Demonstrated Treatment Technologies

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Learning Objectives

What we will learn:

- What technologies are commercial and available now for the treatment of PFAS in both soil and water?
- What developing technologies exist that may be available in the future?
- What are the key features of each technology?
- What are the advantages/disadvantages and limitations of each technology?
PFAS Treatment Technologies

ITRC Defined Three Categories:

- **Field Implemented Technologies** – Technologies that have been demonstrated under full-scale conditions at multiple sites, by multiple practitioners and multiple applications are well documented in peer-reviewed literature.

- **Limited Application Technologies** – Technologies that have been implemented on a limited number of sites, by a limited number of practitioners, and may not have been documented in peer-reviewed literature.

- **Developing Technologies** – Technologies that have been researched at the laboratory or bench scale, but these technologies have not been field demonstrated.
Water Treatment

- Effective conventional approaches, with limitations:
  - Carbon adsorption
  - Resin adsorption
  - Reverse osmosis

- Typically ineffective conventional technologies:
  - Air stripping, air sparging

- Technologies in development:
  - Examples include - bioremediation, chemical oxidation, chemical reduction, thermal desorption, electrochemical, others

- Be aware of precursor transformations via treatment processes, particularly with oxidation and biodegradation

- Treatment objectives can drive the decision making
Activated Carbon

- Granular Activated Carbon (GAC) most widely used technology.
- GAC performance varies based on site-specific conditions, carbon source types and manufacturing methods.
- Shorter-chain PFAS break through faster than longer chain, but generally still within the range considered feasible.
- GAC less effective for PFCAs than PFSAs of same C-F chain length.

Photo used with permission: Calgon Carbon Corporation, 2018
Typical GAC Process Diagram

- **Influent GAC vessel**
  - “Lead”
- **Second GAC vessel**
  - “Lag”
- **Monitoring**
  - Influent
  - Mid-point
  - Effluent
- **Carbon Change Out**
  - Lead to reactivation
  - Lag to lead
  - New to lag

Diagram used with permission: Calgon Carbon Corporation, 2018
Reactivated Carbon

- GAC can be “reactivated” under high temperature and reused.
- Less aggressive “regeneration” methods are not appropriate for PFAS.
- Contract reactivation services provided by most GAC suppliers (e.g., round trip service).
- Reactivated carbon typically used in wastewater and groundwater remediation applications.
- For drinking water applications, reactivated carbon should be used with caution to avoid commingling with carbon from other sources. Must comply with AWWA B605-13 Reactivation of Granular Activated Carbon standard.
GAC Testing

- **Isotherm Testing**
  - Batch test to evaluate GAC adsorptive capacity

- **Rapid Small-Scale Column Tests (RSSCT)**
  - Simulates full-scale performance in short period of time
  - Small diameter (less 1.0 cm ID) are typical
  - Identifies carbon type, breakthrough data, usage rates
  - Can be used to calibrate vendor models

- **Pilot testing**
  - When water quality variability or combinations of processes are necessary.
Isotherm Testing

- Not a dynamic indicator of full scale performance
- Provides screening-level understanding of effectiveness

Solution in contact with increasing amount of carbon

Equilibrium Reached

Graphics used with permission: Calgon Carbon Corporation, 2018
Column Testing Example

- Less effective for shorter chain carbon compounds (PFBS and PFHxA).
- Differences between sulfonates and carboxylates.
- Initial breakthrough above detection:
  - PFBS at 256 days.
  - PFHxA at 311 days.
  - PFHpA at 367 days.

Graph courtesy of Langan, with permission of client.
Ion Exchange (IX) Resin vs. GAC

PFOS – Perfluorooctane Sulfonate

GAC removes by adsorption using hydrophobic “Tail”

Selective IX Resins removes by both ion exchange and adsorption using both “Head” & “Tail”

Figure Courtesy of Langan/Adapted from Purolite
Single-Use Selective Resin + Incineration

- Use Selective Resin + Incineration
- Short Contact Time ~3 mins
- Simple & Effective - Operator Preferred

Treated water

PFAS in water

PFAS loaded resin

Incineration or other disposal alternative

Illustrations courtesy of Purolite, Inc.
Single-Use Selective Resin

- Simple, field-demonstrated
- High removal effectiveness
- Small footprint/headscape
- High operating capacity
  - 100,000 to 350,000 BV
- Operation costs
  - Need to be based upon site-specific resin usage rates and disposal costs

Example Ion Exchange Removal Curves at Specific Influent Concentrations

Data courtesy of Purolite, Inc.
Precautions in Reviewing Data

- Compare apples to apples
  - Empty bed contact time (ECBT)
    - GAC EBCT for this study is half of what is typically (10-12 min) used
    - IX EBCT is shorter (2-3 min)
  - Compare gallons treated before breakthrough, the difference between GAC and IX may be less pronounced
  - Factors that impact effectiveness
    - Site specific geochemical parameters
    - Co-contaminants
    - Other factors

- Consider site-specific testing before selecting sorptive media

Data courtesy of Purolite, Inc.
Regenerable Ion Exchange Resins

- Demonstrated on the bench to be equally effective after multiple regeneration cycles
- Regeneration solution is solvent and brine
- Solvent can be recovered and reused
- Distilled brine runs through GAC then is loaded on high-capacity IX media for incineration
- The low volume, high concentration liquid waste may in the future be able to be destroyed with destructive options (developing technologies such as non-thermal plasma, electrochemical oxidation)
Regenerable Resin Process
In Situ Sorption

- Colloidal activated carbon with a biopolymer
- Technology widely demonstrated for VOCs
- Can be installed as a treatment barrier
- Full-scale demonstrations at several sites
- Unknown longevity, but modeling predicts >100 years

Graphics used with permission of Regenesis, Inc., after: Rick McGregor, Remediation, 2018; 28:33-41
Reverse Osmosis

- Membrane Processes
- Effective for PFAS
  - High pressure membrane
  - High energy usage
  - Reject water disposal
  - Typically used on lower flow rates
  - Questions about sustainability
- Removes a wide range of constituents:
  - Including hardness, dissolved solids, as well as VOCs and PFAS
- Costly
  - Capital
  - Operating
Flocculation/Coagulation

- Pre-treatment technology
- Many products have been tested:
  - Alum, ferrate, ferric sulfate, Polydiallyldimethylammonium chloride (polyDADMAC)
- Multiple flocculants can be used to address varied chain lengths
- Pilot-scale systems in Europe
- Sludge disposal is needed
- Carbon or Resin Polishing
  - Results in less disposal quantities than GAC directly
  - Non-detect concentrations with adsorbent polishing

Photos courtesy of Bill DiGuiseppi, Jacobs
Soil Remediation Technologies

- **Conventional**
  - Excavation and landfill
  - Excavation and offsite incineration
  - Stabilization

- **Developing/Limited demonstrations**
  - Soil Washing
  - Thermal
Soil Remedial Technologies

- Excavation with offsite disposal in a permitted landfill, where allowed.
  - Out of abundance of caution, some landfills no longer will accept PFAS soils. Do not assume this is straightforward.

- Excavation with offsite incineration
  - Must be >1,100°C for PFAS
  - Destruction assumed but not well documented

Photo courtesy of CH2M/Jacobs
Soil Remediation Technology

- Stabilization/Immobilization via sorption
- Combination of powder-based reagents with high surface area and various binding methods:
  - Powdered activated carbon, aluminum hydroxide, kaolin clay
  - Added from 1-5% by weight to soil
  - Fully commercial & demonstrated in Australia
  - Extensive testing, research and demonstration in Europe

Images courtesy of Ziltek™ and AquaBlok Ltd.
Treatability Study: PFOS/PFOA in Soil

- Two commercial airport sites in Australia
- Site soils mixed with proprietary combination of GAC and additives at various addition rates
- Soil leachates prepared using the Toxicity Characteristic Leaching Procedure (TCLP)

Data courtesy of Ziltek Pty Ltd.
Soil Stabilization Example

- 1,100 tons PFAS impacted soils stabilized on-site at two airports during upgrade activities.
- Transport and disposal in a purpose-built burial cell located at a municipal waste landfill site.
- Cell lined and covered with stabilization agent.
- EPA Test Method 1311 and 1320 (TCLP and MEP) to verify performance.

Photos and information courtesy of Ziltek Pty Ltd. Cell design graphic courtesy of Langan
Developing - Treatment Technologies
Stewart Abrams, PE
Langan Engineering and Environmental Services, Inc.
Developing Separation Technologies

- **Zeolites**
  - Microporous aluminosilicate minerals
  - Limited testing beyond PFOS/PFOA
  - Less sorptive than GAC
  - Requires disposal/destruction of media

- **Foam Fractionation**
  - Air microbubbles separate PFAS
  - Demonstrated in Australia

- **Biochar**
  - Pyrolyzed biomass to create charcoal
  - Demonstrated on wide variety of PFAS
  - Limited effectiveness on short-chain PFAS
  - Competitive sorption an issue
  - Requires disposal/destruction of media
PAC+Additives* Ex-Situ Adsorption

- Evaluated in Australia, U.S. and Germany
- Passed PFAS contaminated water (1.8 mg/L) through two different columns, up to 100 pore volumes
  - One column with activated carbon
  - One column with powder activated carbon and additives
- Evaluated short- and long-chain PFAS
- Removed shorter chain PFAS more effectively than activated carbon alone

* Rembind™. Data courtesy of Ziltek Pty Ltd.
Electrochemical Coagulation

- Electrical charges generate metal hydroxide floc
- Floc is polar and sorbs to PFAS
- Optimal energy, plate material, and pH control kinetics
- Zinc anode shown to be best
- Waste sludge disposal is needed

\[
\text{ZnO/Zn}_{0.70}\text{Al}_{0.30}(\text{OH})_2(\text{CO}_3)_{0.15}\times\text{H}_2\text{O}
\]

Figure courtesy of Bill DiGuiseppi, Jacobs
Electrochemical Oxidation

- Use of direct current (DC) to degrade PFAS
  - Electrode material (Boron-doped diamond, MMO, lead-dioxide etc.)
  - Major byproducts: Fluoride ions, shorter-chain PFAS, perchlorate
  - Limitations

Source: Schaefer et al. 2015

Oxidation/Reduction Approaches

- Activated Persulfate
  - High-temperature activation found to oxidize PFCAs, but not PFSA. Subject of current SERDP research.

- Photolysis
  - Typically in presence of catalyst
  - Geochemistry has profound effect

- E-Beam
  - Established, but not common, destructive technology for other recalcitrant chemicals
  - Tested for PFAS in academic lab
  - Oxidizing/reducing chemical reactions
Chemical Reduction

- **Zero Valent Metals**
  - Combination of sorption onto iron as well as reduction via dehydrohalogenation

- **Ultraviolet light + sulfite**
  - Creates hydrated electrons, strong reducing agents that react with carboxylates and sulfonates
  - Could be used for concentrate destruction

- **Vitamin B12 with titanium citrate**
  - Limited bench tests
  - Primarily attacks branched vs linear PFOS
  - Required high heat and pH in some cases

Images courtesy of Timm Strathmann, Colorado School of Mines
Sonolysis (Ultrasound)

- Sound waves >19 kHz create cavities in liquids
- Cavities collapse at maximum radius creating extreme localized conditions
  - High heat (5000K)
  - High pressure (1000 bar)
- PFAS sorb to the cavity interface
- Cavity collapses
  - Cleaves bond between hydrophobic and hydrophilic portions of molecules

Figures courtesy of Michelle Crimi, Clarkson
Plasma Treatment

- Uses electricity to convert water into mixture of highly reactive species
  - OH*, O, H*, HO₂*, O₂*, H₂, O₂, H₂O₂ and aqueous electrons (e⁻<sub>aq</sub>)
- Plasma formed by means of electrical discharge between one high voltage and one groundwater within or contacting the water
- Argon gas pumped through diffuser
  - Produces bubble layer on surface that concentrates PFAS

Photos courtesy of Selma Mededovic, Clarkson


Combined Remedy: Separate and Destroy

- In situ precursor transformation with oxidation
- Ex situ IX: regenerable resin
- Plasma destruction of concentrated PFAS in liquid

Figure courtesy of Michelle Crimi, Clarkson

SERDP ER18-1306; ESTCP ER-5015
Soil Separation/Washing

- A handful of bench and pilot scale tests
  - Torneman, 2017 – Two sites in Sweden
  - Ventia, 2018 – One site in Australia

- Minimally documented, but available results are positive

- Lower throughput for clay-rich soils

- Treatment of multiple waste streams (water, sludge) required

- Dry sieving may concentrate PFAS in limited volume fraction (i.e., clays and organic fines)
Thermal Desorption for PFAS in Soil

- Bench scale information
- Targeted for unsaturated zone AFFF source areas
- Would require wet scrubber and scrubber water treatment (GAC)
- Air discharge control would be needed

<table>
<thead>
<tr>
<th>Initial Total PFAS Conc. (µg/kg)</th>
<th>% Decrease in Total PFAS</th>
<th>Exposure Temperature/Time</th>
<th>Number of PFAS Analyzed</th>
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<tbody>
<tr>
<td>200</td>
<td>26</td>
<td>250°C 8 days</td>
<td>29</td>
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<tr>
<td>151</td>
<td>40 99.4</td>
<td>300°C 4 days 350°C 2 days</td>
<td>29</td>
</tr>
<tr>
<td>290</td>
<td>89.3-99.8 97.3-&gt;99.9* 99.8-&gt;99.9*</td>
<td>400°C 60 mins 550°C 50 mins 700°C 80 mins</td>
<td>29</td>
</tr>
</tbody>
</table>

* >99.9% decreases are based on the limited analytical suite performed and based on decreases below the Limits of Detection

Data courtesy of William DiGuiseppi, Jacobs
PFAS Remediation Technologies: Takeaways

- There are a lot of technologies with promise to treat PFAS
- There are only a few that are considered field implemented
  - Excavation and incineration or sorption/stabilization for soil
  - Pump and treat with GAC, membrane filtration, or ion exchange for water
- Limited application approaches
  - Thermal desorption or soil washing for soil
  - Injectable sorbents, coagulants for water
- Developing technologies
  - Destructive chemical treatment
- Treatment trains (combinations of unit processes) should be considered
- Treatability and pilot studies are the norm