

## **EnviroMetal Technologies Inc.'s Perspective on Nanoscale Iron**

---

Since the concept of nanoscale metallic particles for in-situ environmental remediation was introduced by Dr. Wei-xian Zhang and his colleagues in the late 1990's (Wang and Zhang, 1997), these highly reactive particles have been the subject of considerable laboratory and field testing. The purpose of this memorandum is to present EnviroMetal Technologies Inc.'s (ETI's) technical perspective on the use of nanoscale iron and bimetallic iron particles, in the context of our experience with iron permeable reactive barrier (PRB) technology.

The theoretical potential benefits of these nanoscale particles (1-100 nm) include their ability to flow with groundwater and their ability to promote rapid degradation of organic contaminants (and immobilization of dissolved metals). This memorandum focuses on degradation of volatile organic compounds (VOCs). Liu et al. (2004) present a discussion of trichloroethene (TCE) degradation rates achieved with various nanoscale metals and bimetallic particles. While degradation rates normalized to surface area are similar to those measured with conventional granular iron (Nurmi et al., 2005), the much higher surface area of nanoscale particles means that per unit mass, observed VOC degradation rates are often 10 to 100 times higher. Tratnyek et al. (2004) and Nurmi et al. (2005), discuss the means of correlating VOC degradation rates reported for various nanoscale particles.

Prior to selecting a nanoscale-based remedy, the objective of the remediation scheme needs to be determined, i.e., containment and/or passive treatment of a contaminant plume for a period of years, or short-term mass reduction of high concentrations in a source (DNAPL) area or dissolved plume. Nanoscale iron does not represent a long-term passive treatment remedy, as these particles only remain reactive for days to weeks in the subsurface (e.g., Zhang, 2003; Bickmore and Friem, 2004). Both nanoscale iron and bimetallic particles will be consumed rapidly due to reactions with VOCs with bimetallic particles reacting faster. This consumption of the metal (or bimetal) via VOC reactions does not consider the oxidation of the nanoscale particles by groundwater itself. Even in the absence of VOCs, preliminary work at the University of Waterloo has shown rapid consumption of a common nanoscale iron by water oxidation, with 35% to 50% of the metal being consumed within 12 days (Reardon, 2005).

Given these consumption rates, it is more appropriate to consider nanoscale particles as a mass reduction tool (i.e., similar to molasses, HRC™, or other aquifer amendments) rather than a form of long-term PRB technology. Several re-injections may be required over the lifetime of the project depending on the additional mass flux of VOCs entering the injection zone where these nanoscale particles are applied, from upgradient source areas or free phase DNAPL. Indeed, in one of the few field-scale projects reported to date (Cernik et al., 2005), suspected VOC migration from an upstream source caused a sporadic increase in concentrations in a nanoscale injection well following the injection.

There has been very little work done on the effect of inorganic constituents in groundwater on nanoscale metal reactivity, longevity, and transport. Some preliminary laboratory investigations on the effects of carbonate (e.g., Okinaka et al., 2004, 2005), and nitrate (Xinhua and Zhu, 2005) have been reported, but no clear conclusions can be drawn from these data, especially as these experiments were performed in the absence of aquifer minerals which may influence groundwater geochemistry in the field. The rapid agglomeration of nanoscale particles and the resulting loss of reactivity and mobility is a recognized problem (He and Zhao, 2005), although migration distances in the order of several meters have been reported in the field (Cernik et al., 2005; Elliott and Zhang, 2001). The reactivity of the particles after moving these distances remains uncertain.

There have been several efforts to modify nanoscale particles with surfactant coatings (e.g. Suleh et al., 2005; Kanel et al., 2005) or stabilizers (He and Zhao, 2005), to improve their mobility. Delivery of nanoscale particles with surfactants or oil emulsions (e.g., Kanel et al., 2005; Geiger et al., 2003; O'Hara et al., 2004) has also been investigated to facilitate their use in treating areas of suspected DNAPL source zones, by encouraging the partitioning of the DNAPL into the nanoscale delivery fluid/emulsion. Others have investigated using combined carbon and iron (or bimetallic iron) nanoscale particles as a means of facilitating transport through porous media (Schrack et al., 2004).

In summary, nanoscale iron particles, because of their high reactivity but relatively short life time and limited mobility, 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. 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 \$11 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 in all instances. Given recent advances in installing conventional fine-grained iron using hydraulic/pneumatic fracturing, jetting, and direct push technologies, and the development of other strategies such as Colorado State University's iron-clay technology (Sale et al., 2004) for source zone clean-up, there are several other iron-based alternatives that could be considered as an alternative to nanoscale particles at a given site.

It is our understanding that a report in preparation by Battelle Inc. for the U.S. DoD will report on two nanoscale field pilot tests performed at US Navy sites. ETI will be participating in the USEPA workshop on environmental nanotechnology in October 2005. The results of both these endeavours, when published, will be incorporated into this memorandum.

High reactivity nanoscale metals represent an intriguing development in contaminant remediation, however, significant questions concerning their technical performance and cost need to be answered before these particles can be considered for widespread use as a remedial option.

## References

- Bickmore, C. and Friem, J., 2004. Materials Science Perspectives of Injectable Zero Valent Metals and Alloys. Presented at RTDF Permeable Barriers Action Team Meeting, Albuquerque, New Mexico, October 26-27.
- Cernik, M., Kvapil, P. and Pupeza, M., 2005. Dechlorination of Chlorinated Ethenes in Fractured Sandstone by Zero-Valent Iron Nano-Particles. Symposia Papers Presented Before the Division of Environmental Chemistry American Chemical Society, Washington, DC, August 28-September 1.
- Elliott, D. and Zhang, W., 2001. Field Assessment of Nanoscale Bimetallic Particles for Groundwater Treatment. *Environ. Sci. Technol.* Vol. 35, No. 24, pp. 4922-4926.
- Geiger, C.L., Clausen, C.A., Brooks, K., Coon, C., Huntley, C., Filipek, L., DeVor, R., Krug, T., O'Hara, S., Majors, D. and Quinn, J., 2003. Remediation of DNAPLs Using Emulsified Zero-valent Iron: Laboratory and Field Results. Symposia Papers Presented Before the Division of Environmental Chemistry American Chemical Society, New Orleans, LA, March 23-27.
- He, F. and Zhao, D., 2005. Application of Novel Stabilizers for Enhanced Mobility and Reactivity of Iron-Based Nanoparticles for In-Situ Destruction of Chlorinated Hydrocarbons in Soils. Symposia Papers Present Before the Division of Environmental Chemistry, American Chemical Society, Washington, DC, August 28-September 1.
- Henn, K., Sun, Y.P., Zhang, W. and Waddill, D., 2004. Feasibility of In Situ Nanoscale Iron Remediation: From Laboratory to Field. Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, May 24-27, 2004.
- Kanel, S.R., Kang, S., Jung, H. and Choi, H., 2005. Transport Characteristics of Surfactant Stabilized Iron Nano Particle in Unsaturated Porous Media. Symposia Papers Present Before the Division of Environmental Chemistry, American Chemical Society, Washington, DC, August 28- September 1.

Liu, Y., Majetich, S.A., Tilton, R.D., Sholl, D.S. and Lowry, G.V., 2005. TCE Dechlorination Rates, Pathways and Efficiency of Nanoscale Iron Particles with Different Properties. *Environ. Sci. & Technol.*, Vol. 39, No. 5, pp. 1338-1345.

Nurmi, J.T., Tratnyek, P.G., Sarathy, V., Baer, D.R., Amonette, J.E., Pecher, K., Wang, C., Linehan, J.C., Matson, D.W., Penn, R.L. and Driessen, M.D., 2005. Characterization and Properties of Metallic Iron Nanoparticles: Spectroscopy, Electrochemistry, and Kinetics. *Environ. Sci. & Technol.* Vol. 39, No. 5, pp. 1221-1230.

O'Hara, S., Krug, T., Major, D., Quinn, J., Geiger, C. and Clausen, C., 2004. Treatment of DNAPL Source Zones Using Emulsified Zero-valent Iron. Presented at RTDF Permeable Barriers Action Team Meeting, Albuquerque, New Mexico, October 26-27.

Okinaka, K., Jazdanian, A.D., Dahmani, A.M., Nakano, J., Okita, T and Kakuya, K., 2005. Degradation of Trichloroethene with Reactive Nanoscale Iron Particles in Simulated Ground Water. Symposia Papers Present Before the Division of Environmental Chemistry, American Chemical Society, Washington, DC, August 28-September 1.

Okinaka, K., Jazdanian A.D., Shimizu H., Okita, T. and Kakuya, K., 2004. Treatment of 1,1-Trichloroethane with Reactive Nanoscale Iron Product in Simulated Groundwater. Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, May 24-27, 2004.

Reardon, E.J., 2005. Paper in preparation.

Sale, T., Olsen, M. and Shackelford, C., 2004. Remediation of Chlorinated Solvents Using Zero-Valent Iron and Clay in Conjunction with Soil Mixing. Presented at RTDF Permeable Barriers Action Team Meeting, Albuquerque, New Mexico, October 26-27.

Saleh, N.B., Sirk, K., Sarbu, T., Tilton, R.D., Matyjaszewski, K. and Lowry, G.V., 2005. Transport and DNAPL Targeting of Polyelectrolyte-and Surfactant-Modified Nanoiron. Symposia Papers Present Before the Division of Environmental Chemistry, American Chemical Society, Washington, DC, August 28- September 1.

Schrack, B., Hydutsky, B.W., Blough, J.L. and Mallouk, T.E., 2004. Delivery Vehicles for Zerovalent Metal Nanoparticles in Soil and Groundwater. *Chem. Mater.*, Vol. 16, pp. 2187-2193.

Tratnyek, P.G., Sarathy, V. and Bae, B., 2005. Nanosize Effects on the Kinetics of Contaminant Reduction by Iron and Iron Oxides. Symposia Papers Present Before the Division of Environmental Chemistry, American Chemical Society, Washington, DC, August 28- September 1.

Tratnyek, P.G., Nurmi, J.T. and Sarathy, V., 2004. Advantages of Nano Iron Metal for Remediation of Carbon Tetrachloride. Presented at RTDF Permeable Barriers Action Team Meeting, Albuquerque, New Mexico, October 26-27.

Wang, C. and Zhang, W., 1997. Synthesizing Nanoscale Iron Particles for Dechlorination of TCE and PCBs. *Envir. Sci. Technol.* Vol. 31. No. 7, pp. 2154-2156.

Xinhua, X. and Zhu, X., 2005. Rapid Reductive Denitrification of Nitrate and Nitrite By Nanoscale Compared with Microscale Iron. Symposia Papers Present Before the Division of Environmental Chemistry, American Chemical Society, Washington, DC, August 28- September 1.

Zhang, W., 2003. Nanoscale Iron Particles for Environmental Remediation: An Overview. *Journal of Nanoparticle Research.* Vol 5, pp. 323-332.