Innovative Options for Ex-Situ Removal of Perchlorate and Explosives in Groundwater

National Defense Industry Association
30th Environmental and Energy Symposium and Exhibition

April 7, 2004

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Innovative Technology Evaluation (ITE) Team

- Army National Guard
- Army Environmental Center
- Army Corps of Engineers
- AMEC Earth and Environmental

Acknowledgements

- Shaw Environmental & Infrastructure, Inc.
- US Filter Corporation
- Pennsylvania State University (PSU)
- The Purolite Company
- DL Maher (div. of Boart Longyear, Inc.)
ITE History and Mission

• History - Impact Area and Ranges at Site used for training since 1911

• Mission - Evaluate innovative remediation technologies to treat low levels of perchlorate and explosives in soil and groundwater
Ex Situ Groundwater Treatment Technology Evaluation

Technologies evaluated

- Fluidized Bed Bioreactor (FBBR)
- Granular Activated Carbon (Standard GAC)
- Granular Activated Carbon tailored by the addition of a proprietary cationic monomer (Tailored GAC)
- Ion Exchange Resin (IX Resin)
## Site Contaminant and Aquifer Characteristics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Area #1</th>
<th>Area #2</th>
<th>Area #3</th>
<th>Area #4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perchlorate (µg/L)</td>
<td>100</td>
<td>5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>RDX &amp; HMX (µg/L)</td>
<td>200</td>
<td>0</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Nitrate as N (mg/L)</td>
<td>2.2</td>
<td>&lt;0.12</td>
<td>0.05</td>
<td>0.1</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>4.6</td>
<td>6.1</td>
<td>4.4</td>
<td>5.0</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>7.6</td>
<td>7.9</td>
<td>7.2</td>
<td>8.7</td>
</tr>
<tr>
<td>Total Organic Carbon (mg/L)</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>0.59</td>
<td>0.68</td>
</tr>
<tr>
<td>Orthophosphate as P (mg/L)</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Iron (mg/L)</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>pH (S.U.)</td>
<td>5.8</td>
<td>6.3</td>
<td>5.4</td>
<td>5.7</td>
</tr>
<tr>
<td>Dissolved Oxygen (mg/L)</td>
<td>9.8</td>
<td>9.4</td>
<td>10.6</td>
<td>9.2</td>
</tr>
</tbody>
</table>
Fluidized Bed Bioreactor Overview

- **FBBR experience**
  - In use at DoD and commercial sites - Longhorn AAP (TX), Aerojet (CA)
  - Vendor – Shaw Environmental & Infrastructure, Inc.
  - Prior demonstration at lab scale on TNT but not RDX

- **FBBR study**
  - Bed medium (GAC)
  - Biomass
  - Nutrient substrate
  - Nutrients (N, P)
  - pH control
  - Fluidization control

FBBR Flow Schematic
Credit: Shaw, Inc.
FBBR Area #1 Study Results

Initiation  | Phase 1 - Acclimation  | Phase 2 - HRT = 80 min.  | Phase 3 - HRT = 35 min.

Concentration - ug/L

Date:
04/20/02 05/04/02 05/18/02 06/01/02 06/15/02 06/29/02 07/13/02 07/27/02 08/10/02

- CEIMIC Effluent Analyses
- Envirogen Effluent Analyses
- Envirogen Influent Analyses
- CEIMIC Influent Analyses
- Study Performance Goal

FBBR A (Acetic Acid) Effluent Perchlorate vs. Time

HRT = Hydraulic Retention Time
FBBR Area #2 Study Results

FBBR A (Acetic Acid) Effluent Perchlorate vs. Time

Phase 1. HRT = 16 min.

Phase 2. HRT = 11 min.

Perchlorate Concentration (ug/L)

Date

08/09/02 08/19/02 08/29/02 09/08/02 09/18/02 09/28/02

Envirogen Effluent Analyses

CEIMIC Effluent Analyses

Envirogen Influent Analyses

CEIMIC Influent Analyses

FBBR A (Acetic Acid) Effluent Perchlorate vs. Time
FBBR Study Conclusions

• Area #1 Study (Perchlorate and RDX)
  ° Perchlorate degraded to <1.0 µg/L at Hydraulic Retention Time (HRT) of 35 min.
  ° RDX degraded to <2 µg/L at HRT of 80 min.

• Area #2 Study (Perchlorate alone)
  ° Perchlorate degraded to <1.0 µg/L at HRT of 16 min.
  ° Addition of nitrate is required when perchlorate and other electron acceptors are low.
Granular Activated Carbon (Standard GAC)

- GAC - an old friend to water treatment, used on explosives
- Theory
  - Contaminants held onto carbon surface via adsorption
  - Contaminants removed but not destroyed
  - Initial Breakthrough - after carbon’s capacity is exhausted, levels in effluent are above detection limits
  - Rapid Small Scale Column Tests (RSSCTs) predict performance of a full-scale system
- Goal - Can Standard GAC remove perchlorate from groundwater at very low concentrations?
- Test - RSSCTs to find how much groundwater can be processed before breakthrough
  - Carbon provided by US Filter
  - Tests performed by PSU (Dr. Fred Cannon, Bob Parette)
### Standard GAC RSSCTs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Test #1</th>
<th>Test #2</th>
<th>Test #3</th>
<th>Test #4</th>
<th>Test #5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source Study Area</td>
<td>#4</td>
<td>#1</td>
<td>#1</td>
<td>#1</td>
<td>#3</td>
</tr>
<tr>
<td>Perchlorate (µg/L)</td>
<td>1</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Influent RDX (µg/L)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5.5</td>
</tr>
<tr>
<td>Influent HMX (µg/L)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>EBCT (min)</td>
<td>20</td>
<td>5</td>
<td>7</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>BV to Perchlorate BT</td>
<td>30,000</td>
<td>15,000</td>
<td>20,000</td>
<td>20,000</td>
<td>40,000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>to 25,000</td>
<td>to 24,000</td>
<td></td>
<td>to 46,000</td>
</tr>
<tr>
<td>BV to RDX BT</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>308,000</td>
</tr>
<tr>
<td>Effective Bed Life (mo)¹</td>
<td>13</td>
<td>2</td>
<td>3-4</td>
<td>9-11</td>
<td>9-10</td>
</tr>
</tbody>
</table>

EBCT = Empty Bed Contact Time  
BV = Bed Volumes  
BT = Breakthrough  
¹ Effective Bed Life = time between media change-outs (months)
Modified Granular Activated Carbon (Tailored GAC)

- Theory - Increasing number of positive charges on GAC surface improves perchlorate adsorption
- Goal - Can modified GAC offer an economical alternative to conventional GAC?
- Test - Preload the GAC with organic monomer with a strong positive charge (Tailored GAC)
  - Tests performed by PSU (Dr. Fred Cannon, Bob Parette)
- Materials - Proprietary cationic monomer - NSF approval is pending
# Tailored GAC RSSCTs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Test #6</th>
<th>Test #7</th>
<th>Test #8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source Study Area</td>
<td>#2</td>
<td>#3</td>
<td>#3</td>
</tr>
<tr>
<td>Perchlorate (µg/L)</td>
<td>5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Influent explosives (µg/L)</td>
<td>0</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>EBCT (min)</td>
<td>5</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>BV to Perchlorate BT</td>
<td>77,000 to 170,000</td>
<td>270,000</td>
<td>270,000</td>
</tr>
<tr>
<td>BV to RDX BT</td>
<td>N/A</td>
<td>8,000</td>
<td>308,000</td>
</tr>
<tr>
<td>Effective Bed Life (mo)</td>
<td>9 - 19</td>
<td>56</td>
<td>56</td>
</tr>
</tbody>
</table>

EBCT = Empty Bed Contact Time  
BV = Bed Volumes  
BT = Breakthrough  

1 Effective Bed Life = time between media change-outs (months)  
2 Bed Life applies only to perchlorate treatment, not RDX treatment  
3 Test #8 combines results from Tests #5 & #7 (2 columns: 1 Tailored GAC, followed by 1 Standard GAC)
RSSCT Results & Conclusions

• For 5 µg/L perchlorate in groundwater
  ° Standard GAC - operational life is 3 - 4 months (10-minute EBCT)
  ° Tailored GAC - operational life is ~ 20 months (5- minute EBCT)

• For 1 µg/L perchlorate and 6 µg/L explosives in groundwater
  ° Standard GAC - operational life is ~ 9 months (10-minute EBCT)
  ° Tailored GAC followed by Standard GAC - operational life is ~ 56 months (8.5-minute EBCT)

• Sorption differences
  ° Standard GAC very effective for explosives, slightly effective for perchlorate
  ° Tailored GAC very effective for perchlorate, ineffective for explosives
Ion Exchange Resins (IX Resins)

- **Theory** - Anions held to a +charged surface are exchanged for other anions. These IX resins do not remove explosives/other neutral species.

- **Test** - Field studies using Type I Styrenic Resins & Nitrate-Selective Resins.

- **Perchlorate Selective Resins** evaluated, but appear to have similar effective bed life to Nitrate-Selective Resins for treating perchlorate at the site, at higher expense.

- **Materials** - Purolite A520E, Purolite A600E are NSF approved for use in water supply.
Field Study - Tailored GAC, IX Resins

- Goal #1 - Is Tailored GAC effective at field scale?
- Goal #2 - How much will monomer leach from Tailored GAC?
- Goal #3 - Will a “polishing” GAC vessel capture leached monomer?
- Goal #4 - Can IX resins treat low concentrations of perchlorate?
## Field Study - Tailored GAC, IX Resins

<table>
<thead>
<tr>
<th>Media</th>
<th>Tailored GAC</th>
<th>N – S Resin</th>
<th>T1 - S Resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td>Study Area #2</td>
<td>#2</td>
<td>#2</td>
</tr>
<tr>
<td>Perchlorate (µg/L)</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Explosives (µg/L)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>EBCT (min)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Bed Volumes to date</td>
<td>21,000</td>
<td>21,000</td>
<td>21,000</td>
</tr>
<tr>
<td>Predicted Bed Volumes</td>
<td>&gt;150,000</td>
<td>72,000</td>
<td>15,000</td>
</tr>
<tr>
<td>Predicted Bed Life (mo)</td>
<td>&gt; 16</td>
<td>&gt; 8</td>
<td>&gt; 1.5</td>
</tr>
</tbody>
</table>

N-S = Nitrate Selective ion exchange resin  
T1-S = Type I Styrenic ion exchange resin  
EBCT = Empty Bed Contact Time  
BV = Bed Volumes  
1 Predicted Bed Life = time between change-outs (months)
ITE Field Study Results & Conclusions

• Initial effluent from a Tailored GAC unit contains < 1 mg/L monomer; after one month < 0.1 mg/L.

• Preliminary: The Nitrate Selective Resin will likely remove perchlorate using an EBCT of 5 minutes, for an operation bed life of ~ 8 months.

• Preliminary: The Type I Styrenic Resin will likely remove perchlorate using an EBCT of 5 minutes, for an operation bed life of ~ 2 months.
# Implementation Cost Comparison

<table>
<thead>
<tr>
<th>Treatment Scenario</th>
<th>Comparative Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>5 µg/L perchlorate</strong></td>
<td></td>
</tr>
<tr>
<td>° Standard GAC</td>
<td>2x</td>
</tr>
<tr>
<td>° Tailored GAC</td>
<td>1.5X</td>
</tr>
<tr>
<td>° Nitrate Selective IX Resin</td>
<td>4x</td>
</tr>
<tr>
<td><strong>1 µg/L perchlorate, 6 µg/L explosives</strong></td>
<td></td>
</tr>
<tr>
<td>° Standard GAC</td>
<td>1X</td>
</tr>
<tr>
<td>° Tailored GAC¹</td>
<td>2X</td>
</tr>
<tr>
<td>° Nitrate Selective IX Resin</td>
<td>4X</td>
</tr>
</tbody>
</table>

Assumptions:
- Costs are for media only, except for Tailored GAC, where extra analytical costs are added. If monomer is NSF approved, costs are reduced by 0.5X
- Tailored GAC system requires extra Standard GAC vessel to treat explosives
ITE Study Recommendations

• Standard GAC can treat very low concentrations of perchlorate

• Standard GAC can be especially effective when explosives are present in addition to perchlorate

• Ion Exchange Resins can treat low concentrations of perchlorate to very low treatment goals.

• Tailored GAC may be an economical alternative to ion exchange resins. Further work to obtain NSF approval should be pursued.

• Applicability of ITE results to other sites is dependent on site characteristics -- RSSCTs, field studies recommended
References and Resources

- AMEC Earth & Environmental, Inc.
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