DERP FORUM

Achieving Greater Success Through Strong Partnerships

November 14-17, 2023 • Kansas City, MO

PFAS Treatment Technologies in Practice

Defense Environmental Restoration Program (DERP) Forum

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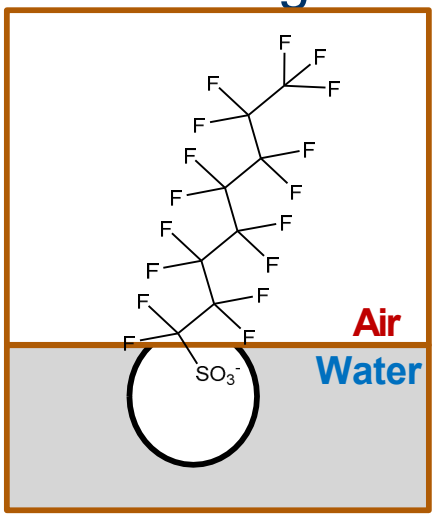
NAVFAC EXWC

Overview – PFAS Treatment

- Brief PFAS Background
- PFAS Separation Technologies (Liquid Streams)
  - Sorption (Granular Activated Carbon, Ion Exchange Resin)
    - *Not* covered (but also important): Organoclays
  - Foam Fractionation
  - Dispose or…
- Destroy PFAS
  - Incineration (Relatively well-developed technology, but some caveats)
  - Selected Methods in Development:
    - Supercritical Water Oxidation (SCWO) and HALT
    - Technologies *not* covered today (but also important): Plasma, Sonolysis, Electrochemical Oxidation
- Ongoing Efforts at EXWC

PFAS Basics in Brief

- PFAS are composed of highly stable carbon-fluorine (C-F) covalent bonds in the hydrophobic tail portion, and various ionizable functional groups in the head group(s)
- Fluorine has a large first ionization energy and electron affinity; it is the most electronegative element known
  - Strongest, shortest, single bond between carbon and any other atom
  - In general, PFAS are very stable and non-reactive (see below)
- C-F bond cleavage requires a *high energy input*
- PFAS "tail" = hydrophobic, polar "head group" = hydrophilic
  - General affinity for air-water interface (e.g., longer chain PFAS like PFOS and PFOA)
  - Short chain PFAS (e.g., PFBS, PFBA, etc.) have less hydrophobic properties than long chain PFAS → tend to remain in solution more than long chain counterparts
  - Hydrophobicity and charged head group also important for adsorption processes



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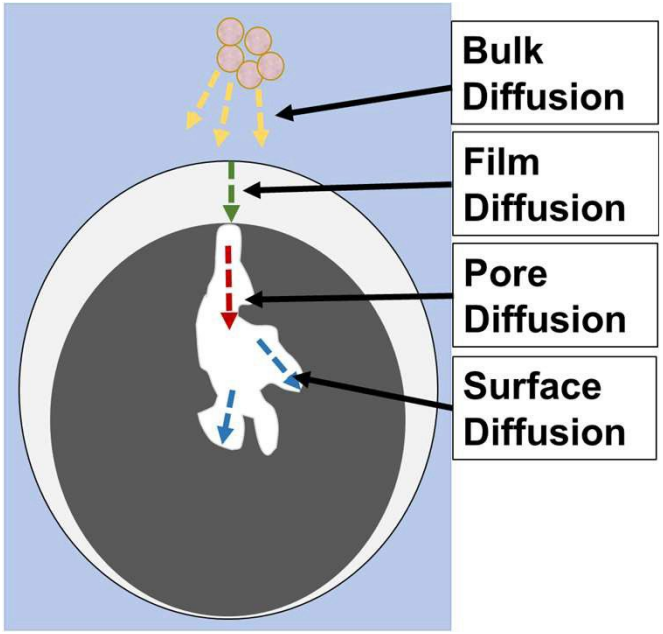
Separation Technologies

PFAS Separation from Liquid Using GAC

- Granular Activated Carbon
- Physical mass transfer from aqueous phase onto solid media
- GAC adsorption: bulk, film, pore, and surface diffusion
  - Van der Waals and/or other weak ionic forces to bind PFAS molecule to the surface
- Diffusion through liquid film (film diffusion); Diffusion through capillaries or pores (pore diffusion); Diffusion along pore surfaces (surface diffusion)
  - Longer contact times allows more time for greater pore diffusion



GAC - Applicability

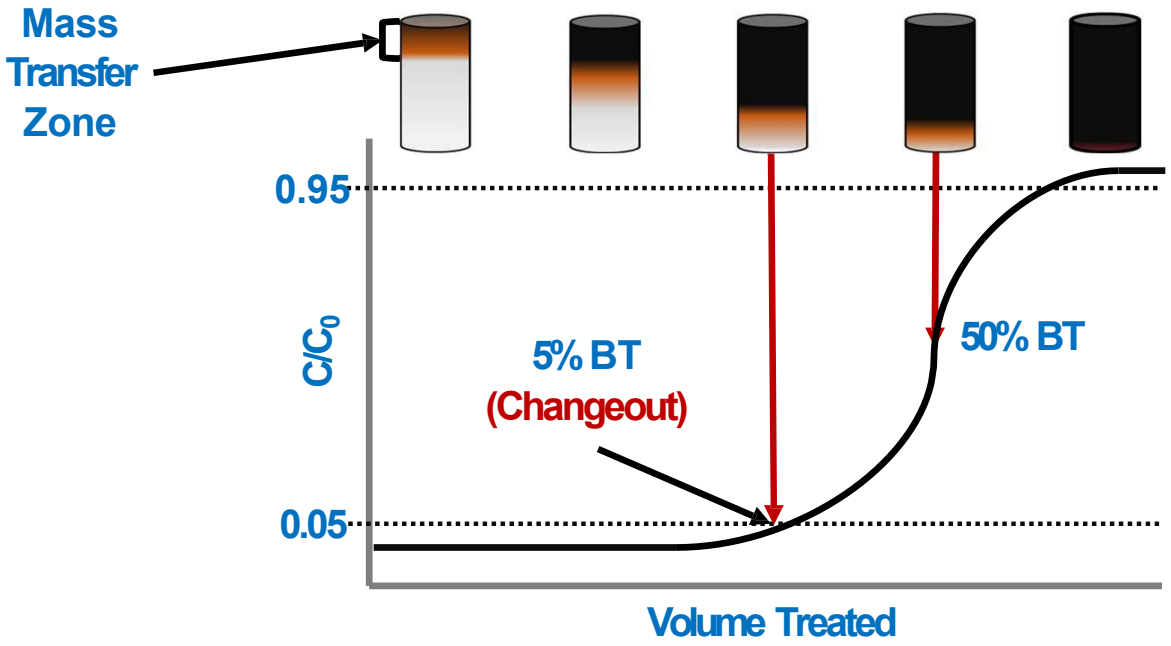
-Pump and treat; drinking water and groundwater (ppt-low ppb level); rapid breakthrough (BT) likely with high concentration PFAS

-Reliable for broad range of influent conditions/chemicals of concern

-May be "reactivated" (PFAS destruction; DiStefano et al., 2022)

-Integration with existing infrastructure

-10-20+ min EBCT effective range; 10-15 min EBCT typical

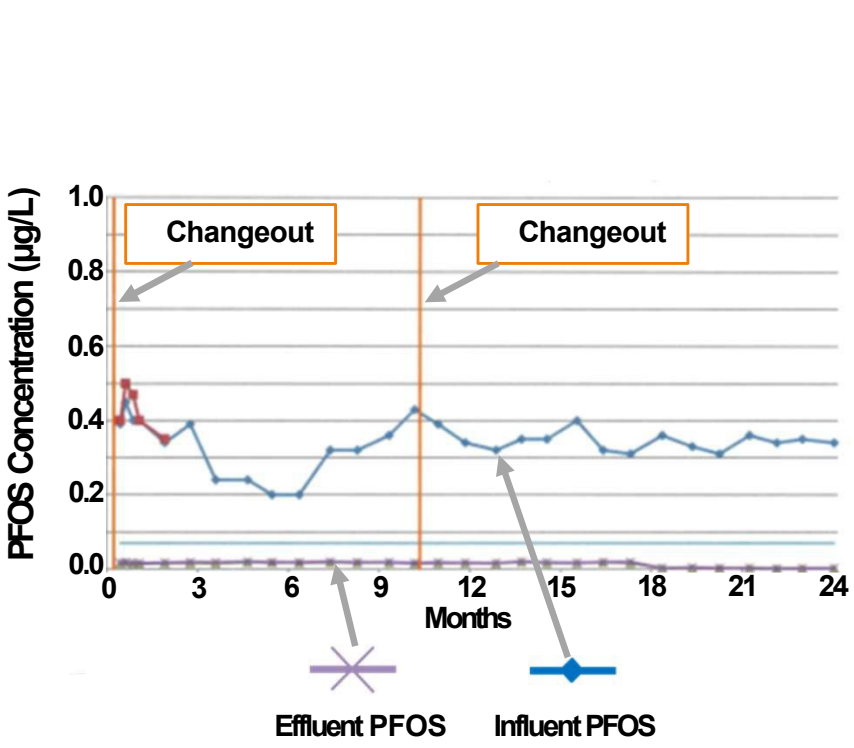


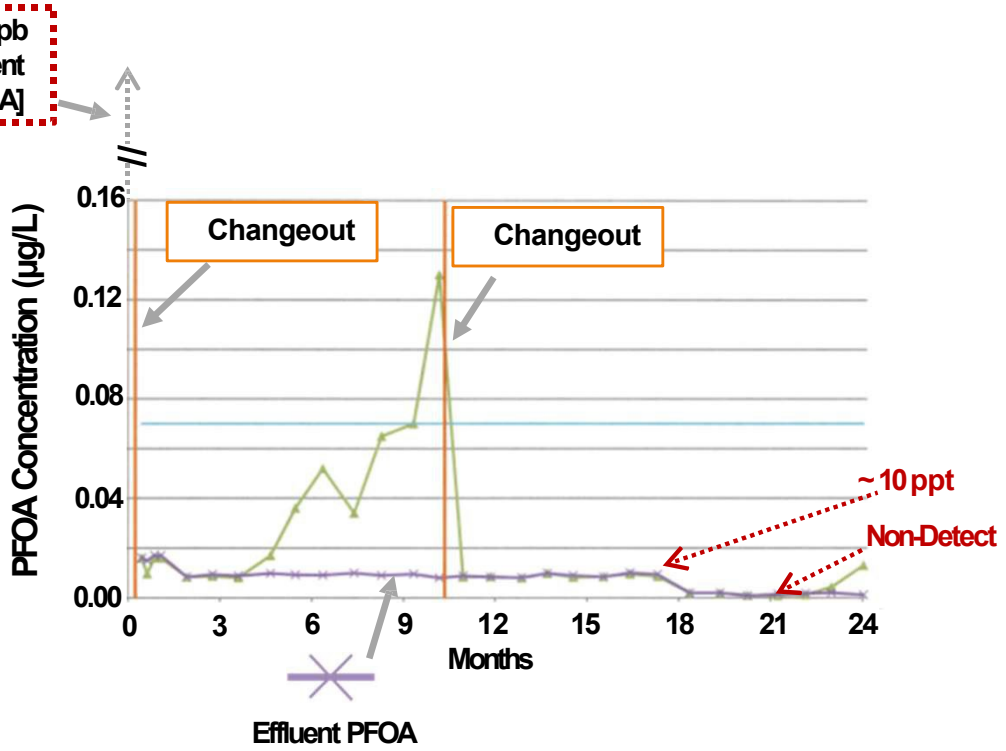
GAC - Process Limitations

- Selective nature of removal: In general, greater removal efficiency for sulfonates (e.g. PFOS, PFHxS, PFBS) vs. carboxylates (e.g. PFOA, PFHxA, PFBA)
- Chain length and sorption: Long chain > Short chain
- Short chain displacement by long chain PFAS & subsequent desorption
- Greater removal for linear isomers of PFOS, PFHxS, and perfluorooctane sulfonamide (FOSA) vs. branched isomers
- May require increased contact time

GAC Case Study

- Case study: NAS Brunswick GAC (F600) System





Note: Adsorption applications to be covered in greater detail in subsequent presentation

Ion Exchange

- **Applicability**
  - -Single use and regenerable resins
    - Single-use PFAS-selective IX resins ideal for low-concentration streams better since change-out would be less frequent
    - Regenerable resins better suited for removal of higher concentration PFAS
      - Savings realized from reusing the treatment media outweighs the cost of frequent replacement of non-regenerable media
  - -Low EBCT (~1.5-5 min), good for short chain PFAS removal
- **Process Limitations**
  - -Competitive adsorption with other anionic substances (e.g. salts)
  - -Fouling caused by NOM, iron, and other heavy organics; pre-treatment likely
  - -Non-regenerable resins: transport and disposal costs
  - -Regenerable resins: brine and flammable regenerant waste streams

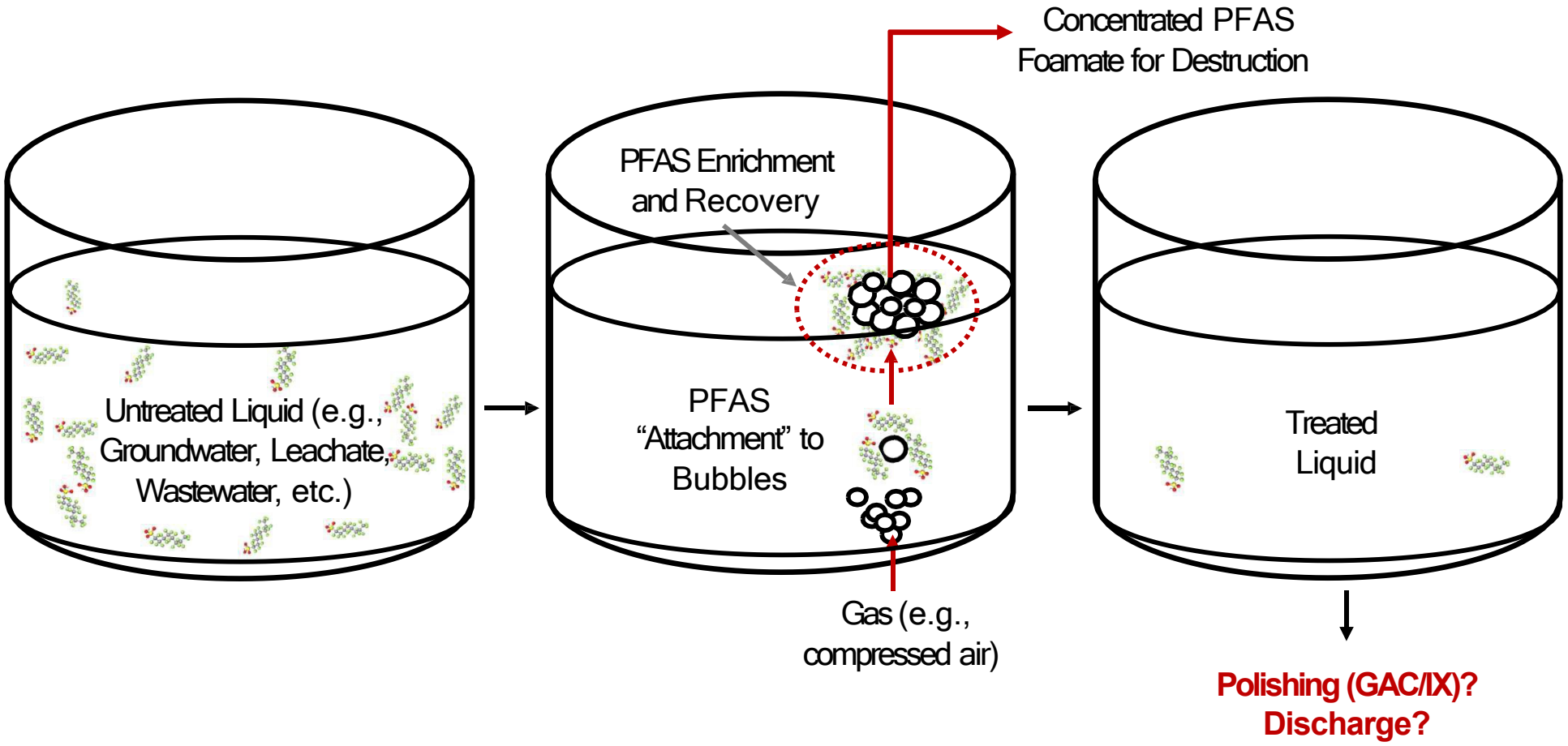
Ion Exchange (cont.)

- **Case Study**
- Comparison of GAC & regenerable IX Processes
- GAC EBCT total 20 min (4 tanks); 100,486 gallons of groundwater
- IX EBCT of 7.5 min; 422,645 gallons of groundwater
- Resin treated over eight times as many bed volumes (BVs) of groundwater as GAC before PFOS exceeded the USEPA Health Advisory (HA) and six times as many BVs for PFOA

From (Woodard et al., 2017)

Foam Fractionation

- Rapidly maturing and conceptually simple process to enrich and separate PFAS from liquids; no consumable media (GAC/IX)



Foam Fractionation

- Long chain PFAS more hydrophobic and greater affinity for air/water interface
  - Cationic surfactants addition can aid in short chain PFAS recovery
- Good process performance in complex streams, but may require post-treatment and/or polishing according to discharge requirements
  - Pretreatment generally non-issue, and ideal for moderate to high-strength PFAS streams
  - Perform economic analysis to evaluate savings potential
- Use as initial PFAS reduction strategy to greatly extend life of adsorption process or as standalone treatment, depending on discharge requirements
- Co-mingled VOCs and vapor phase treatment

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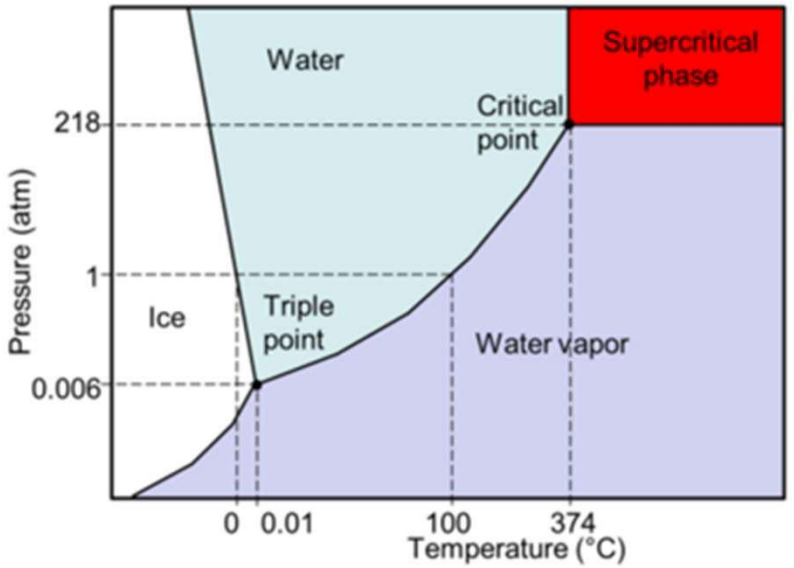
Destruction Technologies

Destructive Methods Currently Used
Incineration

- Solids or liquids are collected and sent to incineration facility
- Requires >1,400 °C for fluorinated organics (PFOS most recalcitrant)
- Cost Estimate: $11.6-23.2/gallon
- Some incineration facilities are restricting acceptance of PFAS-containing waste and soils
- OSD Incineration Prohibition Policy Update (14 July 2023)

Hydrothermal and Supercritical Water Oxidation

- **Theory**
- Combination of heat and pressure to achieve PFAS destruction in a reactor
- Alkaline Hydrothermal - cleavage of PFAS functional group catalyzed by OH-, followed by sequential carboxylation.
  - Addition of hydroxide salts lowers temperature required for destruction
- Supercritical water oxidation (SCWO) is uses unique properties of water above its critical point at 374°C and 3200 psi.
  - Oxygen is fully soluble in SC water and can increase rate of oxidation if supplied



Destructive Technologies
Hydrothermal and Supercritical Water Oxidation

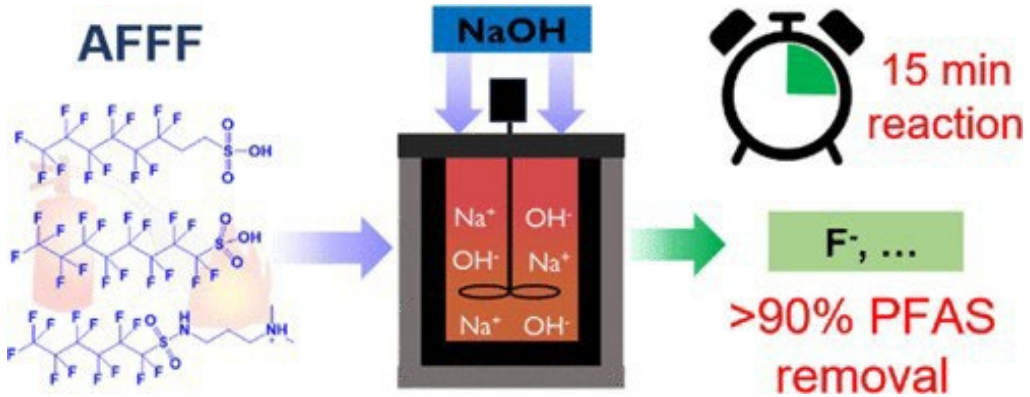
- **Applicability**
- PFAS destruction in high moisture content matrices
  - PFAS impacted liquids, concentrates, wastewater
- Soil, spent IX, and GAC can be slurried for treatment, easier reactor loading/unloading
- Batch and continuous processes under development

- **Limitations and Factors Affecting Performance**
- Requisite for high moisture content
- Capital costs for reactor
- Potential safety issues (high temperature and pressure)

Destructive Technologies

Hydrothermal and Supercritical Water Oxidation

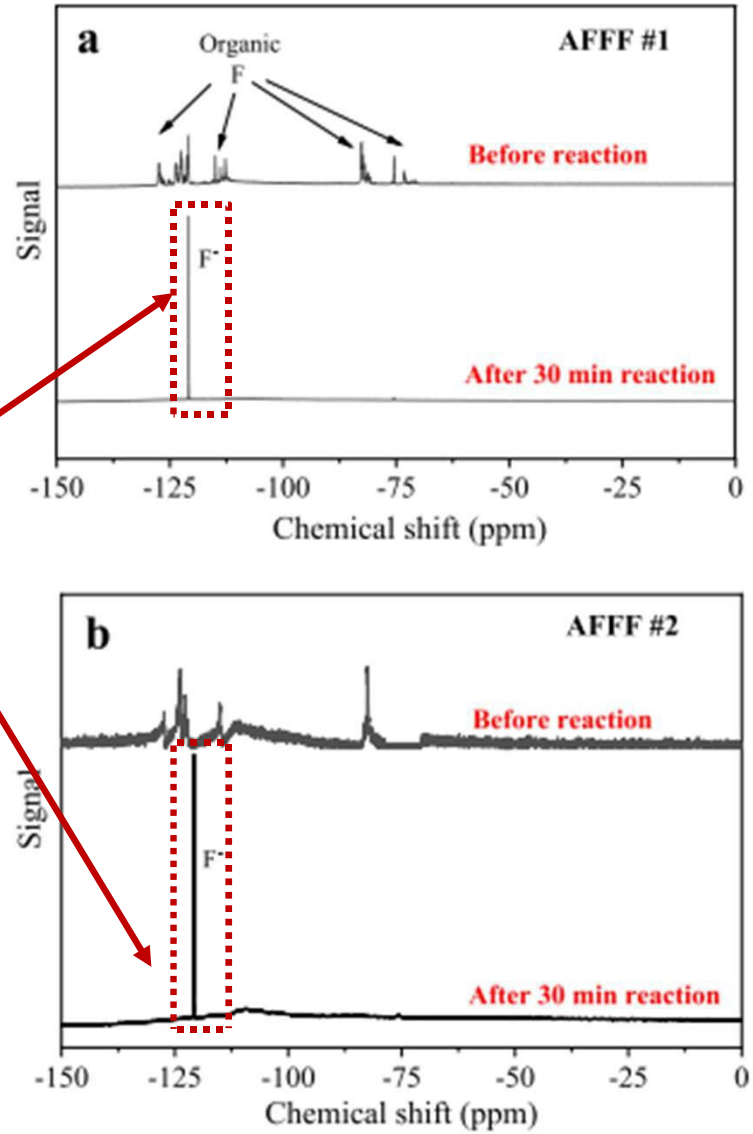
- **Case Study** - HALT
- Colorado School of Mines, Tongji University, Geosyntec
- Alkaline hydrothermal: Near critical temp and pressure (350 °C, 16.5 Mpa); 1-5 M NaOH addition
- Fed reactors with ECF and telomer-based AFFF formulations
- Reactors operated for up to 6 hours



(From Hao et al., 2021)

Hydrothermal and Supercritical Water Oxidation

- **Case Study** - HALT
- Most PFASs were non-detect within 15-30 min
- More recalcitrant PFAS required addition of 5 M NaOH
- ^{19}F NMR revealed mineralization/defluorination

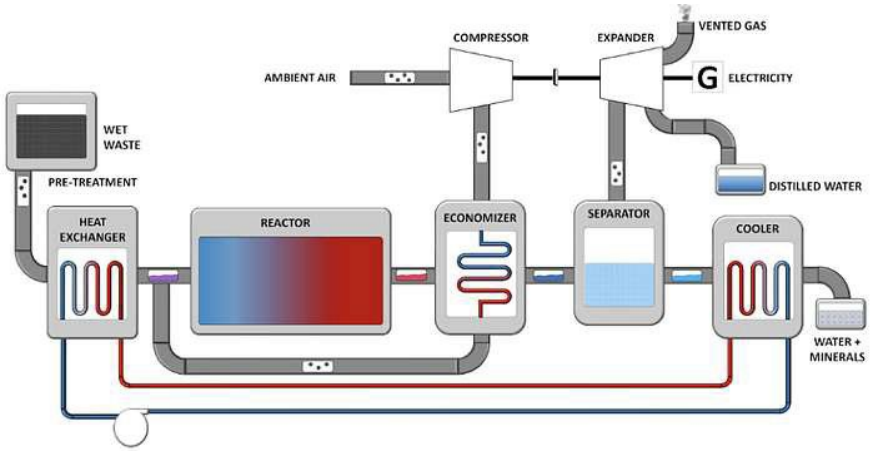


(From Hao et al., 2021)

Destructive Technologies

Hydrothermal and Supercritical Water Oxidation

- **Case Study** - Air-SCWO
- 374 Water, Duke Univ., US EPA PFAS Innovative Treatment Team (PITT)
- PFAS impacted municipal wastewater → Lime stabilized sludge (Maine)
- AFFF -Light Water 3% (diluted 30x)
- Nix1 Air-**SCWO** system
  - Reactor operated above 374 °C and 221 bar; Air introduced into reactor



(From 374 Water)

	Feedstock	Treated Effluent	Elimination
PFOS	110,000 ng/l	0.65 ng/l	99.99%
PFOA	<6200 ng/l	3.15 ng/l	99.99%
PFAS	(24 derivatives)	29.1 ng/l	99.99%

Concluding Remarks

- Many established and maturing technologies available for liquid treatment; soils/solids still catching up
  - General trend: ***concentrate*** from large volume to smaller volume, then ***destroy***
  - Note that "100%" removal is not accurate reporting – inquire about detection limits
- Low ppt treatment possible for a while, but consistently achieving these levels may require some adjustments. *Weigh initial capital vs. O&M costs on an individual site basis*
  - Increase contact time → larger sorbent infrastructure
  - Increase media changeout intervals (shorter BT time) → more consumables and disposal
  - Add "polishing" step(s) with specialized media
  - Complex or high-strength streams → evaluate maturing separation technologies (e.g., foam frac.)
    - "Polish" with filter media, as needed, to achieve lower limits

Select PFAS Treatment Investigations at NAVFAC EXWC

Concentrate PFAS from Liquids
In Situ Foam Fractionation with "D-FAS" Technology, ESTCP; Extracted Groundwater • Dissolved PFAS attaches to gas bubbles and foam is created at surface → PFAS foam captured • Treats wide range of liquids and concentrations: groundwater, wastewater, etc.
Drop-in Sorption Packets for PFAS Treatment of IDW and Stored Water
Concentrate PFAS from Soil
In Situ Thermal Treatment of PFAS in Vadose Zone
Expanding NAVFAC EXWC's PFAS-Impacted Treatment Feasibility Testing Toolbox
Closed Loop *In Situ* Soil Flushing at PFAS-Impacted Sources
Immobilize PFAS In Situ
In Situ Activated Carbon Sorptive Barrier for PFAS Remediation in Coastal Sites
Novel, Hybrid Polyelectrolyte/Hydrophilic Polymer for In-situ PFAS Treatment
Destroy PFAS
Photocatalytic Investigation Derived Waste Treatment of PFAS
Innovative PFAS Destructive Technologies for Treatment of Soil and Other Media
Bench-Scale Evaluation of Supercritical Water Oxidation (SCWO) to Destroy PFAS in Aqueous IDW and Complex Waste Streams
Application of SCWO to Destroy PFAS Impacted Groundwater Waste Streams
Super Critical Water Oxidation of PFAS on Spent Sorbents and Ion Exchange Resins