Presentation Overview

- Evaluating Remediation Technologies
- Sorption
- In Situ Technologies
- Dealing with Investigation-Derived Waste (IDW)
- Wrap-Up

Summary of Available Technologies – Drinking Water Treatment

<table>
<thead>
<tr>
<th>Technology Category</th>
<th>Technology</th>
<th>Maturity/Availability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorption</td>
<td>Activated Carbon*</td>
<td>Commercialized, can be purchased from vendors</td>
</tr>
<tr>
<td></td>
<td>Anion Exchange Resin*</td>
<td>Commercialized, can be purchased from vendors</td>
</tr>
<tr>
<td></td>
<td>Biochar</td>
<td>Field Pilot Scale, not commercially available</td>
</tr>
<tr>
<td></td>
<td>Zeolites/Clay Minerals</td>
<td>Commercialized, can be purchased from vendors</td>
</tr>
<tr>
<td>Membrane Filtration</td>
<td>Reverse Osmosis and Nanofiltration*</td>
<td>Commercialized, can be purchased from vendors</td>
</tr>
<tr>
<td>Coagulation</td>
<td>Specialty Coagulants</td>
<td>Field Pilot Scale, not commercially available</td>
</tr>
<tr>
<td>Redox Change</td>
<td>Electrochemical</td>
<td>Field Pilot Scale, not commercially available</td>
</tr>
<tr>
<td>Other</td>
<td>Sonochemical</td>
<td>Field Pilot Scale, not commercially available</td>
</tr>
</tbody>
</table>

* Technologies that will be discussed

Consider Effect of Prior Remediation for Co-Contaminants on PFAS

- Benzene plume
- Oxygen injections at yellow
- Elevated levels of PFAS at location of historical and present benzene plume – lacking in areas with no O2 injections
- Fourfold difference in Kd between PFHxS and PFOA yet their plume overlapped – likely due to in situ transformation of precursors
- Navy currently conducting similar study under NESDI

Summary of Available Technologies – Soil Treatment

<table>
<thead>
<tr>
<th>Technology Category</th>
<th>Technology</th>
<th>Maturity/Availability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorption and Technologies</td>
<td>Modified Carbon*</td>
<td>Commercialized, can be purchased from vendors</td>
</tr>
<tr>
<td></td>
<td>Minerals/Modified Minerals*</td>
<td>Commercialized, can be purchased from vendors</td>
</tr>
<tr>
<td>Excavation Disposal</td>
<td>To Landfill</td>
<td>Commercialized</td>
</tr>
<tr>
<td></td>
<td>To Incinerator</td>
<td>Commercialized</td>
</tr>
<tr>
<td>Thermal</td>
<td>Field Pilot Scale, commercially available</td>
<td></td>
</tr>
</tbody>
</table>

* Technologies that will be discussed

Pump-and-Treat

- At drinking water wellhead
- At point of use
- To control plume size/spread
- At base boundary to prevent plume migration

Key Point: Only practical treatment for groundwater available
Treatment Technologies for PFAS Site Management

Granular Activated Carbon (GAC)

Material
- Made from bituminous coal or coconut
- Highly porous, large surface area

Application
- Typically used in packed-bed flow-through vessels
- Operate in series (lead-lag) or parallel
- Virgin or Reactivated GAC

Granular Activated Carbon (cont.)

Mechanism
- Adsorption on surface process, physical mass transfer
- No chemical degradation or transformation

Effectiveness
- Capable of 90 to >99% removal efficiency
- Individual PFAS have different GAC breakthrough times
- e.g., GAC capacity for PFOS>PFOA
- Influent conc. for <5 Carbon PFAS typically lower
- High DOC reduces effectiveness

Reactivation of PFAS Contaminated Granular Activated Carbon

Thermal Reactivation Process
- Reactivation temperature 1,300°F
- PFAS pyrolysed to carbon char
- Lower CO₂ footprint than making virgin GAC
- Reactivated carbon may be just as effective as virgin carbon

Bituminous vs. Coconut Carbon

Reagglomerated coal
coconut
70 ppt EPA Health Advisory Exposure Limit
Concentration of PFOA 920 ng/L (ppt)
Simulated Empty Bed Contact Time (EBCT) 10 minutes
Background TOC 1.42 mg/L
Reagglomerated coal
coconut
Key Point
Bituminous carbon appears to perform better than coconut carbon at this specific site

Case Study – POET Vermont

- Initially sampled once per month for 3 months
- Influent, midpoint and effluent
- Influent PFOA Concentration >1,000 ppt; sample every 3 months
- Influent PFOA Concentration >200 ppt to <1,000 ppt sample every 6 months
- Influent PFOA Concentration <200 ppt every 12 months

Case Study – Point of Entry Treatment – Vermont Residences

- PFOA contamination from textile coating at CHEMFAB®
- >541 samples from private wells
- Bottled water delivered to residents
- 11 homes connected to municipal water
- 255 POET systems installed
Treatment Technologies for PFAS Site Management

Case Study POET Vermont – Results
- Influent concentrations vary from <20 ppt to 4,900 ppt
- Volume treated per unit from 50 gal over one month to 37,000 gal over 3 months
- Pre and post filter replaced every 4 months
- UV lap replaced every 12 months
- GAC replacement assumed every 2 years
- Swap lead and lag tank then ship GAC media to vendor

Case Study – NAS Brunswick, ME GWETS
- Former Naval Air Station in Brunswick, ME, BRAC 2011
- Treating CVOCs at GWETS using air stripping and GAC (vapor and liquid phase)
- Recovered over 500 kg VOCs since 1995; removal now limited by back diffusion rate, asymptotic range
- 1,4-Dioxane addressed by addition of HiPOx® unit
- PFAS removed via liquid-phase GAC
  - PFOA breakthrough determines changeout
  - Shorter-chain PFAS, carboxylates, break through earlier

Case Study – NAS Brunswick, ME GWETS – Results (cont.)

Ion Exchange
- Material
  - Synthetic neutral co-polymeric media (plastics) with positively-charged exchange sites
  - Can be regenerated (produces waste stream) or single use (must be disposed of properly)
- Application
  - Removes anionic PFAS binding to negatively-charged functional group
  - Lead-lag including combination of single use and regenered

Material
- Polystyrene polymer chain
- Exchangeable counter ion
- Fixed ion exchange group e.g., quaternary ammonium, — N+, for anion IEX
- Exchangeable counter ion e.g., chloride, Cl–, for anion IEX
- Synthetic neutral co-polymeric media (plastics)
Ion Exchange (cont.)

Mechanism
- Acts as ion exchange resin and adsorbent resin
- Positively charged anion exchange media
- Removes negatively-charged PFAS from water

Effectiveness
- Reaction kinetics faster than GAC
- Operating capacity higher than GAC
- Breakthrough varies for different PFAS
- Less frequent media change-outs

Considerations When Using Ion Exchange
- Type and concentration of inorganic ions in groundwater affect PFAS capacity of resin
- Bench-scale tests recommended to determine most effective resin
- More cost-effective at higher concentrations
- Organic matter may foul resin
- Co-contaminants compete for resin site
- Site-specific testing should be performed

Regeneration of Ion Exchange Resins
- Brine solution can desorb anionic head of PFAS from resin
- Organic solvent-like methanol or ethanol can desorb C-F tail
- Surfactants with both nonionic and anionic properties can be used as regenerants
- Most successful has been organic solvents and sodium chloride
- The solution used to regenerate may then need to be concentrated to minimize the volume of waste

Key Point: Shipped back to vendor for regeneration

Case Study – Comparison of GAC with Ion Exchange at Pease AFB
- Historic use of AFFF for firefighting training
- Note 6.2 FS 2nd highest concentration PFAS
- Ion Exchange – ECT Sorbix A3F
- GAC – Calgon Filtrasorb® 400 (F400)

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Sample Volume</th>
<th>Influent Concentration (mg/L)</th>
<th>Effluent Concentration (mg/L)</th>
<th>Breakthrough (Days)</th>
<th>Average Breakthrough (Days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>Note 6:2</td>
<td>6.2</td>
<td>0.04</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>PFHxS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFOA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFBS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFHpA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFHxA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Case Study – Comparison of GAC with Ion Exchange at Pease AFB (cont.)

GAC
- 4 vessels in series
- Each containing 5 gal F400
- Each vessel 5 min EBCT overall 20 min EBCT
- Samples collected at influent and after each vessel weekly for 8 weeks
- At 1.8 gpm treated 100,486 gal water (11,165 bed volumes)

Ion Exchange
- 3 vessels in series
- Each containing 5 gal resin
- Each vessel 2.5 min EBCT overall 7.5 min EBCT
- At 3.6 gpm treated 422,645 gal water (46,961 BVs)
- Samples collected routinely at influent and effluent

Entire Pilot Scale Setup

Reference: Steve Woodard John Berry Brandon Newman 2018 Ion Exchange Resins for PFAS Remediation Technologies
Case Study – Comparison of GAC with Ion Exchange at Pease AFB (cont.)

- Three regeneration trials using proprietary blend of organic solvent and brine
  - Step 1: Purge lead vessel with 1 BV 10% brine to prime resin for regeneration
  - Step 2: Pump 10 BV regenerant through resin counter flow
  - Step 3: Pump 10 BV potable water to rinse resin counter flow
  - Step 4: Return resin vessel to full service

Regenerant Solution Recovery
- Distill off solvent fraction into regenerant tank for reuse, left with concentrated brine PFAS fraction
- OR conduct superloading – process concentrated brine PFAS solution through adsorption media then recycle brine solution

In Situ Stabilization (ISS)
- Use of amendments for adsorbing and stabilizing PFAS in soil and groundwater
- GAC, stabilizers, and modified minerals (organoclays)
- Commercially available
- Additional amendments being developed
- Critical to monitor soil leachate to determine treatment effectiveness
- Limited full-scale application in U.S. (more overseas)

Activated Carbon for In Situ Water Treatment – PlumeStop®

Material
- Colloidal activated carbon
  - 1-2 µm sized particles of carbon suspended in water by organic polymer dispersion chemistry

Application
- In situ sorbent technology sorbs PFOS and PFOA from aqueous phase
- Treats dissolved-phase contaminants
- Applied by low-pressure injections
**Activated Carbon for In Situ Water Treatment – PlumeStop® (cont.)**

**Mechanism**
- Coats surface of soil
- Contaminants in dissolved phase then sorb to carbon
- Does not destroy PFAS, immobilizes PFAS in place
- Occupies just 0.1% soil pore volume

**Effectiveness**
- Reduces aqueous concentration to below 70 ng/L
- Radius of influence can be up to 25 ft
- Can be applied as multiple barriers perpendicular to plume

---

**In Situ Soil Treatment – Aluminum-Based Sorbent – Rembind Plus®**

**Material**
- Aluminum hydroxide, activated carbon, organic matter, and kaolinite

**Application**
- Apply to soil in ~2 to 5% by weight
- Adjust to 30% moisture content
- Binding occurs in 24 hours
- Pilot tested for water treatment

---

**In Situ Soil Treatment – Aluminum-Based Sorbent – Rembind Plus® (cont.)**

**Mechanism**
- Aluminum hydroxide binds to functional head of PFAS by electrostatic interactions
- Activated carbon and organic matter binds to tail via hydrophobic interactions and Van der Waals forces

---

**In Situ Soil Treatment – Aluminum-Based Sorbent – Rembind Plus® (cont.)**

**Aluminum-Based Sorbent for GW Case Study – Air Force Site**

- Historical use of AFFF at site
- Full-scale GAC system: two 20,000-lb GAC vessels in operation to remove PFOS/PFOA from groundwater
- Goal of pilot study to evaluate sorption capacity of RemBind Plus®

---

**Aluminum-Based Sorbent for GW Case Study – Air Force Site (cont.)**

- 30-gal batch reactor pilot test set up next to GAC system
- 30 gal of contaminated water mixed 1.135 kg aluminum-based sorbent for one hour and allowed to settle overnight
- Next day treated GW moved to effluent tank and contaminated GW added to tank with amendment without replacing amendment
- Run for 2 weeks treating 280 gal water
- Monitored for 53 PFAS compounds and TOP assay
- TOC also monitored
### Types of IDW

**Liquid Waste**
- Purge water from groundwater sampling
- Concentrated AFFF

**Solid Waste**
- Well installation waste (soil cuttings)
- Soil cuttings from core sampling
- Spent GAC
- Spent ion exchange resin
- Soil from excavations

### Challenges with Handling IDW

- PFAS are considered non-hazardous (can be disposed of in any landfill)
- Landfill refusal to accept PFAS waste
- Potential for future liability
- Risk of landfill leachate

### Considerations for Liquid IDW

- If PFAS concentrations are below regulatory levels, water may be considered to be disposed to sanitary sewer/POTW
- At sites where there is a PFAS GWETS, purge water should be considered to be treated in that system with operator approval
- Consideration should be given to have purge water pass through a drum of GAC, held in a receiving tank pending analysis
- If below regulatory values, GW may be able to be discharged to the sanitary sewer/POTW
- Purge water may be able to be sent to an off-site treatment facility willing to accept it

### Considerations for Solid IDW

- Currently sending to a landfill or a treatment facility may be the only choice
- As treatment becomes more common, the soil cuttings may be treatable on-site (e.g., thermal)
- PFAS waste is non-hazardous*, so 90 day rule may not apply
- Option – retain material on site as treatment approaches and policies are developed
- EXWC conducting research on treatment for IDW and source zone soils

### Key Points

- GAC may be the only practical treatment for groundwater to date
- PFAS <5 carbons much shorter breakthrough times
- Bituminous carbon may perform better than coconut carbon but depends on site conditions
- Ion exchange resin may be better at removing PFAS and can be regenerated but may be more expensive
- In situ treatment technologies PlumeStop®, RemBind Plus® and MatCARE™ limited field demonstrations in U.S.
Mechanism of Sorption – Electrostatic Interaction

- Interaction between negative and positive charges
- Strong negative charged shell around CF chain due to fluorine atoms and functional group
- Electrostatic bond mainly at functional group due to stronger negative charge
- To promote electrostatic bond increase ionic strength, ensure pH is not too alkaline
- Example seen in organoclay

Reference:

Mechanism of Sorption – Hydrophobic Interactions

- Occurs at the electronegative CF chain
- Longer chain more hydrophobic
- Leads to formation of micelles
- Is often stronger than electrostatic repulsion (between negatively-charged tail and negatively-charged sorbent)

FRTR 2018: PFAS Emerging Contaminants and Remediation Technologies

In Situ Soil Treatment Modified Organoclay Sorbent – MatCARE™

Material
- Palygorskite-based material modified with oleylamine, i.e., amine modified clay sorbent

Application
- Applied to soil at 10% w/w
- Water content of soil 60%

FRTR 2018: PFAS Emerging Contaminants and Remediation Technologies
In Situ Soil Treatment Modified Organoclay Sorbent – Soil Treatability Studies

- Four soils from fire training areas at overseas Air Force Bases
- Air-dried, homogenized, and passed through 2-mm sieve
- pH, organic carbon content, and PFOS concentration
- 1 kg of each soil adjusted to 60% moisture, amendment added at 10 g per 100 g soil
- PFOS-spiked treatment also included (10 ml of PFOS stock solution) then mixed
- 10 g sample, 3x/yr
- Water extraction

### Physico-Chemical Properties of the Soil

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH</th>
<th>TOC (%)</th>
<th>PFOS (nmol g⁻¹)</th>
<th>Texture</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4.8</td>
<td>0.96</td>
<td>3.66</td>
<td>Sandy clay loam</td>
</tr>
<tr>
<td>B</td>
<td>4.9</td>
<td>1.97</td>
<td>148.72</td>
<td>Clay loam</td>
</tr>
<tr>
<td>C</td>
<td>8.1</td>
<td>0.29</td>
<td>32.33</td>
<td>Sandy loam</td>
</tr>
<tr>
<td>D</td>
<td>6.5</td>
<td>2.03</td>
<td>18.52</td>
<td>Sandy clay loam</td>
</tr>
</tbody>
</table>

### In Situ Soil Treatment Modified Organoclay Sorbent – Results

<table>
<thead>
<tr>
<th>Temperature</th>
<th>25°C no spike</th>
<th>25°C spike with 0.2 mmol/kg PFOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sorbent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil D</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Water Treatment – Aluminum-Based Sorbent/GAC Comparison

<table>
<thead>
<tr>
<th></th>
<th>Aluminum Adsorbent</th>
<th>Activated Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bind short-chain PFAS</td>
<td>High efficiency</td>
<td>Low efficiency</td>
</tr>
<tr>
<td>Easy to apply in field</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Availability of large volumes</td>
<td>1-2 weeks</td>
<td>1-2 Months</td>
</tr>
<tr>
<td>PFOS adsorption capacity</td>
<td>2,000 µg/g</td>
<td>1,500 µg/g</td>
</tr>
</tbody>
</table>

Aluminum-Based Sorbent for Full-Scale Soil Treatment Case Study

- Airport contaminated with PFAS
- Replacing asphalt – excavated 900 tons of PFAS-contaminated soil

Aluminum-Based Sorbent for Full-Scale Soil Treatment Case Study (cont.)

- 900 tons of contaminated soil
- PFOS total concentration <5.7 mg/kg
- PFOS leachable concentration <180 µg/L (by USEPA Method 1311)
Aluminum-Based Sorbent for Full-Scale Soil Treatment Case Study (cont.)

- Transported 900 tonnes of soil to municipal waste landfill site
- Treated hotspots with 10% RemBind®
- Validated samples at accredited lab
- Obtained EPA approval for disposal in a purpose-built burial cell

In Situ Technologies

• Transported 900 tonnes of soil to municipal waste landfill site
• Treated hotspots with 10% RemBind®
• Validated samples at accredited lab
• Obtained EPA approval for disposal in a purpose-built burial cell

In Situ Technologies

Aluminum-Based Sorbent for Full-Scale Soil Treatment Case Study (cont.)

Soil Leachate after Treatment

<table>
<thead>
<tr>
<th>Activity</th>
<th>Approximate Cost ($)</th>
<th>Cost per Ton (900 Tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Landfill disposal fees</td>
<td>$63,500</td>
<td>$67</td>
</tr>
<tr>
<td>Investigation, bench trials, mixing, and reagent supply</td>
<td>$47,500</td>
<td>$50</td>
</tr>
<tr>
<td>Total</td>
<td>$111,000</td>
<td>$117</td>
</tr>
</tbody>
</table>

In Situ Technologies

• A water authority in Cape Cod, MA treated soil with amendment in the bottom of an excavation before backfilling to mitigate the risk of PFAS leaching in a drinking water source

In Situ Technologies

Influence of a commercial adsorbent on the leaching behaviour and bioavailability of selected perfluoroalkyl acids (PFAAs) from soil impacted by PFAS.