

Report for 2003AL8B: In-situ Destruction of PCBs, PCE and TCE in Alabama Soils and Groundwater Using a New Nanoscale Sorptive Catalyst

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Report Follows

SYNOPSIS

IN-SITU DESTRUCTION OF PCBS, PCE AND TCE IN ALABAMA SOILS AND GROUNDWATER USING A NEW CLASS OF NANOSCALE BIMETALLIC PARTICLES

Don Zhao, Principal Investigator (PI), Assistant Professor

Feng He, Graduate Research Assistant and Ph.D. Candidate

Cliff Lange, Co-Principal Investigator
Associate Professor

Mark O. Barnett, Co-Principal Investigator
Assistant Professor

Department of Civil Engineering
238 Harbert Engineering Center, Auburn University, Auburn, AL 36849
Telephone: 334-844 6277; Fax: 334-844 6290; E-mail: dzhao@eng.auburn.edu

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A. PROBLEM STATEMENT AND OBJECTIVE OBJECTIVES

Polychlorinated biphenyls (PCBs), tetrachloroethylene (PCE), and trichloroethylene (TCE) are categorized as chlorinated hydrocarbons, which have been widely used in industries and caused serious groundwater and subsurface contamination in Alabama and hundreds of other sites in the U.S. All three chemicals are believed to be potent carcinogens.

For their non-flammability, stability, and electrical insulating properties, PCBs were used in hundreds of industrial applications (e.g., in electrical transformers and as plasticizers in paints and plastics). More than 1.5 billion pounds of PCBs were manufactured in the United States from its first industrial use in 1927 to the cessation of production in 1977. The U.S. EPA estimates that about half of the total domestically consumed PCBs (625,000 tons) were dumped into the environment (soil and groundwater) before the enactment of federal regulations in 1976. One of the most contaminated sites in the U.S. was discovered in Anniston, AL in the mid 1990's. From 1929 to 1971, large amounts of PCBs were produced at the Anniston Monsanto facility and hundred tons of PCB wastes were dumped into the local environment. In 1990 the Environmental Defense Fund Scorecard ranked Calhoun County, where Anniston is located, among the worst 20% of all counties in the US in terms of an average person's added cancer risk from hazardous waste. The discovery of PCBs in Anniston triggered a costly battle involving the local community, industry, state courts, state government, and US EPA, and has attracted national attention.

PCE and TCE are organic solvents widely used in dry cleaning and metal rinsing. In the past, large amounts of used PCE and TCE were simply dumped into the ground. As a result, high concentrations of PCE and TCE are commonly detected in areas adjacent to dry cleaners, automobile manufacturers or shops, asphalt processing plants, and military bases. The

nationally known PCE/TCE site in Alabama is the “Montgomery capital plume” site, which has been considered to be of the NPL (national priorities list) caliber. To avoid being added to the NPL (which would cost much more), the city of Montgomery has shut down two contaminated wells and initiated an \$18.6 million clean up action.

Chlorinated hydrocarbons are highly persistent to natural degradation. Cleanup of soils and groundwater contaminated by chlorinated hydrocarbons has been a focus of the environmental remediation research. The primary obstacle is the lack of cost-effective remediation techniques. For instance, excavation of contaminated soil has been one of the common practices. However, the associated cost is between 100-700 dollars/yard³. For the capital plume site, since the site is located in the heavily populated downtown area, engineered processes (e.g., excavation) are highly restricted. Therefore, there is an urgent need for developing new cost-effective in-situ techniques for the cleanup of Alabama soils/groundwater contaminated by chlorinated solvents.

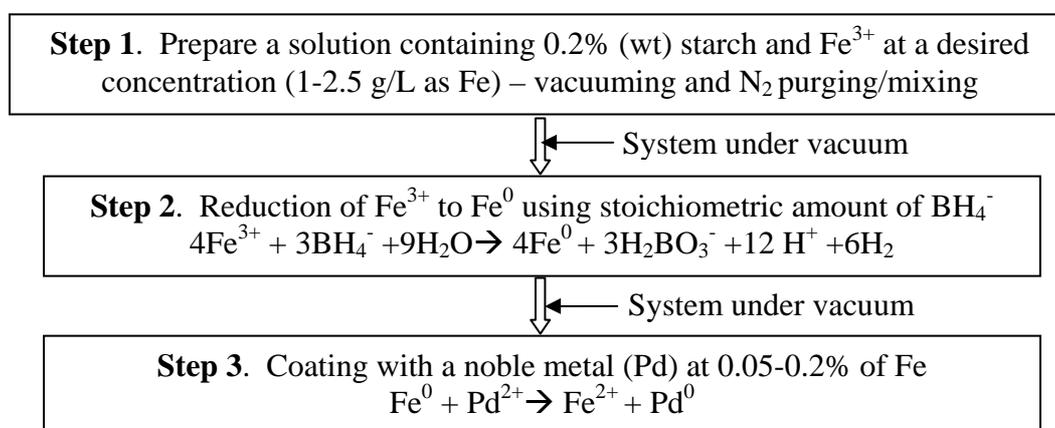
This research aims to develop a new in-situ and cost-effective process for complete destruction of chlorinated hydrocarbons such as PCBs and PCE/TCE in soils and groundwater. The specific research objectives are to:

- 1). Develop a new class of highly reactive, nanoscale bimetallic catalysts that are effective for degradation of the chlorinated organic compounds in soils and groundwater.
- 2). Test the feasibility (reaction equilibrium, kinetics and dynamics) of the new material for in-situ destruction/mineralization of the chlorinated contaminants in selected Alabama soils and groundwater.

B. RESEARCH APPROACH

B1. Preparation of the nanoscale iron particles

The key to this research was the preparation of the reactive nano-materials. In this research, we developed a simple yet highly innovative procedure, which resulted in the production of a new class of truly nanoscale, highly reactive materials. The preparation method is briefed as follows (a U.S. Patent application on this approach is in processing):



Unlike conventional methods, we applied a low-cost and environmentally friendly carbohydrate (starch) in the preparation. The starch serves as a stabilizer that prevents subsequently formed nanoparticles from agglomeration, thereby maintaining their high

surface area and reactivity. Compared to dendrimers we attempted first, starch is much cheaper and much more effective.

In step 2, a stoichiometric amount of a reducing agent NaBH_4 was added to the solution containing Fe^{3+} and the stabilizer. Thereby, Fe^{3+} is reduced to Fe^0 . To ensure efficient use of the reducing agent BH_4^- , the entire reactor system was operated under inert conditions though continuously vacuuming and/or N_2 purging.

In step 3, a small amount (0.05-0.1% of iron loaded) of a noble metal (Pd) is coated on the iron-loaded dendrimer by reducing Pd^{2+} to Pd^0 . Pd serves as a catalyst to speed up the reaction.

B2. Experiments for TCE degradation

Batch experiments were conducted in 65 mL serum bottles, which were filled with 63 mL solution containing the nanoscale particles. The degradation was initiated by adding 2 mL of TCE stock solution, which resulted in an initial TCE concentration of 20 mg/L, to the solution with the nanoscale particles (no headspace). The bottles were then capped with Teflon Mininert valves and mixed on a rotary shaker (40 rpm) at 22 ± 1 °C in an incubator. At selected time intervals, 0.25 mL of the aqueous solution of TCE was withdrawn using a 250 μL gas-tight syringe into a 2 mL GC vial and extracted with 1 mL of hexane. The extract was then analyzed by a HP 6890 GC equipped with electron capture detector (ECD). Blank experiments were also carried out without the addition of the nanoparticles.

B3. Experiments for PCBs degradation

Sacrificial batch experiments were conducted in 2 mL GC vials with Teflon-lined caps. Reaction was initiated by injecting 25 μL Aroclor 1254 (100 mg/L) 1 mL solution per vial containing 1 mg/L nanoscale Fe(0) (Pd-Fe). The initial concentration of PCBs was 2.5 ppm. The vials were then sealed and mixed on a rotary shaker (40 rpm) at 22 ± 1 °C in an incubator. At predetermined times, the solution was transferred to a 10 mL vial and extracted with 1 mL hexane. The emptied GC vial was also washed using hexane twice using hexane (2 mL in wash 1 and 1 mL in wash 2) and during the first wash the vial was also sonicated for 10 minutes to ensure no PCBs were left in the vial. The rinsing hexane was then added into the 10 mL vial containing the solution. Upon mixing and sonication for 5 minutes, the vial was centrifuged for 5 minutes at 1500 rpm to separate the phase. PCBs in the hexane phase were then analyzed using an HP 6890 GC equipped with an HP5 capillary column (32 m long, 0.25 mm ID, Restek Co.) and ECD. Appropriate control tests were also carried out to ensure that the mass loss of PCBs was due to reaction.

C. PRINCIPAL FINDINGS AND SIGNIFICANCE

The most significant findings from this research are briefed as follows:

- For the first time, we developed a new generation of physically stable and chemically reactive nanoparticles with the aid of a low-cost stabilizer and by conducting the preparation process under vacuum. The particles can remain reactive for days without agglomeration.
- Based on the pseudo-first-order reaction rate, the degradation rate of TCE using the new nanoparticles is orders of magnitude faster compared to the best reported Fe-based nano-

materials to date. No toxic intermediate by-products such as VC, 1,1-DCE, cis-DCE and trans-DCE were detected.

- More than 80% of PCBs ($C_0 = 2.5$ ppm) in water solution was destroyed using the stabilized nano-materials within 100 hours, compared to only 24% with non-stabilized Pd-Fe nanoparticles.

The preparation procedure developed in this study resolved a key technical barrier in developing physically stable, reactive nanoparticles. The new materials developed in this study represent a substantial technical advancement in preparing nano-scale, reactive particles for reductive dechlorination. The innovative procedures we developed and the mechanisms behind are also highly valuable in the general realm of nano-technology.

The new nano-materials can be safely injected into contaminated subsurface and actively attack and destroy the contaminant plumes without disturbing the aquifer soil and without causing environmental side effects. Therefore, a cost-effective, environmentally benign, in-situ, active remediation technology can be readily conceived using the new materials.

Given the urgent technical need for remediation of soils and groundwater contaminated with PCBs, PCE and TCE, we foresee a great and immediate practical value of our research products. Because of the superior reactivity and low cost, the new materials and the proposed in-situ, active process will save millions of dollars of remediation costs.