

Application of PRB Technology for Brownfield Redevelopment

Granular iron PRBs are accepted as a viable alternative for the remediation of chlorinated solvents in groundwater, with a 13-year track record of successful field performance. PRBs are remediating contaminated groundwater throughout the United States, Canada, Europe, Japan and Australia. Granular iron PRBs are applicable under most geochemical conditions and do not require reapplication, resulting in a predictable, reliable, long-term treatment solution.

Iron PRBs have been used at 35 sites as part of Brownfield redevelopments, including private sites, U.S. Department of Defence redevelopment sites and dry cleaner sites. The remedial objectives of iron PRBs used at these sites were to:

- Prevent further off-site migration of VOCs (iron PRBs installed at downgradient property boundary); and
- Prevent on-site migration of VOCs (Iron PRBs

placed on upgradient boundary of clean sites).

PRBs are typically used in conjunction with other remedial measures (source treatment or removal) or as part of a site-wide risk minimization strategy.



Iron PRB Placement in Toronto, Ontario

Development of Alternative Iron Sources

As many readers will be aware, current iron based remedial approaches may well involve injection techniques as much as excavation-based approaches. Indeed, some of our injection partners have seen significant increases in these types of

applications during the past several months. This trend, coupled with the continued price instability of cast iron sources, has led us to expand our efforts in developing alternative sources of iron materials. In addition to continued testing of fine-grained materials from Connelly-GPM, Peerless Metal Powders & Abrasive, and Hepure Inc., we have conducted extensive evaluations of iron from Quebec Metal Powders (QMP). QMP products are obtained from processing of ilmenite ore, and consequently are more stable in price than other cast iron products. The morphology and grain size of QMP's 'off-the-shelf' product lends itself to injection applications, and QMP has expended considerable effort in developing a coarser grain iron product for conventional trench type PRBs. QMP materials have been applied at nine field sites, and have been also used in combination with organic carbon amendments at others. Please call us for input as to the most appropriate iron source for use in a specific site application.

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ZVI-Clay Technology for Source-Zone Clean-Up

The ZVI-Clay technology is an *in situ* method of treating source areas containing VOCs at high concentrations including DNAPL. ZVI-Clay involves admixing reactive media (zero valent iron) and stabilizing agents (clay) into soils containing chlorinated compounds using conventional soil mixing equipment. Through mixing, heterogeneous subsurface source zones are transformed into uniform low permeability bodies of soils, contaminants, reactive media, and stabilizing agents. Soil mixing greatly reduces the need to rigorously delineate contaminant distribution within source zones and overcomes the challenge of delivering reactive media through complex geologic media. The ZVI-Clay technology has been applied at seven full-scale sites to date.

Site/ Installation Date	COIs / Source Mass	Soil Mixing Technique	Performance
DuPont Kinston, NC - 1999	TCE	Jet grouting	90% TCE destruction after 1 year
DuPont Martinsville, VA - 2002	CT 20 tons	Shallow Soil Mixing	99.99% CT and 99% total VOC destruction after 2 years
DoD Camp Lejeune, NC - 2005	PCE 10 tons	Shallow Soil Mixing	91% PCE destruction after 1 year
DoD Arnold AFB, TN - 2005	TCE	Surface Soil Mixing	Not available
DoD Vint Hills Farm, VA - 2005	TCE	Shallow Soil Mixing	Not available
Lake City Army Ammunition Depot, Missouri - 2005	TCE	Shallow Soil Mixing	Not available
DuPont, Florence, SC - 2005	VOCs	Surface Soil Mixing	Not available

Update on NSERC Chair Research

In collaboration with the E.I du Pont Canada Co. (DuPont), and the National Sciences and Engineering Research Council of Canada (NSERC), ETI has supported a multi-year research program at the University of Waterloo headed by Dr. Robert Gillham. Recent activities conducted by Dr. Gillham's research group have included the following:

- Investigation of the use of iron-carbon mixtures (including DARAMEND®) for treatment of PETN, an explosive residual found in soil and groundwater;
- Investigation of the ability of iron to degrade chlorinated butenes and butadienes;
- Development of a mathematical model to predict long term PRB performance;
- Investigation of competing affects of nitrate, chromate, and sulphate on VOC degradation rates; and
- Testing of alternative source of iron materials.



Column Testing in Groundwater Research Laboratory, University of Waterloo

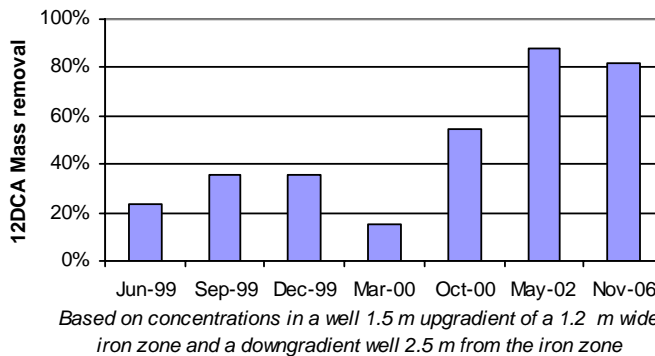
Please call us if you would like information on any of the above. The second, five-year term of Dr. Gillham's Research Chair concluded last spring; we are very pleased to announce that Dr. Gillham has agreed to continue his research in another two-year program, again co-sponsored by DuPont and ETI, which was initiated in September 2007.

We should mention two other research programs that ETI co-sponsors. One involves investigations of alternative iron sources by Dr. J. F. (Rick) Devlin at the University of Kansas, in collaboration with DuPont and Quebec Metal Powders. In past years, ETI has sponsored a portion of Dr. Devlin's research into the development of an *in situ* velocity probe, which is still a significant part of his program at Kansas. The second involves research conducted by Dr. Ramon Aravena at the University of Waterloo. Dr. Aravena's program evaluates the tracking degradation pathways of organic compounds at iron PRB field sites using stable isotope measurements.

Degradation of 1,2-DCA in a Mature Iron PRB

Certain chlorinated aliphatic hydrocarbons, like DCM or 1,2-DCA are not degraded abiotically by iron. Field observations have shown appreciable rates of DCM reduction downgradient of two iron PRBs. This phenomenon was attributed to bioremediation downgradient of iron PRBs stimulated by low Eh, elevated hydrogen gas and dissolved iron concentration. Recently published* iron PRB data document 1,2-DCA degradation within an iron zone and downgradient of it, after about 3 years of operation. Given below is a data summary reprinted with author's permission.

In February 1999 Orica Australia Pty Ltd installed a pilot-scale reactive iron barrier (RIB) to evaluate the effectiveness in destroying dissolved-phase chlorinated hydrocarbons (CHCs). The first 13 months of performance monitoring showed significant reduction of most CHCs with total influent concentrations up to 220 mg/L, but, as expected, little reduction of the 10 mg/L of 1,2-DCA. The inability of ZVI to degrade 1,2-DCA has been historically recognised as a limitation of RIBs. However, recent sampling of the pilot-scale RIB has shown that 1,2-DCA degradation is now occurring. Sampling in November 2006 (month 91) confirmed this with concentration reductions of up to one or two orders of magnitude. Groundwater conditions have changed markedly in the test site, largely due to groundwater extraction and treatment starting up within the last two years altering plume flow direc-



tions. Most CHCs have decreased to a total of less than 60 mg/L, but 1,2-DCA concentrations have risen to up to 127 mg/L. Reaction rates have decreased little with time, but gradual fouling is not yet enough to impair RIB hydraulics. The cause of the 1,2-DCA mass removal is due to microbial colonisation of the barrier by dehalorespiring and/or hydrogen utilising bacteria, including *Dehalococcoides* and *Dehalobacter*. Although this phenomenon has been observed at the laboratory scale for other compounds this is the first instance the authors are aware of that documents this in the field for 1,2-DCA. Exploiting this phenomenon might broaden the capability of RIBs to reductively dechlorinate hitherto recalcitrant compounds.

* Stening, J., Manefield, M., Zemb, O., Przepiora, A., and Vogan, J. 2008. Reductive Dechlorination of 1,2-Dichloroethane in a Reactive Iron Barrier. Proceedings of the Sixth International Conference on Remediation of Chlorinated and Recalcitrant Compounds. Monterey, CA, May 19-22.

IronRefs Database

The internet-based database of published information on contaminant remediation using zero-valent metals (cgr.ese.ogi.edu/ironrefs) provides an excellent bibliographic resource for environmental professionals, students and academics.

An update of the database, partially sponsored by ETI, has recently been completed by Dr. Paul Tratnyek's Group at Oregon Health & Science University. The interactive database contains currently listings of more than 1,360 iron-related publications, including peer-reviewed articles, conference proceeding papers and monographs.

We hope to see your research or case study paper listed soon!

Iron Systems by Numbers*

Number of field-scale iron treatment systems installed worldwide	200
Number of countries PRBs installed	13
Total tons of iron installed	47,000
Number of times the total surface area of all iron placed in PRBs would cover West Virginia	1
Total combined length of all PRBs in the US in miles	7.0
Deepest injected PRB in feet	120
Deepest excavated PRB in feet	70
Longest continuous PRB in feet	1,210
Longest operating PRB in years	13

* Statistics as of April 2008

A Brief Comment on Nanoscale Iron

Since the concept of nanoscale particles for *in situ* environmental remediation was introduced by Dr. Wei-xian Zhang and his colleagues in the late 1990's, these highly reactive particles have been the subject of considerable laboratory and pilot-scale field testing. The theoretical potential benefits of these nanoscale particles (1 to 100 nm) include their ability to flow with groundwater and their ability to promote rapid degradation of organic contaminants (and immobilization of dissolved metals).

However, given that the preponderance of published data shows rapid agglomeration of nanoscale particles and the resulting loss of reactivity and mobility, nanoscale iron particles seem to be best suited to remediation of source zone(s), where they can be used to remove a relatively large quantity of VOCs in a short period of time. For these applications, it is important to consider the effects of back-diffusion from low permeability layers which commonly result(s) in the "rebound" effect. Another concern stemming from the need

for relatively high injection pressures (to prevent nonparticle agglomeration) is the potential for changing the DNAPL architecture and/or secondary contaminant mobilization. One must also consider the cost of applying nanoscale particles (perhaps several times) over the time period needed to achieve any significant mass reduction. Commercially available nanoscale iron prices are currently in the range of \$10 to in excess of \$20 per pound. This compares to a price of about \$0.40 per pound for conventional fine-grained iron materials which will last significantly longer in the subsurface. By simple calculation, it appears that nanoscale particles would have to remain at least 20 times as reactive as conventional sources over their lifetime to be cost-competitive, and this may not be the case. Given recent advances in installing fine-grained ('micro-scale') iron or EHC[®] using hydraulic/pneumatic fracturing, jetting, and direct push technologies, and the development of other strategies such as Colorado State University's ZVI-clay technology for source zone clean-up, there are several other iron-based alternatives that should be considered as an alternative to the use of nanoscale particles at a given site.

Continued Development of Adventus Technologies

By way of several comparative studies and successful field applications, our injectable EHC[®] technology has become established as one of the most effective technologies available for promoting ISCR driven plume remediation. EHC comprises engineered particles combining solid carbon and fine-grained iron, which facilitate the combined

abiotic and microbial degradation of recalcitrant compounds including chlorinated solvents and pesticides in groundwater. Our most recent formulations of EHC (EHC-M) include constituents, which promote the precipitation of trace metals from contaminated groundwater. AquaBlok[®] sediment capping technology has been enhanced with the use of zero valent iron to reduce the flux of VOCs from contaminated sediments to overlying surface water bodies. Please call us for a summary of recent research results supporting these remedial approaches.

For a free estimate or for information,
please contact us!

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