Putting corrosion to use: remediating contaminated groundwater with zero-valent metals

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At first sight, rusty metal may not seem the obvious tool for cleaning up polluted water. But appearances can be deceptive, and corrosion is finding a surprising new role
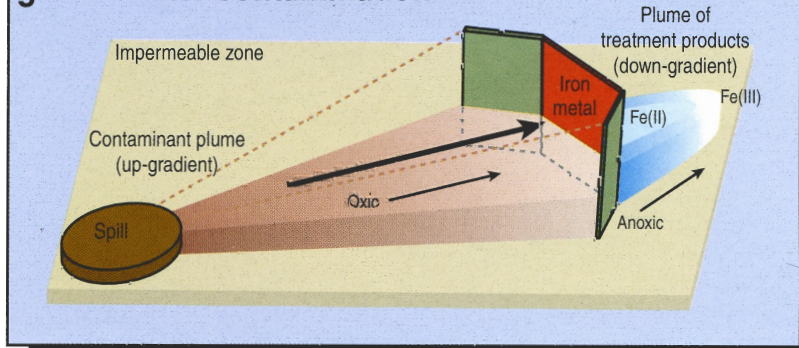
In 1990, a group of hydrogeologists at the University of Waterloo, Ontario, Canada, stumbled on some very old chemistry and made it into one of the most promising new approaches to groundwater remediation. Professor Robert Gillham had a student testing the suitability of various materials for the construction of casings used in groundwater monitoring wells. They were expecting to find that the plastic pipes commonly used as well casings interfered with the detection of chlorinated solvents, which are important groundwater contaminants. Instead, they found that the real problem was with metal pipes, which caused analytes such as perchloroethylene, trichloroethylene and carbon tetrachloride to be degraded at significant rates.[1]

Around this time, dissatisfaction with the established methods of remediating contaminated groundwater was growing, and many groups were involved in the search for alternative techniques. A major issue was with traditional methods that involve continual pumping from treatment wells. These methods typically yield diminishing improvements in groundwater quality with little prospect of decreasing the annual operation costs. In principle, the costs could be reduced by 'passive' treatment methods that require little, if any, maintenance after installation. It had been proposed that passive treatment might be achieved by creating a zone in the subsurface where contaminants are degraded as they are carried along by flowing groundwater.[2]

Gillham recognised that the process responsible for degrading chlorinated solvents by metal well casings might be applicable to the creation of passive treatment zones for remediation. Iron became the metal of primary interest because it is readily available, cheap, non-toxic and it rapidly degraded many chlorinated solvents in preliminary tests.[3] The first field test was performed at Base Borden, Ontario, and involved burying industrial scrap iron filings (from a local machine shop) in a rectangular cell, forming a permeable zone that intercepted a plume of solvent-contaminated groundwater (see Figure 1). Samples taken from the site in the following years showed that groundwater emerging from the treatment zone was largely free of contamination.[4]

The field test at Borden demonstrated the possibility of passive treatment for groundwater contamination using reactive barriers in the ground and, in particular, the potential for using zero-valent metals as the reactive medium. EnviroMetal Technologies in Guelph, Ontario, was formed to pursue the commercial application of the approach, and dozens of pilot and full scale operations are already in operation. Two completed installations that have received considerable press are located in Silicon Valley.[5,6] Another is a pilot system using zero-valent iron to remediate contaminated groundwater at a site in Belfast (see Figure 2).[7] In parallel with commercial developments, a great deal of research has been started into predicting, maintaining and enhancing remediation performance.[8] This work ranges from hydrological studies in large-scale model aquifers (see Figure 3), to chemical investigations of dechlorination at the metal-water interface.

Rediscovering corrosion

Early decisions on where or whether to use in-ground barriers of zero-valent iron were made without knowing how iron caused chlorinated solvents to degrade. This uncertainty was reflected in the nickname 'magic sand', which was given to the iron/sand mixtures used in early installations. The implication that there was something mysterious about the process may have hindered widespread acceptance for a brief period, but this has been overcome by research that began appearing in 1994.

The first report from my own group showed that there are many precedents for chemical reactions that might explain the degradation of chlorinated solvents in the presence of zero-

In-ground reactive barrier for treating groundwater contamination

Impermeable zone
Plume of treatment products (down-gradient)
Iron metal
Fe(III)
Fe(II)
Contaminant plume (up-gradient)
Oxic
Spill
Anoxic

Some important reactions involved in contaminant reduction by zero-valent iron

Anaerobic corrosion	$2H_2O + Fe^0 \rightarrow Fe^{2+} + H_2 + 2OH^-$
Aerobic corrosion	$O_2 + 2Fe^0 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^-$
Dechlorination	$RCl + Fe^0 + H^+ \rightarrow RH + Fe^{2+} + Cl^-$
Nitro reduction	$ArNO_2 + 3Fe^0 + 6H^+ \rightarrow ArNH_2 + 3Fe^{2+} + 2H_2O$

Installation of the reactor vessel 'gate' contained within a cement bentonite slurry wall 'funnel', which is successfully treating a localised plume of TCE at Nortel's site in Belfast

A large experimental aquifer under cons[...]

valent iron.[9] These reactions are remarkably varied and include dissolving metal reductions and catalytic hydrogenations used in organic synthesis; mechanistic and preparative aspects of organic electrochemistry; aqueous and non-aqueous corrosion; and high-pressure lubrication. The literature on each topic contributes a slightly different perspective, and much of the current research into groundwater treatment with zero-valent metals involves sorting out the mechanistic model that is most appropriate under field conditions.

Perhaps the most useful way of interpreting the degradation process is as corrosion of the metal with the organic contaminant as oxidant (see the Table). In the presence of

construction at VEGAS, University of Stuttgart, West Germany

construction of any in-ground permeable barrier. The importance of zone-scale interfaces is illustrated by the results of column studies designed to model a cross section of an in-ground permeable iron barrier by including up-gradient (the area before the barrier), iron-bearing, and down-gradient (the area after the barrier) zones (see Figure 5). As these columns are exposed to dissolved chlorinated solvents, they develop conspicuous zones of precipitation that undoubtedly will influence remediation performance.[11]

At the up-gradient interface, O_2 is rapidly consumed by reaction with Fe^0 and oxidation of Fe^{2+} to Fe^{3+}. Thus, regions beyond this interface will be anoxic and may continue to be anoxic beyond the treatment zone. The pH increases steeply in the iron-bearing zone because of the various corrosion reactions, but it declines gradually in the down-gradient region as a result of precipitation of iron oxides. Precipitation is greatest at the up-gradient interface, where the accumulation of oxides and carbonates can reduce permeability and thereby decrease the amount of contaminated water flowing through the treatment zone. Although this mode of failure has not been observed to date for in-ground treatment walls, it has been a recurrent problem in column tests and various methods for managing the precipitation are under investigation.[12]

During extended application of in-ground reactive barriers, microbiological effects are likely. Bacteria might accelerate corrosion (biocorrosion) in the iron-bearing zone. However, core samples of this zone at the Borden demonstration site have shown no evidence of significant microbial activity. The plume of groundwater emanating from the treatment zone may be high in ferrous iron and dissolved hydrogen and therefore should favour microorganisms that can metabolise these substances. Biodegradation by these and other types of microorganisms may be important to meeting remediation targets if effluent from the iron-bearing zone contains partial degradation products that are still considered hazardous.
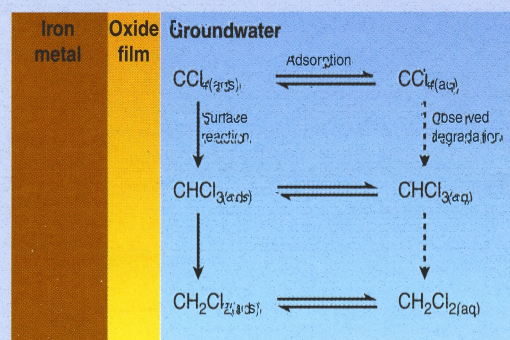
Sizing an iron wall

Zero-valent iron is a mild reductant, so it is not surprising that rates of dehalogenation vary widely for the various chlorinated solvents of environmental interest. This is part of the reason that carbon tetrachloride is rapidly converted to chloroform, but little dechlorination occurs to dichloromethane (see Figure 5). In a similar manner, incomplete dechlorination of the highly chlorinated ethenes could produce vinyl chloride, which is more hazardous and more persistent than the parent compounds under anaerobic conditions. Even small amounts of vinyl chloride in the treatment-zone effluent could limit the success of a project, so a great deal of attention has been devoted to this issue.[13–15] Fortunately, most of these studies indicate that the highly chlorinated ethenes are largely converted to simple

water, iron corrodes through a redox reaction driven preferentially by dissolved O_2, resulting in breakdown of the metal and formation of ferric oxides (rust). Anaerobic corrosion proceeds slowly by reduction of H^+ or H_2O to H_2. Chlorinated hydrocarbons such as perchloroethylene and carbon tetrachloride have almost the same oxidising potential as O_2, and their corrosive properties are well documented.[10] For the contaminant, corrosion yields dechlorination, which results in products that are either less harmful or more amenable to further degradation by other processes.

The aqueous corrosion of metals like iron is mediated by the layer of oxides that forms at the metal-water interface. An enormous amount of research has been done on the properties of this oxide layer because it is the key to maintaining passivation of metal surfaces, and thereby controlling material damage by corrosion. In the application of zero-valent metals to environmental remediation, precipitates at the metal-water interface also mediate the essential chemistry (see Figure 4). Effective treatment, however, requires that passivation of the surface be minimised, at least with respect to the contaminant degradation reaction. Fortunately, the incoherent and porous nature of oxide films on iron (that make it so susceptible to material damage by corrosion) appears to allow adequate contaminant degradation rates to be sustained over years of operation in the ground.

The biogeochemical context

In addition to the small scale interfacial effects involving passive films on individual grains of metal, there are important large scale interfaces that occur between zones created by the

Controlling processes | 4
Process controlling carbon tetrachloride degradation on iron

hydrocarbons, and the release of intermediate dechlorination products is very limited.

Where the groundwater contamination includes a mixture of chlorinated solvents, the design of a reactive barrier is determined by the least reactive constituent. An analysis of available kinetic data on dechlorination by iron confirms that perhalogenated contaminants are reduced more rapidly than their less highly chlorinated congeners, and dechlorination is more rapid at saturated carbon centres (for example, carbon tetrachloride and hexachloroethane) than unsaturated carbons (like perchloroethene or trichlorothene). Rate constants normalised to iron surface area are the most appropriate basis for preliminary design calculations, and we have recently reported representative values.[16] These can be used to calculate the amount of iron needed to achieve a 1000-fold decrease in contaminant concentration using the contaminant transport model developed by Gerald Eykholt of the University of Wisconsin, Madison.[17] The results for a typical iron loading[3] of $1m^2/mL$ and typical hydrologic properties[17] are presented as a function of groundwater flow rate in Figure 6.

Variations new and old
The range in reactivity in Figure 6 highlights the need to achieve more complete degradation of the less labile contaminants. This opportunity to expand the applicability of zero-valent metals in remediation has led to an explosion of research and development in pursuit of enhancements. An early improvement strategy was to increase retention time in the reactive zone by mixing a granular adsorbant, such as activated carbon, in with the granular iron. This approach failed because the time a contaminant spends adsorbed to carbon does not increase time spent adsorbed to the metal, and only the latter contributes to degradation. The oxide layer that passivates iron with respect to corrosion can be removed by various physical and chemical methods, which should result in increased contaminant degradation rates. This works in the laboratory,[9,18] but is unlikely to be practical for full-scale field applications.

So far, the most effective ways to increase contaminant degradation rates involve using metals that are stronger reducing agents than iron, or metal combinations that result in accelerated corrosion. The former approach to enhancement mainly involves magnesium, tin and zinc.[19] The latter involves 'bimetallic' combinations such as nickel/iron, copper/iron and palladium/iron. A team of collaborators at the Oak Ridge National Laboratory, Tennessee, and the University of Arizona, Tucson, has shown that palladised iron not only greatly accelerates the degradation of chlorinated aliphatic compounds,[20] it

apparently is effective at reducing halogenated aromatic compounds such as polychlorinated biphenyls (PCBs).[21] It remains to be determined if these enhancement strategies will be acceptable to regulators or cost-effective. However, they certainly demonstrate the potential for large improvements in remediation performance by manipulating the chemistry of treatment systems based on zero-valent metals.

Enhanced degradation rates make implementations other than in-ground permeable barriers increasingly attractive. For example, pumping contaminated groundwater to the surface and treating it in canisters of zero-valent metal may be preferred if contaminant degradation is rapid enough to allow adequately high pumping rates. Similar considerations apply to 'funnel and gate' systems where impermeable zones are created in an aquifer to concentrate groundwater flow through a narrow treatment zone (as at Belfast).[22] Certainly the most complex implementation of zero-valent metals in remediation proposed to date involves the 'Lasagna' approach developed by a consortium of corporations and the US Department of Energy.[23] This process uses electrokinetics to force contaminants through low-permeability zones and into contact with a treatment zone containing iron or other reactive materials. Other modes of implementation that are currently being studied include injection of colloidal iron to get at contaminants in the deep subsurface, and additional iron to bentonite slurry walls that are used to form impermeable barriers to isolate groundwater contamination zones.[24]
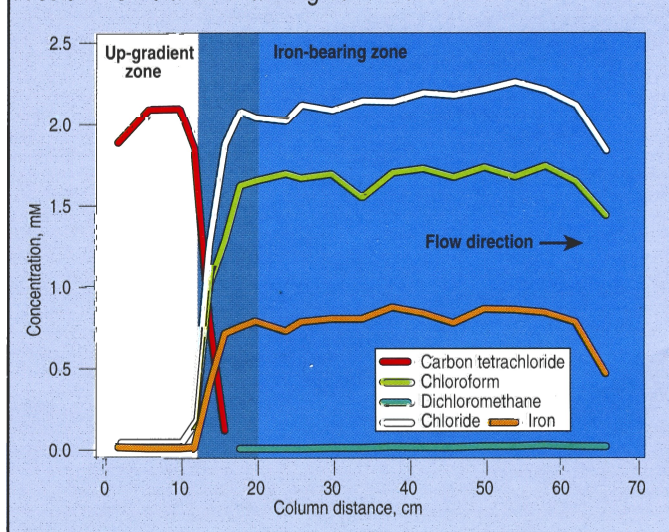
Beyond chlorinated solvents
In addition to degrading chlorinated solvents, zero-valent metals may prove to be useful for remediating other types of environmental contaminants. Other organic contaminants that contain reducible functional groups include pesticides, dyestuffs and munitions. Nitro groups are particularly characteristic of munition compounds and are readily reduced by iron.[18] The resulting amines are still somewhat problematic, but they can be further degraded microbiologically. Even inorganic nitrate can be reduced by zero-valent iron. The use of this reaction to treat groundwater with elevated nitrate levels has been under investigation by Martin Reinhard's group at Stanford University.[25]

In parallel with developments in treating organic contaminants with zero-valent metals, there have been similar developments in treating contamination by toxic metals. Early work in this area focused on removing cadmium and chromate from

Chemical profiles | 5
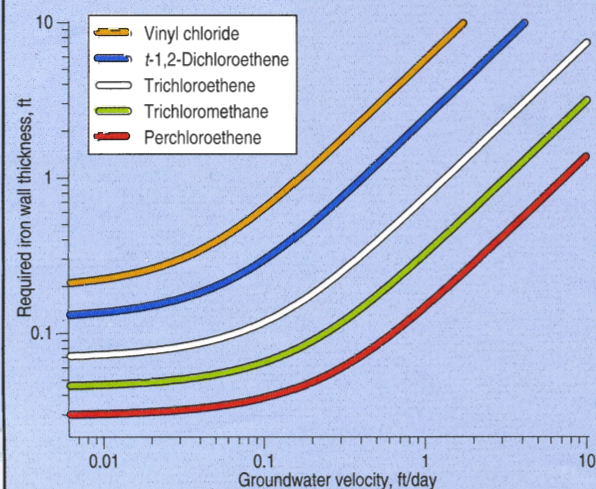A column simulation of an in-ground reactive barrier

Carbon tetrachloride
Chloroform
Dichloromethane
Chloride — Iron

Dechlorination 6

Required wall thicknesses for dechlorinating selected solvents

Courtesy: G Eyhkholt

wastewater by a process described as 'cementation'.[26,273] More recently the emphasis has shifted to metals such as chromium, technetium and uranium, which are mobile groundwater contaminants under oxidising conditions, but can be immobilised by precipitation in the presence of a reductant.[28–31]

The fact that zero-valent iron appears to be effective at treating such a wide variety of groundwater contaminants offers the prospect of a single treatment scenario for some sites with plumes of mixed composition. One combination of contaminants that occurs fairly frequently involves chlorinated solvents and chromate. An in-ground reactive barrier of zero-valent iron is already being tested at such a site in Elizabeth City, North Carolina.[32] If the technology proves useful for treating these co-contaminants, there will undoubtedly be even more ambitious applications attempted in the near future.

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