# Nanoremediation – a Consultant‘s Perspective

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**NanoRem Final Conference**

**Nanoremediation for Soil and Groundwater Clean-up - Possibilities and Future Trends**

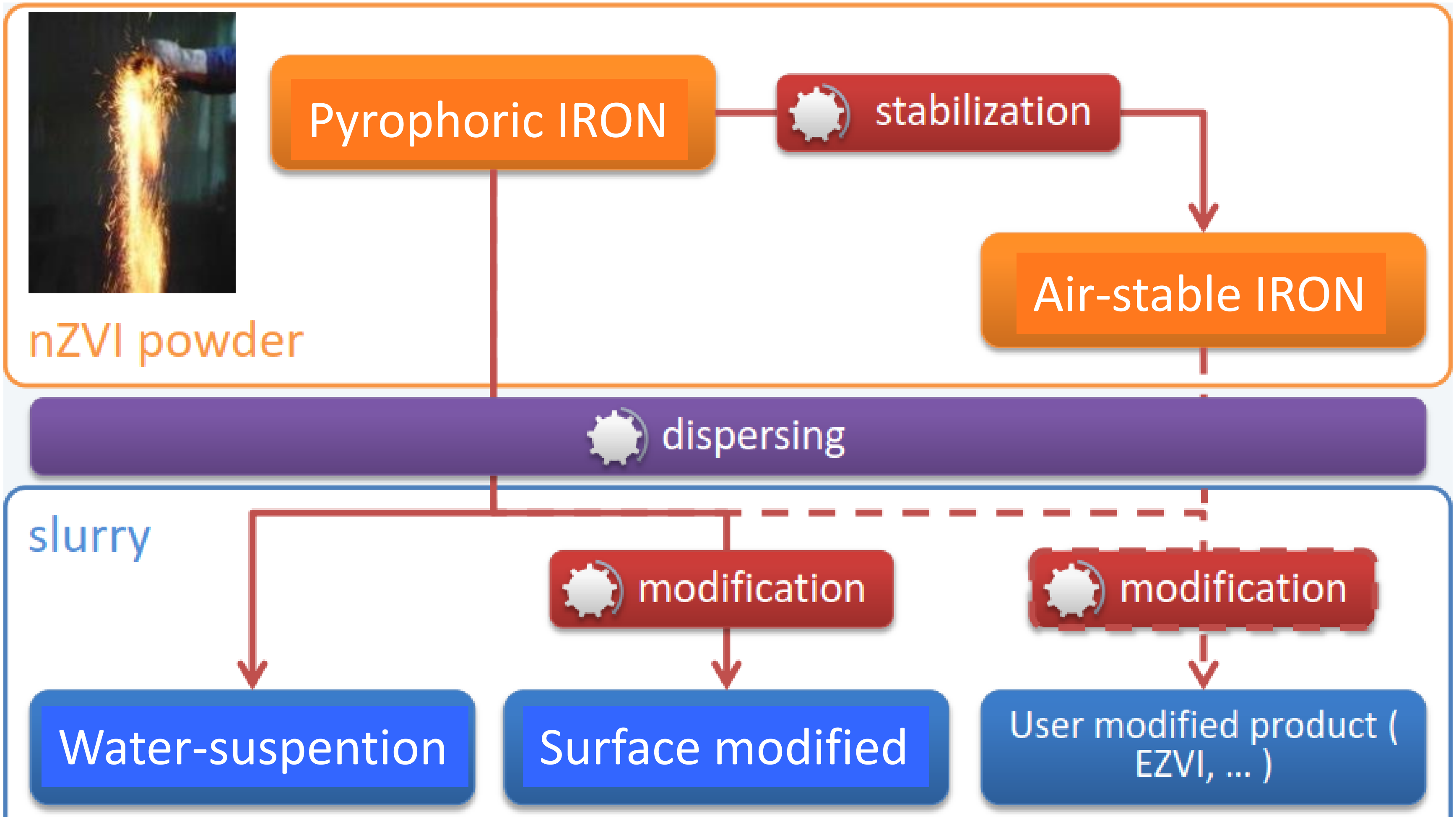
DECHEMA
Gesellschaft für Chemische Technik und Biotechnologie e.V.

Frankfurt am Main, 21st November 2016

# What does it mean NANOREMEDIATION? Consultant view

- IN-SITU remediation technology, where reactive substance is based on nanosized SOLID PHASE material (Nanoparticles, nanotubes, nanocomposites, nanofibres,……).
- where the nanomaterial was used as a part of principal technology or as a part of the treatment train.
- **Process limitations: material, application, monitoring, risks, costs**

# State of art of nano-„materials“ nZVI raw products and grades




*Source: NANOIRON l.t.d.*

# State of art of nano-„materials“ for remediation

- Many materials in different state of development at the market
- Only within NANOREM: nZVI (NANOFER, melted iron), iron oxides, carboiron
- Combined materials – EZVI, bimetallic iron, nano-micro and iron-C composites,

***Limitations – contact between reactive particle and contaminant, longevity of nanoparticles, material costs***

# State of art of nano-„application“ for remediation

- All in-situ injection methods feasible – vertical and horizontal wells or tranches, direct push, multiscreened well – packer injections)

***Limitations***

1. ***Contact between reactive particle and contaminant = > detailed contaminant investigation followed by targeted injection required***
2. ***Migration of particles – hydraulic gradient and induced water flow required***

# Nanoirom application / injection

# State of art of nano-„monitoring“ for remediation

- No cheap method for nanoparticle monitoring at low concentrations (risks)
- Relatively cheap methods for nanoparticle monitoring at high concentrations (magnetic susceptibility measurements, total iron, color) (remediation efficiency)

***Proved: migration at natural hydraulic gradient is negligible, good result when iron found in monitoring wells***

# State of art of nano-„risks“ for remediation

- **No significant toxic effect found**
- Where Nanoiron came from? – from iron oxides or nanooxides
- What happens with nanoiron in soil? – it becomes iron oxides or nanooxides

***Limitation: fear of unknown materials and related „usage“ regulation in certain EU and non EU countries***

- *precursor: ferrihydrite ($5Fe_2O_3.9H_2O$)*
- *mine Zlaté Hory, Oslavany*
- *size 2-6 nm, aggregates 150 nm*
- *Spec. surface 270 $m^2/g$*

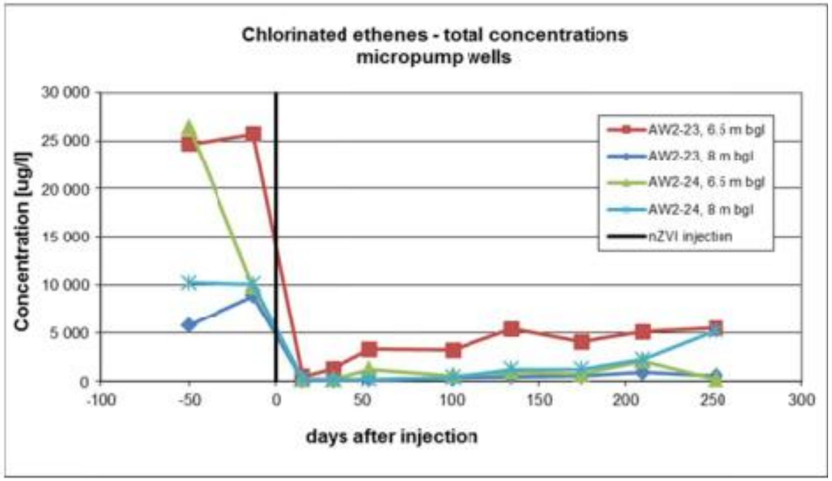
*source: Projekt Nano (PřF UPOL)*

# nZVI Efficiency: List of deployment (CZ.R.)

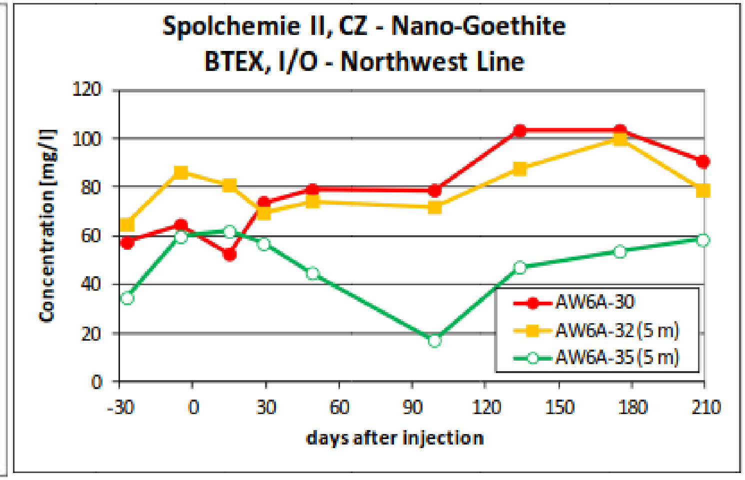
| Site | Contam. | Lab/pilot/ Remed. | | Type of nZVI |
|---|---|---|---|---|
| Spolchemie 2004 | Cl-Ethenes | L,P | | ZHANG |
| Kuřívody 2005, 2006, 2009 | Cl-Ethenes | L,P | ☺ | ZHANG, RNIP |
| Permon 2006 | Cr6+ | L,P | | RNIP |
| Rožmitál 2007 – 2010 | PCB | L,P | ☺ | RNIP, NANOFER |
| Hluk 2007, 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, 2014 - 2017 | Cl-E, Cl-A | L, P, R | ☺ | RNIP, NANOFER |
| Františkovy lázně 2014 | Cl-Eth | L,P | | NANOFER |
| Trutnov, 2011, 2012 | Cr6+, Cl-Eth | L,P, R | ☺ | NANOFER |
| Spolchemie 2009, 2010, 2013 – 2015 | Cl-E, Cl-M | L, P, R | ☺ | NANOFER |

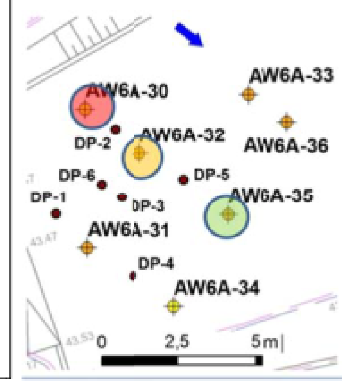
# NANOREM Results

## Spolchemie I (nZVI)

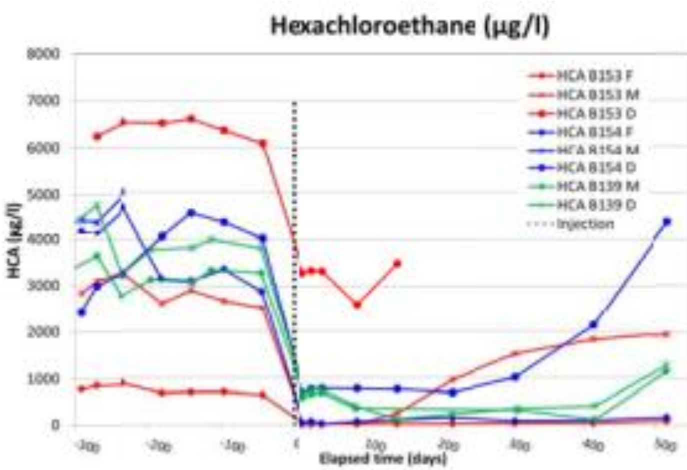


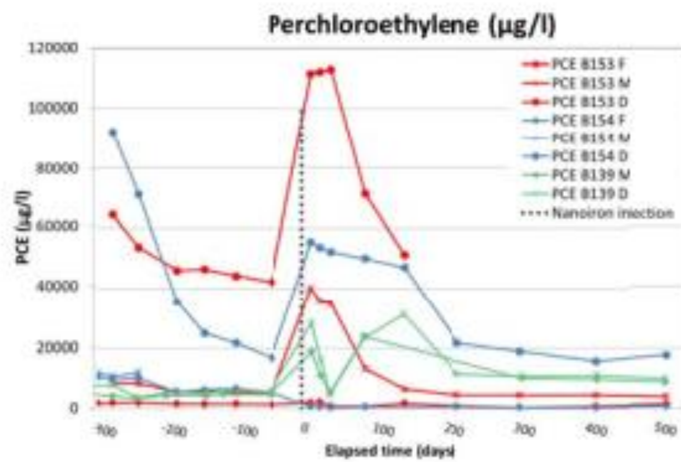

## Spolchemie II (nGoethite)



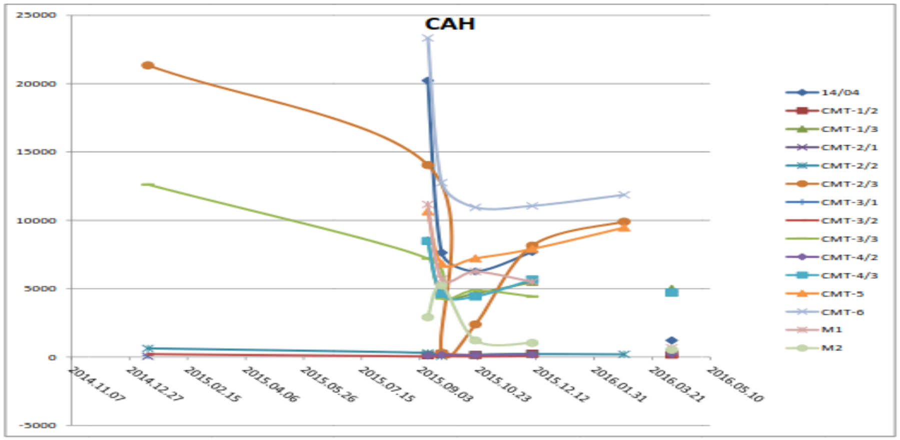

## Solvay (nZVI)

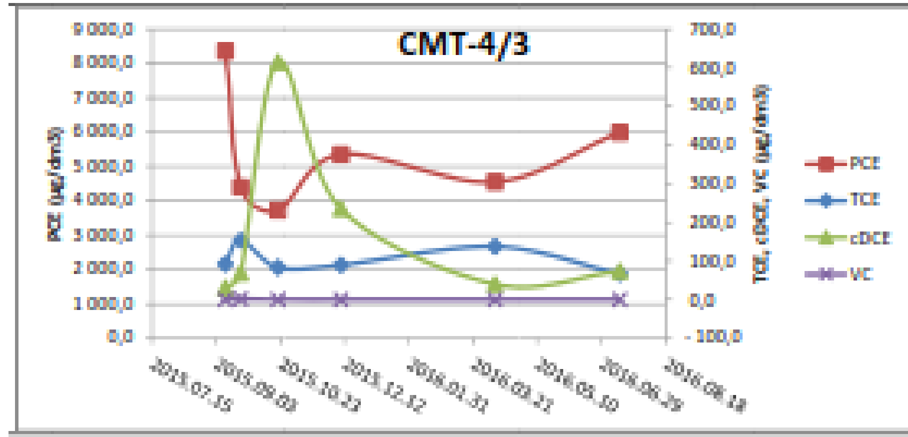


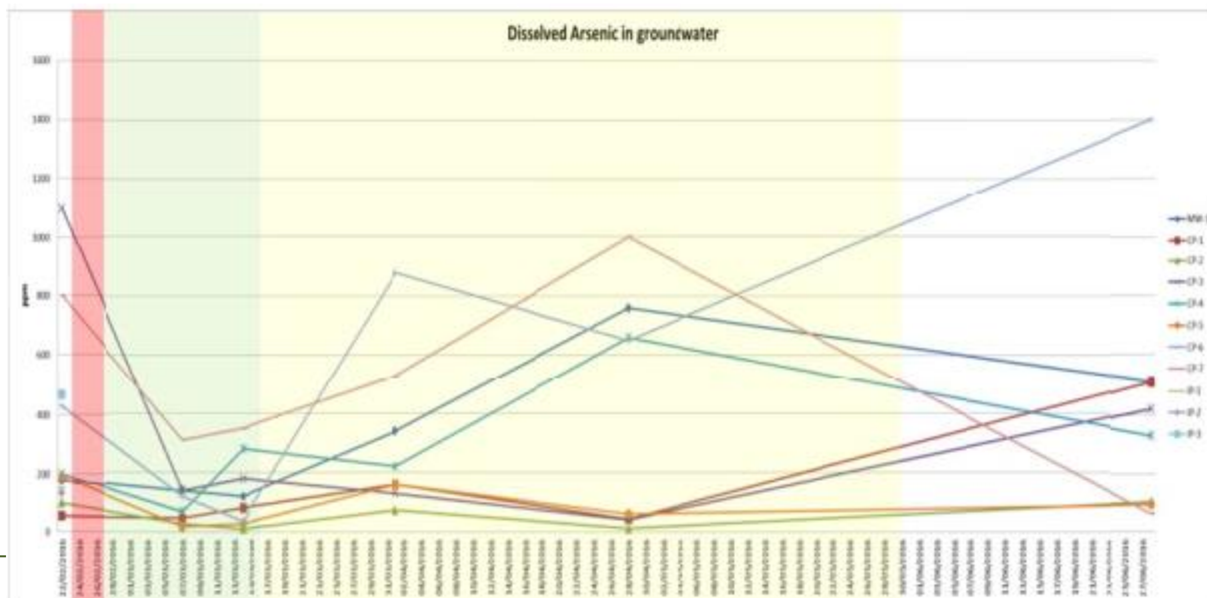
# NANOREM Results

## Balassagyarmat (C-I)




## Nitrastur (nZVI)



# List of deployments (NANOREM)

| Site | Contam. | Result | Type of nZVI |
|---|---|---|---|
| Barreiro PT | Heavy metals | Not applied | Not applied |
| Nitrastur ESP | Heavy metals (As) | Satisfying migration satisfying reaction | NANOFER ☺ |
| Balassagyarmat HU | Cl-Ethenes | Satisfying migration | CARBOIRON |
| Solvay CH | Chlorinated hydrocarbons | Satisfying migration moderate reaction | Milled nZVI |
| Spolchemie I CZ | Cl-Ethenes | Moderate migration satisfying reaction | NANOFER ☺ |
| Spolchemie II CZ | BTEX | Satisfying migration | Goethite |
| Neot Hovav ISR | Not studied | Satisfying migration Reaction not studied | CARBOIRON ☺ |

| | | Nanoremediation | ISCR (mZVI/dithionate) | ISBR |
|---|---|---|---|---|
| **Risks** | Human health | No exposure once successfully deployed.<br>Some NPs are hazardous, some are air stable and safer to handle. 😐 | No exposure once successfully deployed.<br>Some reagents, such as dithionate, are potentially hazardous. 😐 | No exposure once successfully deployed.<br>Materials are safe to handle. 🙂 |
| | Aquifer ecology | Injections are typically in highly disturbed environments. No NP specific ecotoxicity found by NanoRem. Ultimate fate is as iron oxides which are plentiful in soils. 🙂 | Injections are typically in highly disturbed environments. Ecological impacts unstudied, but assumed minimal. 🙂 | Injections are typically in highly disturbed environments. Ecological impacts unstudied, but in the long terms assumed minimal. 🙂 |
| | Water | Injected materials have limited lifetimes and limited travel distance, and are not associated with taint of the subsurface 🙂 | Lifetimes and travel distance of injected dithionite has not been widely studied, may be extensive. The travel distance of mZVI is essentially zero. High levels of sulphate and low pH remaining after dithionate reduction 😐 | Injected substrates to stimulate bioremediation are soluble or release soluble substrates possibly causing taint for water supplies. 😐 |
| | Supporting measures | Pre-deployment risk assessment available and published. 🙂 | No pre-deployment risk assessment tool. 😐 | No pre-deployment risk assessment tool. 😐 |

| | | Nanoremediation | ISCR | ISBR |
|---|---|---|---|---|
| **Benefits** | Breadth of solutions | Wide range of treatable contaminants.<br>Source term and pathway management applications.<br>Suitable for situations inhibitory to microbial dehalorespiration processes. ☺ | Wide range of treatable contaminants.<br>Tendency to pathway management applications.<br>Suitable for situations inhibitory to microbial dehalorespiration processes ☺ | More restricted range of treatable contaminants.<br>Potential for stall (e.g. TCE --> DCE)<br>Tendency to pathway management applications.<br>May be prevented by toxic or other inhibitory conditions 😐 |
| | Speed and completeness of action and synergies | Rapid treatment effects owing to nanoscale processes.<br>Moderate migration in the subsurface.<br>Tendency to complete degradation of contaminants.<br>Synergistic with ISBR and ISCR. ☺ | Slower treatment effects.<br>Microscale ZVI does not readily move in the subsurface.<br>Tendency to complete degradation of contaminants.<br>Synergistic with ISBR and nanoremediation 😐 | Slower treatment effects.<br>Soluble substrates migrate rapidly in the subsurface<br>Tendency to stall for some problems.<br>Synergistic with nanoremediation and ISCR. 😐 |
| | Ease of deployment | Portable systems (not requiring fixed infrastructure).<br>Some systems require specialised deployment interventions.<br>NanoRem is addressing the issue that deployment knowhow not widespread. 😐 | Portable systems (not requiring fixed infrastructure).<br>Widespread know-how and systems. 😐 | Portable systems (not requiring fixed infrastructure).<br>Widespread know-how and systems.<br>No direct contact with contaminant needed. ☺ |
| | Track record | Limited track record, relatively few suppliers. 😐 | Well established technology, many vendors, moderate track record. ☺ | Well established technology, many vendors, substantial track record. ☺ |

| | | Nanoremediation | ISCR | ISBR |
|---|---|---|---|---|
| **Costs** | Cost estimating | Bespoke costings needed for each deployment option appraisal. ☹ | Many consultants have a good knowledge of relative treatment costs. 😐 | Many consultants have a good knowledge of relative treatment costs. ☺ |
| | Cost levels | 100% | 70-90% | 60% |

Cost drivers:

- material  costs = cheaper material = lower reactivity
- installation cost = easier = cheaper
- operation costs = shorter = cheaper
- monitoirng costs = shorter = cheaper

# Potential for nanoremediation

- 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.**
- **For combined processes (nano-BIO or nano-Physical)**

# n/mZVI + DC combination = INR-DC

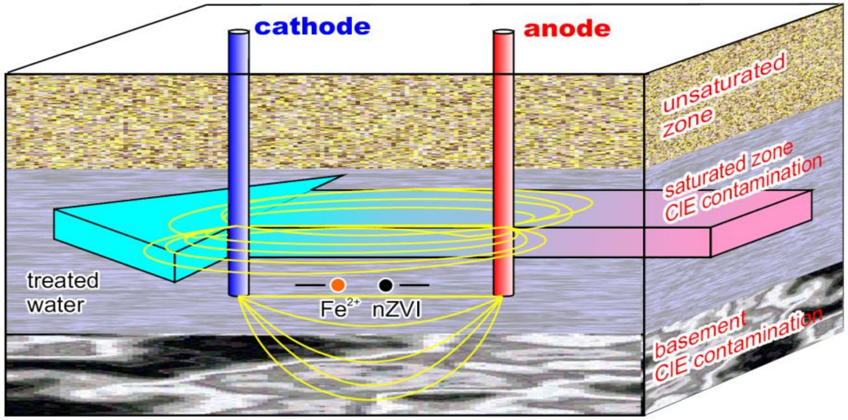
- Chemically supported reductive de-chlorination of CIE is inherently a substitution of chlorine protons, while the electrons are consumed by the equation: $Cl_2C=CCl_2 + 4H^+ + 8e^- \longrightarrow H_2C=CH_2 + 4Cl^-$

- For the successful running of the reaction it is necessary to create a significant excess of protons and electrons in a geochemical system. Both of these conditions are virtually assured by for example **$Fe^0$** reaction with water.

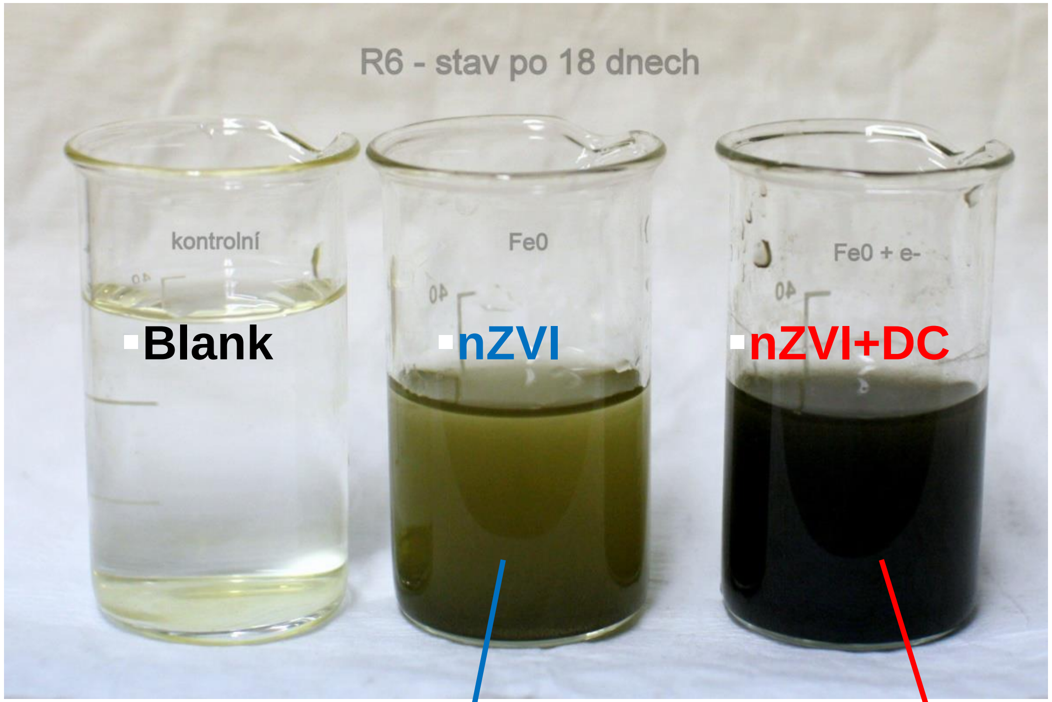
$$5H_2O + Fe^0 \longrightarrow Fe^{3+}(OH)^-_3 + H_2 + 2OH^- + 3H^+ + 3e^-$$

- A similar effect can be achieved by providing electrons into the reorganized structure using the DC electric field. During the appropriate

current density the decomposition of water occurs to form hydrogen and the environment gets overfed by e- for the process of reductive de-chlorination of CIE are created.



# Combinations
# n/mZVI + DC combination = INR-DC



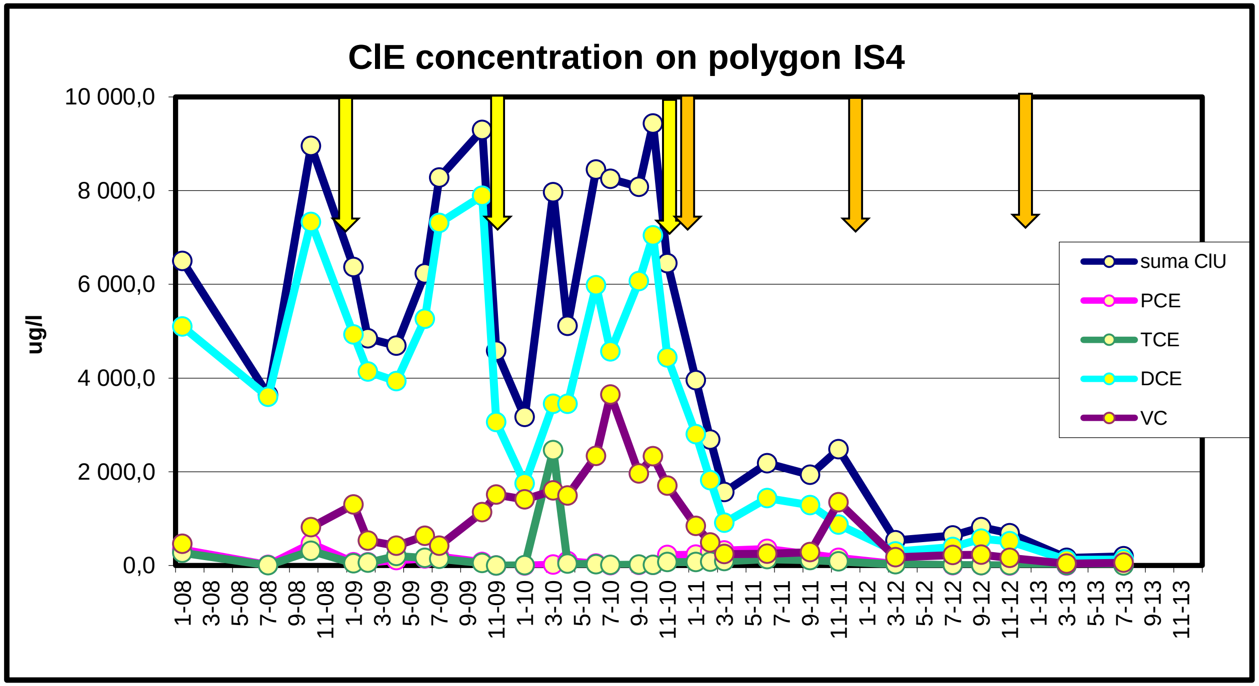

***90% goethit***
***10% magnetit***

***80% magnetit***
***20% $Fe(OH)_2$***

# Combinations
# n/mZVI + DC combination = INR-DC

## ClE concentration

- Observed decrease of ClE concentrations
- After nZVI injection (yellow arrow) dechloration from PCE to DCE
- Stagnancy period – after DC current connection (orange arrow) rapid decrease of sum of ClE (even DCE, VC)



# Economical evaluation for a model case

| | nZVI | ISCR (micro) | ISBR | INR-DC |
|---|---|---|---|---|
| Material mass (bulk) [%] | 100% | 500% | 1000% | 100% |
| Material costs [%] | 100% | 20% | 10% | 40% |
| No of injections / total time | 6 injections / 2 years | 6 injections / 3 years | 9 injections / 3 years | 3 injections and service DC / 2 years |
| Operation costs [%] | 100% | 250% | 150% | 110% |
| Monitoring costs [%] | 100% | 150% | 150% | 100% |
| Total costs [%] | 100% | 90% | 60% | 60% |
| Risk of failure | 100% | 130% | 70% | 80% |

# Conclusions

- **Nanoremediation limitations:**
  - Availability of materials in sufficient quantity and quality
  - Distribution of solid material in soils,
  - Longevity of nanomaterials,
  - Costs,
  - Legal limitations
- **Solutions :**
  - Availability – Demand – Solved limitations
  - Detailed contaminant prospection and site characterisation
  - Targetted injection
  - Combination with physical and biological methods
  - Spreading of information about the use, behaviour, efficiency, fate and toxicity of nanomaterials in groundwater environment

# Thank you for your attention

This project received funding from the European Union Seventh Framework Programme (FP7 / 2007-2013) under Grant Agreement No. 309517.

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