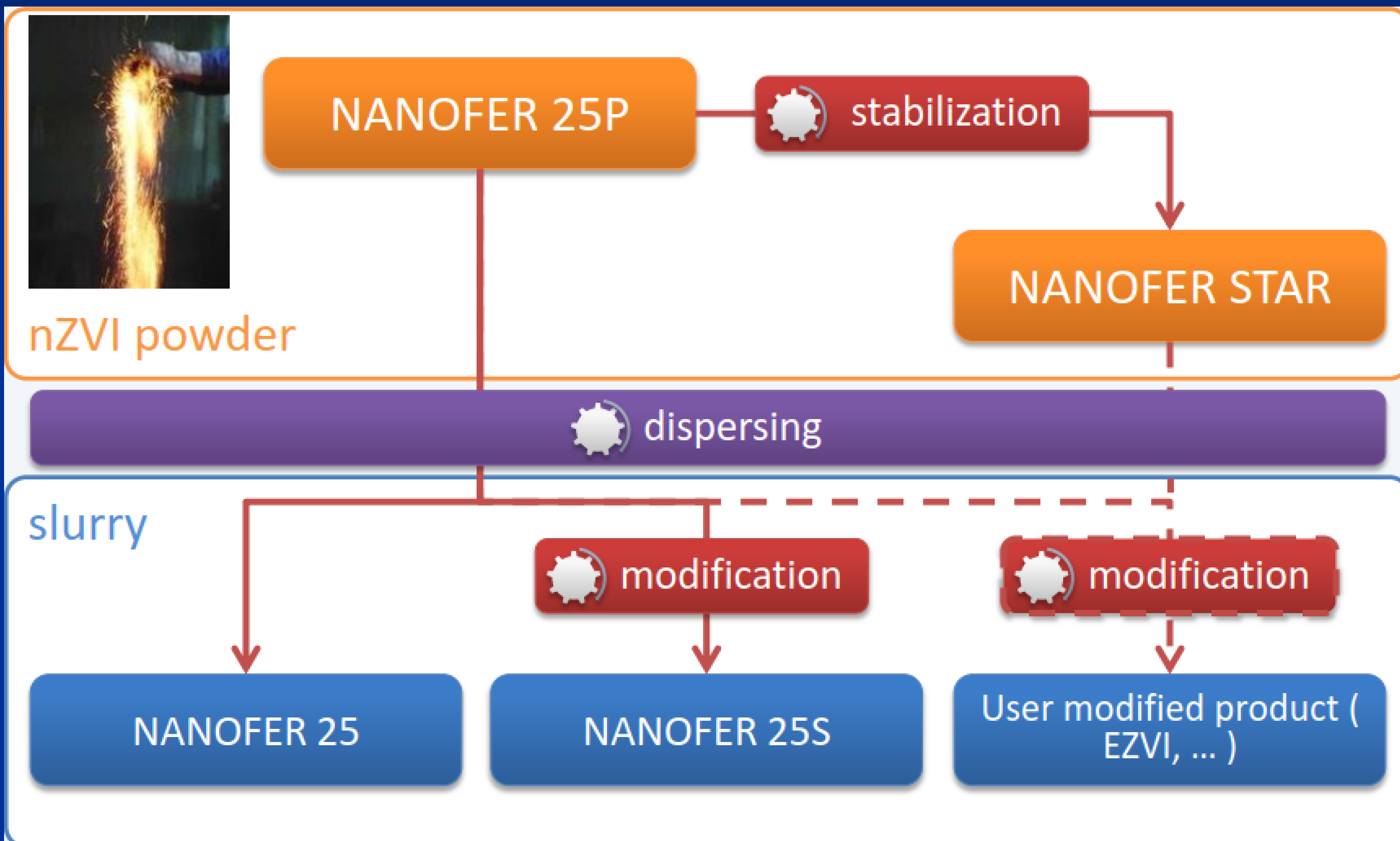
Commercial and field scale experience of nano-iron in use in the Czech Republic and elsewhere in Europe

Petr Kvapil, AQUATEST a.s.

Nanoiron raw products and grades



Source: NANOIRON l.t.d.

Nanoiron applications - CZ

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 - 2016	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

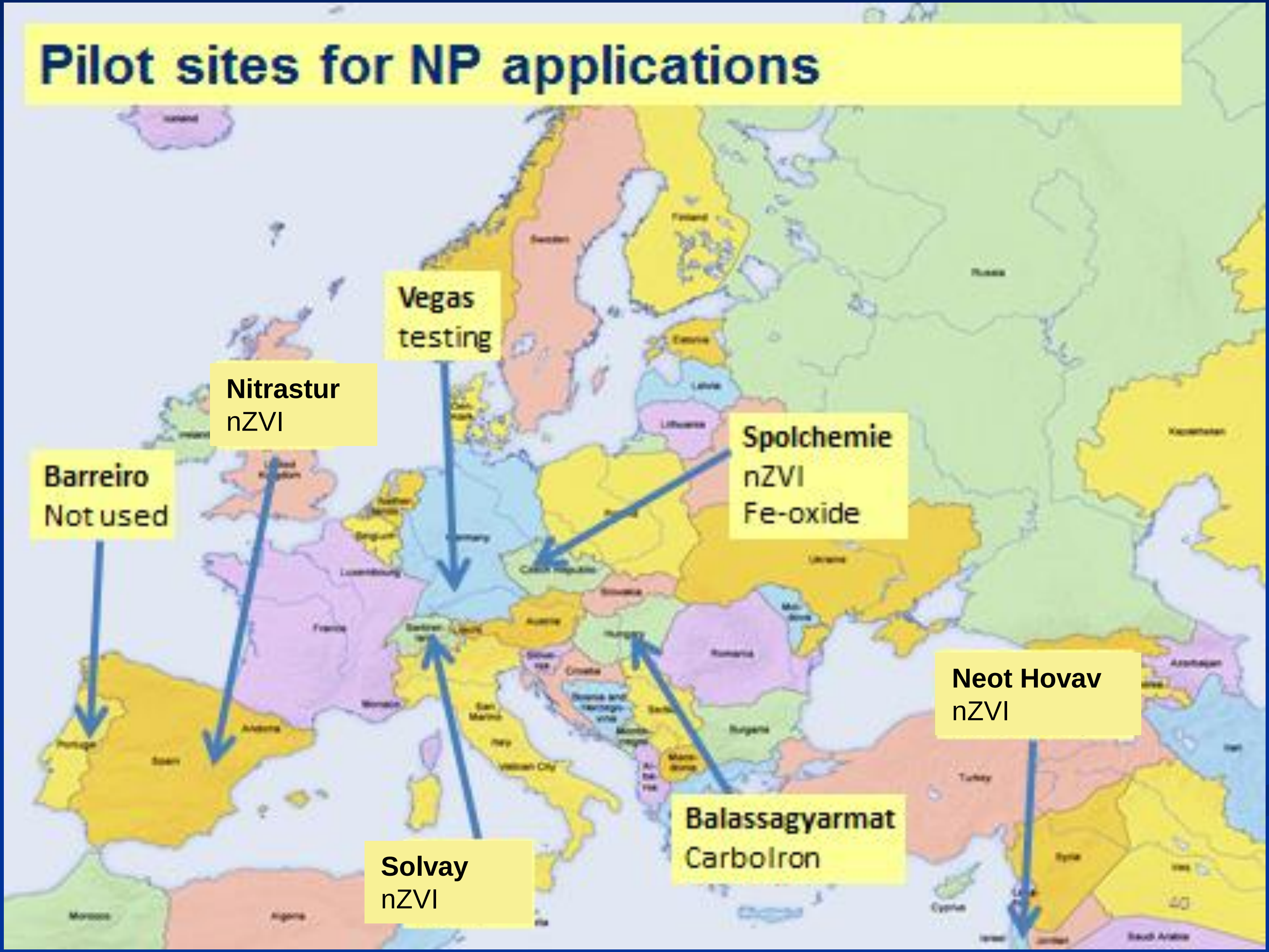
Nanoiron applications – EU (out CZ)

Country	Contam.	Lab/pilot/ Remed.	Type of nZVI
Italy 2005	Cl-Ethenes	L,P	ZHANG
Slovakia 2005	Cl-Ethenes	L,P	ZHANG
France 2009, 2015	Cl-Eth, Cr6+	L,P,R	NANOFER 25S
Hungaria 2014	Cl-Eth,	L,P	Carbo-Iron
Portugal 2011	Heavy metals	L,P	NANOFER 25S
Germany ???	BTEX	L,P	Goethite
Swiss 2015	Cl-Eth, HCA	L,P	Milled Fe
Spain 2015	As	L,P	Nanofer STAR
Danmark (2014, 2015)	Cl-Eth	L,P	Nanofer 25S/STAR

⇒ **Other pilots:** USA, Canada, Belgie, Holland, Italy, South Korea

⇒ **Universities:** Australia/ New Zeland, Malajsia, India, Thajland, South America

Nanoiron applications in frame of NANOREM



General Expectations from Nanoiron Remediation?

Remediation Requirement

- Best technology
- Fast remediation
- Cheap remediation
- Environmental - friendly
- No by-products
- Easy to apply
- No „rebound“ effect
- No legal requirements

Expectation from Nanoiron

- Runs where others failed
- Within several weeks
- For a few tens of thousands
- No toxic
- Intermediates do not arise
- Great dispersion in soils
- One application is sufficient
- Well accepted by regulators

All provide nanoFe ???

Is NanoRemediation accepted by regullators in CZ/World ?

- Yes & No
- Local specific - subject to decision of regional authorities
- NZVI injections regulated by WATER law
  - „Ussualy“ Exception for irregular matters injection
- Ussualy field pilot test required
- Usually the iron is more easily accepted than soluble materials (oxidants or reductants)
- First injection most difficult

Nanoparticles migrates in the aquifer without retardation?

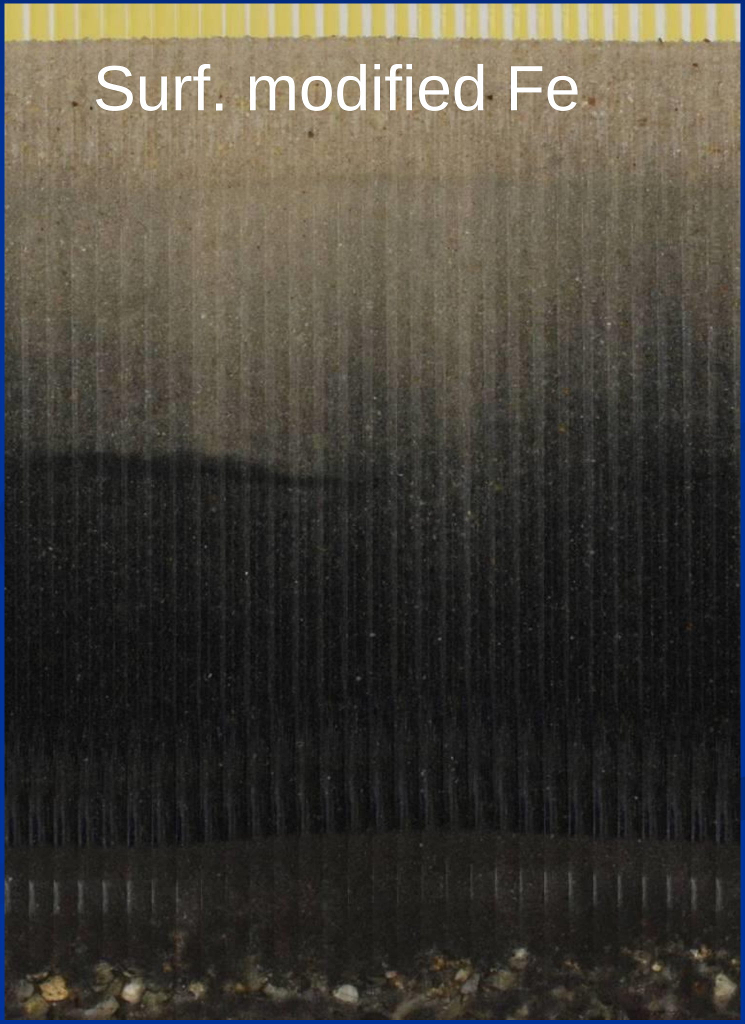
- NO
- Agglomerates quickly when modified and dosed inappropriately
- Migration confirmed in laboratory columns
- Could be transported far away by open fractures
- Example (results of column tests)

⇒ Suspension preparation and surface modification at the site

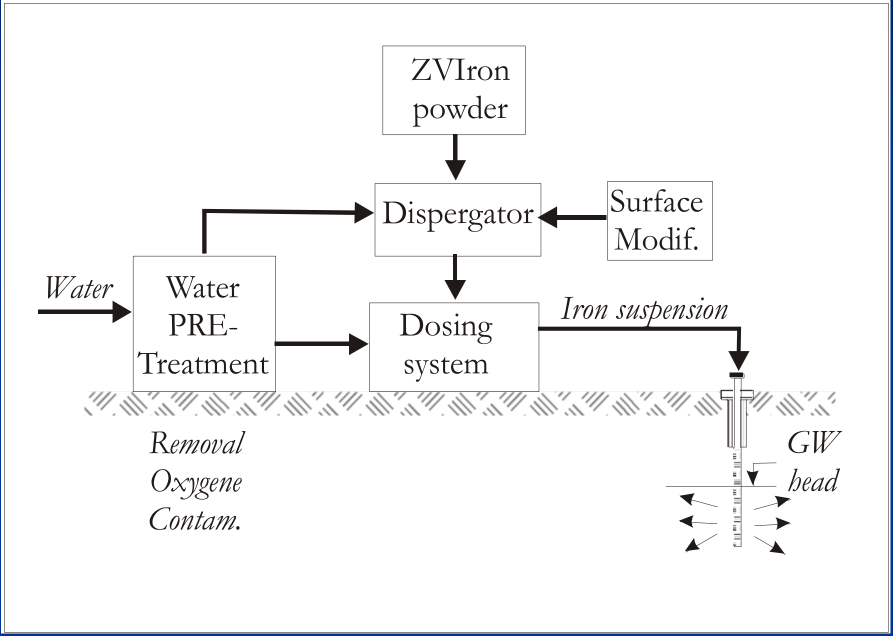
⇒ Subject of NANOREM research

Real migration of nanoparticles

After 45 pore volumes



Field injection and dosing system



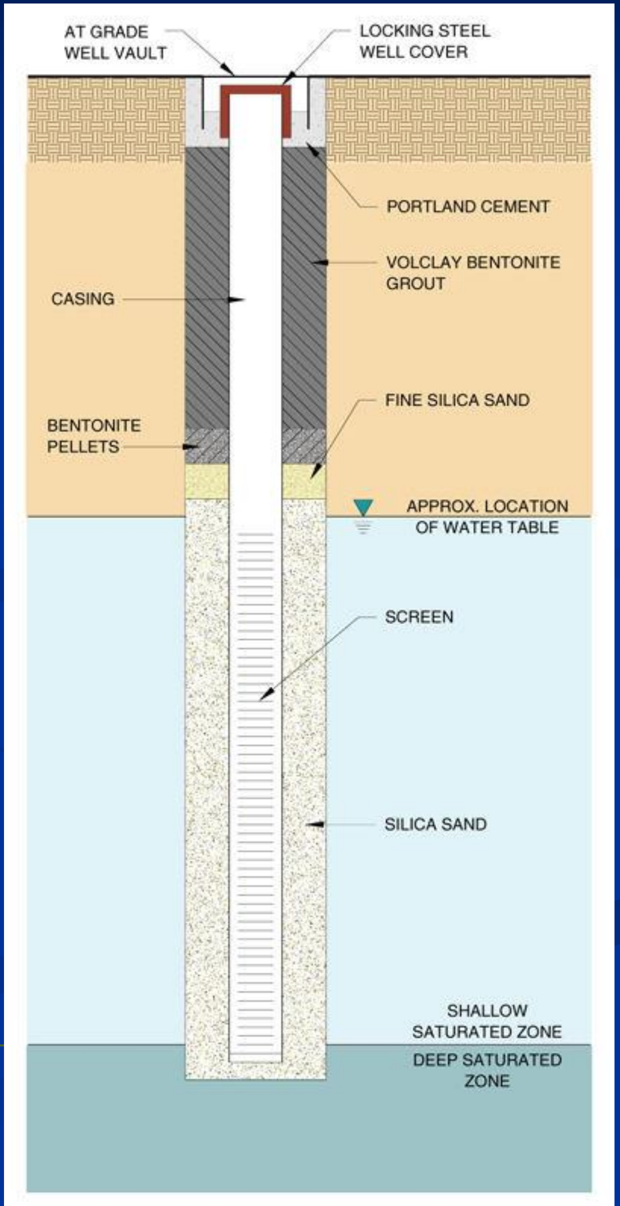
- Dry powder stored and brought to the site
- Reduced transport costs

•Advantage of initial high reactivity
•Mobility and reactivity control

Dispergation & Dosing & Injection

Problems with conventional well injection

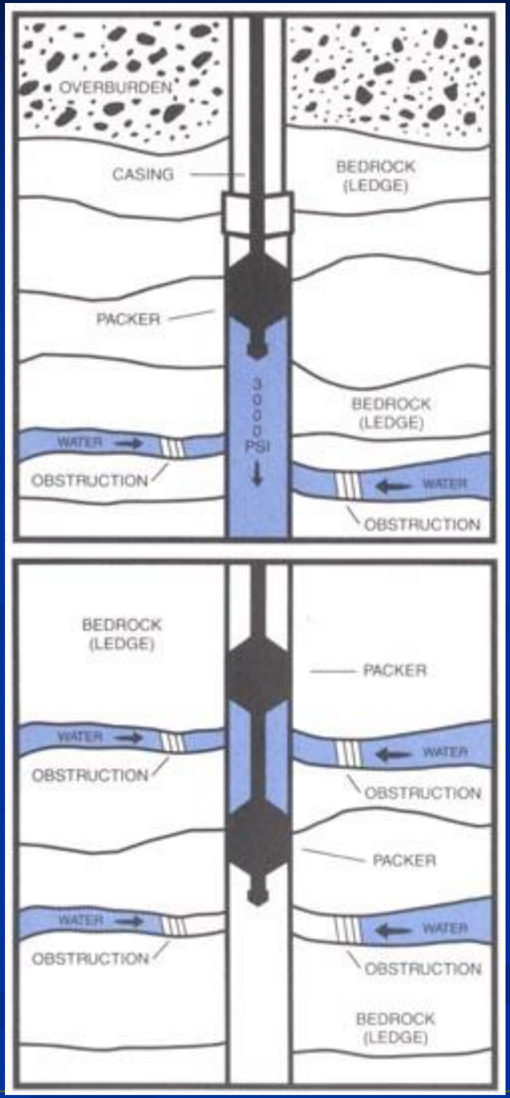
- Top – bottom screened
  - Doesn´t reflect site lithology, contamination
- Screen-slots and well construction
  - Inapropriate for solid suspension injections
  - Inapropriate for pressure injections – day-lighting
- Bigger diameter
  - Decrease water flow velocity
  - Increased volume of well → sedimentation of solid particles in well



Conventional well

Nanoiron Injection in Bedrock Areas

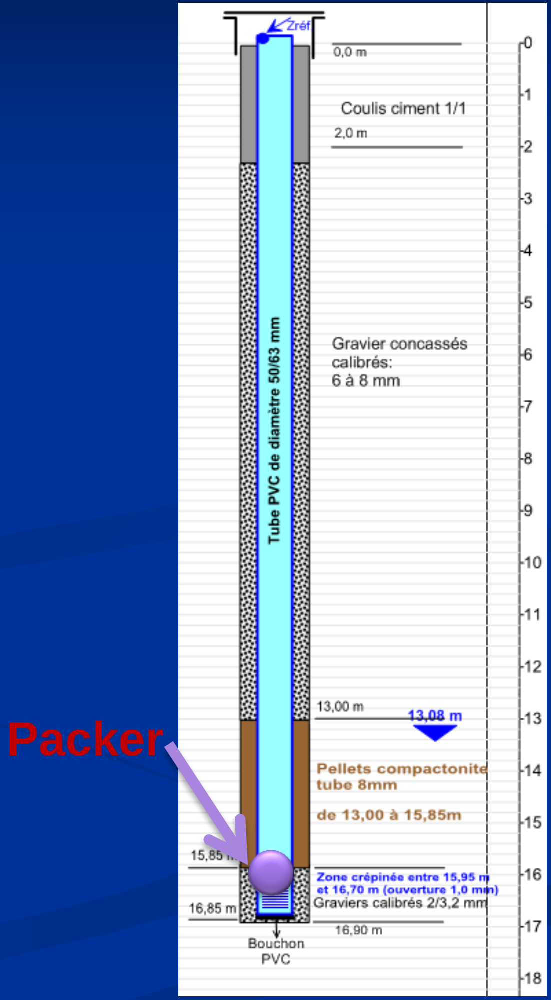
- Required enhancements
  - Adapted number of injection points
  - Well sealed from surface
  - Adapted to pressure injection
    - 1 – 10 atm
  - Adapted to lithology and contaminant distrubution
    - Multiple screen
    - Packer injections
  - Decrease partical sedimentation space
    - Well diameter – small (5 cm)
    - Packer injection



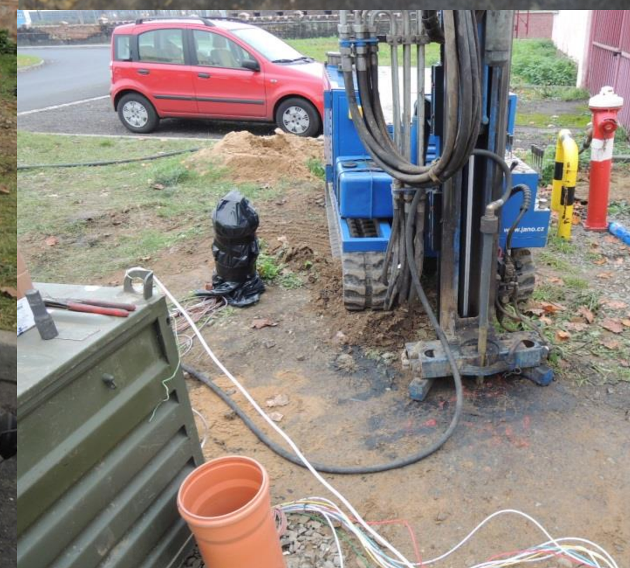
Picture: Southeast water production.com

Well in bedrock

Packer Injection Solvay CH



Direct-push Injection at Spolchemie Site



Hydro-Geological description
Technology for detailed measurement

Do we understund site conditions based on well-core descr

??????

Hydro-Geological description

Technology for detailed measurement – well logging

Do we understund site conditions based on well-core descr

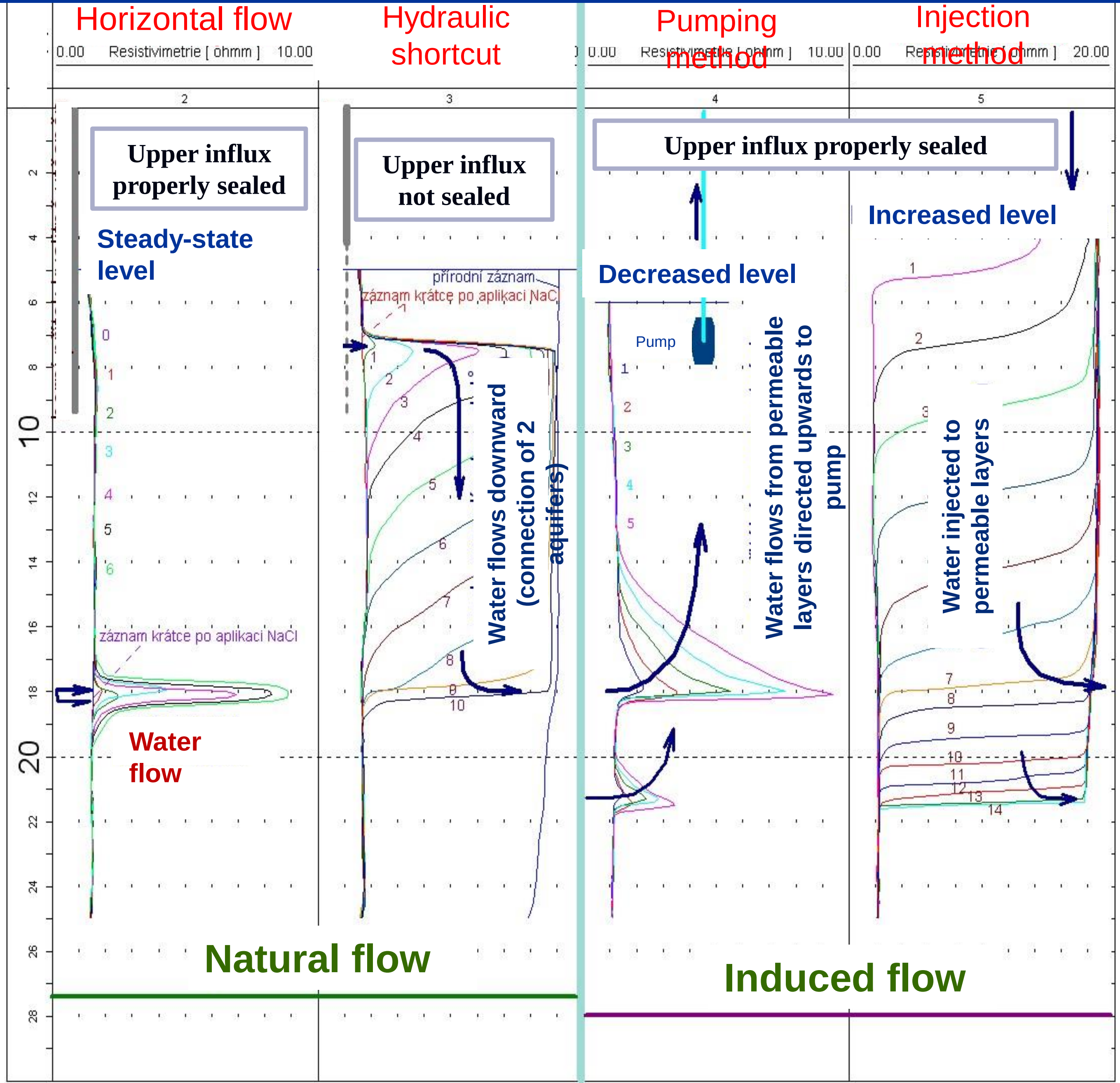
??????

soil
- lithology
- fractures

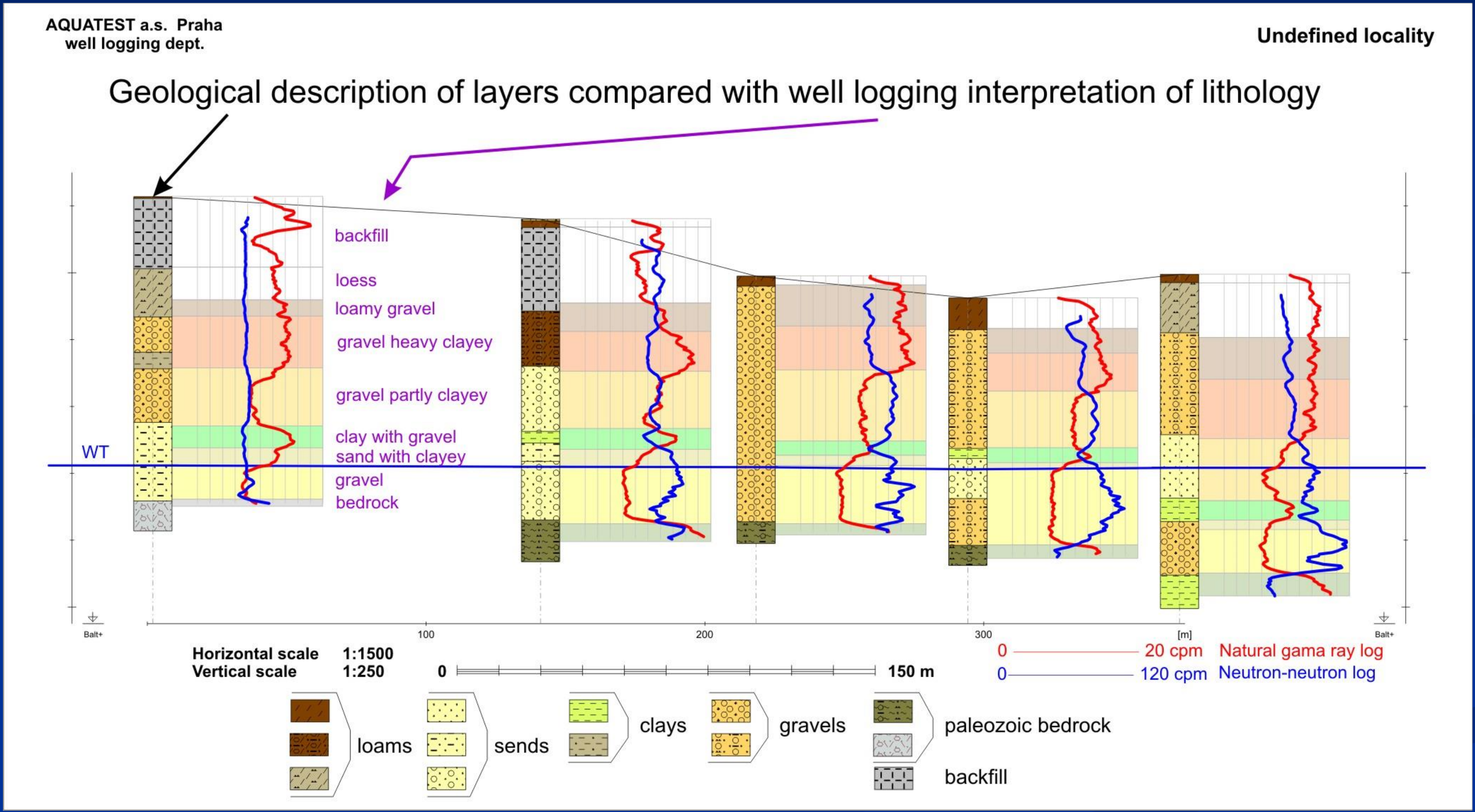
water
- velocity
- direction

aquifer
- permeability
- heterogeneity

Schematic example of in-well flow – technology principles

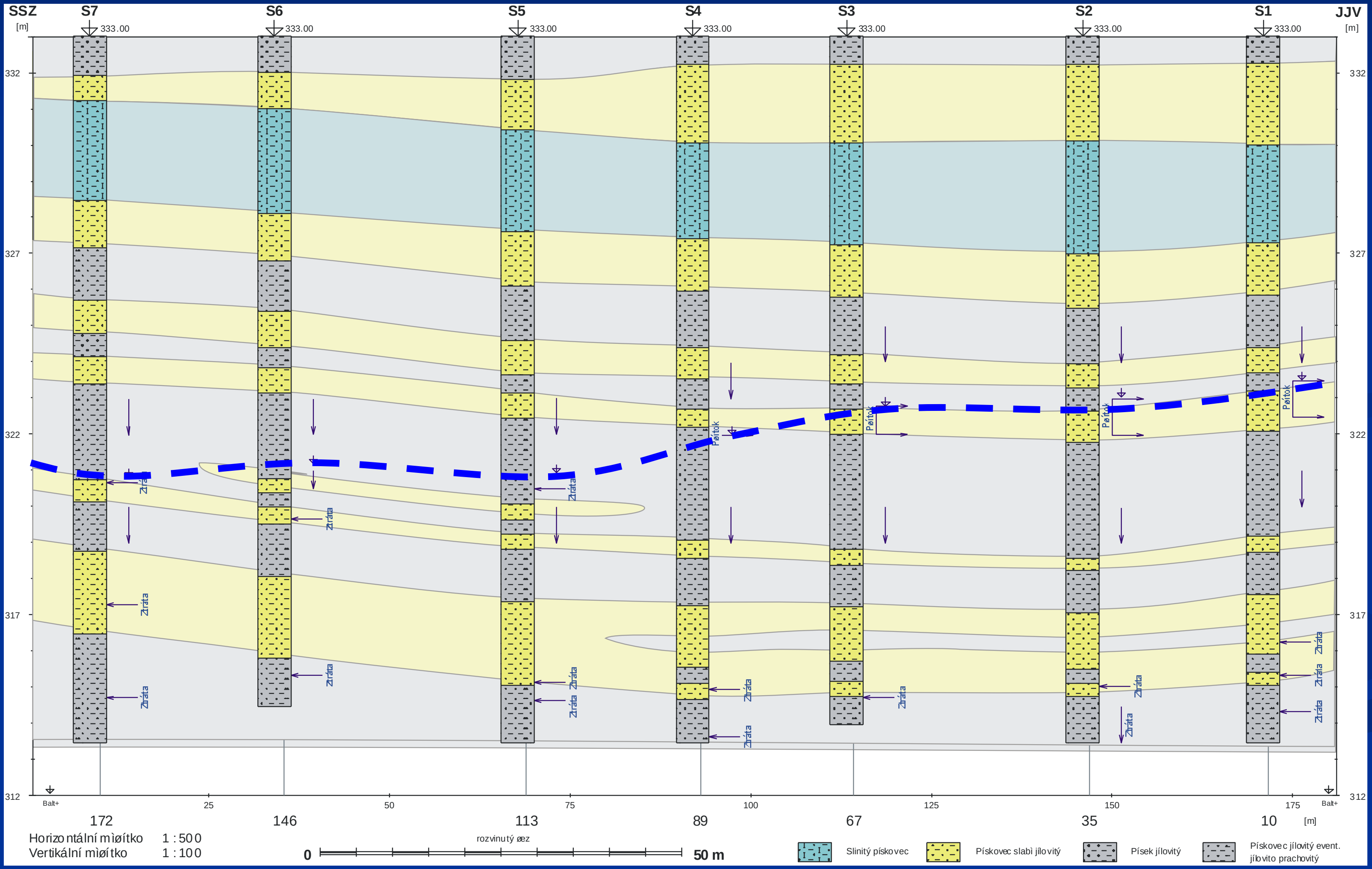


Geological description



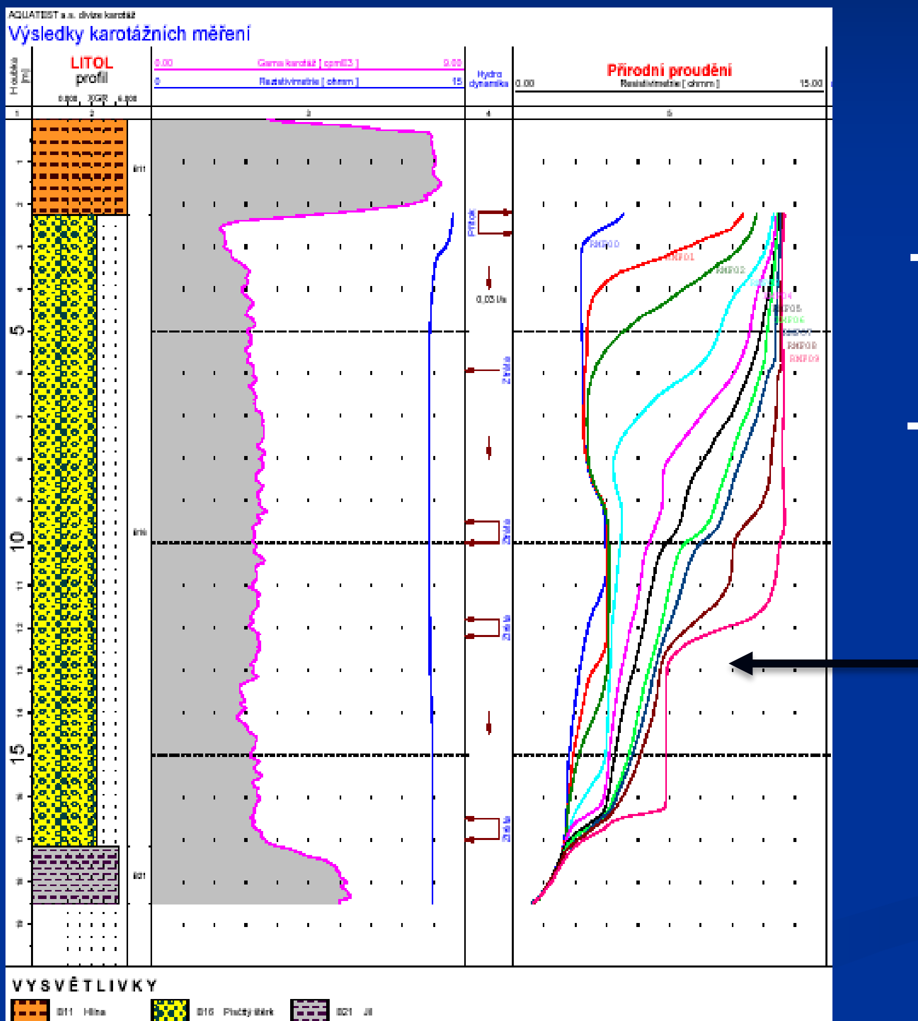
Hydro-Geological description

Example 1 – geo – hydrogeological relation



Hydro-Geological description

Example 2 – vertical stratification of groundwater flow

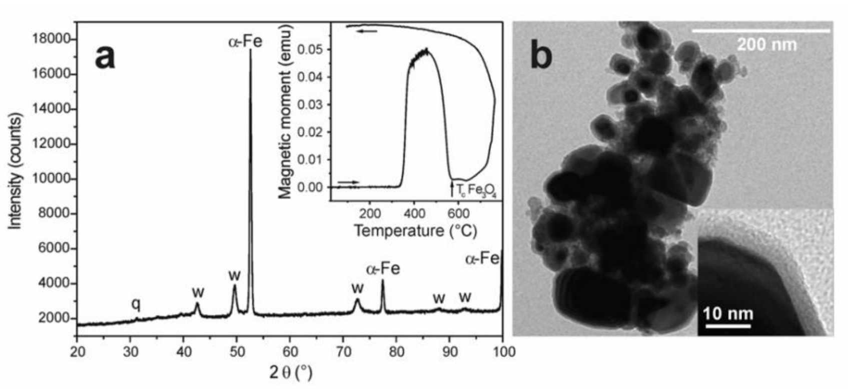


- vertical flow - DOWN

- horizontal velocity up to 4 m per day

Where Nanoiron came from? What happens with nanoiron in soil?

- precursor: ferihydrit ($5Fe_2O_3.9H_2O$)
- mine Zlaté Hory, Oslavany
- size 2-6 nm, aggregates 150 nm
- Spec. surface 270 m^2/g
- reduction v H_2 under 600ºC
- α-Fe + wüstit FeO
- 50-150 nm, 5 nm shell
- High content Fe^0
- stability (dry state)
- reductive properties



source: Projekt Nano (PřF UPOL)

Nanoiron will help where other methods have failed ?

- No & Yes
- Nanoiron can substitute/facilitate bio-enhanced dechlorination
- Nanoiron will help in cases of complex mixture contaminants (mixture of CLM, CLE, some metals, saline waters)
- In areas where are water resources, cellars, danger of explosions, etc.
- Most of real cases…

Nanoiron cleans also soils?

- Yes & No
- Iron cleans, „NANO“ increases efficiency
- Suitable for saturated zone

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

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

- Exemple: PCB, DCA, AOX, some metals, cyanides

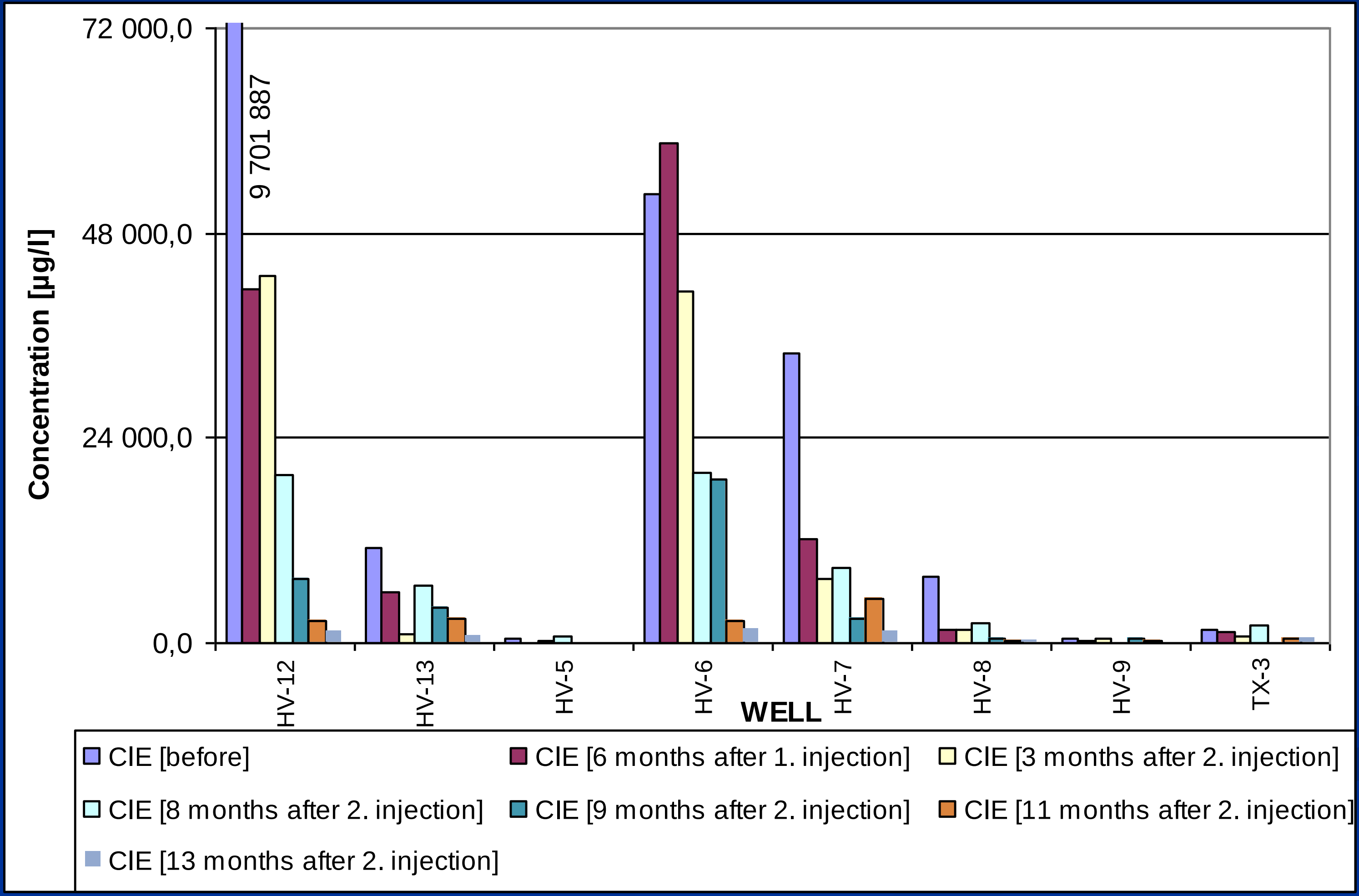
Nanoiron degrades quickly and without intermediates?

- YES & NO
- Reaction rate should be confirmed in laboratory tests
- Fast reactions without intermediates: PCB, metals (Cr, As)
- Slow reactions (cis-DCE, DCA)
- Exemple (Permon, Písečná)

Case – Písečná – 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

Case – Pisecna – full-scale results in remediation wells



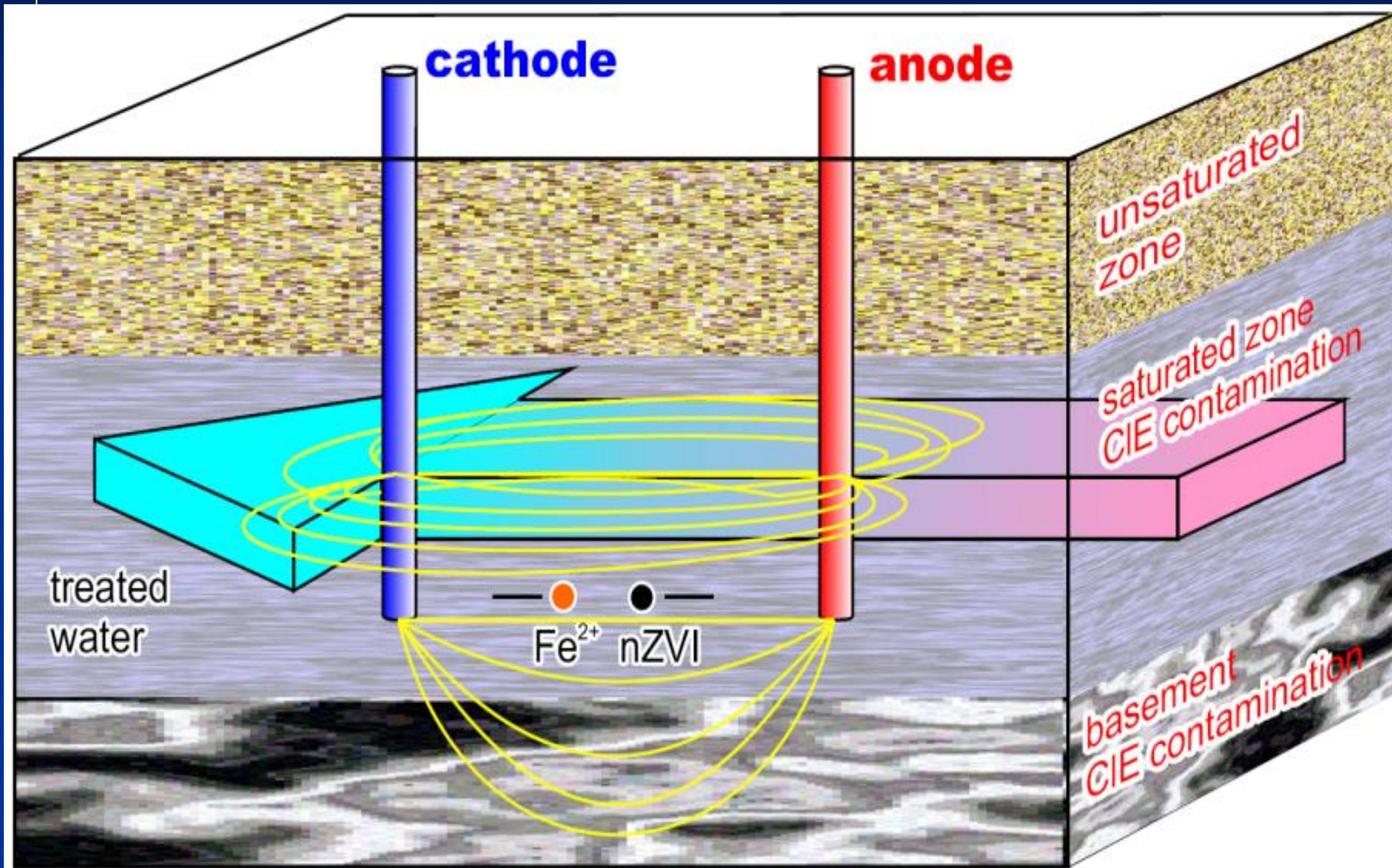
Fast reaction, small doses = low price?

- YES & NO
- Strong reductive agent degrades by competitive reactions such as with water

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

- Need of repeated injections = higher costs
- For now the high cost of reagents = higher costs
- BUT ENHANCED NANOREMEDIATION moderate material price in combined cases (exemple: combinations – BIO or DC)

Combination NZVI - DC



Laboratory tests

- Reactor tests
  - *Study of dissociation of chlorinated ethylenes in contaminated water from locality*
    - *1. just using DC current without nZVI (high voltage, various types of electrodes) >>* ***without success***
    - *2. nZVI + DC current*

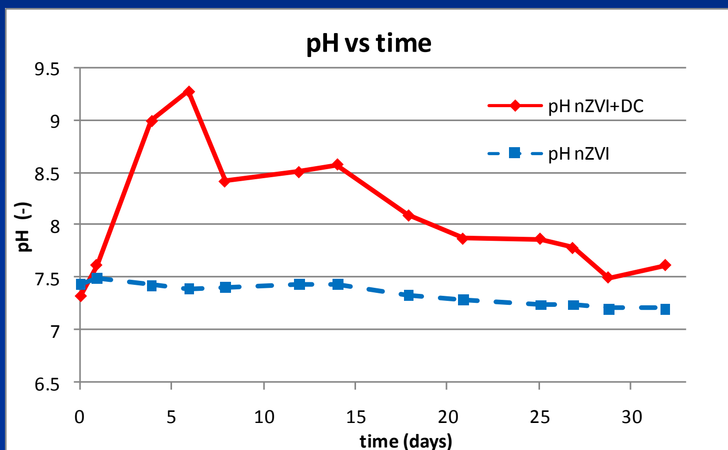
>> Final setup = Closed mixed reactors (2.5 L), steel electrodes, regular sampling, analysis (pH, ORP, conductivity, anions, ClE)

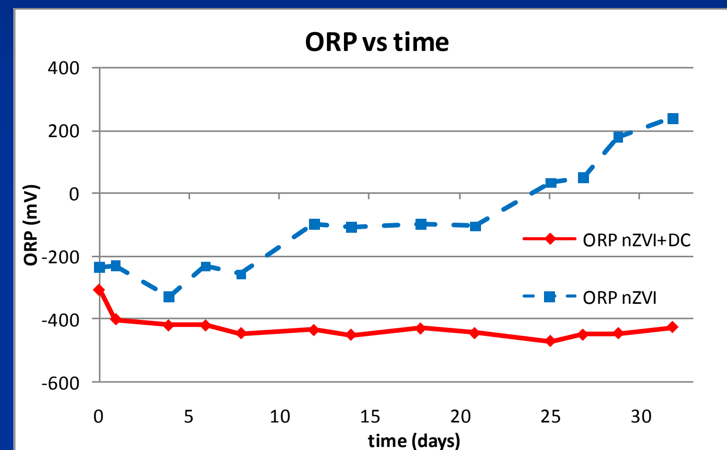
Separated electrodes space (ion membrane)

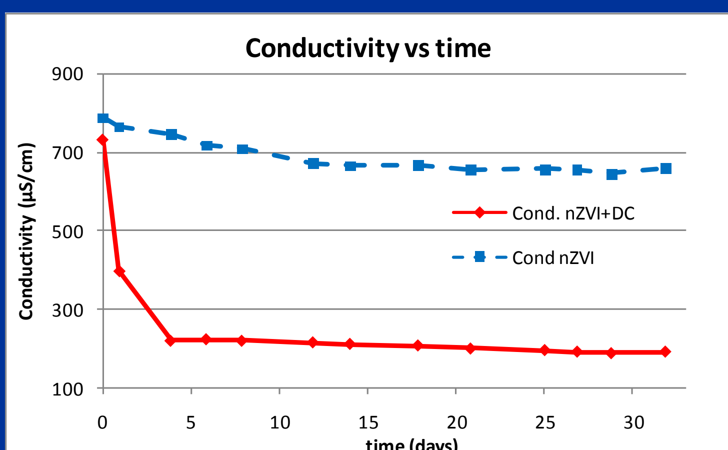
Undivided reactors

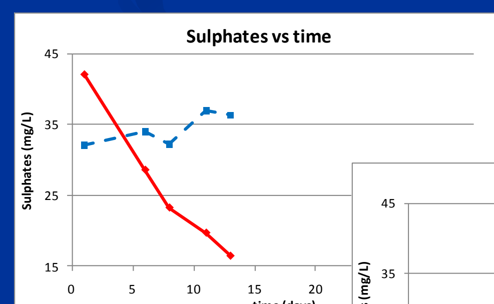
Laboratory tests

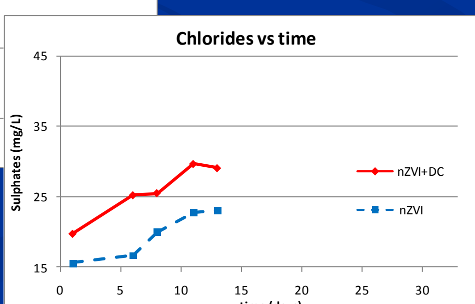
- *Suma of ClE **25 mg/l**, app. **70% of cis-1,2-DCE***
- *Mixture reactors: **nZVI+DC**, **nZVI***
- *nZVI concentration **0,5 g/l**, steel electrodes, voltage **1 V/cm**, **30 days***



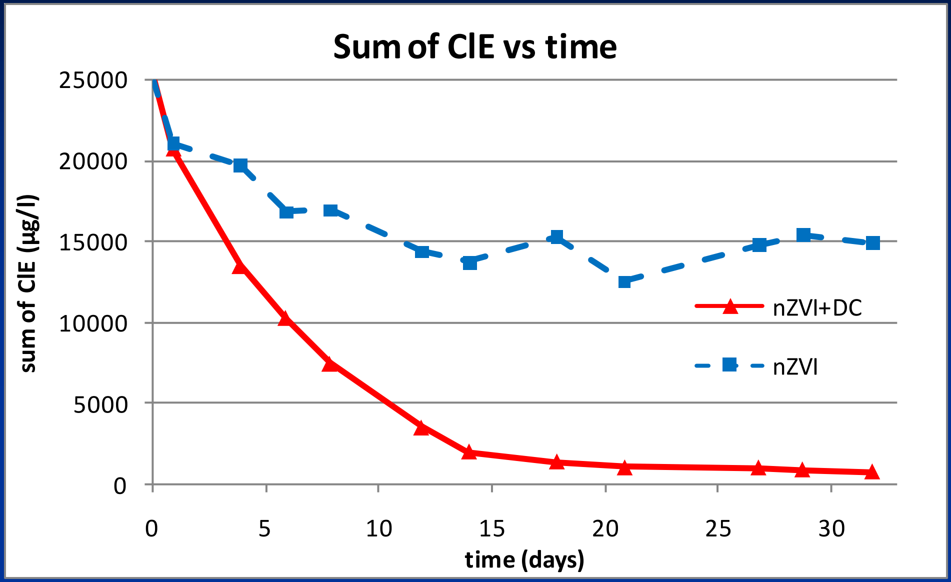




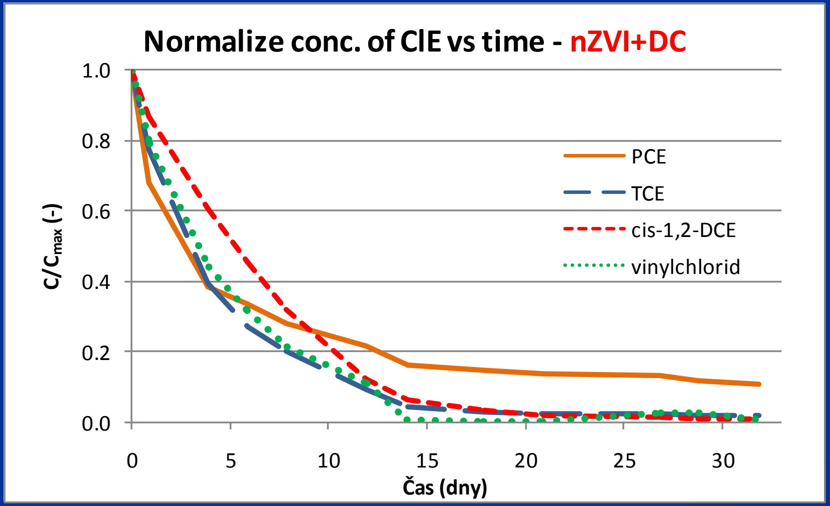


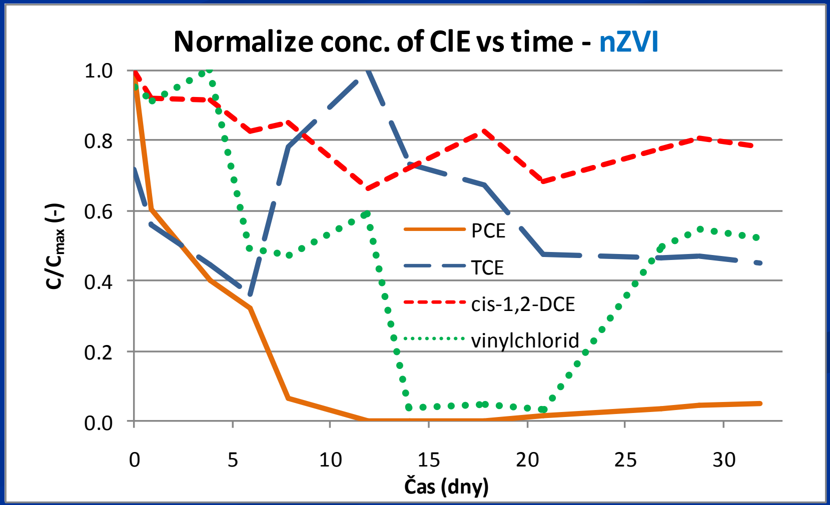


Laboratory tests

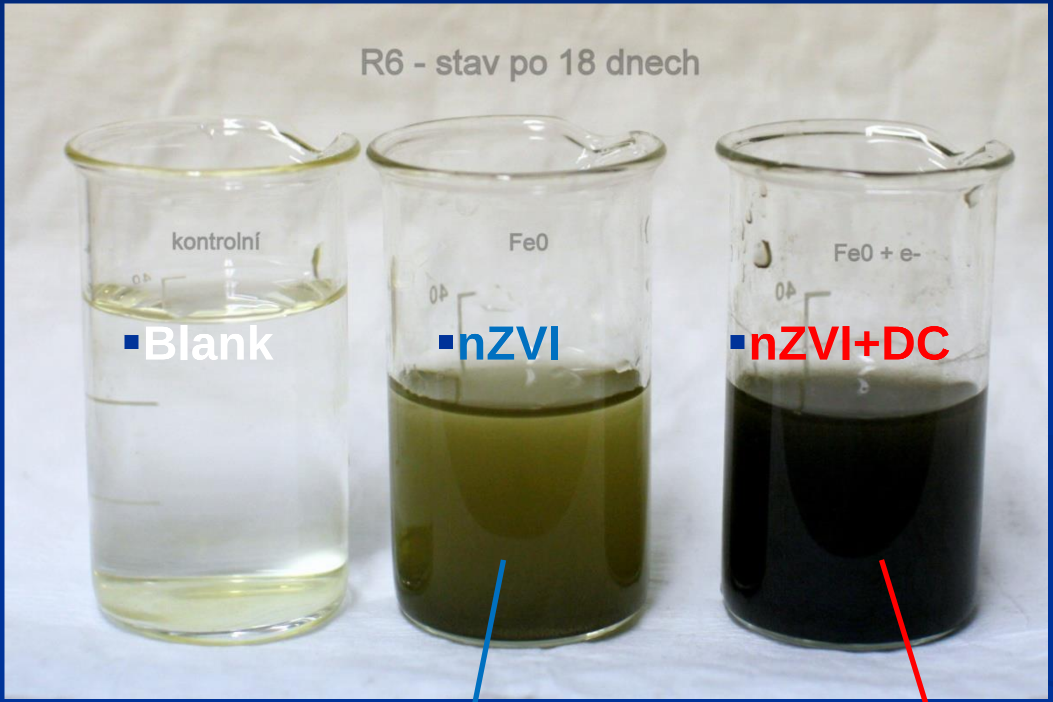


- common application of nZVI and DC current reduce 97% of the sum of ClE (alone nZVI app 40%)
- total power 150 Wh
- app. 4 W/day on 1 g of nZVI





Laboratory tests



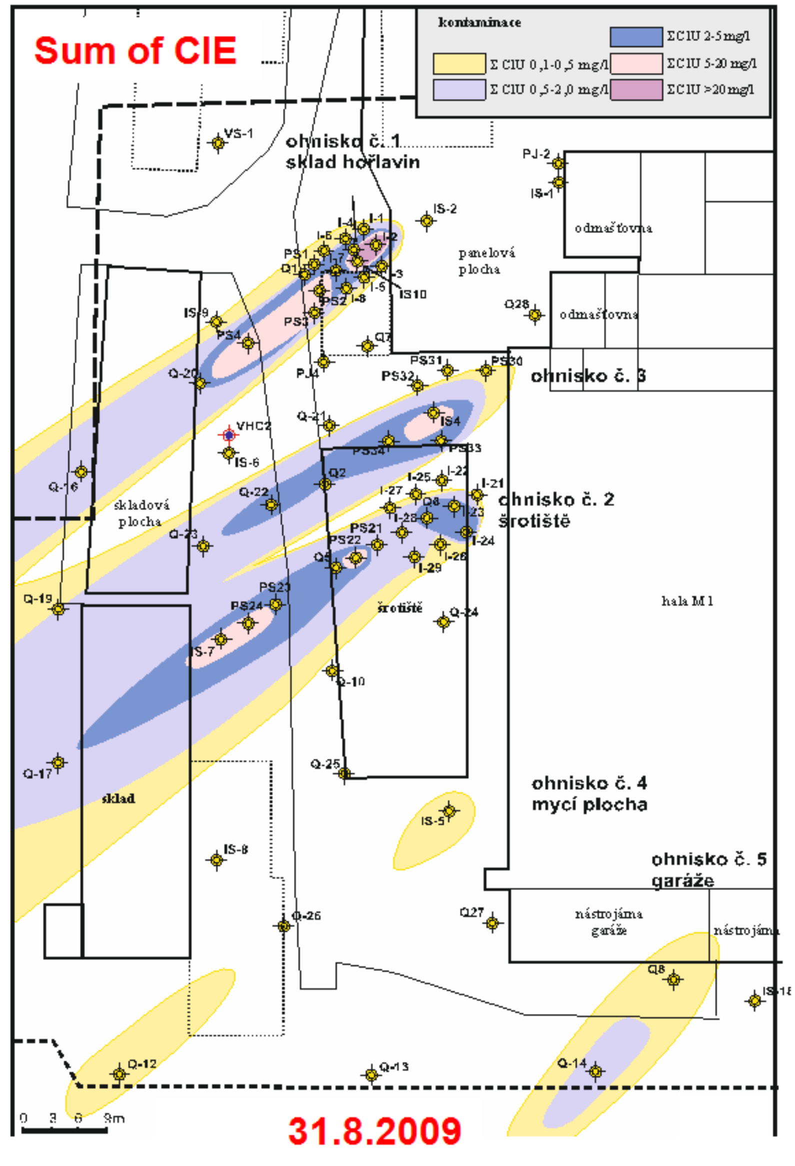
- Blank
- nZVI
- nZVI+DC

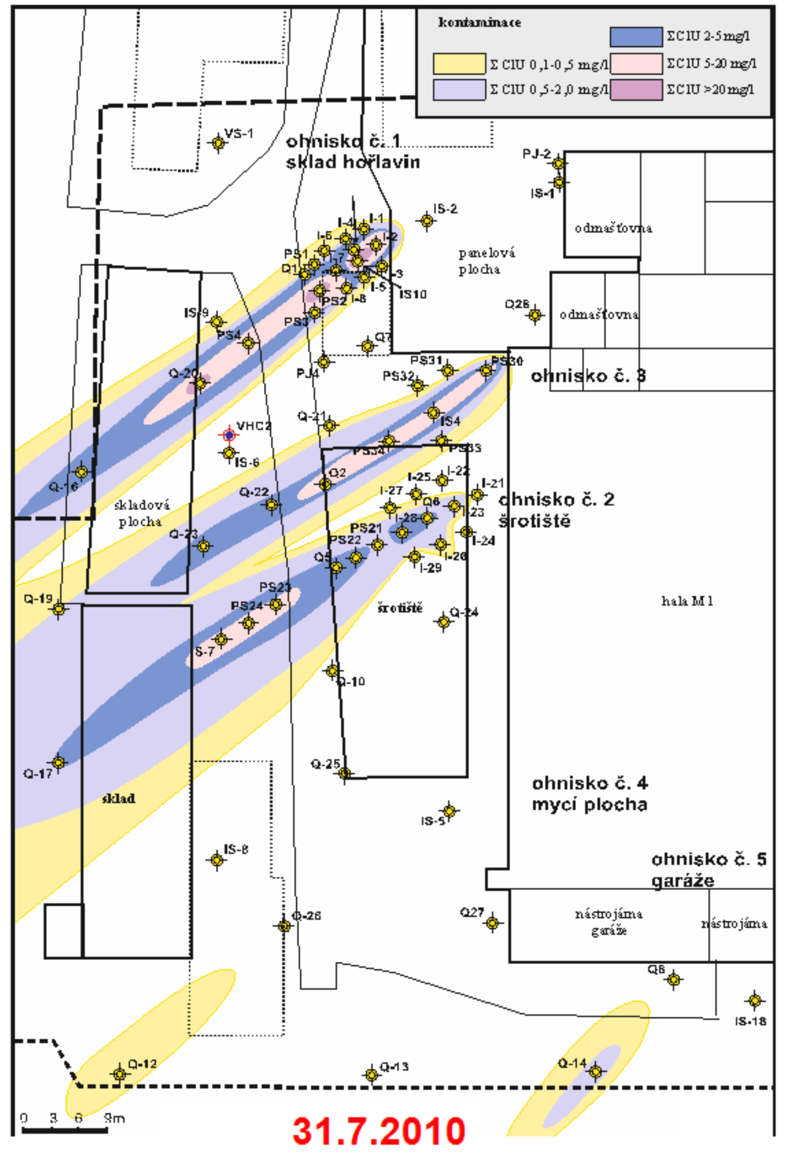
90% goethit
10% magnetit

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

Field verification – Site Hořice

- Beginning of remediation
- State after 3rd nZVI appliaction





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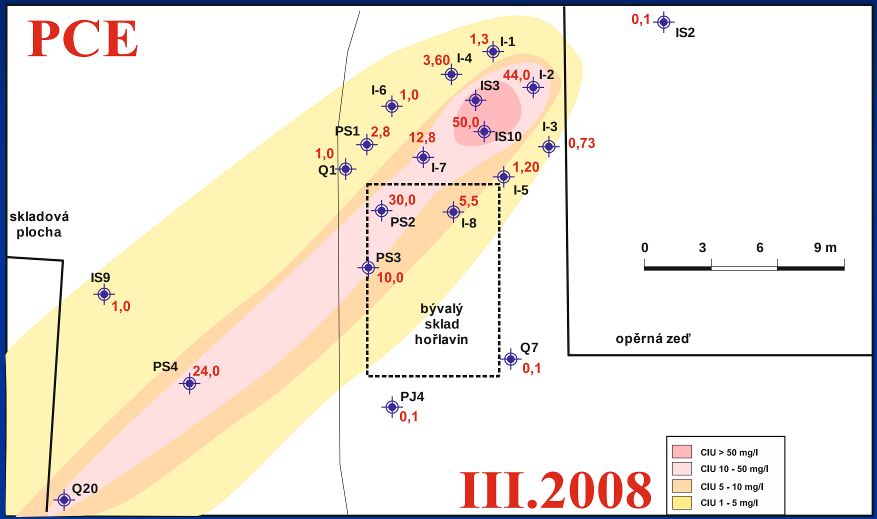
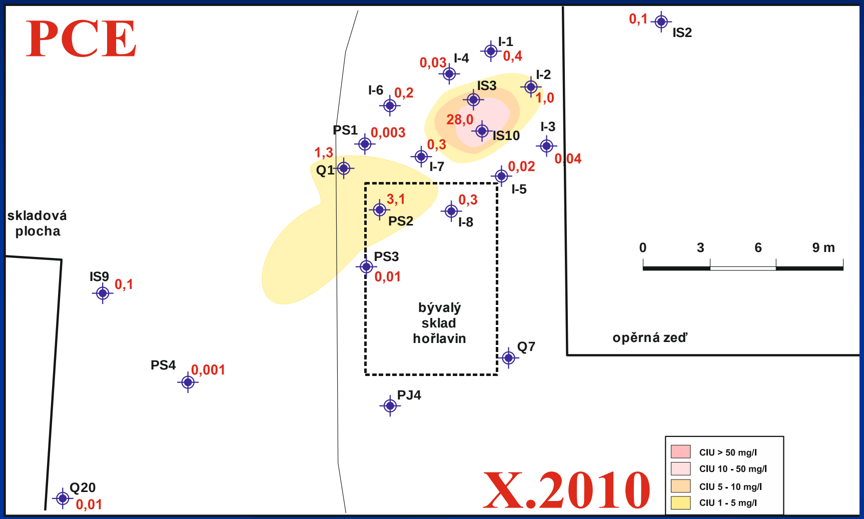
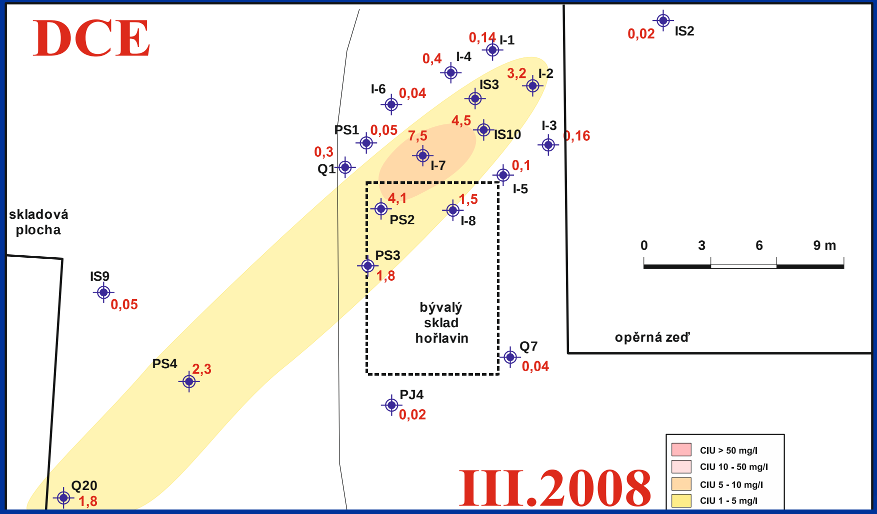
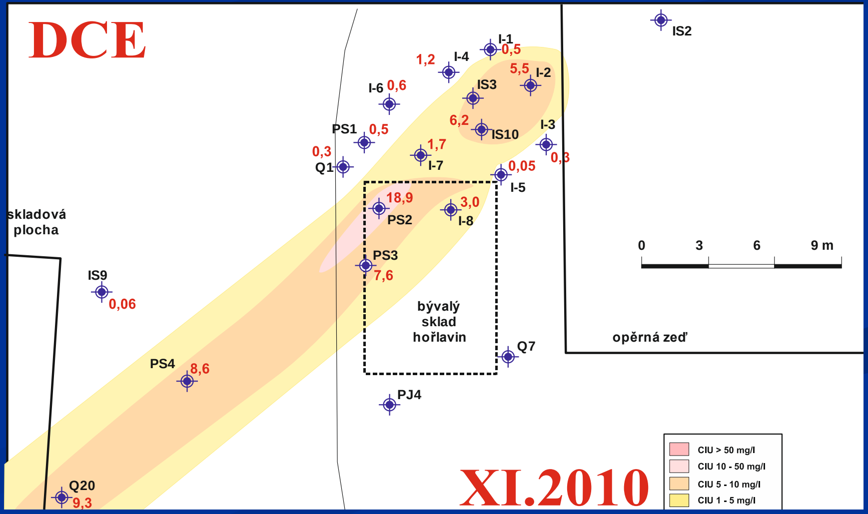
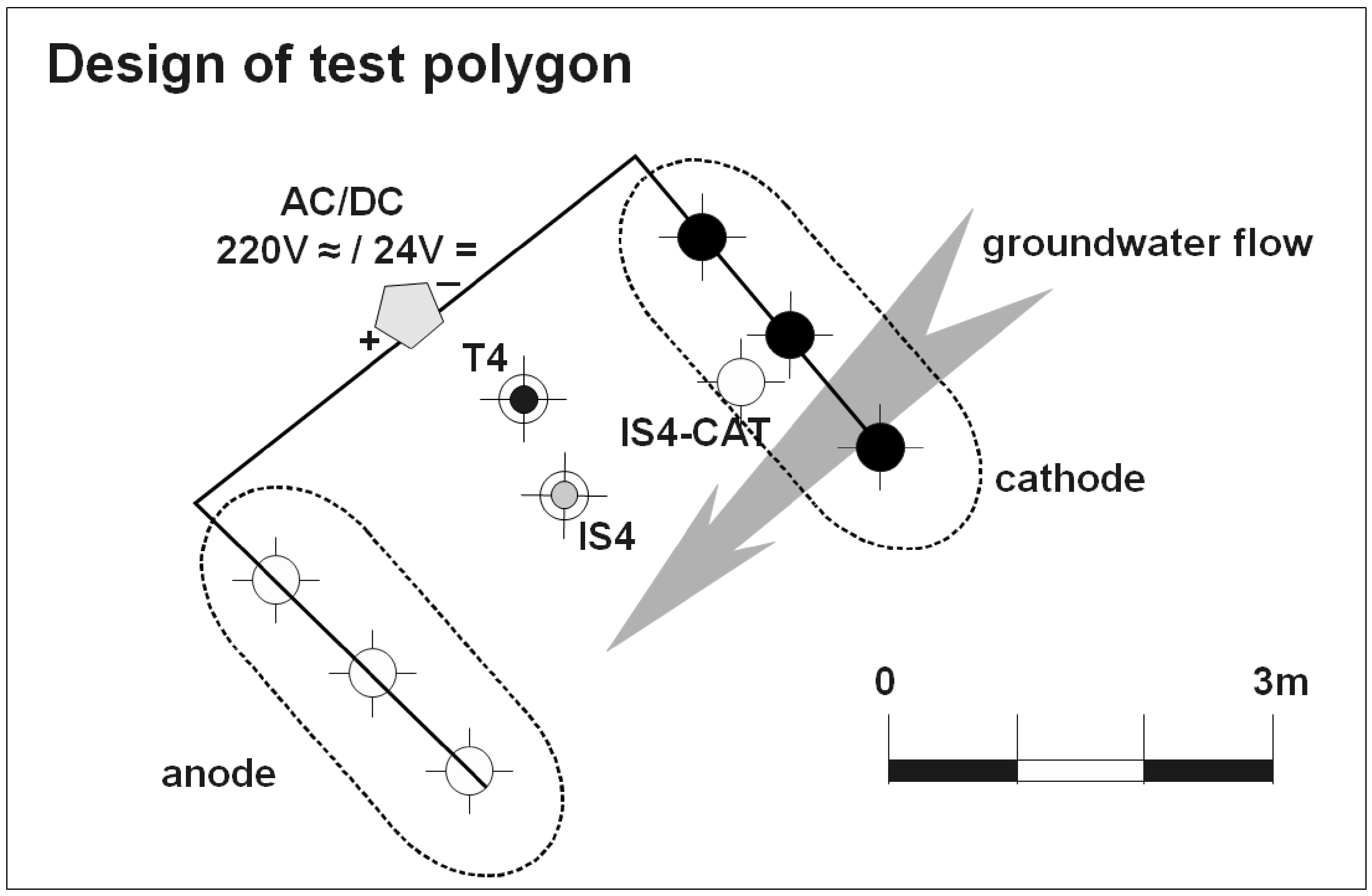








Field verification – Site Hořice

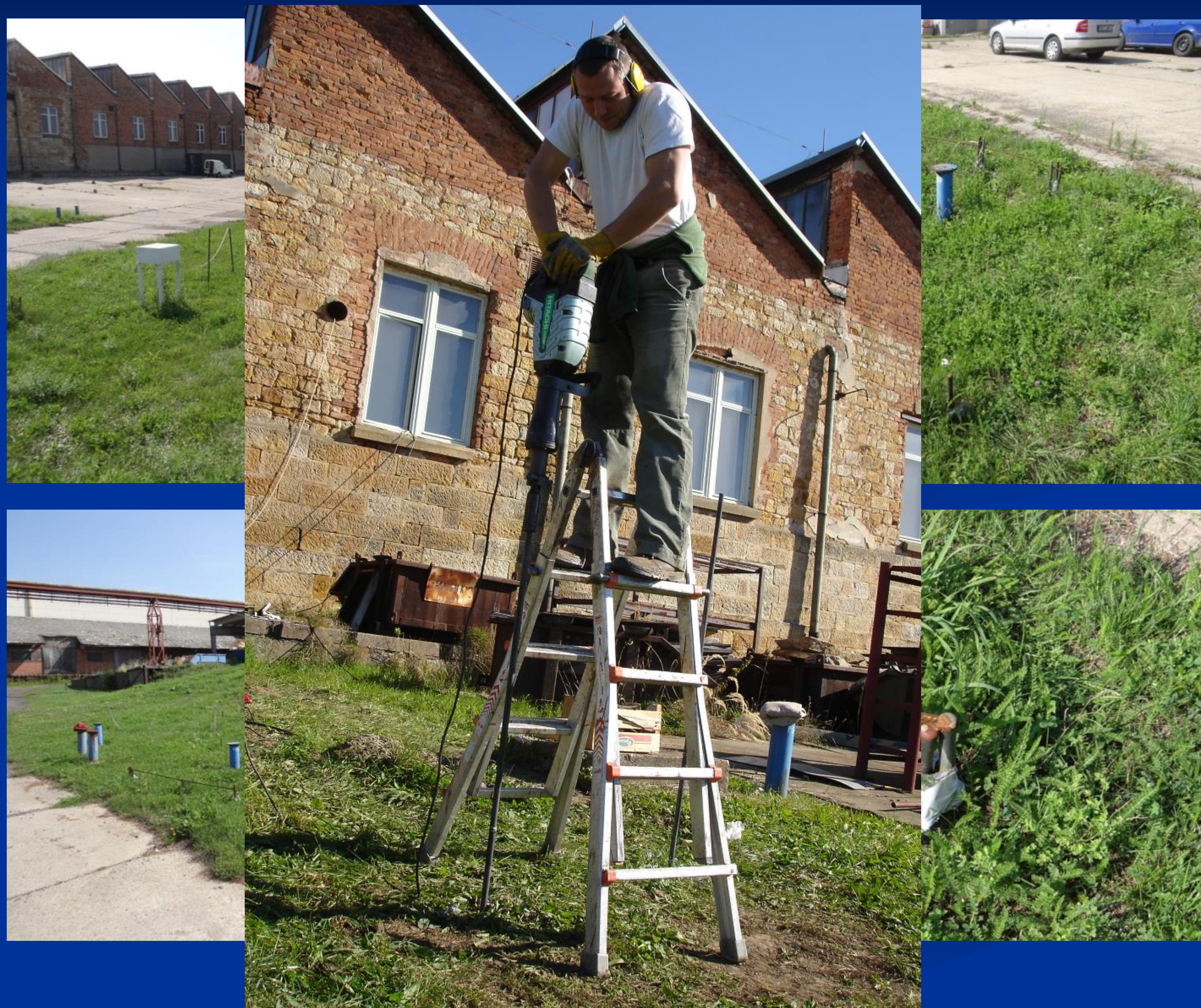


Field verification – Site Hořice

- Remediation polygons

Field verification – Site Hořice

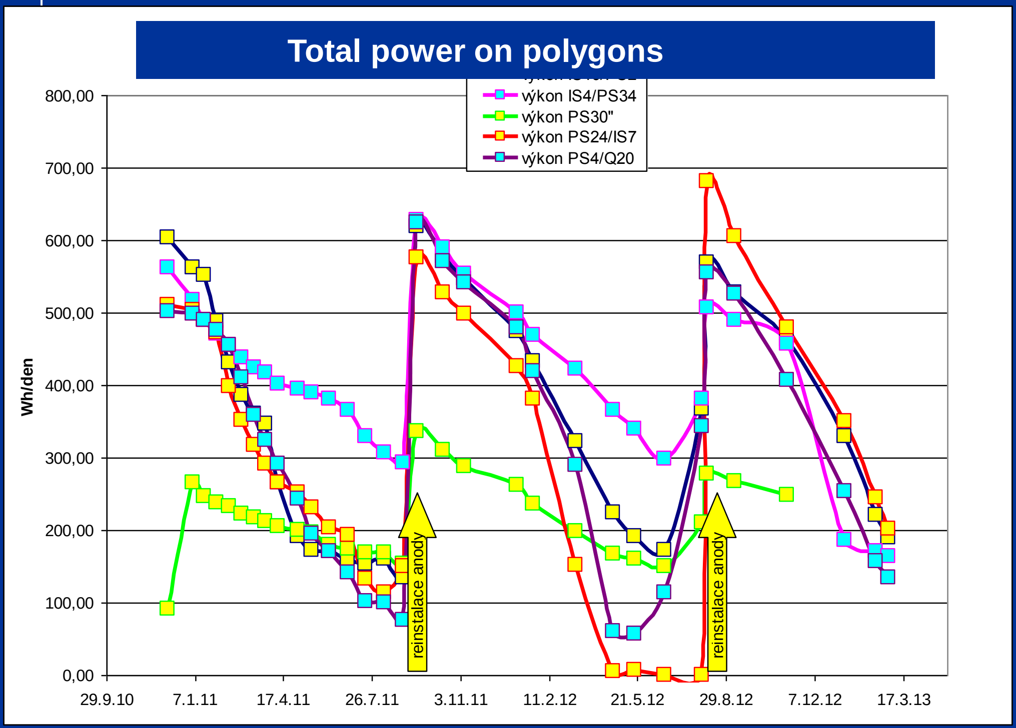
- **Remediation polygons**

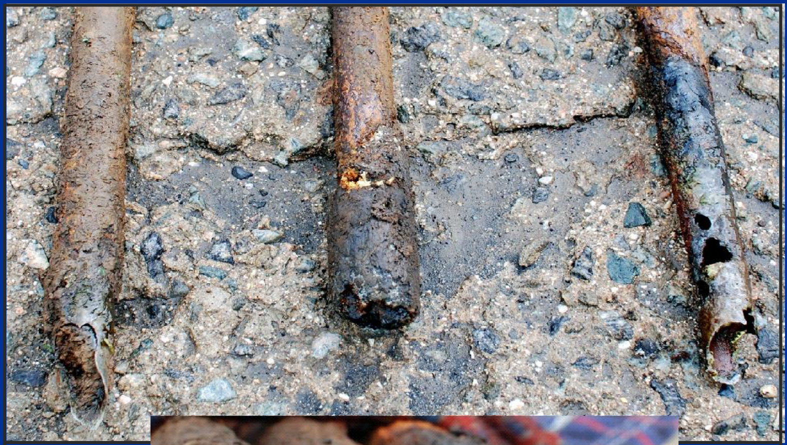


Field verification – Site Hořice

Oxidation of anodes

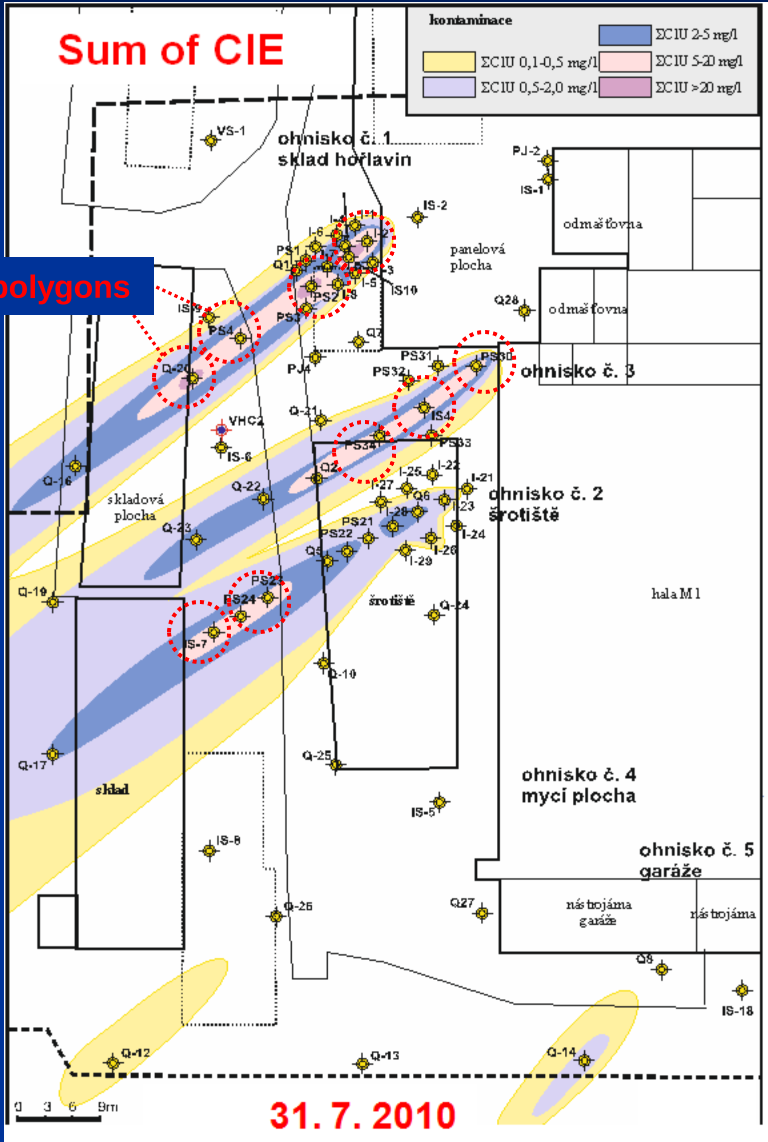
- From **12/2009** runs 2 polygons, from **10/2010** 9 polygons
- DC Voltage restricted on **24 V** and max **350 W** >> anodes degradation >> reinstallation each 6-9 months

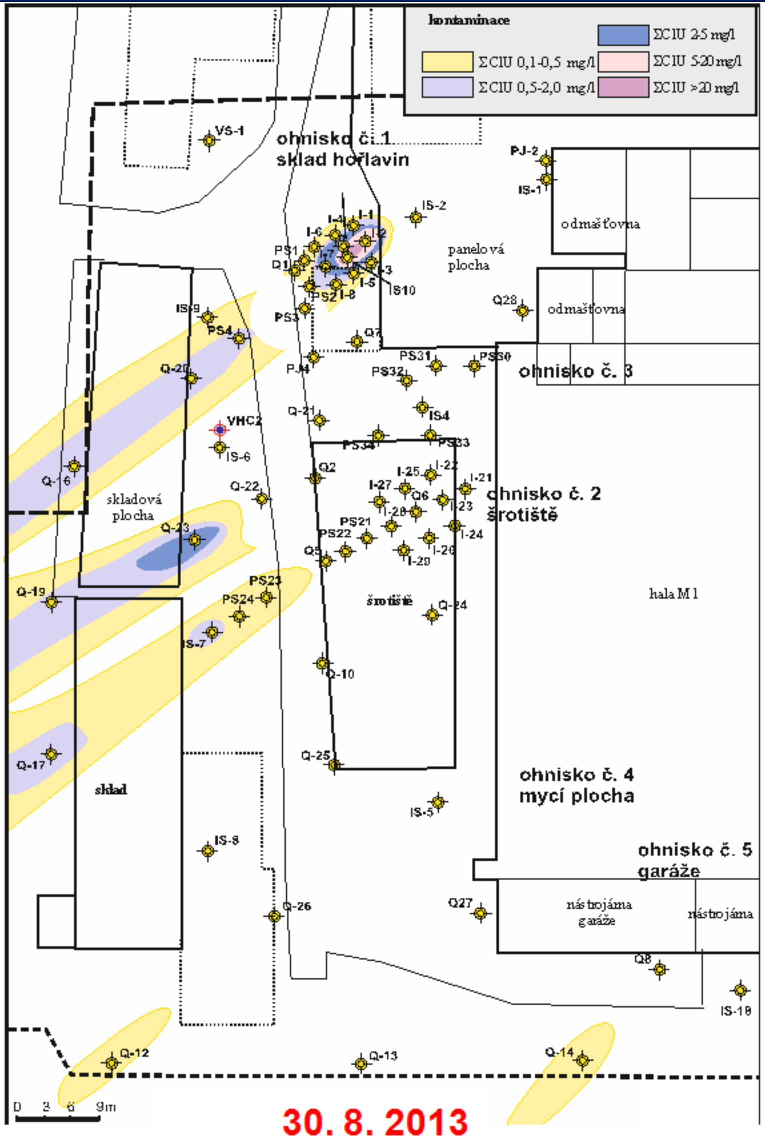




Field verification – Site Hořice

- State before nZVI+DC start
- Today

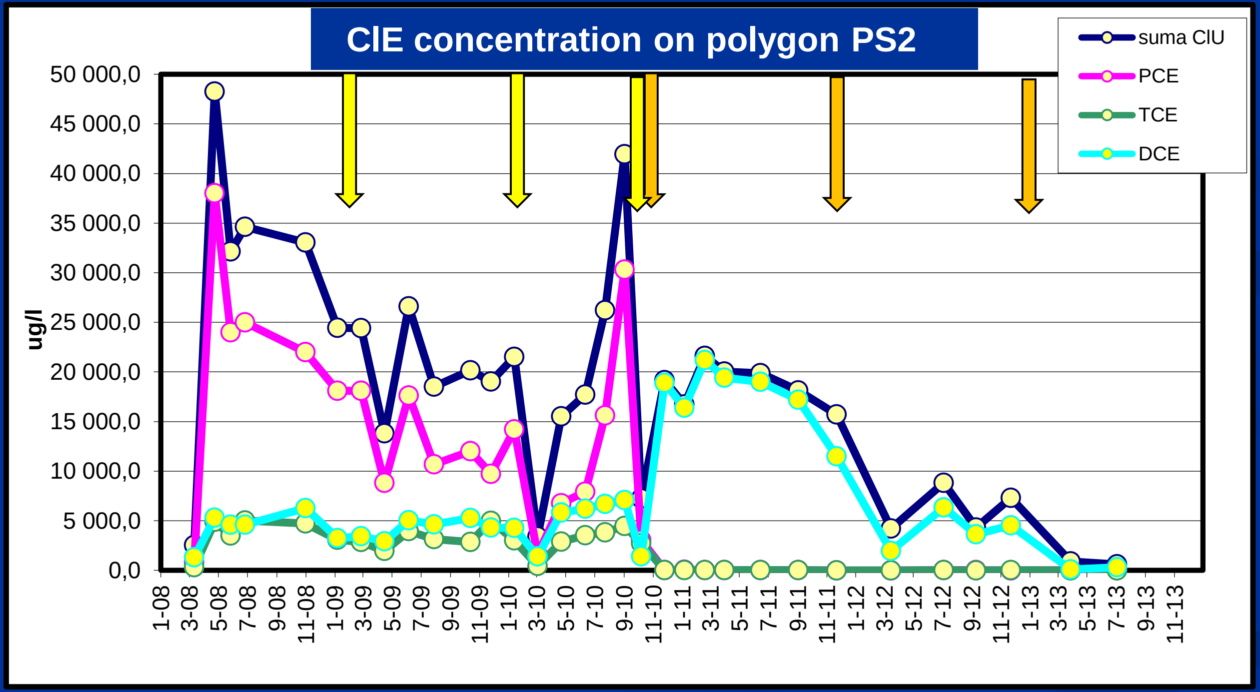




Field verification – Site Hořice

ClE concentration

- On all 9 polygons decreasing of ClE concentration
- 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)



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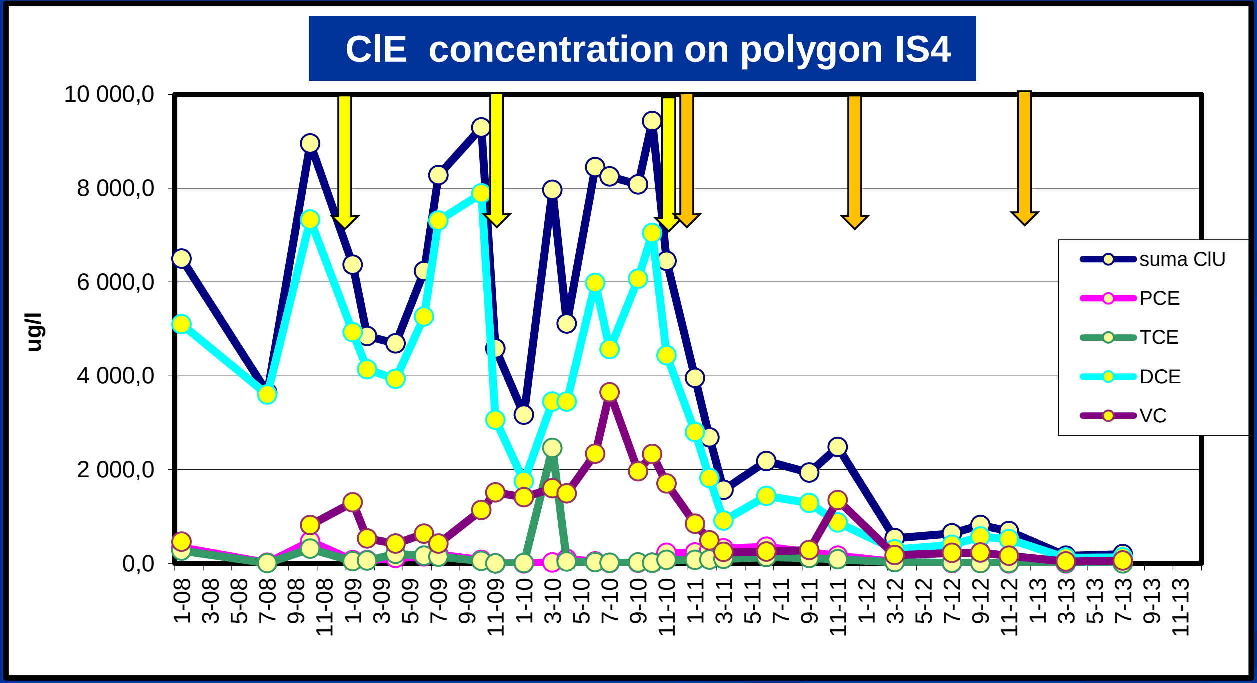
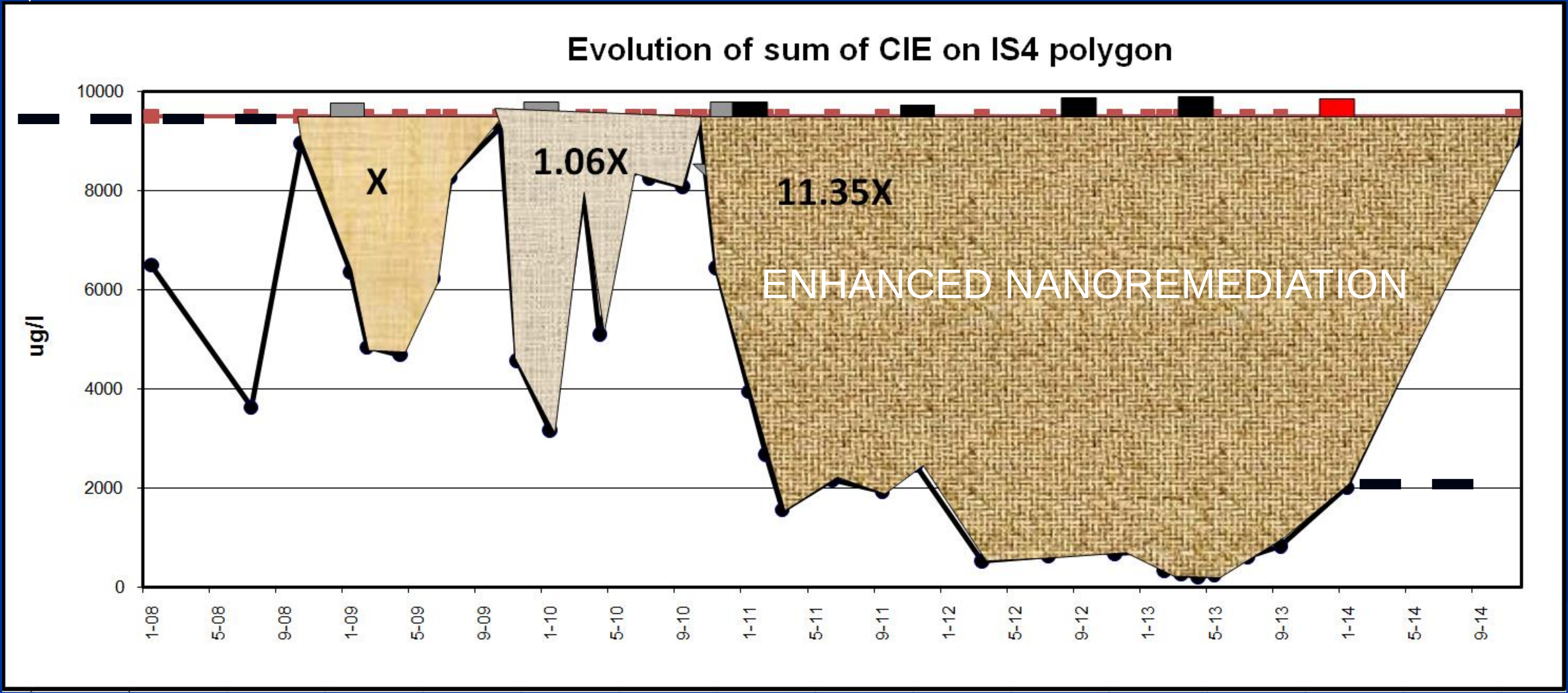


Field verification – Site Hořice

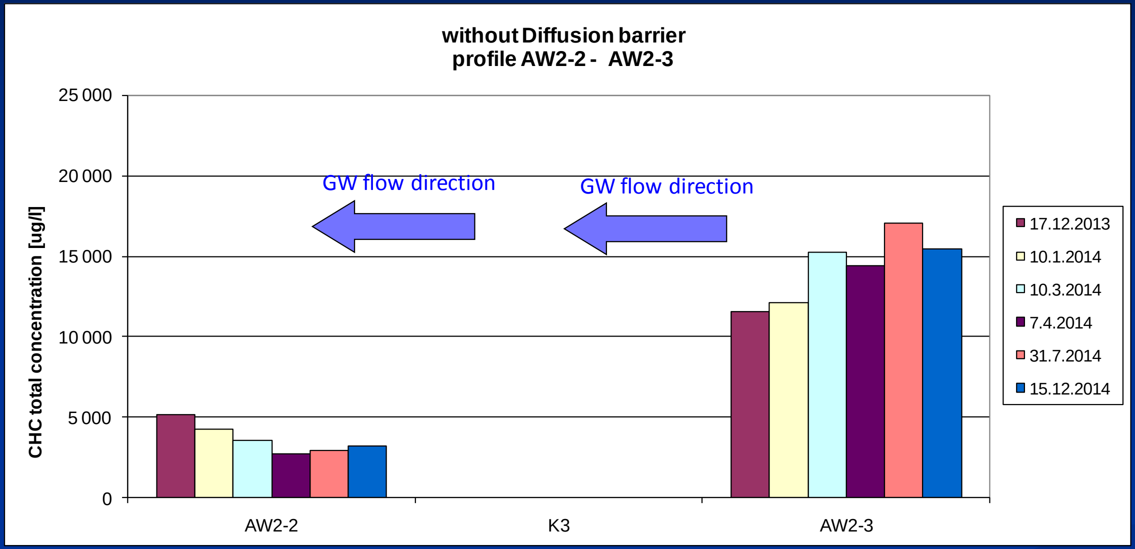
Efficiency comparison

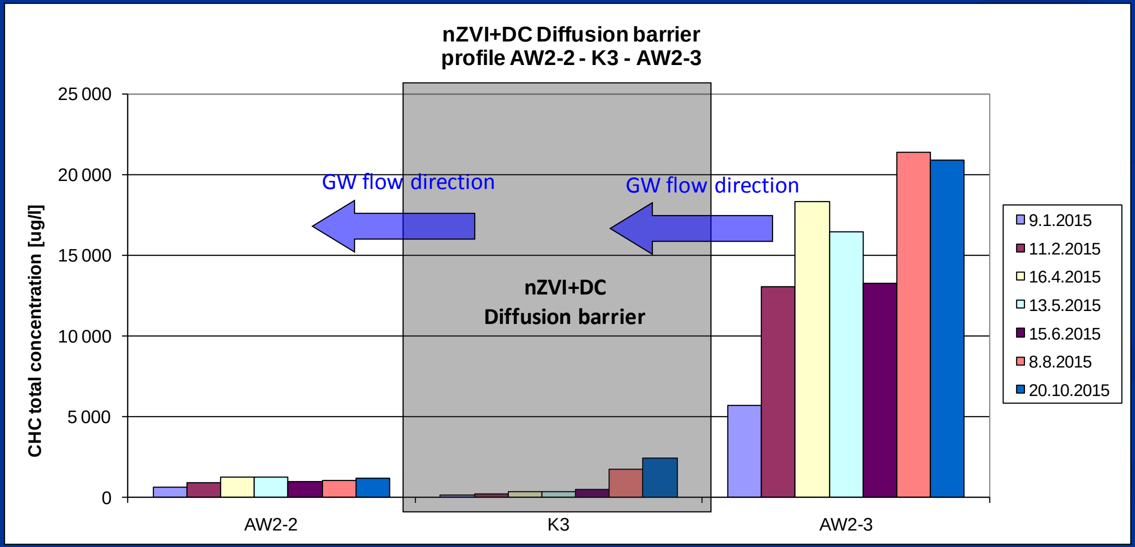
- Surface above the curve >> quantity of decomposed ClE
- Each nZVI (surface **X**) vs nZVI+DC (**10.X**)

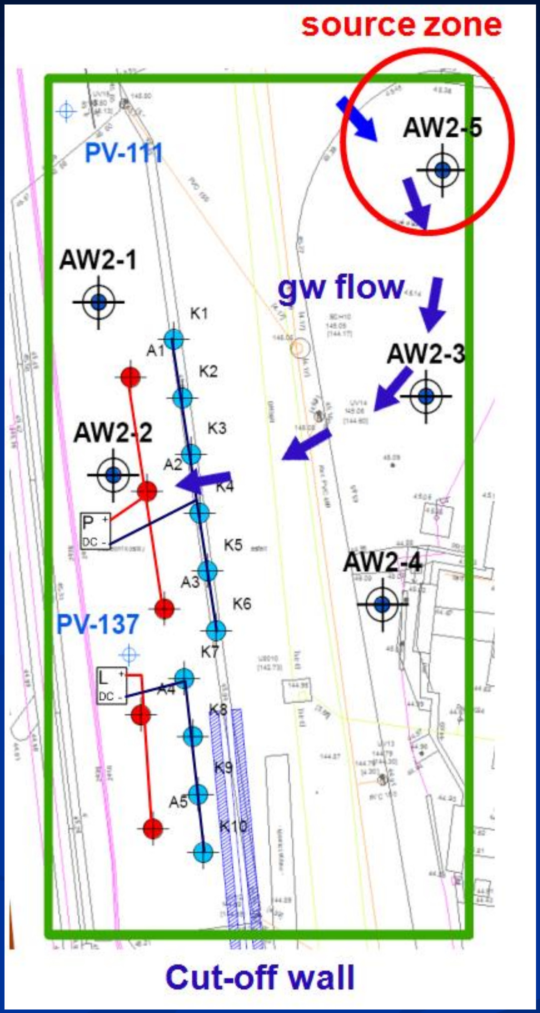


Field verification – Site Spolchemie

Diffusion barrier







Economic comparison – Enhanced Nanoremediation

- **<u>100% nZVI</u>** vs. **<u>100% of nZVI + 10% of DC system</u>** = double active time

  >> Less number of injections

”just” nZVI

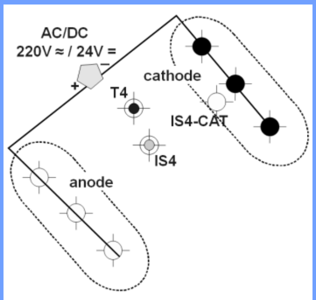
<u>X kg</u> of nZVI per 1 injection
Number of injections: **<u>N</u>**
>>price **<u>Y,- eur</u>**

vs

nZVI + DC

<u>X kg</u> of nZVI per 1 injection
Number of injections: **<u>0.5N</u>**
>>price **<u>0.5Y,- eur</u>**

+



price **<u>0.1Y,- eur</u>**

Same reactivity

Double active time
Save 40% of money

Perspectives of nanoiron applicability

- For combined processes
- 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.

Nano-Rem market position

- New technology = research, universities
- Problematic sites = „go“ Nano where others failed
- Polishing = low cost activity at the end of remediation
- Drinking water sites = other chemicals are not acceptible
- Use NanoRem to have better market position
- „Nano“ = brand, China, India

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Thanks for your attention