



RISK^eLearning

Nanotechnology – Applications and Implications for Superfund



April 19, 2007
Session 4:
"Nanotechnology – Superfund
Site Remediation
Marti Otto, EPA OSRTI
Mary Logan, RPM, EPA Region 5



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Nanoscale Zero-Valent Iron Field-Scale and Full-Scale Studies

Risk e-Learning Internet Seminar Series
"Nanotechnology: Applications and
Implications
for Superfund."

April 19, 2007

Marti Otto

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Outline

Background

Field-scale studies

Tuboscope Site, AK
Launch Complex 34, FL
NAS Jacksonville, FL
NAES Lakehurst, NJ

Outreach and Publications

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Nanotechnology shows great promise for improved sensors. The sensors can lead to improved monitoring and detection capabilities that allow for real-time, accurate sensing of many compounds simultaneously at extremely low concentrations frequently in hostile environments [\[BK1\]](#).

Treatment involves cleaning up waste streams of contaminants, particularly those substances that are highly toxic, persistent within the environment, or difficult to treat. Nanotechnology holds promise for cost-effective, specific, and rapid solutions for treatment of contaminants [\[BK2\]](#).

Remediation addresses problems brought about by prior technologies and past practices. Cleanup of contaminated sites using nanotechnology is one of the initial successes in nano tech applications to the environment. Researchers are developing cost-effective technologies that enable both rapid and effective cleanup of recalcitrant compounds, particularly those located in inaccessible areas [\[BK3\]](#).

There are two aspects of nanotechnology applications in green manufacturing. The first involves using nanotechnology itself to eliminate the generation of waste products and streams by designing in pollution prevention at the source. The second aspect involves the manufacture of nano materials themselves in a benign manner. Both of these involve use of environmentally friendly starting materials and solvents, improved catalysts, and significantly reduced consumption of energy in the manufacturing process [\[BK4\]](#).

Background: OSWER and TIFSD



Office of Solid Waste and Emergency Response



<http://www.osde.state.gov/OSW/cleanup-and-emergency-response/>

Develops hazardous waste standards and regulations (RCRA)
Regulates land disposal and waste (RCRA)
Cleans up contaminated property and prepares it for reuse (Brownfields, RCRA, Superfund)

Helps to prevent, plans for, and responds to emergencies (Oil spills, Chemical releases, Decontamination)
Promotes innovative technologies to assess and clean up contaminated waste sites, soil, and groundwater (Technology Innovation)



Technology Innovation and Field Services Division

Provides information about characterization and treatment technologies (Clu-in, TechDirect, TechTrends, Case Studies, Technical Overviews)

Advocates more effective, less costly technologies

Provides national leadership for the delivery of analytical chemistry services for regional and state decision makers to use at Superfund and Brownfield sites

Environmental Response Team (ERT) provides technical assistance and science support to environmental emergencies



<http://www.epa.gov>

**Background:
Nanotechnology for Site Remediation**

Nanotechnology for Site Remediation

Potential applications include *in situ* injection of nanoscale zero-valent iron (NZVI) particles into source areas of groundwater contamination

Contaminants

Chlorinated hydrocarbons

Metals?

Pesticides?

Over 15 field-scale and full-scale studies

8

Nanotechnology shows great promise for improved sensors. The sensors can lead to improved monitoring and detection capabilities that allow for real-time, accurate sensing of many compounds simultaneously at extremely low concentrations frequently in hostile environments [\[BK1\]](#).

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Field Scale Studies

2 EPA sites with field studies in 2006

Tuboscope site, Alaska
Nease Chemical, Ohio

2 field studies with emulsified nanoscale zero-valent iron (EZVI)

NASA's Launch Complex 34, FL
Parris Island, SC

Majority of field studies

Trichloroethene (TCE), trichloroethane (TCA), degradation products
Gravity-feed or low pressure injection
Source zone remediation

**Tuboscope Site
BP/Prudhoe Bay,
Alaska**

Tuboscope Site
BP/Prudhoe Bay
North Slope, Alaska



Tuboscope Site
BP/Prudhoe Bay
North Slope, Alaska

Cleaned pipes used in oil well construction
from 1978 to 1982

Contaminants

Trichloroethane (TCA)

Diesel fuel

Lead

Tuboscope Site

North Slope, Alaska

Pilot test: injection of NZVI

Objectives/Goals

Reduce the concentrations of TCA and diesel fuel contaminants

Reduce the mobility of lead at the site

Field Test conducted August 2006

First round of sampling: September 2006

More information: hedeen.roberta@epa.gov

Launch Complex 34, FL

Launch Complex 34

**Used as launch site for Saturn rockets from
1960 to 1968**

**Rocket engines cleaned on launch pad using
chlorinated VOCs, including TCE**

**DNAPL (primarily TCE) present in subsurface
EZVI demonstration conducted beneath the
Engineering Support Building**

Properties of Emulsified Zero-Valent Iron



Jacqueline Quinn, NASA

Oil membrane is hydrophobic and miscible with DNAPL

Abiotic degradation by ZVI

Biodegradation enhanced by vegetable oil and surfactant components of EZVI

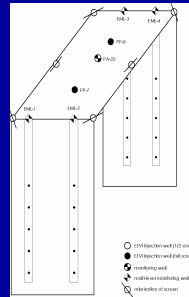
EZVI Injection Set-Up

EZVI injected in 8 injection wells

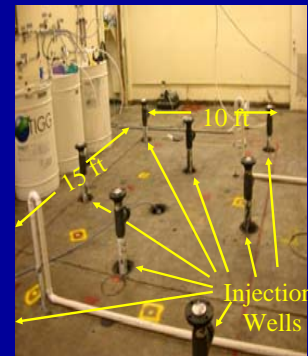
Injection wells along edge of plot directed inwards

Injection wells in center were fully screened

Injection at 2 discrete depth intervals in each well



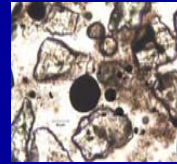
Slide: Jacqueline Quinn, NASA



Soil Core Samples



EZVI in 1- to 3-
inch thick
stringer



Soil core sample

Results

Significant reduction (57 to 100%) of TCE in target depths within 5 months

Significant additional reduction of TCE in groundwater samples collected 18 months after injection

Data suggest longer-term TCE reduction due to biodegradation

Subsequent fieldwork indicates that better distribution of EZVI may be achieved using pneumatic fracturing or direct push rather than pressure pulse injection method

NAS Jacksonville, FL

NAS Jacksonville

Former underground storage tanks

**Source area contaminants: TCE, PCE,
1,1,1-TCA, and 1,2-DCE**

CERCLA cleanup

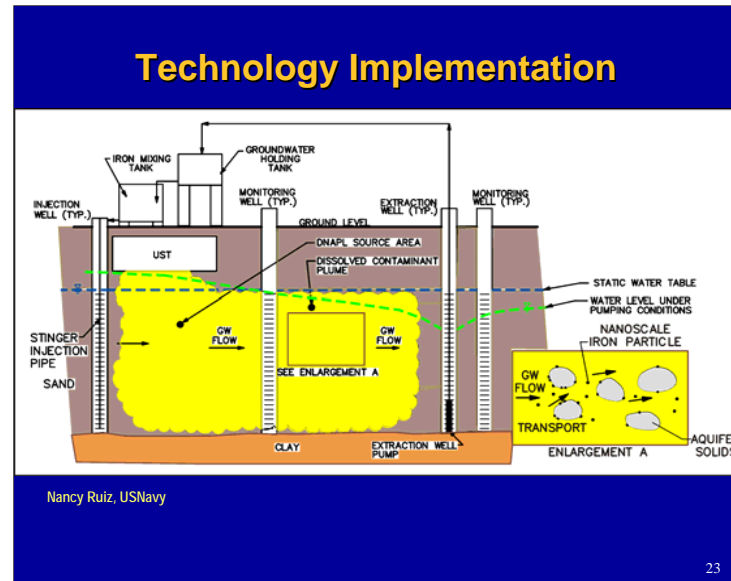
Groundwater monitoring under RCRA

NZVI Injection

Gravity Feed

10 injection points

**300 lb bimetallic nanoparticles (BNP)
(99.9 % Fe, 0.1 % Pd and polymer support)**



300 lb BNP (99.9 % Fe, 0.1 % Pd and polymer support)

Initial direct-push technology injection (40 lb)

1st recirculation event (110 lb) – 2 to 4.5 g/L

2nd recirculation event (150 lb) – 4.5 g/L

Injection at 10 locations; known hot spots

Recirculation system – downgradient groundwater

NZVI continuously added to recirculation water

Gravity flow injection

Results/Conclusions

NZVI significantly reduced dissolved TCE levels in several source zone wells

Some increases in cis-1,2 DCE and 1,1-DCA

Did not achieve strong reducing conditions to generate substantial abiotic degradation of TCE

Potentially deactivated NZVI due to mixing with oxygenated water, or

Insufficient iron may have been injected

NAES Lakehurst, NJ



NAES Lakehurst, NJ

Pilot-scale study in 2003

Full-scale work in 2005 and 2006

PCE, TCE, TCA, *cis*-DCE, VC

Largest amount of contamination 45 to 60 ft
below groundwater table

NAES Lakehurst, NJ

Full-Scale Project

November 2005: Phase I (2300 lb nanoscale bimetallic particles)

January 2006: Phase II (500 lb nanoscale bimetallic particles)

Injection method: direct push wells

Remedial objective: to attain NJ groundwater quality standards using a combination of NZVI and monitored natural attenuation

Full-Scale Project

- Media treated
 - Groundwater
 - Soil
- Initial concentrations up to 360 ppb chlorinated VOCs
- Final concentrations: TBD
- Groundwater quality standards have been obtained for some monitoring wells
- Monitoring continues.

Summary of Navy's Conclusions

NZVI is a promising technology for source zone treatment

Inject sufficient iron to create strongly reducing environment, which is essential for success

Take care to not deactivate NZVI during storage or mixing

Short-term performance monitoring can be misleading. Long term monitoring of treatment zone until ORP levels have returned to pre-treatment levels is essential.

Cost and Performance Report: Nanoscale Zero Valent Iron Technologies for Source Remediation available on <http://www.clu-in.org>

More information: Project Manager at (805) 982-1155

Outreach and Publications

October 2005 Workshop on Nanotechnology for Site Remediation

Held October 20-21, 2005, in Washington, D.C.

Proceedings and presentations:

<http://www.frtr.gov/nano>

Nanotechnology and OSWER: New Opportunities and Challenges

Held July 12-13, 2006, in Washington, D.C.

Presentations:

<http://esc.syrres.com/nanotech/>

Outreach and Publications, Cont.

Issues area on CLU-IN website
<http://clu-in.org/nano>

Upcoming TIFSD products on nanotechnology

Spreadsheet of field tests

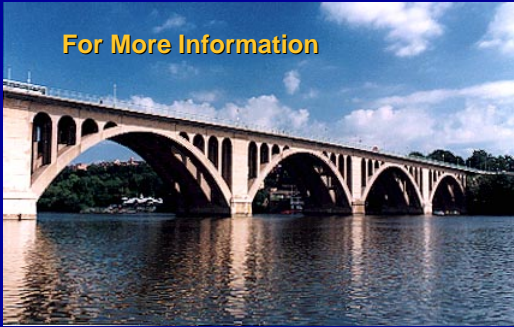
Cost and performance

Media/contaminants

Technology/vendor information

Points of contact

Fact sheet on nanotechnology for site
remediation



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Nease Chemical Site Nanotechnology Update

Risk e-Learning Internet Seminar Series
“Nanotechnology: Applications and Implications for Superfund”

Mary Logan
U.S. EPA, Region 5
April 19, 2007

Objectives

- Provide brief site description
- Brief overview of selected remedy for soil, source areas and groundwater
 - Considerations that led to selection of nanotechnology for groundwater clean up
- Discuss status of groundwater remediation by nanotechnology at the Nease site
 - Preliminary pilot study results

Acknowledgements

- Rutgers Organics Corporation – current site owner, has agreed to conduct work
- Golder Associates – primary contractor for Rutgers, is performing and/or overseeing the work
 - Special thanks for use of figures and pictures
- Ohio EPA – partner oversight agency and technical support
- EPA's technical support – Region 5 and ORD

Nease Chemical Superfund Site Overview

Site Background

Nease facility

Former chemical manufacturing plant

Operated from 1961 - 1973

Spills and on-site waste disposal

The remedy for soil, source areas and groundwater was selected by EPA in 2005

More than 150 contaminants identified

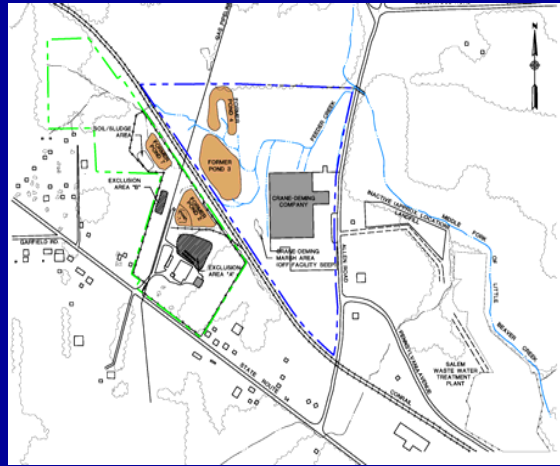
Primary site contaminants include:

Mirex in soil up to 2,080 ppm

VOCs in groundwater over 100 ppm

A future remedy will address mirex in sediment and floodplains

Nease Chemical Superfund Site



Summary of Source Area and Groundwater Contamination

Hydrogeologic units: overburden; transition bedrock; Middle Kittanning Sandstone bedrock

Units are hydraulically connected

Depth to groundwater – a few feet to ~ 9 ft.

Former Ponds 1 & 2 → primary source of contamination to groundwater

50,000 CY waste/fill and underlying soil

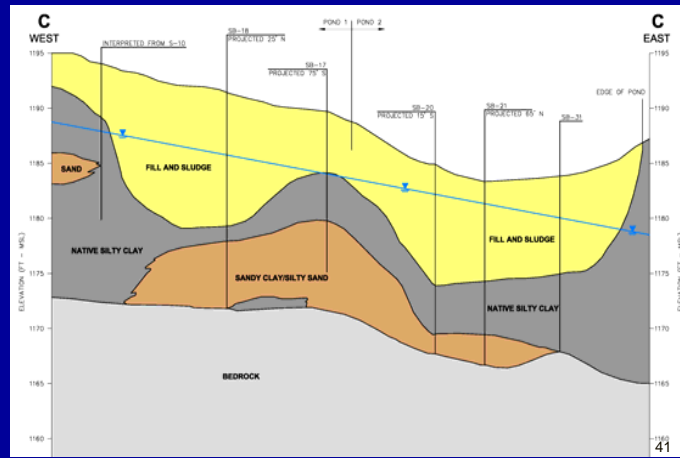
Waste/fill in ponds is generally below the water table

Maximum pond waste concentration: VOCs > 50,000 ppm; SVOCs ~ 11,000 ppm; pesticides 1,000 ppm; NAPL is found in waste and till

Primary groundwater contaminants

chlorinated ethanes and ethenes, benzene, chlorobenzene

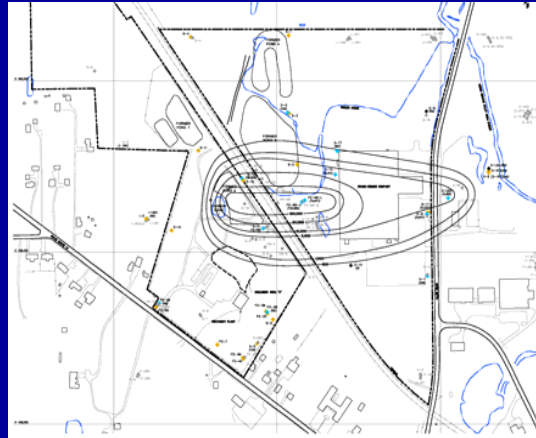
Cross Section – Former Ponds 1 and 2



Bedrock Groundwater

- Middle Kittanning Sandstone
 - Thickness 21 to 53 ft.
 - Velocity ~ 65 to 160 ft/yr
- Bedrock is fractured
 - Flow primarily through bedding plane partings
- DNAPL is present
- Plume length ~ 1650 ft.
- Max. total VOCs > 100 ppm
- Natural attenuation seems to be occurring

Groundwater Contaminant Contours
Total VOCs Bedrock July 2003



Operable Unit 2 Selected Remedy

Former Ponds 1 and 2 → in-situ treatment by soil mixing/air stripping, stabilization and solidification.

Ponds and soil → covered/capped.

Includes Ponds 1 & 2 after treatment

Shallow eastern groundwater → captured in a trench, pumped above ground, treated on site.

Bedrock groundwater → treated by injection of nanoscale zero-valent iron (NZVI).

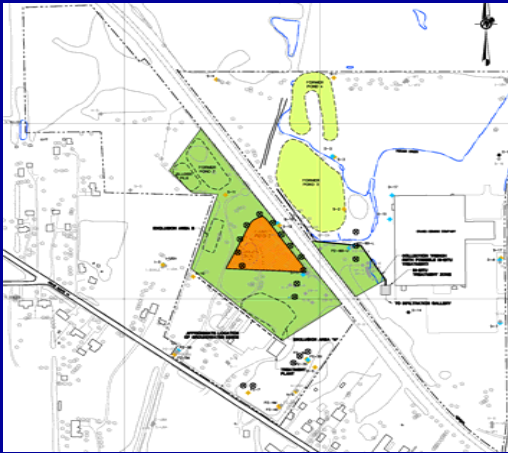
Treatment of plume core, MNA downgradient

NZVI treatment may be coupled with enhanced biological treatment

Pre-design data suggests that the approach for the southern area groundwater must be reconsidered

Long-term O&M, institutional controls.

Conceptual Layout of Remedy



NZVI – Remedy Evaluation Considerations

What is NZVI?

1 100 nanometer sized iron particles

A human hair is 500 to 5000 times wider

Large surface area compared to volume

NZVI is very reactive

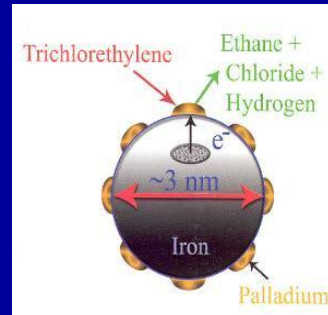
Contaminants are destroyed by a reaction similar to rusting

Non-toxic by-products are formed

Iron can be enhanced

Reactive catalyst

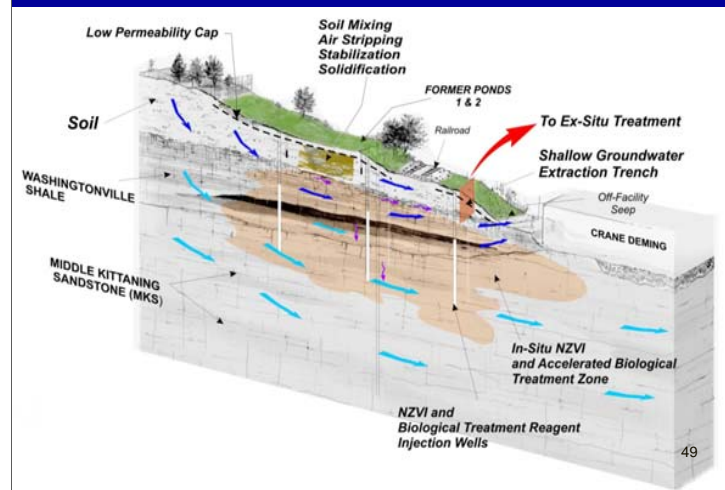
Coatings



How Does NZVI Work?

- An iron-water slurry is injected through wells into the contaminated aquifer.
 - Intended to diffuse/flow with groundwater
 - Need to spread the iron
 - Goal → in-situ treatment of contaminants
- Contaminants are rapidly destroyed by oxidation-reduction reactions.
- With time, iron particles partially settle out and reactivity declines.

Conceptual Diagram of Nease Site Remedy



FS Analysis - Considerations

Types of contaminants and the ability of NZVI to treat the contaminants of concern

Ability to combine NZVI with other approaches for recalcitrant contaminants

Existing conditions

Site hydrogeology

Groundwater geochemistry

Source control

Underground injection requirements

Likely to be ARARs

Cost

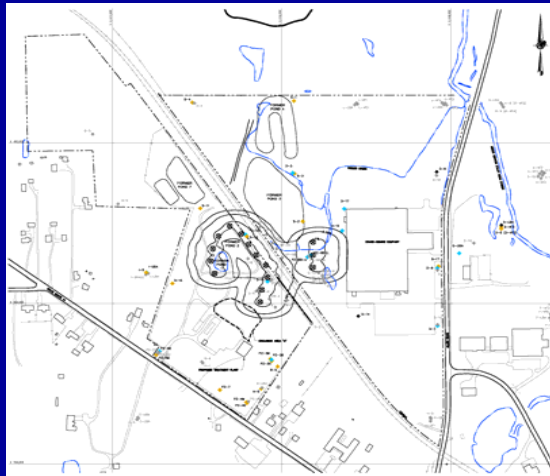
FS Analysis – Considerations (cont.)

- Estimate number of injection wells
 - Radius of influence of treatment zone to determine injection well spacing
 - Simple 2D modeling
- Estimate frequency and timing of injections
 - Calculate NZVI mass requirements
 - Simple stoichiometric calculations
 - Additional iron to account for waste
 - Rebound can occur as NZVI is used up
 - Addressed by multiple injections

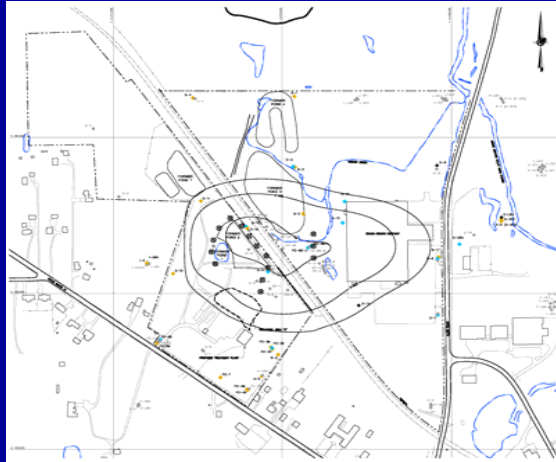
FS Projections - NZVI Area of Influence After a Few Days



FS Projections - NZVI Area of Influence After a Few Weeks



FS Projections - NZVI Area of Influence After a Few Months



Why NZVI at the Nease Site?

Contaminants – generally treatable

Chlorinated ethenes, ethanes

Favorable geochemical conditions

Low dissolved oxygen concentrations

Relatively low nitrate/nitrite and sulfate

Unfavorable conditions for other options

Fractured bedrock (favorable for NZVI)

DNAPL

Desire to maintain/enhance existing site conditions that support natural attenuation

Strongly reducing conditions created by NZVI

Favorable for anaerobic bacteria that may help degrade chemicals not treated by the Iron

Relatively low cost

Nease Chemical Site NZVI Treatability Study

NZVI Treatability Study

- NZVI treatability study is being conducted as part of the pre-design investigation
- NZVI study has two phases
 - Bench scale study
 - Field pilot test
- Final Remedial Design will be based on results
- Bench study started in July 2006
- Field pilot started in November 2006

Bench Scale Study

Bench Study - Objectives

- Assess effectiveness of NZVI for treatment of chlorinated VOCs
- Determine effects (if any) of NZVI on non-chlorinated VOCs
- Evaluate by-product generation
- Determine optimal formulation and dosage
- Evaluate site-specific geochemical influences on treatment effectiveness
- Determine the longevity of NZVI

Bench Study - Approach

Highly contaminated groundwater collected

Baseline analysis

Four different iron materials tested

Mechanically produced or chemically precipitated

With and without palladium catalyst

Jar tests for rate and effectiveness of a range of NZVI concentrations/formulations

0, 0.05, 0.1, 0.5, 1, 2, 5, and 10 g/L

Jar tests to assess the influence of site soils

Capacity tests → effectiveness of iron to treat re-contaminated samples

Bench Test Procedures



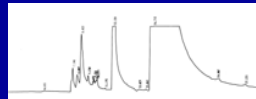
Water Samples
from the Site



Batch Reactors



Gas
Chromatograph



Before



After

Baseline Contaminant Levels

Contaminant	Result (ug/L)
Benzene	7,000
1,2-Dichlorobenzene	15,000
cis-1,2-Dichloroethene	11,000
trans-1,2-Dichloroethene	2,200 J
Methylene chloride	2,100 J
1,1,2,2-Tetrachloroethane	2,300 J
Tetrachloroethene (PCE)	82,000
Toluene	1,500 J
Trichloroethene (TCE)	21,000

Bench Study - Primary Results

Mechanically produced NZVI with 1% palladium at 2 g/L recommended formulation

Chemically produced iron showed slightly better performance than mechanically produced, but both were adequate

NZVI without palladium showed only partial treatment within 2 weeks

No chlorinated by-products were detected

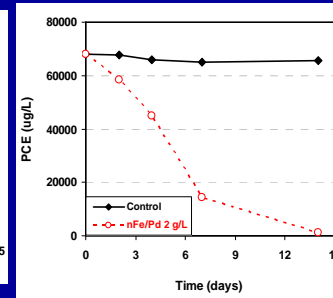
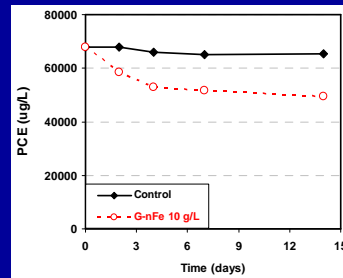
Benzene was not adequately treated and was produced as a by-product by reduction of 1,2-dichlorobenzene

Site soils did not seem to inhibit treatment

Bench test reductions within 2 weeks using mechanically produced NZVI with 1% palladium at 2 g/L.

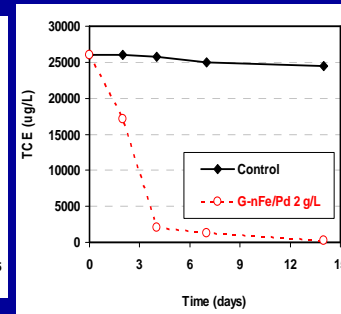
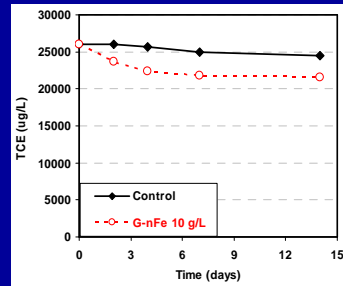
Contaminant	Reduction
PCE	98%
TCE	99%
cis-1,2-DCE	97%
trans-1,2-DCE	>99.9%
1,2-DCA	99%
1,2-Dichlorobenzene	"complete"

Nease Bench Test - PCE Degradation



10 g NanoFe or 2 g NanoFe/Pd per liter groundwater
Pd concentration was 1%wt
PCE initial concentration 68000 µg/L

Nease Bench Test - TCE Degradation



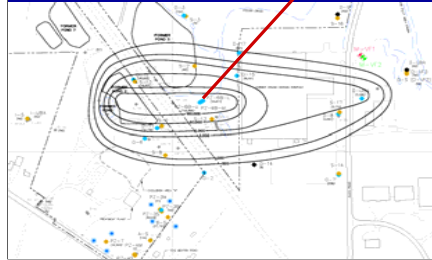
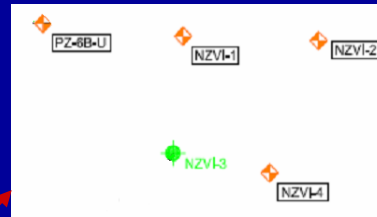
10 g NanoFe or 2 g NanoFe/Pd per liter groundwater
Pd concentration was 1%wt
TCE initial concentration 26000 $\mu\text{g/L}$

Field Pilot Test

Field Pilot Test - Objectives

- Verify laboratory results
- Evaluate treatment under field conditions
 - Confirm in-situ treatment effectiveness
 - Evaluate geochemical changes in the aquifer
- Support the remedial design
 - Evaluate rate of transport/dispersion of NZVI
 - Assess size of effective treatment zone

Study Area and Pilot Study Wells



Field Pilot Well Array



Additional Aquifer Testing

Slug tests performed on wells

Some wells in zones of lower hydraulic conductivity

Tracer testing was conducted using saline

Demonstrated interconnection of wells

Provided data on time for saline to reach wells and time for peak concentrations to be seen

Tests provided estimates of potential injection rates and volume

Resulted in a new well and the planned injection well was changed

Field Pilot Test – Approach

NZVI brought to site as parent slurry, mixed in batches

Parent slurry mixed with potable water to provide injected slurry

Injected concentration 10 g/L

Contained powdered soy (patent pending) as an organic dispersant
20% by weight of NZVI

Most batches contained palladium
1% by weight of NZVI

Last few injections were iron
without palladium



Mixing NZVI Injection Slurry



Field Pilot Test – Approach (cont.)

Injection of NZVI slurry

Injection well

Work plan: Planned to use PZ-6B-U

Actual: Used well NZVI-3

Injection rate

Work plan: Planned at 2 gpm or higher

Actual: 0.15 – 1.54 gpm

Injection time

Work plan: Planned over 3 – 4 days

Actual: Took about 22 days

– NZVI mass

Work plan: Planned to inject 100 kg (75% with palladium)

Actual: Injected 100 kg (~87% with palladium)

Injection volume

Work plan: Planned on 2,600 to 3,500 gallons of slurry

Actual: 2,665 gallons

Summary of NZVI Injections

Date	Injection Method	Injection Pressure (psi)	Average Injection Rate (gallons per minute (GPM))	NZVVPd (KG)	NZVI (KG)	NZVI Slurry (gallons)
11/28/2006	Gravity w/ pumping - open system	NA	0.6	5		132
11/29/2006	Gravity w/ pumping - open system ¹	NA	0.9	6		159
11/30/2006	Gravity w/ pumping - open system ²	NA	0.5	1.5		40
12/1/2006	Gravity w/ pumping - open system ³	NA	<0.5	3		79
12/4/2006	Gravity - open system ⁴	NA	1.25	1.9		50
12/5/2006	Gravity - open system ⁵	NA	0.3	3.4		90
12/6/2006	Gravity - closed system ⁶	4	1	1.9		50
12/7/2006	Gravity - closed system ⁷	NA	0.46	2.6		70
12/8/2006	Pressure Injection - closed system	11	2	4.5		120
12/9/2006	Pressure Injection - closed system ⁸	8	1.54	6.4		170
12/10/2006	Pressure Injection - closed system ⁹	8	1.5	1.1		30
12/11/2006	Pressure Injection - closed system ¹⁰	6	0.77	6.4		170
12/12/2006	Pressure Injection - closed system ¹¹	5 to 19	0.6	4.3		115
12/13/2006	Pressure Injection - closed system	5 to 25	0.7	5.5		145
12/14/2006	Pressure Injection - closed system ¹²	17	0.36	4.9		130
12/15/2006	Gravity - closed system ¹³ (over night)	NA	0.07	2.07		55
12/15/2006	Pressure Injection - closed system ¹⁴	17	0.44	4.54		120
12/16/2006	Pressure Injection - closed system ¹⁵	17-10	0.15	1.89		50
12/18/2006	Pressure Injection - closed system ¹⁶	3-10	1.3	3		80
12/19/2006	Pressure Injection - closed system ¹⁷	7-12	0.95	11.72		310
12/20/2006	Pressure Injection - closed system	10	0.73	5.67		150
		14	0.60		2.27	60
12/21/2006	Pressure Injection - closed system	14	0.69		10.96	290
TOTAL				87.4	13.2	2,665

NZVI Injection



Pressure injection system allows for injection under pressure in a closed system.



Field Pilot Test – Monitoring

Downhole electronic dataloggers

Continuously

Geochemical parameters – conductivity, pH, ORP,
DO, temperature, potentiometric head

Baseline chemical monitoring

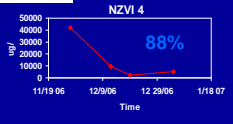
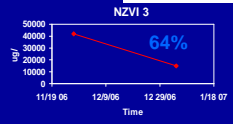
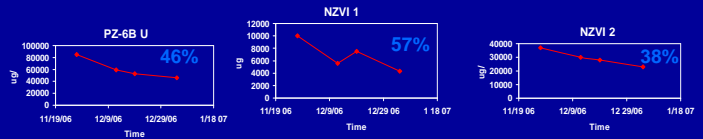
Post-injection chemical monitoring

1, 2, 4, 8, and 12 weeks post-injection planned

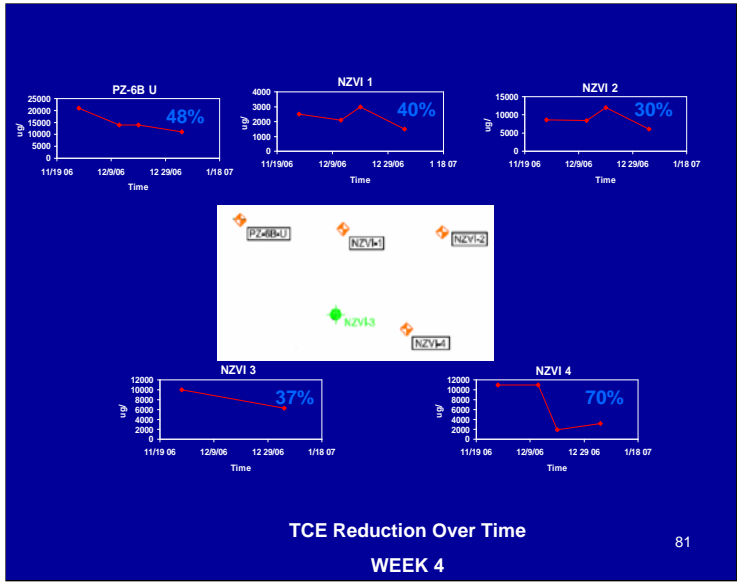
1 week" sample taken about 14 days after injections
started

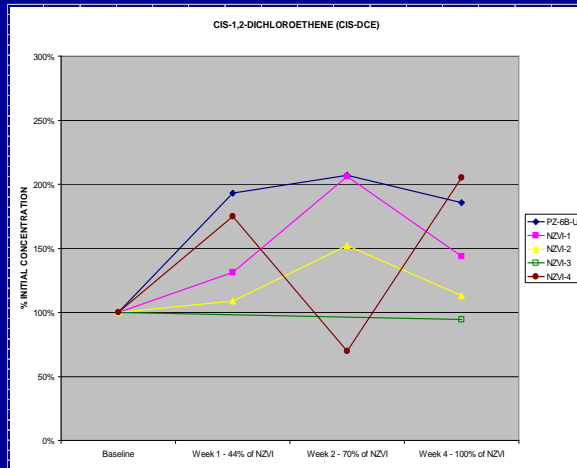
VOCs all sample events

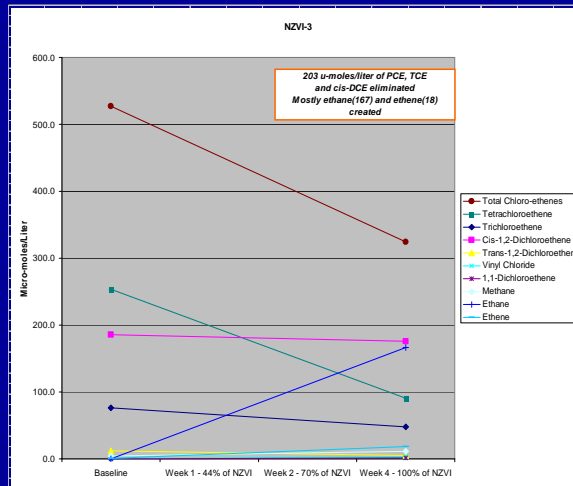
SVOCs and natural attenuation parameters –
select sample events

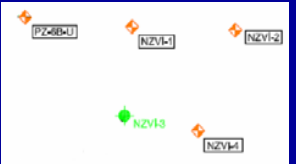
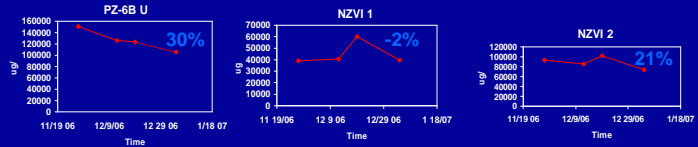


PCE Reduction Over Time
WEEK 4









VOC Reduction Over Time
WEEK 4

Field Pilot - Preliminary Results

DISCLAIMER: All data is not available and
results are just being assessed

Promising results!

Downhole dataloggers showed that all wells
were being influenced

Injection well "best" for overall VOC reduction

NZVI-4 "best" for PCE and TCE reduction

Closest downgradient

cis-DCE produced

Need to track breakdown over time

End breakdown products observed

Next Steps

- Complete analysis of monitoring data
- Work on enhanced biological treatment
- Remedial design
 - Number of injection wells?
 - Well placement?
 - Frequency and timing of injections?
 - NZVI mass requirements?
 - With or without palladium?
 - Use of organic dispersant?
- Construct and implement full-scale system

Nease Site - NZVI Information

- Technical memorandum – later in 2007
 - Results of all tests
 - Recommendations for full scale use
 - Lessons learned
- On the internet
 - <http://www.epa.gov/region5/sites/nease/>
- Contact me:
 - (312) 886-4699
 - logan.mary@epa.gov

Questions/Comments

Thank You

After viewing the links to additional resources,
please complete our online feedback form.

Thank You

[Links to Additional Resources](#)