REGIONAL CENTRE OF ADVANCED TECHNOLOGIES AND MATERIALS

Regionální centrum pokročilých technologií a materiálů

NANOREMEDIATION: What´s in It for Me?

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NanoRem

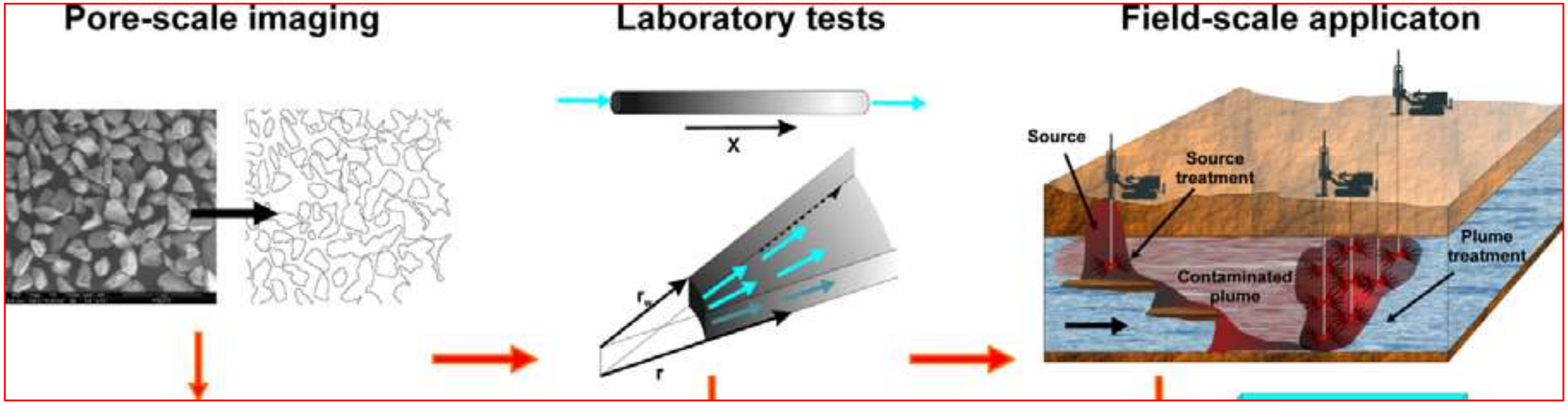
Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

SEVENTH FRAMEWORK PROGRAMME

- 7FP EU project NANOREM
- 29 EU institutions from 15 Countries
- PAG: D. Elliott, G. Lowry, M. Wiesner
- Budget €12 million ($16.8 million); duration 48 months
- Aim: Identification of the most appropriate nano-remediation technological approaches to achieve a step change in practical remediation performance

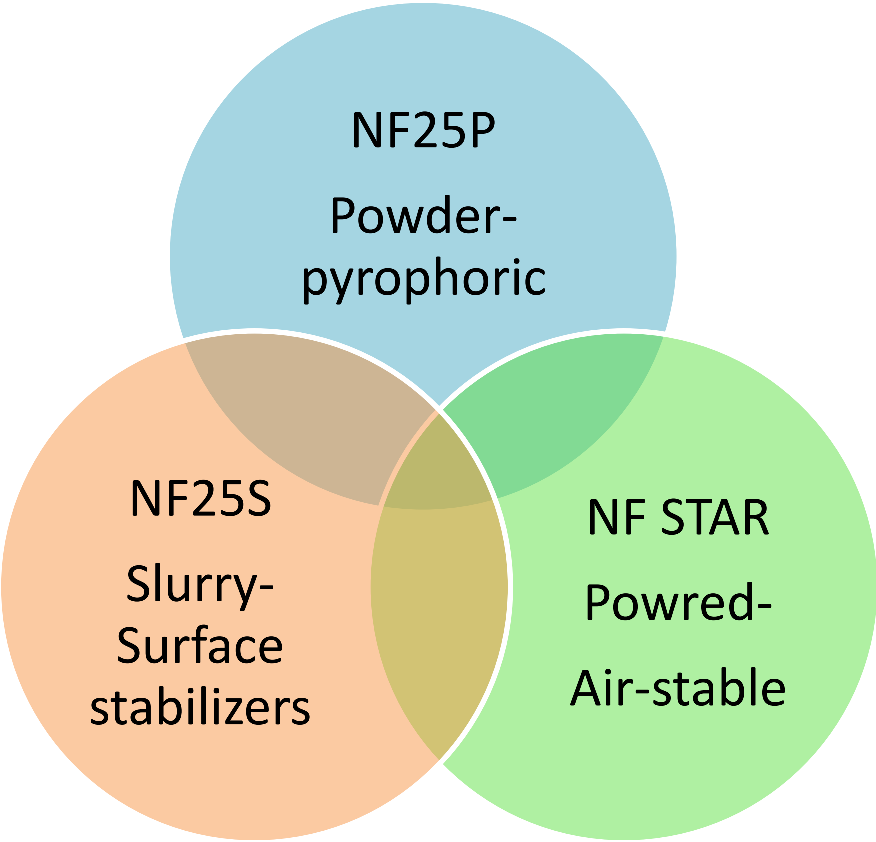
List of activities

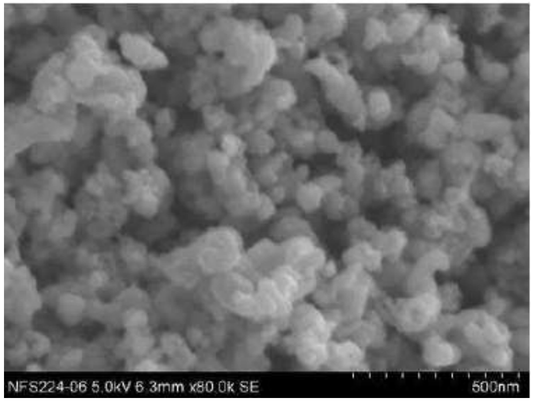
- Design, Improvement and Optimized Production of:
  - Zero-Valent Iron Nanoparticles
  - Non-ZVI and Composite Nanoparticles
- Mobility and Fate of Nanoparticles
- Environmental Impact of Reactive Nanoparticles
- Analytical Methods for In-situ Determination of Nanoparticles Fate
- Upscaling, Risk and Sustainability
- Pilot Site Applications and Field Demonstrations



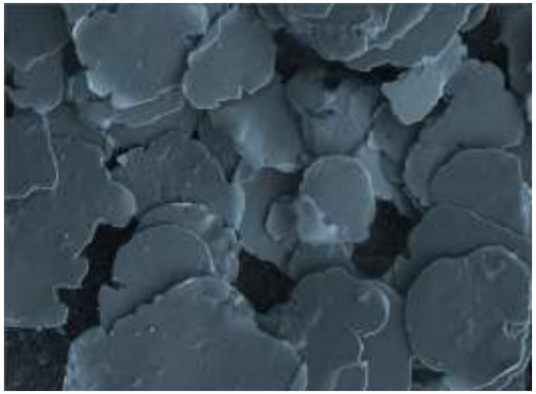
Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

nZVI particles





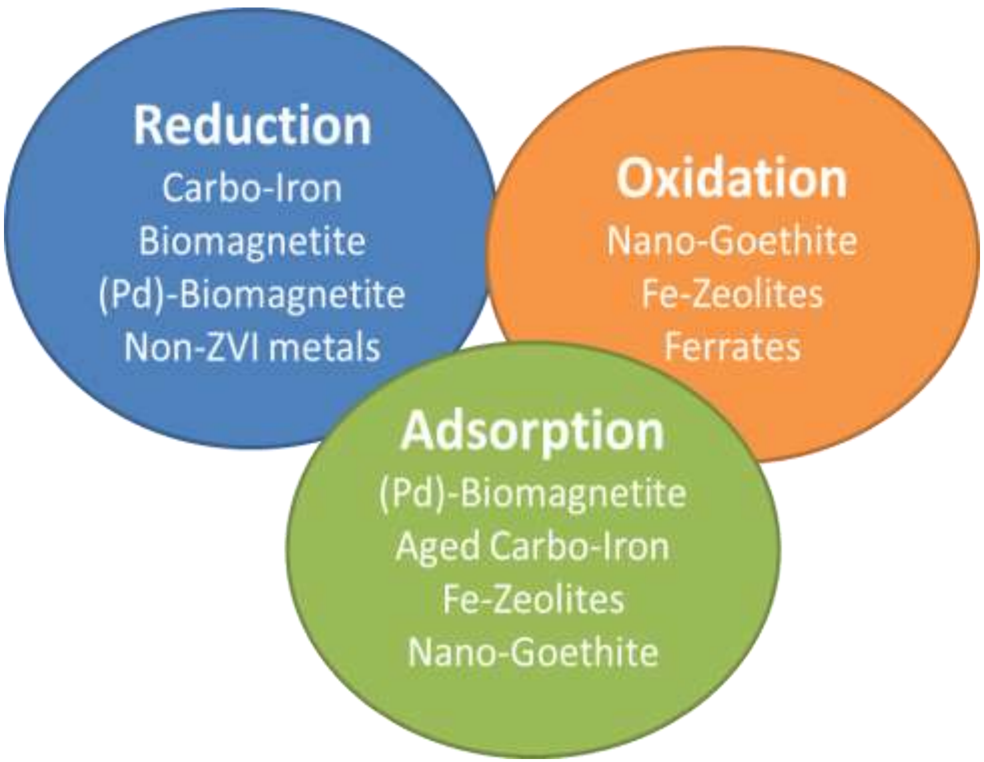
NF STAR

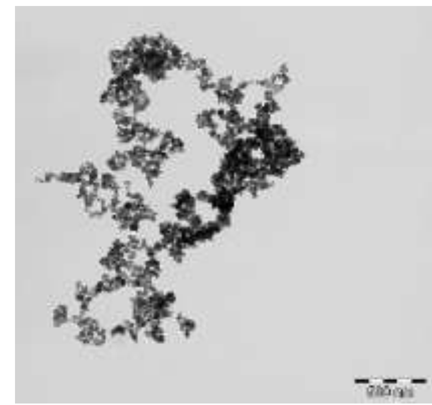


milled NP

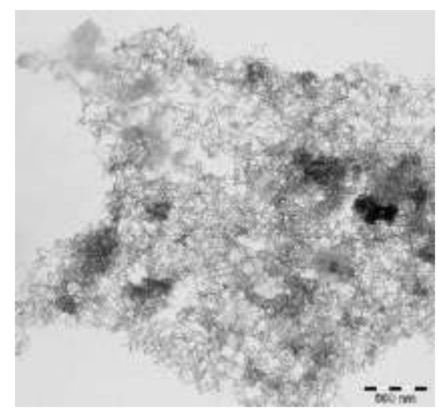
Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

Non-Fe and combined particles





Biomagnetite



Feox NP

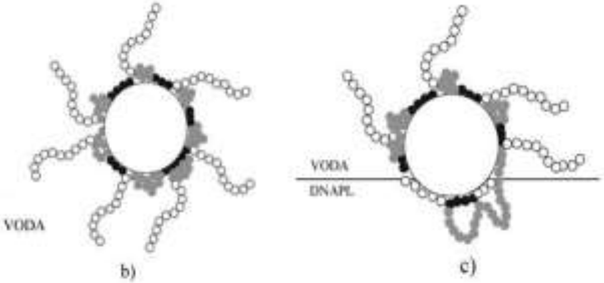
Optimal properties

- reactivity **with contaminants**
- mobility **in the aquifer**
- stability **before application**

- **NO (minimum) of negative environmental effects**
- **price, availability**

Surface modification

Inhicor-T
Starch
Carboxymethyle cellulose
Polyacrylic acid
Cellulose
Tween 60



Innovative nZVI Manufacturing

Field deployment approaches

NANOIRON
FUTURE TECHNOLOGY

SLURRY MANUFACTURING → SHIPPING → STORAGE → DILUTION → INJECTION

Conventional delivery and application process

15-60 days

1 day

POWDER SHIPPING → STORAGE → SLURRY MANUFACTURING → DILUTION → INJECTION

Innovative application process

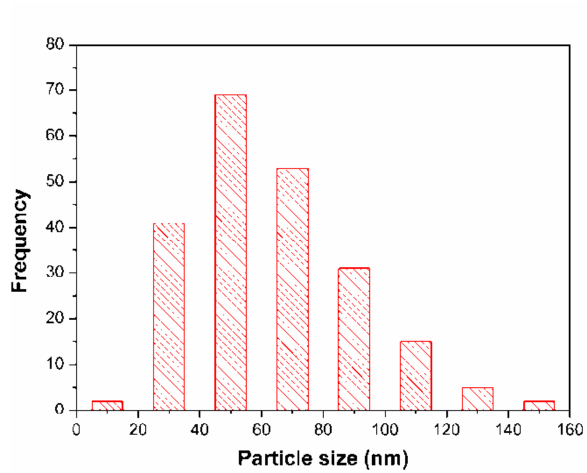
NANOFER STAR- dry nZVI

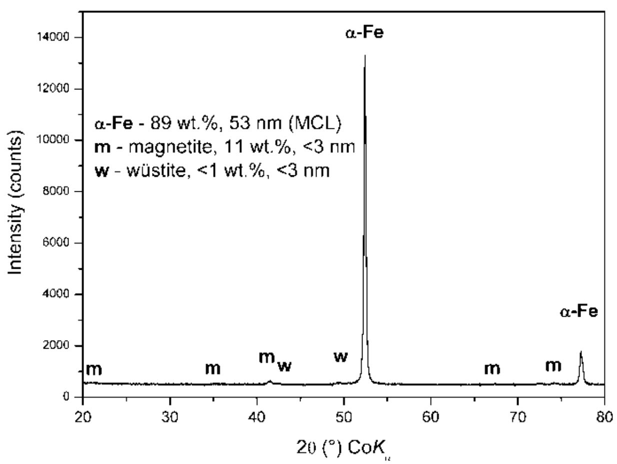
- Dry powder transported to the site
- On site surface activation, stabilization
- Dillution to a final concentration
- advantage → high reactivity, >95% Fe^0

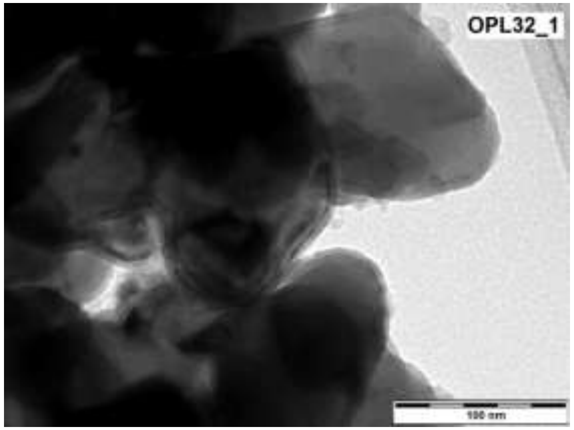
Challenging nZVI materials

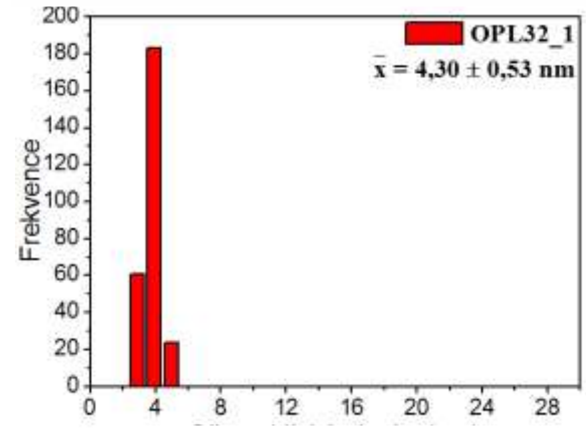
Dry NP powder

- NANOFER STAR – dry NP powder produced by solid-state thermal reduction of Fe-oxide
- Thin oxide shell for NP protection
- Good stability, transpotability
- Sufficient reactivity (activation)
- Mobility (surface modifications)





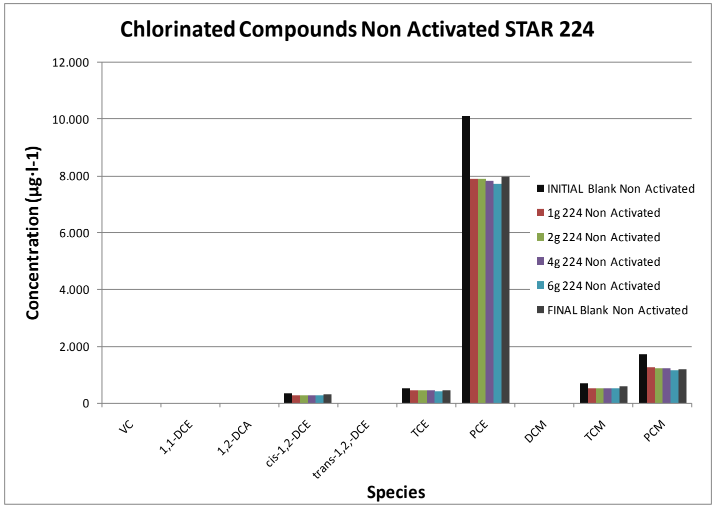


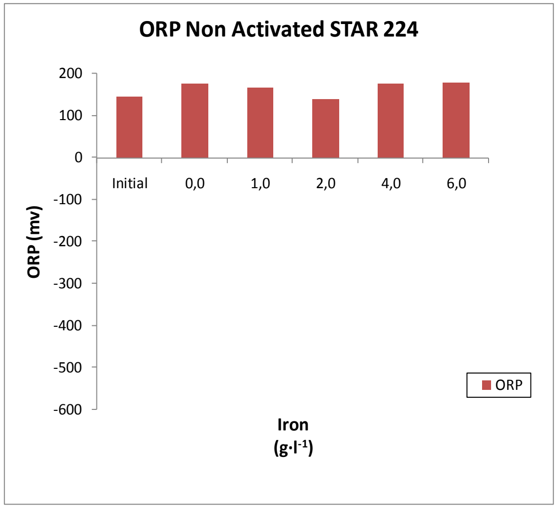


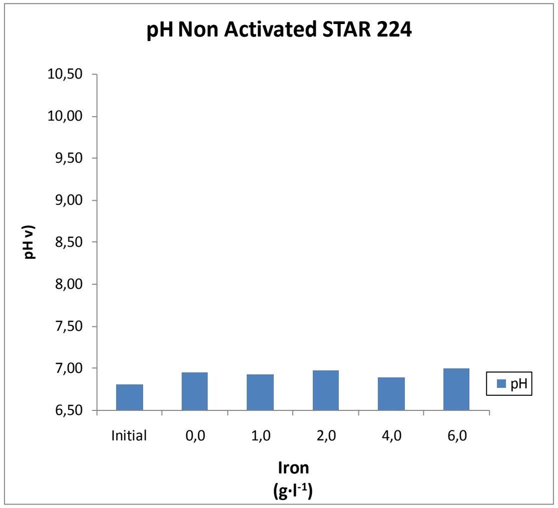
thickness of oxidic layer (nm)

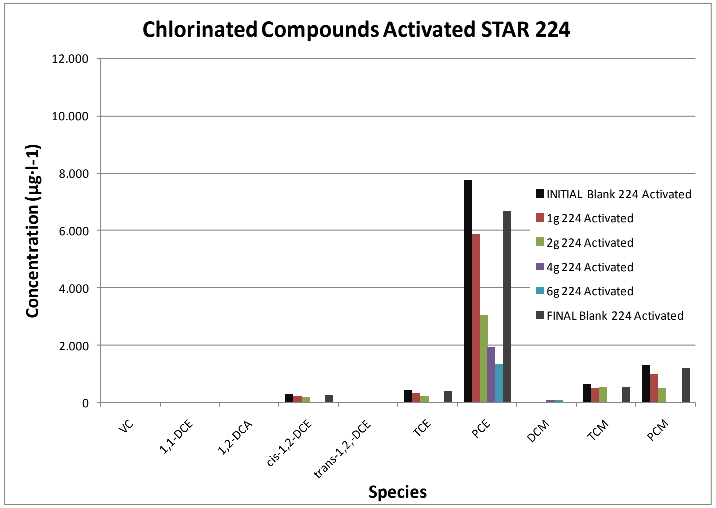
Activation on Zurzach site

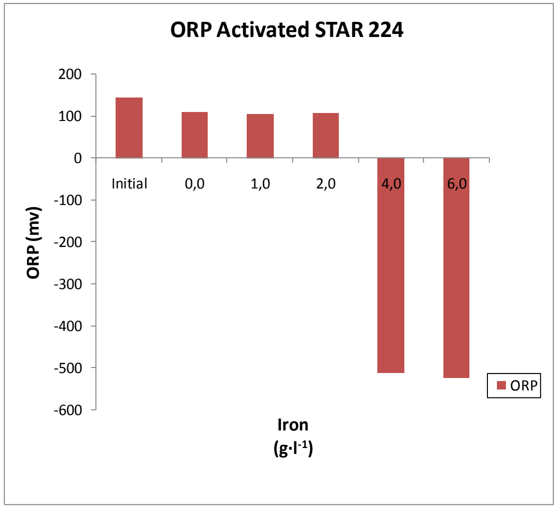
Switzerland

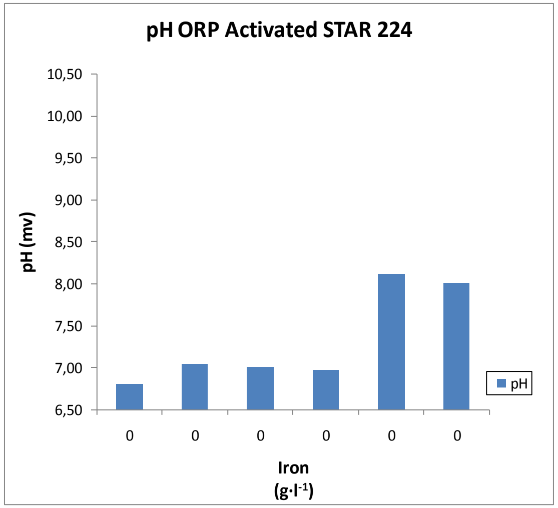








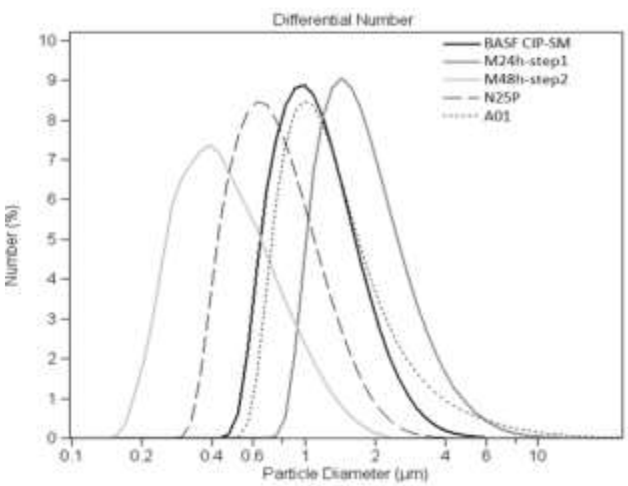




nZVI characterization

3 types of tests

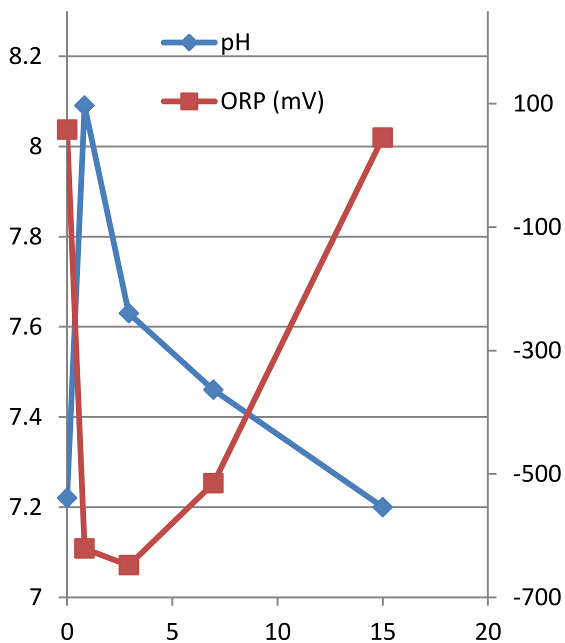
- Physical characteristics:
  - zeta-potential,
  - BET,
  - TEM & SEM, XRD & Mössbauer,
  - Size distribution: DLS & DGC,…
- Reactivity tests:
  - Water (production of H_2 and OH^-)
  - Selected contaminants (spiked in water)
  - Contaminated water
- Mobility tests
  - 1-D simple tests for comparison
  - Complex 1-D tests
  - 2-D and 3-D tests

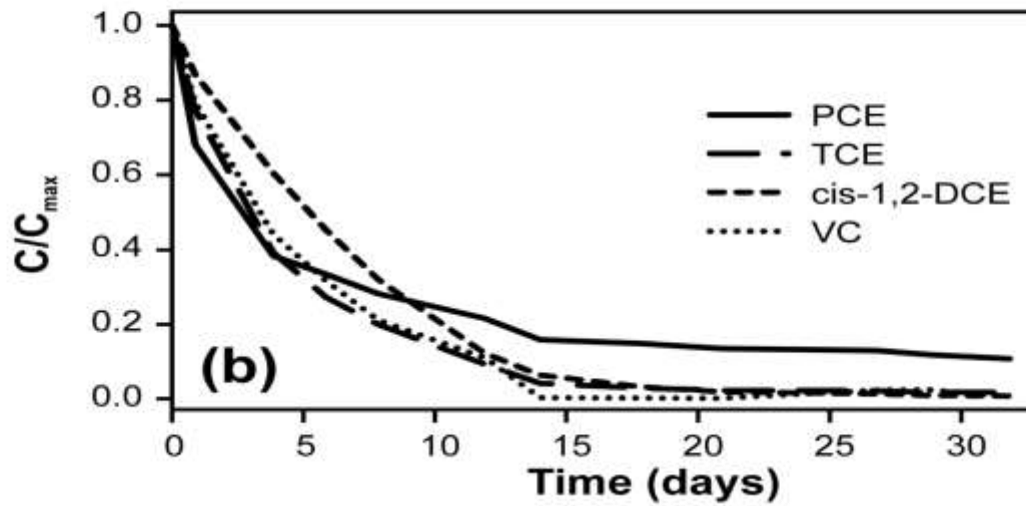


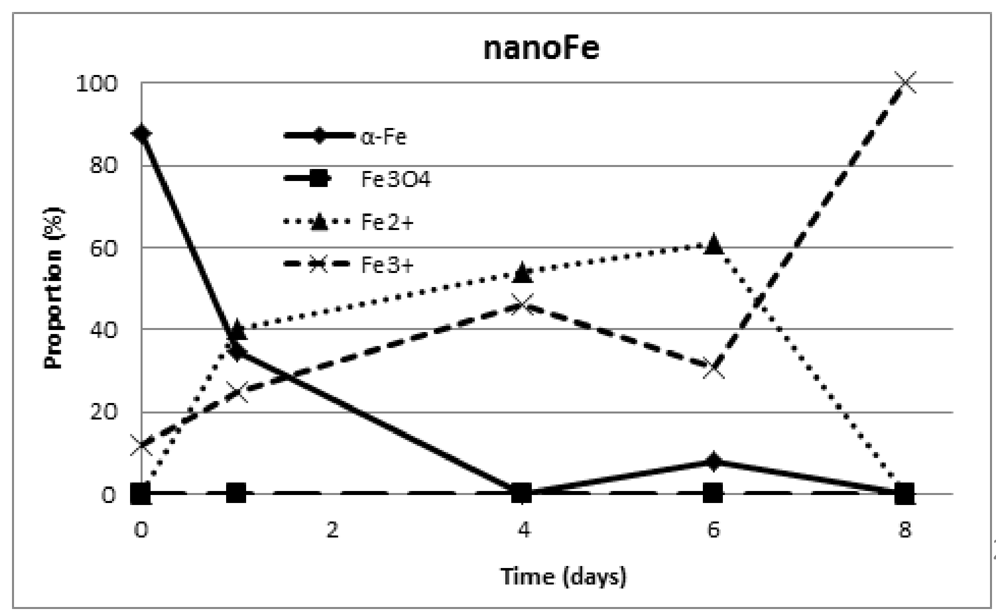
nZVI reactivity

Reaction with contaminated water

- pH and ORP
- Removal of CHC
- Kinetic tests
- Concentration tests



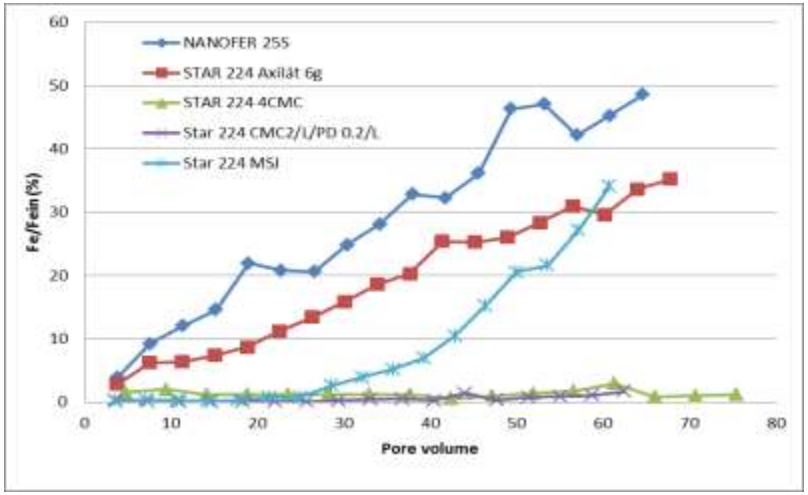




Migration tests

1-D laboratory columns

- Migration bottom-up
- Sandy media
- Low nZVI conc. (<1 g/l)
- Comparison of different modifications



non modified NZVI

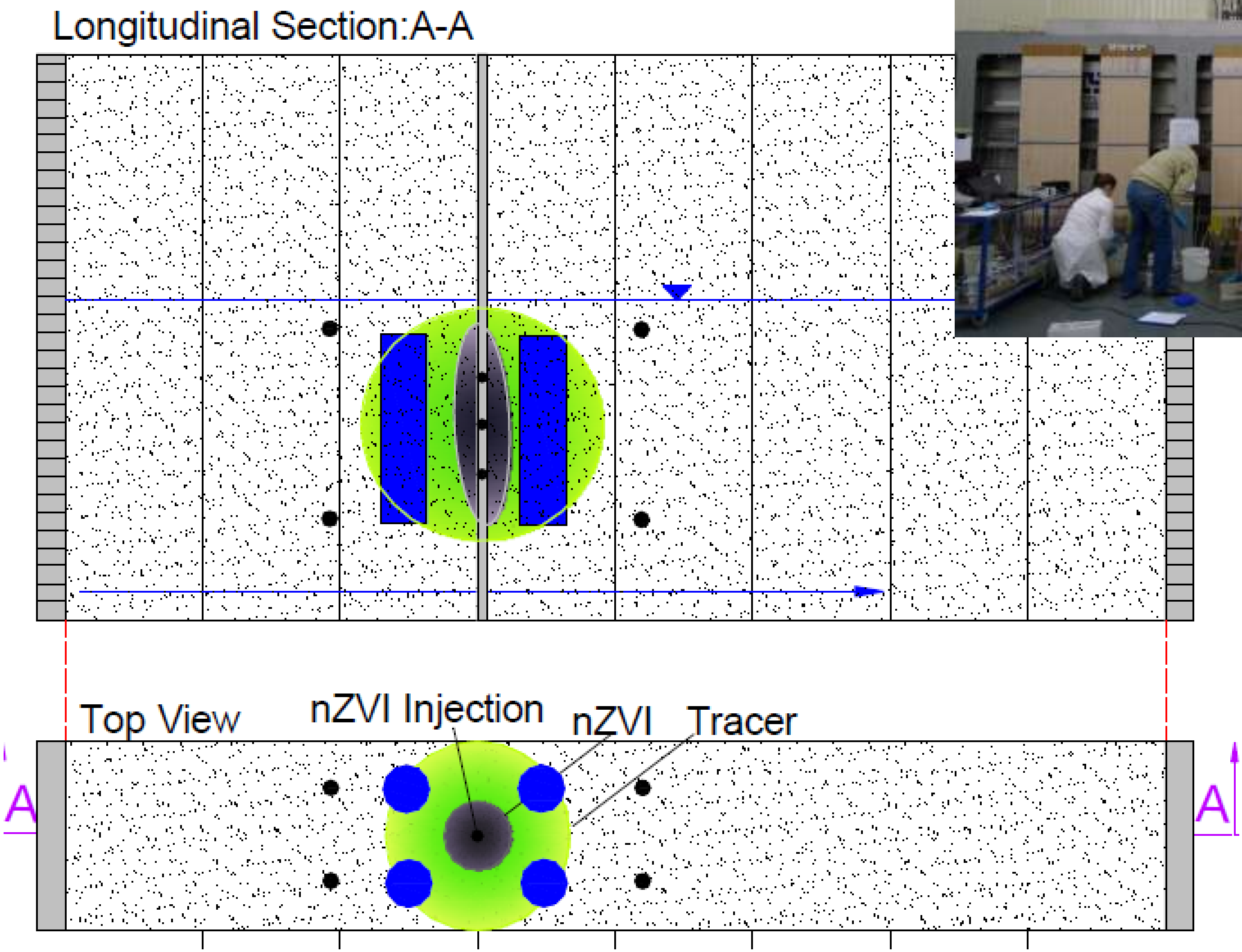
modifications

Migration tests

2-D laboratory columns VEGAS Germany (60l, 10g/l, 7 hours)

VEGAS – large flume test

600 x 300 x 100 cm Vessel



Combination of nZVI with other methods

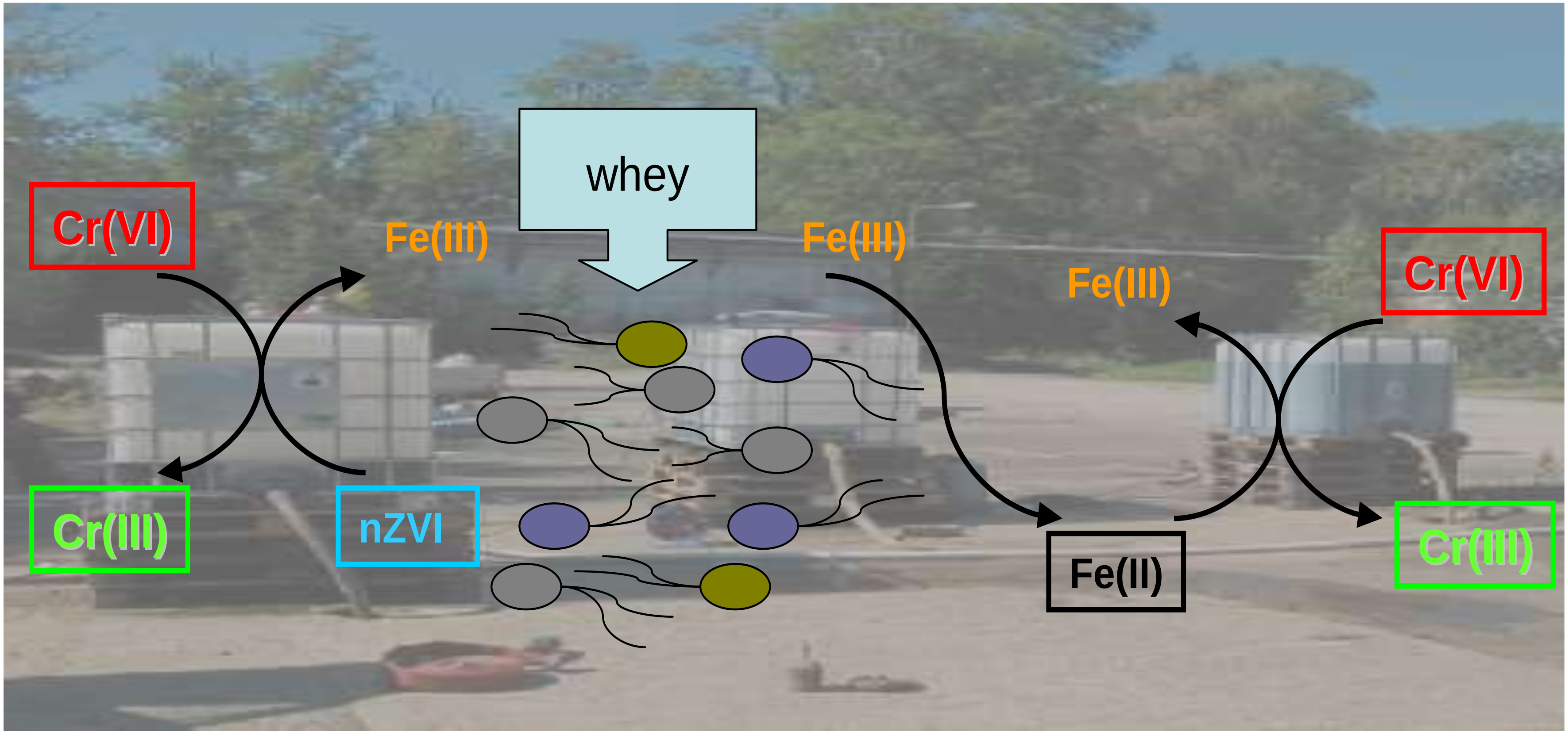
Remediation “trains”

- Why?
- nZVI has limitations
  - High cost (100 €/kg or $65/lb)
  - Limited migration
  - Low hydraulic conductivity
- Bioremediation has limitations
  - Accumulation of daughter unless bioaugmented (e.g. c-DCE from TCE)
  - Lower ORP needed for dechloration
- Combination of nZVI & other methods
  - with anaerobic biostimulation or bioaugmentation
  - with electrokinetics (DC field)

Combination nZVI with bioremediation

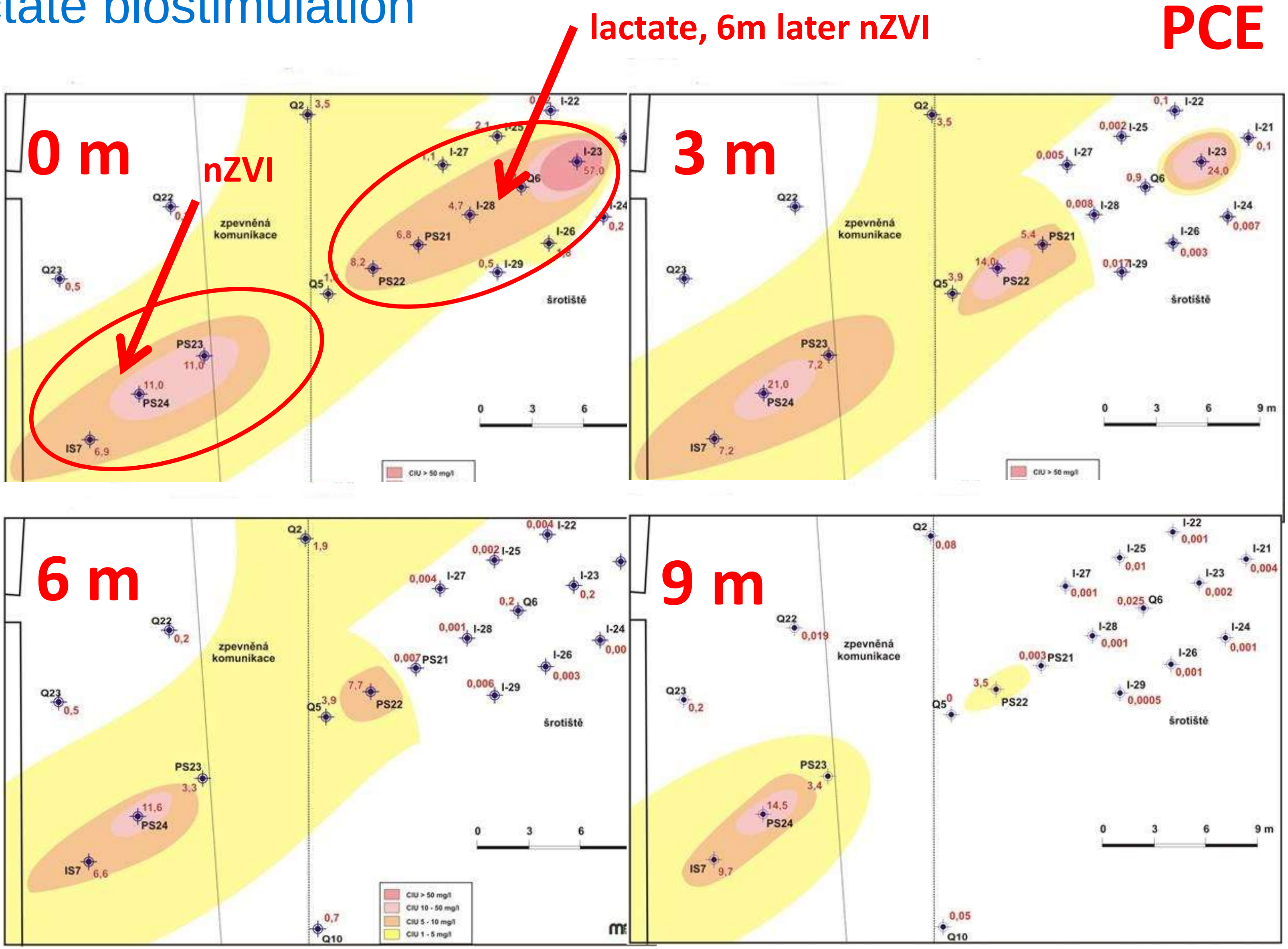
Lactate (biostimulation)

- Lactate → fermentation (CO_2 + CH_4) → source of electrons for anaerobic biodegradation
- Cheap, good migration, higher ORP → c-DCE
- Elimination of nitrates, sulfate, dissolved oxygen



Combination with bioremediation

lactate biostimulation

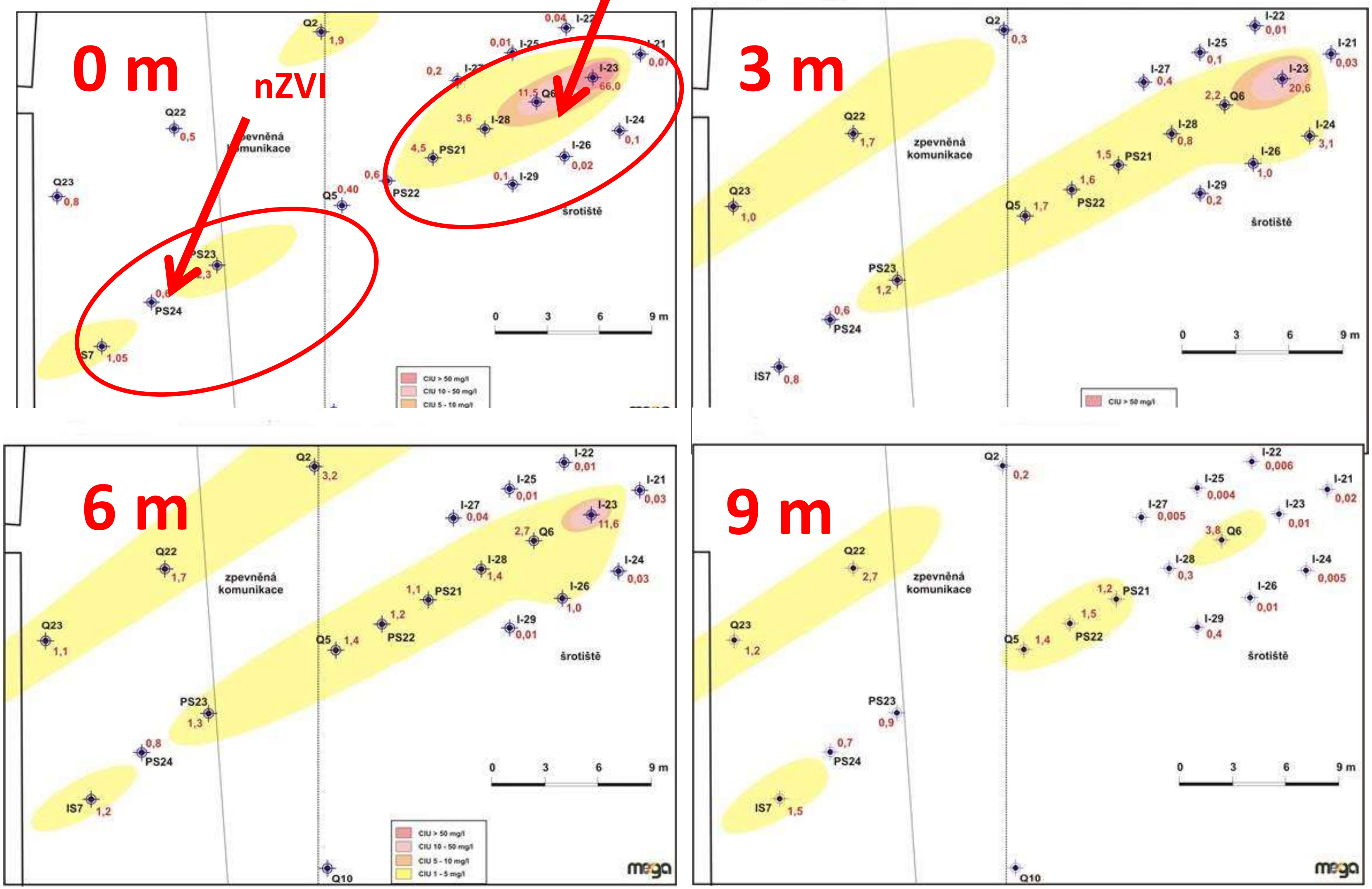


Combination with bioremediation

lactate biostimulation

lactate, 6m later nZVI

DCE



Combination with DC (EK-nZVI)

Principle of reaction

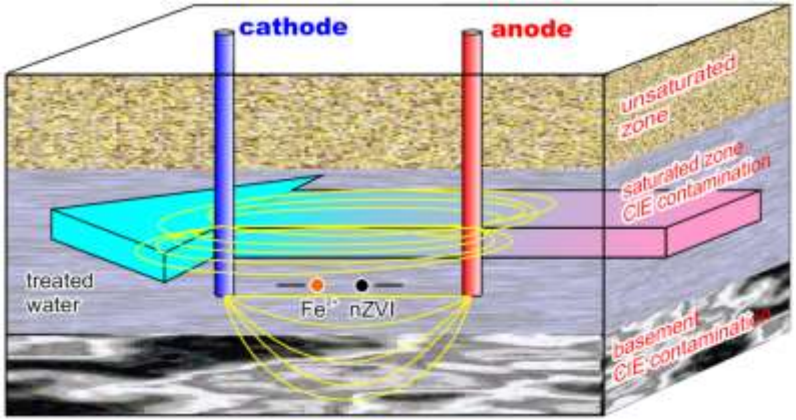
- Chemically supported reductive de-chlorination of CIE
- substitution of chlorine protons – role of electrons:

$$Cl_2C{=}CCl_2 + 4H^+ + 8e^- \longrightarrow H_2C{=}CH_2 + 4Cl^-$$

- For the successful running of the reaction it is necessary to create a significant excess of protons and electrons in a geochemical system.
- By **Fe⁰** reaction with water.

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

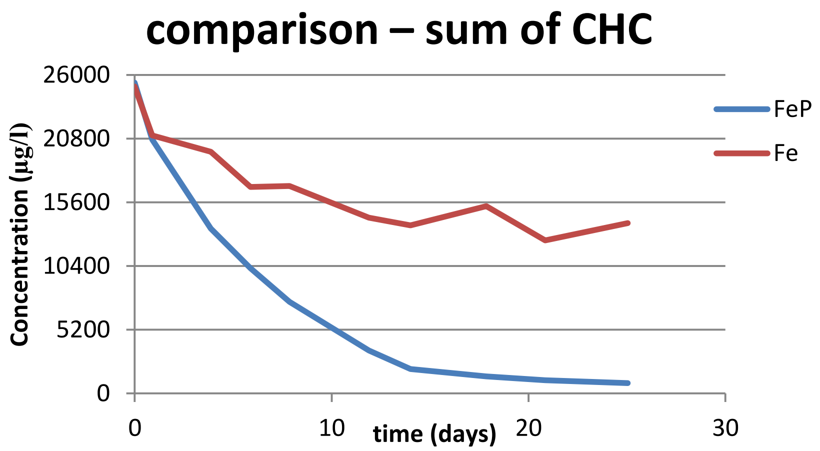
- Similarly by providing electrons using the DC electric field.

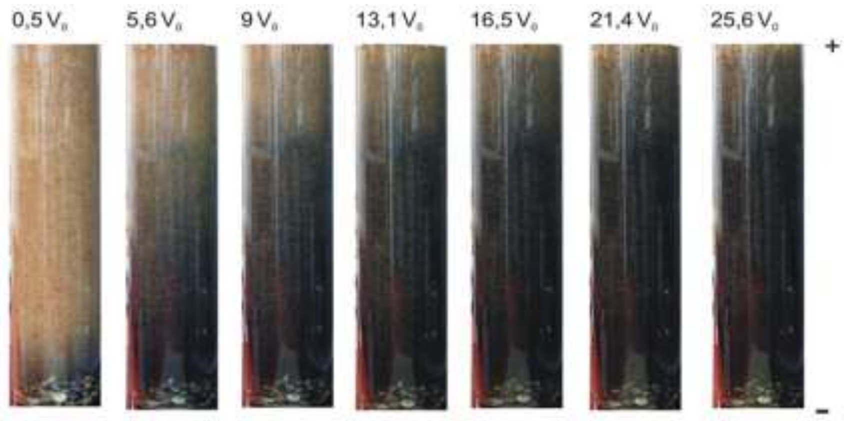


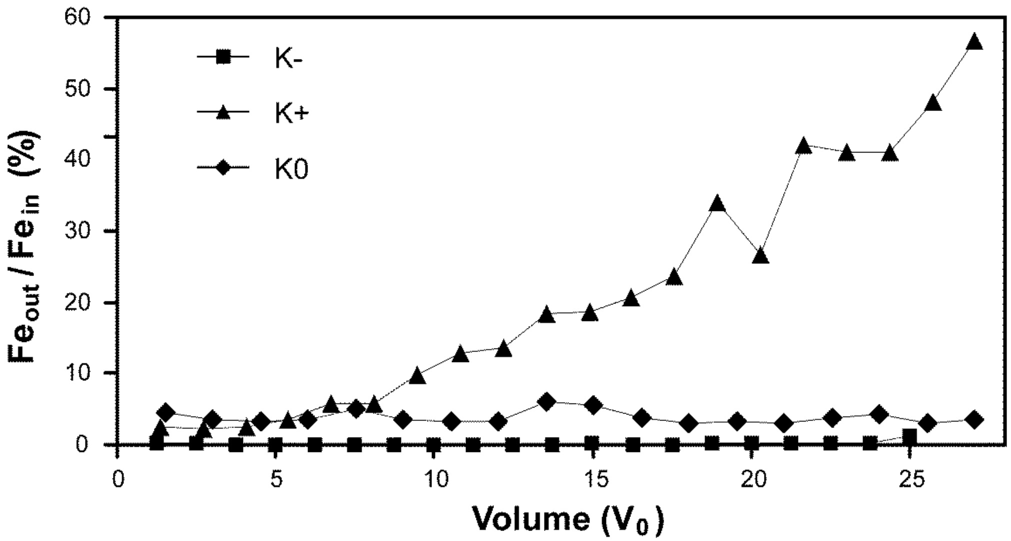
Combination with DC field

Laboratory experiments

- Principle in lab: DC ~1V/cm
- nZVI concentration 0.5 g/l
- Higher Fe^{2+} conc.
- Lower Eh
- Better migration
- Higher reactivity





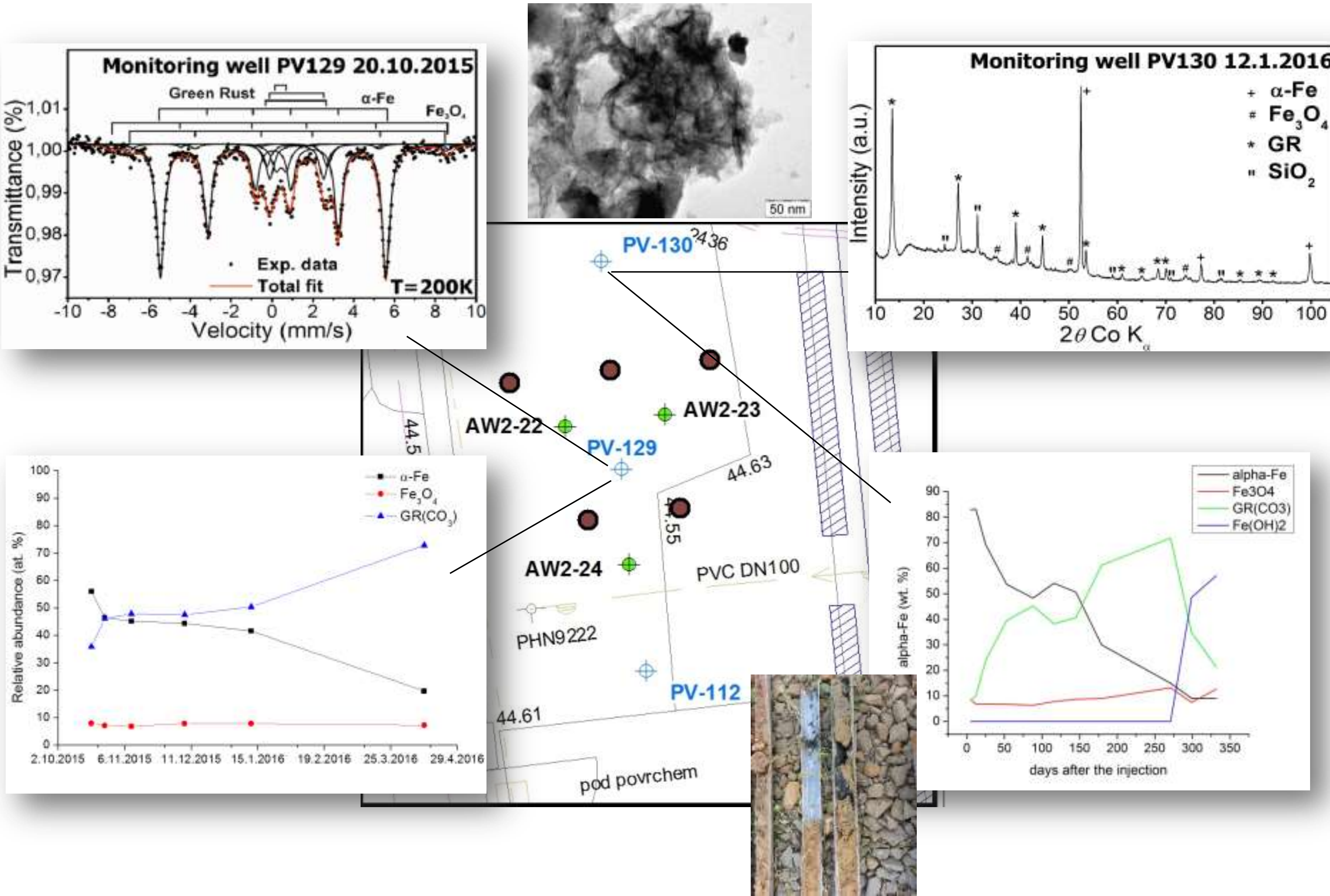


Health and Safety Considerations

NANOREM project

- Health and Safety is an important issue
  - Effects of exposure to NPs is considered for all “nano” products
  - Importance of studying and understanding of product behavior
  - Reduce risk by minimize contact of nanoparticles with persons
- Fate of nanoparticles in environment – *in-situ* & *ex-situ*
- Current knowledge and future direction
  - Toxicity of nZVI towards water organisms
  - EU REACH legislation
- Two most recent studies including NANOFER product
  - Erik J. Joner et al. *DDT degradation efficiency and ecotoxicological effects of two types of nanosized zero-valent iron (nZVI) in water and soil.* Chemosphere, 2016, 144, 2221-2228
  - Arturo A. Keller et al. *Toxicity of Nano-Zero Valent Iron to Freshwater and Marine Organisms. PLoS ONE 7(8): e43983.*

Structural analysis results



The future of nZVI in Europe

State of the art and future developments

State-of-the-Art

- Different nZVI products available (dry, milled, slurry)
- Many lab and field tests accomplished – lectures to learn
- All points of view (reactivity, migration, storability, transportability, toxicity,…)

Technical challenges:

- Successful field-scale applications in EU countries (needed for method acceptance/growth)
- Rigorous cost-effectiveness comparisons with other methods

Thank you for your attention !

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www.nanorem.eu