Impact of nZVI stability on mobility in porous media

Chris M. Kocura, Denis M. O’Carroll⁎, Brent E. Sleep

Civil and Environmental Engineering, Western University, 1151 Richmond Rd., London, ON, Canada N6A 5B8
Civil Engineering, University of Toronto, 35 St. George St. Toronto, ON, Canada M5S 1A4

Article info

Article history:
Received 25 May 2012
Received in revised form 10 September 2012
Accepted 5 November 2012
Available online 17 November 2012

Abstract
Nano-scale zero valent iron (nZVI) has received significant attention because of its potential to rapidly reduce a number of priority source zone contaminants. In order to effectively deliver nZVI to the source zone the nZVI particles must be stable. Previous laboratory studies have demonstrated the mobility of polymer modified suspensions of low concentration nZVI. More recently studies have shown potential for higher concentration nZVI suspensions to be transmitted through porous media. However, with increasing nZVI concentration aggregation is accelerated, reducing the available time for injection before nZVI settles. In this study the colloidal stability and mobility of nZVI concurrently synthesized and stabilized in the presence of carboxy-methyl-cellulose (CMC) are evaluated in one-dimensional column experiments. Low pore water velocity nZVI injections (4, 2, and 0.25 m/day) conducted over periods as long as 80 h with no mixing of the influent reservoir were used to investigate the effects of prolonged aggregation and settling of colloids on transport. A numerical simulator, based on colloid filtration theory, but accounting for particle aggregation and settling was used to evaluate the contributions of aggregation and settling on nZVI mobility. Results suggest that the prediction of nZVI sticking efficiency in column experiments becomes increasingly influenced by aggregation and settling in the influent reservoir as the period of injection increases. Consideration of nZVI stability is required for the prediction of nZVI mobility at the field scale and for the design of successful nZVI remediation plans.

Keywords:
Nanoparticles
Zero valent iron
Carboxymethyl cellulose
Stability
Mobility
nZVI

1. Introduction
Nano-scale zero valent iron (nZVI) particles have significant potential for use in remediating a number of priority source zone pollutants. Chlorinated ethenes, polychlorinated biphenyls (Liu et al., 2007; Wang and Zhang, 1997), chlorinated methanes (Lien and Zhang, 1999), heavy metals (Hoch et al., 2008; Ponder et al., 2000), arsenic (Kanel et al., 2007), and perchlorate (Cao et al., 2005) have all been successfully treated in laboratory studies using nZVI. The coupled benefits of high surface area available for reaction and potential mobility in the subsurface due to small particle size have generated significant interest in their application for the remediation of source zone pollutants (Zhang, 2003); however, a number of challenges remain before the technology can be widely adopted.

A number of studies have shown that nZVI rapidly aggregates (He and Zhao, 2005; Schrick et al., 2004), growing to a critical size, where gravitational forces result in the settling of particles (Phenrat et al., 2007). It is now generally accepted that the surface of nZVI particles must be modified to reduce aggregation and settling so that the particles remain dispersed in aqueous solutions for extended periods of time. This makes it possible to transport nZVI particles to distances of several meters from injection wells to target contaminant zones. Technologies developed for stabilizing nZVI in colloidal form include hydrophilic carbon supported nZVI (Schrick et al., 2004), anionic polymers anchored to nZVI particles (He and Zhao, 2005; He et al., 2007), organic acids absorbed to nZVI particles (Sun et al., 2007), anionic polymers absorbed to nZVI particles (Phenrat et al., 2008), multi-functional polymers
absorbed to nZVI particles (Saleh et al., 2005), nonionic polymers anchored to nZVI particles (Tiraferri et al., 2008), oil in water emulsion encapsulation of nZVI (Berge and Ramsburg, 2009), and shear thinning polymer admixtures (Comba and Sethi, 2009).

Prolonged nZVI stability in aqueous solutions has led to greater nZVI mobility in porous media laboratory experiments (He et al., 2009; Hydutsky et al., 2007; Johnson et al., 2009; Phenrat, 2008; Phenrat et al., 2009; Saleh et al., 2007). However, stability and mobility vary with stabilization technique. In addition conditions used in many laboratory experiments differ than those likely in the field. The pore velocities employed in most column studies are much higher than would be typically used in field scale applications (Berge and Ramsburg, 2009), except in the immediate vicinity of the injection well in very permeable formations (He et al., 2009; Johnson et al., 2009; Kim et al., 2009; Phenrat et al., 2009; Saleh et al., 2007; Zhan et al., 2008), or with high injection pressures (Vecchia et al., 2009; Zhan et al., 2008). Few studies have been conducted at pore water velocities representative of typical of field implementations (Berge and Ramsburg, 2009; Raychoudhury et al., 2011; Tiraferri and Sethi, 2009). Results of laboratory tests at high water velocities may overestimate nZVI mobility in lower velocity field scale applications, due to reduced nZVI attachment to porous media at higher velocities.

In field scale injections, nZVI from a feed vessel is injected into the subsurface. Although significant advances have been made in improving nZVI aqueous phase stability, these particles are meta-stable (Phenrat et al., 2009) and will eventually aggregate and settle to some extent in the feed vessels during field applications. Thus, some settled nZVI may be retained in the feed vessel, and the particle size of injected nZVI may increase as injection progresses. In most lab studies high injection rates and short porous medium residence times have been used so that little settling in the nZVI feed vessels occurred. For example, in a recent study of post-synthesis stabilized nZVI the total time from injection of the nZVI slurry to completion of the column experiment was on the order of 13 min (Phenrat et al., 2009) or less in other stabilized nZVI studies (Kim et al., 2009; Saleh et al., 2007; Schrick et al., 2004; Zhan et al., 2008). In these short duration experiments, little aggregation and settling of nZVI in the feed vessels would be expected to occur, in contrast to field scenarios. In addition, the typical experimental methodology involves sonication or aggressive mixing to suspend nZVI in the feed vessel during column experiments. This applied energy intensity is difficult to replicate with large injection volumes typical of field cases. Thus, it is important to include the effects of nZVI aggregation and settling in the feed vessel during the injection period to accurately represent the nZVI injection process.

The goal of this study is to use column experiments and numerical modeling to assess the impact of polymer-stabilized nZVI particle aggregation and settling on nZVI transport over a range of pore water velocities that may be used in the field (0.25–4 m/day). To replicate likely field conditions, nZVI in the feed vessel was not continually mixed in contrast to other studies in the literature. The suite of column experiments were simulated using a numerical model based on colloid filtration theory (CFT) to investigate the impact of nZVI aggregation and settling in the feed vessel on subsequent nZVI mobility in porous media.

2. Materials and methods

2.1. nZVI synthesis

nZVI was synthesized using a modified chemical precipitation method (He and Zhao, 2005). 0.5 M FeSO4 (Sigma Aldrich, St. Louis, MO) was well mixed in the presence of a food grade anionic polymer (sodium carboxy-methyl-cellulose, 250 kg/mol (CMC250k) (Sigma Aldrich, St. Louis, MO)). The polymer was dissolved overnight in de-ionized water and de-oxygenated to <0.2 mg/L using nitrogen displacement. The solution was then titrated to Fe0 using 2.0 M NaBH4 (Sigma Aldrich, St. Louis, MO) in keeping with the optimal stoichiometric ratio for small nZVI particles (He and Zhao, 2007). The solution was gently agitated for an additional 30 min to ensure complete nucleation of nZVI particles on the polymer. All characterization and column experiments proceeded immediately following synthesis with no effort to re-suspend the nZVI suspension. This synthesis method, modified from another study by He et al. (2007), was selected over other methods because of the enhanced colloidal stability afforded by electro-steric repulsion as well as the ease of synthesis and scalability. This nZVI previously exhibited enhanced colloidal stability and mobility at low nZVI concentrations (He et al., 2009) and higher concentrations (Raychoudhury et al., 2011). Recent results and recommendations from an nZVI field trial suggest particle reactivity and stability is maximized when particles are synthesized immediately prior to injection (i.e., on-site synthesis) (Bennett et al., 2010). Thus, a fresh batch of nZVI was synthesized for each experiment conducted to avoid drying and resuspending the particles. The CMC concentrations were chosen to provide the best available colloidal stability for a given nZVI concentration.

2.2. nZVI characterization

Particle size was determined using transmission electron microscopy (Philips EM 200 TEM) to assess the individual nZVI particle size using previously reported methods (Sakulchaicharoen et al., 2011). Dynamic light scattering (DLS) (90Plus particle size analyzer, Brookhaven Instruments, Holtsville, NY) was used to determine the size of nZVI/CMC aggregates in suspension. Freshly synthesized 0.1 g/L nZVI was prepared in 0.2% wt CMC250k solution and analyzed using DLS. For 2.5 g/L nZVI prepared in 0.8% wt CMC250k solution, optimal light scattering was achieved by diluting nZVI in 0.8% wt. CMC250k. Zeta potential of nZVI was quantified using electrophoretic mobility measurements of the solutions (Zeta pals software, Brookhaven). nZVI concentrations were quantified using a ultraviolet–visible spectrophotometer (UV–vis) at 508 nm wavelength (Helios Alpha, Thermo Fisher). A calibration curve was developed for every experiment by diluting the freshly synthesized nZVI slurry to known aqueous concentrations. The UV–Vis analysis was validated using the ferrozine method (Stoekel, 1970) by comparing replicate samples. Calibration curves were linear, and no effect of changing particle size due to aggregation was detectable.

The stability of the freshly synthesized nZVI suspensions was evaluated using UV–vis. For low concentrations of nZVI (0.1 g/L), 3 mL of freshly synthesized solution was placed in a
sealed quartz cuvette in an anaerobic chamber (Coy, Grass Lake, MI) and scanned at 2 minute intervals for 48 h. It was not possible to use the same analysis to assess the effect of the higher nZVI concentration (2.5 g/L) due to the light path limitations through the sample. Sacrificial 4 mL serum vials (Kimble, Vineland, NJ) containing the freshly synthesized nZVI were placed over an 80 hour period. A 100 μL sample was extracted from the bottom of the vial by inserting a 250 μL gastight syringe (Hamilton, Reno, NV) through the butyl stopper (Kimble, Vineland, NJ) to minimize agitation. Each sample was diluted in 10 mL of DI water and analyzed using the UV–Vis photo-spectrometer.

2.3. Column experiments

Column experiments were conducted in glass columns with PTFE and stainless steel porous bed supports (Kimble/ Kontes — Vineland, NY, dimensions in Table 1). Columns were packed with acid washed F32 quartz sand (Table 1, US Silica, Berkeley Springs, WV) and then flushed with carbon dioxide to displace air in the pore space. 30 pore volumes of de-ionized water were then passed through the column, in an upward direction to displace and dissolve the carbon dioxide, leaving a fully water saturated sand pack. 15 pore volumes of de-oxygenated water were then passed through the column, in an upward direction to displace and dissolve the carbon dioxide, leaving a fully water saturated sand pack. 15 pore volumes of de-ionized water containing 0.1 mM bromide were then pumped into the column in a downward direction through a butyl stopper (Kimble, Vineland, NJ) to minimize exposure to oxygen. The 8 pore volumes of injection solution were then pumped into the column in a downward direction at the desired pore water velocity. During this injection period care was taken to prevent agitation of the injection solution in the syringe. Effluent samples were collected using a fraction collector and nZVI concentrations were determined over an 80 hour period. A 100 μL sample was passed through a 0.2 μm PTFE syringe filter and analyzed using an HPLC (Waters — Milford, MA) equipped with a conductivity detector to determine tracer ion concentrations.

2.4. Modeling nZVI transport using colloid filtration theory

Column experiments were modeled using traditional colloid filtration (Eq. (1)) (Yao et al., 1971):

\[
\frac{\partial C}{\partial t} = \frac{D_H}{\partial x^2} + v_p \frac{\partial C}{\partial x} - K_{Adv} C
\]

where C is the nZVI concentration in the aqueous phase (M/L³), \(D_H\) is the hydrodynamic dispersion coefficient (L²/T), \(v_p\) is the pore water velocity (L/T), t is time (T), and \(K_{Adv}\) is the rate at which nZVI attaches or is deposited on available collector sites (1/T) and can be further described by:

\[
K_{Adv} = \frac{3(1-\theta_w)}{2d_{50}} \alpha \eta_0 v_p
\]

where \(\theta_w\) is the volumetric water content (-), \(d_{50}\) is the median collector grain size (L), \(\alpha\) is the sticking efficiency, or removal efficiency (-) defined as the ratio of particles that attach to the collector to those that strike the collector, and \(\eta_0\) is the theoretical collision efficiency (-) determined using the correlation of Tufenkji and Elimelech (2004):

\[
\eta_0 = \eta_{id} + \eta_i + \eta_c
\]

where the ratio of particles striking the collector to those that approach the collector, \(\eta_{id}\), is calculated as the sum of diffusion \(\eta_d\), interception \(\eta_i\), and gravity \(\eta_c\) contributions. CFT has been applied in previous studies evaluating the transport of nZVI in porous media (He et al., 2009; Johnson et al., 2009; Raychoudhury et al., 2011; Tiraferri and Sethi, 2009). However, the equation of Tufenkji and Elimelech (2004) has been most commonly employed using an analytical solution to Eq. (1) that assumes a constant influent concentration and requires a steady state effluent nZVI concentration to calculate \(\alpha\) from the differential form of Eq. (2). It has been suggested that CFT is inappropriate for nZVI at high concentration because influent concentrations do not reach steady state due to aggregation (Phenrat et al., 2009).

In this study, the governing equations were solved using a one-dimensional finite element code (Liu et al., 2009). Independently determined experimental parameters were used as model inputs (e.g., porosity, pore water velocity, mean grain size) when possible (Table 1). Changes in the influent nZVI concentration (inlet boundary condition) due to settling in the influent reservoir were described using an exponential decay model (Phenrat et al., 2007):

\[
C(t) = A_i + B_i \exp^{-\tau t}
\]

where \(t\) is time and \(A_i\), \(B_i\) and \(\tau_i\) are fitting parameters that describe the decay within the settling regime i.e. \(A_i\), \(B_i\) and \(\tau_i\) were determined by minimizing the difference between observed and model stability profiles (Table 2) and utilized to represent the settling behavior in the feed vessel.

As aggregation was occurring in the inlet reservoir, the particle size passing through the column was assumed to be increasing in time. This increasing size would change the collision efficiency, as calculated by Eq. (3). Therefore, in a subset of model simulations the changing average particle size was described using a first order relationship for particle

---

Table 1

Properties of porous media used for column experiments and modeling.

<table>
<thead>
<tr>
<th>Porous media parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>Column length</td>
</tr>
<tr>
<td>D</td>
<td>Column diameter</td>
</tr>
<tr>
<td>d_{50}</td>
<td>Collector diameter</td>
</tr>
<tr>
<td>I</td>
<td>Uniformity coefficient</td>
</tr>
<tr>
<td>I</td>
<td>Ionic strength</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>n</td>
<td>Porosity</td>
</tr>
<tr>
<td>PV</td>
<td>Pore volume</td>
</tr>
</tbody>
</table>
Table 2
nZVI injection solution and stability properties.

<table>
<thead>
<tr>
<th>nZVI properties</th>
<th>0.1 g/L nZVI</th>
<th>2.5 g/L nZVI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>0.2% wt</td>
<td>0.8% wt</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>250 kg/mol</td>
<td>250 kg/mol</td>
</tr>
<tr>
<td>Degree of substitution</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Viscosity ($\mu$P)</td>
<td>13.8 cP</td>
<td>72.3 cP</td>
</tr>
<tr>
<td>pH</td>
<td>8.5</td>
<td>8.5</td>
</tr>
<tr>
<td>Ionic strength</td>
<td>30 mM</td>
<td>160 mM</td>
</tr>
<tr>
<td>Hamaker (A)</td>
<td>1.0E−19 J</td>
<td>1.0E−19 J</td>
</tr>
</tbody>
</table>

Aggregation and settling properties in first settling regime

- Initial particle diameter ($d_{p,initial}^{final}$) 61 nm
- Final particle diameter ($d_{p,final}$) 123 nm
- $d_{p,initial}$: initial measured particle size (L), and $d_{p,final}$ is the rate of particle growth observed using DLS following synthesis ($\text{T}^{-1}$).
- $T_{cr}$ is the characteristic time ($d_{p,final} - d_{p,initial}$) e$^{K_{dp} T}$

where $d_{p,initial}$ is the stable aggregated particle size (L) measured after $T_{cr}$, $d_{p,initial}$ is the initial measured particle size (L), and $K_{dp}$ is the rate of particle growth observed using DLS following synthesis ($\text{T}^{-1}$). Eq. (5) is used to predict the particle diameter used in calculating collision efficiency with Eq. (3). Parameters in Eq. (5) were determined from the DLS measurements.

The numerical model was coupled to an unconstrained non-linear optimization routine using the simplex search method (Lagarias et al., 1998) to allow determination of sticking efficiency ($\alpha$) for each nZVI suspension and longitudinal dispersivity ($\lambda_L$), by minimizing the root mean square error (RMSE) between observed and simulated nZVI effluent concentration as a function of time.

3. Results and discussion

3.1. nZVI properties

Transmission electron microscopy (TEM) analysis of dried nZVI particles indicated that individual nZVI particles were 2.8 ± 1.6 nm in diameter (Sakulchaicharoen et al., 2011). However, the mean hydrodynamic diameter of the particles from DLS analysis was 61 nm immediately following synthesis for 0.1 g/L of nZVI using 0.2% CMC250k polymer. He and Zhao (2007) reported hydrodynamic diameters of 18.1 nm for 0.1 g/L nZVI using a 90 kg/mol CMC polymer (CMC90k) (He et al., 2009). The hydrodynamic diameter of 0.1 g/L nZVI particles grew from 61 nm to 123.5 nm during the 1 h period following synthesis. The hydrodynamic diameter for the 2.5 g/L nZVI suspension and CMC250k polymer at 0.8%, initially 25 nm, eventually grew to a meta-stable size of 110 nm following synthesis. Particle diameters were observed to grow at different rates in this study (Table 2), as described by Eq. (5), with the particles in the 2.5 g/L nZVI suspension growing at slower rate than in the 0.1 g/L nZVI suspension. Higher suspension viscosity in the case of 2.5 g/L nZVI will contribute to reduced nanoparticle collisions leading to slower particle aggregation. The surface charges on these aggregates, characterized by zeta potential, were -53.8 mV and -52.1 mV for 2.5 and 0.1 g/L nZVI concentration suspensions, respectively. This is consistent with nZVI synthesized by other researchers at 0.2 g/L using a similar polymer (CMC90k at 0.2% wt., ζ = -55.8 ± 0.9 mV) (He et al., 2009).

3.2. nZVI stability

The colloidal stability of both 0.1 g/L nZVI stabilized with 0.2% wt. CMC250k and 2.5 g/L nZVI stabilized with 0.8% wt. CMC250k was assessed (Fig. 1). 0.1 g/L nZVI represents a typical concentration found in both environmental colloid mobility studies (He et al., 2009) and nZVI reactivity studies (He and Zhao, 2008). 2.5 g/L represents a concentration that may be appropriate for field scale application of nZVI (Elliott and Zhang, 2001). Observed characteristic times ($\tau$ in Eq. (4)) in this study are significantly higher than those reported for
unstabilized nZVI (Phenrat et al., 2007), and the threshold time between aggregation and dominant settling, $T_{\text{Crit}}$, exceeds reported values for nZVI/anionic polymer systems that use a post-synthesis stabilization technique (Phenrat et al., 2008). The absence of rapid settling during the stability test (Fig. 1) for both low and high concentration nZVI and the DLS size results (Table 2) confirms that large aggregates are not formed immediately following synthesis. The formation of large aggregates is undesirable for nZVI application in the field. Although slow settling was still observed as the stability test proceeded in this study the combination of increased $\tau$ and $T_{\text{Crit}}$ suggest that nZVI synthesized in the presence of the CMC250k polymer would be stable on the order of days in the suspension. This increases the feasibility of lengthy injection periods as nZVI settling in influent vessels would be limited.

### 3.3. nZVI mobility experiments

A series of sand packed column experiments was designed to evaluate the impact of aggregation and settling, nZVI concentration, and pore water velocity on nZVI transport. The results of the nZVI mobility experiments are shown in Fig. 2. Fig. 2a shows the average of 4 replicate experiments with error bars representing 2 standard deviations from the mean for the 0.1 g/L nZVI injected at a pore water velocity of 4 m/day (individual breakthrough curves can be found in supplementary information 1). Fig. 2b–d each shows the breakthrough curve from one experiment. At 4 m/day with 0.1 g/L nZVI, the maximum normalized effluent concentration plateaued at 0.85 (Fig. 2a) within 3 pore volumes following injection. Other studies with low concentration nZVI suspensions report rapid plateau achievement at similar normalized effluent concentrations, but at higher pore water velocities (15–30 m/day) (He et al., 2009; Phenrat et al., 2009; Saleh et al., 2008). At the same pore water velocity (4 m/day) with 2.5 g/L nZVI and 0.8% polymer concentration a higher maximum normalized effluent concentration was achieved due to improved stability with higher polymer content (nZVI C/Co=0.9, Fig. 2b). A previous study using high influent nZVI concentrations (over 2 g/L) achieved normalized effluent nZVI concentrations of over 95% (Phenrat et al., 2009) using pore water velocities of 27 m/day. The good nZVI mobility was attributed to electro-steric repulsion between particle and collector provided by the adsorbed polymer coating on nZVI. In addition to using higher pore water velocities than those in this study different nZVI synthesis and stabilization methods were used which could result in different nZVI stability and retention.

As the pore velocity was decreased, to 2 m/day and 0.25 m/day with an influent nZVI concentration of 2.5 g/L, normalized effluent concentrations at 1 pore volume were similar to the 4 m/day experiment (Fig. 2c and d). A previous column study that used post-synthesis stabilized nZVI at a pore water velocity of 2.3 m/day reported a normalized breakthrough of 0.6–0.7 for low concentration nZVI (Tiraferri and Sethi, 2009), although a nonionic polymer was used to stabilize the nZVI, making comparison difficult.

---

**Fig. 2.** Experimental breakthrough curves and model fits for a.) 0.1 g/L nZVI at $v_p = 4$ m/day, b.) 2.5 g/L nZVI at $v_p = 4$ m/day, c.) 2.5 g/L nZVI at $v_p = 2$ m/day, d.) 2.5 g/L nZVI at $v_p = 0.25$ m/day. The injection period for each experiment has been included in the time bars.
At a pore water velocity of 4 m/day (Fig. 2b) and a 5 h or 8 PV nZVI injection period no significant decline in effluent C/C₀ with pore volumes flushed was observed. In contrast, at pore water velocities of 2 m/day and 0.25 m/day (Fig. 2c and d) C/C₀ decreased with pore volumes flushed, with greater decreases for the 0.25 m/day case. Similar to the 2 m/day results with 2.5 g/L nZVI, declining C/C₀ with pore volumes flushed was observed at later time during the 4 m/day tests with 0.1 g/L nZVI (Fig. 2a). Consideration of the stability of the nZVI suspensions, as indicated by the settling curves (Fig. 1), indicates that significant settling and aggregation of the 2.5 g/L nZVI solution would have occurred after 8 h. As a result, the mobility experiments with injection periods exceeding 8 h (i.e. the 0.25 and 2 m/day tests) would have involved significant aggregation and settling of nZVI in the influent reservoir. This would cause decreasing influent nZVI concentrations, leading to decreasing effluent nZVI concentrations with time. The 0.1 g/L nZVI suspension was less stable than the 2.5 g/L nZVI suspension as significant aggregation and settling occurred after 2 h. As this is less than the 5 hour injection period for 4 m/day injection velocity, the declining effluent concentrations for the 4 m/day 0.1 g/L nZVI case were also likely due to aggregation and settling in the influent reservoir. This will be further explored through numerical modeling.

Few studies to date have evaluated nZVI mobility with residence times and injection periods sufficient to observe the impact of settling. Johnson et al. (2009), studying the mobility of nZVI stabilized with natural organic matter (NOM), observed rapid nZVI settling in 5 min during a stability test using 1 g/L nZVI. The nZVI was freshly suspended before injection yet significant nZVI retention was reported during column experiments, increasing as pore water velocity decreased. As the pore water velocity decreased the residence time increased from 2.5 min, an insufficient amount of time to expect significant settling, to 25 min wherein aggregation and settling may have occurred. Johnson et al. (2009) used a pulse injection (2 mL) volume, so the effects of aggregation and settling in the influent reservoir were not evaluated, however they presented the first experiments with sufficient residence time to allow for significant aggregation and settling which may have contributed to retention.

Column experiments evaluating the mobility of nZVI modified with guar gum (Tiraferrri and Sethi, 2009) utilized relatively low pore velocities (vₚ = 2.3 m/day and 12 m/day) and reported effluent C/C₀ values between 0.57 and 0.87. They observed declining effluent concentrations even when the influent was agitated, although the experiments were performed at high ionic strength which may have caused electrostatic double layer suppression and aggregation and settling in the influent reservoir in spite of the mixing. Tiraferrri and Sethi (2009) suggest that declining effluent concentrations were due to filter ripening and did not consider the stability of the particles and influent aggregation and settling as a contributing factor. However, an earlier study of 0.5 g/L nZVI stabilized with guar gum reported a low characteristic time of settling, τ = 5230 s (Tiraferrri et al., 2008), settling 25 times faster than nZVI in this study. This suggests that aggregation and settling that was observed by Tiraferrri et al. (2008) in stability tests may have occurred in the column experiments performed by Tiraferrri and Sethi (2009) resulting in declining effluent C/C₀ as they used the same guar gum stabilized nZVI formulation.

In contrast to the decreasing effluent concentrations observed over the duration of injection in this study (e.g. Fig. 2a, reaching a peak C/C₀ value of 0.85, declining to 0.75), increasing effluent nZVI concentrations have been observed in at least one other set of column experiments (Raychoudhury et al., 2010). These researchers performed nZVI column experiments over an 11 h injection period with only moderate mixing applied to the influent reservoir to prevent settling. Raychoudhury et al. (2011) speculate that the increasing effluent concentration was due to aggregation of nZVI particles during the period of injection. This result follows from the collector efficiency relationship of Tufenkji et al. (2004) that predicts decreased collector efficiency (and thus increased mobility) with increasing particle size, in the particle size range studied here. Increasing effluent concentrations were observed in the current study for the first 3 pore volumes of the 0.1 g/L nZVI injection (Fig. 2a) because the collision efficiency (ηb) from the Tufenkji and Elimelech (2004) correlation is at a minimum when particle size is 500 nm (see Fig. S7, Supporting Information). The time to inject 3 PV in the current study is similar to the duration of the experiments performed by Raychoudhury et al. (2011) in which increasing effluent concentrations were observed. This highlights an important shortcoming in many column experiments. It is important to consider the duration of injection and the influent reservoir conditions that will be used in the ultimate field application to ensure that the column experimental conditions are representative of the field.

### 3.4. Modeling one dimensional column experiments

Results of model calibration are given in Table 3 and Fig. 2a–d. Values of α and dispersivity were calibrated. Calibrations were performed assuming that i) α was independent of velocity (i.e., same α for all velocities) and ii) α was dependent on velocity (i.e., distinct α for each velocity). For the first modeling formulation (No Boundary Decay) the influent nZVI concentration was held constant, consistent with previous modeling studies where the influent solution was continuously sonicated or mixed (He et al., 2009; Phenrat et al., 2009; Tiraferrri and Sethi, 2009). In this case the model predicts a constant effluent concentration following breakthrough (Fig. 2, No Boundary Decay). However, in experiments at 0.1 g/L nZVI and 2.5 g/L nZVI, at the lowest velocity of 0.25 m/day, the effluent concentration decreased with increased pore volumes flushed through the column. Under these conditions the No Boundary Decay model underpredicts effluent concentration initially and overpredicts effluent concentrations at the termination of the nZVI suspension injection. Sticking efficiencies (α) of 0.17 and 0.067 were fit for 0.1 g/L and 2.5 g/L nZVI suspensions, respectively. These α values could also be determined using the assumption of steady-state effluent concentration and application of the steady-state CFT analytical solution. However, as effluent C/C₀ changes with pore volumes flushed, the conditions are inconsistent with the assumptions used in the derivation of a steady-state solution to CFT. Application of CFT using effluent C/C₀ measured at different times, without consideration of changes in C₀, results in α decreasing with time.

The second model formulation (Boundary Decay) incorporates settling through decreases in C₀ with time by applying Eq. (4) with parameters fitted to settling data (Fig. 1). For the
4 m/day experiment with 2.5 g/L nZVI, settling in the influent reservoir does not significantly influence effluent concentrations because the experiment is performed over a short period of time relative to the settling times at 2.5 g/L. For the 0.25 m/day experiment with 2.5 g/L nZVI, settling in the influent reservoir starts to become important towards the end of the 80 h injection period resulting in a 30% decrease in the influent concentration. Inclusion of settling (i.e., boundary decay leading to decreasing C0) in the model results in effluent C/C0 model results that are similar in behavior to those observed in experiments (Fig. 2, Boundary Decay). This also leads to significantly lower values of fitted α (Table 3), suggesting that studies that have not considered settling may be overestimating α.

As nZVI particles were observed to aggregate during the period of time in which the stability test was performed (Fig. 1) the third modeling approach includes both a decaying boundary condition (Eq. (4)) and particle aggregation (Eq. (5)) (Fig. 2, Decay + Aggregation). For 0.1 g/L nZVI this model results in a further decrease in the fitted sticking efficiency (Table 3), however, for 2.5 g/L nZVI the sticking efficiency increased. It should be noted that in both cases the fitted sticking efficiency is still on the same order of magnitude as for the second model (i.e., inclusion of settling) and over an order of magnitude smaller than when both settling and aggregation are neglected. The 0.25 m/day model results in Fig. 2d highlight the impact of aggregation in the influent reservoir. Aggregation does not affect the entire breakthrough curve, but impacts the first 3.5 pore volumes of the injection resulting in improvements to the model fit and a lower RMSE.

The change in nZVI particle size can be significant over the injection times used in this study and for field applications. For example, in the 2.5 g/L reservoir, as particles aggregate and grow in size from 25 nm to 110 nm the collector efficiency (ηp) decreases from 4.8 × 10⁻² to 1.5 × 10⁻², indicating that the larger aggregates should be more mobile than the freshly synthesized nZVI particles. Thus, for nZVI that is not colloidal stable, or for lengthy injection periods like those expected for field scale delivery, it is necessary to determine the appropriate parameters describing aggregation and settling and incorporate these into analyses and modeling.

To investigate trends of α with velocity an additional set of model calibrations was performed in which α was assumed to be dependent on pore water velocity and fitted independently for each 2.5 g/L nZVI experiment (Table 3). Similar to the results presented earlier when settling is included in the conceptual model, the fitted α is lower than the value fitted when settling is neglected (Table 3). The inclusion of aggregation and settling further decreases the fitted value of α with the largest decrease for the lowest pore water velocity. These results suggest that α decreases with decreasing pore water velocity when α is dependent on pore water velocity. Additional simulations were used to demonstrate the sensitivity of the nZVI breakthrough to variations in aggregation and settling (shown as supplementary content Figs. S1–S4). nZVI mobility is strongly dependent on the stability of the influent suspension (Eq. (4)) and the rate of aggregation of nanoparticles (Eq. (5)) but somewhat less sensitive to small changes in the final aggregate size (dp_final).

However, as discussed previously, the stable aggregate size must remain within a particle size range to minimize the collision efficiency (Fig. S7, Supporting Information).

Previous studies have suggested that α may be a function of velocity (Bai and Tien, 1999; Elimelech and O’Melia, 1990; Tiraferri and Sethi, 2009) and more recently fluid shear was proposed as a possible mechanism for explaining nano-sized particle deviation from traditional CFT (Phenrat et al., 2009). In these studies, however, transport parameters were determined using higher pore water velocities and larger colloid particles (higher shear conditions) than this study or shear (mixing) was applied to the influent suspension. In these studies only 2 to 3 pore volumes of nanoparticles were injected, leaving insufficient time to account for the onset of particle settling. From the results of the current study, one may conclude that the bench scale test conditions should replicate, as closely as possible, the intended field scale conditions with respect to pore water velocity and injection time.

4. Summary and conclusions

The experimental approach in this study was designed to be representative of conditions expected at field scale injection...
sites: 1) pore water velocities were typical of field conditions 2) nZVI particles were not sonicated or mixed before they were injected into the sand packed column 3) long nZVI injection periods were used. Under these conditions settling and aggregation of nZVI particles in the influent vessel and during subsurface transport to target contaminant zones are likely to be significant. Analysis of column experiments should incorporate aggregation and settling in the influent vessel and during porous media transport to avoid overestimation of nZVI sticking efficiencies. This requires a model that incorporates settling at the influent boundary and changes when nZVI is given sufficient time to aggregate and settle.

Acknowledgments

Funding for this research project was provided in part by the Ontario Centers of Excellence, the Natural Science and Engineering Research Council (NSERC) of Canada and Dow Chemical. The authors would also like to thank the consultants from CH2MILL Canada Ltd. and AMEC Geomatrix for helpful advice.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jconhyd.2012.11.001.

References


