Reactivity tests in columns for simulating source zone and plume remediation of chlorinated hydrocarbons by zero-valent metal particles under subsurface-like conditions

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Introduction

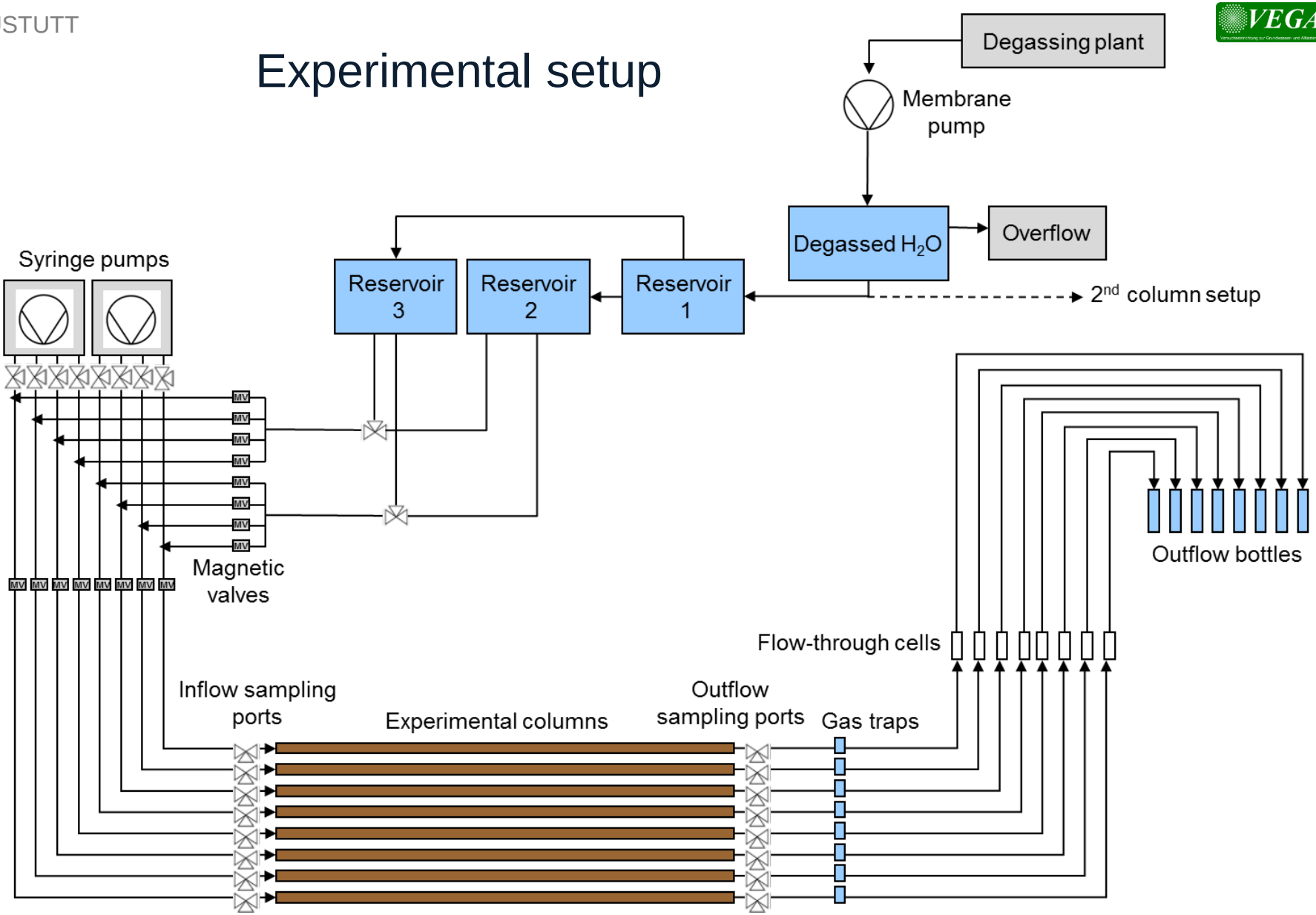
- Chlorinated hydrocarbons - commonly detected groundwater contaminants

- State of the art:
  Permeable reactive barriers (composed of Fe^0)
  → Remediation of the contaminant plume

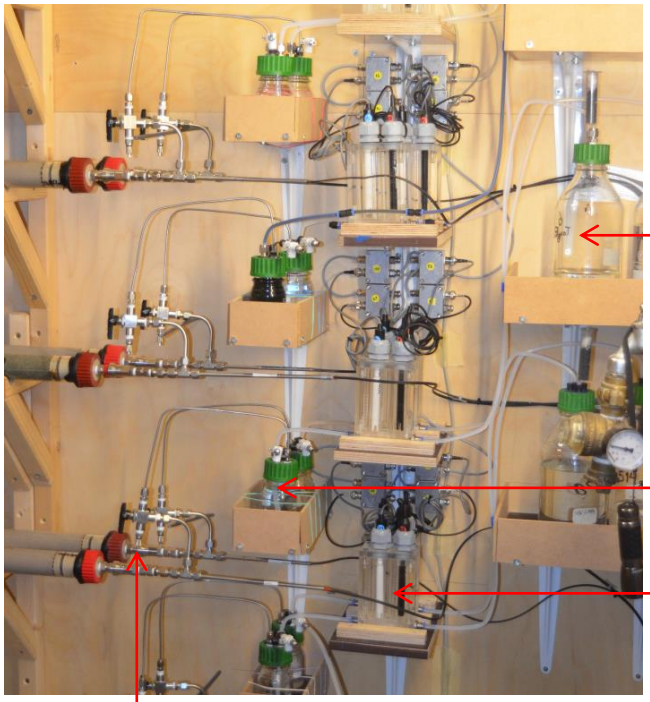
- Objective of current studies (e.g. NanoRem):
  Source zone and plume remediation by injection of zero-valent metal particles into the subsurface
  → Demands on the particles to allow for an effective pollutant degradation:
  1) Good transport properties
  2) Long-term reactivity towards the target contaminant ➡ Reactivity tests in columns

(Batch tests do not reflect conditions in aquifers!)

Experimental setup



Experimental setup



Outflow bottles (Cl^-)

Gas traps (H_2, C_2H_4, C_2H_6)

Flow-through cells (pH and ORP)

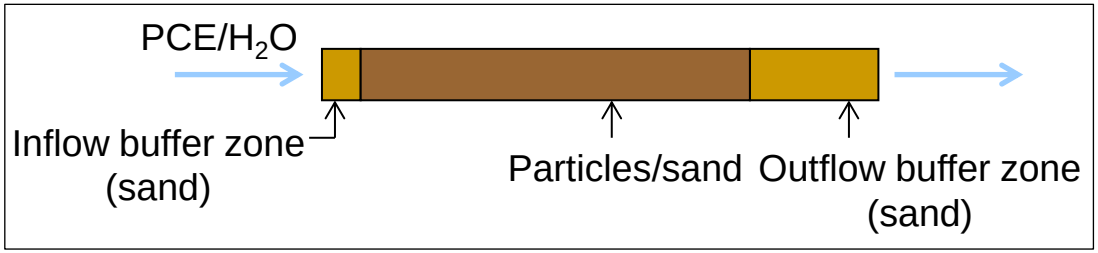
Outflow sampling ports (PCE, metabolites)

- Contaminant: Tetrachloroethene (PCE, C_2Cl_4)
- Tested particles: Fe^0, (Mg^0), Al^0

Experimental setup

- $L_{columns}$: 100 cm or 200 cm, *ID*: 3.6 cm
- Porous media: quartz sand – Dorsilit® 8 (0.3 – 0.8 mm)
- Simulation of source zone and plume remediation under flow-through conditions

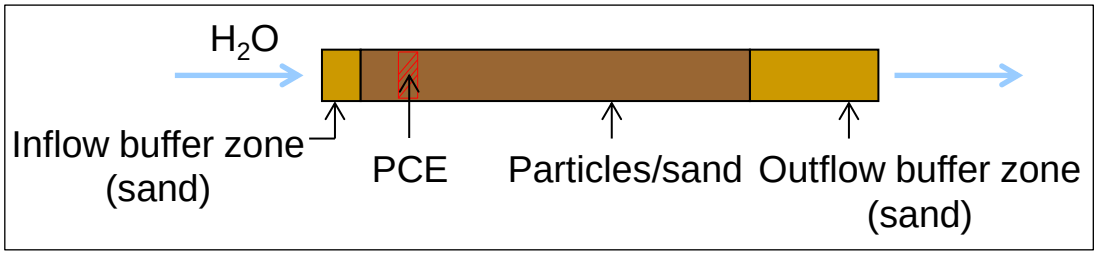
  (Flow rate ~ 175 cm^3/d, seepage velocity ~ 0.5 m/d)



Plume remediation

↓

Al^0



Source zone/plume remediation

↓

Fe^0

Source zone/plume remediation of PCE by Fe^0

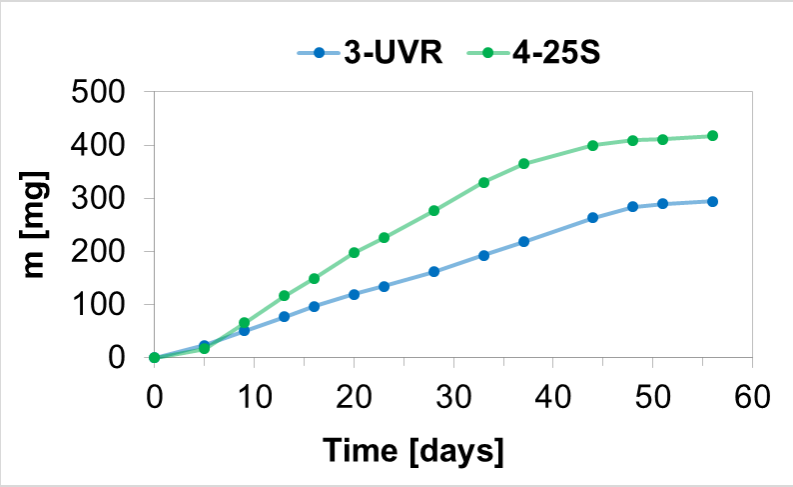
Remediation reaction

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

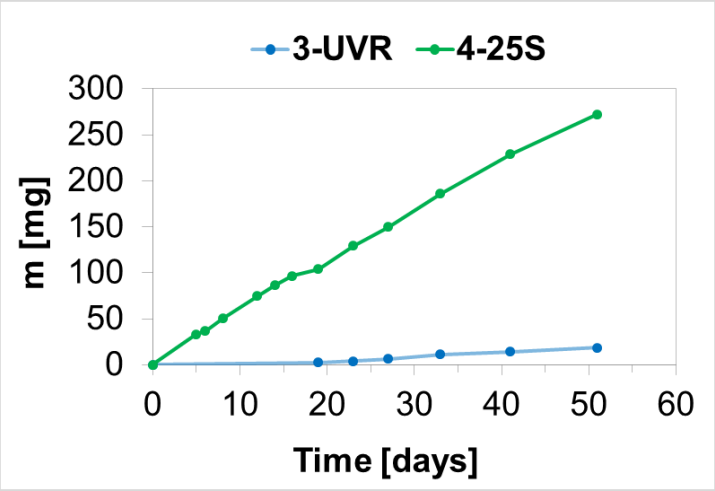
vs. anaerobic corrosion

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

Chloride formation



Hydrogen formation



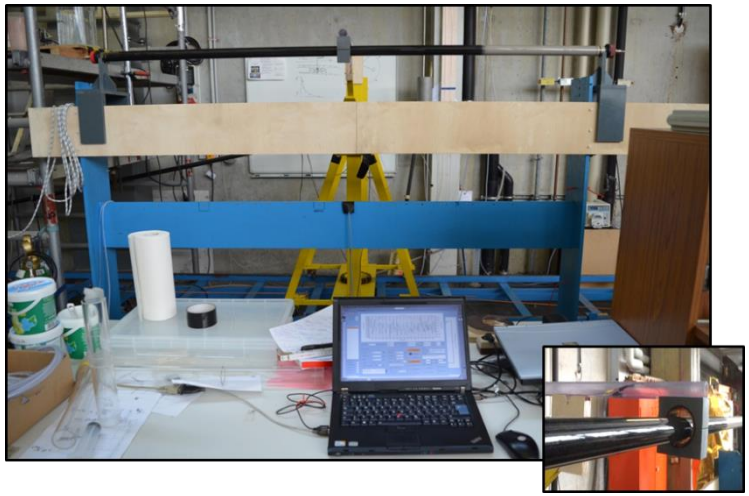
3-UVR: flaky Fe microparticles produced by milling (UVR-FIA GmbH)

4-25S: Fe nanoparticles (NANO IRON s.r.o.)

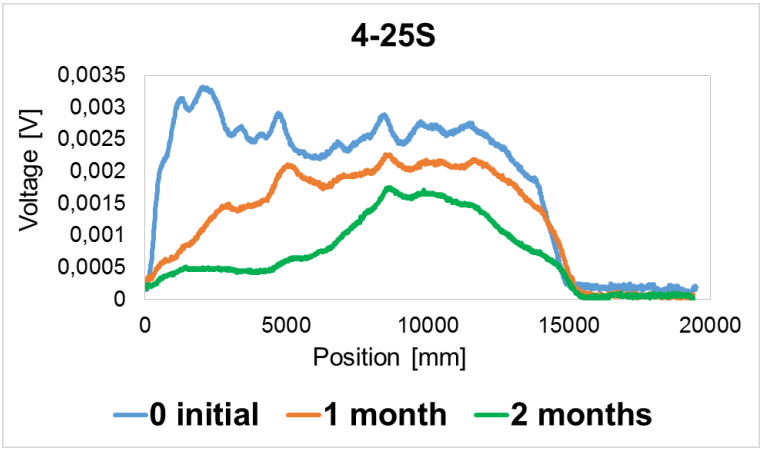
- Formation of intermediates (mainly TCE)
- Higher PCE degradation (to ethene) using iron nanoparticles

Source zone/plume remediation of PCE by Fe^0

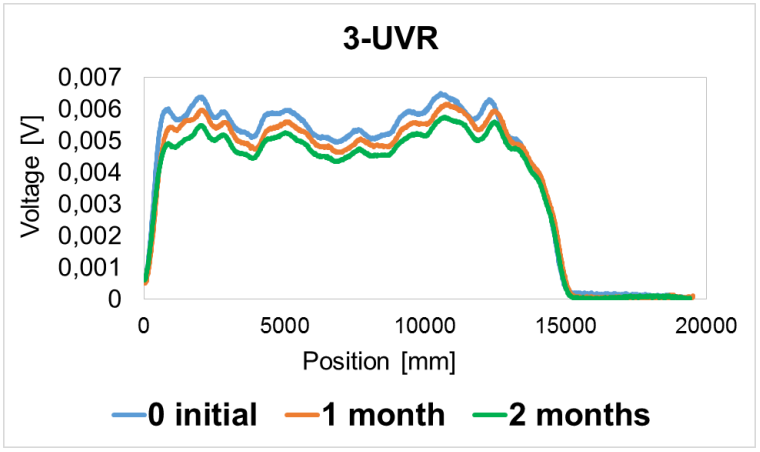
- Higher hydrogen formation/consumption of Fe^0 by anaerobic corrosion for Fe nanoparticles



Magnetic susceptibility measurements
→ changes in Fe^0 concentration
in the course of the experiment



37% Fe^0 remaining after 2 months



89% Fe^0 remaining after 2 months

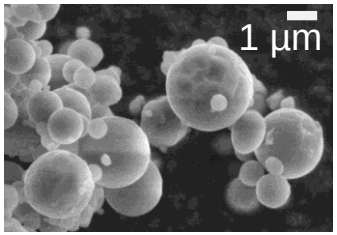
Plume remediation of PCE by Al^0

Al:

- Lower density compared to Fe
- Better stoichiometry related to mass compared to Fe

1 g PCE → 1.34 g Fe^0 (MW: 55.8 g/mol; 2 e^-)

0.43 g Al^0 (MW: 26.9 g/mol; 3 e^-)



Aluminiumgrieß AK 6 WA 23
(ECKART GmbH)

- However, reactivity tests in columns indicate a poor remediation efficiency.
  - Decrease in PCE concentration of ~10%
  - Formation of intermediates (TCE and DCE)

➡ Reactivity enhancement of Al by modification of the particle properties?

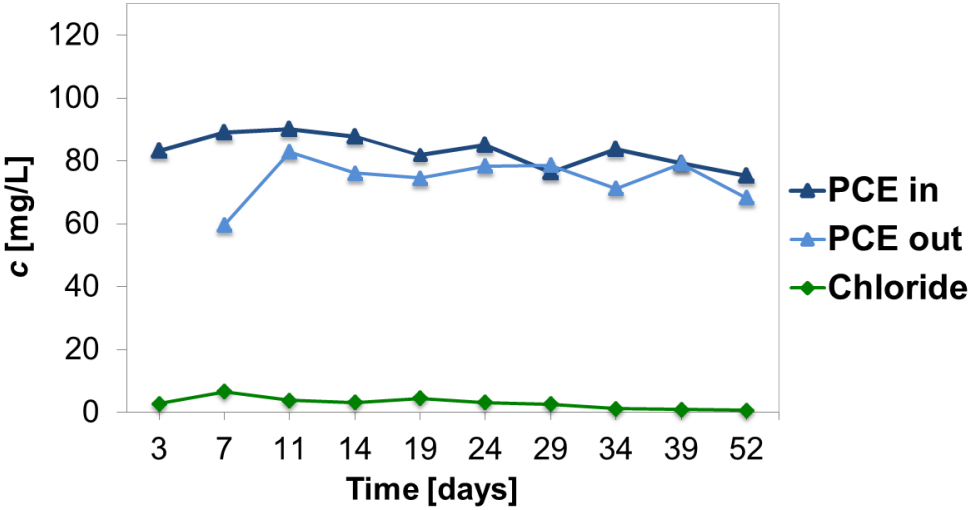
- "Mechanical activation" of Al (by ball milling Al together with Al_2O_3)
- Use of composite particles (e.g. Al/Mg)

Plume remediation of PCE by Al^0

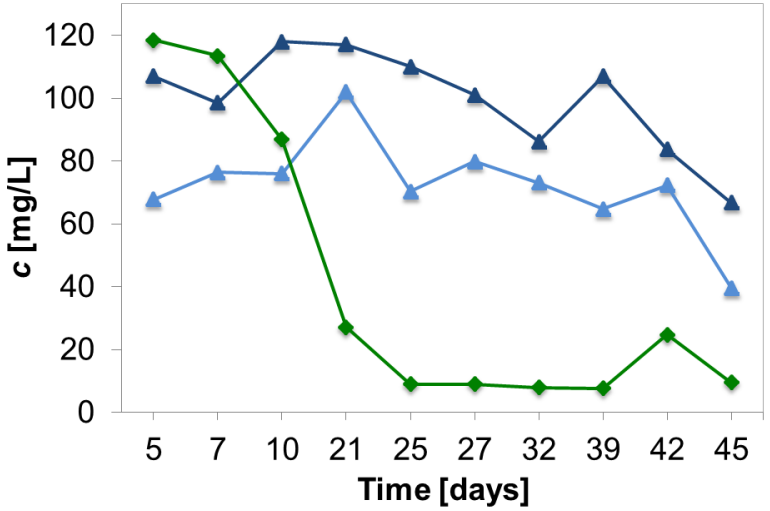
Preliminary results:

- Higher chloride formation using Al/Mg and Al/Al_2O_3
- Improved pollutant degradation
- Detection of ethene as end product

Al



Al/Mg



Conclusions

- Reactivity tests in columns (> 50 days) under flow-through conditions are suitable to study the long-term behaviour of the Fe^0 and Al^0 particles under field-similar conditions.
- Simulation of source zone or plume remediation of PCE possible.
- Al^0 in principle suitable for the reductive dehalogenation of PCE, but modification of the particle properties (or the aquifer properties) necessary!
- Milled Fe microparticles might be promising regarding their longevity and their relationship between dechlorination and anaerobic corrosion.

Thank you for your attention!

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