

## Project Summary

- Title:** Admicelle-Catalyzed Reductive Dechlorination of Perchloroethylene (PCE) by Zero Valent Iron
- Project ID:** R/UW-REM-002
- Investigator:** Dr. Zhaohui Li, Assistant Professor of Geology and Assistant Professor of Chemistry, Geology Department and Chemistry Department, University of Wisconsin – Parkside
- Period of Contract:** 07/01/1999 – 06/30/2001
- Background/Need:** Chlorinated solvents are a major groundwater contaminant at industrial sites, U.S. Department of Energy facilities, and military installations. Recent discovery of using zero valent iron (ZVI) as permeable barriers to degrade chlorinated solvents dissolved in groundwater has attracted great attention. Numerous researches on using ZVI for groundwater remediation have been focused on increasing the degradation rate constant of chlorinated solvents. However, most of them involve in coating the metals with noble metals such as Pt or Pd. Thus a search for an inexpensive, yet effective material, to enhance the rate of degradation of chlorinated solvents becomes more imminent.
- Objectives:** The objectives of this research are to further study a novel observation made by the PI on enhanced perchloroethylene degradation by ZVI under the catalysis of a cationic surfactant hexadecyltrimethylammonium (HDTMA). The influence of surfactant chain length of several quaternary ammonium surfactants, the surfactant coverage and the surfactant surface configuration on ZVI, the initial PCE concentrations, and initial solution pH and ionic strength on PCE reduction kinetics will be studied in batch scale. Column experiments will be conducted as a function of initial PCE concentrations and contaminant injection rates to verify the batch results and to provide further justification for future pilot scale and/or field tests.
- Methods:** Laboratory batch sorption was performed to determine the sorption maxima of surfactants with different hydrophobic chain lengths (8, 12, and 16 carbons in the tail group, respectively). Batch reduction kinetic study was performed to determine the rate constants of PCE degradation and trichloroethylene (TCE) generation due to the degradation of PCE. For column studies, both modified and unmodified ZVIs were packed in duplicates to glass columns of 30 cm long and 2.5 cm in diameter. Contaminant solutions were made in a 12-L collapsible Teflon bags and were delivered by a precision syringe pump with four 10-mL gas-tight syringes attached at different flow rates and different initial PCE and TCE

concentrations to verify the enhancement of PCE reduction catalyzed by HDTMA on ZVI surfaces.

**Results and Discussion:**

Batch results indicate that the longer the surfactant tail group, the more hydrophobic the surfactant is, thus the higher the surfactant sorption. Compared to unmodified ZVI, the rate constants of PCE dechlorination increased by 15 to 20 folds when ZVI was modified by HDTMA. A six to nine fold increase in rate constants was found for ZVI modified with dodecyltrimethylammonium, while a five to seven fold increase was found for ZVI modified with octyltrimethylammonium. The half-life of PCE in the presence of unmodified ZVI was about 10 days, but reduced to 0.4 day when HDTMA-ZVI was used. Solutions with ionic strengths of 0.001, 0.01, and 0.1 M of NaCl, and with initial pHs at 3, 5, and 7 had little effect on PCE reduction rates. Significant slowdown of PCE reduction was found at an initial pH of 11, maybe due to the inhibition of iron corrosion.

Column results show that a 10-fold reduction in effluent PCE concentrations was achieved when HDTMA-ZVI was used compared to unmodified ZVI. With an initial PCE concentration of 20 mg/L and a flow rate of 0.25 mL/min, the effluent PCE concentrations were 0.08-0.1 mg/L and 1.1-2.4 mg/L for modified and unmodified columns, respectively. As the flow rate increased to 2 mL/min, the effluent PCE concentrations increased to 1.5-1.7 mg/L and 13-14 mg/L for modified and unmodified columns, respectively. As the input concentration reduced to 6 mg/L, at a flow rate of 2 mL/min, the effluent PCE concentrations were 0.1-0.2 mg/L and 3.0-3.3 mg/L for modified and unmodified columns, respectively.

**Conclusions/  
Implications/  
Recommendations:**

The research shows that the sorbed cationic surfactant, particularly HDTMA, drastically increase the PCE degradation rate. In addition, the pathway of PCE degradation could be predominant by reductively dechlorination when surfactant was present compared to  $\beta$ -elimination when surfactant was absent. Due to the superior enhancement of PCE reduction under the influence of surfactant, it is recommended for a pilot scale test, which will be proposed to US DOE.

**Related**

**Publications:**

Alessi, D. S. and Li, Z. (2001) Synergistic Effect of Cationic Surfactants on Perchloroethylene Degradation by Zero Valent Iron, *Environ. Sci. Technol.*, in press.

**Key Words:**

Perchloroethylene, Reductive Dechlorination, Trichloroethylene, Surfactant, Zero-Valent Iron

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