

Reductive Dechlorination of Tetrachloroethylene in Soils by Fe(II)-Based Degradative Solidification/Stabilization

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ABSTRACT

An experimental study was conducted to test the feasibility of degradative solidification/stabilization (DS/S) process in treating tetrachloroethylene (PCE) in solid phase systems. The Fe(II)-based ds/s process successfully treated PCE in a soil at the reaction rates that would not allow significant release of the contaminant in the environment. A leach model was also developed that could describe the relative importance of leaching and degradation in ds/s. The first and second Damköhler numbers and dimensionless time were important parameters that determined leaching processes in wastes treated by ds/s.

Key words: chlorinated hydrocarbons, remediation, degradative solidification/stabilization, reductive dechlorination, leach model, ferrous iron

1. INTRODUCTION

Degradative Solidification/Stabilization (DS/S) is a modification of conventional S/S processes that promotes degradation of organic contaminants while containing them as well as containing inorganic contaminants. Reductive dechlorination was studied as a degradative reaction for chlorinated hydrocarbons in DS/S. A preliminary experiment was conducted in our lab to identify an effective DS/S system for chlorinated hydrocarbons. The experiment found Fe(II) was a promising reductant for chlorinated hydrocarbons. Fe(II) could completely dechlorinate tetrachloroethylene (PCE) to non-chlorinated hydrocarbons in 10% cement slurries⁽¹⁾. In this study, the Fe(II)-based DS/S technology was applied to treat a soil contaminated with PCE. Leach models are useful in evaluating the performances of the solidified wastes.⁽²⁾ They can simulate the overall release of the contaminants from treated materials. Leach models for DS/S systems would include description of leaching and degradation.

The objective of this research was to further evaluate the Fe(II)-based DS/S technology by investigating PCE dechlorination in solid phase systems such as would be produced by s/s treatment of soils and sediments. An additional objective was to develop a leach model that could describe the relative importance of degradation and leaching during DS/S.

2. MATERIALS AND METHODS

The soil used for degradation experiments was collected from the first ~20 cm to ~40 cm of the surface at a site in College Station, Texas. The soil was dried and screened to particle sizes below 0.425 mm (No. 40 mesh).

First, the sorption potential of the soil for the target compound (PCE) was tested. An isotherm experiment was conducted at pH 12.1 at a soil to water ratio of 1.29 by using 25-mL glass vials. Seven different initial concentrations of PCE (6.25, 12.5, 25, 52.5, 105, 168, 210 mg/L) were used. The equilibration time was 7 days.

PCE degradation experiments were also carried out by using the same 25-mL glass vials. All samples were prepared in an anaerobic chamber (Coy Laboratory Products). First, appropriate amounts of the soil, cement, water, and Fe(II) stock solutions were transferred to vials and were mixed. KOH (5.3 N) or HCl (5 N) solution was also added to maintain pH of the systems around 12.1. The mass ratio of soil:cement:water was 62.5:7.5:30. Then reactions were initiated by spiking methanolic stock solutions of PCE to yield a PCE concentration of 100 mg/kg soil. The samples were cured at the room temperature. At each sampling time, samples were extracted for PCE and its degradation products using pentane in 250 mL plastic bottles with fluorinated surface.

3. RESULTS AND DISCUSSION

3.1 Degradation Experiments

From the sorption experiment, a value for K_p of 0.622 L/kg was obtained. Using the f_{oc} value for the soil (0.0069), a value for K_{oc} of 90.1 was obtained, which is about a factor of 2 to 4 lower than experimentally determined K_{oc} values of PCE for natural solids in the study of Mouvet et al.⁽³⁾

Figure 1 shows the results of the PCE degradation experiments. Lines in Figure 1 represent first-order fits. TCE was the only chlorinated intermediate product observed in these experiments. The concentrations of TCE did not exceed 7% of the initial concentration of PCE on a molar basis. TCE disappeared within the first 11 days in three higher Fe(II) dose experiments, but persisted throughout the experimental period in the 5.39 g Fe(II)/kg experiment. The absence of the degradation products such as dichloroethylenes and vinyl chloride implies that Fe(II)-based DS/S technology may completely dechlorinate PCE in soils without production of hazardous intermediates. Figure 1 shows that the apparent half-lives of PCE are generally within time frames allowable for DS/S technology, i.e., several months to years. Half-lives of PCE even shorter than those of the present experiments may be obtained by adding Fe(III) and/or an appropriate anion such as sulfate.⁽¹⁾ Such additions were found to increase reaction rates in slurry reactors, possibly by promoting the formation of larger amounts of the reactive agent.

3.2 Development of Leach Model

A model for leaching of a target compound from a waste treated by DS/S is based on a dynamic material balance within the waste form and the following assumptions:

- one dimensional transport by diffusion in a slab
- linear partitioning at equilibrium

○ Control ■ 5.39 g Fe(II)/kg ◆ 13.5 g Fe(II)/kg ▲ 27.0 g Fe(II)/kg ● 53.9 g Fe(II)/kg

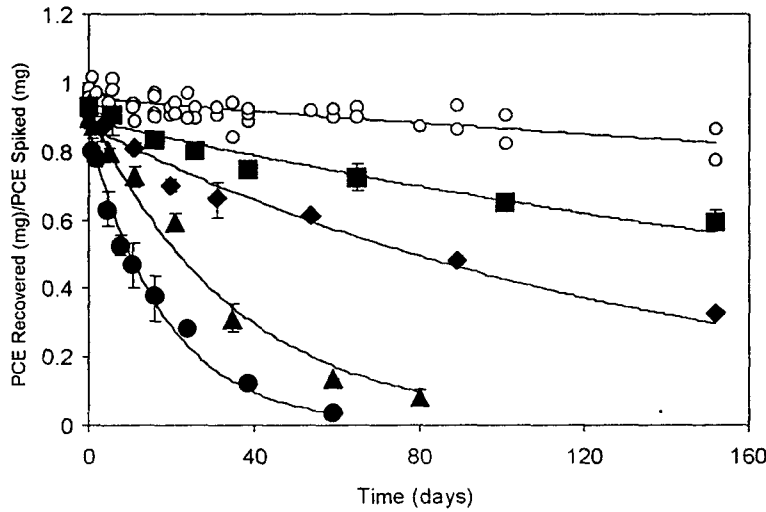


Fig. 1. Kinetics of PCE reduction by Fe(II) in solidified soils.

- first-order degradation rate
- infinite bath (concentrations outside waste form remain very low)

Using these assumptions, the material balance equation expressed in terms of dimensionless variables is as follows:

$$\text{Material balance equation: } \frac{\partial \bar{C}}{\partial \bar{t}} = \frac{\partial^2 \bar{C}}{\partial \bar{x}^2} - D_{a,II} \bar{C} \quad (1)$$

$$\text{where: } \bar{C} = \frac{C}{C_0} ; \quad \bar{x} = \frac{x}{L} ; \quad \bar{t} = \frac{D_e t}{RL^2} ; \quad D_{a,II} = \frac{kL^2}{D_e} ; \quad R = 1 + \rho_b K / \varepsilon$$

The material balance equation has been solved for the case of heat transfer⁽⁴⁾ and the result can be applied to this problem as the following:

$$\frac{M_t}{M_0} = 2 \sum_{i=0}^{\infty} \frac{1 - \exp\left(D_{a,II} + \left(\frac{(2i+1)\pi}{2}\right)^2 \bar{t}\right)}{D_{a,II} + \left(\frac{(2i+1)\pi}{2}\right)^2} \quad (2)$$

where: M_t = amount leached at time t ; M_0 = amount initially in solid.

Figure 2 shows the results of the model plotted for different value of $D_{a,II}$ (second

Damköhler number). This figure shows that for $D_{a,1}$ (first Damköhler number) < 0.1 , all curves are equivalent and linear. In this region, the reaction has not had sufficient time to degrade the target organic so that a model based on no reaction is reasonably valid.⁽²⁾ This figure also shows that the maximum fraction leached is approached as $D_{a,1}$ approaches a value of 1.0.

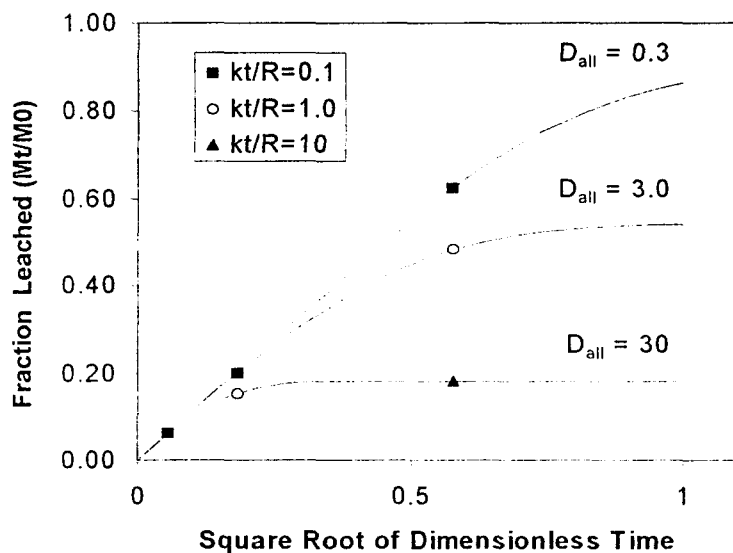


Fig. 2. Model predictions for fraction leached as a function of dimensionless time for different values of the second Damköhler number.

4. CONCLUSIONS

Degradation experiments showed that Fe(II)-based DS/S technology could effectively treat PCE in soils without production of substantial amounts of chlorinated intermediates within times spans acceptable for DS/S technology. The leach model shows that contaminant leaching can be determined by first and second Damköhler numbers and dimensionless time.

5. REFERENCES

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