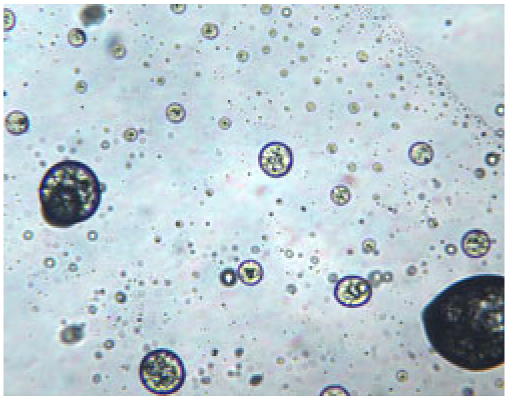
Nanoscale and Microscale Zero Valent Iron (Fe°) Treatability Studies

Nanoscale and microscale zero valent iron (**Fe°**) are emerging remediation technologies used to degrade recalcitrant chemicals by reductive processes. SiREM Fe° treatability studies are designed to address site specific needs in order to optimize your remediation program. The parameters typically evaluated in Fe° treatability studies include:

- Design loading rates;
- Applicability of Fe° to specific compounds of interest; and
- Comparison of Fe° and emulsion formulations, sources or vendors.



Photomicrograpgh of nanoscale zero valent Iron particles shown inside oil droplets, photograph courtesy of Dr. Cherie Geiger, University of Central Florida

SiREM has performed nano-Fe° treatability studies for potential application at variety of Federal and private-sector sites. Our work with nano-Fe° has demonstrated effective and often rapid treatment of numerous groundwater pollutants including:

- Trichloroethene and dichloroethene
- Carbon tetrachloride and chloroform
- 1,1,1-Trichloroethane
- Trichlorofluoromethane
- Ethylene dibromide
- Nitrate
- N-nitrosodimethylamine (NDMA)
- Trichloropropane

Nanoscale Zero Valent Iron Tool

Title: Introduction (1 of 2)
Text: Zero valent iron (ZVI) is a strong reducing agent. It has been successfully used in numerous permeable reactive barrier applications to treat chlorinated organic compounds in groundwater. Injecting fluidized nanoscale zero valent iron (NZVI) into a contaminated source zone is an extension of this concept. Nanoscale iron particles typically have surface areas up to 30 times greater than larger-sized granular iron and are up to 1,000 times more reactive for the degradation of chlorinated organic compounds. Click here to see the relative size of a nanoscale-sized iron particle. NZVI is ideally suited for treating chlorinated organic compounds and dense non-aqueous phase liquid (DNAPL) "hot spots" through injection directly into the source area of contamination. A slurry of NZVI is distributed into the subsurface using a variety of carrying fluids. This helps the iron powders disperse into the subsurface and creates contact between the contaminants and the iron particles.

Title: Introduction (2 of 2)
Text: In the past few years, NZVI has grown and progressed in terms of both its use and regulatory acceptance. This Web tool is designed to assist Navy Remedial Project Managers (RPMs) in the development and implementation of effective NZVI applications. Navy RPMs can use the information in this tool to:

- Learn about the key scientific concepts related to the use of NZVI and the types of NZVI media available.
- Understand the different injection methods used to deliver NZVI to the subsurface.
- Understand what factors influence the applicability of the NZVI technology.
- Benefit from the lessons learned at other sites related to the use of NZVI technology.

Title: Creating Nanoscale Zero Valent Iron
Text: Nanoscale iron particles typically have diameters between 50 to 300 nanometers and surface areas up to 30 times greater than larger-sized granular iron. This results in nanoscale iron particles that are 10 to 1,000 times more reactive than their larger counterparts. NZVI is created using various techniques and is available commercially in several different forms including:

- Solid Nanoscale Particles
- Porous Nanoscale Particles
- Emulsified Nanoscale Particles
- Bimetallic Nanoscale Particles

An example of one method for synthesizing NZVI is shown here. Click here for more information on how this synthesis process works.

Title: NZVI Synthesis
Text: This method uses a solution of sodium borohydride that is added to a solution of iron chloride. The zero valent iron particles precipitate out of solution and are stored wet, in order to avoid an oxidizing reaction with air. Another form of NZVI-type material is a micro-powder made from grinding or milling iron waste stock. A high purity powder (95%+ iron) that uses magnetite as a source rock is also available.

Title: Injection Media
Text: NZVI can be distributed into the subsurface using a variety of carrying fluids. Among the most common are water, nitrogen gas, and vegetable oil.

A slurry of water and NZVI powder can be injected into the contaminated zone using nitrogen gas as a carrier. This helps the iron powder disperse in the subsurface and creates contact between the contaminants and the iron.

Alternatively, NZVI can be mixed with vegetable oil and water to create an emulsion, which is then injected into the contaminant zone. It is conjectured that chlorinated solvents preferentially diffuse through the vegetable oil and react with the iron inside the emulsion droplet.

Title: Iron Reactivity (1 of 2)
Text: Iron Reaction Mechanisms ZVI is a strong reducing agent and its properties are well suited to the treatment of many common dissolved contaminants. Under certain groundwater conditions, elemental iron is slowly oxidized to ferrous iron, releasing two electrons in the process. These electrons participate in a variety of reactions leading to the transformation of the target contaminant. The reaction proceeds through two known pathways. In the beta-elimination pathway, the formation of partially dechlorinated products such as dichloroethene (DCE) and vinyl chloride (VC) is avoided, and trichloroethene (TCE) is transformed directly to ethane via the production of some short-lived intermediates, such as chloroacetylene and acetylene. Most experts believe that chlorinated solvents degrade primarily through the beta-elimination pathway when exposed to iron. Very little DCE or VC have been found in laboratory or field studies with iron, which indicates that the dominant mechanism is probably beta-elimination (Roberts, et al., 1996).

Title: Beta-elimination
Text: Beta-elimination is an elimination reaction in which a proton, which is beta to a leaving group, is removed by a base. The adjacent atoms (usually carbons) typically develop a pi bond.

This pathway for iron degradation was proposed in Roberts, A.L., L.A. Totten, W.A. Arnold, D.R. Burris, and T.J. Campbell. 1996. "Reductive Elimination of Chlorinated Ethylenes by Zero Valent Metals." *Environ.*

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Title: Iron Reactivity (2 of 2)
Text: Iron Reaction Mechanisms

In the hydrogenolysis, or sequential degradation pathway shown here, one chlorine atom is removed in each step, so that TCE degrades to *cis*-1,2 DCE, then to VC, and finally to ethene and ethane.

Title: Hydrogenolysis
Text: The breaking of a chemical bond in an organic molecule with the simultaneous addition of a hydrogen atom to each of the resulting molecular fragments.

Title: Injection Methods (1 of 5)
Text: The injection method used depends on the type of geology found in the treatment zone and the form in which the NZVI will be injected. Typically four methods have been used to inject NZVI into the subsurface:

- Direct push techniques involve a direct push rig or stationary injection point to introduce NZVI into the treatment zone.
- Pneumatic fracturing uses air to create a fracture network of preferential flowpaths around the injection point and enhance NZVI distribution.
- Pressure Pulse Technology (PPT) uses regular pulses of pressure while injecting the NZVI slurry, which forces the slurry forward through the subsurface.
- Liquid atomization injection combines an NZVI-fluid mixture with a carrier gas to create an aerosol that can be dispersed into the treatment zone.

More detailed information for each injection method can be viewed by clicking the number icons in the bottom left corner.

Title: Injection Methods (2 of 5)
Text: Direct injection is a technique that uses a direct push rig to deliver the NZVI slurry into the treatment zone. In this method, the direct push rods are advanced to the target depth and the slurry is pumped into the subsurface. One advantage to using a mobile direct push rig is the ability to move from point to point in the treatment zone to deliver the injections. Another direct injection technique is to install a stationary injection point for use in delivering the NZVI slurry.

The decision to use direct injection is dependent on the geologic conditions in the treatment zone. Direct injection is well-suited for consolidated materials and fractured bedrock because there tends to be sufficiently interconnected pore space to permit the distribution of NZVI slurry throughout the treatment zone. In low permeability materials, such as silt and clay, the NZVI slurry may not advance into the formation, but back up into the injection point during operation.

Site-specific field testing may be necessary to determine the suitability of direct injection techniques for delivering NZVI into the treatment zone.

Title: Injection Method (3 of 5)
Text: Pneumatic fracturing is a technique that injects gas into the subsurface at low pressures and high volume flowrates to develop a network of fractures in the treatment zone. NZVI is then injected into the subsurface, and flows outward through these fractures to create a contact zone between the iron particles and the contaminant.

The distance that fractures propagate outward from the injection point typically range from 20 to 60 feet but depend on the type of rock formation. Fractures do not travel as far in unconsolidated materials such as silts and clays. Because direct injection can be problematic in silts and clays, pneumatic fracturing combined with direct injection offers a way to distribute the NZVI more effectively throughout the contaminant zone.

Title: Injection Methods (4 of 5)
Text: Pressure Pulse Technology (PPT) is a technique that uses regular pulses of pressure to advance an NZVI slurry into the subsurface. The pressure pulses cause the pores in the geologic formation to expand, which forces the slurry forward in a wave-like motion. A pressure pulse can propagate between 15 and 900 ft/s depending on subsurface characteristics, such as permeability, the fluid viscosity of the injected slurry, and the scale of the pressurized pulse (Quinn et al., 2004).

Title: Injection Methods (5 of 5)
Text: Liquid Atomization Injection is a technique that uses a combination liquid-gas stream to inject NZVI into the subsurface. By combining with a carrier gas, the NZVI-liquid mixture becomes an aerosol that more effectively distributes the NZVI particles in the treatment zone than liquid alone. The liquid atomization injection process can be used after pneumatic fracturing in formations with lower permeability, such as silt and clay.

Title: Implementation
Text: It is necessary to follow several steps in order to ensure the efficient design and effective performance of an NZVI injection system. The success of any in situ technology largely depends upon achieving a good understanding of the contaminated subsurface and preparing a suitable design that takes into account the variabilities inherent in aquifer systems. This is especially important for NZVI injection systems

because the NZVI is targeted to a source zone rather than a dispersed plume.

Title: Conceptual Site Model
Text: Developing a conceptual site model includes conducting a preliminary assessment of the available data to determine whether NZVI injection would be an appropriate technology. Factors that can determine whether NZVI injection is a suitable remedial action at a site include:

- Hydrogeology of the aquifer;
- Geochemistry of the groundwater;
- Type and distribution of contaminants;
- Aboveground features and access; and
- Depth of contamination.

Once the conceptual model is developed, a preliminary determination on the suitability of the NZVI injection technology at the specific site is made. Data gaps typically appear, and relate to information about the site characteristics or the suitability of a certain injection technique. Additional site characterization and treatability testing are required to address these data gaps.

Title: Site Characterization
Text: NZVI injection often requires additional characterization in the more localized setting of the prospective injection locations. This includes a determination of several factors that will impact applicability of this treatment technology including:

- Geology of targeted treatment zone;
- Horizontal and vertical distribution of contamination;
- Groundwater flow characteristics;
- Presence of underground obstacles;
- Presence of indigenous microorganisms;
- Depth of contamination and aquitard.

Title: Treatability Testing
Text: Treatability testing provides information on the efficiency of reactions between the reactive medium and the target contaminants under the specific site conditions.

Treatability tests are most often conducted as either batch or column studies. The kinetics of contaminant removal can be determined from these data in terms of a reaction rate or contaminant half-life.

Title: Batch Test
Text: Batch tests can be done to obtain a quick test of the reactivity of the candidate medium, although column tests provide more dynamic and accurate rate information.

Title: Column Test
Text: In a typical column study, groundwater from the site is run through a column packed with soil and NZVI. Water samples are collected through ports along the length of the column. Each port represents a different residence time of the groundwater in the reactive medium.

Column tests provide dynamic and accurate rate information, as well as information on how the groundwater residence time affects the NZVI in soil. Column tests are also a good way of determining the behavior of native groundwater constituents upon contact with the NZVI slurry or emulsion.

Title: Design
Text: The design for an NZVI injection application should be centered over the source zone or areas of highest concentrations if the exact source cannot be found. Common design elements include:

- Dosage of NZVI;
- Mass of primary contaminant within the treatment zone;
- Mass of soil in the treatment zone;
- Injection well/point direction (180º or 360º);
- Injection well/point placement;
- Radius of influence;
- Injection method; and
- Performance assessment monitoring locations.

Title: Construction and Implementation
Text: Constructing an NZVI technology typically involves installing the injection points, groundwater monitoring wells, and possibly a groundwater control system. Injection points can be temporary or permanent depending on the project goals.

Temporary injection points can be abandoned and backfilled with grout after injections are complete. More permanent injection points are constructed similarly to monitoring wells, with permanent casing using stainless steel or polyvinyl chloride (PVC).

Groundwater monitoring wells should be screened within the expected treatment zone to capture the effects of the treatment. Monitoring wells located around the perimeter of the treatment zone may be useful in determining the effective zone of treatment.

If soil sampling will be used for performance assessment, the borings ideally should not be drilled immediately adjacent to NZVI injection points or monitoring wells. This will help avoid potential damage and also minimize the interference that a grouted borehole may have on the distribution of NZVI.

Once all of the design components have been constructed, the selected injection method is used to deliver NZVI to the treatment zone.

Title: Monitoring and Performance Evaluation
Text: A monitoring plan is required to determine how well the NZVI injection met the design objectives of the project. Two main types of monitoring are typically required: compliance monitoring and performance monitoring. Compliance monitoring usually consists of collecting groundwater samples downgradient of contamination on a regular basis. Performance monitoring includes groundwater monitoring and soil sampling that can be used to determine the effectiveness of the NZVI treatment. Groundwater monitoring may include collection of contaminant levels, total organic carbon (TOC), oxidation reduction potential (ORP), pH, manganese, iron, and dissolved gases including ethene, and acetylene. Soil sampling can provide both quantitative data on contaminant levels after treatment and visual confirmation of NZVI in the designated treatment area.

Title: Compliance Monitoring
Text: Compliance monitoring is required to ensure that downgradient groundwater quality is protected. This typically involves placement of one or more monitoring wells to measure the contaminant level at a downgradient compliance point in the aquifer. However, at many sites, it may take months before significant improvements in downgradient levels are observed. Therefore, monitoring wells are often placed in the source zone to evaluate the level of treatment.

Title: Performance Monitoring
Text: Performance monitoring provides important feedback on the degree of treatment achieved by the NZVI injection. Groundwater samples can be collected from inside the treatment zone to determine if the overall quantity of contamination in the source zone has decreased as a result of the treatment and whether or not this decrease is sustainable (i.e., no rebound). Groundwater samples can also be collected immediately downgradient from the treatment zone to determine whether or not the flux of contamination from the source zone to groundwater has been reduced by the treatment. Groundwater samples may also be analyzed for signs of increased biological activity resulting from the NZVI injection as reducing conditions suitable for biodegradation are created.

Soil sampling can also be an important part of performance monitoring. By visually observing soil samples from within the expected treatment zone, problems such as preferential flowpaths, short circuiting, and inefficient distribution can be identified. Soil samples may also be analyzed for the concentration of contaminants remaining after the injection in order to determine the effectiveness of the source zone treatment.

Title: Economics of NZVI Technology
Text: The cost of using NZVI at a site depends to a large extent on the

scale of the application; in particular the size of the treatment zone and the amount of iron needed to achieve reductive dechlorination. Unit costs are reported to range from $117 to $286 per cubic yard of contaminated soil in the identified treatment zone. Field-scale demonstrations have found NZVI injections to be cost-competitive when compared to in situ chemical oxidation applications. Click here for an example of the variables that determined the cost of an NZVI field demonstration at Hunters Point Shipyard, San Francisco, California (Tetra Tech, Inc., 2003). For this site and others, the primary factors affecting unit costs include:

- The size of the contaminated zone;
- Reagent cost (e.g., ZVI);
- Field implementation goals, such as drilling and infrastructure;
- Monitoring requirements; and
- Cleanup goals.

Title: Advantages and Limitations
Text: Advantages:

- Used to treat source zones of contaminants that react with ZVI, such as chlorinated solvents or dense nonaqueous phase liquid (DNAPL)
- Fast reaction time
- Complete reduction pathway to non-toxic end products is possible
- In situ treatment
- Passive operation that requires minimal labor energy/input
- No recurring aboveground waste disposal requirements
- No aboveground structures required
- Potentially less expensive than pump-and-treat systems due to low O&M costs

Limitations:

- May not be cost-effective for large dispersed plumes
- Cost of NZVI material itself is relatively high; therefore injections of this material need to be targeted towards well-defined source areas
- Longevity issues may arise, requiring multiple injections
- Need a thorough understanding of the hydraulic flow characteristics for adequate NZVI delivery
- Specialized equipment for mixing the NZVI and injecting the mixture may be required

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Title: Case Studies
Text: The following three case studies are provided here for a look at demonstrations that have been conducted using the NZVI injection technology. Case Study 1: Hunters Point Shipyard, San Francisco, California Hunters Point Shipyard was operated as a ship repair, maintenance, and commercial facility from 1869 to 1986. In 1991, the Navy designated the site for closure and divided the shipyard into six parcels to facilitate groundwater and soil cleanup activities. This case study highlights the pneumatic fracturing and NZVI injection method implemented at Parcel C, which was characterized as having high chlorinated solvents (primarily TCE) in shallow groundwater. Case

Study 2: Launch Complex 34, Cape Canaveral Air Force Station, Florida Launch Complex 34 was used as a launch site for the National Aeronautics and Space Administration's (NASA's) Saturn rockets from 1960 to 1968. Rocket engines were cleaned in the nearby support building using chlorinated solvents such as TCE. Although the support building was abandoned in 1968, a significant subsurface source of TCE-DNAPL remains. This case study highlights the use of an emulsified form of NZVI to treat a zone of TCE-DNAPL. Case Study 3: Proposed Study of Emulsified Zero Valent Iron (EZVI) to Treat DNAPL Source Areas This case study is currently being developed as a joint project funded by the Department of Defense's Environmental Security Technology Certification Program (ESTCP). The proposed study is to further evaluate the ability of EZVI to reduce DNAPL mass and mass flux. Although a site for the project has not been chosen yet, a description of the proposed project is provided and the case study will be updated as the project progresses.

Title: Introduction to Case Study 1
Text: A field demonstration of an NZVI technology was conducted at Hunters Point Shipyard (HPS), Remedial Unit C4 (RU-C4) of Parcel C, in San Francisco, California, from November 2002 to March 2003. The primary objective of the demonstration was to evaluate the technology's cost and performance in destroying chlorinated volatile organic compounds (VOCs) in source areas at HPS. The chosen technology was Ferox injection, an in situ subsurface remediation technology for chlorinated VOCs.

This project was selected and partially funded by the U.S. Department of Navy's Alternative Restoration Technology Team (ARTT). The project was completed by Naval Facilities Engineering Command, Southwest Division; the ARTT; Tetra Tech EM, Inc.; and ARS (ARS) Technologies, Inc. ARS holds the patent for the Ferox injection technology (Tetra Tech, Inc., 2003).

Title: Case Study 1: Technology Description
Text: The Ferox injection technology implemented at HPS uses the liquid atomization injection method to introduce a slurry of ZVI powder into targeted subsurface zones. The ZVI slurry is injected using nitrogen gas as the carrier fluid. For this demonstration, pneumatic fracturing was used first prior to injecting the slurry, in order to create subsurface fractures and facilitate the distribution of the atomized ZVI. Chemical reduction occurs once the ZVI comes into contact with the chlorinated VOCs.

Title: Case Study 1: Site Description
Text: At HPS, groundwater flow patterns are complex. There are two aquifers and a fractured bedrock zone that bears water within discrete fractures and shear zones. Much of the aquifer consists of artificial fill, which was placed during construction activities that shaped the

topography at HPS. The groundwater elevation was approximately 7 feet below ground surface (bgs), and the groundwater gradient across the site was relatively flat because of the surrounding San Francisco Bay.

Prior to the demonstration, groundwater characterization efforts indicated that TCE was present in concentrations as high as 88,000 µg/L, with a mean concentration of 27,000 µg/L inside the treatment zone. TCE as DNAPL (i.e., greater than 1,100,000 µg/L) was not detected in any of the monitoring wells. Lesser concentrations of DCE and VC were observed, indicating some natural historical attenuation occurred at the site. Chloroform and carbon tetrachloride were also present.

Title: Case Study 1: Technology Demonstration
Text: Based on pre-demonstration groundwater characterization, the proposed treatment zone in Parcel C was approximately 900 square feet by 22 feet in thickness. To determine the dosage of ZVI powder for the injections, the vendor considered the following:

- The estimated mass of TCE;
- The estimated mass of soil within the treatment zone; and
- The mass ratios of iron-to-TCE and iron-to-soil.

Calculations indicated 16,000 pounds of ZVI powder would be sufficient to destroy the TCE in the treatment zone. The estimated top and bottom of the injection zone were the water table (7 feet bgs) to the depth below where DNAPL would potentially be observed (30 feet bgs).

Four injection boreholes were installed to provide sufficient coverage of the treatment zone. Using an integrated injection process in each borehole, pneumatic fracturing was employed first and then immediately followed by the Ferox injection. Nitrogen gas was used for both the pneumatic fracturing and Ferox injection fluid. During fracturing, pressures ranged from 55 to 230 pounds per square inch gauge (psig). Fracturing was conducted in 3-foot intervals, from approximately 30 ft bgs and proceeding upward to at least 10 ft bgs. Packer assemblies were used to isolate the 3-foot intervals.

After the pneumatic fracturing was complete at each 3-foot interval, ZVI powder and potable water were mixed in a tank using a ratio of 1 kg of ZVI powder to 1 gallon of water. The ZVI slurry was added to the nitrogen stream, and the injection took approximately 5 to 20 minutes to complete. During the injection process, subsurface pressures ranged from 40 to 180 psig.

A total of 16,289 pounds of ZVI powder was injected through the four boreholes.

Title: Case Study 1: Monitoring
Text: Three rounds of groundwater monitoring were conducted 2, 6, and 12 weeks after the injections and compared to baseline

concentrations. Ten monitoring wells were located within the treatment zone. Another eight monitoring wells were located around the perimeter of the treatment zone. All eighteen of these wells were screened within the zone of the ZVI injections (7 to 32 feet bgs). One additional well was screened below 32 feet bgs to monitor the area below the treatment zone. The groundwater samples were analyzed by a laboratory for the following:

- PCE, TCE, cis-1,2-DCE, trans-1,2-DCE, VC, chloroform, and carbon tetrachloride;
- Dissolved gases (hydrogen, ethane, and ethane);
- Chloride, alkalinity, and nitrate; and
- Iron, manganese, and arsenic.

In addition, a water quality meter with flow-through cell was used to measure for oxidation-reduction potential (ORP), dissolved oxygen, pH, temperature, conductivity, and turbidity.

Title: Case Study 1: Performance Assessment (1 of 2)
Text: Based on the three post-injection groundwater monitoring events, the TCE plume decreased in both size and concentration as a result of ZVI injection. The plume maps at left compare the TCE plume over the baseline and three post-injection sampling events. Click here to learn more about the magnitude of the decreases in contaminant concentrations post-injection. The pneumatic fracturing and Ferox injections into four boreholes resulted in a treated area of about 1,818 square feet, or approximately twice the original estimated area of 900 square feet. The treatment zone was found to extend at least 15 feet from the point of each injection. The treatment zone also extended 2 feet above and below the targeted depths of 7 to 32 feet bgs. An estimated subsurface volume of 1,683 cubic yards was treated during this demonstration.

Title: Results
Text: The primary results are listed below:

- Nearly 99.2% of the TCE in the treatment zone was reduced to ethane and chloride.
- TCE decreased from a mean pre-injection concentration of 27,000 μg/L to 220 μg/L after the demonstration.
- Decreases in pre-demonstration concentrations of PCE (99.4%), cis-1,2-DCE (94.2%), and VC (99.3%) were also observed.
- Concentration decreases were also observed in chloroform (92.6%) and carbon tetrachloride (96.4%).
- No significant increases in TCE degradation byproducts, such as DCE and VC, were observed as a result of the treatment.

The third event conducted 3 months after the ZVI injections did not show evidence of rebound in dissolved chlorinated VOC concentrations inside the treatment zone. A minor increase in the mean concentration of TCE in groundwater (approximately 15 μg/L) was observed outside the treatment zone. A statistical evaluation confirmed that the increase was not significant at the 95% confidence level. This indicated that the increase was within the range of normal concentration fluctuations and was not due to plume displacement as a result of the injections. The site continues to be monitored for signs of any residual contamination.

Title: Case Study 1: Performance Assessment (2 of 2)
Text: The graphs to the left show the changes in ORP, pH, and dissolved gases compared to the change in TCE concentration before and after the injection.

- ORP decreased to less than -200 mV within 15 feet of the injection boreholes;
- An increase of 1 to 2 pH units was observed in the treatment zone;
- Dissolved gases increased measurably; and
- Changes in chloride levels were obscured by the high background concentrations of chloride initially present in the aquifer.
- Water quality was not adversely impacted by arsenic, manganese, iron, or nitrate in groundwater.

Title: Arsenic, Manganese, Iron, and Nitrate
Text: A statistical evaluation determined that arsenic and manganese did not mobilize from soil to groundwater as a result of the demonstration. Mean dissolved iron concentrations increased from 150 µg/L to 570 µg/L and mean total iron concentrations increased from 3,400 µg/L to 12,000 µg/L. These observed increases were attributed to the injection of ZVI and are expected to subside once the strong reducing conditions have dissipated. The average nitrate concentrations decreased 94.1% in the treatment zone.

Title: Case Study 1: Cost Summary and Comparison
Text: The costs for a small field-scale application of the Ferox technology were estimated based on the HPS demonstration and compared to in situ chemical oxidation, another injection technology. The total cost of the field-scale application at HPS was $289,274, or $172 per cubic yard of the treatment zone. Excluding sampling, analytical, and demonstration-derived waste management costs, the total cost was $196,665, or $117 per cubic yard. The unit costs for in situ chemical oxidation by injecting potassium permanganate (the most common oxidant) were reported to range from $31 to $183 per cubic yard treated.

Title: In Situ Chemical Oxidation Costs
Text: The cost range for in situ chemical oxidation reflects three different delivery methods:

- $31/CY for soil fracturing with potassium permanganate oxidative particle mixture
- $130/CY for soil mixing with potassium permanganate injection
- $183/CY for horizontal well flushing with potassium permanganate

Title: Case Study 1: Lessons Learned
Text: The following considerations are mentioned here based on information in the performance assessment report for the NZVI demonstration using Ferox at Hunters Point Shipyard.

- Pneumatic fracturing combined with liquid atomization injection of the ZVI slurry created a larger treatment zone than originally estimated. Performance assessment and compliance monitoring wells should be sited to anticipate both ideal and less than ideal distribution of ZVI through the treatment zone.
- Flowrates for both nitrogen and ZVI slurry should be optimized in the field based on conditions encountered at the site. Slow nitrogen distribution through the formation at Hunters Point led the vendor to use pulses of nitrogen rather than a steady flow to distribute the ZVI. Pulsing helped to prevent excessive pressure buildup and surface heave.
- Injecting at shallow depths may lead to nitrogen and slurry seeping up to the ground surface. Switching to direct hydraulic pumping may reduce the potential for seeping to the ground surface and the risk of contaminant vapors escaping from the subsurface.
- Some minor heaving of the concrete floor was observed during the demonstration, which generally occurred during shallow injections. However, residual heave up to 1 inch was observed after the injections. If this technology is applied in buildings, the project design might include surveying transits and monitoring with a heave rod before, during, and after each injection.
- Underground utilities such as storm drains may be inspected during the injection to ensure that groundwater or ZVI is not entering the storm water conveyance system.

Title: Case Study 2: Introduction
Text: Nanoscale emulsified zero valent iron (EZVI) was demonstrated in the field at Launch Complex 34, Cape Canaveral Air Station, Florida between June 2002 and January 2003. The goal of the project was to evaluate the cost and technical performance of nanoscale EZVI when applied to a DNAPL source zone. The DNAPL source zone consisted of TCE, with daughter products of dissolved cis-1,2-DCE and VC also present. The demonstration was conducted under NASA's Small Business Technology Transfer Research (STTR) Program. The demonstration was conducted by GeoSyntec Consultants, in partnership with the University of Central Florida (UCF). The demonstration was independently evaluated under the U.S. Environmental Protection Agency's (EPA) Superfund Innovative Technology Evaluation (SITE) Program. The U.S. EPA contracted Battelle to conduct a detailed site characterization and to perform an independent performance assessment(Battelle, 2004 and GeoSyntec Consultants, 2002.)

Title: Case Study 2: Technology Description
Text: The EZVI for this demonstration was composed of surfactant, biodegradable vegetable oil, water, and nanoscale iron. The emulsion

particles (or micelles) that formed from this mixture contained a nucleus of iron suspended in water, surrounded by an oil membrane. The surfactant keeps the micelles intact and well-distributed. This diagram is an animation of the potential EZVI treatment process. For example, TCE diffuses through the oil membrane into the interior aqueous phase of the emulsion particle. There it will undergo reductive dechlorination facilitated by the zero valent iron particles. This will maintain a concentration gradient across the oil membrane and provide a driving force for TCE molecules to continue entering the micelle. The final byproducts of non-chlorinated hydrocarbons from the reaction can then diffuse out of the emulsion into the surrounding groundwater.

Title: Case Study 2: Site Description
Text: At Launch Complex 34, the EZVI demonstration was conducted in a surficial aquifer that was subclassified as having an Upper Sand Unit, a Middle Fine-Grained Unit, and a Lower Sand Unit. The EZVI technology was demonstrated within the Upper Sand Unit because this unit was the most permeable and therefore most likely to have sufficient pore space to accommodate the EZVI injections. Prior to the demonstration, the EZVI treatment plot was characterized using soil and groundwater sampling. In the Upper Sand Unit soil, an estimated 10 to 46 kg of TCE was present, and an estimated 3.8 kg of this may have occurred as DNAPL. Pre-demonstration TCE concentrations in groundwater measured from the Upper Sand Unit were at or near the solubility level of TCE (i.e., 1,100,000 µg/L), suggesting that DNAPL was likely present in the EZVI plot and surrounding area. Based on these results, two separate depths in the Upper Sand Unit (at 18 ft bgs and 22 ft bgs) were targeted for EZVI injection. The groundwater table was approximately 6 ft bgs.

Title: Case Study 2: Technology Demonstration
Text: Eight injection wells were installed in the 9 x 15 foot rectangular demonstration plot. Six of the injection wells were screened 180º around the circumference and placed at the edges of the plot, with the screens oriented inward toward the plot center. The remaining two wells in the middle of the plot were fully screened around the circumference (360º). The target treatment zone was 16 to 24 feet bgs. The estimated volume of EZVI needed to treat the TCE in the demonstration plot ranged from 608 to 845 gallons. The estimated radius of influence was 4.5 feet from the injection well.

Several injection methods were tested outside of the plot to determine which method could overcome the high viscosity of the EZVI mixture (see Case Study 3). Pressure pulse technology (PPT) was selected as the injection method, but was modified to inject water into the aquifer before, during, and after the EZVI injection. This modification overcame the viscosity differences and forced the EZVI further outward into the aquifer. The total volume of EZVI injected was approximately 661 gallons and the total volume of water injected (before, during, and after EZVI) was 1,627 gallons. The injections were completed over the course of 5 days.

A groundwater control system was used to maintain hydraulic control through the EZVI plot. An average flowrate of 0.3 gpm was used during the demonstration. The water was withdrawn from a monitoring well in the center of the plot and reinjected approximately 20 ft upgradient from the plot. This likely produced an inward gradient into the plot.

Title: Case Study 2: Performance Assessment (1 of 2)
Text: Soil sampling was employed to estimate the changes in total TCE and DNAPL mass in the Upper Sand Unit as a result of the EZVI injection. Nearly 200 soil samples were collected during pre- and post-demonstration characterization. Soil sampling also provided the opportunity to visually observe EZVI in the treatment zone. Two different methods were used to estimate TCE concentrations and mass in the treatment plot including linear interpolation by contouring and kriging. For example, the linear interpolation method estimated that an 86% reduction in total TCE mass occurred after the demonstration, from 17.8 kg to 2.6 kg. Of that total TCE mass, the estimated reduction in TCE-DNAPL mass was 84%, from 3.8 kg to 0.6 kg using this same method.

Title: Case Study 2: Performance Assessment (2 of 2)
Text: Plume maps shown here compare the pre- and post-demonstration groundwater concentrations in the Upper Sand Unit. Groundwater samples were collected from monitoring wells both inside and around the perimeter of the treatment plot. The highest pre-demonstration concentrations of TCE were observed at 1,180,000 µg/L in the center of the test plot. The TCE concentrations decreased to less than 9,000 µg/L immediately after the demonstration. Significant increases in cis-1,2-DCE and VC were also observed after the EZVI injections. This accumulation suggests that multiple TCE degradation mechanisms may have been stimulated by the EZVI injection. Abiotic degradation of TCE by ZVI primarily bypasses the formation of these two intermediates and results in the direct formation of ethene. However, these are byproducts of biological degradation of TCE, which may be stimulated by the addition of an electron donor source such as the vegetable oil in the EZVI. Approximately one year after the EZVI injections, TCE had decreased to less than 5 µg/L in the test plot. DCE and VC concentrations also decreased further, while ethene concentrations increased to over 9,000 µg/L. These later samples indicated that contaminant degradation continued for several months after the EZVI injection.

Title: Case Study 2: Cost Summary and Comparison
Text: The cost estimation for the EZVI technology demonstration performed at Launch Complex 34 involved three major components:
- The application cost of EZVI was $327,000;
- The site preparation and waste disposal cost was $25,000; and

- The site characterization and performance assessment costs were $250,000 and $275,000 respectively.

An economic present value (PV) analysis of the EZVI technology and a groundwater pump-and-treat system was conducted as part of the performance assessment report. The PV of the pump-and-treat costs over 30 years was estimated to be $1,365,000. An equivalent treatment cost for full-scale deployment of the EZVI treatment technology was estimated to be $452,000.

There is one important long-term cost benefit to using a DNAPL source remediation technology such as EZVI injection. Even if the contaminant source zone is only partially removed by the EZVI treatment, and natural attenuation is insufficient to meet downgradient cleanup goals, it is anticipated that the weakened source will lead to a weakened plume that can be contained in a cost-effective fashion.

Title: Case Study 2: Lessons Learned
Text: The following lessons were learned during the demonstration of EZVI injection at Launch Complex 34:

- The application of EZVI resulted in a reduction in TCE-DNAPL mass.
- The results indicated that both abiotic and microbial reductive dechlorination may have occurred. The accumulation of degradation intermediates (i.e., DCE and VC) and methane suggested that biodegradation played a role in the transformation of TCE.
- Improvements in injection techniques are necessary to overcome the viscosity issues associated with the EZVI.

Title: Introduction to Case Study 3
Text: This case study is currently being developed as a joint project funded under ESTCP. The project team is composed of representatives from NAVFAC, NASA, and GeoSyntec Consultants. The proposal for this work is based on the promising results from the laboratory studies and pilot test of EZVI conducted at the Cape Canaveral site (see Case Study 2). As part of this project, NAVFAC proposes to conduct additional work to:

- Improve the EZVI delivery approach;
- Evaluate the contribution of both ZVI and vegetable oil to DNAPL degradation; and
- Demonstrate and validate the technology for widespread use at DoD sites.

This project is a new start in Fiscal Year 2004 and the plans for the project are discussed here. This case study will be updated with future results as the demonstration site is selected and the project progresses (GeoSyntec Consultants, 2004 and Quinn, et al., 2004).

Title: Case Study 3: Technology Description
Text: EZVI is composed of food-grade surfactant, biodegradable vegetable oil, water, and nano- or micro-scale ZVI. When these are mixed together, the iron particles in water become surrounded by an

oil-liquid membrane to form emulsion droplets. Because the oil membrane of the droplet has hydrophobic properties similar to DNAPL, the two phases can mix.

The chlorinated volatile organic compounds (CVOCs) in the DNAPL diffuse through the oil membrane and undergo reductive dechlorination as they come into contact with the ZVI in the interior aqueous phase.

In addition to this abiotic degradation pathway, the vegetable oil and surfactant are long-term electron donors that may stimulate biological degradation of contaminants.

Title: Case Study 3: Site Selection
Text: The site for this project has not been chosen yet, but several are under review. To narrow the choices, the project team identified key characteristics a site should have. Those characteristics are:

- Known TCE or PCE DNAPL source area;
- Appropriate depth to the DNAPL source;
- Existing site characterization data;
- Appropriate hydraulic conditions;
- Regulators will accept the injection approach;
- Existing on-site support and infrastructure;
- Minimal site issues; and
- A RPM who will be supportive of the demonstration.

Title: Case Study 3: Laboratory Microcosms
Text: Laboratory studies will be conducted as part of this project to evaluate two pathways for DNAPL degradation: abiotic dehalogenation and enhanced biodegradation. To accomplish this, EZVI will be added to one biologically active microcosm of soil and groundwater and one sterile microcosm. A second set of experiments will be conducted using the vegetable oil-surfactant-water mix (i.e., EZVI without the iron!) in one biologically active and one sterile microcosm. The microcosms will be monitored for CVOC degradation over a 12-week period.

Title: Case Study 3: Injection Methods
Text: This project proposes to evaluate four injection technologies for their ability to deliver EZVI to the subsurface:

- Hydraulic fracturing
- Pneumatic fracturing
- Pressure pulse technology
- Direct injection.

Soil and groundwater samples will be collected over 9 months to characterize the EZVI distribution and assess the changes in DNAPL mass and mass flux.

Title: Case Study 3: Summary and Future Plans
Text: In summary, this project proposes to validate the EZVI injection technology by combining laboratory microcosms with field deployment. The size and duration of the technology demonstration is intended to generate realistic information for scale-up design and to evaluate the short- and long-term impacts of the technology on DNAPL mass and mass flux.

The data and lessons learned from the demonstration will be used to develop a guidance manual and application protocol for DoD RPMs to use in designing, implementing, and evaluating the EZVI injection technology. This case study will be updated as the project progresses.

Title: Lessons Learned
Text: The following lessons were learned from NZVI technologies applied at demonstration sites:

- Significant improvements to injection technologies are necessary to more efficiently and effectively distribute NZVI throughout a treatment zone.
- Certain byproducts (such as iron and chloride) are subject to secondary, nonhealth-based drinking water standards under the Safe Drinking Water Act, and may require sufficient time and distance to dissipate.
- The NZVI technologies led to significant removal of contaminant mass from a source zone. However, because technology, site, and economic limitations may limit contaminant mass removal to less than 100%, it may not always be possible to meet groundwater cleanup targets in the source region in the short term.
- Biological degradation of contaminants may be stimulated when using an injection media that also contains an electron donor (such as the vegetable oil portion of EZVI). As a result, contaminant degradation may continue after the iron is exhausted, but the biological degradation mechanism may result in accumulation of DCE and VC. Additional injections of NZVI may be necessary to counteract this effect.
- To improve long-term effectiveness and prevent rebound, care must be exercised before injection in preventing NZVI from getting passivated, understanding the site geology, and injecting a sufficient mass of NZVI.

Title: Summary
Text: The NZVI injection technology can be a suitable remedy for eliminating or mitigating a contaminant source zone (e.g., DNAPL). The technology is in situ and the injections may be reapplied as necessary. Although the NZVI injection technology itself is fairly young, the use of zero valent iron to treat chlorinated contaminants is well-established and accepted. As the technology is validated and more widely applied, regulatory guidelines for compliance should follow.

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