In-situ groundwater remediation with iron particles:

Studies on long-term stability, reactivity and transport

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VEGAS Versuchseinrichtung zur Grundwasser- und Altlastensanierung

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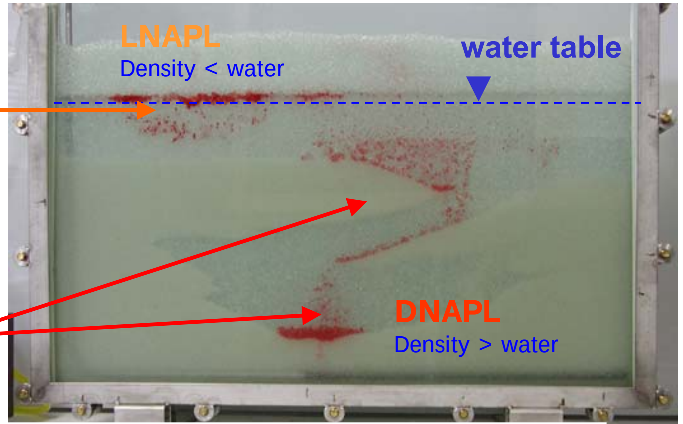
Remediation technologies required

LNAPL

DNAPL



NAPL = Non-aqueous phase liquid (not miscible with water**)**

Bench-scale

- Well controlled conditions (discharge, temperature, pH, Eh, conc.)
- Well-known mass and distribution of contaminants
- Homogeneous filling
- Completely mixed systems (stirred reactors) or 1D flow (soil columns)
- Reproducible experiments

⇨ mass balances
small amount of samples necessary

Investigation of single processes

VEGAS

IFARE, LEAP

? Scaling Factors ?

Influence of variability in space and time

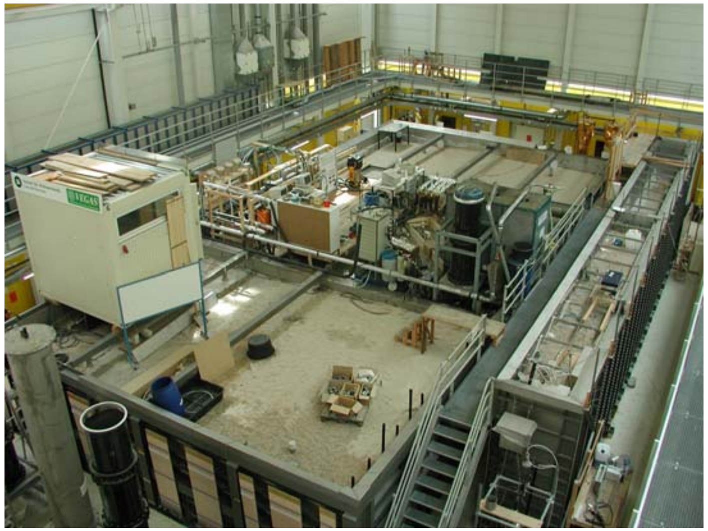
Interaction of different processes

Field-scale

- Unknown contaminant mass and distribution
- Partially uncontrollable boundary conditions
- Heterogeneous soil structure
- 3D flow
- Non-reproducible experiments

⇨ High uncertainty
Large amount of needed samples

„The real world problem“



Length: 18.5 m
Width: 9 m
Height: 4.5 m
More than 1000 sampling and measurement ports

Division into three compartments
(9m x 6.2m x 4.5m)

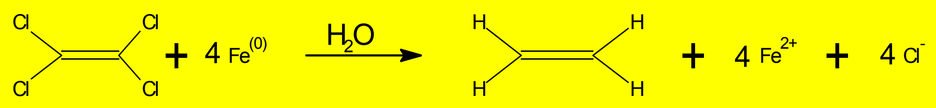
Former / current projects
Surfactant flushing
Steam/steam-air injection
Thermal wells
Groundwater circulation wells
Alcohol flushing
Fuel spill and detection
Geothermal energy use

Development of in situ Remediation Technologies

VEGAS	Source		Plume
	Thermally enhanced	Physical / chemical Flushing Technologies	
Unsaturated Zone	Steam-Air-Injection		
	Thermal Wells (THERIS)		
Saturated Zone (Groundwater)	Steam-Air-Injection	Alcohol-Flooding	„Dichtwand-Heber-Reaktor“ (DHR)
		Microemulsion Flushing	Enhanced Natural Attenuation (ENA)
	Thermal Wells	Surfactant Flushing	
		ISCO *(under investigation)*	
		Nano Iron *(under investigation)*	

Chemical Reduction by Iron

- **Reaction of Zero Valent Iron with CHC**



- **Also possible**
  - Heavy metals (Chromium VI, etc)
  - Other chlorinated compounds

Motivation for Injecting Colloidal Zero Valent Iron

- ZVI reacts with a wide variety of contaminants
- "Semi-Passive" method
- Low cost for installation
- Possible under buildings
- No limit to depth of injection (except economic)
- After all iron is used (or activity ceases), new injection possible
- Innovative method

→ **Experimental proof necessary**

Open Questions

- **Transport**
  - What **transport distances** are achievable under field conditions?
    - → *Distance between injection wells, source or plume treatment*
  - What **influences / controls** the transport **distances** and iron **distribution**?
    - → *Pre-treatment, rate-, concentration- and duration of injection*
  - How to **determine / prove** injected iron **concentrations** in the aquifer?
    - → *Duration of injection*
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  - What is the longevity of nano/micro-iron colloids?
  - How much nano/micro-iron is necessary?
- **Monitoring**
  - Short term: **Location** of nano/micro-iron **after** injection?
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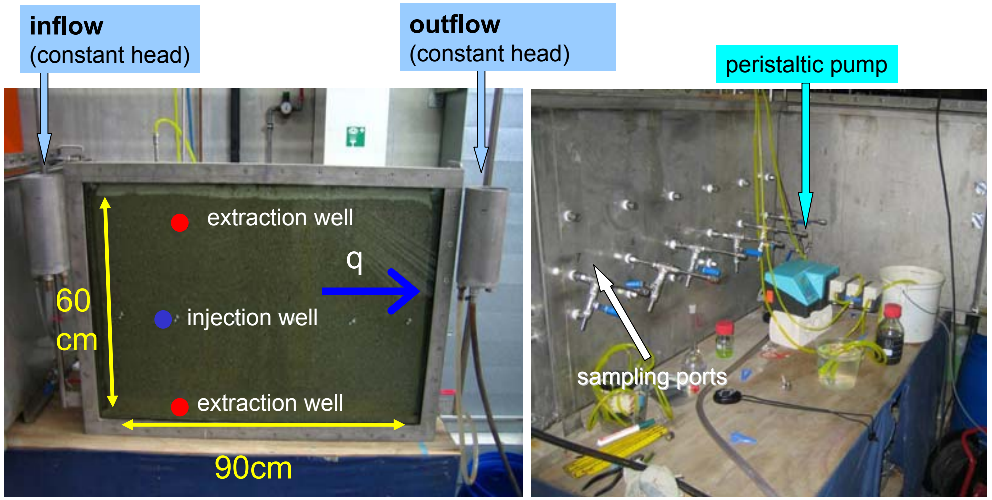
Preliminary Investigations - 2D Flume



First Transport Results

- **First experiments** indicated a very poor transport behavior of the particles:

→ Systematic transport experiments necessary

- **Further problem** How can Fe(0) be measured on a level of mg/kg with a geogenic background in soil of 40 g/kg?

Transport Investigations in Columns - New Measurement Technology

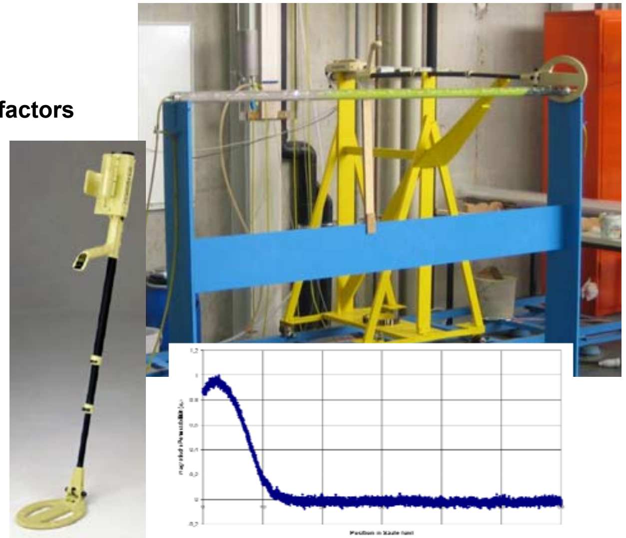
Column experiments

systematic investigations of factors influencing the transport

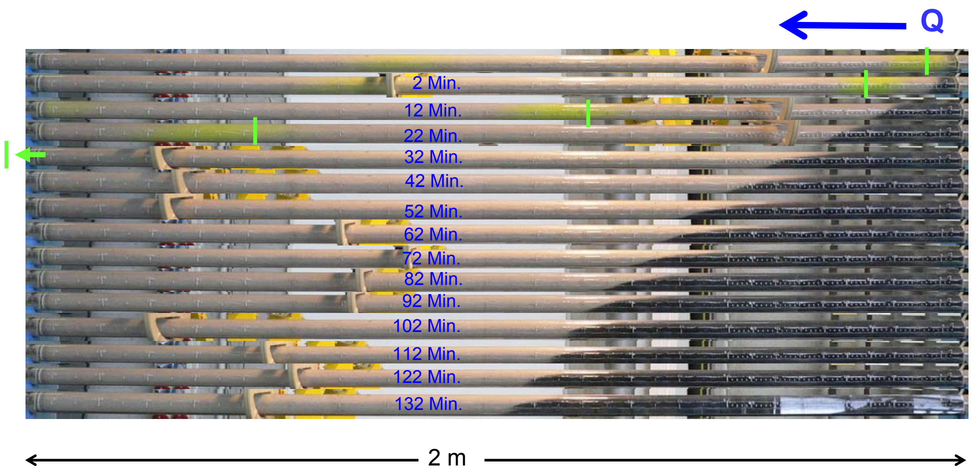
- Grain size distribution
- Injections rate
- Formulation of suspension
- Concentration of suspension

Non-destructive measurement system based on a modified commercial metal detector

→ Detection of changes in magnetic susceptibility



ZVI Front Propagation



$v = 9 \cdot 10^{-4}$ m/s	$K = 1.25 \cdot 10^{-3}$ m/s
$n = 0.33$	$C_{inj} = 10$ g/l

Open Questions – Transport Investigation in Large 3D Container

- **Transport**
  - What **transport distances** are achievable under field conditions?
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  - What **influences / controls** the transport **distances** and iron **distribution**?
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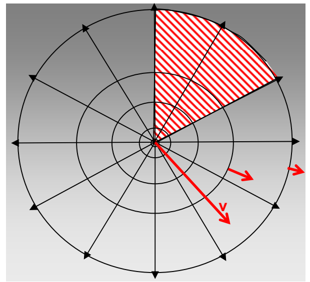
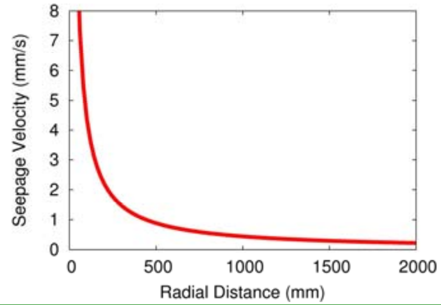
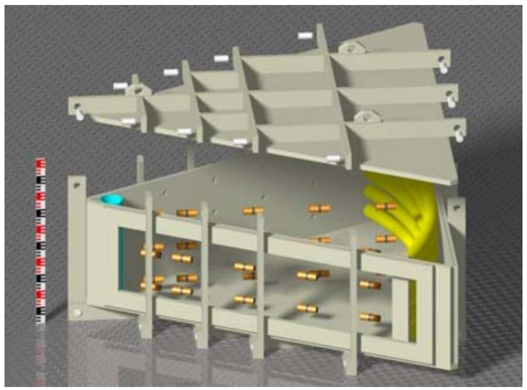
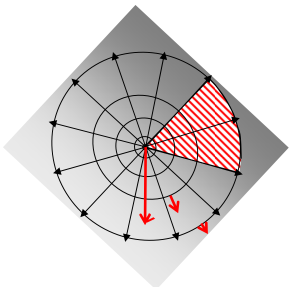




2-D Depth Averaged Radial Flow Experiment

- 60° triangular container to simulate the injection in a confined aquifer
- In-situ sensors record Fe^0-break through curves at different locations during the injection
- Realistic field flow velocities and concentrations



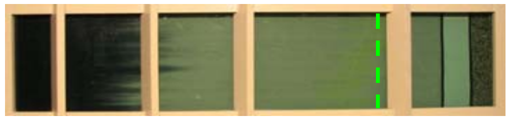


3D Drawing of the Container

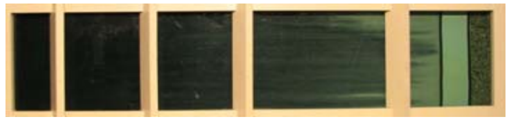
(r: 2 m, α: 60°, h: 0.6 m)

Transport Investigation Large Container - Results

t = 200 s, Uranin front near iron front



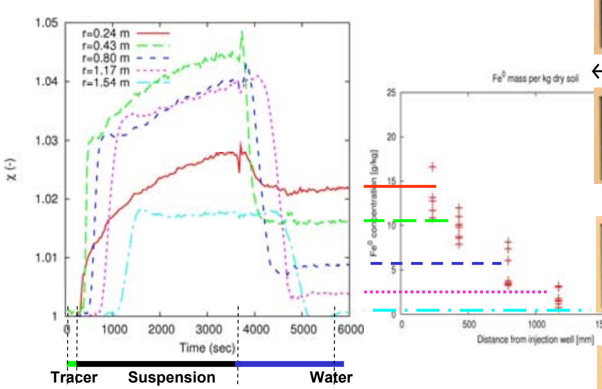
t = 700 s, Uranin front (green) near outflow, iron front retarded



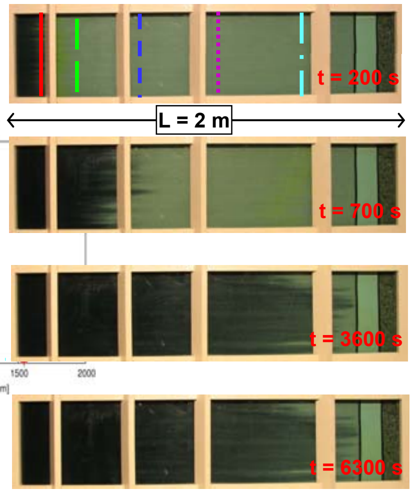
t = 3600 s, iron front near outflow

t = 6300 s, iron front stable = max. transport distance

Quantitative Measurement and Qualitative Observation



Magnetic susceptibility measured during the injection experiment

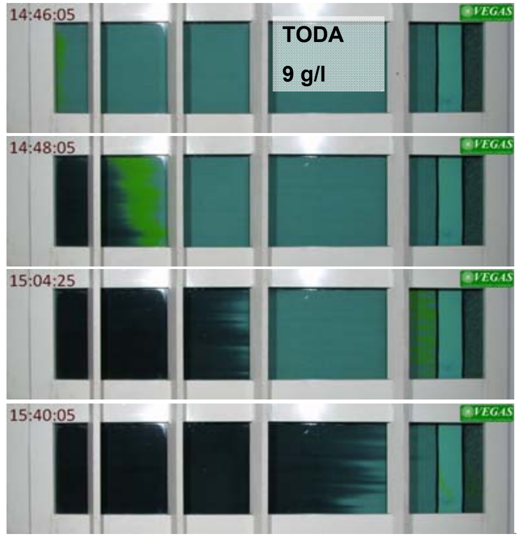


Four sequential images of the cross sectional glass plate

Large Scale Transport Experiments – Current Summary

By optimisation of the suspension and the Injection a distance of 2 m could be reached

➔ **Basis for the layout of field applications**



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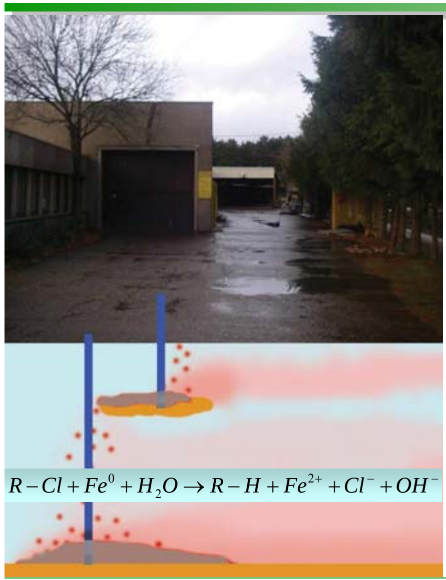
Open Questions

$$R-Cl+Fe^{0}+H_2O\rightarrow R-H+Fe^{2+}+Cl^{-}+OH^{-}$$

- **Reactivity**
  - What is the longevity of nano/micro-iron colloids?
  - How much nano/micro-iron is necessary?
- **How to predict reactivity at the field scale?**

How to Predict Reactivity at the Field Scale?



Methods

Batch	**0-D**
Column	**1-D**
Flume	**2-D**
(Container	**3-D)**

Numerical Simulation

Experimental Methods to determine Reactivity

Batch

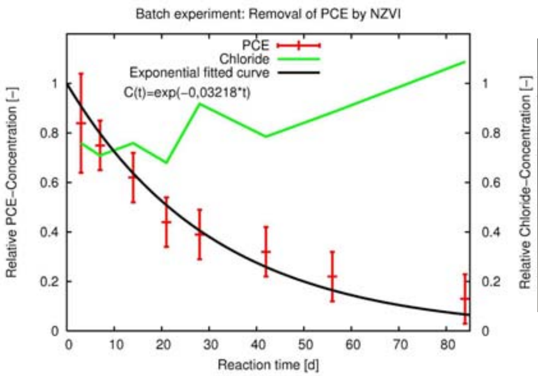
- Closed system
- Thermodynamic equilibrium
- Reproducible
- Maximum contact between components
- With or without matrix material or matrix components
- Variation of single parameters

- Identification of controlling and limiting parameters
- Suitability of reactant to remove a target compound
- Side reactions or incomplete break down

Information Obtained from Batch with Fe^0

Removal of 50 mg/l PCE with 1 g/l Fe^0

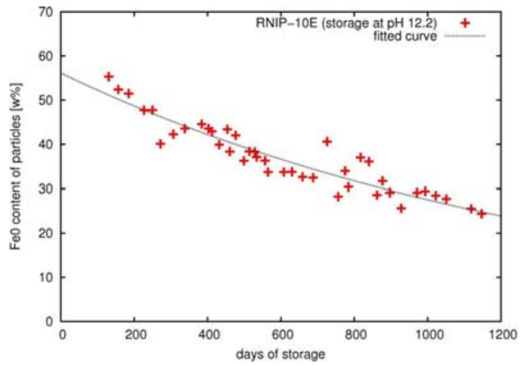
$$C_2Cl_4 + 4\,Fe^0 + 4\,H_2O \rightarrow C_2H_4 + 4\,Fe^{2+} + 4\,Cl^- + 4\,OH^-$$ pH↑



Information Obtained from Batch with Fe^0

- Hydrogen production can be used to determine Fe^0-concentration
- Freeze-dry of a Fe^0 sample
- $Fe^0 \rightarrow Fe^{2+}$ with hydrochloric acid
- Measurement of the released hydrogen gas volume

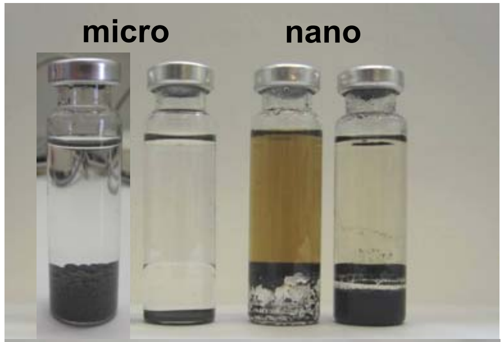
$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2$$



Information Obtained from Batch with Fe^0

Pure phase PCE with micro- and nano iron in separate vials

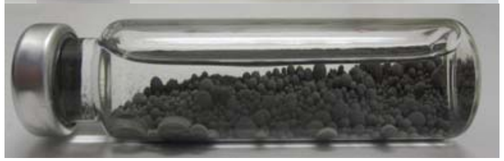
Either water or PCE as wetting phase



From Left to Right:

- Micro, water wet
- Micro, PCE wet
- Nano, water wet
- Nano, PCE wet

Micro Fe water wetting at interface between PCE and Water

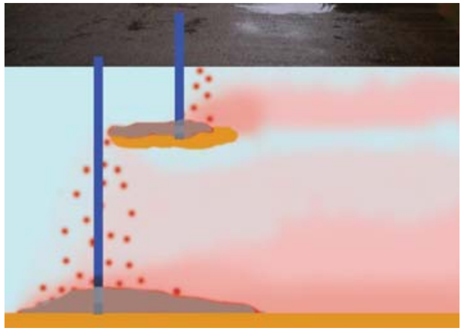


Batch Results Alone Insufficient

- Large scale not at chemical equilibrium
- Interaction between different parameters
- pH buffer due to continuous input of fresh ground water (in most aquifers)

?

How to approach the „real world“ ?



Experimental Requirements to Determine Reactivity

Realistic conditions

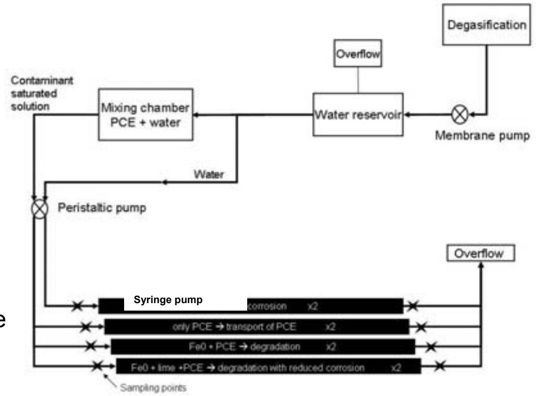
- Natural groundwater flow conditions
- Very slow and constant water flux (v ≈ 0.5 m/d)
- Realistic horizontal flow conditions
- No O_2 in the system
- No (sun) light
- Constant temperature
- Long term stable system (minimum 6 months)

→ 1-D Column experiments

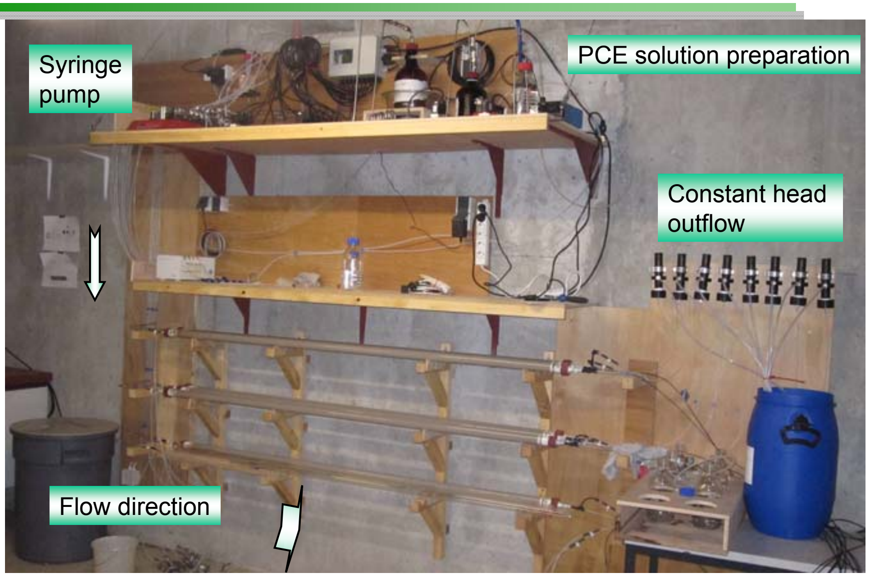
Column Experiments

Variable Boundary and Initial Conditions

- Fe^0 injected in the column
- Matrix premixed with Fe^0
- Continuous flux of water
- Concentration of contaminant variable
- Additional components in water possible
- Addition of slaked lime to increase pH
- Contact time variable through flow rate
- Residual NAPL in column possible



Column Experiments



Information obtained from Column Experiments

- Anaerobic corrosion makes Zero-valent iron unstable in aqueous solutions
  - causes hydrogen production
  - is pH-value dependent (and increases the pH-value in closed systems → self inhibition in batch experiments)

$$Fe^{0} + 2\,H_2O \rightarrow Fe^{2+} + H_2(g) + 2\,(OH)^{-}$$

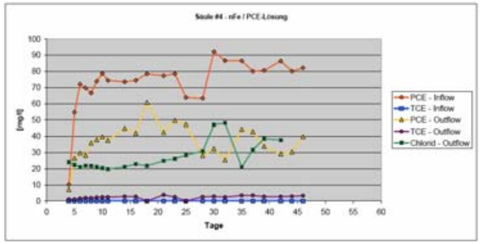
- Addition of slaked lime powder ($Ca(OH)_2$) to the iron suspension could reduce the H_2-gas production significantly
- Slaked lime increases the pH, thus reduces the anaerobic corrosion

With $Ca(OH)_2$

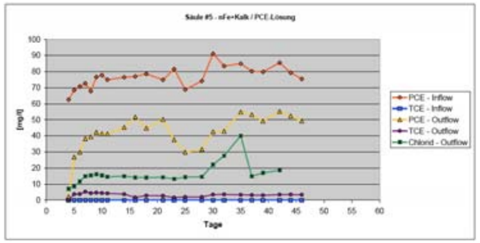
Without $Ca(OH)_2$ → $H_2(g)$

Results of Reactivity Experiments

- The results show that an addition of $Ca(OH)_2$ reduces the formation of H_2 significantly
- The iron particles were more than 100 days active
- In columns without $Ca(OH)_2$ large amounts of hydrogen evolved
- The reactivity in columns with $Ca(OH)_2$ was slightly reduced



Without $Ca(OH)_2$



With $Ca(OH)_2$

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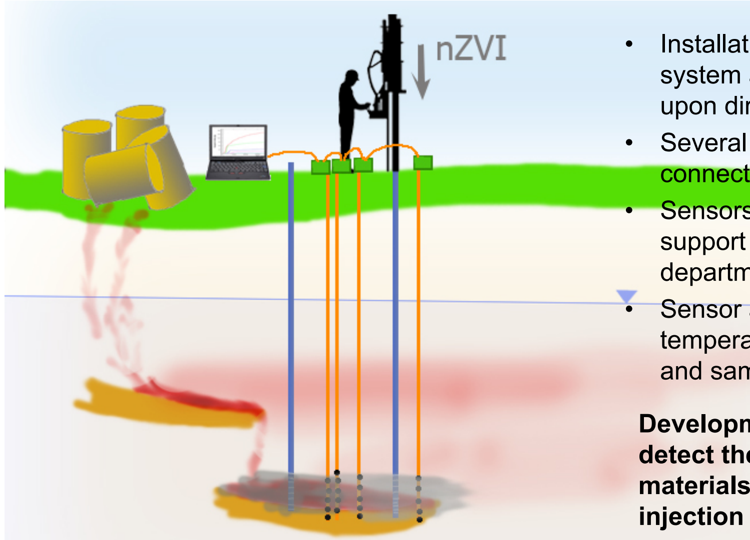
Development of a Field-Ready Measurement System

- **Requirements**
  - Based on magnetic susceptibility measurements
  - One master system with data acquisition and remote data transfer
  - Several slaves distributed over the field site each with several sensors for different depths
  - Robust and stand alone (battery driven)
  - 2 operation modes:
    - Live mode during injection
    - Long term mode for following the reaction (consumption of Iron)

"Final" field design 2011

1st concept; Lab: uncoated, coated; 1st field concept, (horizontal) 2nd field concept (vertical installation)

Principle



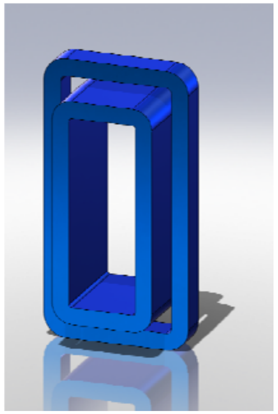
- Installation of measurement system and injection based upon direct push techniques
- Several slave systems are connected to a master
- Sensors optimized with support by electronic department of the university
- Sensor arrays with temperature measument and sampling ports

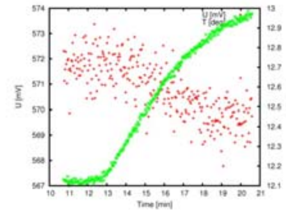
Development of methods to detect the Fe-based reactive materials during and after injection into the subsurface

Some Impressions From the First Field Application in Belgium

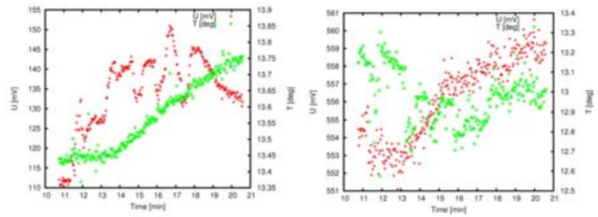
Sensor and Results

- **Final sensor currently in production**





Temperature
Fe-Signals



Measurements are ongoing…

What else do we need?

- Improve the economy
  - The cost of Nano-Iron is still too high (>100 €/kg)
  - Micro-Iron is much cheaper (~2-5 €/kg), but difficult to inject and the reactivity is lower
- Tackle sources instead of plumes (really reduce remediation times)
- Improve the formulations/injection for a better distribution in the subsurface
- Reduce the corrosion as a competing reaction ($Ca(OH)_2$?)
- Assess the ecotoxicity of the particles and their reaction products to minimize risks to natural systems (=> authorities)
- Develop numerical tools for planning of field applications

Successful Field Demonstrations…

Successful Field Demonstrations…

Successful Field Demonstrations…

Last but not least

Thanks to our staff, the involved students and partners

and the funding

NAPASAN Nanopartikel zur Grundwassersanierung

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