Project 86981

Transport, Targeting and Applications of Functional Nanoparticles for Degradation of Chlorinated Organic Solvents

Lowry, Gregory V.
Carnegie Mellon University

RESULTS TO DATE: Project Objectives This project addresses the need for methods to remove or degrade subsurface contaminants that are present as dense non-aqueous phase liquids (DNAPLs), and act as long-term sources of groundwater contamination. The goal is to build on a particle-based approach to subsurface contaminant remediation that is based partly on the recent success in using nanoiron to degrade chlorinated compounds dissolved in groundwater, and knowledge of how colloids migrate in porous media. The objective is to engineer reactive nanoparticles that can decompose and potentially isolate DNAPL pollutants in the subsurface. Delivering reactive particles directly to the surface of the DNAPL will decompose the pollutant into benign materials, reduce the migration of pollutant during treatment, possibly lead to encapsulation of the DNAPL, and reduce the time needed to remove residual pollution by other means, such as natural attenuation.

Contributions from several basic science fields are used to advance a particle-based strategy for in situ DNAPL degradation by providing targeted delivery of reactive particles directly to the DNAPL. Specific project elements are the following.

1. Particle synthesis and characterization. Synthesize reactive Fe0 particles and bimetallics that rapidly and efficiently dechlorinate TCE to harmless products. 2. Particle surface modification. Amphiphilic block copolymers are synthesized using ATRP and methods to attach the polymers to the particles are determined. 3. Particle and polymer characterization. The physical and chemical properties of synthesized polymers and polymer-coated particles are characterized, including their NAPL targeting ability. 4. Particle reactivity analysis. The efficacy and efficiency of Fe0 nanoparticles synthesized by different methods are determined. The effect of water quality parameters and the absorbed polymers on the reactivity and efficiency are also determined. 5. Particle mobility. The transportability and water-DNAPL partitioning of particles in saturated porous media is determined using micro-model and intermediate scale experiments in porous media. The effect of how physical, chemical, and hydrologic regimes existing in the subsurface affect nanoparticle migration is also investigated. 6. Particle-level computer model. Develop a predictive numerical model for the transport and DNAPL partitioning of surface modified nanoparticles in bench-scale and meso-scale experiments.

The end date of this project is scheduled for September 14, 2005. We have project funds (and project cost share) remaining to carry the project through to December 31, 2005, and possibly through March 14, 2006. We will apply for a 6-month no cost extension for the project. A full final project report will be submitted at that time. This brief report describes the remaining project tasks.

Good progress has been made on all elements of the project. The status of each project element is briefly described here.

1) Particle synthesis and characterization.

These are complete and no further activities will take place in this area. Two peer reviewed publications have resulted from this effort to date (1 accepted, 1 submitted). A third publication is forthcoming.

2) Particle surface modification.

The project goal was to create a reactive nanoiron particle that could transport effectively through water saturated porous media, and target the NAPL/water interface. This goal has been achieved. The final product is a Fe0/Fe3O4 core shell nanoiron particle (25-100nm), modified with a PMAA42-b-PMMA26-b-PSS466 triblock copolymer. A Nanoletters manuscript describing these particles is in preparation and should be submitted by August, 2005.

Work continues on characterizing these particles, determine the effects of altering the ratios of hydrophobic and hydrophilic blocks, and demonstrating their ability to target the NAPL/water interface under flow conditions, but no additional surface modifications are being developed.

3) Polymer and polymer-coated particle characterization and NAPL-water interface targeting. DLS and TCE/water/nanoparticle emulsion studies are continuing. The goal is to fully characterize the colloidal stability, NAPL/water targeting, and silica/nanoparticle interactions.

4) Particle reactivity. The reactivity of two types of nanoiron particles was fully explored. The results from this investigation lead to the conclusion that one particle type (RNIP) was superior in performance to the other type (made from borohydride reduction of Fe2+). All future studies are being investigated on the more promising type of nanoiron (RNIP). Two manuscripts resulted from these studies (ES&T and Chemistry of Materials).

Studies continue on the effects of pH and groundwater solutes on RNIP reactivity and lifetime. The effect of polymer modification is also under investigation. Preliminary data suggests that the impact of modifications is minimal (less that a factor of 4).

5) Particle mobility. Transport studies on polymer-modified RNIP continue. We have demonstrated that the polymer modifications make RNIP easily transportable through water saturated porous media, even at high particle concentrations that would be required for field application (3g/L). Continuing studies are investigating the effect of pH, flow velocity, and ionic strength on the transportability of the polymer-modified RNIP. In addition, commercial surfactants and polymers that may be able to impart the desired amphiphilicty to RNIP are being evaluated. The performance of these commercially available products is being compared to the polymer developed here. Low cost alternatives to the triblock copolymer are needed to make this a cost-effective approach.

6) Developing numerical models to predict transport and partitioning behavior of the nanoparticles.

A BD model has been developed that can evaluate the ability of nanoparticles to target the oil/water interface as a function of the architecture of the polymer coating. These results will be submitted for publication shortly. The models developed have achieved the goals of the project and no further model development will be conducted. A study comparing the modeled and experimental responses of polymer-modified nanoiron may still be conducted.