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Travel distance and transformation of injected emulsified zerovalent iron nanoparticles in the subsurface during two and half years

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ABSTRACT

Nanoscale zerovalent iron (NZVI) such as Toda Kogyo RNIP-10DS has been used for site remediation, yet information is lacking regarding how far injected NZVI can travel, how long it lasts, and how it transforms to other minerals in a groundwater system. Previously we reported effective mass destruction of chlorinated ethenes dominated by tetrachloroethene (PCE) using emulsified zerovalent iron (EZVI) nanoparticles of RNIP-10DS in a shallow aquifer (1–6 m below ground surface, BGS) at Site 45, Marine Corps Recruit Depot, Parris Island, South Carolina, USA. Here we report test results on transport and transformation of injected EZVI in the subsurface. We employed two EZVI delivery methods: pneumatic injection and direct injection. Effective delivery of EZVI to the targeted zone was achieved with pneumatic injection showing a travel distance from injection points of up to 2.1 m and direct injection showing a travel distance up to 0.89 m. X-ray diffraction and scanning electron microscopy studies on particles harvested from well purge waters indicated that injected black colored NZVI (α-Fe^0) was transformed largely to black colored cube-like and plate-like magnetites (Fe_3O_4, 0.1–1 μm, 0–9 months), then to orange colored irregularly shaped lepidocrocite (γ-FeOOH, 0.1–1 μm, 9 months to 2.5 years), then to yellowish lath-like goethite (α-FeOOH, 2–5 μm, 2.5 years) and ferrihydrite-like spherical particles (0.05–0.1 μm) in the top portion of the aquifer (1–2 m BGS). No α-Fe^0 was found in most monitoring wells three months after injection. The formed iron oxides appeared to have a wider range of particle size (submicron to 5 μm) than the pristine NZVI (35–140 nm). Injected NZVI was largely transformed to magnetite (0.1–1 μm) during two and half years in the lower portion of the aquifer (3–6 m).

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1. Introduction

There has been increasing interest in the fate and transport of nanoscale zerovalent iron (NZVI) in the subsurface since it was first field tested for degrading groundwater trichloroethene (TCE) (Elliott and Zhang, 2001). NZVI is a promising material for environmental remediation (Zhang, 2003; Li et al., 2006; Otto et al., 2008). One limitation is that NZVI particles are ferromagnetic so that they form aggregates in aqueous suspension (Schrick et al., 2004; Nurmi et al., 2005; Phenrat et al., 2007; Hotze et al., 2010) that renders them difficult to deliver to the targeted subsurface zone. Consequently, a number of laboratory and field studies have been conducted to enhance NZVI colloidal stability by modifying NZVI surfaces with polymers thereby increasing their mobility in the subsurface once injected (Henn and Waddill, 2006; Kanel and Choi, 2007; Saleh et al., 2008; Vecchia et al., 2009; Phenrat et al., 2010a,b; Bennett et al., 2010; He et al., 2009, 2010; Sunkara et al., 2010; Zhan et al., 2009, 2011; Phenrat et al., 2011). Among the modified forms of nanoiron, emulsified zerovalent iron (EZVI), was developed in laboratory (Geiger et al., 2003) and then field tested and monitored for up to two years to treat source-zone chlorinated volatile organic compounds (CVOCs) dominated by TCE at a site in Florida, USA (Quinn et al., 2005; O'Hara et al., 2006). At that site, EZVI was injected using pressure pulse technology. Additional injection tests by NASA in Florida indicated that pneumatic fracturing and direct injection methods performed better than pressure pulse injection because the pneumatic fracturing and direct injection led to more uniform distribution of EZVI than did pressure pulse injection. Consequently, an additional field test was conducted at Site 45, Marine Corps Recruit Depot, Parris Island, South Carolina, USA using two different injection technologies (pneumatic fracturing and direct injection) that showed 86% decrease in total CVOCs mass two and half years after injection (Su et al., 2012).

EZVI has unique properties in that emulsion droplets on the order of 10 μm contain NZVI particles in water surrounded by an oil-liquid membrane (food-grade surfactant, biodegradable vegetable oil). The oil layer of the emulsion is miscible with the dense nonaqueous phase liquid (DNAPL). CVOCs diffuse through the oil membrane and are degraded in the presence of the NZVI in the interior aqueous phase. Dechlorination rates are proportional to the concentration of water present within the DNAPL (Berge and Ramsburg, 2010). EZVI can be used to enhance degradation of DNAPL by enhancing contact between the DNAPL and the NZVI particles. NZVI itself does not show bactericidal effect (Kirschling et al., 2010) possibly due to aging to form the oxide shell (benign to bacteria) or adsorption of polymers and natural organic matter to NZVI (Li et al., 2010). Due to vegetable oil and surfactant which act as long-term electron donors (Borden, 2007; Borden et al., 2007), EZVI also promotes anaerobic biodegradation. Other advantages of the EZVI technology are that EZVI can be injected into areas where conventional permeable reactive barrier (PRB) construction may not be feasible (e.g., due to depth restrictions, geological media) and that EZVI can be injected directly into DNAPL source zones.

Our previous report focused on treatment effectiveness and mechanisms of CVOCs degradation (Su et al., 2012). Here we provide information on the fate and transformation of injected EZVI. Previous studies showed that Toda Kogyo RNIP-10DS aged for six months in concentrated slurry acquires properties that are relatively stable over weeks or even months (Sarathy et al., 2008). Anaerobic corrosion of RNIP-10DS in moist quartz sand is slower than in water alone due to the effect of dissolved silica sorbing onto iron reaction sites and acting as an anodic inhibitor, which reduces the metallic iron's susceptibility to oxidation by water (Reardon et al., 2008). X-ray absorption and X-ray diffraction studies of RNIP-10DS in simulated anaerobic groundwater containing separately a common anion (10 mN of Cl^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}, and HCO_3^-) show oxidation of the iron to form magnetite (Fe_3O_4), vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) and iron sulfate species, possibly schwertmannite ($Fe_{16}O_{16}(OH, SO_4)_{12-13} \cdot 10-12H_2O$) after six months, whereas oxidation in the presence of excess dissolved oxygen leads to rapid (<24 h) loss of Fe^0 and formation of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) (Reinsch et al., 2010). The longevity and mineralogical transformation of this iron in a field groundwater system has not been reported. In another study, microsized ZVI (2 ± 1 μm) was injected in a shear-thinning fluid to treat groundwater TCE effectively (Truex et al., 2010, 2011), yet no detailed information was given about the transformation of injected iron. Our study aims at filling the knowledge gap of nanoiron fate and transport in the field.

2. Materials and methods

2.1. *Site description*

Detailed site description was reported previously (Vroblesky et al., 2009, 2011; Su et al., 2012). Four above ground storage tanks (ASTs) (of unknown volumes) were historically situated along the northern side of former Building 193 (SI Fig. S1). These tanks were first put into place in 1988 following the removal of a previously existing underground storage system where hydrocarbon-cleaning solvents were stored. The exact location and volume of the former underground storage system are not known. The new storage tanks were positioned within a concrete catch basin used to contain any overflow during tank filling. It was reported on March 11, 1994, that one of the tanks had been overfilled with tetrachloroethene (PCE) and an unknown amount of the chemical flowed into the concrete catch basin. The PCE overflow was not collected at that time, and heavy rainfall subsequently washed the chemical onto the surrounding soil and caused the soil to be contaminated. A possible second source of contamination is in the rear (west end) of former Building 193. Waste solvents may have been handled or accumulated in this area. No documented leaks or spills occurred in this location. A third possible location of contamination is within the northwestern corner of former Building 193, where the dry cleaning process was conducted. A concrete floor that would serve as secondary containment was noted in this area prior to building demolition. Again, no documented leaks or spills occurred in this location.