

Supporting Information

Abiotic reductive dechlorination of *cis*-dichloroethylene by Fe species formed during iron- or sulfate-reduction

Hoon Y. Jeong,^{†,*} Karthik Anantharaman,[‡] Young-Soo Han,[‡] and Kim F. Hayes[‡]

[†]Department of Geological Sciences, Pusan National University, Busan 609-735, Korea.

[‡]Department of Civil and Environmental Engineering, University of Michigan, Ann Arbor, MI 48109, USA.

*Corresponding author: Hoon Y. Jeong

Department of Geological Sciences, Pusan National University, Busan 609-735, Korea.

Phone number: 82-51-510-2249; fax: 82-51-517-6389; e-mail: hjeong@pusan.ac.kr.

Submitted to Environmental Science & Technology

Revised manuscript was prepared on April 27, 2011.

Pages (including the cover page): 8

Number of figures: 3 (S1–S3)

Gas Chromatography (GC) analysis.

cis-DCE and its potential dechlorination products including vinyl chloride (VC), acetylene, ethylene, and ethane were analyzed on a combination of a Tekmar 7000 headspace autosampler and a HP 5890 GC equipped with flame ionization detector (FID) and electron capture detector (ECD). The headspace vials were equilibrated for 20 min at 80°C in the autosampler. After the carrier gas from the autosampler passed through a J&W Scientific DB-624 column (30 m × 0.53 mm i.d. with 3 µm film thickness), it was split into a second DB-624 column connected to ECD and a J&W Scientific GS-Q column (30 m × 0.5 mm i.d.) connected to FID. Oven temperature was changed as follows: isothermal at 40°C for 10 min, ramping to 90°C at 5°C/min, ramping to 220°C at 15°C/min, and isothermal at 220°C for 5 min. Concentrations of *cis*-DCE, VC, acetylene, and ethylene were determined by comparison of GC peak areas to five-point standard curves. For *cis*-DCE, GC peak area was normalized with respect to that of *trans*-DCE.

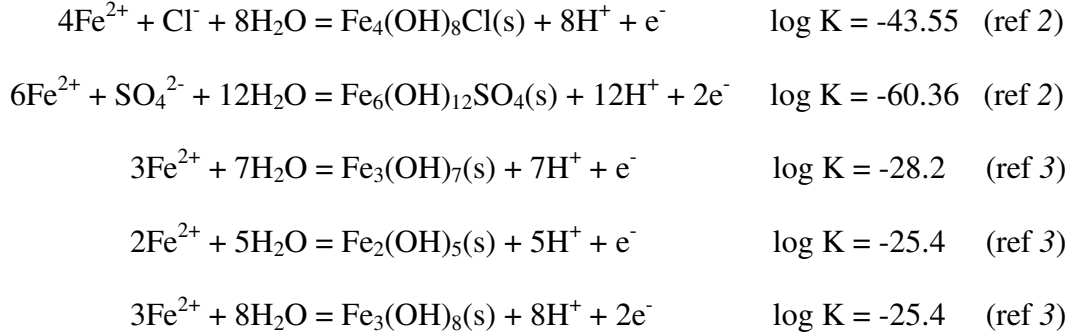
Equilibrium calculations for the prediction of bulk-phase Fe precipitates using MINEQL+4.5 (ref 1).

For equilibrium calculations, the initial concentrations of components (Fe^{2+} , Fe^{3+} , HS^- , SO_4^{2-} , and Cl^-) were input according to the compositions in Table 1. The pH and pe values were measured using a pH electrode and an ORP combination electrode, respectively. In these calculations, the ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple was allowed to float in response to the pe value. However, the ratio of $\text{HS}^-/\text{SO}_4^{2-}$ redox couple was fixed to their initial ratio to reflect the slow conversion between the two under anoxic conditions. It should be noted that the floating of the ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple redox allows mixed Fe(II)-Fe(III) solids (e.g., green rusts) to form even when no Fe(III) is initially present (i.e., $\text{Fe(III)}_0 = 0$). This is possible since the ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ is calculated in response to the pe values rather than the initial concentrations of Fe(II) and Fe(III). The justification for allowing for this possibility in equilibrium calculations is that anoxic corrosion reactions of Fe(II) precipitates with water or slight oxygen contamination can produce Fe(III) even when Fe(III) concentration is initially zero. For aqueous species (Type II species), the default thermodynamic data in MINEQL+ 4.5 were used without change. In case of dissolved solids (Type V species), some modification was made as follows:

For the evaluation of stable Fe precipitates

The default equilibrium constants (K) were used for goethite, magnetite, $\text{Fe(OH)}_2(\text{s})$, mackinawite, greigite, and pyrite. Updated equilibrium constants (K) were used for

chloride green rust ($\text{Fe}_4(\text{OH})_8\text{Cl}$), sulfate green rust ($\text{Fe}_6(\text{OH})_{12}\text{SO}_4$), and hydroxy green rusts ($\text{Fe}_3(\text{OH})_7$, $\text{Fe}_2(\text{OH})_5$, and $\text{Fe}_3(\text{OH})_8$) as follows:



For the evaluation of metastable Fe precipitates

Among the above solids, goethite, magnetite, pyrite, and hydroxy green rusts were removed for calculations.

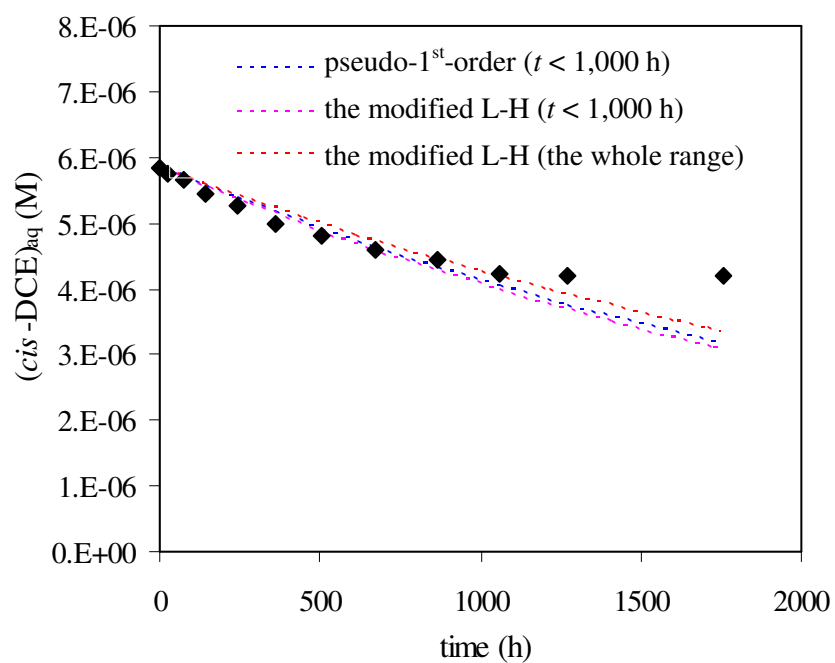


Figure S1. Model fits with a pseudo-first-order rate law and the modified Langmuir-Hinshelwood (L-H) rate law (see the main text for the description of these rate laws). The data range fitted is provided in parenthesis.

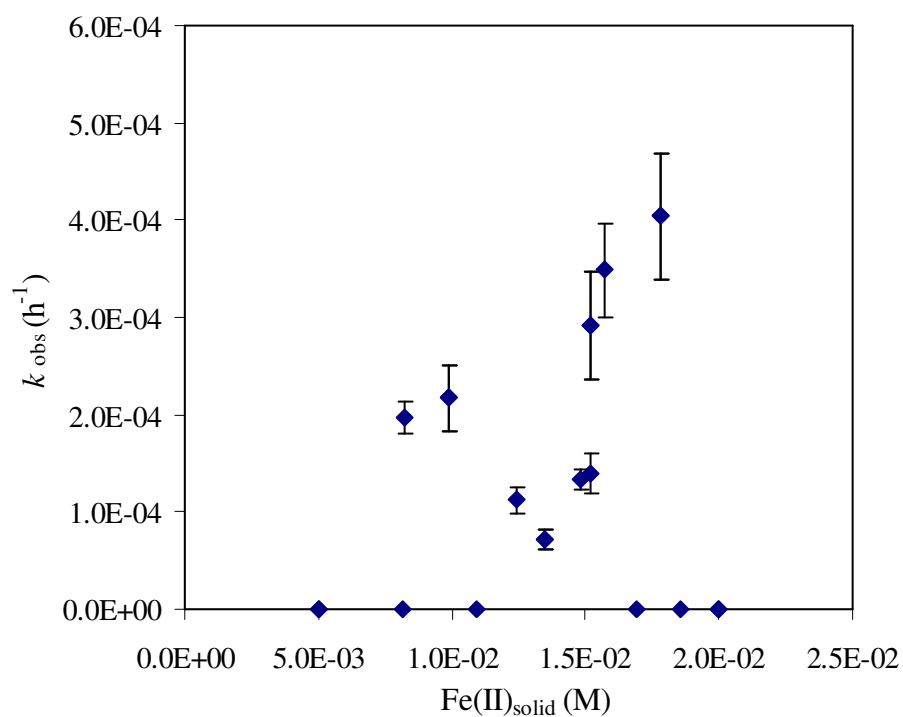


Figure S2. Relationship between solid-phase Fe(II) concentrations ($\text{Fe(II)}_{\text{solid}}$) and pseudo-first-order rate constants (k_{obs}). Error bars represent one standard deviation.

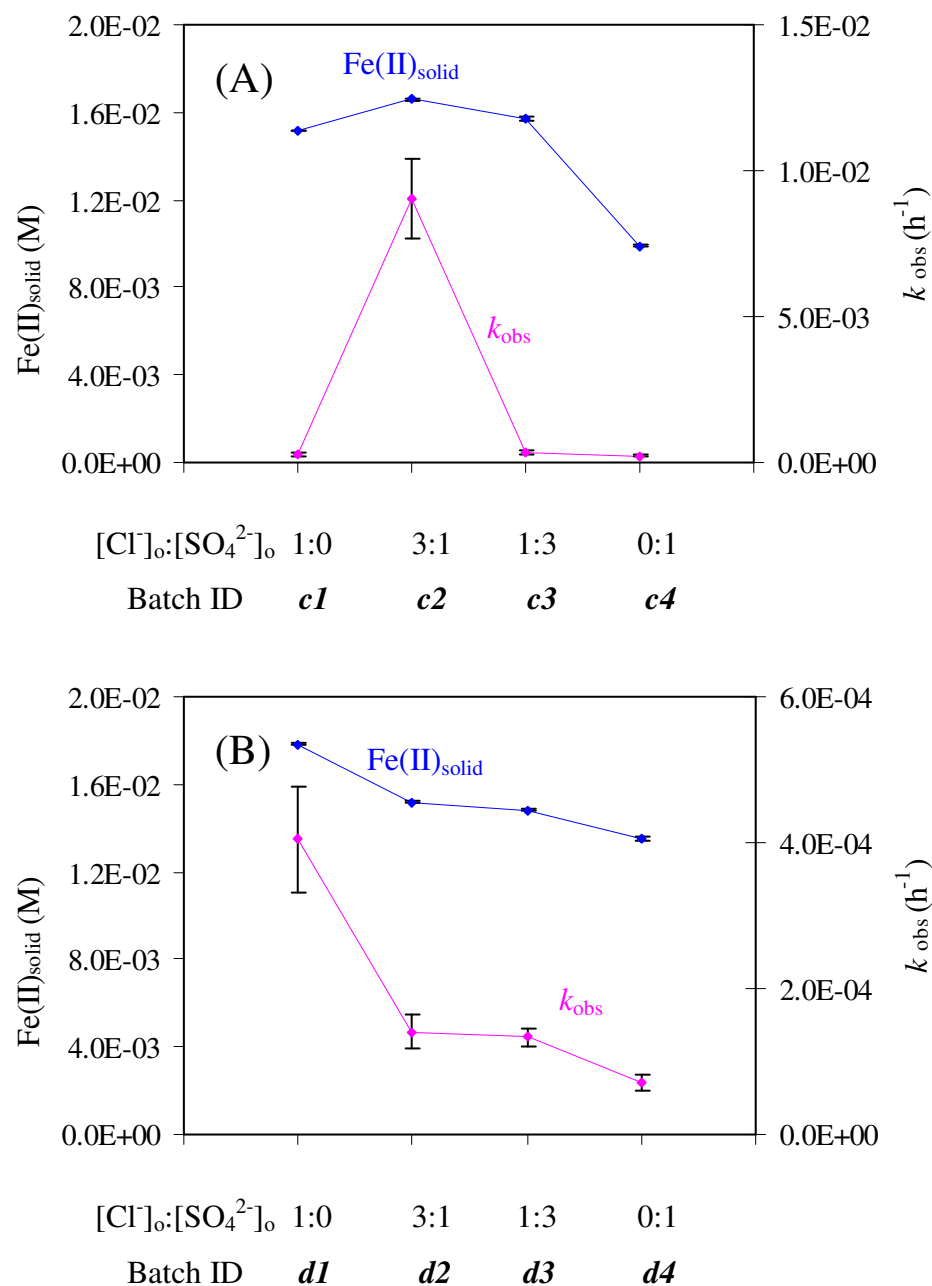


Figure S3. Relationship between solid-phase Fe(II) concentrations ($\text{Fe(II)}_{\text{solid}}$) and pseudo-first-order rate constants (k_{obs}) for the batches in Figure 3A (part A) and the batches in Figure 3B (part B). Error bars for $\text{Fe(II)}_{\text{solid}}$ represent one standard deviation, and those for k_{obs} represent 95% confidence interval.

References cited in Supporting Information

1. Schecher, W.D.; McAvoy, D.C. *MINEQL+ 4.5*; Environmental Research Software: Hallowell, ME, 2001.
2. Génin, J.-M.R.; Bourrié, G.; Trolard, F.; Abdelmoula, M.; Jaffrezic, A.; Refait, P.; Maitre, V.; Humbert, B.; Herbillon, A. Thermodynamic equilibria in aqueous suspensions of synthetic and natural Fe(II)-Fe(III) green rusts: occurrences of the mineral in hydromorphic soils. *Environ. Sci. Technol.* **1998**, *32*, 1058-1068.
3. Bourrié, G.; Trolard, F.; Génin, J.-M.R.; Jaffrezic, A.; Maitre, V.; Abdelmoula, M. Iron control by equilibria between hydroxy-green rusts and solutions in hydromorphic soils. *Geochim. Cosmochim. Acta* **1999**, *63*, 3417-3427.