

## Supporting Information

**Relative Importance of Mass Transfer and Reaction Kinetics.** As described in Figure S-1, mass transfer of a solute from the solution to the reactive surface can be described by diffusion through a stagnant layer. Fick's law describes the diffusive transport as follows (Clark 1996):

$$J = D_m \frac{(C_b - C_s)}{\delta} = k_m (C_b - C_s) \quad (\text{S-1})$$

where  $J$  is the flux of a compound at the surface ( $\text{ML}^{-2}\text{T}^{-1}$ ),  $D_m$  is the molecular diffusivity of the compound ( $\text{L}^2\text{T}^{-1}$ ),  $C_b$  is the concentration of the compound in the bulk liquid ( $\text{ML}^{-3}$ ),  $C_s$  is the concentration of the compound at the surface ( $\text{ML}^{-3}$ ),  $\delta$  is the thickness of the stagnant layer (L), and  $k_m$  is the mass transfer coefficient ( $\text{LT}^{-1}$ ). If a first-order reaction occurs on the surface, the material balance around the surface gives the following equation at steady state:

$$k_s C_s = k_m (C_b - C_s) \quad (\text{S-2})$$

where  $k_s$  = surface reaction rate ( $\text{LT}^{-1}$ ). Upon manipulation, eq (S-2) becomes

$$C_s = \frac{C_b}{\left(\frac{k_s}{k_m} + 1\right)} \quad (\text{S-3})$$

A term,  $k_s/k_m$ , in eq (S-3) is a dimensionless number known as the second Damköhler number ( $D_{a,II}$ ) (Clark 1996). This number is the ratio of the diffusion and reaction time scales.

Therefore, when  $D_{a,II} \ll 1$ , the observed rate is limited by reaction. When  $D_{a,II} \gg 1$ , the observed rate is limited by diffusive mass transfer. Eq (S-3) can be used to derive a rate expression for a batch reactor system as follows:

$$\dot{m} = V k_{app} C_b = A k_s C_s = \frac{A k_s C_b}{\left(\frac{k_s}{k_m} + 1\right)} \quad (\text{S-4})$$

where  $\dot{m}$  is the rate of change of the compound mass in the reactor ( $\text{MT}^{-1}$ ),  $V$  is the volume of the liquid ( $\text{L}^3$ ),  $k_{app}$  is the apparent first-order rate constant ( $\text{T}^{-1}$ ), and  $A$  is the surface area of the reactive surface ( $\text{L}^2$ ). From eq (S-4),

$$k_s = \frac{k_{app} \left(\frac{V}{A}\right)}{\left\{1 - \frac{k_{app} \left(\frac{V}{A}\right)}{k_m}\right\}} \quad (\text{S-5})$$

From eq (S-1), the mass transfer coefficient ( $k_m$ ) can be expressed as the ratio,  $D_m/\delta$ . Therefore,  $D_{a,II}$  is expressed as follows:

$$D_{a,II} = \frac{k_s}{k_m} = \frac{k_{app} \left(\frac{V}{A}\right)}{\left\{\frac{D_m}{\delta} - k_{app} \left(\frac{V}{A}\right)\right\}} \quad (\text{S-6})$$

The thickness of the stagnant layer ( $\delta$ ) in a porous solid could be approximated as the radius of the pore, if there is a sufficient number of active sites so that diffusion of target compound to an active site is primarily radial. If the number of active sites is not sufficiently high, then diffusion would also have a substantial longitudinal component and the thickness of the stagnant layer would be some multiple of the pore radius.

To evaluate the relative importance of mass transfer and reaction kinetics in the solid phase systems, the second Damköhler number ( $D_{a,II}$ ) for the experiment that showed the most rapid degradation kinetics (53.9 g Fe(II)/kg experiment) was calculated. First,  $\delta$  was approximated as 0.2 mm, which lies within the size range that occupies the largest portion of the soil sample (Table S-1). As such, it is a generous estimate of the pore radius. Then, it was assumed that the chloride-containing green rust (GR1(Cl)) was an effective reagent and that 5% of the Fe(II) initially added in the system transformed to GR1(Cl). This amount of the reactive agent is equivalent to 10 times the stoichiometric amount needed to reduce PCE spiked into the system completely to ethylene. The specific surface area of the chloride-containing green rust measured in our lab (109 m<sup>2</sup>/g) was used to estimate the area of reactive surfaces. The values for  $k_{app}$  (column 3 in Table 4) and  $V$  (aqueous phase volume) are  $6.13 \times 10^{-7}$  1/s and  $9.46 \times 10^{-6}$  m<sup>3</sup>, respectively. The diffusivity of PCE was estimated as  $8.7 \times 10^{-10}$  m<sup>2</sup>/s (Hayduk and Laudie 1974)

The resulting  $D_{a,II}$  for this case is shown in Table S-2 (case 1). The value calculated is much less than 1, which indicates that the surface reaction controlled the overall kinetics of PCE degradation and that mass transfer did not limit the observed rates. The effect of larger  $\delta$  (10 x) and smaller A (1/10 x) were evaluated as case 2 (Table S-2). A larger estimate of  $D_{a,II}$  was

obtained, but it is still substantially less than one. In the case of the experiments with lower Fe(II) doses, similar or lower estimates for  $D_{a,II}$  will be obtained. Thus, it is unlikely that mass transfer kinetics limited the observed PCE degradation kinetics in the solid-phase systems.

### Literature Cited

Clark, M. M. *Transport Modeling for Environmental Engineers and Scientists*; John Wiley & Sons: New York, NY, 1996.

Hayduk, W. and Laudie, H. "Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions," *AIChE J*, 20(3): 611-15, 1974.

Soil Science Society of America. *Methods of Soil Analysis, Part I. Physical and Mineralogical Methods-Agronomy Monograph No. 9*; 2nd ed.; Soil Science Society of America: Madison, WI, 1986.

Table S-1. Particle Size Distribution of the Silawa Soil<sup>a</sup>.

type	sand						silt		clay	
size (mm)	2.0- 1.0	1.0- 0.5	0.5- 0.25	0.25- 0.10	0.10- 0.05	total (2.0-0.05)	0.02- 0.002	total (0.05-0.002)	< 0.0002	total (<0.002)
Content (%)	0.3	0.6	15.5	46.0	18.7	81.1	5.5	12.2	3.7	6.7

<sup>a</sup>Determined by the pipette method (SSSA 1986)

Table S-2. Estimation of the Second Damköhler Number ( $D_{a,II}$ ) for the Solid Phase Experiments

case No.	$\delta$ (mm)	$k_m$ (m/s)	A (m <sup>2</sup> )	$D_{a,II}$
1	0.2	$4.35 \times 10^{-6}$	13.6	$9.81 \times 10^{-8}$
2	2	$4.35 \times 10^{-7}$	1.36	$9.82 \times 10^{-6}$

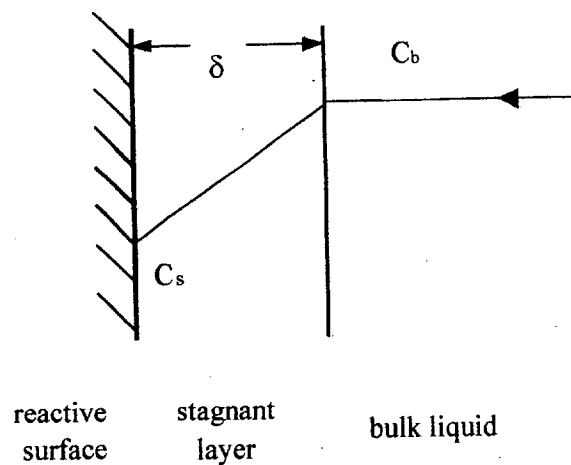


Figure S-1. Conceptual Basis for the Diffusive Transport of a Compound toward a Surface.