



## Dechlorination of pentachloroethane by commercial Fe and ferruginous smectite

Javiera Cervini-Silva <sup>a,\*</sup>, Richard A. Larson <sup>b</sup>, Jun Wu <sup>b</sup>, Joseph W. Stucki <sup>b</sup>

<sup>a</sup> Department of Environmental Science, Policy, and Management, University of California, 151 Hilgard Hall #3110, Berkeley, CA 94720-3110, USA

<sup>b</sup> Department of Natural Resources and Environmental Sciences, University of Illinois, W-521 Turner Hall, 1102 South Goodwin Avenue, Urbana, IL 61801, USA

Received 1 May 2001; received in revised form 25 January 2002; accepted 25 January 2002

### Abstract

Short-term experiments were conducted to investigate the effect of a commercial Fe and an iron-bearing clay mineral, ferruginous smectite (SWa-1), on the degradation of pentachloroethane (PCA). After 3 h of contact time, SWa-1 catalyzed PCA dehydrochlorination to tetrachloroethene (PCE, 65% conversion), whereas commercial Fe promoted PCA stepwise dechlorination via dehydrochlorination ( $\approx 40\%$  conversion) and subsequent PCE hydrogenolysis to trichloroethene (TCE). The addition of unaltered SWa-1 to commercial Fe led to a complete inhibition on TCE production, whereas the addition of reduced SWa-1 barely resulted in a 30% decrease. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Structural-Fe oxidation state; Smectites; Dechlorination; Permeable reactive barriers; Groundwater remediation

### 1. Introduction

The transformation of chlorinated aliphatic compounds in the presence of metallic Fe has been the subject of several studies in recent years (Johnson et al., 1996; Fiorenza et al., 2000, and references therein) as part of an effort to assess the effectiveness of reactive barriers for groundwater treatment. Workers (Powell and Puls, 1997) have considered amending clay minerals e.g., well crystallized kaolin, KGa-2; mica montmorillonite, SYn-1, to commercial Fe to enhance dehalogenation reactions by means of in situ proton release. Another study (Shen and Rabideau, 1998) reports that mixing commercial Fe(0) with smectites such as Ca-

montmorillonite (STx-1), hectorite (SHCa-1), montmorillonite (SAz-1), among others, at high temperatures (300–550 °C) enhanced trichloroethene dechlorination. These workers noted a correlation between the degradation rate of trichloroethene and the surface area of the mixture of clay and Fe. Comparing the reactivity of smectites with different structures based solely on the clay surface area could be misleading, however, because of key controlling factors in smectite surface chemistry being overlooked, such as the distribution (Manceau et al., 2000) and oxidation state of structural Fe (Yan and Stucki, 1999), particularly as they relate to hydration (Yan and Stucki, 2000). Furthermore, recent studies show that the oxidation state of structural Fe in smectite clays alters the Brønsted (Cervini-Silva et al., 2000a, 2001) and Lewis (Amonette et al., 1998; Cervini-Silva et al., 2000b) basicity towards chlorinated aliphatics and provide evidence to support a strong correlation between the Fe(II) content in clay minerals, {Fe(II)}, and the rate of dechlorination of chlorinated aliphatics via

\* Corresponding author. Tel.: +1-510-643-9951; fax: +1-510-643-5098.

E-mail address: jcervini@nature.berkeley.edu (J. Cervini-Silva).

dehydrochlorination (1,1,2,2-tetrachloroethane, TeCA and pentachloroethane, PCA; Cervini-Silva et al., 2000a, 2001) and reduction (trichloronitromethane and trichloroacetonitrile; Cervini-Silva et al., 2000b, 2001).

PCA (pentalin®), a common degreasing agent, is used as a chemical intermediate in the manufacture of trichloroethene and is listed as priority pollutant by the US EPA. In spite of that, few mechanistic reports have examined the transformation pathways of PCA in aquatic environments bearing Fe (e.g., Butler and Hayes, 2000; Larson and Cervini-Silva, 2000), and even less attention has been paid to study the fate of PCA in the presence of Fe-bearing clay minerals (Cervini-Silva et al., 2000a, 2001). The purpose of this study was to study the effect of ferruginous smectite in the degradation pathway(s) of PCA in the presence of commercial Fe.

## 2. Materials and methods

### 2.1. Materials

PCA (98%), TeCA (98%), sodium dithionite (98%) were purchased from Aldrich Chemical Company (Milwaukee, WI). Tri- and tetrachloroethene (PCE), sodium citrate dihydrate (99+%), sodium carbonate, and sodium chloride were purchased from Fisher (Fair Lawn, NJ). Industrial ethanol (USP) from McCormick Distilling Company (Weston, MO), and pentane for THM analysis HP from Burdick and Jackson (Muskegon, MI). All the reagents were used as received.

Ferruginous smectite [SWa-1,  $\text{Na}_{0.87}(\text{Si}_{7.38}\text{Al}_{0.62})\text{-(Al}_{1.08}\text{Fe}_{2.67}^{3+}\text{Fe}_{0.01}^{2+}\text{Mg}_{0.23}\text{O}_{20}(\text{OH})_4$ ; Manceau et al., 2000] from Grant County, Washington was purchased from the Source Clays Repository of The Clay Minerals Society.

### 2.2. Clay preparation

A sample of <2  $\mu\text{m}$  particle-size fraction of SWa-1 was saturated with  $\text{Na}^+$ , dialyzed, and freeze-dried. 30 mg portions of the freeze dried SWa-1 were dispersed in 50-ml polycarbonate centrifuge tubes with 20 ml of 5 mM NaCl by shaking gently overnight. This sample, with no reduction treatment, was designated the unaltered sample (SWa-U). Reduction was performed according to the method of Stucki et al. (1984) (using dithionite and a citrate-bicarbonate buffer solution at  $\text{pH} = 8.4$ ). An aliquot of the clay suspension was taken to determine  $\{\text{Fe(II)}\}$ , and total Fe,  $\{\text{Fe}_\text{T}\}$ , using a colorimetric method (Komadel and Stucki, 1988) scaled to microtiter plate format (Stucki, 1981). The content of Fe(III) was deduced by difference,  $\{\text{Fe}_\text{T}\} = \{\text{Fe(II)}\} + \{\text{Fe(III)}\}$ . The  $\{\text{Fe}_\text{T}\}$  in the clay sample was 15.5/100 g clay (2.77 mmol Fe/g clay);  $\{\text{Fe(III)}\}$  and  $\{\text{Fe(II)}\}$  in SWa-U were 15.44 and 0.06/100 g clay, respectively.

After chemical reduction,  $93 \pm 5\%$  of the total Fe was reduced from Fe(III) to Fe(II);  $\{\text{Fe(III)}\}$  and  $\{\text{Fe(II)}\}$  in SWa-R were 0.36 and 15.14/100 g clay, correspondingly.

### 2.3. Reaction of PCA and SWa-1

A 0.2 mM solution of PCA was prepared in 9:1 water–ethanol under an argon atmosphere. 2 ml of PCA stock solution and 2 ml of clay suspension (10 mg clay) were added to a 4.5-ml vessel. Each vessel (15 samples) was septum-sealed and the headspace was saturated with high-purity argon with the aid of thin needles (gauge 25). The final concentration of PCA was 0.1 mM; total clay content was 2.5 mg/ml; NaCl concentration was 2.5 mM. The vessels were placed horizontally in a wrist-action shaker, and removed periodically to collect samples. Samples without clay (0.1 mM PCA and 2.5 mM NaCl) were used as blank solutions.

### 2.4. Reaction of PCA with commercial Fe and commercial Fe + SWa-1

50 mg of commercial Fe (GX-027, Master Builder, Cleveland, OH) as received, 2 ml of PCA stock solution, and 2 ml of deoxygenated water–ethanol mixture were placed in the 4.5 ml capped teflon vessels (PCA-commercial Fe). 50 mg of commercial Fe, 2 ml of PCA stock solution, and 2 ml of clay suspension (SWa-U or SWa-R), were combined (PCA-SWa-commercial Fe). In both experiments the volume mixture was adjusted to 4 ml and no buffer was added. Experiments were also conducted to study the fate of TeCA in binary mixtures to assess its participation as reaction intermediate during PCA degradation.

### 2.5. Analytical techniques

Aliquots of 0.1 ml of the reaction mixture, of either SWa-1, commercial Fe, or SWa-1 and commercial Fe and PCA were collected, filtered with Puradisc™ syringe filters (nylon filters with polypropylene housing, 0.45  $\mu\text{m} \times 1.3$  mm ID, Whatman, Clifton, NJ), diluted with distilled water (1:100), and extracted once with pentane (1:1). A 0.1- $\mu\text{l}$  aliquot of the pentane fraction was injected directly into the gas chromatograph detection port for analysis; the temperature program was the same as that described above. The identification of reactants and products was confirmed using a Hewlett–Packard 5890 quadrupole GC/MS, equipped with an ECD detector (range 10) and a Hewlett–Packard column (HP-5, 12 m  $\times$  0.2 mm ID, and 0.33- $\mu\text{m}$  film thickness). The makeup and carrier gas was nitrogen. After 3 and 18 h of contact time, 1-ml aliquots of the reaction mixtures were filtered and, without diluting,

extracted once with pentane (1:1). The pentane fraction ( $\approx 1$  ml) was separated with a syringe and concentrated once to 0.1 ml by solid-phase extraction using Analytichem Bond Elut solid phase cartridges (C-18, 1 cm<sup>3</sup>/100 mg, Varian, Harbor City, CA). A 0.5- $\mu$ l aliquot of the pentane fraction was injected directly into the GC/MS detection port for analysis.

The proton activity of the supernatant solution of the reaction mixtures was measured right after filtration with a pH meter (Orion 720 A) and Ross combination electrode calibrated with buffer solutions at pH 4 and 7.

### 3. Results and discussion

#### 3.1. Reaction products and kinetics of PCA dechlorination

The disappearance of PCA and the formation of reaction products was monitored by gas chromatography, as described in Section 2. In all the experiments,  $\{\text{Fe}_T\}$  was in molar excess with respect to PCA and the time course of [PCA] in the presence of SWa was approximated by a pseudo-first order kinetic model with its integrated form as

$$[\text{PCA}] = [\text{PCA}]_0 e^{-k_{\text{obs}} t} \quad (1)$$

where  $k_{\text{obs}}$  is the observed pseudo-first order rate constant (Table 1). Values of  $k_{\text{obs}}$  were calculated from the slope of semilogarithmic plots of concentration versus time using data collected over three half-lives for PCA. These plots were approximately linear over one half-life. Linear regression analysis of the data was performed using ANOVA with 95% confidence intervals.

After shaking for 5 h, blank experiments showed 3–5% and 9–12% mass losses for PCA and PCE and trichloroethene (TCE), respectively. Headspace sampling and analysis, GC-ECD and GC/MS, confirmed the enrichment of the gas phase with PCA with time; yet the amount of PCA observed did not account for the mass loss observed from suspension, therefore, it is likely that a fraction of PCA remained sorbed at the clay surface. Degradation products present below detection limits and polar products (e.g., nonchlorinated organic acids), presumably formed because of PCA (slow) hydrolysis via substitution mechanism(s), were not quantified. Consequently, the observed disappearance of PCA may not be attributed solely to adsorption at the clay surface.

**PCA and SWa-1.** The presence of SWa-R facilitated the dehydrochlorination of PCA (Eq. (2); Fig. 1) to PCE when compared to hydrolysis in bulk water under the same pH conditions. These results agree with previous work (Cervini-Silva et al., 2000a,b, 2001) in that the  $k_{\text{obs}}$  increases with the reduction of the structural Fe of the clay (Table 1). Incubations of PCA with treated

Table 1  
Dechlorination of PCA in the presence of commercial Fe, SWa-1, and commercial Fe + SWa-1

Source of Fe	$k_{\text{obs}}$ (h <sup>-1</sup> ) <sup>a</sup>	Reaction products	Conversion (%)
Commercial Fe <sup>b,c</sup>	$0.81 \pm 0.21$	PCE	$39.8 \pm 1.2^d$
		TCE	$42.8 \pm 4.2^e$
SWa-U <sup>b,c</sup>	$0.26 \pm 0.05$	PCE	$44.6 \pm 0.8^d$
SWa-R <sup>b,c</sup>	$>5.5^f$	PCE	$58.6 \pm 8.3^d$
Commercial Fe + SWa-U <sup>c</sup>	$0.24 \pm 0.06$	PCE	$42.4 \pm 1.6^d$
Commercial Fe + SWa-R <sup>c</sup>	$0.38 \pm 0.08$	PCE	$45.5 \pm 2^d$
		TCE	$6.9 \pm 1.4^e$

<sup>a</sup>  $k_{\text{obs}}$  was calculated as described in the text by linear regression analysis of the data using ANOVA with 95% confidence intervals. The average number of data sets used to calculate  $k_{\text{obs}}$  was 5.

<sup>b</sup> The specific surface area of commercial Fe, and SWa-U and SWa-R was 3.3 (Johnson et al., 1996), and 700.4 and 559.3 m<sup>2</sup> g<sup>-1</sup> (Lear and Stucki, 1989), correspondingly.

<sup>c</sup> The mass concentration of the surface was 12.5 and 2.5 g l<sup>-1</sup> suspension for commercial Fe and SWa(-U or -R), respectively.

<sup>d</sup> The conversion refers to the number of moles of PCE that have formed per mole of PCA initially present in the reactor after 5 h of contact time and monitored periodically in the following 24 h.

<sup>e</sup> The conversion refers to the number of moles of TCE that have formed per mole of PCA initially present in the reactor after 5 h of contact time and monitored periodically in the following 24 h.

<sup>f</sup> “>” refers to too fast to measure  $k_{\text{obs}}$  accurately using the integral method. The hydrolysis-rate constant found for PCA in 5 mM NaCl was  $8.05 \times 10^{-3}$  h in agreement with previous studies (Roberts and Gschwend, 1991).

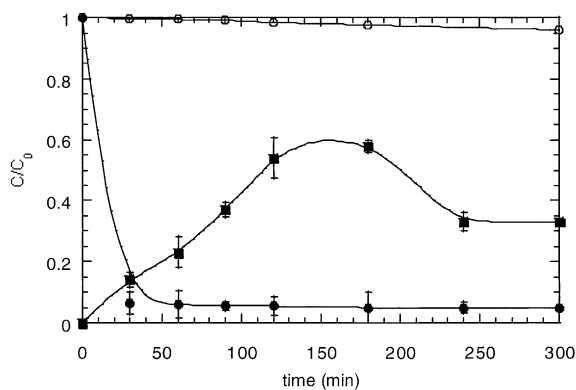


Fig. 1. The reaction of PCA (circles) with reduced SWa. The production of PCE (squares) is normalized to the initial concentration of PCA,  $C_0$ . Open squares denote control experiment for PCA in distilled water. Error bars indicate twice the standard deviation of triplicate sample measurements. Lines are to aid the eye and do not indicate a model fit.

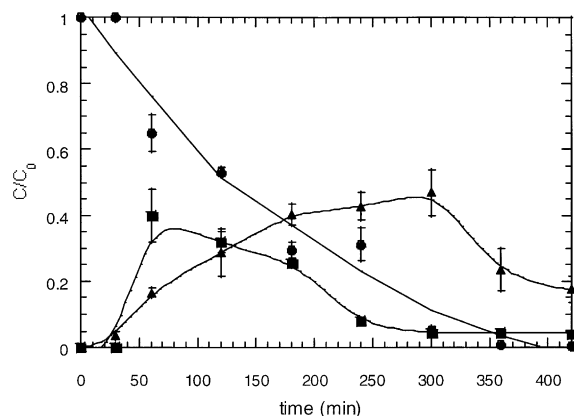
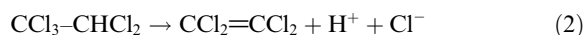
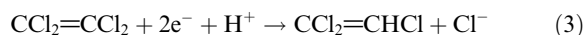


Fig. 2. The reaction of PCA (circles) with commercial Fe. The production of PCE (squares) and TCE (triangles) is normalized to the initial concentration of PCA,  $C_0$ . Error bars indicate twice the standard deviation of triplicate sample measurements. Lines are to aid the eye and do not indicate a model fit.

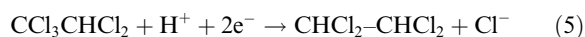
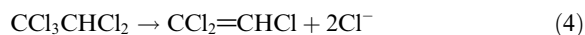
and nontreated clay by citrate led to similar trends in the PCA disappearance and conversion to PCE.



**PCA-commercial Fe.** Fig. 2 shows the formation of PCE and TCE as major products of the reaction between PCA and commercial Fe. PCE was formed first and its concentration decreased, while the concentration of TCE increased as the reaction progressed, which indicates two consecutive dechlorination reactions: PCA dehydrochlorination to PCE and subsequent PCE hydrogenolysis to TCE (Eqs. 2 and 3). Furthermore, experiments in which the supernatant solution of a commercial Fe–water mixture was incubated with PCA (contact time = 0–5 h) showed no formation of TCE suggesting that Fe, which acts as reductant towards PCA, may be active only in either Fe(0) or Fe(II)-bound form.



Like SWa-1, commercial Fe accelerated the formation of PCE when compared to PCE production during PCA base-promoted dehydrohalogenation (Roberts and Gschwend, 1991) or hydrolysis (Jeffers et al., 1989) in bulk water. Fig. 2 illustrates that PCA contributed to TCE production because of either reductive dechlorination (Eq. (4)), or hydrogenolysis to TeCA (Eq. (5)) and subsequent TeCA dehydrochlorination (Eq. (6)). However, it is likely that the reductive dechlorination pathway prevailed because incubations of TeCA with Fe(0) for 5 h showed no formation of TCE.



**PCA-SWa-commercial Fe.** PCE was the main product formed from the reaction between PCA with SWa-R and commercial Fe (Table 1). The addition of clay, either in the unaltered or reduced form, to commercial Fe retarded PCA dehydrochlorination to PCE and PCE hydrogenolysis to TCE (Eq. (3)). The inhibition of PCA dechlorination was independent of the oxidation state of structural Fe and the clay surface area (Table 1). These results suggest a decrease in the active sites at the commercial Fe surface because of (a) clogging by clay deposition or (b) clay-catalyzed complexation and precipitation of Fe(III) at the commercial Fe surface (Thompson and Tahir, 1991).

Aging (Stucki et al., 1984), pH (Rozenon and Heller-Kallai, 1976), temperature (Rozenon and Heller-Kallai, 1978) and composition (Amonette et al., 1998) have an effect in clay dissolution and, consequently, in the amount of  $\text{Fe}^{2+}$  released to suspension, thereby altering the redox chemistry at the clay–water interface, which could enhance the formation of reduction products. Ongoing experiments show that the accumulation of  $\text{Fe}^{2+}$  on the clay surface in the reduced form, as result of grinding with commercial Fe, contributes to the simultaneous hydrogenolysis (Eq. (5)) and dehydrochlorination (Eq. (4)) of PCA to TeCA (28%) and PCE (18%), respectively, and inhibits the formation of TCE (Fig. 3).

### 3.2. pH effect on PCA degradation

Similar steady increases in pH from 7.5 to 8.3 were observed during incubations of PCA with commercial

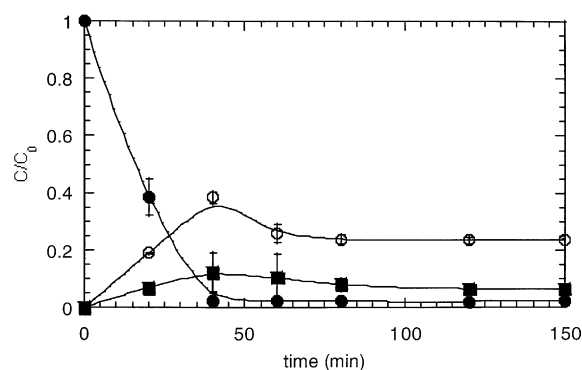


Fig. 3. Hydrogenolysis and dehydrochlorination of PCA (closed circles) in the presence of SWa-R and  $\text{Fe}^{2+}$  to TeCA (squares) and PCE (open circles), respectively. Suspension composition: 0.1 mM PCA, 0.5 M  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , 2.5 mg clay  $\text{ml}^{-1}$  suspension, and 2.5 mM NaCl concentration. No pH buffer was added. Error bars indicate twice the standard deviation of triplicate sample measurements. Lines are to aid the eye and do not indicate a model fit.

Fe, commercial Fe and SWa-U, or commercial Fe and SWa-R. From the second-rate constant for PCA base-promoted dehydrochlorination reaction ( $9.8 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ ; Roberts and Gschwend, 1991),  $k_{\text{OH}}^-$  the pseudo-first order constant for the base-promoted dehydrochlorination is expected to be  $3.1 \times 10^{-2} \text{ h}^{-1}$  at pH 7.5 and  $3.1 \times 10^{-1} \text{ h}^{-1}$  at pH 8.5. It amounts to nearly 40%, of the PCA  $k_{\text{obs}}$  in the presence of commercial Fe (Table 1), thus the formation of PCE is partially caused by the increase in  $[\text{OH}^-]$  because of commercial Fe anoxic corrosion. In contrast, the supernatant solution of PCA-SWa (U or R) suspensions showed little pH variation,  $7.3 \pm 0.1$ , and the expected pseudo-first order constant for the base-promoted dehydrochlorination,  $3.8 \times 10^{-2} \text{ h}^{-1}$ , barely accounts for 15 and 0.7% of PCA  $k_{\text{obs}}$  in the presence of SWa-U, and SWa-R, respectively. These results are consistent with the idea that clay minerals catalyze the hydrolysis of halogenated aliphatics (El-Amery and Mill, 1984).

The outcome of this study shows that conducting fundamental research on the surface chemistry of Fe(0)-smectite mixtures merits further scrutiny as a preliminary step to assess the potential implementation of smectites in large-scale systems (e.g., reactive slurry walls) for the removal of chlorinated solvents from natural waters.

## Acknowledgements

The authors thank Karen A. Marley (University of Illinois at Urbana-Champaign) and Dr Charles B. Roth (Purdue University) for helpful discussions, and the analytical support for iron elemental analysis to the microanalysis laboratory of the School of Chemical Sciences of the University of Illinois at Urbana-Champaign. This work was supported in part by the US Department of Agriculture (Grant Numbers NRI-CRGP 93-37102-8957 and 98-35107-6313) and the National Science Foundation (Grant Number EAR 95-23902).

## References

- Amonette, J.E., Fruchter, J.S., Gorby, Y.A., Cole, C.R., Cantrell, K.J., Kaplan, D.I., 1998. Method of removing oxidized contaminants from water. US Patent 5 783 088.
- Butler, E.C., Hayes, K.F., 2000. Kinetics of the transformation of halogenated aliphatic compounds by iron sulfide. *Environmental Science and Technology* 34, 422–429.
- Cervini-Silva, J., Wu, J., Stucki, J.W., Larson, R.A., 2000a. Adsorption kinetics of pentachloroethane in iron-bearing smectites. *Clays and Clay Minerals* 48, 132–138.
- Cervini-Silva, J., Wu, J., Larson, R.A., Stucki, J.W., 2000b. Transformation of chloropicrin in the presence of iron(II)-bearing clay minerals. *Environmental Science and Technology* 34, 915–917.
- Cervini-Silva, J., Larson, R.A., Wu, J., Stucki, J.W., 2001. Transformation of chlorinated aliphatic compounds by ferruginous smectite. *Environmental Science and Technology* 35, 405–409.
- El-Amery, M.M., Mill, T., 1984. Hydrolysis kinetics of organic chemicals on montmorillonite and kaolinite surfaces as related to moisture content. *Clays and Clay Minerals* 32, 67–73.
- Fiorenza, S., Oubre, C.L., Ward, C.H., 2000. *Sequenced Reactive Barriers for Groundwater Remediation*. Lewis Publishers, Boca Raton.
- Jeffers, P.M., Ward, L.M., Woytowitch, L.M., Wolfe, N.L., 1989. Homogeneous hydrolysis rate constants for selected chlorinated methanes ethanes and propanes. *Environmental Science and Technology* 23, 965–969.
- Johnson, T.L., Scherer, M.M., Tratnyek, P.G., 1996. Kinetics of halogenated organic compound degradation by iron metal. *Environmental Science and Technology* 30, 2634–2640.
- Komadel, P., Stucki, J.W., 1988. Quantitative assay of minerals for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  using 1,10-phenanthroline: III. A rapid photochemical method. *Clays and Clay Minerals* 36, 379–385.
- Larson, R.A., Cervini-Silva, J., 2000. Dechlorination of substituted trichloromethanes by an iron(II) porphyrin. *Environmental Toxicology and Chemistry* 19, 543–548.
- Lear, P., Stucki, J.W., 1989. Effects of iron oxidation state on the specific surface area of nontronite. *Clays and Clay Minerals* 37, 547–552.
- Manceau, A., Lanson, B., Drits, V.A., Chateigner, D., Gates, W.P., Wu, J., Huo, D., Stucki, J.W., 2000. Oxidation–reduction mechanism of iron in dioctahedral smectites. 1. Structural chemistry of oxidized reference nontronites. *American Mineralogist* 85, 133–145.
- Powell, R.M., Puls, R.W., 1997. Proton generation by dissolution of intrinsic or augmented aluminosilicate minerals for in situ contaminant remediation by zero-valence-state iron. *Environmental Science and Technology* 31, 2244–2251.
- Roberts, A.L., Gschwend, P.M., 1991. Mechanism of pentachloroethane dehydrochlorination to tetrachloroethylene. *Environmental Science and Technology* 25, 76–86.
- Rozenson, I., Heller-Kallai, L., 1976. Reduction and oxidation of  $\text{Fe}^{3+}$  in dioctahedral smectites. 1. Reduction with hydrazine and dithionite. *Clays and Clay Minerals* 24, 271–282.
- Rozenson, I., Heller-Kallai, L., 1978. Reduction and oxidation of  $\text{Fe}^{3+}$  in dioctahedral smectites. 3. Oxidation of octahedral iron in montmorillonite. *Clays and Clay Minerals* 26, 88–92.
- Shen, P., Rabideau, A.J., 1998. Enhanced degradation of trichloroethylene in the presence of metallic iron and soil smectites. In: *Proceedings of the 13th Mid-Atlantic Industrial and Hazardous Waste Conference*, vol. 5. Pittsburgh, PA, USA, July 12–15, pp. 349–357.
- Stucki, J.W., 1981. The quantitative assay of minerals for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  using 1,10-phenanthroline: 2. A photochemical method. *Soil Science Society of America Journal* 45, 638–641.
- Stucki, J.W., Golden, D.C., Roth, C.B., 1984. The preparation and handling of dithionite-reduced smectites suspensions. *Clays and Clay Minerals* 39, 191–197.

- Thompson, D.W., Tahir, N.M., 1991. The influence of a smectites clay on the hydrolysis of iron(III). *Colloids and Surfaces A* 60, 369–398.
- Yan, L.B., Stucki, J.W., 1999. Effects of structural Fe oxidation state on the coupling of interlayer water and structural Si–O stretching vibrations in montmorillonite. *Langmuir* 15, 4648–4657.
- Yan, L.B., Stucki, J.W., 2000. Structural perturbations in the solid–water interface of the redox transformed nontronite. *Journal of Colloid and Interface Science* 225, 429–439.