Utilization of Zero-Valent Iron nanoparticles (nZVI) for in-situ groundwater remediation including recent field scale application and remediation experience

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Applications of Nanotechnology for Safe and Sustainable Environmental Remediations
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Presentation outline

• Introduction: nZVI products & characteristic
• nZVI processing and application
• Technology implementation
• Field groundwater remediation experiences
• Conclusions
NANO IRON, s.r.o. established in 2008
Zero-Valent Iron nanoparticles (nZVI) industrial production in large quantities
Worldwide distribution
Technical support
Technology development
Scientific research
PRODUCTS CHARACTERISTICS

- Average particle size: 50nm
- Narrow particle size distribution: 20-100nm
- Average surface area: 20-25m$^2$/g

BET adsorption-desorption isotherms
XRD pattern
Mössbauer spectrum
PRODUCTS

nZVI powder

NANOFER 25P

stabilization

NANOFER STAR

dispersing

slurry

NANOFER 25

modification

NANOFER 25S

modification

User modified product (EZVI, ...)

www.nanoiron.cz
NANOFER 25P dry nanopowder

- Product composition (weight):
  - 80-90% of nZVI
  - 20-10% of iron oxides

- No degradation (unlimited storage time)
- Highest reactivity (high efficiency)
- Cheaper shipping (comparing to slurry)
- No waste production (reusable packaging)
- Dangerous classified (UN 1383 - pyrophoric)
- Refused from plane transportation

NANOFER 25P certified packaging according to international ADR/RID and IMDG standard
Pyrophoric properties

**IMPORTANT NOTICE**

**Pyrophoric DOES MEAN** the powder ignites spontaneously in air = rapid oxidation of Fe(0) in case of nZVI

**Pyrophoric DOES NOT MEAN** the powder is explosive, calling nZVI explosive is wrong interpretation!

- Pyrophoric substance can be handled safely in atmospheres of argon or nitrogen.
- Pyrophoric properties of nZVI = rapid oxidation of Fe(0):
  - \( 4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + \text{heat} \)
  - *nZVI powder is stored in certified packaging and processed in dispersing unit under protective atmosphere in order to prevent undesirable transformation of Fe(0) to Fe\(_2\)O\(_3\)*
NANOFER STAR dry nanopowder

FeO (wustite) stabilized nZVI

• Product composition (weight):
  – 60-80% of nZVI
  – 40-20% of iron oxides

• Product is:
  – Surface stabilized
  – Transportable
  – Air-stable
  – Reactive

<table>
<thead>
<tr>
<th>No degradation (unlimited storage time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High reactivity (comparable to NANOFER 25P)</td>
</tr>
<tr>
<td>Even cheaper shipping (comparing to NANOFER 25P)</td>
</tr>
<tr>
<td>Air stability</td>
</tr>
</tbody>
</table>

Dangerous classified (UN 3089 - flammable)

Lower amount of nZVI (comparing to NANOFER 25P)
NANOFER STAR dry nanopowder

effect of shell thickness

TCE 35 mg/L (40 mL)
15 mg nZVI
analyzed by GC
nZVI SLURRY MANUFACTURING
from dry nano-powder

Schematic principle

Industrial Dispersing unit

The technology prevents spontaneous release of dry nanoparticles to the environment
NANOFER 25S slurry (liquid)
in-situ groundwater remediation product

• Product composition (weight):
  – 20% of solid nanoparticles
  – 80% of water including stabilizer

Direct application after dilution
No special processing technology required
Fast express shipping (samples, low volumes)
Improved migration

Aging (degradation)
Expensive shipping (high volumes)

REACTIVITY
with contaminants (reaction time)

STABILITY
before application (lifetime)

MIGRATION
in aquifer (mobility)

NANOFER 25S
NANOFER 25
DISADVANTAGES of nZVI water slurry products

- Extreme reactivity of nanoparticles causes degradation (ageing) of the product in water environment during time.

  Risks esp. in case of large projects

Parameters affecting product degradation:
- Air oxygen
- Dissolved oxygen
- Temperature

### NANOFER 25S long-term degradation behavior

- Cooled sample (2-4°C)~(36-39°F)
- Room temperature sample (20-22°C)~(68-72°F)
nZVI TESTER
slurry quality measurement

- Simple, cheap and fast measurement of nZVI content
- Principle: measurement of hydrogen volume, which is evolving during chemical reaction of nZVI and an acid
- The method is comparable to Mössbauer spectroscopy and X-ray powder diffraction
nZVI delivery: large-scale projects

**Question:**
Why to ship 800g of water in each kilogram of the product (80% of the weight) by expensive express shipping, when water is available on site? And what about slurry storage?

**Answer:**
Slurry direct manufacturing from a dry nano-powder on site!
nZVI APPLICATION

matter of time

Conventional delivery and application process of nZVI

Innovative application process of nZVI
IN-LINE DILUTION
proportional dosing system

Automatic dosing unit
- Set required dosing (g/L)
- Proportional to water flow
- Slurry consumption depends on injection rate
- Easy to operate
- Autonomous
- Clean process comparing to manual dosing

II. Generation in development
- Includes water filtering and degassing
nZVI REMEDIATION CONCERNS

• Delivery and utilization of technology
• Implementation of technology
• Regulatory approval process
nZVI IMPLEMENTATION

- **LABORATORY EXPERIMENTS** – feasibility approval
  - Batch experiments: groundwater + soil + nZVI concentration
  - Concentration dependency (efficient concentration) in g/L
  - Kinetic (reaction rate)
  - Comparison of different products

- **REGULATORY APPROVAL**
  - Subjected to decision of local authority

- **FIELD PILOT STUDY**
  - Usually 100-500kg of NANOFER 25S

- **FULL SCALE REMEDIATION**
nZVI REMEDIATION EXPERIENCE
• Fur processing site
• Contamination: Chlorinated ethenes (PCE, TCE, DCE, VC) and chromium (Cr6+)
• Previous treatment: pump&treat, venting, vapor deposition, ISCO
KARA TRUTNOV
laboratory study

**ME-24: PCE**

**ME-24: Cr⁶⁺**

- **SOIL + 0 g/L nZVI**
- **SOIL + LACTATE + 0 g/L nZVI**
- **SOIL + 1 g/L nZVI**
KARA TRUTNOV
pilot injection

NANOFER 25S
- 200kg
- 2 injection wells

Results after 2 months

### Chemical composition of ground water - well ME-24

<table>
<thead>
<tr>
<th>parameter</th>
<th>unit</th>
<th>September 8\textsuperscript{th}</th>
<th>September 20\textsuperscript{th}</th>
<th>October 22\textsuperscript{nd}</th>
<th>October 31\textsuperscript{st}</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>6,94</td>
<td>8,58</td>
<td>7,98</td>
<td>7,87</td>
</tr>
<tr>
<td>Total chromium (Cr tot.)</td>
<td>mg/L</td>
<td>42,5</td>
<td>&lt;0,001</td>
<td>0,874</td>
<td>&lt;0,001</td>
</tr>
<tr>
<td>Hexavalent chromium (Cr\textsuperscript{6+})</td>
<td>mg/L</td>
<td>42,2</td>
<td>&lt;0,005</td>
<td>0,873</td>
<td>&lt;0,005</td>
</tr>
<tr>
<td>Vinylchloride (VC)</td>
<td>μg/L</td>
<td>278</td>
<td>70,4</td>
<td>&lt;4</td>
<td>&lt;4</td>
</tr>
<tr>
<td>trans-1,2-Dichlorethene (t-DCE)</td>
<td>μg/L</td>
<td>14,1</td>
<td>1,9</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>1,1-Dichlorethene (DCE)</td>
<td>μg/L</td>
<td>4,4</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>cis-1,2-Dichlorethene (c-DCE)</td>
<td>μg/L</td>
<td>2340</td>
<td>1060</td>
<td>3,1</td>
<td>18,9</td>
</tr>
<tr>
<td>Trichloroethene (TCE)</td>
<td>μg/L</td>
<td>642</td>
<td>92,4</td>
<td>1,64</td>
<td>&lt;0,50</td>
</tr>
<tr>
<td>Tetrachloroethene (PCE)</td>
<td>μg/L</td>
<td>903</td>
<td>62,6</td>
<td>3,77</td>
<td>&lt;0,50</td>
</tr>
<tr>
<td>sum of CHC including VC</td>
<td>μg/L</td>
<td>4182</td>
<td>1287</td>
<td>8,5</td>
<td>18,9</td>
</tr>
</tbody>
</table>

Notes:
- Concentrations below detection limit are marked as <0,001.
- The map shows the distribution of contaminants in the groundwater, with color coding indicating concentration levels.
KARA TRUTNOV
full-scale remediation

NANOFER 25S
• 2000kg - winter/2011
• 1800kg - spring/2012

DCE: 02/2012
DCE: 06/2012
KARA TRUTNOV
full-scale remediation – latest results 2013
• Former dangerous waste landfill, drinking water source in neighborhood
• Contamination: chlorinated ethanes and ethenes
• High reactivity of nZVI is needed for TCA degradation
• Fractured bedrock area
Degradation of CHC during time

Concentration (µg/L)

Hydrogeological wells

HW-12  HW-13  HW-5  HW-6  HW-7  HW-8  HW-9  TX-3

- CHC (before application)
- CHC (6 months after 1. application)
- CHC (3 months after 2. application)
- CHC (8 months after 2. application)
- CHC (3 months after 3. application)
• Former tarmacadam plant
• Contamination: DELOR 103 = PCB
• ZVI is feasible, but only nZVI is efficient
• Previous treatment: 20 years of hydraulic barrier
• Pilot injection of 100kg of nZVI
• Former Soviet military base – dry cleaner contamination
• Chlorinated hydrocarbons – mainly PCE; DNAPL
• 1990: first site investigation
• 1992-2004: pump&treat, venting
• 2004-2012: in-situ methods (ISCO, LACTATES, nZVI)
KUŘIVODY
LACTATES + nZVI combined method

<table>
<thead>
<tr>
<th>Well</th>
<th>HJ-908</th>
<th>RW-9</th>
<th>RW-37</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contaminants</td>
<td>PCE (100%)</td>
<td>PCE (30%)</td>
<td>c-DCE (82%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TCE (26%)</td>
<td>VC (16%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DCE (39%)</td>
<td></td>
</tr>
<tr>
<td>Quantity</td>
<td>200kg</td>
<td>50kg</td>
<td>200kg</td>
</tr>
<tr>
<td>Quantity</td>
<td>200kg</td>
<td>200kg</td>
<td>30kg</td>
</tr>
</tbody>
</table>

Legend:
- Groundwater monitoring point
- CHC concentration contourlines in mg/l
- Groundwater flow direction
- Scale bar: 0 20 40 60 80m

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KUŘIVODY
LACTATES + nZVI combined method

TOTAL molar concentrations [C/C₀]

Time [date]

Lactates
nZVI
Lactates + nZVI

RW-9
RW-37
HJ-908
HOŘICE (MEGA)

- Chlorinated hydrocarbons (PCE, TCE, DCE)
- Lactates vs. nZVI tested
- nZVI selected

no toxic intermediates observed
HOŘICE (MEGA)

Sum of CIU in turon

Before nZVI injection

December 31st 2011
SPOLCHEMIE

- Chemical factory
- Contamination: chlorinated methanes and ethenes
- Clay, sand, gravel aquifer
- 400kg of NANOFER 25P, on-site manufacturing
VCE, DCE and Cl-Eth in monitoring well HP-6 – PILOT INJECTION

Date: 09.12.2008

Application of nZVI (100kg)
OTHER SITES and STUDIES

- CHC Pilot injection in Netherlands (4 sites)
- CHC Pilot injection in Portugal
- CHC Pilot injection in USA
- Pesticides pilot injection (CZ)
- TNT laboratory study (Portugal)
- Mine tailings remediation (CAN, CZ)
- Wastewater treatment (selenium, arsenic, chromium, …)
- More than 20 tons of NANOFER 25S applied on various sites around Europe.
- Others: 350 free-samples of NANOFER products shipped worldwide in past years, 75 to USA and Canada, mainly to universities, research institutes and remediation companies.
COSTS

nZVI comparing to other products

• Application cost is important
  – Lower amount of nZVI is needed
  – Better mobility of nanoparticles = less injection wells
  – Faster application
  – Higher efficiency

All parameters affect remediation cost

Absolute cost of material ($/kg) is not representative

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SAFETY and TOXICITY

- Reduced contact with nanoparticles by using semiautomatic and automatic equipment.
- Iron oxides/hydroxides are final products after reaction of nZVI with water.
- Nanoscale zero-valent iron is not a new chemical substance, nanosize provides different physical properties to nanoparticles.
- US TSCA:
  - “Although a nanoscale substance that has the same molecular identity as a non-nanoscale substance listed on the Inventory differs in particle size and may differ in certain physical and/or chemical properties resulting from the difference in particle size, EPA considers the two forms to be the same chemical substance because they have the same molecular identity. The inventory listing in this case is considered to represent both the nanoscale and non-nanoscale forms of the substance and, as such, does not distinguish between two forms having the same molecular identity that differ only in particle size and/or physical/chemical properties resulting from difference in particle size.”

- ALS Laboratories Results: Toxicity towards water organisms – included in MSDS of NANOFERs.
- Dr. Keller: Toxicity of Nano-Zero Valent Iron to Freshwater and Marine Organisms
  (http://www.plosone.org/article/info%3Adoi%2F10.1371%2Fjournal.pone.0043983;jsessionid=15869797BB1E5D27B1CD84693AB8FEA0)
NANOREM (EU FP7 Project)

Nanotechnology solutions for in-situ soil and groundwater remediation NMP.2012.1.2-1
Project No: 309517
CONCLUSION

• nZVI works where others failed

• Product development
  – Air stable nZVI
  – nZVI based nanocomposites (Fe₃C-C having 80m²/g)
  – Combined methods (lactates, vegetable oil, …)
  – Ferrates (oxidation technology)

• DISPERSING TECHNOLOGY & IN-LINE DOSING
  – Unique technical solution for groundwater remediation polluted mainly by chlorinated hydrocarbons, hexavalent chromium and many other substances.
  – Fresh slurry ensures extraordinary reduction efficiency.
  – Processing of nZVI powder is safe, when operation and safety procedures are kept.
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- MEGA – RNDr. Jaroslav Hrabal at al.

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Thank you for your attention

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