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Use of iron-based technologies in contaminated land and groundwater remediation: A review

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ABSTRACT

Reactions involving iron play a major role in the environmental cycling of a wide range of important organic, inorganic and radioactive contaminants. Consequently, a range of environmental clean-up technologies have been proposed or developed which utilise iron chemistry to remediate contaminated land and surface and subsurface waters, e.g. the use of injected zero zero-valent iron nanoparticles to remediate organic contaminant plumes; the generation of iron oxyhydroxide-based substrates for arsenic removal from contaminated waters; etc. This paper reviews some of the latest iron-based technologies in contaminated land and groundwater remediation, their current state of development, and their potential applications and limitations.

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1. Introduction

The management of contaminated land and groundwater is a major current environmental issue, where recent (and historical) industrial and urban activities have led to the presence of elevated concentrations of a wide range of contaminants in soils, sediments and surface- and groundwaters, affecting the health of millions of people worldwide. In Europe alone, the European Environment Agency estimates that soil contamination requiring clean-up is present at approximately 250,000 sites in the EEA member countries, while potentially polluting activities are estimated to have occurred at nearly 3 million sites (EEA, 2007). A range of national and regional legislation has consequently been implemented to enforce the clean-up or remediation of contaminated land, and the clean-up or protection of surface and groundwater resources. This, alongside the recognition that “traditional” methods of contaminated land and groundwater treatment (e.g. disposal to

landfill, isolation, pump-and-treat) are not sustainable (or indeed effective) in many situations, has led to a massive increase in research into the development of alternative *in-situ* and *ex-situ* treatment technologies for land and water remediation. A number of these alternative remediation techniques utilise the sorptive and reductive properties of iron and its mineral products to remove or stabilise inorganic, organic and radioactive contaminants. This paper reviews these iron-based land and water remediation technologies and their current state of development, and evaluates their applicability (and limitations) in remediating a range of common groundwater and soil/sediment contaminants.

2. The environmental chemistry of iron

Iron is the fourth most abundant element in the Earth's crust, and reactions involving iron play a major role in the

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environmental cycling of a range of important contaminants. Iron exists in the environment dominantly in two valence states — the relatively water-soluble Fe(II) (ferrous iron) and the highly water-insoluble Fe(III) (ferric iron), with the latter being the stable form in oxygen-rich environments under neutral to alkaline pH conditions. Zero-valent (or elemental/native) iron (Fe(0)) is also found under some specific environmental and geological conditions (e.g. in some mafic and ultramafic rocks, and in meteorites, Read, 1970). It is, however, rarely formed at the Earth's surface due to the high reactivity of elemental iron. The common iron-bearing minerals are shown in Table 1. The variable oxidation state of iron, its ability to co-ordinate to oxygen, nitrogen and sulphur atoms, and to bind additional small molecules, mean that iron is one of the most important trace elements in biological systems, and plays an important role in many reactions in the human body. In the environment, iron plays an important role in contaminant mobility, sorption and breakdown due to its role as an electron donor (i.e. during the oxidation of Fe^{2+} to Fe^{3+}), and, in its various mineral forms, as a precipitant/sorbent substrate. Freshly-precipitated, amorphous Fe oxyhydroxides (hydrous ferric oxides, or HFO) are known to be particularly effective adsorbents of a range of contaminants (e.g. Bendell-Young and Harvey, 1992; Cundy and Croudace, 1995; Cundy and Hopkinson, 2005), due to their high (reactive) specific surface area. Indeed, removal of contaminants from waste streams through precipitation with

(hydrous) ferric oxides is an established methodology in a number of industrial processes, for example the use of high density sludge systems for arsenic control in effluents from the mining industry, and in the treatment of textile dye effluent (e.g. Kumar et al., 2007). Over time, however, HFO gradually transforms (crystallises) to more ordered forms such as goethite or hematite, which have reduced surface areas and so are generally less reactive and effective as sorbent substrates (Smedley and Kinniburgh, 2002). Sorbed metals and radionuclides can either be surface adsorbed, co-precipitated or incorporated into the (Fe)oxide structure. Non-oxide Fe phases (sulphides, carbonates, phosphates) also act as effective sorbents or (co)precipitants for a range of contaminants.

The long-term storage of contaminant metals and radionuclides on iron oxyhydroxide and oxide phases is, however, clearly pH and Eh dependant, as chemical and/or microbially-driven reduction reactions or an increase in acidity may lead to breakdown and solubilisation of iron phases and release of associated contaminants (e.g. Smedley and Kinniburgh, 2002). A clear illustration of this is in the reductive release of Fe-oxide associated As from organic-rich alluvial sediments in the Bengal delta, which has caused extensive groundwater contamination and large large-scale health problems in the local population (see Section 3.1.2). Similarly, contaminant sorption to Fe sulphides, carbonates and phosphates is also highly dependant on local Eh/pH conditions and so may be reversible. In the case of iron sulphides, a prominent example is the (chemical and microbially-mediated) release of metals following oxidation of pyrite and marcasite-rich mining wastes exposed to air and water during and following mining operations. In this case, iron sulphide oxidation (and oxidation of other metal sulphide phases), coupled with ferrous iron oxidation and ferric iron hydrolysis, may generate persistent and widespread acid mine drainage (AMD) and associated trace metal enrichments, causing severe environmental degradation (see reviews by Kalin et al., 2006 and Blodau, 2006).

Many of the reactions involving Fe in soils, sediments and groundwater are microbially-mediated, with Fe(III) acting as the dominant electron acceptor for microbial respiration in many subsurface environments. Microbially-mediated reactions involving Fe have been shown to both sequester and release contaminants, e.g. the activity of Fe(III)-reducing micro-organisms can reduce and precipitate a range of high-valency contaminant metals (such as U, Cr, and Tc) through direct enzymatic reduction and via indirect reduction catalysed by biogenic Fe(II), but can also release trace metals formerly bound to Fe(III) phases (e.g. Lloyd, 2003). A detailed description of the properties, reactions and mechanisms of formation and dissolution of the various major iron minerals and phases is beyond the scope of this article, but comprehensive recent reviews can be found in Cornell and Schertmann (2003) and Vaughan (2006).

Table 1 – Some common iron-bearing minerals present in surface and near-surface environments

Mineral class	Name	Formula
Native or metal form (rare) Oxides/hydrated oxides	Zero-valent iron (ZVI)	Fe
	Hematite	α - Fe_2O_3
		γ - Fe_2O_3
	Magnetite	Fe_3O_4
	Goethite	α - $\text{FeO} \cdot \text{OH}$
	Lepidocrocite	γ - $\text{FeO}(\text{OH})$
	Ferrihydrite	$\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$
	Green rusts	Fe(II–III) hydroxysalts, general formula: $[\text{Fe}^{\text{II}}_{(1-x)}\text{Fe}^{\text{III}}_x(\text{OH})_2]^{x+}$ $[(x/n)\text{A}^{n-} \cdot (m/n)\text{H}_2\text{O}]^{x-}$, where x is the ratio $\text{Fe}^{\text{III}}/\text{Fe}_{\text{tot}}$.
Carbonates	Siderite	FeCO_3
	Ankerite	$\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$
Phosphates	Vivianite	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$
	Strengite	$\text{FePO}_4 \cdot 2(\text{H}_2\text{O})$
Sulphates	Hydrated ferrous sulphate (copperas)	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (melanterite form)
Sulphides	Pyrite	FeS_2
	Marcasite	FeS_2
	Pyrrhotite	$\text{Fe}(1-x)\text{S}$
	Mackinawite	$(\text{Fe}, \text{Ni})_{1+x}\text{S}$ (where $x=0$ to 0.11)
Silicates	Greigite	$\text{Fe}^{2+}\text{Fe}_2^{3+}\text{S}_4$
	Berthierine	$(\text{Fe}_4^{2+}\text{Al}_2)(\text{Si}_2\text{Al}_2)\text{O}_{10}(\text{OH})_8$
	Chamosite	$(\text{Fe}_5^{2+}\text{Al})(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$
	Greenalite	$\text{Fe}_6^{2+}\text{Si}_4\text{O}_{10}(\text{OH})_8$
	Glaucconite	$\text{KMg}(\text{FeAl})(\text{SiO}_3)_6 \cdot 3\text{H}_2\text{O}$

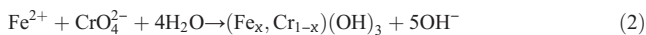
3. Iron as a remediation tool

The use of iron-based technologies in contaminated land and groundwater remediation is a rapidly developing field, with a range of techniques proposed which make use of iron as a reductant, or as a sorbent, which have been tested at various

scales of application. The ability of iron (both in its zero-valent form and as Fe^{2+}) to reduce (and so immobilise or reduce the availability of) redox sensitive elements such as Cr and Tc or to dechlorinate various organic groundwater contaminants has been demonstrated at both laboratory scale and in field tests (e.g. Liang et al., 1996; Puls et al., 1999; CL:AIRE, 2001; Kim et al., 2007; Ludwig et al., 2007). Zero-valent iron has been shown to be a strong reducing agent capable of reducing many halogenated methanes, ethanes, and ethenes and other halogenated compounds at ambient temperatures (e.g. Deng and Hu, 2001), e.g.:



Surface-bound Fe^{2+} can also act as a possible reductant for chlorinated compounds (Deng and Hu, 2001). Reactions for Cr reduction and immobilisation include:



in which the toxic or carcinogenic hexavalent form of Cr is reduced to the less toxic Cr^{3+} form, which readily precipitates as $\text{Cr}(\text{OH})_3$ or as the solid solution $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3$ (Puls et al., 1999).

A range of other systems have proposed the use of iron oxides and oxyhydroxides, and sulphides, to sorb or immobilise contaminants from groundwater and in wastes (e.g. Heal et al., 2003; Kumpiene et al., 2006; Mohan and Pittman, 2007; Contin et al., 2007; Naveau et al., 2007). Contaminant interaction with iron-bearing minerals, and microbially-mediated reactions involving iron as an electron acceptor, may also be an important component of monitored natural attenuation strategies (i.e. whereby naturally-occurring surface and subsurface biogeochemical reactions are used to reduce contaminant loads or concentrations in land remediation programmes) and in passive treatment systems such as constructed wetlands (e.g. Schirmer and Butler, 2004, Kalin et al., 2006).

Current applications of iron-based technologies in contaminated land or groundwater remediation can be broadly divided into two (overlapping) groups, based on the chemistry involved in the remediation process: technologies which use iron as a sorbent, (co-)precipitant or contaminant immobilising agent (referred to here as sorptive/ stabilisation technologies); and those which use iron as an electron donor to break down or to convert contaminants into a less toxic or mobile form (reductive technologies). It should be noted however that many technologies utilise both processes to a greater or lesser degree. Specific examples are discussed below.

3.1. Sorptive/stabilisation technologies

3.1.1. Iron as a sorbent in “assisted natural remediation” schemes

Several authors have examined the use of iron oxides as *in-situ* soil amendments, to reduce the bioavailability of various contaminants at former industrial sites. Iron-rich soil amendments, such as goethite and iron grit (an angular cast steel abrasive, of < 0.1mm size, containing 97% $\text{Fe}(0)$), may be applied as part of “assisted natural remediation” schemes at highly contaminated sites, to immobilise contaminants, and so improve vegetation growth and microbial diversity, and

reduce offsite metal transport. For example, Kumpiene et al. (2006) examined the efficiency of $\text{Fe}(0)$ to reduce the mobility and bioavailability of Cr, Cu, As and Zn in a chromated copper arsenate (CCA)-contaminated soil. The treatment significantly decreased As and Cr concentrations in soil leachates (by 98% and 45%, respectively), in soil pore water (by 99% and 94%, respectively) and in plant shoots (by 84% and 95%, respectively). The stabilization technique also restored soil enzyme activities and reduced microbial toxicity, as evaluated by toxicity tests.

The use of iron-based soil amendments has shown promising results over relatively long treatment periods (e.g. up to six years, Mench et al., 2006) and in a variety of contaminated soils (e.g. As-contaminated agricultural soils, Mench et al., 2006; CCA-contaminated soils, Kumpiene et al., 2006). Some amendments, however, may have detrimental effects on plant growth (Hartley and Lepp, 2008), and may not be equally effective on all contaminants present. For example, in Kumpiene et al.’s (2006) study, detailed above, despite the relative success of $\text{Fe}(0)$ -based soil amendments in reducing the bioavailability of Cr and As in CCA-contaminated soils, exchangeable and bioaccessible fractions of Cu remained high, causing some residual toxicity in the treated soil (Kumpiene et al., 2006). In addition, careful (long-term) monitoring of soil leachates and contaminant bioaccessibility is required following application of the amendments, due to possible changes in Fe (and contaminant) mineralogy and speciation over time.

3.1.2. Iron-based technologies for the removal of arsenic from ground and drinking waters

In recent years, a range of inexpensive, iron-based, water clean-up technologies have been developed to address the major problem of arsenic contamination in groundwater-sourced drinking water. This problem is particularly severe in the Bangladesh and West Bengal area, where up to 70 million people are exposed to elevated arsenic concentrations in drinking water, due to consumption of local groundwater contaminated with arsenic following its release from As-bearing aquifer sediments (Lepkowski, 1999). Aquifers in a range of other countries are also severely affected by elevated arsenic concentrations, including the USA, China, Argentina, Chile, Mexico, Hungary, Romania and Vietnam (Smedley and Kinniburgh, 2002). A large number of authors have examined the adsorption of arsenic by iron oxides (see reviews by Smedley and Kinniburgh, 2002; Mohan and Pittman, 2007), highlighting (a) the tendency of As (in both of its common As (III) and As(V) states) to strongly bind to (hydrated) Fe oxides (as monodentate or bidentate inner sphere complexes), even at very low arsenic concentrations, and (b) the important environmental role of amorphous, freshly-precipitated, Fe oxides as sorbents of arsenic. Iron-based As removal technologies make use of this strong (geo)chemical association of As with Fe, removing As by direct adsorption processes (e.g. Yuan et al., 2002; Mohan and Pittman, 2007; Sylvester et al., 2007) (Fig. 1), or co-precipitation (e.g. chemical co-precipitation using ferric chloride, e.g. Meng and Korfiatis, 2001), with many systems reporting > 90% arsenic removal from treated water. These high removal rates are, however, frequently achieved using batch adsorption experiments on solutions

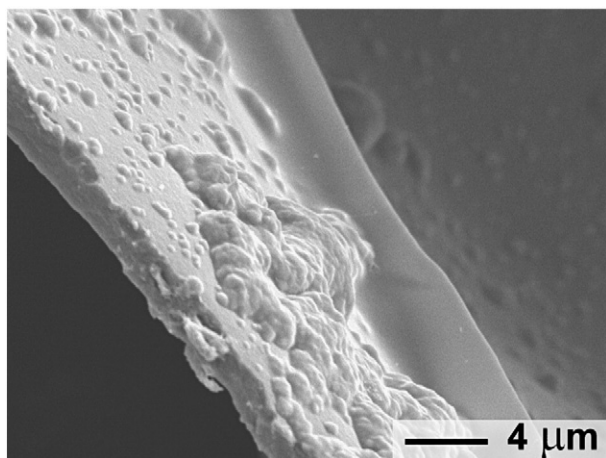


Fig. 1 – Scanning electron microscope image of iron:polymer composite material for wastewater treatment, developed at the University of Brighton, and shown to be effective at removing >99% of As from test solutions. Sub-micron scale agglomerations of hydrous Fe oxides are stabilized on the polymer surface, providing a large surface area for As adsorption. Authors' unpublished data, image courtesy of I. Savina.

spiked to mg/l As concentrations, although a number of authors have reported effective arsenic removal from solutions with more environmentally-realistic (100–800 μg/l) As concentrations (Mohan and Pittman, 2007). A detailed review of the performance of the main arsenic-removal technologies, including those utilising iron as an adsorbent or precipitant, is given in Mohan and Pittman (2007).

Most iron-based treatment methods are more effective in removing arsenic in its pentavalent (As(V) or arsenate) state, rather than as the more toxic trivalent (As(III) or arsenite) species, and so may involve oxidation as a pre-treatment (Rao and Karthikeyan, 2007). Adsorption of As may also be less effective at higher pHs (Mohan and Pittman, 2007). The need for effective, robust and low-cost devices for widespread small-scale (i.e. at the scale of an individual household) application has led a number of researchers to examine the use of low-cost, local and/or waste materials such as iron-coated sand, cast iron filings, steel wool, and amended blast furnace slags, which may provide effective components of point-of-use filters for As removal (as shown by Joshi and Chaudhuri, 1996; and Rao and Karthikeyan, 2007; see also Mohan and Pittman, 2007). In addition, Sarkar et al. (2007) discuss the large-scale field (i.e. well-head) application of regenerable iron nanoparticle-based hybrid anion exchangers, wherein the higher cost of these devices is partly offset by their ability to be repeatedly re-used, following simple regeneration at a central regeneration facility. Regeneration of As sorbent devices, in common with chemical co-precipitation methods, may however generate arsenic-rich sludges which require landfill disposal, which in itself may lead to further environmental release of arsenic. Many of these technologies, while still at a relatively early stage of development or application, do however show significant potential for effective removal of arsenic from relatively large volumes of contaminated drinking water.

3.2. Reductive technologies

3.2.1. Iron-based chemical treatment methods

The ability of iron to act as an electron donor or reducing agent is utilised in so-called Fenton treatment techniques, whereby Fe^{2+} or Fe^0 are used to reduce hydrogen peroxide and generate the highly reactive $\cdot\text{OH}$ radical, e.g. for Fe^{2+} (Hong et al., 2007):



The hydroxyl radical is a strong oxidising agent capable of non-selectively oxidising a variety of organic compounds (e.g. Villa et al., 2008). Commonly applied to industrial wastes, Fenton techniques have also shown considerable efficiency in the remediation of contaminated soils containing (among other contaminants) pesticides, fuel and explosives (Villa et al., 2008). Traditional Fenton's treatment requires low pH conditions, but a number of authors have examined the use of modified Fenton processes for field-scale application without acidification of the treated media. For example, Kakarla et al. (2002) observed a 90% reduction in chlorinated contaminants in groundwater at a former dry-cleaning facility in Florida, USA, using a modified Fenton's processes which utilised chelated-iron catalysts and stabilized hydrogen peroxide, to allow effective *in-situ* field application under local pH conditions (i.e. pH 5–7), while also extending the longevity of the reaction process. These Fenton treatment techniques form one of a number of *in-situ* (iron-based) chemical methods that may be applied for removal of a range of organic (and some inorganic) contaminants from groundwater and soils. Other iron-based chemical remediation technologies include ferrous sulphate and ferrous ammonium sulphate injection. The former is a traditional reducing agent for the treatment of metal industry process effluents, which has also been successfully applied as an *in-situ* groundwater treatment method, e.g. Brown et al. (1998) note the successful *in-situ* application of an acidified solution of ferrous sulphate heptahydrate (via a combination of wells and trenches) to remove Cr(VI) by reductive precipitation at the site of a former paper mill on the Delaware River, USA. In this example, concentrations of Cr(VI) in groundwater were reduced from 85,000 μg/l to 50 μg/l. Ferrous ammonium sulphate may also be applied, which has the advantage over ferrous sulphate of reacting relatively rapidly over neutral to alkaline pHs, thus avoiding the need for acidification (e.g. CL:AIRE, 2007).

Despite a number of successful large-scale applications of these chemical injection methods, further research is still needed on their field-scale limitations and practicalities, particularly regarding the interaction of iron with the intermediate products of contaminant degradation (e.g. Hong et al., 2007), the role of soil organic matter in the efficiency of the treatment process, and the behaviour of other, non-target, site contaminants during treatment.

3.2.2. Iron-based nanoparticles as tools for soil and groundwater remediation

The recent rapid development of the field of nanotechnology has driven a considerable volume of research into the use of iron-based nanoparticles as soil and groundwater remediation tools. The use of iron-based nanoparticles to remediate contaminated land and groundwater makes use of the enhanced reactivity,

surface area, and/or enhanced mobility of nanometre (10^{-9} m)-scale iron particles, to produce more rapid or cost-effective clean-up of wastes compared to conventional iron-based (and other) technologies (USEPA, 2007). Laboratory studies have indicated that nanoscale iron particles can effectively remediate a range of (chloro)organic compounds in groundwater, including chlorinated methanes, ethanes, benzenes and chlorinated biphenyls, principally using zero-valent iron (ZVI) as a bulk reducing agent (Elliott and Zhang, 2001). In addition, Quinn et al. (2005) note the potential of zero-valent iron nanoparticles to not only treat dissolved chlorinated solvents *in-situ*, but also to remediate dense nonaqueous phase liquid (DNAPL) contaminant source zones in aquifers.

A number of field trials into the effectiveness of groundwater remediation by iron-based nanoparticles have therefore been undertaken or are being developed (e.g. Elliott and Zhang, 2001; Zhang, 2003; ITRC, 2005; Quinn et al., 2005). The particles used are typically injected as a slurry directly into the subsurface environment to remediate contaminated groundwater plumes or contaminant source zones (thus avoiding the need for intrusive digging methods), and may be suspended in a hydrophobic fluid (i.e. injected as an emulsion) to prevent particle agglomeration and enhance reactivity and mobility. The nanoparticles themselves commonly consist of zero-valent iron or bimetallic nanoparticles (iron nanoparticles coated with catalytic metals such as Pd and Pt). Some technologies make use of the magnetic properties of certain iron minerals (e.g. Fe_3O_4) as a post-treatment separation tool (e.g. Yantasee et al., 2007). High remediation efficiencies have been observed: in field trials in the USA, O'Hara et al. (2006) and Quinn et al. (2005) reported substantial reductions in soil concentrations (greater than 80 percent) of the DNAPL contaminant trichloroethylene (TCE) and significant reductions in TCE groundwater concentrations (60% to 100% reduction) during a field-scale demonstration of the injection of emulsified zero-valent iron nanoparticles at Cape Canaveral Air Force Station, Florida, USA. Pilot source remediation trials at Jacksonville and Lakehurst (USA) using bimetallic nanoparticles, however, while showing some promising results (specifically, reduction in TCE concentrations in some test wells), were generally less successful than those using emulsified zero-valent iron nanoparticles, possibly due to early passivation of the nanoparticles used, or use of an insufficiently high iron:soil ratio to generate reducing conditions in the aquifers treated (Gavaskar et al., 2005).

While there has been much emphasis on the use of nano-iron for the removal of DNAPL and other organic contaminants, the utility of iron nanoparticles in removing or stabilizing metallic and metalloid contaminants has also been demonstrated in a variety of soil and water media. For example, the use of nanoscale zero-valent iron to adsorb arsenite and arsenate in the subsurface, and so reduce As mobility in groundwaters, has been proposed (Kanel et al., 2005, 2006), and the use of nanoscale magnetite crystals to remove Cr(VI) from wastewaters has also been examined (Hu et al., 2004). In recent work, Liu and Zhao (2007) and Xu and Zhao (2007) note the potential of using stabilized Fe (ZVI and iron phosphate-based) nanoparticles as soil amendments, to reductively immobilize immobilise Cr(VI) and also to reduce the bioaccessibility of Cu in soils (see also Section 3.1.1).

In general, there has been a comparatively rapid transfer of nano-iron-based remediation technologies from laboratory to field-scale application, and full-scale commercial applications of nano-zero-valent iron in land and groundwater remediation have rapidly developed (Tratnyek and Johnson, 2006). As outlined above, these field-based approaches typically involve the free-release of engineered nanoparticles to the environment. There are, however, a number of potentially serious issues concerning the environmental fate of engineered nanoparticles, and their potential impacts on human health (e.g. Colvin, 2003). For the latter, various concerns have been raised which derive largely from the small size and high reactivity and potential mobility (in both environmental and biological systems) of engineered nanoparticles. For example, environmental exposure to nanoparticles may allow their penetration into the deep lung via inhalation, where the clearance mechanism may not eject highly anisotropic, non-biodegradable nanomaterials (e.g. Lam et al., 2004). In addition, the passage of nanoparticles across cell membranes directly into cells or tissues may interfere with important cellular functions, while their enhanced reactivity may also have free-radical-releasing, pro-inflammatory properties (Royal Society, Royal Academy of Engineering, 2004). While the exposure of cells and tissues to engineered nanoparticles has also been shown to have a beneficial effect with respect to their use as therapeutic biomaterials (e.g. Matsumoto et al., 2007), these beneficial effects usually occur under controlled exposure conditions. In general, the transport mechanisms of engineered nanoparticles through the environment and into plant and animal life, and the associated risks, remain poorly understood (e.g. Nowack and Bucheli, 2007), and this may significantly limit their widespread application as remediation tools. In the UK, the Royal Society and Royal Academy of Engineering recommends "that the use of free (that is, not fixed in a matrix) manufactured nanoparticles in environmental applications such as remediation be prohibited until appropriate research has been undertaken and it can be demonstrated that the potential benefits outweigh the potential risks", while the USEPA have made the environmental fate of, and exposure to, nanoparticles, a high priority research area (USEPA, 2007), and has introduced regulation on the use of certain nanoparticles used as bactericides (Chatterjee, 2007).

The use of nanoparticles in a static, or contained, system may avoid many of the problems outlined above, although the application of nanoscale iron particles and their agglomerates in systems such as fixed-bed columns, *in-situ* reactive barriers and similar flow-through applications is not possible due to extremely high pressure drops in conventional systems, and their lack of durability and mechanical strength (Cumbal et al., 2003). Recent technologies have attempted to develop this area however by producing porous polymer-based materials of higher mechanical strength e.g. the ArsenX^{DP} system (Sylvester et al., 2007), which is a hybrid (regenerable) sorbent consisting of nanoparticles of hydrous iron oxide distributed through porous polymeric beads, and N-CAS (Nano-composite arsenic sorbent), a polymer:FeOOH composite developed by the Idaho National Laboratory, USA. Most focus has been on the development of post-abstraction, *ex-situ* water filtration devices (e.g. Sarkar et al., 2007, see Section 3.1.2), but there is significant scope for the development of fixed nanoparticle-based *in-situ* devices, provided that manufacturing costs can be kept sufficiently low.

3.3. A combined chemical approach: Reactive barrier technologies

The use of iron as a reactive material in permeable reactive barriers was pioneered in the 1990s (e.g. Blowes and Ptacek, 1994, USEPA, 1998) and has been the subject of considerable research and development since that date. A permeable reactive barrier (PRB) is an engineered zone of reactive material, extending below the water table, designed to intercept and treat contaminated groundwater. Contaminants passing through the PRB are either degraded by, or retained in, the reactive barrier material. A variety of PRBs have been developed and installed at contaminated sites to treat a range of inorganic, organic, and radioactive contaminants. Typical PRB designs involve the excavation and backfilling of a continuous trench with reactive material (such as iron, limestone, calcium phosphate-based minerals, activated carbon, compost, zeolites etc., with the choice of material depending on the target contaminant(s)), which is perpendicular to and intercepts a groundwater plume, or consist of a so-called “funnel and gate” system in which low-permeability walls are used to direct contaminated groundwater towards a permeable treatment zone. Zero-valent iron (ZVI) has been used particularly successfully as a reactive media in a number of field-scale PRB systems (e.g. Lo et al., 2007), particularly those designed to remediate chlorinated organic, metal and radionuclide contamination. Of ca. 200 PRBs installed worldwide by 2004, 120 were iron-based (i.e. utilising zero-valent iron, steel wool, cast iron, amorphous HFO etc.) (ITRC, 2005).

Zero-valent iron PRB systems may remove chlorinated organics by reductive dechlorination (see discussion in Deng and Hu, 2001), whereas metals, metalloids and radionuclides may be removed via reductive precipitation, surface adsorption or complexation, or co-precipitation with the Fe oxyhydroxides that form on the ZVI surfaces (Scherer et al., 2000; ITRC, 2005). Contaminant removal processes may be effective over considerable timescales, e.g. Wilkin et al. (2005) report the continued effectiveness (after 8 years of operation) of reductive precipitation in removing groundwater Cr contamination in the zero-valent iron PRB at the US Coastguard Support Centre near Elizabeth City, NC, USA. Well-documented limitations of PRB systems however include the need for intrusive engineering methods for installation, the need for well-constrained and discrete groundwater flow paths, and loss of reactivity and build up of mineral precipitates within the PRB over time. For the latter, many authors have reported significant loss of porosity and permeability within PRB systems due to the build up of mineral precipitates (such as aragonite, calcite and siderite) derived from reactions with local groundwater and the formation of iron corrosion products such as goethite, mackinawite and green rusts (e.g. Phillips et al., 2003; Liang et al., 2005; Morrison et al., 2006; Henderson and Demond, 2007). Furukawa et al. (2002) and Wilkin et al. (2005) however note that the development of secondary iron-bearing mineral phases (such as iron sulphides and ferrihydrite) within zero-valent iron PRBs may in fact enhance their removal efficiency for various contaminants. Henderson and Demond (2007) have carried out a detailed analysis and review of the parameters contributing to PRB failure in field installations of zero-valent iron-based PRB systems, and note that the most

common causes of PRB failures are design flaws (e.g. improper hydraulic characterisation of a site prior to PRB installation) rather than loss of reactivity or clogging via mineral precipitation (although these latter factors may limit PRB longevity in the field).

Recent work has also examined the remote, electrical generation of reactive subsurface iron barriers (Hopkinson and Cundy, 2003; Cundy and Hopkinson, 2005; Faulkner et al., 2005). Using electrokinetic techniques which mimic natural reactions in soil/sediments, subsurface reactive (i.e. sorptive) iron barriers can be generated in various geometries using a low-magnitude (< 2V/cm) electrical potential generated between vertical iron-rich electrodes. This process also generates an intense pH gradient in the treated material which is used to remobilise and concentrate contaminants around the iron barrier, which can then be excavated (Fig. 2).

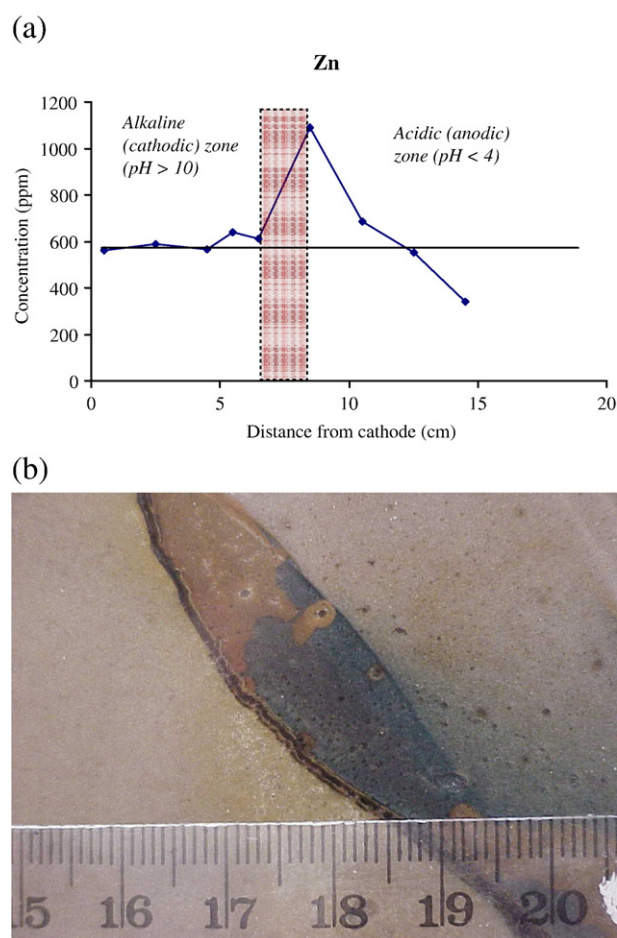


Fig. 2 – (a) Remobilisation (from the acidic anodic compartment) and re-concentration of zinc onto subsurface, sub-vertical, Fe barrier (illustrated in (b) — scale bar in cm), generated in-situ in industrial site soils following bench-scale electrokinetic treatment (Hopkinson and Cundy, 2003; Cundy and Hopkinson, 2005). Filled bar on (a) shows position of Fe barrier, horizontal bar shows Zn concentration prior to treatment (569 ± 3 ppm). This iron-based electrokinetic method has been shown to be effective on a range of soil materials, for the removal or stabilization of various contaminants, including Zn, Cu, Pu, Am, As, U, Pb and Cr. Part (b) after Cundy and Hopkinson (2005).

Forced dissolution of the electrodes can also be used to deliberately mobilise dissolved iron into an area of soil, to act as a reductant to immobilise elements such as Cr. Recent bench trials on Cr-contaminated waste soils using this method show 85 to 96% reduction in Cr(VI) concentrations in soil leachates, with a concomitant increase in concentration of mixed iron–chromium mineral phases within the treated soil (Hopkinson et al., *in press*).

4. Discussion

As illustrated above, a range of novel, iron-based technologies have been proposed or are under active development for the remediation of a range of common soil and groundwater contaminants. Many of the techniques developed are still at

an experimental or pilot stage, however, and there is a need to demonstrate their large-scale field, rather than laboratory, effectiveness, i.e. to show that they are capable of safe, low low-cost upscaling and (for some applications) mass production. Many laboratory studies have examined remediation performance under extremely high contaminant concentrations, short timescales and controlled conditions which may not reflect those present at (or in) contaminated sites. A major development issue is therefore posed by the need for the technologies to work at low (environmental) contaminant concentrations, in the presence of a range of competing ions. For example, As (V) and phosphate have been observed to compete for sites on hydrous ferric oxide, so high phosphate concentrations in groundwater may significantly inhibit As sorption (Smedley and Kinniburgh, 2002). Groundwater major ion chemistry may also significantly affect permeable reactive

Table 2 – Stage of development, mode of application, and published or estimated costs of selected iron-based remediation technologies discussed in the text

Technology	Stage of development	<i>In-situ</i> or <i>ex-situ</i>	Remedial mechanism	Estimated cost (US \$)
Assisted natural remediation	Laboratory and pilot field trials	<i>In-situ</i>	Contaminant immobilisation	Little info, but likely to be relatively low (<\$50 per ton material treated).
Chemical oxidation using Fenton's reagent	Commercial systems available	<i>In-situ</i> or <i>ex-situ</i>	Chemical oxidation	Cost varies depending on depth, nature and quantity of contaminant, and local geology. As an example, \$220,000 estimated for treatment of ca. 80,000 gal. of DNAPL contaminated groundwater, King's Bay naval submarine base, Georgia, USA (USEPA data, Federal Remediation Technologies Round Table, http://costperformance.org).
Chemical reduction via addition of Fe(II)-containing solutions	Commercial systems available	<i>In-situ</i> or <i>ex-situ</i>	Reductive precipitation	Cost varies depending on depth, nature and quantity of contaminant, and local geology. Cost of \$250,000 reported for treatment of Cr(VI) contaminated soils and ca. 75,000–100,000 gal. of Cr(VI)-contaminated groundwater using ferrous sulphate heptahydrate (Brown et al., 1998).
Source remediation via nZVI injection	Pilot trials implemented, commercial systems available	<i>In-situ</i>	Dechlorination (of DNAPL contaminants)	Cost varies depending on depth, nature and quantity of contaminant, and local geology. \$250,000–\$300,000 per site (based on pilot trials reported in Gavaskar et al., 2005)
Permeable reactive barriers	Commercial systems available	<i>In-situ</i>	Sorption or degradation of contaminants in barrier	\$60–\$245 per ton material treated (Mulligan et al., 2001)
Excavation and disposal	Established, traditional "treatment" method	–	–	Variable, depending on local landfills taxes, legislative framework and type of contaminant. In the UK, ca. \$90–\$450 (equivalent) per ton, but reaching ca. \$10,000 (equivalent) per ton for low level radioactive wastes.
Pump and treat	Established traditional treatment method	<i>Ex-situ</i>	Removal of contaminated groundwater by pumping, followed by contaminant removal via sorption, precipitation, air stripping etc.	Cost varies depending on site size, nature and volume of contaminant, and local geology. Project life cycle however may be 30–50 years, with costs in the order of millions of dollars (Brown et al., 1998).
Soil vapour extraction	Commercial systems available	<i>In-situ</i>	Extraction and treatment	Cost varies depending on site size, nature and volume of contaminant, and local geology. Cost range ca. \$400–\$1500 per ton material treated (Federal Remediation Technologies Round Table, http://www.frttr.gov)
Soil washing	Commercial systems available	<i>Ex-situ</i>	Removal of soluble contaminants, or waste reduction/minimisation	\$25–\$300 per ton material treated (Mulligan et al., 2001)

Estimated costs for alternative *in-situ* and *ex-situ* remediation technologies (italicized) are included for comparison.

barrier lifetimes due to mineral precipitation (see Section 3.3 above). The use of non-selective contaminant treatment techniques which mimic, or harness, natural soil reactions (including biological and geological analogue methods) may therefore provide a productive area of research and development (e.g. Cundy and Hopkinson, 2005).

A range of iron-based techniques however have been successfully demonstrated at field-scale (see Section 3), and are slowly gaining acceptance from industry and regulators, although the risk-averse nature of the contaminated land industry, and the fact that many of the techniques are limited to certain specific types of sites or contaminants, means that it may be several years yet before they become industry-standard tools. Zero-valent iron-based permeable reactive barrier technologies are arguably an exception to this, as these have been widely used over the past 10 years, although more research is needed on their modes of failure (e.g. Henderson and Demond, 2007), and the detailed chemistry (and microbiology) behind their long-term field performance. Despite their widespread application, however, PRBs are still generally regarded as a developing technique. In the UK and the rest of Europe, there remains a heavy reliance on excavation and removal/disposal (commonly referred to as “dig and dump”) as a management method for contaminated soils, despite a range of legislative, cost and sustainability drivers to develop alternative treatment methods. *In-situ* iron-based treatment methods have, through a range of large-scale trials, proven to be potentially cost-effective remediation options (Table 2). Indeed, Brown et al. (1998) estimate that the total project cost of \$250,000 in remediating Cr(VI) contaminated soils and groundwater via ferrous sulphate heptahydrate addition at a former paper mill on the Delaware River (USA) was approximately equal to the cost of capital equipment that would have been required merely to initiate conventional pump-and-treat methods (Table 2). Such *in-situ* treatment methods may dramatically reduce project life cycles and costs compared to *ex-situ* treatment methods, and particularly compared to traditional pump-and-treat and excavation and disposal practices (see discussion in Brown et al., 1998). They can also be a more sustainable option, and may reduce the risk from exposure to contaminated media (Environmental KTN, 2008). One of the key issues limiting the adoption of novel *in-situ* remediation techniques in general is not that of cost, but of industry and regulator confidence, specifically the need to show that the techniques can be reliably, repeatably and safely applied in a range of different settings/sites. Recent work, therefore, has proposed the development of regional verification/demonstration centres for innovative remediation technologies, to encourage their widespread adoption (see Spira et al., 2006). In the case of source remediation using engineered iron nanoparticles, current barriers to adoption generally relate to uncertainty over the environmental fate and safety of these particles, which is likely to form a major focus of research over coming years.

5. Conclusions

Iron-based remediation or water treatment technologies are commonly used in a range of industries, and are being increasingly applied in contaminated land and groundwater remediation. A wide range of methods have been developed

which use iron (in a variety of chemical and mineral forms) as a reductant or as a precipitant/sorbent, and have been proposed for both *in-situ* and *ex-situ* application (e.g. removal of As from drinking water by adsorption to or co-precipitation with iron oxide phases; zero-valent iron-based permeable reactive barriers; chemical remediation via ferrous sulphate injection etc.). For widespread application/adoption however these methods need to be shown to be low-cost, and capable of being applied at field-scale (i.e. robust), at often relatively low contaminant concentrations in chemically (and biologically) complex and heterogeneous soil and water media. Zero-valent iron-based permeable reactive barriers are one of the more established so-called “novel” iron-based treatment tools, however predicting the long-term performance of these systems remains problematic due to their complex chemistry. There has been much recent interest in the use of engineered iron-based nanoparticles as an *in-situ*, relatively non-invasive tool for groundwater remediation, particularly for the direct treatment of contaminant source zones, but uncertainties over the health impacts and environmental fate of these particles need to be addressed before their widespread application.

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