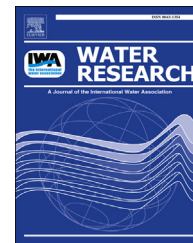


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Influences of nanoscale zero valent iron loadings and bicarbonate and calcium concentrations on hydrogen evolution in anaerobic column experiments

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ABSTRACT

The estimation of nanoscale zero-valent iron (nZVI) reactivity after its injection into the subsurface is essential for its application in groundwater remediation. In the present study H₂ generation of commercially available nZVI and novel milled nZVI flakes were investigated in column experiments with varying nZVI loads (ranging from 8 to 43 g nZVI per kg sand). H₂ evolution rates were determined for column experiments without and with hydrogen carbonate and/or calcium. On average 0.29 mmol H₂/L per g Fe⁰ evolved within the first 30 days in column experiments with spherical, commercial nZVI particles. The H₂ evolution developed almost independently of the water matrices applied. The application of nZVI flakes resulted in lower H₂ generation rates. In general corrosion rates accelerated linearly with increasing initial amounts of iron. This was evident in experiments with both particle types. Concentration profiles of carbonate and calcium in influent and effluent were used to estimate corrosion products and precipitates. Despite the presence of high concentrations of inorganic carbon, Fe²⁺ reacted preferably with hydroxide ions to form ferrous hydroxide which is the precursor of magnetite. As a result only minor passivation of the reactive nZVI was observed.

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1. Introduction

Groundwater remediation with nanoscale zero-valent iron (nZVI) is a promising alternative to ZVI permeable reactive barriers (PRB) or conventional pump-and-treat techniques. The nZVI water slurry can be injected into the contaminated subsurface to avoid excavation of aquifer material or pumping of contaminated groundwater. In-situ remediation with nZVI

is especially advantageous for poorly accessible contaminated sites (e.g. contamination underneath a building). Besides the transport behavior, the particle reactivity after its injection into the subsurface is a key factor for the successful application of nZVI.

The high reactivity of nZVI is linked to its large surface area (Nurmi et al., 2005; Tratnyek and Johnson, 2006). Depending on the manufacturing process, suspensions of nZVI often contain particles with a core–shell structure. The (protecting) particle

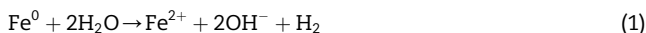
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shells consist of a thin iron oxide layer (Fe_3O_4 , FeO) of a few nanometers (Martin et al., 2008; Sarathy et al., 2008) which encloses the Fe^0 core (core–shell structure). The aging of core–shell nanoparticles is described by the shrinking of the metallic core while no changes in the particle size and surface area are evident (Liu and Lowry, 2006; Crane and Scott, 2012).



Under anaerobic conditions zero-valent iron reacts with water to form ferrous iron (Fe^{2+}), hydroxide ions and hydrogen. The reaction consists of two reaction steps with different reaction rates (Wang and Farrell, 2003): 1) Formation of H^0 -atoms adsorbed on the iron surface and 2) reaction to H_2 . The formation of adsorbed H^0 -atoms is linked to the availability of electrons from the core and is reported to be the rate controlling step in the corrosion of nZVI (Liu and Lowry, 2006). According to another kinetic model, the diffusion of reactants and products through the particle shell limits the reaction rate (Reardon et al., 2008).

Under anaerobic conditions magnetite (Fe_3O_4) is the final corrosion product of the ZVI oxidation in de-ionised water (Ruhl et al., 2012), with ferrous hydroxide ($\text{Fe}(\text{OH})_2$) as its precursor (Reardon et al., 2008; Ruhl et al., 2012). In complex groundwater matrices, the formation of secondary minerals depends on the concentration of inorganic groundwater solutes and the local pH value.

Corrosion experiments with granular iron have indicated that the formation of mineral precipitates affect the long-term reactivity of PRB (Kober et al., 2002; Klausen et al., 2003; Kohn et al., 2005; Parbs et al., 2007; Weber et al., 2013). In particular, mainly iron hydroxide carbonate (chukanovite, $\text{Fe}_2\text{CO}_3(\text{OH})_2$) is formed in the presence of carbonate on the iron surface (Ruhl et al., 2011) and influences significantly the reactivity (Jeen et al., 2006; Lee and Wilkin, 2010; Ruhl et al., 2012). High concentrations of inorganic carbon increase not only the dehalogenation rates of chlorinated groundwater contaminants but also the inhibition of reactive sites in the long-term (Parbs et al., 2007). Based on results of field-scale PRBs, Lee and Wilkin (2010) calculated the phase stability of siderite (FeCO_3), chukanovite and ferrous hydroxide in a $\text{Fe}(\text{II})$ – CO_2 – H_2O -system. The thermodynamic calculations indicated that the formation of siderite and ferrous hydroxide in anaerobic Fe^0 -groundwater systems is preferred either under carbonate rich (siderite) or carbonate limited (ferrous hydroxide) groundwater conditions (Lee and Wilkin, 2010).

Liu et al. (2007) investigated the influence of various groundwater anions (except nitrate) on the reactivity of nZVI in well-mixed batch reactors. The presence of different groundwater solutes decelerated the dehalogenation rate of trichloroethylene (TCE), but no significant differences in the H_2 evolution were found in similar batch experiments without contaminants. Solid phase characterization of nZVI particle surfaces which were oxidized in the absence and presences of common groundwater anions (except nitrate) without contaminants by Reinsch et al. (2010) supports these results. Investigation of H_2 generation in batch experiments with nZVI and quartz sand indicated that the aquifer material probably decelerates the anaerobic corrosion reaction (Reardon et al., 2008).

Direct remediation of a contaminant source requires the injection of high nZVI amounts into the subsurface. The influence of various nZVI loads (g iron per kg sand) on the long-term aging under realistic flow conditions in the long-term is not yet fully understood. In the present study, column experiments with different types of nZVI, including novel milled nZVI flakes, were carried out to investigate the influences of a) varying loads of iron per kg sand inside the column and of b) hydrogen carbonate and calcium on the rate of anaerobic corrosion. Köber et al. (2014) reported recently the development of novel milled nZVI flakes for groundwater remediation. In the present study H_2 generation of these milled nZVI flakes was intensively investigated in column experiments.

2. Material and methods

2.1. ZVI nano particles

Corrosion experiments were performed with two types of nZVI: 1) Commercial nZVI particles (Nanofer25, Nanofer25S) supplied by NanoIron s.r.o., Czech republic and 2) novel milled nZVI flakes supplied by UVR-FIA GmbH, Freiberg, Germany, which were produced only for research purposes.

The particles of Nanofer25 and Nanofer25S have a BET surface area of 25 m^2/g and 22 m^2/g (Zhuang et al., 2012) and an average particle size of 50 nm. The particles consist of a metallic ZVI core and an iron oxide (Fe_3O_4 , FeO) shell (core-shell-structure). Particles of the type Nanofer25S were coated with polyacrylic acid by the manufacturer to support colloidal stability. The particles in suspensions of Nanofer25 and Nanofer25S contained about 80% (by weight) of Fe^0 .

The milled particles are a new type of flake, like nZVI, which are being developed for groundwater remediation (Köber et al. (2014)). The nZVI flakes are manufactured in a two-step process by milling iron powder (ATOMED 57, Rio Tinto) in a ball mill under anaerobic conditions. During the milling process the particles are coated with additives to improve colloidal stability. A description of the manufacturing process and characterizations including reactivity and transport behavior in porous media is given by Köber et al. (2014). The nZVI flakes (lateral size several micrometer, thickness < 200 nm) have a BET surface area of 18 m^2/g . The particle suspension contains agglomerates of different sizes in the range of 45 μm and 200 nm related to the milling process. A fresh particle suspension contains approximately 85% of Fe^0 . Before use the suspension was stored in ethylene glycol to avoid oxidation (Köber et al., 2014).

Before each experiment the Fe^0 content of the nZVI was determined by complete digestion under acidic conditions and quantification of the hydrogen production (triplicate analyses).

2.2. Column experiments

Glass columns (inner diameter: 36 mm, lengths: 70 mm) were filled with 120 g of quartz sand (Dorsolit D8, grain size 0.3–0.8 mm) and loaded with different product types and

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