Biodegradation of Hydrocarbons under Nitrate and Sulfate Reducing Conditions

David Abranovic P.E., ERM, Scottsdale, AZ
Paula Chang, ERM, Scottsdale, AZ
Richard Brown, ERM, Ewing, NJ

WaterTech 2008
Contents

• Summary of Sulfate Nitrate Reduction
• Site Background and Setting
• Environmental Setting
• Laboratory Testing Results
• Pilot Test Design and Implementation
• Pilot Test Results
• Full Scale Remediation Strategy
Electron Acceptors Products
1. Oxygen >>> Water, CO₂
2. Nitrate >>> Nitrogen, CO₂
3. Fe(III) >>> Fe(II), CO₂
4. Mn(IV) >>> Mn(II), CO₂
5. Sulfate >>> Sulfide, CO₂
6. None (fermentation) >>> Methane, CO₂

Hydrocarbon Biodegradation
Contaminant (Electron donor) e.g. BTEX

Microbial Growth

Electron Acceptors

Energy
e⁻

Products

High Energy Yield
Fast Kinetics in lab experiments

Low Energy Yield
Slow Kinetics in lab experiments

Yield

High

Fast

Microbial Growth

Low

Slow

1. Oxygen >>> Water, CO₂
2. Nitrate >>> Nitrogen, CO₂
3. Fe(III) >>> Fe(II), CO₂
4. Mn(IV) >>> Mn(II), CO₂
5. Sulfate >>> Sulfide, CO₂
6. None (fermentation) >>> Methane, CO₂

Delivering sustainable solutions in a more competitive world
### Why Sulfate?

<table>
<thead>
<tr>
<th>Electron Acceptor (EA)</th>
<th>Maximum Concentration (mg/L)</th>
<th>Mass of benzene degraded per unit mass of EA</th>
<th>Potential Benzene Degraded (mg/L)</th>
<th>Issues</th>
</tr>
</thead>
</table>
| Oxygen (in air)        | 9 - 10                       | 0.33                                       | 3.0 – 3.3                        | • Limited solubility  
                         |                              |                             |                                  | • Numerous oxygen sinks  
                         |                              |                             |                                  | • Potential aquifer clogging  
                         |                              |                             |                                  | • Biofouling near injection point |
| Pure Oxygen            | 60 - 70                      | 0.33                                       | 19.8 – 23.1                      |        |
| Sulfate                | 100 – 250*                   | 0.22                                       | 22.0 – 55.0                      | • Hydrogen sulfide; never documented as an issue in the field  
                         |                              |                             |                                  | • Secondary MCL for sulfate – 250 mg/L* |
| Nitrate                | 80 - 100                     | 0.21                                       | 16.8 – 21.0                      | • DW concern  
                         |                              |                             |                                  | • Primary MCL – 10 mg/L NO₃-N (45 mg/L NO₃) |
| Iron (III)             | 0 - 1                        | 0.024                                      | 0 – 0.024                        | • Very low solubility  
                         |                              |                             |                                  | • Aquifer clogging |

*Secondary MCL for sulfate – 250 mg/L*
Sulfate/Nitrate Advantages

- Most HC plumes are anaerobic and depleted of soluble electron acceptors (nitrate and sulfate)
- Sulfate reducing bacteria are ubiquitous and rapidly grow in HC rich anaerobic conditions
- Nitrate may oxidize iron sulfides to sulfate and boost the total electron acceptor pool
- Suitable for a variety of hydrocarbons – gasoline, gas condensate, alkanes, PAH, diesel…
- Nitrate and sulfate salts are much more soluble than oxygen
- Lower cost alternative $ 19 to 150/t vs $16,500/ton for ORC
Installation Restoration Program (IRP)
Site 25, 148th Fighter Wing (FW), Duluth, MN

Looking East

025-MW003 and 003 Deep

East-southeast

025-MW011

025-MW010

Looking East
Site Background and Setting

- Water table from 3 to 12 ft bgs, due to topographic slope
- Interbedded silts and clay to approximately 20 ft bgs
- Primary contaminant of concern: Benzene
- Abandoned upgradient UST source for BTEX, GRO and DRO
- Receptor of concern is a nearby wetland
Contaminant Concentrations
Treatability Study Set-up

• Site groundwater and soil
• BTEX, GRO and DRO spiked at time zero
• Treatment Conditions:
  • Sterile Groundwater Control – groundwater only
  • Ambient (Live) Control – groundwater and soil
  • Sulfate Amended – 400 to 1,000 mg/L
  • Sulfate and Nitrate Amended – 400 to 1,000 mg/L and 4 to 8 mg/L, respectively
Treatability Study Results

Delivering sustainable solutions in a more competitive world
Treatability Results Summary

- From 0 to 13 weeks, the nitrate+sulfate treatment show >98% decrease in Benzene, Toluene, Xylenes and GRO.
- From 13 to 26 weeks the % change is almost equal in the ambient, sulfate and sulfate+nitrate treatments, indicating that the degradation rate caught up after the longer incubation period.
- Soil GRO and DRO concentrations dropped significantly in all three treatments over the 26 week period.
Pilot Test Design

- Sulfate (Epsom Salt, MgSO₄, 400 mg/L) Nitrate (as KNO₃, 4 mg/L) and dosages from treatability test
- 850 lb of 40% MgSO₄
- 6 lb of 62% KNO₃
- 4,650 gal GAC filters tap water used to batch-mix injection solutions
- ROI of 20 ft, targeted top 12 feet below water table
- Injection grid of 10 points
- Distribution testing at 5, 10 and 15 ft from two injection points
Pilot Test Design

10 Injection Points
7' Radius of Influence
20' on Center

DIRECTION OF GROUNDWATER FLOW

MW009
MW010
MW011
MW006
MW003
MW D003

Delivering sustainable solutions in a more competitive world
Ideal Field Conditions vs. Reality - a Difference of 40 Degrees
Field Set-up
Pressure Pulse Injection – Wavefront™

• Pressure wave induces pore throat dilation

• Hornet – Model Name

• Injections were performed with and without the pressure pulse

• The unit is pressure sensitive – needs a minimum pressure (can be set by manufacturer)

• Affects ability to valve down injection pressures/rates
ROI Confirmation Sampling

- Injections were performed downgradient to upgradient
- 6 of the 10 injection points used Wavefront
- Groundwater samples were collected a radia distances from injection points at 5, 10, and 15 feet
- Analyzed using a LaMotte Field Test Kit for Sulfate, range 0 – 200 ppm
### ROI Monitoring

<table>
<thead>
<tr>
<th>Location</th>
<th>Sulfate (mg/L)</th>
<th>Wavefront</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1-5</td>
<td>160-200</td>
<td>Y</td>
</tr>
<tr>
<td>I1-10</td>
<td>160-200</td>
<td>Y</td>
</tr>
<tr>
<td>I1-15</td>
<td>50-80</td>
<td>Y</td>
</tr>
<tr>
<td>I2-5</td>
<td>160-200</td>
<td>NA</td>
</tr>
<tr>
<td>I2-10</td>
<td>160-200</td>
<td>NA</td>
</tr>
<tr>
<td>I2-15</td>
<td>160-200</td>
<td>NA</td>
</tr>
<tr>
<td>I2-5</td>
<td>&gt;200</td>
<td>N</td>
</tr>
<tr>
<td>I2-10</td>
<td>&gt;200</td>
<td>N</td>
</tr>
<tr>
<td>I2-15</td>
<td>80-120</td>
<td>N</td>
</tr>
</tbody>
</table>

**Diagram Notes:**
- **Injection Points**
- 7’ Radius of Influence
- 20’ on Center
Results – Test Area Shallow Well

025-003MW

HC Concentration (ug/l)

Monitoring Date

Sulfate mg/l
Results – Down Gradient Shallow Well

[Graph showing monitoring data for different compounds over a period from Sep-06 to Dec-07. The x-axis represents monitoring dates, and the y-axis represents concentration in ug/l for HC and mg/l for Sulfate.]
Pilot Test Conclusions

• Sulfate/nitrate reduction is an effective tool for accelerating natural attenuation of HCs in groundwater

• Removal of free-phase hydrocarbons is necessary for successful application sulfate reduction

• Based on the rapid consumption rates, high sulfate/nitrate dosing will likely not result in groundwater exceeding secondary standards
Future Site Work

- High Vacuum Extraction for source area separate phase HC removal
- Sulfate/Nitrate amendments to address residual dissolved phase HC remediation
- Monitored Natural Attenuation as final polishing step
Questions