THE DESIGN AND TRANSPORT OF ZEROVALENT IRON PARTICLES FOR ENVIRONMENTAL REMEDIATION

A Thesis in
Chemistry
by
Bianca Will Hydutsky

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The thesis of Bianca Will Hydutsky was reviewed and approved* by the following:

Thomas E. Mallouk
DuPont Professor of Materials Chemistry and Physics
Thesis Advisor
Chair of Committee

Christine D. Keating
Assistant Professor of Chemistry

David L. Allara
Professor of Polymer Science and Chemistry

Susan L. Brantley
Professor of Geosciences

Ayusman Sen
Professor of Chemistry
Head of the Department of Chemistry

*Signatures are on file in the Graduate School
ABSTRACT

Environmental contamination is a worldwide problem due to the persistence of chlorinated hydrocarbons and toxic metals in the soil and groundwater. Often these contaminants are located in regions very difficult to reach by conventional methods. However, suspensions of specifically tailored zerovalent iron particles transport through packed beds or soil to effectively remediate halogenated hydrocarbon contaminants, such as trichloroethylene (TCE), by chemical reduction to non-toxic products. In order to study the transport of particles through the subsurface, sand and soil packed columns were designed. With these columns, it is possible to quantify the amount of iron retained by the column and determine where in the column the iron particles are retained. Experimental elution results were compared to contemporary transport models based on particle filtration through granular media. Control experiments showed that unmodified iron particles rapidly agglomerated in water, and were filtered efficiently by the columns. However, colloidal suspensions formed by combining iron particles with anionic transport agents achieved drastically improved iron particle elution through sand and soil packed columns. Additional experiments showed that adding specific combinations of anionic hydrocolloids and polyelectrolytes to iron suspensions further enhanced particle transport, mainly by controlling particle aggregation. Iron particle aggregation and subsequent sedimentation resulted for higher iron particle concentrations. The incorporation of anionic hydrocolloids was found to affect aggregation, though further studies are underway. Through collaboration with industry, this technology has already been successfully implemented in full-scale remediation field studies.
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This thesis discusses the use of zerovalent particles for the remediation of chlorinated hydrocarbon contaminants in soil and groundwater. Chapter 1 provides an overview of the contamination problems and conventional remediation methods. This chapter reviews zerovalent iron as an environmental remediant and considers the transport capabilities of these particles in porous media.

Chapter 2 investigates the transport of nanometer sized zerovalent iron particles through soil and sand packed columns by comparing the elution of unsupported iron particles to particles associated with an anionic support. A portion of the work discussed in Chapter 2 was published in the journal article "Delivery Vehicles for Zerovalent Metal Nanoparticles in Soil and Groundwater" (Schrick, B.; Hydutsky, B. W.; Blough, J. L.; Mallouk, T. E. Chemistry of Materials 2004, 16, 2187-2193). Bettina Schrick worked on the initial proof of concepts that this work is based upon. She also obtained ICP-AES, XPS, and BET measurements for the nanoiron. I synthesized the particles used in the experiments as well as the hydrophilic carbon support material, and conducted the microscopy work. Jennifer Blough and I designed and carried out the breakthrough studies using the particles I synthesized and isolated. For the reactivity studies, I synthesized Fe\textsuperscript{0}-Pd particles and carried out all of the measurements. Dr. Mallouk and I worked on the TE and RT numerical simulations with the help of Dr. Bruce Logan.

Chapter 3 further investigates the transport of zerovalent iron particles by measuring the elution of two commercially available iron samples, CIP and RNIP. These samples were modified with anionic polymers or clay and were passed through sand
packed columns. Much of the work in Chapter 3 was submitted for publication to Environmental Science & Technology in February 2007 as "Optimization of nano- and micro-iron transport through sand columns using polyelectrolyte mixtures". Elizabeth J. Mack, Benjamin Beckerman, Joanna M. Skluzacek, and Tom Mallouk assisted this research. The iron samples used in this chapter were obtained commercially, however the anionic polymers and hydrocolloids were incorporated with the iron particles by me, or in some cases, by Ben Beckerman. Ben assisted me with the CIP transport studies using sand packed columns. Elizabeth Mack assisted me periodically throughout this work. Joanna Skluzacek assisted me with the zeta potential work described in Chapters 3 and 4. Dr. Mallouk and I both contributed to the sticking coefficient calculations and the R-T and T-E predictions. Adrian Goodey helped collect SEM images.

Chapter 4 investigates the aggregation of RNIP and CIP iron particles. The effects of iron concentration and the incorporation of several support materials were studied in a variety of ways. Sedimentation, visible aggregation, and elution through sand packed columns were all examined. I developed the procedures, conducted the preliminary work and collected a majority of the data. Elizabeth Mack and Jessica Hershman assisted me with a portion of the data collection and are planning to continue with these investigations. The work in Chapter 4 has not been submitted for publication at this time.

Chapter 5 included the summary and conclusions of the thesis. In Section 5.2, the full-scale remediation of a contaminated site in Hamilton Township, NJ is described (Varadhi, S. N., Gill, H. S., Apoldo, L. J., Liao, K., Blackman, R. A., and Wittman, W. K., Full-Scale Nanoiron Injection for Treatment of Groundwater Contaminated with
Chlorinated Hydrocarbons. *Natural Gas Technologies 2005 2005, February.*. The full-scale application was made possible by collaboration between PARS Environmental, Inc., Dr. Mallouk, and the people who worked on this research project. PARS utilized the zerovalent iron remediation technology we developed in our laboratory to treat this site.
Chapter 1

Introduction

Chlorinated hydrocarbon contamination in the environment is a worldwide problem due to the heavy use of these compounds as solvents, lubricants, degreasing agents, pesticides and even in dry cleaning. Whether from leaks, breaks in pipes, or by other means, the release of toxic halocarbons has resulted in heavily contaminated soil and groundwater in our surrounding environment. The contaminants are often widely dispersed in the soil, rock, and water layers, making the remediation of these sites exceptionally challenging, especially considering the limitations of conventional remediation technologies\textsuperscript{1,2}

Although our research group studied toxic metals and a range of halogenated organic contaminants\textsuperscript{3,4} the present work will focus mainly on trichloroethylene (TCE) as a model contaminant. TCE has been used in many industrial applications. According to Environmental Protection Agency reports, over 291,000 lbs of TCE were released into the land and water between 1987 and 1993.\textsuperscript{5} Since prolonged exposure to high levels of TCE may result in liver damage and increased risk for cancer, the EPA has set the maximum allowed contaminant level (MCL) in drinking water as 5 ppb.\textsuperscript{5} However, it is not uncommon to record ppm levels of TCE in contaminated sites, often in the presence of a veritable cocktail of halogenated contaminants and toxic metals.
1.1 Transport of contaminants in the environment

When contaminants such as TCE are leaked, spilled or otherwise enter the soil, they migrate through the unsaturated (vadose) zone, which is the region between the ground surface composed of soil, sand, clay, organic matter, and some water, and the groundwater level. As hydrophobic organic contaminants pass through the vadose zone, a portion of the contamination adsorbs to organic and inorganic colloidal materials, such as soil organic matter and mineral surfaces in the subsurface leaving behind a trail of pure-phase contaminant, called ganglia, as it spreads into the soil. These ganglia are trapped in the soil and are held between the soil grains by capillary forces. Figure 1.1 shows a schematic description of the probable path that TCE or a similar dense non-aqueous phase liquid (DNAPL) might take as the contaminant spreads and eventually enters the groundwater saturated zone. DNAPLs have a higher density than water, so they sink down through the water accumulating as a pool on the impermeable layer beneath. The DNAPL is slightly water soluble, so a large concentration gradient that spreads easily to contaminate a large area of groundwater surrounds the pool at the bottom of the aquifer. DNAPL chemicals, such as TCE, remain in the soil and groundwater for years due to their low solubility. The distribution of contaminants throughout the subsurface zones suggests that a successful remediation strategy must address the high concentration of contaminants in the soil layers of the vadose zone and the underlying groundwater.
When considering options for the remediation of sites contaminated with organic compounds, many conventional remediation strategies are unable to reach all contaminated subsurface regions. Several conventional technologies have been used for the remediation of halocarbon contaminants by physical or chemical means, such as soil vapor extraction, pump-and-treat methods, heat treatment, bioremediation, electroosmosis, injection of reactive material (e.g., oxidizers) via hydrofracturing, and the in-situ placement of permeable reactive metal barriers (PRB). 1,8, 9,1, 10, 11

Pump-and-treat becomes an expensive and inefficient approach, due to the length of time it can take to remove contamination from a site.12 Reactive subsurface barriers were among the first to incorporate iron filings to react with organic contaminants as

**Figure 1.1.** Slightly soluble DNAPL contaminants are trapped in the subsurface through capillary forces as ganglia or as a pool surrounded by a concentration gradient.2
contaminated water passed through the permeable wall, forming mainly non-toxic products such as hydrocarbons and chloride ions.\textsuperscript{13} However, permeable reactive barriers work very slowly, are costly to install, and are unable to access the contaminant source zone. Another concern is the lifetime of the barrier, since the low surface area iron filings making up the permeable barrier passivate over time. Additionally, the hydraulic conductivity can be diminished, if the permeability of the barrier is not equal or greater than that of the aquifer. For example, when considering these methods for the remediation of an industrial site in New Jersey, it was estimated that pump and treat would require about $4,160,000, whereas a permeable reactive barrier of zerovalent iron filings would cost approximately $2,200,000, mainly due to excavation costs.\textsuperscript{14} Both of these techniques are limited to the treatment of only shallow aquifers and are unable to treat the contaminants trapped in the vadose zone.

DNAPL contamination in soil and groundwater is difficult to access by conventional remediation technologies due to its limited solubility in water and its location in both the unsaturated and groundwater saturated zones. Hydrofracturing uses pressurized water to inject a slurry or suspension of reactive iron particles through wells forming cracks in the subsurface.\textsuperscript{10} More recently, injection methods have been developed in an effort to overcome some of the limitations of the aforementioned techniques. Zhang and coworkers have contributed significant advancements for zerovalent iron remediation by injecting slurries of zerovalent iron nanoparticles into injection wells. Cantrell and coworkers have developed shear thinning methods which rely on certain polymer additives to decrease the viscosity of an injection fluid in order to increase the mobility of micron size iron particles for transport through porous media.\textsuperscript{15}
In other work, reactive nanoscale zerovalent iron particles (RNIP) have been formed into a surface stabilized biodegradable emulsion in which droplets consisting of an oil-liquid membrane surround zerovalent iron particles. This emulsified zerovalent iron (EZVI) can be delivered to subsurface contamination via injection wells.  

Though iron injection techniques are more effective and are a significant improvement over the conventional methods discussed above, these techniques have a range of drawbacks as well. None can fully decontaminate each and every site in a reliable and effective manner. Nanoiron injection methods are plagued by particle aggregation, as small Fe\(^0\) particles attach together to minimize surface energy. These large aggregates clog transport routes\(^2\)\(^,\)\(^17\) and injection wells, which may prevent particle transport completely. The high viscosity of the EZVI solution (1,942 cp)\(^16\) will hinder its transport though the subsurface. According to Cantrell et al., a higher viscosity solution has a decreased kinematic velocity, which results in more particle loss due to gravitational sedimentation.\(^15\)

1.3 Proposed remediation approach

We seek to tailor zerovalent iron particles in such a way to enable transport through soil and water to reach contaminated zones. This approach has several key features which make it an excellent alternative to conventional remediation technologies. The transport of modified iron particles to contaminated zones eliminates the need for expensive excavation of the site, making it inexpensive to put in place and to maintain. Instead of simply adsorbing or relocating the contaminants in the site, this low
maintenance in-situ method is able to access contaminants regardless of the depth or geological complexity of the site and reduce TCE and other toxic metals to non-toxic forms through reductive dehalogenation, utilizing reaction mechanisms that avoid toxic byproducts that may be more persistent or more toxic.\textsuperscript{18} Zerovalent iron and the transport materials we have selected are safe for use in the environment, affordable, and readily available for large scale operations.

Prior to use in full-scale remediation applications, much more will need to be understood about the mechanisms involved iron transport technology. This work focuses on investigating several of the scientific aspects involved in the remediation of halogenated organic contaminants by iron transport. We need to better understand the transport mechanisms, reaction mechanisms, kinetics of contaminant reactions at the surface of the iron particle, particle corrosion, and contaminant targeting. Here we will expound upon our findings in many of these areas. Specifically, we will look at the transport of nano- and micro-iron particles through soil and sand packed columns, consult colloid filtration literature\textsuperscript{19-21} to gain a better understanding of the collisions and forces involved, develop ways to enhance subsurface mobility, and develop analytical techniques to study changes in the transport capabilities of a variety of iron particle samples. Upon synthesizing nanometer sized iron particles, we further tailor the samples by incorporating a second, catalytic metal to increase dehalogenation reaction kinetics and further modify the samples with delivery vehicle additives.
1.4 Dehalogenation by zerovalent iron particles

For the chemical reduction of halo- genated organic contaminants, zerovalent iron has been shown to be particularly effective and versatile, transforming halogenated hydrocarbons such as trichloroethylene (TCE), as well as a range of toxic metal ions, into less toxic or mobile substances.9, 13, 22-26, 27-33 When the zerovalent iron particle surface oxidizes in the presence of a halogenated organic contaminant, TCE for example, electrons donated from the corrosion of iron are accepted by the TCE. The contaminants are reductively dehalogenated by the surface mediated redox reaction:

\[ \text{C}_2\text{HCl}_3 + 3\text{Fe}^0 + 3\text{H}^+ \rightarrow \text{C}_2\text{H}_4 + 3\text{Fe}^{2+} + 3\text{Cl}^- \]

TCE is reduced to non-toxic ethene and/or ethane as chlorine is replaced by hydrogen. Complete dehalogenation of chlorinated compounds is vital to avoid the formation of toxic intermediates, such as vinyl chloride (VC), which is more toxic than TCE and is only slowly reduced by iron.13, 24, 25, 27, 33 Because these reactions occur at the surface of iron particles, larger particles (e.g., iron filings) have lower reactivity than smaller, higher surface area iron particles. For this reason, an increasing number of laboratory and field studies of in situ remediation have been carried out using iron nano and microparticles4, 14, 27, 32, 34-38 Ponder utilized zerovalent iron nanoparticles to study the reduction of toxic metals to insoluble forms3 and Schrick looked at the hydrodechlorination of trichloroethylene to non-toxic products.4 Lowry, et al. compared TCE dehalogenation capabilities of zerovalent iron nanoparticles synthesized via Zhang’s sodium borohydride reduction36 (discussed in Section 1.4.1) with RNIP produced by Toda America39 (discussed further and used in Chapter 3). Lowry and coworkers found that both samples
successfully reduced TCE to non-chlorinated hydrocarbons without forming toxic intermediate byproducts. Using excess Fe/B, 80% ethane and 20% C3-C6 non-chlorinated hydrocarbon resulted. Reduction experiments using excess RNIP produced 74.5% ethene and 20.9% ethane. In his comparison, he also explains that the sodium borohydride reduced iron nanoparticles are mainly amorphous with a thin oxide layer, whereas RNIP particles are surrounded by a thicker more crystalline shell of Fe3O4. He suggests this shell is responsible for slowing the TCE dehalogenation reaction, however, the particle reactivity is still rapid enough for in-situ remediation use, and the lifetime of the particle is believed to be extended due to the shell protecting some of the Fe0.27

1.4.1 Nanoiron background

In 1996 Wei-Xian Zhang and his research group at Lehigh University developed a synthetic method which used sodium borohydride to reduce iron salts to nanometer sized zerovalent iron particles ranging from 10-100 nm in diameter by the following reaction:36

\[
4Fe^{3+} + 3BH_4^- + 9 H_2O \rightarrow 4Fe^{0}↓ + 3H_2BO_3^- + 12H^+ + 6H_2
\]

Here iron salt is mixed with excess sodium borohydride to ensure a fast reduction and uniform iron crystal growth. The iron particles produced by the sodium borohydride reduction method average 66±12 nm diameter and have BET surface areas of approximately 35±3 m²/g.36 These nanoparticles are composed of approximately 95% zerovalent iron and 5% boron.

Zhang’s group also determined that palladium can be attached to the iron particle surface by soaking freshly synthesized nanometer sized iron particles in a solution of 1
wt% palladium acetate in ethanol. Simply washing the fresh particles in the palladium acetate solution results in the reduction and subsequent deposition of Pd onto the Fe surface via the following reaction:

$$\text{Pd}^{2+} + \text{Fe}^0 \rightarrow \text{Pd}^0 + \text{Fe}^{2+}$$

the palladium attached to the surface of the zerovalent iron particle acts as a second, catalytic metal. These palladized iron particles display a more rapid dehalogenation rate, much higher than is owed to their increased surface area, without producing toxic, less easily reduced intermediate halocarbons. Reactivity and transport studies using palladized iron nanoparticles are further discussed in Chapter 2.

For in-situ remediation of contamination plumes, a slurry formed by mixing unmodified nanoiron particles with water can be injected into groundwater aquifers using injection wells, as was mentioned before. However, once the particle slurry is injected, if the iron particles rapidly agglomerate, they may be quickly filtered by the packing medium and immobilized. Therefore, many injections would be required at a contaminated site and deep plumes remain inaccessible by this method.

1.5 Colloid filtration theories for iron particle transport

Much of the contamination in the subsurface, distributed throughout vadose and groundwater zones, exists in inaccessible locations or at depths difficult or impossible to reach by conventional remediation methods. In order to develop a remediation material able to follow the contaminant path and transport deep into the subsurface to reach all of the trapped contaminants in sites, we consider modifying iron particles for use as reactive
transport agents. Highly reactive nanoscale zero-valent iron particles are a very promising remediation material, because they effectively reduce a wide variety of halogenated contaminants and toxic metal ions, as was mentioned before, however, the colloidal chemistry of these metallic particles is such that they have very poor transport properties in the soil and groundwater, mainly due to their tendency to aggregate, adhere to soil surface, and because of their small size.

The transport of iron particles in the subsurface environment has been modeled using colloid filtration theory (CFT). CFT provides a useful approximation for environmental transport in the form of a first-order kinetic model for particle collection by a uniform porous medium. However, particle transport in the natural environment is actually quite a complicated problem involving such factors as the flow rate of mobile phase, porosity of the packed media, the diameter and surface charge of the particles and collectors, and substantial heterogeneity in the surface chemistry of soils and soil organic matter. In an effort to optimize the transport of reactive zerovalent iron particles, we have focused on chemical methods to minimize aggregation and adhesions to soils and have used CFT to determine the relative effectiveness of different chemistries in enhancing particle transport through packed beds of water-saturated sand and soils.

Chemical “delivery vehicles” are well known in biomedical applications such as drug delivery, gene transfection, and tissue compatibility for transplants. However, until recently this concept had not been applied to the delivery of nanoparticles to the deep sub-surface environment. Many components of the soil, clay, sand, silica, and mineral surfaces are negatively charged at near neutral or slightly acidic pH and easily capture metallic particles. In Chapters 2 and 3, we investigate how anionic
polymers and hydrocolloids impart an overall negative surface charge to iron nano- and microparticles. In the case of nanoparticles, a highly negative surface charge helps stabilize colloidal suspensions, preventing particle aggregation by maximizing the columbiaic repulsion between particles. For both nano- and microparticles, particle-collector interactions are made more repulsive by increasing the negative charge on the particle (and possibly the collector) surface. The negative surface charge imparted by the anionic additives make them less likely to be captured by sand and soil components. Excess polyelectrolyte in solution may inhibit particle adhesion to favorable sites though blocking\textsuperscript{44} and macromolecular crowding\textsuperscript{45} effects, discussed in Chapter 3.

Recent transport models by Tufenkji and Elimelech, based on (CFT)\textsuperscript{19,20} have been very helpful in creating a more accurate model of the forces involved. Classical filtration theory (CFT)\textsuperscript{19,20} explains the seemingly counterintuitive result that very small particles, below 200 nm or so, are most readily collected by porous filtration media. Nanosized iron particles are subject to Brownian motion, and therefore follow random trajectories that move them from fluid streamlines to the surface of the collector grains, where the fluid velocity is zero. The random paths these small particles take increases the number of particle-particle and particle-collector collisions that occur during transport through a packed bed.\textsuperscript{2} In order to maximize the transport capabilities of iron particles, we take measures to minimize particle-particle and particle-collector interactions during transport, and ensure that collisions that do occur are less successful.

From these models we have developed methods to quantitatively determine whether particles permeate through a packed bed or adhere to collector grains and are retained. Chapters 2 and 3 study the effects of these factors involved in iron particle
transport through soils and packed media. Suspensions of iron particles are passed through sand and soil packed columns, and the suspension and elution are both analyzed for iron concentration to quantify the iron retained by the column. Two methods are used to accomplish this. In one case, the iron is complexed into a form measurable by UV-vis spectroscopy. Another approach uses electron microscopy to visually compare iron suspensions before and after elution through packed columns to determine changes in particle size distributions.

1.6 Motivation

The design, synthesis and transport capabilities of zerovalent iron nanoparticles produced by sodium borohydride reduction (Fe/B) are discussed in Chapter 2. The reactivity of Fe/B is examined by measuring TCE dehalogenation rates and special attention is paid to the effects of surface area and the addition of a second catalytic metal on these reaction rates. The retention of these particles by packed media is examined through breakthrough studies using a variety of soil types in saturated columns. In Chapter 3, bench top transport studies, based on colloid filtration theory (CFT) models, delve deeper into the effects of particle diameter, flow rate, and delivery additives on the transport of various iron particle samples through saturated sand packed columns. Particle-particle and particle-collector interactions are minimized by incorporating anionic delivery additives. Using a factorial Design of Experiments approach, several transport parameters are varied in a systematic manner to optimize the elution of an iron particle suspension through packed columns.
Chapter 4 focuses on the aggregation properties of nanometer sized iron particles. The aggregation of zerovalent iron particles leads to filtration and clogging of porous media. Larger, micron-sized iron particles do not aggregate to the same extent, but are far less reactive for hydrocarbon dehalogenation due to their lower surface area. In this chapter, we examine the transport, sedimentation and visual aggregation traits of RNIP combined with several polymer mixtures. We see that iron particles modified with anionic polymers have different aggregation and sedimentation traits than unmodified iron particles.

Finally, in Chapter 5, field studies and full scale remediation projects using modified RNIP are discussed. In collaboration with PARS Environmental, Inc., the iron suspension technology developed in our laboratory was utilized to remediate hydrocarbon contamination over a half-acre heavily contaminated disposal site in New Jersey. The results showed that our modified RNIP sample had the transport and reactivity capabilities necessary to significantly decrease the total volatile organic compound (VOC) levels through hydrodehalogenation without the production of toxic intermediates or products.
1.7 References


Chapter 2
Design, Synthesis, and Transport of Zerovalent Iron Nanoparticles

2.1 Introduction

Reliable remediation technologies are needed for the decontamination of chlorinated hydrocarbons and toxic metals in soil and groundwater. Contamination introduced into the subsurface travels through the unsaturated (or vadose) zone and spreads into the saturated groundwater zone beneath. As hydrophobic, sparingly soluble contaminants migrate though the unsaturated zone, pure phase ganglia are retained by capillary forces and by adsorption to organic or inorganic colloidal materials in the soil layers.\textsuperscript{1,2} Consequently, sites can have a high concentration of organic contaminants in soil layers and in the groundwater below.\textsuperscript{3}

It is necessary that remediation strategies are tailored for both unsaturated and saturated zones. In Chapter 1, conventional remediation techniques such as pump and treat methods and permeable reactive barriers were discussed and their limitations were noted. Among the most critical was their inability to access and treat source zones of contamination deep in the subsurface. In situ methods that more directly treat the contaminant at the source, such as the injection of reactive slurries or suspended solids, overcome some of these limitations. Hydrofracturing accomplishes this by injecting pressurized water through wells to develop cracks in the subsurface prior to particle injection.\textsuperscript{4} Shear thinning fluids have been shown in column tests to enhance the transport of micro-iron particles by decreasing the fluid viscosity in order to minimize particle capture by gravitational sedimentation.\textsuperscript{5} However, because shear thinning additives
actually increase the viscosity of the suspension at low flow rates typical of dispersion in ground water, it is not clear that this approach can be effective in the field. Nanoscale iron particles have been gravity fed through injection wells to study their reactivity and transport in an aquifer.\(^6\) The advantages and drawbacks of these methods were discussed in Chapter 1, and it was noted that all are plagued by the limited dispersion of unmodified iron colloids in soils.\(^7\)

When colloid filtration theories are applied to environmental transport processes, numerical simulations show that particle collisions with the soil matrix are most frequent for very small particles (<100 nm) and larger (>3 \(\mu\)m) particles due to diffusion and sedimentation mechanisms, respectively. Logan has shown that even for particles of optimal size, the collision frequency with collector grains can be on the order of hundreds per meter.\(^1\) For particles to transport effectively, nearly all of these collisions must be unsuccessful, i.e., the sticking probability must be very low. Therefore controlling the absorptive properties of particles in soils is a key factor to their effective utilization. As was mentioned earlier, it is also critical to prevent particle aggregation, as colloidal metal particles tend to aggregate. This aggregation prevents their flow through porous media and they are efficiently filtered by the interception mechanism.\(^1\)

In Chapter 1, we proposed a strategy whereby zerovalent iron particles, which can chemically reduce halogenated organic contaminants such as trichloroethylene (TCE) to less toxic products, would be tailored in size and surface charge enabling their transport through packed media. In this chapter, the subsurface transport of highly reactive zerovalent iron nanoparticles is assisted by anionic, polymeric additives that prevent particle aggregation and lower their sticking probability in collisions with collector
grains. The polymeric additive presumably binds strongly to the iron oxide surface by chelation. Strong binding between the additive and the particle is expected to be important for delivery to contamination sites that are deep in the subsurface, because otherwise the particle could be chromatographically separated from the polymer during transport. Sites at depths greater than 20 meters, under buildings, etc., are of particular interest, because they cannot be accessed easily by hydrofracturing techniques or other conventional emplacement methods.8, 9

Anionic hydrophilic carbon and poly(acrylic acid) (PAA) are used in this chapter to quantify the effects of anionic polymer additives on the transport of zerovalent iron nanoparticles. We compare the elution of iron nanoparticles synthesized in the presence of hydrophilic carbon or PAA (hereafter referred to Fe/C and Fe/PAA) to that of unsupported nanoiron particles, using saturated columns packed with Ottawa sand and three model soils taken from different regions of the USDA soil textural triangle. We also confirm the reactivity of eluted nanoparticles using trichloroethylene (TCE) as a model contaminant.

2.2 Experimental Section

2.2.1 Materials and Methods

*Synthesis of Iron nanoparticles by Sodium Borohydride Reduction*

Zerovalent iron nanoparticles were prepared using procedures modified from Ponder et al. and Wang, et al.10, 11 Briefly, 6.5 g of FeSO₄·H₂O (Aldrich) was dissolved
in 100 mL of deionized water with stirring, about 15 min. After adjusting the pH to 6.2-7.0 with 3.8 M NaOH, the metal salts were reduced to black particles using 4.0 g of solid NaBH₄ (Aldrich) which was added in one portion. No precautions were taken to eliminate oxygen from the reaction vessel. A large reaction vessel should be used to avoid foam spillover, and the reduction should be carried out in the fume hood due to the H₂ evolved.

After the NaBH₄ was added, the mixture was stirred for 30 min or until visible hydrogen evolution had ceased, and the solid particles were separated from the liquid reaction mixture using a laboratory centrifuge spun at 8000 rpm (approximately 8600 g). The solid product was re-suspended in water, then twice in ethanol and once in acetone, centrifuging between each step to remove the solvent from the solid particles. The iron particles could also be isolated by vacuum filtration using a 0.2-µm pore-size nylon filter.

In both cases, the isolated particles were rinsed with water, ethanol, and acetone to eliminate water and prevent air oxidation, before being spread out over a large glass surface to be dried overnight under vacuum at room temperature. The next day the vacuum chamber was returned to ambient pressure by slowly introducing nitrogen or argon, being careful to avoid the rapid exothermic reaction with oxygen during passivation of the surface of the fresh Fe⁰ particles. This reaction creates a significant amount of heat and will easily sinter or even ignite the particles.

*Synthesis of Fe⁰Pd Nanoparticles*

For the synthesis of palladium-coated nanoiron (Fe-Pd), a slight modification of the procedure described by Wang and Zhang was used.¹¹ Nanoiron was prepared using
6.2 g of FeSO₄·7H₂O (Aldrich) in 100 mL of deionized water (with pH adjusted to 6.2-7.0 as described above), which was reduced with 3.1 g of solid NaBH₄ (Aldrich). The iron nanoparticles were then centrifuged, washed with water, and then immediately suspended in a solution of 0.1 g of palladium (II) acetate trimer ([Pd(C₂H₃O₂)]₃, 47.5% Pd, Alfa Aesar) in 20 mL of ethanol. This procedure coated the iron surface with Pd via a displacement reaction. The Pd-coated particles were then centrifuged, washed with ethanol and acetone, and dried in a vacuum oven overnight at room temperature, as described above.

**Synthesis of Hydrophilic Carbon Support**

As is further described by Schrick et. al, the carbon support, Vulcan XC-72 carbon (Cabot Corp.), was made hydrophilic by reaction with the diazonium salt derived from sulfanilic acid.¹² This reaction is thought to decorate the edges and defects of graphitic sheets with covalently linked benzenesulfonic acid groups.¹³ An aqueous suspension of 16.8 g of carbon was combined with a solution of 1.2 g of NaNO₂ and 2.6 g of sulfanilic acid in water, to which 1.5 mL of concentrated hydrochloric acid was added. The mixture was stirred overnight and the solvent was then evaporated in a crystallizing dish held at 120°C for 24 h. The resulting black flakes were then Soxhlet-extracted with ethanol for 24 hours.¹² The hydrophilic carbon was analyzed by combustion analysis for C, H, N, and S content, and the surface composition was determined by X-ray photoelectron spectroscopy (XPS).¹²
Addition of Anionic Polymers or Colloids to Modify Particles for Transport

By modifying the iron nanoparticle synthesis described above, a polymeric or colloidal additive may be incorporated to aid in the suspension and transport properties of the particles. Once the iron salt is dissolved in water, the additive, either 6.1 g of hydrophilic carbon (Cabot XC-72) or PAA (poly(acrylic acid)), average $M_w$ ca. 3500, was stirred into the reaction vessel. The rest of the particle synthesis was carried out exactly as described above. The pH was adjusted with NaOH and NaBH$_4$ reduced the mixture to Fe$^0$ particles associated with the polymer or carbon colloid. The modified particles were isolated by either filtration or centrifugation. The fresh modified particles were washed with palladium acetate in ethanol at this point, if desired. Steps to isolate and dry the particles were followed as described above. PAA was either combined with the iron salt prior to sodium borohydride reduction or was mixed with isolated iron particles in water. The sodium salt of PAA was used throughout this work.

2.2.2 Characterization of Modified Particles and Transport Agents

X-ray photoelectron spectroscopy (XPS) was performed on a Kratos XSAM800 pci spectrometer. Nitrogen Brunauer-Emmet-Teller (BET) adsorption isotherms were obtained using a Micromeritics ASAP 2010 surface area analyzer. Iron and boron bulk content were determined using a Leeman Labs PS3000UV inductively coupled plasma spectrophotometer (ICP-AES) at the Penn State Materials Characterization Laboratory. Analysis of samples for C, H, N, and S was carried out by Atlantic Microlabs, Norcross, GA. Transmission electron microscope (TEM) images were obtained at the Electron
Microscope Facility for the Life Sciences in the Biotechnology Institute at Pennsylvania State University using a JEOL 1200EXII microscope.

### 2.2.3 Analytical Measurements of Reactivity

TCE dehalogenation was tested using a purge and trap apparatus (Tekmar LCS-2) coupled to a gas chromatograph (Buck Scientific) equipped with a Restek MXT-502.2 60 m metal capillary column (0.53 mm i.d., carrier He, 3.0 µm df) and a dry electrolytic conductivity detector (DELCD) measuring Cl and Br containing compounds. The sample was purged for 6 min in a water bath kept at 35°C, then desorbed for 5 min at 180°C. The temperature program for the GC began at 40°C for 5 min, followed by a ramp at 10°C/min to 200°C. The sample was held at 200°C until the end of the run at 22 min.

To test the reactivity of Fe-Pd/C suspensions before and after elution through sand columns, the stock (5 mg particles/mL) or eluted suspensions, 4 mL, were loaded into 20-mL IChem vials (VWR) with a Teflon-silicone septum, which contained 4 mL of 26 ppm TCE in water. The vials were monitored for TCE removal via purge and trap sampling by recording the concentration of TCE, initially 13 ppm, at several times post mixing. The sample purge removed all of the TCE from the reaction vessel; therefore, each measurement required an individual reaction vial. All of the reaction vials were rotated on a roller drum about their vertical axis at 11 rpm.
2.2.4 Elution of Supported and Unsupported Nanoparticles Through Model soils

To test the transport of the support materials and particles in model soils on the bench-top, glass buret columns with an inner diameter of 1.2 cm were used. The packing material was either standard Ottawa sand (200-700-mm particle size, E&M Science, CAS 14808-60-7) or one of three soils: Hagerstown, Pope, or Chagrin. These three soils were characterized at the Pennsylvania State University Soil Characterization Laboratory (Table 2.1). They were stored at 4°C and passed through a 2-mm-mesh sieve prior to use.

The column ends were equipped with a two-way valve which was used to control the flow rate of solution through the column. A small glass wool plug was pushed to the bottom of each column to prevent drainage of the sand or soil through the column ends. Prior to the addition of nanoparticle suspension, the columns were slurry-packed to a height of 13 cm. The porosity of the packing material was measured by comparing the weight of wet and dry soil columns. Porosity and hydraulic conductivity values for these sand and soil columns are given in Table 1. Water used to make the sand or soil slurries and the iron suspensions was first passed through a Nanopure ion-exchange system, and had a resistivity of 18.3 MΩ·cm and a pH of 6.7. Water was added to borohydride reduced nanometer size iron particles alone, borohydride nanoiron with hydrophilic carbon support and borohydride nanoiron particles with a PAA delivery additive to make stock solutions.

In the column breakthrough studies, stock solutions of suspended iron nanoparticles (5 mg/mL) were introduced to the top of the column continuously and the
eluent was collected in 1.5-mL fractions. For analysis of these fractions in Fe and Fe/PAA experiments, 150-µL aliquots from each fraction were transferred by micropipet into 3.0 mL of an orthophenanthroline (Aldrich, 3 mg/mL) aqueous solution, pH 6.5. A UV-vis spectrophotometer was used to quantify iron complex formation by measuring absorbance at 508 nm. The dissolution of iron to form the [Fe(phen)_3]^{2+} complex was typically complete within 10 min, as judged from the lack of turbidity of the solution and the constant absorbance reading at 508 nm. Because iron dissolution was rapid, it was not necessary to add HCl. For the analysis of Fe/C fractions, 2.0 mL of orthophenanthroline solution (3 mg/mL) and 1 mL of 6 M HCl were mixed with each aliquot. The mixture was then centrifuged at 14,000 rpm (approximately 22,000 g) for 30 min to remove the carbon support. The amount of iron in the supernatant was determined from the absorbance at 508 nm. To ensure that all the iron was removed from the carbon support, fresh orthophenanthroline/HCl solution was added to the carbon pellet. After centrifuging, the supernatant was colorless and no absorbance above background could be detected at 508 nm. The same spectrophotometric methods were used to determine the iron contents of dry Fe/C, Fe/PAA, and Fe-Pd/PAA samples, and of aqueous stock suspensions. In Chapters 3 and 4 the phenanthroline complexation procedure is modified to provide a more quantitative analysis. In later studies, the samples were first acidified to dissolve all iron, and then hydroxylamine HCl was added to ensure all of the iron was in the 2+ state needed for complexation.
2.4 Results and Discussion

Transmission electron micrographs show that the hydrophilic carbon obtained by reaction of Vulcan XC-72 consists primarily of platelets that are 50-200 nm in diameter. These particles are sufficiently large for centrifugal separation, but are much smaller than the average particle sizes of the sand and soils used in our experiments. These carbon particles, either with or without a supported metal, form a persistent suspension in water (settling time > 1 day) because of the negatively charged sulfonate groups that decorate the carbon surface. Elemental analysis and XPS were used to characterize the carbon particles before and after reaction with the diazonium salt derived from sulfanilic acid. The untreated carbon contained 99% C, 0.43% S, and 0% N. After the derivatization, the carbon particles contained 1.61% S and 0.28% N, and the carbon content decreased to 90%. The remaining percentage is most likely oxygen and sodium, which charge balances the sulfonate groups. XPS data confirmed an increase in sulfur on the carbon surface from 0.3 to 1.8%. The surface oxygen content increased by 6%, the sodium content increased by 1.1%, and the carbon content decreased by 9%. The sulfur in the treated samples is oxidized, which is consistent with the presence of sulfonate groups. The sulfonate groups are expected to be located on the edges of the carbon flakes and at defect sites on the basal planes, as has been observed previously for carbon treated with concentrated nitric and sulfuric acids. The strongly acidic sulfonate groups ensure that the carbon particles are negatively charged in the range of pH relevant to soil and groundwater remediation; this high negative surface charge is a key property in preventing the agglomeration of the supported metal particles. The overall negatively
charged iron particles repel each other and are thus less likely to aggregate. Not only do we rely on the overall negative charge to prevent particle agglomeration, but the negative charge also serves to prevent the loss of iron particles to favorable adhesion sites in soil or sand matrices.

Figure 2.1. TEM image of Fe$^0$ particles with hydrophilic carbon support.

A TEM image of Fe nanoparticles synthesized by sodium borohydride reduction in the presence of hydrophilic carbon, Figure 2.1, shows the 30-100 nm iron particles enveloped by the sulfonated carbon particles. Because of its lower electron density, carbon appears as a lower contrast material than iron in these images. Lower magnification micrographs showed substantial amounts of free carbon, but little or no iron that was not associated with carbon sheets. From these images it is apparent that there is a strong association between the sheets and the iron particles.

Soil is a complex matrix composed of sand, silt, clay, minerals, organic material, etc. To better understand the transport of iron nanoparticles in a wide range of soils, we chose soils of representative textures from the USDA soil textural triangle, Figure 2.2. The USDA soil textural triangle describes the textural makeup of soils in terms of the
fraction of particles from three size ranges. Sand particles range from 2 – 0.2 mm in diameter, silt covers the 20 - 2µm size range, and clay particles are less than 2 µm. The three soils we used are marked in their appropriate textural classes on the USDA soil textural triangle (H = Hagerstown, C = Chagrin, P = Pope, and S = Sand), and their characterization details are shown in Table 2.1.

Figure 2.2. The USDA soil textural triangle compares the sand, silt, and clay sized particles that make up soils. Ottawa sand and the three model soils used are marked in their respective location on the triangle, H = Hagerstown, C = Chagrin, P = Pope, and S = Sand.

To study the transport of supported nano-iron in more environmentally relevant porous media, model soils of different textures were used. These soils varied in sand, silt, or clay content, shown in Figure 2.2 and Table 2.1. Also in Table 2.1, pH, cation exchange capacity, percent organic matter, dry and wet specific gravity, porosity, and hydraulic conductivity measurements are shown for each. The physical and chemical characteristics of soil are very important to particle transport. Hagerstown, formed in limestone residuum,\(^{17}\) is rich in silt texture (size 20-2 µm). The Pope soil, containing shale, siltstone, and sandstone,\(^{17}\) is rich in sand texture (size 2-0.2 mm). Both soils have relatively acidic pH. The swelling clay (montmorillonite) fraction of the clay in
Hagerstown and Pope soils is only 5%, the balance being consisting of mainly kaolinite, illite, and vermiculite. This is consistent with the relatively low pH and low cation exchange capacity of these soils. Chagrin soil, containing limestone, sandstone, and shale,17 is rich in clay texture (<2 µm in size) and has a slightly alkaline pH. The order of increasing particle size for the packing materials based on the percentages of sand, silt, and clay of those samples is therefore: Chagrin < Hagerstown < Pope < Ottawa sand.

Table 2.1. Textural composition and properties of model soil and sand-packed columns

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Hagerstown (high silt)</th>
<th>Pope (high sand)</th>
<th>Chagrin (high clay)</th>
<th>Ottawa sand (sand)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand %</td>
<td>29.9</td>
<td>55.9</td>
<td>27.7</td>
<td>100</td>
</tr>
<tr>
<td>Silt %</td>
<td>46.2</td>
<td>25.4</td>
<td>38.0</td>
<td>-</td>
</tr>
<tr>
<td>Clay %</td>
<td>24.0</td>
<td>18.7</td>
<td>34.2</td>
<td>-</td>
</tr>
<tr>
<td>Texture</td>
<td>Loam</td>
<td>Sandy Loam</td>
<td>Clay Loam</td>
<td>Sand</td>
</tr>
<tr>
<td>CEC (meq/100g)</td>
<td>9.2</td>
<td>9.8</td>
<td>17.0</td>
<td>-</td>
</tr>
<tr>
<td>pH in water</td>
<td>6.2</td>
<td>5.1</td>
<td>7.6</td>
<td>6.9</td>
</tr>
<tr>
<td>Organic matter %</td>
<td>2.7</td>
<td>3.3</td>
<td>2.8</td>
<td>-</td>
</tr>
<tr>
<td>Dry soil specific gravity (g/mL)</td>
<td>1.12</td>
<td>1.13</td>
<td>0.99</td>
<td>1.52</td>
</tr>
<tr>
<td>Wet soil specific gravity (g/mL)</td>
<td>1.57</td>
<td>1.53</td>
<td>1.46</td>
<td>1.94</td>
</tr>
<tr>
<td>Porosity %</td>
<td>45</td>
<td>40</td>
<td>48</td>
<td>42</td>
</tr>
<tr>
<td>Hydraulic conductivity (m/s)</td>
<td>$(5 \pm 2) \times 10^{-4}$</td>
<td>$(9.0 \pm 0.8) \times 10^{-4}$</td>
<td>$(1.7 \pm 0.2) \times 10^{-3}$</td>
<td>$(2.6 \pm 0.2) \times 10^{-3}$</td>
</tr>
</tbody>
</table>
The hydraulic conductivities of packed columns of these soils and sand were determined from gravity flow rates (Table 2.1). In column breakthrough studies with iron nanoparticles, the hydraulic conductivity was dependent on the support material used. The flow rate with Fe/PAA was not significantly different from the water flow rate for any of the soils tested. In sand and Chagrin soil, the flow rate was fast (> 10 mL/min) for water and all of the suspensions. These two packing materials have very different particle sizes, as the Chagrin soil consists of only 28% sand, the balance being relatively small silt and clay particles. The flow rate through Pope soil was somewhat slower, but again there was very little difference between the suspensions. The flow rate of water and of all suspensions was slower (1-5 mL/min, depending on column age and packing conditions) through the silt-rich Hagerstown soil. In this case, the suspended particles impeded the flow of water. This effect was particularly pronounced with the unsupported Fe nanoparticles. For Hagerstown soil, freshly packed columns with relatively fast gravity flow rates (5 mL/min) were used for breakthrough studies.

Breakthrough curves were obtained for 5 mg/mL suspensions of Fe/C, Fe/PAA, and unsupported nanoor iron, and the results are shown in Figure 2.3. In the case of Fe/C, nearly quantitative elution of particles was found for Ottawa sand and Chagrin (high clay) columns, consistent with the results shown in Figure 2.3. There was minimal elution of Fe/C through Hagerstown and Pope soils. Sand and Chagrin columns retained about 40% of the Fe/PAA injected. In the case of Fe/PAA in Chagrin soil, a downturn of the fraction eluted is observed after several pore volumes (column pore volume = 3-4 mL in each case), suggesting that Fe/PAA particles are retained and ultimately clog the pores in Chagrin soil. Unsupported iron nanoparticles were strongly retained by all the soils.
tested. Interestingly, unsupported particles appear to elute most effectively from the Chagrin column, despite the small grain size of the clay-rich soil. This result suggests that some of the anionic clay particles may play a role similar to that of anionic hydrophilic carbon. It is well-known that clay platelets assist in the transport of sorbed cations through soils, particularly at low ionic strength where their electrostatic repulsions are maximized. Clay platelets in water may also increase the effective negative charge on the soil grains through blocking and macromolecular crowding effects.

In Chapter 3, bentonite clay is used as a support material to study the hypothesis that anionic swelling clays may enhance iron particle transport at low ionic strength. To address a related concern, it is possible that there may be an error in the measurement of Fe elution through Chagrin soil. The results in Figure 2.3 display an iron concentration (normalized absorbance measurement) ranging 0.23 to 0.29. Had the Fe nanoparticles eluted from the column, one would expect the initial fractions collected to measure very low, or almost no iron and the iron concentration should increase with volume eluted. If the measured iron was due to background iron in the Chagrin column, this should been seen in the Fe/C and Fe/PAA columns as well. In Chapters 3 and 4, special consideration is paid to background correction and the phenanthroline analysis is modified to ensure more quantitative results.
**Figure 2.3.** Column breakthrough data for elution of unsupported iron nanoparticles, and nanoparticles supported by PAA and hydrophilic carbon. Each suspension contained 5 g/L solids. Vertical axis shows absorbance at 508 nm of the [Fe(phen)$_3$]$^{2+}$ complex formed by dissolution and complexation of eluted iron nanoparticle fractions, normalized to the same suspensions before elution.
The reactivity of the Pd-Fe/C particles was unaffected by elution through the sand columns, as shown in Figure 2.4. The carbon particles by themselves reversibly sorb TCE under these conditions. In groundwater applications involving low concentrations of TCE and other organic contaminants, the carbon support may help to preconcentrate organics for reduction by the supported iron nanoparticles.

![Figure 2.4](image.png)

**Figure 2.4** shows that the dehalogenation 8 mL of 13 ppm TCE using 0.020 g of Fe-Pd/C (20 wt % metal, Fe/Pd atomic ratio 50:1) before and after elution through an Ottawa sand column. Although the carbon support material adsorbs 40% of the TCE initially present under the same conditions, a second purge and trap cycle desorbs the TCE from the carbon.

The elution of iron particles modified with PAA and carbon transport additives through clay-rich soil and sand is important for environmental applications. A soil-
permeable support could make the injection and dispersion of colloidal iron and other materials more efficient, particularly in the remediation of very insoluble and hence immobile contaminants in subsurface deposits that are not easily excavated. However, the relatively poor transport of PAA and hydrophilic carbon modified nano-iron in low-clay soils (Pope and Hagerstown) presents a potential problem for such applications.

Particle filtration theory can be used to help understand the different transport properties of supported nanoparticles in these soils and to develop some ideas for improving the particles and supports. There are three basic mechanisms for capture of colloidal particles in porous media: diffusion, which dominates with particles below a few hundred nanometers in diameter, gravitational sedimentation, which dominates with larger particles (particularly those of significantly higher density than water), and interception, which is also important for larger particles and aggregates of primary particles. The additive probability of particle collision by the three mechanisms with the collector grains is the collector efficiency ($\eta$). The exponential attenuation of particle concentration by filtration is also dependent on the sticking coefficient ($\alpha$), which represents the fraction of these collisions that are successful in immobilizing a particle.

Early models of particle filtration overestimated and underestimated the effects of the diffusion and interception mechanisms, respectively, because they did not accurately consider hydrodynamic and universal van der Waals interactions. Recently, Tufenkji and Elimelech (T-E) have re-worked this problem by obtaining an accurate numerical solution to the convection-diffusion equation, which includes these terms. By fitting their results to a power law expression in the same dimensionless parameters used in earlier models, they obtained an accurate expression for collector efficiency:
\[ \eta = 2.4 A_S^{1/3} N_R^{-0.081} N_{Pe}^{-0.715} N_{vdW}^{0.052} + 0.55 A_S N_R^{1.675} N_A^{0.125} + 0.22 N_R^{-0.24} N_G^{1.11} N_{vdW}^{0.053} \] (2.1)

In the T-E equation, the effects of the three filtration mechanisms remain separable: the additive terms represent filtration by particle diffusion, interception, and sedimentation, respectively. The dimensionless parameters \( A_S, N_R, N_{Pe}, N_{vdW}, N_A, \) and \( N_G \) can be calculated from the soil porosity, particle size, soil grain size, Darcy (or superficial) fluid velocity, particle density, fluid temperature and viscosity, and particle Hamaker constant (*). This equation has been successfully used to fit a large body of literature data on particle transport through porous media. While the model should be applied cautiously to real soils (which contain a range of grain sizes), it can nevertheless be used to obtain an estimate of filtration lengths and to understand the effects of particle size and flow rate on transport.

In the “clean bed” limit, in which adsorbed particles do not cover an appreciable fraction of the surface of the porous medium, the particle concentration \( N \) decays exponentially according to equation (2.2), where \( N_0 \) is the concentration at the inlet and \( L \) is the distance traveled through the column¹. The filtration constant, \( \lambda \), may be calculated from \( \eta \) by using equation (2.3), in which \( \theta \) is the column porosity and \( d_c \) is the collector (or grain) size of the soil.

\[ \ln \left( \frac{N}{N_0} \right) = -\alpha \lambda L \] (2.2)

\[ \lambda = \frac{3}{2 d_c} (1 - \theta) \eta \] (2.3)

Figure 2.5 shows a calculation of the filtration length \( (\lambda)^{-1} \) vs. particle size from equations (2.1)-(2.3) under the conditions of our experiments for sand \( (d_c = 300 \mu m) \) and
soil \((d_c = 100 \, \mu m)\) columns. The filtration length corresponds to the column length at which the particle concentration falls to \(1/e\) of its initial value if the sticking coefficient \(\alpha = 1\). Experimentally, \(\alpha\) may be obtained by comparing experimental filtration lengths \((\alpha \lambda)^{-1}\) with calculated \(\lambda^{-1}\) values.

By comparing the results shown in Figs. 2.3, and 2.5, one may draw two important conclusions. First, sticking coefficients are lower than unity for Fe/PAA and Fe/C in Ottawa sand and Chagrin soils. We can estimate \(\alpha\) for Fe/PAA in Ottawa sand from the observation that about 60% elutes from a 13 cm column. Using equation (2.2), we obtain \((\alpha \lambda)^{-1} \approx 25 \, \text{Å}\). From Fig. 2.6, using \(d_p \approx 50\, \text{nm}\), the calculated \(\lambda^{-1}\) value is 9.1 cm, and therefore \(\alpha \approx 0.36\). Similarly, for Fe/PAA in Chagrin soil \((\lambda^{-1} \approx 1.1 \, \text{cm})\), we can estimate \(\alpha \approx 0.05\). For unsupported iron nanoparticles in Chagrin soil, \(\alpha \approx 0.14\), because the observed elution of 20% implies \((\alpha \lambda)^{-1} \approx 8 \, \text{Å}\). For Fe/C in sand and Chagrin soil, the nearly quantitative elution from 13 cm columns implies \(\alpha\) values \(< 0.07\) and \(< 0.01\), respectively. In general, \(\alpha\) values are lowest for Chagrin soil, which has the highest cation exchange capacity and therefore the highest negative surface charge density. This is consistent with the idea of repulsive interactions between the negatively charged support materials and negatively charged soil grains.

The second important conclusion one can draw, particularly from Figure 2.5, is that the filtration of nanoparticles is dominated by the diffusion mechanism, due to their far higher collision frequency. Better transport can be anticipated for larger particles that are less affected by diffusion from Brownian forces. The particles studied in our experiments (30-100 nm diameter) appear at the extreme low end of the plots in Fig. 2.5.
For 50 nm iron nanoparticles in sand, for example, we calculate a filtration length of 9 cm, whereas for 0.5 µm particles, the filtration length is 39 cm. Under the conditions shown in Fig. 2.5, the optimum particle size to minimize collisions and filtration is 0.40-0.50 µm for both sand and soil columns. The fact that the maximum in calculated elution length is roughly independent of collector grain size and flow rate seems counterintuitive; it can be explained by the fact that the probability of particle filtration by both the diffusion and interception mechanisms increases as the grain size decreases. Although particle collection by the diffusion mechanism is more sensitive to flow rate than is collection by interception, the predicted optimum particle diameter varies between narrow limits of 0.38 and 0.55 µm for all reasonable values of Darcy flow velocity (U ≥ 0.003 cm/s).

These simulations illustrate the importance of controlling both particle size and sticking coefficient in order to achieve transport over distances of tens of centimeters in packed columns of model soils. These Laboratory column transport experiments to some extent represent a “worst case” model for transport in the field, where a hierarchy of pore sizes exists and the dispersion of particles occurs in three dimensions. Nevertheless these studies are useful for understanding the factors that contribute to particle retention, and they can provide a ranking of the effectiveness of different additives in different soils. In Chapter 3, the transport of polymer-modified iron particles is considered more quantitatively using well characterized distributions of spherical carbonyl iron powder (CIP).

Equation 2.1 and Figure 2.5 suggest that nanometer size iron particles are more easily filtered by the column, mainly due to Brownian forces. For example, 50 nm
particles are calculated to have a filtration length of approximately 9 cm, whereas 500 nm particles are predicted to have a filtration length of 39 cm. Better transport should be achieved by larger particles that are not controlled by these forces. According to the predictions made by this simulation, particles in the 400 - 500 nm diameter size range would be optimal for transport through both sand and soil systems.

**Figure 2.5:** Open circles: Calculated filtration length ($\lambda^{-1}$) as a function of iron particle diameter, $d_p$, from equations 1.1-1.3. Upper curve shows a calculation for Ottawa sand (porosity $\Theta = 0.42$, $d_c = 300 \, \mu m$, Darcy flow velocity $u = 0.3 \, \text{cm/s}$). Lower curve shows a calculation for an average soil ($\Theta = 0.42$, $d_c = 100 \, \mu m$, $U = 0.2 \, \text{cm/s}$). Shaded region highlights the optimal particle diameter range predictions.
2.5 Conclusions

Anionic support materials such as hydrophilic carbon and PAA inhibit aggregation and significantly reduce the sticking coefficient of iron nanoparticles in Ottawa sand and in a high clay soil. In Chapter 3, bentonite clay is used as an anionic support material to further investigate the role of clay in iron particle transport. The relatively poor transport of these iron particles in the other soils tested implies that particles have higher sticking coefficients in soils having lower cation exchange capacity (see Table 2.1). The calculation of filtration lengths using the T-E model shows that nanoparticles will have poor transport properties compared to particles that are 400-500 nm in diameter. Chapter 3 follows these predictions with transport studies using micron sized iron particles modified with PAA. Also in Chapter 3, the transport properties of a reactive zerovalent nanoiron sample are studied by systematically varying three delivery additives. Because larger particles with less surface areas have lower reactivity, the aggregation of small reactive particles into larger reactive iron clusters will be investigated in future work. Chapter 4 studies particle aggregation and investigates ideal transport diameter.

2.6 References


(*) The porosity function $A_S$ is defined as $A_S = \left( \frac{2(1 - \gamma^5)}{2 - 3\gamma + 3\gamma^2 - 2\gamma^3} \right)$, where $\gamma = (1-\theta)^{1/3}$. The Peclet number $N_{Pe} = \frac{Ud_c}{D_p}$, where $D_p = \frac{k_BT}{3\pi\mu d_p}$. $U$ is the superficial (or Darcy) flow rate, $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature, and $\mu$ is the fluid viscosity. The other parameters are given by $N_{vdW} = \frac{A}{k_BT}$, $N_A = \frac{A}{3\pi d_p^2 \mu U}$, $N_R = d_p/d_c$, and $N_G = \frac{d_p^2 g \Delta \rho}{18 \mu U}$, where $A$ is the particle Hamaker constant, $g$ is the gravitational constant, $\Delta \rho$ the difference in specific gravity between the particle and the fluid, and $d_p$ and $d_c$ are the particle and soil grain diameters, respectively. See (ref 22) for complete details. For iron nanoparticles, we used $\Delta \rho = 6$ g/cm$^3$, $A = 1 \times 10^{-20}$ J, and $T = 288$ K. Variation of these parameters within reasonable limits did not significantly affect the results shown in Fig. 2.5.
Chapter 3

Optimization of nano- and micro-iron transport through sand columns using polyelectrolyte mixtures

3.1 Introduction

Industrial and agricultural processes have created many contaminated soil and groundwater sites that contain dense non-aqueous phase liquids (DNAPLs), metal ions such as Cr(VI), and other persistent hazardous compounds. DNAPLs, as hydrophobic contaminants, exist in the subsurface environment in a variety of forms, including liquid ganglia and adsorbed phases in pores that equilibrate very slowly with the groundwater.\textsuperscript{1,2} In these cases, pump-and-treat remediation methods have had limited effectiveness and \textit{in situ} remediation technologies, in particular chemical oxidation and reduction, are now being intensively studied.\textsuperscript{3} Among the available reductants, zero valent iron has been shown to be particularly effective and versatile, transforming halogenated hydrocarbons such as trichloroethylene (TCE), as well as a range of toxic metal ions, into less toxic or mobile substances.\textsuperscript{4-13} Because these reactions occur at the surface of iron particles, larger particles (e.g., iron filings) have lower reactivity than smaller, higher surface area iron particles. For this reason, an increasing number of laboratory and field studies of in situ remediation have been carried out using iron nano and microparticles.\textsuperscript{14-22}

Delivering zero valent iron particles to contamination sources in soil and groundwater is an interesting challenge for in situ remediation. The particles are typically
injected as an aqueous slurry, and they must travel distances of meters through soil or aquifers to reach the contamination source zones. Although nanoparticles have higher reactivity with DNAPLs and metal ions, they have poorer transport properties than microparticles for two reasons. First, according to classical filtration theory, particles below about 200 nm in diameter undergo collisions much more frequently with soil grains than larger particles because they are subject to Brownian motion. Second, iron nanoparticles do not form stable colloids. At a given mass concentration, the number density of nanoparticles is orders of magnitude higher than that of microparticles, and they are therefore more subject to aggregation. Large aggregates of nanoparticles are readily filtered and cause clogging of pores in soils. These factors complicate not only the delivery of nanoparticles to contaminant sources, but also the quantitative analysis of laboratory transport data.

Several strategies have been studied for improving the transport properties of iron nano- and microparticles in soils. Cantrell and coworkers used shear-thinning polymer additives to alter the fluid viscosity in soil pores and thereby decrease the frequency with which iron microparticles collide with soil grains. More recently, several groups have studied hydrophilic polymers and anionic carbons as coatings for iron nanoparticles. These “delivery vehicles” stabilize suspensions of nanoparticles and dramatically decrease the fraction of particle-soil collisions that result in particle immobilization. Oil-based microemulsions have also recently been found to stabilize nanoparticle suspensions and enhance their transport in saturated soil.

The transport of particles in the subsurface is often studied and modeled by using data from laboratory column tests. Quantitatively, one expects particles to travel over
greater distances in the field, where the dispersion pathways are three-dimensional and involve a hierarchy of pore sizes. Bench-scale column tests can nevertheless provide a ranking of the effectiveness of different delivery vehicles, and can provide useful kinetic information about particle filtration. One of the difficulties in modeling and optimizing the transport of iron nano- and microparticles in column tests however is the heterogeneity of both the particles and the collector (soil) grains. Soils are typically composed of a chemically diverse set of surfaces that include mineral grains, soil organic matter, and the DNAPL of interest. The particle-polymer-surfactant suspensions that are used for in situ remediation are also complex in that they contain both iron and iron oxide particles in a distribution of sizes. Clean-bed filtration models typically consider a uniform collector size and particle size, and model the interaction between them to obtain a single kinetic parameter, the sticking coefficient ($\alpha$). A more sophisticated filtration model recently developed by Tufenkji and Elimelech considers a range of particle-collector interaction energies. So far, this model has been tested with uniform polystyrene particles, but not with more heterogeneous samples that resemble the broad distributions used in field studies of micro- and nano-iron transport and remediation.

In this paper, we examine the transport of well characterized distributions of iron microparticles in saturated sand packed columns. We find that first-order kinetic models do not accurately describe the profile of retained particles in the columns or the size distribution of the eluted particles. However, the qualitative features of both the retention profile and size distribution are consistent with the more recent Tufenkji-Elimelech model. Iron microparticle transport is enhanced substantially by adding poly(acrylate) to the particle suspensions, and under these conditions the particles with the most
negative zeta potentials have the best transport properties. We also carried out a factorial optimization of iron nanoparticle (Toda RNIP) transport, using a mixture of anionic polymer and clay dispersants. We find that bentonite clay and poly(styrene sulfonate) added to poly(acrylate) significantly enhance the transport of nanoparticles relative to poly(acrylate) alone. Interestingly, there is no correlation of sticking coefficient with total concentration of polyelectrolyte, suggesting that the synergistic effect of mixing polyelectrolytes affects some other parameter, such as particle aggregation.

3.2 Experimental Section

3.2.2 Materials

Ottawa sand from VWR Scientific (CAS 7631-86-9) was dry sieved through a series of mesh screens to narrow the grain size dispersity for sand-packed columns. Sand that passed through a 40 mesh screen, but was unable to pass the 60 mesh screen, is hereafter referred to as 40 mesh sand. The 40 mesh sand was measured to be 160 ± 45 µm in diameter by optical microscopy. Three carbonyl iron powders, CIP-OM, CIP-HF, and CIP-HQ were obtained from BASF. The measured diameters of these approximately spherical iron microparticles were fitted to log normal distributions as shown in Figure 3.2, and an SEM image of CIP-HQ particles is shown in Figure 3.3. Nanocrystalline iron (Reactive Nano-Iron Particles, or RNIP), also shown in Figure 3.3, was provided by Toda America as a 25 wt% aqueous suspension. The RNIP samples were stored in sealed plastic containers, as received from the supplier, and were refrigerated at 1.7°C to prevent
air oxidation and anaerobic corrosion. RNIP stock suspensions were made by diluting the received suspensions with water. The stock suspensions were used within 2-4 days of preparation. Polyacrylic acid sodium salt (PAA), average MW 3500, was provided by Toda Kogyo, Ltd. Poly(sodium 4-styrenesulfonate) (PSS, 20 % wt. in water, average MW 1,000,000) was purchased from Aldrich. A bentonite clay sample, provided by PARS Environmental, Inc., was analyzed at Agricultural Analytical Services Laboratory, Penn State University. This bentonite sample had a cation exchange capacity (CEC) of 22.1 meq/100g. The percent saturation of the CEC was 67.7 % Ca, 28.0% Mg, and 4.3% K. The sample contained a high level of calcium (total calcium content 3400 ppm) suggesting the presence of a soluble calcium phase. Scanning electron microscopy (SEM) - Energy dispersive spectroscopy (EDS) confirmed the high calcium content. Therefore the CEC and percent saturations were calculated using a maximum exchangeable calcium level of 15 meq/100g. Textural analysis of the bentonite clay gave 75.1% clay, 9.5% silt, and 15.4% sand.

3.2.2 Iron particle transport experiments

Sample preparation. Iron particle suspensions, or stock suspensions, were made by adding the appropriate polymer(s) or clay to the iron sample in water, followed by thorough mixing. From batch to batch, the concentration of iron in the suspensions varied ± 10%; each sample was analyzed for iron prior to use, as described below, and the accuracy in the analysis was estimated to be ± 2%. Nanopure water, resistivity of 18.2 MΩ-cm, was used to make all solutions/suspensions and to pack the columns used
in transport experiments. All stock suspensions were shaken prior to injection into the columns.

*Column preparation.* One meter long glass columns (internal diameter 1.6 cm) with a two-way valve at the lower end were used for column transport studies (Figure 3.1). First, a glass wool plug was pushed to the bottom of each column. The columns were filled with water and dry 40 mesh sand was then poured in to minimize trapping of air bubbles in the water-saturated sand. The porosity of the sand-packed columns was found to be 42% by comparing the mass of wet and dry columns. The columns contained a reservoir bulb above the top of the sand in order to provide a slight pressure head for water flow through the column. Flow rates were controlled by adjusting the two-way valve at the lower end of each column, and measuring the flow rate of water prior to the iron elution experiment.

After rinsing the sand packed column with several pore volumes of water, 2.00 mL of CIP particle suspension (5.0 ± 0.5 mg/mL, or approximately 6 x 10⁷ – 5 x 10⁸ particles/mL) was introduced at the top of the column. The suspension was eluted in each case with deionized water. Particles not retained by the column were collected in 200 mL of eluted volume. All column tests were run at least in duplicate, and
the iron content of each stock suspension and elution was quantified by a phenanthroline complexation method, described below.

Iron analysis by phenanthroline complexation. The phenanthroline method was used to quantitate the iron in both stock suspensions and in the eluted fraction collected from the columns. In each measurement, 1.00 mL of eluent or 0.050 mL of stock suspension was added to 4.0 mL hydrochloric acid (1.0 M) to dissolve the iron sample, followed by 1.0 mL hydroxylamine hydrochloride (100g/L) to ensure complete conversion to the Fe\(^{2+}\) oxidation state. To increase the pH, 7.0 mL sodium acetate (100g/L) was then added. Then, 7.0 mL 1,10-phenanthroline (1.0 g/L) was added to form the red-orange iron tris-phenanthroline complex \([\text{Fe(phen)}_3]^{2+}\). The resulting solution was centrifuged and the absorbance at \(\lambda = 508\) nm was measured by UV-visible spectroscopy, following calibration with a standard \((\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4\cdot6\text{H}_2\text{O})\) iron solution.\(^{35}\) A linear calibration curve was obtained between absorbance values of 0.2 and 1.0. The iron concentration in each eluted sample, corrected for dilution, was compared to the concentration of iron in the particle stock suspension to determine the fraction that eluted from the column and the amount of iron retained.

Background iron correction. A 1.0 mg/mL aqueous solution of PAA (2.0 mL) was eluted with 200 mL water through sand-packed columns of various lengths, following the procedure for injection of an iron stock solution. The eluted solutions collected from each column were analyzed for iron by the phenanthroline method. The iron released from the column by the PAA solution was subtracted from elution measurements as a background correction.
**Analysis by scanning electron microscopy (SEM).** Stock suspensions and collected elutions were imaged by SEM. The sizes of individual iron particles in each image were measured, and the frequency of each particle size was used to determine the particle size distribution of each sample, as shown in Figure 3.2.

**CIP transport as a function of polymer concentration and flow rate.** To investigate the effects of PAA in CIP iron stock suspensions, four different concentrations of PAA, 0.5 mg/mL, 1.0 mg/mL, 2.0 mg/mL, and 5.0 mg/mL were added to 5.0 ± 0.5 mg/mL of CIP iron (6 x 10^7 – 5 x 10^8 particles/mL) in water. These stock suspensions were passed through 26 ± 2 cm long sand packed columns at a flow rate of 18 mL/min (0.152 cm/s). The amount of iron eluted from each column was determined by the phenanthroline method. Flow rate effects were studied by comparing the elution of CIP through 52 ± 3 cm long sand packed columns at 5, 10, and 18 mL/min. The two-way valve at the bottom of the column was adjusted to set each flow rate. The CIP and PAA concentrations in the stock suspensions were held constant at 5.0 ± 0.5 mg/mL and 1.0 mg/mL, respectively. Each 200 mL elution and the stock suspension were analyzed by the phenanthroline method and by SEM.

**Quantification of retained iron.** To measure the iron particles retained in the packing material, a specially designed glass transport column was used. This column consisted of two cylindrical sections connected by a short piece of flexible tubing, allowing the top reservoir section to be removed from the lower packed region. Following the elution experiment, the top section of the column was removed. The lower packed section was inverted, and the packing material exited the column as a plug that maintained its cylindrical shape. The packing material was extruded across aluminum
foil folded to separate the column packing into individual segments. Each segment was air dried, weighed, and analyzed for iron content by using the phenanthroline method. To account for the background levels of iron in the packing material, a control sample was also analyzed for iron.

_Transport of RNIP with polymer/clay mixtures._ To study the effect of polyanion mixtures on iron nanoparticle filtration, different amounts of PAA, bentonite clay, and polystyrene sulfonate (PSS) were mixed with RNIP via a factorial design-of-experiment approach for three variables. Fifteen stock suspensions were made by mixing 10.0 mg/mL of RNIP with combinations of PAA, PSS and clay in water. The RNIP suspension was first diluted with water, and then the appropriate amount of solid PAA was added. PSS was added from a 20% solution, followed by the solid clay. Between each addition (PAA, PSS, clay), the suspension was agitated for 5 min. The composition of each additive was determined by a central composite factorial design. For these experiments, the column lengths were 71 ± 4 cm and the flow rate was held constant at 18 mL/min. The iron content in each stock suspension and elution was quantified by the phenanthroline method.

### 3.2.3 Particle Characterization and Instrumentation

Transmission electron microscope (TEM) images were obtained using a JEOL 1200EXII microscope. Scanning electron microscope (SEM) images, taken with an FEI Quanta 200 ESEM, were used to determine the particle size distributions for the CIP samples. Iron particles in each image were individually measured and counted to
determine the distribution of particle diameters in each sample. The diameter distribution of sand particles was determined by a similar procedure using optical microscope images from an Olympus SX60 microscope operated in bright field mode.

A Hewlett Packard 8452A diode array spectrophotometer was used for UV-visible analysis of iron-phenanthroline samples. X-ray powder diffraction patterns were obtained with a Philips X’Pert MPD diffractometer, using monochromatized Cu Kα₁ (λ = 1.54053 Å) radiation. The electrokinetic properties of the carbonyl iron powder samples (CIP-HQ, CIP-HF, and CIP-OM) in varying concentrations of PAA were measured using a ZetaPALS zeta potential analyzer (Brookhaven Instruments Corporation, Holtsville, NY). The iron powders were first suspended in the PAA solution and then allowed to settle before small aliquots were taken from the top of the supernatant. This procedure allows the largest particles to settle and gave reproducible mobility results. Electrokinetic analyses of iron powder control samples were also performed using deionized water to suspend the particles. The electrophoretic mobility was measured at 25°C, and the Smoluchowski model was used to convert the raw electrophoretic mobility data into zeta potential. Each reported result is the average of 5 replicate runs.

3.3 Results and Discussion

3.3.1 Particle Size Distributions

Figure 3.2 shows the diameter distributions of carbonyl iron powder (CIP) samples BASF CIP-HQ, -HF, and -OM, and Figure 3.3 shows electron micrographs of Toda Reactive
Nanoiron Powder (RNIP) and CIP-HQ. Images similar to that shown in Figure 3.3c were obtained for CIP-HF and OM. The CIP particles and have a range of diameters. The diameter ($d_p$) distributions for these particles were fitted to log normal distributions (Eqn. 3.3), and the best fits are shown in Figure 3.2. The maxima in these diameter distributions were similar for HQ and HF (0.77 and 0.93 µm, respectively), but larger for OM (1.56 µm). Within the limit of detection by X-ray powder diffraction, all three CIP samples consisted of pure $\alpha$-Fe and did not contain significant amounts of oxide.

\[
P(d_p) = \frac{1}{d_p \sigma \sqrt{2\pi}} \exp\left(-\frac{[\ln d_p - \mu]^2}{2\sigma^2}\right)
\]

(3.1)

**Figure 3.2.** Particle diameter distributions for CIP samples. Lines represent fits to Eqn (3.1).
The RNIP particles, in contrast, were irregularly shaped and had average dimensions of 50-100 nm. Larger cubic particles with well defined faces were observed in some images (Fig. 3.3b). X-ray powder diffraction patterns showed the presence of a significant quantity of magnetite (Fe₃O₄) in these samples in addition to α-Fe, and the larger particles in the TEM images of RNIP are believed to be magnetite.

![Figure 3.3. Nano- and micro-iron samples. (a), (b) TEM images of Toda RNIP and (c) SEM image of CIP-HQ.](image)

### 3.3.2 Micro-iron Particle Transport

CIP iron particles were dispersed in aqueous PAA solutions, and their transport through sand columns was measured by analyzing both the eluted and retained fractions. In these experiments, we sought to mimic the conditions of iron particle injection in field tests¹⁹ and full-scale remediation projects.²² In those applications, the particles are typically pressure-injected or gravity fed into the soil as 1-10 g/L aqueous suspensions,
and in many cases the injection is followed by additional surface water and/or recirculated ground water. In our experiments, a 2.0 mL plug of iron suspension (5.0 ± 0.5 g/L) was introduced at the top of the column and was followed by 200 mL water (approximately 5 pore volumes) in order to quantitatively elute unretained particles. The diameter distribution of the eluted particles was measured by SEM, and in the case of CIP-HQ the amount of retained iron was analyzed as a function of column length. When the sum of the eluted and retained fractions was background corrected (by analyzing eluted blanks that contained only PAA and no iron), mass balance results were typically accurate to 10-15%, as shown in Table 3.1.

Table 3.1. Analytical results for eluted and retained CIP-HQ iron.

<table>
<thead>
<tr>
<th>Iron (mg)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CIP</td>
<td>flow rate (cm/s)</td>
<td>initial</td>
<td>eluted</td>
<td>retained</td>
</tr>
<tr>
<td>HQ</td>
<td>0.084</td>
<td>9.0</td>
<td>6.8</td>
<td>4.8</td>
</tr>
<tr>
<td>HQ</td>
<td>0.042</td>
<td>9.0</td>
<td>6.3</td>
<td>4.8</td>
</tr>
</tbody>
</table>

For each kind of CIP iron, eluted particle size distributions were measured at three different flow rates (5, 10, and 18 mL/min, = 0.042, 0.084, and 0.152 cm/s). Figure 3.4 shows representative results for larger (CIP-OM) and smaller diameter (CIP-HQ) initial distributions. In all cases, the distribution of eluted particle diameters could be approximated well by Equation 3.1. The eluted particle size distributions were normalized by constraining the mass of eluted iron to match the mass-weighted integral of the log normal distribution. This normalization procedure is however very sensitive to
counting errors at the high end of the distributions, because the particle mass is proportional to the third power of the diameter. In some cases, this procedure gave the physically reasonable result that the eluted distributions contained fewer particles of every size than the initial distribution. In other cases, (see, e.g., Fig. 3.4), the calculated maximum in the eluted distribution exceeded the number of particles of the same size in the initial distribution. While the scale factors for these fits are therefore uncertain, the maxima in the eluted distributions were more accurate and were consistent between duplicate runs.

**Figure 3.4.** Initial (open circles) and eluted (solid squares) particle size distributions for CIP-OM and CIP-HQ elution. Best fits to Eqn 3.1 are shown. Lower traces in each plot are the calculated eluted distributions from classical filtration theory, using the RT and TE models, Eqns. (3.6) and (3.7). Mass normalization was used to scale the eluted distributions.
Figure 3.4 also shows fits of the eluted quantity of iron to classical filtration theory (CFT). In CFT, which is essentially a first-order kinetic model for particle collection, the number density of particles in the mobile phase at the end of a column at

$$\ln\left(\frac{N}{N_0}\right) = -\alpha \lambda L$$

(3.2)

length L is given by Eqn. (3.2), where the product \((\alpha \lambda)^{-1}\) is a filtration length. The sticking coefficient \(\alpha\) is the probability that a particle-collector collision results in immobilization. In the “clean bed” limit, in which adsorbed particles do not cover an appreciable fraction of the surface of the porous medium, \(\lambda\) is obtained from Eqn. (3.3), in which \(\eta\) is the collector efficiency, \(d_c\) is the diameter of a collector grain, and \(\theta\) is the soil porosity. The collector efficiency is further composed of three terms as shown in Eqn. (3.4), which represent the three basic mechanisms for the capture of colloidal particles in a packed bed: diffusion \((\eta_D)\), which dominates for particles below 200 nm in diameter, interception \((\eta_I)\), and gravitational sedimentation \((\eta_G)\), which dominate for larger particles and aggregates of particles. The Rajagopalan-Tien (or RT) model (Eqn. 3.5) has been widely used to calculate these \(\eta\) values from experimental parameters, and thereby calculate the sticking coefficient from

$$\eta = 4.04b_H^{1/3}Pe^{-2/3} + b_HL_0^{1/8}R_s^{41/8} + 0.00338b_HS^{1/2}R_s^{-0.4}$$

(3.5)
the fraction of particles eluted. In this equation, the three additive terms represent \( \eta_D \), \( \eta_r \), and \( \eta_G \), respectively, and the parameters \( b_H \), \( Pe \), \( L_0 \), \( R^* \), and \( S^* \) can be calculated from the soil porosity, particle size, soil grain size, Darcy (or superficial) fluid velocity, particle density, and Hamaker constant.\(^{24}\) A more recent model, which includes hydrodynamic and universal van der Waals interactions, has been developed by Tufenkji and Elimelech (TE).\(^{33}\) In the TE equation (Eqn. 3.6), the three additive terms have the same meaning as in the RT equation, and the dimensionless parameters \( A_S \), \( N_R \), \( N_{Pe} \), \( N_{vdW} \), \( N_A \), and \( N_G \) can be calculated from the same set of physical parameters.\(^{36}\)

\[
\eta = 2.4 A_S^{1/3} N_R^{0.081} N_{Pe}^{-0.715} N_{vdW}^{0.052} + 0.55 A_S N_R^{1.675} N_A^{0.125} + 0.22 N_{vdW}^{0.053} \] (3.6)

Figure 3.4 also shows calculations of the eluted CIP particle distributions according to the RT and TE models. The data for all CIP samples, along with \( \alpha \) values derived from the RT and TE models, are compiled in Table 3.2. An important parameter to compare in this table is \( d_{p,max} \), the particle diameter at the maximum in the distributions. Because the experimental and calculated \( d_{p,max} \) values are not sensitive to mass normalization, they provide a useful way to compare the eluted particle size distribution to the CFT calculations.
Table 3.2. Experimental and calculated $d_{p,max}$ values and calculated sticking coefficients.

<table>
<thead>
<tr>
<th>CIP</th>
<th>flow rate (cm/s)</th>
<th>fraction eluted</th>
<th>Experimental $d_{p,max}$ (µm)</th>
<th>TE model</th>
<th>RT model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Initial</td>
<td>Eluted</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>HQ</td>
<td>0.152</td>
<td>0.88</td>
<td>0.77</td>
<td>0.88</td>
<td>0.004</td>
</tr>
<tr>
<td>HQ</td>
<td>0.042</td>
<td>0.33</td>
<td>0.77</td>
<td>0.73</td>
<td>0.021</td>
</tr>
<tr>
<td>HF</td>
<td>0.152</td>
<td>0.57</td>
<td>0.93</td>
<td>0.93</td>
<td>0.019</td>
</tr>
<tr>
<td>HF</td>
<td>0.042</td>
<td>0.34</td>
<td>0.93</td>
<td>0.73</td>
<td>0.017</td>
</tr>
<tr>
<td>OM</td>
<td>0.152</td>
<td>0.20</td>
<td>1.56</td>
<td>0.88</td>
<td>0.033</td>
</tr>
<tr>
<td>OM</td>
<td>0.084</td>
<td>0.047</td>
<td>1.56</td>
<td>0.88</td>
<td>0.057</td>
</tr>
</tbody>
</table>

As expected, for all three CIP samples the fraction eluted increases with increasing flow rate. However, two deviations from the predictions of CFT are apparent in the data. First, the derived $\alpha$ values are generally lower (for a given sample) at the higher flow rate, i.e. at a higher fraction of eluted particles. Second, the experimental $d_{p,max}$ is in the range 0.73-0.93 µm for all eluted samples and the range is narrower (0.73-0.88 µm) at lower flow rates. In contrast, for CIP-OM, which initially contains larger particles, CFT predicts a significantly larger value of $d_{p,max}$ (1.22-1.37 µm). It is also apparent from Fig. 3.4 that the eluted particle diameter distributions predicted by the CFT models are both broader than the observed distribution for CIP-OM.

Further insight into the deviation from CFT may be obtained by examining the fraction of retained iron as a function of column length. With a single particle diameter $d_p$, CFT predicts an exponential profile of retained particles according to Eqn. (3.2). However, with a distribution of particle sizes the situation is more complex. Because the
largest and smallest particles in the distribution are filtered more efficiently, the average filtration length $(\alpha \lambda)^{-1}$ increases slightly with increasing column length $L$. Re-writing Eqn. (3.2) in exponential form, we obtain Eqn. (3.7).

$$\frac{N}{N_0} = e^{-\alpha \lambda L} \quad (3.7)$$

For a distribution of particles this must be re-written as Eqn. (3.8), which is a sum over all values of particle diameter $d_p$. The number density of particles $N$ (particles/cm$^3$) can be converted to the mass concentration of iron in the mobile phase, $M(L)$ (mass/cm$^3$), by using Eqn. (3.9), where $V$ is the particle volume ($V = \frac{4}{3} \pi r^3$) and $\rho$ is the specific gravity of iron. Finally, the retained fraction (mass of iron retained per unit length) can be calculated from the gradient of $M(L)$ according to Eqn. (3.10), where $\theta$ is the column porosity and $A$ is the cross-sectional area.

$$N(L) = \sum_{d_p} N_0(d_p) e^{-\alpha \lambda (d_p) L} \quad (3.8)$$

$$M(L) = \rho \sum_{d_p} N_0(d_p) V(d_p) e^{-\alpha \lambda (d_p) L} \quad (3.9)$$

$$\frac{dM_{\text{retained}}(L)}{dL} = -\frac{dM(L)}{dL} \times \theta \times A \quad (3.10)$$

Figure 3.5 compares the experimental retained mass distribution of CIP-HQ iron with the distributions calculated from Eqns. (3.9-3.10), using $\alpha$ values obtained from the TE and RT models. The distribution of particle sizes introduces a slight upward curvature into the calculated retained profile. However, the experimental profiles are much more sharply curved. This behavior is consistent with the more recent model of Tufenkji and Elimelech, which considers a range of particle-collector interaction energies.
and rate constants. In this model, larger particles are collected at a faster rate, because they are trapped by van der Waals forces in a secondary energy minimum that is deep relative to the thermal energy. Very similar curvature in retained profiles was seen in their experiments with latex particles and columns of glass collectors. This effect is consistent with several observations in our data: the sharpening of eluted particle size distributions (Fig. 3.4), the shift to $d_{p,max}$ values smaller than expected from CFT (Table 3.3), the increase in apparent $\alpha$ values with decreasing flow rate (Table 3.3), and the decrease in apparent $\alpha$ values with increasing column length (see Fig. 3.6 below).
3.3.3 Effect of PAA Concentration on the Transport of Micro-Iron Particles

In order to gain insight into the effect of added PAA on the sticking coefficient ($\alpha$), the concentration of PAA in the stock CIP iron suspensions was varied between 0.5 and 5.0 mg/mL. Sticking coefficients were calculated from the fraction of iron eluted using the TE model, and the results are shown in Fig. 3.6. These results are compared with zeta potential measurements of the same particles over a broader range of PAA concentrations (0-100 mg/mL).

The addition of PAA to the suspensions imparts substantial negative charge to the particles, most likely by chelation of the polyacid to the iron oxide or hydroxide at the particle surface. In pure water, the measured $\zeta$ values were -15, -19, and -20 ± 2 mV for CIP-HQ, OM, and HF, respectively. At the PAA concentrations used in the sand column experiments, $\zeta$ values were in the range of -60 to -90 mV. The primary effect of the large negative charge on the particle surface is to cause electrostatic repulsion between the particles and the negatively charged collector grains. For CIP-HF, $\alpha$ decreases substantially as the PAA concentrations is increased from 1 to 5 mg/mL, and there is also a significant change in the zeta potential. For CIP-HQ, the changes in both quantities are more gradual. There is apparently a subtle difference in the surface chemistry of these otherwise very similar particles. CIP-HQ particles retain their negative charge after exposure to concentrated PAA solutions (1000 mg/mL) and rinsing with deionized water ($\zeta = -61$), but with the same treatment $\zeta = -28$ and -32 mV for CIP-OM and HF, respectively. At the concentrations of PAA used in the transport experiments, there is a very large excess of polymer relative to the number of surface
sites on the low surface area micro-iron particles. It is therefore possible that secondary effects of the excess polyelectrolyte, such as blocking of strong adsorption sites on the collector grains\textsuperscript{37} or macromolecular crowding,\textsuperscript{38} also contribute to the decrease in $\alpha$ with increasing PAA concentration. However, the dominant effect of increasing polyanion concentration is clearly to increase the negative surface charge of the particles.

Figure 3.6. Left: Sticking coefficient, $\alpha$(TE) vs. PAA concentration for CIP-HQ, HF, and OM elution from 26.1 cm (open plot symbols) and 51.7 cm (solid plot symbols) columns. Flow rate = 0.151 cm/s. Right: $\zeta$ vs. PAA concentration for CIP-HQ and HF.
3.3.4 Effect of Polyelectrolytes on the Transport of Nanoiron Suspensions

The transport of nano-iron is more complex than that of micro-iron, primarily because of the tendency of nanoparticles to aggregate and the strong dependence of \((\alpha \lambda)^{-1}\) on particle size in the nanoscale regime. Saleh et al. have recently studied RNIP modified with anionic block copolymers and found that particle zeta potential does not correlate directly with filtration length.\(^\text{29}\) The dependence of eluted fraction on particle concentration that they observed also suggests that aggregation plays a role, and that aggregate straining rather than filtration is an important component of particle capture. These factors complicate the problem of developing and testing a quantitative model for RNIP transport. Despite this problem, it is important to optimize the transport of iron nanoparticles, because they have the most utility for in situ remediation.

In our earlier study, we found that PAA enhanced nanoparticle transport, and was especially effective in a clay-rich soil.\(^\text{26}\) This result seems counterintuitive, given the fine texture of clay soils and the strong dependence of filtration length on collector diameter. It is important to recall however that swelling clays are also anionic polyelectrolytes and may thus affect particle zeta potential or block strong adsorption sites on other collector surfaces. In order to explore these effects, we conducted RNIP transport studies with mixtures of polyelectrolytes: PAA, a low molecular weight coordinating polyanion, poly(sodium 4-styrenesulfonate) (PSS), a high molecular weight, non-coordinating polyanion, and bentonite clay, a swelling clay. Fifteen different electrolyte mixtures were chosen, based on a three-parameter central composite design (CCD) factorial array, as illustrated in Figure 3.7.
Figure 3.7. Left: Three factor orthogonal central composite design (CCD)\(^{39}\) showing percent of RNIP eluted. Right: Each circle on the cartesian axes represents a ternary mixture of polyelectrolytes with a high, middle, or low concentration of one component, and the center point represents an average value of all three concentrations. The eight factorial points at the corners of the cube represent mixtures with intermediate concentration values. Right: Scatter plot of percent elution vs. total polyelectrolyte composition. Column length (71 cm), flow rate (18 mL/min), and RNIP concentration (10 mg/mL) were held constant.

The fraction of RNIP eluted in these experiments depended sensitively on the composition of the electrolyte mixture. With 71 cm sand columns, this fraction ranged between 6 and 40\%, with the highest elution fraction at relatively high PSS concentration (2.5 mg/mL) and lower concentrations of PAA and clay (1.0 and 0.8 mg/mL,
respectively). Surprisingly, there was no apparent trend with total poly(anion) concentration, contrary to the results obtained with micro-iron (see Fig. 3.6). This suggests that the most important effects of the other added electrolytes may be to control particle aggregation or other factors, rather than simply to change the zeta potential and thereby affect the particle-collector interaction potential. Ditsch et al., used similar mixtures of PAA, PSS, and copolymers, to show that aggregation of oxide nanoparticles can be controlled by properly controlling the molecular weight and order of addition of the components. Recently, Lowry and coworkers have quantified the aggregation of unmodified RNIP particles as a function of particle concentration and time. Given the strong sensitivity of the filtration length to particle (or aggregate) size in the nanoscale regime, this can clearly be an important parameter in the transport of RNIP.

3.4 Conclusions

The transport of polyacrylate-modified micro- and nano-iron in sand columns was examined for particle size distributions like those used for in situ zero valent iron remediation. With micron-size iron particles, the eluted size distributions were narrower than predicted by classical filtration theory, and apparent sticking coefficients varied with flow rate and column length. The profile of retained iron in the columns did not follow the log linear dependence expected from CFT. These observations could be rationalized in terms of a distribution of collection rate constants, as recently proposed by Tufenkji and Elimelech. The correlation of apparent $\alpha$ values with particle zeta potentials and
polymer concentration suggests that the primary role of PAA in these suspensions is to increase the electrostatic repulsion between individual particles and soil collector grains.

The transport behavior of RNIP nano-iron suspensions was qualitatively different in that there was no clear correlation between filtration length and total electrolyte concentration. These trends appear to merit further study, particularly in understanding the role of clays and polymeric electrolytes in controlling nanoparticle aggregation. Phenomenologically, we have observed that the filtration length of RNIP is sensitive to the composition of the polyelectrolyte suspension. With ternary mixtures containing PAA, PSS, and bentonite clay, the filtration length can be extended by a factor of 3-4 relative to polyacrylate alone. This finding may have useful consequences for remediation studies like that described in reference 22.
3.5 References


10. Liang, L.; Korte, N; Goodlaxson, JD; Clausen, J; Fernando, Q; Muftikian, R. Byproduct formation during the reduction of TCE by zero-valence iron and palladized iron. *Ground Water Monitoring and Remediation*. Winter **1997**, 122-127.


36. The porosity function \( A_S \) is defined as

\[
A_S = \left( \frac{2(1 - \gamma^5)}{2 - 3 \gamma + 3 \gamma^5 - 2 \gamma^6} \right),
\]

where \( \gamma = (1-\theta)^{1/3} \).

The Peclet number \( N_P = \frac{ud_c}{D_p} \), where \( D_p = \frac{k_B T}{3\pi\mu d_p} \). \( u \) is the Darcy flow velocity, \( k_B \) is Boltzmann’s constant, \( T \) is the absolute temperature, and \( \mu \) is the fluid viscosity. The other parameters are given by

\[
N_{vdw} = \frac{A}{k_B T}, \quad N_A = \frac{A}{3\pi d_p^2 \mu u},
\]

\[
N_R = \frac{d_p}{d_c}, \quad N_G = \frac{d_p^2 g \Delta \rho}{18 \mu u},
\]

where \( A \) is the particle Hamaker constant, \( g \) is the gravitational constant, \( \Delta \rho \) is the difference in specific gravity between the particle and the fluid, and \( d_p \) and \( d_c \) are the particle and collector grain diameters, respectively. See (33) for complete details. For iron microparticle transport calculations, we used \( \Delta \rho = 6 \text{ g/cm}^3 \), \( A = 1 \times 10^{-20} \text{ J} \), and \( T = 298 \text{ K} \).


Chapter 4

Controlling the Aggregation of Iron Particles

4.1 Background, Theory, Motivation

It is well recognized that zero-valent metal nanoparticles are powerful reducing agents for chlorinated hydrocarbons\textsuperscript{1-6} and reducible metal ions such as Cr(VI)\textsuperscript{7-10} and Pb(II),\textsuperscript{7} and it is well known that contaminant reduction rates by Fe\textsuperscript{0} increase with surface area.\textsuperscript{11-14} However, the colloidal chemistry of these particles is such that they tend to aggregate in solution, which prevents their flow through porous media such as soils. The magnetic properties of iron particles are also a concern with respect to aggregation.\textsuperscript{15} Although our prior work,\textsuperscript{16, 17} discussed earlier in Chapters 2 and 3, has shown that there are ways to form stable suspensions of iron nanoparticles,\textsuperscript{16} the conclusions of those studies, along with colloid filtration models, suggest that the diameter of the iron particle or particle aggregate plays a significant role in subsurface transport and mobility\textsuperscript{16-18}. These results suggest that the small highly reactive particles are not ideal for transport, and in fact larger, micron sized particles will have much better transport properties in soils and ground water. However, since the dehalogenation of TCE is a surface mediated reaction, the reactivity of a larger particle is much lower because of a significantly lower surface area per volume of iron. The sodium borohydride reduced zerovalent nanoiron and reactive nanosized iron particles (RNIP) used in Chapters 2 and 3 have high surface areas (20-40 m\textsuperscript{2}/g) and are consequently very reactive.\textsuperscript{14, 16, 19-21}
The zerovalent iron nanoparticles, synthesized by the Zhang method\textsuperscript{22} using sodium borohydride, are impractical for scale-up for reasons of cost and safety. The RNIP provided by Toda America has similar particle size and surface area, has a high level of reactivity and is commercially available in large quantities.\textsuperscript{23} Because a key motivation of this work is to develop an iron injection remediation technology for practical use in the real world, we use reactive nanoiron particles (RNIP) provided by Toda America here to study controlled particle aggregation. The RNIP sample is quite practical for use in field studies, because it is reactive and relatively inexpensive in comparison to the nanoiron produced by sodium borohydride reduction of iron sulfate.

Here we focus on the further investigation of the effects of polymeric additives on the aggregation of iron particles. The goal of this study is to develop reactive micron sized clusters of nanoscale iron that retain their high reactivity for the in-situ remediation of halogenated contaminants in the subsurface environment. Anionic polymers are again utilized to provide an overall negative surface charge in order to prevent uncontrolled aggregation and decrease sticking coefficients for successful particle transport.

Other work using RNIP principles has shown some success. Lowry \textit{et al.} have studied the dehalogenation properties of RNIP and have also examined its use in targeting chlorinated organics in a packed medium.\textsuperscript{20, 24} Quinn \textit{et al.} encapsulated RNIP in a technique they call EZVI (emulsified zero-valent iron), whereby an emulsion made of vegetable oil and water encapsulates a collection of iron particles into biodegradable membrane.\textsuperscript{25} PARS Environmental, Inc., a company based in Robbinsville, NJ, has used RNIP to remediate several pilot and full-scale remediation sites by incorporating polymeric additives with the help of our group\textsuperscript{26}. 
4.1.1 Transport effects of size and surface charge

According to filtration models discussed earlier, an ideal particle diameter for transport is one that is small enough for particles to follow the fluid flow and fit between the packed bed of collectors, however the particles must be large enough, and have sufficient mass to avoid being controlled by Brownian forces\textsuperscript{18, 27, 28}. A numerical simulation based on colloid filtration theories, Figure 2.5, predicted that particles approximately 0.5 micrometers in diameter should be the ideal size for transport through soil and sand. Chapter 3 discussed the transport of carbonyl iron powders (CIP) through packed columns, which showed that polymer-modified particles ranging from 0.5 to 1.5 micrometers in diameter transport well through the sand-packed columns we used.

Surface charge has been shown to be critical for the optimization of particle transport. Additives discussed in Chapters 2 and 3 were used to impart an overall negative charge to iron particles, resulting in enhanced transport. Previously we have shown that incorporating an anionic polymer, such as PAA, lowered the sticking coefficients of zerovalent iron particles. This resulted in enhanced transport through columns packed with model soils or sand.

In an effort to further develop this remediation technique for practical application in field studies, we address the transport size and surface charge restrictions while considering the need for high reactivity for halocarbon reduction. We used nanometer size reactive iron particles (RNIP) along with a variety of polymers of diverse functional groups and chain lengths to study the aggregation of nanometer size iron into micron size clusters suitable for transport. According to work by Ditsch et al., magnetite particles can
be clustered together in a controlled manner using a limited amount of short chain polymer, followed by a stabilization step with additional polymer by properly controlling the molecular weight and order of addition of the components.\textsuperscript{29} Recently, Lowry and coworkers have quantified the aggregation of unmodified RNIP particles as a function of particle concentration and time.\textsuperscript{15} Given the strong sensitivity of the filtration length to particle (or aggregate) size in the nanoscale regime, this can clearly be an important parameter in the transport of RNIP.

In this work, we begin to look into controlled aggregation by various polymers by several approaches. In one approach, polyethylenimine (PEI), a cationic polymer was used as a clustering agent, followed by an anionic polymer, polyacrylic acid sodium salt (PAA\textsubscript{long}), to stabilize and provide an overall negative charge, as we commonly do to minimize particle-collector interactions. Polyacrylic acid sodium salt (PAA\textsubscript{short}) was used alone and in conjunction with other polymers. Because the factorial experiment in Chapter 3 produced interesting results with PAA\textsubscript{short}, PSS, and clay, some of these combinations were also investigated. Additionally, a longer length (higher MW) polyacrylic acid sodium salt was used in conjunction with PAA\textsubscript{short} and PEI.

Zeta potential measurements compared the surface charge imparted by each polymer to the iron particle surface. TEM, SEM and optical microscopy were utilized to further investigate the size, shape, and other physical organization of the particle mixtures. A video capture optical microscopy setup was used to watch particle aggregation. This method was also used to briefly look at the magnetic effects of the particle aggregates. A UV-Vis spectrophotometer was used to measure the sedimentation time of the suspensions.
4.2 Experimental Section

4.2.1 Materials

Ottawa sand from VWR Scientific (CAS 7631-86-9) was dry sieved through a series of mesh screens to narrow the grain size dispersity for sand-packed columns. Sand that passed through a 40 mesh screen, but was unable to pass the 60 mesh screen, is hereafter referred to as 40 mesh sand. The 40 mesh sand was measured to be $160 \pm 45 \mu m$ in diameter by optical microscopy. The carbonyl iron powder (CIP-HQ) was obtained from BASF. The measured diameters of these approximately spherical iron microparticles were fitted to log normal distributions as shown in Figure 3.1, and an SEM image of CIP-HQ particles is shown in Figure 3.2. Nanocrystalline iron (Reactive Nano-Iron Particles, or RNIP), also shown in Figure 3.2, was provided by Toda America as a 25 wt% aqueous suspension. The RNIP samples were stored in sealed plastic containers, as received from the supplier, and were refrigerated at 1.7°C to prevent air oxidation and anaerobic corrosion. A portion of the RNIP suspension received from Toda America was centrifuged and dried in a vacuum over overnight. The particles were stored on the bench top in a sealed plastic container. RNIP stock suspensions were made by massing out the desired quantity of dried particles into glass vials, and a glass stirring rod was used to break up larger pieces of the dehydrated sample. The desired amount of water was added to the vial, and the mixture was sonicated for 30 min. The stock suspensions were used within 2-4 days of preparation.
Polyacrylic acid sodium salt (PAA_{short}), average MW 3500, was provided by Toda Kogyo, Ltd. A second polyacrylic acid sodium salt (PAA_{long}) had an average MW of 60,000. This PAA_{long} sample was obtained as a 35% aqueous solution from Polysciences, Inc. Poly(sodium 4-styrenesulfonate) (PSS, 20 % wt. in water, average MW 1,000,000) was purchased from Aldrich. Polyethylenimine (PEI), approximate MW 750,000, 50% w/v aqueous solution was purchased from Sigma. A bentonite clay sample, provided by PARS Environmental, Inc., was analyzed at Agricultural Analytical Services Laboratory, Penn State University. This bentonite sample had a cation exchange capacity (CEC) of 22.1 meq/100 g. The percent saturation of the CEC was 67.7 % Ca, 28.0% Mg, and 4.3% K. The sample contained a high level of calcium (total calcium content 3400 ppm) suggesting the presence of a soluble calcium phase. Scanning electron microscopy (SEM) - Energy dispersive spectroscopy (EDS) confirmed the high calcium content. Therefore the CEC and percent saturations were calculated using a maximum exchangeable calcium level of 15 meq/100 g. Textural analysis of the bentonite clay gave 75.1% clay, 9.5% silt, and 15.4% sand.

4.2.2 Iron particle transport experiments

Sample preparation.

Iron particle suspensions, or stock suspensions, were made by adding the appropriate polymer(s) or clay to the iron sample in water, followed by thorough mixing. From batch to batch, and depending on the experiment, the concentration of iron in the suspensions varied. However, each sample was analyzed for iron prior to use, as
described below, and the accuracy in the analysis was estimated to be ± 2%. Nanopure water, resistivity of 18.2 MΩ\(\cdot\)cm, was used to make all solutions/suspensions and to pack the columns used in transport experiments. All stock suspensions were shaken prior to injection into the columns, sedimentation measurements, and imaging.

*Column preparation.*

One meter long glass columns (internal diameter 1.6 cm) with a two-way valve at the lower end were used for column transport studies. First, a glass wool plug was pushed to the bottom of each column. The columns were filled with water and dry 40 mesh sand was then poured in to minimize trapping of air bubbles in the water-saturated sand. The porosity of the sand-packed columns was found to be 42% by comparing the mass of wet and dry columns. The columns contained a reservoir bulb above the top of the sand in order to provide a slight pressure head for water flow through the column. Flow rates were controlled by adjusting the two-way valve at the lower end of each column, and measuring the flow rate of water prior to the iron elution experiment. In this work, the flow rate was set to 10 mL/min, or 0.084 cm/s.

After rinsing the sand packed column with several pore volumes of water, 2.00 mL of CIP particle suspension (5.0 ± 0.5 mg/mL, or approximately \(6 \times 10^7 \text{ – } 5 \times 10^8\) particles/mL) was introduced at the top of the saturated column. The suspension was eluted in each case with deionized water. Particles not retained by the column were collected in 200 mL of eluted volume. All column tests were run at least in duplicate, and the iron content of each stock suspension and elution was quantified by a phenanthroline complexation method, described below.

*Iron analysis by phenanthroline complexation.*
The phenanthroline method was used to quantitate the iron in both stock suspensions and in the eluted fraction collected from the columns. This varies slightly from the analysis method in Chapter 3. In each measurement, 5.00 mL of eluent or 0.100 mL of stock suspension was added to 4.0 mL hydrochloric acid (8.0M) to dissolve the iron sample, followed by 1.0 mL hydroxylamine hydrochloride (100g/L) to ensure complete conversion to the Fe$^{2+}$ oxidation state. To increase the pH, 14.00 mL sodium acetate (200g/L) was then added. Then, 5.0 mL 1,10-phenanthroline (1.0 g/L) was added to form the red-orange iron tris-phenanthroline complex [Fe(phen)$_3$]$^{2+}$. The resulting solution was centrifuged and the absorbance at $\lambda = 508$ nm was measured by UV-visible spectroscopy, following calibration with a standard (FeSO$_4$(NH$_4$)$_2$SO$_4$·6H$_2$O) iron solution.$^{30}$ A linear calibration curve was obtained between absorbance values of 0.2 and 1.0. The iron concentration in each eluted sample, corrected for dilution, was compared to the concentration of iron in the particle stock suspension to determine the fraction that eluted from the column and the amount of iron retained.

*Background iron correction.*

A 1.0 mg/mL aqueous solution of PAA (2.0 mL) was eluted with 200 mL water through sand-packed columns of various lengths, following the procedure for injection of an iron stock solution. The eluted solutions collected from each column were analyzed for iron by the phenanthroline method. The iron released from the column by the PAA solution was subtracted from elution measurements as a background correction.

*Quantification of retained iron.*

To measure the iron particles retained in the packing material, a specially designed glass transport column was used. This column consisted of two cylindrical
sections connected by a short piece of flexible tubing, allowing the top reservoir section to be removed from the lower packed region. Following the elution experiment, the top section of the column was removed. The lower packed section was inverted, and the packing material exited the column as a plug that maintained its cylindrical shape. The packing material was extruded across aluminum foil folded to separate the column packing into individual segments. Each segment was air dried, weighed, and analyzed for iron content by using the phenanthroline method. To account for the background levels of iron in the packing material, a control sample was also analyzed for iron.

### 4.2.3 Iron particle aggregation experiments

*Aggregation of RNIP with polymer/clay additives.*

Different amounts of PAA\_short, PAA\_long, PEI, polystyrene sulfonate (PSS), and bentonite clay were mixed with RNIP in water to study aggregation effects. Solid RNIP was mixed with water and sonicated for 30 minutes. In separate vials, solid PAA\_short, PAA\_long from a 35% solution, PSS from a 20% solution, PEI 50% w/v aqueous solution, and solid bentonite clay were each mixed with the desired amount of water and briefly sonicated. Desired amounts of RNIP and polymer suspensions were mixed together and agitated periodically. When more than one polymer was added, the suspension was agitated for 5 min. between additions. The iron content in each stock suspension was quantified by the phenanthroline method.
4.2.4 Aggregation measurements

*Analysis of aggregation by optical microscopy.*

Particle suspensions (250mg/L) were visually analyzed by optical microscopy in order to study particle aggregation with respect to time. A thin, flat capillary (approximately 2 mm x 0.2 mm x 6 cm) was dipped into a particle suspension and a video of the particle aggregation was captured for approximately 45 minutes.

*Particle sedimentation study.*

Iron particle suspensions were made as described above. Dry iron powder was mixed with water and sonicated approximately 30 minutes. The desired mass of dry polymer, or aqueous solution, was mixed with water and sonicated about 5 minutes. RNIP samples without polymer additives were made by diluting the stock suspension with additional water, whereas RNIP/PAA and RNIP/PSS samples were made by mixing the iron and polymer solutions in a specific ratio. In order to study the sedimentation rates of each particle suspension, the sample was poured into a disposable plastic cuvette and the absorbance measurement at 508 nm was made every 30 seconds for 3600 seconds (1 hour). The beam of light was shown through the sample 1.5 cm from the bottom of a 4.5 cm tall cuvette with a path length of 1.0 cm. A range of CIP-HQ and RNIP concentrations were studied and mixtures of the iron particles with PAA or PSS were also examined. For RNIP and CIP-HQ, several concentrations of unsupported particles mixed in water were analyzed to make a calibration relating initial iron concentration with absorbance at 508 nm. This procedure was adapted from reference 15.
4.2.5 Particle Characterization and Instrumentation

*Analysis by electron microscopy (TEM, SEM, and optical microscopy).*

Stock suspensions were spotted onto formvar coated copper TEM grids, excess solution was wicked away with a kimwipe, and the sample was allowed to dry completely before being imaged by TEM. For SEM samples, the suspension was dropped onto clean gold coated glass slides which had been mounted on SEM stubs using double sided carbon tape. Again, the excess solution was wicked away and the sample was dried. The samples were placed into a gold evaporator before analysis. To determine the particle or aggregate size and morphology for each sample, transmission electron microscope (TEM) images were obtained using a JEOL 1200EXII microscope. Scanning electron microscope (SEM) images were taken with an FEI Quanta 200 ESEM. The sizes of individual iron particles in each image were measured to determine the representative particle sizes for each sample. The aggregation and particle morphology visible in these images was also studied. The diameter distribution of sand particles was determined from optical microscope images taken with an Olympus SX60 microscope operated in bright field mode. The Olympus SX60 microscope was operated both in bright field mode and in dark field mode, depending on the sample. Video capture was accomplished using MGI Videowave-4 software. A Hewlett Packard 8452A diode array spectrophotometer was used for UV-visible analysis of iron-phenanthroline samples. The Hewlett Packard spectrophotometer also measured the sedimentation times of each sample by using the kinetic function. The electrokinetic properties of the iron polymer mixtures were measured using a ZetaPALS zeta potential analyzer (Brookhaven
Instruments Corporation, Holtsville, NY). RNIP was first suspended in the polymer solution and then allowed to settle before small aliquots were taken from the top of the supernatant. This procedure allows the largest particles to settle and gave reproducible mobility results. The electrophoretic mobility was measured at 25°C, and the Smoluchowski model was used to convert the raw electrophoretic mobility data into zeta potential. Each reported result is the average of 5 replicate runs.

4.3 Results and Discussion

4.3.1 Zeta potential in solution

Although in previous work the primary effect of the large negative charge imparted by polymer adsorption onto the particle surface was to cause electrostatic repulsion between the particles and the negatively charged collector grains, we are now considering the use of the same polymers for controlled aggregation. Ditsch suggests that, a significant surface charge as well as excess polymer in solution could hinder aggregation. To investigate the surface charge of RNIP when combined with polymer additives, electrophoretic mobility measurements were taken for a variety of samples. RNIP (Toda) (5mg/mL massed) was combined with several different polymer additives (2 mg/mL) as described earlier. The solutions were either analyzed following dilution with water, or the particles were isolated by centrifugation, rinsed and resuspended in water prior to analysis. The samples are labeled in Table 4.1 as unwashed or washed, respectively. Electrophoretic mobility was measured and zeta potential values were calculated using the Smoluchowski equation.
Table 4.1. Zeta potentials calculated from electrophoretic mobility measurements of RNIP (Toda) samples (5mg/mL) mixed with polymer (2mg/mL). Measurements were taken two ways: samples suspended in solution with polymer or rinsed to remove unbound polyelectrolyte.

Table 4.1 shows that for each sample measured, PAA_{short}, PSS, and PEI, the magnitude of the zeta potential decreased significantly upon washing the particles. This is evidence that the adsorption of charged polymers onto RNIP is reversible. When the excess, unbound polyelectrolyte is rinsed away, the electrophoretic mobility and therefore the absolute value of the zeta potential are decreased. Also of note, all of the above samples were negatively charged except PEI. This cationic polymer will be used in the next section in combination with a longer chain anionic polymer, PAA.

### 4.3.2 Cationic – Anionic polymer mixture compared to Anionic mixture
Transport studies were carried out to investigate the effects of polyelectrolyte additives on mobility through sand packed columns, similar to experiments discussed earlier (Chapters 2 and 3). The images in Figure 4.1 display two different samples. On the left, an RNIP dispersion was mixed with a solution of cationic PEI with the intention of aggregating the nanosized particles into clusters. This was followed by mixing with PAA to give the clusters an overall negative charge, to promote the formation of suspensions in water and transport though sand packed columns. On the right of the

**Figure 4.1.** In each of these three comparisons, RNIP particles mixed first with PEI, then with PAA_{long} are shown on the left side and on the right are RNIP particles mixed with PAA_{short}. a) particle suspensions in water, b) SEM images of particle clusters dried on gold coated glass slides, c) transport columns and elution.
images, an RNIP dispersion was mixed just with PAA. Figure 4.1 compares the two samples. In a), both samples appear to suspend well and look very similar. Figure 4.1 b) shows SEM images of both samples. The samples differ in that the RNIP/PEI-PAA on the left appears to be inconsistent in size shape and overall organization. The RNIP/PAA image on the right is polydisperse in size, but the aggregates are more consistently shaped, although the effects of drying the sample during SEM preparation are unclear. Therefore, transport studies were conducted to compare the mobility of the two samples in sand packed columns. In c) we clearly see that the RNIP/PEI-PAA sample is retained by the column, and the elution does not contain any detectable amount of iron upon phenanthroline complexation method (Table 4.3). The RNIP/PAA sample on the right transports very well through the column and achieves over 80% by mass elution, upon comparing the iron concentration in the stock and eluted solutions. Later, we look at the elution and sedimentation characteristics of more concentrated RNIP/PAA samples.

4.3.3 Microscopy of particles and aggregates

The SEM image of RNIP/PAA in Figure 4.1b suggests that the particles are significantly larger than 1µm in diameter. Chapters 2 and 3 predicted the ideal particle diameter for transport through the sand packed columns to be in the 0.5 and 1.5 micrometer size range. The SEM may be unable to fully cover the size range of interest, therefore TEM images of RNIP/PAA particles were taken to examine a smaller size regime, see representative images in Figure 4.2. TEM images suggest that the sample consists of aggregates of approximately 2µm or smaller. Theses aggregates are not shown in the SEM, whereas, aggregates larger than about 2 µm were not seen in any
TEM images. Although dilute solutions were used, it is unclear what effects drying may have had on these samples, such as drying-induced aggregation. Therefore, SEM and TEM imaging may not be able to clearly describe the size range of particles and aggregates for our samples.

Figure 4.2. TEM images of RNIP/PAA particles on formvar coated copper grids.

4.3.4 Sedimentation using UV-Visible spectroscopy

The aggregation and sedimentation of RNIP and CIP-HQ samples were studied by monitoring the sedimentation of particle dispersions as a function of time. \(^{15, 31}\) Three RNIP particle concentrations were studied (250 mg/L, 500 mg/L and 1000 mg/L), as were two concentrations of RNIP/PAA and RNIP/PSS mixtures (250 mg/L and 500 mg/L). Absorbance measurements were taken at 508 nm for 1 hour through a 4.5 cm x 1 cm x 1 cm cuvette, 1.5 cm from the bottom of the sample. The initial absorbance measurement at 508 nm for each sample of known concentration was used for a calibration of absorbance vs. concentration. This relationship was then used to plot \(C/C_0\) (or \(C_t/C_0\)), where the initial concentration is \(C_0\), and \(C_t\) is the concentration at a given time, \(t\). Sedimentation data, plotted in the form \(C/C_0\) (or \(C_t/C_0\)) vs. time in seconds is shown in Figure 4.3.
Each sedimentation curve in Figure 4.3 was divided into three sedimentation regions (Table 4.2): aggregation I, sedimentation II, and sedimentation III. By visual inspection of the curves in Figure 4.3, divisions were chosen as indicated by changes in the slope of the log \((C/C_0) vs.\) time curve. The time range selected for each division is listed in Figure 4.3. Using RNIP without any transport additives, Phenrat et al. suggest that the first regime (aggregation I) represents the aggregation of iron particles into discrete micrometer-sized aggregates. Here the particles begin to aggregate and start to form chains but remain suspended, so the sedimentation rate is low. In the second regime (sedimentation II), the aggregates grow, and sedimentation becomes rapid due to chain formation and gelation of micrometer sized aggregates. The sedimentation slows at the end of stage II where particles and smaller aggregates that did not form large chain-like clusters slowly sediment from solution, sedimentation region III.

Figure 4.3 shows the individual regions for each curve as well as exponential fits for each region. Equation 4.1 describes the time dependent concentration and is used to monitor the concentration of particles suspended with respect to time. Using Equation 4.1, the characteristic time in seconds, \(\tau\), was determined by taking the inverse of the exponent of each fit.
Figure 4.3. Sedimentation of RNIP particles with and without anionic polymer additives. Exponential fits are drawn to indicate sedimentation regions of polymer modified samples.

\[ C(t) = C_0 e^{-t/\tau} \] (4.1)

\[ \tau = \frac{9\eta(\beta - p_i)}{2g^2(\rho_s - \rho_i)^2R_H^2} \] (4.2)

\[ \beta = 5 \times 10^9(R_{11}) - 1.5 \times 10^3 \] (4.3)

Calculated values of the characteristic time (\( \tau \)) are included in Table 4.2, as are the R² of each fit. Equation 4.2 shows the relationship between \( \tau \), \( \beta \), and \( R_H \), where \( \beta \), in units of
kg/m·s², is a function of pressure and is dependent on the permeability of the fractal aggregates and $R_H$ is the hydrodynamic radius of an aggregate in meters. The pressure of the fluid, $p_f$ (294 kg/m·s²) is a product of the solution density (1000 kg/m³), the height of the fluid in the cuvette above the point where the beam of light shines through (0.03 m), and the acceleration due to gravity (9.8 m/s²). In Equation 4.2, $\eta$ is the fluid viscosity (0.001 kg/m·s), $\rho_s$ is the density of the solid (6150 kg/m³), and $\rho_l$ is the density of the liquid (1000 kg/m³).

In this work, estimations for the hydrodynamic radius ($R_H$) for the fractal aggregates were calculated based on a fit to the data presented in Reference 15. Here, Phenrat et al. use dynamic light scattering (DLS) to measure $R_H$ for low particle concentrations. For higher concentration iron mixtures, where DLS is unable to accurately measure $R_H$ values due to multiple scattering, $R_H$ values are estimated from the sedimentation curves using the empirically derived constants in Equation 4.3 to express $\beta$ as a function of $R_H$ for iron nanoparticles.

In Table 4.2, $\tau$ increases as estimated $R_H$ decreases. This agrees well with earlier predictions that sedimentation regions having high $\tau$ indicate that smaller particles or aggregates settle more slowly. Regions with low $\tau$ represent more the more rapid sedimentation of larger aggregates or chains. Upon comparing the sedimentation of RNIP with that of RNIP mixed with anionic polymer, several differences are apparent. At 500 mg/L and 250 mg/L, unmodified RNIP follows the predictions of Phenrat et al., which suggest that the second sedimentation region has a lower $\tau$, indicating that large aggregates and chains are sedimenting during this time frame.
Table 4.2. Summary of fitting parameters for the determination of estimated $R_H$ for concentrated dispersions of RNIP. Three concentrations of RNIP and two concentrations of RNIP/PAA and RNIP/PSS are included.

<table>
<thead>
<tr>
<th>[RNIP] (mg/L)</th>
<th>Sedimentation Region</th>
<th>Time Range (sec)</th>
<th>$\tau$</th>
<th>$R^2$</th>
<th>Estimated $R_H$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RNIP - No Polymer</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>I</td>
<td>0-120</td>
<td>400</td>
<td>0.914</td>
<td>21.7</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>150-660</td>
<td>420</td>
<td>0.962</td>
<td>20.6</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>1050-3600</td>
<td>20000</td>
<td>0.810</td>
<td>0.1</td>
</tr>
<tr>
<td>500</td>
<td>I</td>
<td>0-390</td>
<td>1700</td>
<td>0.994</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>420-1080</td>
<td>1100</td>
<td>0.991</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>1260-3600</td>
<td>20000</td>
<td>0.860</td>
<td>0.1</td>
</tr>
<tr>
<td>250</td>
<td>I</td>
<td>0-750</td>
<td>5000</td>
<td>0.984</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>780-1860</td>
<td>3300</td>
<td>0.985</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>1890-3600</td>
<td>10000</td>
<td>0.950</td>
<td>0.3</td>
</tr>
<tr>
<td><strong>RNIP with Polymer</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>RNIP/PAA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>I</td>
<td>0-330</td>
<td>1250</td>
<td>0.989</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>420-710</td>
<td>2000</td>
<td>0.946</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>2190-3600</td>
<td>20000</td>
<td>0.962</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>RNIP/PSS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>I</td>
<td>0-330</td>
<td>1700</td>
<td>0.988</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>420-1860</td>
<td>2500</td>
<td>0.957</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>2190-3600</td>
<td>20000</td>
<td>0.978</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>RNIP/PAA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>I</td>
<td>0-420</td>
<td>3300</td>
<td>0.987</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>630-2010</td>
<td>5000</td>
<td>0.911</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>2280-3600</td>
<td>20000</td>
<td>0.949</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>RNIP/PSS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>I</td>
<td>0-540</td>
<td>5000</td>
<td>0.996</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>660-2010</td>
<td>5000</td>
<td>0.975</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>2280-3600</td>
<td>20000</td>
<td>0.966</td>
<td>0.1</td>
</tr>
</tbody>
</table>

However, this is not the case for the higher concentration of 1000 mg/L. This is likely due to earlier aggregation in a more concentrated sample. For the RNIP/polymer samples, $\tau$ increases from region I to II to III in almost every sample. This is indicative of a change in aggregation behavior, compared to unmodified RNIP. In the
RNIP/polymer samples, larger aggregates fall first, followed by medium sized aggregates and finally smaller aggregates. High levels of aggregation, such as the formation of large chains and the gelation of the aggregates is not shown in these results.

The data also suggest that larger particles fall out of solution first, followed by medium size and finally smaller particles. These curves also show that at higher initial particle concentrations, aggregation is more rapid and the stages occur earlier. This is of interest, because higher iron concentrations are used for field studies (3-30mg/mL)\(^2\). These results also suggest that either polymer, when used with low RNIP concentrations (250 mg/L), prevents the formation of large aggregates (>3µm) that would be efficiently intercepted in sand columns.

4.3.5 **Transport studies using more concentrated RNIP/polymer mixtures**

Prior to studying sedimentation, more concentrated iron mixtures (RNIP/PAA and RNIP/PSS), were passed through sand-packed columns to compare the transport capabilities of each sample. Higher iron concentrations were used to more closely compare to concentration ranges used for injection in soil (3-30 g/L)\(^2\). For these studies, one aliquot of RNIP suspension was mixed into a solution of PAA and another aliquot was mixed into a solution of PSS. The resulting solutions consisted of 2.7 mg/mL RNIP and 1 mg/mL polymer. As was described earlier, the solutions were passed through sand packed columns at a flow rate of 10 mL/min (0.084 cm/s) and the elution was collected upon exiting the column. The concentration of iron in the initial solution was compared to the iron concentration in the elution via phenanthroline complexation. Results of this study (Table 4.3) show that RNIP/PAA attained better elution than the RNIP/PSS sample.
However, when the less concentrated RNIP/PAA sample was passed through the columns, a higher percentage of iron eluted than the more concentrated RNIP/PAA. Both RNIP/PAA samples and the RNIP/PSS sample are an improvement upon unmodified RNIP, which has poor elution by itself.

4.3.6 Particle aggregation viewed with microscopy

In an effort to further investigate the aggregation and sedimentation of some of these samples, unmodified RNIP, Figure 4.4 (a), RNIP modified with PAA_{short} (b), and unmodified CIP-HQ (c) were mixed in water as described earlier and the samples filled thin glass capillaries. Using optical microscopy, 45 minute videos captured the aggregation and individual images taken from the videos are shown in Figure 4.4, with time increasing from left to right, and the scalebar equal to 10 \( \mu \)m. The videos show that all three samples aggregate over time; however, the CIP aggregates the least. This is expected, because larger iron particles are less prone to aggregate than small, nanometer sized iron particles.

Table 4.3. Transport of RNIP suspensions through 26 cm sand packed columns. The fluid flow rate was set to 10 mL/min, 0.084 cm/s for each column.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Iron Concentration Stock (g/L)</th>
<th>Iron Eluted % by mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>RNIP/PEI-PAA</td>
<td>0.40</td>
<td>below limit</td>
</tr>
<tr>
<td>RNIP/PAA</td>
<td>0.40</td>
<td>83.0</td>
</tr>
<tr>
<td>RNIP/PAA</td>
<td>2.7</td>
<td>47.3</td>
</tr>
<tr>
<td>RNIP/PSS</td>
<td>2.7</td>
<td>20.6</td>
</tr>
</tbody>
</table>
Figure 4.4. Optical microscope is used to capture approximately 45 minutes of particle aggregation video for a) unmodified RNIP, b) RNIP modified with PAA, and c) unmodified CIP-HQ in water, time increasing left to right. Scalebar is 10 µm.

4.4 Conclusions

In previous chapters, we discuss the addition of anionic support materials to increase the negative surface charge on the iron particles, with the intention of minimizing aggregation, and to enhance the effective negative charge on the soil grains for blocking and macromolecular crowding mechanisms to aid delivery. Here we
discussed the aggregation of iron particles and our attempt to control aggregation in order to form reactive nanoiron clusters in the low micron size regime. Sedimentation studies show that the iron particle concentration plays as significant a role in aggregation as do anionic polymer additives. When samples of similar iron particle concentration were compared by sedimentation, resulting estimated hydrodynamic radii indicated that the gelation and formation of chains of aggregates commonly seen in region II, is much less prevalent in samples with anionic support materials. This is expected to aid in particle transport and subsurface mobility. Transport studies agreed with these predictions, and the polymer modified samples showed moderate success when passed through sand-packed columns. Aggregation videos suggest that the particles aggregate with or without the polymeric additives. Further studies are needed to thoroughly investigate the controlled clustering of RNIP as well as the aggregation of these particles in solution.

4.5 Future work

Although improved transport was achieved, to further optimize and thoroughly investigate this system, some additional work must be done. It would be exceptionally helpful to compare the overall particle size distributions of each of the aggregate suspensions. From our findings, TEM measurements tend to exclude larger, micron size particles and SEM is unable to clearly image nanometer size particles; therefore the distributions provided by each method do not agree. A technique capable of measuring particle from 10 nm to 10 µm would make a comparison of the distributions of particle diameters in each sample. Dynamic light scattering (DLS) may be able to provide particle diameter distributions covering this range. Our previous attempts to utilize this
instrument were unsuccessful, most likely due to high concentrations, the lack of dispersants in the samples we analyzed, and inexperience using the instrument. Based on more recent literature,\textsuperscript{15} it may be possible to successfully use DLS to determine the particle distributions in our suspensions. This would be extremely helpful to quantitatively determine the sticking coefficients of the suspensions from our transport studies. We are unable to accurately calculate the sticking coefficient ($\alpha$) without particle diameter, see Appendix A.

The reactivity of each of these particle suspensions should be investigated for TCE dechlorination. Nurmi mentions that dehalogenation kinetics will likely change upon aggregation of nanometer size particles.\textsuperscript{14} Kinetic dehalogenation studies could be carried out using the purge-and-trap gas chromatograph system described in Chapter 2. It is imperative that the clusters not only achieve successful transport through packed media, but are also highly reactive. Although the CIP samples used in Chapter 3 showed improved mobility, their low surface area limits their dehalogenation ability. We hypothesize that high surface area clusters will have faster dehalogenation kinetics than CIP samples. On a related note, measuring the surface area of the particle clusters would enable surface area normalized rate constants to be calculated and compared to those in literature.\textsuperscript{6, 11, 14, 22, 34, 35}

Measuring iron elution as a function of particle concentration for RNIP/PAA would be helpful in further optimizing iron transport in the subsurface. The effects of particle concentration shown above suggest that lower particle concentrations may be more effectively transported than higher concentrations, due to aggregation effects. It
may also be useful to know how aggregation and transport properties of mixtures change over time, as older samples may have different mobility than newer samples.

4.6 References


Chapter 5
Conclusions

5.1 Summary

This work has focused on designing iron particles for the in-situ remediation of soil and groundwater contaminated by chlorinated hydrocarbons, such as TCE. In particular, the studies discussed here address the size, shape, and surface charge of various iron particles and the incorporation of polymeric “delivery vehicles.”

Anionic, hydrophilic carbon (Fe/C) and poly(acrylic acid)-supported (Fe/PAA) zerovalent iron nanoparticles were studied as a reactive material for the dehalogenation of chlorinated hydrocarbons in groundwater and soils. The transport of Fe/C nanoparticles was studied by elution through columns packed with model soils from different regions of the USDA soil textural triangle, and was compared to that of unsupported Fe nanoparticles. The Fe/C and Fe/PAA particles form colloidal suspensions in water, and their anionic surface charge facilitates transport through soil- and sand-packed columns.

Elution lengths from column breakthrough studies were compared with calculations based on the Tufenkji-Elimelech (TE) model. It can be concluded from this comparison that nanoparticle diffusion is the dominant filtration mechanism, and that Fe/PAA and Fe/C particles have sticking coefficients on the order of 0.36 and $\alpha=0.07$, respectively, in sand and 0.05 and $\alpha=0.01$, respectively, in clay-rich Chagrin soil. In contrast,
unsupported Fe nanoparticles rapidly agglomerate in water and are efficiently filtered by all of the soils tested, except for the clay-rich soil in which clay platelets may also act as an anionic support material. Trichloroethylene reduction by Pd-catalyzed Fe/C is rapid, and the reaction is unchanged by elution of a suspension of the material through a sand column.

Sand-packed columns were used to study the transport of micro- and nano-iron particle suspensions modified with anionic polyelectrolytes. Microscale carbonyl iron powders (CIP) were combined with PAA, and the profiles of initial and eluted particle diameters were compared with simulations based on classical filtration theory (CFT), using both the Tufenkji-Elimelech (TE) and Rajagopalan-Tien (RT) models. With particle size distributions that peaked in the sub-micron range, there was reasonable agreement between both models and the eluted distributions. With distributions that peaked in the 1.5 µm range, however, the eluted distributions were narrower and shifted to smaller particle size than predicted by CFT. Apparent sticking coefficients depended on column length and flow rate, and the profile of retained iron in the columns did not follow the log-linear form expected from CFT. These observations could be rationalized in terms of the secondary energy minimum model proposed by Tufenkji and Elimelech.

For micro-iron, sticking coefficients correlated well with particle zeta potentials and polyacrylate (PAA) concentration. With nanoscale iron particles, there was no apparent correlation between filtration length and total electrolyte concentration. However, mixtures of PAA with poly(4-styrenesulfonate) (PSS) and bentonite clay significantly enhanced nano-iron transport, possibly by affecting the aggregation of the particles.
Further investigation into the aggregation of RNIP was carried out through sedimentation studies, in addition to microscopy and transport experiments. As was predicted, unmodified RNIP, especially at high concentration, undergo aggregation to the extent of chain formation and gelation. This was shown in sedimentation results as well as optical microscopy videos. However, when an anionic polymer, such as PAA or PSS are mixed into the RNIP dispersions, the samples do not aggregate as rapidly or to such a high degree. Transport studies compared the two modified suspensions and determined that RNIP/PAA has greater mobility through sand-packed columns than RNIP/PSS, though both were an improvement over unmodified RNIP.

5.2 Remediation Field Study Collaboration

Several remediation technologies were considered when planning the full-scale subsurface remediation of an industrial site in Hamilton Township, New Jersey that had been used for the disposal of broken utility poles, construction and demolition debris and a variety of other wastes. The results of a cost analysis for this case study found that pump and treat would require about $4,160,000, and a permeable reactive barrier of zerovalent iron filings would cost approximately $2,200,000. However, according to PARS Environmental, Inc., based in Robbinsville, NJ, zerovalent nanoiron injection could remediate the site for only $250,000.\(^1\) In collaboration with PARS, our iron remediation delivery technology has been used to dehalogenate several contaminated pilot and test sites in New Jersey. Based on the results of the bench-top studies conducted in our laboratory and several pilot sites, reactive nanosized zerovalent iron
particles modified with anionic polymers and hydrocolloids were chosen for the full scale remediation of this site.

Prior to the injection, the site geology was carefully mapped to determine the depths of the unsaturated (vadose) and saturated zones making up the subsurface. The Perched Water level ranged from 2-8 feet below ground surface (bgs) and the water table aquifer depth ranged from 21-24 feet bgs. A series of monitoring wells were put in place to determine the types and quantities of contaminants present across the site. Initial findings confirmed that 1,1-dichloroethane (1,1-DCA), 1,1-dichloroethene (1,1-DCE), 1,1,1-trichloroethane (1,1,1-TCA), 1,2-dichloroethane (1,1-DCA), and trichloroethylene (TCE) were present at total chlorinated VOC levels as high as 1,600 ppb. The highest concentrations covered approximately one-half acre of land. The pH in the Perched Water area was very low (<4). Measurements of Oxidation Reduction Potential, pH, Conductivity, Turbidity, Temperature, and Dissolved Oxygen were made in each monitoring well to determine initial conditions and to evaluate the effectiveness of the nanoiron injection.

In large drums, RNIP (reactive nano-iron particles from Toda America) was mixed with a tested anionic polymer additive in water. The suspension was directly injected with low pressure (<20 psi) into the ground in a grid pattern across the one-half acre hot spot where contaminant levels were measured to be the highest. The suspension concentrations varied from 3 – 30 g/L and were injected at depths of 8 – 12 feet bgs.

Over the course of two injection phases, over 4500 pounds of iron particles modified with a mixture of anionic polymers and hydrocolloids was injected into the contaminated zone. During Phase I, 3,000 pounds of our particle mixture was injected
throughout the treatment area over a 20 day period. For Phase II, a total 1,500 pounds of material was injected over 10 days.\textsuperscript{1}

The results of this study suggest that the modified nanoiron had the transport and reactivity capabilities necessary to significantly decrease the total volatile organic compound (VOC) levels through hydrodehalogenation without the production of toxic intermediates or products.\textsuperscript{1}

5.3 Conclusions

In our effort to tailor reactive zerovalent iron particles into a new environmental remediation technology, we have investigated several critical aspects. To tailor reactivity, we see that the particle size is directly related to the surface area and that reactivity can be further enhanced by an additional catalytic metal, even at low levels. We have shown that the mobility of iron particles though sand packed columns can be dramatically improved with the incorporation of soluble anionic additives. Several anionic materials (organic polymers, sulfonated carbons, clays) have been shown to limit particle-particle as well as particle-collector interactions so that iron particle suspensions can be passed through saturated packed media.

In our studies of several types of iron particles, some synthesized and some available commercially, we find that although RNIP is a good material for use in practical environmental remediation applications, due to practical aspects of cost and large scale availability, it is a difficult material to use in controlled scientific experiments. The material contains particles with a distribution of sizes, shapes, iron content, and
degree of oxidation. Carbonyl iron powders are also inexpensive and readily available in large quantities, and the particle diameter (1-2 µm) is nearly ideal for transport. However, CIP’s are far less reactive for the reductive dehalogenation of chlorinated contaminants, likely due to their low surface area and oxidized surface. Although future endeavors may improve on these iron particle compositions and provide better tailored reactive particles, this work has already impacted the environment in a few areas, and continues to be utilized in injection sites.

5.4 Future Directions

The incorporation of biodegradable polymers is also of great interest in our group, as the use of these polymers would minimize the addition of long lasting materials in the environment. Although the transport additives we used in this work are considered safe for the environment and are commonly used in everyday products, for example, poly(acrylic acid) PAA is non-toxic and is commonly used in laundry detergents and even in disposable diapers, however, it is not biodegradable, as would be preferred for environmental remediation use. Ideally, we would like to develop an alternative delivery method using biodegradable polymers, such as alginate or cellulose derivatives. This approach may assist in the incorporation of helpful bacteria or enzymatic additives into the particle suspension mixture. By recruiting microbes, contaminant site remediation could address a broader range of contaminants, including those that are unreactive with nanoscale iron particles.
As was mentioned in Chapter 4, dynamic light scattering (DLS), a technique used to determine particle size, may provide particle diameter distributions in either powder or solution form. This would be helpful in studying the overall distribution of particle size in our suspensions. Although TEM and SEM provide high resolution images of the particles used in these studies, drying-induced aggregation occurs and so these techniques cannot be used to measure the sizes of particle aggregates in the suspensions we have studied. A technique capable of measuring particle aggregate diameters from 100 nm to 10 µm in both initial and eluted suspensions would allow us to understand in more detail the relationship between particle aggregation and transport.

5.5 References

Appendix A

Calculation of Sticking Coefficients

Sticking coefficients (\(\alpha\)) and elution predictions were calculated based on theories developed by Rajagopalan - Tien and Tufenkji - Elimelech. By using an excel spreadsheet shown below, the experimental transport results of iron particles passing through sand packed columns were utilized to develop a comparison between the two theories. As was described earlier, the RT filtration theories neglect to consider the effects of interparticle interactions and van der Waals forces for very small particles; those which are controlled by Brownian diffusion forces. This is of particular importance when nanometer sized iron particles are used, but is also pertinent for larger sized samples, such as the CIP iron and iron particle aggregates.

Several factors must be considered in order to properly determine the sticking coefficient for a given system. The parameters used are described herein. The Hamaker constant (A) for iron particles is \(1.00 \times 10^{-13}\) erg. The Darcy flow velocity (U) is set for each experiment and ranges from 0.042 to 0.152 cm/s. The percent of iron eluted from the column was determined experimentally by measuring the difference in iron concentration between the stock and eluted solutions; this is further described in Chapters 2 and 3. The column length (L) is measured from the top of the packing material to the top of the glass wool plug. Soil porosity (\(\Theta\)) is determined using the mass of the column before and after packing along with the volume of the packing material. The porosity of a column packed with 40 mesh sand was determined to be 42%. The collector diameter
(d_c) is a measured average using an optical microscope. For 40 mesh Ottawa sand, the collector grain diameter was determined to be 162 ± 45 µm. Particle diameter (d_p), or in this case, particle size distribution, was measured using SEM imaging. The particle size distributions for CIP samples, for example, are shown in Figure 3.2. Iron particle density (ρ) was set at 7 g/cm³, determined for a particle consisting of iron and iron oxide.

From these spreadsheet calculations, we determine the predicted elution of the stock sample and the sticking coefficient for both TE and RT transport models. The results of these calculations are further discussed in Chapter 3. A portion of the spreadsheet is shown below. This example is set-up to determine the TE and RT sticking coefficients (Alpha) for CIP-OM.

<table>
<thead>
<tr>
<th>soil porosity</th>
<th>gamma</th>
<th>gamma^5</th>
<th>gamma^6</th>
<th>As</th>
<th>As^1/3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.42</td>
<td>0.833956606</td>
<td>0.403382697</td>
<td>0.336403665</td>
<td>33.63977575</td>
<td>3.227751827</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Darcy vel (cm/s)</th>
<th>Column length (cm)</th>
<th>grain size (um)</th>
<th>grain density</th>
<th>Hamaker constant (erg)</th>
<th>bH</th>
<th>bH^1/3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.084</td>
<td>51.7</td>
<td>162</td>
<td>7</td>
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VITA

Bianca Will Hydutsky

Education
Ph.D., Chemistry – May 2007
Pennsylvania State University, University Park, PA
B.S., Chemistry – ACS accredited – May 2000
Millersville University, Millersville, PA

Professional Experience
2001-present Doctoral Research for Professor Thomas E. Mallouk
Pennsylvania State University, University Park, PA
2003-2004 Scientific Consultant - Environmental Chemistry
PARS Environmental, Inc., Robbinsville, NJ
2000-2003 Supervising Teaching Assistant and Teaching Assistant
Pennsylvania State University, University Park, PA
2000-2001 Mass Spectrometry Laboratory Technician and Researcher
Pennsylvania State University, University Park, PA
1998-2000 Senior Laboratory Technician
Lancaster Laboratories, Inc., Lancaster, PA

Presentations

Publications and Patents