IN-SITU CONDITIONING AND STABILIZATION OF DREDGING AND MINERAL SLUDGE


5th International Conference on Remediation of Contaminated Sediments
2 to 5/02/09, Jacksonville, Florida
Introduction

• Sediments often dredged for nautic reasons but also due to contamination with heavy metals and organic pollutants

• Sediments stored in ponds but:
  – Large volumes of sediment with a high water content and low strength
  – Ponds are full
  – Pollutants can leach and cause a risk to the environment
Disadvantages hydraulic filling ponds

South-Africa, 1994, spills 3 million m³

Spain, 1998, spills 7 million m³
Introduction

• MIP project wants to find a solution for:
  – The water content of the sludge: decrease water volume
  – A way to stimulate the immobilization of HM or degradation of organic pollutants in these sludges: chemically / biologically
Aim MIP project

1. Chemical and biological stabilization and consolidation of sludge

2. Chemical and biological removal of contamination (heavy metals, mineral oil, PAHs, PCBs)

3. Tests:
   1. Lab tests by research partners
   2. *In situ* tests by industrial partners: focus on injection techniques and additives
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Chemical stabilization and consolidation sludge: University of Ghent

- Addition of additives to:
  - Decrease sedimentation and consolidation time
  - Increase final density (compaction)
  - Increase final shear resistance
  - Decrease pollutant leaching
Chemical stabilization and consolidation sludge: University of Ghent

• Seepage consolidation tests:
Biological stabilization sludge
Catholic University College of Bruges-Ostend

• *In situ* stabilization by bacterial calcification
• Principle:
  – Degradation of ureum to $\text{NH}_4^+$ and $\text{CO}_3^{2-}$
  – Due to pH increase: shift of $\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$ to $\text{CO}_3^{2-}$
  – Reaction of $\text{CO}_3^{2-}$ with $\text{Ca}^{2+}$ to $\text{CaCO}_3$
  – $\text{CaCO}_3$: stabilization of sludge and fixation of pollutants
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2. Chemical and biological removal of contamination (heavy metals, mineral oil, PAHs, PCBs)
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   1. Lab tests by research partners
   2. *In situ* tests by industrial partners: focus on injection techniques additives
Biological degradation of organic pollutants:
Catholic University of Leuven

• Bacterial capacity present in sludge for degradation of organic pollutants?:
  • Degradation naphthalene?
  • Degradation chlorobenzenes?

• Stimulation biological degradation?
• Influence of chemical additives on biological degradation?
Chemical removal of pollutants:
Flemish Institute for Technological Research (VITO)

• Chemical oxidation and chemical reduction of organic pollutants
In situ chemical oxidation (ISCO) of pollutants in sediments

- **Chemical oxidation:**
  - Degradation of organic pollutants:
    - mineral oil, BTEX, PAHs, MTBE, chlorinated compounds
  - Oxidants:

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>ORP (V)</th>
<th>Reactive species</th>
<th>Target pollutants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenton’s: $H_2O_2 + Fe(II)$</td>
<td>2.8</td>
<td>$\cdot OH, \cdot O_2^-, \cdot HO_2^-, HO_2^-$</td>
<td>Petroleum hydrocarbons, Chlorinated solvents (ethenes: PCE, TCE), BTEX, MTBE, PCBs, CBs, PAHs, phenols</td>
</tr>
<tr>
<td>Activated persulfate: $Na_2S_2O_8 + Fe/heat/acid/base$</td>
<td>2.6</td>
<td>$SO_4^{2-}$</td>
<td>Petroleum hydrocarbons, Chlorinated solvents (ethenes: PCE, TCE; ethanes:TCA, DCA; methanes), BTEX, MTBE, PCBs, PAHs</td>
</tr>
<tr>
<td>Ozone</td>
<td>2.1</td>
<td>$O_3$</td>
<td>Petroleum hydrocarbons, Chlorinated solvents (ethenes: PCE, TCE), BTEX, MTBE, PAHs, PCBs</td>
</tr>
<tr>
<td>Persulfate: $Na_2S_2O_8$</td>
<td>2.1</td>
<td>$S_2O_8^{2-}$</td>
<td>Petroleum hydrocarbons, Chlorinated solvents (ethenes: PCE, TCE; ethanes:TCA, DCA; methanes)</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>1.8</td>
<td>$H_2O_2$</td>
<td></td>
</tr>
<tr>
<td>Permanganate: $KMnO_4$, $NaMnO_4$</td>
<td>1.7</td>
<td>$MnO_4^-$</td>
<td>Petroleum hydrocarbons, BTEX, PAHs, Chlorinated solvents (ethenes: PCE, TCE), phenols</td>
</tr>
</tbody>
</table>
In situ chemical oxidation (ISCO) of pollutants in sediments

- **Total oxidant demand**
  - Contaminant demand
  - **natural oxidant demand**: organic matter, reduced metals, sulfides
  - Oxidant decomposition

- **Oxidation of sediments**:
  - Often **high organic matter content** (MIP sediments: 2.4 – 10% OM)
    → high natural oxidant demand
  - Often **mixed pollution** of organics + heavy metals:
    - Oxidation of reduced/precipitated heavy metals
    - Fenton’s/ Persulfate oxidation: acidic conditions/ pH↓
      → risk of heavy metal **mobilisation**
Chemical oxidation of pollutants in sludge Berendrechtsluis

<table>
<thead>
<tr>
<th>Sludge characteristics</th>
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</thead>
<tbody>
<tr>
<td>dry matter content (%)</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>organic matter content (%)</td>
</tr>
<tr>
<td>Clay content (%)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Organic contaminants</th>
</tr>
</thead>
<tbody>
<tr>
<td>mineral oil (mg/kg DM)</td>
</tr>
<tr>
<td>PAH 16 (mg/kg DM)</td>
</tr>
<tr>
<td>PCBs (mg/kg DM)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heavy metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total content</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>As</td>
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<tr>
<td>Cd</td>
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<tr>
<td>Cr</td>
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<tr>
<td>Fe</td>
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<tr>
<td>Cu</td>
</tr>
<tr>
<td>Hg</td>
</tr>
<tr>
<td>Pb</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>Zn</td>
</tr>
</tbody>
</table>
In situ chemical oxidation (ISCO) of pollutants in sediments

- Preliminary results: Natural oxidant demand with different oxidants
  - Sediment sample tested: 6.9% OM
  - Oxidants: KMnO₄ and Na₂S₂O₈
  - Laboratory test: natural oxidant demand measured after 14 days

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Natural oxidant demand</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g/kg DM)</td>
<td>(Euro/tonDM)</td>
</tr>
<tr>
<td>Na₂S₂O₈</td>
<td>50-100</td>
<td>140-280</td>
</tr>
<tr>
<td>KMnO₄</td>
<td>300-450</td>
<td>1200-1800</td>
</tr>
</tbody>
</table>

- Economically feasible?
- Lower natural oxidant demand with persulfate compared to permanganate
In situ chemical oxidation (ISCO) of pollutants in sediments

- Preliminary results: Natural oxidant demand (permanganate) in sediments with different organic matter content
  - Oxidant: KMnO₄
  - Laboratory test:
    natural oxidant demand measured after 14 days

<table>
<thead>
<tr>
<th>Sediment sample</th>
<th>Organic matter content (%)</th>
<th>Natural oxidant demand (g/kg DM)</th>
<th>Cost (Euro/tonDM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zandwinningsput</td>
<td>2.4</td>
<td>50-100</td>
<td>200-400</td>
</tr>
<tr>
<td>Berendrechtsluis</td>
<td>6.9</td>
<td>300-450</td>
<td>1200-1800</td>
</tr>
<tr>
<td>leper-IJzer kanaal</td>
<td>7.6</td>
<td>150-300</td>
<td>600-1200</td>
</tr>
</tbody>
</table>

- Natural oxidant demand increases with amount of organic matter?
- Natural oxidant demand is lower for ‘older’ organic matter?
In situ chemical oxidation (ISCO) of pollutants in sediments

- Preliminary results: mobilisation of heavy metals
  - Sediment sample tested: 7% OM
  - Oxidant: Na₂S₂O₈

<table>
<thead>
<tr>
<th>oxidant dose (g/kg DM)</th>
<th>pH</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Pb</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7,5</td>
<td>0,09</td>
<td>&lt;0,026</td>
<td>0,12</td>
<td>&lt;0,13</td>
<td>0,71</td>
<td>0,22</td>
<td>&lt;0,04</td>
<td>0,05</td>
</tr>
<tr>
<td>50</td>
<td>6,5</td>
<td>0,08</td>
<td>0,08</td>
<td>0,10</td>
<td>0,16</td>
<td>0,14</td>
<td>2,42</td>
<td>0,16</td>
<td>7,0</td>
</tr>
<tr>
<td>100</td>
<td>6,2</td>
<td>0,09</td>
<td>0,11</td>
<td>0,09</td>
<td>0,37</td>
<td>0,42</td>
<td>4,03</td>
<td>0,40</td>
<td>14,9</td>
</tr>
<tr>
<td>150</td>
<td>6,1</td>
<td>0,08</td>
<td>0,12</td>
<td>0,09</td>
<td>0,48</td>
<td>0,65</td>
<td>4,81</td>
<td>0,47</td>
<td>17,2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total initial content of metals (mg/kg DM)</th>
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<tbody>
<tr>
<td>32</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Leachable metals (DIN-S4 extraction) (mg/kg DM)</th>
</tr>
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<tbody>
<tr>
<td>0,43</td>
</tr>
</tbody>
</table>

- decrease of pH from 7,5 to 6,2
- release of Pb, Ni and Zn: <5% of total initial content
Aim MIP project

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2. Chemical and biological removal of contamination (heavy metals, mineral oil, PAHs, PCBs)

3. Tests:
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Injection techniques additives

1. Injection techniques additives
   - *In-situ* fracturing (Envisan, Rasenberg)
   - Soft Soil Injection System (DEC)
   - Dredging cutter with additives (Ghent Dredging)
   - Inline injection additives during filling ponds

2. Removal pore water
   - Vacuum consolidation (Envisan)
   - Soil drainage (Envisan)
   - Wings (Ghent Dredging)
Partners

Research partners
• VITO NV (Flemish Institute for Technological Research), Belgium, Sandra Van Roy, Frederik Accoe, Ludo Diels, Winnie.Dejonghe@vito.be
• K.U.L. (Catholic University of Leuven), Belgium, Danka Cichocka, Dirk.Springael@agr.kuleuven.ac.be
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• WVRB, Belgium, Gerrit.Vanrompaey@wvrb.be

Problem Owners
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• Agency for Maritime and Coastal Services, Belgium, Miguel.Berteloot@mow.vlaanderen.be
• Nyrstar, Belgium, Michel.Dubois@zinc.nyrstar.com
• Tessenderlo Chemie, Belgium, Jules.Houtmeyers@tessenderlo.com

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• Research partners: MIP
• Industrial partners: IWT