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Field scale Remediation Experience using Iron Nanoparticles and Evolving Risk-Benefit Understanding

Sponsored by: U.S. EPA Technology Innovation and Field Services Division and Contaminated Land: Applications in Real Environments (CL:AIRE)

Delivered: December 14, 2010, 10:00 AM - 12:15 PM, EST (15:00-17:15 GMT)

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Visit the Clean Up Information Network online at www.cluin.org

Although I'm sure that some of you have these rules memorized from previous CLU-IN events, let's run through them quickly for our new participants.

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You should note that throughout the seminar, we will ask for your feedback. You do not need to wait for Q&A breaks to ask questions or provide comments. To submit comments/questions and report technical problems, please use the ? Icon at the top of your screen. You can move forward/backward in the slides by using the single arrow buttons (left moves back 1 slide, right moves advances 1 slide). The double arrowed buttons will take you to 1st and last slides respectively. You may also advance to any slide using the numbered links that appear on the left side of your screen. The button with a house icon will take you back to main seminar page which displays our agenda, speaker information, links to the slides and additional resources. Lastly, the button with a computer disc can be used to download and save today's presentation materials.

With that, please move to slide 3.

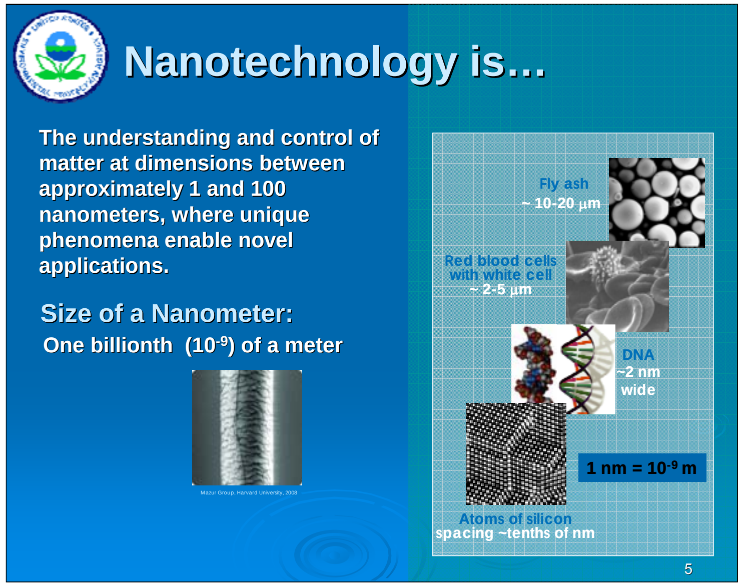
Use of Nanoscale Zero-Valent Iron for Site Remediation

December 14, 2010

Martha Otto
Technology Innovation and Field Services Division
Office of Superfund Remediation and Technology Innovation
U.S. Environmental Protection Agency
Washington, D.C.

Outline

- Background
- Overview of the Technology
- Benefits and Limitations
- Extent of Use
- Outreach/Programs/Projects
- Needs/Next Steps



Double helix is about 2 nm wide

What is Nanotechnology?

Nanotechnology is the science of the very small and involves the manipulation of matter at the atomic or molecular levels. A nanometer is 100,000 times thinner than a strand of hair.

Nanotechnology has three important aspects: size, structure and resulting novel properties.

Estimated Number of Sites and Cleanup Costs

2004 - 2033

Program	Sites/Properties	Cleanup Cost
Superfund Remedial	1,146 – 1,926	$41 - 103 B
RCRA Corrective Action	3,829	$31 - 58 B
Underground Storage Tanks	215,827-395,827	$27 – 49 B
Department of Defense	6,199	$31 B
Department of Energy	5,000	$73 B
Civilian Agencies	3,000	$15 – 22 B
States & Private	150,000	$ 30 B
Total Range *Middle Value*	385,001-565,781 *475,000*	$248 – 366 B *$302 B*

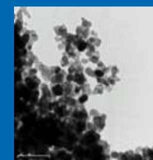
Groundwater Contamination Challenges

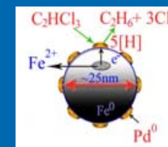
- Contaminated groundwater is a major problem.
- Pump and treat has been traditional remedy
  - Of the 725 pump and treat Superfund remedial projects, few have met clean up goals.
  - Can be costly and time-consuming.
- We are getting better, but remediation remains a challenge, especially for some sites with Dense Nonaqueous Phase Liquids (DNAPL) (e.g., TCE, PCE).

Nanoscale Zero-Valent Iron

Wei-xian Zhang, Lehigh

(ES&T, March 2006)





- ***In situ*** **applications include the use of nanoscale zero-valent iron (nZVI) particles to address groundwater contamination**
- **Reductive dechlorination – most important reaction mechanisms**
  - -**Beta elimination**
  - -**Hydrogenolysis**

Potential Benefits of Iron Nanoparticles

- Small particle size (100-200 nm)
- High surface area to weight ratio
- Highly reactive
- Direct injection into aquifers
- Faster cleanups/potentially lower cost
- Degrades multiple contaminants
  - Chlorinated hydrocarbons (e.g.,trichloroethene, trichloroethane)
  - Pesticides
  - Metals
  - Inorganic anions

Wei-Xian Zhang, Lehigh University

nZVI - Limitations

- Geologic conditions
  - Soil matrix composition
  - Hydraulic properties of the aquifer
  - Depth to groundwater
  - Geochemical properties
- Concentration of contaminants
- Challenge to monitor the distribution of the injected nanoparticles
- Issues of potential toxicity and safety

Potential Implications

Fate and Transport

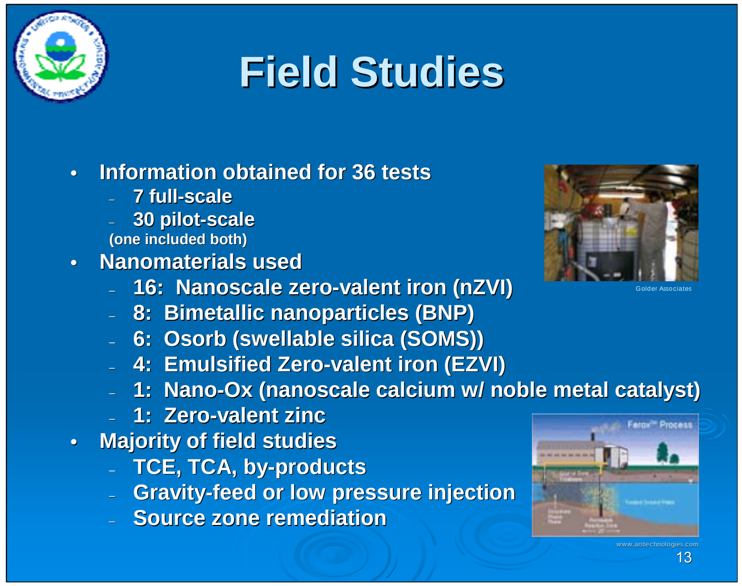
- Possibility of nanoclusters carrying sorbed contaminants (Gilbert, 2007)
- Surface modification of nZVI particles improve stability and increase mobility (Lin, 2010)

Toxicity

- Inhalation exposures to nZVI lead to reactive oxidative stress (Keenan, 2008)
- Mammalian nerve cells experience oxidative stress, although fresh nZVI >"aged" nZVI>surface-modified nZVI (Phenrat, 2008)
- Surface modification significantly reduces toxicity of nZVI to E. coli (Li, 2010)

nZVI: Improvements

- Use pressurized injection
- Modify particle surface to improve stability and mobility and to decrease toxicity
- Encase nanoparticles
  - Emulsified oil
  - Swellable silica or carbon
- Create nanomaterials *in situ*
- Form a “soft curtain” permeable reactive barrier

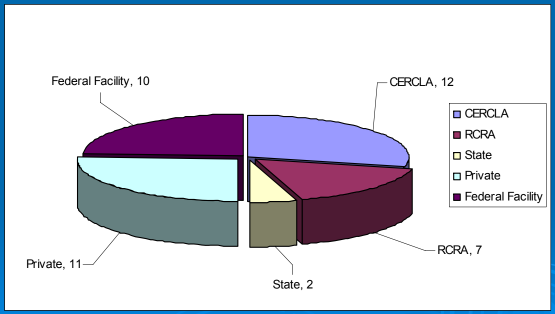


•Data has been collected on sites currently using or testing nanoparticles for environmental remediation as well as sites that are preparing to use or test the use of nanoparticles.

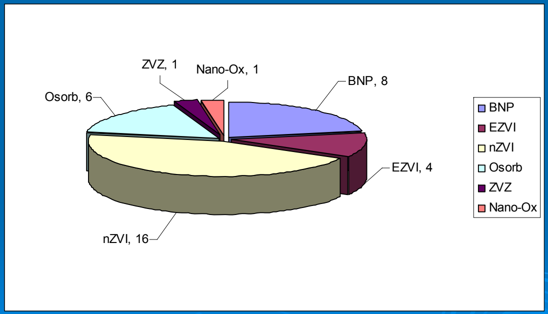
•Some of the full-scale sites include:

- •Naval Air Engineering Station, Lakehurst, NJ
- •Naval Air Station, Jacksonville, FL
- •Patrick AFB, FL
- •Cape Canaveral Air Force Station Launch Complex 15, FL

Type of Site,
36 Field Tests



Nanomaterial Type, 36 Field Tests



Tuboscope Site, BP/Prudhoe Bay North Slope, AK

BP Tuboscope Site

- Cleaned pipes used in oil well construction from 1978 to 1982
- Contaminants
  - Trichloroethane (TCA)
  - Diesel fuel, lead
- Max conc TCA before treatment = >58 mg/L
- Pilot scale using bimetallic nanoparticles
- Shallow test
  - 0 – 4 feet bgs, physical mixing
  - TCA reduction 60%
- Deep test
  - 0 – 7.5 feet bgs, pressurized injection
  - TCA reduction up to 90%

Emulsified Zero-Valent Iron

Jacqueline Quinn, NASA

Launch Complex 15

- Cape Canaveral, FL
- Abandoned space launch complex
- Full scale
- Initial TCE concentrations as high as 439 mg/L
- Post treatment dropped to 0.028 mg/L
- Currently in long term performance monitoring, evaluating impacts to plume post source reduction

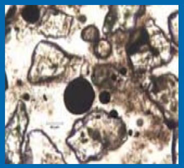
Industrial site on Patrick Air Force Base, FL

- Full scale
- High-pressure pneumatic injection
- Initial TCE concentrations were 150 mg/L
- Post treatment, highest concentrations were 3.58 mg/L

Hangar K, Cape Canaveral, FL

Soil Core Samples

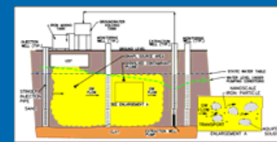
Jacqueline Quinn, NASA



Soil core sample

U.S. Navy NZVI Field Tests

- **Tests at Navy Superfund sites**
  - NAES Lakehurst, NJ
  - NAS Jacksonville, FL
  - Hunters Point, CA



USNavy, Jacksonville project

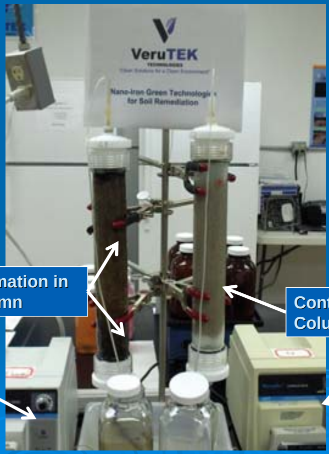
- **Navy's Conclusions**
  - nZVI is a promising technology for source zone treatment
  - Inject sufficient iron to create strongly reducing environment, which is essential for success
  - Take care to not deactivate nZVI during storage or mixing
  - Short-term performance monitoring can be misleading. Long-term monitoring of treatment zone until ORP levels have returned to pre-treatment levels is essential.


USNavy, Lakehurst

- <u>Cost and Performance Report: Nanoscale Zero-Valent Iron Technologies for Source Remediation</u>

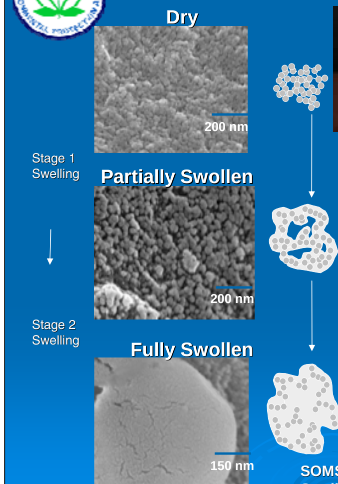
  available on http://www.clu-in.org

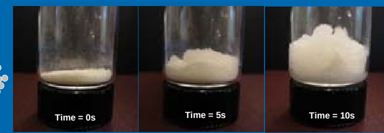
In Situ Formation of Nanoparticle Zero Valent Iron in Soils with Lemon Balm Extract and $Fe(NO_3)_3$



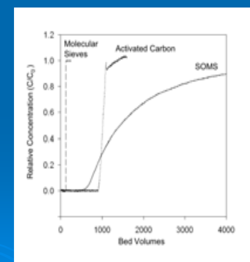
Slide courtesy of Rajender S. Varma, USEPA

SOMS: Nano-Engineered Organosilica





Breakthrough curve, Toluene in water:
Swellable Organically Modified Silica (SOMS)

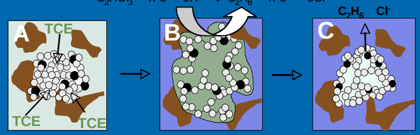


SOMS absorbs all small molecule organics from water
Swelling is completely reversible (organic sponge)

SOMS: Dehalogenation of TCE in Groundwater

Synthesis can accommodate incorporation of nano zero-valent iron (nanoZVI) into the expandable SOMS matrix.

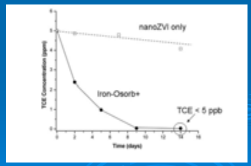
$$C_2HCl_3 + 4Fe^0 + 5H^+ \rightarrow C_2H_6 + 4Fe^{2+} + 3Cl^-$$



○ = crosslinked organosilicaparticle ● = nanoZVI

Advantages:

1. Matrix absorbs large amounts of TCE.
2. Iron is sequestered preventing deactivation.
3. Intermediates (ex. vinyl chloride) retained until complete dechlorination is achieved.



Slides on SOMS prepared by Dr. Paul L. Edmiston
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www.absmaterials.com
Patented Organosilica material.

References:

Chemistry of Materials, 20, 1312-1321, (2008).
Separation and Purification Technology, in press (2009).

Outreach/Programs/Products

- EPA CLU-IN website (cleanup information website, http://clu-in.org/)
  - Fact sheet on nanotechnology for site remediation and information on field test sites
    http://clu-in.org/542f08009
  - Technology focus area on nanotechnology applications for site remediation
    http://clu-in.org/nano
  - Internet Seminars on Nanotechnology and Superfund
    http://clu-in.org/training
- Karn,B., Kuiken T., Otto, M. 2009. Nanotechnology and *In Situ* Remediation: A Review of the Benefits and Potential Risks. Environmental Health Perspectives 117 (12): 1823-1831.

New Technology Focus Area

Needs/Next Steps

- **Research**
  - Technology Implementation
    - Improving the nanomaterials (stability, mobility, reactivity, reducing toxicity by design)
    - Fine-tuning the field application
  - Toxicology
    - Potential health and environmental effects
    - Potential effects on soil microbial populations
  - Fate, Transport, Transformation
    - Detecting nanoparticles in environmental media
    - Determining concentration of nanoparticles
    - Measuring valence state of iron
    - Measuring distance travelled in groundwater
- **Outreach**
  - Providing technical support to field offices
  - Documenting cost and performance of the technology

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For More Information

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nZVI Field Application Case Studies in the U.S.

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Geosyntec Consultants, UNC-Chapel Hill

Field-Scale Iron Nanoparticle Remediation Experience and Evolving Risk Benefit Understanding

USEPA CLU-IN Webinar

14 December 2010

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Outline

i. Introduction to field-scale use of nZVI
ii. Overview of the case study
iii. A decade of nZVI injections in NJ
iv. Field-scale implications and issues
v. Final thoughts

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i. nZVI from lab to field

- Significant experience with demonstrating that the chemistry works
  - Amenable reductates: CAHs, oxidized Me^{x+}, pesticides, Cl & NO_2-aromatics, ClO_4^-, etc.
- Lab success may not follow in field
  - Batch study complexity << field conditions
  - Mixing differences and contact
- Scaling-up and benchmarking difficult
  - Variability in site conditions and nZVI
  - Very costly to rigorously assess performance

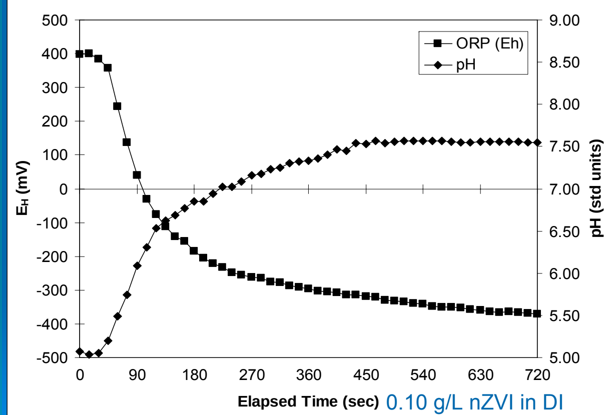
i. Drivers for nZVI in remediation

- Multiple delivery options/broad efficacy:
  - Injection of nZVI slurries through MW and DPT technology
  - Diffuse CAH plumes in GW & DNAPL zones
  - Immobilization of redox-sensitive metals
- Technology synergies:
  - Profound water chemistry impacts

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$$

  - Anaerobic biodegradation and nZVI

i. Profound water chemistry impacts



0.10 g/L nZVI in DI

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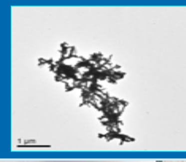
i. Perspectives on nZVI



- Rapid evolution of technology
  - Developed at Lehigh in 1996
  - 1st field deployment in 2000
  - Burgeoning interest in academia, industry, regulators
- Attributes
  - Enhanced reactivity
  - Target hot-spot areas & tough reductates
- nZVI vendor developments
  - 2000 = None
  - 2010 = Many, worldwide
  - Various manufacturing methods

i. Variety of iron nanoparticles

- Bare nZVI
- Bimetallics (Fe/Pd, etc.)
- Supported nZVI
  - Carbon or polymeric bead substrate
- Emulsified ZVI (eZVI)
  - nZVI or mZVI within emulsified oil micelles
- Surface-modified nZVI
  - Surfactant/polymer-based surface architectures

ii. Case study site overview

- Manufacturing site in Trenton, NJ
  - Active since 1937
  - Springs, appliances, HVAC equipment
- RI began 1990
  - Multiple interim remedial measures
- Soils and groundwater impact
  - Well-characterized TCE plume
  - Ongoing reductive dechlorination
- NJDEP case team very involved
  - Meetings, submittal of benchscale study & nZVI data, permit-by-rule for injection

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ii. Objectives

- Field efficacy
  - Works in the lab but…
  - Degradation products?
  - Mobility in the subsurface?
- Enhance ongoing NA processes
  - Lower TCE & E_H, Increase $Fe^{2+,3+}$
  - Drive anaerobic biodegradation processes
- Role of nZVI in site remediation strategy
  - Evaluation of different injection techniques
  - Cost-effectiveness

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iii. Overview of treatment areas

- Two key areas of site:
  - DGC-15 & AOC-3
- DGC-15:
  - Downgrad of bldg & mfg areas, NW corner
  - DGC-12, DGC-15, MW-18
- AOC-3:
  - Former 5,000-gal TCE AST, upgrad of bldg
  - DGC-9, DGC-9D, MW-28

iii. Aerial view of site – Trenton, NJ

iii. Three nZVI injection campaigns

- June-Aug 2000
  - 1st field demonstration of technology
  - Small-scale injections, proof-of-concept
- June-Nov 2003
  - Utilization of supported nZVI
  - Demonstrated efficacy of larger-scale injection
- May-Dec 2007
  - Surface-modified nZVI
  - Large-scale injection (500 lbs) under building

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iii. Pre-injection conditions

- Key contaminants: TCE & daughters
- Surficial aquifer impacted
  - Silty sands & clays, saprolite above bedrock (35 ft bgs)
- Key hydrogeological parameters:
  - K ~10^{-2} m/s, i ~0.01, v ~0.3-3 m/d
- Field parameters (DGC-15, AOC-3):
  - D.O. ~0-2 mg/L; ORP ~+200 mV; pH ~4.5-5.5
- Chloroethenes (DGC-15, AOC-3):
  - TCE ~400-600 μg/L; c-DCE ~200 μg/L; VC ~10 μg/L
  - TCE ~200-300 μg/L; c-DCE ~50 μg/L; VC ~1-10 μg/L

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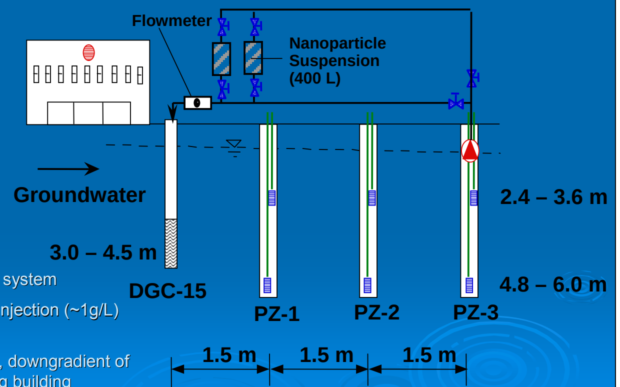
iii. DGC-15 area schematic (2000, 2003)



Recirculation system

Gravity feed injection (~1g/L) nZVI slurry

Within plume, downgradient of manufacturing building

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iv. nZVI injection underway (2000)

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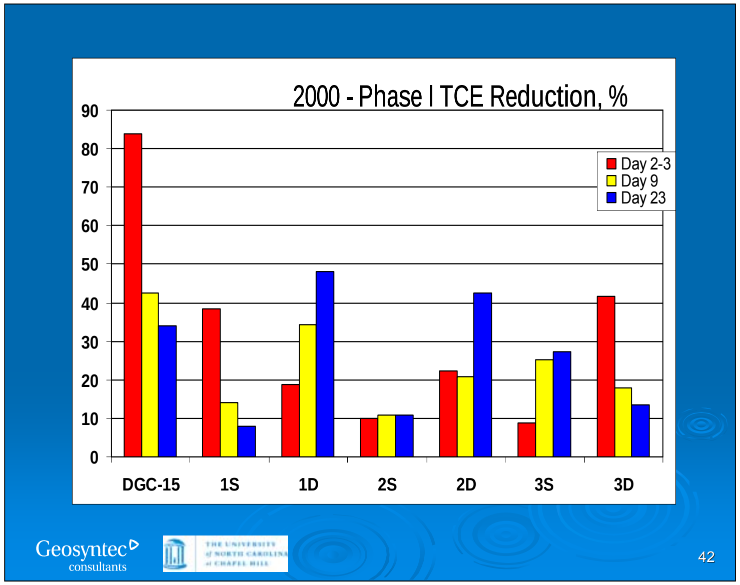
2000 - Phase I TCE Reduction, %
90
80
70
60
50
40
30
20
10
0
Day 2-3
Day 9
Day 23
DGC-15
1S
1D
2S
2D
3S
3D
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iii. 2007 Geoprobe injection strategy

- Two approaches:
  - (1) Wells INJ-1 & INJ-2 & (2) DPT (Geoprobe)
- Geoprobe 6610 used to inject 300 lbs iron
  - Sodium polymethacrylate (Na^{+}PMA) stabilized
  - 2-150 gal poly tanks containing ~20 g/L nZVI slurry
  - Formation water from INJ-1 used to dilute nZVI
- DPT injection strategy
  - 2 transects of borings
  - 3 depth intervals: 8-12, 14-16, 23-25 ft bgs
  - Approx 20-25 lbs nZVI per boring, some “double-shots”
  - 8-12 ft depth interval very low permeability

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iii. Infrastructure for Geoprobe injection

iii. 2007 nZVI injection results

- Within Area 3, significant redox chemistry Δ
  - ORP: ~ +200 mV to -300 mV
  - pH: ~0.5 to 1 std unit increase
- Boring B-7 (middle of test area)

Injection	TCE (μg/L)	c-DCE (μg/L)	t-DCE (μg/L)
Pre	220	45	ND
Post (6 months)	145	10	10

- nZVI reducing TCE, 2^0 bio more important?
- Effects of surface-modification
  - nZVI traveled >30 ft, evident in cores beneath bldg
  - Potentially some loss of reactivity, too much Na^+PMA?

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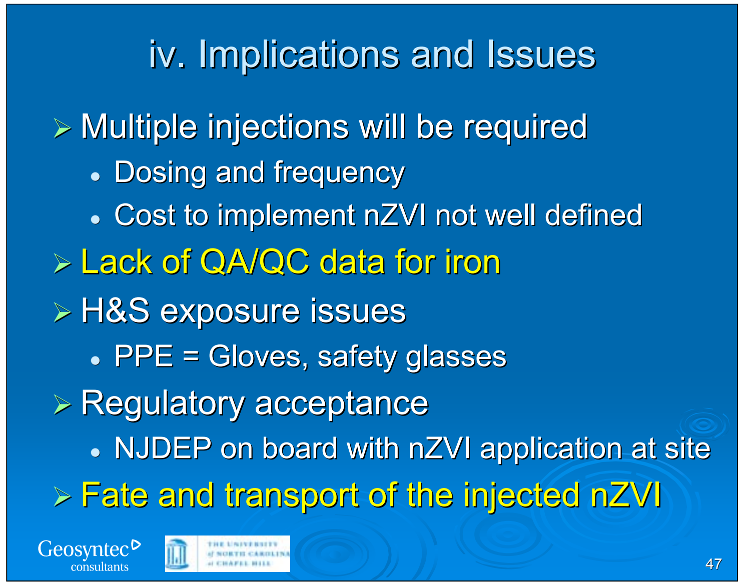
iii. Longer-term look at DGC-15 & AOC-3

- 2010 data (basis 2000)

	TCE	% Red	c-DCE	% Red	VC	% Red
DGC-15	220	45-60	170	15	15	-50
AOC-3	100	55	30	33	<1 (ND)	0

- Difficult to interpret results
  - Contaminant trends are decreasing
  - Overlapping attenuation mechanisms
  - Activity of iron?


iv. Implications and Issues
Multiple injections will be required
Dosing and frequency
Cost to implement nZVI not well defined
Lack of QA/QC data for iron
H&S exposure issues
PPE = Gloves, safety glasses
Regulatory acceptance
NJDEP on board with nZVI application at site
Fate and transport of the injected nZVI
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iv. nZV QA/QC – major data gaps

- Documentation provided = MSDS
  - Info focuses on safety not efficacy
- How do you know if the nZVI is still active?
  - Minimal product lifecycle analyses
  - Variable mfg methods and storage periods
- What performance or quality data is needed from vendor?

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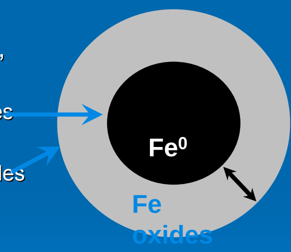
iv. Potential QA/QC parameters

- "Born on date" & storage method
- pH/ORP profile
- Particle size distribution (PSD)
- Specific surface area (SSA)
- Zeta potential (ζ) & Isoelectric point (IEP)
- Batch reactivity test

QA/QC should be low cost, rapid, and easy to develop

iv. Environmental fate considerations

- Rapid aggregation of nZVI
- Core-shell structure
- Fe^0 core shrinks over time, oxide shell grows
  - Magnetite (Fe_3O_4) rich oxides → Fe in +2.67 ox. state
  - Maghemite (Fe_2O_3) rich oxides → Fe in +3 ox. state
- Iron oxides removed by aquifer media
  - Activity 0.5-1 yr or longer?



e^- transfer across oxide shell

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v. Major considerations

- Performance vs. cost
  - Typically 5-20 g/L but how many rounds? Frequency?
  - Effect of non-target reductates (water, e-acceptors, etc.) when treating relatively dilute contaminant plumes
  - ~$30/lb vs. ~$1-10/lb for mZVI
- Delivery issues
  - Reasonable hydrogeology
  - Injection well(s), recirc. loops, transects of borings
- Interpretation of post-injection data
  - Complicated & overlapping attenuation mechanisms
- Proximity of receptors
  - Exposure issues: VI, off-site considerations, GW discharge areas
- Amenability of regulators

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v. Final thoughts

- nZVI a useful complementary remedial technology
- Major hurdle limiting growth is lack of robust cost-effectiveness data
- Environmental fate of nZVI likely a lesser concern in comparison to worker exposure

Thanks! Any questions?

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Field scale application, case studies from the EU (CZR)

Kvapil Petr, Černík Miroslav
(Lacinová L., Nosek J., Zbořil R.,)

Presentation objectives

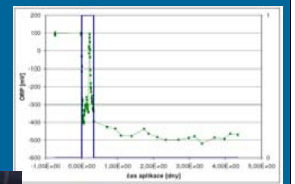
To start discussion about:

- the risk management problem being addressed,
- the practical delivery and use of the technology,
- the regulatory approval process,
- the project outcomes and ongoing monitoring.
- the risks versus the benefits of iron nano-particle use for remediation.

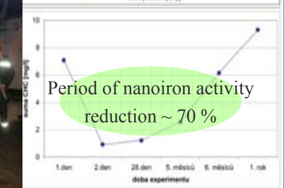
History of nanoiron (nZVI) in ČR

- First application of nZVI in ČR – in 2004

•Spolchemie
•source - Zhang
•GOLDER Assoc.
•Laboratory tests
•Field tests

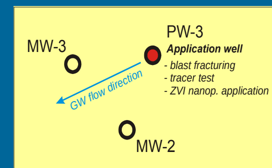


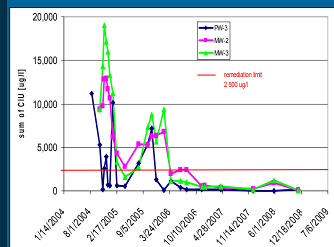
•ORP decrease
•pH increase
•CHC decrease
6 months



Kurivody site – first successfull

- 2005
- FRACTURED BEDROCK FLOW
- Tracer test
- Blast fracturing
- Low final concentrations
- No rebound





Zhang´s nZVI

Nanoiron applications - overview

Site	Contam.	Lab/pilot/ Remed.	Type of nZVI
Spolchemie 2004	Cl-Ethenes	L,P	ZHANG
Kuřívody 2005, 2006	Cl-Ethenes	L,P	ZHANG, RNIP
Piešťany 2005	Cl-Ethenes	L,P	ZHANG
Permon 2006	Cr6+	L,P	RNIP
Rožmitál 2007 – 2010	***PCB***	***L,P***	***RNIP, NANOFER***
Hluk 2007, 2008 (PRB)	Cl-Ethenes	L,P	RNIP, NANOFER
Hořice 2008, 2009	***Cl-Ethenes***	***L, P, R***	***RNIP, NANOFER***
Uherský Brod 2008	Cl-Ethenes	P	NANOFER
Písečná 2008, 2009	***Cl-E, Cl-A***	***L, P, R***	***RNIP, NANOFER***
Spolchemie 2010	***Cl-E, Cl-M***	***L, P, R***	***NANOFER***

Laboratory: AOX, U, As, nitrobenzene, acid mine waters, other CHC

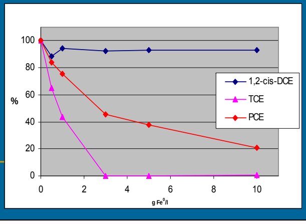
Steps to FULL-SCALE

- Feasibility approval - laboratory test
  - Concentration test
  - Kinetic test
- Regulatory approval process in CZR
- Feasibility approval - field pilot test
  - Geological & hydrogeological descriptions
  - Tracer tests
  - Applications of nanoiron
- Full scale

Feasibility - Laboratory tests

Aim: Feasibility approval

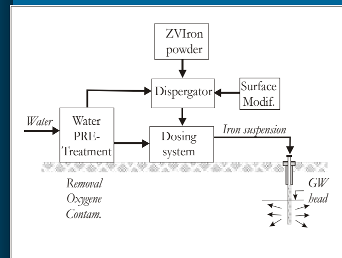
- description: Batch tests:
  system nanoparticles x water x soil
- 2 phases:
  - 1. phase – verification of efficient concentration
  - 2. phase – verification of reaction rate



Nano-iron project regullations

- NZVI injections regulated by WATER law
  - „Ussualy“ Exception for irregular matters injection
- Subject to decision of regional authorities
- Ussualy field pilot test required
- Usually the iron is more easily accepted than soluble materials (oxidants or reductants)

Field system – from 2009



- Dry powder stored and brought to the site
- Reduced surface oxidation by Oxygen (pretreatment)

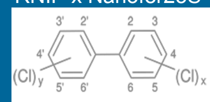
•Advantage of initial high reactivity
•Mobility and reactivity control

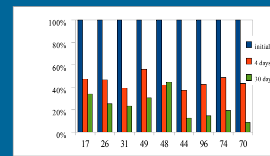
Case #1: PCB – Rozmital p.T.

- 20 years of hydraulic barrier
- Former tarmacadam plant, DELOR 103
- Recently contaminated soil waste deposit
- Iron is feasible, but only nanoscale is efficient
- No exception from Water law needed for this site

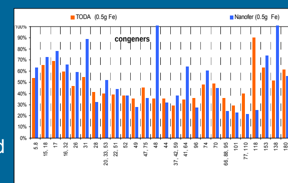
Case #1: PCB – Rozmital p.T.

- Laboratory experiments
  - kinetics for 4, 10, 30, 60 days
  - concentration dependency
- Indicative congeners x all
- RNIP x Nanofer25S



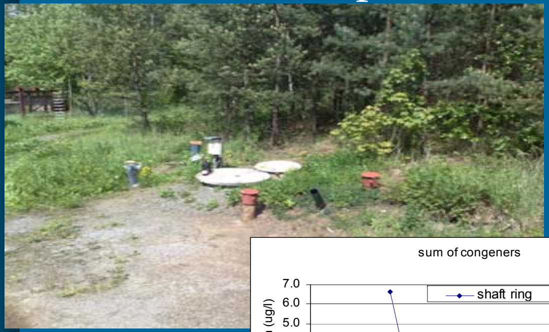


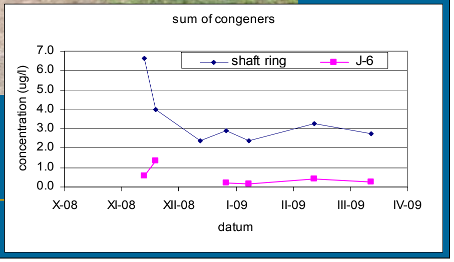
Kinetics: Nanofer25 – indicative congeners



•Significant decrease after 4 days
•NanoFe active during whole period
•TODA x Nanofer similar
•Lower efficiency for more chlorinated
•Sorption questions?

Case #1: PCB – pilot test

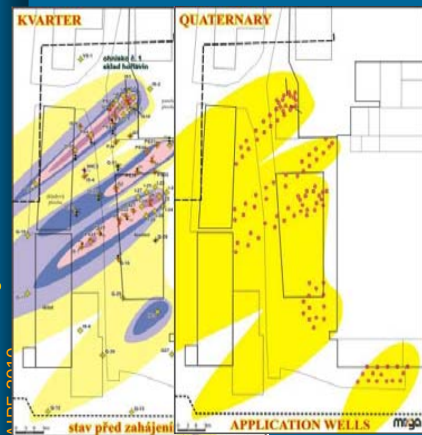




Case #2 – Horice

- Provided by MEGA and TUL
- Tested nanoiron vs. Lactates
- During first stages nanoiron more efficient, later simillar efficiency
- Decission of client to use nanoiron, no toxic intermediate degradation product observed.
- No Water law exception needed for this site

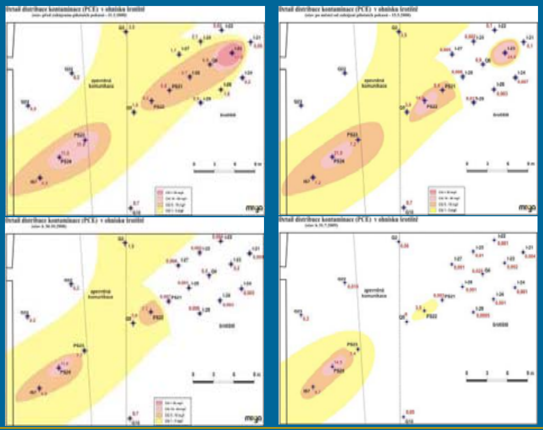
Case #2 – Horice – full scale



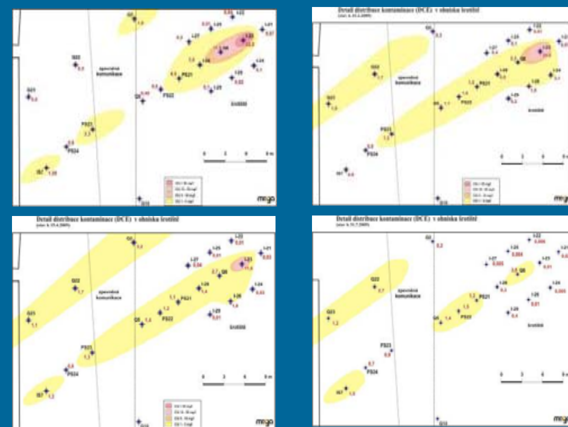
- PCE, TCE, DCE, 70 mg/l
- 120 x 60 m
- I.stage (11/2008)
- 82 injection wells
- depth 10 m
- 300 kg nZVI
- II.stage
- 300 kg nZVI (11/2009)

aquatest

Case #2 – Horice - PCE: ini, 3m, 6m



Case #2 – Horice - DCE: ini, 3m, 6m 9m



Case #2 – Horice – I. stage econ

Direct push well network
– 80 w x 10 m x 40€ = 32 k€

nanoFe
- 300 kg x 5 x 23€ = 35 k€

Other (water, electricity, management)
- 30 k€

Monitoring (not part of remediation)
- 100 k€

TOTAL = 200 k€

II. Stage = 100 k€ (shared monitoring)

Case #3: Pisecna site

- Former dangerous waste landfill
- Fractured – bedrock area
- CLE and CLA contamination
- Drinking water sources in the neighbourhood
- High reactivity needed for TCA degradation
- No exception from Water law needed

Case #3 – Pisecna Comparative lab-tests

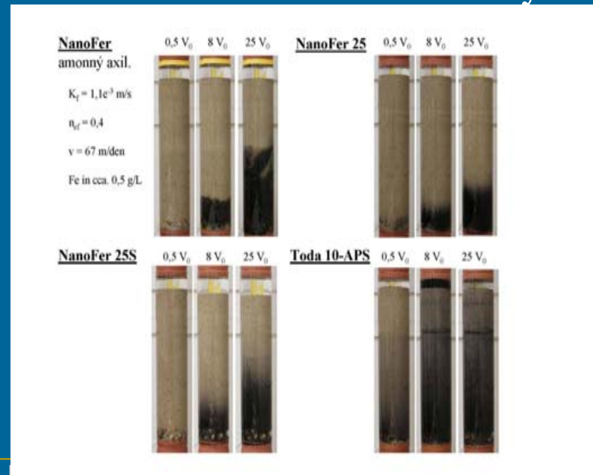
Comparative test for 5 nZVI types:

- prepared by Zhang (2003)
- RNIP (Toda)
- NANOFER 25 – without surfactant
- NANOFER 25S – modifyed by TWEEN
- NANOFER …– modifyed by axilate

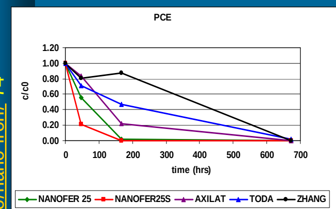
Tested properties:

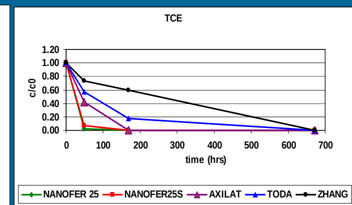
- aggregation - DLS
- sedimentation – column tests
- mobility - column tests
- reactivity – kinetic tests, various nZVI concentration
  3 real ground water
  2 artifficaly mixed water

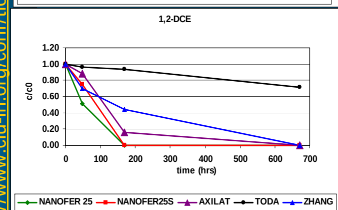
Case #3 – Pisecna – mobility tests

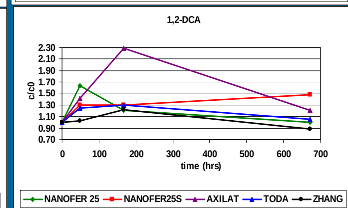


Case #3 – Pisecna – reactivity tests





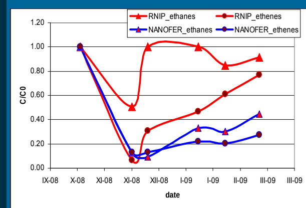




aquatest

Case #3 – Pisecna – pilot application

- RNIP x NANOFER25
- Geological conditions not equal
- CHC concentrations similar
- Cl-Ethenes O.K. both (o)
- Cl-Ethanes TODA worse (Δ)

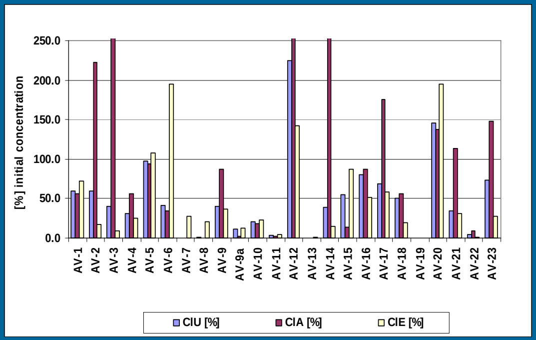


Case #3 – Pisecna – full-scale

- Pretreatment of technological water
  - Contaminant removal
  - Oxygen removal
- Preparation nZVI slurry:
  - 1000 kg dry powder iron NANOFER25N (containers in N_2 atmosphere)
  - diluting by field slurry dispergator to 5000 kg of 20% suspension of nZVI NANOFER 25 and NANOFER 25S
  - On-site
- Semi-automatic dosing system

Case #3 – Pisecna – Full
em

Case #3 – Pisecna – full-scale results in application wells



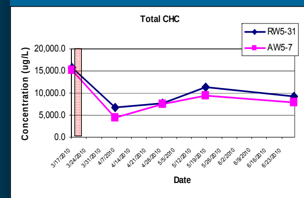
Case #3 – Pisecna – economics

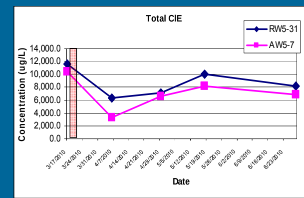
- Estim. contaminants = 1 ton
- Contam. Area = 2000 m3
- Depth of contam.= 20 -35 mbs
- nZVI plan = 1.3 tons
- Number of wells = 30
- Duration = 1 test + 2 full a.
- cost: nZVI = 140 k€
  - Wells = 60 k€
  - Other = 40 k€
  - Monitoring = 120 K€
- TOTAL = 360 K€

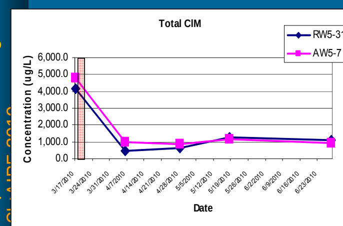
Case #4 – Spolchemie

- Exception from Water law needed
- Exploited cellars in contaminated area
- CLE and CLM contamination
- Clay, sand, gravel aquifer
- Chemical factory

Case #4 – Spolchemie - Pilot







30 kg of pure iron injected
6 months period of monitoring

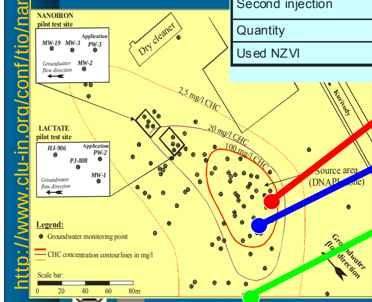
Reduction CHC – 30 – 40%
Reduction CIE – 20 – 30%
Reduction CIM – 70 – 80%

Case #4 – Spolchemie – full scale

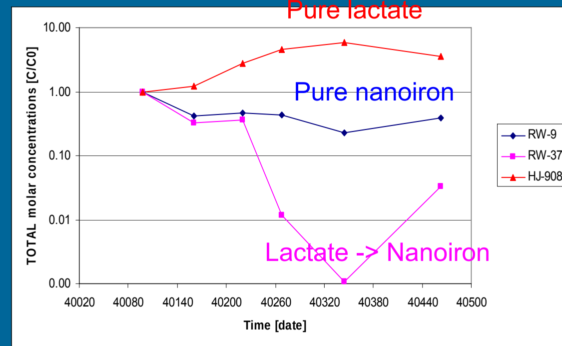
Full scale:
- 10 direct pushed wells
- 3 rotary drilled wells
- 3-12m bgs
- 1000 kg of pure iron
- In 2-3 injection steps
- 3 years

Case #5 – Combination – NZVI - lactate

Well	HJ-908	RW-9	RW-37
Contaminant composition	PCE (100%)	PCE (30%), TCE (26%), DCE (39%)	c-DCE (82%), VC (16%)
First injection	Lactic acid (2009)	NZVI (2009)	Lactic acid (2008)
Quantity	200 kg	50 kg	200 kg
Injected concentration	0,5%	0,2%	0,2%
Second injection	Lactic acid (2010)	Lactic acid (2010)	NZVI (2009)
Quantity	200 kg	200 kg	30 kg
Used NZVI	----	NANOFER 25S	NANOFER 25S



Case #5 - combination



Perspectives of nanoiron

- For contaminations types where high reactivity is needed (for ex. PCB)
- For sites where presence of toxic intermediates (VC) is hazardous (also buildings and cellars)
- In the proximity of used cellars or underground facilities (where also the bad smell is undesirable)
- In the proximity of water sources, the iron is not much soluble, the Iron will not harm the quality of water (bad smell, black color).
- To enhance remediation proceess started by other technologies.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Hálkova 6, Liberec
Thanks for your attention

Golder Associates nZVI Experience

Similarities and Contrasts Between Field-scale Applications in the United States, Canada, and Europe

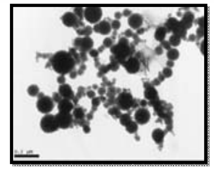
Golder Associates

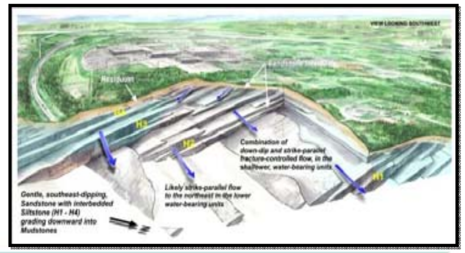
INTRODUCTION

- Keys to Success Based on Golder's Global nZVI Experience
- Creating a Positive Global Perception of the Technology
- Golder's Global Academic Network
- Summary of Golder Projects
- Case Studies and Commentary
  - United States
  - Canada
  - Germany
  - United Kingdom

KEYS TO SUCCESS

- Well-developed Conceptual Site Model
- ZVI Material and Additive Selection
- Regulatory Acceptance
- Reactivity
- Deliverability
- Treatment Longevity





MANAGING GLOBAL EXPECTATIONS

FACT	FICTION	WHY?
60 – 80% dechlorination in one (1) year	100% dechlorination in hours	bench scale, thorough mixing, good contact
Estimated zones of influence	nZVI travels indefinitely with groundwater	Flocculation, settling, interaction of oxide with aquifer
nZVI is a nano size material at production, not in subsurface	nZVI is a "true" nano-material	no change in electronic properties, flocculation occurs rapidly in subsurface

GOLDER'S ACADEMIC NETWORK

- **United States**
  - Lehigh University
  - Carnegie Mellon University
  - Oregon University of Health Sciences
- **Canada**
  - McGill University
  - University of Calgary
- **Europe**
  - Polytechnic University of Turin (Italy)
  - Queen's University Belfast (Northern Ireland)
  - University of Redding (United Kingdom)
  - University of Leipzig (Germany)
  - Technical University of Denmark
  - University of Venice (Italy)

SUMMARY OF GOLDER PROJECTS

By the numbers…

- 23 Locations World-Wide
  - 14 in US (61%)
  - 6 in Europe (26%)
  - 2 in Canada (9%)
  - 1 in Caribbean (4%)
- 19 Chlorinated ethene Sites (83%)
- 2 PCB Sites (9%)
- 1 Chlorinated Methane and Ethane Site (4%)
- 1 Chromium Site (4%)
- nZVI Materials
  - Mechanically crushed (78%)
  - Well-head precipitated nZVI (18%)
  - Laboratory precipitated (4%)

Site Information	[illegible]	[illegible]	[illegible]	[illegible]
Pharmaceutical Facility	Res			3-2005 florin@golder.com
Manufacturing/Research Facility	Res			and Florin Gheorghiu +1 856-793-2005
Nease Chemical				) and Florin Gheorghiu +1 856-793-2005
Brownfield				173 akane@golder.com
Industrial Plant				173 akane@golder.com
Industrial Plant				50 jpaul@golder.com
Brownfield				893 cpaul@golder.com
Former Chemical Storage Facility				-2005 hlin@golder.com
Industrial Plant				893 dley@golder.com
Lake Lucina Cleaners				430 kbaltz@golder.com
Adams Cleaners				430 kbaltz@golder.com
Town-N-Country Cleaners				430 kbaltz@golder.com
Touch of Quality Cleaners				430 kbaltz@golder.com
Malnove / Potlatch				430 kbaltz@golder.com
Valcartier Garrison				285 SHains@golder.com
Industrial Plant				3-2005 florin@golder.com
Solvent Manufacturing Plant				39 (348) 450 0375 QUATEST a.s., Czech @tul.cz
Industrial Plant				39 (348) 450 0375 QUATEST a.s., Czech @tul.cz
Industrial Plant				89614 jbruns@golder.com
Industrial Plant				39 (348) 450 0375
Brownfield	Slovakia	Unconsolidated sediments	TCE, DCE	39 (348) 450 0375 mpupeza@golder.com; Miroslav Cerník (AQUATEST a.s., Czech Republic), Miroslav.Cernik@tul.cz

December 14, 2010

Golder Associates

United States

Golder Associates Inc.

Bedrock nZVI Injection using Hydraulic Fracturing
North Carolina, USA

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Florin Gheorghiu, PG, CPG, Golder Associates +1 856-793-2005
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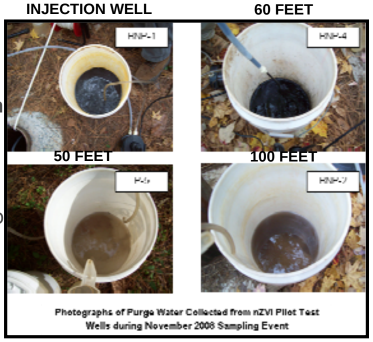
PROJECT SUMMARY - NORTH CAROLINA

- **Well-developed CSM**
  - cVOCs in fractured bedrock, heterogeneous distribution of hydraulic K-values
- **Material and Additive Selection**
  - Golder nZVI, Pd, Soy Protein
- **Reactivity**
  - Significant cVOCs treatment, >160,000 ppb to <20,000 ppb
- **Deliverability**
  - Hydraulic fracturing to connect low-K areas with high-K areas
- **Treatment Longevity**
  - Not evaluated during pilot-scale



Photographs of Purge Water Collected from nZVI Pilot Test Wells during November 2008 Sampling Event

Canada

Golder Associates Ltd.

Injection of nZVI in Permeable Unconsolidated Sediments, Quebec, Canada

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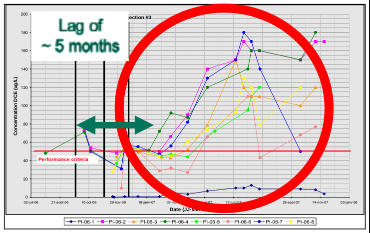
Denis Millette, Golder Associates Ltd. + 1 514-383-0990 Dmillette@golder.com

PROJECT SUMMARY - QUEBEC

- **Well-developed CSM**
  - cVOCs in high transmissivity glacial outwash sand aquifer
- **Material and Additive Selection**
  - Golder nZVI, Soy Protein
- **Reactivity**
  - Significant cVOCs treatment, TCE from >400 ppb to <5 ppb
- **Deliverability**
  - Pressurized injection and GW recirculation
- **Treatment Longevity**
  - >2 years, conversion to enhanced bioremediation observed



Golder Associates

Germany

Golder Associates GmbH

Helmholtz Zentrum für Umweltforschung

UFZ Joint Research Project (FE-NANOSIT)

For additional information contact:

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and
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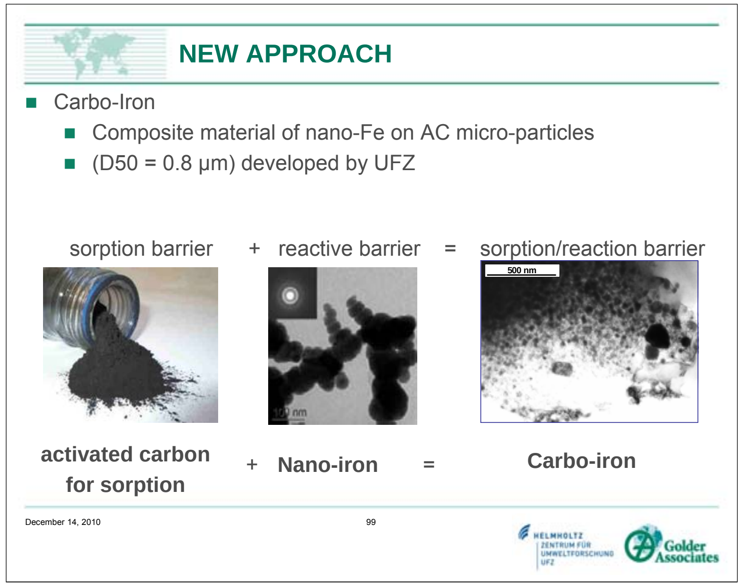
RESEARCH PROJECT IN GERMANY

- Golder Associates GmbH & Helmholtz Zentrum für Umweltforschung UFZ: Application for a joint research project (FE-NANOSIT)
- Lab investigation and field application
- Financing: BMBF (German Federal Ministry of Research and Technology)
- Start: May 2010, duration: 3 years



They use activated carbon which is the most widely used sorbent in environmental technology. Here is, what they do: Step 1 - They grind down AC to particle sizes of about 1µm and found that those particles form stable colloidal suspensions. That means they have a quasi soluble injectable strong sorption material. Step 2 – They decided to give the activated carbon additional reactivity by deposition of zero-valent iron on the carrier particles.

Right from the start we wanted an injectable material for the formation of sorption barriers. The first experiments were done with soluble humic substances. But their sorption potential and the way they form sorption layers was not really satisfactory. Therefore, we started to think about taking activated carbon which is the most widely used sorbent in environmental technology. Activated carbon had just one drawback: it is not soluble. How can it become injectable? We tried to grind down to particle sizes of about 1µm and found that those particles form stable colloidal suspensions. That means we now have a quasi soluble injectable strong sorption material. Mobility testes and barrier formation went very well, so that we decided in a second project to give the activated carbon additional reactivity by deposition of zero-valent iron on the carrier particles.

With Carbo-Iron a new remediation strategy can be followed – the *in situ* generation of a permeable sorption/reaction barrier in contaminated aquifers.

United Kingdom

Golder Associates (UK) Ltd.

Current Regulatory Issues in the UK

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CURRENT UK STATUS

- Policy
- defra Funded Research
  - What will it deliver?
  - When will it be available?
- The Way Forward
  - Further Research?
  - Bench-scale Trials?
  - Pilot-scale Trials?
  - Timeframes?
- REACH considerations

Golder Associates

WHAT'S ON THE HORIZON FOR nZVI

- Advances in "green" dispersants
- Continuing research on toxicity
- Enhancing deliverability with injection technologies, Electro-Kinetics
- New iron materials, particle sizes, mixtures of iron

- **CLOSING**
  - nZVI is *not* a remedial panacea
  - Must be applied after careful development of CSM, proper remedial technology screening, material and additive selection, emplacement technology, etc.
  - nZVI research and implementation community must help to alleviate regulatory concerns based on sound science

Golder Associates

Initial view on the benefits vs. the risks of nano-scale iron use for *in situ* remediation

Paul Bardos, r3 Environmental Technology Ltd, UK
John Henstock, CL:AIRE, UK

CL:AIRE

Contents

- Project Introduction
- Benefits of using Iron Nanoparticles
- Risks of using Iron Nanoparticles
- Provisional Conclusions for Discussion

"A Risk/Benefit Approach to the Application of Iron Nanoparticles for the Remediation of Contaminated Sites in the Environment"

- Project funded by UK Government's *Department of Environment, Food and Rural Affairs* (Defra)
- 6 Month Project
- Literature based investigation to identify and outline the risk/benefits of the use of iron nanoparticles
- Revaluate recommendations from 'precautionary approach' advocated in 2004 paper*, for release of nanoparticles into the environment
- Will provide a pre-application list for key controls (policy tool)
- Report due Spring 2011

**Royal Society and Royal Academy of Engineering 'Nanosciences and Nanotechnologies' report (2004)*

Project Team

- CL:AIRE (UK)
- r3 Environmental Technology (UK)
- The University of Nottingham (UK)
- Geosyntec (USA)
- Deltares (NL)

CL:AIRE

The University of Nottingham

UNITED KINGDOM · CHINA · MALAYSIA

Geosyntec consultants

Deltares Enabling Delta Life

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Benefits

- Extending the range of treatable contaminants
- Gap between lab and field scale proven treatable contaminants
- Source Term Treatments
- Majority of nZVI field applications for pathway management / plume treatment
- Effectiveness of Contaminant Removal

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Benefits

- Efficiency of treatment
- Ease of Use (in situ)
- Applications
- Longevity of Action
- Wider Benefits

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Risks

- Perceived Risks
- Why is nano considered to be so different?
- Fate of iron nanoparticles in the environment

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Risks

- Toxicology
- Ecotoxicology
- Potential for Human Exposure
- Future Research Needs

Provisional Conclusions

- Niche benefits/conditions for operation
  - Recalcitrant contaminants, particularly chlorinated solvents
  - Plume management
  - Where quick reactions are highly desired
- Not a substantive step-change over what has been previously available?
- Anecdotal view that transporting the iron sufficient distance in its non-passivated form to contact the contaminant, is the greater issue than risk of uncontrolled migration to pose health risks.
- Anecdotal view that risks of nano-iron use in the environment unlikely to prove unacceptable

Provisional Conclusions 2

- The technical evidence base appears insufficient for some key stakeholders to support the release of nano-iron particles into the environment
  - Pre-cautionary approach favoured by corporate clients and regulators alike, while better understanding of health risks formulated
  - Notoriously difficult to adequately monitor both the nano-iron fate and the decontamination effects
  - Relatively expensive whilst absence of consensus on efficacy is well documented nor uniformly understood (‘over-engineering’ necessary to prove)
  - Aside from with chlorinated solvents, a gap exists for other contaminants between ‘promising’ lab results which aren’t being proven/tested in the field.

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Provisional Conclusions 3

- "Research Essentials" or "Optional Reassurance": is it presently justified to invest large sums of money on evidence gaps such as animal toxicity, special detection methods for iron NPs in the environment?
- A good first step might be to use expert elicitation workshop(s)
  - structured workshops to explore expert views of 'best case' and 'worst-case' risk scenarios, and model probabilistically how "bad" the worst case is.

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Voluntary Iron Nanoparticle Register

As part of the webinar we have set up a 'Voluntary Register to record Field-applications of Iron Nanoparticles', which is designed to capture industry use of iron nanoparticle deployments, so that volunteered case studies can be used in US EPA's development work and for inclusion in the UK Governments' 2011 report publication: "A risk benefit approach to the application of iron nanoparticles for the remediation of contaminated sites in the environment".

We particularly welcome recent examples not yet well represented in the academic literature.

Please ensure you are permitted to post information on this temporary register. http://www.surveymonkey.com/s/nanoiron

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Thank you

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Resources & Feedback

- To view a complete list of resources for this seminar, please visit the **Additional Resources**
- Please complete the **Feedback Form** to help ensure events like this are offered in the future

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