Latest Findings in In-situ Remediation of Hydrocarbon Impacted Soils using Hydrogen Peroxide

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Background

- Hydrogen peroxide (H$_2$O$_2$) a strong oxidant is used to cleanup residual contaminants adjacent to structures with restricted access (Mahmoud et al. 2000)
  - H$_2$O$_2$ + Fe$^{2+}$ → Fe$^{3+}$ + OH$^-$ + OH·
  - OH· + C$_x$H$_y$ → H$_2$O + CO$_2$ + heat
  - H$_2$O$_2$ + Fe$^{3+}$ → Fe$^{2+}$ + H$^+$ + HO$_2$
  - OH· + Fe$^{2+}$ → OH$^-$ + Fe$^{3+}$
  - HO$_2$· + Fe$^{3+}$ → O$_2$ + H$^+$ + Fe$^{2+}$
  - H$_2$O$_2$ + OH· → H$_2$O + HO$_2$·
2 tiltplates installed for monitoring ground movements during injections
Restricted Access
Two $\text{H}_2\text{O}_2$ Applications

- Initial concentration pre-determined based on contaminant concentrations and type of contaminant
- Typical concentrations: 10 - 25%

  - First: 16% concentration
  - Second: 20% concentration
H$_2$O$_2$ Treatment Apparatus

Drums of 50% concentration H$_2$O$_2$
H₂O₂ Injection

Assessing required concentration
Laboratory Program

- Impact of hydrogen peroxide on heave of soil
- Investigate major process variables in use of hydrogen peroxide for remediation
  - Influence of iron catalyst
  - Use of surfactant
  - Multiple applications of hydrogen peroxide
- Study the distribution of hydrogen peroxide in soil upon injection
- Impact of hydrogen peroxide injection hydraulic conductivity
Test Conditions

♦ Major contaminant - diesel

♦ Heave Study
  - Sandy soil (with 0.55 % organic content)
  - concentrations of 0, 2000, and 5000 mg/kg
  - $\text{H}_2\text{O}_2$ concentrations of 5%, 10%, 15%, 25% and 30% by volume

♦ Other Experiments
  - Three soil types
    - Sandy silt (UC soil; 63.9% sand, 26.1% silt and 7.9% clay, 0.4% orgs., 1.9% iron content)
    - Silty clay (SH soil; 44% sand, 23.2% silt and 31.4% clay, 1.87% orgs., 1.55% iron content)
    - Ottawa sand (as control)
  - concentrations of 0, 500, 1000, 5000 & 10,000 mg/kg
  - $\text{H}_2\text{O}_2$ concentrations of 5%, 10% and 20% by volume
No. 2 diesel: C9 – C20, 160 °C and 360 °C

**Major physical properties**

<table>
<thead>
<tr>
<th>Index</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.82 – 0.87</td>
</tr>
<tr>
<td>Viscosity (cSt)</td>
<td>1.3 – 4.1</td>
</tr>
</tbody>
</table>
| Solubility (mg/L) | 2.3 – 8.3 (Distilled Water)  
                  | 2.8 – 39.1 (Fresh water)                      |
| Volatility (%)  | 57 (5 day evaporation @22 C)                 |

**Major chemical compounds**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes (normal, branched &amp; cycloalkanes)</td>
<td>70 - 80</td>
</tr>
<tr>
<td>Aromatics</td>
<td>20 - 30</td>
</tr>
</tbody>
</table>
Results – heave of soil

- Initial volumetric change in specimens

Graph showing H₂O₂ Concentration (%) on the x-axis and % Change Void Ratio on the y-axis for unspiked specimens and spiked specimens with 2000 mg Diesel/kg and 5000 mg Diesel/kg.
Results – heave of soil

- Long term volumetric change in specimens

![Graph showing % Change in Void Ratio vs. H₂O₂ Concentration (%)]

- 2000 mg Diesel/kg
- 5000 mg Diesel/kg
Results - Major process variables

6  H$_2$O$_2$ consumption
6  Soil buffering capacity and pH effect on DROs degradation
6  Iron catalysts and mineral iron oxides
6  Gas quantification/qualification
6  Enhancement of diesel degradation
H$_2$O$_2$ consumption during remediation of Ottawa sand

♦ No iron added
♦ Iron added (720 mg/L)

- 5% hydrogen peroxide
- 10% hydrogen peroxide
- 20% hydrogen peroxide

5% peroxide
- Ferrous ion
- Ferric ion

20% peroxide
- Ferrous ion
- Ferric ion

Residual hydrogen peroxide (%)

Duration of H$_2$O$_2$ application (min)

Residual H$_2$O$_2$ (%) 

Reaction time (min)
Low soil pH – Beneficial but difficult to attain

♦ Forcing a decrease in soil pH

♦ Impact of soil pH on DRO removal

![Graph showing pH of soils and DROs removal](image)

- Sandy silt (UC soil)
- Silty clay (SH soil)
- Ottawa sand (OS soil)

![Graph showing pH of Ottawa sand and DROs removal](image)

- Ottawa sand
  - 5 ml, 10% peroxide
Impact of External Iron Addition to UC and SH soils

![Graph showing the impact of external iron addition to UC and SH soils. The x-axis represents the H$_2$O$_2$ concentration (%), ranging from 0 to 30. The y-axis represents the DROs removal, C/Co, (%), ranging from 0 to 100. The graph includes data for UC soil and SH soil at 0 mg/L, 720 mg/L, 1800 mg/L, and 3600 mg/L.]
Impact of External Iron Addition to Ottawa Sand

![Graph showing the impact of external iron addition to Ottawa Sand on DROs removal. The x-axis represents Fe²⁺ amendment (mg/L) and the y-axis represents DROs removal, C/Co (%). The graph includes data points for 5 ml, 20% peroxide, 5 ml, 10% peroxide, and 5 ml, 5% peroxide.]
Degradation Efficiency and Gas Production

- Diesel Degradation Efficiency
- Oxygen generation – indication of scavenging of H$_2$O$_2$

![Graphs showing DROs removal and oxygen production over time for different conditions](image-url)
Effect on Diesel Concentration on DRO removal

- 10 ml of 10% H$_2$O$_2$ used

![Graph showing DRO removal vs. Diesel concentration for Sandy silt (UC soil) and Silty clay (SH soil).]
Degradation efficiency – ratio of \( \text{H}_2\text{O}_2 \) consumed to diesel degraded

- **Sandy silt**
  - 5% Peroxide
  - 10% Peroxide
  - 20% Peroxide

- **Silty clay**
  - 5% Peroxide
  - 10% Peroxide
  - 20% Peroxide
Surfactant Enhanced Diesel Degradation

- 5% Peroxide
- 10% Peroxide
- Sandy silt (UC soil)
- Silty clay (SH soil)
- Sandy silt (UC soil)
- Silty clay (SH soil)
Impact of Multiple Applications

♦ Sandy silt

♦ Silty clay

10% Peroxide
5,000 mg/kg diesel

△ One application
★ Multiple application

DROs removal, C/Co, (%)

Volume of H₂O₂ used (mL)
H$_2$O$_2$ Infiltration & Injection
Injection Test Results
Injection Test Results

- Two major concerns

  - Uneven distribution of \( \text{H}_2\text{O}_2 \) and remediation
  - \( \text{H}_2\text{O}_2 \) making its way to the top along the injector due to “refusal”
Hydraulic Conductivity Results

- Hydraulic conductivity of $\text{H}_2\text{O}_2$ is 30 times lower than that of water
- Reason – gas generation and increased resistance due to gas pressure
- Surface application not very effective due to reaction at the surface
Conclusions

♦ Soil volume changes encountered
♦ Heave
  – Below a 15% H₂O₂ concentration, treated soil experience immediate settlement
  – Settlement decreases as H₂O₂ concentration increases
  – Above 10% H₂O₂ concentration immediate settlement is followed by rebound
  – At 30% H₂O₂ concentration and high diesel content significant volume increase (heave) takes place
Conclusions

♦ Process variables
  – Presence of iron necessary
  – Concentration and volume of H₂O₂ are both important process variables
  – High concentration of H₂O₂ had higher degradation, at a lower efficiency
  – Soil pH, if it can be lowered, would increase degradation
  – Optimum dosage for remediation: 8 mL of 5% H₂O₂ (or 4 mL of 10% H₂O₂) per gram of 5000 mg/kg diesel contaminated soil
Conclusions

- SDS improves the treatment efficiency when SDS concentration > than CMC
- Multiple application somewhat increased degradation efficiency

♦ Injection and Infiltration Tests
- Uneven distribution of \( \text{H}_2\text{O}_2 \) during injection
- Refusal due to reaction and gas production may be concern
- Hydraulic conductivity lowered by gas production
Acknowledgements

- Hatem Mohamed, Matrix Solutions
- Nichols Environmental Ltd.
- NSERC for funding the project