Zero-Valent Iron Nanoparticles for Abatement of Environmental Pollutants: Materials and Engineering Aspects

Xiao-qin Li, Daniel W. Elliott, and Wei-xian Zhang*
Center for Advanced Materials and Nanotechnology, Department of Civil and Environmental Engineering, Lehigh University, Bethlehem, Pennsylvania, USA

Zero-valent iron nanoparticle technology is becoming an increasingly popular choice for treatment of hazardous and toxic wastes, and for remediation of contaminated sites. In the U.S. alone, more than 20 projects have been completed since 2001. More are planned or ongoing in North America, Europe, and Asia. The diminutive size of the iron nanoparticles helps to foster effective subsurface dispersion whereas their large specific surface area corresponds to enhanced reactivity for rapid contaminant transformation. Recent innovations in nanoparticle synthesis and production have resulted in substantial cost reductions and increased availability of nanoscale zero-valent iron (nZVI) for large scale applications. In this work, methods of nZVI synthesis and characterization are highlighted. Applications of nZVI for treatment of both organic and inorganic contaminants are reviewed. Key issues related to field applications such as fate/transport and potential environmental impact are also explored.

Keywords zero-valent iron, nanoparticle, remediation, environmental nanotechnology, synthesis, characterization, toxic waste

Table of Contents

1. INTRODUCTION ............................................................................................................................... 111

2. IRON NANOPARTICLES FOR ENVIRONMENTAL REMEDIATION .................................................. 112
   2.1 Synthesis of Iron Nanoparticles .................................................................................................. 113
   2.2 Characterization of Iron Nanoparticles ................................................................................. 114
   2.3 Degradation of Organic Contaminants .................................................................................. 116
   2.4 Remediation of Inorganic Contaminants ............................................................................... 118
   2.5 Transport of the Iron Nanoparticles ....................................................................................... 119

3. CHALLENGES AHEAD ................................................................................................................... 121

ACKNOWLEDGMENTS ..................................................................................................................... 121

REFERENCES ........................................................................................................................................ 121

1. INTRODUCTION

Due to their subcolloidal size and unique molecular and/or atomic structures, many nanomaterials have been shown to possess distinctive mechanical, magnetic, optical, electronic, catalytic, and chemical properties that contribute to promising applications in machinery, energy, optics, electronics, drug delivery, and medical diagnostics.1–6 The large surface-to-volume ratio of nanomaterials can lead to surprising surface and quantum size effects. As particle size decreases, the proportion of surface and near surface atoms increases. Surface atoms tend to have more unsatisfied or dangling bonds with concomitantly higher surface energy. Thus, the surface atoms have a stronger

*E-mail: wez3@lehigh.edu
tendency to interact, adsorb, and react with other atoms or molecules in order to achieve surface stabilization. For example, carbon nanotubes have been widely reported to exhibit an extremely high storage capacity for hydrogen and may serve as an ideal material for fuel cells, energy storage, and transmission.

New discoveries on nanomaterials are being reported at an ever-increasing rate. Generally speaking, gold is considered to be a rather stable and inert substance. However, nano-gold particles (<10 nm) exhibit very high affinity for many functionalized species including amino and nucleic acids and have been used as molecular delivery carriers. When functionalized with oligonucleotides, gold nanoparticles can act as intracellular gene regulation agents for the control of protein expression in cells. Moreover, titania nanoparticles have far better chemical stability, optical properties, and higher photochemical reactivity than their conventional microscale counterparts. It has been suggested that titania nanoparticles are more suitable for photoelectrical energy conversion and photocatalysis. At the nanoscale, the energy and electronic properties of materials are discrete rather than existent in a continuum as is the case for bulk materials. The quantum size effect of nanomaterials has found many interesting applications, notably in electronics, information storage, and also in nanosensors. The quantum size effect even allows detection of single molecules and/or single biological cells.

Interestingly, nanoscale materials also exist ubiquitously in the natural environment. Biomolecules such as DNAs and proteins have characteristic dimension(s) in the nano domain (1–100 nm). The particle sizes of natural materials, such as viruses, smog aerosols, and weathered minerals such as iron oxides and silicates, are often on the nanoscale or have nanoscale components. Engineered nanomaterials have found increasing environmental applications, notably in electronics, information storage, and also in nanosensors. The quantum size effect even allows detection of single molecules and/or single biological cells.

FIG. 1. The core-shell model of zero-valent iron nanoparticles. The core consists of mainly zero-valent iron and provides the reducing power for reactions with environmental contaminants. The shell is largely iron oxides/hydroxides formed from the oxidation of zero-valent iron. The shell provides sites for chemical complex formation (e.g., chemosorption).

2. IRON NANOPARTICLES FOR ENVIRONMENTAL REMEDIATION

The nanoparticles (<100 nm) discussed in this contribution are zero-valent iron (ZVI) particles and exhibit a typical core-shell structure as illustrated in Figure 1. The core consists primarily of zero-valent or metallic iron while the mixed valent [i.e., Fe(II) and Fe(III)] oxide shell is formed as a result of oxidation of the metallic iron. Iron typically exists in the environment as iron(II)- and iron(III)-oxides, and as such, ZVI is a manufactured material. Thus far, applications of ZVI have focused primarily on the electron-donating properties of ZVI. Under ambient conditions, ZVI is fairly reactive in water and can serve as an excellent electron donor, which makes it a versatile remediation material.

The use of ZVI as a remediation agent in groundwater treatment started in early 1990s when granular ZVI was first employed in permeable reactive barrier (PRBs) systems. In a PRB structure, groundwater flows passively through an engineered iron wall while contaminants are precipitated, adsorbed, or transformed in contact with the ZVI surface. Over 100 such PRB structures have been constructed in the U.S. since the early 1990s. Although PRBs containing ZVI powders may serve as useful in-situ remedies for some sites, important challenges still exist for this technology that may limit its practical application. For example, a large amount (e.g., tons) of iron powder is usually needed even for a modest PRB structure. Costs associated with the PRB construction, especially for deep aquifers, remains too high for many potential users of the technology. Another important limitation is the relative lack of flexibility after a PRB is
installed. Relocation or major modifications to the PRB infrastructure is often impractical.

The nanoscale iron (nZVI) technology discussed herein can be regarded as an extension of the ZVI technology. In some cases, it may serve as an alternative to the conventional ZVI PRBs. For other sites, the nZVI process can complement (or supplement) the fixed PRBs. For example, nZVI injections can be used to address the heavily contaminated source area or other “hot spots” whereas ZVI PRB functions as barrier to contain the dispersion of contaminants. Because of their small size, nanoparticle slurries in water can be injected under pressure and/or even by gravity flow to the contaminated area and under certain conditions remain in suspension and flow with water for extended periods of time. An in-situ treatment zone may thus be formed. Alternatively, iron nanoparticles also can be used in some ex-situ applications.

Over the past decade, extensive studies have demonstrated that ZVI nanoparticles are effective for the treatment of many pollutants commonly identified in groundwater, including perchloroethylene (PCE) and trichloroethylene (TCE), carbon tetrachloride (CT), nitrate, energetic munitions such as TNT and RDX, legacy organohalogen pesticides such as lindane and DDT; as well as heavy metals like chromium and lead. Examples of some recent field applications using ZVI nanoparticles are presented in Table 1.

There are two general strategies in terms of nanoparticle synthesis: top-down and bottom-up approaches. The former starts with large size (i.e., granular or microscale) materials with the generation of nanoparticles by mechanical and/or chemical steps including milling, etching, and/or machining. The latter approach entails the “growth” of nanostructures atom-by-atom or molecule-by-molecule via chemical synthesis, self-assembling, positional assembling, and so on.

Both approaches have been successfully applied in the preparation of nZVI nanoparticles. For example, ZVI nanoparticles have been fabricated by vacuum sputtering synthesized from the reduction of goethite and hematite particles with hydrogen gas at elevated temperatures (e.g., 200–600°C), by decomposing iron pentacarbonyl (Fe(CO)₅) in organic solvents or in argon, and by electrodeposition of ferrous salts. The generation of nZVI by the “bottom-up” reduction of ferric (Fe(III)) or ferrous (Fe(II)) salts with sodium borohydride has been used by many research groups.

\[
4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^{0} \downarrow + 3H_2BO_3^- + 12H^+ + 6H_2 \uparrow \tag{1}
\]

This table is partially based information provided by Marti Otto (U.S. EPA).

<table>
<thead>
<tr>
<th>Site</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phoenix—Goodyear Airport (Unidynamics)</td>
<td>Phoenix, AZ</td>
</tr>
<tr>
<td>Defense Contractor Site</td>
<td>CA</td>
</tr>
<tr>
<td>Jacksonville dry cleaner sites, pilot tests using nZVI (several sites)</td>
<td>FL</td>
</tr>
<tr>
<td>State Lead Site</td>
<td>ID</td>
</tr>
<tr>
<td>Groveland Wells Superfund Site</td>
<td>Groveland, MA</td>
</tr>
<tr>
<td>Aberdeen site</td>
<td>MD</td>
</tr>
<tr>
<td>Sierra Army Depot</td>
<td>NV</td>
</tr>
<tr>
<td>Pharmaceutical plant. Pilot test</td>
<td>Research Triangle Park, NC</td>
</tr>
<tr>
<td>Industrial Site</td>
<td>Edison, NJ</td>
</tr>
<tr>
<td>Picattiny Arsenal</td>
<td>Dover, NJ</td>
</tr>
<tr>
<td>Shieldalloy plant</td>
<td>NJ</td>
</tr>
<tr>
<td>Manufacturing Site</td>
<td>Passaic, NJ</td>
</tr>
<tr>
<td>Klocker Road Site</td>
<td>Hamilton Township, NJ</td>
</tr>
<tr>
<td>Manufacturing Plant</td>
<td>Trenton, NJ</td>
</tr>
<tr>
<td>Naval Air Engineering Station</td>
<td>Lakehurst, NJ</td>
</tr>
<tr>
<td>Confidential site. Pilot test</td>
<td>Winslow Township, NJ</td>
</tr>
<tr>
<td>Confidential site. Pilot test</td>
<td>Rochester, NY</td>
</tr>
<tr>
<td>Nease superfund site, Pilot test</td>
<td>OH</td>
</tr>
<tr>
<td>Former Electronics Manufacturing Plant</td>
<td>PA</td>
</tr>
<tr>
<td>Rock Hill, pharmaceutical plant, full scale using nZVI</td>
<td>SC</td>
</tr>
<tr>
<td>Memphis Defense Depot</td>
<td>TN</td>
</tr>
<tr>
<td>Grand Plaza Drycleaning Site</td>
<td>Dallas, TX</td>
</tr>
<tr>
<td>Industrial plant, pilot tests using nZVI</td>
<td>Ontario, Canada</td>
</tr>
<tr>
<td>Public domain, pilot test using nZVI</td>
<td>Quebec, Canada</td>
</tr>
<tr>
<td>Solvent manufacturing plant, pilot testing using nZVI</td>
<td>Czech Republic</td>
</tr>
<tr>
<td>Industrial plant, pilot testing using nZVI</td>
<td>Czech Republic</td>
</tr>
<tr>
<td>Industrial plant, pilot testing using nZVI</td>
<td>Germany</td>
</tr>
<tr>
<td>Industrial plant, pilot testing using nZVI</td>
<td>Italy</td>
</tr>
<tr>
<td>Brownfields, pilot test using nZVI</td>
<td>Slovakia</td>
</tr>
</tbody>
</table>

2.1 Synthesis of Iron Nanoparticles

Robust methods for large-scale and cost-effective production of nanomaterials are essential to the growth of nanotechnology. Environmental applications often require usage of considerable quantities of treatment reagents and/or amendments for the remediation of huge volumes of contaminated water and soil. Unlike many industrial applications, environmental technologies often exhibit relatively low market values. Therefore, the application of these technologies can be particularly sensitive to the costs of nanomaterials. This may have been the main factor for the relatively slow adaptation of some environmental nanotechnologies.

There are two general strategies in terms of nanoparticle synthesis: top-down and bottom-up approaches. The former starts with large size (i.e., granular or microscale) materials with the generation of nanoparticles by mechanical and/or chemical steps including milling, etching, and/or machining. The latter approach entails the “growth” of nanostructures atom-by-atom or molecule-by-molecule via chemical synthesis, self-assembling, positional assembling, and so on.

Both approaches have been successfully applied in the preparation of nZVI nanoparticles. For example, ZVI nanoparticles have been fabricated by vacuum sputtering. synthesized from the reduction of goethite and hematite particles with hydrogen gas at elevated temperatures (e.g., 200–600°C), by decomposing iron pentacarbonyl (Fe(CO)₅) in organic solvents or in argon, and by electrodeposition of ferrous salts. The generation of nZVI by the “bottom-up” reduction of ferric (Fe(III)) or ferrous (Fe(II)) salts with sodium borohydride has been used by many research groups:

\[
4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^{0} \downarrow + 3H_2BO_3^- + 12H^+ + 6H_2 \uparrow \tag{1}
\]
A major advantage of this method is its relative simplicity with the need of only two common reagents and no need for any special equipment/instrument, it can be done in almost any wet chemistry lab. In our laboratory at Lehigh University, we have used this approach to produce high-quality iron nanoparticles for over ten years. Typically it is achieved by slowly adding 1:1 volume ratio of 0.25 M sodium borohydride into 0.045 M ferric chloride solution. Nevertheless, there are important health and safety considerations associated with the borohydride reduction approach. The synthesis needs to be conducted in a fume hood as the chemical reactions produce hydrogen gas as a byproduct. Moreover, explosion-resistant mixers should be used to minimize the possibility of sparks, and so on. The jet-black nanoparticle aggregates can be collected by vacuum filtration. Selected images of nZVI are given in Figure 2.

Bimetallic iron nanoparticles, in which a second and often less reactive metal such as Pd, Ni, Pt, or Ag can be prepared simply by soaking the freshly prepared nZVI in a solution of the second metal salt.\textsuperscript{23} It is believed that the second noble metal promotes iron oxidation and may act as a catalyst for electron transfer and hydrogenation. Several studies have demonstrated that bimetallic iron nanoparticles (Pd-Fe, Pt-Fe, Ni-Fe, Ag-Fe) can achieve significantly higher degradation rates and prevent or reduce the formation of toxic byproducts.\textsuperscript{20,43}

The iron nanoparticles are colloidal in nature and exhibit a strong tendency to aggregate as well as adhere to the surfaces of natural materials such as soil and sediment. Increasing efforts have been directed on the dispersion of iron nanoparticles. For example, He and Zhao used water-soluble starch as a potential nanoparticle stabilizer.\textsuperscript{27} The average size of iron nanoparticles was reduced to 14.1 nm in diameter. In another work, Mallouk and co-workers have synthesized carbon platelets with 50–200 nm in diameter and water soluble polyelectrolyte like poly(acrylic acid) (PAA) as supports and dispersants.\textsuperscript{34} Saleh et al. used poly(methacrylic acid)-block-poly(methyl methacrylate)-block-poly(styrenesulfonate) to modify the iron nanoparticle surface. Although the hydrodynamic diameter of the modified particles increased 30–50 nm, the colloidal stability of the modified nZVI was enhanced.\textsuperscript{44}

Over the last decade, the costs for ZVI nanoparticles have been reduced dramatically (e.g., from >$500/kg to $50–100/kg). At the time of the initial field demonstration of the nZVI technology in 2001, there were no commercial suppliers of iron nanoparticles while presently multiple vendor options exist. Still, prices remain too high for many applications. Compared to laboratory prepared ZVI particles, the quality and efficacy of commercially available nZVI products can be highly variable as inadequate quality assurance and quality control and characterization protocols exist to support the products.

2.2 Characterization of Iron Nanoparticles

Only limited work has been published thus far on the surface characterization of ZVI nanoparticles. A detailed knowledge of the surface properties is vital for understanding the salient reaction mechanisms, kinetics, and intermediate/product profiles. The transport, distribution, and fate of nanoparticles in the environment also depend on these surface properties. However, it is often not practical to define an average or typical iron nanoparticle because ZVI nanoparticles produced with different methods may exhibit widely varying properties. Fundamentally, iron nanoparticles are reactive species and their surface properties change rapidly and profoundly over time and solution chemistry and with environmental conditions. In practice, the term “aging” has often been used to describe the observed changes of iron nanoparticles.

Figure 2 presents the Transmission Electron Microscopy (TEM) images of iron nanoparticles synthesized using the sodium borohydride method. The nanoparticles are mostly spherical in shape and exist as chain-like aggregates. An accumulative size distribution survey of over 400 nanoparticles from TEM images suggests that over 80% of the nanoparticles have diameters of less than 100 nm whereas 50% are less than 60 nm (Figure 3).\textsuperscript{45} The average BET surface area is about 30,000–35,000 m\textsuperscript{2}/kg.

According to the core-shell model, the mixed valence iron oxide shell is largely insoluble under neutral pH conditions and may protect the ZVI core from rapid oxidation. The speciation of the actual oxide layer is complicated due to the lack of long-range order and its amorphous structures. The composition of the oxide shell may also depend on the fabrication processes and environmental conditions. For example, the oxide shell of α-Fe nanoparticles generated by sputtering consists mainly of...
FIG. 3. An accumulative size distribution of zero-valent iron nanoparticles. More than 420 nanoparticles were measured from TEM images.

maghaemite (γ-Fe₂O₃) or partially oxidized magnetite (Fe₃O₄). Nanoparticles formed via nucleation of metallic vapor also contain γ-Fe₂O₃ and Fe₃O₄, with richer γ-Fe₂O₃ for smaller particles due to the higher surface-to-volume ratio and rapid surface oxidation. On the other hand, particles produced by hydrogen reduction of goethite and hematite particles reportedly have only Fe₃O₄ in the shell. The presence of wustite (FeO) has also been noted. It is not clear from the existing literature whether variations in the shell structure and composition have any effect on the iron nanoparticle reactivity, aggregation, and transport.

Detailed X-ray Photoelectron Spectroscopy (XPS) studies on the ZVI nanoparticles have been performed in our laboratory. Figure 4 shows the XPS survey on the Fe2p3/2 and O1s regions. For the Fe2p3/2 spectrum, the binding energy of the main peak was located at ca. 711 eV, which is attributable to ferric iron [Fe(III)]. The smaller peak at ca. 707 eV suggests the presence of the elemental metallic iron. The photoelectron peak of O1s in Figure 4b can be decomposed into three separate peaks at 529.9 eV, 531.2 eV, and 532.5 eV, representing the binding energies of oxygen in O²⁻, OH⁻, and chemically or physically adsorbed water, respectively. The oxygen species are similar to those on the surface of iron oxides in water.

Further examination of the peak area ratios of Fe/OH and OH⁻/O²⁻ suggest that the oxide shell is composed of mainly iron hydroxides or iron oxyhydroxide. As a result of iron oxidation, Fe²⁺ is first formed on the surface:

$$2 \text{Fe} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{OH}^-$$ \[2\]
$$\text{Fe} + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^-$$ \[3\]

Fe²⁺ can be further oxidized to Fe³⁺:

$$4\text{Fe}^{2+} + 4\text{H}^+ + \text{O}_2 \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}$$ \[4\]

FIG. 4. (a) XPS survey on Fe 2p3/2 and (b) XPS survey on O 1s of zero-valent iron nanoparticles. Results suggest that the iron on the particles surface is extensively oxidized.

Fe³⁺ reacts with OH⁻ or H₂O and to yield hydroxide or oxyhydroxide:

$$\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3$$ \[5\]
$$\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{FeOOH} + 3\text{H}^+$$ \[6\]

Fe(OH)₃ can also dehydrate to form FeOOH:

$$\text{Fe(OH)}_3 + 3\text{H}^+ \rightarrow \text{FeOOH} + \text{H}_2\text{O}$$ \[7\]

The results constitute the foundation of the conceptual model of the nZVI nanoparticle as illustrated in Figure 1. In water, ZVI nanoparticles can exhibit metal-like or ligand-like coordination properties depending on the solution chemistry. At low pH (\(<pH_{zpc} ≈ 8\)), iron oxides are positively charged and attract anionic ligands including key environmental species such as sulfate and phosphate. When the solution pH is above the isoelectric point, the oxide surface becomes negatively charged and can form surface complexes with cations (e.g., metal ions). As described previously, zero valent iron can serve as very effective electron donors (i.e., reductants). ZVI (Fe²⁺/Fe) has a standard
reduction potential (E°) of −0.44 V, which is lower than many metals such as Pb, Cd, Ni, and Cr, as well as many organic compounds like chlorinated hydrocarbons. These compounds are thus susceptible to the reduction by ZVI nanoparticles.

Reactions at the nZVI surface involve many steps, for example, mass transport of molecules to the surface and electron transfer (ET) from the ZVI to the surface adsorbed molecules. Kinetic analysis suggests that for many organic compounds such as PCE and TCE, the surface reaction or electron transfer is the dominant factor or the rate limiting step. There are several potential pathways for the electron transfer (ET) to occur: (1) direct ET from Fe(0) through defects such as pits or pinholes, where the oxide layer acts as a physical barrier; (2) indirect ET from Fe(0) through the oxide layer via the oxide conduction band, impurity bands, or localized bands; or (3) ET from sorbed or lattice Fe(II) surface site.48,49 In this regard, the iron oxide shell can appropriately be considered as n-type semiconductor. On the other hand, we are not aware of direct evidence on the ET mechanisms at this time.

2.3 Degradation of Organic Contaminants

A substantial portion of the peer-reviewed nZVI literature has been limited to the degradation of various organic contaminants such as chlorinated organic solvents, organochlorine pesticides, polychlorinated biphenyls (PCBs), and organic dyes. Selected compounds studied in our laboratory at Lehigh University are listed in Table 2.

The chemical principles underlying the transformation of halogenated hydrocarbons have been particularly well documented as those compounds are among the most commonly detected soil and groundwater pollutants. Metallic iron (Fe0) serves effectively as an electron donor:

\[
\text{Fe}^0 \rightarrow \text{Fe}^{2+} + 2e^- \quad [8]
\]

Chlorinated hydrocarbons on the other hand accept the electrons and undergo reductive dechlorination:50,51

\[
\text{RCl} + \text{H}^+ + 2e^- \rightarrow \text{RH} + \text{Cl}^- \quad [9]
\]

From a thermodynamic perspective, the coupling of the reactions [8] and [9] is often energetically highly favorable:

\[
\text{RCl} + \text{Fe}^0 + \text{H}^+ \rightarrow \text{RH} + \text{Fe}^{2+} + \text{Cl}^- \quad [10]
\]

For example, tetrachloroethene (C2Cl4), a common solvent, can be completely reduced to ethane by nZVI in accordance with the following overall equation:

\[
\text{C}_2\text{Cl}_4 + 5\text{Fe}^0 + 6\text{H}^+ \rightarrow \text{C}_2\text{H}_6 + 5\text{Fe}^{2+} + 4\text{Cl}^- \quad [11]
\]

Figure 5 presents an example of a laboratory study on a mixture of chlorinated hydrocarbons. Six common compounds including trans-dichloroethene (t-DCE), cis-dichloroethene (c-DCE), 1,1,1-trichloroethane (1,1,1-TCA), tetrachloroethylene (PCE), trichloroethylene (TCE), and tetrachloromethane were investigated. The initial concentration was 10 mg/L for each of the six compounds and the total nZVI loading was 5 g/L. As illustrated by the trend illustrated in the gas chromatograms over the reaction time course, all of the six compounds were reduced by the ZVI nanoparticles. Within one hour, over 99% removal of tetrachloroethylene was observed. Greater than 95% removal efficiency of the 6 compounds was achieved within 120 hours.

The importance of electron donors in the reduction of chlorinated hydrocarbons has received significant attention in the research and environmental remediation communities. Extensive research on both biological and chemical dechlorination
has been published over the last two decades. In general, the rate of dechlorination increases with the number of chlorine substituents. For dechlorination with ZVI, three potential transformation mechanisms have been proposed: (1) direct reduction at the metal surface; (2) reduction by ferrous iron at the surface; and (3) reduction by hydrogen.\textsuperscript{51} Ferrous iron, in concert with certain ligands, can slowly reduce the chlorinated hydrocarbons. However, electron transfer from ligand ferrous ions through the nZVI oxide shell is thought to be relatively slow and is probably not of great consequence. Dissolved hydrogen gas has been shown of little reactivity in the absence of a suitable catalytic surface (e.g., Pd).
The incorporation of a noble or catalytic metal such as Pd, Ni, Pt, or Ag, can substantially enhance the overall nZVI reaction rate. It has been observed that the surface area normalized rate constant \( (K_{SA}) \) of Fe/Pd nanoparticles for the degradation of tetrachloromethane is over two orders of magnitude higher than that of microscale iron particles. The activation energy of Fe/Pd nanoparticles in the transformation of tetrachloroethylene (PCE) was calculated to be 31.1 kJ/mole, compared to 44.9 kJ/mole for iron nanoparticles.\(^5\) The fast reactions generated by the bimetallic nanoparticles also reduce possibility of toxic byproduct formation and accumulation. Although chlorinated aliphatic compounds with 1 or 2 carbons have been studied extensively, chlorinated alicyclic and aromatic compounds have received far less attention. Without a doubt, chlorinated alicyclic and aromatic compounds feature more complicated chemical structures, are less aqueous soluble, react more slowly with nZVI, and often generate more intermediates and byproducts. Limited research indicates that iron nanoparticles can exhibit fairly high reactivity toward these compounds even though some researches with micro- and millimeter iron particles reported little reactions. Xu et al. evaluated the degradability of hexachlorobenzene (HCB) by Fe/Ag bimetallic nanoparticles.\(^4\) With an initial HCB concentration of 4 mg/L and an applied loading of 25 g/L nZVI, over 50% of HCB was reduced from aqueous solution within 30 minutes. HCB concentrations were reduced below the detection limit (<1 μg/L) within approximately 4 days. HCB was gradually transformed to a series of lesser chlorinated benzenes such as 1,2,4,5-tetrachlorobenzene, 1,2,4-trichlorobenzene, and 1,4-dichlorobenzene.

The degradation of lindane (γ-hexachlorocyclohexane, γ-HCH), one of the most widely used organochlorine pesticides over the timeframe from the 1940s through the 1990s, was investigated by Elliott.\(^5\) Experiments conducted with a groundwater contaminated with lindane (~700 μg/L of ΣHCH, a summation of the 4 environmentally significant HCH isomers identified) showed that over 95% of the lindane was removed from solution within 48 hours by 2.2–27.0 g/L nZVI. In contrast, about 59% of HCH was removed in solution after 24 hours with 49.0 g/L microscale iron particles (Figure 6). It is hypothesized that lindane is reduced via a dihaloelimination reaction to γ-TeCCH:

\[
C_6H_4Cl_6 + Fe^0 \rightarrow C_6H_4Cl_4 + Fe^{2+} + 2Cl^- \quad [12]
\]

It was further determined that at least 35–65% of the chlorine initially present in lindane was converted into chloride. The reaction followed pseudo first-order rate with the observed rate constant \( (k_{obs}) \) in the range of 0.04–0.65 hr\(^{-1}\).

### 2.4 Remediation of Inorganic Contaminants

Several recent studies provided valuable insights into key nZVI properties associated with the potential to transform metal ions such as Cd, Ni, Zn, As, Cr, Ag, and Pb, as well as notorious inorganic anions like perchlorate and nitrate.\(^3\)\(^4\)\(^5\)\(^6\)\(^7\) ZVI nanoparticles can rapidly remove and/or reduce these inorganic ions and also have relatively higher capacity than conventional sorptive media and granular iron particles. As an example, studies with chromium ore processing residual (COPR) containing highly concentrated hexavalent chromium show that one gram of ZVI nanoparticles can reduce and immobilize 65–110 mg Cr(VI).\(^3\)\(^4\) In comparison, the capacity for Cr(VI) removal by microscale ZVI is only 1–3 mg Cr(VI)/g Fe. Furthermore, the reaction rate with the ZVI nanoparticles is at least 25–30 times faster.

The work on reductive precipitation of Cr(VI) also confirmed that the nZVI reactions are surface-mediated. The initial reaction can be treated as a pseudo first order reaction in which the rate constant is normalized to the total surface area of iron. Cr(VI) is reduced to Cr(III), which is then incorporated into the iron oxide layer as \((\text{Cr}_x\text{Fe}_{1-x})(\text{OH})_3\) or \(\text{Cr}_x\text{Fe}_{1-x}(\text{OOH})\).

While reduction is the predominant mechanism for Cr(VI) removal, both reduction and surface complex formation (sorption) are observed for Ni(II) removal. The capacity was experimentally determined to be 0.13 g Ni(II)/g Fe or 4.43 meq Ni(II)/g, which is well over 100% higher than the best inorganic sorbents (e.g., zeolites) available. High-resolution X-ray photoelectron spectroscopy (HR-XPS) reveals that the amount of reduced Ni(0) at the iron nanoparticle surface increases with time. At equilibrium, about 50% of Ni(II) is reduced as Ni(0) at the surface and 50% Ni(II) remains adsorbed at the iron nanoparticle surface (Figure 7). The surface complex is primarily nickel hydroxide.\(^5\)

Iron nanoparticles can also reduce some relatively stable inorganic compounds such as perchlorate and nitrate. According to the several studies on the reduction of nitrate by granular and microscale ZVI particles published thus far the reduction
The reduction of nitrate by iron nanoparticles is fast even at relatively high pH (e.g., 8–10), a range that is known to be inhibitory to the iron oxidation reactions. For example, Sohn et al. designed repetitive experiments and observed that reaction rates remained about the same even after exposed to new nitrate solutions for 6 times. It is speculated that in alkaline solutions, the anionic hydroxide species ($\text{Fe(OH)}_{x}^{2-x}$ or $\text{Fe(OH)}_{3}^{3-x}$) are dissolved and then precipitated yielding different phase of iron oxide, most likely magnetite ($\text{Fe}_3\text{O}_4$). The phase transformation may expose fresh ZVI iron surface to nitrate, resulting in a relatively stable reaction rate.

Perchlorate is another high profile contaminant in the U.S., particularly in the western states. It is persistent in the environment due to its intrinsic chemical stability. Consequently, rates of natural attention under most cases are very slow. Because of its stability in water, only few reductants, such as complexes of tin(II), vanadium(II, III), molybdenum(III), titanium(III), and ruthenium(III, IV), have been identified as being capable of reducing perchlorate. Still, the half-lives of perchlorate may range from 0.83 years to up to 11.3 years for these transition metal reductants. In a study by Cao et al., ZVI nanoparticles were observed to reduce perchlorate to chloride with no observance of the sequential degradation products. The nZVI-mediated reduction of perchlorate proceeds according to Equation 14:

$$\text{ClO}_4^- + 4\text{Fe}^{0} + 8\text{H}^+ \rightarrow \text{Cl}^- + 4\text{Fe}^{2+} + 4\text{H}_2\text{O} \quad [14]$$

In contrast, the reduction by microscale iron particles is negligibly slow. Not surprisingly, the activation energy was calculated to be 79 kJ/mole, indicative that the reduction is limited by the slow kinetics.

### 2.5 Transport of the Iron Nanoparticles

Because ZVI nanoparticles are increasingly being used in site remediation, a critical issue for the future development of the technology involves nZVI transport, dispersion, and fate in the subsurface environment. At present, little information is available on the transport and fate of ZVI nanoparticles in the environment. In laboratory soil column experiments, the mobility of pure iron nanoparticles has been observed to be limited due to the colloidal nature and efficient filtration mechanisms of aquifer materials. Data from some recent field tests indicate that the iron nanoparticles may migrate only a few inches to a few feet from the point of injection. The mobility of nanoparticles in the subsurface environment depends on many factors including the particle size, solution pH, ionic strength, soil composition, ground water flow velocity, and so on.

Recent research indicates that promising new synthetic methods are being developed to produce more mobile ZVI nanoparticles without sacrificing significant surface reactivity. Mallouk and his group at Penn State have successfully synthesized ZVI nanoparticles on supports, which feature a high density of negative charges (dubbed as delivery vehicles) to aid in electrostatic repulsion among particles and an increase in particle aggregation. Laboratory soil column tests with Fe/C, Fe/PAA, and unsupported iron nanoparticles suggest that the anionic surface charges can enhance the transport of iron nanoparticle through soil- and sand-packed columns, where as the unsupported iron nanoparticles aggregate and impede the flow of water through the column. Further analysis show that the Fe/C and Fe/PAA nanoparticles have lower sticking coefficients.

Work by Y. P. Sun at Lehigh University on the use of poly(vinyl alcohol-co-vinyl acetate-co-itaconic acid) (PV3A) as a dispersant also helped to generate a new class of nZVI with substantially better subsurface mobility potential. As illustrated in Figure 8, the iron nanoparticles were well dispersed with most of the resulted particles less than 20–30 nm. Further analysis using acoustic spectrometry indicated that the dispersed iron nanoparticles have a mean size at 15.5 nm with 90% of the particles smaller than 33.2 nm. The stabilized particles also have...
FIG. 8. Characterization of iron nanoparticles (a–d) dispersed with poly(vinyl alcohol-co-vinyl acetate-co-itaconic acid) (PV3A), and (e) to (h): pure nanoparticles.
high reactivity and high stability in terms of suspension (over 6 months). Measurements of ξ-potential suggest that dispersed iron nanoparticles have net negative charge at pH 4.5, likely the result of the dissociation of the carboxylic acid groups within the PV3A molecules. In comparison, the original or bare iron nanoparticles have much larger particle size and settle out of solution in less than 10 minutes. The bare iron actually has slight positive charges in the neutral pH range. This may help to explain the low mobility of ZVI nanoparticles.

3. CHALLENGES AHEAD

Since the initial field demonstration of the nZVI technology in 2001, significant progress has been made in research and development of iron nanoparticles for soil and groundwater treatment. New research and development efforts should be directed toward enhancing real-world performance and minimizing potential economic and environmental risks. The following sections present some questions, problem, and/or challenges we have experienced in our laboratory and field work.

Materials chemistry. The synthesis of iron nanoparticles represents the foundation of this technology. Several nZVI synthetic methods have been identified but the economics of each is considerably different. The challenge is to scale up the processes and produce nano iron in large enough quantity such that further price reductions into the $10–25 per pound range become feasible. Methods for quality control and assurance (e.g., particle size, reactivity, surface charge, and mobility) should be established. Other issues requiring resolution might include optimization or customization of the ZVI surface properties (hydrophobicity, charge, functional group, etc.) for efficient subsurface transport under site-specific conditions and for degradation of targeted contaminants (e.g., perchlorate, PCBs, DNAPL).

Environmental Chemistry. This work includes the study of reaction rate, mechanism, and effect of environmental factors (e.g., pH, ionic strength, competing contaminants) on the transformation of targeted environmental contaminants. As discussed earlier, the published work so far has been largely limited to 1- and 2-carbon chlorinated aliphatic compounds. Details on the reaction mechanisms at the nanoparticle-water interface are still scarce. More work needs to be focused on exploring the feasibility of using nZVI for the treatment of halogenated aromatic compounds, PCBs, dioxins, pesticides, and other organic complex pollutants. Remediation of metal contaminated sites also presents interesting opportunities and challenges.

Geochemistry. This entails the nZVI reactions with both surface and ground water, interactions (sorption, desorption) with soil and sediment, settling, aggregation, and transport phenomena in porous media. Evaluating the long-term fate of iron nanoparticles represents another topic worthy of more focused attention. To date, virtually no studies in this key area have been published.

Environmental Impact. Thus far, no reports on the ecotoxicity of low-level ZVI in soil and water have been published in the peer-reviewed literature. However, it is the authors’ view that systematic research on the environmental transport, fate, and ecotoxicity is needed to overcome increasing concerns and fear in the environmental use of nanomaterials, and minimize any unintended impact. To date, the overwhelming proportion of nZVI research deals with the applications of the technology and work is needed to adequately assess its implications.

Iron nanoparticles may actually provide a valuable opportunity to demonstrate the positive effect on environmental quality. Iron is the fifth most used element; only hydrogen, carbon, oxygen, and calcium were consumed in greater quantities. It has been found at the active center of many biological molecules and likely plays an important role in the chemistry of living organisms. It is well documented that iron is an essential constituent of the blood and tissues. Iron in the body is mostly present as iron porphyrin or heme proteins, which include hemoglobin in the blood, myoglobin, and the heme enzymes. The challenge is to determine eco-and human toxicity of highly reactive ZVI nanoparticles.

ACKNOWLEDGMENTS

Research described in this work has been supported by Pennsylvania Infrastructure Technology Alliance (PITA), the U.S. National Science Foundation (NSF), and by the U.S. Environmental Protection Agency (U.S. EPA). The authors thank Mr. Sisheng Zhong for his able assistance in the preparation of this manuscript and Marti Otto (U.S. EPA) for information presented in Table 1.

REFERENCES

14. BCC Research, Nanotechnology in Environmental Applications (RNAN039A).