



## **Nanomaterial Risk Assessment Worksheet**

### **Zero Valent Nano Sized Iron Nanoparticles (nZVI) for Environmental Remediation**

**Synopsis:** The information contained in this document is based on a literature survey conducted March 2007 as well as on unpublished experiments conducted in DuPont's laboratories. DuPont is monitoring the continuing development of this technology and competing technologies, for treatment of contaminated aquifers. Based on currently available information, DuPont has no immediate plans to implement this technology at any DuPont site.

#### **Step 1. Describe Materials and Applications**

Zero valent nano-sized iron particles (nZVI), with primary particle size less than 100nm, are expected to be made by a variety of vendors and shipped as highly concentrated slurries to contractors, for use as a reagent to destroy organic contaminants in ground water. nZVI will typically be received as stabilized aqueous slurry. The iron particles would be mixed into water and then injected into subsurface aquifers through small-diameter wells. It is intended that toxic contaminants (e.g., tetrachloroethylene, trichloroethylene) would be reductively dechlorinated to an essentially non-toxic mixture of ethane, ethene, and acetylene. Under normal conditions at a remediation site, workers will already be dressed in full protective suits. The technology has been pilot tested at roughly 15 field sites by various parties, using materials provided by different vendors. DuPont is not itself a producer or user of nZVI at this time.

#### **Step 2. Profile Life Cycles**

##### **Properties Profile**

The nZVI is manufactured by a variety of processes. Such processes include, for example, reduction of iron oxide particles; precipitation from  $\text{FeCl}_3$  using sodium borohydride; and flame synthesis. The primary particle size, particle size distribution, and degree of agglomeration/aggregation of nZVI are different for each manufacturer, and are considered proprietary by each supplier. Considered even more proprietary is the use of stabilizers to achieve the necessary balance between chemical activity and shelf life.

##### **Hazard and Exposure Profile**

Toxicity, human hazard, and environmental fate and effects data available from potential suppliers are highly variable in both quality and completeness. In many cases, it is not clear from the information provided whether the EHS data is based on the nZVI or on larger sized "simple iron powder." Typical warnings include:

- Skin irritation
- Eye irritation
- Harmful if inhaled – irritating to mucous membranes and upper respiratory tract.
- May be harmful if swallowed. Large doses will produce a laxative effect.
- Toxicological properties have not been thoroughly investigated.
- Dissolved iron and manganese concentrations in ground water may increase.

In addition to such warnings, the following factors need to be taken into consideration to anticipate and avoid potential hazards:

- In order for treatment reactions to occur there must be direct contact between nZVI particles and the contaminant molecules. Incomplete destruction reactions could result from poor contact, from adding insufficient quantities of nZVI, or from aquifer conditions that limit the reaction (e.g., unfavorable pH, low temperature).
- nZVI does not react with or destroy all ground water contaminants. Incomplete destruction could result in the generation of toxic partial degradation products.<sup>1</sup> At this stage of development, a laboratory feasibility study, followed by appropriate field studies, are recommended to demonstrate contaminant destruction and treatment mechanisms.

### **Environmental Fate and Transport Profile**

Since the nZVI is injected directly into the environment, it is important to characterize the fate and transport of this material in the aquifer. Very similar reactions occur with micro and macro scale ZVI as are reported for nZVI. The reactions and reaction products for coarser iron particles have been well documented in the peer-reviewed scientific literature. Based on publications, our experiments, and analogy we expect the reaction products and their environmental fate to be very similar for macro ZVI and nZVI. The iron is generally released as dissolved ferrous iron. Typically the iron then precipitates as carbonate or sulfide minerals down gradient of the treatment area.

### **Step 3. Assess Risks**

DuPont has not conducted a full risk assessment due to the stage of technology development and due to DuPont's decision not to move forward with either field pilot tests or full-scale applications.

### **Step 4. Risk Mitigation**

DuPont has not evaluated risk mitigation measures in detail due to the stage of technology development and due to DuPont's decision not to move forward with either field pilot tests or full-scale applications.

### **Step 5. Decide, Document and Act**

DuPont would not consider using this technology at a DuPont site until the end products of the reactions following injection, or following a spill, are determined and adequately assessed. Of particular importance is the question of whether persistent nanoparticles are generated, or whether the material is rapidly converted into a soluble iron salt or a hydroxide. Presently DuPont is monitoring the continuing development of this technology and competing technologies, for treatment of contaminated aquifers.

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<sup>1</sup> See USEPA, "Nanotechnology White Paper," Office of Science Advisor, Report EPA 100/B-07/001, February 2007, p. 57, available at <http://www.epa.gov/OSA/pdfs/nanotech/epa-nanotechnology-whitepaper-0207.pdf>.

Before the technology can be accepted in the field, the following additional questions must be addressed.

1. When dried, the slurry probably becomes pyrophoric, which suggests that materials used to clean up a spill may present a fire hazard. That potential should be determined and the MSDS should contain an appropriate warning.
2. The fate of the nZVI after a spill has dried has not been resolved. If it rapidly and completely reacts to form soluble iron salts or hydroxides, the risk should no different from other sources of iron contamination which are more abundant by far. Alternatively, if nano-sized iron oxide particles are present, the particles should be compared to those (rust particles) already abundant in the environment. This should start with comparisons of physical-chemical properties and tests for bioaccumulation potential along with the base set of toxicology and environmental fate and effects tests, as appropriate.
3. The most likely human exposure pathway is accidental skin contact with the slurry. Skin sensitization tests should be conducted for the nano iron slurry and compared to similar tests on slurries of larger sized iron particles. (There is an inherent problem here, in that such slurries are already fairly acidic, which carries its own level of toxicity.)
4. The ultimate fate of the nZVI once it has been used in the aquifer appears not to have been fully determined. It seems likely that the final products would be soluble iron hydroxides and salts after a few weeks. If so, there may be no cause for long-term concern specific to the nanoscale-related properties of nZVI. If the reaction products include nano sized iron oxide particles, their soil binding energy should be determined and the same EHS questions as in #2 (above) should be resolved.
5. As noted earlier, it has been reported that incomplete contaminant destruction reactions can occur if contact times are insufficient, if the amount of nZVI added to an aquifer is insufficient, or if used on untested contaminants. Careful design and testing of treatment systems is necessary to avoid these potential problems.

There is presently no way to determine the degree to which most of the suppliers have collected health and environmental safety data, conducted an exposure analysis or determined what engineering controls and personal protective equipment they should employ. Should any valid tests result in an adverse finding, these should be shared with the suppliers and potential customers. Appropriate controls should be discussed.

#### **Step 6. Review and Update**

DuPont will monitor the status of this technology to review and update the decision as additional information becomes available.

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