Case History:

Removal of Perchlorate from Groundwater at the Longhorn Army Ammunition Plant

Presented at the Sixth In Situ and On-Site Bioremediation Conference

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Dawn Knight

Complete Environmental Systems
Deerinwater Environmental Systems
Aerojet
U.S. Filter/Envirex
Envirogen’s Engineering Group
Presentation Overview

1. Sources of perchlorate
2. Biological degradation of perchlorate
3. Fluid Bed Reactor
4. Aerojet Full Scale System Success
5. Longhorn Army Ammunition Plant
   - History
   - Problem
   - Full Scale System Success
6. Summary
Sources of Perchlorate

• Fireworks and matches
• Airbag inflators
• Nuclear reactors and electronic tubes
• Lubricating oils
• Tanning and finishing leather
• Mordant for fabrics and dyes
• Electroplating aluminum refining
• Rubber manufacturing
• Paints and enamels
• Fertilizers
Sources of Perchlorate

It has been estimated that 90% of ammonium perchlorate released is as an oxidizer for solid rocket propellant.
Bacterial Metabolism

Requirements:

• Energy Source (organic or inorganic)
• Electron Acceptor (O₂, NO₃, SO₄, CO₂)
• Carbon Source (organic or CO₂)
• Macronutrients (N,P,S)
• Mineral Ions (Ca, K, Mg, Fe, Cu, Zn, Co, et al.)
• Vitamins and/or Amino Acids
**Biological Perchlorate Reduction**

*Terminal Electron Acceptor:*

$$\text{ClO}_4^- \rightarrow \text{ClO}_3^- \rightarrow \text{ClO}_2^- \rightarrow \text{O}_2 + \text{Cl}^-$$

(perchlorate) (chlorate) (chlorite)

H$_2$O
Organic Pollutants

Biomass + CO₂

Nutrients (N,P)

H₂O

O₂

Benzene (substrate)
Perchlorate Reduction

Biomass + CO₂

Cl⁻ + O₂ → ClO₄⁻

Nutrients (N,P)

Organic Substrate
(Ethanol, Acetate, Lactate, Molasses, Sucrose)

(H₂O)

(Anoxic Conditions; i.e. Low O₂)
Utilization of Electron Acceptors

- 250

Redox (mV)

+ 800

Groundwater + Substrate

Methanogenesis

Denitrification

CO₂ → CH₄

SO₄²⁻ → S⁻

ClO₄⁻ → Cl⁻

NO₃⁻ → N₂

O₂ → H₂O
Bioreactor System Options for Treatment of Organic Chemicals

![Diagram of bioreactor systems]

FLOWRATE, GPM

mg/l

CONTAMINATED WATER OR WASTEWATER FEED
pH CONTROL
NUTRIENTS
OXYGEN

MEMBRANE BIOLOGICAL REACTOR SYSTEM

TREATED EFFLUENT
FBR Flow Schematic

**FLUIDIZED BED REACTOR**

**EFFLUENT**

**FEED**
(i.e., CONTAMINATED GROUNDWATER)

**NUTRIENT(S)**

**ELECTRON DONOR**

**RECYCLE**

**BED HEIGHT CONTROL SYSTEM**

**INFLUENT**
FBR Advantages

• High biomass concentration means long SRT and short HRT

• High volumetric efficiency translates to compact system; installation in a building

• Simplicity of operation minimizes need for operator attention

• Small impact from changing feed conditions, as feed is combined with recycle before entering the reactor
Key Mechanical Components

• Device and method used to distribute influent flow to the reactor

• Device and method used to control the expansion of the fluidized bed due to biofilm growth

• Method to control electron donor dosage rate
Aerojet’s Full Scale Perchlorate Treatment Plant

- 4 Fluidized Bed Reactors available
- Each reactor has a design capacity of
  - 1800 gpm Fluidization Rate
  - 900 gpm Feed Rate
- 4 reactors currently in use with combined feed rate of ~3500 gpm (~875 gpm each)
- Treating ~ five million gallons per day
### Aerojet’s Full Scale Perchlorate Treatment Plant

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Influent</th>
<th>Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved $O_2$</td>
<td>5.3 ppm</td>
<td>&lt;0.5 ppm</td>
</tr>
<tr>
<td>CLO4</td>
<td>~3500 ppb</td>
<td>&lt;4.0 ppb</td>
</tr>
<tr>
<td>TCE</td>
<td>1500 ppb</td>
<td>1500 ppb</td>
</tr>
<tr>
<td>NDMA</td>
<td>110 ppt</td>
<td>110 ppt</td>
</tr>
<tr>
<td>Nitrate-N</td>
<td>1.5 ppm</td>
<td>&lt;0.11 ppm</td>
</tr>
<tr>
<td>Nitrite-N</td>
<td>&lt;0.076 ppm</td>
<td>&lt;0.076 ppm</td>
</tr>
<tr>
<td>Sulfate-S</td>
<td>6.0 ppm</td>
<td>6.0 ppm</td>
</tr>
<tr>
<td>Ethanol</td>
<td>NA</td>
<td>&lt;1.0 ppm</td>
</tr>
<tr>
<td>pH</td>
<td>~7.5</td>
<td>~7.5</td>
</tr>
</tbody>
</table>
Longhorn Army Ammunition Plant
### LHAAP History

<table>
<thead>
<tr>
<th>Year Range</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1942-1945</td>
<td>LHAAP opened; Monsanto Chemical Company - TNT</td>
</tr>
<tr>
<td>1952-1956</td>
<td>Universal Match Corporation - pyrotechnic ammunition</td>
</tr>
<tr>
<td>1955-1965</td>
<td>Thiokol Corporation - rocket motor facility</td>
</tr>
<tr>
<td>1965</td>
<td>Pyrotechnic and illuminating ammunition re-established</td>
</tr>
<tr>
<td>1965-1997</td>
<td>Multi-functional; INF</td>
</tr>
<tr>
<td>1990</td>
<td>NPL</td>
</tr>
<tr>
<td>1991</td>
<td>Federal Facilities Agreement</td>
</tr>
<tr>
<td>1997</td>
<td>Caretaker Status</td>
</tr>
<tr>
<td>2000</td>
<td>Fish and Wildlife Service Memorandum of Agreement</td>
</tr>
</tbody>
</table>
Bench Scale FBR Glass Reactor
## Results of Phase 1 - Sample Characterization

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Units</th>
<th>Drum #1</th>
<th>Drum #2</th>
<th>Drum #3</th>
<th>Average</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen (O₂)</td>
<td>D.O. Probe</td>
<td>mg/L</td>
<td>4.0</td>
<td>3.5</td>
<td>Not Analyzed</td>
<td>3.8</td>
<td>0.4</td>
</tr>
<tr>
<td>Perchlorate (ClO₄⁻)</td>
<td>EPA 300.0</td>
<td>mg/L</td>
<td>15.1</td>
<td>14.7</td>
<td>14.4</td>
<td>14.7</td>
<td>0.4</td>
</tr>
<tr>
<td>Chlorate (ClO₃⁻)</td>
<td>EPA 300.0</td>
<td>mg/L</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>Nitrate-N (NO₃⁻-N)</td>
<td>EPA 300.0</td>
<td>mg/L</td>
<td>1.9</td>
<td>1.9</td>
<td>1.8</td>
<td>1.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Nitrite-N (NO₂⁻-N)¹</td>
<td>HACH Method 8507</td>
<td>mg/L</td>
<td>0.016</td>
<td>0.013</td>
<td>0.011</td>
<td>0.013</td>
<td>0.003</td>
</tr>
<tr>
<td>Ortho-phosphate-P (PO₄⁻-P)</td>
<td>EPA 300.0</td>
<td>mg/L</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>N/A</td>
</tr>
<tr>
<td>Ammonia-N (NH₃-N)</td>
<td>EPA 350.2</td>
<td>mg/L</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>N/A</td>
</tr>
<tr>
<td>Sulfate (SO₄²⁻)</td>
<td>EPA 300.0</td>
<td>mg/L</td>
<td>290</td>
<td>310</td>
<td>310</td>
<td>303</td>
<td>11.5</td>
</tr>
<tr>
<td>Chemical Oxygen Demand (COD)</td>
<td>EPA 410.4</td>
<td>mg/L</td>
<td>56</td>
<td>21</td>
<td>12</td>
<td>30</td>
<td>23.2</td>
</tr>
<tr>
<td>Total Organic Carbon (TOC)</td>
<td>EPA 415.1</td>
<td>mg/L</td>
<td>&lt;1</td>
<td>1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>N/A</td>
</tr>
<tr>
<td>Oil &amp; Grease (O&amp;G)</td>
<td>EPA 413.1</td>
<td>mg/L</td>
<td>Less than 10 mg/L for a composite sample</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Suspended Solids (TSS)</td>
<td>EPA 160.2</td>
<td>mg/L</td>
<td>12</td>
<td>14</td>
<td>4</td>
<td>10</td>
<td>5.3</td>
</tr>
<tr>
<td>Volatile Organic Contaminants (VOCs)</td>
<td>SW-846 8260</td>
<td>mg/L</td>
<td>Not Analyzed</td>
<td>Less than 0.10 to 0.05 mg/L for all on 8260 list except for acetone @ 0.18 mg/L</td>
<td>Less than 0.10 to 0.05 mg/L for all on 8260 list</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Priority Pollutant Metals</td>
<td>EPA 200.7 and EPA 245.1 (Hg)</td>
<td>ug/L</td>
<td>Less than PQL for all on 200.7 list (and Hg) except for Ni @ 1.7 ug/L and Zn @ 198 ug/L</td>
<td>Less than PQL for all on 200.7 list (and Hg) except for Ni @ 1.8 ug/L and Zn @ 131 ug/L</td>
<td>Not Analyzed</td>
<td>1.8 for Ni and 165 for Zn</td>
<td>0.1 for Ni and 47.4 for Zn</td>
</tr>
<tr>
<td>Broth Tube Toxicity/Inhibition Test</td>
<td>Internal SOP</td>
<td>N/A</td>
<td>Not Toxic or Inhibitory</td>
<td>Not Toxic or Inhibitory</td>
<td>Not Toxic or Inhibitory</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

¹ EPA Method 300.0 (Ion Chromatography) gave initial results of 330, 340, and 320 mg/L for nitrite-N. The samples were re-run, and the peak was determined to be chloride (Cl⁻) at an average concentration of 710 mg/L. The nitrite-N results were confirmed by an independent laboratory using Method EPA 353.2.
Longhorn Army Ammunition Plant
Bench-Sale Results

Perchlorate Concentration (ug/L)

Date

Influent
Effluent

Low carbon substrate feed

Longhorn Army Ammunition Plant
Full Scale FBR Installation
(Perchlorate Reduction)

• Design Basis
  – 50 gpm
  – One 5 ft. dia. unit
  – Acetic acid as electron donor
  – GAC media
  – Perchlorate up to 22,000 ppb
UPDATE

Longhorn Army Ammunition Depot

ENVIROGEN FBR System Performance

Days Since Inoculation

Perchlorate Concentration (ppb)

- Influent Perchlorate
- Effluent Perchlorate
Summary

• Biological Fluid Bed Reactor successfully treating more than 7.0 million gallon per day of groundwater containing perchlorate
• Consistent effluent perchlorate levels below practical quantitation limits (4 ppb)
• Single FBR treats from 50 to 1,000 gpm
• No flow rate limits with multiple units
• Thank you - Bill Guarini, Envirogen, Inc.
  609 - 936-9300 x 135