SCRENNING OF DECHLORINATION SYSTEMS FOR DEGRADATIVE SOLIDIFICATION/STABILIZATION OF TETRACHLOROETHYLENE

Inseong Hwang and Joo-Yang Park

Department of Civil Engineering, Texas A&M University, College Station, Texas 77840, USA
Department of Civil Engineering, Hanyang University, Seoul 133-791, Korea
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Abstract: Degradative solidification/stabilization (DS/S) is a potential new technology to remediate sites contaminated with chlorinated hydrocarbons or mixtures of chlorinated hydrocarbons and inorganics such as heavy metals. Experimental studies were conducted to screen a wide range of reagents that could be used to treat chlorinated hydrocarbons. Tetrachloroethylene was used as a model chlorinated hydrocarbon. The screening experiments tested a total of 36 systems that included combinations of different types of binders, electron donors, and electron carriers. A combination of ferrous iron and Portland cement was identified as a potentially effective DS/S system for chlorinated hydrocarbons.

Key Words: solidification/stabilization, ferrous iron, polysulfide, tetrachloroethylene, chlorinated hydrocarbons, reductive dechlorination, Portland cement

INTRODUCTION

Remediation of sites contaminated by hazardous wastes is a major environmental problem and solidification/stabilization (S/S) is the most commonly used remedial alternative at superfund sites in the United States. The conventional S/S can immobilize inorganic contaminants at high pH using binders such as Portland cement, fly ash, and lime. Degradative solidification/stabilization (DS/S) is a modification of S/S that combines degradative processes for organic contaminants destruction with the low cost of conventional S/S. Destruction of organic contaminants can be achieved by adding degrading reagents in the conventional S/S systems.

Reductive dechlorination is a major degradation process for chlorinated hydrocarbons in reducing environments. Reduced forms of sulfur and iron are the most abundant electron donors in natural reducing environments. Sulfide, polysulfide (S₂⁻), dithionite (S₂O₄⁻₂), pyrite (FeS₂), and ferrous iron are among iron or sulfur-containing compounds that are known to reduce chlorinated hydrocarbons in the environment. Studies in natural systems have found that electron carriers mediate the reduction by accepting electrons from electron donors and transferring them to the substrates. The addition of electron carriers to the systems containing electron donors is reported to greatly accelerate the reduction rates. Common electron carriers are iron porphyrins, humic acids, and quinoid type compounds. Hematin, which is the electron carrier tested in this study, is a type of iron porphyrin. Therefore,
the most effective DS/S systems for chlorinated hydrocarbons can be expected to include binders (e.g. Portland cement), a source of electrons (e.g. ferrous iron), and electron carriers (e.g. hematin).

Despite the attractiveness of DS/S as a remedial technology for chlorinated hydrocarbons, there is little data to support its use. Thus, experimental studies were carried out to screen a variety of combinations of reagents that could be used for DS/S of chlorinated hydrocarbons. Tetrachloroethylene (PCE) was chosen as a model chlorinated hydrocarbon. Experiments were conducted in slurry reactors at high pH conditions similar to cementitious systems.

MATERIALS AND METHODS

Materials

The following chemicals were used as received: tetrachloroethylene (99.9+%, HPLC grade, Aldrich), toluene (99.9%, glass distilled, EM), methanol (99.8%, HPLC grade, EM), hexane (99.9+%, Burdick & Jackson), sodium sulfide (nonahydrate, 98.0+%, Sigma), sulfur powder (99+%, EM), pyrite (<200 mesh, American Minerals), sodium dithionite (85.3%, Sigma), ferrous sulfate (heptahydrate, 99+%, Sigma), hematin (from porcine gall, Sigma), sodium carbonate (99.5+%, Sigma), Portland cement (type I, Capitol Cement), fly ash (class C, Depauw Fly Ash), and calcium hydroxide (Fisher Scientific). The chemical composition of the Portland cement was determined by the manufacturer and is shown in Table 1. The chemical composition is expressed in terms of oxides that would be present if the cement consisted of the pertinent oxides.

Deoxygenated deionized water (water, hereafter) was prepared by sparging the water purified by a Barnstead Nanopure system for at least 12 hours with the atmosphere of an anaerobic chamber (Coy Laboratory Products) containing 95% N2 and 5% H2. Methanolic stock solutions of PCE were prepared daily. Stock solutions of sulfide, Fe(II), and dithionite were also prepared daily by dissolving appropriate amounts of the reagents in the water in the anaerobic chamber. The stock solution of polysulfide was prepared based on the procedure used by Licht and Davis. Sulfur powder and Na2S were mixed in a molar ratio of 3 to 1 and were dissolved for 2 days in the anaerobic chamber. The stock solution of hematin was prepared by dissolving 0.12 g of hematin and 0.6 g of Na2CO3 in a 250-mL volumetric flask. Na2CO3 was added to facilitate the dissolution of the hematin.

Experimental Methods

Screening experiments: Screening experiments were conducted in two phases. In the first-level screening, 36 systems were tested. They consisted of all possible combinations of 3 solids (none, fly ash, Portland cement), 6 electron donors (none, sulfide, polysulfide, dithionite, pyrite, ferrous iron), and 2 electron carriers (none, hematin). The first-level screening identified Portland cement as an effective solid, and polysulfide and Fe(II) as promising reductants for PCE. Then a second-level screening experiment was conducted to select the more promising DS/S system.

Clear borosilicate glass vials (nominally 20 mL) were used as batch slurry reactors. Closures of the vials were designed to minimize intrusion of oxygen and volatilization losses of PCE. To accomplish this, a lead foil tape (3M, adhesive backed) was chosen as a sealing material and was attached to the face of Teflon lined silicon septum of the closure. The recoveries of controls that contained PCE and water were at least 97% over the reaction period of the screening experiment (30 days), suggesting that the reac-

| Table 1. Chemical composition of the Portland cement |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Oxide           | CaO             | SiO2            | Al2O3           | Fe2O3           | MgO             | SO3             | Loss on ignition residue |
| wt %            | 64.85           | 20.26           | 5.46            | 2.52            | 1.26            | 3.20            | 1.65            | 0.1                 |


tor system could effectively contain PCE.

In the first-level screening experiment, all samples were prepared in triplicate in the anaerobic chamber. The lime was used as a buffer to maintain pH of the slurries higher than 10.3. The mass of the solids was 1.2 g and the lime 0.222 g. The dose of the electron donors was 100 times the stoichiometric amount to reduce spiked PCE completely to ethylene. The following half reactions for the reduction of PCE and the oxidation of the electron donors were used to calculate the amounts of the electron donors required:

\[
PCE + C_2Cl_4 + 8e^- + 4H^+ \rightarrow C_2H_4 + 4Cl^- \\
(1)
\]

sulfide: \[ S^{2-} \rightarrow S^{2-} + 2e^- \] (2)

Polysulfide: \[ S_n^{2-} \rightarrow S_n^{2-} + 2e^- \] (3)

Dithionite: \[ (S_2O_3)^2- + 8OH^- \rightarrow 2(SO_3)^2- + 4H_2O + 6e^- \] (4)

pyrite: \[ FeS_2 \rightarrow Fe^{3+} + 2S^{2-} + 3e^- \] (5)

Fe(II): \[ Fe^{2+} \rightarrow Fe^{3+} + e^- \] (6)

The dose of the electron carrier (hematin) was 40 mg/L. The solution volume of the slurries was 12 mL, hence the mass ratio of solid to solution was 0.1. Headspace volumes for the slurries containing solids and without the solids were ~12.3 mL and ~12.7 mL, respectively.

The reaction was initiated by spiking 10 μL of the methanolic stock solution of PCE into the slurries to yield a PCE concentration of 0.48 mg/vial (40 mg/L). After PCE spiking, the vials were capped rapidly using the closure. The vials were mounted on an incubator shaker that provided orbital shaking at a speed of 170 rpm at 60 °C. The vial containers were covered with an aluminum foil to prevent the effect of light. After 30 days of incubation, vials were taken from the incubator shaker for sampling. To extract PCE from the slurries, 6 mL of the hexane extractant containing toluene as an internal standard was injected through the septum of the 20-mL vials using a 10-mL gas-tight syringe. The vials containing the extractant were then shaken at 250 rpm for 30 min using an orbital shaker at room temperature. After extraction, ~1 mL of the hexane layer was transferred to 1 mL autosampler vial for GC analysis. pH values of the samples were measured after 1 and 30 days at 60 °C. For selected experiments, chloride in the solution was analyzed for chloride balance study.

The sample preparation procedure for the second-level screening experiment was the same as the one for the first-level screening experiment. The samples were incubated at 40 °C for 10 days and extracted with the hexane extractant.

**Effect of lead foil liner**: In the first-level screening experiment, complete removal of PCE was observed in the system containing the lime buffer but without an electron donor. It was initially assumed that this degradation was due to alkaline hydrolysis reactions, because a recent study demonstrated the effectiveness of basic solutions in dechlorinating a chlorinated ethylene. Gu and Siegrist[11] reported that TCE could be completely hydrolyzed in the 2 M NaOH solution at 40 °C. A question was not raised as to whether the lead foil liner of the closure could act as an electron donor for PCE until the second-level screening was completed. Sound recoveries of PCE in the controls suggested that the lead foil effect was negligible at neutral pH. However, its effect in the high pH region had been unknown. Therefore, an experiment was carried out to study the effect of the lead foil at high pH after the second-level screening was completed. Recoveries of PCE in slurries containing the extra lead foil were compared to those of slurries having only the lead foil liner. The specimen of the lead foil with a dimension of 37.7 mm by 37.7 mm was cut into 14 rectangular pieces and was added to vials containing the lime buffer. These lead foil pieces had a surface area equivalent to 11 times that of the liner of the closure. The vials were placed in the incubator shaker at 60 °C. Sampling for PCE was conducted as described in the screening experiment after 3 and 8 days of incubation.
Analytical Methods

PCE and its chlorinated degradation products, trichloroethylene (TCE), 1,1-dichloroethylene (1,1-DCE), cis-dichloroethylene (c-DCE), trans-dichloroethylene (t-DCE), vinyl chloride (VC), dichloroacetylene, and chloroacetylene were analyzed by the Hewlett-Packard G1800A GC equipped with a DB-VRX column (J&W Scientific), 60 m 0.25 mm i.d., with a film thickness of 1.8 μm and operated with electron impact ionization and a mass selective detector. Extractants were injected using an autosampler with a split ratio of 30:1 at 230 °C. Helium was used as a carrier gas at 1 mL/min. The oven temperature program was as follows: 80 °C for 8 min, ramp 20 °C/min to 160 °C, and hold for 2 min. The temperature of the detector was 300 °C.

Chloride was analyzed by a Dionex DX-500 IC/HPLC equipped with a self-regenerating suppressor, a CD-20 conductivity detector, and an IonPac® AS4A-SC analytical column, 250 mm 4 mm i.d. The eluent was 1.8 mM Na₂CO₃/1.7 mM NaHCO₃, and the flow rate was 3 mL/min. The filtered solution was manually injected into the column through a 25-μL sample loop.

RESULTS AND DISCUSSION

Level 1 Screening of Dechlorination Systems

Figures 1 and 2 show the results from the first-level screening experiment that tested a total of 36 systems consisting of a variety of solids, electron donors, and electron carriers. Error bars in the Figures 1 and 2 represent ranges of observed removals in the triplicate samples. Performances of different systems are presented in terms of PCE removal in 30 days at 60 °C. pH values of most of the experiments were controlled between 11.4 and 12.0 by the lime buffer. pH values of the systems containing Fe(II) were generally lower, ranging from 9.1 to 11.6. With the data available, it was not possible to draw a relationship between pH and system performances. As shown in Figure 1,

![Figure 1](image1.png)

**Figure 1.** PCE removal in systems without electron donor and systems containing Fe(II) or pyrite (PC = Portland cement, FA = fly ash, P = pyrite, Fe = Fe(II), H = hematin).

![Figure 2](image2.png)

**Figure 2.** PCE removal in systems containing dithionite, sulfide, and polysulfide (PC = Portland cement, FA = fly ash, D = dithionite, S = sulfide, PS = polysulfide, H = hematin).

almost complete removal (> 99.8%) of PCE was achieved in the systems containing the lime buffer or Portland cement without electron
donor. It was initially assumed that PCE was removed by alkaline hydrolysis in these systems. However, it was later found that the lead foil liner of the closure acted as an electron donor. The results of the experiment on the effect of the lead foil are presented in Table 2. The addition of lead substantially increased PCE removal rates both at the neutral pH (~7) and at the high pH (11.4). In the high pH experiments, the reaction rate is approximately proportional to the amount of lead present in the systems. These results clearly show that Pb(0) from the lead foil liner can donate electrons to PCE and that the reaction is enhanced at high pH. This enhancement must be due to increased corrosion rate of the lead at high pH. Lead is documented to form amphoteric oxides in high pH environments, and thereby readily corrodes. Lead is also subject to attack by lime, Portland cement, mortar, and concrete.

Despite the expected dominance of the lead in dechlorination reactions in the DS/S systems tested, different reactivities are shown among different systems. Complete degradation of PCE was rarely observed in the systems containing pyrite, dithionite, and sulfide. On the other hand, PCE concentration decreased below the detection limit (0.066 mg/L) in most of the systems containing Fe(II) and polysulfide. In the experiments without electron donor (Figure 1), fly ash and hematin appear to have inhibited dechlorination reactions by the lead foil. However, effects of fly ash and hematin on dechlorination reactions cannot be clearly delineated in the experiments with electron donors. Fly ash and hematin generally did not substantially change the extent of PCE removal in these experiments. Figure 2 shows that reactivities of dithionite and sulfide systems are considerably lower than those of the other systems. Dithionite and sulfide ions might have coated surfaces of the lead foil by forming precipitates such as PbS and prevented further corrosion of the lead. Therefore, PCE removal in these systems could have been mainly due to reductions by dithionite and sulfide as electron donors rather than the lead foil. If this were true, dithionite and sulfide could be regarded as poorer reductants for PCE than the lead.

Based on the performances shown in the level 1 screening experiment, Fe(II) and polysulfide were selected as promising electron donors and Portland cement as a solid (binder). Portland cement was chosen in preference to fly ash, because the performances of these two binders were similar but the former was the more commonly used binder in the field. The effect of the lead foil had not been elucidated when these decisions were made. PCE reductions observed in Fe(II) and polysulfide systems could have been entirely due to reduction reactions by the lead foil.

Major polysulfide species in aqueous solutions are $S_2^{2-}$, $S_3^{2-}$, $S_4^{2-}$, and $S_5^{2-}$. Concentrations of these polysulfide species and sulfides in DS/S systems containing polysulfide at 60 °C were estimated using the equilibrium equations given in the literature and the results are presented in Table 3. Table 3 shows that the polysulfide would account for more than 95% of the sulfide species present in the systems containing polysulfide and that $S_4^{2-}$ and $S_5^{2-}$ would be major polysulfide species with $S_4^{2-}$ being the most predominant.

### Table 2. PCE degradation by the lead foil

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>PCE removal after 8 days (%)</th>
<th>Apparent first-order rate constant (day$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water + lead (1)</td>
<td>2.0</td>
<td>0.0025</td>
</tr>
<tr>
<td>Water + extra lead (× 12)</td>
<td>72</td>
<td>0.088</td>
</tr>
<tr>
<td>Water + lime$^\ddagger$ + lead (× 1)</td>
<td>90</td>
<td>0.29</td>
</tr>
<tr>
<td>Water + lime$^\ddagger$ + extra lead (× 12)</td>
<td>100</td>
<td>&gt; 2.14$^d$</td>
</tr>
</tbody>
</table>

$^a$Lead from the lead foil liner (2.84 cm$^2$), $^b$Lead from the lead foil liner plus extra lead foil added (34.1 cm$^2$), $^c$0.25 M Ca(OH)$_2$, $^d$100% removal was observed after 3 days. The rate was calculated based on this.
Table 3. Sulfide and polysulfide speciations in DS/S systems containing polysulfide

<table>
<thead>
<tr>
<th>species</th>
<th>$H_2S$</th>
<th>$HS^-$</th>
<th>$S^{2-}$</th>
<th>$S_2^{2-}$</th>
<th>$S_3^{2-}$</th>
<th>$S_4^{2-}$</th>
<th>$S_5^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>conc. (M)</td>
<td>$6.60 \times 10^{-4}$</td>
<td>$4.38 \times 10^{-1}$</td>
<td>$5.75 \times 10^{-4}$</td>
<td>$5.28 \times 10^{-6}$</td>
<td>$2.71 \times 10^{-1}$</td>
<td>$8.26 \times 10^{-7}$</td>
<td>$8.95 \times 10^{-1}$</td>
</tr>
<tr>
<td>% dist.</td>
<td>0.00007</td>
<td>4.65</td>
<td>0.00006</td>
<td>0.00560</td>
<td>2.87</td>
<td>87.6</td>
<td>9.49</td>
</tr>
</tbody>
</table>

Table 4. Degradation products in Fe(II) and polysulfide systems

<table>
<thead>
<tr>
<th>exp.</th>
<th>PCE conc. after 10 days (mg/L)</th>
<th>peak height (abundance)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PCE</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt; 0.066</td>
<td>N.D.</td>
</tr>
<tr>
<td>PC + Fe</td>
<td>&lt; 0.066</td>
<td>N.D.</td>
</tr>
<tr>
<td>PS</td>
<td>5.04</td>
<td>17,000</td>
</tr>
<tr>
<td>PC + PS</td>
<td>14.71</td>
<td>N.A.</td>
</tr>
<tr>
<td>buffer</td>
<td>30.9</td>
<td>50,000</td>
</tr>
</tbody>
</table>

N.D. = not detected, N.A. = not available

![Figure 3](image-url)

Figure 3. Comparison of the performances of Fe(II) and polysulfide systems at 40°C (PC = Portland cement, Fe = Fe(II), PS = polysulfide).

Fe(II) and polysulfide in dechlorinating PCE. Figure 3 shows the results in terms of PCE removal after 10 days at 40 °C. Error bars in the figure represent ranges of observed removals in the triplicate samples. pH values of the slurries were maintained near 12.0. The system with only buffer was still able to remove PCE because of the activity of the lead foil liner. However, PCE removal in this system was much slower than in Fe(II) and polysulfide systems, indicating that Fe(II) and polysulfide were effective electron donors for PCE. Fe(II) performed better than polysulfide. In the case of Fe(II) systems, a half-life of less than 15 days for PCE at 20 °C can be obtained, assuming a first-order degradation kinetics and a typical activation energy for abiotic transformation of halogenated organics (100 kJ/mol). This range of reaction rates is well suited to time spans allowable for DS/S of wastes. A leach model predicts that conventional S/S systems can contain most of wastes within the solidified matrices for periods like several years to scores of years.

Degradation products in these five experiments were analyzed to closely investigate the reactions. The analytical method allowed detection of TCE, 1,1-DCE, c-DCE, t-DCE, and VC. Table 4 shows peak heights of the chromatograms of the degradation products found in the experiments measured manually. In the experiment with Fe(II) without cement, substantial amounts of TCE and t-DCE were found. When Fe(II) was present in the cement system, however, chlorinated ethylenes were not detected. This suggests an important role of the cement in dechlorination reactions. Chlorinated ethylene intermediates were not detected in the polysulfide systems. When the lead foil acted as an electron donor (buffer system), TCE was produced. VC was not detected in any systems. To collect more infor-
formation on degradation products, selected samples from the level I screening experiment were retrieved and analyzed for chloride. Samples from the following three experiments were available: 1) buffer only, 2) Fe(II) with hematin (Fe + H), and 3) polysulfide (PS) only. All of these systems had shown more than 99.8% removal of PCE during the level I screening experiment. Chloride recoveries of the experiments were 36.0%, 99.7%, and 61.6% for buffer, Fe + H, and PS experiments, respectively. The chloride data suggest that the Fe(II) system was able to almost completely dechlorinate PCE to produce non-chlorinated products, but that the polysulfide-based reduction produced substantial amounts of chlorinated intermediates. Chlorinated intermediates in this experiment were probably not the chlorinated ethylenes because they were not found in the product analysis conducted for the polysulfide system from the level II screening. Therefore, it may be hypothesized that PCE reduction by polysulfide occurs via pathways other than hydrogenolysis (equation (1) in section II). A considerable portion of PCE removal in polysulfide systems might be attributable to nucleophilic addition reactions rather than electron transfer reactions, thereby releasing less chloride into the solution than predicted by assuming reductive reactions. Polysulfide is known to be a strong nucleophile.\(^{17,18}\)

The experimental results show that Fe(II) has advantages over polysulfide as a degrading agent for chlorinated hydrocarbons. This is based on the observation that Fe(II) degraded PCE most rapidly among the electron donors tested and it also did not appear to produce chlorinated intermediates. Furthermore, Fe(II) is an inexpensive agent that can be obtained as an industrial byproduct and is more environmentally favorable than polysulfide.

**CONCLUSIONS**

Slurry reactor experiments were conducted to identify the most effective dechlorination system for degradative solidification/stabilization (DS/S) of chlorinated hydrocarbons. A variety of degradation systems were tested that consisted of binder, electron donor, and electron carrier by using tetrachloroethylene (PCE) as a model chlorinated hydrocarbon. The conclusions obtained are as follows:

1. A combination of Portland cement and Fe(II) shows a potential to be developed into an innovative DS/S system to treat chlorinated hydrocarbons. The estimated half-life of PCE in Portland cement/Fe(II) systems at an ambient temperature (20 °C) was 15 days.
2. Portland cement/Fe(II) systems did not appear to produce chlorinated byproducts during the reductive transformation of PCE.
3. Hematin as an electron carrier did not enhance PCE reduction reactions in DS/S systems.
4. The lead foil liner of the closure for the slurry reactor system employed in this study had a substantial capacity to reduce PCE at the experimental conditions. This, however, did not affect the conclusions of the current study because the lead foil had much lower PCE reduction capacity than the electron donors such as Fe(II) and polysulfide.

**REFERENCES**

5. Roberts, A. L., Sanborn, P. N., and Gschwend, P. M., “Nucleophilic substitution reac-


