



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



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## ABSTRACT

The limited transport of nanoscale zero-valent iron (nZVI) in porous media is a major obstacle to its widespread application for *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 predominate 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 *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 electrosteric 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.

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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 homogenous (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

PAA-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). 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, Austria) was used as the quartz porous medium. Limestone (with ~97.0% CaCO<sub>3</sub>, ~2% MgCO<sub>3</sub>, 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 PAA-nZVI suspension

The PAA-nZVI stock suspension (~8 g L<sup>-1</sup>) was prepared by suspending the aqueous suspension of NANOFER 25S (50 g) provided by the producer in a 1 mM

NaHCO<sub>3</sub> 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 PAA-nZVI stock suspension in 1 mM NaHCO<sub>3</sub> 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 PAA-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 ~1000 particles mL<sup>-1</sup>, Eyetechn™, Ambivalu, The Netherlands). 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 NaHCO<sub>3</sub> and 0.3 mM CaCO<sub>3</sub>, 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 cell was equilibrated by circulating the background solution (1 mM phosphate 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 Fairbrother–Mastin equation (Fairbrother and Mastin, 1924). In addition, the alteration of the surface charge as a function of pH (pH 5–10) has been studied in a 1 mM NaCl background solution.

### 2.5. Column experiments

Transport studies were performed in borosilicate glass columns (1 cm i.d., 10 cm length, Omnifit, 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),  $3 \times 10^{-4}$  m s<sup>-1</sup> and  $6 \times 10^{-4}$  m s<sup>-1</sup> were performed in pure quartz and pure carbonate sand. The injection velocity of  $6 \times 10^{-4}$  m s<sup>-1</sup> 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 NaHCO<sub>3</sub> 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 porosities 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<sup>-1</sup> total Fe in 1 mM NaHCO<sub>3</sub> 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/C<sub>0</sub>) 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

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