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PCE dissolution and simultaneous dechlorination by nanoscale zero-valent iron particles in a DNAPL source zone

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ABSTRACT

While the capability of nanoscale zero-valent iron (NZVI) to dechlorinate organic compounds in aqueous solutions has been demonstrated, the ability of NZVI to remove dense non-aqueous phase liquid (DNAPL) from source zones under flow-through conditions similar to a field scale application has not yet been thoroughly investigated. To gain insight on simultaneous DNAPL dissolution and NZVI-mediated dechlorination reactions after direct placement of NZVI into a DNAPL source zone, a combined experimental and modeling study was performed. First, a DNAPL tetrachloroethene (PCE) source zone with emplaced NZVI was built inside a small custom-made flow cell and the effluent PCE and dechlorination byproducts were monitored over time. Second, a model for rate-limited DNAPL dissolution and NZVI-mediated dechlorination of PCE to its three main reaction byproducts with a possibility for partitioning of these byproducts back into the DNAPL was formulated. The coupled processes occurring in the flow cell were simulated and analyzed using a detailed three-dimensional numerical model. It was found that subsurface emplacement of NZVI did not markedly accelerate DNAPL dissolution or the DNAPL mass-depletion rate, when NZVI at a particle concentration of 10 g/L was directly emplaced in the DNAPL source zone. To react with NZVI the DNAPL PCE must first dissolve into the groundwater and the rate of dissolution controls the longevity of the DNAPL source. The modeling study further indicated that faster reacting particles would decrease aqueous contaminant concentrations but there is a limit to how much the mass removal rate can be increased by increasing the dechlorination reaction rate. To ensure reduction of aqueous contaminant concentrations, remediation of DNAPL contaminants with NZVI should include emplacement in a capture zone down-gradient of the DNAPL source.

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1. Introduction

Dense non-aqueous phase liquid (DNAPL) source zones are long term sources of ground water contamination that cannot be treated effectively using passive remediation technologies such as pump-and-treat and permeable reactive barriers (ITRC, 2002; O'Carroll, 2008). Delivering reactive nanoscale zerovalent iron (NZVI) particles in situ to reductively dechlorinate entrapped DNAPL has been expected to provide DNAPL mass reduction and provide residual treatment capacity to mitigate mass flux from diffusion-controlled low permeability zones (Bennett et al., 2010; Berge and Ramsburg, 2009; Henn and Waddill, 2006; O'Carroll, 2008; Phenrat et al., 2009a, 2009b, 2009c, 2010; Tratnyek and Johnson, 2006). Field experiments have shown that in-situ injection of NZVI may constitute an attractive remediation technique

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for contaminated soil and groundwater (Elliott and Zhang, 2001; Quinn et al., 2005; Bennett et al., 2010; Henn and Waddill, 2006). Several laboratory studies using batch reactors have confirmed that NZVI is superior to its counterpart bulk ZVI for degradation of dissolved chlorinated organics such as trichloroethylene (TCE) and perchloroethylene (PCE) due to the large specific surface area of nanoparticles. The general pathways and kinetics of dehalogenation by Fe^0 nanoparticles have been described by Liu et al. (2005). The reactivity of NZVI may be further enhanced by adding a catalyst metal such as Pd (Lien and Zhang, 2007; Yan et al., 2010; Zhang et al., 1998) and the mobility in-situ may be enhanced by surface coatings (Saleh et al., 2005 — Fe^0 particles; He et al., 2007 — bimetallic particles) or emulsions (Berge and Ramsburg, 2009).

While reactivity under different aqueous chemistries and with various NZVI to contaminant ratios has been investigated in closed batch reactors (Liu and Lowry, 2006; Liu et al., 2007; Phenrat et al., 2009b), only limited investigations under controlled laboratory conditions on the reactivity of NZVI inside porous media with groundwater flow (e.g. Kim, 2009; Taghavy et al., 2010) have been undertaken. In addition, the behavior of NZVI in the subsurface and its direct interactions with DNAPL sources are still poorly understood. Improved understanding based on careful experimentation at all relevant scales of interest is necessary for the design of cost-effective in situ DNAPL source zone remediation using NZVI.

As the exact location of entrapment will not be known at field sites, to address the question of whether NZVI can be used to efficiently remediate DNAPL source zones, it is necessary to understand how the NZVI interacts with the DNAPL and its dissolved components in the vicinity of the source. As a first step in a multi-scale investigation, we first conducted experiments in a small (15 mL) flow cell, where emplaced NZVI particles were allowed to react and interact with a PCE DNAPL pool, while steady groundwater flow was maintained through the flow cell. Experiments were conducted at two different groundwater flow velocities using reactive nanoscale iron particles (RNIP), a commercially available NZVI manufactured by Toda Kogyo Corp., Japan. Second, we developed a detailed model of the three-dimensional flow cell to further analyze the experimental results and their implications for the reactive processes in the DNAPL source zone. The model was developed within the framework of a finite difference groundwater flow code; MODFLOW-2000 (Harbaugh et al., 2000), and the reaction module RT3D (Clement, 1997), which is an extension of the transport code MT3DMS (Zheng and Wang, 1999) allowing addition of user-specific code describing the reactive processes. Here we implemented a Gilland–Sherwood type model of rate-limited DNAPL dissolution (Saba and Illangasekare, 2000; Saenton and Illangasekare, 2007) coupled to a first order model for NZVI-mediated degradation of PCE producing the three main reaction byproducts acetylene, ethene and ethane. An extension to this model which allows partitioning of the reaction products into the DNAPL was also developed.

A joint analysis of experimental and modeling results allowed a detailed analysis of the different processes occurring when NZVI was emplaced in a DNAPL source zone. The modeling allowed testing of the relative importance of the different processes (dechlorination reactions, mass-transfer and partitioning) as these could be turned on or off in the model and thereby be studied both occurring simultaneously and in isolation. In summary, with the ultimate goal of understanding much more complex field settings, the objectives of this study were to generate experimental data in small physical model of a DNAPL source undergoing remediation by NZVI, develop modeling tools for this system, and analyze the simultaneously occurring DNAPL dissolution and PCE dechlorination processes.

2. Experimental methods and materials

2.1. Nanoscale zero-valent iron (NZVI)

The NZVI used were RNIP (reactive nanoscale iron particles) obtained from Toda Kogyo Corp., Onoda, Japan. The particles were shipped and stored in water at pH 10.6 but before use they were dried in water under vacuum. The Fe^0 content of the particles was 22% by weight as measured from H2 formation during acid digestion of the particles and the specific surface area was approximately 15 $m^2\ g^{-1}$ as previously measured by N_2 adsorption and BET theory (Liu et al., 2005). Further details on the physical and chemical properties of these particles have also been reported by Liu et al. (2005).

2.2. Batch reactivity study and GC methods

The reactivity of RNIP with PCE was first measured using experiments in batch reactors. Dry RNIP powder was mixed with de-aired water containing 5 mM $NaHCO_3$ to provide a 10 g/L RNIP concentration. Reactors were prepared in 60 mL Serum bottles, with 50% aqueous solution and 50% headspace, and capped with gastight Teflon Mininert valves. The reactors were left in an anaerobic chamber for 2 days to allow initially formed H_2 to degas. Then PCE (99% grade, Sigma-Aldrich) was added and the concentrations of PCE and its reaction byproducts were monitored over time by taking headspace samples and directly analyzing them on a HP-6890 gas chromatograph with a HP-PLOT/Q 30 m × 0.53 mm column and flame ionization detector (FID). Samples were injected splitless at 250 °C with oven temperature 50 °C for 2 min then ramping 40 °C/min to 220 °C and holding for 9 min. This method was modified from Liu et al. (2005) and provides adequate separation between PCE and reaction byproducts. The method was calibrated for PCE (99% grade, Sigma-Aldrich), trichloroethene (TCE) (99% grade, Sigma-Aldrich), 1-1-dichloroethene (DCE) (US-EPA, 1000 mg/L standard in methanol), cis-1-2-DCE (US-EPA, 5000 mg/L standard in methanol), and trans-1-2-DCE (US-EPA, 5000 mg/L standard in methanol), as well as for the following gases (all Matheson Portable Gas Standards (MicroMat 10 and 14) purchased from Alltech): vinyl chloride (VC) (10 ppm in nitrogen), ethane (100 ppm and 1000 ppm in helium), ethene (100 ppm and 1000 ppm in helium), acetylene (100 ppm and 1000 ppm in helium), C4 hydrocarbons (15 ppm each in nitrogen). Liquid standards were prepared in 120 mL Serum bottles, with 50% aqueous solution and 50% headspace, capped with gastight Teflon Mininert valves. These were prepared by diluting a multi-component stock solution and were chosen to cover the range of concentrations observed in the batch reactors and flow-cell samples (the latter described in more detail below). Calibration of gas concentrations over the relevant ranges was done by injecting different volumes of the Matheson MicroMat gas standards (listed above), thus obtaining calibration curves for a known injected mass.

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