Agenda

• Perfluoroalkyl Substances (PFAS)

• Granular Activated Carbon (GAC)
  – PFAS treatment history
  – Base Material
  – Testing

• Treating PFAS with GAC
  – PFAS removal data
    ▪ Long & short chain PFAS
    ▪ Comparing different GAC
    ▪ Lab vs. full scale performance
    ▪ Reactivation
PFAS Molecular Characteristics

- Chemically Stable
  - C-F Bond
- High Molecular Weight
- Low Vapor Pressure
- Easily infiltrates into groundwater and soil
- Easily absorbs into organisms
- Resistant to oxidation, biodegradation, and air stripping
EPA-Recognized Contaminant

In May 2016 the EPA established a Health Advisory Exposure limit for PFOA and PFOS at 70 ppt concentration (combined limit).
Granular Activated Carbon
The safest way to treat water is to **remove** harmful compounds

- No unnecessary chemical addition
- No concentrated waste stream

GAC is the leading technology for removal of PFAS from groundwater

- Effective for PFAS removal in drinking water and remediation applications
- Chosen since 2001 for PFAS removal in over 45 large installations and over 1,000 POE systems

Spent GAC containing adsorbed PFAS can be reactivated

- Eliminates future liability for the contaminant
- Safe, sustainable, environmentally responsible
- GAC is recycled and reused
Calgon Carbon PFAS Treatment Locations

45+ Installations Across the U.S.
Differentiating GAC Products
Starting Materials

- Wood
- Dislocation
- Coconut
- Lignite
- Bituminous Coal
- Graphitic plate
Starting Materials

Wood

Coconut

Lignite

Bituminous Coal

Graphitic plate

Graphitic plate

Graphitic plate

Graphitic plate
Starting Materials

Raw material dictates all of the product possibilities

- Ash impurities
- Density
- Hardness
- Adsorption capacity
- Adsorption kinetics
Testing is Critical

Why

• Many factors influence the effective service life of GAC
  • Temperature
  • pH
  • EBCT
  • Concentration
  • Competitive Adsorption
  • Extremely difficult to quantify without testing

Objectives

• Application Research
  • Best GAC for the application
  • Design recommendations
• Customer Specific
  • Feasibility
  • Exchange frequency

Methods

• Column Testing (ACT or RSSCT)
  • Define the kinetics of adsorption or minimum contact time required
  • Define accurate carbon use rates impacted by competitive adsorbing compounds
Bench Scale Column Tests

• Accelerated Column Test (ACT)
  – Calgon Carbon developed test
  – Scaled to hydraulically simulate Empty Bed Contact Time (EBCT) and superficial velocity of full scale system
  – Scaling factors are experimentally determined
  – Used to estimate CUR for full scale system

• Rapid Small Scale Column Test (RSSCT)
  – ASTM D6586 Bench Scale Column Test
  – Scaling factors assume constant or proportional diffusivity
  – Relative comparison between carbons
Carbon Comparison for PFAS Removal
Summary of Test Data from Previous Work

RSSCT PFOA Breakthrough Comparison

RSSCT PFOS Breakthrough Comparison

Removal of various PFAS

CalgonCarbon
A Kuraray Company
Research RSSCT Study:
Comparison of GAC Types for PFOA and PFOS Removal

- Four GAC products marketed for PFOA/PFOS treatment were evaluated under identical operating conditions and influent water quality

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Apparent Density, Oven (g/cc)</th>
<th>Ash (%)</th>
<th>Iodine Number (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagglomerated Bituminous</td>
<td>0.561</td>
<td>7.8</td>
<td>999</td>
</tr>
<tr>
<td>Lignite</td>
<td>0.377</td>
<td>12.4</td>
<td>616</td>
</tr>
<tr>
<td>Enhanced Coconut</td>
<td>0.414</td>
<td>4.1</td>
<td>1291</td>
</tr>
<tr>
<td>Enhanced Coconut (Blend)</td>
<td>0.388</td>
<td>6.9</td>
<td>1070</td>
</tr>
</tbody>
</table>
Research RSSCT Study:
Comparison of GAC Types for PFOA and PFOS Removal

- Multiple PFAS, variety of chain lengths
  - Each compounds spiked to approximately 200 ppt

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>CAS Number</th>
<th>Carbon Chain Length</th>
<th>Molecular Weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluoro octanesulfonic acid</td>
<td>PFOS</td>
<td>1763-23-1</td>
<td>C8</td>
<td>500.13</td>
</tr>
<tr>
<td>Perfluoro octanoic acid</td>
<td>PFOA</td>
<td>335-67-1</td>
<td>C8</td>
<td>414.07</td>
</tr>
<tr>
<td>Perfluorohexanesulfonic acid</td>
<td>PFHxS</td>
<td>355-46-4</td>
<td>C6</td>
<td>400.11</td>
</tr>
<tr>
<td>Perfluoro hexanoic acid</td>
<td>PFHxA</td>
<td>307-24-4</td>
<td>C6</td>
<td>314.05</td>
</tr>
<tr>
<td>Perfluoro butanesulfonic acid</td>
<td>PFBS</td>
<td>375-73-5</td>
<td>C4</td>
<td>300.1</td>
</tr>
<tr>
<td>Perfluoro butanoic acid</td>
<td>PFBA</td>
<td>375-22-4</td>
<td>C4</td>
<td>214.04</td>
</tr>
</tbody>
</table>

- Background TOC – 0.16 ppm
- Simulated EBCT – 10 minutes
PFOA Removal vs Simulated Days

RSSCT Breakthrough Curves

- PFOA Concentration (ppt)
- Simulated Days
- Feed PFOA
- Bituminous
- Lignite
- Enhanced Coconut
- Enhanced Coconut (Blend)

70 ppt USEPA HAL
PFOS Removal vs Simulated Days

RSSCT Breakthrough Curves

PFOS Concentration (ppt) vs Simulated Days

- Feed PFOS
- Bituminous
- Lignite
- Enhanced Coconut
- Enhanced Coconut (Blend)

70 ppt USEPA HAL
PFHxS Removal vs Simulated Days

RSSCT Breakthrough Curves

PFHxS Concentration (ppt) vs Simulated Days

- Feed PFHxS
- Bituminous
- Lignite
- Enhanced Coconut
- Enhanced Coconut (Blend)
PFBS Removal vs Simulated Days

RSSCT Breakthrough Curves

PFBS Concentration (ppt)

Simulated Days

- Feed PFBS
- Bituminous
- Lignite
- Enhanced Coconut
- Enhanced Coconut (Blend)
Conclusions:

Reagglomerated bituminous coal GAC significantly outperformed:
• Lignite
• Enhanced Coconut
• Enhanced Coconut (Blend)

GAC was still effective for the shorter chain compounds (C4, C6)
• Able to remove PFBS and PFHxS to non-detect
• Breakthrough occurred very quickly for Lignite and both Enhanced Coconuts
• Rapid PFBS breakthrough observed for Lignite and both Enhanced Coconuts
Hypothetical Economic Analysis

- **Treatment Objective:**
  - PFOA <70 ppt HAL

- **Factors considered:**
  - Performance by each material using results of study
  - Density difference
  - Carbon cost ($/lb)

Let’s look at what the “total cost” for each option would be using assumed market pricing....
## Total Cost of Ownership Comparison

<table>
<thead>
<tr>
<th></th>
<th>Reagglomerated Bituminous</th>
<th>Enhanced Coconut</th>
<th>Lignite</th>
</tr>
</thead>
<tbody>
<tr>
<td># of days online</td>
<td>1,095 (3 years)</td>
<td>1,095 (3 years)</td>
<td>1,095 (3 years)</td>
</tr>
<tr>
<td># of Exchanges (in period)</td>
<td>1.38</td>
<td>4.56</td>
<td>7.30</td>
</tr>
<tr>
<td>Total Cost Impact *</td>
<td>$113,617</td>
<td>$223,011</td>
<td>$216,126</td>
</tr>
<tr>
<td>$/1,000 gallons*</td>
<td>$0.14</td>
<td>$0.28</td>
<td>$0.27</td>
</tr>
</tbody>
</table>

*Based on Model 10 System, field service not included

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### Elasticity of Total Cost

- **Bituminous Filtrasorb 400**
- **Enhanced Coconut**
- **Lignite**

- +20% GAC cost increase ($/lb)
- -20% GAC cost decrease ($/lb)
Conclusions

• Performance will have a significant impact on total cost

• Lowest GAC cost ($/lb) doesn’t mean the lowest lifecycle cost

• Testing with representative source water is **ALWAYS** recommended to better understand future costs and optimize system design

Unit Cost ($/lb) ≠ Total Treatment Cost
Municipal Case Study

• Municipality in NY encounters PFOA in drinking water

• ACT column test
  – Determine efficacy of proposed treatment system
    ▪ 2 vessels, lead-lag operation
    ▪ 40,000 lbs GAC per vessel
    ▪ 13.2 minutes EBCT
**ACT Data**

**Simulated Days of Operation vs. PFOA and TOC**

**13 minutes EBCT**

Non detect after 620 simulated days of operation
Customer Field Data

Temporary Model 10 System
10 minutes EBCT

Days of Operation
PFOA Concentration (ppt)

- Lead Vessel Effluent
- Lag Vessel Effluent
- Influent PFOA
- Average Influent PFOA
- Health Advisory Level
Customer Field Data

Permanent Model 12-40 System
13 minutes EBCT

- Influent
- Average Influent
- Lead Effluent
- Lag Effluent
- USEPA HAL

PFOA Concentration (ppt) vs. Days of Operation
Activated Carbon Reactivation
What is Reactivation?

- Granular activated carbon has a finite bed life until the treatment objective is no longer reached.

- Reactivation is a process to restore the entirety of GAC’s adsorption capacity.

- The process is carried out at reactivation centers throughout the world.

- Generally, Industrial GAC furnaces reach temperatures up to 1800ºF.

- Adsorbed material is thermally destroyed and further treated through a series of abatement technologies.
### Experimental Design & Results

<table>
<thead>
<tr>
<th>PFAS</th>
<th>CMR Spent treating ppt levels</th>
<th>Lab React Spent treating ppb levels PFAS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PFBA</strong></td>
<td>1.9</td>
<td>1.3(^{J})</td>
</tr>
<tr>
<td><strong>PFPeA</strong></td>
<td>&lt;0.43</td>
<td>&lt;0.42</td>
</tr>
<tr>
<td><strong>PFHxA</strong></td>
<td>&lt;0.51</td>
<td>&lt;0.50</td>
</tr>
<tr>
<td><strong>PFHpA</strong></td>
<td>&lt;0.22</td>
<td>&lt;0.21</td>
</tr>
<tr>
<td><strong>PFOA</strong></td>
<td>&lt;0.75</td>
<td>&lt;0.73</td>
</tr>
<tr>
<td><strong>PFNA</strong></td>
<td>&lt;0.24</td>
<td>&lt;0.23</td>
</tr>
<tr>
<td><strong>PFDA</strong></td>
<td>&lt;0.27</td>
<td>&lt;0.27</td>
</tr>
<tr>
<td><strong>PFUnA</strong></td>
<td>&lt;0.97</td>
<td>&lt;0.95</td>
</tr>
<tr>
<td><strong>PFDoA</strong></td>
<td>&lt;0.049</td>
<td>&lt;0.47</td>
</tr>
<tr>
<td><strong>PFTrIDA</strong></td>
<td>&lt;1.1</td>
<td>&lt;1.1</td>
</tr>
<tr>
<td><strong>PFTeA</strong></td>
<td>&lt;0.26</td>
<td>&lt;0.25</td>
</tr>
<tr>
<td><strong>PFBS</strong></td>
<td>&lt;0.18</td>
<td>&lt;0.17</td>
</tr>
<tr>
<td><strong>PFHxS</strong></td>
<td>0.23(^{JB})</td>
<td>0.22(^{JB})</td>
</tr>
<tr>
<td><strong>PFHpS</strong></td>
<td>&lt;0.17</td>
<td>&lt;0.16</td>
</tr>
<tr>
<td><strong>PFOS</strong></td>
<td>&lt;0.48</td>
<td>&lt;0.46</td>
</tr>
<tr>
<td><strong>PFDS</strong></td>
<td>&lt;0.28</td>
<td>&lt;0.28</td>
</tr>
</tbody>
</table>

**Leach Test Procedure:**

- Load reactivated carbon into columns
- Backwashed for ~8 BV with NSF42 water (50 ppm TDS, 0.5ppm Cl\(^{-}\), pH 6.75)
- Soak 24 hours.
- Sample 1 BV.
- Repeat two more times compositing all 3 samples
- Analyze for PFAS per EPA 537

B: Compound was found in blank
J: Result is less than the RL but greater than or equal to the MDL and the concentration is an approximate value
Final Takeaways

GAC is effective and proven for removal of PFAS
- Long and short chain

Not all GAC is created equal
- Reagglomerated bituminous coal GAC is the preferred product type
- Field and lab data corroborate superior performance

Testing required to accurately predict service life
- Column > Isotherm
- Performance impacts cost
Thank you!

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