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Polyacrylic acids for enhanced transport of nanoscale zero-valent iron particles

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Jiemvarangkul, Pijit

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

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Of Lehigh University

In Candidacy for the Degree of

Master of Scicnce

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Civil and Environmcntal Enginccring

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This thesis is accepted and approved in partial fulfillment of the requirements for the Master of Science.

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Finally, I would like to thank my family in Thailand. They always give me love and support. That means a lot to me.

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ABSTRACT

Nanoscale Zero-valent iron (nZYI) has been studied at Lehigh University since 1996. In recent years, nZYI, 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 nZYI in ground water. Several methods have been proposed and tested to improve the nZYI 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 llushing 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 I 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 m^2/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 aI., 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, thc excessivc costs and engineering challcnges associated with constructing iron walls in decp aquifers can bc avoided. The feasibility of injection of iron nanoparticlcs into groundwater relics on the small size of the particles. A ficld test was conducted in Ncw Jersey in 2000 and data from this work showed that over 90% of total chlorinated VOCs was reduced in a few days. conccntrations of PCE. TCE. and DCE reached ncar or below thc groundwatcr quality standards within six wceks with no VC detectcd. 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:

- I. Enhancing the suspension and dispersion of nanoscale zero-valent iron particles by using poly Poly acrylic acid (PAA).
- 2. 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:

$$
Fe^{0} \to Fe^{2+} + 2e^{-} \qquad \qquad E^{0} = +0.447 \text{ V}
$$

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).

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

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 m²/g) than the conventional granular iron or microiron particles, which have specific surface areas less than $1 \text{ m}^2/\text{g}$ (Wang and Zhang 1997). nZVI particle synthesis using the borohydride (BH₄) reaction has been used in many laboratories (Wang and Zhang 1997; lhang 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** stabilit),

Colloidal particles have size betwecn I nm to 1,000 nm. A system containing colloidal particles is termed "stable" whcn it is slowly changing its state of dispersion. Unstable particle suspension leads to particles aggregation. coagulation. and sedimcntation 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 uscd in thc dcscription of the colloidal stability is thc DLVO thcory. which was devclopcd by Dcrjaguin and Landau in \941 in Russia and independently by Verwey and Overbeck in 1948 in Holland (Stumn and Morgan. 1996). According to the DLYO theory, the total energy of a suspension of fine particles can be described as:

$$
V_T = V_R + V_A
$$

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 moleculcs also carry charges (e.g.. polyelectrolytes). creating combined electro-steric repulsion and conscquently enhancing colloidal stability.

2.3 **Dispersion of nZVI**

Colloidal iron nanoparticles have the potential to be a mobile rcmcdiation method (Wang and Zhang. 1997: Elliott and Zhang. 200 I). Iron nanoparticlcs 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 cnvironmcntal conditions. Groundwater in general has relati\ely high \alues 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:

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

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 $0.2 \mu m$ 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 kY. The TEM samples were prepared by depositing two to three droplets of the nanoparticle suspension onto a Holcy carbon film (Erncst 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. Λ 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 I 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: Thcrmo Orion model 420 was used as pH mctcr 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 stabilizcr for the iron nanoparticlcs. Thc structure of PAA is illustrated below.

$$
\begin{array}{c}\n0 \\
1 \\
c - \infty \\
1 \\
(-\text{CH CH}_2 - \cdot) \\
\cdot\n\end{array}
$$

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 (SiO₂) (>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 I 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 placcd at two ends of the column to prevent the loss of thc sand and distributing the flow. During the experiment. the column was set up vertically and scaled with scrcw caps at both cnds. 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

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CHAPTER 4

Results and Discussion

4.1 Suspension of nZYI

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. Yaried PAA amounts were added at $0\%, 5\%, 10\%, 20\%, 30\%, 50\%$ and 100% of the nZVI. Iron solutions were mixed at high speed \sim 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 nanoparticlcs. 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 (O%PAA). thc imagcs 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 cach solution is prcscntcd in Figurc 4-8. Thc rcsults shown that pH incrcascd with highcr PAA conccntration 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 ironparticlcs movcmcnt tcsting as shown in Figurc 3-2. In thc cxpcrimcnt. thc column was set up in vertical and scaled with screw caps at both ends. 200 mL of 10 g Fc L nZVI particles or various Polymcrizcd nano iron particlcs wcre pumpcd 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 thc rcsults wcrc shown in Figure 4-10. At no PAA and 5% PAA. solids in cffluent solution were low or ncarly nothing coming out from the column over thc cxpcrimcnt time. Increasing %PAA showcd that more solids move though thc column. Morc solids mass could pass though thc column in highcr %PAA. Most of solids came out at time around $2 - 7.5$ pore volumes.

Total Fc of solution passing though thc column was mcasurcd with thc scrics of timcs as pore volumc. The rcsults wcrc illustratcd in Figurc 4-11. For no PAA. thc results showed that no iron came out from thc column ovcr thc cxpcrimcnt timc. All nZVI wcre rctaincd in thc sand mcdia. At 5%PAA. thc similar rcsults 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 Fell for 10% PAA and 1.8 g Fell 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 *Fell* and 0.82 g Fell 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 DLYO 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 negativc chargcs. which crcatc rcpulsive forcc bctwccn particlcs and sand surfacc that has natural ncgativc chargcs. Howcvcr. the attractivc (van dcr 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 ncgativc surfacc chargc incrcascs substantially (Schrick. B.. ct al 2004). Whcn thc 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.

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

0% PAA

20% PAA

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

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

50% PAA

100% PAA

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

 23

Solids in solution (%)

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 24

Figure 4-6. nZVI solution after 180 minute sedimentation

Fe in solution

Figure 4-7. Fe concentrations in solution

26

Figure 4-8. **pH** of mixed solution

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Figure 4-10. Solids in effluent

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0Jb PAA o **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

32

Figure 4-14. Distribution of iron

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Figure 4-15. Bare iron nanoparticles in porous media

CHAPTERS

Conclusion

Use of nZVI 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 $nZVI$. 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 nZVI.

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

- 1. 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.
- 2. The mass of iron that can transport through the sand column varies directly to ~~ ofPAA added into the solution.
- 3. Normally nZVI will increase solution pH. Eyent though in high pH condition nZVi particles hayc ncgatiyc surfacc chargcs (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.
- 6. 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