Carbonate minerals in porous media decrease mobility of polyacrylic acid modified zero-valent iron nanoparticles used for groundwater remediation

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A B S T R A C T

The limited transport of nanoscale zero-valent iron (nZVI) in porous media is a major obstacle to its widespread application for \textit{in situ} groundwater remediation. Previous studies on nZVI transport have mainly been carried out in quartz porous media. The effect of carbonate minerals, which often pre- dominate in aquifers, has not been evaluated to date. This study assessed the influence of the carbonate minerals in porous media on the transport of polyacrylic acid modified nZVI (PAA-nZVI). Increasing the proportion of carbonate sand in the porous media resulted in less transport of PAA-nZVI. Predicted travel distances were reduced to a few centimeters in pure carbonate sand compared to approximately 1.6 m in quartz sand. Transport modeling showed that the attachment efficiency and deposition rate coefficient increased linearly with increasing proportion of carbonate sand.

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1. Introduction

The application of nanoscale zero-valent iron (nZVI) for \textit{in situ} groundwater remediation has received increasing attention as a beneficial and novel remediation technique; nZVI is a strong reducing agent capable of rapid dechlorination of chlorinated organics and immobilization of heavy metals in contaminated groundwater (Grieger et al., 2010; Karn et al., 2009; Zhang, 2003). A precondition for effective nZVI application is its successful delivery to the contaminated source zones. This has proved to be a major obstacle to widespread utilization of this technology (O’Carroll et al., 2013; Tratnyek and Johnson, 2006). The reported transport distances for nZVI-based particles range from centimeters (Schrick et al., 2004) to hundreds of meters (Saleh et al., 2008) in sand columns (predicted using colloid filtration theory), to just a few meters measured in a field demonstration in fractured sandstone (Zhang and Elliott, 2006).

The limited nZVI transport in porous media is due to particle aggregation and deposition onto the aquifer grains. Both of these processes depend on the particle properties, such as size, composition, ZVI content, and surface charge (Phenrat et al., 2009, 2007), as well as on the site-specific hydrochemical and hydrogeological parameters. These include the groundwater chemistry (i.e., water composition, ionic strength, and pH; Kim et al., 2012; Phenrat et al., 2010a,b; Saleh et al., 2008) and the properties of the aquifer material (such as grain size distribution, surface charge heterogeneities, and mineral and organic matter content, He et al., 2009; Kim et al., 2012; Phenrat et al., 2011; Song et al., 2011). Although the previous studies showed the effects of certain parameters on nZVI transport, predicting nZVI mobility in a specific type of porous media is still not possible, since the most influential chemical and physical heterogeneities have not been identified yet.

Particle aggregation and deposition can be reduced by nZVI surface modification with polymers, polyelectrolytes, and surfactants, or by incorporation of nZVI into silica or activated carbon matrices (Bleyl et al., 2012; Mackenzie et al., 2012; Phenrat et al., 2010a; Zhan et al., 2008). Adsorbed anionic polyelectrolytes, such as polyacrylic acid (PAA), impart a negative surface charge on the nZVI and provide electrostatic double layer repulsions and electrostatic repulsions to counter attractive magnetic and van der Waals forces (Phenrat et al., 2010a; Raychoudhury et al., 2012; Schrick et al., 2004). The repulsive forces hinder nZVI deposition onto negatively charged aquifer material, which is prevalent in most subsurface media (Kim et al., 2012), therefore promoting nZVI mobility.
Even though nZVI transport can be promoted by PAA-modification in negatively charged quartz media, it is still affected by the physical and chemical heterogeneities encountered in aquifers, including variations in grain size, surface charge, and type and content of natural organic matter and clay. Studies on the transport of latex and silica microspheres have demonstrated that chemical heterogeneities can be a major factor controlling colloid deposition in porous media (Chen et al., 2001; Johnson et al., 1996; Yang et al., 2010). The same effect is expected for much denser nZVI particles used for remediation. Previous studies investigating nZVI transport were mainly carried out in mineralogically uniform media and quartz as a model aquifer material (Kim et al., 2009; Raychoudhury et al., 2012; Saleh et al., 2008). In addition, the presence of kaolinite clay in porous media at 2 wt.% has been shown to significantly decrease the nZVI mobility, which was attributed to heteroaggregation between kaolinite and nZVI particles and charge heterogeneities on the clay surface (Kim et al., 2012). Carbonate minerals are common constituents of aquifers (e.g., Borden Aquifer, Mackay et al., 1986) and they can (locally) comprise more than 80% of the porous aquifer (Geological Survey of Austria, 1994). What effect these minerals exert on the transport of nZVI has not been addressed in any study to date.

In this study we have evaluated the effect of carbonate minerals in porous media on the transport of commercially available PAA-nZVI (NANOFER 25S) for five model porous media, starting from pure quartz sand and systematically increasing the carbonate sand content. The comparison between the transport in homogeneous (pure quartz) media and in media with mineralogical heterogeneities caused by the presence of carbonate has been performed in well-controlled column experiments. The experimental transport data were analyzed and modeled using colloid filtration theory and a one dimensional convection–dispersion equation. A detailed characterization of the NANOFER 25S suspension was conducted to support these calculations. To our knowledge, this is the first study investigating the transport of commercially available NANOFER 25S particles, including two prevailing aquifer materials, quartz and carbonate, under injection conditions applied in groundwater remediation.

2. Material and methods

2.1. Nanoscale zero-valent iron particles

PAAS-nZVI (NANOFER 25S) was supplied by NANOIRON, s.r.o. (Czech Republic) in form of an aqueous suspension (pH 11) with a mean primary particle diameter below 50 nm and a total iron concentration of ~ 20 wt.% (as given by the producer). The particles are modified by an inorganic iron oxide layer and an organic PAA coating (Kadar et al., 2011). The production method for NANOFER 25S certainly differs from that of nZVI commonly reported in scientific literature (reactive iron nanoparticles, RNIP, Toda Kogyo, Japan or borohydride reduced nZVI particles). The particles are modiﬁed by an inorganic iron oxide layer and an organic PAA coating (Kadar et al., 2011). The production method for NANOFER 25S certainly differs from that of nZVI commonly reported in scientific literature (reactive iron nanoparticles, RNIP, Toda Kogyo, Japan or borohydride reduced nZVI particles).

These different production methods will likely result in different structural configurations of particles, size distributions, and specific surface area (Mueller and Nowack, 2010: U.S. EPA, 2005), the properties that can affect the deposition and transport of nZVI particles.

2.2. Porous media

Standard Ottawa sand (20–30 mesh, 0.4–0.85 mm, extra pure, Fisher Scientiﬁc, USA) was used as the quartz porous medium. Limestone (with ~97% CaCO₃, ~5% MgCO₃, and ~1% aluminum and iron oxides, Table S1, Supplementary Data) was obtained from the Dachstein Formation (Lower Austria, Austria). The limestone was crushed with a jaw crusher and then sieved to between 0.5 and 1 mm, in order to obtain a size fraction as similar as possible to that of the Ottawa sand.

2.3. Preparation and characterization of PAAS-nZVI suspension

The PAAS-nZVI stock suspension (~8 g L⁻¹) was prepared bysuspendine the aqueous suspension of NANOFER 25S (50 g) provided by the producer in a 1 mM NaHCO₃ solution (pH 8.3), using an ultrasonic bath (Sonorex RK 106, Ø 240 mm, 130 mm high, 120 W indicated power, Bandelin electronic, Germany). Suspensions for the transport experiments and for particle characterization were prepared by further dilution of the PAAS-nZVI stock suspension in 1 mM NaHCO₃ to the desired concentrations. The total iron (Fe) content was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 5300DV, PerkinElmer, USA) after acid digestion.

Morphology and primary particle size were examined using scanning electron microscopy (SUPRA®40 FE-SEM, Carl Zeiss, Germany). Aggregate size of PAAS-nZVI in suspension was further determined by analyzing the obscuration time (pulse length) of a particle in a suspension being illuminated by a rotating laser beam, with a CCD camera positioned behind the measurement vessel as the detector (time of transition principle, 0.6–300 μm operation range, 0.2 μm resolution, limit of detection: 0.6 μm). Particle sedimentation was monitored by measuring the transmittance of monochromatic light (wavelength 880 nm) from the suspension (TurbiScan LAB, Quantachrome, Germany, Comba and Sethi, 2009), acquiring the transmittance data for 25 min over the entire height of the sample suspension (~55 mm) in steps of 40 μm.

Electrophoretic mobility and particle size were determined using dynamic light scattering and laser Doppler anemometry (Zetasizer Nano ZS, Malvern Instruments, UK) in the supernatant after two hours sedimentation. The electrophoretic mobility was determined as a function of pH (pH 2–10) and in the presence of monovalent and bivalent cations (in 1 mM NaNO₃ and 0.3 mM CaCl₂, respectively). The electrophoretic mobility was converted into apparent zeta potential by applying the Smoluchowski relationship.

2.4. Preparation and characterization of porous media

The quartz sand (QS) was acid washed before use, as described by Yang et al. (2010), in order to remove metal oxide impurities from the grain surfaces. The carbonate sand (CS) was rinsed with deionized water to remove any soluble solids and fine materials. Carbonate and quartz grains were mixed in varying proportions to obtain five different classes of porous media: (1) pure quartz sand (100% QS), (2) 90:10% QS:CS, (3) 50:50%QS:CS, (4) 10:90% QS:CS, and (5) pure carbonate sand (100% CS).

The streaming potentials of the porous media were measured with an Electrokinetic Analyzer (SurPASS, Anton Paar, Austria) equipped with a cylindrical cell. The streaming potential was determined by circling the background solution (1 mM NaCl buffered saline, pH 7.4) in alternate directions for a period of ~15 min prior to each measurement. The streaming potential was converted into zeta potential using the Smoluchowski equation.

2.5. Column experiments

Transport studies were performed in borosilicate glass columns (1 cm i.d., 10 cm length, Ommunft, Germany). A peristaltic pump (Ismatec, Germany) was used to feed background electrolyte and the PAA-nZVI suspension into the columns. In order to confirm the effects of different injection velocity for these particles, two experiments with different velocities that correspond to the injection velocities commonly applied at field sites (Phenrat et al., 2010a), 3 × 10⁻⁶ m s⁻¹ and 6 × 10⁻⁶ m s⁻¹ were performed in pure quartz and pure carbonate sand. The injection velocity of 6 × 10⁻⁶ m s⁻¹ was chosen for the set of transport experiments involving five porous media with increasing carbonate content.

Each column was wet packed with porous media until ~8 cm height, and then flushed with at least ten pore volumes with a 1 mM NaHCO₃ background solution in order to remove background turbidity. Changes in the electrical conductivity and the pH due to dissolution of calcium carbonate are reported in Table S2 (Supplementary Data). A tracer test using NaBr was then conducted, and effluent bromide concentrations were analyzed by ion chromatography (ICS-1000, Dionex, Austria). The sorptivities of the media ranged between 0.38 (in pure quartz) and 0.46 (in pure carbonate). Following elution of the bromide tracer the entire PAA-nZVI suspension containing ~200 mg L⁻¹ total Fe in 1 mM NaHCO₃ was introduced into the columns. In order to prevent aggregation and sedimentation, the particle suspension was sonicated prior to and during the injection (ultrasonic bath, Sonorex RK 106, Ø 240 mm, 130 mm high, 120 W indicated power, Bandelin electronic, Germany). The column effluent was collected every 30 s and analyzed for total Fe. The breakthrough curve for each transport experiment was plotted as the normalized total Fe concentration (C/C₀) versus number of pore volumes. The presented data are the mean results from duplicate measurements.

2.6. Transport models

2.6.1. Colloid filtration theory

Colloid filtration theory (CFT) describes the deposition of particles in a porous medium involving two sequential steps: transport from the fluid to the grains of the medium, and attachment to the grains (Elimelech and O’Melia, 1990). These
processes are described by the single-collector contact efficiency and the attachment efficiency. The single-collector contact efficiency ($\eta_0$), calculated following Tufniski and Elimelech (2004) describes the transport of particles to a collector as a cumulative effect of diffusion ($n_d$), interception ($n_i$), and gravitational sedimentation ($n_s$): $\eta = n_d + n_i + n_s$. The attachment efficiency ($\alpha$) is the proportion of collisions between the particles and collectors that result in attachment. It was calculated empirically using the normalized Fe concentration ($C/C_0$) at the plateau of the dispersion equation (CDE), and afterwards calculated after Kretzschmar et al. (1999) and Tufniski and Elimelech (2004):

$$\alpha = \frac{2d_d}{3(1 - n_d)n_0} \ln\left(\frac{C}{C_0}\right)$$

In Equation (1), $d_d$ represents the average diameter of the collector, $n$ the porosity of the porous medium, and $l$ the length of the column (8 cm in this case). The particle deposition rate coefficient ($k_{CDE}$) was then calculated after Kretzschmar et al. (1999) and Tufniski and Elimelech (2004):

$$k_{CDE} = \frac{v}{l} \ln\left(\frac{C}{C_0}\right) - \frac{3(1 - n)}{2d_d} \eta_0$$

where $v$ is the pore water velocity.

The transport distance ($L_T$) of PAA-nZVI at which 50% and 99.9% of particles are removed ($C/C_0 = 0.5$ and 0.001, respectively) was calculated using the column properties (the average diameter of the collector and the porosity), the single-collector contact efficiency, and the attachment efficiency (Elimelech et al., 1995) as:

$$L_T = \frac{2d_d}{3(1 - n)\eta_0} \ln\left(\frac{C}{C_0}\right)$$

2.6.2. One dimensional transport equation

The transport of particles through a saturated porous media under steady state flow conditions can be described by the convection–dispersion equation (CDE), including a term for first-order particle removal (Kretzschmar and Sticher, 1998):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \frac{v}{l} \frac{\partial C}{\partial x} - k_{CDE} C$$

where $t$ is the elapsed time, $x$ is the travel distance, $D$ is the dispersion coefficient for PAA-nZVI particles, and $k$ is the first-order particle removal rate coefficient. The dispersion coefficient and first-order removal ($k_{CDE}$) values were obtained by fitting the convection–dispersion equation to the PAA-nZVI breakthrough curves, using the velocity applied in column experiments (CXTFIT, STANMOD software, version 2.08.1130). The removal rate coefficient ($k_{CDE}$) was compared to the deposition rate coefficient ($k_{CDE}$) calculated using colloid filtration theory.

Mineralogical variations within the subsurface can be incorporated into the model simulations by considering a two-patch charge heterogeneity. In the patchwise heterogeneity model (PHM) the surface area of the porous media is divided into favorable and unfavorable fractions (Song et al., 1994), which in this study comprise the carbonate and quartz sands, respectively. The heterogeneity parameter $\lambda$ is defined as the proportion of favorable deposition sites in the porous medium, which is in our study equal to the proportion of carbonated sand. The average deposition rate coefficient ($k_{PHM}$) is then expressed as a linear combination of the deposition rates onto pure quartz ($k_{Q}$) and pure carbonate ($k_{C}$) sand (Chen et al., 2001):

$$k_{PHM} = \lambda k_{Q} + (1 - \lambda) k_{C}$$

3. Results and discussion

3.1. PAA-nZVI characterization

The SEM images of the PAA-nZVI particles showed irregularly-shaped aggregates ranging in size from 200 nm to >1 μm (Fig. 1). Irregular shaped particles have been previously observed for other nZVI particles (e.g., RNIP, Toda Kogyo, Japan; Nurmi et al., 2005; Liu et al., 2005). Deviation between the primary particle size given by the manufacturer (<50 nm) and the observed aggregates are a result of particle aggregation and sample preparation, i.e., drying the PAA-nZVI suspension on the grid (Domingos et al., 2009). The SEM images therefore provide the information about the morphology of the primary particles and aggregates, but the estimated aggregate size may not be representative of the actual particle size in the suspension. For that purpose the PAA-nZVI suspension was in addition characterized with the available complementary techniques to obtain a more thorough characterization.

The laser obscuration time measurement of the PAA-nZVI suspension (≈100 mg L$^{-1}$ total Fe in 1 mM NaHCO$_3$, pH 8.3) resulted in a mean particle size of 1.6 ± 1.4 μm. This revealed a predominance of large aggregates in the particle suspension, and also indicated a polydisperse system with a broad particle size distribution. Determination of the dispersion state was further investigated by means of particle sedimentation in the PAA-nZVI suspension (with 200 mg L$^{-1}$ total Fe in 1 mM NaHCO$_3$, pH 8.3). This resulted in a sedimentation rate of 0.35 mm min$^{-1}$ and corresponds to a PAA-nZVI diameter of 1.2 μm of the settled fraction based on Stokes Law (PAA-nZVI density: 7.87 g cm$^{-3}$, fluid density: 1 g cm$^{-3}$, fluid viscosity: 1 kg m$^{-1}$ s$^{-1}$). This size is in agreement with the mean particle size delivered by the laser obscuration time method. The total Fe concentration in the stable fraction (supernatant after 2 h of sedimentation) was a factor of ten smaller (≈20 mg L$^{-1}$) than in the initial suspension, demonstrating that ~90% of the particles had already settled by this time. The hydrodynamic diameter of the stable PAA-nZVI particles determined by dynamic light scattering was 235 ± 3 nm. The zeta potential of these stable PAA-nZVI particles was −41.1 ± 0.5 mV (at neutral pH and in the presence of 1 mM NaHCO$_3$). With decreasing pH the zeta potential increased, reaching the isoelectric point at pH ~ 3 (Figure S1, Supplementary Data). The zeta potential of these particles was additionally measured in the presence of a 0.3 mM CaCO$_3$ background solution, and the particles exhibited a less negative charge over the whole pH range investigated. This indicated that calcium screened the PAA-nZVI surface charge, an effect that has previously been observed for polysaspartate-, triblock copolymer-, and surfactant-modified nZVI particles (Saleh et al., 2008).

3.2. Surface charge of porous media

The streaming potentials for the five classes of porous media (0–100% CS) were determined at a pH of 7.4 and ionic strength of 1 mM. The results showed that the pure quartz sand was negatively charged (−50 mV), with the zeta potential becoming less negative with increasing proportions of carbonate sand (Fig. 2a). Pure carbonate sand carried a weak negative charge under the same experimental conditions (−16 mV, 100% CS, Fig. 2a).

Previous studies have reported that the zeta potential of a heterogeneous porous medium at a given pH is a linear combination of
the zeta potential values of the two original materials (Elimelech et al., 2000; Johnson, 1999). It should therefore be expected that

$$\zeta_{\text{tot}} = \lambda \zeta_{\text{CS}} + (1 - \lambda) \zeta_{\text{QS}},$$

(6)

where $\zeta_{\text{QS}}$ is the zeta potential of quartz sand, $\zeta_{\text{CS}}$ that of carbonate sand, and $\lambda$ is the heterogeneity parameter (in our study, equal to the proportion of carbonate sand).

Our results showed that the zeta potential increased approximately linearly with increasing carbonate content (solid line, Fig. 2a). The values obtained for the mixtures containing 10 and 50% carbonate sand were, however, slightly less negative than the linear combination of the zeta potentials of pure quartz and carbonate sands (dashed line, Fig. 2a).

The zeta potential was further determined as a function of pH in all investigated media (Fig. 2b). Quartz sand carried a high negative charge over the whole pH range investigated, with the zeta potential increasing slightly from $-45$ mV (at pH 10) to $-39$ mV (at pH 5). The surface charge of the quartz and carbonate mixtures exhibited a less negative zeta potential in this pH range. The surface charge of pure carbonate sand increased slightly from an initial $-12$ mV (at pH 10) to $-8$ mV (at pH 5.7). We hereby acknowledge that at pH values below 8.27 calcite starts dissolving at atmospheric CO₂ pressure and values obtained below this value represent conditions at thermodynamic non-equilibrium.

The differences in zeta potential for quartz and carbonate sand at pH 7.4 (Fig. 2a and b) resulted from the different background solutions applied. Carbonate sand and especially quartz sand, were more negatively charged in the presence of the phosphate buffer (Fig. 2a) than in the presence of NaCl (Fig. 2b). This can be explained by phosphate adsorption onto the porous media surface, resulting in decreased zeta potentials, as previously reported for the surface charge of quartz sand under different phosphate concentrations (Wang et al., 2011).

Overall, the surface charge measurements suggest that the repulsive forces between the negatively charged PAA-nZVI particles and the carbonate sand surfaces will be lower than for quartz sand. This assumption is supported by the interaction energy profiles between quartz and carbonate sands and PAA-nZVI particles. We calculated the electrostatic interactions between the particles and the mineral grains according to the DLVO theory (calculated after Christian et al. (2008), Figure S2, Supplementary Data). The height of the repulsive energy barrier decreased with increasing carbonate content and decreasing surface charge, disappearing completely when the proportion of carbonate sand exceeds 50%. In the absence of a repulsive energy barrier, PAA-nZVI should have a strong tendency to deposit onto carbonate-rich porous media.

3.3. Effect of injection velocity on PAA-nZVI deposition and transport

The effect that the injection velocity has on PAA-nZVI deposition and transport was confirmed in two different experimental setups, with pure quartz sand and pure carbonate sand. Like for the previously studied reactive iron nanoparticles (RNIP, Toda Kogyo, Japan) and iron nanoparticles produced by borohydride reduction, the PAA-nZVI transport (NANOFER 25S) depended on the injection velocity, in both quartz and carbonate sands. Doubling the injection velocity from $3 \times 10^{-4}$ m s⁻¹ to $6 \times 10^{-4}$ m s⁻¹ significantly decreased the deposition and enhanced the PAA-nZVI transport. In quartz sand the PAA-nZVI breakthrough ($C/C_0$) increased from 0.32 to 0.70, while in carbonate sand the observed increase was from 0.08 to 0.22 (Figure S3, Supplementary Data). The lower observed deposition at higher injection velocities can be attributed to the smaller volumes of stagnation zones and higher drag forces, as reported for previously investigated nZVI particles (Phenrat et al., 2010a, 2009; Raychoudhury et al., 2010).

3.4. Effect of carbonate minerals in porous media on PAA-nZVI deposition and transport

Five model porous media with increasing proportions of carbonate sand were used to study effects of carbonate minerals on the PAA-nZVI transport. The results demonstrated that as the proportion of carbonate sand increased the PAA-nZVI deposition also increased and therefore the transport decreased (Fig. 3). The PAA-nZVI breakthrough ($C/C_0$) decreased from 0.70 in pure quartz sand to 0.18 and 0.22 in porous media containing 90% and 100% of carbonate sand, respectively (Fig. 3). The PAA-nZVI breakthrough in the experiments with 90% and 100% of carbonate sand were not different from each other. This suggests that the deposition was dominated by the carbonate surfaces at carbonate loading higher than 90%.

The PAA-nZVI breakthrough occurred slightly ahead of the bromide tracer (Fig. 3). This reflects the well-documented size exclusion effect, where the PAA-nZVI particles are excluded from
strength $\frac{1}{4}$

The therefore recognized as the dominant mechanism for PAA-nZVI increasing contribution of gravitational sedimentation (Figure S4, single-collector contact efficiency ($h$) for particle sizes between 200 and 500 nm. These correspond to the particle diameter, Darcy velocity, porosity, all of which were almost identical for the porous media. The lowest values were obtained for PAA-NZVI particle sizes between 200 and 500 nm. These correspond to the particle sizes for which the highest subsurface mobility of PAA-nZVI can be expected in an ideal porous media (Elimelech and O’Melia, 1990). The $\eta_0$ values increased for particles larger than 500 nm due to the increasing contribution of gravitational sedimentation (Figure S4, Supplementary Data). Gravitational sedimentation ($\eta_c$) was therefore recognized as the dominant mechanism for PAA-nZVI deposition in all investigated porous media (Table 1), which is attributed to the high density of the used nZVI particles (7.87 g cm$^{-3}$) and the relatively large size of the nZVI aggregates flowing through the column.

The increase in PAA-nZVI deposition with an increasing proportion of carbonate sand is assumed to be a result of favorable particle attachment to carbonate grains. This assumption is supported by the linear increase in the attachment efficiency ($z$) from 0.2 in pure quartz sand to approximately 1.2 in the porous media containing 90–100% carbonate sand (Table 1, Fig. 4a). Values for $z$ greater than 1 are physically impossible; however, particle aggregation during the column experiment can result in overestimation of attachment, as observed previously by Phenrat et al. (2010a). A linear increase with increasing proportion of carbonate sand was also observed for the particle deposition rate coefficient ($k_{CDE}$), which increased from 0.003 s$^{-1}$ for 100% QS to 0.011 s$^{-1}$ for 100% CS. No difference was observed in the particle deposition rate between sand mixtures with 90% and 100% carbonate sand (Table 1).

The PAA-nZVI transport was further described by fitting the convection—dispersion equation (Equation (4)) to the experimental breakthrough curves. The results showed an excellent agreement between the experimental and fitted breakthrough curves with $R^2 > 0.968$ (Table 2, Fig. 3), supporting the assumption that the PAA-nZVI deposition was controlled by a first-order kinetic mechanism.

The CXTFIT-fitted first-order deposition rate coefficient ($k_{CDE}$) ranged from 0.002 to 0.013 s$^{-1}$, with the highest values recorded in

![Fig. 3. Experimental breakthrough curves and model fits of PAA-nZVI in porous media containing various amounts of quartz sand (QS) and carbonate sand (CS). Experimental conditions were as follows: influent iron concentration $- 200$ mg L$^{-1}$, ionic strength $- 1$ mM NaHCO$_3$, solution pH = 8.3–9.0.](image)

Colloid filtration theory can explain the deposition of particles onto porous media in terms of different transport mechanisms and particle sizes. The calculations of the single-collector contact efficiency ($\eta_0$) according to Tufenkji and Elimelech (2004) showed that the values for $\eta_0$ were almost the same for all porous media investigated (Table 1). This can be attributed to the values of the input parameters used for the $\eta_0$ calculation (i.e., mean collector diameter, Darcy velocity, porosity, fluid viscosity, and temperature), all of which were almost identical for the five classes of porous media.

The $\eta_0$ values were obtained for PAA-NZVI particle sizes between 200 and 500 nm. These correspond to the particle sizes for which the highest subsurface mobility of PAA-nZVI can be expected in an ideal porous media (Elimelech and O’Melia, 1990). The $\eta_0$ values increased for particles larger than 500 nm due to the increasing contribution of gravitational sedimentation (Figure S4, Supplementary Data). Gravitational sedimentation ($\eta_c$) was therefore recognized as the dominant mechanism for PAA-nZVI deposition in all investigated porous media (Table 1), which is attributed to the high density of the used nZVI particles (7.87 g cm$^{-3}$) and the relatively large size of the nZVI aggregates flowing through the column.

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![Fig. 4. Influence of carbonate content on the (a) attachment and (b) deposition kinetics of PAA-nZVI in heterogeneous porous media. The solid lines are linear fits of the results. The dashed line in (b) indicates the linear combination of the removal rates of pure quartz sand (QS) and pure carbonate sand (CS) sand, according to Equation (5).](image)

### Table 1

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<th>Porous media</th>
<th>$\eta_0$</th>
<th>$\eta_1$</th>
<th>$\eta_c$</th>
<th>$\eta_c$</th>
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<td>0.0111</td>
<td>0.34</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Contribution of diffusion ($\eta_0$), interception ($\eta_1$), gravitational sedimentation ($\eta_c$), single-collector contact efficiency ($\eta_0$), attachment efficiency ($z$), deposition rate coefficient ($k_{CFT}$), and travel distance to remove 99.9% and 50% of the PAA-nZVI particles ($L_0$, $L_1$).
the porous media with 90 and 100% carbonate sand (Table 2). Since the hydrodynamic dispersion coefficient differs from zero (Table 2), the attachment efficiency was additionally determined using $k_{\text{DDE}}$ and Equation (2) in order to exclude dispersion as the dominant transport process. The values for $k_{\text{DDE}}$ ranged between 0.16 and 1.33 (Table 2). The values for $k_{\text{DDE}}$ and $\alpha_{\text{DDE}}$ were similar to those for the deposition rate coefficient and attachment efficiency calculated by applying the colloid filtration theory (Table 1), indicating that both approaches are applicable for describing the PAA-nZVI deposition kinetics and that dispersion is not the dominating transport process. The particle removal rate coefficients ($k_{\text{RMM}}$) for the five porous media are presented in Fig. 4b. The results showed that the removal rate increased approximately linearly as the proportion of carbonate sand increased. The linear increase can be explained by the patchwise heterogeneity model (Song et al., 1994), which assumes that the average removal rate is a linear combination of the removal rates onto pure quartz sand ($k_{\text{QS}} = 0.024 s^{-1}$) and pure carbonate sand ($k_{\text{CS}} = 0.011 s^{-1}$) (Equation (5); dashed line in Fig. 4b). The removal rates for 10% and 90% carbonate sand were nevertheless slightly higher than the average removal rates ($k_{\text{RMM}}$) calculated using the patchwise heterogeneity model (Table 2).

The PAA-nZVI travel length was predicted by applying the colloid filtration theory (Equation (3)) and setting the removal of the particles to 99.9% (close to total removal) or 50% (removal of half of the particles). The maximum predicted travel length in pure quartz sand was 1.55 m (after 99.9% particle removal), but with more than a half of the injected particles traveling no further than 0.16 m (Table 1). In the presence of carbonate sand the predicted travel distance was even shorter, ranging between 0.03 m (for 50% particle removal) and 0.34 m (for 99.9% particle removal; Table 1).

Travel distances (99% particle removal) reported by Saleh et al. (2008) for other surface modified nZVI particles (polyspartate-, triblock copolymer-, sodium dodecyl benzyl sulfonate-nZVI) in pure quartz sand were significantly higher than the values in this study, ranging from 0.6 m to ~500 m, depending on the ionic strength and nZVI surface coating. However, Saleh et al. (2008) performed their experiments with the stable nZVI fraction (after sedimentation) at a low nZVI concentration (~30 mg L$^{-1}$), while in this study the entire polycarbonate suspension, as used in field applications, had concentrations ~200 mg L$^{-1}$, was utilized. In addition to the higher concentration, the polycarbonate of the nZVI used here may have decreased the transport. Phenrat et al. (2009) found that the larger nZVI particles aggregated much more readily than the smaller ones, leading to increased aggregation and lower transport. Travel distances reported by Schrick et al. (2004) for polycarbonate acid modified nZVI in pure quartz sand, using very high particle concentrations (5 g L$^{-1}$), were lower than values in this study, ranging from 9 to 39 cm and depending on the particle size. The high concentration might have contributed to the decreased travel distance. Travel distances (99% particle removal) reported for guar gum-coated nZVI in pure quartz sand (Tirafferi and Sethi, 2009) were comparable with the values in this study. The calculated distances ranged between 0.59 and 2.37 m, depending on ionic strength and injection velocity. The highest value was obtained applying the highest injection velocity, which is therefore considered to be an essential factor in enhancing the transport. Once the injection is terminated and groundwater flow velocity returns to background levels (that are well below those during injection), the PAA-nZVI particles will be retained in the porous media (Phenrat et al., 2010b).

Overall, the linear increase in particle deposition and attachment efficiency with increasing proportions of carbonate sand demonstrated that the attachment and deposition kinetics of PAA-nZVI are controlled by the mineralogical variations within the subsurface. Our results are in agreement with those of Elimelech et al. (2000), who observed a similar linear trend for deposition of colloidal silica particles onto porous media containing various amounts of positively charged patches (aminsilane-modified quartz grains). Our study showed that not only the positively charged minerals (such as iron oxides and the edges of clay minerals) act as favorable deposition sites for nZVI particles, but also carbonate minerals that carry a weak negative surface charge in the pH range typically found in groundwater. Both will decrease the transport of nanoparticles in heterogeneous porous media and therefore need to be taken into account in the design of nZVI-based in situ remediation. It should be noted that higher ionic strength due to the dissolution of calcium carbonate (Table S2, Supplementary Data) can alter the stability of PAA-nZVI by electrostatic double layer compression and increase its deposition onto the aquifer grains (Petosa et al., 2010). In addition, higher dissolved calcium concentrations can destabilize the PAA-nZVI suspension and therefore decrease transport. This is due to specific adsorption of calcium ions onto nZVI surfaces, as well as complexation of calcium ions by carboxylic groups of the PAA, which results in an associated loss of repulsive negative charges (Ottofuelling et al., 2011; Saleh et al., 2008). The effect of calcium concentration on the PAA-nZVI deposition and transport was evaluated in different experimental setups; with pure quartz and pure carbonate sand, and including three different calcium concentrations (1 mM, 2.5 mM, and 5 mM CaCl$_2$). In quartz sand the PAA-nZVI breakthrough ($C/C_0$) decreased from 0.36 (in 1 mM CaCl$_2$) to 0.14 (in 5 mM CaCl$_2$), while in carbonate sand the observed decrease was from 0.10 (in 1 mM CaCl$_2$) to 0.03 (in 5 mM CaCl$_2$) (Table S3, Supplementary Data). High aqueous calcium concentrations, which can be expected in carbonate-rich aquifers, are therefore additionally limiting the PAA-nZVI transport, as previously reported by Saleh et al. (2008).

Similar to the complexation of carboxylic groups in the PAA with dissolved calcium, the PAA can also adsorb on the calcite through complexation of calcium at the sand surface (Geffroy et al., 1999; Taylor and Sigmund, 2010). The latter may result in bridging effects between the PAA-nZVI and carbonate minerals and therefore enhance the particle deposition onto carbonate sand. These interactions and their effects on the nZVI transport need also to be considered when designing a nZVI application in carbonate-rich aquifers.

4. Conclusions and implications for field application

Our study has revealed that the PAA-nZVI (NANOFER 25S) suspension, with a mean aggregate size of approximately 1.4 μm, is polydisperse and not stable. The stable fraction of this suspension (after two hours of sedimentation) contains significantly smaller particles with a diameter of ~235 nm. However, the concentration of nZVI in this stable fraction is only about 10% of the original suspension.
We demonstrated that carbonate minerals in aquifers and with them introduced surface charge heterogeneities, have a strong effect on the transport of a polydisperse suspension of PAA-nZVI. The results showed that even a low proportion of carbonate minerals (10%) in the subsurface may cause an increase in the deposition of PAA-nZVI particles and aggregates, and consequently limit their transport. The favorable deposition of PAA-nZVI particles onto carbonate rather than quartz sand is attributed to the lower negative surface charge of carbonate sand. It should be further noted that surface complexations of PAA coating with calcite might additionally occur, as well as particle aggregation due to dissolved calcium. Both effects are expected to be more pronounced in carbonate-rich porous media and will result in increased particle deposition.

The model simulations based on colloid filtration theory and the one dimensional transport equation showed that the PAA-nZVI attachment efficiency and deposition rate increase linearly with increasing proportions of carbonate sand, under the investigated conditions. The maximum predicted travel distances for PAA-nZVI in carbonate sand was approximately five times shorter than in quartz sand and not more than 0.3 m in our study, which in praxis may reduce chances that the nZVI suspension reaches the contaminated source zone. We acknowledge that the hereby performed small-scale experiments are not direct analogues for large-scale settings. However, the reported differences in nZVI deposition onto quartz and carbonate sands are also likely to manifest themselves at larger scales. The transport distance for nZVI based particles is therefore likely to be low in carbonate-rich porous media, thus requiring more injection wells in the treatment zone and potentially a larger mass of nZVI, which increases the overall remediation costs. Since carbonate sands are common constituents of aquifers, their effects on nZVI transport needs to be taken into account in the design of nZVI-based remediation.

New strategies are therefore required in order to improve PAA-nZVI transport in such heterogeneous porous media. It might be possible to optimize those nZVI particle properties that affect their mobility in porous media, or to enhance delivery by improving the injection techniques. Another strategy might be to inject natural polyelectrolytes (with no adverse effects on the environment) prior to, or during the application of nZVI suspensions. Such natural organic polyelectrolytes can adsorb on the porous media, provide a greater and more uniform negative surface charge and thus minimizing the deposition of negatively charged nZVI particles, as previously demonstrated by Johnson et al. (2009) and Kim et al. (2012). The effects that organic (and biodegradable) polyelectrolyte coatings have on aquifer surfaces will need to be considered in future studies, which aim for improved nZVI transport in heterogeneous porous media. Furthermore, the ecotoxicological effects that these coatings may have on the subsurface organisms will also have to be determined. These introduced polyelectrolyte coatings could promote bacterial growth in the subsurface (Kirschling et al., 2010; Xie et al., 2010) and subsequently enhance the remediation by combining nZVI treatment with bioremediation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2013.04.004.

References


