Enhanced transport of Si-coated nanoscale zero-valent iron particles in porous media

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ABSTRACT
Laboratory column experiments were conducted to evaluate the effect of previously described silica coating method on the transport of nanoscale zero-valent iron (nZVI) in porous media. The silica coating method showed the potential to prevent the agglomeration of nZVI. Transport experiments were conducted using laboratory-scale sand-packed columns at conditions that were very similar of natural groundwater. Transport properties of non-coated and silica-coated nZVI are investigated in columns of 40 cm length, which were filled with porous media. A suspension was injected in three different Fe particle concentrations (100, 500, and 1000 mg/L) at flow 5 mL/min. Experimental results were compared using nanoparticle attachment efficiency and travel distances which were calculated by classical particle filtration theory. It was found that non-coated particles were essentially immobile in porous media. In contrast, silica-coated particles showed significant transport distances at the tested conditions. Results of this study suggest that silica can increase nZVI mobility in the subsurface.

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1. Introduction
Application of nanoscale zero-valent iron (nZVI) represents a progressive subsurface remediation tool [1,2] for the treatment of aquifers contaminated by both organic pollutants and heavy metals.[3–8] In comparison with sub-micron iron particles, nZVI have much higher specific surface area that provides abundant sites for degradation, and results in higher surface reactivity. [9,10] However, high reactivity alone is not sufficient to make nZVI a good remediation agent. One of the greatest challenges of nZVI technology is the successful delivery of iron nanoparticles to the contaminated zone in the subsurface. Processes that affect the mobility of nZVI particles start to occur immediately after its transfer into a suspension and continue during the transport and storage. It has been shown that nZVI particles are produced with a primary size of approximately 50–100 nm. [11–13] Iron nanoparticles then due to their colloidal instability start to aggregate and form secondary particles with sizes approaching the micron scale.[14,15] Colloidal stability depends upon the balance of the repulsive and attractive forces that exist between particles as they approach one another.[16] In the case of nZVI suspension, attractive van der Waals forces and magnetic forces [15] prevail over the repulsive one, thus determining their tendency to aggregate.[17] It is expected that the secondary particles do not exhibit the properties that are expected from ‘true’ nanosize particles.

Many investigations focused on the transport of nZVI demonstrated that nZVI particles do not transport easily in the subsurface and are not delivered for more than few centimetres from an injection well.[14,18,19] Iron nanoparticles injected into the subsurface can colloid or attach to soil grain. The shell of nZVI consisted of iron oxides which have a high affinity for adsorption onto surfaces of soil grains.[20] Natural geochemical conditions (pH and ionic strength) can destabilize nanoparticles and allow aggregation. Formation of aggregates promotes plugging of the porous media, thus affecting the mobility of nZVI due to straining and gravitational sedimentation.[21] To improve nZVI mobility through the subsurface, it is necessary to prevent the formation of large aggregates that tend to be easily filtered and reduce the attachment of nZVI to the soil.[14,22] Surface modification of nZVI can facilitate mobility through the porous media by reducing their affinity to the surfaces of the soil grains and by increasing their colloidal stability.[23]

Suitable modifiers need to have several characteristics. They have to be able to effectively coat nZVI surface, thus preventing aggregation and reducing the attachment to soil grains. They must be also insensitive to variations in
hydrogeochemistry of the aquifer (e.g. pH, ionic strength), [24] be harmless, and easy to dose in field.

Investigations focused on nZVI stabilization have been carried out using, for instance, polyacrylate,[18,25] anionic hydrophilic carbon,[18] polyacrylic acid, [18,25,26] alone or mixed with polyethylene 4-styrenesulphonate,[27] block copolymers,[14] or oil-based microemulsion.[28]

In our recent study,[29] we demonstrated that silica is a suitable coating agent which prevents particles aggregation through electrosteric stabilization. In addition, silica-coated particles were not sensitive to different ionic strengths, which suggested its suitability for subsurface applications. However, stability against aggregation does not demonstrate good mobility in porous media. The most critical factor of nZVI application is the ability to access a contaminant in the subsurface. Investigations focused on the transport of nZVI demonstrated that nZVI does not transport easily in saturated porous media and is not delivered for more than few centimetres from an injection well. Therefore, the objective of this work is to evaluate the effect of silica coating on the mobility of three nZVI commercial products through water-saturated porous media.

2. Materials and methods

2.1. Materials

All chemicals were reagent grade (99 + % pure) and were used as received, including sodium silicate solution (26.5% SiO2, Sigma-Aldrich, Germany), sulphuric acid (96%, Penta Chrudim, Czech Republic), calcium chloride dihydrate (Lachema, Czech Republic), magnesium chloride hexahydrate (Penta, Czech Republic), sodium bicarbonate (Penta, Czech Republic), potassium bicarbonate (Lachema, Czech Republic), and hydrochloric acid (35%, Lachner, Czech Republic). Freshly distilled water (DW) was used in all experiments. Ostion KS acid ion exchange resin was regenerated by subsequent rinsing with DW and 2M H2SO4 solution.

2.2. Iron nanoparticles

Three nZVI commercial products were used within the work – NANOFER 25 (N25), NANOFER 25S (N25S) produced by NANO IRON, Ltd, Czech Republic, and RNIP-10APS (RNIP) produced by Toda Kogyo Corp., Japan. All the three products were delivered in the form of aqueous suspensions with the elementary iron content of 14–18% wt. for N25 and N25S, and 5–17% wt. for RNIP. N25S and RNIP included stabilizing agents, whose characteristics were not provided. To coat the products with silica, the method described in Honetschlagerova et al. [29] was used.

2.3. Particles characterization

Bare and silica-coated N25, N25S, and RNIP were characterized for size by dynamic light scattering using a Zetasizer Nano ZS (Malvern Instruments Ltd., United Kingdom). X-ray powder diffraction (XRD) analysis was used for the identification of nZVI phase composition. XRD data were collected with AXS D8 0-0 powder diffractometer (BRUKER-AXS, Germany). Transmission electron microscopy (TEM) was used to visually identify the morphology of bare and silica-coated N25, N25S, and RNIP. TEM was performed on a TECNAI Spirit G2 (FEI Czech Republic Ltd.) instrument (LaB6 cathode; accelerating voltage of 120 kV; point-to-point resolution of 0.24 nm). A sample was dropped onto a holey-carbon film supported by a copper-mesh TEM grid and dried in air at room temperature.

2.4. Column experiments

Soil used for the column experiments was taken from the sandpit in Libcice nad Vltavou (Czech Republic). Approximately 50 kg of sand collected was dried at room temperature and homogenized in a plastic barrel. The sand was thoroughly cleaned to remove any organic impurities. Natural concentration of iron was determined by the atomic absorption spectrometer Sensaa (GBC Scientific Equipment, Australia) after acid digestion of sand in concentrated HCl. For each column experiment fraction 0–2.5 mm was used. Results from the sieve analysis and soil characterization are provided in the Supporting Information (Figure S1, Table S1, S2). The surface area of the sand was determined using Coulter SA 3100 BET Surface Area Analyser after drying the samples in an inert atmosphere (Beckman Coulter, USA). The sand was cleaned to remove any metal and organic impurities by soaking the sand in 5M HCl for 12 h, rinsing with DW and baking at 400°C for 8 h.

Columns were Plexiglas (4.8 cm inner diameter x 40 cm length). All tubing was Tygon or Teflon. Peristaltic pump (Ismatec 123) was used to feed background electrolyte solution (0.5 mM CaCl2·2H2O, 0.5 mM MgCl2·6H2O, 0.5 mM NaHCO3, 0.5 mM KHCO3) and the nZVI suspensions into the columns. Approximately 1200 g of soil was packed wet in each column, with a target bulk density (soil dry weight in g/volume of soil in mL) of approximately 0.4 g/mL. Pore volume (PV) was determined to as soil moisture and used water for the column packing. Each packed column was flushed with 2 L of background electrolyte solution (evaluated for at
least 11 PV) to remove background turbidity and to provide uniform collector surface charge. The nZVI suspensions with the ionic strength same as background electrolyte suspension were injected in three different Fe particle concentrations (100, 500, and 1000 mg/L) at flow 5 mL/min. The suspensions were continuously bubbled with nitrogen during injection to avoid particle sedimentation. The column was flushed with 1 L of background electrolyte solution after suspension injection. The samples of effluent (corresponding to 1 PV) were collected during the injection of nZVI suspensions, and following flushing with background electrolyte solution and then analysed for total Fe content. Iron concentration in the effluent was determined using the atomic spectrometer Sensaa (GBC Scientific Equipment, Australia) after acid digestion of samples in concentrated HCl.

In this work, sodium chloride (NaCl) was used as non-adsorbing and non-retarded tracer. NaCl was dissolved in DW at a concentration of 1 mM. The tracer was continuously pumped into the column till the effluent concentration is equal to the influent. NaCl was detected by continuously measuring the conductivity at the effluent.

All column experiments were made in duplicate and the elution data are expressed as the mean of two replicate data. Parameters of column experiments are provided in the supporting information (Table S3).

2.5. Modelling nZVI transport using colloidal filtration theory

Column experiments were modelled using traditional colloid filtration. The classic filtration theory assumes that the theoretical single collector efficiency ($\eta_0$) is the sum of the contact efficiencies due to interception ($\eta_i$), sedimentation ($\eta_s$), and diffusion ($\eta_d$) (Equation (1)):

$$\eta_0 = \eta_i + \eta_s + \eta_d.$$  

Essentially, $\eta_0$ is the probability that a particle will collide with the collector grain through one of the three transport mechanisms, considering system hydrodynamics, particle size, and density can be rewritten using Equation (2):

$$\eta_0 = \frac{3}{2} \left( \frac{d_p}{d_c} \right)^2 + \left( \frac{\rho_p - \rho}{\rho} \right) g d_p^2 \frac{\mu d_p^2 v_0}{18 \mu_0} + \frac{0.9}{\mu d_p d_c v_0} \left( \frac{kT}{\mu d_p d_c v_0} \right)^{2/3},$$  

where $d_p$ is particle diameter, $d_c$ is collector (grain) diameter, $\rho_p$ is particle density, $\rho$ is fluid density, $\mu$ is fluid viscosity, $v_0$ is fluid velocity, $T$ is absolute temperature, and $k$ is the Boltzmann constant.

The traditional model does not consider the influence of hydrodynamic (viscous) interactions and van der Waal’s forces. To accurately predict colloid filtration, Rajagopalan and Tien [30] introduced a semi-empirical equation for $\eta_0$ by solving numerically the trajectory equation for non-Brownian particles. Tufenkji and Elimelech [31] further developed this traditional model considering a range of particle collector interaction energies (see supporting information S1).

The transport of colloids in subsurface is usually studied and modelled by using data from laboratory column experiments. One of the difficulties in modelling and optimizing the transport of materials such as nZVI is heterogeneity of collector grains. To represent the heterogeneity of the porous media, soil parameters such as grain size distribution, porosity, and hydraulic conductivity can be used instead of $d_c$. The relationship between grain size distribution and hydraulic conductivity has been studied by many scientists.[32,33] Mehrabi and Milne-Home [34] modified Equation (2) and replaced $d_c$ by $d_{10}$, which generally refers to effective size of grain in sample. Martin et al. [35] found that $d_{10}$ is the best characteristic diameter for filtration calculations for heterogeneous media.

3. Result and discussion

3.1. Particles characterization

The hydrodynamic diameter ($D_h$) of bare N25, N25S, and RNIP ranged from 1000 to 3500 nm, which indicated the presence of aggregated particles. The treatment with silica decreased the particle $D_h$ to values 100–200 nm.

The identification of nZVI phase composition was performed using XRD analysis. The samples were lyophilized before the analysis to avoid destroying their physical structure and oxidation during the drying on air. The XRD examination of N25 and N25S indicated two phases, $\alpha$-Fe and $Fe_3O_4/\gamma-Fe_2O_3$, where N25 exhibited $\alpha$-Fe content of 96% wt. and $Fe_3O_4/\gamma-Fe_2O_3$ content of 4% wt. and N25S $\alpha$-Fe content of 92% wt. and $Fe_3O_4/\gamma-Fe_2O_3$ content of 8% wt. The same two phases were indicated also for RNIP, which showed $\alpha$-Fe content of 28% wt. and $Fe_3O_4/\gamma-Fe_2O_3$ content of 78% wt.

Figure 1 presents TEM images that illustrate morphology and particle size of non-coated (Figure 1(a)) and silica-coated (Figure 1(b)) nZVI particles. Although the morphology of nZVI is controlled by production process, TEM images of non-coated N25, N25S, and RNIP appeared similar to one another. The individual particles (10–100 nm) have irregular shape and visible core shell structure, where the shell is probably due to iron oxide(s), while the core is attributed to Fe$^0$. TEM images also demonstrate that in case of non-coated
N25, N25S, and RNIP, most particles formed aggregates which reach the size of microns, and that the coating with silica led to disintegration of these aggregates.

3.2. Column experiments

A series of sand-packed column experiments was designed to evaluate the effect of the silica coating on the mobility of N25, N25S, and RNIP through water-saturated porous media. Transport of non-coated and silica-coated particles through water-saturated sand-packed columns was evaluated at three Fe particle concentrations (100, 500, and 1000 mg/L), low ionic strength (2 mM), and pore-water velocity \(\sim 4\) m/day to simulate injection into contaminated sandy aquifer.

In the case of non-coated particles, only clear solution passed through the columns and most of the particles were observed to accumulate on the bottom section (the entrance end) of the columns, which became visibly black (Figure S2). This indicates that non-coated particles were immobile because they aggregate rapidly and deposit on the porous media.

The elution of silica-coated particles was much higher. Black particles of coated nZVI moved up in the column and the black colour was clearly visible in the effluent. Subsequent analysing for Fe showed increasing concentration in the effluent after the injection of 2 PV. Figure 2 shows breakthrough curves (BTCs) for silica-coated N25 (Figure 2(a)), N25S (Figure 2(b)), and RNIP (Figure 2(c)). BTCs of non-coated nZVI are not shown because no iron was detected in the effluent. BTCs are plotted as the relative concentration of Fe \((C/C_0)\) in the effluent, versus PV. A tracer (NaCl 1 g/L) was used for control and baseline measurement. The tracer BTC shown in Figure 2 has symmetrical shape and no tailing, indicating that the physical non-equilibrium process, such as rate-limited mass transfer into regions of immobile water and preferential flow paths, was not presented during the transport. Column experiments for Si-N25 showed a relatively small fraction of Fe in the effluent, indicating the aggregation and deposition of the particles on the porous media. The maximum value achieved by the ratio between eluted and injected Fe concentration \((C/C_0)\), in the case of column A (100 mg/L) is 0.50, in the case of column B (500 mg/L) is 0.17, and in the case of column C (1000 mg/L) is 0.09, indicating that the deposition onto porous media increases with increasing particle concentration. Although only a small fraction of particles was detected in the effluent, the results indicate that silica coating enhances the transport of N25 through porous media. For Si-N25S column A (100 mg/L), iron concentration in the effluent reached the maximum \((C/C_0 = 0.87)\) in 6 PV, compared to 3 PV of the tracer. This shows slight retardation of Si-N25S (100 mg/L) in the column. In contrast, the relative concentration \((C/C_0)\) in the effluent from columns B and C (500 and 1000 mg/L) is no more 0.23 and 0.09, respectively. This finding indicates that Si-N25S may also undergo some aggregation within the column. This aggregation and further deposition of Si-N25S on porous media increased with increasing particle concentration. However, silica is found to significantly enhance N25S mobility through the saturated packed column.

For Si-RNIP the maximum values achieved by the ratio between eluted and injected iron concentration \((C/C_0)\), in the case of column A (100 mg/L) is 0.91, in the case...
of column B (500 mg/L) is 0.31, and in the case of column C (1000 mg/L) is 0.14. These findings show that the transport of silica-coated RNIP depends highly on the particle concentration. The elutability decreases as the particle concentration increases. This suggests that at higher concentration a higher percentage of silica-coated RNIP particles may accumulate within the columns. The results indicate that silica coating is necessary for reasonable transport of RNIP, even at low ionic strength.

3.3. Usability in the remedial process

When injected into natural aquifer, a considerable amount of the injected nZVI mass needs to be transported from the injection point to the contaminated zone. Field application of nZVI usually requires the nZVI transport to be at least on the order of 10 m or more away from the injection point. Small-scale column experiments are commonly used to evaluate nZVI mobility under a range of representative subsurface conditions. One method to compare experimental results has been to compare the attachment efficiency $\alpha$. Assuming clean bed condition for nZVI in heterogeneity porous media, $\alpha$ is estimated from column breakthrough data using Equation (3):

$$\alpha = - \frac{2d_{10}}{3(1-\varepsilon)\eta_0 L} \ln \left( \frac{C}{C_0} \right),$$

where $d_{10}$ is effective collector (grain) diameter, $\varepsilon$ is packed bed porosity, $\eta_0$ is single collector efficiency, $L$ is the length of the column, and $C_0$ and $C$ are influent and effluent particle concentrations. Sticking coefficient $\alpha$ is estimated.

Figure 2. BTCs of (a) Si-N25, (b) Si-N25S, (c) Si-RNIP at three particle concentrations (column A = 100 mg/L, column B = 500 mg/L, and column C = 1000 mg/L) at low ionic strength (2 mM) obtained from the samples taken during the injection of Si-nZVIs and following flushing with background (BG) electrolyte solution.
depends on surface charge and other surface interaction forces and on hydrogeochemical conditions evaluated, and expresses the probability that a particle–collector collision results in immobilization of particles.[45]

This work compares the mobility of three commercial nZVI products and evaluates the effect of the silica coating on their transportability through porous media using data obtained within the column experiments. Moreover, it indicates the significance of the results of this work in comparison to previous studies.[18,42] The data obtained are summarized in Table 1. First, non-coated N25, N25S, and RNIP are essentially immobile in porous media. This limited transport may be caused by the rapid aggregation of non-coated particles which was indicated during the particles characterization. It has been shown that nanoparticles with high magnetic moments such as nZVI exhibit poor mobility in porous media due to rapid particle aggregation.[46] Furthermore, experiments showed that silica-coated N25, N25S, and RNIP can be mobile under specific groundwater conditions; however, particle concentration will significantly affect their mobility in porous media. Although the real soil was used within the experiments, it is impossible to precisely predict the transport distance of nZVI in the subsurface. Moreover, there are some limitations to applying standard deep-bed filtration models in natural systems.[38] Therefore, α values determined in this study can be used to estimate transport distance for Si-N25, Si-N25S, and Si-RNIP in an unconsolidated sandy aquifer.

In general, a smaller α implies a longer transport distance for nanoparticles. The calculated α for Si-N25 are 0.0077 (100 mg/L), 0.0196 (500 mg/L), and 0.0276 (1000 mg/L). Although being coated with similar amount of silica,[29] highly concentrated suspensions showed higher α values. It is not surprising that α values increase with increasing particle concentrations. Experience shows that at high particle concentrations, particle–grain interactions and aggregation in porous media play an important role.[14,38,47,48] Increasing nZVI concentration results in closer range interaction forces between particles, and thus increasing aggregation. Greater attractive forces occurred between particles, leading to aggregate formation and retention, due to increased size, dispersivity, and magnetic Fe^0 content. [38] These attractive forces were found to be sufficient to prevail over any fluid drag forces that would otherwise cause breakage or dislodging of aggregates. Furthermore, once aggregates are formed and retained in a column, they subsequently attract additional particles, resulting in straining. In general, straining occurs when the pore throats between grains are too small to allow the passage of particles. The same phenomenon was observed also in the case of Si-N25S and Si-RNIP. In general, α ranged from 0.0014 to 0.0077 for particle concentration 100 mg/L, from 0.0141 to 0.0279 for particle concentration 500 mg/L, and 0.0231 to 0.0485 for particle concentration 1000 mg/L. Reported sticking coefficient for non-coated and coated nZVI varies based on used porous media, type of nZVI, and the hydrogeochemistry of the system (e.g. pore-water velocity, ionic strength). Yang et al. [26] tested the mobility of non-coated and Poly(acrylic acid) (PAA)-coated Fe(B) particles (particle concentration 2.5 g/L) in vertical silica sand/soil columns. The calculated α value for non-coated nZVI was 0.5628 and for PAA-coated particles 0.1078. Lower α for Fe(B)/PAA nanoparticles (particle concentration 5 g/L) in silica sand/soil columns in comparison to non-coated particles was also observed by Schrick et al.[18] They reported α of 0.14 for non-coated particles and 0.05 for Fe(B)/PAA particles in clay-rich soil. Tiraferri and Sethi [40] tested the mobility of non-coated RNIP, RNIP-10AP, and guar-gum-coated RNIP (particle concentration 154 mg/L) in sand columns. The non-coated RNIP was immobile in tested conditions. They reported α of 0.107 and 0.060 for non-coated RNIP-10AP and guar-gum-coated RNIP, respectively. In the present work, as shown in Table 1 a much lower sticking coefficient was obtained for silica-coated nZVIs. Phenrat et al. [38] investigated the mobility of poly(styrene sulphonate) (PSS) RNIP with three different particle size distributions at different particle concentrations through 25.5 cm long silica sand columns (d_p = 0.3 mm, 5 mM NaCl/5 mM NaHCO3, pore-water velocity of 3.2 × 10^-4 m/s). The reported α were for fraction 1 (6% of particles average D_H = 45 nm, 94% of particles average D_H = 328 nm) of 0.012 and 0.066, for fraction 2 (40% of particles average D_H = 25 nm, 60% of particles average D_H = 367 nm) of 0.005 and 0.011, and for fraction 3 (average D_H = 25 nm) of 0.002 and 0.0007, for particle concentrations 30 mg/L and 6 g/L, respectively. The reported α values [38] for fraction 1 are much lower than those for silica-coated RNIP particles presented in this study (Table 1). However, this fraction contained ~0.8% of particles by mass, columns were 25.5 cm long compared to 40 cm long used in this study, and they used higher pore-water velocity during the experiment. Moreover, PSS is not a natural component of the subsurface as the silica is, and in some cases may cause adverse health effects.[49] The results indicate that the silica coating improved mobility of N25, N25S, and RNIP by providing electrosteric stabilization. However, magnetically induced aggregation and subsequent straining may result in retention of silica-coated particles with increasing particle concentration.

To estimate the transport distance over which 99% removal of nanoparticles would occur as a function of
subsurface characteristics and the sticking coefficient, the single collector efficiency approach [48] and deep-bed filtration theory were used. Using a determined in column experiments and the column properties (e.g. $d_{10}$, $\varepsilon$, $\eta_0$), the filtration travel length required to remove 99% of the particles, where $C/C_0 = 0.01$, was calculated using Equation (4):

$$L_T = -\ln \left( \frac{C}{C_0} \right) \frac{2d_{10}}{3(1-\varepsilon)\alpha \eta_0}.$$  

The estimated transport distances at which 99% of the particles will be filtered are summarized in Table 1. The best transportability in tested soil revealed Si-RNIP at particle concentration 100 mg/L. As indicated from values, the transport distances decrease with increasing particle concentrations. As shown in Table 1, calculated travel distances of Si-N25, Si-N25S, and Si-RNIP at particle concentration 1000 mg/L are less than 1 m. In comparison with the results obtained by other authors, the calculated travel distances determined within this study are much higher than those presented so far in the literature for the mobility of iron nanoparticles in sand columns. It should be noted that velocities used in the presented experiments (~4 m/day) are smaller and more similar of natural groundwater, than those chosen by other authors.[40,50] Moreover, predicted filtration lengths calculated based on filtration theory are usually smaller than distances associated with experimental deposition profiles. Therefore, travel distances of Si-N25, Si-N25S, and Si-RNIP in the environment should be believed to be higher than those predicted from the calculations.

### 4. Conclusions

Because of the potential reducing power, nZVI has found increasing environmental applications. However, both laboratory and field data show limited mobility of nZVI in a porous media under the natural groundwater conditions. We have examined the effect of a previously reported stabilization method [29] on the mobility of three nZVI commercial products. The results obtained from the investigation showed strongly enhanced mobility of silica-coated nZVIs compared to non-coated particles. Non-coated NANOFER 25, NANOFER 25S, and RNIP-10APS were essentially immobile in porous media. The column experiments showed that silica-coated nZVI can transport through the column; however, retardation effects were observed. For silica-coated particles and injection condition evaluated here (pore-water velocity ~4 m/day, ionic strength 2 mM), transmission through 40 cm column was the best for particle concentration 100 mg/L (50–91%). This value decreased with increasing particle concentration and was 9–14% for particle concentration 1000 mg/L, suggesting transport distance ~1 m. The concentrations typically applied in the field ranged from 1 to 10 g/L.[50,51] The results obtained from the study showed that using highly concentrated silica-coated nZVI slurries could make nZVI emplacement over large contaminated regions impractical. However, the calculated travel distances determined within this study are still much higher than those presented so far in the literature for the mobility of iron nanoparticles in sand columns.[25,26,38] Although laboratory experiments have indicated enhanced stability, and mobility of silica-coated nZVIs, it is difficult to transfer obtained

| Suspension type | Particle concentration (mg/L) | Particle $D_{10}$ (µm) | Single collector efficiency ($\eta_d$) | Pore-water velocity (m/s) | Maximum $C/C_0$ | Attachment efficiency ($\alpha$) | Filtration length $L_T$ (m) $^a$ | $L_{T10}$ | $L_{T1}$ |
|----------------|-----------------------------|------------------------|-------------------------------------|-------------------------|----------------|-----------------------------|-----------------------------|---------|---------|
| N25            | 100                         | 5                      | 335.1178                           | $5.0 \times 10^{-5}$   | 0              | --                          | --                          | --      | --      |
|                | 500                         | 5                      | 351.3290                           | $4.8 \times 10^{-5}$   | 0              | --                          | --                          | --      | --      |
| Si-N25         | 100                         | 0.18                   | 0.4172                             | $5.0 \times 10^{-5}$   | 0.5            | 0.0077                      | 2.66                        | 0.40    | 0.06    |
|                | 500                         | 0.18                   | 0.4172                             | $5.0 \times 10^{-5}$   | 0.17           | 0.0196                      | 1.04                        | 0.16    | 0.02    |
| N2SS           | 100                         | 3.5                    | 157.4211                           | $4.8 \times 10^{-5}$   | 0              | --                          | --                          | --      | --      |
|                | 500                         | 3.5                    | 173.3836                           | $5.2 \times 10^{-5}$   | 0              | --                          | --                          | --      | --      |
| Si-N2SS        | 100                         | 0.19                   | 0.4420                             | $5.2 \times 10^{-5}$   | 0.87           | 0.0014                      | 13.23                       | 1.09    | 0.30    |
|                | 500                         | 0.19                   | 0.4686                             | $4.8 \times 10^{-5}$   | 0.23           | 0.0141                      | 1.25                        | 0.19    | 0.03    |
| RNIP           | 100                         | 1.1                    | 18.3396                            | $4.6 \times 10^{-5}$   | 0              | --                          | --                          | --      | --      |
|                | 500                         | 1.1                    | 17.5271                            | $4.8 \times 10^{-5}$   | 0              | --                          | --                          | --      | --      |
| Si-RNIP        | 100                         | 0.12                   | 0.1960                             | $4.8 \times 10^{-5}$   | 0.91           | 0.0023                      | 19.53                       | 2.94    | 0.45    |
|                | 500                         | 0.12                   | 0.1960                             | $4.8 \times 10^{-5}$   | 0.31           | 0.0279                      | 1.57                        | 0.24    | 0.04    |
|                | 1000                        | 0.12                   | 0.1869                             | $5.0 \times 10^{-5}$   | 0.14           | 0.0485                      | 0.94                        | 0.14    | 0.02    |

$^a$Filtration length required to remove 99% of particles.
$^b$Filtration length required to remove 50% of particles.
$^c$Filtration length required to remove 10% of particles.

Table 1. Complete calculations for attachment efficiency, single collector efficiency, and filtration length for all tested suspensions.
results to aquifer system. Thus, the feasibility for application of silica-coated nZVI in groundwater remediation needs to be further tested in the field.

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