Treatability Testing for In-Situ Chemical Oxidation

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Overview

- Definition of Treatability Testing
- Benefits and Limitations
- Types of Treatability Tests
- Case Study
- Summary

“The strongest arguments prove nothing so long as the conclusions are not verified by experience.”

- Roger Bacon
What is Treatability Testing?

- Measurement of Treatment Under “Ideal” Conditions
- Controlled Tests Performed on Water and Soil Samples
- Proof of Concept
- Establish Parameters for Pilot / Full-Scale ISCO
- Common Objectives
  > Determine reactivity of soil
  > Select the optimum chemistry
  > Evaluate potential adverse reactions
  > Develop cost estimate
Benefits of Treatability Testing

- Generates Site-Specific Data
- Allows Optimization Prior to Full-Scale Implementation
  - Refine chemistry
  - Incorporate efficiencies
  - Cost savings potential
- Enhances Pilot Testing / Full-Scale Implementation
  - Expected results guide next phase of work
  - Simplifies evaluation of field scale results
Limitations of Treatability Testing

- **Linear Scale-Up Limitations**
  - Difficult to simulate heterogeneity in test column
  - Small sample volume compared to site
  - Well-mixed static system

- **Contact and Mixing**
  - May favorably bias results
  - Not possible to evaluate delivery process

- **Pilot Study Required (usually)**
Types of Treatability Tests

- **Laboratory Tests**
  - Simple, inexpensive tests
  - Incorporate into RI
  - SOD, peroxide reactivity

- **Bench-Scale Study**
  - Proof of concept
  - Basis of design
  - Scale-up for pilot test

- **Pilot Testing**
  - Discussed in next session
  - Provides full-scale design parameters
  - Requires extensive monitoring
Stoichiometric Evaluation

- Starting Point for All Treatability Tests
- Establish Baseline for Comparison
- Facilitates Oxidizer Selection
  - Mass/volume requirements
  - Reaction kinetics
  - Catalyst requirements

Equations:
1. $15\text{Na}_2\text{S}_2\text{O}_3 + \text{C}_8\text{H}_8 + 12\text{H}_2\text{O} \rightarrow 6\text{CO}_2 + 30\text{SO}_4^{2-} + 30\text{Na}^+ + 30\text{H}^+$
2. $18\text{Na}_2\text{S}_2\text{O}_3 + \text{C}_8\text{H}_8 + 14\text{H}_2\text{O} \rightarrow 6\text{CO}_2 + 36\text{SO}_4^{2-} + 36\text{Na}^+ + 36\text{H}^+$
3. $21\text{Na}_2\text{S}_2\text{O}_3 + \text{C}_9\text{H}_{10} - 16\text{H}_2\text{O} \rightarrow 6\text{CO}_2 + 42\text{SO}_4^{2-} + 42\text{Na}^+ + 42\text{H}^+$
4. $25\text{Na}_2\text{S}_2\text{O}_3 + \text{C}_8\text{H}_{18} - 16\text{H}_2\text{O} \rightarrow 8\text{CO}_2 + 50\text{SO}_4^{2-} + 50\text{Na}^+ + 50\text{H}^+$
5. $49\text{Na}_2\text{S}_2\text{O}_3 + \text{C}_{12}\text{H}_{34} + 32\text{H}_2\text{O} \rightarrow 16\text{CO}_2 + 98\text{SO}_4^{2-} + 98\text{Na}^+ + 98\text{H}^+$
Gas Evolution and Generation

Stoichiometric Oxygen Gas Production

Peroxide Injection Rate (gpm) vs. Oxygen Gas Production (SCFM)

Reference: 2011 Pilot Test Work Plan, GES
Soil Oxidant Demand

- Measure of Oxidant Depletion Over Time
  - Grams of oxidant per kilogram of soil (g/kg)
  - Range: 0.1 to 20 g/kg
- Standard Methods
  - Permanganate: USEPA Method – PSOD and ASTM D7262-10
  - Other oxidants: Varies
- Variables – Soil Related
  - Natural organic matter
  - Reduced solid species
  - Soil structure / mineralogy
- Variables – Process Related
  - Oxidant
  - Oxidant concentration
  - Time of measurement
Oxidant Demand – Primary Design Factor

- Soil Matrix is Generally Dominant
  - 2 to 3 orders of magnitude
  - Groundwater constituents relatively unimportant
- Matrix Demand May Exceed Contaminant Demand
- Interpreting the Results
  - Cost of full-scale implementation
  - Evaluate oxidant mass versus pore volume
  - SOD ignores relative reaction rates
Soil Oxidant Demand vs. Dose

- Initial Oxidizer Concentration
- Activator / Catalyst
- Oxidant Dependent
- SOD Measurement Time
- Other Factors

Reference: 2010 PRIMA Environmental, Inc.
Bench-scale Testing

- Establish Basis of Design
  - Oxidizer selection
  - Dose optimization
  - Oxidant/stabilizer concentration
  - Catalyst selection
  - Secondary considerations

- Address Concerns
  - Contaminant desorption
  - Metals mobilization
  - Cr(VI) formation
  - pH shift
  - By-product formation
Dose Optimization

![Bar chart showing remaining PCE (μg/L) over different treatment times and levels of persulfate. The chart compares 2 g/L, 5 g/L, and 10 g/L persulfate treatments at 4 days, 8 days, and 21 days.](chart.png)
Some metals can be mobilized by oxidizing conditions
Redox sensitive metals must be considered
\[ \text{Cr}^{3+} \rightarrow \text{Cr}^{6+} \]
Bench-Scale and Pilot Test Important
- Directly measure constituent concentrations
- Evaluate “buffering” capacity of site
Catalyst Optimization

Activation Method Optimization

Intermediates in MTBE-Persulfate Reaction

Reference: Optimization of In-Situ Chemical Oxidation Design Parameters, Amine Dahmani, PhD, ERI
Pilot Tests

Pilot tests are performed on targeted area(s) of the site

- Common Objectives
  - Radius of influence
  - Rate of application
  - Field-scale inefficiencies
  - Field oxidant volume estimates
  - Evaluate injection design

- Cost Estimate for Full-Scale Implementation
- Another Opportunity to Say “No”
Case Study: Bulk Storage Facility

- **Background**
  - Petroleum bulk storage facility
  - 125 million gallon storage capacity
  - 200 acres
  - COCs – gasoline, diesel, heavy fuel oil

- **Geology**
  - Heterogeneous deposits
  - Sand, silt, clay, some gravel
  - Clay unit underlies superficial water bearing unit

- **Hydrogeology**
  - Aquifer: 5 – 35 feet thick
  - DTW: 1 – 29 feet bgs
  - Hydraulic gradient: 0.04 ft/ft to 0.005 ft/ft
  - Hydraulic conductivity: 0.003 ft/min to 0.024 ft/min
Case Study: ISCO Target Areas

Legend:
- ○: NPA PROGRAM GEOPROBE WELLS
- ☐: PROPOSED PILOT TEST WELLS
- □: LOW AREA
- ---: APPROXIMATE CENTERLINE OF Dike
- ---: APPROXIMATE TOP EDGE OF HOLDING POND
- ✓: LOCATION OF TANKS COMPARED FROM AERIAL MAPS

Diesel Range Organics

Gasoline Range Organics
Case Study: Geologic Cross-Section

Gasoline Range Organics

Diesel Range Organics
Case Study: Treatability Study Objectives

Process Variable Evaluation/Optimization

- Chemistry Optimization
- Oxidant Stability / Gas Evolution
- Soil Oxidant Demand
- Soil Buffering Capacity
- Optimize Reaction Chemistry
  - Oxidizer Dose
  - Oxidant Determination
- Address Concerns
  - pH reduction (persulfate)
  - Chromium VI
Case Study: Chemistry Optimization

- Sodium Persulfate / Hydrogen Peroxide Activation
  - Activate with $\text{H}_2\text{O}_2$ / Persulfate
  - Activate with EDTA-Iron
- Hydrogen Peroxide
  - EDTA-Iron
  - Stability of peroxide
- Catalyst Evaluation
  - EDTA only
  - Utilize “native” iron
Case Study: Oxidant Stability / Gas Evolution

Hydrogen Peroxide Longevity Test
Case Study: SOD vs. Concentration

<table>
<thead>
<tr>
<th>Time, Days</th>
<th>Na$_2$S$_2$O$_8$ Remaining, g/L</th>
<th>Na$_2$S$_2$O$_8$ Consumed, g/kg Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Soln. Low Dose</td>
<td>High Dose</td>
</tr>
<tr>
<td>0</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>3.6</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>2.3</td>
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<tr>
<td>7</td>
<td>1.9</td>
<td>11</td>
</tr>
<tr>
<td>21</td>
<td>1.3</td>
<td>6.0</td>
</tr>
</tbody>
</table>

• Dose Optimization
• Higher Dose – Higher SOD

Low Dose
• Concentration: 5 g/L
• SOD: 11 g Na$_2$S$_2$O$_8$/kg

High Dose
• Concentration: 15 g/L
• SOD: 27 g Na$_2$S$_2$O$_8$/kg
Case Study: Soil Buffering Capacity

- Assess pH drop following persulfate injection
- Mild buffering capacity of soil
- May require pH adjustment following persulfate injection
- All samples similar results
Case Study: Test Multiple Locations

- Oxidant/Catalyst Evaluation
- Multiple Samples per AOC
- Very Different Results

**Pair #1 – GRO Optimized**
- peroxide / persulfate – 70%
- EDTA-Fe / peroxide – 68%

**Pair #3 – GRO Optimized**
- EDTA-Fe / persulfate – 100%
- EDTA-Fe / peroxide – 80%
Case Study: Optimization Results

- **EDTA-Iron Catalyst**
  - EDTA solution = 1,100 mg/L
  - Chelated iron concentration = 150 mg/L
  - EDTA : Iron = 10:1

- **Persulfate – Peroxide**
  - H2O2 : Persulfate = 5 : 1

- **Persulfate – EDTA-Iron**
  - EDTA : Persulfate = 1 : 4
Summary

- Treatability Testing is Valuable
  - Process optimization
  - Cost information
- Decision Making Enhanced
  - Site-specific data
  - Go / No-go earlier in design process
- Lessons Learned
  - Optimize chemistry
  - Develop contingencies for concerns
  - Even “Simple Sites” benefit

"Happy is he who gets to know the reason for things.”
- Virgil
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