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# Abiotic Reductive Dechlorination of Chlorinated Ethylenes by Iron-Bearing Soil Minerals. 2. Green Rust

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Abiotic reductive dechlorination of chlorinated ethylenes by the sulfate form of green rust (GR<sub>SO4</sub>) was examined in batch reactors. Dechlorination kinetics were described by a modified Langmuir–Hinshelwood model. The rate constant for reductive dechlorination of chlorinated ethylenes at reactive GR<sub>SO4</sub> surfaces was in the range of 0.592 (±4.4%) to 1.59 (±6.3%) day<sup>-1</sup>. The specific reductive capacity of GR<sub>SO4</sub> for target organics was in the range of 9.86 (±10.1%) to 18.0 (±4.3%) μM/g and sorption coefficient was in the range of 0.53 (±2.4%) to 1.22 (±4.3%) mM<sup>-1</sup>. Surface area-normalized pseudo-first-order initial rate constants for chlorinated ethylenes by GR<sub>SO4</sub> were 3.4 to 8.2 times greater than those by pyrite. Chlorinated ethylenes were mainly transformed to acetylene, and no detectable amounts of chlorinated intermediates were observed. The rate constants for the reductive dechlorination of trichloroethylene (TCE) increased as pH increased (6.8 to 10.1) but were independent of solid concentration and initial TCE concentration. Magnetite and/or maghemite were produced by the oxidation of GR<sub>SO4</sub> by TCE. These findings are relevant to the understanding of the role of abiotic reductive dechlorination during natural attenuation in environments that contain GR<sub>SO4</sub>.

## Introduction

The well-known prevalence (1, 2) and persistence (3, 4) of chlorinated ethylenes in natural environments have driven substantial research to characterize the reductive dechlorination of chlorinated ethylenes under various environmental conditions. Substantial research on biodegradation of chlorinated organics has been conducted for the last few decades (5, 6). Recently, the effort to characterize natural reductants causing abiotic reductive dechlorination has attracted attention not only due in part to the limitations of biodegradation but also due to the potential interactions between biotic and abiotic processes. Sulfides (7, 8), natural organic matter (8, 9), macrocycles (10, 11), and mineral surfaces (12, 13) in natural environments have been reported to increase the dechlorination rates of chlorinated organics by acting as electron donors and mediators/carriers. Research has been conducted to measure the reactivity of iron-bearing

soil minerals. It has been reported that iron sulfide minerals (e.g., pyrite (12, 14), troilite (15), and mackinawite (16, 17)) and iron oxide minerals (e.g., magnetite (15, 18, 19)) can transform chlorinated ethanes and ethylenes primarily to non-chlorinated products (acetylene, ethylene, ethane). The reduction of nitrobenzenes and chlorinated ethylenes at iron oxide surfaces has been reported to be accelerated by the addition of Fe(II) (13, 18). Green rust (GR; [Fe<sup>II</sup><sub>6-x</sub>Fe<sup>III</sup><sub>x</sub>(OH)<sub>12</sub>]<sup>x+</sup>[(A)<sub>x/n</sub>·yH<sub>2</sub>O]<sup>x-</sup>) is a mixed Fe(II)-Fe(III) hydroxide that has a pyroaurite-type structure consisting of brucite-like layers i.e., positively charged trioctahedral metal-hydroxide layers and negatively charged interlayer of anions and water molecules (20). It has attracted attention because it may be produced in both natural (21) and engineered systems (22, 23) and it can reduce many inorganic and organic contaminants. GR has been reported to occur naturally in reductomorphic soils (21) and during the corrosion of iron, where it is believed to be an intermediate in the formation of end products such as goethite, lepidocrocite, or magnetite (24, 25). It has been reported that nitrate (26, 27) and Cr(VI) (28) are transformed by suspensions of sulfate GR (GR<sub>SO4</sub>; 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) and carbonate GR (GR<sub>CO3</sub>; Fe<sup>II</sup><sub>4</sub>Fe<sup>III</sup><sub>2</sub>(OH)<sub>12</sub>CO<sub>3</sub>·yH<sub>2</sub>O) at similar or higher rates than those reported for microorganisms. Carbon tetrachloride (CT), hexachloroethane (HCA), pentachloroethane (PCA), and tetrachloroethylene (PCE) have been shown to undergo reductive transformation in the presence of GR<sub>SO4</sub> (18, 29, 30). However, no significant research on the reductive dechlorination of chlorinated ethylenes by GR has been systemically conducted to date.

The characterization of reductive dechlorination of chlorinated ethylenes by iron-bearing soil minerals is important because it can produce basic knowledge that could be used to predict the fate of chlorinated ethylenes in natural environments and to effectively operate remedial technologies. Although GR has not been reported as being present in natural systems contaminated with chlorinated organics, it could be formed in such systems under iron-reducing conditions. The objective of this research was to characterize the kinetics of reductive dechlorination of chlorinated ethylenes by the sulfate form of GR and to identify the products formed by the reaction. A series of chlorinated ethylenes (PCE, trichloroethylene (TCE), *cis*-dichloroethylene (*cis*-DCE), and vinyl chloride (VC)) were used as target chlorinated organics.

## Experimental Section

**Materials.** Anaerobic environments required for the preparation of reagents and samples were previously described (31). Chlorinated organics used for this research were ACS grade: PCE (99.9%, Sigma), TCE (99.6%, Sigma), *cis*-DCE, (97.0%, Sigma), *trans*-dichloroethylene (*trans*-DCE, 98%, Sigma), 1,1-dichloroethylene (1,1-DCE, 99.0%, Sigma), and VC (20 000 mg/L, Sigma). Standard gases of ethane (99.0%), ethylene (1.0%), and acetylene (1000 mg/L) (Scott Specialty Gases) were used for the analysis of non-chlorinated transformation products. Methanol (99.8%, HPLC grade, EM) was used as a diluent for target organic stock solutions.

Deaerated deionized water (ddw) was prepared by deoxygenating 18 MΩ·cm deionized water with 99.99% nitrogen for 2 h and then by deoxygenating with the mixed gases in an anaerobic chamber for 12 h (31). A bicarbonate buffer (10 mM) was prepared by adding an exact amount of NaHCO<sub>3</sub> (100.3%, Sigma) to ddw. Acid and base solutions were prepared by diluting H<sub>2</sub>SO<sub>4</sub> (95.7%, Sigma) and NaOH (97.0%, EM) with ddw. The following biological buffers were

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used to investigate the effect of pH on the dechlorination kinetics. They were purchased from Sigma and were ACS or higher grades: 2-[N-Morpholino]ethanesulfonic acid (MES,  $pK_a = 6.1$ , for pH 6.8 suspension), 3-[N-Morpholino]propanesulfonic acid (MOPS,  $pK_a = 7.2$ , for pH 7.3 suspension), mixture of Tris[hydroxymethyl]aminomethane and Tris[hydroxymethyl]aminomethane hydrochloride (Tris,  $pK_a = 8.1$ , for pH 8.1 and 9.2 suspensions), and 3-[cyclohexylamino]-1-propanesulfonic acid (CAPS,  $pK_a = 10.4$ , for pH 10.1 suspension). Aqueous solutions (0.05 M) were prepared by adding exact amounts of buffers to ddw and adjusting to the exact pH with 1 M NaOH solution.

GR<sub>SO4</sub> was prepared by a method modified by Koch et al. (26) in which a solution of FeSO<sub>4</sub> is partially oxidized by contact with air. The suspension of dark blue-green precipitates was introduced into an anaerobic chamber immediately after GR<sub>SO4</sub> synthesis and washed several times with ddw until no Fe(II) was detected in supernatant. Because GR<sub>SO4</sub> would be oxidized during freeze-drying, it was spread on the plate and dried under an anaerobic atmosphere. The dried GR<sub>SO4</sub> was ground with pestle and mortar, sieved (<63  $\mu\text{m}$ ), and stored in the anaerobic chamber for no more than 7 days before being used in order to preclude an aging effect (32). The characteristics of GR<sub>SO4</sub> used for this research were identified previously (31). The Fe(II) and Fe(III) contents of GR<sub>SO4</sub> were 464 and 212 mg/g. The surface area measured by ethylene glycol monoethyl ether (EGME) method in the anaerobic chamber was 86.3 m<sup>2</sup>/g. The identity and purity of synthesized GR<sub>SO4</sub> was confirmed by X-ray diffraction (XRD) (See Figure S-1, Supporting Information).

**Experimental Procedures.** Batch kinetic experiments to investigate the dechlorination kinetics of target organics and transformation products in GR<sub>SO4</sub> suspension were conducted as previously described (31). The experiments were conducted in 20-mL glass vials at room temperature ( $22 \pm 0.5$  °C). Exact amounts of GR<sub>SO4</sub> were transferred to the vials followed by a bicarbonate buffer in the anaerobic chamber. The mass ratio of solid to water was 0.007 resulting in the surface area concentration of 604 m<sup>2</sup>/L. pH of GR<sub>SO4</sub> suspensions was adjusted to 7 by adding the acid or base solutions and kept constant during the experiments. A partial conversion of GR<sub>SO4</sub> to mixed GR<sub>CO3</sub>/GR<sub>SO4</sub> could occur by the substitution of CO<sub>3</sub><sup>2-</sup> for SO<sub>4</sub><sup>2-</sup> in GR<sub>SO4</sub>, but the anion exchange was not observed under the experimental condition employed for the experiments. Target organic stock solutions (10–50  $\mu\text{L}$ ) were spiked into GR<sub>SO4</sub> suspensions to obtain initial concentrations of 0.19 mM PCE, 0.25 mM TCE, 0.41 mM *cis*-DCE, and 0.40 mM VC.

Based on the results of batch kinetic experiments, TCE was chosen as a target chlorinated organic to investigate the effects of pH, concentration of GR<sub>SO4</sub>, and concentration of target organic on dechlorination kinetics. For a batch experiment where pH was an experimental parameter, 0.05 M biological buffers were added to vials to keep pH of GR<sub>SO4</sub> suspensions constant throughout the experiment. The pH range investigated was 6.8 to 10.1 and mass ratio of solid to liquid in the suspension was 0.01. Controls were prepared by spiking TCE to aqueous solutions of the biological buffers. To identify the effect of GR<sub>SO4</sub> concentration, exact amounts of GR<sub>SO4</sub> were added to vials at mass ratios of 0.001 to 0.04. Tris buffer solution (0.05 M) was added to keep suspension pH at 8.1. The experiment started by spiking 10  $\mu\text{L}$  of 0.76 M TCE stock solution to GR<sub>SO4</sub> suspension to provide an initial concentration of 300  $\mu\text{M}$ . To investigate the effect of target organic concentration, 5 to 20  $\mu\text{L}$  TCE stock solutions were spiked to GR<sub>SO4</sub> suspension with mass ratio of 0.01 at pH 8.1 resulting in 4 levels of TCE concentrations (150, 300, 450, and 600  $\mu\text{M}$ ). All experiments were conducted at room temperature and samples for analysis were prepared in the same way described in the batch kinetic experiments. The

concentration of target organic in aqueous solution was monitored at each sampling time.

A batch experiment was also conducted in 200-mL amber bottle (Kimble) with open-top cap and three-layered septum system to identify oxidation products of GR<sub>SO4</sub> after reaction with TCE. An exact amount of pure TCE was spiked to GR<sub>SO4</sub> suspension including a bicarbonate buffer. The initial concentration of TCE was 0.22 M and mass ratio of GR<sub>SO4</sub> was 0.01. Controls were prepared in the same way without TCE. pH value of the suspension was adjusted and kept constant at 7 as described for the batch kinetic experiments. Reaction was initiated by mixing the bottle in an anaerobic chamber using an orbital shaker at 180 rpm at room temperature. The oxidation products of GR<sub>SO4</sub> were identified and Fe(II) and Cl<sup>-</sup> concentrations in aqueous solution and GR<sub>SO4</sub> were monitored at each sampling time. All the controls and samples for this research were run in duplicates or triplicates.

**Analytical Procedures.** Fe(II) and total iron in aqueous solution and in GR<sub>SO4</sub> suspension were measured by using a Hewlett-Packard (HP) 8452A Diode-Array Spectrophotometer using the Ferrozine method (33). Aliquots of the suspension (2.5 mL) were rapidly withdrawn with a 5-mL gastight syringe (Hamilton) and filtered with a 0.2  $\mu\text{m}$  membrane filter (Whatman). Each 1 mL filtrate was transferred to polypropylene tube (VWR) and diluted with 1 to 9 mL ddw. GR<sub>SO4</sub> suspension (0.5 mL) without separation of oxidation products was transferred to 1.2 M acid solution (9.5 mL) and shaken for 5 min to extract iron. A 10% hydroxylamine solution was added to the sample to reduce Fe(III) to Fe(II) for the measurement of total iron.

The product of the reaction of TCE with GR<sub>SO4</sub> was identified by XRD. An aliquot of GR<sub>SO4</sub> suspension was withdrawn with a 5-mL gastight syringe and filtered with a 0.2  $\mu\text{m}$  membrane filter. The filtered GR<sub>SO4</sub> sample was treated with 1:1 (v:v) glycerol solution to minimize oxidation by atmospheric oxygen (26, 27) and was scanned between 0° and 70° 2 $\theta$  with a scan speed of 1° 2 $\theta$ /min by a Rigaku automated diffractometer (Cu K $\alpha$  radiation).

Chlorinated ethylenes and chlorinated transformation products were measured by using a HP G1800A gas chromatography detector (GCD) equipped with a DB-VRX column and a mass spectrometer detector. After extraction of supernatant and GR<sub>SO4</sub> with pentane on an orbital shaker at 250 rpm, an aliquot of extractant (1  $\mu\text{L}$ ) was injected into an injection port at a split ratio of 30:1. The extraction efficiency of target organics for aqueous samples was generally greater than 92% and that for solid samples was greater than 88%. Non-chlorinated transformation products (C<sub>2</sub> hydrocarbons) were measured by using a HP 6890 gas chromatograph (GC) equipped with a GS-Alumina column and a flame ionization detector. After headspace sampling, an aliquot of gas sample was introduced into the injection port at a split ratio of 5:1. The concentrations of C<sub>2</sub> hydrocarbons in headspace were converted to those in aqueous solution by using dimensionless Henry's law constants (34, 35).

Chloride was measured by using a Dionex 500 ion chromatograph (IC) equipped with AS9-HC column and conductivity detector. An aqueous sample was filtered with a 0.2  $\mu\text{m}$  membrane filter, and an aliquot amount of filtrate was introduced to the injection port.

## Results and Discussion

**Treatment of Kinetic Data.** The dechlorination kinetics of chlorinated ethylenes in GR<sub>SO4</sub> suspension was similar to that observed in pyrite and magnetite suspensions (36). Target organics rapidly disappeared initially, followed by more slow removals and ultimately approached constant concentrations. This behavior was attributed to consumption of the

TABLE 1. Kinetic Parameters, Transformation Products and Their Recoveries, and Target Organic Remaining in GR<sub>SO4</sub> Suspension<sup>a</sup> at the Last Sampling Time

target organics <sup>b</sup> (last sampling time)	$S_R$ ( $\mu\text{M/g}$ )	$K$ ( $\text{mM}^{-1}$ )	$k^c$ ( $\text{day}^{-1}$ )	$R^{2d}$	$k_{1,sa}$ ( $\text{Lm}^{-2}\text{day}^{-1}$ ) <sup>e</sup>	product recovery and target organic remaining (%)
PCE (60.4 day)	9.86 ( $\pm 10.1\%$ ) <sup>g</sup>	1.22 ( $\pm 4.3\%$ )	1.59 ( $\pm 6.3\%$ )	0.911	$1.62 \times 10^{-4}$	C <sub>2</sub> H <sub>2</sub> : 5.1 C <sub>2</sub> H <sub>4</sub> : 0.7 PCE: 64.7 total <sup>f</sup> : 70.5
TCE (60.4 day)	14.4 ( $\pm 13.2\%$ )	0.76 ( $\pm 4.4\%$ )	0.90 ( $\pm 8.6\%$ )	0.841	$8.55 \times 10^{-5}$	C <sub>2</sub> H <sub>2</sub> : 8.8 C <sub>2</sub> H <sub>4</sub> : 1.2 TCE: 60 total <sup>f</sup> : 70
<i>cis</i> -DCE (64.4 day)	16.9 ( $\pm 6.0\%$ )	0.633 ( $\pm 2.0\%$ )	0.592 ( $\pm 4.4\%$ )	0.937	$5.19 \times 10^{-5}$	C <sub>2</sub> H <sub>2</sub> : 0.8 C <sub>2</sub> H <sub>6</sub> : 8.5 C <sub>2</sub> H <sub>4</sub> : 5.0 <i>cis</i> -DCE: 71 total <sup>f</sup> : 85.3
VC (64.4 day)	18.0 ( $\pm 4.3\%$ )	0.53 ( $\pm 2.4\%$ )	0.94 ( $\pm 2.8\%$ )	0.970	$7.77 \times 10^{-5}$	C <sub>2</sub> H <sub>4</sub> : 20.3 C <sub>2</sub> H <sub>6</sub> : 2.5 VC: 68 total <sup>f</sup> : 90.8

<sup>a</sup> Concentration of GR<sub>SO4</sub> ( $M_0$ ) = 7 g/L. <sup>b</sup> Initial target organic concentration: 0.19 (PCE), 0.25 (TCE), 0.41 (*cis*-DCE), and 0.40 mM (VC). <sup>c</sup> Partitioning factors ( $p_{CE}$ ) for  $k$ : 1.12 (PCE), 1.08 (TCE), 1.06 (*cis*-DCE), and 1.07 (VC). <sup>d</sup>  $R^2$  values of nonlinear regression for kinetic parameters. <sup>e</sup> Surface area-normalized pseudo-first-order initial rate constant for reductive dechlorination of chlorinated ethylenes, surface area concentration of GR<sub>SO4</sub> was 604 m<sup>2</sup>/L. <sup>f</sup> Total is total carbon mass balance in GR<sub>SO4</sub> suspension. <sup>g</sup> Uncertainties represent 95% confidence limits.

finite reductive capacity of GR<sub>SO4</sub> as it was oxidized. Oxidation products could have formed as separate phases or as a coating on the GR<sub>SO4</sub> surfaces. A modified Langmuir–Hinshelwood kinetic model was developed to describe this behavior (see pp S1–S2, Supporting Information) (36). The material balance equation of target organic combined with the rate equation in a batch reactor follows

$$\frac{dC_{CE}}{dt} = -\frac{(k/p_{CE})\{C_{RC}^0 - p_{CE}(C_{CE}^0 - C_{CE})\}C_{CE}}{1/K + C_{CE}} \quad (1)$$

$$p_{CE} = \left(1 + H_{CE} \frac{V_g}{V_{aq}} + K_s\right) \quad (2)$$

$$C_{RC}^0 = M_R S_R \quad (3)$$

where  $C_{CE}$  is the target organic concentration in aqueous solution;  $k$  is the rate constant for reductive dechlorination of target organic at the reactive sites of GR<sub>SO4</sub>;  $C_{RC}^0$  is the initial concentration of reductive capacity of GR<sub>SO4</sub> for a target organic and represents the total amount of the target organic that GR<sub>SO4</sub> can reduce per unit volume of water;  $C_{CE}^0$  is the initial target organic concentration;  $K$  is the sorption coefficient of target organic;  $p_{CE}$  is the partitioning factor that considers the partitioning of target organics to gas, aqueous, and solid phases assuming instantaneous equilibrium in the phases;  $H_{CE}$  is the dimensionless Henry's law constant for chlorinated ethylenes;  $V_g$  and  $V_{aq}$  are the volumes of headspace and aqueous solution;  $K_s$  is the solid-phase partitioning coefficient for chlorinated ethylenes (See Table S-1, Supporting Information);  $M_R$  is the concentration of GR<sub>SO4</sub>; and  $S_R$  is the specific initial reductive capacity of GR<sub>SO4</sub>. The parameters ( $k$ ,  $K$ , and  $C_{RC}^0$ ) were estimated by an optimization procedure using MATLAB (MathWorks Inc.) that solves the differential equation numerically by a fourth-order Runge–Kutta method and calculates the sum of squares repeatedly to find its minimum value by adjusting values of the parameters with the Marquardt–Levenberg algorithm. The corrected pseudo-first-order initial rate constants ( $k_1$ ) were calculated using the following eq 4 in order to compare the dechlorination kinetics of chlorinated ethylenes in GR<sub>SO4</sub> suspension to those for other systems that were reported in terms of first-order rate constants. The surface area-normal-

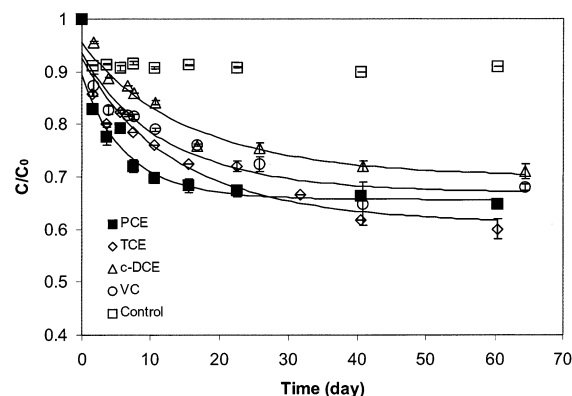


FIGURE 1. Reductive dechlorination of chlorinated ethylenes in GR<sub>SO4</sub> suspension (0.007 g/g). Error bars are ranges of relative concentration of target organics. Curves represent kinetic model fits. Control is the control sample for PCE.

ized pseudo-first-order initial rate constant ( $k_{1,sa}$ ) was also calculated by normalizing  $k_1$  by the surface area of GR<sub>SO4</sub>.

$$k_1 = \frac{(k/p_{CE})C_{RC}^0}{1/K + C_{CE}^0} \quad (4)$$

**Reductive Dechlorination of Chlorinated Ethylenes by Green Rust.** The decay of target organics in controls and GR<sub>SO4</sub> suspension is represented in Figure 1. PCE concentration in controls rapidly decreased due to the partitioning to the solid phases and reached equilibrium concentration (91.2% of initial PCE concentration) at the first sampling point (1.6 day). The concentrations of TCE, *cis*-DCE, and VC (not shown) in controls also dropped rapidly and reached equilibrium (95.9, 97, and 98% of initial target organic concentrations, respectively) at 1.6 day. When a first-order rate law is assumed to account for the partitioning of target organics to the solid phases, the partitioning rates of target organics to solid phases were at least 11 times faster than the highest dechlorination rate of target organics in GR<sub>SO4</sub> suspension.

Reductive dechlorination of chlorinated ethylenes in the presence of GR<sub>SO4</sub> is well fitted by the kinetic model as shown in Figure 1. The rate constants for the dechlorination of target



organics in GR<sub>SO4</sub> suspension (Table 1) are similar to those observed in pyrite suspension (36), but differ by factors of 0.6 to 1.9. The rate constant for the dechlorination of PCE at the reactive surfaces of GR<sub>SO4</sub> was greatest followed by those of VC, TCE, and *cis*-DCE, which is a different order compared to that shown in the reductive dechlorination of target organics by iron sulfide and iron oxide minerals (36). Because the reductive dechlorination by iron-bearing soil minerals is probably the result of a variety of serial and parallel reactions, the dechlorination kinetics of each target organic may appear to be different depending on the type of reductants and experimental conditions. The rate constant for the dechlorination of *cis*-DCE by GR<sub>SO4</sub> was the smallest among the target organics, which is similar to results that have been reported for the reductive dechlorination of chlorinated ethylenes by pyrite, magnetite, and Zn(0) (34, 36). The corrected pseudo-first-order initial rate constants for target organics normalized by GR<sub>SO4</sub> surface area (Table 1) were 3.4 to 8.2 times greater than those in pyrite suspension (36). They were 31 to 850 times smaller than corresponding constants for the dechlorination of target organics in the presence of mackinawite (17), troilite (15), and zerovalent metals (15, 34). The specific initial reductive capacity of GR<sub>SO4</sub> for target organics was between 9.9 and 18  $\mu\text{M/g}$ . The reductive capacity measures the ability of the reductant to react with a specific target compound. Therefore, it may be different for different compounds, and it does not necessarily equal the reductive capacity that could be calculated by assuming all Fe(II) in GR<sub>SO4</sub> can be oxidized to Fe(III). The values calculated from Fe(II) content are approximately 2–3 orders of magnitude greater than those observed in these experiments, which may be the result of limited reactivity of different types of Fe(II) in GR<sub>SO4</sub> (e.g., Fe(II) species at edges or external surfaces) or the blocking effect of Fe(III) surface coatings.

Approximately, 29 to 40% of initial target organics were removed (i.e., not measured in aqueous solution) in 70 days and the total amount of carbon recovered at the last sampling time was 70 to 90.8% of the initial amount. The low total carbon recovery may be mainly caused by unrecovered target organics in a sorbed state and volatilization loss during the sampling procedure. The formation of nondetectable products and inaccuracy in Henry's law constants may affect the incompleteness of total carbon recovery. The main transformation products for the reductive dechlorination of PCE were acetylene and ethylene, which accounted for 14.5 and 2.0% of the removed PCE, respectively (See Figure S-2, Supporting Information). In contrast to what is usually observed in the microbial hydrogenolysis of PCE (5, 37) and the reductive transformation of PCE by Vitamin B<sub>12</sub> with Ti(III)-citrate (10, 38), no chlorinated daughter products were observed during the reaction. No further reduction of ethylene to ethane was observed either. Figure 2 represents the distribution of transformation products for the reductive transformation of target organics by GR<sub>SO4</sub>. A possible reaction pathway for the reductive transformation of PCE by GR<sub>SO4</sub> can be suggested based on the observed product distribution. PCE could be reduced to acetylene via a dechlorination path and then to ethylene. Because TCE, dichloroethylenes (DCEs), and VC were not detected above the method detection limits (TCE: 0.8  $\mu\text{M}$ , *cis*-DCE: 2.06  $\mu\text{M}$ , *trans*-DCE: 8.3  $\mu\text{M}$ , 1,1-DCE: 2.4  $\mu\text{M}$ , and VC: 16  $\mu\text{M}$ ), these compounds are not likely intermediates for the transformation of PCE. However, unstable intermediates such as dichloroacetylene and chloroacetylene could be formed (PCE  $\rightarrow$  dichloroacetylene  $\rightarrow$  chloroacetylene  $\rightarrow$  acetylene) (17, 18, 22). Compared to the parallel transformation pathways usually found in the reductive dechlorination of PCE by zerovalent metals (34, 39) and iron sulfides (17, 18), the main pathway for the transformation of PCE by GR<sub>SO4</sub> is probably the reductive

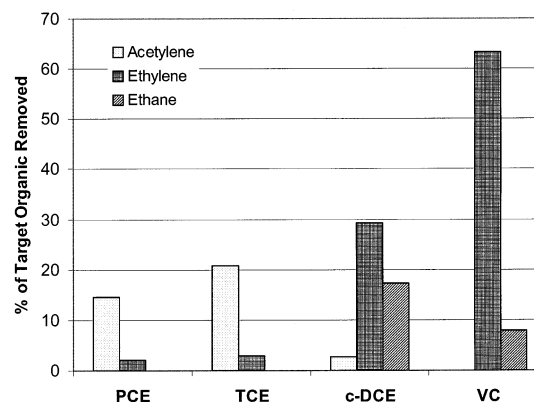


FIGURE 2. The product distribution for the reductive dechlorination of target organics in GR<sub>SO4</sub> suspension (0.007 g/g).

elimination pathway with further reduction to ethylene (PCE  $\rightarrow$  dichloroacetylene  $\rightarrow$  chloroacetylene  $\rightarrow$  acetylene  $\rightarrow$  ethylene).

The principal transformation products for the reductive dechlorination of TCE in the presence of GR<sub>SO4</sub> were acetylene and ethylene. Because transformation products expected by a hydrogenolysis pathway (e.g., DCEs and VC) were not observed above the method detection limits, they are not likely to be an important intermediate for the transformation of TCE to acetylene. This also suggests that a highly reactive intermediate (e.g., chloroacetylene) is produced during the reductive transformation of TCE to acetylene (17, 18). Based on the product distribution observed, it appears that reductive elimination with further reduction to ethylene (TCE  $\rightarrow$  chloroacetylene  $\rightarrow$  acetylene  $\rightarrow$  ethylene) is the principal reaction pathway for the transformation of TCE by GR<sub>SO4</sub>.

The main transformation product for the reductive dechlorination of *cis*-DCE was ethylene. Compared to the product distribution for *cis*-DCE dechlorination by pyrite (36) and zerovalent metals, ethylene was further reduced to ethane and no VC was detected at concentrations above the method detection limit. A possible reaction pathway has been suggested to explain abiotic reductive transformation of *cis*-DCE that includes reduction to acetylene followed by sequential reduction to ethylene and ethane. The formation of acetylene increased until 25.8 days and then decreased as the formation of ethylene increased. Although the amount of acetylene produced was smaller than that estimated by stoichiometric calculation, the pathway of *cis*-DCE  $\rightarrow$  acetylene  $\rightarrow$  ethylene  $\rightarrow$  ethane would be a reasonable pathway for the reductive transformation of *cis*-DCE in GR<sub>SO4</sub> suspension.

The removal of VC by GR<sub>SO4</sub> was approximately 30% at 37 days (graphical estimation), which is 4–6 times greater than the microbial removals of VC by methanogenic and Fe(III)-reducing bacteria (40). 63.4% of VC removed was transformed to ethylene as a principal product and 7.8% was transformed to ethane. No acetylene was detected during the reaction. A similar product distribution was shown in the reductive transformation of VC by pyrite (36). These results suggest a hydrogenolysis pathway with further reduction to ethane (VC  $\rightarrow$  ethylene  $\rightarrow$  ethane) for the reductive transformation of VC in GR<sub>SO4</sub> suspension. Both *cis*-DCE and VC were reductively transformed to ethane in GR<sub>SO4</sub> suspension, while the transformation of PCE and TCE to ethane was not observed. This could be due to the limitations of stoichiometry and/or kinetics. In the system with *c*-DCE or VC, there was a higher ratio of reductive capacity in GR<sub>SO4</sub> than oxidative capacity in *cis*-DCE or VC. Therefore, less of the reductive capacity of GR<sub>SO4</sub> was consumed in converting the target organics to ethylene and there was more available to convert ethylene to ethane. Lower reductive capacity re-

TABLE 2. Kinetic Parameters for the Reductive Dechlorination of TCE as Functions of pH, Mass Ratio, and Initial Target Organic Concentration

pH	mass ratio (g/g)	$C_{TCE}^0$ (mM)	$S_R$ ( $\mu$ M/g)	$K$ (mM $^{-1}$ )	$k$ (day $^{-1}$ )	$R^2$
6.8	0.01	0.3	9.6( $\pm$ 2.1%) <sup>b</sup>	0.80( $\pm$ 3.6%)	0.56( $\pm$ 2.7%)	0.972
7.3	0.01	0.3	10.2( $\pm$ 1.8%)	0.80( $\pm$ 2.3%)	0.92( $\pm$ 1.9%)	0.98
8.1	0.01	0.3	10.6( $\pm$ 3.3%)	0.80( $\pm$ 3.2%)	1.21( $\pm$ 1.9%)	0.984
9.2	0.01	0.3	12.5( $\pm$ 2.5%)	0.80( $\pm$ 2.6%)	1.71( $\pm$ 3.3%)	0.968
10.1	0.01	0.3	15.1( $\pm$ 5.1%)	0.801( $\pm$ 4.4%)	2.22( $\pm$ 6.1%)	0.907
8.1	0.001	0.3	12.0( $\pm$ 3.3%)	0.789( $\pm$ 3.1%)	1.20( $\pm$ 3.2%)	0.971
8.1	0.005	0.3	13.8( $\pm$ 4.1%)	0.80( $\pm$ 5.3%)	1.21( $\pm$ 3.6%)	0.962
8.1	0.02	0.3	13.0( $\pm$ 3.5%)	0.80( $\pm$ 4.6%)	1.18( $\pm$ 3.4%)	0.964
8.1	0.04	0.3	12.8( $\pm$ 4.9%)	0.791( $\pm$ 4.2%)	1.22( $\pm$ 4.0%)	0.931
8.1	0.01	0.15	10.5( $\pm$ 2.7%)	0.803( $\pm$ 1.9%)	1.19( $\pm$ 1.3%)	0.987
8.1	0.01	0.45	11.2( $\pm$ 8.8%)	0.798( $\pm$ 6.5%)	1.24( $\pm$ 4.5%)	0.921
8.1	0.01	0.6	10.9( $\pm$ 7.0%)	0.80( $\pm$ 8.4%)	1.22( $\pm$ 5.9%)	0.897

<sup>a</sup> Initial concentration of TCE (mM). <sup>b</sup> Uncertainties represent 95% confidence intervals. <sup>c</sup>  $R^2$  values of nonlinear regression for kinetic parameters.

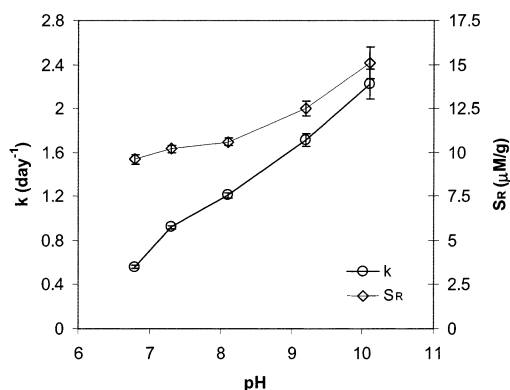


FIGURE 3. Rate constant ( $k$ ) and specific initial reductive capacity of  $GR_{SO4}$  ( $S_R$ ) as a function of pH for the reductive dechlorination of 0.3 mM TCE in 0.01 g/g  $GR_{SO4}$  suspension. Error bars for  $k$  and  $S_R$  represent 95% confidence intervals.

maining in a system with PCE or TCE could limit the observed production of ethane by slowing dechlorination kinetics or if very low, by stoichiometry.

**Factors Affecting Dechlorination Kinetics.** The effect of pH, solid concentration, and target organic concentration on the reductive dechlorination of TCE was investigated in  $GR_{SO4}$  suspensions. The estimated parameters to describe the dechlorination kinetics are reported in Table 2.

**Influence of pH.** The pH dependence of dechlorination rate constant is demonstrated in Figure 3. The uncertainties of estimated rate constants representing 95% confidence interval were less than 6.1% and the  $R^2$  values are greater than 0.90, which indicate that the kinetic model adequately described the reductive dechlorination of TCE by  $GR_{SO4}$  in these experiments. An increase of suspension pH increased dechlorination rate constants. This result may be described by the effect of pH on thermodynamics of the redox reaction. Since the dechlorination reaction produces hydrogen ions, an increase of pH would increase the driving force for the reaction and possibly increase its rate. Alternatively, the pH dependence of TCE dechlorination by  $GR_{SO4}$  could be explained by assuming that the hydrated  $GR_{SO4}$  surfaces are composed of hydroxide functional groups (e.g.,  $\equiv Fe(II)OH_2^+$ ,  $\equiv Fe(III)OH_2^+$ ,  $\equiv Fe(II)OH$ , and  $\equiv Fe(III)OH$ ). These groups originate from the hydrolysis of partially uncoordinated surface iron and undergo protonation and deprotonation as pH changes, resulting in changes in surface charge (41). Deprotonated surface groups are more reactive than protonated ones (16); therefore, the increase of deprotonated species on  $GR_{SO4}$  surfaces due to the increases of pH would tend to increase the rate constant. If nonreactive sites were

converted to active sites, the increases in pH would tend to increase the initial reductive capacity, which was observed (Figure 3). Increases in either of these parameters would increase the rate of TCE dechlorination. Similar effects of pH have been observed for the reduction of nitroaromatics by magnetite with Fe(II) (13) and by iron porphyrin with  $H_2S$  (9) as well as in the reductive dechlorination of HCA by mackinawite (16). However, the increase of dechlorination rate constant due to the pH increase in  $GR_{SO4}$  suspension was approximately 1.6 to 8.5 times smaller than those observed in systems (9, 13, 16) containing mackinawite, magnetite with Fe(II), and iron porphyrin with  $H_2S$  although the surface area concentration of  $GR_{SO4}$  was approximately 1 to 3 orders of magnitude higher than that of the other reductants. In contrast to the pH effect described above, it has been reported that an optimum pH was observed for PCE dechlorination by suspensions of Portland cement and Fe(II) (22). An optimum pH for PCE degradation with  $GR_{SO4}$  might be observed if experiments were conducted at higher pH values.

**Influence of Solid Concentration.** A statistical inference test showed that the slopes of the rate constant ( $k$ ), specific initial reductive capacity ( $S_R$ ) and sorption coefficient ( $K$ ) versus concentration of  $GR_{SO4}$  solids were not significantly different from zero at the 95% confidence level (See Figure S-3, Supporting Information). The independence of these parameters from affect of solid concentration supports the validity of the kinetic model. An average specific initial reductive capacity was calculated as  $12.4 \pm 1.5 \mu M/g$ , which is generally consistent with that measured in previous experiments (31), differing by about a factor of 1.1. The kinetic model predicts that the pseudo-first-order initial rate constant ( $k_i$ ) should be a linear function of mass ratio. Similar behavior has been reported for other reductants/target organics, such as Fe(0)/chlorinated ethylenes (42, 43) and magnetite/nitroaromatics (13).

The results of this kinetic study can be extrapolated to predict first-order decay coefficients and half-lives of TCE in aquifers that contain green rust. The initial reductive capacity concentration ( $C_{RC}^0$ ) in the aquifer can be calculated by assuming that green rust represents 1% of the iron content of the soil. The mass of iron per volume water in a typical saturated soil can be calculated as 91 g/L by assuming an iron content of 2.6%, bulk density of 1.4 kg/L, and porosity of 0.40. This provides a green rust concentration of 1.73 g/L assuming that GR is 52.6% iron. Combining these results with those in Table 2 produces a value for  $C_{RC}^0$  of 0.0225 mM. A partitioning factor ( $p_{CE}$ ) for TCE of 4.66 can be calculated by assuming a soil organic fraction of 0.005 and an organic carbon partition coefficient of 206 L/kg. Equation 4 can be used to calculate a pseudo-first-order rate constant of 0.0037

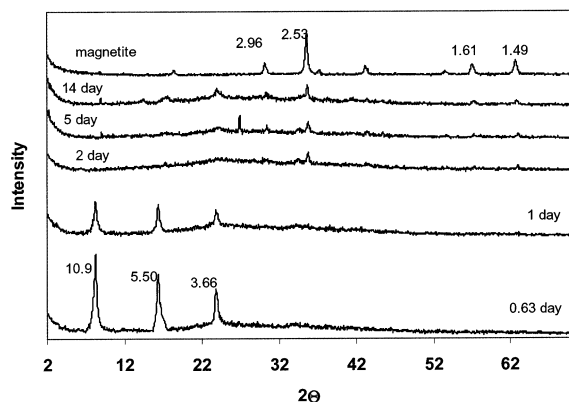


FIGURE 4. The change of XRD patterns for the oxidation product during the reaction between GR<sub>SO4</sub> and TCE. The values near peaks represent their *d*-spacing values (Å).

day<sup>-1</sup> which gives an apparent half-life of 190 days. This is on the order of reported half-lives of chlorinated organics during natural attenuation and demonstrates the potential for soil minerals such as green rust to play an important role in determining the fate of chlorinated organics in natural systems.

**Influence of Target Organic Concentration.** The coefficients in the kinetic model (*k*, *S<sub>R</sub>*, *K*) are not affected by the initial concentration of TCE (See Figure S-4, Supporting Information). This further supports the validity of the modified Langmuir–Hinshelwood kinetic model. The definition of the pseudo-first-order initial rate constant (Equation 4) predicts that it will be a nonlinear, decreasing function of initial concentration of TCE. A similar trend has been found in the reduction of nitroaromatics by magnetite with Fe(II) under different initial concentrations (13) and in the reductive dechlorination of chlorinated ethylenes by Fe(0) (44). The pseudo-first-order rate constant for dechlorination of TCE by 40 m<sup>2</sup>/L Fe(0) decreased with increasing initial target organic concentration (4 to 175 μM) by a factor of 10 (44), while the rate constant by GR<sub>SO4</sub> decreased by a factor of 1.3 as initial TCE concentration increased (150 to 600 μM). This result may be caused by high initial TCE concentration in GR<sub>SO4</sub> suspension and low reductive capacity of GR<sub>SO4</sub> for target organic due to limited number of reactive sites.

**Oxidation Product of GR<sub>SO4</sub>.** The ratio between the decrease in total Fe(II) and the increase in aqueous Cl<sup>-</sup> in GR<sub>SO4</sub> suspension at the last sampling time was 2.96 ± 0.02, which is greater than the theoretical value for the conversion of TCE to ethane (2.67). This result indicates that there may be other undefined reactions that consume Fe(II) in this system.

GR<sub>SO4</sub> samples at each sampling time were analyzed with XRD to identify the oxidation product of GR<sub>SO4</sub>. Figure 4 shows the change of oxidation product during the reaction of GR<sub>SO4</sub> with TCE. *d*-spacing values of three main peaks at 0.63 day were 10.9, 5.50, and 3.66 Å, which are good accordance with XRD data for GR<sub>SO4</sub> reported by Hansen (45). The location of peaks in the X-ray diffraction pattern of GR<sub>SO4</sub> did not change after 1 day, but the intensity of three main peaks remarkably decreased. The three main peaks disappeared and a new peak of an oxidation product at 2.53 Å started to form at 2 days. As the reaction proceeded, the crystallization of the oxidation product continued. The X-ray diffraction pattern at 14 days shows main peaks of an oxidation product for which *d*-spacing values are 2.96, 2.53, 1.61, and 1.49 Å. This pattern is consistent with that of magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>) (46). It is difficult to unequivocally identify the oxidation product of GR<sub>SO4</sub> only using XRD analysis, because of the similarities in diffractograms of magnetite and maghemite.

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## Supporting Information Available

Table of measured solid phase partitioning coefficients and partitioning factors of chlorinated ethylenes in GR<sub>SO4</sub> suspension and figures of diffractogram of GR<sub>SO4</sub>, reductive transformation of PCE by GR<sub>SO4</sub> and rate constant, specific initial reductive capacity, and sorption coefficient as a function of mass ratio and as a function of initial target organic concentration for the reductive dechlorination of TCE. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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