Project Title: Transport, Targeting, and Applications of Metallic Functional Nanoparticles for Degradation of DNAPL Chlorinated Organic solvents

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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 nanoparticle iron 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 will be needed 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.** Synthesize reactive Fe^0 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 Fe^0 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.

Status

This project was initiated September 15, 2002. Parallel research tracks have focused on all objectives of the project simultaneously. The following outlines the research progress for each objective, the implications of results to date, and the future work planned for the remaining 15 months of the project.

1) Particle synthesis. Two types of unmodified iron nanoparticles were investigated, Reactive Nanoscale Iron Particles (RNIP, supplied by Toda American, Inc.) and Fe^0 nanoparticles (Fe^0/B) synthesized in our laboratory using a slightly modified aqueous sodium borohydride reduction method previously reported⁷. The modification focused on minimizing the size distribution of the nanoparticles. The modifications include using a diluted synthesis solution (lower Fe^{2+} conc.) and adding an aqueous NaBH_4 solution instead of solid NaBH_4 . Particles were separated from the suspension solution by centrifuge, dried at 120°C under N_2 , and stabilized in air overnight. RNIP particles are synthesized

commercially by reduction of Fe-oxides in H_2/CO gas, and available in large quantities.

Transmission electron microscopy (TEM) and N_2 -BET indicate that particle sizes and specific surface areas of each particle type are similar. (Fe/B: primary particle size (30-40nm) and specific surface area ($36.5m^2/g$); RNIP primary particle size (40-60nm) and specific surface area ($23m^2/g$)).

The Fe^0 content (wt %) of fresh particles (determined from H_2 evolution upon digestion in concentrated HCl) is 97% for Fe/B and 27% for RNIP. TEM indicates a core/shell morphology for both particle types (Figure 5(a)-(b)). EELS indicates that oxygen concentrated in the shell of the particles so it is likely that the inner core consists of Fe^0 and the outer shell some iron oxide phase. Transmission Electron Microscopy confirmed the core/shell structure of RNIP particles reported by the manufacturer. Electron Diffraction (ED) and X-Ray Diffraction (XRD) confirmed the existence of Fe^0 in each type of the particles and Fe_3O_4 in RNIP particles while didn't identify any oxide phase in the Fe/B particles.

Figure 1.1. TEM images of fresh particles; a) Fe^0/B and b) RNIP

Implications. Both particles synthesis methods produce Fe^0 nanoparticles that with similar sizes and surface areas. This implies that both types will degrade TCE at similar rates and with similar efficiency. The lower Fe^0 content of RNIP particles compared to Fe/B particles means that RNIP particles do not have the same TCE dechlorination potential as the Fe/B particles, assuming all Fe^0 is available and used for TCE dechlorination. The lower cost and commercial availability of the RNIP particles, however, makes them an attractive candidate particle.

Future work. Particle properties, especially the boron in Fe/B particles, will be correlated with their ability to dechlorinate TCE to optimize the properties of the iron nanoparticles.

2) Particle surface modification.

2a) Designing and synthesizing inorganic-organic hybrid particles with the appropriate water solubility and TCE partitioning behavior. - The nanoparticles with hydrophobic-hydrophilic shell were synthesized by Atom Transfer Radical Polymerization (ATRP), which is well-known as a robust technique for control/living radical polymerization¹⁻⁴. ATRP allows the synthesis of well defined materials with prescribed block length and narrow polydispersity.

The hybrid nanoparticles consist of an inorganic core (SiO_2 or Fe^0) surrounded by a hydrophobic inner shell and a hydrophilic outer shell. The role of the hydrophobic block is to protect the core against contact with water, while the hydrophilic part was designed to enable the transport of the particles through groundwater layers and to provide NAPL-water targeting. Our studies showed that a ratio 1/5 – 1/10 between hydrophobic and hydrophilic blocks is sufficient to provide water solubility of the hybrid nanoparticles. Studies performed on unattached block copolymers showed that polystyrene (PSt) and poly(methyl methacrylate) (PMMA) are good candidates for the hydrophobic blocks. Sulfonated polystyrene (SPSt) was selected as the hydrophilic block due to its excellent water solubility. Other segments, such as methacrylate macromonomers with poly(ethylene oxide) side chains strongly adhered to silica due to the polyether blocks, obstructing the transport of the hybrid nanoparticles in the subsurface.

SiO₂-polymer coated particles

Inorganic-organic particles (silica core-organic (polymer) shell) are being used as model nanoparticles for transport studies until reactive polymer-modified Fe^0 particles are developed and optimized. The synthesis of silica-supported initiators, starting from 20 nm silica dispersed in methyl ethyl ketone, was described elsewhere⁵. Using the ATRP initiators covalently attached to the silica surface, we formed a polystyrene shell with ~120 nm size via ATRP (Figure 2.1). The shell was then sulfonated using acetyl sulfate method⁶. The sulfonated nanoparticles (~90 nm) were completely soluble in water. The water soluble particles have a slightly smaller size than the unsulfonated precursors (Figure 2.1), which can be explained by shrinkage of the hydrophobic part in water. The Si-O-C bond formed in this synthesis method, however, is susceptible to hydrolysis and the polymer can be released from the particles.

Figure 2.1. Particle-size measurements of bare silica, silica initiator, silica polystyrene, and silica-sulfonated polystyrene nanoparticles. Measurements were performed using a Malvern Dynamic Light Scattering instrument.

To avoid hydrolysis of the Si-O-C bond and release of polymer, silica-grown nanoparticles were also synthesized by using a silica initiator with Si-O-Si bond, which is more stable in water than Si-O-C bond. The procedure is presented in Figure 2.2. The 1-(chlorodimethylsilyl)propyl 2-bromoisobutyrate was synthesized from chlorodimethylsilane and allyl 2-bromo-2-methyl propionate in the presence of Karstedt's catalyst. The product was purified by vacuum distillation. $^1\text{H-NMR}$ spectrum indicated high purity of the 1-(chlorodimethylsilyl)propyl 2-bromoisobutyrate. Further, 2-bromoisobutyrate silica initiator was synthesized using a silica dispersion in methyl isobutyl ketone (commercial name MIBK-ST from Nissan). The unmodified OH groups on the silica particles were reacted with hexamethyldisilazane. The silica initiator was repeatedly washed with hexane and centrifuged, then dried under vacuum.

Figure 2.2. Synthesis of silica initiator

Polystyrene was then grafted onto the particles by reaction with the initiator and then sulfonated using the acetyl sulfate method. GPC analysis of cleaved polymer showed $M_n=12,400$ (approximately 120 structural repeat units). After sulfonation, the PSS-modified silica nanoparticles (Figure 2.3) were completely soluble in water, and the Si-O-Si bond formed was stable in water.

Figure 2.3. PSS-modified Silica nanoparticles.

A third type of polymer-modified silica particle was developed by us, consisting of hydrophobic-hydrophilic block copolymers grown from silica particles (Figure 2.4).

Figure 2.4. Polymer modified silica nanoparticles. A hydrophobic and hydrophilic block is provided.

This type of hybrid particles was synthesized by polymerizing methyl methacrylate using silica initiators, and then by chain extension with styrene. Further, the silica-supported block copolymers underwent sulfonation, to allow the formation of water soluble nanoparticles even for block copolymers with higher molecular weights. Thus, silica-supported nanoparticles with molecular weight of the PMMA segment $M_n=2800$ g/mol and $M_n=21,000$ g/mol of PMMA-block-SPSt showed temperature size dependence as presented in Figure 2.5. Changes in hydrodynamic radius are likely due to polymer extension and/or particle aggregation. The nature of these changes is under investigation.

Figure 2.5. Temperature dependence of particle hydrodynamic radius for polymer-modified silica nanoparticles Si-(PMMA)₂₈₀₀-block-(SPSt)₁₈₂₀₀. The measurements were performed on water solution of nanoparticles (1 g/l).

Fe⁰-polymer particles.

We developed a technique for building hydrophobic-hydrophilic hybrids which consist of a short anchoring poly(methacrylic acid) block, a hydrophobic PMMA protective shell, and a hydrophilic SPSt outer block. (Fig. 2.6)

Figure 2.6. Hydrophobic-hydrophilic triblock copolymers containing a short anchoring group.

The anchoring poly(methacrylic acid) block was obtained by hydrolysis of t-butyl groups from poly (t-butyl methacrylate), while the sulfonation reaction of polystyrene was performed following the same procedure as used for silica particles. The possibility of anchoring block copolymers on Fe⁰ nanoparticles by means of poly(methacrylic acid) (PMAA) units was confirmed from our experiments. Thus, when using triblock copolymers (PMAA)₂₉₀₀-(PMMA)₂₀₀₀-(SPSt)₆₃₀₀ we obtained water soluble Fe⁰ nanoparticles whose size dependence upon temperature is presented in Figure 2.7. Changes in hydrodynamic radius are likely due to polymer extension and/or particle aggregation. The nature of these changes is under investigation.

Figure 2.7. Temperature dependence of Fe⁰-polymer nanoparticles in water.

Optimizing block length and type.

Polymer attachment, water solubility, and NAPL-water partitioning are all affected by the polymer block type and relative lengths. To establish the optimum ratio between the anchoring part and hydrophobic and hydrophilic blocks, other triblock copolymers with different block size were synthesized and evaluated.

A triblock copolymer poly(methacrylic acid)-b-(MMA)-b-sulfonated polystyrene with $M_n=6000$ (PMA); 2600 (MMA); 48600 (SS) is water soluble (Figure 2.8), but - due to its high molecular weight - it requires long time under stirring for solubilization.

Code: PMAMMASS

$M_n=6000$

$M_n=2600$

$M_n=48600$

Figure 2.8. . Hydrophobic-hydrophilic triblock copolymer Poly(MAA)₄₂-b-(MMA)₂₆-b-StS₄₆₆

A triblock copolymer poly(methacrylic acid)-b-(MMA)-b-Sulfonated polystyrene with shorter anchoring block and longer PMMA block was synthesized (Figure 2.9). Molecular weights of each block are: $M_n=2000$ (PMA); 5700 (MMA); 8340 (SS). Properties of this polymer are under investigation.

Figure 2.9. . Hydrophobic-hydrophilic triblock copolymer Poly(MAA)₁₄-b-(MMA)₅₇-b-StS₈₀

The triblock copolymers presented above contain PMMA as hydrophobic block. PMMA is a rigid block, while its T_g is about 100-120 °C. Since the role of the hydrophilic block - as we designed it - is to protect the Fe⁰ nanoparticle, we synthesized triblock copolymers with poly(*n*-butyl methacrylate) as the hydrophobic block; poly(*n*-BMA) has a lower glass transition temperature, close to room temperature ($T_g=20$ °C), and will provide a less rigid protective shell.

A triblock copolymer poly(methacrylic acid)-b-(BMA)-b-sulfonated polystyrene was synthesized in three steps. First, a short PtBMA block was synthesized using *p*-tosyl chloride as initiator, followed by chain extension with *n*-BMA. The purified diblock was further used as macroinitiator in the polymerization of styrene. The styrene block underwent sulfonation using the acetyl sulfate method, simultaneously with *t*-butyl groups hydrolysis. The molecular weights of each block were: $M_n=2170$ (PMA); 9030 (BMA); 22170 (SS) (Figure 2.10) .

Figure 2.10. Hydrophobic-hydrophilic triblock copolymer Poly(MAA)₁₅-b-(BMA)₆₄-b-StS₂₁₃

To study the influence of the length of hydrophobic block on hybrid nanoparticles, we synthesized a triblock copolymer with the same size of anchoring and hydrophobic blocks, but with shorter hydrophilic block. The experimental procedure was similar to that used for the previous blocks. The triblock copolymer (Figure 2.11) poly(BMA)-b-(MMA)-b-St with $M_n=2170$ (PBMA); 9030 (nBMA); 7580 (St) is not water soluble (due to its short hydrophilic block), but forms very stable emulsions when organic solvents (e.g. toluene) are present in water.

Figure 2.11. Hydrophobic-hydrophilic triblock copolymer Poly(MAA)₁₅-b-(BMA)₆₄-b-StS₇₆

Implications. Appropriate hydrophobic and hydrophilic polymer blocks were identified and the first generation of inorganic-organic hybrid nanoparticles is now available for characterization and transport experiments. Characterization/testing of these particles will provide feedback to improve the next generation of particles. The ability to functionalize SiO_2 and Fe^0 particles has been demonstrated.

Future work. Work is in progress, including additional variation of the ratios of hydrophilic/hydrophobic blocks for a better control of the water solubility, transport, and particle protection provided by the hydrophobic block. Methods to produce particles with Si-C polymer linkages are being developed. The Si-C bonds are more stable than the Si-O-C bonds in polymer coated particles, improving the long term stability of these particles. A manuscript presenting the results from the development/characterization of functionalized SiO_2 and Fe^0 particles is in preparation.

2b) Sorption isotherms for polymers on Fe-oxide and SiO_2 . Sorption of the synthesized tri-block co-polymers to Fe nanoparticles was measured by the solution depletion technique. The synthesized polymers sorb to two types of iron nano-particles (RNIP and Fe_2O_3).

A fixed amount of Fe was added to varying amount of polymers in solution at a pH of 7-8. The samples were then mixed for a week under room temperature to establish sorption equilibrium. Samples then were centrifuged at 2000 rpm for 10 minutes and the supernatant was analyzed for polymer concentration using a Total Organic Carbon (TOC) Analyzer (OI Analytical, TOC1010).

Sorption of the triblock copolymer to RNIP particles are shown in Figure 2.12. The saturation coverage of 2900(PMA)2000(MMA)6300(SS) onto RNIP was 7 mg/m^2 (approx), assuming RNIP surface area to be $25 \text{ m}^2/\text{g}$. Sorption of all the synthesized tri-block co-polymers to Fe_2O_3 (hematite) nanoparticles was qualitatively observed and is now being quantified using the same technique.

Figure 2.12. Triblock Sorption Isotherm on RNIP Fe⁰ particles.

Implications. This demonstrates that polymers do adsorb to the iron surfaces and in sufficient quantity to stabilize nanoparticle suspensions in water. It also demonstrates that the polymer sorption to iron is fairly strong (steep isotherm). Therefore it is possible to modify the iron particle surfaces to provide them with NAPL-water targeting ability.

Future Work: Quantification of sorption of the tri-block co-polymers to the Fe₂O₃ and SiO₂ nano-particles. Stabilization of Fe₂O₃ particles with polymer sorption is going to be achieved using these measurements of sorption isotherms and at different pH and ionic strength. The desorption rate of polymers attached to particles will also be determined to confirm that polymers are sorbed essentially irreversibly. The effect of adsorbed polymers on particle reactivity will also be determined.

3) Polymer and polymer-coated particle characterization and NAPL-water interface targeting.

3a) *Polymer and polymer-coated particle characterization.* To investigate the interfacial targeting ability of the PMAA₄₂-b-PMMA₂₆-b-PSS₄₆₆ triblock polymer, interfacial tension measurements were performed for several different concentrations in a 1mM NaHCO₃/TCE two-phase system using the Du Nouy ring method. Figure 3.1 shows the plot of interfacial tension vs. polymer concentration. For the polymer free sample, the measured interfacial tension was 35 dynes/cm. The break in the interfacial tension shows a critical micelle concentration (CMC) of approximately 3 mg/ml, indicating that these triblock copolymer amphiphiles self-assemble at high concentrations in solution.

Figure 3.1. Interfacial tension plot for PMAA₄₂-b-PMMA₂₆-b-PSS₄₆₆ triblock polymer

Static light scattering (SLS) experiments were performed on the same polymer and the results are shown in the Zimm plot fashion in Figure 3.2. The polymer was dissolved in a 1mM NaHCO₃ solution with no exposure to TCE.

Figure 3.2. Zimm Plot for PMAA₄₂-b-PMMA₂₆-b-PSS₄₆₆ triblock polymer.

The concentrations used in the SLS experiments were the same as those used in the interfacial tension experiments, providing a common frame of reference. From the Zimm plot, the calculated molecular weight of the scattering objects (58,000 g/mole) is approximately the same as the molecular weight of individual polymer chains as measured by size exclusion chromatography. SLS results did not indicate a change in either apparent molecular weight or radius of gyration above the CMC that had been determined from the TCE/water interfacial tension measurements. One would expect these parameters to increase in the presence of micelles. We hypothesize that TCE solubilization promoted the polymer self-assembly in the interfacial tension measurements. No TCE was present for the light scattering experiments. We are currently conducting additional light

scattering studies in the presence of TCE, and air/water surface tension measurements in the absence of TCE to test this hypothesis.

For the polymer-coated particles, we characterized a system of silica particles with polystyrene sulfonate (PSS) grafted from its surface. Figure 3.3 shows a typical particle size distribution obtained from dynamic light scattering (DLS).

Figure 3.3. DLS of PSS grafted silica particles in 1mM NaHCO₃

From the plot, the z-averaged hydrodynamic diameter is 110 nm with a second smaller peak around 20 nm. We suspect that this smaller peak is a result of some free polymer in solution. Centrifugation/decantation procedures are being developed to test for and then eliminate the presence of free polymer.

3b) NAPL-water interface targeting. To test the targeting ability of the polymer-coated particles, we measured their influence on the interfacial tension of the TCE/water interface. Whereas bare silica particles do not lower the interfacial tension, these particles caused surface tension lowering in excess of ~23 dyne/cm (Figure 3.4). This confirms that the PSS grafts cause the particles to adsorb at the TCE/aqueous interface - demonstrating target capability. Interestingly, the targeting was achieved with only the hydrophilic polyelectrolyte. Continuing studies are underway to test the need for hydrophobic blocks.

Further evidence for the interfacial targeting capabilities of the PSS-grafted particles is provided by our observation that they stabilize emulsions of TCE and water, an effect that can only be achieved by adsorption to the interface. Experiments using TCE and heptane with PSS-Si particles demonstrated that the particles partition to the TCE and heptane interface and forms emulsions with a droplet size of approximately 5-20 μm (when Water:TCE = 5:1 and particle concentration was 1g/L). The emulsion droplets were observed using Olympus IMT-2 inverted microscope equipped with long working distance objectives. The

Figure 3.4. Surface tension lowering provided by PSS-coated silica nanoparticles.

images were recorded by using a SONY 77 CCD camera and the image analysis software Scion Image 1.62a with a Macintosh G3 computer. The magnification used was 1.0x intermediates lens and a 40x objective lens. Figures 3.5 (a)-(b) shows the stabilized droplets using PSS-Si particles.

Figure 3.5a: Stabilized Droplets of TCE

Figure 3.5b: Stabilize Droplets of Heptane

Implications. The $\text{PMAA}_{42}\text{-b-PMMA}_{26}\text{-b-PSS}_{466}$ triblock polymer and PSS-grafted particles do target TCE/water interface. These experiments demonstrate the ability of an inexpensive PSS polymer to provide targeting of the NAPL-water interface.

Future Work. Follow-up SLS experiments on TCE saturated aqueous polymer samples will be done to determine if TCE promotes micellization or if it has no effect on it. The effects of aqueous pH and ionic strength on the self-assembly, adsorption and targeting will be systematically examined. Adsorption studies of this and similar polymers onto silica and hematite nanoparticles will be performed in order to determine the colloidal stabilization and colloidal targeting properties of these polymers.

A systematic study of emulsification of TCE/Heptane using PSS-Si (hydrophilic particles). This study of Pickering Emulsion would involve constructing a ternary phase diagram altering TCE/Heptane:Water:PSS-Si Particles ratio and observe the emulsification behavior.

4) Particle reactivity. Both Fe/B and RNIP are highly reactive and rapidly transform trichloroethylene (TCE) to nontoxic compounds.

Fe/B: Using excess iron, Fe/B transformed TCE into ethane (80%) and C3-C6 coupling products with a surface-area normalized rate constant ($1.4 \times 10^{-2} \text{ L} \cdot \text{hr}^{-1} \cdot \text{m}^{-2}$) that is ~4-fold higher than RNIP ($3.1 \times 10^{-3} \text{ L} \cdot \text{hr}^{-1} \cdot \text{m}^{-2}$). Using limited iron, Fe/B transformed TCE into ethane (70%) and C3-C6 coupling products. The reaction displayed zero-order kinetics without deactivation. All Fe^0 in the Fe/B particles was accessible for TCE dechlorination and 92 wt. % ($\pm 0.7\%$) of the Fe^0 was used to reduce TCE. H_2 evolved from Fe/B with TCE presence was used to reduce TCE and adding H_2 to the reactor increased both the rate and efficiency of TCE dechlorination, indicating a catalytic hydrodechlorination pathway exists. Termination of the reaction with sufficient H_2 remained suggests that the catalyst may be Fe^0 or a transient Fe-(hydr)oxide phase. Zero-order kinetics implies strong binding of TCE on the oxide shell.

RNIP: RNIP particles yielded unsaturated products acetylene using limited iron and ethylene using excess iron. Reactions displayed first-order kinetics for both cases. Acetylene as the main intermediate indicates β -elimination is the dominant pathway of RNIP for TCE reduction. Approximately 44 wt. % of Fe^0 in the RNIP particles was unavailable for TCE dechlorination and remained in the particles. Adding H_2 did not change the reaction rate or efficiency of RNIP particles. Reaction rates, pathways, and products distribution indicate that RNIP behaves as micro-scale iron filings on TCE dechlorination. First order kinetics suggests that a weak binding of the TCE and the products on the surface of RNIP particles.

Implications. Particles made from a borohydride reduction of aqueous Fe^{2+} generate H_2 quickly in water and lose their reactivity for TCE degradation. The polymerization may protect the particles and maintain the reactivity until targeting NDAPL TCE. The ability of RNIP to be stabilized in water and retain their activity makes handling and subsurface delivery easier. However, the strong binding of TCE onto the Fe/B surface and weak binding onto RNIP surface imply similar trend of polymer adsorption on the particles which would make it more difficult to graft polymer onto RNIP surface. The efficiency of the RNIP particles is

comparable with that of Fe/B particles in terms of TCE degraded by unit mass of Fe⁰, however the cost to produce these particles is roughly 1 order of magnitude less (\$300/kg for Fe⁰/B vs. \$15/kg for RNIP).

Future work. Further investigation will be conducted on the pathways and kinetics of the two nanoparticles for TCE dechlorination. The effects of dissolved solutes (e.g. carbonate, sulfate, chloride, organic matter, adsorbed polymers) on particle reactivity and efficiency will be determined. The properties responsible for the catalytic pathway of Fe/B particles will also be studied. Additional characterization of each type of particle will be performed using XRD or NEXAFS to obtain information about the minor oxide phases of particles. Particle properties will be correlated with their ability to dechlorinate TCE to optimize the properties of the iron nanoparticles. A manuscript presenting the factors affecting the reactivity and efficiency of these two Fe⁰ particles was submitted to ES&T (May, 2004) and a second on the kinetics and pathways is in preparation.

5) Particle mobility. Transport studies were conducted in 1-D column experiments using silica sand (ASTM D-1556) with an effective porosity of 0.33. The transport studies were performed for several of the synthesized polymers and particle-polymers to observe the breakthrough in packed sand beds.

Stainless steel tubing was used to construct the flow system having a column OD of 0.5" and the flow rate used was 0.5 ml/min (velocity of 7.7 m/day). UV-vis Spectrophotometry (Spectra Physics, Spectra-100) was used as the detector, fixed at the wavelength providing maximum signal response for a particular polymer/particle (typically 200-300nm). A finite square pulse of polymers/particles was introduced to the column (up-flow) and the breakthrough was measured at the column exit using the UV-Vis detector in real time.

Polymers

All the polymers evaluated did not show significant hold up (i.e. greater than 80% mass transported in all cases) or retardation in the sand bed (Figure 5.1). Mass balances were calculated by integrating the breakthrough curves and comparing them to the area expected for the pulse. A second peak observed in the breakthrough curves suggests two population of polymers. This will be studied further to verify this occurrence and also find the nature this behavior.

Figure 5.1: Breakthrough curve of 6000 (PMA)2600(MMA)48600(SS). Replicate experiments were performed. The conservative tracer (NaNO₂) is included for comparison.

PSS-modified silica particles

The PSS-Si particles (silica core and organic shell) were transported through the column and more than 92% of the mass eluted. Mass was calculated by integrating under the curve. There was no significant retardation in the transportability.

Figure 5.2: Breakthrough curve of PSS-modified Silica particles. Replicate experiments were performed. The conservative tracer (NaNO₂) is included for comparison.

Implications. These initial studies indicate that the polymers and polymer coated particles are transported readily through sand packed columns. The impacts of organic matter, heterogeneity, and dissolved solutes may decrease the transportability. Also, the flow velocity will greatly impact the efficiency of transport.

Future Work: Glass column of 2.5" OD will be used instead of the 0.5" OD to decrease the flow velocity and obtain transportability data under more realistic groundwater flow velocities. NAPL-Water interface targeting will also be evaluated. Dodecane will be used in the packed column experiments at 10% saturation level to observe the change in the breakthrough behaviors of the PSS-Si particles and the polymers. The impact of dissolved solutes and organic matter on transportability is also under investigation.

6) Developing numerical models to predict transport and partitioning behavior of the nanoparticles. The diffusion rates of nanoscale particles, particularly in inhomogeneous environments such as water/DNAPL interfaces, are sensitive to the microscopic particle structure. Their structure is challenging to fully characterize experimentally, so computer simulations on molecular length-scales (Brownian Dynamics (BD) simulations) are being conducted to describe the dynamics and structure of polymer-grafted metal nanoparticles. These

simulations will complement experimental particle characterization and, ultimately, will provide parametric inputs for macroscale simulations of particle transport in porous media.

- Modeling a nanoparticle. For our purposes, simulating the Brownian Dynamics of a solid nanoparticle in a solvent is somewhat more challenging than simply reproducing the known translational diffusivity of solid particles, since we aim to correctly describe the dynamics of polymers grafted to the particle. As a result, the description of the solid particle must reproduce the correct translational and rotational diffusivities. Furthermore, the rigid nature of the particle must be included in the simulation. These tasks were accomplished by performing BD simulations of a set of nodes distributed on the surface of the nanoparticle subject to distance constraints⁸⁻¹¹.
- BD simulations of bare particles incorporating hydrodynamic interactions. We define the diffusion tensor in terms of a modified form of the Rotne-Prager-Yamakawa formulation¹². Correlated random numbers were obtained by performing a Chebyshev series expansion of the square root of the diffusion tensor as described by Fixman¹³ and implemented by others^{14,15}. We tested the translational and rotational diffusions of a bare particle and compared them to theoretical predictions, as Figure 6.1 shows. We find that the bead radius affects the diffusion properties of the particle. As the number of beads is increased, and the bead radius is decreased, the predicted hydrodynamic radius approaches the theoretical limit. Moreover, we find that we can account for the bead radius effect on the diffusion by a simple formula, enabling us to tailor the design such that the simulation gives the correct hydrodynamic radius for the bare particle.
- BD simulations of stabilized nanoparticles. Since we are looking for a representation of a stabilized particle with a limited number of beads, there must be then a balance between the number of beads representing the particle and polymer bead size. If the number of particle beads is small, we have to compensate by making the polymer beads larger in size to be able to occupy space, and thus be able to extend outwards. We test the model against data for the hydrodynamic radius of a polystyrene-stabilized silica particle from Savin et al.¹⁶, as Figure 6.2 shows. As expected, compensation in terms of polymer bead size is necessary in order to have an agreement with experimental data. Similar simulations were carried out using different number of particle beads. The information obtained from those simulations can be used to model systems with various grafting densities.

Implications. Measurements of the polymer structure and the translational diffusivity of the composite particle are providing information that can be closely related to the experimental data available from light scattering. Working in tandem with light scattering experiments, we expect to be able to develop our BD simulations to a level where they can provide quantitative information supporting

choices of graft densities, polymer chain lengths, etc. within the overall context of this project.

Future work. The aim of our future work is to study particles stabilized by block copolymers and to study diffusion and spatial configuration of stabilized particles in the presence of oil-water interface. In order to achieve this goal, simulation runs of block-copolymers at oil-water interfaces will be carried out and compared to block-copolymer interfacial studies that are currently performed by other team members.

Figure 6.1: Hydrodynamic radius (R_h) vs. number of beads (N) representing the bare particle. The triangles are results from calculation of R_h using translational diffusion, while the diamond-shaped symbols are obtained from rotational diffusion calculations. The radius of the bare particle is unity, while the radius of the beads on the particle surface decreases with the increase of the number of beads.

Figure 6.2: Hydrodynamic radius (R_h) vs. molecular weight of grafted polystyrene chains. N_b denotes the number of beads that represent the bare particle.

References

1. Wang, J. S.; Matyjaszewski, K. J. Am. Chem. Soc. 1995, 117, 5614.
2. Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. Science 1996, 272, 866.
3. Matyjaszewski, K.; Wang, J. S., US 5,763,548, 1995.
4. Pyun, J.; Matyjaszewski, K. Chem. Mater. 2001, 13, 3436.
5. Pyun, J. Jia, S.; Kowalewski, T., Patterson, G. D.; Matyjaszewski, K. Macromolecules 2003, 36, 5094.
6. Y. Tran, P. Auroy, J. Am. Chem. Soc. 2001, 123, 3644.
7. Zhang, Wei-xian, J. Nanoparticle Research, 2003, 5(3-4), 323-332.
8. Ryckaert, J.-P.; Ciccotti, G.; Berendsen, H. J. C. Journal of Computational Physics 1977, 23, 327-341.
9. Ciccotti, G.; Ferrario, M.; Ryckaert, J.-P. Molecular Physics 1982, 47, 1253-1264.
10. Liu, T. W. Journal of Chemical Physics 1989, 90, 5826-5842.
11. Doyle, P. S.; Shaqfeh, E. S. G.; Gast, A. P. Journal of Fluid Mechanics 1997, 334, 251-291.
12. de la Torre, J. G.; Bloomfield, V. A. Biopolymers 1977, 16, 1747-1763.
13. Fixman, M. Macromolecules 1986, 19, 1204-1207.
14. Kroger, M.; A., A.-P.; Laso, M.; Ottinger, H. C. Journal of Chemical Physics 2000, 113, 4767-4773.
15. Jendrejack, R. M.; Graham, M. D.; de Pablo, J. J. Journal of Chemical Physics 2000, 113, 2894-2900.
16. Savin, D. A.; Pyun, J.; Patterson, G. D.; Kowalewski, T.; Matyjaszewski, K. Journal of Polymer Science: Part B: Polymer Physics 2002, 40, 2667-2676.

Publications/Presentations

1. Lowry, G., Redden, G., Tilton, R., Sholl, D., Majetich, S., Matyjaszewski, K., Meakin, P., Rollins, H., "Transport, Targeting, and Applications of Metallic Functional Nanoparticles for Degradation of DNAPL Chlorinated Organic solvents". Presented at the DOE Environmental Management Science Program FY2003 Annual Meeting, Pasco, WA, May 7, 2003.
2. Liu, Y., Lowry, G., Majetich, S., "TCE Dechlorination by Iron Nanoparticles: Effect of the Surface Oxide Layer Growth on the TCE Dechlorination Rate", Presented at the American Chemical Society 35th Central Regional Meeting. Pittsburgh, PA October 19-22.
3. Lowry, G., Liu, Y., Majetich, S., "Factors Affecting the Reactivity, Efficiency, and Lifetime of Iron Nanoparticles for In Situ Degradation of TCE". Presented at the American Geophysical Union Fall Meeting 2003, San Francisco, CA, December 8-12, 2003.
4. Lowry, G., Redden, G., Tilton, R., Sholl, D., Majetich, S., Matyjaszewski, K., Meakin, P., Rollins, H., "Transport, Targeting, and Applications of Metallic Functional Nanoparticles for Degradation of DNAPL Chlorinated Organic

- solvents". In the proceedings of the 227th American Chemical Society National Meeting, March 31, 2004. Vol. 44(1), p. 488.
5. Lowry, G., Tilton, R., Sholl, D., Majetich, S., Matyjaszewski, K., "Developing Functional Fe⁰-based Nanoparticles for In Situ Degradation of DNAPL Chlorinated Organic Solvents", Presented at the 227th American Chemical Society National Meeting, April 1, 2004, Anaheim, CA.
6. Lowry, G., "Nanomaterials: Novel Applications for DNAPL and PCB Impacted Sites". Presented at the April meeting of the Three Rivers Chapter of the Academy of Certified Hazardous Materials Managers, Pittsburgh, PA, April 8, 2004.
7. Tilton, Robert, Sirk, K., Saleh, N., Lowry, G., "Development of Polymer-Decorated Nanoparticles for Targeted Delivery of Remediation Agents to the Trichloroethylene/Water Interface", 78th ACS COLLOID AND SURFACE SCIENCE SYMPOSIUM, New Haven, CT. June 20-23, 2004.
8. "Tiny engineered particles could one day remove common pollutant", by Byron Spice, science and technology writer for Pittsburgh Post Gazette, feature article in science and technology section of post Gazette, 4/1/04. (<http://www.post-gazette.com/pg/04092/294409.stm>).
9. "Nanoparticles seek out solvents in groundwater", by Liz Kalaugher, editor NanotechWeb.org, feature article in Nanotechweb.org on 4/13/04 (<http://nanotechweb.org/articles/news/3/4/8/1>).
10. Liu, Y., Lowry, G.V., "Comparative evaluation of the reactivity and efficiency of two types of nanoscale zero-valent iron for reductive dehalogenation of TCE DNAPL". In the Proceedings of the Environmental Chemistry Division, 228th American Chemical Society National Meeting, Philadelphia, PA, Aug 22-26. Vol. 45(1).
11. K. Sirk, N.B. Saleh, Y. Liu, T. Sarbu, A.S. Almusallam, G. Lowry, K. Matyjaszewski, S. Majetich, D. Sholl, R. Tilton, "Development of Polymer-Modified Nanoparticles for Targeted Delivery of Remediation Agents to DNAPL/Water Interfaces", AIChE 2004 National Meeting, November 7-12, 2004, Austin, TX.
12. Liu Y., Majetich, S. A., Tilton, R. D., Sholl, D. S., Lowry, G.V., "TCE Dechlorination Rates, Pathways, and Efficiency of Nanoscale Iron Particles with Different Properties", submitted to *Environ. Sci. & Technol.* May 31, 2004.
13. Almusallam, A. and Sholl, D., "Brownian dynamics study of polymer-stabilized nanoparticles". Presented at the Midwest Thermodynamics and Statistical Mechanics Conference, June 4, 2004, Buffalo, New York.