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Review

Nanoscale iron particles for environmental remediation: An overview

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Abstract

Nanoscale iron particles represent a new generation of environmental remediation technologies that could provide cost-effective solutions to some of the most challenging environmental cleanup problems. Nanoscale iron particles have large surface areas and high surface reactivity. Equally important, they provide enormous flexibility for *in situ* applications. Research has shown that nanoscale iron particles are very effective for the transformation and detoxification of a wide variety of common environmental contaminants, such as chlorinated organic solvents, organochlorine pesticides, and PCBs. Modified iron nanoparticles, such as catalyzed and supported nanoparticles have been synthesized to further enhance the speed and efficiency of remediation. In this paper, recent developments in both laboratory and pilot studies are assessed, including: (1) synthesis of nanoscale iron particles (10–100 nm, >99.5% Fe) from common precursors such as Fe(II) and Fe(III); (2) reactivity of the nanoparticles towards contaminants in soil and water over extended periods of time (e.g., weeks); (3) field tests validating the injection of nanoparticles into aquifer, and (4) *in situ* reactions of the nanoparticles in the subsurface.

Introduction

The scale of soil and groundwater contamination is enormous and the complexity is seemingly intractable. Consider just a few examples. A few blocks from this author's office is one of the largest brownfields in the US, the former Bethlehem Steel site occupying more than 2500 acres. There are more than 50 Superfund sites within 2 h of driving time from Lehigh University. Nationwide, more than 1500 sites have been put on the Superfund list (EPA, 2003a). Less than one third of them have been cleaned up in the past decade. The average cost for cleaning up a Superfund site has been reported to be more than 25 million dollars. According to US EPA, over 418,000 underground storage tank (UST) releases had been confirmed as of September 30, 2001. While much work has been and continues to be done, there are still about 150,000 UST sites remaining to be cleaned up (EPA, 2003b). The numbers of other contaminated sites such as abandoned mining sites, landfills, and industrial sites are just as staggering. The Federal government, including the Departments of Defense, Interior, and Energy is the owner of thousands of contaminated sites. The Department of Energy (DOE) alone has about 6.4 billion cubic meters of contaminated soil, groundwater, and other environmental media at the DOE sites with a wide variety of contaminants, from radionuclides to metals and dense nonaqueous phase liquids (DNAPL) (DOE, 2002). If \$100/ton or \$100/m^3 (a commonly used yardstick by consultants) is needed to cleanup the contaminated soil and/or water, the aggregated financial burden for site cleanup is truly colossal.

Despite their minuscule status, nanoscale particles may hold the potential to cost-effectively address some of the challenges of site remediation (Masciangioli and Zhang, 2003; EPA, 2003d,e). Two factors contribute to the nanoparticles' capabilities as an extremely versatile remediation tool. The first is their small particle sizes (1–100 nm). In comparison, a typical bacterial cell has a diameter on the order of 1 μm (1000 nm). Nanoparticles can be transported effectively by the flow of groundwater. Due to this attribute, the nanoparticle–water slurry can be injected under pressure and/or by gravity to the contaminated plume where treatment is needed. The nanoparticles can also remain in suspension for extended periods of time to establish an *in situ* treatment zone. Equally important, they provide enormous flexibility for both *in situ* and *ex situ* applications. For example, nanoparticles are easily deployed in slurry reactors for the treatment of contaminated soils, sediments, and solid wastes. Alternatively, nanoparticles can be anchored onto a solid matrix such as activated carbon and/or zeolite for enhanced treatment of water, wastewater, or gaseous process streams. Direct subsurface injection, whether under gravity-fed or pressurized conditions, has already been shown to effectively transform chlorinated organic compounds (Elliott & Zhang, 2001; Glazier et al., 2003). The technology holds great promise for immobilizing heavy metals and radionuclides as well. Examples of potential applications of nanoscale iron particles for site remediation are further illustrated in Figure 1.

In this paper, an overview is provided on the recent progress in laboratory studies and field tests of nanoscale iron particles for environmental remediation. Synthesis and characterization of supported and unsupported nanoparticles are reviewed. Examples are presented from laboratory studies of the nanoparticles for transformation of common soil and groundwater contaminants. A field test of the nanoscale iron particles is summarized.

Nanoscale iron particles

Metallic or zero-valent iron (Fe^0) is a moderate reducing reagent, which can react with dissolved oxygen (DO) and to some extent with water:

$$2Fe^{0}_{(s)} + 4H^{+}_{(aq)} + O_{2(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \qquad (1)$$

$$Fe^{0}_{(s)} + 2H_2O_{(aq)} \rightarrow Fe^{2+}_{(aq)} + H_{2(g)} + 2OH^{-}_{(aq)} \qquad (2)$$

The above equations are the classical electrochemical/corrosion reactions by which iron is oxidized from exposure to oxygen and water. The corrosion reactions can be accelerated or inhibited by manipulating the solution chemistry and/or solid (metal) composition. Since early 1990s, the iron corrosion chemistry has been put into productive use in the treatment of hazardous and toxic chemicals, thanks to the discovery of Gillham and co-worker (Gillham & O'Hannesin, 1994; Orth & Gillham, 1996; O'Hannesin & Gillham, 1998) and works by many others. The environmental chemistry of metallic or zero-valent iron has been extensively documented (EPA, 2003c). Contaminants

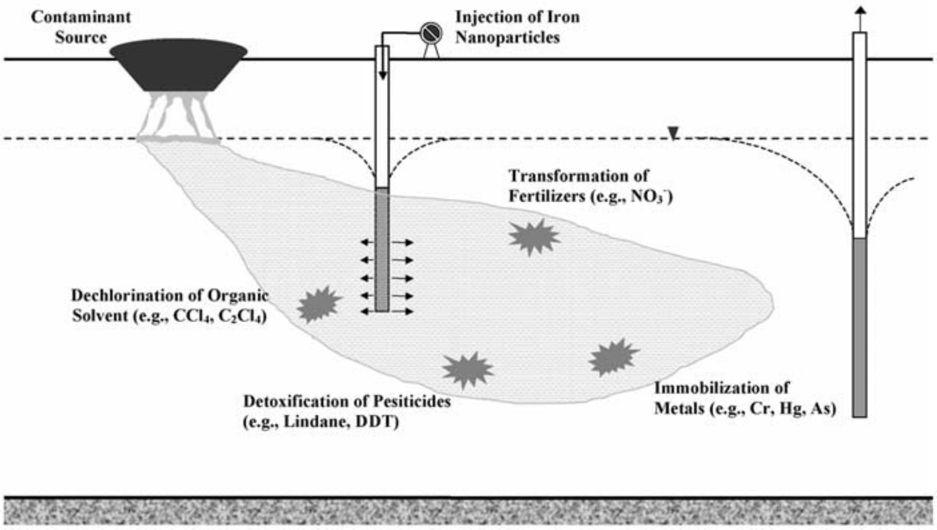

Figure 1. Nanoscale iron particles for *in situ* remediation. Recent research has suggested that as a remediation technique, nanoscale iron particles have several advantages: (1) effective for the transformation of a large variety of environmental contaminants, (2) inexpensive, and (3) nontoxic.

such as tetrachloroethene (C_2Cl_4), a common solvent, can readily accept the electrons from iron oxidation and be reduced to ethene in accordance with the following stoichiometry:

$$C_2Cl_4 + 4Fe^0 + 4H^+ \rightarrow C_2H_4 + 4Fe^{2+} + 4Cl^- \quad (3)$$

Environmental applications of metallic iron have been enthusiastically accepted by many users and regulatory agencies, largely due to the low costs and absence of any known toxicity induced by the use of iron. Use of metallic iron in the form of packed bed reactors and permeable reactive barriers has been widely reported (EPA, 2003c).

Work at the author's laboratory at Lehigh University has focused on the research and development of nanoscale iron particles for environmental remediation. In 1996, we developed a method to synthesize nanoscale iron particles (Wang & Zhang, 1997; Zhang et al., 1998). Typically, nanoparticles can be prepared by using sodium borohydride as the key reductant. For example, $NaBH_4$ (0.2 M) is added into $FeCl_3 \cdot 6H_2O$ (0.05 M) solution (~1 : 1 volume ratio). Ferric iron is reduced by the borohydride according to the following reaction (Wang & Zhang, 1997):

$$\begin{aligned} &4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow \\ &\qquad 4Fe^0 \downarrow + 3H_2BO_3^- + 12H^+ + 6H_2 \end{aligned} \quad (4)$$

Note that excessive borohydride is typically needed to accelerate the synthesis reaction and ensure uniform growth of iron crystals. Synthesis at much lower concentrations and the use of ferrous iron has also successfully performed.

Palladized Fe particles are prepared by soaking the freshly prepared nanoscale iron particles with an ethanol solution containing 1 wt % of palladium acetate ($[Pd(C_2H_3O_2)_2]_3$). This causes the reduction and subsequent deposition of Pd on the Fe surface (Wang & Zhang, 1997):

$$Pd^{2+} + Fe^0 \rightarrow Pd^0 + Fe^{2+} \quad (5)$$

Similar methods were used to prepare Fe/Pt, Fe/Ag, Fe/Ni, Fe/Co, Fe/Cu bimetallic particles (Xu & Zhang, 2000). A photomicrographic image of the iron nanoparticles was recorded with a Philips EM 400T Transmission Electron Microscopy (TEM) as shown in Figure 2. Nanoparticle samples were prepared by depositing two or three droplets of dilute Fe nanoparticle containing ethanol solution onto carbon films (Ernest Fullan Inc.). Measurement of over 150 particles yielded a mean value of particle diameter at 66.6 ± 12.6. The median size was 60.2 nm. Most particles (>80%) had diameters less than 100 nm with 30% less than 50 nm. The average specific BET surface area of the nanoscale Pd/Fe particles was about $35 \pm 2.7\ m^2/g$.

While it is well recognized that the metallic iron nanoparticles are powerful remediants, the colloidal chemistry of these particles is such that they tend to agglomerate and adhere to soil surfaces. Work in Mallouk's group at Pennsylvania State University has explored carbon nanoparticles used as a support for iron and bimetallic (e.g., Fe/Ni) compositions (Ponder et al., 2000; 2001; Schrick et al., 2002). The carbon consists of platelets that are 50–200 nm in diameter, i.e., smaller than the slit size in essentially all soils. The platelets are first made anionic by the reaction

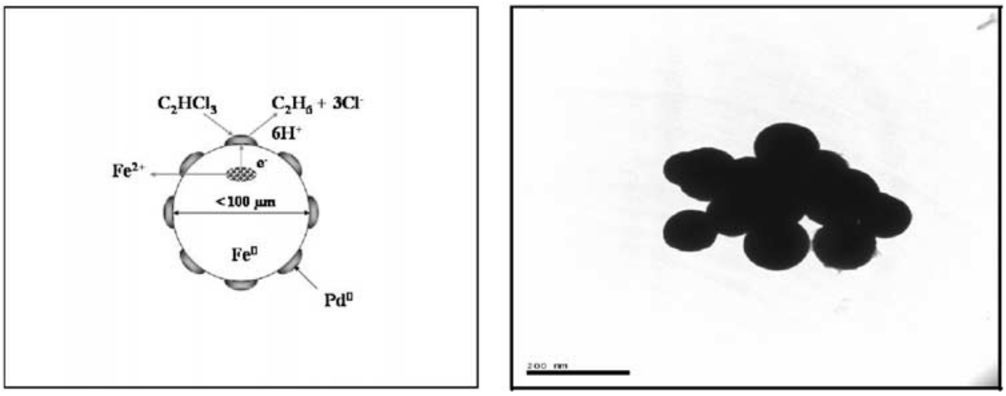

Figure 2. (a) Schematic depiction of the nanoparticle-mediated reduction of trichloroethene in water. (b) Transmission electron microscope photomicrograph of a nanoparticle cluster. Size bar is 200 nm.

of their edges with a diazonium salt of benzenesulfonic acid, the same process used to make dispersable inks and toners from carbon black. It was hypothesized that the diazonium salt of benzenesulfonic acid reacts primarily at the edges of the carbon sheets, and that the metal nanoparticles are supported on the carbon basal planes. The resulting material can form a permanent suspension in water and can be used in this form during the standard borohydride synthesis of zero-valent metal nanoparticles. The microstructure of the support/metal particles is relevant to their reactions with many hydrophobic organic contaminants that are known to adsorb strongly to carbon materials. In a similar manner, water-soluble polyelectrolytes such as poly(acrylic acid) (PAA) have been used as nanoparticle supports. Dramatic enhancement in permeability was observed with PAA-supported nanoparticles using both sand and soils (Ponder et al., 2000; 2001; Schrick et al., 2002).

Laboratory assessment

Recent laboratory research has largely established nanoscale iron particles as effective reductants and catalysts for a wide variety of common environmental contaminants including chlorinated organic compounds and metal ions (Lien, 2000; Lien & Zhang, 1999, 2001; Zhang et al., 1998). Examples are given in Table 1. For halogenated hydrocarbons, almost all can be reduced to benign hydrocarbons by the nano-Fe particles. Ample evidence indicates that iron based materials have been successful in the transformation of many other contaminants, including anions (e.g., NO_3^-, $Cr_2O_7^{2-}$), heavy metals (e.g., Ni^{2+}, Hg^{2+}), and radionuclides (e.g., UO_2^{2+}).

In this section, results from a recent laboratory experiment are presented. The laboratory study was conducted as a part of a project to evaluate the potential of using nanoscale iron particles for *in situ* remediation of chlorinated organic solvents (e.g., 1,1,1-trichloroethane (TCA), trichloroethene (TCE)) found in the soil and groundwater at an US Naval site. Groundwater and soil samples were collected at the site and were shipped to Lehigh University for various laboratory tests. The tests were conducted during the period of August 2002 to March 2003. Experiments were designed to determine the concentrations of organic contaminants, to investigate changes of groundwater chemistry as a result of the addition of the nano iron

Table 1. Common environmental contaminants that can be transformed by nanoscale iron particles

- Chlorinated methanes
  - Carbon tetrachloride (CCl_4)
  - Chloroform ($CHCl_3$)
  - Dichloromethane (CH_2Cl_2)
  - Chloromethane (CH_3Cl)
- Chlorinated benzenes
  - Hexachlorobenzene (C_6Cl_6)
  - Pentachlorobenzene (C_6HCl_5)
  - Tetrachlorobenzenes ($C_6H_2Cl_4$)
  - Trichlorobenzenes ($C_6H_3Cl_3$)
  - Dichlorobenzenes ($C_6H_4Cl_2$)
  - Chlorobenzene (C_6H_5Cl)
- Pesticides
  - DDT ($C_{14}H_9Cl_5$)
  - Lindane ($C_6H_6Cl_6$)
- Organic dyes
  - Orange II ($C_{16}H_{11}N_2NaO_4S$)
  - Chrysoidine ($C_{12}H_{13}ClN_4$)
  - Tropaeolin O ($C_{12}H_9N_2NaO_5S$)
  - Acid Orange
  - Acid Red
- Heavy metal ions
  - Mercury (Hg^{2+})
  - Nickel (Ni^{2+})
  - Silver (Ag^+)
  - Cadmium (Cd^{2+})
- Trihalomethanes
  - Bromoform ($CHBr_3$)
  - Dibromochloromethane ($CHBr_2Cl$)
  - Dichlorobromomethane ($CHBrCl_2$)
- Chlorinated ethenes
  - Tetrachloroethene (C_2Cl_4)
  - Trichloroethene (C_2HCl_3)
  - *cis*-Dichloroethene ($C_2H_2Cl_2$)
  - *trans*-Dichloroethene ($C_2H_2Cl_2$)
  - 1,1-Dichloroethene ($C_2H_2Cl_2$)
  - Vinyl chloride (C_2H_3Cl)
- Other polychlorinated hydrocarbons
  - PCBs
  - Dioxins
  - Pentachlorophenol (C_6HCl_5O)
- Other organic contaminants
  - N-nitrosodimethylamine (NDMA) ($C_4H_{10}N_2O$)
  - TNT ($C_7H_5N_3O_6$)
- Inorganic anions
  - Dichromate ($Cr_2O_7^{2-}$)
  - Arsenic (AsO_4^{3-})
  - Perchlorate (ClO_4^-)
  - Nitrate (NO_3^-)

particles, and to examine the efficacy of the nanoparticles for dechlorination of major chlorinated organic compounds found in the groundwater and soil.

The groundwater contained approximately 6070 μg/l of TCA, 4680 μg/l of TCE and a few other chlorinated hydrocarbons (e.g., tetrachloroethene, dichloroethene) at lower concentrations (<100 μg/l). Batch reactors were loaded with 80 ml water, 0–20 g soil, and nanoparticles at varied concentrations. At selected time intervals, a 5–10 μl headspace aliquot was withdrawn from the batch bottle for analysis. Organic concentrations were measured by the static headspace gas chromatograph (GC) method. Concentrations of chlorinated volatile compounds were measured using a HP5890 GC equipped with a DB-624 capillary column (30 m × 0.32 mm) and an electron capture detector (ECD). Hydrocarbon products in the headspace were qualitatively identified with a Shimadzu QP5000 GC-MS and further quantified with GC analysis by comparing retention times and peak areas with standard gas samples (ethane, ethene, acetylene, methane and carbon dioxide etc.).

According to Eqs. (1) and (2), iron-mediated reactions should produce a characteristic increase in pH and decline in solution redox potential (E_H). A highly reducing environment ($E_H \ll 0$) is created through the rapid consumption of oxygen and other potential oxidants and production of hydrogen. Figure 3 presents the pH/ORP (oxidation–reduction potential) trends after the addition of the nanoscale iron particles into a batch reactor. Typically in a closed batch reactor, a pH increase of 2–3 units was observed while ORP reduction was in the range of 500–900 mV. It is expected that the pH and ORP changes would be less dramatic for field applications wherein diffusion and other mechanisms dilute the chemical changes. Our previous field experiments suggest that the water pH was increased by about one pH unit, and ORP can be maintained at -300 to -500 mV (Elliott & Zhang, 2001; Glazier et al., 2003). The pH increase and potential decrease at the site should favor the growth of anaerobic microorganisms, which could be beneficial for accelerated biodegradation. Production of hydrogen gas and also ferrous iron ion should further encourage microbial growth. It has been suggested that the nanoscale iron particles can be used as an efficient reducing reagent for regulating the standard potential in the subsurface and for chemical and/or biological dechlorination.

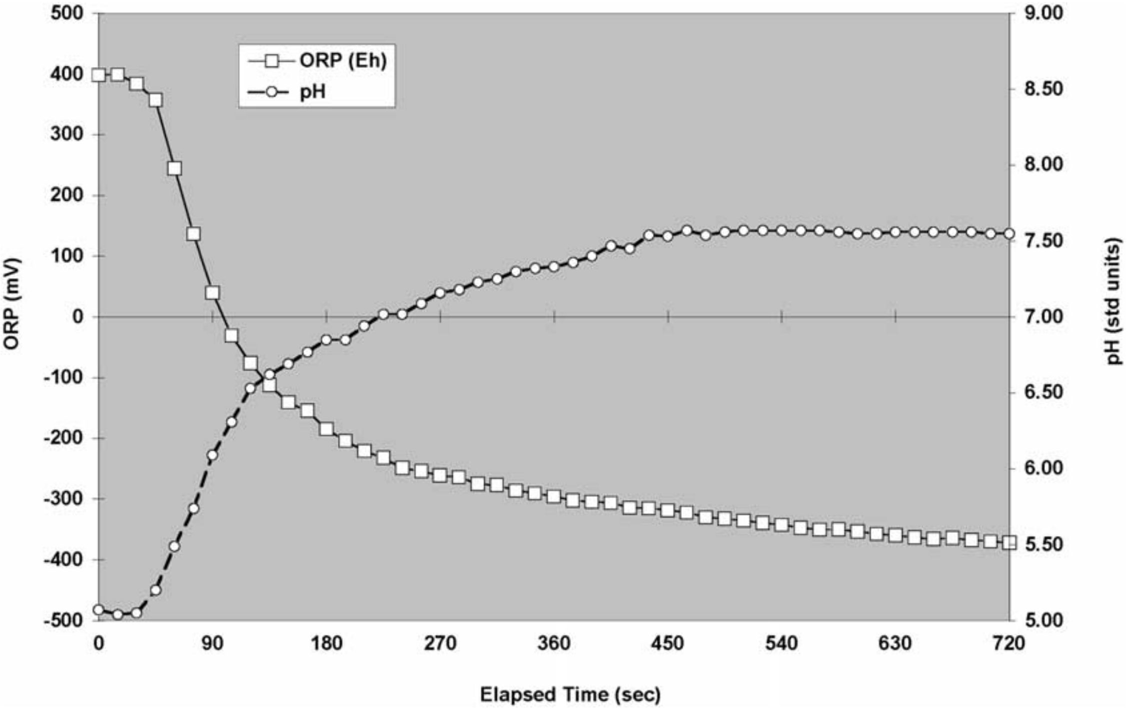

Figure 3. Water chemistry of nanoscale iron particles. Rapid pH and Oxidation Reduction Potential (ORP) changes were observed after the addition of 0.11 g/l of the Pd/Fe nanoparticles in water. Very low ORP can be established in 200 s.

Rapid and complete dechlorination of all chlorinated contaminants was achieved within the water and soil–water slurries. For example, with a nanoscale Pd/Fe particle dose at 6.25 g/l, all chlorinated compounds were reduced to below detection limits (<10 μg/l) within 8 h (with and without soil). Ethane was the major product in all tests. Greater than 99% removal was achieved with nanoscale iron particle (no palladium) in 24 h (Figure 4). Experiments with repeated spiking of TCE suggest that the laboratory-synthesized nanoscale particles can remain reactive within the soil and water environments for extended periods of time

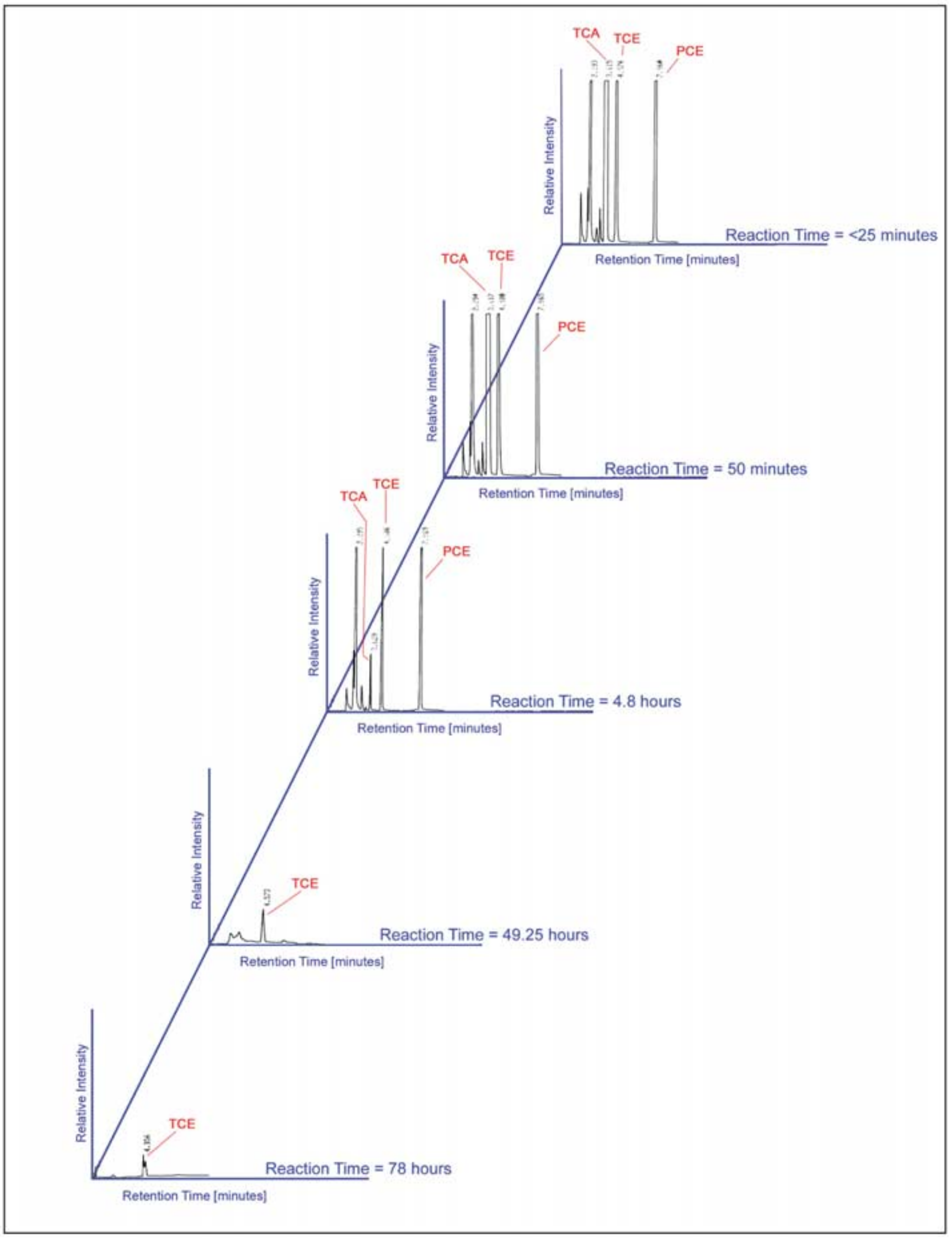

Figure 4. GC chromatograms from a batch reactor, which contained 80 ml of groundwater and 1.1 g nano Fe (no pallidium). Initial concentrations of TCA, TCE, and PCE (tetrachloroethene) were 6070, 4680, and 100 μg/l, respectively.

(6–8 weeks). Laboratory tests also demonstrated that the addition of the nanoparticles creates highly reducing conditions with low standard potentials (-300 to -500 mV).

Further analysis of the batch test data suggests that the nanoscale Pd/Fe particles can achieve a dechlorination rate of ~1 mg TCE/g nano Fe/h and a total capacity of approximately 100–200 mg TCE/g nano Fe. The rate and capacity parameters are approximately 1–3 orders of magnitude higher than conventional iron powders (e.g., >10 μm).

Field assessment

In this section, results from a recent field-demonstration of the nanoscale iron nanoparticles for *in situ* groundwater treatment is reviewed (Glazier et al., 2003). The test was carried out at an industrial/research facility located in Research Triangle Park, North Carolina. Based on a review of potentially applicable technologies, the nanoscale iron particle technology was retained for evaluation by the site owner because of its potential effectiveness in the treatment of chlorinated solvents found at the site. Following regulatory agency approval, the pilot test was implemented in September 2002. The following section summarizes the hydrogeologic setting of the site, the steps taken to implement the pilot test, and the degree of treatment achieved.

The site is located in the west-central portion of the Durham subbasin, one of a string of half-graben structures that formed during Late Mesozoic age continental rifting that occurred along the Atlantic seaboard of North America. The stratigraphy of Triassic age sedimentary bedrock at the Site has been compiled from subsurface investigations including rock cores, suites of downhole geophysical logs, as well as, televiewer and downhole video data collected from a large number of boreholes. Integration of the large data set within a hydrostratigraphic framework allowed the recognition of distinct, stacked, and repeating sedimentary packages consisting of sandstone grading and fining upward into siltstone.

In general, groundwater flow at the site is radial (Figure 5), with a hydraulic divide along the topographic ridge. In bedrock, groundwater flow is structurally controlled. Rock core and optical televiewer data have shown that the most abundant discontinuities in the bedrock are gently dipping bedding planes. Although, higher angle fractures appear to be more frequent within the sandstone–siltstone package, with somewhat higher frequency within the siltstone package. Hydraulic conductivity data used in conjunction with geologic structural data indicates that the geologic contact between rock packages and rock horizons (i.e., bedding plane partings) are the most permeable features at the site. Therefore, groundwater flow is influenced by the changing nature of the bedding plane hydraulic conductivity as shown by the boundary analysis of the pumping tests conducted at the site.

The hydraulic conductivity in the test area is approximately 10^{-3} cm/s. However, the hydraulic conductivity decreases with depth. This prevents migration of groundwater downdip along bedding planes to the east–southeast. In addition, the lower vertical component of hydraulic conductivity across bedding planes also reduces downward migration of groundwater.

The following pilot test activities were conducted: (i) installation of the injection well and monitoring wells; (ii) analysis of groundwater samples from the injection well and monitoring wells to define baseline conditions prior to the commencement of the pilot test; (iii) pilot test field implementation and nanoparticle injection monitoring using continuous electronic measurements of flow rate, water level, ORP, DO, pH, specific conductance, and temperature; and (iv) post-injection monitoring.

The pilot test was conducted in an area approximately 38 m (125 feet) downgradient from, a former waste disposal area. Wastes previously were excavated from this area; however, residual impact to the subsurface environment remained. This area was selected because of the relatively high groundwater contaminant concentrations historically detected in this portion of the site. The nanoparticle injection well (BNP-4) was installed into shallow bedrock approximately 38 m northeast of the former waste disposal area. Downgradient monitoring wells (BNP-3 and BNP-2) were drilled into shallow bedrock at 6.6 m (22 feet) to the north and 13 m (43 feet) to the east–northeast of BNP-4, respectively. Existing monitoring well (GW-4) was used as the third monitoring point located at 19 m (63 feet) northeast of the injection point.

Baseline groundwater sampling provided data regarding the groundwater geochemistry and contaminant concentrations at the test location prior to the nanoparticle injection. On September 12, 2002, one day before the injection, groundwater samples were collected from the injection well and the three monitoring wells (BNP-2, BNP-3, and GW-4). Two additional existing wells were also sampled to provide pre-injection

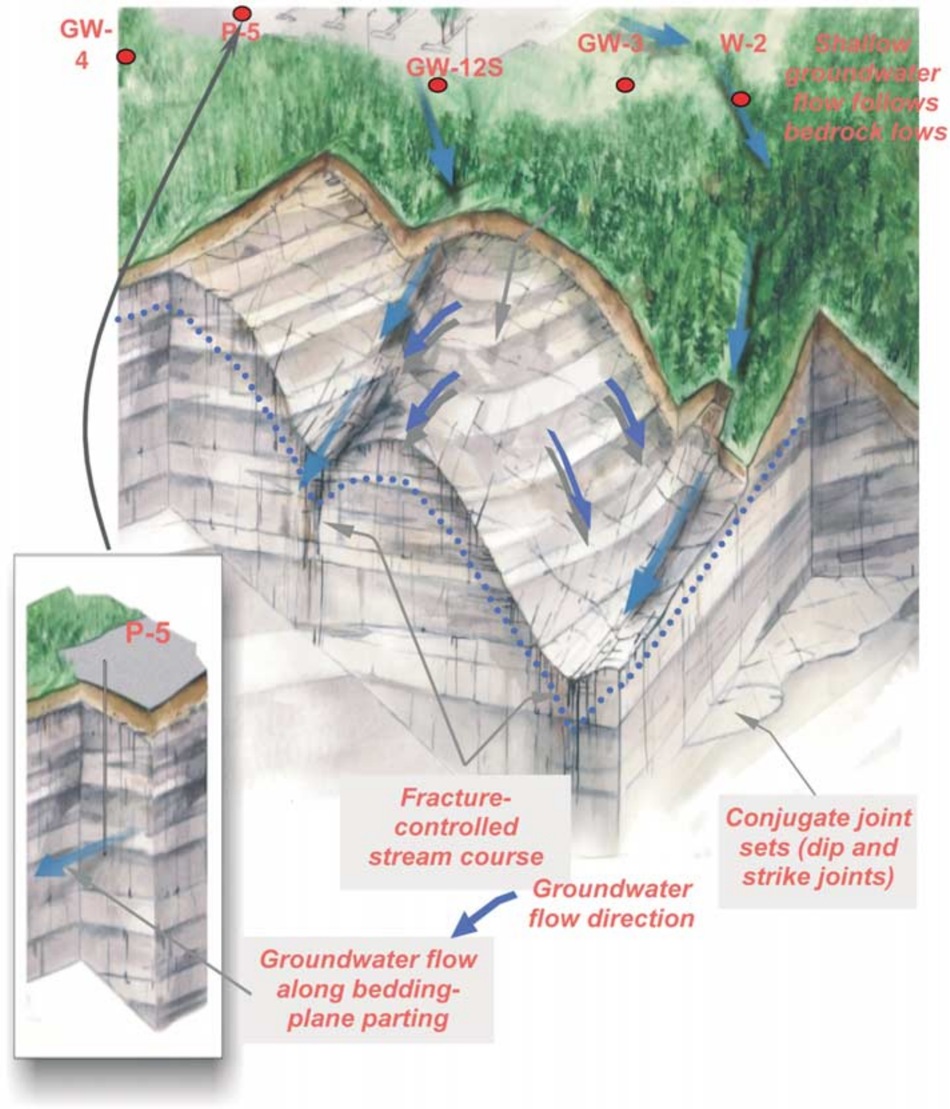

Figure 5. Conceptual model of *in situ* application of nanoscale iron particles. The nanoparticles were introduced into the aquifer by gravitational flow (Glazier et al., 2003).

baseline chemistry data. The baseline samples were analyzed for various volatile organic compounds (VOCs), metals, chloride, and a suite of redox-sensitive biogeochemical parameters.

The iron nanoparticles were injected as a slurry suspension that was prepared on-site using potable water. The total slurry volume injected was 6056 l (1600 gallons) at a nanoparticle concentration of 1.9 g/l in the slurry. The total nanoparticle mass injected was 11.2 kg. The injection was carried out from September 13 through September 15, 2002, at an average injection rate of 0.6 gallons per minute (gpm).

Potable water and nanoparticles were mixed in a 1500 l (400 gallon) tank, and the injection was carried out by pumping the slurry into the well. During injection, the slurry in the tank was mixed continuously to prevent settlement of the larger size particle aggregates. In-well mixing during injection was also provided using a submersible pump placed at the bottom of the injection well and equipped with short discharge tubing (below the water level). This allowed continuous recirculation of the nanoparticle slurry within the well screen area of the injection well.

The injection flow rate was monitored with an electronic flowmeter and the water level change in the injection well (BNP-4) was monitored with a vented pressure transducer attached to a datalogger. The monitoring wells (BNP-2, BNP-3, and GW-4) were monitored with multi-parameter Troll 9000 dataloggers to record water level, ORP, DO, pH, specific conductance, and temperature. The multi-parameter dataloggers were maintained in the monitoring wells for long-term monitoring. During the treatment phase monitoring, field indicator parameters (i.e., water level, ORP, DO, pH, specific conductance, and temperature) were measured continuously with electronic dataloggers in three of the wells. These parameters were also monitored *ex situ* during purging using a flow-thru cell.

The results of the field-scale treatability pilot test agree favorably with those of previously published laboratory tests (Wang & Zhang, 1997; Lien & Zhang, 1999; 2001; Xu & Zhang, 2000) and field tests (Elliott & Zhang, 2001). Over 90% reduction in the pre-injection baseline concentration of approximately 14,000 μg/l of total chlorinated VOCs was achieved within several days in the injection well (BNP-4) and observation well BNP-3 (Figure 6). PCE, TCE, and DCE concentrations were also reduced to levels near or below groundwater quality standards within six weeks of nanoparticle injection without increases in the concentrations of the daughter product vinyl chloride.

The pre-injection baseline ORP conditions in most of the test area were indicative of iron-reducing conditions (i.e., approximately +50 mV to −100 mV redox potential), and were lowered to methanogenic conditions during and after the injection, with measured *in situ* redox potentials of approximately −700 mV in the injection well, and −500 mV in the nearby monitoring wells.

The radius of influence of the injection, as measured by significant contamiant concentration reduction, was approximately 6–10 m around the injection well. It is possible that a wider radius could be achieved by modifying the injection procedure to either (1) inject the nanoparticle slurry under pressure, or (2) pump groundwater from a nearby cross-gradient well in order to draw the slurry into an elongate slug with the long axis perpendicular to the direction of groundwater flow.

Concluding remarks

Our recent work has demonstrated that: (1) nanoscale iron particles (10–100 nm) can be synthesized from

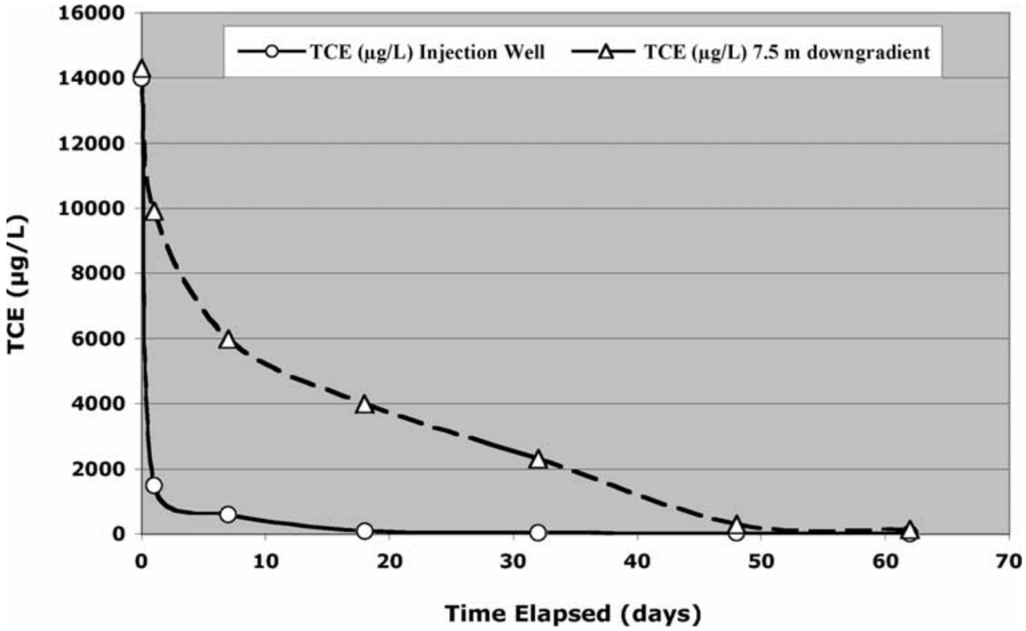

Figure 6. Reduction of TCE following the *in situ* application of nanoscale iron particles.

common precursors such as Fe(II) and Fe(III); (2) the nanoparticles can remain reactive towards contaminants in soil and water for extended periods of time (>4–8 weeks); (3) field tests showed that the injection of nanoparticle slurry into aquifer is relatively uncomplicated, (4) the nanoparticles can flow with groundwater over 20 m distance, (5) rapid *in situ* reactions have been observed with TCE reduction up to 99% in a few days after the nanoparticle injection. More attention should be directed to the fundamentals of nanochemistry in the environment, i.e., contaminant transformation at the nanoparticle–water interface. More field-scale studies to investigate the transport and reaction mechanisms are clearly needed to further determine the potential and limits of the technology. Through improved understanding of geochemistry of nanoparticles in both basic and field demonstrations in well-characterized environments, the prospect for successful exploiting the nanoscale technology for environmental applications appears very good.

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