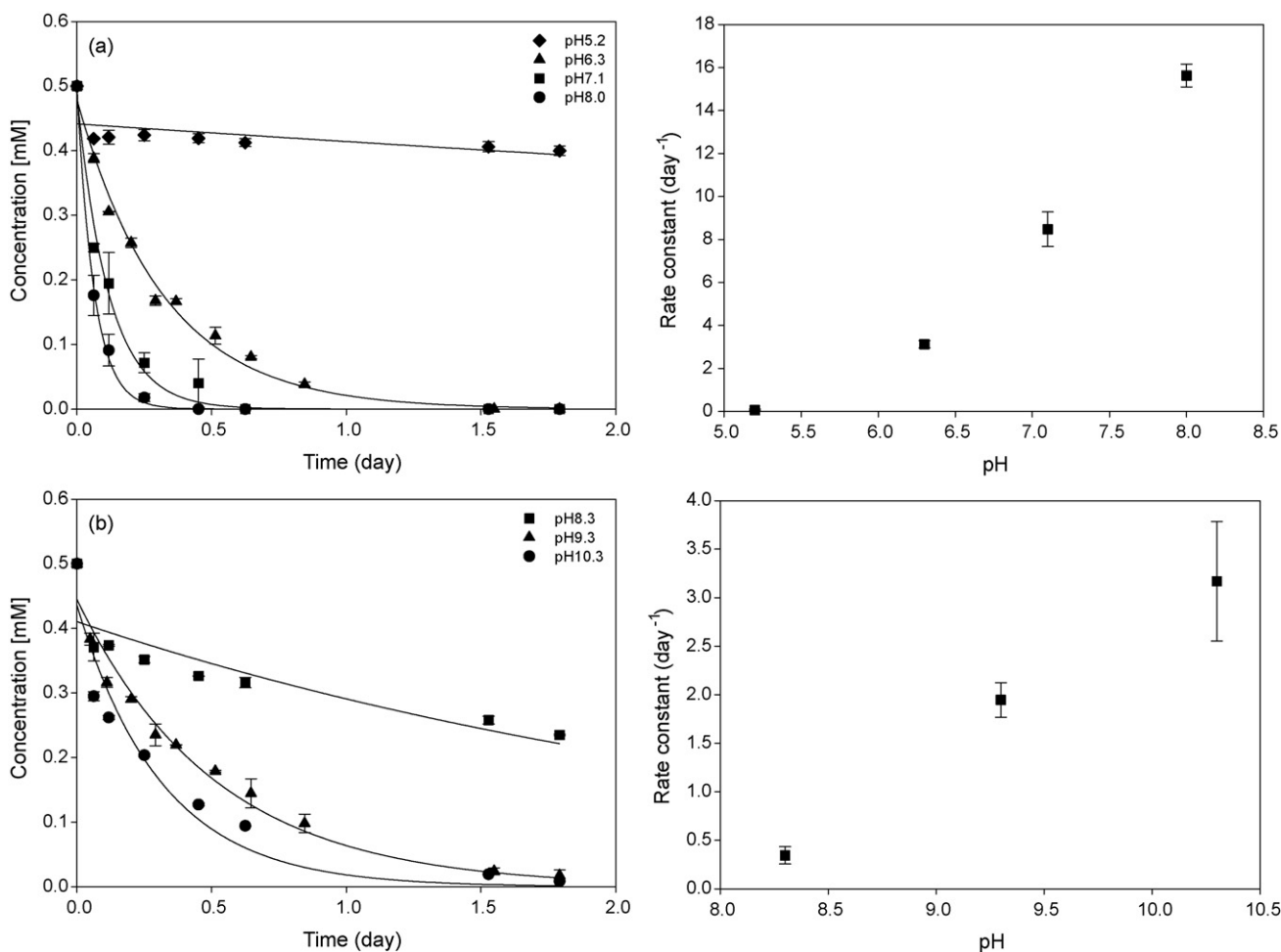


Fig. 4. Reductive dechlorination of CT by soil treated with (a) Fe(II) and (b) HS<sup>-</sup> under different pHs.

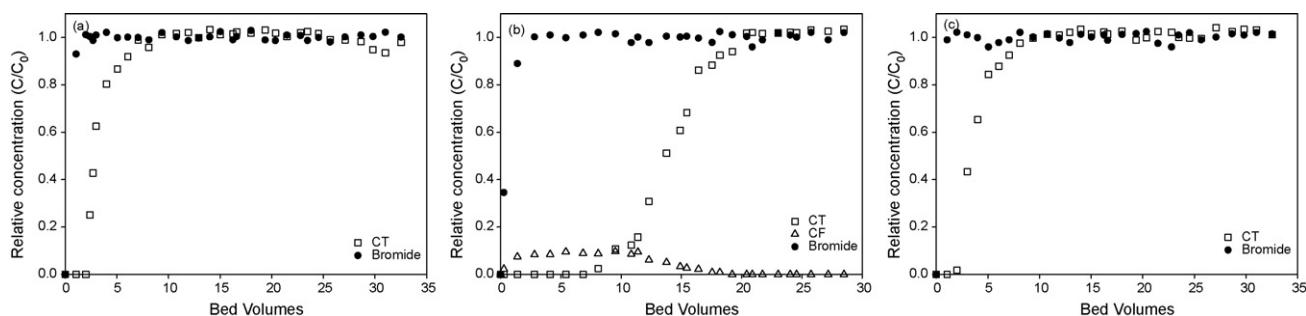


Fig. 5. CT degradation in acidic soil columns filled with (a) soil, (b) soil treated with Fe(II), and (c) soil treated with HS<sup>-</sup>. No pH adjustment. CF: chloroform.

but was not measured in this experiment. Less chlorinated products such as mono- and dichloromethanes were not detected in both suspensions either. Researchers have reported that CF was the main transformation product through hydrogenolysis pathway and that the distribution of products was dependent on reductant types [11–13,26,27]. An estimated rate constant for the reductive dechlorination of CT in soil suspension with Fe(II) ( $3.1219 \pm 0.1720 \text{ d}^{-1}$ ) was greater than that for HS<sup>-</sup> ( $1.9785 \pm 0.1687 \text{ d}^{-1}$ ) indicating a faster degradation kinetics by the addition of Fe(II). The addition of Fe(II) or HS<sup>-</sup> into the soil suspension produces iron or sulfur complexes/precipitates bound on the soil surfaces such as  $\equiv\text{Fe(II)OH}_2^+$ ,  $\equiv\text{Fe(II)OH}$ ,  $\equiv\text{Fe(III)OH}_2^+$ ,  $\equiv\text{Fe(III)OH}$  [28] and  $\equiv\text{FeSH}_2^+$ ,  $\equiv\text{FeSH}$ ,  $\equiv\text{FeS}^-$  [9]. The distribution of these reactive surface species is strongly dependent on the pH of soil suspension. The pHs of soil suspensions treated with Fe(II) and HS<sup>-</sup> were 6.3 and 9.3, respectively, showing that the soil suspension treated with Fe(II) seemed to have more favorable pH condition for the formation of the reactive surface species. Fe(II) could be considered as more effective reducing agent for the reductive degradation of CT in the acidic soil.

### 3.2. Factors affecting the reductive dechlorination kinetics

#### 3.2.1. Influence of reductant concentration

The effect of reductant concentration on the dechlorination kinetics of CT (Fig. 2(a) and (b)) was investigated by monitoring the target compound in the batch system. pH was kept constant at 6.3 and 9.3 in Fe(II) and HS<sup>-</sup> systems, respectively. As the amount of Fe(II) increased, we could observe the faster dechlorination kinetic of CT. The increase of HS<sup>-</sup> also accelerated the dechlorination kinetics in soil suspensions with HS<sup>-</sup>. This may be due to the increase of reactive Fe(II) complexes on the soil surfaces and/or surface

precipitation (i.e., Fe(OH)<sub>2</sub>) enhancing the degradation kinetics of CT [29,30] as the reductant concentrations increase. In case of HS<sup>-</sup> system, reactive iron sulfides may form on the soil surfaces and their contents may increase as HS<sup>-</sup> concentration increases. Reactive iron species on the soil surfaces can also be reduced by HS<sup>-</sup>. The newly formed iron sulfide and/or increased reactive Fe(II) species can degrade CT and increase reaction rate by facilitating electron transfer to chlorinated organic compounds [10,18]. No direct spectroscopic analysis has been conducted to identify the reactive iron and sulfur species on the soil surfaces in this study. The kinetic rate constant of soil treated with Fe(II) showed greater values than that with HS<sup>-</sup> as the concentrations of reductants increased, indicating that Fe(II) was more effective reductant than HS<sup>-</sup> for the reductive dechlorination of CT in the soil suspension.

#### 3.2.2. Influence of contact time for soil with reductants

The contact time for soil with reductants is a very important factor for enhancing reductive capacity of the soil. Fig. 3 shows that effect of contact time for soil with reductants on the reductive dechlorination of CT. Kinetic rate constant for Fe(II) system was typically greater than that of HS<sup>-</sup>, which is consistent with the experimental results above (Section 3.2.1). In case of Fe(II) system, the rate constant decreased as the contact time increased, therefore the optimal contact time for the Fe(II) system can be determined to be 4 h. This may be due to the oxidation of reactive Fe(II) species bound on soil surfaces to Fe(II)/Fe(III) forms caused by an aging effect. Butler and Hayes reported that amorphous iron(II) sulfide was reactive but its reactivity was declined as it was oxidized to greigite (Fe<sub>3</sub>S<sub>4</sub>) caused by the aging effect [10]. They also reported that iron sulfide transformed hexachloroethane (HCA) to tetrachloroethylene but it cannot dechlorinate trichloroethylene (TCE)

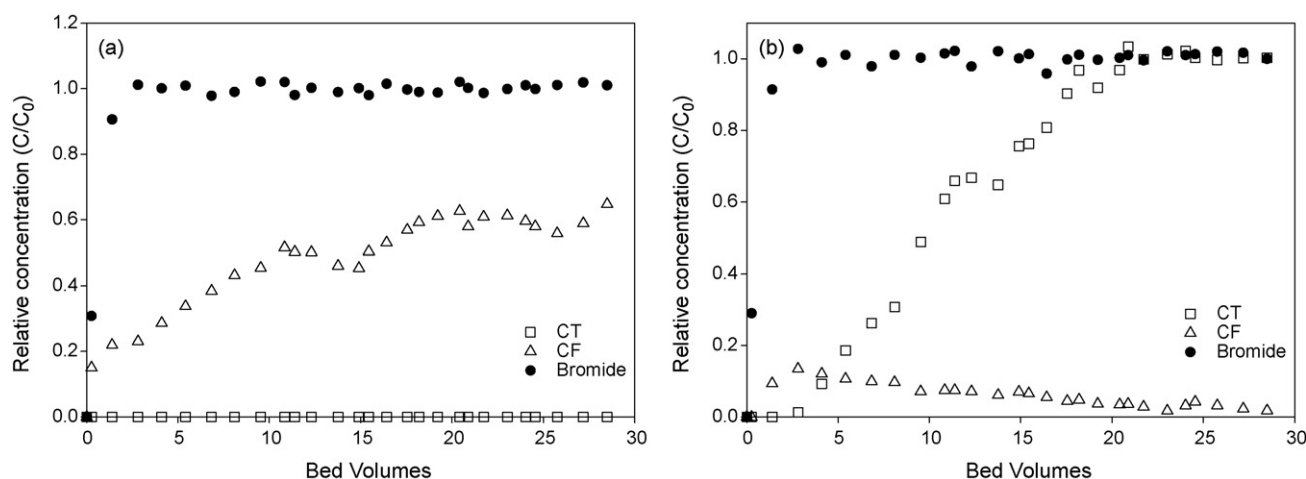
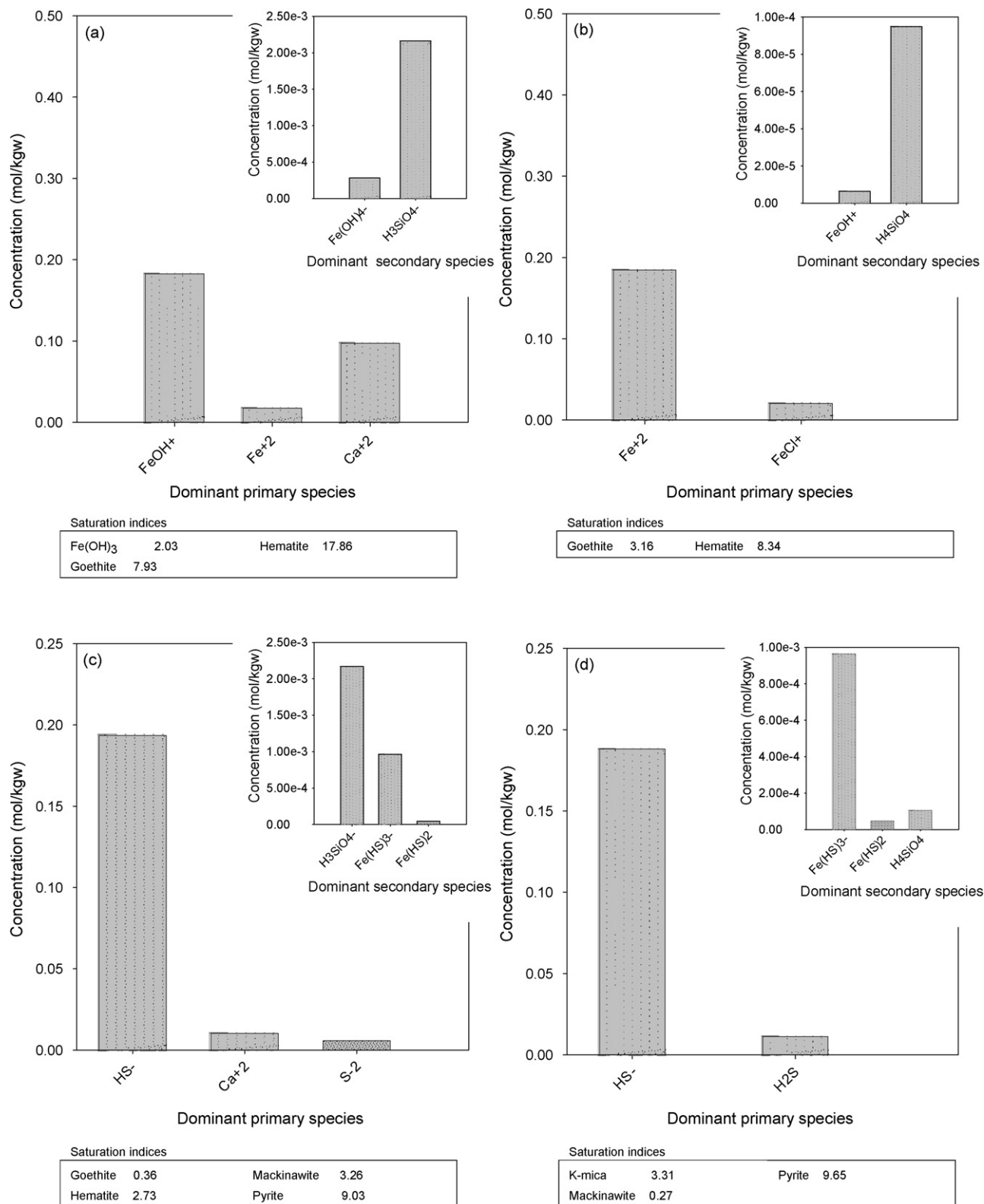


Fig. 6. CT degradation in soil column treated with (a) Fe(II) and (b) HS<sup>-</sup> under pH adjustment. CF: chloroform.

for 6.5 months. This may be due to the lower reduction potential of the aged iron sulfide than that of HCA but higher than that of TCE. As the contact time increased, the rate constant for  $\text{HS}^-$  system showed its peak value at 1 d, showing that 1 d is an optimal contact time for the soil treated with  $\text{HS}^-$ . The kinetics for the reduc-

tion of soil forming reactive surface complexes/precipitates by  $\text{HS}^-$  looked much slower than that by  $\text{Fe(II)}$ . The reductive capacity of soil treated with  $\text{HS}^-$  decreased, as the contact time increased after its peak value at 1 d. This may be due to the aging effect described above.



**Fig. 7.** Distribution of dominant (primary and secondary) chemical species on the soil surfaces predicted by PHREEQC.  $\text{Fe(II)}$  system (a) with and (b) without pH adjustment;  $\text{HS}^-$  system (c) with and (d) without pH adjustment.

### 3.2.3. Influence of pH

The effect of pH on the degradation kinetics of CT by soils manipulated with Fe(II) and HS<sup>-</sup> is shown in Fig. 4. Sodium hydroxide was used to adjust suspension pHs, instead of organic buffers because they may affect the dechlorination kinetics of CT and distribution of transformation products [29]. The increase of pH increased the dechlorination rate of CT in the Fe(II) system (Fig. 4a). Suspension pH can significantly affect the surface charge of the soil, i.e. when the pH is higher than point of zero charge (pHpzc), soil surface is negatively charged and can adsorb more Fe(II) resulting in the formation of reactive surface complexes/precipitates. This may explain the proportional increase of rate constants as the increase of pH shown in Fig. 4(a). Fig. 4(b) shows the effect of pH on the dechlorination kinetics of CT in the HS<sup>-</sup> system. The rate constants also proportionally increased with increasing pH in HS<sup>-</sup> system. HS<sup>-</sup> can produce hydrated iron sulfide species on the soil surfaces which may be oxidized to hydrophobic elemental sulfur by transferring electrons to CT, resulting in more sorption of CT on the surfaces and facilitating the electron transfer [25]. As the pH increased, more reactive iron sulfide and hydroxide species can form on the soil surfaces. The surfaces can be further deprotonated and more reactive deprotonated surface species (e.g., -OH<sup>-</sup> and -O<sup>2-</sup>) can be produced for the reductive dechlorination of CT. Consequently, the reductive dechlorination of CT in the HS<sup>-</sup> system could be accelerated by faster electron transfer at high pH through these processes.

### 3.3. Enhanced reductive dechlorination of CT in soil column

#### 3.3.1. Degradation of CT in soil columns treated by Fe(II) and HS<sup>-</sup>

Fig. 5 shows CT removal in soil columns with and without treatment of Fe(II) and HS<sup>-</sup> under no pH adjustment. There was no color change in the soil column with Fe(II), while soil color changed to black in the column with HS<sup>-</sup>, indicating the formation of iron sulfide. No XRD analysis has been conducted to confirm its formation. The bed volumes (BV) to reach a column breakthrough of CT assuming it to be the relative concentration ( $C/C_0$ ) of 0.5 were 2.8 (control), 13.76 (Fe(II)), and 4.0 (HS<sup>-</sup>), respectively, which indicates that the soil column treated with Fe(II) has the greatest reductive capacity for CT followed by column treated with HS<sup>-</sup> and control. This result is very similar to that of batch experiment above. The removal of CT in control column (Fig. 5(a)) is due mainly to the adsorption on the soil surfaces. The removal caused by intrinsic reduction capacity of the soil surfaces did not seem to play a pivotal role because no transformation products were observed during the control test. CT was reductively degraded to CF in the soil column treated with Fe(II) (Fig. 5(b)), while CT was removed but CF was not detected under the detection limit in the column treated with HS<sup>-</sup> (Fig. 5(c)). The result indicates that CT was reductively degraded in the column treated with Fe(II). In the soil column treated with HS<sup>-</sup>, CT may be reductively transformed to potential transformation products (CS<sub>2</sub>, CO<sub>2</sub>, CO, and HCOO<sup>-</sup>) during the reductive dechlorination of CT by sulfides. We did not measure the transformation products in this experiment.

#### 3.3.2. Degradation of CT in soil columns treated by Fe(II) and HS<sup>-</sup> under pH adjustment

Fig. 6 shows the reductive dechlorination of CT in the treated soil columns with pH adjustment with CaO. Relative concentration ( $C/C_0$ ) of CT for the soil column treated with Fe(II) under pH adjustment was almost zero and that of CF increased to 0.65 at the BV of 28.49 indicating no significant loss in its full reductive capacity during the column test. The relative concentration of CT for the soil column treated with HS<sup>-</sup> reached 1 at BV of 20.88 and the amount of CF produced in HS<sup>-</sup> system was much smaller than that in Fe(II) system. The results obtained from pH adjustment tests are quite different to those under no pH adjustment (Fig. 5(b) and (c)), i.e. the BV

of HS<sup>-</sup> system under pH adjustment with CaO to reach at  $C/C_0 = 1$  was twice longer than that under no pH adjustment. The column breakthrough for HS<sup>-</sup> system with CaO was 9.52 BV and that for Fe(II) with CaO cannot be determined until 28.49 BV. CaO, initially added into soil column to buffer the acidic soil, was reported to catalyze the formation of reactive soil minerals such as sulfate green rust (Fe<sup>II</sup><sub>4</sub>Fe<sup>III</sup><sub>2</sub>(OH)<sub>12</sub>SO<sub>4</sub>·yH<sub>2</sub>O) crystals in hematite/Fe(II) system [3]. Breakthrough curves of bromide and CT observed in the control and reduced soil columns showed that retardation occurred during the degradation of CT in the columns.

Fig. 7 shows the distribution of surface chemical species predicted by PHREEQC. Fig. 7(a) shows that FeOH<sup>+</sup> and Fe(OH)<sub>4</sub><sup>-</sup> complexes on the soil surfaces formed by the decrease of Fe(II) were dominant reactive surface species. These species can contribute to the enhancement of reductive capacity of soil treated with Fe(II) under pH adjustment for the reductive dechlorination of CT. However, the soil column without pH adjustment contained very low content of iron hydroxide species, which did not significantly affect the acceleration of the dechlorination kinetics (Fig. 7(b)). We also estimated the contents of iron sulfide complexes (i.e., Fe(HS)<sub>2</sub> and Fe(HS)<sub>3</sub><sup>-</sup>) and reactive precipitates such as mackinawite (FeS) formed on the soil surfaces in the columns treated with HS<sup>-</sup> with and without pH adjustment. The contents of iron sulfide complexes in each column were very low and similar but the column with pH adjustment had 12 times higher content of mackinawite than that without pH adjustment, explaining the faster reaction kinetics of the column with pH adjustment (Fig. 7(c) and (d)). This indicates that the pH adjustment with CaO is a very significant treatment to enhance the degradation kinetics for the reductive dechlorination of CT by forming reactive metal hydroxide species in the acidic soil column treated with reductants.

## 4. Conclusions

The research was conducted to investigate the effect of significant geochemical factors on the dechlorination kinetics of CT by soils treated with Fe(II) and HS<sup>-</sup>. Batch kinetic results for reductant concentration effect on the dechlorination kinetics showed a significant enhancement of kinetic rates as the reductant concentration increased to 100 mM. This indicates that a proper amount of reductant to accelerate the dechlorination kinetics can be estimated based on the experimental results and applied to the sites contaminated with CT during the natural attenuation. The results for contact time for soil with the reductants to enhance system reactivity represented different tendency. Fe(II) system showed the decreased kinetic rate with increasing the contact time, while HS<sup>-</sup> system have an optimal contact time during the reaction period. Aging effect should be considered to obtain best reactivity of the reduced soil, when the reductants are injected to the sites contaminated with CT. Longer contact time accompanying the aging effect cannot ensure better reductive degradation of CT. The reductive dechlorination rates increased as the suspension pH increased in each soil system. Proper soil pH needs to be estimated and retained to maximize the reactivity of reduced soil and to avoid an excessive use of buffering agent before performing the reductant injection to the sites. The soil treated with Fe(II) showed higher reactivity than that with HS<sup>-</sup>, indicating that Fe(II) treatment could be more effective for the remediation of acidic soil contaminated with CT. In contrast, HS<sup>-</sup> treatment not producing a toxic product such as CF can be considered as an environmentally favorable treatment so that it could be better applied for the remediation of the contaminated soil. We observed similar tendencies of pH effect and reductant type on the dechlorination kinetics in continuous column test. Soil column treated with Fe(II) showed higher reactivity than that with HS<sup>-</sup> and the pH increase by CaO addition increased

the reactivity of reduced soils. The distribution of reactive surface species ( $\text{FeOH}^+$ ,  $\text{Fe}(\text{OH})_4^-$ , and  $\text{FeS}$ ) during the reductive dechlorination was estimated by an equilibrium model, PHREEQC, which can provide basic knowledge to properly operate the modified natural attenuation and in situ redox manipulation.

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