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Polyacrylic Acids for Enhanced Transport of Nanoscale Zero-Valent Iron Particles

May 2007

Polyacrylic Acids for Enhanced Transport of

Nanoscale Zero-Valent Iron Particles

By

Pijit Jiemvarangkul

A Thesis

Presented to the Graduate and Research Committee

Of Lehigh University

In Candidacy for the Degree of

Master of Science

in

Civil and Environmental Engineering

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May 2007

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ABSTRACT

Nanoscale Zero-valent iron (nZVI) has been studied at Lehigh University since 1996. In recent years, nZVI, has increasingly been utilized in groundwater and hazardous waste treatment because of its large specific surface, high reductive reactivity and potential mobility in the subsurface envrionment. However, several recent researches report rapid aggregatation and settling of nZVI in ground water. Several methods have been proposed and tested to improve the nZVI mobility. A common approach is electro-steric stabilization of the nanoparticles. Poly (acrylic acid) or PAA, a frequently used polymeric stabilizer, is evaluated in this work for enhanced nZVI dispersion and transport.

Batch experiments suggest that PAA increases the amount of nZVI in suspension. However, excessive PAA reverses the dispersion and results in aggregation of iron nanoparticles. From sand column experiments, our results demonstrate that PAA enhances of the transport of iron nanoparticles in sand columns. Mass of iron in the column effluent increased from 0% with no PAA to 5 and 40.7% for solutions amended with 5% to 50% of PAA. Further flushing of columns with water and/or PAA solution can further increase the outflow of nZVI. Nonetheless, a substantial portion of the nZVI remained within the sand columns. In summary, this work does show the potential of PAA for enhanced nZVI transport. More work to optimize the experimental conditions and test other stabilizers are still needed.

CHAPTER 1

Introduction

Nanoscale Zero-valent iron particles (nZVI) with sizes between 1 and 100 nm diameters have been studied at Lehigh University since 1996. The colloidal iron nanoparticles have very higher specific surface areas (SSA), around 35 m²/g (Wang and Zhang 1997). In comparison granular iron has SSA less than 1 m²/g. The property of nZVI to rapid and completely reduce halogenated aliphatic compounds containing either one or two carbon atoms has been widely documented. (Zhang et al., 1998). In recent years, nZVI has increasingly been utilized in groundwater and hazardous waste treatment. Many laboratory studies have discovered that nZVI can effectively transform a variety of environmental contaminants such as chlorinated solvents, organochlorine pesticides, PCBs, organic dyes, and inorganic pollutants such as perchlorate, nitrate, and heavy metal ions (Li, Elliott, and Zhang 2006).

A potential advantage of iron nanoparticles is the potential of direct injection into subsurface for in situ treatment. In this manner, the excessive costs and engineering challenges associated with constructing iron walls in deep aquifers can be avoided. The feasibility of injection of iron nanoparticles into groundwater relies on the small size of the particles. A field test was conducted in New Jersey in 2000 and data from this work showed that over 90% of total chlorinated VOCs was reduced in a few days, concentrations of PCE, TCE, and DCE reached near or below the groundwater quality standards within six weeks with no VC detected. Iron nanoparticles remained reactive for more than 4-8 weeks. The radius of influence was around 20 – 60 feet in the subsurface (Elliott and Zhang, 2001). A common problem for using nZVI particles is their limited mobility in the subsurface environment. Iron particles have relatively high settling velocities because of their high density at 7,800 kg/m³ and very short settling distances in underground conditions. Moreover, groundwater in general has relatively high values of ionic strength, which reduces electrostatic repulsion between particles and increase of colloidal aggregation in water (Otterstedt and Brandreth 1998). Based on these reasons, nZVI has been observed to migrate only a few feet from the point of injection.

The objectives of this research include:

- 1. Enhancing the suspension and dispersion of nanoscale zero-valent iron particles by using poly Poly acrylic acid (PAA).
- Studying the transport of nanoscale zero-valent iron particles and stabilized nZVI with PAA through the packed-sand column.

CHAPTER 2

A Literature Review

2.1 Nano zero-valent iron (nZVI)

Zero-valent iron, ZVI, is an efficient electron donor in water:

$$Fe^0 \rightarrow Fe^{2+} + 2e^ E^0 = +0.447 V$$

Many environmental contaminants such as polychlorinated hydrocarbon and heavy metals can serve as the electron acceptors. For example, the dechlorination of chlorinated hydrocarbon solvents such as trichloroethene and tetrachloroethene serves as a good example (Matheson, and Tratnyek, 1994; Burris, Campbell, and Manoranjan, 1995; Orth, and Gillham, 1996).

$$RCI + H' + 2e' \rightarrow RH + CI'$$

ZVI has been used widely as a groundwater treatment remediation agent since early 1990s in the permeable reactive barrier (PRBs) systems (Reynolds, G.W., Hoff, J.T., and Gillham, R.W. 1990; Gu, B et al 1999). In 1996, nanoscale zero-valent iron particles (nZVI) with sizes less than 100 nm diameter were synthesized at Lehigh University. nZVI have much higher specific surface areas ($35 \text{ m}^2/\text{g}$) than the conventional granular iron or microiron particles, which have specific surface areas less than 1 m²/g (Wang and Zhang 1997). nZVI particle synthesis using the borohydride (BH₄⁻) reaction has been used in many laboratories (Wang and Zhang 1997; Zhang and Masciangioli 2003; Sun et al 2006). It is also feasible to produce ultrafine iron particles using mechanical attrition.

A major problem for using nZVI particles is their limited mobility in the subsurface environment. Iron particles have relatively high settling velocities because of their high density at 7,800 kg/m³ and very short settling distances in the underground conditions. Moreover, groundwater in general has relatively high values of ionic strength, which reduces electrostatic repulsion between particles and increases of colloidal aggregation in water (Otterstedt and Brandreth 1998). Based on these reasons, nZVI has been observed to migrate only a few feet from the point of injection.

2.2 Colloidal stability

Colloidal particles have size between 1 nm to 1,000 nm. A system containing colloidal particles is termed "stable" when it is slowly changing its state of dispersion. Unstable particle suspension leads to particles aggregation, coagulation, and sedimentation as results of attractive forces between particles. Several techniques have been developed to prepare colloidal suspension, mainly by creating or increasing repulsive force between particles via electrostatic, steric, and other physical/chemical interactions (Rosensweig, 1985; Everett, 1989; Morrison and Ross, 2002).

The theory commonly used in the description of the colloidal stability is the DLVO theory, which was developed by Derjaguin and Landau in 1941 in Russia and independently by Verwey and Overbeek in 1948 in Holland (Stumn and Morgan,

1996). According to the DLVO theory, the total energy of a suspension of fine particles can be described as:

$$V_{\rm T} = V_{\rm R} + V_{\rm A}$$

When V_T = the total energy of interactions between the particles

- V_R = the repulsive (electrostatic) potential energy
- V_A = the attractive (van der Waals) force

The potential energy curve (a plot of V_T versus distance H from the surface) is illustrated in Figure 2-1. Based upon the potential energy curve, stabilization of colloidal suspension is therefore related to the establishment of a energy barrier between particles that can prevent the collapse of the colloidal state. Two approaches have been commonly used in the preparation of colloidal suspensions: electrostatic repulsion and steric stabilization. Electrostatic repulsion is achieved by imparting or increasing the surface charge while steric stabilization is typically attained by the adsorption of long-chain organic molecules (e.g., surfactants). Large polymeric molecules also carry charges (e.g., polyelectrolytes), creating combined electro-steric repulsion and consequently enhancing colloidal stability.

2.3 Dispersion of nZVI

Colloidal iron nanoparticles have the potential to be a mobile remediation method (Wang and Zhang, 1997; Elliott and Zhang, 2001). Iron nanoparticles have been shown to be amenable to direct injection into the subsurface environment. However, stable iron suspension is needed for particle transport in groundwater because flocculation and aggregation between particles always occurs under the environmental conditions. Groundwater in general has relatively high values of ionic strength, which is favorable for the reduction of electrostatic repulsion between particles and increase of colloidal aggregation in water (Otterstedt and Brandreth 1998). With a density at 7,800 kg/m³, iron particles and aggregates have relatively high settling velocities. Furthermore, aquifers have very narrow channels for the flow of water and short settling distances for particle removal.



Figure 2-1. Potential energy curve (a plot of V_T versus distance H

from the surface)

CHAPTER 3

Materials and Methods

3.1 Synthesis of iron nanoparticles

nZVI particles were prepared by mixing equal volumes of 0.94 M NaBH₄ and 0.18 M FeCl₃, following the reaction:

$$4Fe^{3}(aq) + 3BH_4(aq) + 9H_2O \rightarrow 4Fe^{0}(s) + 3H_2BO_3(aq) + 12H^4(aq) + 6H_2(g)$$

The borohydride solution was slowly added into the ferric chloride with stirring speed at ~400 rpm. The iron nanoparticles were formed and harvested by using vacuum filtration through 0.2 μ m filter papers. The synthesized iron particles were washed several times with water and ethanol before use or stored.

3.2 Characterization of nZVI particles

Transmission Electron Microscopy (TEM): Images of iron nanoparticles were recorded with a Philips EM 400T TEM (Philips Electronics Co., Eindhoven, Netherlands) operated at 100 kV. The TEM samples were prepared by depositing two to three droplets of the nanoparticle suspension onto a Holey carbon film (Ernest Fullam Inc., Latham, NY), which was completely dried in a fume hood prior to the TEM analysis.

3.3 Analytical methods

Total Solids: Evaporation method was used to measure the solids content of a solution. A 43 mm small aluminum dish, used for measuring moisture content in soils

samples, was weighted and solution sample was poured into the aluminum foil cup and weighted. Then, the cup was put into an oven at 105°C for one day. The weight of dry sample cup was measured. The net weight difference represents the solid residue in the water sample.

Total Iron: Atomic absorption (AA) method was used to measure iron concentration in solution samples. Solution samples were taken to 100 mL volumetric flask and 50 mL solution of 2.4 N of HCl plus 0.27 N of HNO₃ were added into the sample flask. Next, the solution was mixed and leaved for 1 hour. DI water was then added to make up the solution to 100 mL. Then, the solution was diluted to the limits of AA instrument. Perkin Elmer AAnalyst 200 Atomic Absorption Spectrometer was in this work.

pH: Thermo Orion model 420 was used as pH meter for this research.

3.4 Nanoparticle suspension

Polymer iron nsnoparticles: Poly(acrylic acid), sodium salt (PAA) [9003-04-07], molecular formula $[CH_2CH(CO_2Na)]_n$, with MW~3,000 in 40% aqueous solution was used as the stabilizer for the iron nanoparticles. The structure of PAA is illustrated below.

$$\begin{pmatrix} 0 \\ C - CN_{B} \\ 1 \\ -CHCH_{2} - \end{pmatrix}_{T}$$

Suspension batch experiments: A 250 mL flask reactor with three open necks was set up for the nZVI suspension batch experiment as shown in Figure 3-1. The center

neck hosted a mechanical stirrer with a speed set at 500 rpm. 200 mL solution of nZVI particles was added with PAA, with concentrations at 10 g Fe/L and varied PAA. The solution was mixed for 2 hours at room temperature. Total solids, Fe and pH were measured after mixing and each solution sample was taken for TEM images. Afterward, the solution was put into 100 mL cylinders to observe its sedimentation for 180 minutes. After settling for 180 minutes, total solids, Fe in solution were measured again.

3.5 Nanoparticles transportation through sand column

Porous media: Standard Ottawa sand, designated as ASTM 20/30 (American Society for Testing and Materials), was used as the column porous material. The ASTM 20/30 sand is mainly composed of mineral quartz, whose main ingredient is silicon dioxide (SiO_2) (>99.8%). Its color is white, the specific density is 2.65 g/cm³, and the grain shape is closely rounded. The particle size of ASTM 20/30 is mainly in the range of 0.60-0.85 mm (Sun. dissertation 2006).

Column experiments: A 30 cm. length and 1 inch inner diameter was packed with sand media for nano ironparticles transport studies as shown in Figure 3-2. A few glass beads of 3 mm diameter were placed at two ends of the column to prevent the loss of the sand and distributing the flow. During the experiment, the column was set up vertically and sealed with screw caps at both ends. 200 mL solution of nZVI particles or various polymerized nano iron particles were pumped upward through the column. The flow rate was 10 mL/min. After pumping all the iron particle solution, 700 mL water was pumped into the column.



Figure 3-1. Schematic of batch experiment set up



Figure 3-2. Schematic of column experiment set up

CHAPTER 4

Results and Discussion

4.1 Suspension of nZVI

Batch experiments were conducted to assess dispersion or suspension of nZVI particles and polymerized nZVI. The 250 ml round-bottom flask reactor with three open necks was used as small reactor as shown in Figure 3-1. The center open neck was placed with a mechanical stirrer with tunable speeds. 200 mL solution of 10 g/L iron nanoparticles and PAA were mixed in the small reactor for 2 hours. Varied PAA amounts were added at 0%, 5%, 10%, 20%, 30%, 50% and 100% of the nZVI. Iron solutions were mixed at high speed ~ 500 rpm at room temperature. Afterward the solutions were taken to 100 ml cylinder to observe the settlement of iron particles for 180 minutes. Before settlement experiment, iron samples were taken to measure the mixed Fe concentration by AA method and to characterize by using TEM and pH of each mixed solution was detected. Total solids and Fe concentration in solutions after settling for 180 minutes were detected.

Figure 4-1 – 4-4 showed the TEM images of nZVI particles with 0%, 20%, 50% and 100% PAA respectively. At 0% PAA or pure iron nanoparticles, iron nanoparticles formed big clusters of spherical particles. A single sphere size was around 60-70 nm (Y.P.Sun dissertation 2006). In Figure 4-1 (0%PAA), the images also showed that most particles formed chain-like cluster shape. For 20% PAA (Figure 4-2), the images presented that iron nanoparticles formed several small groups and distributed well in solutions. However, when increasing %PAA in solution such

as 50% and 100% PAA in Figure 4-3 and 4-4., iron nanoparticles reformed the chainlike clusters.

Figure 4-5 shows solids % in solution after settling for 180 minutes. With 0% and 5% PAA, the solutions had low percent of solids at 0.05% and no color (very clear) as shown in Figure 4-6. Solids concentration in solution rapidly increased at 10% PAA at 0.25% of solids and continuously increased through 50% PAA at 0.55%. The slowly increasing of % solids was continuous to 100% PAA at 0.63% of solids.

Iron in solution after settling was shown in Figure 4-7 in term of C/Co when Co is the initial concentration of iron before settling. At no PAA and 5% PAA, very low Fe concentration nearly to nothing remained in the solution. Fe concentration rapidly increased to 0.13 (C/Co) or 13% in concentration of initial. The Fe concentrations increased to 0.144 (C/Co) at 20% PAA solution and were nearly constant around 0.14 - 0.16 from 20% PAA to 100% PAA.

pH of each solution is presented in Figure 4-8. The results shown that pH increased with higher PAA concentration in solution.

4.2 Transport of nZVI in porous media

A 30 cm. length and 1 inch inner diameter was packed with sand media for nano ironparticles movement testing as shown in Figure 3-2. In the experiment, the column was set up in vertical and sealed with screw caps at both ends. 200 mL of 10 g Fe L nZV1 particles or various Polymerized nano iron particles were pumped upward through the column by following 0, 5, 10 20, 30 and 50 mass percentage of PAA compared with iron mass. The flow rate of pumping was 10 mL/min. After pumping all iron particle solution, water was pumped into the column for observing the movement ability of particles. The effluent solution samples were taken at series times. Total solids and total iron concentration of the samples were measured.

Figure 4-9 showed the initial concentration of iron in mixed solution that was injected into the glass column. The expected iron concentration of mixed solutions was 10 g/L. However, the results presented the initial concentration of iron measured by AA method was around 6.47 - 8.95 g/L.

Solids passing through the column compared with pore volume were measured and the results were shown in Figure 4-10. At no PAA and 5% PAA, solids in effluent solution were low or nearly nothing coming out from the column over the experiment time. Increasing %PAA showed that more solids move though the column. More solids mass could pass though the column in higher %PAA. Most of solids came out at time around 2 - 7.5 pore volumes.

Total Fe of solution passing though the column was measured with the series of times as pore volume. The results were illustrated in Figure 4-11. For no PAA, the results showed that no iron came out from the column over the experiment time. All nZVI were retained in the sand media. At 5%PAA, the similar results with no PAA were presented. Very little concentration of Fe showed up around 4 - 7 pore volume. Higher % PAA in solution resulted in higher concentration of Fe passing though the column. At 10% and 20% of PAA, most of Fe arrived at 1 pore volume until 7.3 pore volume. Both showed the peak of Fe concentration at around 5 - 6 pore

volumes with 1.5 g Fe/L for 10% PAA and 1.8 g Fe/L for 20% PAA. The shapes of distribution curves looked similar to bell curve. For 30% and 50% PAA, the distribution curves illustrated two peak curves of Fe concentration. 30% PAA solution had two peaks at 5.2 and 8.3 pore volumes with 1.31 g Fe/L and 1.30 g Fe/L respectively. For 50% PAA solution, the peaks of distribution curve arrived at 5.2 and 8.3 pore volumes (similar time with 30% PAA curve) with 3.3 g Fe/L and 0.82 g Fe/L respectively.

Figure 4-12 presented the sand columns after injected nZVI and PAA-nZVI solutions for 60 minutes in three different % of PAA from 0%, 30% and 50%. At 0% PAA, all iron particles stuck at around 10 cm. from the injection end of the sand column and nothing came out event though water was pumped through the column. Pure iron particles were able to transport through the filter media just few inches. Adding PAA to nZVI solution helped improve iron particles mobility as shown in Figure 4-12 at 30% and 50% PAA. Iron particles at 30% and 50% PAA were distributed through out the column and eventually passed through the sand column. Nevertheless, some of particles still stuck in the column in 30% and 50% PAA as the gray color zone in columns (Figure 4-12).

Based upon the Fe concentration results of each % PAA solution, calculations of accumulative Fe mass in effluent displayed in percentage of Fe mass in effluent solution compared with the total Fe mass injected into the column were illustrated in Figure 4-13. From the calculation results, the higher % PAA added in solution, the higher iron came out from the column. At no PAA and 5% PAA, the accumulative curves showed very little percent of iron came out from the column. Figure 4-14 showed Fe staying in column and Fe coming out from column as mass percentage compared with total Fe injected into the column. Almost nZVI were stuck in the column at 0% PAA and 5% PAA solutions and %Fe coming out increased in 10% PAA to 17% and slowly raising to 19.4% at 20% PAA, then linearly increasing to 29% at 30%PAA and 40.7% for 50% PAA. Based upon these results, mass of iron coming out from the column directly relates to % of PAA mixed in the solution.

Polymers such as Poly(vinyl alcohaol-co-vinyl acetate-co-itaconic acid) (PV3A) and PAA were achieved to enhance nZVI mobility and dispersion. Work by Y. P. Sun at Lehigh University used PV3A as a dispersant generated nZVI with substantially better subsurface mobility potential (Y.P.Sun dissertation 2006). Mallouk and his group research at Penn State have confirmed that PAA binding to nZVI creating highly negative surfaces effectively reduces the filtration removal by aquifer materials (Schrick, B., et al 2004). Based upon this work, TEM images (Figure 4-1 to 4-4) showed the dispersion of nZVI particles when adding PAA; however after increasing % PAA, particles tended to form cluster again. On the other hand, the transport results confirmed that higher %PAA increased nZVI mass coming out from the sand column as shown in Figure 4-13. PAA creates highly negative surface charges that help nZVI transport through the sand filter (Schrick, B., et al 2004).

Based on work of Y. P. Sun, nZVI in high pH condition (> 8.5) have slightly negative surface changes, but bare iron particles were not able to be pumped through the column. Even though adding small amount of PAA still were not enough to make sufficient repulsive force to transport through the sand media. Increasing PAA enhances negative surface of nZVI and repulsive force between nZVI and sand particles (Y.P.Sun dissertation 2006). Therefore, more nZVI mass came out form the sand column as shown in Figure 4-13.

From Figure 4-13, at 30% PAA, nZVI mass that came out from the sand column increased rapidly and tended to increase with more % PAA. Therefore, the repulsive force formed by negative surface was more dominant than attractive force between iron particle and sand particles at 20% - 30% PAA in this work. Event though PAA can help nZVI increasing in mobility, from the results in Figure 4-14, most of iron mass still stuck in the sand column. Therefore, there may be other forces or factors such as mechanical force or gravity force that hold iron particles in the sand filter.

4.3 A conceptual model for nZVI transport

Based upon the DLVO theory discussed in chapter 2, there are two major forces related to the nZVI transport in porous media : repulsive force and attractive force. For the bare nano iron particles under high pH conditions (e.g., >8.5), iron particle surface has negative charges, which create repulsive force between particles and sand surface that has natural negative charges. However, the attractive (van der Waals) force still is dominant and makes filter media attractive to nZVI particles as shown in model A in Figure 4-15. After PAA is added to ntheZVI solution, the the negative surface charge increases substantially (Schrick, B., et al 2004). When the negative charge on surface of PAA-nZVI particles increase to the level that can produce enough repulsive force to overcome the attractive force, the nZVI particles are stabilized and can remain in solution for extended period of time as illustrated in model B in Figure 4-16.



ł



0% PAA

Figure 4-1. TEM images of 0% PAA iron nanoparticles





20% PAA

Figure 4-2. TEM images of 20% PAA iron nanoparticles

<u>p</u>



l

Figure 4-3. TEM images of 50% PAA iron nanoparticles

50% PAA



100% PAA

Figure 4-4. TEM images of 100% PAA iron nanoparticles



Solids in solution (%)

(



%PAA

Figure 4-6. nZVI solution after 180 minute sedimentation



Fe in solution

Figure 4-7. Fe concentrations in solution





Figure 4-8. pH of mixed solution





Figure 4-10. Solids in effluent



Figure 4-11. Fe concentration in effluent





% PAA 0 30 50

Figure 4-12. The sand columns after 60 minutes injected by nZVI at different % of PAA



Figure 4-13. Fe concentration accumulative % in effluent in different %PAA



Figure 4-14. Distribution of iron

ذن در



Figure 4-15. Bare iron nanoparticles in porous media



Figure 4-16. PAA stabilized iron nanoparticles in porous media

CHAPTER 5

Conclusion

Use of nZV1 in hazardous waste treatment especially in groundwater remediation is becoming increasingly popular in U.S. because of the high specific surface area and high reducing ability of nZV1. It has been widely used to degrade chlorinated hydrocarbons in groundwater. However, laboratory and field data suggest that its mobility under the groundwater conditions is limited. Several methods have been suggested to improve its mobility. Surface stabilization is one of those methods. This research was designed to assess one of polymers, Poly acrylic acid (PAA) that have been suggested to increase the transport efficiency of nZV1.

Based upon the observed experimental results, the following conclusions can be made:

- TEM images reveal that nZVI particles are stabilized by PAA in the range of 20 - 30 %. Lower % of PAA dose not promotes the dispersion, but at higher % of PAA, reverses the dispersion and result in rapid aggregation.
- The mass of iron that can transport through the sand column varies directly to % of PAA added into the solution.
- 3. Normally nZVI will increase solution pH. Event though in high pH condition nZVi particles have negative surface charges (Y.P.Sun dissertation 2006), those negative charges are not sufficient to produce repulsive force taking over

attractive force. This causes nZVI particles stick in the filter media as shown in modal A (Figure 4-15).

- 4. Addition of PAA increases negative charge on the surface of nZVI particles and help to improve the mobility of the particles. PAA-nZVi particles have high repulsive force that helps them passing through the filter media as shown in modal B (Figure 4-16).
- 5. Possibly, there are other factors such as magnetic forces, which hold the particles in the sand column.
- Preparation of PAA-nZVI solution by mixing nZVI and PAA can be succeeded to improve the nano iron particles and no need to control many condition such as pH and ORP. The solution can be prepared in an easy method.

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END OF TITLE