Geosyntec consultants

REMTECH
Remediation Technologies and Requalification of the Territory

Practical Applications for Nanoremediation

Session 1

RemTech, Ferrara Exhibition Center, Ferrara, Italy

21 September 2016

aquatest

NanoRem

TECHNICAL UNIVERSITY OF LIBEREC
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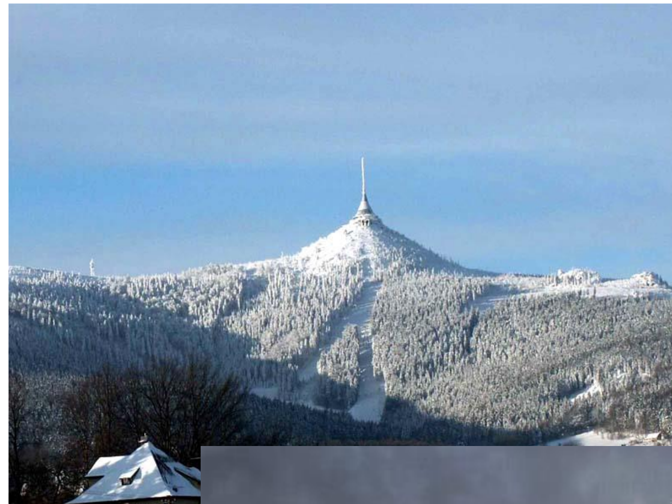
Agenda for Session 1

Time (Hrs)	Title	Presenter
0930 - 1030	A Primer on Nanoremediation – History, Applications, and Issues	D.W. Elliott
1030 - 1045	Break	
1045 - 1145	Nanoremediation in the EU - Impacts of NanoRem and Technology Combinations	M. Cernik
1145 - 1200	Break	
1200 - 1300	Key Field Applications of Nanoremediation – Lessons Learned and Future Directions	P. Kvapil

Technical university of Liberec



1100 employes
9000 students
6 faculties
+ 2 institutes

- **Institute for Nanomaterials, Advanced Technologies and Innovation**

Nanoremediation in EU

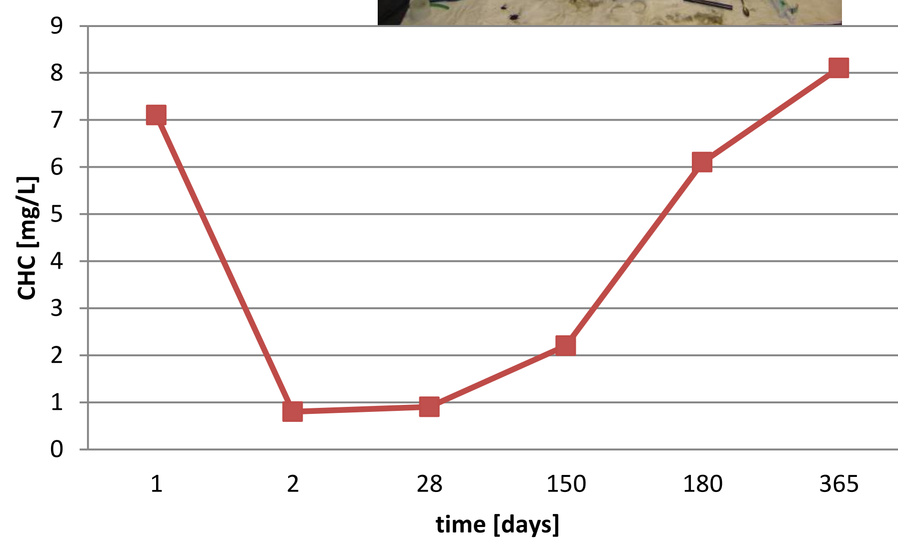
- History
  - 2004: 1st application outside of USA
  - 2005: pilot test at Kurovody
  - Overview of Czech sites
- Characterization of the nanoparticles
  - Different techniques for nZVI characterization
  - Slurry, Dry particles, Milled particles
  - Reactivity with samples of contaminated water
- Novel deployment approaches
  - Combination of nZVI and bioremediation (ARD)
  - Electrokinetics (EK) and nZVI

History of nZVI in Europe

1st application in the Czech Republic

- 2004 – 1st pilot test (Spolchemie, with Golder)
  based on information from M. Pupeza

- Results:
  - ORP decrease (from +100 to -500 mV)
  - pH increase (from 6.5 to 8.5)
  - CHC decrease for 6 months

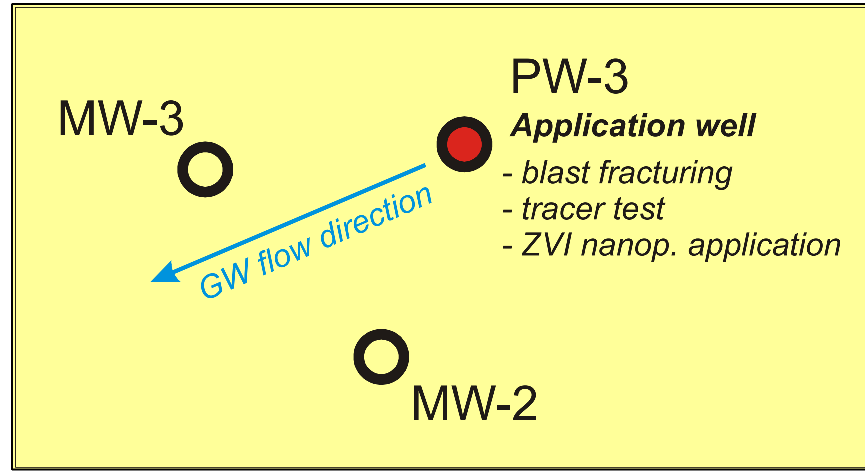


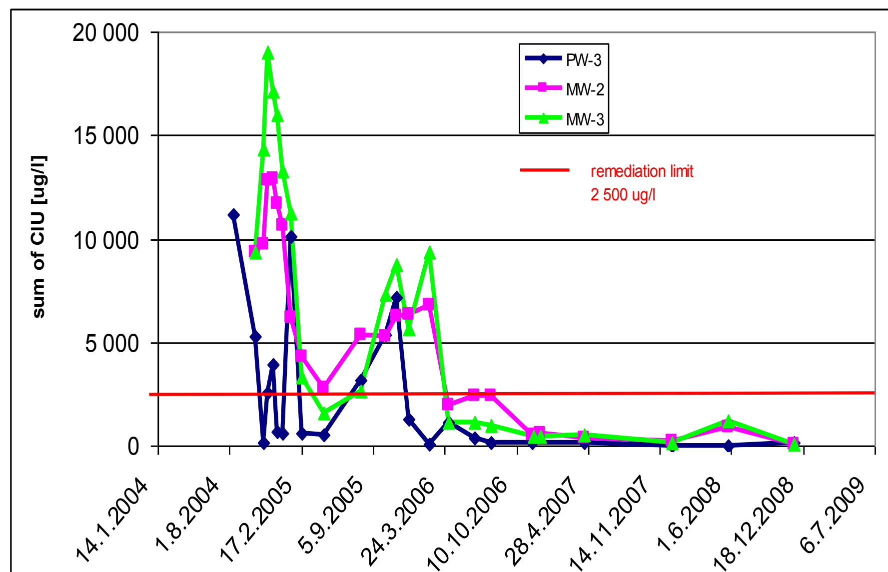
Czech nZVI experience

2nd nZVI application

- 2005 – fractured bedrock (Kurivody, CZ)

- Tracer test
- Pilot test
- No rebound effect





Czech nZVI experience

Site	Cont.	Lab (L)/Pilot(P)/ Remediation (R)	nZVI
Spolchemie 2004	Cl-Ethenes	L,P – 20 kg	ZHANG,
Kuřívody 2005, 2006	Cl-Ethenes	L,P – 50 kg	ZHANG, RNIP
Piešťany 2005	Cl-Ethenes	L,P – 20 kg	ZHANG
Permon 2006	Cr6+	L,P – 7 kg	RNIP
Rožmitál 2007-9	PCB	L,P – 150 kg	RNIP, NANOFER
Hluk 2007, 2008 (PRB)	Cl-Ethenes	L,P – 150 kg	RNIP, NANOFER
Hořice 2008, 2009-2013	**Cl-Ethenes**	**L,P,R – 600 kg**	**RNIP, NANOFER, DC, BIO**
Uherský Brod 2008	Cl-Ethenes	P – 50 kg	NANOFER
Písečná 2008-2011, 2014-17	**Cl-E, Cl-A**	**L,P,R – 250 kg**	**RNIP, NANOFER**
Uzin 2009	Cl-E	L,P – 150 kg	NANOFER
Spolchemie 2009-2017	**Cl-E**	**L,P,R – 1000 kg**	**NANOFER, DC**
MARS 2012-2015	**Cl-E**	**L,P,R – 1000 kg**	**NANOFER, DC, BIO**

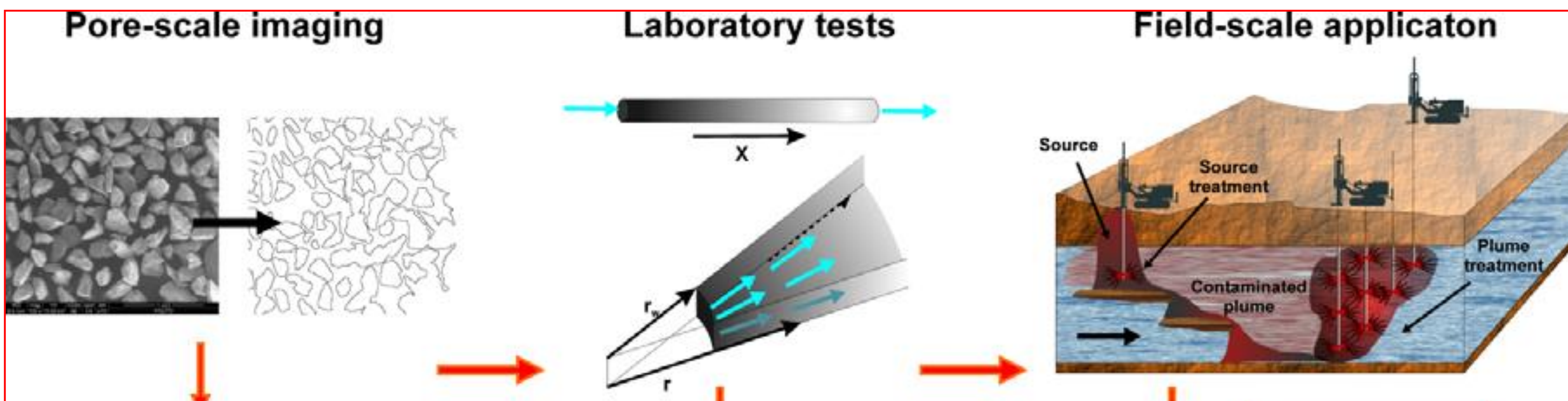
History of Czech nZVI scientific actions

Why just in the Czech Republic?

- No eco-friendly production → changes of political system → privatization → commitment of remediation
- Pump & treat, venting – not effective enough
- Authorities support innovative technologies
- Czech project (2006-8): *"Development of nZVI production and application for treatment of contaminated groundwater"*
- Cooperation of TUL+ UPOL + AQUATEST consultancy → NANOIRON establishment
- Pilot and full scale applications, new products development
- Observatory Nano EU project → EU project NANOREM

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

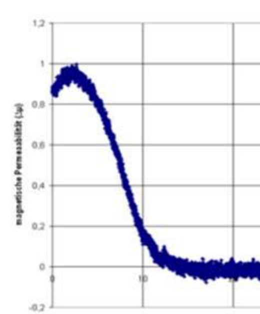
- EU project NANOREM
- 29 EU institutions from 15 Countries
- PAG: D. Elliott, G. Lowry, M. Wiesner
- Budget €12 million ($16.8 million); duration 48 months
- Aim: Identification of the most appropriate nano-remediation technological approaches to achieve a step change in practical remediation performance



List of activities (WPs)

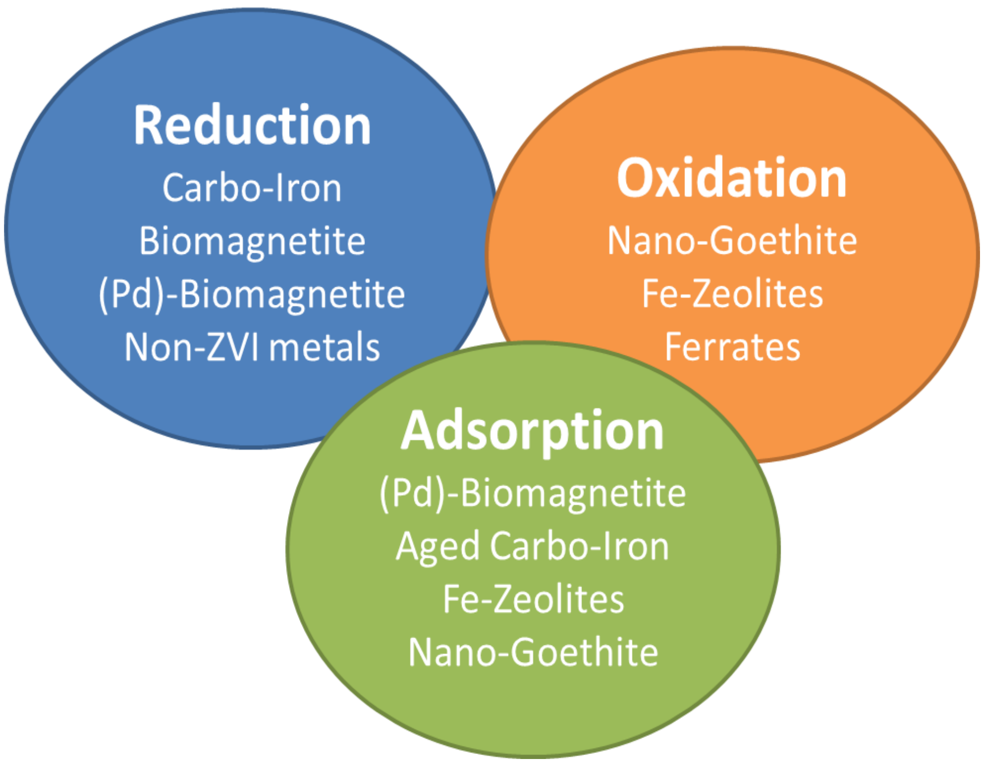
& their objectives

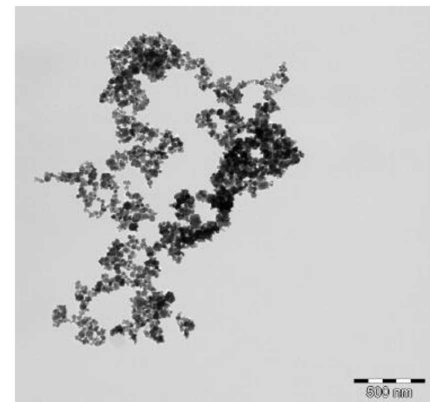
- Design, Improvement and Optimized Production of:
  - Zero-Valent Iron Nanoparticles (WP2)
  - Non-ZVI and Composite Nanoparticles (WP3)
- Mobility and Fate of Nanoparticles (WP4)
- Environmental Impact of Reactive Nanoparticles (WP5)
- Analytical Methods for In-situ Determination of Nanoparticles Fate (WP6)
- Upscaling, Risk and Sustainability (WP8)
- Pilot Site Applications and Field Demonstrations (WP10)



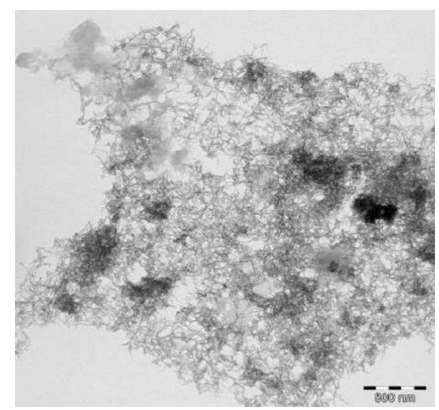
Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

WP3: Non-Fe and combined particles





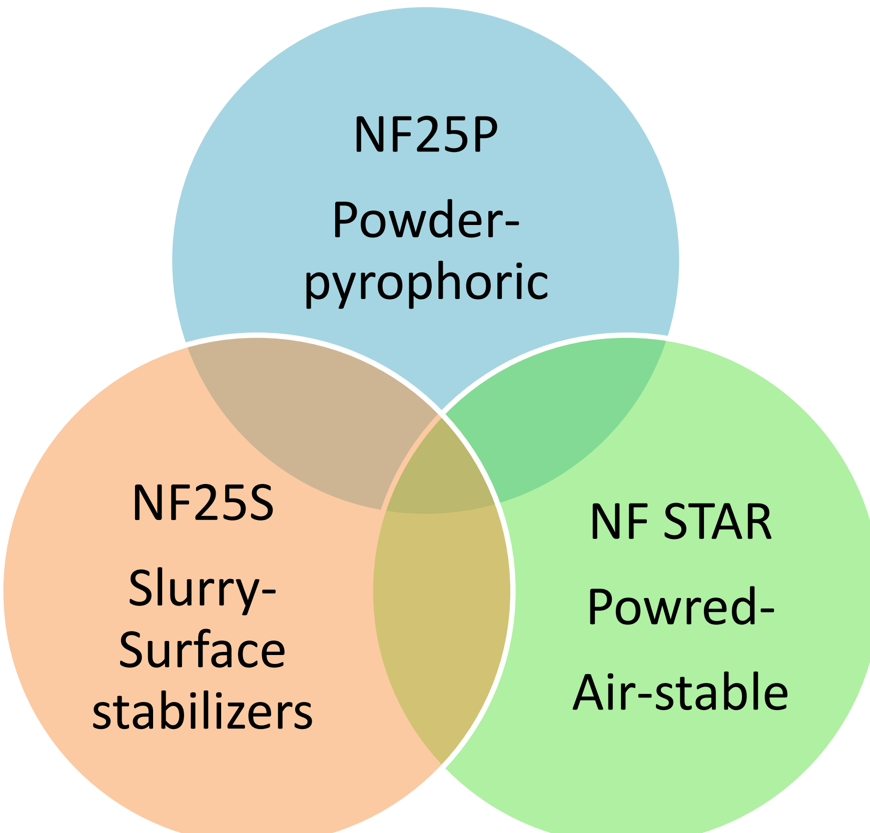
Biomagnetite

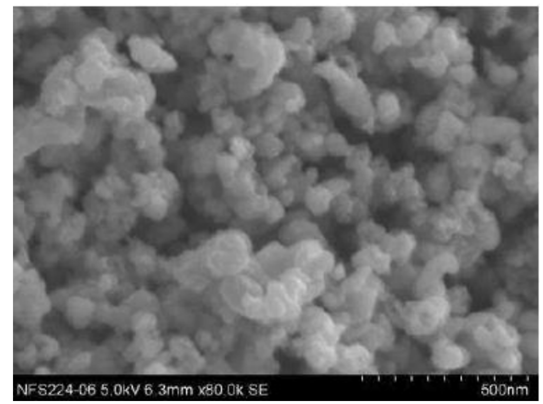


Feox NP

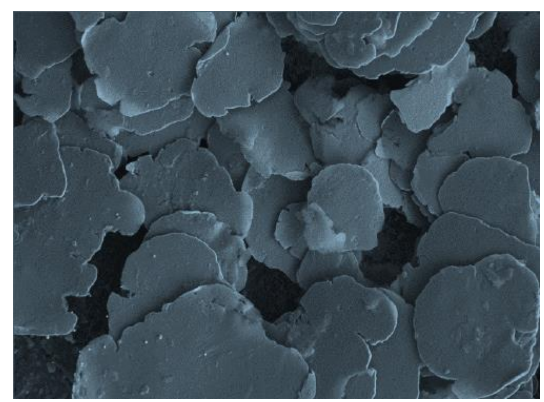
Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

WP2: nZVI particles





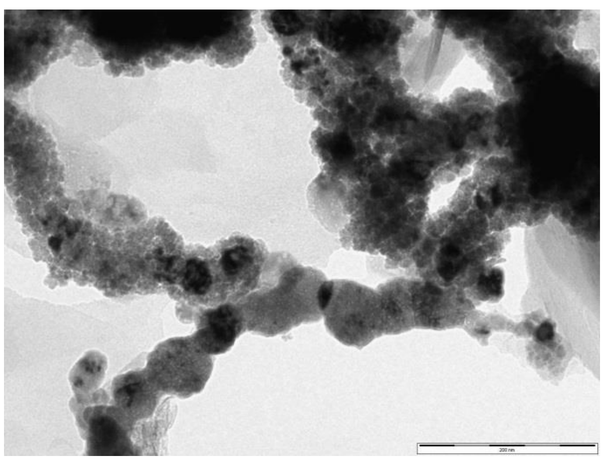
NF STAR

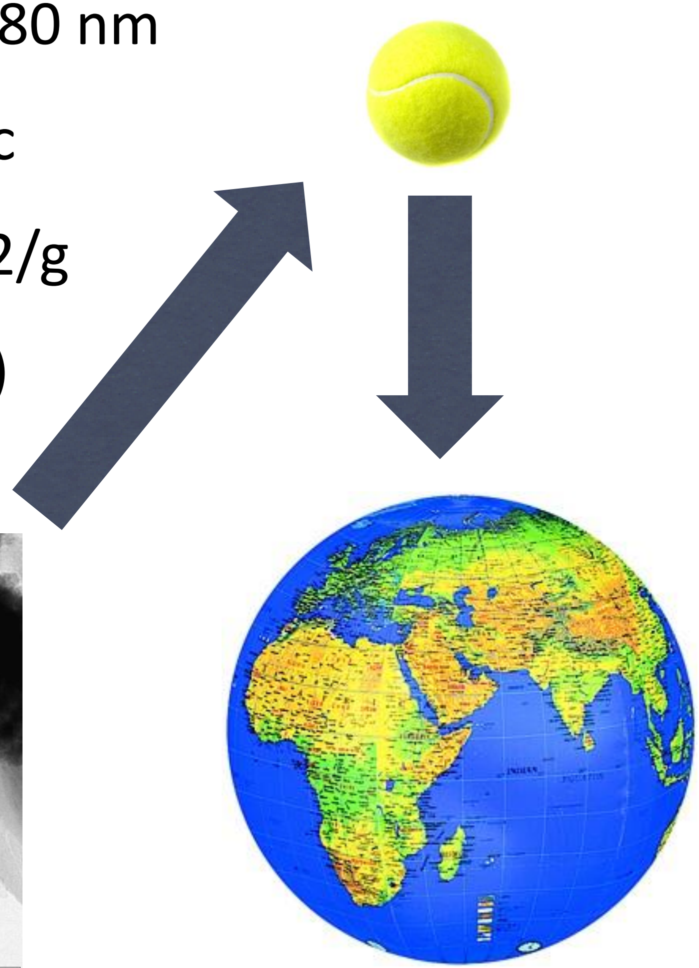


milled NP

Basic nZVI characteristics

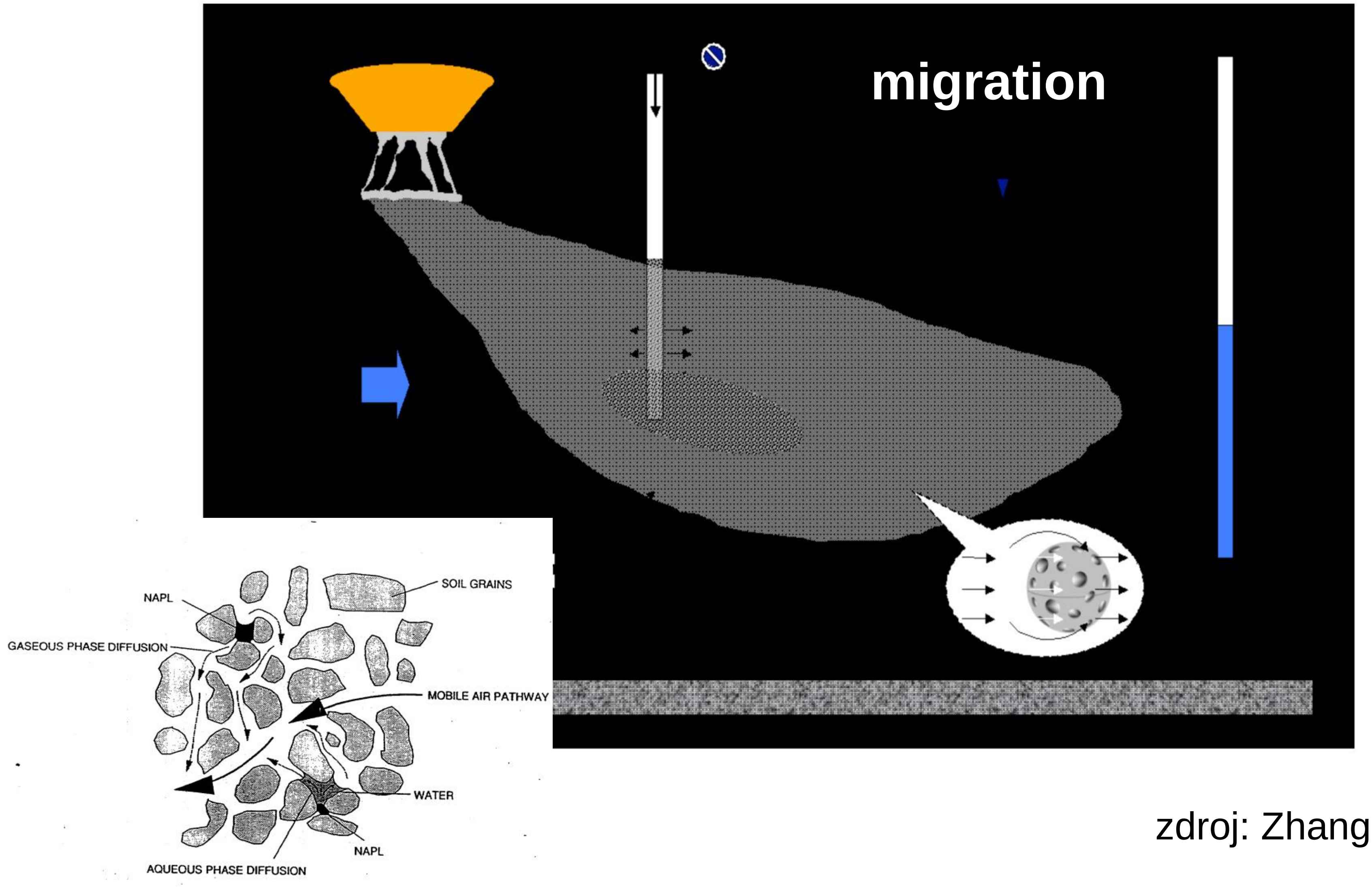
- Nanoscale particles ~ 80 nm
- Reactivity - pyrophoric
- Surface area 20-30 m2/g
- Majority of Fe^0 (>90%)





100 nm

Basic of nanoremediation



zdroj: Zhang

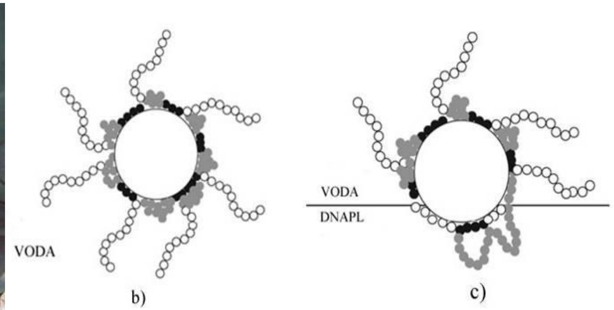
Optimal properties

- reactivity **with contam.**
- mobility **in the aquifer**
- stability **before appl.**

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

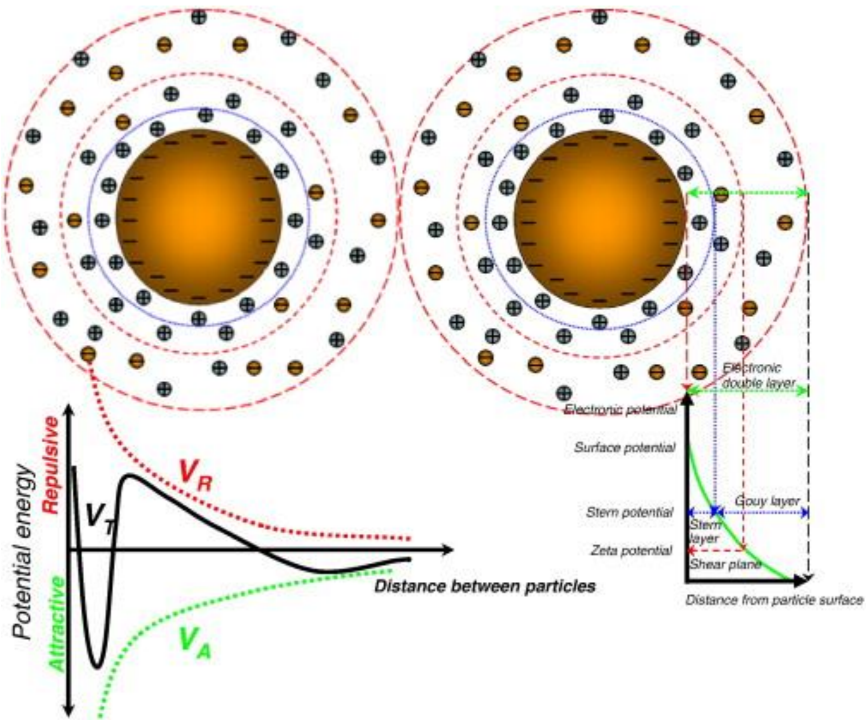
Surface modification

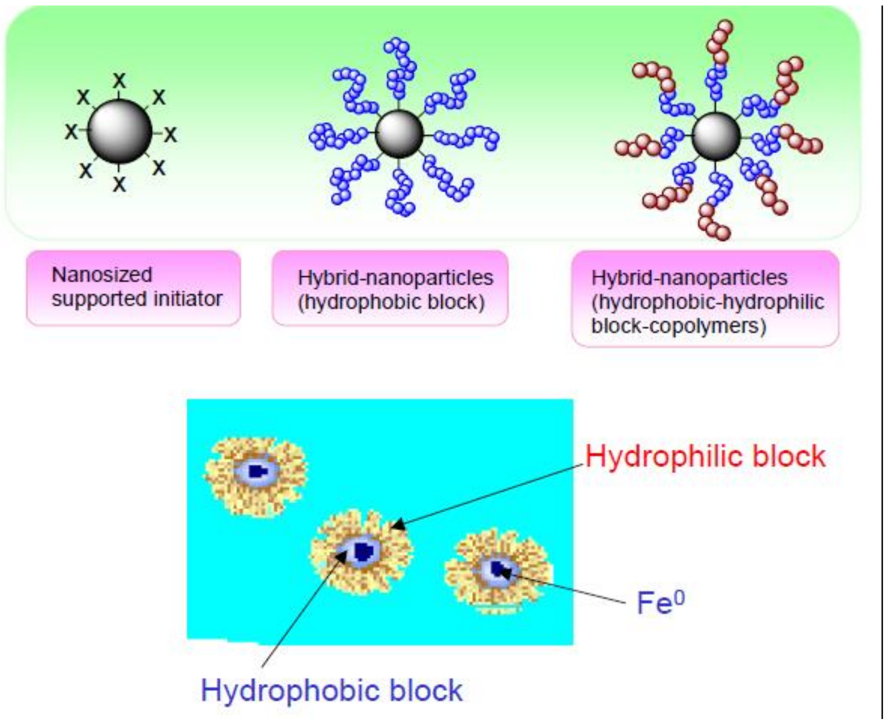
Inhicor-T
Starch
Carboxymethyle cellulose
Polyacrylic acid
Cellulose
Tween 60



Princip of stabilization

- Electrostatic: increase of surface charge → repulsion
- Sterical → increase of nZVI distance

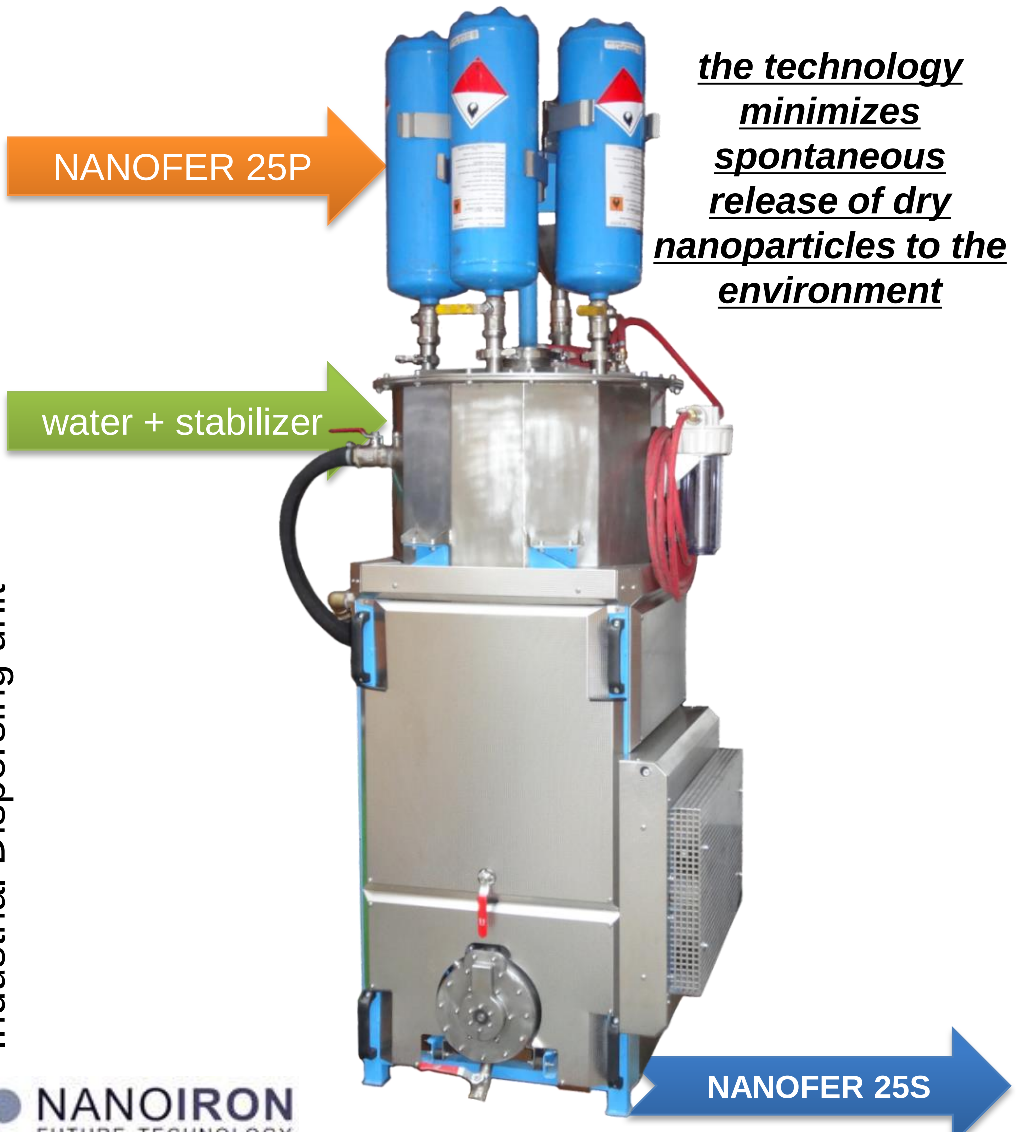




nZVI Slurry Manufacturing

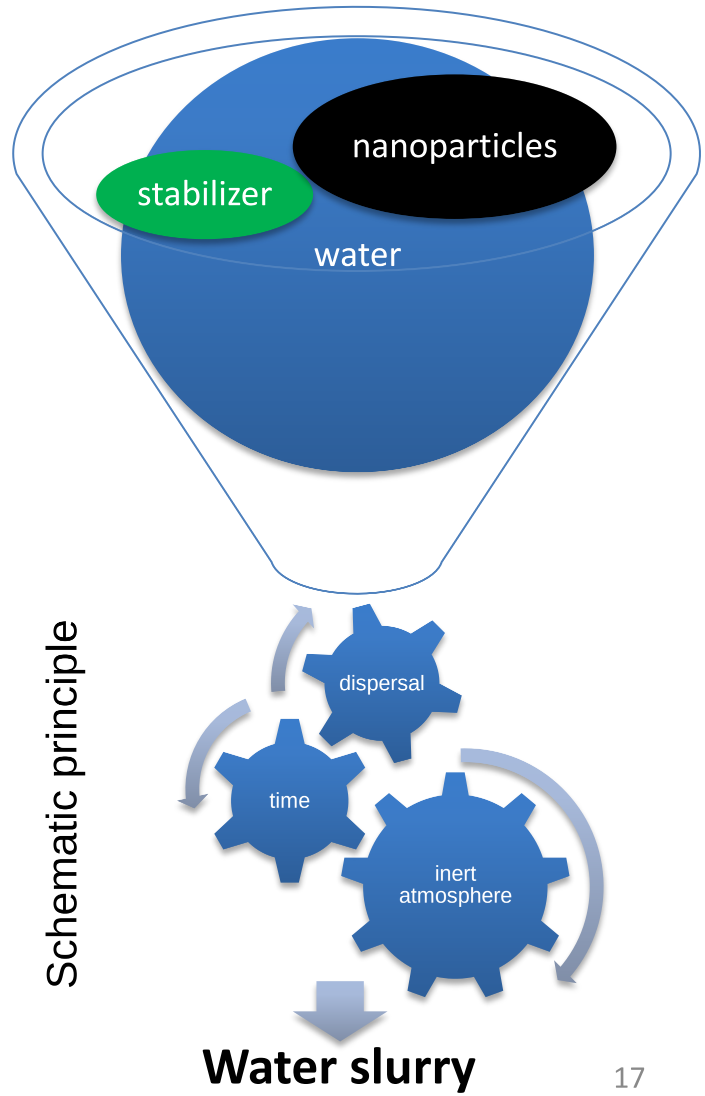
Dispersing process: preparation of fresh nZVI slurry

Industrial Dispersing unit



the technology minimizes spontaneous release of dry nanoparticles to the environment

Schematic principle



NANOIRON
FUTURE TECHNOLOGY

NANOFER STAR

Dry air-stable powder

Innovative nZVI Manufacturing

Field deployment approaches

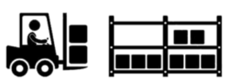
SLURRY MANUFACTURING → SHIPPING → STORAGE → DILUTION → INJECTION

Conventional delivery and application process

15-60 days

1 day

POWDER SHIPPING → STORAGE → SLURRY MANUFACTURING → DILUTION → INJECTION



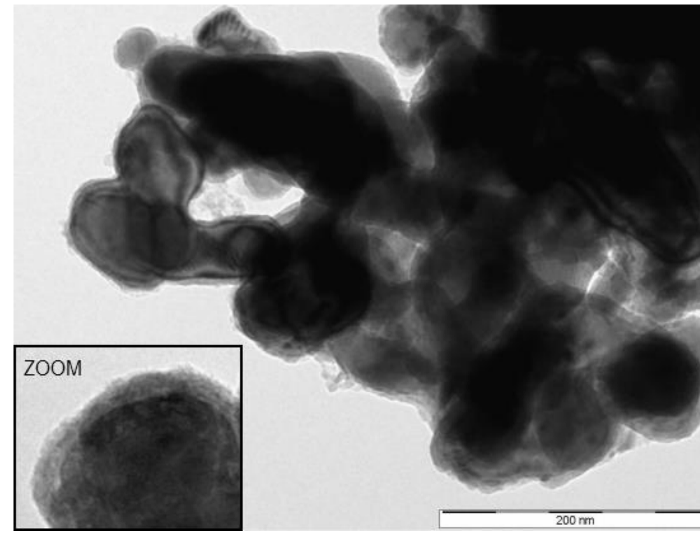
Innovative application process

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

Innovative nZVI Manufacturing

NANOFER STAR: air-stable powder



- Composition (wt%):
  - Min 80% of nZVI
  - Max 20% of iron oxides
- Primary stabilization technique

- STAR means:
  - **S**urface stabilized
  - **T**ransportable
  - **A**ir-stable
  - **R**eactive

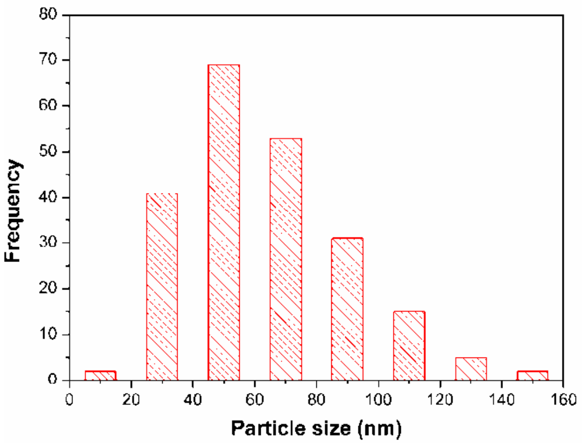
+	−
No degradation (unlimited storage time)	Dangerous classified (UN 3089 - flammable)
High reactivity (comparable to NANOFER 25P)	Lower amount of nZVI (comparing to NANOFER 25P)
Even cheaper shipping (comparing to NANOFER 25P)	
Air stability	

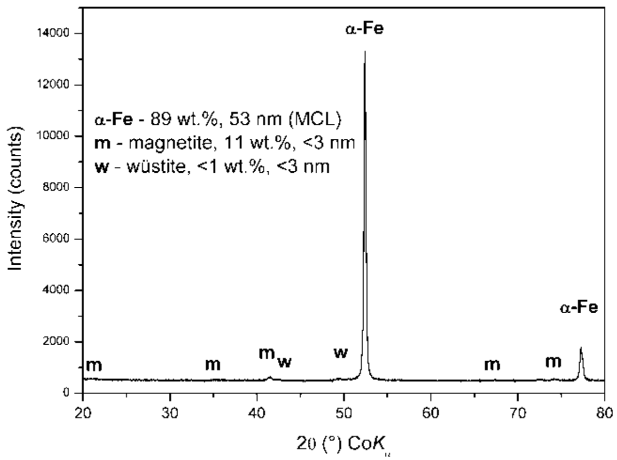
NANOIRON FUTURE TECHNOLOGY

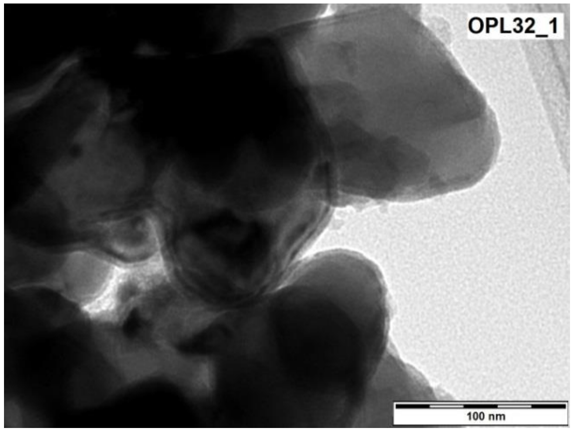
Challenging nZVI materials

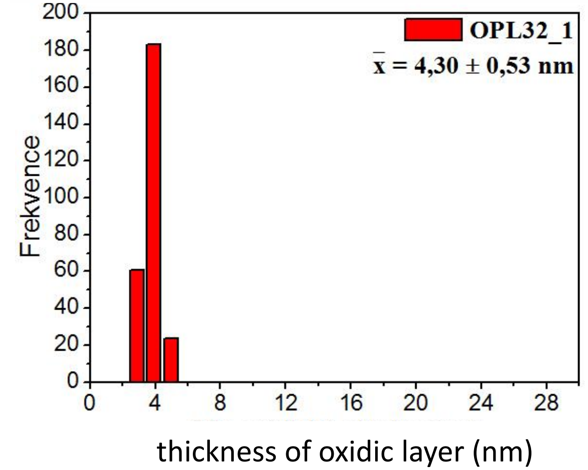
Dry NP powder

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







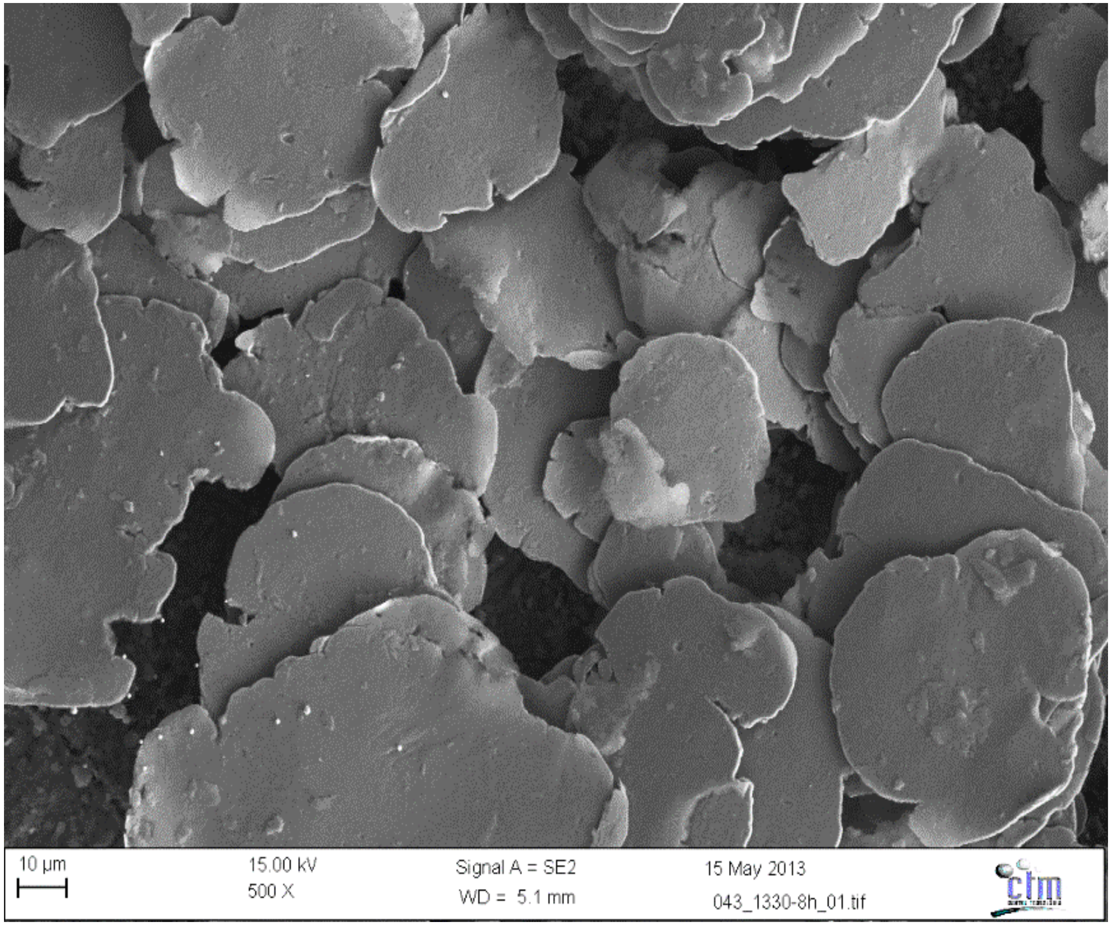


Milling process

Alternative nZVI preparation

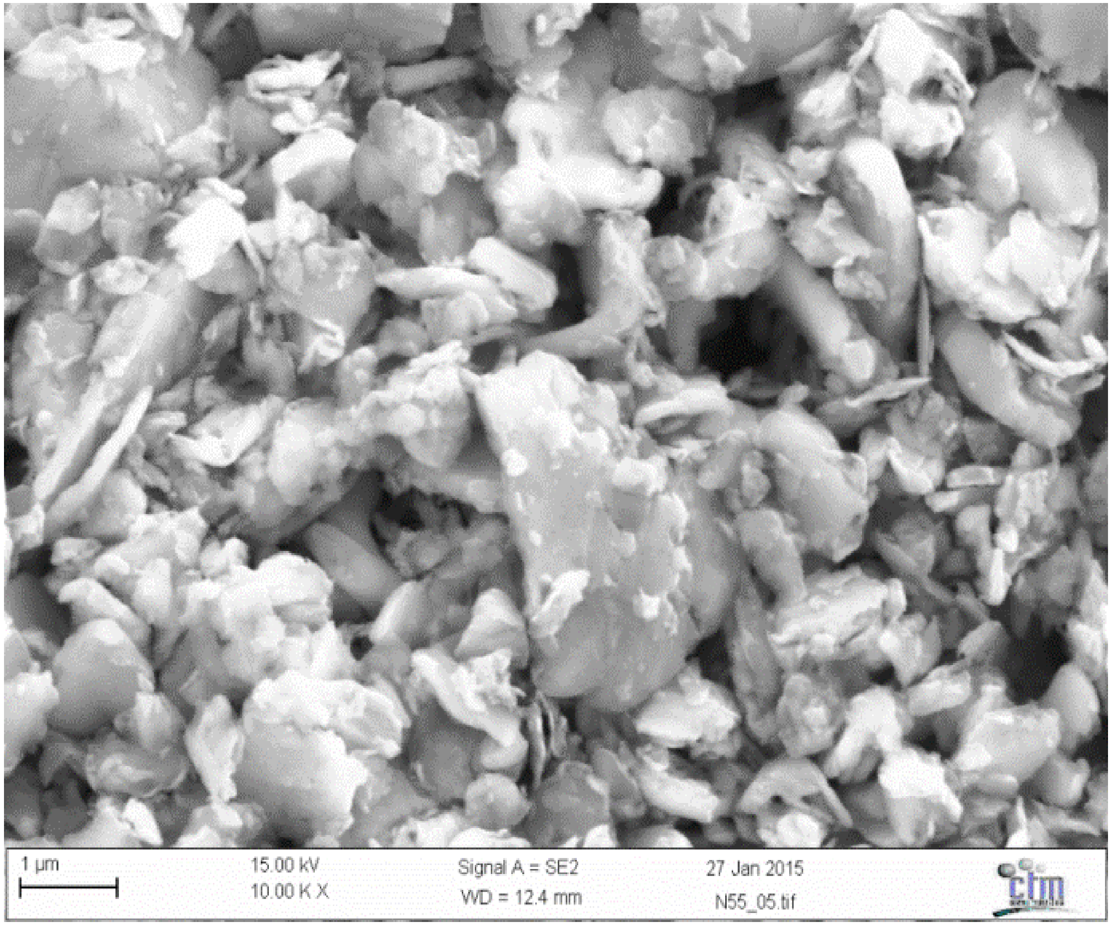
ZVI milling from micro scale

- Preparation of “nano” ZVI particles
- Water or ethanol → flakes (< 100 nm thickness)



ZVI milling

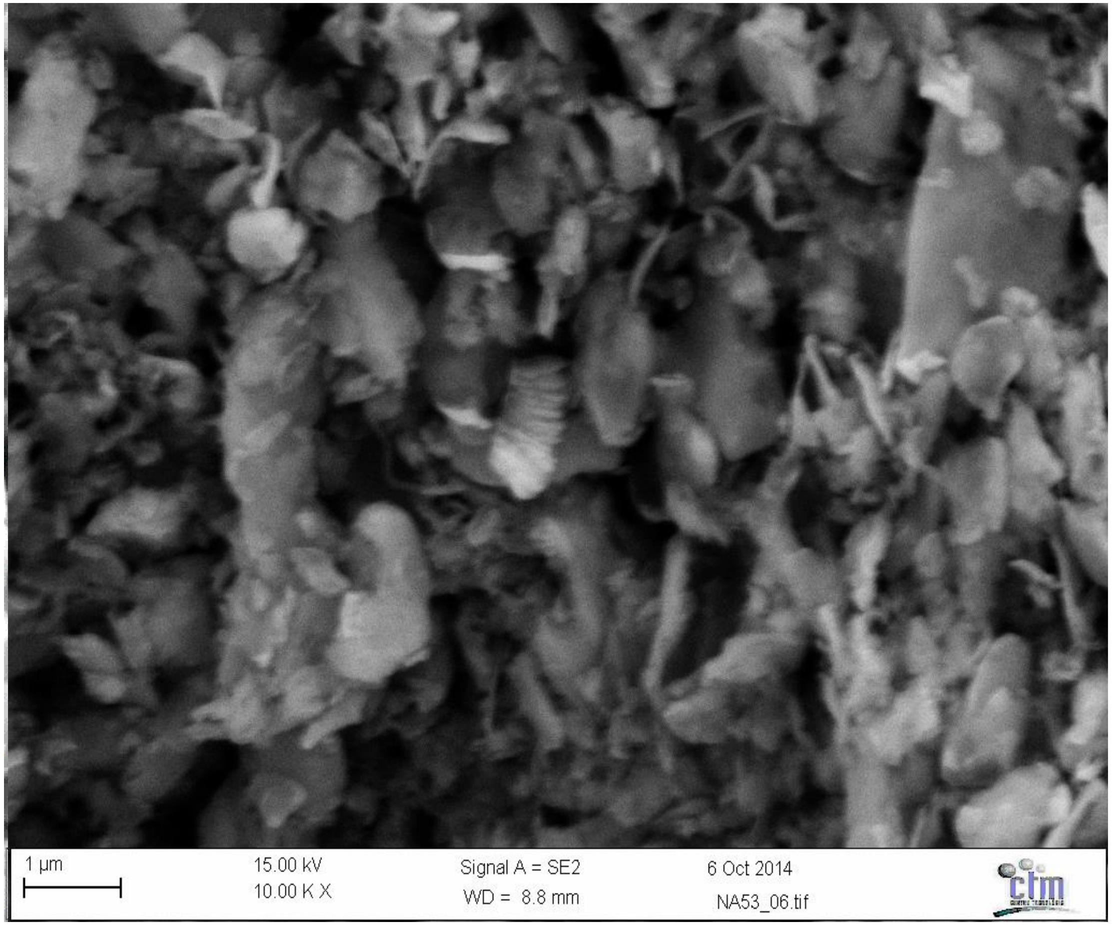
- Preparation of “nano” ZVI particles
- MEG solution



original

ZVI milling

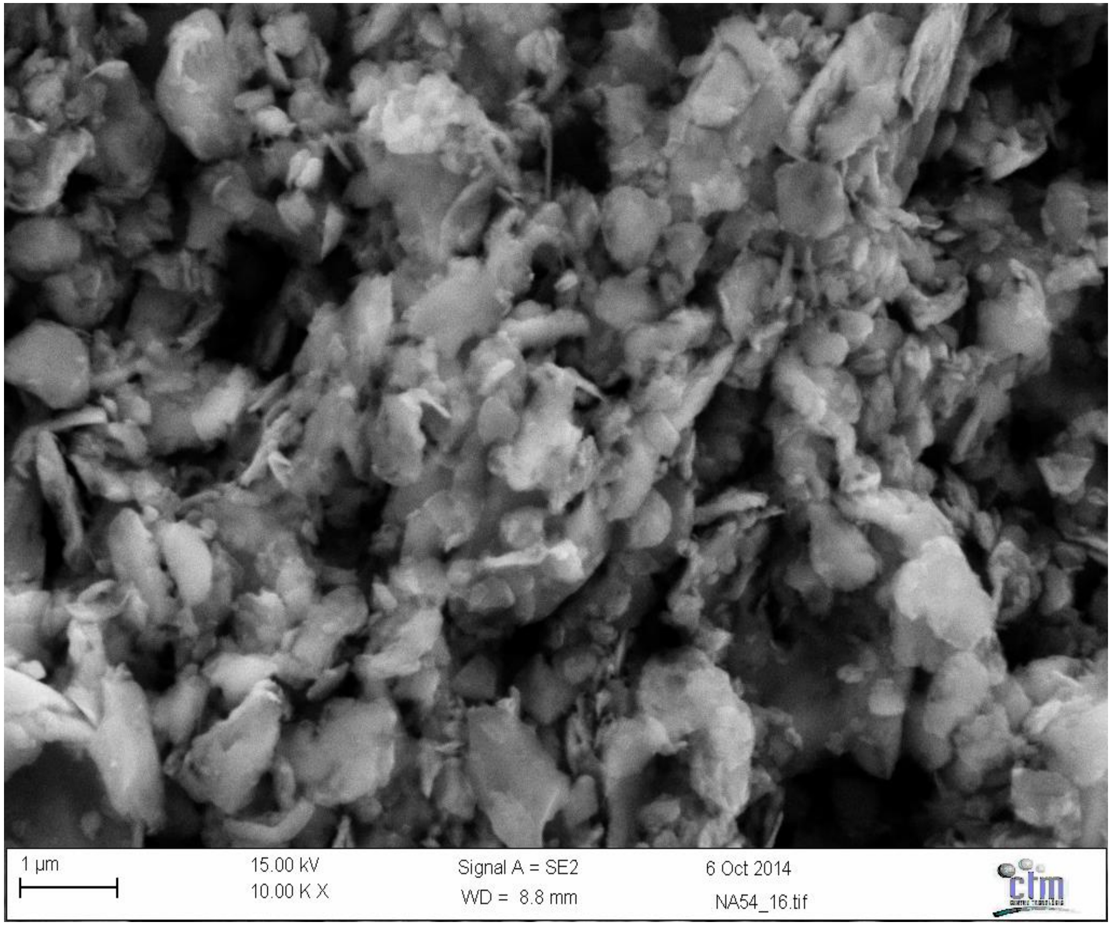
- Preparation of “nano” ZVI particles
- MEG solution



1 g alumina

ZVI milling

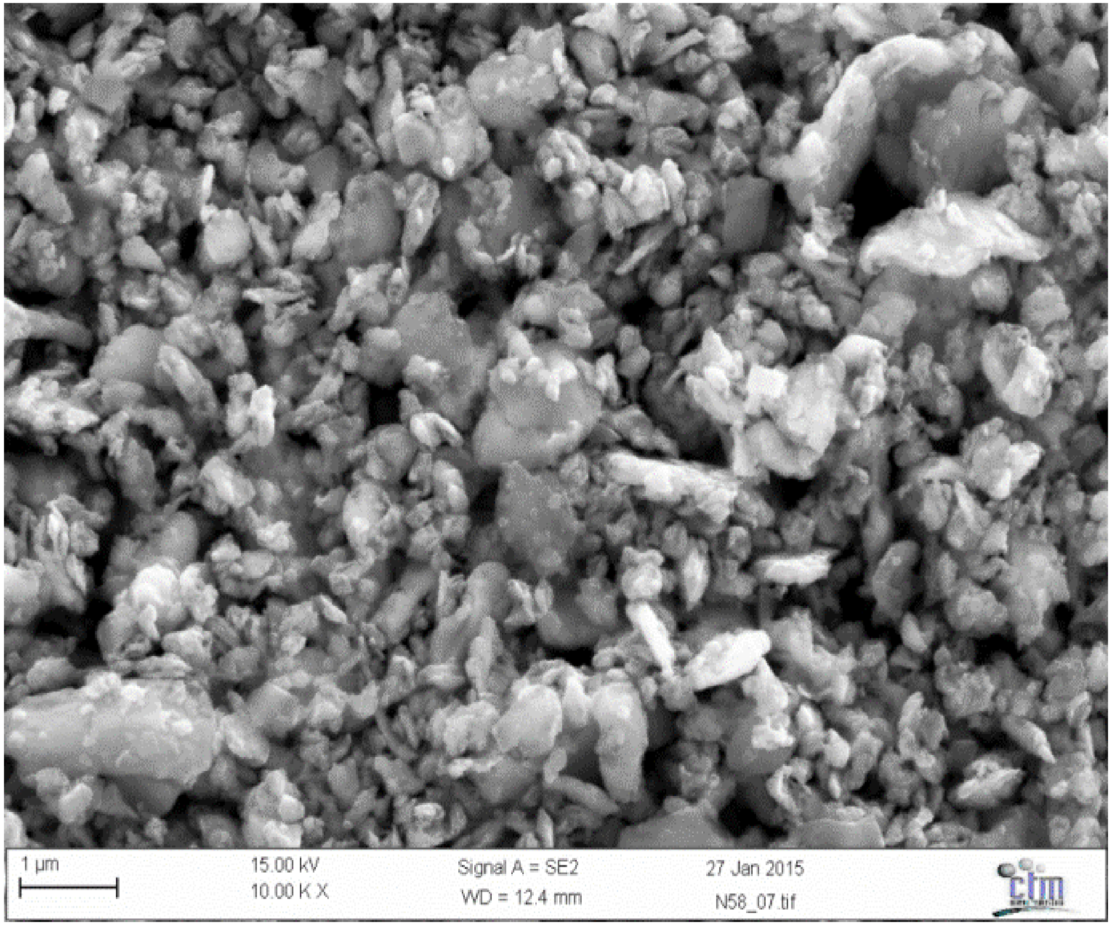
- Preparation of “nano” ZVI particles
- MEG solution



3 g alumina

ZVI milling

- Preparation of “nano” ZVI particles
- MEG solution



10 g alumina

400 nm (med)
Size < 1 µm
(70% volume)

Spherical NP

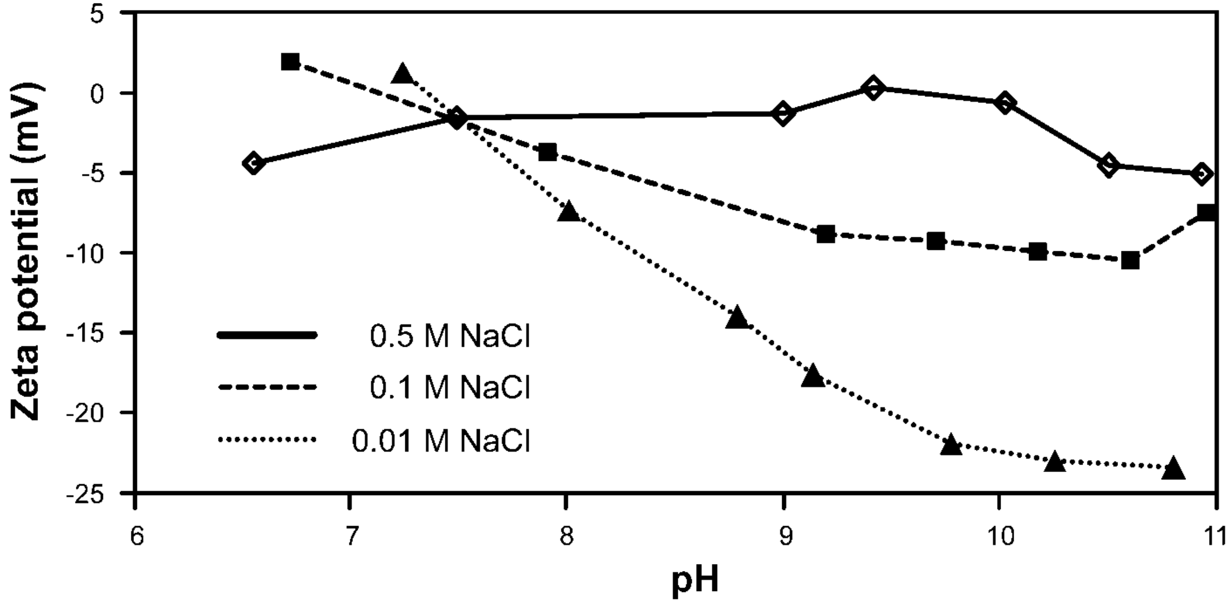
nZVI characterization

3 types of tests

- Structural characteristics:
  - zeta-potential,
  - BET,
  - TEM & SEM, XRD & Mössbauer,
  - Size distribution: DLS & DSC,…
- 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

ZVI characteristics

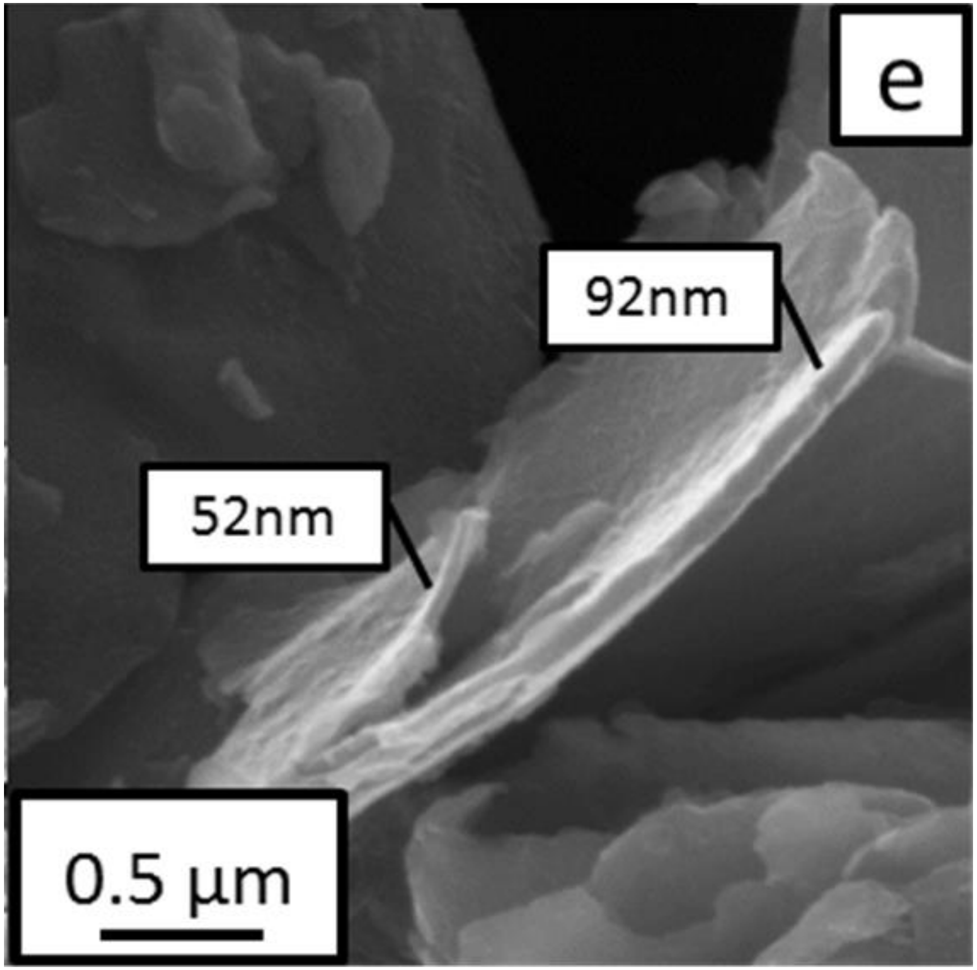
- Zeta-potential



- Addition of NaOH → pH increase
- PZC
- Sign and size at gw pH

nZVI characteristics

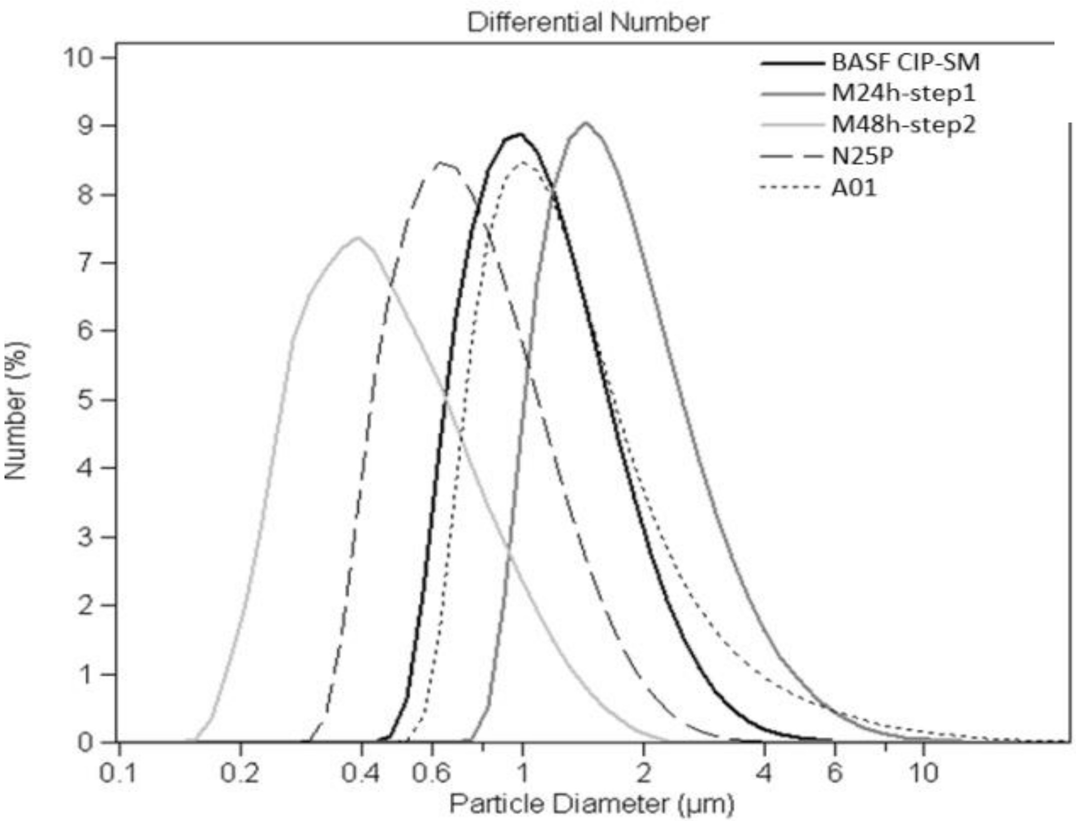
- SEM and TEM pictures

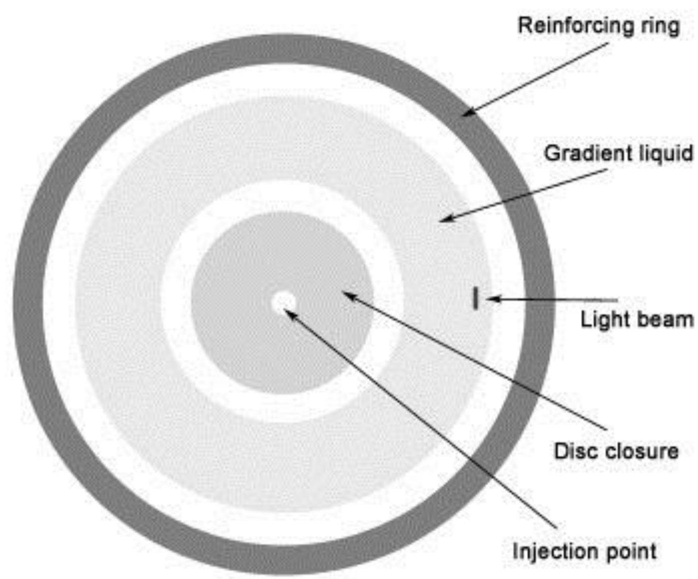


SEM of nZVI after 48h of milling

ZVI characteristics

- Disc gel centrifuge

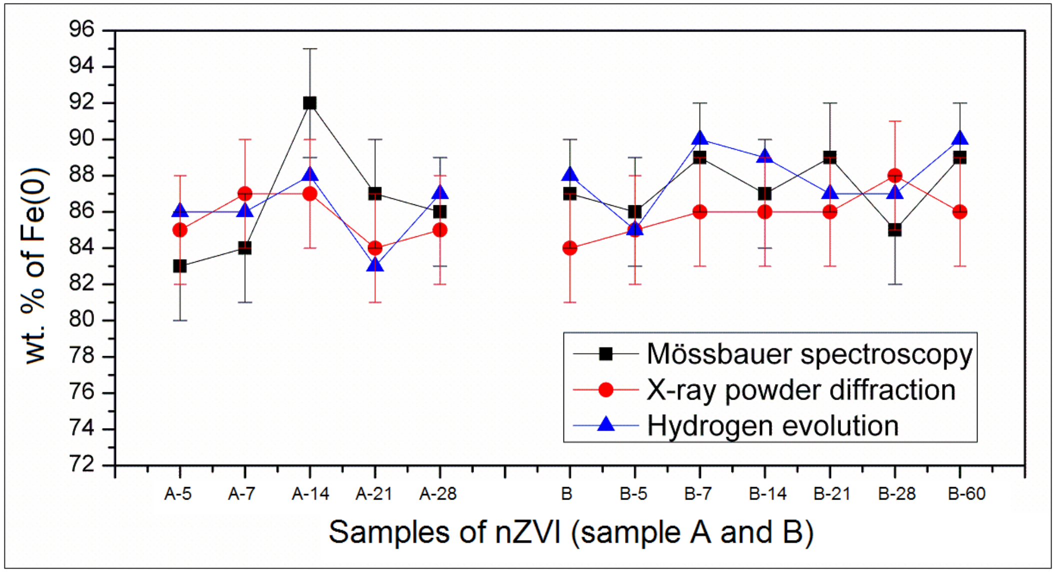




Simple method for reactivity check

QA/QC: Hydrogen evolution method

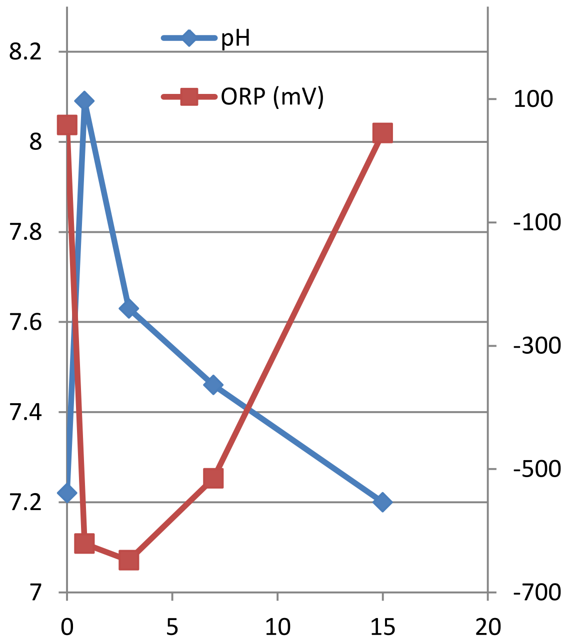
- Simple, cheap and fast measurement of nZVI content.
- Principle: measurement of hydrogen volume, which evolves due to chemical reaction of nZVI and an acid.
- The method has been compared to Mössbauer spectroscopy and X-ray powder diffraction.

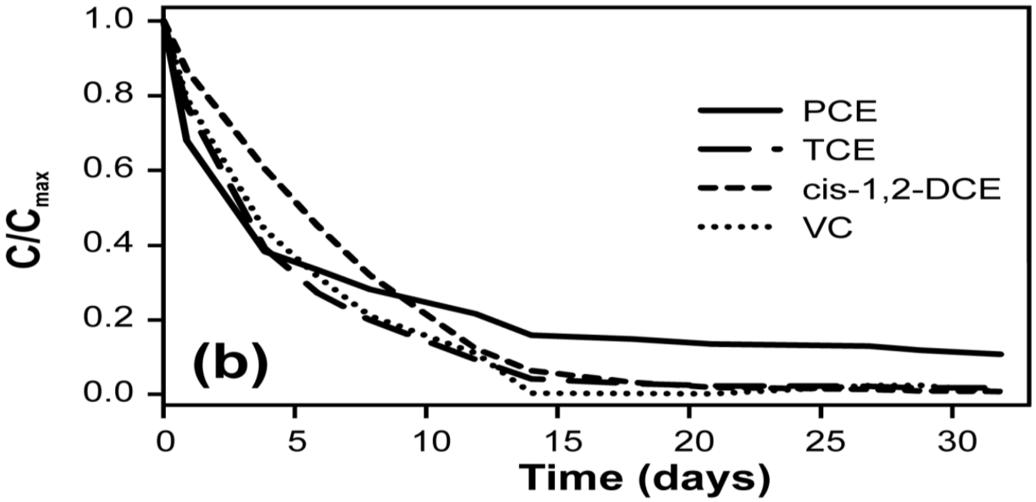


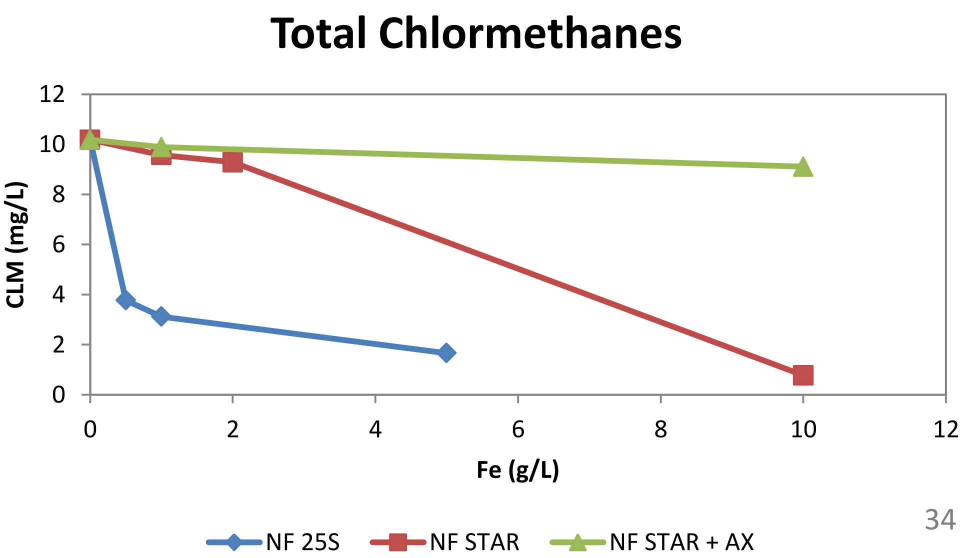
nZVI reactivity

Reaction with contaminated water

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



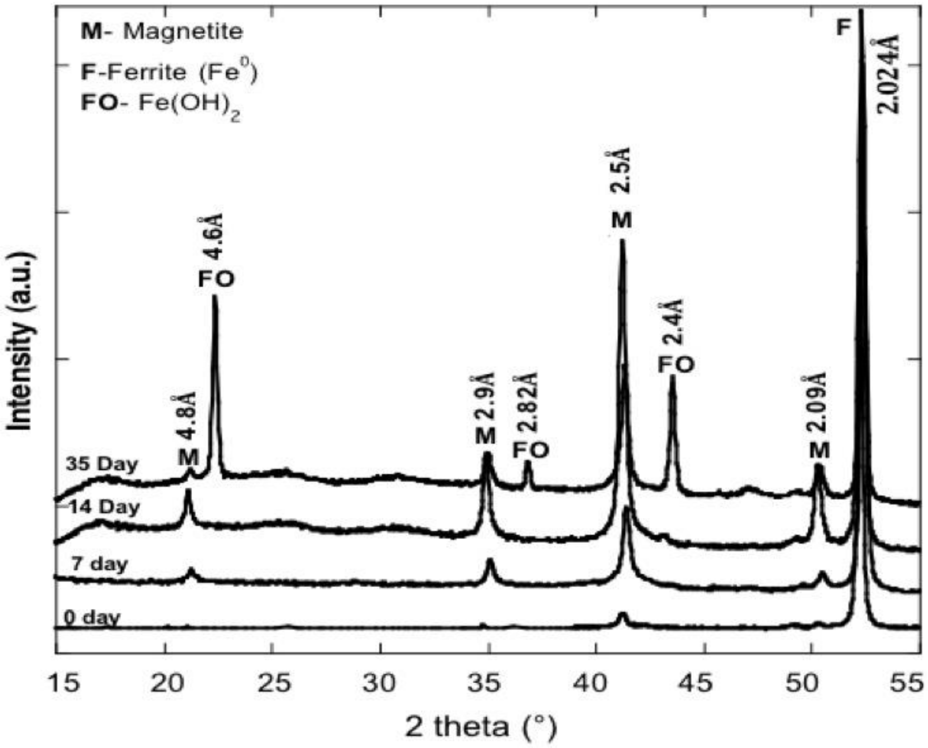


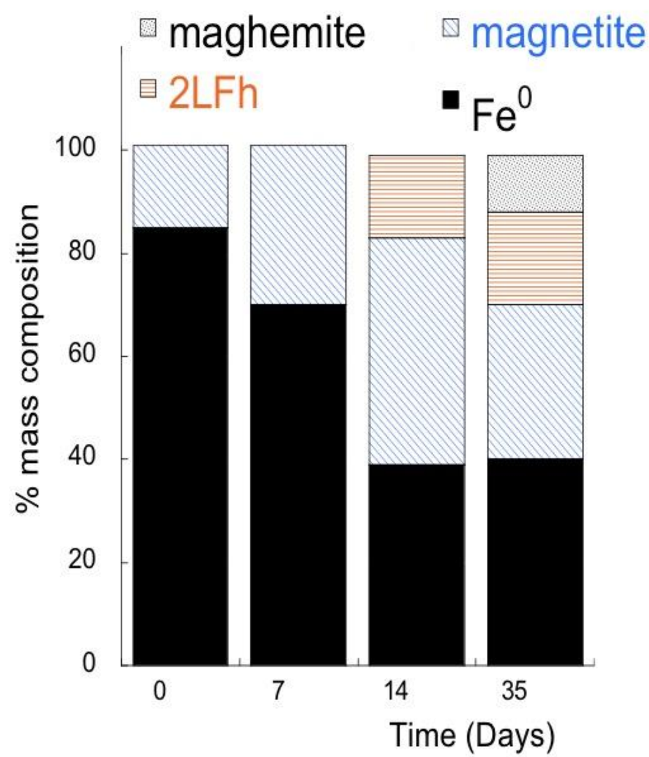


nZVI reactivity

Reaction with distilled water

- Reaction in nitrogen atmosphere
- XRD diffractogram→ mass composition of nZVI

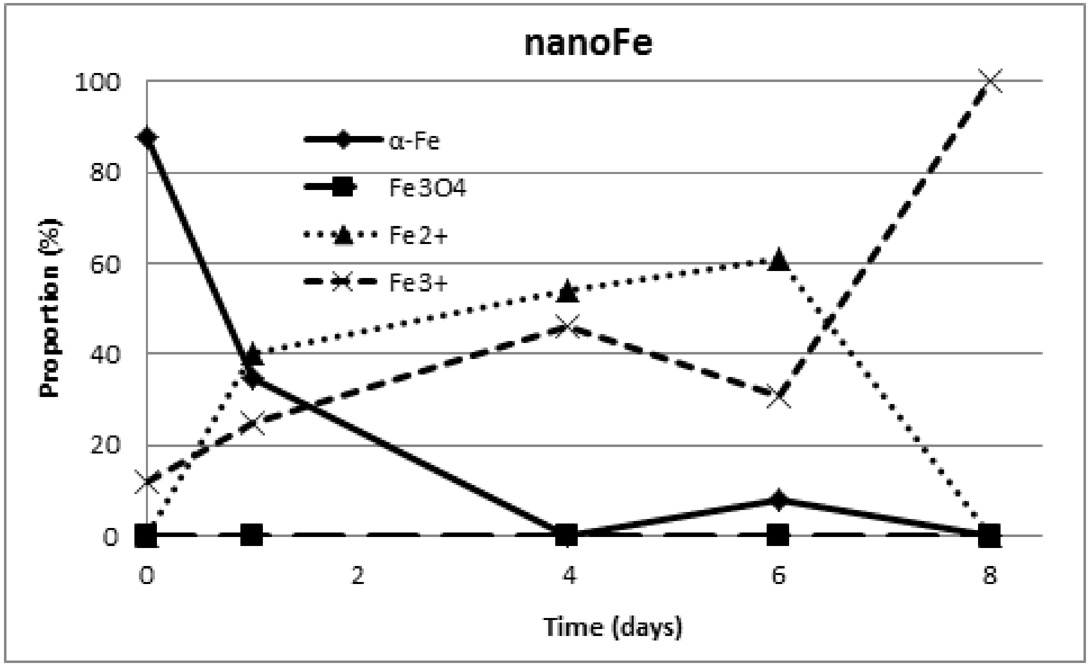




nZVI reactivity

Reaction with contaminated water

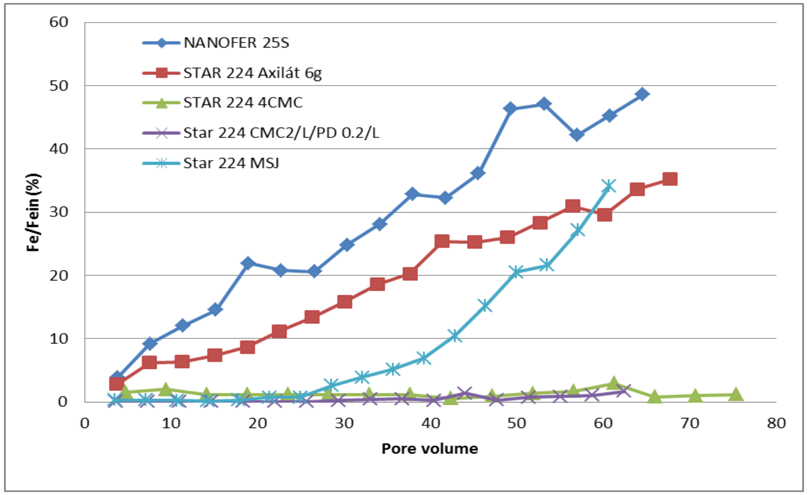
- CHC contaminated water
- Changes in Fe oxidation state composition in time
- Limited nZVI reactivity
- Fe(III)ox final product

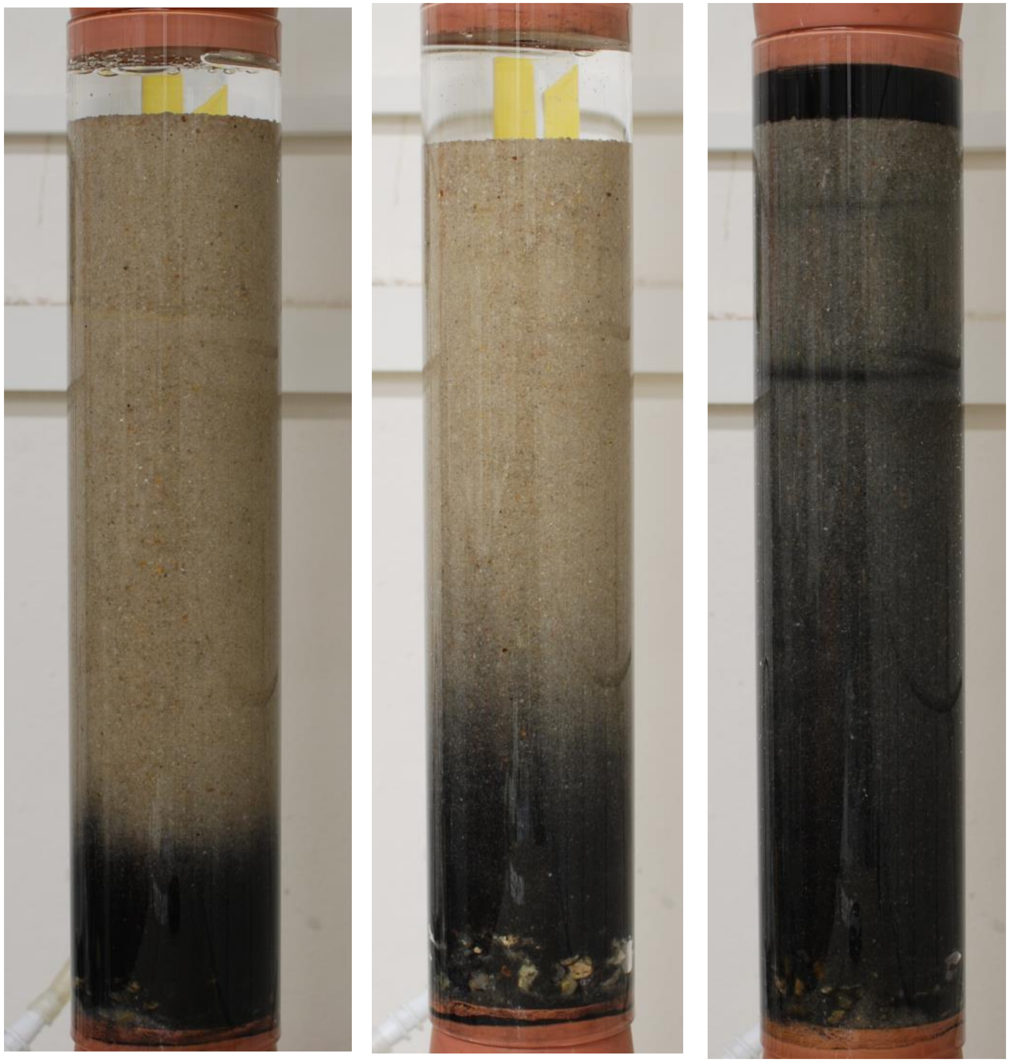


Migration tests

1-D laboratory columns

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





non modified NZVI

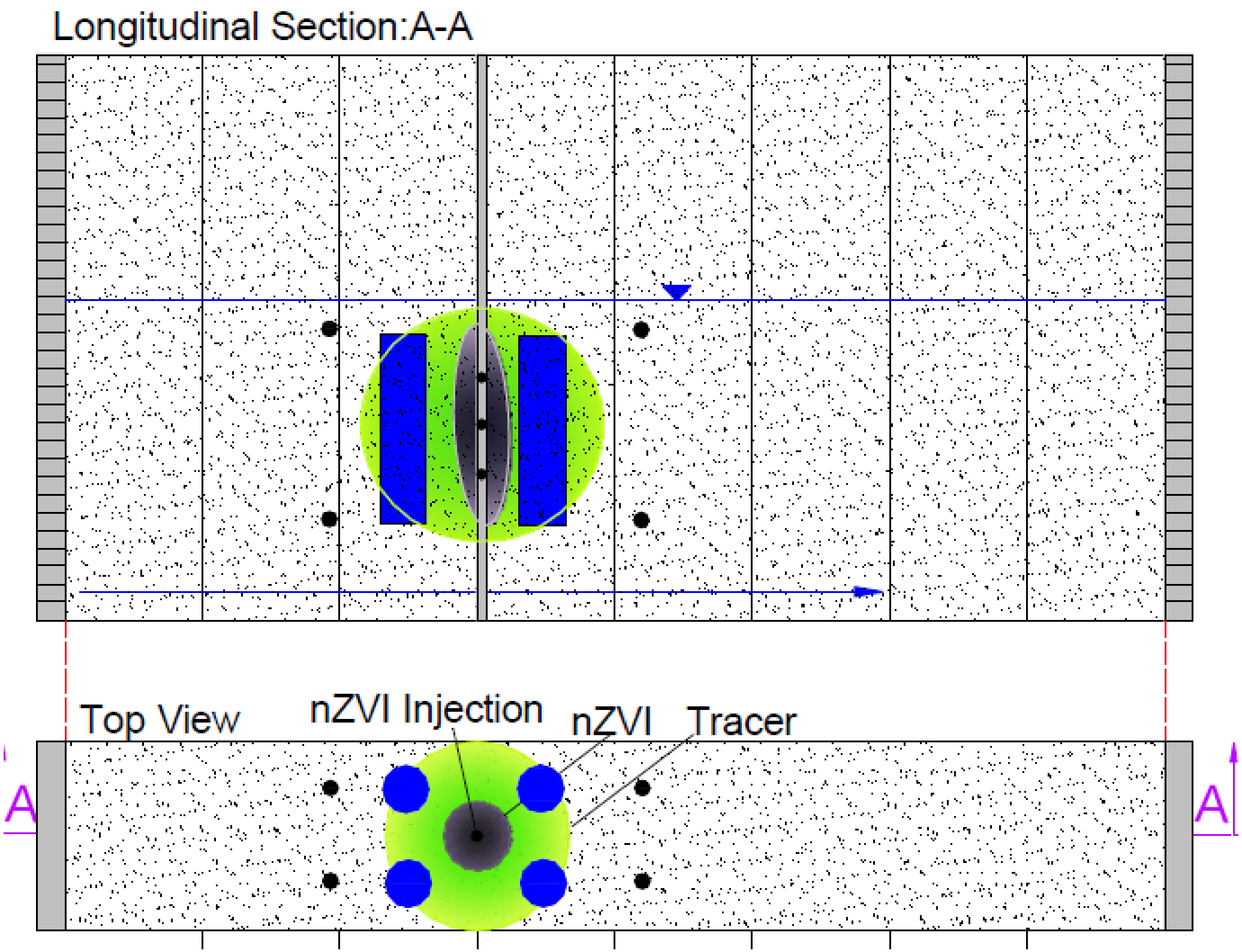
modifications

Migration tests

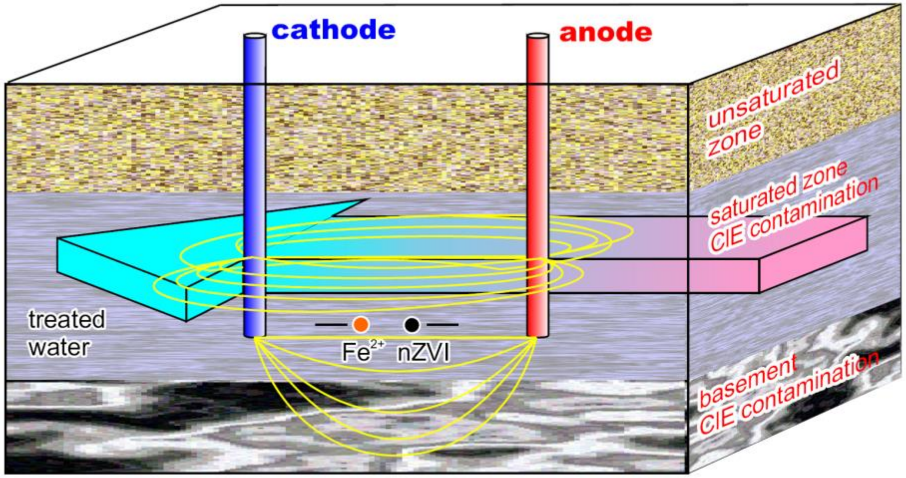
2-D laboratory columns VEGAS Germany (60l, 10g/l, 7 hours)

VEGAS – large flume test

600 x 300 x 100 cm Vessel



Combined methods



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)

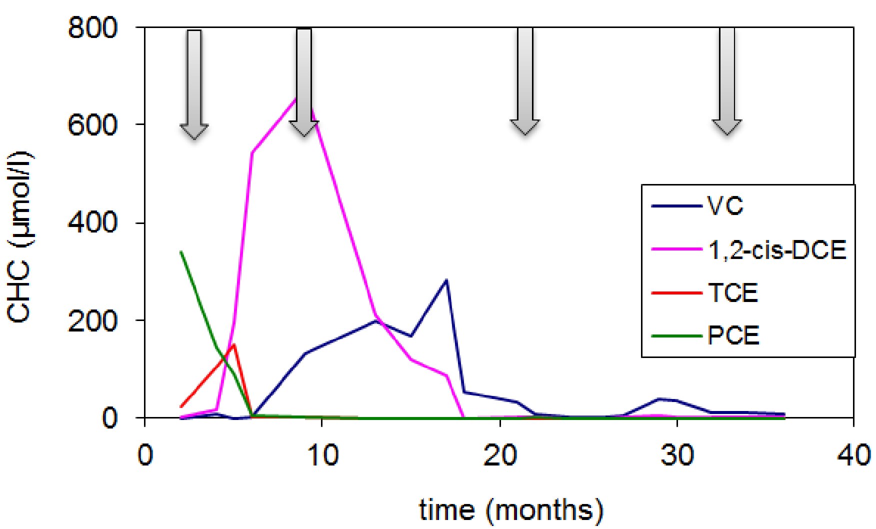
Combination nZVI with bioremediation

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

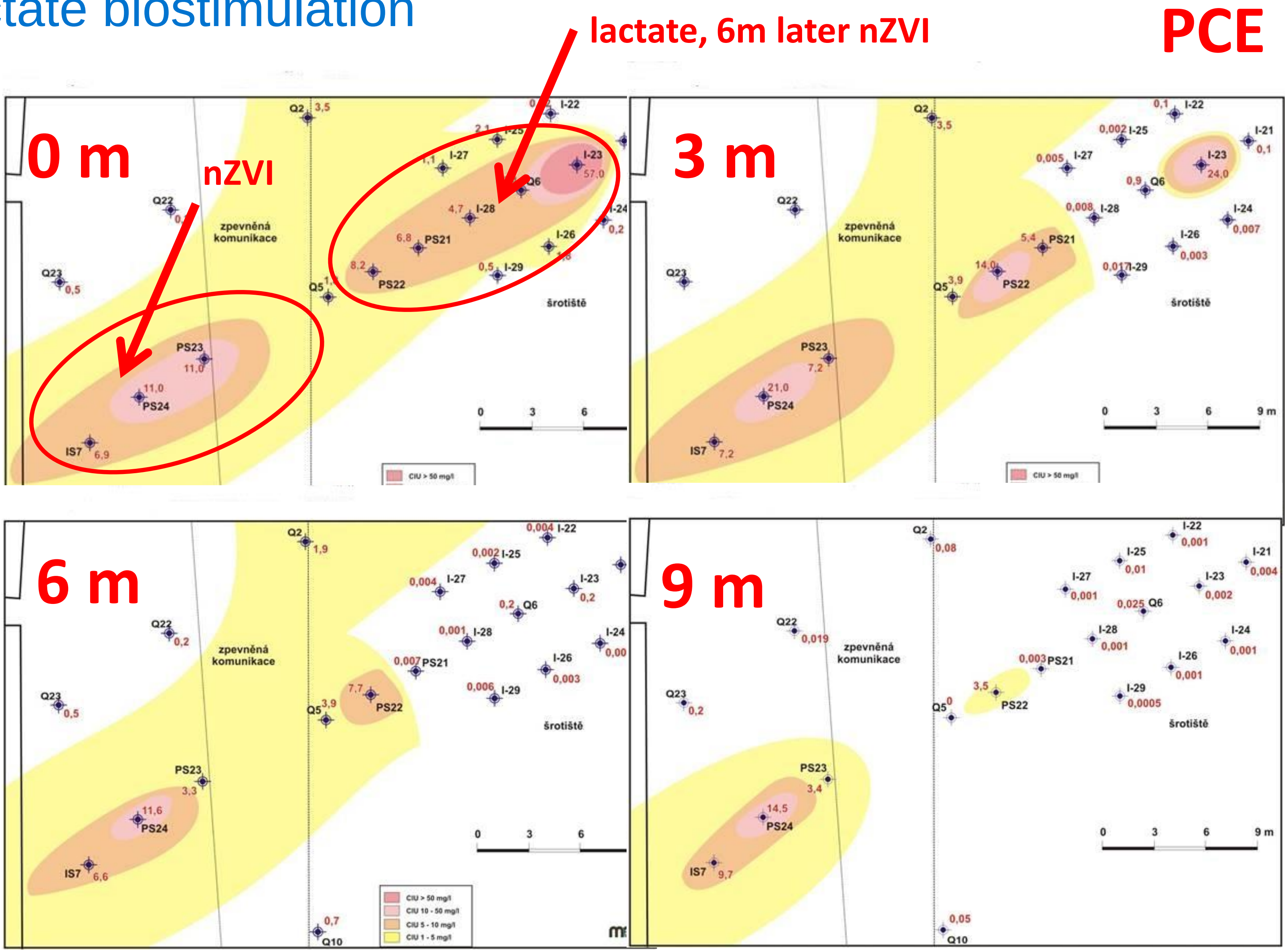
Horice site (CZ)

- Application of lactate
- 3x application nZVI
- Reduction by nZVI (48%)
- Combined reduction (76%)



Combination with bioremediation

lactate biostimulation

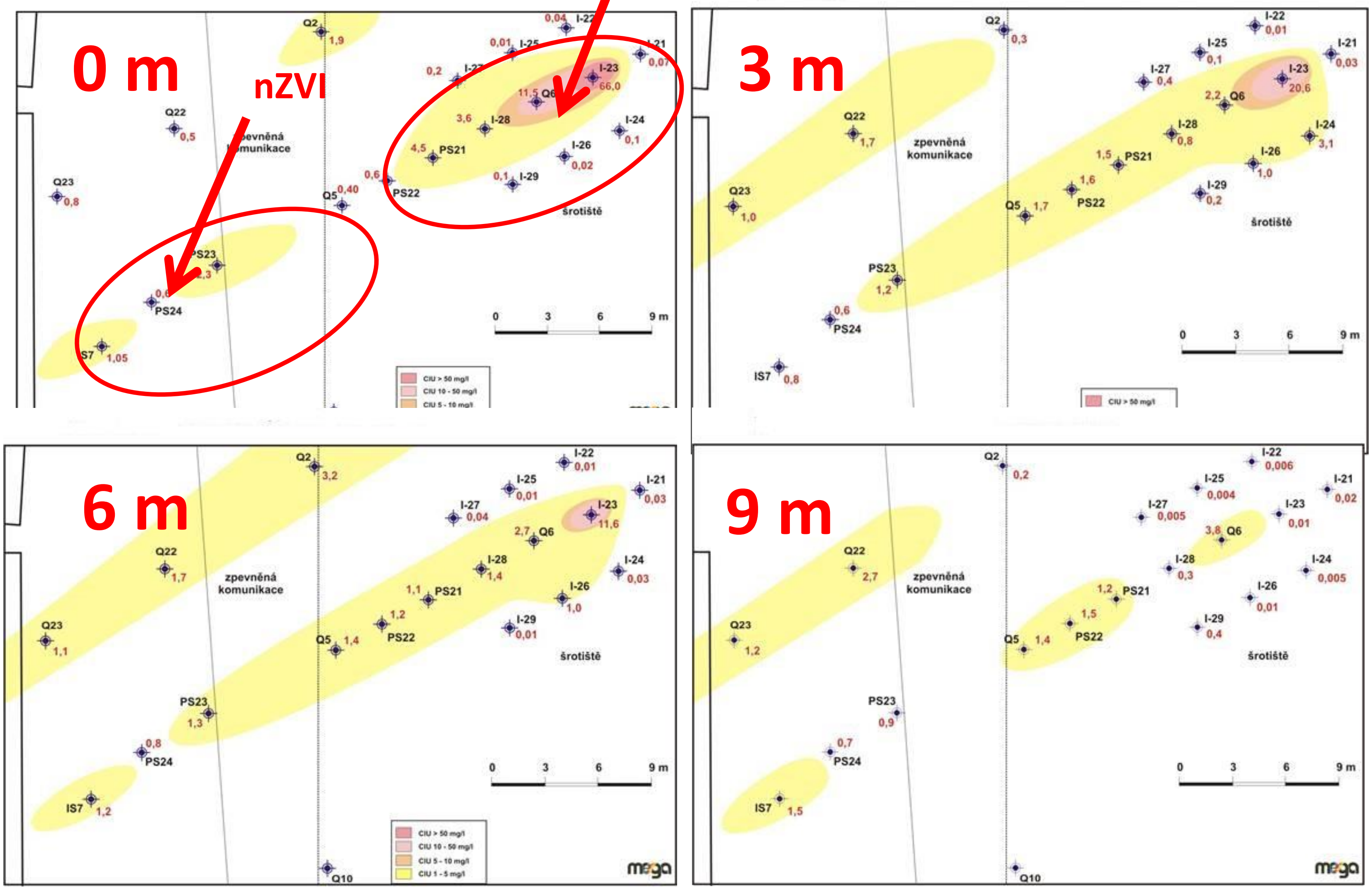


Combination with bioremediation

lactate biostimulation

lactate, 6m later nZVI

DCE



Combination with DC (EK-nZVI)

Principle of reaction

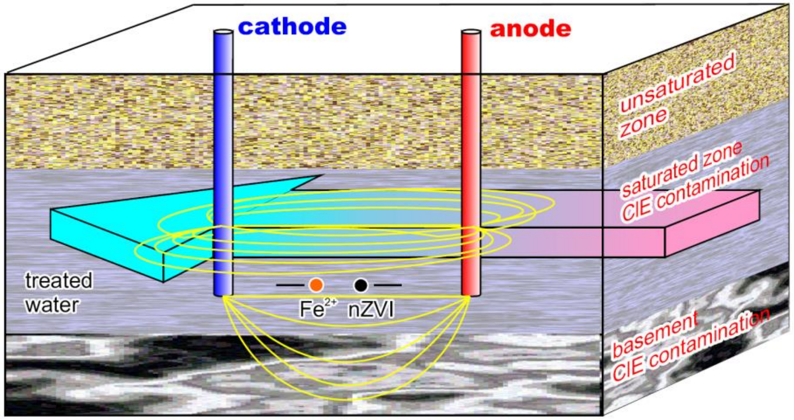
- Chemically supported reductive de-chlorination of CIE
- substitution of chlorine protons, while the electrons

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

- 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 (EK-nZVI)

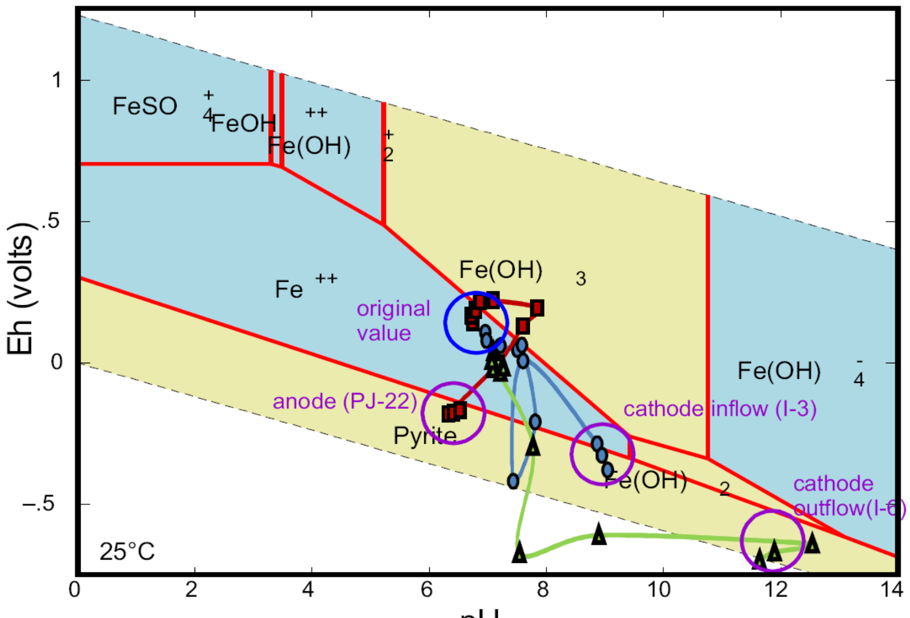
Principle of reaction

Cathode (RED)	Anode (OX)
Water reduction	Water oxidation
pH increase	pH decrease
O_2 reduction	
ORP decrease	ORP increase

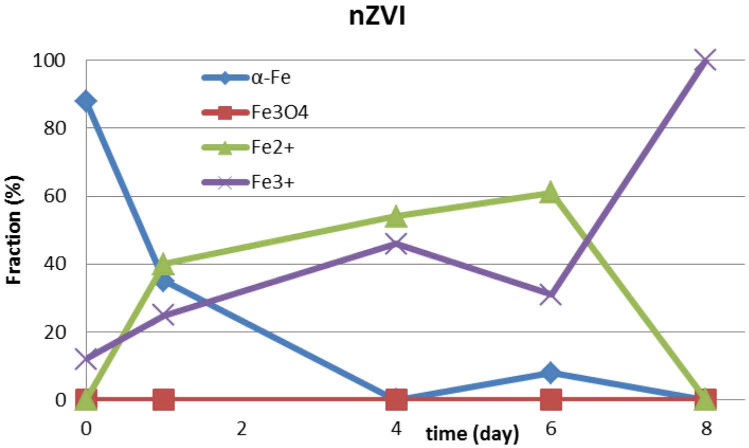
Combination with DC (EK-nZVI)

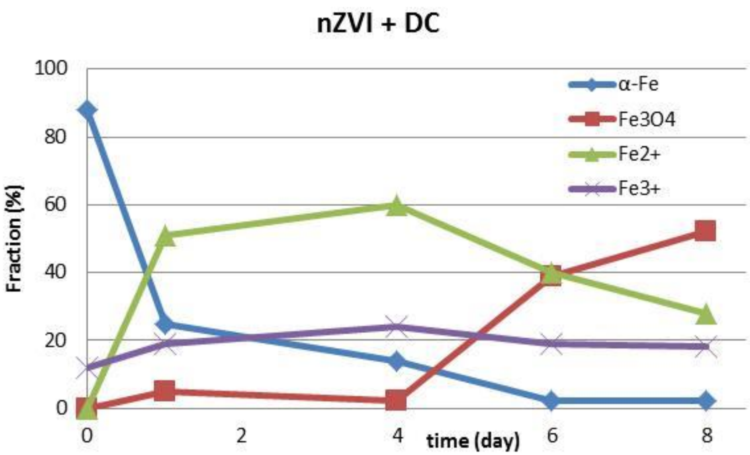
Final products of oxidation

After 30 days 20% of Fe^{2+}



Evaluating the developments of pH and Eh

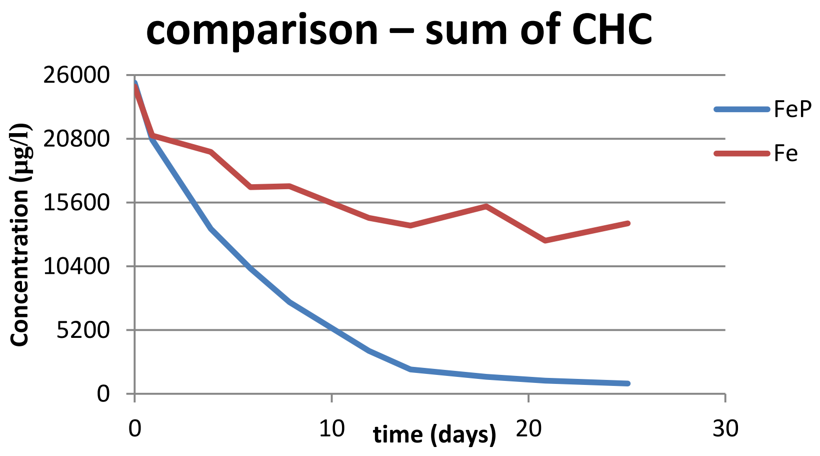


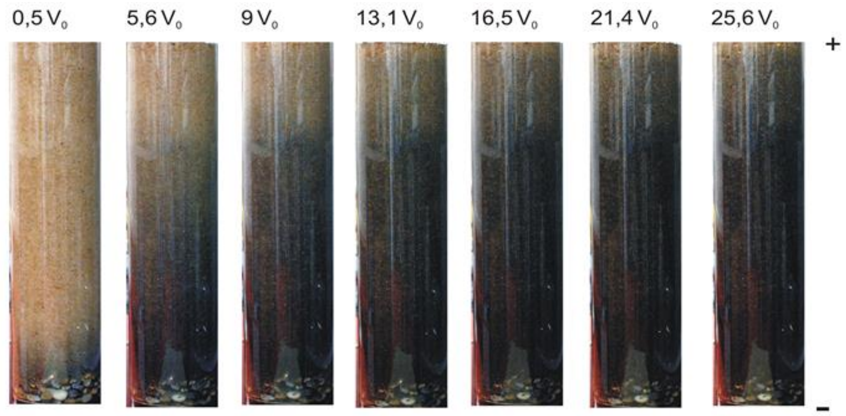


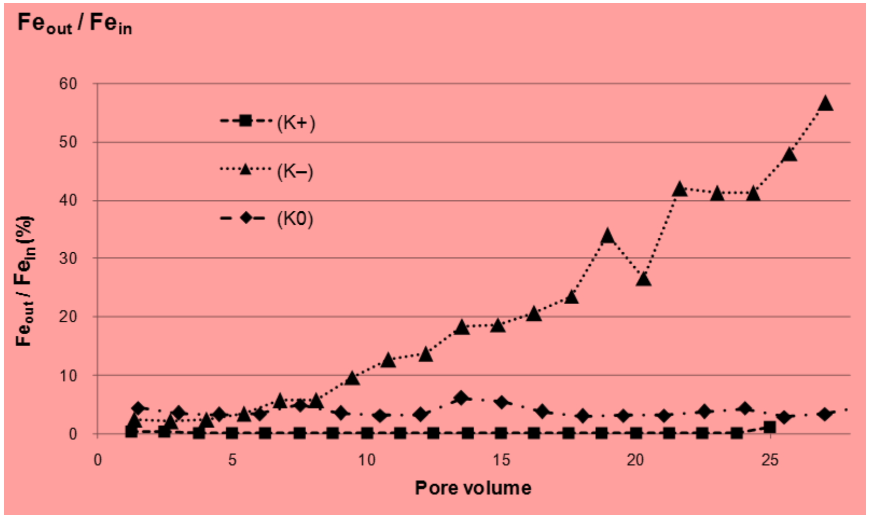
Combination with DC field

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
  - Exposure to NPs. should be 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 – NANOREM
  - Possibility of controlled agglomeration by application of $CaCl_2$
- 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*
  - Arturo A. Keller et al. *Toxicity of Nano-Zero Valent Iron to Freshwater and Marine Organisms*

Innovative nZVI Manufacturing

Toxicity

Soil Slurry: ecotoxicological effects and DDT degradation					
Organism	Endpoint	nZVI-B		NANOFER 25S	
		Aqueous p.	Solid p.	Aqueous p.	Solid p.
Earthworms	Mortality	n.a.	+	n.a.	0
	Growth	n.a.	-	n.a.	+
	Reproduction	n.a.	-	n.a.	+
Ostracods	Mortality	-	-	0	0
	Growth	-	-	0	+
Bacteria	Growth	-	n.a.	0	n.a.
Barley	Germination	+	-	0	-
	Root growth	-	-	+	+
Flax	Germination	-	-	0	0
	Root growth	-	-	+	0
DDT reduction in 24h		92.4%		78.3%	

DDT degradation efficiency and ecotoxicological effects of two types of nanosized zero-valent iron (nZVI) in water and soil

Pisecna – site view

Pisecna – site view

Pisecna site

- Former hazardous waste landfill
- Fractured – bedrock area
- Chlorinated ethenes (Cl-E) and chlorinated ethanes (Cl-A) contamination
- Drinking water sources in the neighbourhood
- High reactivity needed for TCA degradation
- No special permits needed from water authority

Pisecna – Comparative lab-tests

Comparative test for 5 nZVI types:

- borohydride nZVI (Zhang 2003)
- RNIP (Toda)
- NANOFER 25 – without surfactant
- NANOFER 25S – modified by TWEEN
- NANOFER …– modified by axilate
  - Axilate = Na salt of polyacrylic acid

Tested properties:

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

Pisecna – mobility tests

NanoFer

Ammonia axilat

K_f = 1,1 e^{-3}m/s

N_{ef} = 0,4

V = 67 m/day

Fe dose cca. 0,5 g/l

0,5 V_0 8 V_0 25 V_0

NanoFer 25

0,5 V_0 8 V_0 25 V_0

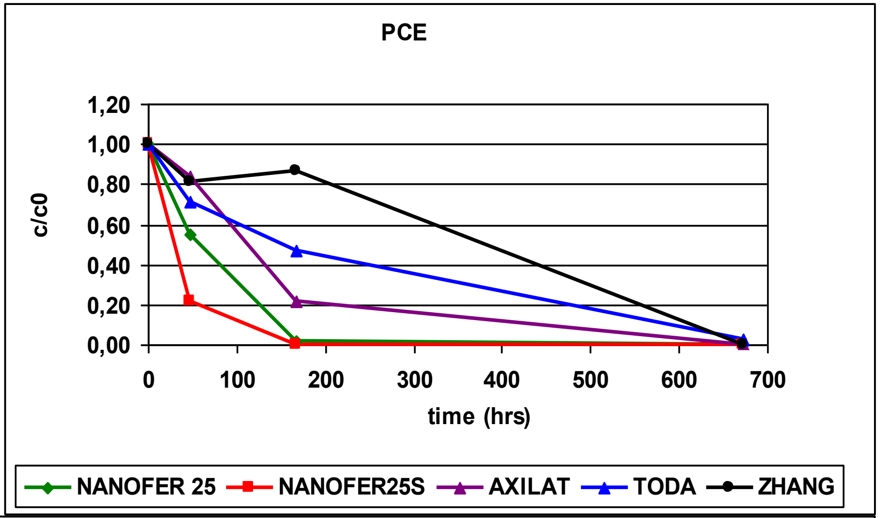
NanoFer 25S

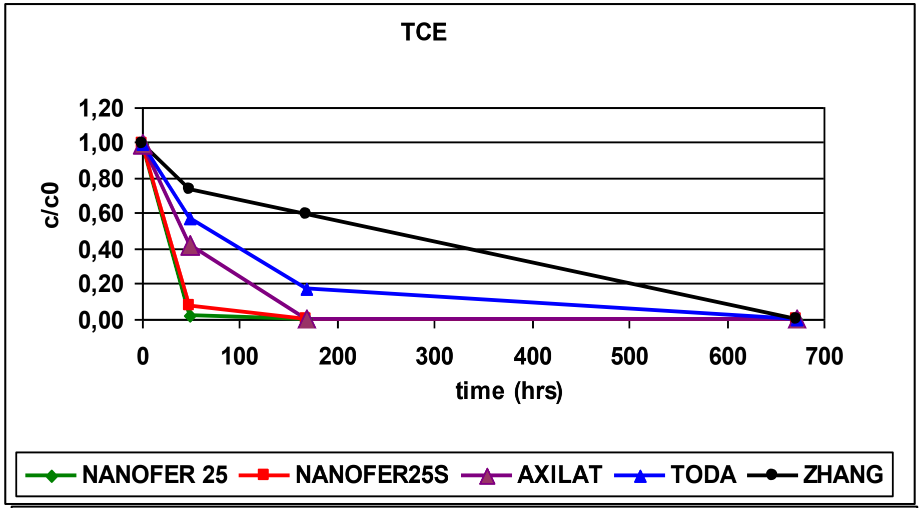
0,5 V_0 8 V_0 25 V_0

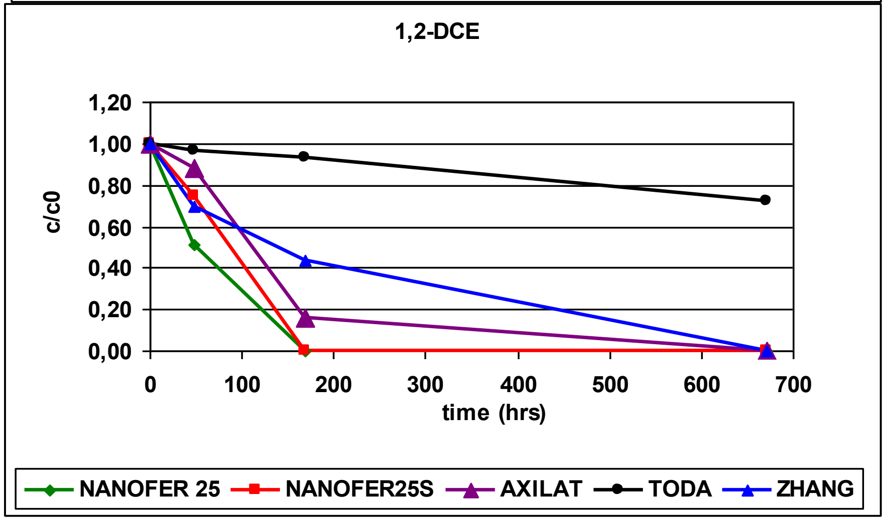
Toda 10-APS

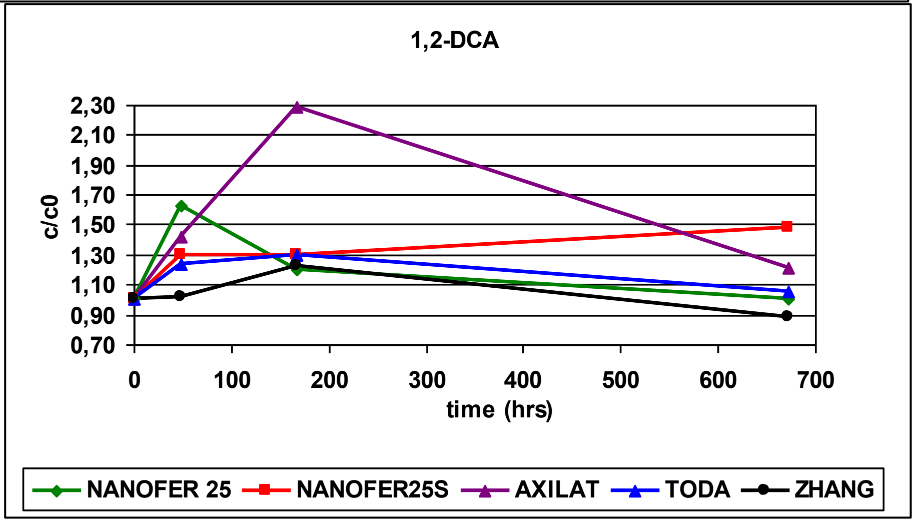
0,5 V_0 8 V_0 25 V_0

Pisecna – reactivity tests



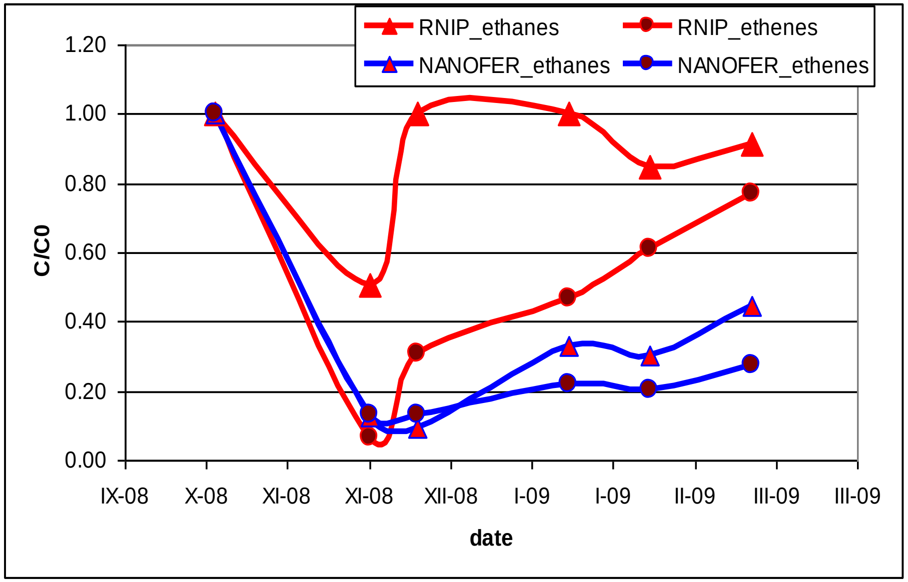


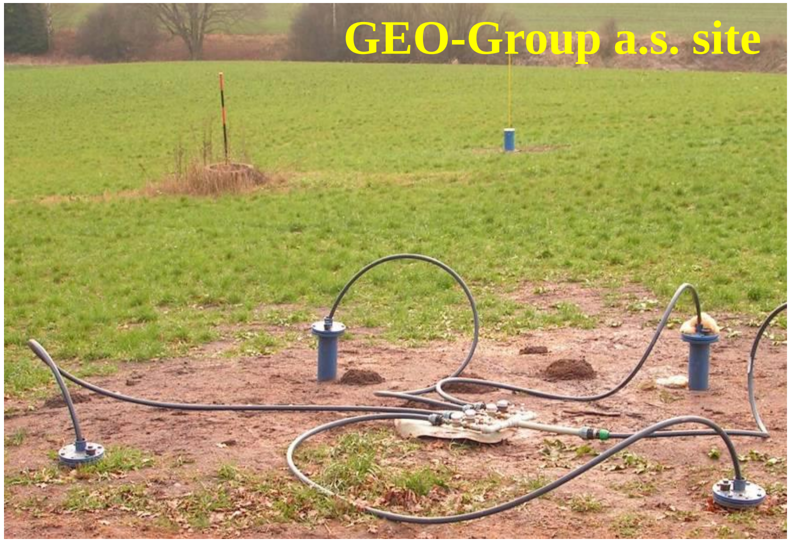




Pisecna – pilot application

- RNIP vs. NANOFER25
- Geological conditions not equal
- CHC concentrations similar
- Cl-Ethenes = both irons performed well
- Cl-Ethanes = TODA iron worse (Δ)





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, storativity, transportability, toxicity,…)

Technical challenges:

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

Caveat

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Thank you for your attention