Concepts of Chemical Oxidation vs. Chemical Oxygenation and Considerations for Engineered Remediation Design

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AGENDA

- Feasibility and Challenges of Engineered Bio & Chemical Remediation Applications
- Reaction Kinetics: Oxidation vs. Oxygenation
- Selection and Engineering Design Factors and Applications for Oxidation
- Health and Safety Considerations
- Case Studies – Chemical Oxidation by Enhanced Hydrogen Peroxide at contaminated sites
Engineered Bio or Chemical Remediation

- Controlled vs. Natural Environment
- Technically feasible not financially viable in most cases.
- Perceptions vs. Reality
- Misunderstanding between Oxidation (Mineralization – Chemical Remediation) and Oxygenation (Aeration - Bioremediation)
### Chemical Oxidants vs. Oxygen Release Chemicals

<table>
<thead>
<tr>
<th>Chemical Oxidants</th>
<th>Oxygen Release Chemicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enhanced Hydrogen Peroxide (H₂O₂)</td>
<td>Peroxide Compounds</td>
</tr>
<tr>
<td>Permanganate (MnO₄⁻)</td>
<td>e.g. Calcium Peroxide (CaO₂)</td>
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<tr>
<td>Persulphate (S₂O₈²⁻)</td>
<td>Commercially available ORC products</td>
</tr>
<tr>
<td>Ozone (O₃)</td>
<td>Raw Hydrogen Peroxide</td>
</tr>
<tr>
<td><strong>To generate Reactive Species</strong></td>
<td><strong>To provide Oxygen</strong> (aeration)</td>
</tr>
</tbody>
</table>

Only successful chelation and activation of chemical oxidants can generate effective reactive species in the field applications!
Reaction Kinetics - Oxygenation

- Part of stimulation of microbial activities in bioremediation.
- Process itself is not a contaminant mass removal process.
- A slow oxygen release compound is often misunderstood as a remediation agent.
Example - Oxygenation

- Calcium peroxide naturally decomposes very slowly to form calcium hydroxide and oxygen.
- Usage: Bioremediation and baking industry.

\[
2\text{CaO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Ca(OH)}_2 + \text{O}_2 \\
\text{or} \\
\text{CaO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{H}_2\text{O}_2 \\
2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2
\]
Reaction Kinetics – Oxidation by Enhanced Hydrogen Peroxide

Oxidation – Decomposition of Organic Compounds

Reaction continues to reduce original contaminants and breakdown products as it continues.
Ex-situ Application - Oxidation by Enhanced Hydrogen Peroxide

- Unsaturated soils
- Shallow soils (<4 mbg)
- Typically fine grained
- Large volume treatment per day
- Remote or local access
- Rapid treatment (<3 days)
- Low input requirements
- Cost/Time/Safety/Sustainability

[Image of agricultural field with a tractor]
In-situ Application - Oxidation by Enhanced Hydrogen Peroxide

- Groundwater (Vadose Zone)
- Remote or local access
- Dissolved phase impacts
- Year round
- Deeper units (>3 mbg)
- Low input requirements
- High conductivity/bedrock
- Cost/Time/Safety/Sustainability

CHEMOX®
Design Basis and Parameters for Oxidation by Enhanced Hydrogen Peroxide

- Geological / hydrogeological characterization
- Background analytical parameters
- Partitioning in soil and groundwater
- Size of plume
- Oxidant demands – SOD & NOD
- Selection of a suitable oxidant
- Chelation / activation strategies
- Target timeframe and end points
- and etc.

CHEMOX®
Heath & Safety Concerns

- Not a Routine Set-up
  - Regulation & supplier requirements
  - Client engagement & readiness (H&S, asset integrity, etc)
  - Project/stakeholder requirements
  - Controls – Administrative/Engineered/PPE/Competency
Corrosion Testing - Enhanced Hydrogen Peroxide Surface observation (FBE)

• Before exposure

• After 30 days
Corrosion Testing - Enhanced Hydrogen Peroxide Surface observation (YJ)

• Before exposure

• After 30 days
Case Study 1
Ex-situ Chemical Oxidation

Optimized mixing for effective reactions

Generate aimed chemical oxidation reactions in fine grained soils
Details
- Abandoned Pipeline – Alberta, Canada
- When: 2012 – 2013
- Contaminants of Concern: BTEX/F1-F4
- Impacted Media and Volume: >10,000 m³ of Fine Grained Soil
- Tasks: Ground Disturbance and Proximity Arrangement, Field Screening, Procurement, Blending, Field Applications, Sampling
- Project Value: $1,300,000
- Completion: 100%

The Problem
- Contaminated soil discovered by landowner when drilling fence posts
- Sandy silt/clay soils
- Minimal site disturbance required
- External stakeholder sensitivities
- Contamination:
  - BTEX: up to 7 mg/kg
  - PHC F1: up to 700 mg/kg
  - PHC F2: up to 950 mg/kg
  - PHC F3: up to 1400 mg/kg

The Approach - ChemOx®
- Ex-Situ Chemical Oxidation Program (EXCO®)
  - Direct application of 250,000 L of TRIUM’s ChemOx® enhanced hydrogen peroxide over period of 10 weeks
  - Remediation Train® approach to supplement EXCO® with landfill program of 3,500 m³ of highly impacted soils

The Results
- Samples collected within 24 hours of treatment completion satisfied de minimus remediation criteria (AENV Tier I, Agricultural Areas) or were below lab detection limits
- Cost savings versus complete landfill option
- Low footprint and program support by landowner
- Zero health and safety events
**Case Study 1**

**Ex-situ Chemical Oxidation**

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**Excavator Process**
- Increased variability
- Reduced reproducibility

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**Mulcher Process**
- Reduced variability
- Increased reproducibility
Case Study 2
In-Situ Chemical Oxidation

Mass destruction to overcome residual impacts

Overcome rebounding and site closure within the target timeframe
**Details**
- Active Retail Gas Station – Edson, Alberta
- When: 2013/2014
- Contaminants of Concern: BTEX
- Impacted Media and Volume: Groundwater, Discrete Point Source Treatment
- Tasks: Program Design, Injection Well Installation, Procurement, Blending, Field Applications, Sampling
- Project Value - $111,000
- Completion - 100%

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**The Problem**
- Property sale pending, expedited results required
- High vehicle/pedestrian traffic area
- Minimal site disturbance and small footprint required
- Winter season
- Contamination from UST area
- Silty Clay soils, shallow groundwater table (< 3 mbg)
- Contamination:
  - Groundwater
    - Benzene, ethylbenzene: Marginally impacted, exceeding site criteria by less than <1 mg/L
    - Benzene criteria - 0.005 mg/L
    - Ethylbenzene criteria - 0.0024 mg/L

**The Approach - ChemOx®**
- Pre and post treatment verification sampling
- In-Situ Chemical Oxidation Program (ISOTEC®)
  - Install 6 injection wells discretely within contaminated interval
  - Secure site for oxidant storage and exposure control
  - Conduct injection activities over night to avoid conflict with gas station operations
  - Heated injection units allow winter execution
  - Inject 7,600 L of TRIUM’s ChemOx® enhanced hydrogen peroxide over 3 programs of <5 days each

**The Results**
- Post treatment samples satisfied remediation target and allowed for approval of sale
- Real-time performance monitoring and reporting to client
- No on-site disturbance to site operations
- Zero lost time or first aid health and safety events
Case Study 3 – Sulfolane in GW

- Treatment at the most heavily impacted monitoring well location.

- Over 3 days of injections a total volume of 320L of 15% Enhanced Hydrogen Peroxide was administered.

- Four groundwater samples were taken 3, 10, 24 and 52 days from the beginning of the pilot.
Analytical Results for Field Pilot

Sulfolane Concentration

- **Concentration (mg/L)**
- **Time (days)**

Graph showing the concentration of Sulfolane over time.
Proof of Concept

- Does not use dedicated monitoring wells as injection wells, as short term analytical results can be biased by various other injection related factors (i.e. dilution, dispersion, etc).
  - Closed system dilution
  - Closed system displacement
  - Groundwater flow/chemical diffusion
  - Open system diffusion
  - Open system hydraulic dispersion
  - Closed system mass destruction
Summary

- The groundwater flow and open system dispersion models provide good correlation and evidence of the effects of “dilution” to the system.
- This extends up to the “24/52” day sampling events, where the linear relationships of the models deviate.
- This deviation could be considered reflective of reductions due to oxidation, with a potential reaction efficiency of up to 80% being observed.
- The 100 day sampling event is planned for early October.
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Reality is Our Product

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Leading Applied Chemical Remediation Strategies

Locations
Cochrane (HQ) / Edmonton / Drayton Valley

International
USA / S. Korea / Middle East / China
Thank you

Acknowledgment