In-situ remediation of an anthropogenic arsenic contamination due to chemical warfare agents

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Introduction

Chemical warfare agents containing arsenic compounds
- Arsenic was used due to its high toxicity
- Their compounds are persistent in the environment

Chemical warfare agents on contaminated military sites
- More than 3,200 potential sites within Germany (Thieme, 1996)
  - 27 production facilities
  - 132 filler points
  - 480 training sites
  - 45 experimental test sites
- Theses sites are potential contaminated with organic-arsenic compounds

Objective
- Development of a sustainable in-situ technique to immobilize inorganic (As$_{\text{inorg}}$) and organic (As$_{\text{org}}$) arsenic compounds
- Contaminated military site in Northern Germany
- Groundwater contains $\text{As}_{\text{org}}$ and $\text{As}_{\text{inorg}}$
- Pump-and-treat facility in place using a two step As-removal

<table>
<thead>
<tr>
<th>Well</th>
<th>Depth [m]</th>
<th>As-total</th>
<th>As(III)</th>
<th>As(V)</th>
<th>As(org)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observation well 69-02-02</td>
<td>23</td>
<td>550</td>
<td>250</td>
<td>50</td>
<td>250</td>
</tr>
<tr>
<td>Pumping well FB 21 A/95</td>
<td>NA</td>
<td>970</td>
<td>80</td>
<td>10</td>
<td>730</td>
</tr>
<tr>
<td>Observation well 69-01-02</td>
<td>8</td>
<td>8800</td>
<td>2180</td>
<td>380</td>
<td>6020</td>
</tr>
<tr>
<td>Observation well 26/91</td>
<td>40</td>
<td>2400</td>
<td>210</td>
<td>20</td>
<td>1860</td>
</tr>
<tr>
<td>Observation well 5/89</td>
<td>14</td>
<td>80</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>60</td>
</tr>
</tbody>
</table>
Cross section
### Batch experiment (I)

200 ml sample:
- initial As: 8.8 mg/l (33% As\textsubscript{inorg})
- coagulant equals 50 mg Fe (250 mg Fe/l)

<table>
<thead>
<tr>
<th>No.</th>
<th>Iron compound</th>
<th>Aeration [h]</th>
<th>As [mg/l]</th>
<th>Immobilisation [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FeCl\textsubscript{3}-solu.(10.000 ppm/ 0,1n HCl)</td>
<td>22</td>
<td>5.4</td>
<td>38.6</td>
</tr>
<tr>
<td>2</td>
<td>FeCl\textsubscript{3} x 6H\textsubscript{2}O</td>
<td>20</td>
<td>8.0</td>
<td>9.1</td>
</tr>
<tr>
<td>3</td>
<td>NH\textsubscript{4}Fe(SO\textsubscript{4})\textsubscript{2} x 12H\textsubscript{2}O</td>
<td>144</td>
<td>5.2</td>
<td>40.9</td>
</tr>
<tr>
<td>4</td>
<td>FeSO\textsubscript{4} x 7H\textsubscript{2}O</td>
<td>22</td>
<td>1.9</td>
<td>78.4</td>
</tr>
<tr>
<td>5</td>
<td>FeCl\textsubscript{2} x 4H\textsubscript{2}O</td>
<td>4.5</td>
<td>1.8</td>
<td>79.5</td>
</tr>
<tr>
<td>6</td>
<td>Fe (Ferrum reductum &lt; 150 µm)</td>
<td>144</td>
<td>8.3</td>
<td>5.7</td>
</tr>
<tr>
<td>7</td>
<td>nano-particles Fe+Ni\textsubscript{3}</td>
<td>20</td>
<td>3.8</td>
<td>56.8</td>
</tr>
</tbody>
</table>

⇒ **Immobilization of As\textsubscript{org}**
200 ml sample:
180 mg FeCl$_2$ × 4H$_2$O (50 mg Fe)

partial pH increase to fasten Fe(OH)$_3$ formation

<table>
<thead>
<tr>
<th>No.</th>
<th>Aeration</th>
<th>Initial concentration</th>
<th>Final concentration</th>
<th>Immobilisation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\text{As}_{\text{inorg}}$ [mg/l]</td>
<td>$\text{As}_{\text{org}}$ [mg/l]</td>
<td>$\text{As}_{\text{inorg}}$ [mg/l]</td>
</tr>
<tr>
<td>1</td>
<td>4h</td>
<td>3.04</td>
<td>6.26</td>
<td>0.032</td>
</tr>
<tr>
<td>2</td>
<td>over night</td>
<td>0.91</td>
<td>0.27</td>
<td>0.008</td>
</tr>
<tr>
<td>3</td>
<td>over night</td>
<td>0.12</td>
<td>1.49</td>
<td>0.008</td>
</tr>
<tr>
<td>4</td>
<td>8h</td>
<td>2.59</td>
<td>5.24</td>
<td>0.042</td>
</tr>
</tbody>
</table>
Position of the pilot plant
Fe(II) → iron hydroxide co-precipitation of As

Sorption of As at iron hydroxide
Results

- Two years of treatment including a 40 days pumping-only-period
- Increasing FeCl$_2$-Dosage up to 1000 ml/cycle (280 mg Fe)
- Reduction of As from ~1.8 mg/l to 0.2 mg/l
- Both wells produce similar results (effect of direct water exchange)
Results

- Initially the reduction of $\text{As}_{\text{inorg}}$ and $\text{As}_{\text{org}}$ is linear (up to 30% immobilization)
- Maximal immobilization of $\text{As}_{\text{inorg}}$ (~100%) > $\text{As}_{\text{org}}$ (~82%)
- Increase of $\text{As}_{\text{inorg}}$ fraction is stronger during pumping-only-period compared to $\text{As}_{\text{org}}$
• Fe-As ratio ~10:1 below 200 ml FeCl₂-dosage (55 mg Fe/l)
• Fe-As ratio ~12:1 up to 700 ml FeCl₂-dosage (195 mg Fe/l)
• High Fe-As ratio (up to 40:1) is needed to reduce As from 0.5 mg/l to 0.2 mg/l (risk of Fe(II) in recovered groundwater)
Sustainability: iron incrustations

- Fe(II) < 0.05 mg/l up to a 700 ml FeCl₂-dosage (195 mg Fe/l)
- No detection of Fe(II) during pumping-only-period

⇒ Redox conditions are stable, no or low risk of immediate As-desorption
Sustainability: iron incrustations

Well 1: iron incrustation after two years of service at a depth 10.40 m

Well 1: iron incrustation after two years of service at a depth 12.40 m
Sustainability: As remobilisation

After one year of treatment

- Soil sampling (disturbed drilling) up and down gradient of both wells
- Sequential extraction of the samples (Wenzel et al., 2001)

<table>
<thead>
<tr>
<th>fraction</th>
<th>extracted fraction</th>
<th>solution</th>
<th>environment</th>
<th>soil-solution ratio</th>
<th>purification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>unspecific sorbed</td>
<td>0.05 M (NH₄)₂SO₄</td>
<td>20°C/4h</td>
<td>1 : 25</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>specific sorbed</td>
<td>0.05 M NH₄H₂PO₄</td>
<td>20°C/16h</td>
<td>1 : 25</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>bound in amorphous iron hydroxides</td>
<td>0.2 M NH₄-oxalate buffer</td>
<td>pH 3.25, 20°C/4h</td>
<td>1 : 25</td>
<td>0.2 M NH₄-oxalate; pH 3.25; soil-solution 1:12.5 10 min shaking in dark conditions</td>
</tr>
<tr>
<td>4</td>
<td>bound in crystalline iron hydroxides</td>
<td>0.2 M NH₄-oxalate buffer + ascorbic acid</td>
<td>pH 3.25, 96°C/0.5h</td>
<td>1 : 25</td>
<td>0.2 M NH₄-oxalate; pH 3.25; soil-solution 1:12.5 10 min shaking in dark conditions</td>
</tr>
<tr>
<td>5</td>
<td>residual phase</td>
<td>HNO₃/H₂O₂</td>
<td>micro wave</td>
<td>1 : 50</td>
<td></td>
</tr>
</tbody>
</table>
Sustainability: As remobilisation

\[ w. \ a. = \frac{1}{n} \sum_{i=1}^{n} \frac{F_{iU} - F_{iL}}{2} + F_{iL} \]

with:
- \( F_{iU} \): upper limit of \( i \)th fraction
- \( F_{iL} \): lower limit of \( i \)th fraction

- Samples with higher mean values released less As
- Released As equals about fraction 1

- Both wells: minor amount of unspecific sorbed As (~15%) (high remobilization risk)
- Down-gradient samples show higher remobilization risk
- Well 1: mainly specific sorbed As (~45%) and As bound in amorphous iron hydroxides (~30%)
- Well 2: mainly specific sorbed As (~65%)
Conclusions

• Laboratory experiments
  – FeCl₂ und FeSO₄ were best capable to immobilise As
  – Immobilisation of As₉₀ >50% and As₈₀ >90%
  – Fe-As ratio derived in soil columns ranged from 5:1 to 20:1

• Field experiment
  – As-concentration reduced from ~1.8 mg/l to ~ 0.2 mg/l
  – Immobilisation of As₉₀ ~82 % and As₈₀ ~100%
  – Fe-As ratio around 12:1 (at stable conditions: Fe <0.05 mg/l)

• Sustainability
  – Changes in well hydraulic have not been detected
  – Fe-incrustations only in the area of the outlet of the Fe(II) in the wells after two years of service
  – As is mainly available as specific sorbed and amorphous Fe-compounds
  – Remobilization of unspecific sorbed As in laboratory experiments
Thank you very much for your attention!

**Acknowledgements:**
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**References:**