In-situ groundwater remediation with iron particles: Studies on long-term stability, reactivity and transport

Hans-Peter Koschitzky, Cjestmir de Boer, André Matheis, Jürgen Braun, Norbert Klaas, Research Facility for Subsurface Remediation University of Stuttgart, Germany

VEGAS Versuchseinrichtung zur Grundwasser- und Altlastensanierung

Seminar “Current Issues in Environmental Geosciences” Department of Environmental Geosciences, Vienna, January, 23th 2012

LNAPL / DNAPL Source Remediation

Remediation technologies required

LNAPL

Density < water

DNAPL

Density > water

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

The Scaling Problem

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

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

Scaling Factors
- Influence of variability in space and time
- Interaction of different processes

High uncertainty
- Large amount of needed samples
- “The real world problem”

VEGAS - Large Container

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

<table>
<thead>
<tr>
<th>Source</th>
<th>Plume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermally enhanced</td>
<td>Physical / chemical flushing technologies</td>
</tr>
<tr>
<td>Steam-Air-Injection</td>
<td></td>
</tr>
<tr>
<td>Thermal Wells (THERIS)</td>
<td></td>
</tr>
<tr>
<td>Unsaturated Zone</td>
<td></td>
</tr>
<tr>
<td>Saturated Zone (Groundwater)</td>
<td>Steam-Air-Injection</td>
</tr>
<tr>
<td></td>
<td>Alcohol-Flooding</td>
</tr>
<tr>
<td></td>
<td>„Dichtwand-Weber-Reaktor“ (DHR)</td>
</tr>
<tr>
<td></td>
<td>Microemulsion Flushing</td>
</tr>
<tr>
<td></td>
<td>Enhanced Natural Attenuation (ENA)</td>
</tr>
<tr>
<td></td>
<td>Surfactant Flushing</td>
</tr>
<tr>
<td></td>
<td>ISCO (under investigation)</td>
</tr>
<tr>
<td></td>
<td>Nano Iron (under investigation)</td>
</tr>
</tbody>
</table>

### Chemical Reduction by Iron

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

\[
\text{CHC} + 4 \text{Fe}^{0} \rightarrow \text{H} + 4 \text{Fe}^{2+} + 4 \text{Cl}^{-}
\]

- **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
- **Reactivity**
  - 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?
  - Long term: **When** is a re-injection 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

- **Reactivity**
  - 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?
  - Long term: When is a re-injection necessary?

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?

Preliminary Investigations - 2D Flume

- **inflow** (constant head)
- **outflow** (constant head)
- **peristaltic pump**
  - **extraction well**
  - **injection well**
  - **extraction well**

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

- Transport
  - What transport distances are achievable under field conditions?
  - What influences / controls the transport distances and iron distribution?
  - How to determine / prove injected iron concentrations in the aquifer?

2-D Depth Averaged Radial Flow Experiment

- 60° triangular container to simulate the injection in a confined aquifer
- In-situ sensors record Fe⁰-break through curves at different locations during the injection
- Realistic field flow velocities and concentrations

Open Questions – Transport Investigation in Large 3D Container

- Transport
  - Distance between injection wells, source or plume treatment
  - Pre-treatment, rate-, concentration- and duration of injection
  - Duration of injection

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_

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

- **Reactivity**
  - 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?
  - Long term: When is a re-injection necessary?

Open Questions

- **Reactivity**
  - What is the longevity of nano/micro-iron colloids?
  - How much nano/micro-iron is necessary?

  \[ R - Cl + Fe^0 + H_2O \rightarrow R - H + Fe^{2+} + Cl^- + OH^- \]
# How to Predict Reactivity at the Field Scale?

## Methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch 0-D</td>
<td>Closed system</td>
</tr>
<tr>
<td>Column 1-D</td>
<td>Thermodynamic equilibrium</td>
</tr>
<tr>
<td>Flume 2-D</td>
<td>Reproducible</td>
</tr>
<tr>
<td>(Container 3-D)</td>
<td>Maximum contact between components</td>
</tr>
<tr>
<td>Numerical Simulation</td>
<td>Variation of single parameters</td>
</tr>
</tbody>
</table>

## Information Obtained from Batch with Fe⁰

Removal of 50 mg/l PCE with 1 g/l Fe⁰

\[ C_2Cl_4 + 4 Fe^0 + 4 H_2O \rightarrow C_2H_4 + 4 Fe^{2+} + 4 Cl^- + 4 OH^- \]  \( pH \uparrow \)

## 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 breakdown

### Information Obtained from Batch with Fe⁰

- Hydrogen production can be used to determine Fe⁰-concentration
- Freeze-dry of a Fe⁰ sample
- Fe⁰ → Fe²⁺ with hydrochloric acid
- Measurement of the released hydrogen gas volume

\[ Fe^0 + 2 H^+ \rightarrow Fe^{2+} + H_2 \]
Information Obtained from Batch with Fe⁰

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)

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 O² 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
- Fe⁰ injected in the column
- Matrix premixed with Fe⁰
- 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

- Syringe pump
- PCE solution preparation
- Constant head outflow
- Flow direction

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

\[ \text{Fe}^{0} + 2 \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_2 (g) + 2 (\text{OH})^- \]

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

Results of Reactivity Experiments

- The results show that an addition of Ca(OH)\(_2\) reduces the formation of \( \text{H}_2 \) 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

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

- Reactivity
  - 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?
  - Long term: When is a re-injection necessary?
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)

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 measurement 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

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...

Thanks to our staff, the involved students and partners

and the funding

Funding provided by:
The EU in the 7th Framework Programme
FP7 ENV 2008.3.1.1.1.
AQUAREHAB

koschitzky@iws.uni-stuttgart.de
http://www.vegas.uni-stuttgart.de

Dr.-Ing. Hans-Peter Koschitzky,
Technical Director
VEGAS,
Versuchseinrichtung zur Grundwasser- und Altlastensanierung, Universität Stuttgart