Effects of transition metal and sulfide on the reductive dechlorination of carbon tetrachloride and 1,1,1-trichloroethane by FeS

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Abstract

Reductive dechlorination of carbon tetrachloride (CT) and 1,1,1-trichloroethane (1,1,1-TCA) by FeS with transition metals (Cu(II), Co(II), and Ni(II)) and hydrosulfide was characterized in this study. The batch kinetic experiments were conducted by spiking each stock solution of CT and 1,1,1-TCA into 33 g/L of FeS suspensions with and without transition metals at pH 7.5. No significant enhancement was observed in the reductive dechlorination of target compounds by FeS with 1 mM transition metals. However, except the addition of Cu(II), the reduction rate of 1,1,1-TCA increased with increasing the concentration of transition metals. The rate constants with 10 mM Co(II) and Ni(II) were 0.06 and 0.11 h⁻¹, approximately 1.3 and 3.0 times greater than those by FeS alone. The addition of 20 mM HS⁻ also increased the rate constants of 1,1,1-TCA by FeS by one order of magnitude. SEM analysis showed that the addition of transition metal (Ni(II)) and HS⁻ caused a noticeable morphologic change of FeS surface. The transition metal added was substituted by the structural iron resulting in the decrease of iron content of FeS (52.6–46.9%). One third of the transition metal in FeS suspension existed as zero-valent form playing a catalyst role to accelerate the reaction kinetics.

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1. Introduction

Chlorinated aliphatic hydrocarbons have been widely utilized as solvents, degreasers, and extractants in industrial processes for several decades. Carbon tetrachloride (CT) and 1,1,1-trichloroethane (1,1,1-TCA) are most commonly used among the chlorinated aliphatic compounds and have been widely observed in the National Priority List (NPL) sites of USA [1–3]. The appearance of these chemical compounds in soil and groundwater caused by improper use and disposal has been of great concern because of their potential toxicity and recalcitrant characteristics [1,3]. The concentration of these compounds in drinking water has been regulated under the Safe Drinking Water Act (SDWA), which set the maximum contaminant level (MCL) of CT and 1,1,1-TCA at 5 and 200 μg L⁻¹, respectively [1,4].

Studies have been carried out to effectively remove these toxic chlorinated compounds using natural soil minerals such as iron sulfides, iron oxides, and iron hydroxides in reducing environments. FeS is one of meta-stable phase iron sulfides with the chemical formula of Fe_{1+x}S, where 0 < x < 0.07. It is one of abundant minerals found in reduced soil and sediment environments and produced by the biologically mediated reduction of sulfate to sulfide followed by sequential reactions with iron species [5]. FeS has been believed to play a pivotal role in degrading chlorinated organic compounds in soil and sediment systems [16,7]. Research has shown that FeS transformed chlorinated aliphatic hydrocarbons such as perchloroethylene (PCE), trichloroethylene (TCE), hexachloroethane (HCA), and trichloroethane (TCA) to less chlorinated compounds and further to acetylene, ethylene, and ethane [5,6,8,9].

Recently, considerable effort has been made to enhance the reactivity of reductants used for the reductive degradation of chlorinated compounds. Researchers have added transition metals such as Pd, Pt, Ni, and Cu to zero-valent metals for this purpose [10–12]. Others have frequently used Pd to enhance the degradation rate of the chlorinated aliphatic and aromatic compounds by zero-valent iron (ZVI) and zero-valent zinc [13,14]. Ni and Cu have been coated on the surfaces of ZVI to increase the kinetic rate of the reductive dechlorination of 1,1,1-TCA [10]. The addition of sulfide has been also observed to improve the reactivity of ZVI [15] and soil minerals [16]. The reaction rates for the reductive degradation of halogenated hydrocarbons by ZVI reacted with sulfide increased as the concentration of sulfide increased [15]. It has been reported that the sulfide added to iron-bearing soil minerals significantly
affected the degradation kinetics of CT [16]. However, little research has been conducted to systematically investigate the enhancement of reactivity of iron-bearing soil minerals, which can produce basic understanding on geochemistry and background knowledge to be applied to the development of novel remedial alternatives.

In this study, we conducted batch kinetic experiments to characterize the reductive dechlorination of CT and 1,1,1-TCA by FeS in the presence of transition metals and sulfide. Three transition metals (Co(II), Cu(II), and Ni(II)) and HS⁻ were selected to improve the reduction capacity of FeS. The effect of transition metal and sulfide concentrations on the reductive dechlorination of target compounds was investigated at different concentrations. Finally, surface analysis was carried out to examine the underlying reaction mechanism of reactivity enhancement of FeS and to identify the coordination chemistry on the FeS surfaces with transition metals and HS⁻.

2. Experimental

2.1. Anaerobic system

The synthesis of FeS and preparation of experiments were conducted in an anaerobic chamber (Coy Laboratory Products Inc.) filled with 95% nitrogen and 5% hydrogen. Deaerated deionized water (DDW) was prepared by purging 18 MΩ cm deionized water (Barnstead) with nitrogen for 2 h and with the anaerobic atmosphere for 12 h in the anaerobic chamber. DDW was used for the preparation of aqueous solutions, solid suspensions, and chemical agents.

2.2. Chemicals

The following chemicals were used for target compounds and potential by-products: carbon tetrachloride (CT, 99.5%, Junsei), chloroform (CF, 99%, Junsei), methylene chloride (MC, 98.0%, Junsei), 1,1,1-trichloroethylene (1,1-TCA, 99%+, Sigma–Aldrich), 1,1-dichloroethane (1,1-DCA, 200 μg/mL in Methanol, Supelco), mixed gas (1% of methane, ethane, ethylene, and acetylene in nitrogen gas, Alltech). FeCl₂·4H₂O (99%, Wako) and Na₂S (98%+, Sigma–Aldrich) were used to synthesize FeS. CuCl₂ (97%, Junsei), NiCl₂ (96%, Junsei) and CoCl₂ (97%, Junsei) were used as a source of transition metals and NaSH (Sigma–Aldrich) was used for the source of sulfide. A mixture of tris(hydroxymethyl)aminomethane (99.8%, Sigma–Aldrich) and tris(hydroxymethyl)aminomethane hydrochloride (99%, Sigma) (Tris buffer) were used to keep the pHs of aqueous solution and FeS suspensions constant at 7.5 during the reaction time.

2.3. Preparation of FeS

FeS was synthesized by adding 1.236 M of Na₂S to the same volume of FeCl₂·4H₂O (1.068 M) and mixing them with a magnetic stirrer in the anaerobic chamber for 3 d [5]. It was washed four times with DDW to remove sulfide and Fe(II) in the suspension through the following steps. FeS suspension was centrifuged at 3000 rpm for 15 min to separate solid from the suspension, the supernatant was replaced by DDW, and the solid was re-suspended. Tris buffer solution was used instead of DDW at the last washing step to keep the pH of suspension constant.

2.4. Experimental procedures

Amber borosilicate glass vials (24 mL) were used as batch reactors for the kinetic experiments. Each vial was sealed by an open-top cap with three layers (silicon septum + lead foil + PTFE film), which successfully maintained anaerobic condition and prevented the loss of chlorinated volatile compounds in the previous study [17]. These reactors were kept in an anaerobic chamber for more than 1 d to remove oxygen, which was possibly attached on the reactor wall. Twenty-three and eight-tenth millilitre of FeS suspension (33 g/L) was transferred to each vial while it was mixed by a magnetite stirrer. An exact amount of stock transition metal solution or HS⁻ solution (500 mM, respectively) was added to FeS suspension. The concentrations of transition metals in the suspensions were 1, 2.5, 5, and 10 mM and those of HS⁻ were 5, 10, 15, and 20 mM. The suspensions were mixed for 1 h to allow chemical equilibrium and then transferred to each vial to identify the effect of transition metals and HS⁻ on the reductive dechlorination of target compounds. The reaction was initiated by spiking 100 μL of stock target compound solutions resulting in 1 mM of CT and 0.5 mM of 1,1,1-TCA, respectively. Controls containing Tris buffer and the target compounds were prepared to check the loss of target compounds due to sorption and volatilization during the reaction. The vials were placed on a tumbler that provided end-over-end rotation at 8 rpm. All samples were prepared in duplicate. The degradation kinetics of CT and 1,1,1-TCA by FeS with and without transition metals and HS⁻ were determined by sacrificial sampling and monitoring the concentration of the target compounds at each sampling point.

2.5. Analytical methods

CT and 1,1,1-TCA, and their chlorinated daughter products (CF, MC, and 1,1-DCA) were analyzed using a gas chromatograph (GC, Hewlett-Packard 6890) equipped with a flame ionization detector and DB-5 column (J&W Co.: 30 m length, 0.32 mm i.d., and 0.25 μm thickness). Headspace samples (50 μL) were obtained by a gas-tight micro-syringe (100 μL, Hamilton). Headspace samples were injected manually into the injection port of the GC under the following condition: inlet temperature, 250°C; split ratio, 5:1; column temperature, isothermal at 60°C; column flow rate, 1.5 mL/min; detector temperature, 300°C.

The same sample preparation procedure was used for the measurement of non-chlorinated products (methane, ethane, ethylene, and acetylene). They were quantified by the GC equipped with a micro-packed column (2 m length, 1/16″ OD, 0.75 mm i.d.) containing 80/100 Carboxen-1004 under the following condition: inlet temperature, 250°C; column temperature, isothermal at 120°C; column flow rate, 6 mL/min; detector temperature, 250°C; splitless mode.

Solid phase extraction was conducted to determine the amount of target and transformation products sorbed on FeS, septum, and reactor wall. After supernatant was separated from the suspension by centrifugation, it was decanted and replaced by an exact amount of extractant (hexane, HPLC grade, Sigma–Aldrich). Extraction was continued for 2 h on the orbital shaker at 200 rpm. The extractant was analyzed by a GC (HP 5890) with an electron capture detector and HP-5 column (J&W Co.: 30 m length, 0.32 mm i.d., and 0.25 μm thickness).

Scanning electron microscope (SEM: FEI XL-30 FEG) with energy dispersive spectrometer (EDS) was used to analyze the morphology of FeS. A droplet of diluted FeS suspension with and without transition metal and HS⁻ was dried on aluminum foil under the anaerobic atmosphere of anaerobic chamber and then coated with Os, respectively.
X-ray photoelectron spectroscopy (XPS: PHI 5800) analysis was conducted to identify the oxidation state of iron, sulfur, and transition metals on the surface of FeS using mono-chromatized Al Kα X-ray (1486.6 eV) with the source power of 15 kV and 24 mA. The data were fitted by the Shirley baseline and Gaussian–Lorentzian peak shape. A droplet of FeS suspension with and without transition metal was carefully dried on the aluminum foil in the anaerobic chamber. There was no further effort to prevent the oxidation of samples during the XPS analysis.

2.6. Treatment of kinetic data

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

\[
\frac{d C_L}{dt} = \frac{-k C_L}{1 + H(V_g/V_L)} = -\left(\frac{k}{\rho}\right) C_L = -k_{app} C_L
\]

where \(C_L\) is the concentration of the target chlorinated compounds in the 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 the CT and 1,1,1-TCA (CT: 1.20; 1,1,1-TCA: 0.709) [18], \(V_g\) and \(V_L\) are volumes of the gas and aqueous phases, respectively, \(\rho\) is the partitioning factor, and \(k_{app}\) is the apparent pseudo-first-order rate constant. The calculated \(P\) for CT and 1,1,1-TCA in this study was 1.01 and 1.005, respectively. \(k_{app}\) was obtained by conducting a nonlinear regression of aqueous-phase target compound concentrations using a Gauss–Newton algorithm in MATLAB® (Math works Inc.), \(k\) was calculated by multiplying \(P\) and \(k_{app}\) and used to account for the effect of partitioning of target compounds between the aqueous and gas phases.

3. Results and discussion

3.1. Reductive dechlorination of CT and 1,1,1-TCA by FeS with a transition metal

Fig. 1a shows the reductive dechlorination of CT by FeS at pH 7.5 in which a first-order rate law reasonably described the reductive dechlorination of target compound. Ninety percent of 1 mM CT was reductively degraded in 3 h and the formation of CF gradually increased to 0.4 mM. CF slightly decreased at 2 h and then showed constant concentration. Less chlorinated compounds (e.g., MC) were not detected in this research. In addition, non-chlorinated \(C_1\) and \(C_2\) hydrocarbons such as \(CH_4, C_2H_4,\) and \(C_2H_6\) which were possibly produced during the reductive dechlorination of CT [19] were not measured either. We also investigated if the target compound and transformation products were adsorbed on the solid surface. However, no detectable amounts of target and products were recovered from the solid samples during the reaction. Based on the measurement of CT and its products, the total carbon mass balance was about 50% at the end of reaction. Many studies have reported that CT was mainly transformed to CF through hydrogenolysis pathway by iron-bearing soil minerals and that the extent of CF production was dependent on the type of soil minerals [20–23]. In the experimental results reported by Zwank et al., the portions of CF formation during the reductive dechlorination of 10 μM CT by mackinawite, goethite, magnetite, lepidocrocite, hematite, and siderite were 55%, 33%, 80%, 14%, 17%, and 33%, respectively [23]. Some researchers proposed different reaction pathways through which CT could reductively transformed to \(CS_2, CO_2, CO\) and \(HCOO^-\) [4,23]. Therefore, the low total carbon mass balance obtained in this study may be due to the formation of other transformation products (e.g., \(CS_2, CO_2, CO\) and \(HCOO^-\)), which were not analyzed during the reaction.

The effect of transition metals (Cu(II) and Ni(II)) on the degrada-
tion kinetics of CT by FeS was examined in this study and shown in Fig. 1b. The reaction rate constants of FeS with Cu(II) and Ni(II) were 1.59(±0.357) and 1.32(±0.363) h\(^{-1}\), respectively, which were slightly greater than the rate constant without a transition metal (1.24(±0.266) h\(^{-1}\)). Approximately, 40% of initial CT was transformed to CF by FeS with Cu(II) and Ni(II) at the last sampling time. No chlorinated methanes and non-chlorinated products were detected from the samples during the reaction.

Fig. 2a shows the reductive dechlorination of 1,1,1-TCA by FeS. The degradation rate of 1,1,1-TCA was lower than that of CT. Eighty-two percent of initial 1,1,1-TCA (0.5 mM) was removed by FeS within 48 h and the rate constant for the reductive dechlorination of 1,1,1-TCA obtained by first-order linear fit was 0.0375(±0.0018) h\(^{-1}\). 1,1-DCA was observed as a significant transformation product in the concentration range of 0.003–0.02 mM (~4% of total removal) showing that 1,1,1-TCA was reductively transformed via hydrogenolysis pathway [10]. Ethylene was also measured...
Fig. 2. (a) Reductive degradation of 1,1,1-TCA by FeS and (b) kinetic rate constants for the reductive degradation of 1,1,1-TCA by FeS with a transition metal (Cu, Co and Ni). FeS suspension was 33 g/L and pH was kept constant at pH 7.5. The initial concentration of 1,1,1-TCA was 0.5 mM. A solid line represent pseudo-first-order model fitting by Eq. (1) and dot lines are plotted (not fit) to guide the eye and error bars represent 95% confidence intervals of rate constants.

Fig. 3 shows the reductive dechlorination of 1,1,1-TCA by FeS at various HS\(^-\) concentrations (5–20 mM). The reaction kinetics of 1,1,1-TCA was properly described by a pseudo-first-order rate law. The kinetic rate constant in the presence of 5 mM HS\(^-\) was three times greater than that in the absence of HS\(^-\) (0.0375(±0.0018) h\(^{-1}\)) and increased at the rate of 0.0054 h\(^{-1}\)mM\(^{-1}\) by 15 mM HS\(^-\). The reactivity of FeS for the reductive dechlorination of 1,1,1-TCA was accelerated by the addition of 20 mM HS\(^-\). The rate constant of 20 mM HS\(^-\) addition was 0.37(±0.0225) h\(^{-1}\), which was one order of magnitude lower.
Fig. 4. SEM and EDS analysis, (a) the surface of FeS, (b) the surface of FeS with Ni(II), and (c) the surface of FeS with HS⁻.
of magnitude higher than that of FeS without HS\(^{-}\). This may be due to the enhanced deprotonation on the surface of FeS at higher pH, which produces more reactive deprotonated surface species (e.g., –OH\(^{-}\) and –O\(^{2-}\)) for the reductive dechlorination of 1,1,1-TCA. The pHs of FeS suspensions with HS\(^{-}\) in the range of 5–15 mM were constant at pH 7.5 during the reaction, while that with 20 mM HS\(^{-}\) increased to pH 8.5. Previous studies demonstrated that the reductive dechlorination rate by FeS was strongly dependent on the suspension pH and generally increased with increasing the pH [5,6].

In control samples containing 20 mM HS\(^{-}\) solution, 1,1,1-TCA was gradually degraded and 10% of its initial concentration was removed at the last sampling time (18 h). This indicates that 1,1,1-TCA can be reductively degraded in homogeneous HS\(^{-}\) solution to a certain extent but that the enhancement of reaction rate was mostly accomplished by the presence of FeS. The addition of HS\(^{-}\) into iron-bearing soil minerals such as magnetite and hematite increased the reaction rates for the reductive dechlorination of chlorinated compounds, while the addition of HS\(^{-}\) into non iron-bearing soil minerals such as kaolinite did not [16]. This suggests that HS\(^{-}\) may react with surface iron species and produce reactive iron sulfides on the mineral surfaces resulting in increased reaction rates. In addition, the sulfur added into iron metal suspension has been observed to dissolve iron metal surface and yield iron sulfide, which can significantly accelerate the reaction kinetics through the following reaction mechanism. The iron sulfide can be deposited on the surface of iron metal and facilitate the electron transfer from iron metal to chlorinated organic compounds. It can also degrade chlorinated organic compounds by playing a role of reactive reductant [6,15]. Therefore, we can assume that HS\(^{-}\) added into FeS suspension may be bound on the surface of FeS and enhance the reaction rate of 1,1,1-TCA by facilitating the electron transfer and/or forming the reactive iron sulfide species on the surface of FeS. No direct spectroscopic analysis has been conducted to identify the reactive sulfur species on the surface of FeS in this study.

3.3. Role of transition metals and HS\(^{-}\) on the surfaces of FeS

Fig. 4 shows SEM images (left side) and EDS measurements (right side) of FeS surfaces without (a) and with a transition metal (Ni(II)) (b) and HS\(^{-}\) (c). SEM image of FeS shown in Fig. 4a illustrates that the amorphous and disordered FeS particles were irregularly aggregated [25]. We did not observe any specific shapes of bulk FeS solids. The X-ray diffraction analysis result of FeS also showed broad peaks at 5.08, 2.96, 2.30, and 1.83 d-spacing values, where broad peaks represent that solid was not well crystallized (data not shown). The EDS analysis showed that these particles were composed of iron (52.6%) and sulfur (47.4%). The aluminum peak in the EDS analysis shown in Fig. 4a was due to the aluminum foil on which the diluted FeS suspension was dried. The shape of solids and surfaces of FeS were significantly changed after the addition of Ni(II) and HS\(^{-}\) as shown in Fig. 4b and c.

Fig. 4b shows that the amassed FeS particles formed big bulk solids and the surface of bulk solids has small cracks. The chemical composition of the bulk solid by the EDS analysis was iron, sulfur, and nickel and their portion was 46.9%, 48.4%, and 4.7%, respectively. The decrease of iron content may be due to the isomorphous substitution with the added Ni(II). Fig. 4c illustrated the SEM image of FeS in the presence of HS\(^{-}\). The noticeable surface change was observed on the surface of FeS after the addition of HS\(^{-}\). The smooth amorphous FeS particles were obliquely and convolutedly aggregated and formed a small sized irregular sphere about 100–500 nm in diameter. The shape of these particles was very similar to that of iron sulfide precipitates observed in the growth media of sulfate-reducing bacteria [26]. The EDS result demonstrated that the portion of S was slightly increased from 47.4% to 48.3% after the addition of HS\(^{-}\), indicating that the added HS\(^{-}\) may be adsorbed on the surface of FeS.

The oxidation states of Fe, S, and Ni were investigated using XPS analyses and those results were shown in Fig. 5. This shows...
the narrow scans of Fe(2p3/2), S(2p3/2), O(1s), and Ni(2p3/2) spectra of FeS with Ni(II). Each raw spectrum of Fe, S, O, and Ni was smoothed and fitted by the Shirley baseline and Gaussian–Lorentzian peak shape. The Fe(2p3/2) spectrum consists of three peaks at 706.0 eV (Fe(II)–S), 709.0 eV (Fe(III)–S), and 711.9 eV (Fe(III)–O), while S(2p3/2) spectrum consists of two peaks at 160.2 eV (S2−) and 162.1 eV (S2−), respectively [27,28].

In determining the identity of peaks around 711.9 eV, Herbert et al. [26] reported them as Fe(III)–S, while Thomas et al. [27] identified them as Fe(III)–O. This peak at 711.9 eV obtained in this experiment was identified as Fe(III)–O, which can be supported by the presence of O2− shown in Fig. 5d. The surface of FeS was composed of 47.6% Fe(II)–S, 34.4% Fe(III)–S, and 17.9% Fe(III)–O. The area percentage of each target chemical component (Fe and S) was similar to that in mackinawite reported by Mullet et al. [28]. The area percentage of reduced chemical species (Fe(II)–S and S2−) on the surface of FeS after the addition of Ni(II) was 11.9% and 64%, respectively, which was relatively lower than that without Ni(II). This result indicates that Fe(II)–S and S2− on the surfaces of FeS were oxidized during the reduction of Ni(II). Fig. 5c shows that Ni(2p3/2) spectrum was composed of two identical peaks at 852.6 and 854.3 eV. The peak at 852.6 eV represents zero-valent Ni(0) and its area percentage is about 25%, while the peak at 854.3 eV represents Ni(II) and its area percentage was 75% [29].

Based on SEM and XPS results, it can be suggested that Ni(II) was bound on the surface of FeS, reductively transformed to Ni(0) by the reduced iron and sulfur species on FeS surfaces, and increased the reaction rates of reductive dechlorination by facilitating the electron transfer reaction. The metal type of Ni on the surface of reactive solids has been reported to be able to increase the reaction rates of reductive dechlorination [10,13]. Ni(0) can reduce chlorinated organic compounds as fast as ZVI can [14]. In addition, based on the previous research papers, a couple of possible reaction mechanisms could also be proposed to explain the role of trace metal on the reactive solid surfaces in the reductive dechlorination of target compounds. Ni(II) adsorbed on the surfaces of FeS could replace Fe(II) in the FeS structure and/or was co-precipitated with FeS resulting in the formation of metal-substituted FeS, such as Fe1−xNi2xS [30]. The formation of metal-substitute FeS can significantly affect the reaction kinetics for the reductive dechlorination of chlorinated aliphatic by FeS with a transition metal [7]. Ni(II) can react with S2− and form NiS [31] resulting in the increase of reductive dechlorination rates by one order of magnitude compared to that by FeS alone [7]. However, no experimental and analytical efforts have been made to verify these assumptions in this study.

4. Conclusions

The experimental results of this research indicated that the addition of a transition metal into FeS suspension was an effective method to improve the reduction capacity of FeS in reductive dechlorination of CT and 1,1,1-TCA. The extent of enhancement on the reactivity of FeS was strongly influenced by the type of transition metals. Cu and Co were revealed to be reactive transition metals to increase the reductive dechlorination rate of CT, whereas Co and Ni were reactive for the reductive dechlorination of 1,1,1-TCA by FeS. A linear relationship was observed between the amount of transition metal (Co and Ni) added and the increased reaction rate for the reductive dechlorination of 1,1,1-TCA. XPS result showed the reduction of 25% Ni(II) to Ni(0) coupled to the simultaneous oxidation of Fe(II) and S2− on the surface of FeS. The enhancement of reaction rates for the reductive dechlorination of target compounds by the addition of a transition metal may be achieved by the catalytic effect of Ni(0) facilitating electron transfer from FeS to target chlorinated compounds and/or the formation of Ni substituted FeS having high reductive capacity for target compounds.

The addition of HS− was another effective method to improve the reductive capacity of FeS for the target compounds in this study. The concentration of 1,1,1-TCA was slowly decreased in aqueous HS− solution. The degradation rate by aqueous HS− was much lower than those by FeS with and without HS− at pH 7.5. FeS suspension with HS− showed higher reductive capacity for the target compound than those of FeS and HS− alone. This is due mainly to the formation of reactive HS− sites on the surface of FeS. The experimental results presented in this study can provide the basic knowledge to better understand the reaction kinetics and mechanism for the reductive dechlorination of chlorinated aliphatics by FeS and support novel ideas about the effect and role of additives (e.g., transition metal and HS−) on the enhancement of reductive dechlorination by FeS.

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