Field Assessment of Nanoscale Bimetallic Particles for Groundwater Treatment

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A field demonstration was performed in which nanoscale bimetallic (Fe/Pd) particles were gravity-fed into groundwater contaminated by trichloroethene and other chlorinated aliphatic hydrocarbons at a manufacturing site. With diameters on the order of 100–200 nm, the nanoparticles are uniquely suited to rapidly degrade redox-amenable contaminants and for optimal subsurface delivery and dispersion. Approximately 1.7 kg of the nanoparticles was fed into the test area over a 2-day period, resulting in minimal clogging of the injection well. The test area was located within a well-characterized region of the contaminant plume and included an injection well and three piezometer couplets spaced 1.5 m apart. Despite the low nanoparticle dosage, trichloroethene reduction efficiencies of up to 96% were observed over a 4-week monitoring period with the highest values observed at the injection well and adjacent piezometers. Data from the field assessment were consistent with the results of pre-injection laboratory studies, which showed rapid dechlorination of target chlorinated compounds accompanied by a sharp decrease of standard oxidation potential and an increase in pH.

Introduction

Efficient injection and dispersion of colloidal or particulate amendments represents a formidable technical hurdle when considering an in situ groundwater remediation technology. Aquifer materials in the vicinity of the injection well(s) behave like filters by removing such amendments from solution, thus significantly reducing their mobility within the subsurface (1, 2). For example, sand filters used in water filtration (typically <1 m deep) routinely remove nearly all of the naturally occurring colloids (1–3). Extensive research has demonstrated that solution and surface chemistry effects can significantly influence the filtration efficiency and hence the mobility and ultimate subsurface fate of colloidal amendments in groundwater (1, 2).

One might assume that smaller particles should be able to move more freely in porous media such as aquifers. However, both theoretical and experimental research indicates that this assumption may not be entirely correct. Filtration of colloids injected into or migrating within porous media generally depends on three major mechanisms: (i) Brownian or molecular diffusion by which random motion of colloidal particles is brought about by thermal effects, (ii) convective fluid flow wherein particles flow with water, and (iii) gravitational effects producing vertical movement of particles (1, 2, 4, 5). Filtration caused by Brownian motion tends to dominate for small particles (e.g., <0.1 μm) whereas filtration induced by gravity outweighs Brownian diffusion for large particles (e.g., >1 μm). Therefore, there should exist a size range wherein the filtration efficiency of colloidal particles is minimized or, stated conversely, the injection and dispersion potential is maximized (6–9). In addition to solution chemistry, the “optimal” size range is a function of many environmental factors such as groundwater flow velocity, particle size of the aquifer material, density of migrating colloids, temperature, etc. For naturally occurring colloidal particles with densities close to that of water, the size range is on the order of 1 μm, which is approximately equivalent to the size of a single bacterial cell (1, 2, 4). For iron colloids with density of 7.8 g/L, the optimal size for subsurface injection is on the order of 100–200 nm under typical groundwater flow conditions (0.1–10 m/day). Methodologies for such sizedeterminations are well-documented and can be found elsewhere (6–8).

Previously, we reported the methods used to synthesize nanoscale iron and iron/palladium bimetallic particles with diameters typically less than 200 nm (10). A wider particle size range can be synthesized with a majority in the range of 100–200 nm in diameter (10). Laboratory studies have demonstrated that the nanoparticles are very effective reductants for a wide array of chlorinated hydrocarbons including chlorinated methanes, ethanes, benzenes, and polychlorinated biphenyls (10–13). The high reactivity of the nanoparticles can partly be attributed to their very high specific surface area (33.5 m²/g) as compared to that of conventional microscale iron (typically <1 m²/g). The reactivity can be dramatically increased by depositing a thin, discontinuous layer (<1 wt %) of noble metal on the iron surface. Many bimetallic combinations (e.g., Fe/Pd, Fe/Pt, Fe/Ag, Fe/Ni) have since been evaluated (10–14).

The metallic iron technology used in groundwater treatment, a striking manifestation of classic corrosion chemistry, has been extensively studied (15, 16). As is the case in corrosion chemistry, water and molecular oxygen typically serve as the electron acceptors in aqueous environments. Elemental iron acts as the electron donor while relatively oxidized compounds serve as the electron acceptors (e.g., are reduced). Burgeoning research over the past decade effectively demonstrates that reduction of many common environmental contaminants, both organic and inorganic, can be coupled to iron oxidation (15–20). Generally speaking, these contaminants are transformed into less toxic or even benign end products. For example, trichloroethene (TCE) can be reduced to ethane in accordance with the following stoichiometry:

\[
C_2HCl_3 + 4Fe^{0} + 5H^+ \rightarrow C_2H_6 + 4Fe^{2+} + 3Cl^- \quad (1)
\]

Iron is oxidized more rapidly when it is attached to a less active (noble) metal (e.g., Pd, Ag, Cu, Co, Ni). Therefore, the transformation of environmental contaminants can be enhanced by coupling iron to a noble metal (10–14, 21, 22). The iron–noble metal couple essentially creates numerous galvanic cells wherein iron serves as the anode and becomes preferably oxidized. Meanwhile, the noble metal (cathode) is protected and remains unchanged. Studies also suggest that noble metals such as palladium can promote dechlorination through catalytic functions such as hydrogenation (23, 24).

While most of the published research concerns granular or “microscale” iron particles (typically ≥50 μm), our work...
focusing on nanoscale iron. The combination of high reactivity and small size make the nanoparticles highly flexible remediation vehicles in a variety of environmental applications. For example, nanoparticles could be added in slurry reactors for the treatment of contaminated soil and sediment as they can penetrate intraparticle pores of soil and sediment aggregates that are inaccessible even to many microorganisms. Alternatively, the nanoparticles can be anchored onto granular activated carbon and other media in wastetreatment applications.

We report herein a field scale, “proof of concept” study involving the injection of the nanoscale bimetallic particles into a contaminated groundwater under gravity-feed conditions. Subsurface delivery of nanoparticles in this manner exemplifies the portability of the technology and its suitability for addressing contaminant hot spot and/or source areas. Moreover, because the nanoparticles are capable of “flowing” to some extent with groundwater, the nanoparticles can theoretically reach areas of contamination inaccessible by many conventional methods (e.g., beneath buildings and airport runways). Specific objectives for this study were to (i) evaluate the amenability of the synthesized nanoparticles for subsurface injection, (ii) assess changes of groundwater chemistry following the injection, and (iii) evaluate the efficacy of the nanoparticles for the transformation of chlorinated hydrocarbons.

Experimental Methods

Site Selection and Test Area Description. The site selected for the pilot scale test is an active manufacturing facility in Trenton, NJ. The test area is located within a relatively well-characterized plume downgradient of a former aboveground trichloroethylene (TCE) storage tank. The dimensions of the test area were approximately 4.5 by 3.0 m and encompassed a saturated thickness of about 6.0 m. Groundwater in the contaminated surficial aquifer is typically encountered at a depth of 1.8–2.1 m below ground surface (bgs) extending to saprolitic clay and bedrock at about 9 m bgs. A monitoring well, denoted DGC-15, served as the point of injection for the test (Figure 1). The test area also contained three nested piezometer pairs at 1.5-m intervals downgradient of the injection well along the principal direction of groundwater flow. The piezometer pairs were designated as PZ-1S and 1D, PZ-2S and 2D, and PZ-3S and 3D with the S and D referring to shallow and deep, respectively. DGC-15 was screened between 3 and 4.5 m bgs generally corresponding to shallow and deep, respectively. DGC-15 was screened between 1.5 m bgs, and the D piezometers were screened between 4.7 and 5.9 m bgs. The hydraulic conductivity (K) of the aquifer within the test zone was determined to be 0.2 cm/s, suggesting a reasonably permeable formation. Using this K and estimated values of the hydraulic gradient (0.001), the natural groundwater seepage velocity within the test area was estimated to be approximately 0.3 m/day. On the basis of an average saturated thickness of approximately 6.0 m and a porosity of 0.25, the estimated volume of groundwater in the test area was 14.1 m^3.

Groundwater Quality in the Test Area. Groundwater quality within the test area is well-characterized, having been monitored regularly for more than a decade. Several chlorinated hydrocarbon contaminants including tetrachloroethene (PCE), TCE, cis-dichloroethylene (c-DCE), vinyl chloride (VC), chloroform (CF), carbon tetrachloride (CT), and 1,1-dichloroethylene (1,1-DCE) at levels ranging from just above detection limits (1–3 μg/L) to 4600 μg/L have been recorded. The concentration of the principal contaminant, TCE, within the test area ranged from 445 to 800 μg/L just before the field study. Field determinations of pH and ORP were made using a Horiba U-22 multi-parameter meter and a flow-through cell. A certified analytical laboratory using U.S. EPA standard protocols furnished the analyses of volatile organic chemicals, total iron, and dissolved iron. The latter samples were field filtered through a 0.45-μm filter just prior to collection.

Test Area Equipment. Key components of the process train are shown in Figure 1. The system included two 625-L polyethylene storage tanks, one of which was used to feed the nanoparticle suspension while the other was on standby or was used to store recirculation volume. The feed tank was fitted with a mechanical agitator and a nitrogen gas feed system to maintain low dissolved oxygen conditions in the tank. The feed line included a totalizer to measure flow from the feed tank into the injection well. Recirculation was accomplished by pumping groundwater from piezometers 3S and 3D into the storage tank or the feed tank. Flowmeters and controllers were fitted onto dedicated Grundfos submersible pumps in piezometers 3S and 3D to enable control of the recirculation flow. The remaining piezometer pairs (PZ-1S/D and PZ-2S/D) were fitted with dedicated low flow sampling pumps to facilitate sample collection with minimal disturbance to the flow of groundwater.

Nanoparticle Synthetic Procedure. The nanoscale iron particles were synthesized by mixing equal volumes of 0.50 M NaBH₄ and 0.09M FeCl₃ solutions according to the following reaction (10–13):

\[
4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^{0} + 3H_2BO_3^- + 12H^+ + 6H_2
\]

Bimetallic particles were then prepared by reductive deposition of Pd²⁺ (from [Pd(C₂H₃O₂)₂]³⁻) on the freshly made iron nanoparticles:

\[
Fe^{0} + Pd^{2+} \rightarrow Fe^{2+} + Pd^{0}
\]

The palladium to iron ratio was controlled at less than 1:300 (w/w). As previously mentioned, the majority (~70%) of the bimetallic particles exhibited a relatively homogeneous size distribution between 100 and 200 nm as observed with a JEOL 6300F high-resolution field-emission scanning electron microscope (SEM).

Laboratory Feasibility Studies. Prior to the field test, laboratory feasibility experiments were conducted using groundwater and aquifer materials from the test area. Bench-scale batch experiments using 0.1 or 0.25 g of the nanoscale Fe⁰ or Fe⁰/Pd⁰ particles were mixed with 40 mL of groundwater and 40 g of sediment. The batch bottles were crimp-sealed with Teflon-lined septa and placed on a rotary shaker at 30 rpm. Parallel control experiments were performed under identical experimental conditions but without the nanoparticles.
The parameters of interest included TCE and its potential daughter compounds such as cis- and trans-DCEs, VC, ethene, ethane, and chloride. The concentrations of the chlorinated ethenes were determined by a HP5890 GC equipped with a DB-624 capillary column (Agilent, 30 m × 0.32 mm) and an electron capture detector (ECD). Hydrocarbons such as methane, ethene, and ethane were measured with the same model GC equipped with an AT-Q capillary column (Altitech, 30 m × 0.32 mm) and a flame ionization detector (FID) (10–13).

Results and Discussion

Bench-Scale Testing Results. Figure 2a depicts the reduction of TCE in batch tests with site groundwater and aquifer sediment samples. Complete dechlorination of TCE was achieved within 12 h for the samples containing 0.25 g of Fe/Pd, approximately 2 days for the samples containing 0.1 g of Fe/Pd, and about 1 month for the samples containing 0.25 g of iron particles. Ethylene and ethane were the principal end products in the bimetallic particle systems. The formation of ethylene and ethane provided evidence that TCE was reductively dechlorinated. The batches with palladium-coated iron particles produced much more ethane (74%) than ethene (6.2%), while only ethene (62%) was observed in the nonpalladized batches. Complete reduction (> 99%) of cis-DCE (~20 μg/L) and CT (~140 μg/L) in the groundwater was also observed.

Figure 2b shows the results from a multiple spiking experiment designed to assess the stability and durability of the nanoparticles. Each spike corresponds to an increase in TCE concentration from near zero to 2000 μg/L with no new addition of nanoparticles. Complete reduction of TCE was observed within 24 h for every TCE spike over the 62-day period.

Nanoparticle Injection Results. Prior to the introduction of the nanoparticles, recirculation of groundwater within the test area was performed over a period of 2 days. It involved withdrawal of groundwater at an average flow rate of 3–5 L/min from piezometers PZ-35 and PZ-3D and re-injection into DGC-15. The induced flow seepage velocities were not determined. However, a transient increase in the groundwater flow velocity was expected. The purpose of this recirculation was to establish more uniform contaminant concentrations within the test zone and to increase the mixing intensity during the injection. Within the test area, TCE concentrations ranged between 400 and 800 μg/L prior to recirculation. Following the injection process, monitoring well DGC-15 and the piezometer couplets were sampled over a period of approximately 4 weeks at an average frequency of two events per week.

On the first day of injection, approximately 890 L of a 1.5 g/L nanoparticle suspension (1.34 kg of nanoparticles) was fed into the injection well by gravity over a period of 6.3 h. During the second day, approximately 450 L of 0.75 g/L nanoparticle suspension (0.34 kg of nanoparticles) was fed over a period of 4 h. The injection process went smoothly. On day 1, an injection flow rate of 7.5 L/min was achieved over the initial hour but decreased to and was maintained at 3.7 L/min. A slug test conducted at the injection well 6 weeks later revealed that the hydraulic conductivity of the aquifer remained unchanged at 0.2 cm/s. In other words, the injection of the nanoparticles did not result in deterioration of aquifer permeability.

TCE Transformation during the Field Test. The test area is located in the middle of a much larger contaminant plume. Given that the mass of injected nanoparticles was relatively small and that “fresh” contaminated groundwater constantly entered the test area, we did not expect to completely eliminate the presence of TCE. Following the injection, TCE concentrations throughout the test zone declined rapidly before exhibiting varying degrees of recovery. Table 1 summarizes the reduction efficiency range obtained in the 4-week period following the injection of nanoparticles. TCE removal efficiencies ranged from 1.5% to 96.5%, exhibiting much spatial and temporal variability (Figure 3a). Not surprisingly, the highest removal efficiencies were achieved at the injection well (DGC-15) and closest piezometer. The TCE and iron concentration data generally exhibited a wavelike pattern consistent with the advection, dispersion, retardation, and reactions of the nanoparticle plume as it migrated within the test area. This behavior is consistent with the classic concepts of colloid transport and reactions in porous media.

Iron Transport in the Test Area. In lieu of monitoring the migration of the nanoparticles directly, we monitored total (FeT) and dissolved iron (Fe 2+) concentrations at each monitoring location throughout the test. Background total and dissolved iron concentrations were typically on the order of 1.0 mg/L or less. During the injection, total iron levels generally rose throughout the test area reaching levels of 135 mg/L in the injection well before declining to 32.2 mg/L 3 weeks after injection. Peak FeT concentrations of approximately 10–20 mg/L were also realized in piezometers PZ-1S, 2S, 2D, and 3S. As expected, the majority (> 50–75%) of the total iron detected could be attributed to Fe 2+ based upon the reducing redox conditions that prevailed as the leading edge of nanoparticles passed. A sizable percentage of the injected iron mass reached the more downgradient piezometers, and not surprisingly, declining Fe 2+ values were observed with increasing distance from the injection well. Using FeT concentration maxima as an indicator, the nanoparticle plume traveled at an apparent velocity of about 0.8 m/d, exceeding the natural seepage velocity of 0.3 m/d. Among others, factors including the residual effects of
recirculation and nanoparticle dispersion may have contributed to this result.

**ORP Changes Due to Nanoparticle Reactions.** The presence of nanoparticles temporarily altered the prevailing groundwater chemistry as they migrated through the subsurface. The parameters most affected were oxidation/reduction potential (ORP), dissolved oxygen (DO), and pH. Also known as redox potential, ORP is a measure of electron activity in a solution and indicates its relative tendency to accept or transfer electrons. In the literature, it is typically reported in terms of $E_n$ (millivolts, mV). Positive values of ORP generally imply oxidizing conditions while negative ORP values usually indicate reducing conditions. The interpretation of ORP data in groundwater must be performed with great care given that redox-liable species may not be in equilibrium under field conditions and that mixed potentials are often measured (2).

Historic ORP levels (i.e., data from 1995 to 1999) in the test area were generally between +150 and +250 mV. As displayed in Figure 3b, post-injection ORP levels declined significantly throughout the test area with reductions of more than 200 mV observed in DGC-15 and reductions of 100–160 mV observed in piezometers 1S, 2S, and 3S. Strongly reducing conditions were established (−360 mV) at DGC-15 within 4 days while slightly reducing (−20 to −75 mV) conditions were achieved at PZ-1S, 2S, and 3S 4–15 days after injection. This is attributable to the consumption of dissolved oxygen and other oxidants by the nanoparticles as they migrated within the aquifer. The TCE reduction efficiencies correlated well with the ORP at a given monitoring location (Figure 3c). For the more downgradient monitoring locations, we observed a lag period between the onset of ORP decline and the subsequent decline of TCE levels. The lag period was on the order of one to several days and increased with increasing distance from DGC-15. Such a lag period was not observed at DGC-15 or the adjacent piezometer couplet (PZ-1S and 1D) where essentially simultaneous ORP and TCE decline was observed. Interestingly, the ORP profile for PZ-3S did not follow the trend observed for DGC-15, PZ-1S, and PZ-2S as the ORP declined earlier than would have been expected given its distance from DGC-15. The cause of this apparent anomaly is not known but could be attributed to possible short-circuiting or preferential flow pathways, a localized reducing zone in that area unrelated to the nanoparticle plume, etc.

**Groundwater pH Changes Elicited.** In addition to the ORP response, the nanoparticles also cause the groundwater pH to rise at least temporarily as a result of their reactions with water and chlorinated hydrocarbons (also see eq 1):

$$\text{Fe}^{0} + 2H^{+} \rightarrow \text{Fe}^{2+} + H_2$$  (4)

In poorly buffered groundwaters, the pH rise can be significant (>2 standard pH units) and prolonged. However, most groundwaters contain some buffering capacity such that the anticipated pH rise would be less pronounced and transient due to natural dilution. Prior to the injection, the pH at all monitoring locations within the test area ranged between 4.6 and 5.2, indicating weakly acidic groundwater. After the nanoparticle injection, the pH range increased to 5.1–7.7 with the highest pH values observed at the injection well and adjacent piezometers. As was the case with ORP, the pH profile displayed a recovery as the localized nanoparticle-contaminant reactions neared completion and dilution and buffering reactions took place.

**Other Possible Benefits of the Nanoparticle Reactions.** We believe it is also worth mentioning that the ORP and pH changes following nanoparticle injection will likely foster creation of a more favorable environment for the growth of anaerobic microorganisms. Residual dissolved oxygen ($<0.2$ mg/L) was completely eliminated, and prevailing ORP was transformed into a moderately reducing ($-100$ to $-200$ mV) environment. The acidic pre-injection groundwater pH was moderate, and dissolved iron (predominantly Fe$^{3+}$) concentrations were significantly increased. Moreover, the lower post-injection TCE concentrations would be less inhibitory of microbial growth. Taken together, these factors should encourage the growth of iron reducing bacteria, which can participate in further natural attenuation processes (25).

**Ongoing Research Needs.** Although higher nanoparticle concentrations and more frequent dosing would be needed to achieve appreciable contaminant removal over an area of meaningful size, the nanoscale bimetallic particles were effective for the transformation of TCE. TCE was reduced to benign hydrocarbons including ethane and ethene. Results from this work support our contention that the nanoparticles technology is suited as an effective, flexible, and portable remedial technique for amenable groundwater contaminants such as chlorinated hydrocarbons. The ability to deliver nanoparticles directly to contaminant hot spots or source areas, and the relative simplicity of the process could make the nanoparticle technology effective for many applications. Additional work both in the lab and in the field are planned or ongoing and include the following: fate and transport of nanoparticles in soil columns and in subsurface; reactivity assessments of the injected nanoparticles with other amenable contaminants; development of suitable modeling tools to characterize the subsurface transport and reactivity of the nanoparticles; and long-term evaluations of the compatibility...
of the nanoparticles and microbially mediated reductive dehalogenation processes. The latter are central to a burgeoning number of monitored natural attenuation-based remediation strategies at numerous sites in the United States. Results from these studies will be reported in due course.

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