Review

Nanoscale zero-valent iron: Future prospects for an emerging water treatment technology

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A B S T R A C T

For the past 15 years, nanoscale metallic iron (nZVI) has been investigated as a new tool for the treatment of contaminated water and soil. The technology has reached commercial status in many countries worldwide, however is yet to gain universal acceptance. This review summarises our contemporary knowledge of nZVI aqueous corrosion, manufacture and deployment, along with methods to enhance particle reactivity, stability and subsurface mobility. Reasons for a lack of universal acceptance are also explored. Key factors include: concerns over the long-term fate, transformation and ecotoxicity of nZVI in environmental systems and, a lack of comparable studies for different nZVI materials and deployment strategies. It is highlighted that few investigations to date have examined systems directly analogous to the chemistry, biology and architecture of the terrestrial environment. Such emerging studies have highlighted new concerns, including the prospect for remobilisation of heavy metals and radionuclides over extended periods. The fundamental importance of being able to accurately predict the long-term physical, chemical and biological fate of contaminated sites following nZVI treatment is emphasised and, as part of this, a universal empirical testing framework for nZVI is suggested.

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1. Introduction

1.1. Engineered nanoparticles: a new tool for water treatment

By virtue of their size, nanomaterials have been shown to possess distinctive chemical, catalytic, electronic, magnetic, mechanical and optical properties [1]. In a little over 15 years, the multidisciplinary nano 'boom' has led to the development of a wide array of novel technologies for both domestic and industrial applications; ranging from enhanced drug delivery to new methods for the treatment of contaminated water.

As particle size decreases, the proportion of atoms located at the surface increases, which raises its tendency to adsorb, interact and react with other atoms, molecules and complexes to achieve charge stabilisation. Additionally, their miniscule size allows nanoparticles to be incorporated within aqueous suspensions and behave as a colloid. Such unique properties have been shown as beneficial for a wide range of applications. For example, macroscale silver is considered chemically inert, but at the nanoscale, silver is used for a wide range of applications including antimicrobial sterilisation, solar energy absorption and as a catalyst for numerous chemical reactions [2]. Today, engineered nanomaterials are in many of the products that we use on a daily basis. The Woodrow Wilson nanotechnology consumer product inventory lists over 1000 everyday items [3]. For example, carbon nanotubes are used to enhance the strength of sports equipment and construction materials, titanium dioxide nanoparticles are used for "self cleaning" surfaces and enhanced UV protection, whilst nano-silicon is used to increase the speed and efficiency of computer processors [3].
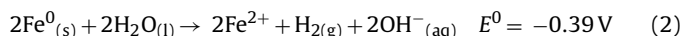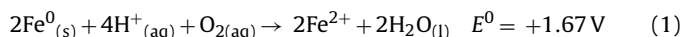
As just one aspect of the global nano-revolution, the potential use of engineered nanomaterials for the treatment of polluted waters has sparked a great deal of interest. Compared to conventional macroscale materials, nanomaterials exhibit significant improvements in surface area as a function of mass. By using a smaller mass of material to achieve the same objective, both raw materials and energy can be theoretically conserved [4] with significant associated cost savings. Additionally (and significantly) their colloidal size allows subsurface deployment via injection with the rapid treatment of aqueous contaminants at almost any location and depth in terrestrial groundwater systems.

Conceptually, the key properties required for the use of any engineered nanoparticle for in situ remediation of polluted groundwater are: (i) high reactivity for contaminant removal; (ii) sufficient mobility within porous media; (iii) sufficient reactive longevity; and (iv) low toxicity. These properties are operational drivers but at the same time the material must be manufactured and deployed at a cost that is competitive with other existing technologies. Not many engineered nanoparticles fulfil the above mentioned requirements. For example, silver nanoparticles are well recognised for their reactivity with aqueous contaminants and also their stability as colloidal suspensions [2]. However, for groundwater remediation, the material's expense for kilogram quantities, in addition to the well recognised environmental toxicity issues, precludes their use [5]. Due to its cheap cost, environmental compatibility and
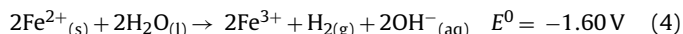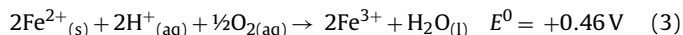
high reactivity, the most widely studied nanomaterial for water treatment is metallic iron (hereafter referred to as nZVI) [6].

1.2. The aqueous corrosion of iron

From a simple perspective, corrosion is the degradation of a material caused by the environment in which it resides. The manufacture of all metals from oxide requires an input of energy and as a result the material has a strong thermodynamic driving force to return to its native low-energy state. This process of reversion is most commonly referred to as corrosion; an inevitable process but one which may be controlled using various methods. Metallic iron (Fe^0), also referred to as zero-valent iron, is well recognised as being highly susceptible to corrosion in aqueous media. Its corrosion is considered to occur primarily through an electrochemical process, with anodic and cathodic components. The anodic reaction involves the dissolution of Fe^0 (forming soluble ionic products or insoluble oxide/hydroxide) and is coupled with reduction of redox amenable species at the cathode. In natural waters, the primary components available for corrosion reactions are dissolved oxygen (DO) and water, with the former being thermodynamically favoured (Eqs. (1) and (2)).

$$2Fe^0_{(s)} + 4H^+_{(aq)} + O_{2(aq)} \rightarrow 2Fe^{2+} + 2H_2O_{(l)} \quad E^0 = +1.67\,V \quad (1)$$

$$2Fe^0_{(s)} + 2H_2O_{(l)} \rightarrow 2Fe^{2+} + H_{2(g)} + 2OH^-_{(aq)} \quad E^0 = -0.39\,V \quad (2)$$

Ferrous iron (Fe^{2+}) is a primary product from these reactions and, in turn, can undergo further oxidative transformation (Eqs. (3) and (4)).

$$2Fe^{2+}_{(s)} + 2H^+_{(aq)} + \tfrac{1}{2}O_{2(aq)} \rightarrow 2Fe^{3+} + H_2O_{(l)} \quad E^0 = +0.46\,V \quad (3)$$

$$2Fe^{2+}_{(s)} + 2H_2O_{(l)} \rightarrow 2Fe^{3+} + H_{2(g)} + 2OH^-_{(aq)} \quad E^0 = -1.60\,V \quad (4)$$

Implicit in the above reactions is an increase of solution pH as either protons are consumed or hydroxyl ions are produced. This is commonly observed during the early stages of laboratory-scale nZVI aqueous reaction experiments. Similarly, due to the high reactive surface area of nZVI (up to $100\,m^2\,g^{-1}$), when a significant mass of material is added to an aqueous system, chemically reducing conditions can be very rapidly achieved through the production of H_2 (Eqs. (2) and (4)); inducing local conditions far from equilibrium and favourable for contaminant removal.

1.3. Environmental reactivity: metallic iron or iron oxide?

During aqueous corrosion both Fe^0 and Fe^{2+} are an active source of $Fe^{3+}_{(aq)}$, H_2 and various precipitates such as $Fe(OH)_2$, $Fe(OH)_3$, Fe_3O_4, Fe_2O_3, $FeOOH$, $Fe_5HO_8 \cdot 4H_2O$ and green rusts. It is these corrosion reactions and the product(s) thereof which are responsible for the reductive transformation and/or physical removal (sorption or enmeshment) of exposed chemical species. As surface precipitated iron oxide/hydroxide is initially porous, the material can develop a "core–shell" structure during the early stages of reaction with both sorption (at the oxide/hydroxide) and chemical reduction (at the metallic iron oxide/hydroxide interface) able to occur

Table 1
Calculated cell potential (E^0 Cell (V)) using the Nernst equation for iron-contaminant metal systems, where Fe^0 is considered the anode material. E^{mx1} Cell (V) and E^{mx2} Cell (V) represent excess $Fe^{2+}_{(aq)}$ with respect to the other aqueous metal at molar ratios of 100:1 and 10,000:1 respectively.

Redox couple	E^0 Cell (V)	E^{mx1} Cell (V)	E^{mx2} Cell (V)	Predominant removal mechanism using Fe^0	Eq.
$Fe^0 + Zn^{2+} \rightarrow Zn^0 + Fe^{2+}$	−0.35	−0.29	−0.23	Sorption/surface complexation	(5)
$Cd^{2+} + Fe^0 \rightarrow Cd^0 + Fe^{2+}$	0.01	0.07	0.13	Sorption/surface complexation	(6)
$Pb^{2+} + Fe^0 \rightarrow Pb^0 + Fe^{2+}$	0.28	0.34	0.39	Sorption with partial chemical reduction	(7)
$Ni^{2+} + Fe^0 \rightarrow Ni^0 + Fe^{2+}$	0.17	0.23	0.29	Sorption with partial chemical reduction	(8)
$Hg^{2+} + Fe^0 \rightarrow Hg^0 + Fe^{2+}$	0.68	0.74	0.80	Reductive precipitation	(9)
$Cu^{2+} + Fe^0 \rightarrow Cu^0 + Fe^{2+}$	0.78	0.81	0.87	Reductive precipitation	(10)

simultaneously. However, as the reaction progresses, increasing quantities of corrosion product(s) and a commensurate lowering in the material's porosity can significantly limit direct Fe^0–H_2O/O_2 and Fe^0–contaminant interactions [7]. It should also be noted at this stage that because the kinetics of the initial stages of Fe^0 oxidation are so rapid, corrosion will proceed even in extremely controlled conditions. Consequently, Fe^0 that is introduced to an environmental system (whether as granular or nZVI) will already have a film of surface oxide acquired directly after synthesis. Therefore, from the outset, it should be understood that although this nanomaterial is referred to as being metallic, each particle exists in natural conditions with a thin but encapsulating layer of surface oxide [8,9].

1.4. nZVI: a versatile material for water treatment

Building on original work by Glavee et al. [10], nZVI was first tested for contaminated water treatment by Wang and Zhang at Lehigh University, USA, [11]. Since then nZVI has been proven as highly effective for the removal/degradation of a wide range of chemical pollutants, including: β-lactam and nitroimidazole-based antibiotics [12,13]; azo dyes [14,15]; chlorinated solvents [11,16–18]; chlorinated pesticides [19–22]; organophosphates [23]; nitroamines [24]; nitroaromatics [17,25,26]; p-chlorophenol [27]; polybrominated diphenyl ethers [28,29]; polychlorinated biphenyls [11,30]; inorganic anions, including nitrate [31,32], and perchlorate [33]; alkaline earth metals, including barium [34] and beryllium [35]; transition metals, including chromium [35–38], cobalt [39], copper [35,38,40,41], lead [37,40], molybdenum [38], nickel [35,40], silver [40], technetium [42] and vanadium [35]; post-transition metals, including zinc [35,40] and cadmium [35,40]; metalloids, including arsenic [35,43–46], selenium [47]; and actinides, including uranium [8,35,37,48–50] and plutonium [51]. Due to the significant variation in contaminant chemistry, numerous possible contaminant removal pathways have been determined, including sorption, complexation, (co)precipitation and surface mediated chemical reduction (Table 1) [52].

As suggested by Li and Zhang [40], for metal ions such as Cd^{2+} and Zn^{2+} which have standard electrode potentials (E^0) for reduction to a metallic state that are very close to, or more negative than, Fe^0 (−0.41 V), the removal mechanism by nZVI is occurs predominantly via sorption/surface complexation. In comparison, with metal ions such as Hg^{2+} and Cu^{2+}, which have E^0 much more positive than Fe^0, removal occurs predominantly via surface mediated reductive precipitation. Where metal cations are only slightly more electropositive than iron, such as Ni^{2+} and Pb^{2+}, sorption, with partial chemical reduction, has been shown to occur. It is recognised, however, that aqueous nZVI treatment systems do not exist at standard conditions and consequently the above comparison of potentials is somewhat invalidated. Instead the Nernst equation may be used to relate standard cell potentials to those actually existing. As displayed in Table 1, the presence of a significant molar excess of aqueous Fe^{2+} derived from the rapid anodic dissolution of the nZVI can significantly alter the cell potential from the standard value (due to alteration of the thermodynamic reaction quotient), making contaminant reduction reactions more favourable.

The most recognised mechanism by which Fe^0 and Fe^{2+} solid materials remove contaminants from groundwater is via chemical reduction, and typically requires the contaminant to be adsorbed or in close proximity (electronic range) of the iron surface. For the treatment of organic contaminants, such as chlorinated organics and polychlorinated biphenyls, removal generally occurs via the reductive degradation of the chemical, i.e. the contaminant is physically destroyed. In comparison, for the treatment of many heavy metals and radionuclides removal typically occurs via immobilisation. Contaminants are merely removed from the water and trapped in an immobile state without physical destruction. For in situ remediation of heavy metals and radionuclides it is therefore significant to note that, as recovery of the injected nanomaterials (with associated contaminants) is unfeasible, contaminants are neither destroyed nor extracted from the system. This presents the prospect for future contaminant remobilisation should geochemical conditions change. Considering the significant geochemical perturbation caused by nZVI injection, subsurface treatment zones are often highly metastable, and even a gradual reversion in groundwater conditions toward a pre-injection state may be enough for significant remobilisation to occur. This is a key issue which may limit the development of the technology and is discussed in Section 3.

2. NZVI synthesis

To date, numerous methods have been developed for the manufacture of metallic nanoparticles, including chemical vapour deposition, inert gas condensation, pulsed laser ablation, spark discharge generation, sputtering gas-aggregation, thermal decomposition, thermal reduction of oxide compounds, hydrogenation of metallic complexes and the aqueous reduction of iron salts. These manufacturing methods can be considered as either "bottom up" or "top down" approaches. The former involves physical or chemical methods to construct a nanomaterial from basic building blocks, such as atoms or molecules. The latter involves physical or chemical methods to breakdown or restructure a bulk material to the nanoscale. Fig. 1 highlights the differences in particle morphology obtained by different manufacturing routes.

With the manufacture of gram-quantity nZVI achieved using simple chemical reagents and minimal specialist lab equipment, the borohydride reduction of ferrous salts is the most widely studied method within academia (Fig. 1A) [11]. The method produces highly reactive nZVI; however, the nanoparticles are often highly polydispersed, ranging over tens to hundreds of nanometres in size and thus significantly prone to agglomeration [9,56,57]. Expensive reagents and the production of large volumes of hydrogen gas also preclude its industrial application [54].

2.1. How much does nZVI cost?

Although iron is inexpensive in bulk form, reactive nanoparticles are much more expensive because of the materials and processes needed to make them. Additional to this, site remediation is an unwanted (and often unplanned) financial burden and as such
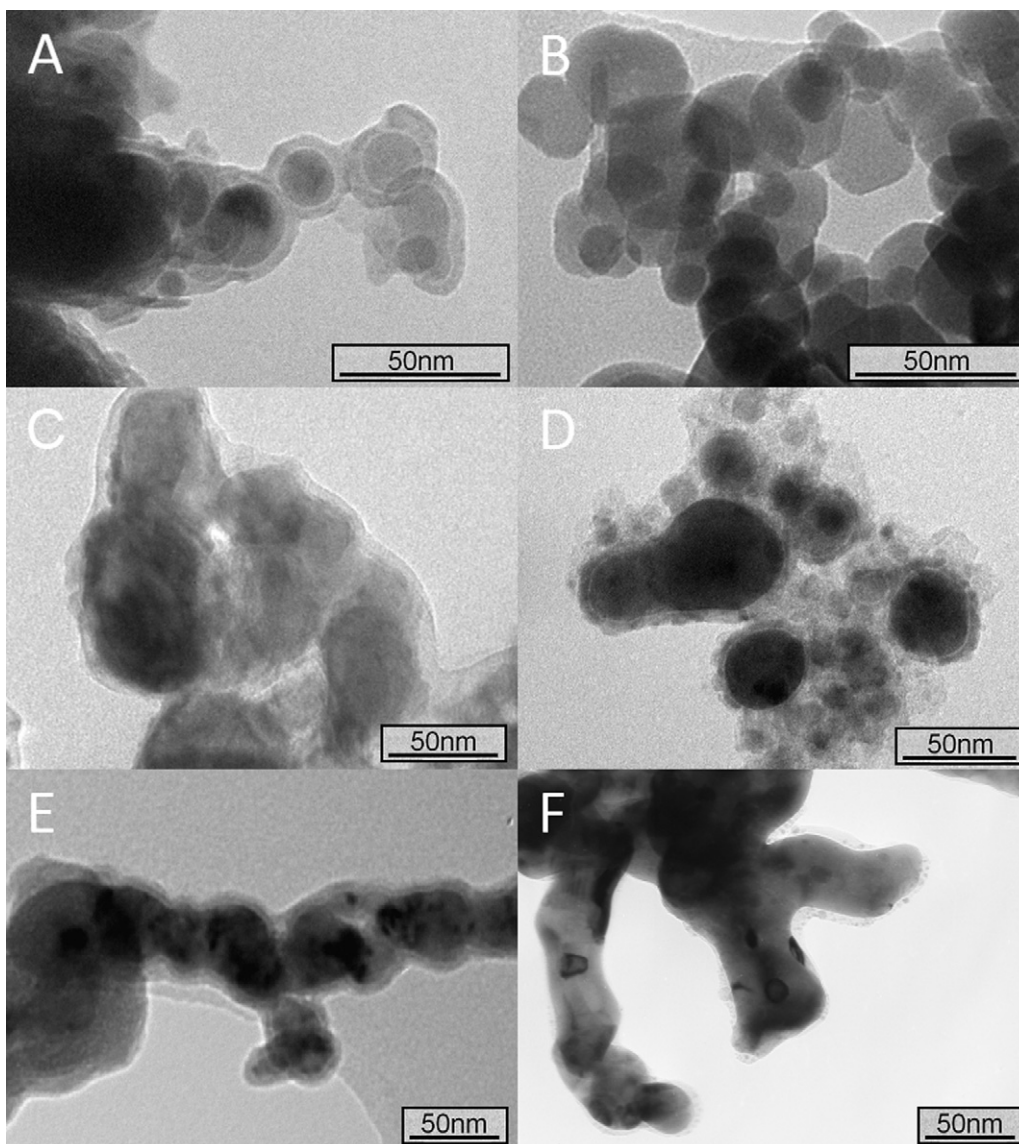
Fig. 1. Transmission electron microscopy (TEM) images of different iron nanoparticles manufactured or purchased by the authors for this review. (A) nZVI synthesised by the reduction of aqueous Fe^{2+} using sodium borohydride [11]; (B) nanoscale magnetite, purchased from Sigma–Aldrich (PubChem Substance ID: 24882829) [8]; (C) NANOFER STAR, purchased from NANO IRON, s.r.o. [53]; (D) nZVI synthesised by the carbothermal reduction of aqueous Fe^{2+} [54]; (E) nZVI synthesised by the reduction of aqueous Fe^{2+} using green tea polyphenols [55]; and (F) nZVI synthesised by the reduction of aqueous Fe^{2+} using sodium borohydride then annealed under vacuum (at least 10^{-6} mbar) at 500 °C for 24 h [9].

environmental technologies typically exhibit a relatively low market value [58]. In 2004 the price for nZVI varied between £15 and £100 per kg, whilst micro and granular Fe^0 were available for less than £1 per kg [59]. Depending on the type and amount ordered nZVI today costs in the range of £50–150 per kg. In order to compete against existing water treatment methods, such as in situ chemical oxidation, the price of nZVI must reduce to approximately <£10 per kg [60]. Consequently, in recent years there has been much investigation into the development of methods to produce cheap multi-kilogram quantities of nZVI, whilst maintaining reactivity and/or functionality.

In 2006, Toda Kogyo Ltd. developed a method that uses hydrogen as a reducing agent for iron oxide nanoparticles at 350–600 °C [61]. Although the process is scalable and has reached commercial status it involves a number of chemical processing steps to synthesise the oxide nanoparticles and then reduce them in a batch process. In recent years, the market leader for large-scale field deployment of nZVI has arguably been Golder Associates Inc., who produce nZVI

in large quantities by the mechanical attrition of macroscale Fe^0 in planetary ball mill systems [62]. Whilst it is a straight forward method, it is highly energy intensive; and newly formed particles exhibit a very high surface energy and are thus prone to aggregation.

2.1.1. The thermal reduction of ferrous iron

The carbothermal reduction of ferrous iron has recently been investigated as a potential method for the manufacture of cheap and functional nZVI (Fig. 1D). Analogous to the production of iron and steel from ore, the method regards the use of thermal energy and gaseous reducing agents (H_2, CO_2, CO, etc.) produced during the thermal decomposition of carbon-based materials (carbon black, carbon nanoparticles, hollow carbon, ultra-fine graphite powder, etc.) to drive the reduction of iron oxide nanoparticles [63] or aqueous Fe^{2+} [54]. With high surface area carbon an extremely cheap and readily available material (e.g. carbon black is a waste product from the fossil fuel industry), both methods represent cheap methods for

the manufacture of various different nZVI physicochemical forms. Additional to this, despite the high temperatures (>500 °C) required for the formation of Fe^0 in preference to its oxides, the reaction is endothermic, with only gaseous by-products, and therefore represents a scalable process.

2.1.2. Electrolysis

As a well-established industrial method for the sequestration of metals from ionic solution, electrolysis has recently been investigated for nZVI synthesis. Requiring only: Fe^{2+} salt solution, a conductive substrate, a direct current and a method to disperse electro-deposited nanoparticles, the method represents an extremely simple, cheap and quick method for the production of nZVI. The only issue is determining appropriate methods for the dispersion of newly formed metallic nanoparticles at the cathode. Recent attempts include Chen et al. using ultrasonication [64], and Wang et al., 2008 using ion-exchange in nafion film [65], represent highly promising methods.

2.1.3. Polyphenolic plant extracts

Perhaps the most environmentally compatible process developed so far for the synthesis of nZVI is the reduction of Fe^{2+} using polyphenolic plant extracts (Fig. 1E). This method, developed by scientists at VeruTEK and the US EPA involves the preparation of a polyphenolic solution by heating specific plant extracts (coffee, green tea, lemon balm, sorghum bran, etc.) in water to near-boiling temperature, extracting the supernatant and mixing it with a Fe^{2+} solution [55]. The method has also been shown as possible at ambient temperature, allowing the potential for nZVI synthesis in situ and eliminating the need for offsite manufacture, storage and transport. Primarily developed as an in situ soil catalyst to improve the performance of in situ chemical oxidation, the process is yet to be tailored to synthesise nZVI that can be used for water treatment as a chemical reducing agent.

3. Is nZVI as good as some studies suggest?

With nZVI proven as highly effective for the removal of a wide range of contaminant species from simple synthetic solutions, subsequent work has focussed on determining the material's performance for the treatment of chemically complex and/or "real" solutions. It has been outlined that some previous studies using 'simple solution' tests, lacking complexing agents and/or competitive chemical reactions, have largely overestimated nZVI performance [8,48,50,66]. This is also evidenced by the limited number of field studies that have reported poorer than expected nZVI performance, with an unexpected need to provide multiple treatments to attain successful clean-up [67,68].

This behaviour was clearly demonstrated in a recent study [8], where nZVI were tested for the removal of U from groundwater samples containing high concentrations of dissolved bicarbonate, in comparison to a laboratory synthetic water system. The nZVI were observed as highly effective for the rapid removal of U from the groundwater despite their complex chemistry and provided a comparable performance to the simple U-only water system. However, over extended time periods (>1 week) near-total re-release of U was recorded from the groundwater system, which was not observed in the simple U-only system over the entire three month treatment period, Fig. 2.

The mechanism was attributed to incomplete chemical reduction of surface-precipitated U (from soluble U^{VI} to insoluble U^{IV}) within the groundwater samples, allowing the re-release of U^{VI} during nanoparticle corrosion [8,69,70] and the reformation of highly stable (nominally carbonate) aqueous U-complexes. Taking uranium as an example, Table 2 shows the significantly enhanced
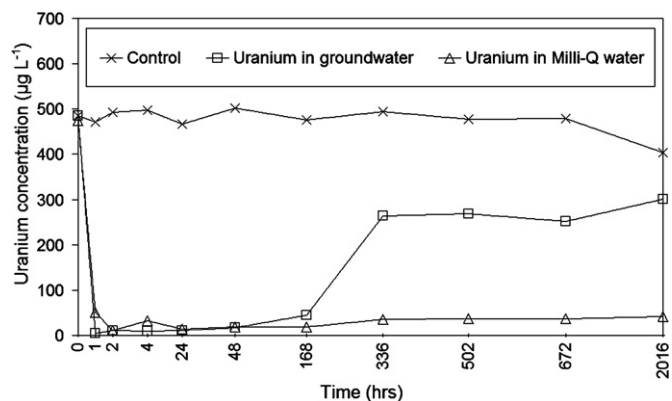

Fig. 2. The removal of aqueous uranium from groundwater and Mill-Q water using nZVI at $0.25\,g\,L^{-1}$ over a 3 month time period [8].

aqueous stability of U^{6+} in the presence of certain complexing agents which are common in natural waters.

A typical groundwater in the vadose zone has a CO_2 pressure of 10^{-2} bar which is elevated with respect to rivers and other surface waters ($10^{-3.8}$ bar) [73]. For uranium, the presence of CO_2 and also bicarbonate (HCO_3^-) in water promotes the formation of uranyl-carbonate complexes UO_2CO_3 (pH 3–5), $UO_2(CO_3)_2^{2-}$ (pH 5–8) and $UO_2(CO_3)_3^{4-}$ (pH > 8) in favour of uranyl-hydrate complexes, which have lower thermodynamic stability. This is recognised to have a profound effect on the adsorption behaviour and commensurate mobility of dissolved uranium in its hexavalent state and thus its affinity for remediation [8,69,70].

As studies to date have largely overlooked the influence of complexing agents ubiquitous to natural waters, more empirical tests are required to characterise the extent at which other heavy metals and radionuclides will display the same remobilisation trend. An obvious mitigation strategy in field applications would be to either: (i) deploy a mass of nZVI significantly in excess of that required; or (ii) to resupply the contaminated zone with nZVI on a regular basis. Both strategies have been reported in field trials as ways to improve efficacy, but likely have not been fully understood from a geochemical perspective. There accordingly exists a fundamental future need to examine the reversible nature of remediation in complex and/or natural waters using nZVI. This will provide validation of the technology for sites where assurance of medium to long-term immobilisation of contaminant heavy metal and radionuclides is required.

4. Operational drivers for water treatment

The structure, geochemistry and hydrogeology of each polluted site is unique. Resultantly the strategy adopted for nZVI deployment must take into account various operational parameters.

Table 2
Stability constants of aqueous U^{6+} in the presence and absence of certain complexing agents found in environmental waters.

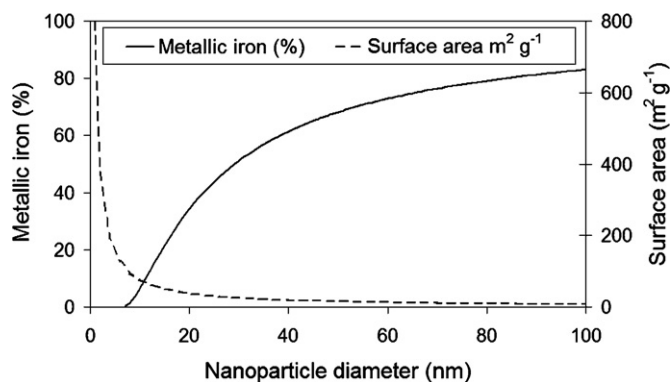| Association reaction	Log K	Eq.
$UO_2^{2+} + CO_3^{2-} = UO_2CO_3$	9.68[a]	(11)
$UO_2^{2+} + 2CO_3^{2-} = UO_2(CO_3)_2^{2-}$	16.94[a]	(12)
$UO_2^{2+} + 3CO_3^{2-} = UO_2(CO_3)_3^{4-}$	21.60[a]	(13)
$UO_2^{2+} + PO_4^{3-} = UO_2PO_4^-$	13.23[a]	(14)
$UO_2^{2+} + SO_4^{2-} = UO_2SO_4$	3.15[a]	(15)
$UO_2^{2+} + H_2O = UO_2OH^+ + H^+$	−5.2[b]	(16)
$UO_2^{2+} + 2H_2O = UO_2(OH)_2 + 2H^+$	−12.0[b]	(17)
$UO_2^{2+} + 3H_2O = UO_2(OH)_3^- + 3H^+$	−19.2[b]	(18)

[a] Grenthe et al. [71].
[b] Langmuir [72]

Fig. 3. Metallic iron content (%) and surface area (m² g⁻¹) calculated as a function of nanoparticle diameter. Both variables are calculated for perfectly spherical nanoparticles and are therefore not intended to directly represent empirical data. Metallic iron (%) assumes a surface oxide thickness of 3 nm, independent of nanoparticle diameter. Surface area (m² g⁻¹) assumes perfectly dispersed nanoparticles, and therefore does not include changes in surface area due to nanoparticulate agglomeration/aggregation.

Variables that may be altered to optimise nZVI performance include the particle size range (Section 4.1), mobility (Section 4.2), reactivity and longevity (Sections 4.3 and 4.4), injection strategy (Section 4.5) and the material's ecotoxicity (Section 4.6).

4.1. NZVI size

It is logical to suggest that by providing the highest surface area for reaction, the very smallest nZVI would provide the best performance for contaminant removal. However, there exists the possibility that at this size range (<20 nm) the resultant particles are too reactive to be useful for in situ environmental applications, with reactive exhaustion likely to be achieved in a very short timescale. Indeed, for achieving optimal nZVI performance at any given site, it should be acknowledged that there is a conceptual play-off between the reactivity and longevity of the material. Particles of sufficient size must be selected to guarantee in situ reactivity and avoid reactive exhaustion during storage, transit and subsurface deployment.

When considering the reactive capacity of nZVI, an additional factor to acknowledge is the proportion of the particle which is oxide compared to Fe^0, as a function of particle size. Assuming an oxide thickness independent of nanoparticulate size, in some circumstances it may account for significantly more of the volumetric fraction than Fe^0. For example, a spherical nZVI particle of 25 nm total diameter with a surface oxide 3 nm thick would be 56% oxide by volume, Fig. 3. Consequently, in typical conditions the smaller the particle the higher the volume of constituent oxide, implying that at very small nano-size (<10 nm) Fe^0 may only represent a small fraction of total nanoparticulate volume.

4.2. Improving the aqueous mobility of nZVI

There is abundant evidence and now a broad consensus that the mobility of nZVI in porous media is very limited under almost all conditions; see [74] and references therein. Without the application of surface coatings to aid colloidal stability, rapid aqueous aggregation of standard nZVI is frequently observed. Indeed, early pilot scale field trials have indicated extremely poor nZVI subsurface migration, with maximum practical transport distances of only a few metres reported for bare unsupported particles in saturated sediments [74]. Particle aggregation and pore clogging were determined as the causal mechanism, with the very limited mobility of nZVI explained by three primary mechanisms:
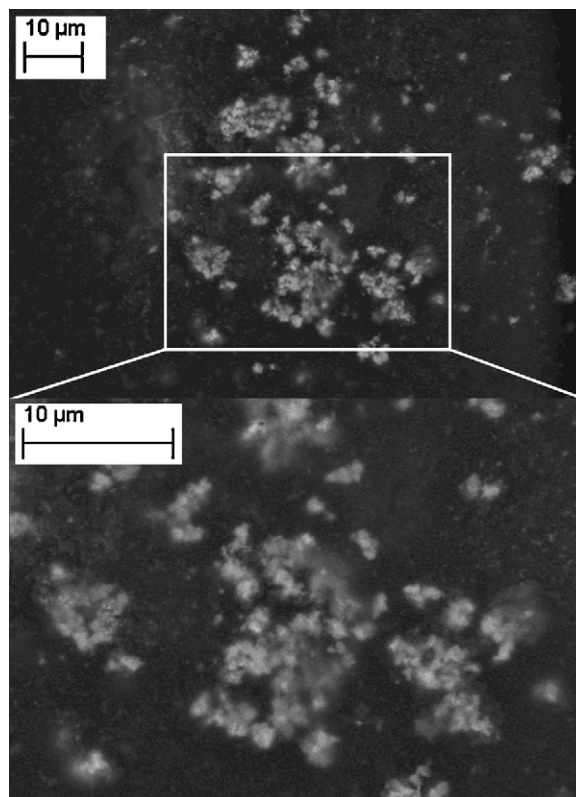

Fig. 4. A backscattered electron microscopy image of unmodified nZVI in Milli-Q water buffered to pH 7.

(i) particle aggregation and subsequent gelation caused by poor colloidal stability; (ii) the formation of voluminous corrosion product precipitates from particle oxidation/corrosion; and (iii) particle removal from solution by interaction with subsurface components, e.g. attachment to mineral surfaces and carbonaceous materials or via microbial removal. See [75–77], and references therein for a more comprehensive review.

An illustrative example of rapid aqueous aggregation is evidenced in Fig. 4 which displays a backscattered electron microscopy image taken of unmodified nZVI in Milli-Q water buffered at pH 7. The image was taken using a Quanto-mix capsule to hold the fluid suspension.

In groundwaters, it is certain that the interaction of injected nZVI with mineral surfaces will be continual. Particle collisions with these immobile subsurface components are estimated to occur on the order of hundreds per metre travelled [78]. Thus, for particles to be effectively transported nearly all of these collisions must be unsuccessful, i.e. the "sticking probability" must be very low. Consequently, the key to improving particle mobility is found in modifying their surface properties such that the nZVI have significantly improved colloidal stability and an associated reduction in the likelihood of adherence to mineral surfaces. Yet the challenge with any nZVI modification is to simultaneously maintain the material's reactive performance. An alternative method to improve the material's mobility without changing its surface properties is to increase the particle size. The consensus within the industry is that, depending on the permeability of the soil, particles within the size range of 0.1–2 μm have the highest mobility [60,79]. An additional advantage of using such particle size fractions is that any nano eco-toxicological issues are precluded. Additional to this, larger particle size fractions (>0.5 μm) can be handled as powder (rather than as slurry), reducing the material's volume and thus improving material handling. Large-scale field tests are planned at

the VEGAS research facility to investigate this [60]. Accompanying this, fundamental investigations into the extent at which an increase in particle size affects the material's reactivity, functionality and contaminant removal efficacy are required.

4.2.1. Surfactants

It is well accepted that particle mobility may be improved through the use of surfactant and other polymer coatings. Work first carried out in the 1960s based on ferrofluids [79] applicable for magnetics, optics, biophysics, medicine, rheology and even thermodynamics has since provided the basis for current nZVI coating technologies. Ferrofluids are classified as stabilised colloidal mixtures of magnetic nanoparticles suspended in a carrier fluid that become strongly polarised in the presence of a magnetic field. Particle stabilisation is achieved through the use of surfactants, polymeric surface coatings and chemicals to control the surface particle charge.

Applied to nZVI, the steric hindrances provided by such coating molecules counteract the electrical and dipolar attractions between particles and promote colloidal stability. This is only achieved when a sufficient mass of coating material or surfactant is present to form a complete micelle. Resultantly, the use of surfactants in nZVI injection technology has limited environmental applicability because, following injection, particle dispersion will be commensurate with rapid desorption of the surfactant into the groundwater, effectively losing any previously imbued particle stability.

4.2.2. Polyelectrolyte coatings

As an alternative to surfactants, the controlled coating of nZVI with high molecular weight polymers may be considered an irreversible process and therefore provides a more appropriate method for increasing the hydraulic mobility of nZVI in subsurface systems. Working in the same way as surfactants to promote colloidal stability (steric hindrances) the polymer is physically or chemically grafted to the nanoparticle surface [80]. An additional benefit is that the polymer coatings may also act as an energy source to stimulate microbial activity, which may aid contaminant removal particularly in carbon limited environments [81].

Numerous polyelectrolyte (polymer) coatings have been tested with varying success, including butyl methacrylate [82], caboxymethyl cellulose [66] and [83], guar gum [84], poly(4-styrenesulphonate) [85], polyacrylic acid [74], polyaspartate [83,86], polyoxyethylene sorbitan monolaurate [46], polymethylmethacrylate [82], polymethacrylic acid [82], polystyrene sulphonate [83], polyvinyl alcohol-co-vinyl acetate-co-itaconic [87], triblock copolymers [88], and xanthan gum [89]. Over a broad range of groundwater conditions these types of coatings are observed to persist for periods of several months [81].

Two commonly studied materials are carboxymethyl cellulose and guar gum. Formed from cellulose and guar beans respectively, both polysaccharides are extremely cheap, non-toxic, natural water-soluble and biodegradable. In water, both species are non-ionic and hydrocolloidal, remaining neutrally charged and unaffected by ionic strength or pH across an environmentally relevant range (pH 5–9) [66,84]. It seems likely that other approaches for improving colloidal stability of nZVI will arise in the future based upon exploiting the plethora of cheaply available biopolymers, improving on production cost, functionality and environmental compatibility. Biopolymers such as alginate and potato starch have already been examined and proven as unsuccessful [84], but other more successful candidates may well arise in the near future.

4.2.3. Improving the mobility of nZVI for the remediation of non-aqueous phase liquids

Researchers at the Kennedy Space Center (NASA) and the University of Central Florida have recently developed a new method for the treatment of non-aqueous phase liquids (NAPL) called "emulsified nZVI" (E-nZVI) [90]. It is one of only a few methods invented which can be used for effective in situ treatment of a dense non-aqueous phase liquid (DNAPL) plume. E-nZVI is comprised of an agglomerate of nZVI particles packed into a droplet surrounded by surfactant and oil layer which forms an oil-liquid membrane. The hydrophobic membrane allows the DNAPL to diffuse through, whereupon it undergoes reductive dechlorination by the E-nZVI in the aqueous phase. The protective membrane also allows the E-nZVI to: move through the subsurface as a DNAPL, therefore improving its chances for DNAPL exposure; and operate in sites of high dissolved oxygen and/or salinity, with iron particles inside the membrane protected from corrosion. Encapsulating the nZVI in a hydrophobic membrane also protects the material from reactions with unwanted groundwater constituents such as inorganics that might otherwise act to decrease its reactive capacity. Additional methods include the use of triblock copolymers [88], and a range of surfactants and biodegradable non-polar oils [91–94].

4.2.4. Protective shells and solid supports

The use of protective shells, originally designed for magnetic applications including data storage [95,96], drug-delivery [97], medical imaging [98] and protein purification [99], has also received interest with regard to improving the hydraulic mobility and longevity of nZVI. Coatings tested include silica [100], polymers [101] and carbon [54,102], and have been observed to improve nZVI stability to a level comparable with polyelectrolyte coatings. Due to its high stability in acidic or basic media and proven biocompatibility, the use of carbon has typically been preferred.

The use of solid supports has also been tested. A method developed by scientists at the Helmholtz Centre for Environmental Research in Germany [103] has combined iron nanoparticles with activated carbon to produce "Carbo-Iron" platelets of between 50 and 200 nm diameter. The combined NAPL sorbent properties of the activated carbon with the reductive capacity of the Fe^0 has proven very promising for the reduction of a range of chlorinated organics whilst also exhibiting hydraulic mobility comparable to surfactants and polyelectrolyte coatings.

4.3. Improving reactivity; bimetallic nanoparticles

A well documented method for increasing the chemical reactivity of nZVI has been to alloy it with a nobler metal (Pd, Pt, Ag, Ni, Cu, etc.). In recent years numerous experimental studies of bimetallic nZVI for contaminant remediation have been made, including Fe/Pd [68,104,16,105–107], Fe/Pt, [104], Fe/Ag [108] and Fe/Ni [104,109–112]. In such electrochemical couples, Fe^0 is considered to behave as an anode, becoming sacrificially oxidised to galvanically protect the noble metal. Experiments have yielded varying results for particle performance, with Fe–Pd generally outperforming the other combinations. Chemical reduction of sorbed contaminants at the bimetallic nZVI surface is considered to occur through either direct electron transfer with the noble metal or through reaction with hydrogen produced by oxidation of Fe^0. Hydrogen is likely present as a dissolved gas, some of which is adsorbed to the particle surfaces, with an undetermined fraction possibly present as active metal hydride having undergone diatomic dissociation and reaction with the exposed noble metal [104].

For the clean-up of chlorinated organic contaminants such as TCE or PCP, hydrogen is observed to be the predominant driver for degradation, by breaking C–Cl bonds and swapping itself for chlorine, which is liberated as a gas [109]. For bimetallic nZVI, an advantageous consequence of the inferred catalysis is that dichloroethelyenes (DCE) and vinyl chloride (VC), which are generated by

TCE breakdown, are observed to be rapidly hydrogenated at the particle surfaces and do not accumulate in the reaction [109]. By comparison, TCE reduction has been recorded as significantly limited by monometallic nZVI [109,112], with the accumulation of DCE and VCs often observed [18,113]. This occurs because direct reduction of water by Fe^0 proceeds more slowly without a galvanic influence and resultantly the hydrogenolysis of the contaminant specie is limited.

4.3.1. Will bimetallics prevail over monometallics?

In the US, approximately 40% of all nZVI remediation projects use bimetallic nZVI (approximately 50% use standard nZVI) whilst in Europe no field application using bimetallic particles is yet to take place [60]. For the commercial deployment of bimetallic nZVI, two unavoidable facts are that: (i) they will only be adopted in preference to monometallic nZVI if they offer significantly improved performance at a competitive price (high value metals such as Pt, Pd and Ag are likely to prove too costly); and (ii) there are still considerable concerns over the ecotoxicity of some of the noble metals chosen for alloying. For example, Ni is considered a hazardous substance by the UK Environment Agency [114].

Within bimetallic nZVI systems, efficiency of the cathodic reaction is found to determine the particle corrosion rate. If the rate is high, contaminant reactivity will also be high but reactive longevity will be poor. Consequently, it is suggested that, bimetallic nZVI is generally best suited for remediation applications where only short migration times to the contaminant plume are required. It is apparent from the literature that bimetallic nZVI reactivity this depends on a range of factors, including nanoparticle size, physicochemistry, and the choice and quantity (%) of the noble metal. Some studies have documented minimal improvement with respect to their monometallic counterpart, [50] whilst others report an enhancement by several orders of magnitude [110]. There is a resultant need for fundamental characterisation and quantification of the reactivity of different bimetallic nZVI materials, Section 6.

4.4. Thermal treatments

Recent attempts to improve the physico-chemical structure of nZVI without the use of alloying or dopant materials (and their aforementioned disadvantages) have examined the use of thermal treatments in vacuo.

It is well established that a wide variety of nZVI synthesis methods, including the most common method, the borohydride reduction of Fe^{2+}, are observed to result in the formation of significant physicochemical imperfections within the forming crystal lattices, within both the bulk metal and the surface oxide layer [9]. This is seen to significantly alter particle reactivity [8,9,48,50,115,116]. As a consequence, thermal treatment (or annealing), a process commonly used in metallurgy to relieve internal stress, refine grain structure and produce equilibrium conditions within a metal has been considered as an appropriate method to improve the physicochemical composition of nZVI [8,9,48,50].

Vacuum annealing of nZVI at 500 °C at less than 10^{-5} mbar for 24 h is observed to result in numerous physicochemical effects on nZVI structure [9]. Changes include a reduction in surface area by up to 75% (from $19.0 \, m^2 \, g^{-1}$ to $4.8 \, m^2 \, g^{-1}$) related to diffusion bonding of previously discreet particles, but, with an accompanying improvement in physical structure and surface chemistry, including: (i) reordering and recrystallisation of the metallic cores; (ii) concurrent thinning, dehydration and stoichiometric refinement of the surface oxide; and (iii) migration of impurities toward the particle surfaces and grain boundaries. A comparative study of annealed and non-annealed nZVI for contaminant remediation has since shown that vacuum annealed nZVI exhibit similar or improved levels of contaminant removal, but with a marked decrease in Fe dissolution [50]. Taking into account the reduced surface area, annealing was demonstrated to significantly increase particle reactivity and has been ascribed to the formation of an effective electronic network within the annealed nZVI structures, related to the increase of Fe^{2+} relative to Fe^{3+} in the surface oxide and its refinement into a uniformly structured magnetite (Fe_3O_4) layer around the metal core [50].

Magnetite has an inverse spinel structure that accommodates both Fe^{2+} and Fe^{3+} in octahedral sites and exhibits effective electron hopping between these sites. Consequently magnetite is a strong semiconductor (10^2–$10^3 \, \Omega^{-1} \, cm^{-1}$) and when formed as a film on Fe^0 is likely to provide a catalytic surface site, facilitating electron transfer from the metal to the oxide, as previously reported [117]. In unmodified nZVI the surface magnetite is defective, poorly crystalline and may co-exist with other non-conductive oxide phases. Consequently, the catalytic behaviour of the surface oxide is considered to be limited and in the early stages of aqueous activity, where direct electrochemical corrosion and dissolution of the Fe^0 may be observed until a uniform oxide is formed. By comparison, the magnetite present on annealed nZVI is determined to be uniform with refined stoichiometry and good electron conductivity such that conductive behaviour is greatly improved and direct contact of the zero valent iron with water (or constituent contaminants) is prevented, Fig. 5.

Resultantly, particle reactivity is improved whilst also limiting initial corrosion rates. Results have also indicated that contaminants such as uranium are retained for longer periods on annealed nZVI, perhaps indicating that in the early stages of reaction a greater proportion of the sequestered U^{6+} is converted to U^{4+} oxide via surface catalysed reductive precipitation [77].

4.5. NZVI injection strategy

With nanoparticle injection conceptually possible at almost any location and depth in a terrestrial groundwater system, the method employed, and the distribution and quantity of injection wells, typically depends on the geology and geochemistry of a contaminated site and not on the location of the contaminant plume. This is unless plume depth is great enough to incur project-limiting deployment costs due to requirements for higher injection pressures and/or larger infrastructure. Subsurface inhomogeneities, such as highly consolidated layers, cobblestones, cracks and fissures, and sub-aerial features, such as monoliths, rivers, buildings and roads, may also affect the proposed injection location(s). However, most vendors typically use a relatively aggressive injection method, often involving hydraulic and/or pneumatic fracturing of the medium to facilitate nZVI movement into soil pores.

In order to perform an effective site evaluation, all geologic and plume heterogeneities must be determined along with a model of all hydraulic and chemical parameters. Once this has been achieved can the geo-environmental engineer theoretically and/or empirically determine (using water and sediment samples taken from the site) whether nZVI is appropriate, and if so: (i) the approximate nZVI composition and; (ii) the deployment strategy. A pilot test is then performed in a small area of the site to determine any unforeseen challenges associated with the project. Data and evidence can then be collated to determine a tailored remediation strategy, including: the composition, quantity and concentration of the nZVI slurry mixture, along with the injection apparatus, location(s), depth, orientation, pressure, flowrate and duration. Other logistical factors that must be considered include: workforce safety, the potential
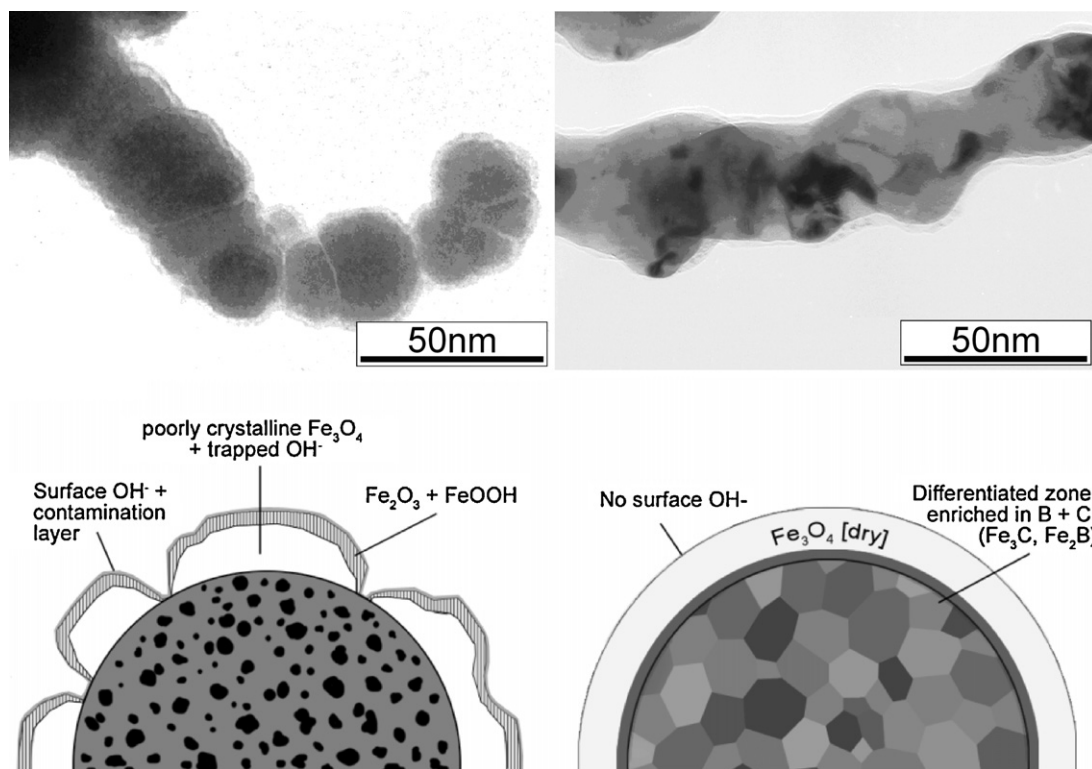
Fig. 5. A transmission electron microscope (TEM) image of: as-formed nZVI (top left) and; (B) vacuum annealed nZVI (top right). An illustration of the perceived structural transformation of: as-formed nZVI before (bottom left) and; vacuum annealed nZVI (bottom right) [9].

for accidental nZVI release, the impact the project may have on local flora and fauna populations and, the strategy for monitoring and any repeated treatments.

As proposed by Tratnyek and Johnson [118], the method of nZVI injection can be tailored for the treatment of mobile or immobile contamination, Fig. 6.

For the treatment of mobile contaminant plumes, low mobility nZVI is typically used for the formation of a "reactive treatment zone". The nanoparticles are sequentially injected and adsorb to native aquifer material, forming a physicochemical filter. For the treatment of a static contaminant body, namely non-aqueous phase liquids (NAPL), mobile nZVI is typically selected and injected upstream for direct treatment. Whilst theoretically robust from a simplistic perspective, both methods are reliant on extremely accurate control over site conditions and nZVI corrosion rate. Compared to permeable reactive barrier technologies, very little is known about the effect of pore clogging (size exclusion) caused by the physical presence of nZVI and its voluminous corrosion products. For example, ferrihydrite ($Fe_2O_3 \cdot H_2O$) is up to 600% larger than an equal mass of Fe^0 [119]. In certain circumstances this could prove beneficial. However, if applied incorrectly, the contaminant plume could be inadvertently directed to a different location. This is an extremely significant factor and has largely been overlooked in the literature [119].

As mentioned in Section 3, the type and concentration of groundwater geochemical constituents (including contaminants) has a strong bearing on the nZVI deployment mechanism, with a large quantity of nZVI typically required for chemically complex waters, and to prevent the remobilisation of heavy metals and radionuclides. Also, the presence of electron donors, especially in aquifer sites that have glacial outwash sediment from bedrock, can cause unwanted nZVI agglomeration and subsequent gelation and pore clogging. Consequently, in addition to standard site monitoring procedures, a determination of the physical distribution and chemical form of nZVI in the subsurface would be highly desirable;

to provide direct feedback as to the progression/evolution of the deployment system. At present, there is no field-portable device available that can detect nanoparticles in situ. However, measurement of groundwater oxidation–reduction potential (ORP) is an effective long-term nZVI performance parameter.

4.6. The environmental toxicology of nZVI

Nanoparticles are in many of the products that we use on a daily basis and are surreptitiously entering the environment in ever increasing volumes. Although the current mass balance for nanoparticles in the environment system is presently undefined it is conceivable that a large amount of anthropogenic nanoparticles, from an increasing variety of sources, could find their way into the soil, atmosphere and aquatic systems [120].

By association, the concept of deliberately injecting engineered nanoparticles into environmental water systems, albeit as a remedial measure, has consequently attracted scrutiny and concern from both academic and environmental authorities. The same properties that make nZVI potentially useful for environmental remediation, specifically their small size and high redox reactivity, also make them potentially harmful to living organisms [121]. To date, a limited number of studies have reported demonstrable toxicity to cells of different types [122–128].

Keenan et al. [128] demonstrated that nZVI can rapidly react with oxygen and cause lung cells to die whilst Pisanic et al. [125] observed limited growth and damage in nerve cells exposed to nZVI. The primary mechanism for cellular damage is considered to be related to nZVI oxidation reactions, where redox cycling and the generation of reactive oxygen species (ROS) from reduced Fe within a cell can cause lipid peroxidation and damage to internal structures such as DNA [129–131]. Evidence also suggests nZVI to have greater ecotoxicity than nanoscale magnetite [127], highlighting the significant role of reduced iron (Fe^0 or Fe^{2+}) in causing toxic effects. This result also suggests that iron oxides/hydroxides produced by
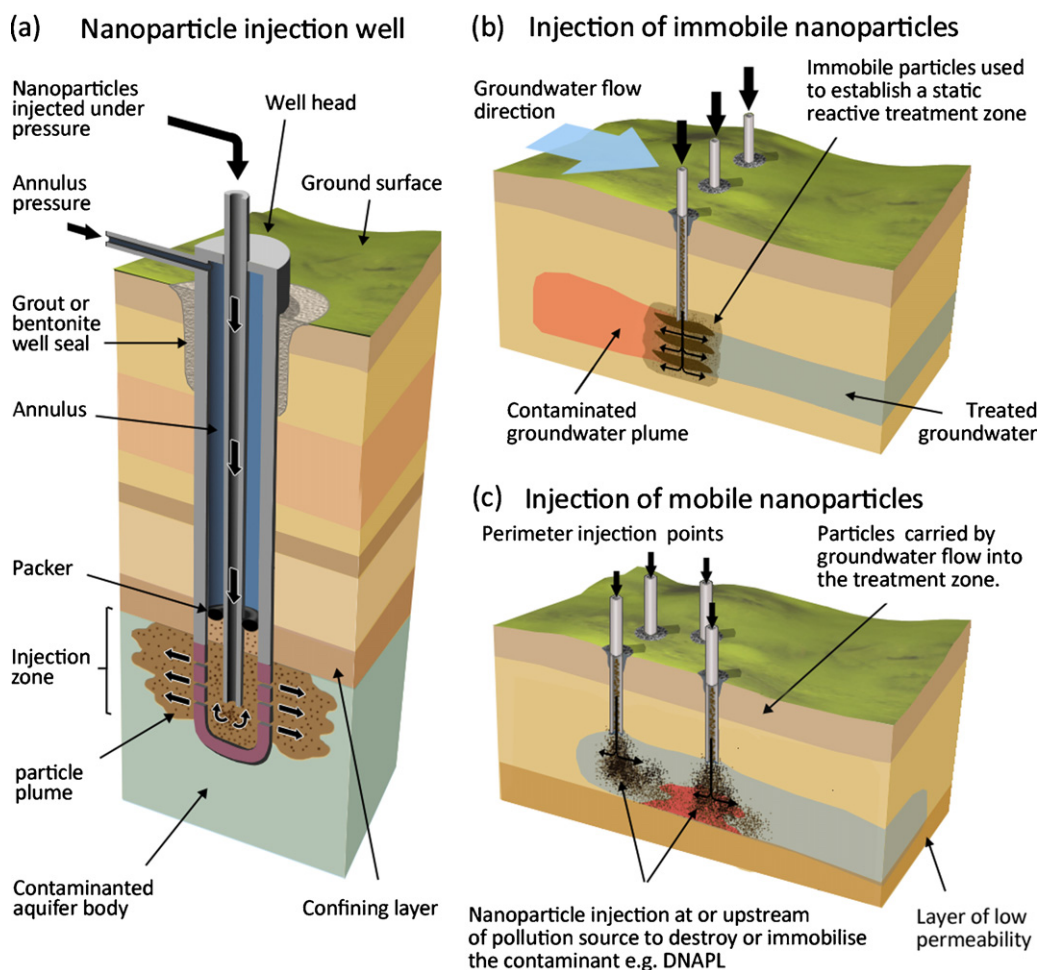
Fig. 6. (A) The layout of a typical nanoparticle injection well. The technology is very similar to that used for injection of CO_2 into subterranean storage reservoirs. Right: the use of nanoparticle injection technology for treating contaminant bodies that are (B) mobile; and (C) immobile [118]. The location and number of particle injection wells is site specific and tailored to achieve the best possible remediation.

nZVI corrosion present significantly less risk, because their inherent nano-toxicity is lower and their increased volume (into the macro-scale) significantly reduces the likelihood of cellular uptake.

A study by Pisanic et al. [125] showed that nZVI with stabilisation coatings, such as polyacrylic acid, resulted in more cellular damage since the particles existed for a longer period without degradation. The shape and size of particles has also been linked to the uptake and toxicology of nanoparticles, with increasingly smaller particles displaying intensifying toxicity.

So far, laboratory 'in vitro' tests have demonstrated nZVI toxicity on isolated cell cultures and test organisms in sterile deionised water or phosphate buffered saline (PBS) over relatively short timescales (<1 h), but research using "real" samples and environmentally relevant timescales are extremely limited [132]. It may prove that nanoparticles in natural environments will be less toxic than indicated by laboratory experiments using synthetic parameters. For example, in a study by Tong et al. [133], C_{60} fullerenes, which in the laboratory have destroyed microbes, were not observed to seriously damage the microbial cultures present in soil after 30 days' exposure.

As the reactions which determine the fate of Fe^0 are well understood, the fate of nZVI in subsurface and aqueous environments can be reasonably well predicted [134]. The acute redox sensitivity of nZVI, which drives the high rates of contaminant reaction and corrosion observed, dictates that their persistence in subsurface environments will be limited. Without fundamentally changing the composition and structure of nZVI it is likely that even the most effectively stabilised and engineered nZVI is likely to be immobilised in the subsurface via aggregation, mineral sorption or oxidative degradation within timescales in the order of days to weeks. Resultantly, nZVI in groundwater is highly unlikely to make it into humans or other mammals as they will have broken down long before contact.

The greatest risk that nZVI pose to humans is most obviously during handling, via inhalation and not when it is in the ground. Suitable care and precautions should quite obviously be taken when handling loose, dry nZVI but by using the material in the way they are intended i.e. in liquid suspension, any immediate human danger is removed.

4.6.1. nZVI in assisted natural remediation

Regardless of the performance of nZVI for environmental remediation, contaminated sites rely on bioremediation as a concurrent or terminal process and to prevent metal and/or metalloid pollutant re-release [135]. Microbially mediated reactions involving Fe can both aid and hinder aqueous contaminant removal reactions. For example, Fe^{3+}-reducing micro-organisms can reduce and precipitate a wide range of high-valence contaminant metals (such as U, Cr and Tc) through direct enzymatic reduction and via indirect reduction catalysed by biogenic Fe^{2+}, but have also been shown to release a wide range of trace metals formerly bound to Fe^{3+} phases [136].

Preliminary studies using nZVI have reported mixed results depending on the chosen experimental parameters. However,

most studies using "real" samples at low nanoparticle concentrations have reported minimal adverse affect on the functioning of plants, microorganisms and soils [137,138]. Whilst, the chemically reducing conditions imbued by the application of nZVI is comparable to the conditions in which anaerobic bacteria develop and proliferate, the capability of micro-organisms to survive in strongly reducing conditions (e.g. -500 to -600 mV) needs further documentation. In addition, mild reducing conditions (e.g. -100 to -300 mV) have been proven as amenable for some anaerobic microbial communities, such as methanogens, but further research is required into determining the fundamental metabolic pathways involved, including whether soil amendments, such as lactate in soils with insufficient electron donors and/or total organic carbon (TOC) are required [139].

As explained in Section 3, the potential re-release of metal and/or metalloid contaminants following a period of apparent remediation is an issue which may significantly limit the extent to which this technology is developed and deployed. There exists a fundamental need to examine the reversible nature of such chemical and/or biological pathways in order to determine appropriate nZVI physicochemical composition, complimentary materials/chemicals that may be used in conjunction with nZVI and injection procedures that are synergistic to the long-term chemistry and biology of the contaminated site.

5. UK legislation

The use of nZVI for in situ environmental applications has reached regulated status in many countries, including the USA, Canada, the Czech Republic, Germany, Italy and Slovakia [140]. Other countries, such as the UK, are yet to establish a legislative framework for commercial application. Since the Royal Society and Royal Academy of Engineering 'Nanoscience and Nanotechnologies: Opportunities and Uncertainties' report in 2004 [141] it has been advocated that a "precautionary approach" should be applied to the introduction of engineered nanoparticles to the environment, until further research has been performed on the potential environmental impacts. This recommendation was generic to all types of nanomaterials, and also predates a significant amount of the aforementioned studies on the toxicology and environmental fate of nZVI. Consequently, in 2010 the UK Department for Environment, Food and Rural Affairs commissioned a literature-based survey to determine "A risk/benefit approach to the application of iron nanoparticles for the remediation of contaminated sites in the environment". The organisation CL:AIRE (Contaminated Land: Applications in Real Environments) was chosen to lead the study. The report is expected in the public domain by late 2011 and will provide a scientific foundation for a more accurate UK legislative framework [142]. What is considered implicit for the future acceptance of nZVI as a remediation technology is a demonstrable and fundamental understanding of nZVI behaviour in subsurface environmental systems. As part of this, the accurate prediction of nZVI mobility, reactivity, fate and ecological impact will be critical. Future research must seek to rapidly address these areas, providing a sound body of scientific evidence upon which legislative decisions may be made.

6. A universal nZVI testing framework

Due to the extremely wide array of different nZVI materials available, the selection of an appropriate material for site remediation can be bewildering for even the most capable geo-environmental engineer. Moreover, due to the highly reactive nature of nZVI it is a perishable product, meaning that one can never assure that the material will maintain its reactivity after its manufacture/purchase date; even under extremely controlled storage

conditions. It therefore makes logical sense to establish a universal testing procedure, so different nZVI-based materials may be compared and contrasted. Such parameters would be of specific use in academia, to ensure emerging nZVI investigations are directly comparable, and, in the commercial sector, to ensure quality assurance and quality control (QA/QC).

6.1. Standard testing parameters

In addition to the standard safety information supplied by nZVI vendors it is recommended that, as a minimum, nZVI products should also be supplied with the following information: fabrication date, storage conditions, bulk and surface elemental composition, oxide thickness, particle size distribution (PSD), specific surface area (SSA), zeta potential (ζ) and isoelectric point (IEP). Testing data should also be included related to reactivity and mobility. The former could include data on pH/ORP manipulation as a function of time for a known volume of deionised water and also batch degradation results for a well characterised aqueous contaminant specie, such as methylene blue [143]. The latter could be tested using soil column experiments [144], magnetic induction coils [145] or simply by measuring the transmittance of a beam of light through a nZVI suspension as a function of time.

The establishment of a universal set of materials performance data for nZVI would be significant for developing future studies concerned with investigating the fundamental environmental behaviour and impact of nZVI.

6.2. Universal NZVI reactivity test

Due to the inherent complexity of using ORP manipulation to determine nZVI reactivity [146], an alternative method could be to measure the evolution of hydrogen gas, produced from the hydrolysis of water, during the material's aqueous corrosion (Eqs. (2) and (4)) [147,148,58,149,150]. The method regards the exposure of a known quantity of nZVI, with a known volume of an aqueous reagent, in a sealed container of known headspace. For the reaction of nZVI with deionised water, one mole of $H_{2(g)}$ is produced from one equivalent mole of Fe^0, so the amount of H_2 produced is directly proportional to amount of Fe^0 in a material. The method can therefore also be used to quantify: (i) the extent at which the material's reactivity is limited by oxide/hydroxide formation; and (ii) the proportion of non-H_2 generating components (such as oxide/hydroxides and impurities, e.g. C, H_2O, OH^-).

As the mass and volumetric density of $H_{2(g)}$ in Fe^0 are 0.036 g g^{-1} and 0.284 g cm^{-3} respectively, the method can be achieved using relatively small quantities of nZVI powder and minimal experimental apparatus. The method can therefore be used in the field, to measure the nZVI content of a slurry prior to deployment; NANO IRON, s.r.o. offer a commercial product, their "nZVI tester" [151].

7. Conclusions

Nanotechnology is one of the most rapidly growing sectors of the global economy. Over a thousand products using nanomaterials are currently available for a diverse range of applications within the private and public sector. For the treatment of contaminated water and soils, a growing body of theoretical and empirical evidence has proven nZVI as both highly effective and versatile. In recent years there have been significant innovations in terms of manufacture techniques, physicochemical functionalisations and enhancements in subsurface stability and mobility. However, the competiveness of nZVI against other in situ treatments such as chemical oxidation is still widely disputed. The wide variety of different nZVI physico-chemical compositions available and discrepancies in the literature

with regard to the chosen testing parameters had led to a confusing array of data. Consequently, in order for different nZVI materials to be effectively contrasted with each other and/or conventional site remediation techniques, a universal empirical testing framework is required, and has been reported herein.

The current review has also highlighted that whilst much emphasis has been placed on methods to enhance particle reactivity (bimetallic combinations, thermal treatments, etc.), seemingly little attention has been paid to reducing production costs or determining the material's ecological impact.

The universal acceptance of nZVI as a remediation technology may well occur, but not until a fundamental understanding of behaviour, interactions and impact has been demonstrated. Future research must seek to establish a sound body of evidence upon which predictions of nZVI mobility, reactivity, fate and ecological impact may be accurately made. Such evidence combined with expected reductions in production costs will prove invaluable for successfully establishing this technology in the land remediation toolbox alongside other more conventional methods.

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