Effect of kaolinite, silica fines and pH on transport of polymer-modified zero valent iron nano-particles in heterogeneous porous media

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**Abstract**

Polymer coatings on nano-sized remediation agents and subsurface heterogeneity will affect their transport, likely in a pH-dependent manner. The effect of pH on the aggregation of polymer-coated nanoscale zerovalent iron (nZVI) and its deposition onto sand and clay (kaolinite) surfaces was studied. nZVI coatings included a high molecular weight (90 kg/mol) strong polyanion, poly(methacrylic acid)-b-(methacrylate)-b-(styrenesulfonate) (PMAA-PMMA-PSS) and a low molecular weight (2.5 kg/mol) weak polyanion, polyaspartate. Aggregation and deposition increased with decreasing pH for both polyelectrolytes. The extent was greater for the low MW polyaspartate coated nZVI. Enhanced deposition at lower pH was indicated because the elutability of polyaspartate-modified hematite (which did not aggregate) also decreased at lower pH. The greater deposition onto clay minerals compared to similar sized silica fines is attributed to charge heterogeneity on clay mineral surfaces, which is sensitive to pH. Heteroaggregation between kaolinite particles and nZVI over the pH range 6–8 confirmed this assertion. Excess unadsorbed polyelectrolyte in solution (100 mg/L) enhanced the transport of modified nZVI by minimizing aggregation and deposition onto sand and clay. These results indicate that site physical and chemical heterogeneity must be considered when designing an nZVI emplacement strategy.

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**1. Introduction**

Nano-scale zerovalent iron (nZVI) and other nanoscale remedial agents (e.g. hydrophobic polymer beads and nano-hydroxyapatite) have been proposed as groundwater remediation agents. The oxidation of the zero valent iron (Fe\(^0\)) is coupled with the reduction of chlorinated hydrocarbons to benign products or the reduction and immobilization of heavy metals. Their small size (5–70 nm) makes it possible to deliver these reactive materials [1–6] in situ directly to the contamination source [7–9]. However, the transport of nZVI in laboratory scale columns is limited by aggregation and by deposition onto porous media, even under ideal flow conditions in relatively homogeneous porous media [7,10,11]. Consistent with this finding, field applications with bimetallic Fe/Pd nano-particles [4,12,13] have indicated that it is indeed difficult to emplace the nano-particles in the subsurface.

Adsorbed anionic polyelectrolyte surface coatings enhance nZVI transport by providing repulsive electrosteric forces that hinder nZVI aggregation and deposition onto porous subsurface media which also usually has a net negative charge at near neutral pH, typical of most groundwater [10,14–17]. Still, varying pH and ionic conditions can limit the nZVI transport [16,18,19] by affecting the nZVI surface charge, which subsequently affects its aggregation and deposition to porous media. When subsurface media is physically or surface chemically heterogeneous, as when mixtures of larger and smaller sized particles co-exist or when clay minerals are present in interstitial spaces between larger grains, differential interactions with each subsurface component may determine the transport of nZVI. Fig. 1 illustrates the possible mechanisms by which pH and the presence of subsurface media of varying size, mineralogy, and charge heterogeneity can affect nZVI transport.

Both pH and the surface polyanion type can affect nZVI aggregation and transport. At pH < pH of the isoelectric point (pH\(_{\text{Iep}}\)) of nZVI, aggregation may result from a change in the conformation of the adsorbed polyanion layer as the underlying particle surface becomes positively charged (Fig. 1a). The charge and associated electrostatic repulsion of an adsorbed weak polyanion would be more sensitive to pH than a strong polyanion because the weak polyanion has a higher pKa [20–25]. Polyaspartate is a weak polyelectrolyte with a pKa near pH 3.5–5 [22]. Its maximum deprotonation occurs above pH 7 [23], so for pH < 7 the decreased
charge in the polyaspartate layer will contribute to aggregation because of the compression of electric double layer. Conversely, a strong polyelectrolyte such as PSS with a pKa near pH 2 should be less affected by low pH. Aggregation of nZVI to large enough aggregates can enhance deposition onto porous media due to increased gravitational settling or mechanical filtration through narrow pore throats [24,25].

Even in the absence of nZVI aggregation, low pH can also enhance nZVI deposition onto porous media with metal oxide surface impurities (e.g. Fe-oxides or Al-oxides) that have a relatively high isoelectric point (pH_{iep} = pH 7–9.5) [26–32] compared to silica (pH_{iep} 2–3) [28,33] or with clay minerals that can develop positively charged edge sites at low pH (Fig. 1b). Metal oxide impurities on mineral surfaces with relatively high pH_{iep} provide positively charged favorable deposition sites that limit nanoparticle transport through porous media at low pH. Even a small amount of hematite on quartz sand has been shown to increase colloid deposition by 2 or 3 orders of magnitude compared to clean quartz sand surfaces due to the positively charged hematite surface at neutral pH [29,31,33].

Deposition of negatively charged engineered nanomaterials onto positively charged clay minerals may decrease the transport of nanomaterials in the subsurface. Clay minerals such as kaolinite are ubiquitous in the subsurface [34–37]. Clays can have both a permanent negative charge on the basal plane because of isomorphous substitution of minerals (Si, Al) for lower positive valent ions and pH dependent edge charge due to surface hydroxyl groups (Al-OH, Si-OH) created from broken bonds which can protonate or deprotonate depending on the pH in the solution [34,38]. The reported pH_{pzc-edge} of kaolinite edge sites ranges from pH 5.8 to 7.5 [34,39–41]. The positively charged edge sites on clay may serve as deposition sites for negatively charged nZVI (Fig. 1b, 1c) at low pH, thereby decreasing transport through porous media. Heteroaggregation between positively charged iron oxide colloids and negatively charged clay particles has been reported [38,42,43]. Fang et al. (2009) observed that retention of nano-sized TiO_2 (without surface modification) was higher in saturated soil columns with higher clay content [44]. However, polymer-coated nZVI nano-particles are expected to behave differently from previously studied iron oxide and metal oxide particle due to the anionic polymer coating.

Real subsurface materials are not only chemically heterogeneous but also physically heterogeneous. Fine particles (less than 2 μm), including clay minerals, are ubiquitous inorganic natural
colloids in the subsurface, making up from less than 1% to tens of percent of subsurface materials [45,46]. The presence of fine particles in pore spaces between larger sized media grains may further limit nanoparticle transport by mechanical filtration. This is particularly true for many clay minerals that exhibit “edge to face heteroaggregation” to form large aggregates which can fill pore throats (Fig. 1c) [34,38,43]. This occurs predominantly at low pH where the positive edge sites are attracted to the negative face sites of the clay particles. This process will be more significant if the nano-particles also aggregate to larger sized particles.

Currently, we lack a fundamental understanding of how pH affects the aggregation, deposition, and transport of polyelectrolyte-modified nano-particles in heterogeneous subsurface media. Such understanding is needed to design appropriate nanoparticle polymeric modifiers for use in natural environments that are physically and chemically heterogeneous. The objectives of this study are to determine the effects of pH and presence of excess free polymer in solution on (1) polyanion-modified nZVI aggregation, and deposition onto sand and clay minerals, and on (2) polyanion-modified nZVI transport through physically heterogeneous porous media containing large and small sized silica sand, or containing silica sand and clay minerals.

2. Materials and methods

2.1. Iron based nano-particles

One form of nZVI, Reactive Nano Iron Particles (RNIP), with Fe0 cores and Fe2O3 shells were provided by Toda Kogyo Corp. (Onoda, Japan). RNIP has no polymer coating and consists of polydisperse particles with a primary particle size ranging from 5 to 70 nm with a median radius of ~20 nm. The unmodified particles were stored anaerobically in water at pH 10.6 at ~300 g/L. The synthesis and properties of these particles have been described previously [5,10,47]. RNIP modified with adsorbed polyaspartate (MRNIP) with a molecular weight of 2–3 kg/mol (PAP2.5K) was also supplied by Toda Kogyo Corp. (Onoda, Japan). Hematite nano-particles (α-Fe2O3) with an average radius of 20 nm were obtained from Nanostructured and Amorphous Materials Inc. (Los Alamos, NM). H2 generation measurements [5] indicated that the Fe0 contents of the slurry reported in Supplementary Material Fig. S2. Silica fines (MINUSIL 5) with a similar size (d50 = 1.7 μm) as kaolinite were supplied by US silica. The size distribution as reported by the manufacturer is given in Supplementary Material Fig. S3.

2.2. Polyanion surface modifiers

Two polyanionic surface modifiers were used including a low molecular weight, weak polyanion, sodium polypaspartate, a synthetic homopolypeptide (PAP2.5K), and a higher molecular weight triblock copolymer (90 kg/mol) containing a strong polyanion, poly(styrene sulfonate)-block (p(MAA)42-p(MMA)26-p(SS)462). The PSS block is the strong polyanion, and the PMAA and PMMA blocks serve to anchor the block copolymer to the iron oxide surface. Subscripts denote the degree of polymerization of each block. Polypaspartate was either supplied by Toda Kogyo (Onoda, Japan) pre-adsorbed to RNIP (MRNIP), or by Lanxess as sodium polypaspartate (2–3 kg/mol). The latter was used to modify hematite nano-particles. The p(MAA)42-p(MMA)26-p(SS)462 triblock copolymer was synthesized using atom transfer radical polymerization (ATRP) as previously described [7,9,15,16].

2.3. Porous matrix

Silica sand with a 300 μm average diameter (d50) and a specific gravity of 2.65 g/cm³ was used as a model porous matrix (Agisco Corp., Hashbrouck Heights, NJ). The Fe2O3 and Al2O3 weight% in the sand reported by the manufacturer were 0.14% and 0.49% respectively. The grain size distribution and other physical properties are provided as Supplementary Material in Fig. S1. Acid-washed sand was prepared using a previously reported procedure to remove metal oxide impurities from the sand [30]. The procedure included reaction with sodium dithionite (0.1 M) for 2 h followed by immersion in a chromic and sulfuric acid mixture (Fisher Scientific, Pittsburgh PA) overnight to remove metal oxide impurities. Then, the sand was soaked in hydrogen peroxide (5% H2O2) for 3 h to remove organic contaminants, followed by acid washing in sulfuric/chromic acid overnight. Finally, the sand was immersed in hydrochloric acid (12 N HCl) overnight and then rinsed repeatedly in DI water until the pH of the water sand mixture remained constant at 7. Kaolinite clay (kaolinite) with an average diameter of 1.3 μm was purchased from ACROS Organics. The grain size distribution is shown in Supplementary Material Fig. S2. Silica fines (MINUSIL 5) with a similar size (d50 = 1.7 μm) as kaolinite were supplied by US silica. The size distribution as reported by the manufacturer is given in Supplementary Material Fig. S3.

2.4. Particle preparation for aggregation and transport studies

MRNIP was provided with PAP2.5K pre-adsorbed in concentrated slurry that contains excess unadsorbed polypaspartate. The mass ratio of polymer to MRNIP was 1.6. This slurry was diluted to 6 g/L with 1 mM NaHCO3 solution (pH = 8.3). Triblock copolymer modified RNIP (Triblock-RNIP) was prepared using the following procedure. The stock slurry of (unmodified) RNIP was sonicated with an ultrasonic probe (550 Sonic Dismembrator, Fisher Scientific) for 30 min to break agglomerates formed during storage. Triblock copolymer (1 g/L) and RNIP (6 g/L) were mixed and equilibrated by end-over-end rotation at 3 rpm for 2 days. For both MRNIP and Triblock-RNIP, suspensions were settled for 5 min to exclude very large aggregates. The upper 80 vol.% of the supernatant was taken and ultracentrifuged (Sorvall, OTD65B) at 27,000 rpm (68,400 g) for 80 min to separate the nano-particles from the unadsorbed polymer solution. The supernatant was discarded and the particles were re-suspended in 1 mM sodium bicarbonate (NaHCO3) solution (pH 8.3) with sonication (550 Sonic Dismembrator, Fisher Scientific). This washing process was repeated three times to completely remove free polyelectrolyte from the suspension [15]. For consistency, and because oxidation of nZVI can affect its aggregation and transport [48], the unmodified RNIP suspension used the same rinsing procedure as for the surface modified RNIP. After rinsing, the unmodified or modified RNIP was suspended in 1 mM NaHCO3 solution to be used as stock for heteroaggregation and transport studies. The concentrations of unmodified and PAP modified and, triblock copolymer modified RNIP stock suspensions were 1.78 g/L, 3.42 g/L and 3.23 g/L, respectively.

With a comparable surface chemistry to MRNIP, polypaspartate-modified hematite particles (PAP-hematite) that were stable against aggregation were used to distinguish effects of aggregation from effects of deposition on RNIP transport. PAP-hematite was prepared by adsorbing PAP2.5K at pH 5 in 1 mM NaHCO3 + 10 mM NaCl solution. It should be noted that at pH = 5 some or all of the added bicarbonate may leave the system through volatilization of CO2(g). The isoelectric point of hematite occurs at pHiep = 7–9.5 [49] so a pH of 5 was used to maximize the adsorbed mass of PAP to ensure good stabilization against aggregation (Fig. S4). The excess unadsorbed polymer was removed with same pH and ionic strength solution using the same washing protocol as described above to provide a stock suspension (10.68 g/L) of PAP-hematite.
2.5. Characterization of surface modified nano-particles and porous media

The electrophoretic mobility (EPM) of polyelectrolyte-modified RNIP or hematite was measured at pH 6 and 8. The electrophoretic mobility (EPM) of MRNIP, triblock-RNIP, and PAP-hematite was measured on dilute suspensions (~15 mg/L) in aqueous NaCl solutions (from 5 mM to 60 mM NaCl) containing 1 mM NaHCO₃ using a Malvern Zetasizer 3000 (Southborough, MA). While loss of CO₂(g) from the system may occur at pH 7, the pH of these suspensions measured before and after measurements remained at the target pH.

Aggregation of surface modified nano-particles was determined at pH 6 and 8 in 10 mM NaCl + 1 mM NaHCO₃ by dynamic light scattering (DLS) (Malvern Zetasizer 3000, Southborough, MA) at 300 mg/L, which is the same concentration used in the column transport studies. The aggregate size of kaolinite clay at pH 4 and 8 was also measured by DLS at 200 mg/L in 10 mM NaCl + 1 mM NaHCO₃ + NaCl background electrolyte. It should be noted that at pH = 4 the added bicarbonate likely leaves through volatilization of CO₂(g), but the pH was well buffered by the acidiity of the system. The CONTIN algorithm was used to convert intensity autocorrelation functions to intensity-weighted particle hydrodynamic diameter distributions assuming that the particles are spherical. Samples for both electrophoretic mobility and size measurement were sonicated in a water bath (Branson U2510) for 5 min just prior to the measurement to break any weak agglomerates formed during storage.

The streaming potential of the porous medium (sand and acid washed sand) was measured as a function of pH using an Electro Kinetic Analyzer (Anton Paar GmbH, Graz, Austria) equipped with a cylindrical cell to house the granular porous medium. Sand or acid treated sand was wet-packed into the cylindrical cell (1.5 cm inside diameter × 3 cm length) in a solution having the same ionic composition and pH as the solution used during the corresponding column experiments. Before the start of each measurement, the cell was equilibrated by circulating the solution in alternate directions for 20 min [50]. Streaming potentials were converted to zeta potentials using the Helmholz–Smoluchowski equation.

To further demonstrate the existence of pH dependent chemical charge heterogeneity on the sand surface, PAP2.5K adsorption onto the sand was determined by quantifying adsorbed PAP mass at pH 6 and 8 in 1 mM NaHCO₃ + 10 mM NaCl. Adsorption to the sand surface was measured by solution depletion in 20 mL slurries containing 300 g/L sand at different initial concentrations of PAP2.5K. The sand slurry and the stock polymer solution were prepared separately and sonicated at either pH 6 or 8 for 3 days. The pH was adjusted every 12 h until there was no change in the pH, and then the sand and PAP were mixed. In this process the added carbonate had likely escaped from the system for the pH = 6 condition. After 2 days, the PAP2.5K concentration in the supernatant was measured using a total organic carbon analyzer (OI Analytical) as described in Kim et al. [15].

The EPM of kaolinite clay was determined between pH 5 and 8 using a Malvern Zetasizer 3000 (Southborough, MA). Dilute suspensions (~15 mg/L) prepared in 1 mM NaHCO₃ plus 10 mM NaCl were analyzed. Some carbonate had likely volatilized from the system at pH = 5. The measured EPM were converted to the apparent zeta potential using the Smoluchowski approximation. Clay suspensions were sonicated in a water bath (Branson 2510) for 5 min just prior to EPM measurement, and pH was adjusted by adding NaOH (0.1 or 0.01 N) or HCl (0.1 or 0.01 N) as needed.

2.6. Heteroaggregation of surface modified RNIP and clay particles

Heteroaggregation of uncoated or modified RNIP and kaolinite particles was determined by monitoring the optical density change of colloidal suspensions using UV–vis spectrophotometry at 508 nm (Varian Palo Alto, CA) for 1 day. A suspension of kaolinite clay (6 g/L) was dispersed in 1 mM NaHCO₃ solution and was allowed to settle quiescently for 1 day to remove the largest aggregates and to obtain a clay suspension that is highly stable against aggregation. The upper 80 vol.% of the supernatant clay suspension was used as stock for the heteroaggregation study. A kaolinite suspension at 800 mg/L and a suspension of kaolinite (800 mg/L) plus RNIP (200 mg/L) were prepared in 10 mM NaCl plus 1 mM NaHCO₃. The pH was adjusted to pH 6, 7 or 8 by adding HCl or NaOH (0.1 N or 0.01 N). Samples were sonicated in a water bath (Branson 2510) for 5 min before the measurement. pH measured after the measurements indicated that the pH had not changed over the time frame of the measurement. All the samples were prepared in triplicate and the reported values are the average and one standard deviation of the three measurements. By comparing the optical density-based sedimentation curves for kaolinite alone and for the mixture of RNIP and kaolinite at different pH, the extent of heteroaggregation between RNIP and kaolinite is determined. To assess the ability of excess unadsorbed polymer to minimize heteroaggregation, the measurements were repeated in the presence of 270 mg/L of excess unadsorbed PAP2.5K in solution. The temperature was controlled at 25 °C over the time of measurement.

2.7. Transport in porous media

Column experiments were conducted to determine how pH, clay minerals, and free polymer in solution affect the transport of surface modified RNIP in heterogeneous porous media. To evaluate the simultaneously acting effects of aggregation and deposition on transport, RNIP transport was measured as a function of pH. To evaluate the effect of pH on deposition only, independent of aggregation, transport was measured as a function of pH using PAP-hematite nano-particles that do not aggregate under the current conditions. To isolate the effect of grain size on the transport, without heterogeneously charged clay minerals, silica fines with a similar size as the clay minerals were added to the sand.

Transport studies were performed using MRNIP, Triblock-RNIP, and non-aggregating PAP-hematite particles in stainless steel columns (15-cm length × 1.25 cm o.d.) as described previously [7]. The porosity was 0.33 and the linear pore water velocity was maintained at 3.2 × 10⁻⁴ m/s using a peristaltic pump. This velocity represents that for an injection well or injection–extraction well pair used for emplacing nZVI in porous media. Either 2 wt.% of silica fines (D₅₀ ≈ 1.7 μm) or 2 wt.% of kaolinite (D₅₀ ≈ 1.36 μm) were mixed with sand (d₅₀ = 300 μm) and a small amount of water and dried in the oven at 40 °C to create a relatively uniform mixture of sand and silica fines or of sand and clay [51]. Column experiments were conducted as follows. After the columns were packed, at least 20 pore volumes (PV) of background solution containing 10 mM NaCl plus 1 mM NaHCO₃ at pH 6, 7, or 8 were eluted through the columns at 3.2 × 10⁻⁴ m/s until the effluent pH equaled the influent pH. A square pulse (1 PV) of nZVI or hematite suspension at 300 mg/L in 10 mM NaCl and 1 mM NaHCO₃ adjusted to pH 6, 7 or 8 was introduced into the column at 3.2 × 10⁻⁴ m/s, then the column was flushed with background electrolyte solution (particle free) for three additional pore volumes. The column effluent was collected for four pore volumes. The ability of excess polymer in solution to enhance the transport of nZVI through the column was determined by introducing one square pulse of MRNIP mixed with 100 mg/L of PAP. During injection, the particle suspension was sonicated with an ultrasonic probe to prevent aggregation prior to introduction into the column. An aliquot of the effluent was acid digested in concentrated HCl (trace metal grade) and analyzed for total Fe using flame atomic absorption spectrometry (GBC at 248.3 nm within the range of 0–10 mg/L Fe) as previously described [7,10,15]. The influent
uncoated or modified RNIP, or hematite particle concentration, was measured in the same way. All transport experiments were conducted in duplicate. The reported values are the average and error bars represent one standard deviation of the replicate measurements.

3. Results and discussion

3.1. pH affects charge and aggregation of surface modified RNIP

The electrophoretic mobility of the surface modified RNIP at pH 6 and 8 are shown in Fig. 2. Although both the MRNIP and triblock-RNIP are negatively charged at pH 6 and 8, the magnitude of the EPM is lower at pH 6 compared to pH 8 even for the triblock copolymer with the strong PSS polyanion. This is likely a result of the positive charge on the underlying RNIP particle at pH 6 ($\text{pH}_{\text{pzc}} = 6.3$) compared to pH 8 [15]. The triblock-RNIP exhibited a more negative electrophoretic mobility compared to MRNIP at each pH tested, and the change in the magnitude for triblock-RNIP was less than for MRNIP when pH was decreased from 8 to 6. The greater apparent charge and lower sensitivity to pH for the triblock-RNIP compared to MRNIP is consistent with expectation for the strong PSS polyanion as compared to the weak PAP polyanion. The decreased magnitude of EPM at low pH compared to the higher pH is consistent with decreased charge in the surface and adsorbed layer which could decrease the repulsion between particles and in turn enhance aggregation. The magnitude of the EPM for PAP modified hematite was greater than for either modified RNIP and was independent of pH for pH 6 to pH 8. The greater charge of hematite compared to either of the RNIP’s is likely due to a greater adsorbed mass of PAP since the negatively charged PAP was adsorbed to hematite at pH = 5 where it is positively charged [52].

Low pH promoted the aggregation of the surface modified RNIP. The measured aggregate size distributions at pH 6 and 8 for each nanoparticle type are shown in Fig. 3. At pH 6, the aggregate sizes of both MRNIP and triblock-RNIP were larger than at pH 8. Notably, the aggregate sizes for both RNIP systems were >1.5 $\mu$m at pH 6.

The greater aggregation of surface modified RNIP at pH 6 compared to pH 8 is consistent with the decreased electrophoretic mobility at pH 6. At pH = 6 the underlying RNIP becomes positively charged ($\text{pH}_{\text{pzc}} = 6.3$) [15] so the interactions between the particle surface and the negatively charged adsorbed polyelectrolyte become more favorable. This can result in a flatter adsorbed layer conformation compared with the higher pH where RNIP is negatively charged when there is no excess unadsorbed polymer in the solution. This flattening would decrease the electrosteric repulsive force between particles and increase aggregation as was observed [20]. The effect of RNIP aggregation on its transport in porous media is discussed later.

3.2. pH affects deposition onto heterogeneous sand surfaces

Limited mobility of polyelectrolyte modified RNIP in sand columns can result from aggregation of the RNIP or RNIP deposition onto the sand surface, or both. A lower mobility of surface modified RNIP through the sand column was observed at pH 6 compared to pH 8 (Fig. 4) for all of coated nano-particles used here. Data in Fig. 4 are for sand that was not acid-treated to remove metal oxide impurities and contained no clay minerals or silica fines, and the nanoparticles were all washed – there was no unadsorbed polyelectrolyte in solution for these measurements. A clear trend of increasing mobility through the column with increasing pH is observed. For nZVI transport, the effect of aggregation (average particle size) on its mobility cannot be distinguished from the effect of pH on deposition because both factors vary at the same time. However, comparing the transport of aggregating nZVI (MRNIP and triblock-RNIP) through sand was less than for MRNIP when pH was decreased from 8 to 6. The greater deposition (and hence lower transport) at pH 6 compared to pH 8 for all coated RNIP evaluated may also be due to the presence of metal oxide (particularly Fe-oxide) impurities on the sand surface. These impurities may be positively charged at pH 6 and promote deposition of the negatively charged modified RNIP. To test this hypothesis, the transport of PAP-hematite nanoparticles, in the absence of excess unadsorbed polyelectrolyte, was measured using sand that was acid washed to remove the impurities (Fig. 5). Transport of the nano-particles at pH 6 was significantly greater for the acid washed sand than for the untreated sand, suggesting that the metal oxide impurities were indeed providing favorable deposition sites. The zeta potential of the acid washed sand (Fig. 6) was significantly more negative and closer to that expected for silica than for the untreated sand, further suggesting the presence of metal oxide impurities. Acid treatment of the sand also affected adsorption of PAP to the sand (Fig. 7). PAP adsorption to untreated sand at pH 6 was approximately one order of magnitude greater than at pH 8, even though the zeta potential of the untreated sand was nearly independent of pH. This suggests...
that at the lower pH, anionic PAP may be adsorbing preferentially to positively charged impurities on the sand surface that have a pH_{iep} higher than pH 6. This may be an important consideration when extrapolating transport results from laboratory studies using clean sands to real field soils where chemical heterogeneity such as adsorbed iron oxide are likely to be present and may affect transport considerably.

Fig. 3. Intensity-weighted aggregate size distribution measured by dynamic light scattering at a time of 3 min after ending sonication. (a) MRNIP, (b) triblock-RNIP and (c) PAP-hematite in 1 mM NaHCO₃ and 10 mM NaCl at pH 6 and 8. The open circles (○) are for pH 8 and the closed circles (●) are for pH 6.

Fig. 4. Percent of mass eluted for MRNIP, triblock-RNIP, and PAP-hematite eluted through 15 cm columns filled with silica sand at pH 6, 7 and 8. The eluted mass of triblock-RNIP was near zero at pH = 6. The initial RNIP or hematite particle concentration was 300 mg/L, porosity of 0.33, linear pore water velocity was $3.2 \times 10^{-4}$ m/s and ionic strength was controlled at 10 mM NaCl plus 1 mM NaHCO₃.

Fig. 5. Percent of PAP-hematite mass eluted through 15 cm columns filled with sand and acid washed sand at pH = 6, pH = 7 and pH = 8 with porosity of 0.33. The initial hematite particle concentration was 300 mg/L, linear pore water velocity was $3.2 \times 10^{-4}$ m/s and ionic strength was controlled at 10 mM NaCl plus 1 mM NaHCO₃.

Fig. 6. Zeta potential of sand and acid washed sand at pH 6, 7 and 8. Zeta potentials were calculated from measured streaming potentials. Experiments were conducted with 10 mM NaCl plus 1 mM NaHCO₃ and as a background electrolyte at 25 °C.

Fig. 7. Adsorption isotherm of PAP onto untreated sand at pH 6 (closed triangle ▲) and pH 8 (open triangle ▲) in the presence of 10 mM NaCl + 1 mM NaHCO₃. The fitted line is based on the Langmuir isotherm for convenience.

3.3. Heteroaggregation between clay and bare or modified RNIP in suspension

A heteroaggregation study was performed to determine if there is pH dependent deposition of uncoated or modified RNIP onto kaolinite particles to support measurements of the effect of kaolinite on column transport discussed below. In each case, the aggregation and sedimentation of a mixture of RNIP (bare or coated,
200 mg/L) and kaolinite (800 mg/L) was monitored and compared to the homoaggregation and sedimentation of bare or modified RNIP or kaolinite at the same pH. Heteroaggregation is indicated by a shift in the critical time for sedimentation to occur [10,14]. Heteroaggregation between bare or surface modified RNIP and kaolinite occurred at pH \( \leq 7 \), but not at pH 8 (Fig. 8 shows data for bare RNIP; results for both uncoated and modified RNIP types are summarized in Table 1). The pH where heteroaggregation occurs in this study falls into the reported range of pH_{pzc-clay edge} (from pH 5.8 to 7.3) and pH_{pzc-RNIP} = 6.3 [34,38], suggesting that uncoated and modified RNIP are depositing onto the positively charged edge sites of the kaolinite at pH < 7 or that the net repulsive force between the RNIP and the kaolinite is decreasing due to a lower net charge on both at the lower pH.

The homoaggregation measurements reveal other kaolinite behaviors that can affect uncoated and coated RNIP transport in sand amended with kaolinite. At pH < 7, the critical time to homoaggregation for kaolinite was decreased relative to high pH. This is a result of “edge-to-face aggregation” among kaolinite particles having both the permanent negatively charged face and positively charged edge sites simultaneously in the structure. This is further supported by the overall decrease in the kaolinite zeta potential with decreasing pH due to the positive charge development at the edge sites of kaolinite (Fig. 9), as well as an increase in kaolinite aggregate size from that measured at pH 8 (\( \sim 800 \text{ nm} \)) to that measured at low pH (\( \sim 4 \mu \text{m} \)) (Fig. S5). Also, aggregation of kaolinite in porous media was observed at pH \( \leq 6 \) (Fig. S6) which could plug pore spaces and prevent transport via mechanical filtration. In summary, the heteroaggregation study suggests that at pH < 7 there is enhanced deposition of coated or uncoated RNIP onto kaolinite clay particles. Also, enhanced mechanical filtration of RNIP due to aggregation of the kaolinite in the pore spaces is possible. Either process may decrease the mobility of nZVI through subsurface media as described next.

### 3.4. Effect of clay minerals or silica fines on the transport of surface modified RNIP

The effect of the presence of kaolinite or silica fines in sand columns on nZVI transport was investigated by comparing the transport of coated RNIP in sand columns amended with either 2 wt.% silica fines or 2 wt.% kaolinite (Figs. 10–12). The presence of either silica fines or kaolinite increases the available surface area for potential RNIP deposition and can decrease the effective pore size between sand grains, which can in turn decrease transport by mechanical filtration. Even though the silica fines and the kaolinite particles were the same size (\( d_p \sim 1.5 \mu \text{m} \)), the presence of 2 wt.% of one or the other of these particles had a different effect on transport due differences in their surface chemistry. Despite the increased surface area for deposition, the presence of silica fines increased transport compared to unamended sand columns for triblock-RNIP and for PAP-hematite (Figs. 11 and 12). Silica fines had little effect on transport of MRNIP which was less stable against aggregation and deposition compared to triblock-RNIP (Fig. 10). The greater transport for triblock-RNIP and for PAP-hematite in the presence of silica fines is due in part due to the increase in average porewater velocity in the pore throats due to the presence of fines [48], however, the increased velocity cannot explain all of the increase in transport. (Supporting Information Fig. S7). This suggests that the presence of silica fines (without surface impurities) is also blocking access to favorable deposition sites on the sand surfaces.

In contrast to the silica fines, the presence of 2 wt.% kaolinite in porous media generally decreased the mobility of RNIP relative to the silica fines at all pH conditions evaluated (Figs. 10 and 11). The triblock-RNIP was less affected than MRNIP, likely due to the greater electrosteric repulsion [14,16] from the negatively charged kaolinite faces afforded by this polymer relative to the PAP. Enhanced deposition onto kaolinite occurred even for the PAP-coated hematite (Fig. 12) which had the greatest overall surface charge (Fig. 2) and did not aggregate. Deposition was greatest at pH 6 where heteroaggregation between uncoated or modified RNIP and the kaolinite occurs in suspension, and where the kaolinite tends to undergo face-to-edge aggregation and can block pore spaces.
3.5. Effect of excess polymer on the transport of surface modified RNIP

Excess PAP in solution was shown to increase transport of MRNIP and hematite in (untreated) sand columns (Fig. 13) by adsorbing to and modifying the sand surface (Fig. 7). Similar behavior was observed for transport in the presence of silica fines and kaolinite in the presence of excess PAP in solution. Adding a small amount of excess polymer (100 mg/L) to the injection solution dramatically improved the mobility of MRNIP through all of three types of porous media used (sand, sand + 2 wt.% silica fines, and sand + 2 wt.% kaolinite clay) (Fig. 13a). The presence of excess unadsorbed polymer prevented heteroaggregation between kaolinite and MRNIP at all pH values evaluated (Table 1), as well as edge to face aggregation of kaolinite. These effects can all be attributed to polyanionic PAP adsorbing to positively charged metal oxide impurities on untreated sand and edge sites on kaolinite. These results suggest that excess PAP in the nZVI injection solution may inhibit nZVI deposition onto the positively charged sites of kaolinite and decreases aggregation of clay in the pore spaces between sand grains. Eliminating these two mechanisms for filtering nZVI results in significantly less deposition and greater transport. It is noteworthy that 100 mg/L of excess unadsorbed PAP in solution appears to have mobilized a fraction of the clay within the column, as judged by the visual appearance of the eluted suspension (Fig. 13b). This may have also enhanced transport of the MRNIP, if some MRNIP were adsorbed to, but shuttled by, mobilized kaolinite.

### Table 1
Summary of the heteroaggregation study.

<table>
<thead>
<tr>
<th>Critical sedimentation time (min)</th>
<th>pH 8</th>
<th>pH 7</th>
<th>pH 6</th>
<th>pH 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>197 ± 6</td>
<td>200</td>
<td>120 ± 17</td>
<td>17 ± 1</td>
</tr>
<tr>
<td>Kaolinite + uncoated RNIP</td>
<td>197 ± 6</td>
<td>108 ± 21</td>
<td>7 ± 1</td>
<td>4 ± 1</td>
</tr>
<tr>
<td>Kaolinite + MRNIP</td>
<td>263 ± 21</td>
<td>203 ± 6</td>
<td>14 ± 1</td>
<td>9 ± 1</td>
</tr>
<tr>
<td>Kaolinite + triblock-RNIP</td>
<td>220 ± 17</td>
<td>200 ± 10</td>
<td>13 ± 1</td>
<td>9</td>
</tr>
<tr>
<td>Kaolinite + excess PAP (267 mg/L)</td>
<td>223 ± 21</td>
<td>173 ± 36</td>
<td>178 ± 21</td>
<td>180 ± 12</td>
</tr>
<tr>
<td>Kaolinite + MRNIP + excess PAP (267 mg/L)</td>
<td>210 ± 12</td>
<td>200</td>
<td>193 ± 12</td>
<td>193 ± 12</td>
</tr>
</tbody>
</table>

* Values were measured from triplicate samples and the average values and ±standard deviations are reported.
4. Conclusions and environmental implications

This study highlights the importance of commonly occurring site specific hydrogeochemical factors such as physical and chemical heterogeneity of porous media and groundwater pH on subsurface transport of surface modified nZVI. At pH 6, aggregation and direct deposition of polyanion-modified RNIP limited its transport. At higher pH, aggregation continues to play a role in decreased transport, but the strong polyanion coatings better serve to decrease direct deposition. Direct deposition to impurities with pH_{pzc} between 6 and 8 on the sand surface limited surface modified RNIP transport. Even for seemingly favorable conditions for transport, (i.e. sandy materials with less than 1% metal oxide impurities), the presence of small percentages of clay minerals resulted in RNIP deposition and severely limited surface modified RNIP transport at pH 6 to 8.

For the nZVI types and injection conditions evaluated here, transmission of nZVI through the 15 cm column was less than 70% without addition of excess polymer. This suggests transport distances of ~1 m for 90% removal of particles, which could make nZVI emplacement over large contaminated regions impractical without addition of excess polymer. One way to improve nZVI transport may be to co-inject small amounts of excess unadsorbed polymer in solution [13]. Excess polymer in the injection can minimize surface modified nZVI deposition onto sand or clay surfaces by adsorbing to positively charged sites in the subsurface media, making the surface charge of porous media uniformly negative and increasing the electrostatic repulsions between nZVI and the media. In mildly acidic soils, and where the porous medium contains a high portion of surface charge heterogeneity due to metal oxide or clay minerals, using excess free polymer in the injection solution can increase surface modified nZVI mobility through subsurface media. The results are based on an injected nZVI concentration of 0.3 g/L, which is much lower than is typically applied in the field (2–10 g/L). While aggregation and enhanced deposition onto favorable deposition sites on the porous media can both limit transport of nZVI, the higher nZVI concentrations used in practice will promote aggregation, potentially making physical straining the dominant factor limiting transport [25,48]. Ionic strength and composition (held constant in this study), and adsorbed natural organic matter on the coated nZVI and the sand and clay surfaces will also affect the deposition and transport behavior of nZVI. All of these variables must be evaluated to better predict coated nZVI transport behavior in natural porous media.

Acknowledgments

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Appendix A. Supplementary material

Additional information about the grain size distributions of sand, silica fines, kaolinite clay, adsorption isotherm of polysaccharate 2.5 K on hematite nano-particles, pH dependent aggregate size of kaolinite clay and microscopic observations of MRNIP aggregation and deposition onto kaolinite clay in a sand–clay mixed media in a micro-fluidic cell. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jcis.2011.12.059.

References