What can you expect? ➔ flash lights

- The problem: Soil and groundwater contamination
- Source – plume
- Remediation methods ➔ *in-situ* technologies
  - Physical
  - thermal
  - chemical
  - biological
- Nanoremediation
- Contribution NanoRem
Industrial heritage:
soil and groundwater contamination

Characterization, Remediation, Monitoring

Water Supply (receptor)  Contaminant Plume in Groundwater (path)  Contaminant Source (source)

Our heritage

Sustainability Workshop, Oslo, 2. – 4. December 2014

Dealing with soil and groundwater contamination

1.) Source Zone Treatment

2.) Plume Management

Source/plume treatment

Sustainability Workshop, Oslo, 2. – 4. December 2014
LNAPL / DNAPL problem

LNAPL: Density < water

DNAPL: Density > water

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

Source
Sustainability Workshop, Oslo, 2. – 4. December 2014

VEGAS Large Flume

Length: 16 m
Width: 1 m
Hight: 3 m
Glas front
CHC spill in an aquifer

Source aquifer

Geology and "image" of a source zone in a fractured aquifer

Source fractured
Plume lengths

Source: Dr. D. Stupp, 2011

Contamination treated *in-situ*

Inventory of 239 cases

Held, Th., Schroers, St.; 2012, Länderfinanzierungsprogramm „Wasser, Boden und Abfall“ 2010, „Auswertung von Fällen mit In-situ-Anwendungen in der gesättigten Zone bei der Altlastenbearbeitung (Projekt B 3.10)

http://www.laenderfinanzierungsprogramm.de/cms/WaBoAb_produ/WaBoAb/Vorhaben/LABO/B_3.10/index.jsp
Soil and groundwater remediation

Remediation Methods

- Restriction Measures
- In-Situ Techniques
  - Biochemical Methods
    - MNA
    - Enhanced NA
  - Hydraulic Methods
    - Pump & Treat
    - Flushing Methods
  - Thermal Methods
    - Steam
    - Steamair
    - Solid Heating Sources
    - Oxidative Methods (ISCO)
    - H$_2$O$_2$
    - Peroxide
    - Persulfate
    - Ozon
    - ORC
  - Chemical Methods
  - Reductive Methods
  - Elementa Metals
  - Molasses
  - HRC
- Ex-Situ Techniques
  - Separation/Reduction
  - Thermal Treatment
- To other location

Applied in-situ methods

n = 258

- Tensid-Spülung 7; 3%
- Sonstige 9; 3%
- ISCO 36; 14%
- SCR (nFe$^0$) 3; 1%
- Funnel & Gate 14; 5%
- Airsparging 43; 17%
- UVB / GSB 8; 3%
- Thermische Verfahren 5; 2%
- Mikrobielle Verfahren 133; 52%

Inventory of 239 cases

Held, Th., Schivo, St.: 2012, Länderfinanzierungsprogramm „Wasser, Boden und Abfall“ 2010, „Auswertung von Fällen mit In-situ-Anwendungen in der gesättigten Zone bei der Altlastenbearbeitung (Projekt B 3.10)"
http://www.laenderfinanzierungsprogramm.de/cms/WaBoAb_prod/WaBoAb/Vorhaben/LABO/B_3.10/index.jsp
Microbiological methods

Inventory of 239 cases

Held, Th., Schroers, St.: 2012, Länderfinanzierungsprogramm „Wasser, Boden und Abfall“ 2010, „Auswertung von Fällen mit In-situ-Anwendungen in der gesättigten Zone bei der Altlastenbearbeitung (Projekt B 3.10)
http://www.laenderfinanzierungsprogramm.de/cms/WaBoAb_prod/WaBoAb/Vorhaben/LABO/B_3.10/index.jsp

Nitrat
14; 12%

H₂O₂
22; 18%

Melasse
24; 20%

Andere Organik
16; 13%

HRC
6; 5%

Bakterien
4; 3%

ISOC
4; 3%

Sauerstoff / Luft
18; 15%

Inventory of 239 cases

Held, Th., Schroers, St.: 2012, Länderfinanzierungsprogramm „Wasser, Boden und Abfall“ 2010, „Auswertung von Fällen mit In-situ-Anwendungen in der gesättigten Zone bei der Altlastenbearbeitung (Projekt B 3.10)
http://www.laenderfinanzierungsprogramm.de/cms/WaBoAb_prod/WaBoAb/Vorhaben/LABO/B_3.10/index.jsp

Applied ISCO techniques

Inventory of 239 cases

Held, Th., Schroers, St.: 2012, Länderfinanzierungsprogramm „Wasser, Boden und Abfall“ 2010, „Auswertung von Fällen mit In-situ-Anwendungen in der gesättigten Zone bei der Altlastenbearbeitung (Projekt B 3.10)
http://www.laenderfinanzierungsprogramm.de/cms/WaBoAb_prod/WaBoAb/Vorhaben/LABO/B_3.10/index.jsp
Thermal In-situ Technologies

- Convection \(\rightarrow\) Conduction
- Ohm \(\rightarrow\) di-electric

- Organic compounds (LNAPL & DNAPL)
- Increase of vapor pressure of contaminant by heating of subsurface / steam distillation
  - \(\rightarrow\) by factors enhanced extraction rates
- Extraction of contaminants as gas (SVE Soil Vapour Extraction)
- Fast and reliable (and controllable) remediation process
  - Selection of technique dependent on site conditions and “composition” of contaminants (mixtures)
  - Expert knowledge required

Operating Windows

- 10 °C
- 50 °C
- 100 °C
- 150 °C

- Thermally enhanced microbiology
- Steam distillation (co-boiling) of many LNAPL and DNAPL
- Contaminant transformation due to other chemical processes
- Natural subsurface temperature
- Thermal in-situ remediation
- Soil drying
Steam–Air–Injection (SAI)

Operation windows
DNAPL and LNAPL, light and medium volatile, boiling points < 180°C
UZ: Unconsolidated soil, mean to good permeability (silt → gravel)
GZ: Pore aquifer (sand to silt) k_f: 5 x 10⁻⁵ to 1 x 10⁻³ m/s
Features
➢ Simultaneous remediation of aquifer and unsaturated soil zone

Steam-air-injection
Sustainability Workshop, Oslo, 2. – 4. December 2014

ISCO in-situ chemical oxidation
Water treatment

Injection of reagent
Grund water extraction
Oxidable or reducible contaminants

**Oxidable contaminants**
- hydrocarbons
- PAH
- BTEX
- CHC
- (ammonium \(\rightarrow\) nitrate)

\[ \text{end products:} \]
- CO\(_2\), water

**Reducible contaminants**
- CHC
- (nitrate \(\rightarrow\) N\(_2\))
- (chromium (VI) \(\rightarrow\) chromium (III))

\[ \text{end products:} \]
- hydrocarbons, chloride

ISCO and ISCR reagents

<table>
<thead>
<tr>
<th>Oxidizing agents</th>
<th>active agents</th>
<th>(E_0) [V]</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permanganate</td>
<td>(\text{MnO}_4^-)</td>
<td>1.7</td>
<td>(\text{MnO}_2) formed</td>
</tr>
<tr>
<td>Fenton's reagent</td>
<td>(\text{H}_2\text{O}_2)</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{OH}^3)</td>
<td>2.8</td>
<td>complex chemism, reaction (pH)</td>
</tr>
<tr>
<td></td>
<td>(\text{HO}_2$)</td>
<td>1.7</td>
<td>difficult to handle</td>
</tr>
<tr>
<td></td>
<td>(\text{O}_2$)</td>
<td>-2.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{HO}_2^-)</td>
<td>-0.88</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reduction agents</th>
<th>active Reagent</th>
<th>(E_0) [V]</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>(\text{Fe})</td>
<td>-0.4</td>
<td>well investigated, high density (transport?)</td>
</tr>
<tr>
<td>Non-Iron metals</td>
<td>(\text{Al})</td>
<td>-1.66</td>
<td>little investigated, corrosion problems?</td>
</tr>
<tr>
<td></td>
<td>(\text{Mg})</td>
<td>-2.36</td>
<td></td>
</tr>
<tr>
<td>&quot;(\text{H}_2)&quot; : HRC, molasses, soy oil...</td>
<td>&quot;(\text{H}_2)&quot;</td>
<td>&lt;=0.2</td>
<td>microbial reaction</td>
</tr>
</tbody>
</table>
Nanoparticles for *in-situ* remediation

- Small size ➔ higher surface area ➔ more reactive
- NPs (in a carrier fluid) injected into saturated zone via wells
- Focus on source treatment
- Applicable below buildings
- “independent” of application depth
- „semi-passive“ technology
- particles e.g. nZVI
- innovative technology

**Carbo-Iron as In-situ reagent**

**Composite Material ➔ Carbo-Iron:**
- Surface properties optimized for max. transport
- Reactivity supported by sorption at Carbon particles
NanoRem Structure

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

Project Structure

Sustainability Workshop, Oslo, 2. – 4. December 2014

Approach

NanoRem’s three level approach

I Development and production: WP2 and WP3

II Properties and behavior in the environment: WP4 to WP7

III Application, permission (approval) and promotion
  • Large scale experiments and pilot sites: WP8 and WP10
  • Dissemination, communication and exploitation: WP9
NanoRem’s Overall Goals

- Identification of the most appropriate nanoremediation technological approaches that could achieve a step-change in practical remediation performance.
- Development of lower cost production techniques and production at commercially relevant scales, also for large-scale applications.
- Determination of the mobility and migration potential of nanoparticles in the subsurface, and their potential to cause harm, focusing on the NP types most likely to be adopted into practical use in the EU.
- Development of a comprehensive toolbox for the design of nanoremediation operations, field scale nanoremediation performance and determination of the fate of NPs in the subsurface.
- Dissemination and stakeholder dialog to ensure that research, development and demonstration meets end-user and regulatory requirements.
- Pre-deployment risk assessment, regulatory requirement, sustainability, market niche
- Provision of tests at representative scales to validate cost, performance, and fate and transport findings.

NanoRem

NanoRem aims to

- unlock the true potential of nanoremediation
- support appropriate use of nanotechnology in restoring land and aquifer resources
- develop knowledge-based and economical remediation technology at a world leading level for the benefit of a wide range of users in the EU environmental sector
- enhance the development of nanoremediation markets and its applications in the EU and beyond
### Production

<table>
<thead>
<tr>
<th>Particle name</th>
<th>Manufacturer</th>
<th>Comment / used in NanoRem</th>
</tr>
</thead>
<tbody>
<tr>
<td>NANOFER 25s</td>
<td>Nanolron</td>
<td>Reference particle, WP10: Large Scale Flume, Pilot sites CZ (DNAPL)</td>
</tr>
<tr>
<td>NANOFER STAR</td>
<td>Nanolron</td>
<td>WP4: Cannot be transported, To be optimized</td>
</tr>
<tr>
<td>(air stable)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NANOFER STAR*</td>
<td>Nanolron</td>
<td>Modified NANOFER STAR, Needed in WP 10: Large Scale Flume, Pilot site IS</td>
</tr>
<tr>
<td>(air stable)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Milled Fe(0)</td>
<td>UVR-FIA</td>
<td>Needed in WP 10, Pilot site Zurzach, CH</td>
</tr>
<tr>
<td>Carbo-Iron (lab)</td>
<td>UFZ</td>
<td>Needed in WP10: Large Scale Flume</td>
</tr>
<tr>
<td>Carbo-Iron (industry)</td>
<td>SciDre Dresden</td>
<td>Pilot site HU</td>
</tr>
<tr>
<td>Fe-Oxide</td>
<td>HMGU</td>
<td>Needed in WP 10 : Large Scale Container, Pilot Site CZ (LNAPL), PO, ES</td>
</tr>
<tr>
<td>Bio-Fe-oxides</td>
<td>UMAN</td>
<td>Research status</td>
</tr>
<tr>
<td>Fe-Zeolites</td>
<td>UFZ</td>
<td>Research status</td>
</tr>
<tr>
<td>Nano-Metals (Mg, Al)</td>
<td>USTUTT</td>
<td>No final product available yet</td>
</tr>
<tr>
<td>Ferrates</td>
<td>USTUTT</td>
<td>No final product available yet</td>
</tr>
</tbody>
</table>

### NanoRem Pilot Sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Country</th>
<th>Site Primary Investigator</th>
<th>Target Cont.</th>
<th>NP-Type</th>
<th>Reaction Principle</th>
<th>Aquifer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zurzach</td>
<td>CH</td>
<td>Solvay</td>
<td>CHC</td>
<td>milled nZVI</td>
<td>Reduction/Sorption</td>
<td>porous / unconfined</td>
</tr>
<tr>
<td>Spolchemie 1</td>
<td>CZ</td>
<td>Aquatest</td>
<td>CHC</td>
<td>NANOFER 25s</td>
<td>Reduction</td>
<td>porous / unconfined</td>
</tr>
<tr>
<td>Spolchemie 2</td>
<td>CZ</td>
<td>Aquatest</td>
<td>BTEX</td>
<td>Iron-Oxide</td>
<td>Oxidation/microbial Enhancement</td>
<td>porous / unconfined</td>
</tr>
<tr>
<td>Barreiro</td>
<td>PO</td>
<td>GeoPlano</td>
<td>HM</td>
<td>Iron-Oxide</td>
<td>Immobilisation</td>
<td>porous / unconfined</td>
</tr>
<tr>
<td>Besor-Secher</td>
<td>IS</td>
<td>Negev, BGU</td>
<td>CHC</td>
<td>air-stable nZVI NANOFER STAR*</td>
<td>Reduction</td>
<td>fractured</td>
</tr>
<tr>
<td>Neot Hovar</td>
<td>IS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Balassagyarmat</td>
<td>H</td>
<td>Golder</td>
<td>CHC</td>
<td>Carbo-Iron</td>
<td>Reduction/Sorption</td>
<td>porous / unconfined</td>
</tr>
<tr>
<td>Bizkaia</td>
<td>ES</td>
<td>Tecnalia</td>
<td>HM</td>
<td>Iron-Oxide</td>
<td>Reduction/Immobilisation</td>
<td>porous / unconfined</td>
</tr>
</tbody>
</table>
Potential benefits

- Faster reaction
- Increased range of treatable contaminants
- Complete degradation / transformation
- Capacity for source term treatment
- Compatibility with \textit{in situ} bio
- Limited environmental persistence
- More sustainable; no excavation, transport nor disposal is necessary

Thank you for your interest and the EU for the funding

This project received funding from the European Union Seventh Framework Programme (FP7 / 2007-2013) under Grant Agreement No. 309517.

\textit{This presentation reflects only the author's views and that the European Union is not liable for any use that may be made of the information contained therein.}