Report as of FY2006 for 2006AL48B: "Pilot Testing an Innovative Remediation Technology for In-situ Destruction of Chlorinated Organic Contaminants in Alabama Soils and Groundwater Using a New Class of Zero Valent Iron Nanoparticles"

Publications

- Articles in Refereed Scientific Journals:
    - Zhao, D. and F. He, 2007, Field Assessment of Carboxymethyl Cellulose Stabilized Fe/Pd Bimetallic Nanoparticles for Groundwater Remediation, Environmental Science and Technology. (Manuscript Submitted).
- Conference Proceedings:
    - He, F. and D. Zhao, In-situ Destruction of Chlorinated Solvents in Soils and Groundwater Using a New Class of Stabilized Fe-Pd Nanoparticles, Proceedings of The 20th Annual Alabama Water Resources Conference, Perdido Beach, AL., Sept. 6-8, 2006.

Report Follows

PILOT-TESTING AN INNOVATIVE REMEDIATION TECHNOLOGY FOR IN-SITU DESTRUCTION OF CHLORINATED ORGANIC CONTAMINANTS IN ALABAMA SOILS AND GROUNDWATER USING A NEW CLASS OF ZERO VALENT IRON NANOPARTICLES

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A. PROBLEM STATEMENT AND OBJECTIVES

Chlorinated hydrocarbons, such as polychlorinated biphenyls (PCBs), tetrachloroethylene (PCE) and trichloroethylene (TCE), are well-known potent toxins to human health and the environment. Although the uses of chlorinated hydrocarbons have now been either banned or highly restricted, the past massive production and applications have left an environmental legacy that large areas of soils and groundwater in Alabama are contaminated with dangerously high concentrations of chlorinated hydrocarbons.

Unfortunately, there have been no cost-effective and environmentally benign remediation technologies available for remediation of chlorinated soils and groundwater despite tremendous research efforts in the past three decades. To a great extent, current remediation practices rely on excavation and landfill of contaminated soils, which are extremely costly and environmentally disruptive (the associated cost is between 100-700 dollars/yard^3). For cases like the capital plume site, since the site is located in the heavily populated downtown area, engineered processes (e.g., excavation) are highly restricted. Currently, Alabama owns 12 EPA-designated NPL (National Priorities List) sites and 2 proposed NPL sites. Of all toxins detected at these sites, chlorinated hydrocarbons are among the most wide-spread and most harmful contaminants to our groundwater, which serves as over 60% of the State’s drinking water source. Using current technologies, clean up of each of these sites would claim for multi-millions of dollars over the next several decades, which constitutes a serious threat to the sustainable development of Alabama economy. Consequently, there is an urgent need for developing new cost-effective in-situ technologies for the clean-up of Alabama soils/groundwater contaminated by chlorinated hydrocarbons.

Our prior highly successful AWRRI project resulted in a new class of zero-valent iron (ZVI) nanoparticles and a patented remediation technology based on the nanoparticles. The nanoparticles have been considered suitable for in situ dechlorination uses, and the technology has attracted national interest. To ultimately apply this promising technology in the field, pilot-test is a critical and logical step, and will yield critical information on the technical and cost effectiveness and necessary design and operating parameters.

Therefore, this research aims to pilot-test this cutting edge in-situ remediation technology for rapid and complete destruction of chlorinated hydrocarbons such as PCE, TCE and PCBs in Alabama soils and groundwater. The specific research objectives are to:

1). Test the feasibility (dispersibility, reactivity, and reactive longevity) of the iron nanoparticles when applied under field conditions at a chlorinated solvent site in Northern Alabama; and

2). Probe the effects of field environmental conditions (pH, dissolved oxygen (DO), oxidation and reduction potential (ORP), ionic strength, and dissolved organic matter (DOM)) on the effectiveness.

B. RESEARCH APPROACH

B1. Bench-Scale Feasibility Studies.

Prior to the field-scale tests, laboratory feasibility studies were conducted using the groundwater from the site. During the tests, 20 mL stabilized Fe suspension (1 g/L, 0.5% sodium carboxymethyl cellulose or CMC, Pd/Fe = 0.1% w/w) was mixed with 23 mL groundwater obtained from a monitoring well (MW-3). The batch vials (43 mL) were then cap-sealed with Teflon-lined septa and placed on a rotary shaker at 50 rpm for degradation tests. Parallel experiments were also performed to degrade PCE and TCE in deionized water solution. To test the change in particle reactivity with the particle aging (i.e. storage time in water), replicate samples of 0.1 g/L lab-synthesized Fe-Pd nanoparticle suspension were stored in sealed glass vials (with zero headspace) and kept in a refrigerator at 4 ^{o}C for up to 9 days before being tested. The particle reactivity was then tested through the degradation experiments of TCE following the procedure described in our prior work (He and Zhao, 2005, *Environmental Science and Technology*, 39, 3314-3320).

The soil mobility of the CMC-stabilized Fe-Pd nanoparticles was tested by measuring the breakthrough behaviors of the nanoparticles through a 2.7 mL of a loamy sand soil bed (obtained from Auburn, AL) packed in a glass column (1 cm I.D.). For comparison, parallel tests were also carried out with a tracer (0.6 g/L KBr) and non-stabilized Fe-Pd particles. The salient soil properties are as follows: porosity = 0.35; hydraulic conductivity = 0.25 cm/min; sand content = 84%; silt = 10%; clay = 6% clay. In the breakthrough tests, a solution containing the tracer, 1.0 g/L (as Fe) of non-stabilized or CMC-stabilized (1% w/w CMC) iron nanoparticles was passed through the soil bed under a constant static hydraulic head of 7.1 cm. The particle breakthrough history was then followed by analyzing the total iron in the effluent until the full breakthrough was achieved. Then, DI water was pumped into the column by an HPLC pump at a constant superficial liquid velocity of 0.23 cm/min. Iron elution history was then followed for ~10 pore volumes.

B2. On-site preparation of CMC-stabilized iron nanoparticles

The field preparation of the stabilized Fe suspension is briefed as follows. Approximately 28 gallons of tap water were placed in a 65 gallon polyethylene reactor and rapidly stirred with a 1/3 horsepower motorized impeller. Then, 564 g of sodium carboxymethyl cellulose (CMC) was then added near the impeller while mixing, and the solution was mixed until no visible clumps (i.e. CMC was fully dissolved) were observed (~ 3 hours). During mixing, nitrogen gas was also supplied to purge the oxygen out of the reactor and facilitate mixing. Then, approximately 564 g of $FeSO_4·7H_2O$ (Fisher, Fair Lawn, NJ) was first dissolved in 1 gallon nitrogen-purged tap water and added into the reactor. While the stirring and N_2 purging continued, 146 g of $NaBH_4$ (98%, Acros Organics, Morris Plains, NJ) was first dissolved in 1 gallon nitrogen-purged tap water, and then, pumped into the reactor at a flow rate of 0.5

L/min to reduce Fe^{2+} to Fe^0. The solution in the tank turned from a milky white to inky black as the nanoparticles were produced. Finally, about 0.5 g of $Na_2PdCl_4 \cdot 3H_2O$ (Strem, Newburyport, MA) was dissolved in 100 mL tap water and slowly added into the reactor. In this way, Pd was coated on the surface of iron nanoparticles to form CMC-stabilized Fe-Pd bimetallic nanoparticles. The resultant nanoparticle suspension contained 0.5% by weight CMC, 1 g/L of Fe, 1 mg/L Pd (or Pd/Fe = 0.1% (w/w)). Before injections, the 1 g/L Fe suspension was then diluted by pumping it into a 200-gallon tank containing 120 gallons of nitrogen-purged tap water. The final diluted Fe suspension (150 gallons) contained 0.2 g/L Fe, 0.1% CMC and 0.2 mg/L Pd. Before the injection, 34 g of KBr as a tracer (dissolved in 100 mL water) was added into nanoparticle suspension. Figure 1 shows the reactor used for the nanoparticle preparation and the black nanoparticle suspension.

Figure 1. A picture of the CMC-stabilized Fe-Pd particles (Fe = 1 g/L) taken from the reactor 5 min after preparation. The dark color indicates the presence of ZVI nanoparticles which are fully dispersed in the water solution.

B3. Suspension injection and groundwater monitoring

The field test was carried out at a northern Alabama site in collaboration with the Golder Associates. This abandoned site was contaminated with high concentrations of PCBs, TCE, PCE and other chlorinated hydrocarbons. The subsurface is characterized as heterogeneous with a relatively shallow semi-confined aquifer. The head gradient at the site before the test 0.012. The hydraulic conductivity ranged from 20 feet/day. The effective porosity is about 0.15. Based on all the pump tests that were done at the site, the epikarst always acts confined although technically it should be semi-confined. The 0.2 g/L nanoparticle suspension was injected into the ground through a 5-ft screened interval at 44.5-49.5 ft below ground of injection well IW-1. A peristaltic pump was set at a rate of ~0.67 gallon/min to deliver the nanoparticle suspension to the injection well, however, the pump did not exert additional pressure, i.e. the suspension was driven into the aquifer only by the static hydraulic gradient (or gravity flow) between injection well and the aquifer. Groundwater samples were collected from two monitoring wells MW-1 (5 ft down gradient) and MW-2 (10 ft down gradient) before and after injection. Samples were collected without purging using 12V submersible pumps installed at each of the monitoring wells. Also, a multi-parameter probe with a flow-through cell was used to measure pH, specific conductance, oxidation-reduction potential (ORP), dissolved oxygen (DO), and temperature readings during sampling activities.

C. PRINCIPAL FINDINGS AND SIGNIFICANCE

The key findings from this research are briefed as follows:

- It is practically feasible to synthesize the CMC-stabilized ZVI nanoparticles on site and on a relatively large scale. The resultant nanoparticles can be easily introduced into the contaminated aquifer under gravity.
- In accord with our prior experimental data, the CMC-stabilized nanoparticles exhibited unprecedented soil mobility and reactivity for destroying the primary contaminants such as PCE, TCE and PCBs under field conditions. The concentrations of PCE, TCE and PCB1242 in MW1 were lowered by up to 77%, 85%, and 83%, respectively, after deducting dilution effect in the first 10 days and continuously reduced by 59%, 96%, and 10% at the end of 29 days. In MW2, the concentrations of PCE, TCE and PCB1242 were lowered by up to 98%, 82%, and 95% respectively in the first 10 days and continuously reduced by 99%, 100%, and 93% at the end of 29 days.
- Application of the nanoparticles greatly boosted sustained biodegradation of the primary contaminants. As the degradation data are still being monitored, steady degradation of all the three chlorinated compounds was continuously observed four months after the treatment.

The results indicate that the in situ technology is technically highly feasible and can potentially save millions of remediation costs. Given the current and future impacts of chlorinated organic contaminants on our economy and human health, the successful implementation of this low-cost cutting-edge technology will save millions of dollars for both Alabama and the nation at large.