Lines of Evidence Approach to Confirm the Efficacy of Conventional and Destructive PFAS Treatment Technologies

Midwest Environmental Compliance Conference
24 September 2024

AGENDA

PFAS 101

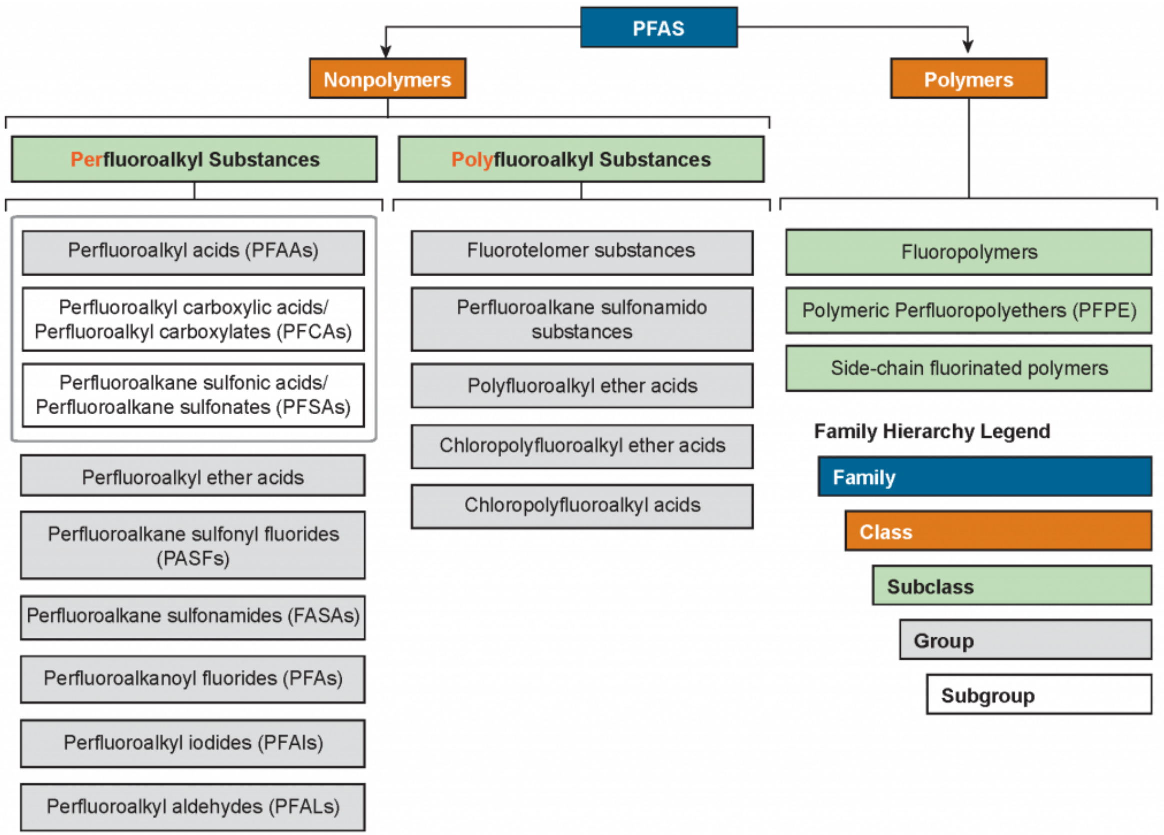
PFAS Regulation Updates

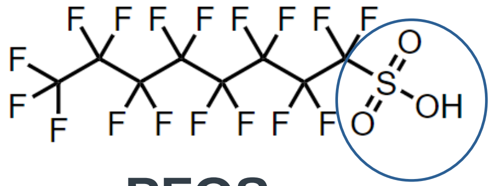
PFAS Treatment

Questions?

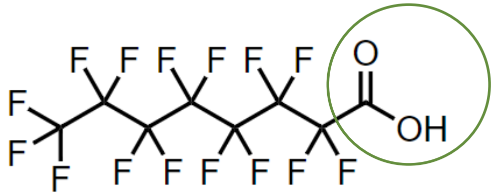
PFAS 101

WHAT ARE PFAS?

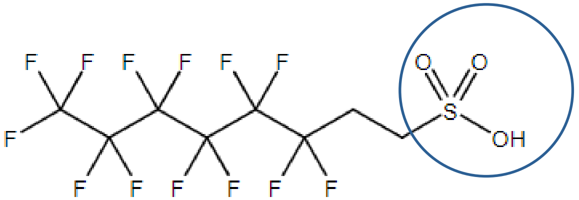




PFOS



PFOA



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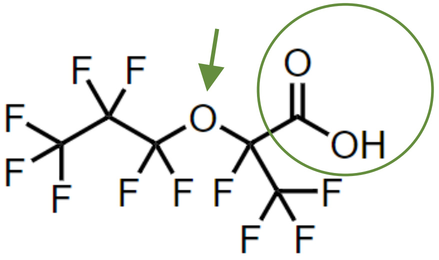


GenX

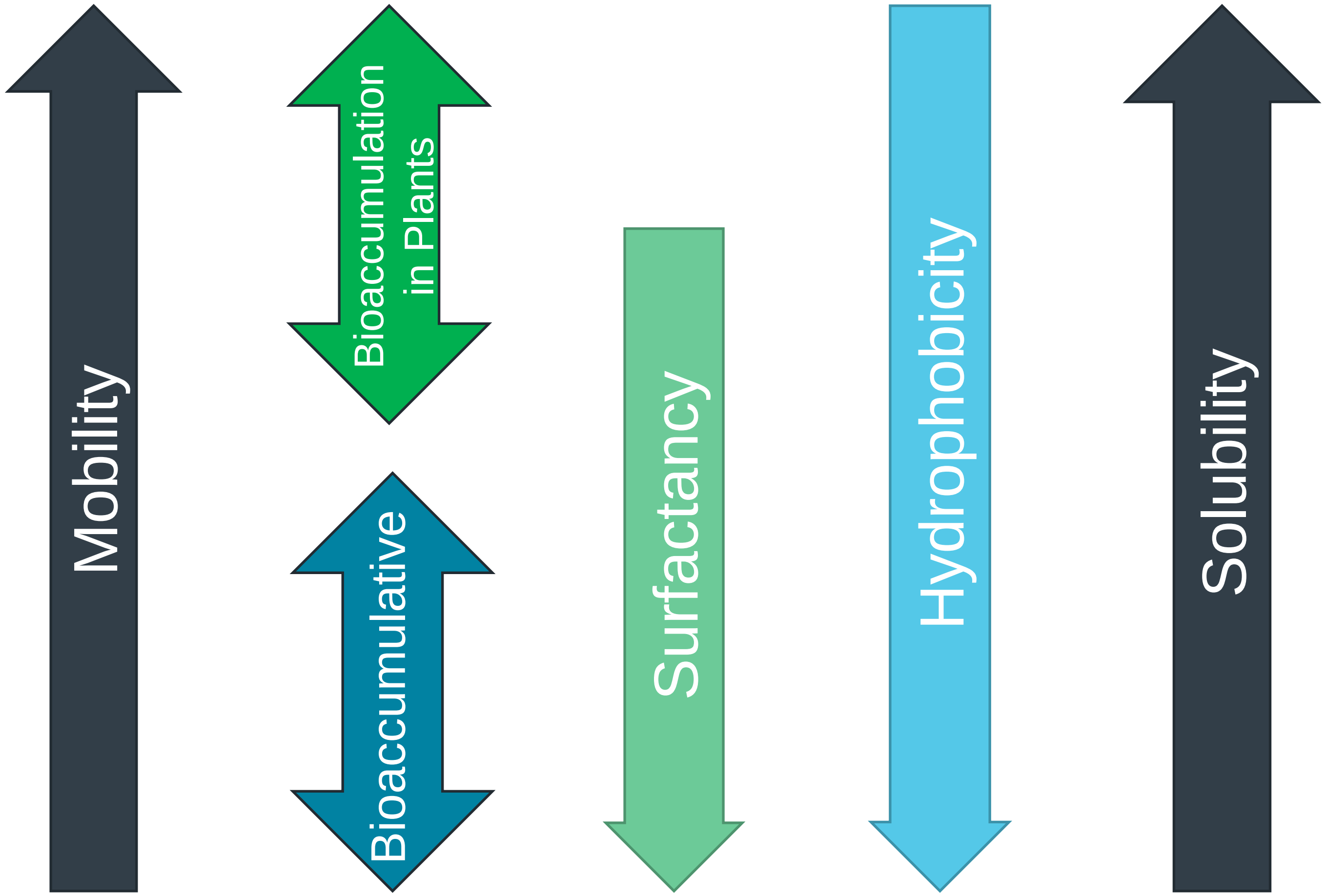
Source: ITRC

PFAS ≈ ORGANIC CHEMISTRY + FLUORINE

PFAS Attribute	General Outcome
Molecule Size (# of Carbons)	Smaller ≈ more mobile, harder to treat
Linear v. Branched	Branched ≈ more mobile
Degree of fluorination	Fewer fluorenes ≈ more mobile
Functional Groups	
- *Charge*	*Charged ≈ more mobile*
- *Transformations*	*Degrade into terminal PFAS*

NGWA, PFAS Fate and Transport 2021

PFAS CHAIN LENGTHS



Ultrashor C1-C3
- C2 Perfluoroethanoic acid (PFEA)
- C3 Perfluoropropanoic acid (PFPrA)

Short C4-C7
- C4 Perfluorobutanoic acid (PFBA)
- C5 Perfluoropentanoic acid (PFPeA)
- C6 Perfluorohexanoic acid (PFHxA)
- C7 Perfluoroheptanoic acid (PFHpA)

Long >C8
- C8 Perfluorooctanoic acid (PFOA)
- C9 Perfluorononanoic acid (PFNA)
- C14 Perfluorotetradecanoic acid (PFTeDA)

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PFAS REGULATION UPDATES

STATE OF REGULATIONS

DRINKING WATER

- Maximum Contaminant Limits (MCLs)
- MCL Goals (MCLGs)
- Hazard Index

CERCLA

- PFOA and PFOS, plus precursors
- “Categories of PFAS”

RCRA

- Proposed Rule in Federal Register Feb. 2024
- Nine PFAS as COCs
- Expand definition of “hazardous waste”

TSCA/TRI

TSCA Reporting

- Final Rule
- Manufactures and importers must report PFAS

TRI Reporting

- Requires reporting of 196 PFAS compounds
- Not subject to *de minimis* exemption

FEDERAL DRINKING WATER REGULATION

PFAS	Individual MCL	Hazard Index MCL*	Health-Based Water Concentration
PFOA	4.0 ppt	--	--
PFOS	4.0 ppt	--	--
PFHxS	10 ppt	1 (unitless)	10 ppt
PFNA	10 ppt		10 ppt
HFPO-DA (GenX Chemicals)	10 ppt		10 ppt
PFBS	--		2,000 ppt

MCL = Maximum Contaminant Level;
ppt = parts per trillion; *for mixtures of ≥ 2 PFAS

CERCLA

- On April 19, 2024, EPA announced the designation of PFOA and PFOS as hazardous substances under CERCLA
  - PFOA and PFOS salts and structural isomers also included
- “When released into the environment, [hazardous substances] may present substantial danger to the public health or welfare or the environment”
- In April 2023, EPA issued an Advance Notice of Proposed Rulemaking seeking input on potentially listing the following PFAS as hazardous substances:
  - PFBS, PFHxS, PFNA, GenX, PFBA, PFHxA, and PFDA
  - Precursors to PFOA, PFOS, and the PFAS listed above
  - Categories of PFAS
- Focus on parties that “significantly contributed to the release of PFAS into the environment”
  - Manufactured PFAS
  - Used PFAS in manufacturing
  - Federal facilities
  - Other industrial parties

CERCLA

Release Notifications

- Releases of hazardous substances at or above their reportable quantities (RQs) within a 24-hour period must be immediately reported to the National Response Center
- A default RQ of one pound has been established for PFOA and PFOS
- Impacted communities must also be notified of releases

Environmental Due Diligence

- Phase I ESAs are used to obtain certain CERCLA liability protections and identify Recognized Environmental Conditions (RECs)
- Previously, PFAS could be considered non-scope considerations and/or Business Environmental Risks (BERs) in Phase I ESAs
- As hazardous substances, PFOA/PFOS releases now must be considered when identifying RECs as part of the Phase I ESA process

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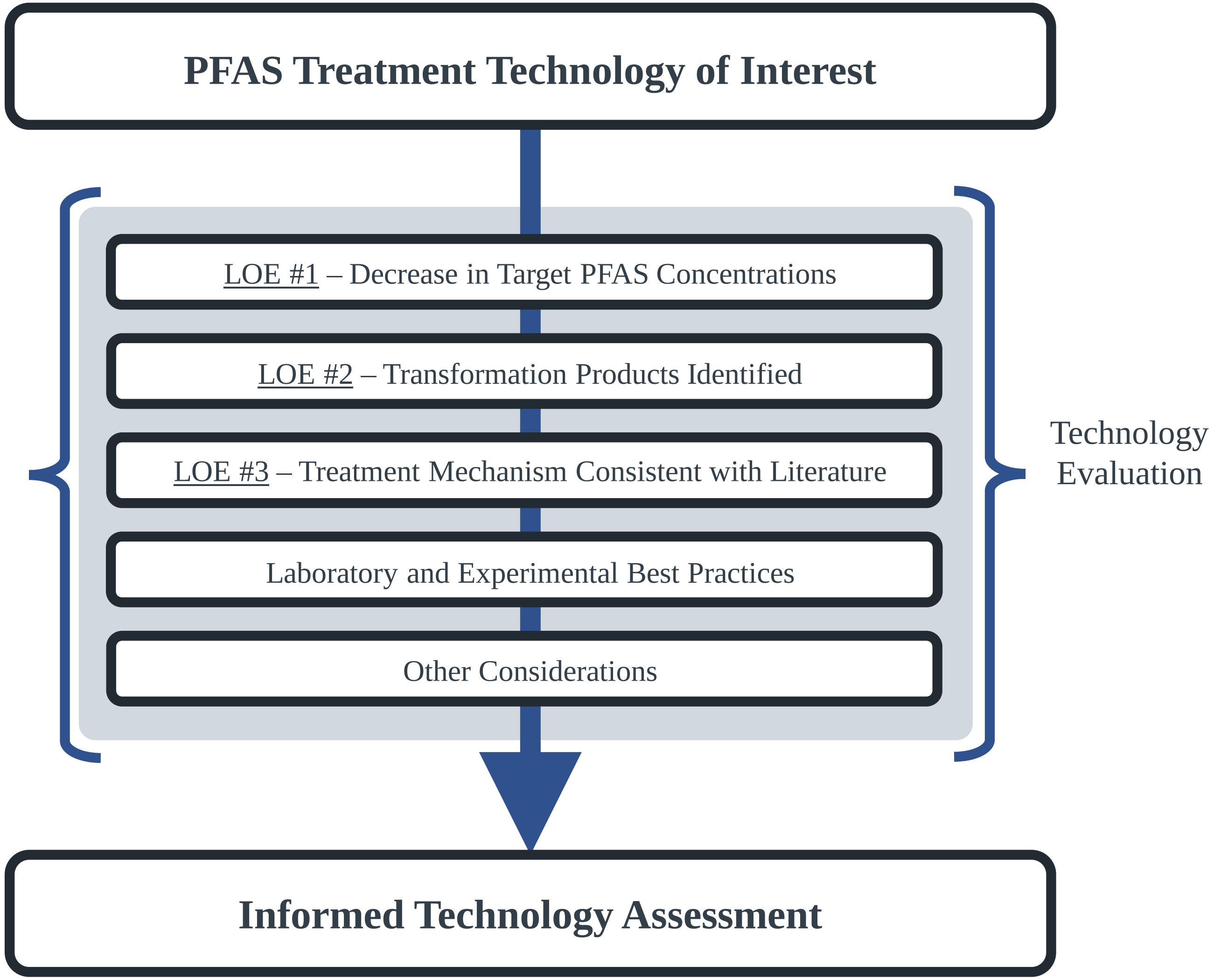
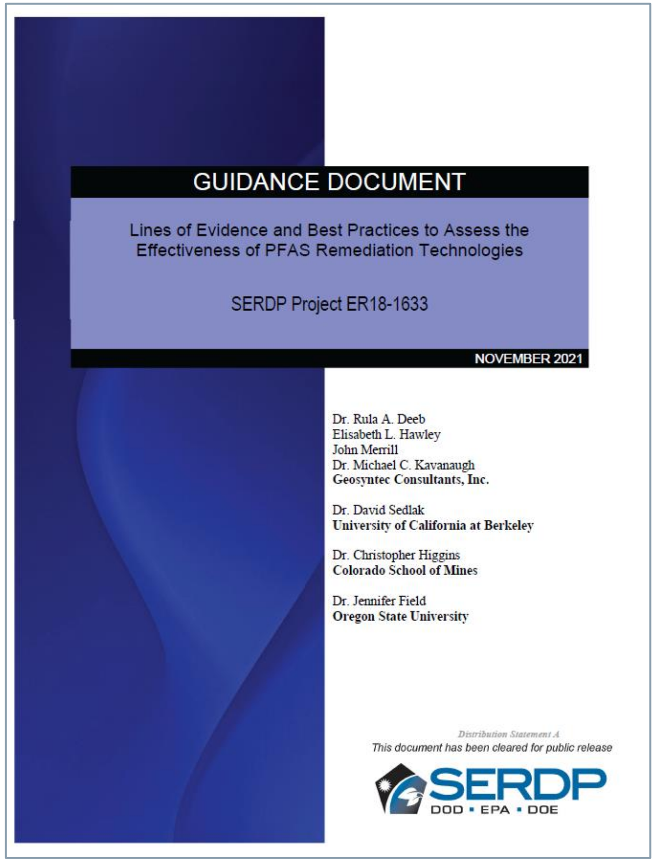
PFAS TREATMENT

LINES OF EVIDENCE




GUIDANCE DOCUMENT

Lines of Evidence and Best Practices to Assess the Effectiveness of PFAS Remediation Technologies

SERDP Project ER18-1633

NOVEMBER 2021

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Distribution Statement A
This document has been cleared for public release

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LINES OF EVIDENCE

#1 Decrease in target PFAS concentrations is observed and explained in the context of a mass balance

#2 Treatment mechanism proposed is consistent with previous studies and supported by data

#3 PFAS treatment transformation products have been identified and quantified

#1 – DECREASE IN TARGET PFAS CONCENTRATIONS

Define PFAS of interest

- Analytical techniques
- Treatment system application
- Chemical properties
- Human health risk

Conduct a mass balance

- Consider gains and losses

Possible losses:
Sorption, association with NAPL and interfaces, volatilization, dilution

Possible gains:
Precursor transformation, desorption/release from surfaces or NAPL, cross-contamination from sampling materials or equipment

#2 – TREATMENT MECHANISM IS SUPPORTED

Is the mechanism consistent with known chemistry of PFAS?

Is the mechanism already known or proven?

What is the evidence that treatment occurs according to the expected mechanism?

Sequestration

- Sorption onto GAC and other sorbents

Transformation/destruction

- Thermal combustion/incineration
- Oxidation/reduction

#3 – TRANSFORMATION PRODUCTS IDENTIFIED AND QUANTIFIED

PFAS transformation products

- Shorter-chain PFAS
- Volatilized PFAS
- Fluoride

Why does this matter?

- Gauge the efficacy of PFAS mineralization
- Close mass balance
- Understand mechanism

Other potential issues may require risk assessment or additional treatment (e.g., metals mobilization due to pH changes)

BEST PRACTICES

#1 Use verified analytical methods for PFAS that are commonly analyzed

#2 Use established research analytical methods for PFAS precursors and other PFAS

#3 Follow and document laboratory best practices for sample preparation and analysis

#4 Include controls in the study design

#5 Account for statistical significance in study design and presentation of results

OTHER CONSIDERATIONS

Effect of PFAS mixtures

- Relevant concentrations of PFAS mixtures
- Co-occurring chemicals
- Other water quality parameters (e.g., temperature, pH, ionic strength, DOC)

Long-term treatment system performance

- Rapid column tests, variety of testing conditions, longevity experiments

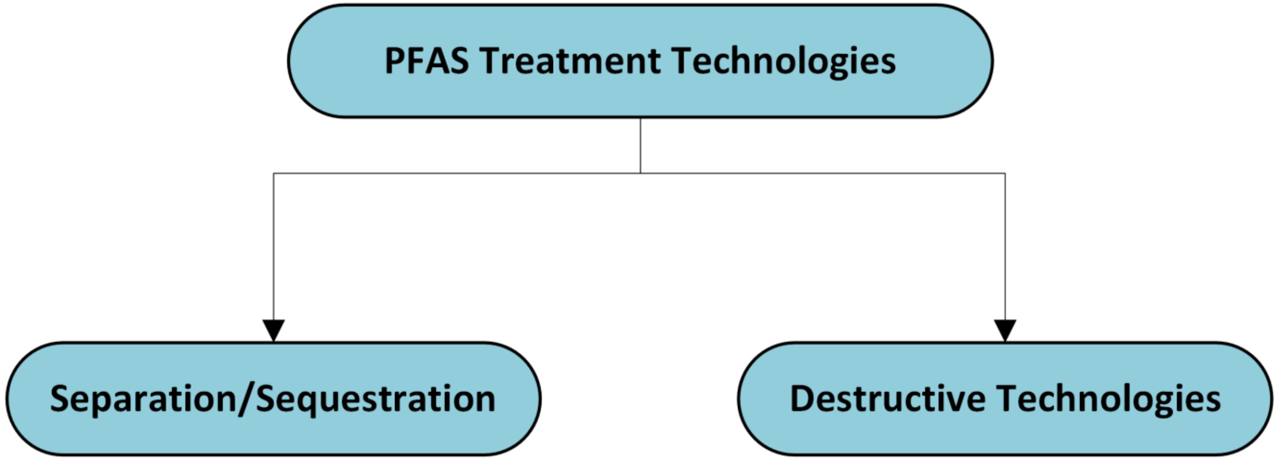
Generation of harmful byproducts

- Be aware of the formation of other (non-PFAS) treatment transformation products

Value relative to other available technologies

- Feasibility, usability, and cost and energy advantages

TREATMENT TECHNOLOGY TYPES



Separation/Sequestration

- Ion Exchange – Single Use and Regenerable
- Granular Activated Carbon
- Reverse Osmosis
- Nanofiltration
- Foam Fractionation
- Incineration

Destructive Technologies

- Activated Persulfate
- Smoldering Combustion
- Hydrothermal Alkaline
- Advanced oxidation processes/advanced reductive processes
- Photolysis/Photocatalysis
- Electrochemical
- Plasma
- Electron Beam

ESTABLISHED TREATMENT TECHNOLOGIES

Granular Activated Carbon (GAC)

- More effective on longer chain PFAS
- PFAS adsorption impacted by TOC, pH and contact time
- Generates solid waste

Ion exchange Resin (IX)

- Can effectively remove long and short chain PFAS
- Regeneration available, but most often single use
- Competition from sulfate, iron, manganese, bicarbonate, and chloride, TOC
- Generates solid waste

Combination of GAC followed by IX

- High O&M costs
- May require significant pretreatment

ESTABLISHED TREATMENT TECHNOLOGIES

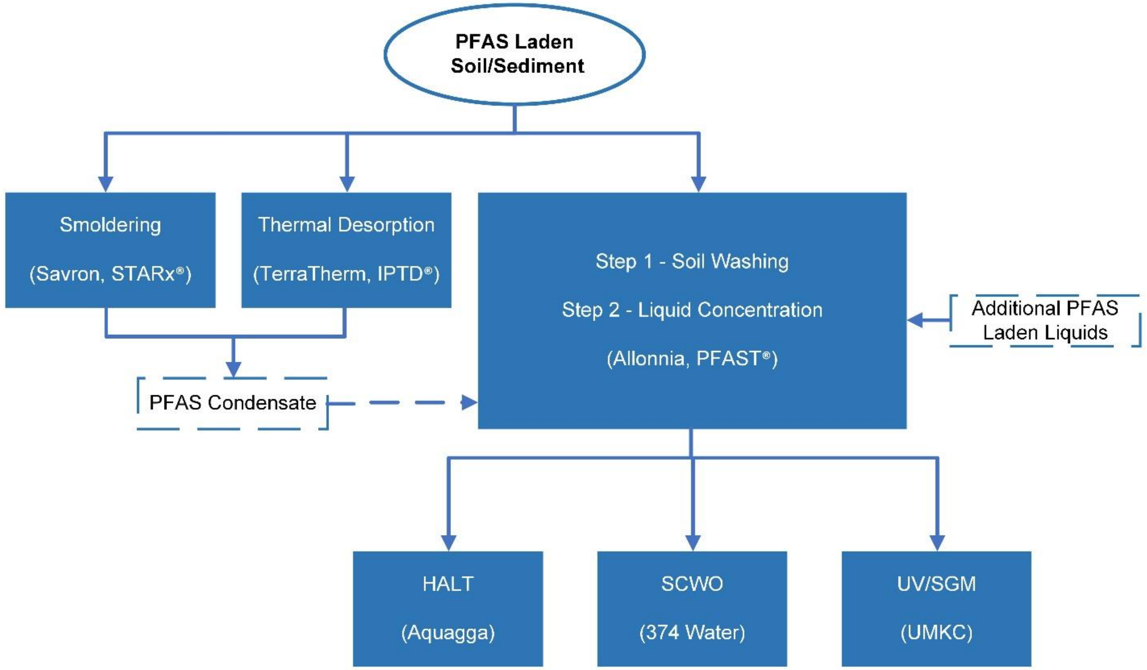
Reverse Osmosis (RO) or Nanofiltration

- Effective for both long and short chain PFAS compounds
- Requires significant pretreatment to reduce negative impact on membrane performance
- Generates liquid waste with high concentration of PFAS that requires disposal
- High capital and energy costs

Reverse Osmosis or Nanofiltration (RO or NF)

Source: OCWD PFAS Workshop 2022

DEVELOPING PFAS DESTRUCTION & REMOVAL TECHNOLOGIES



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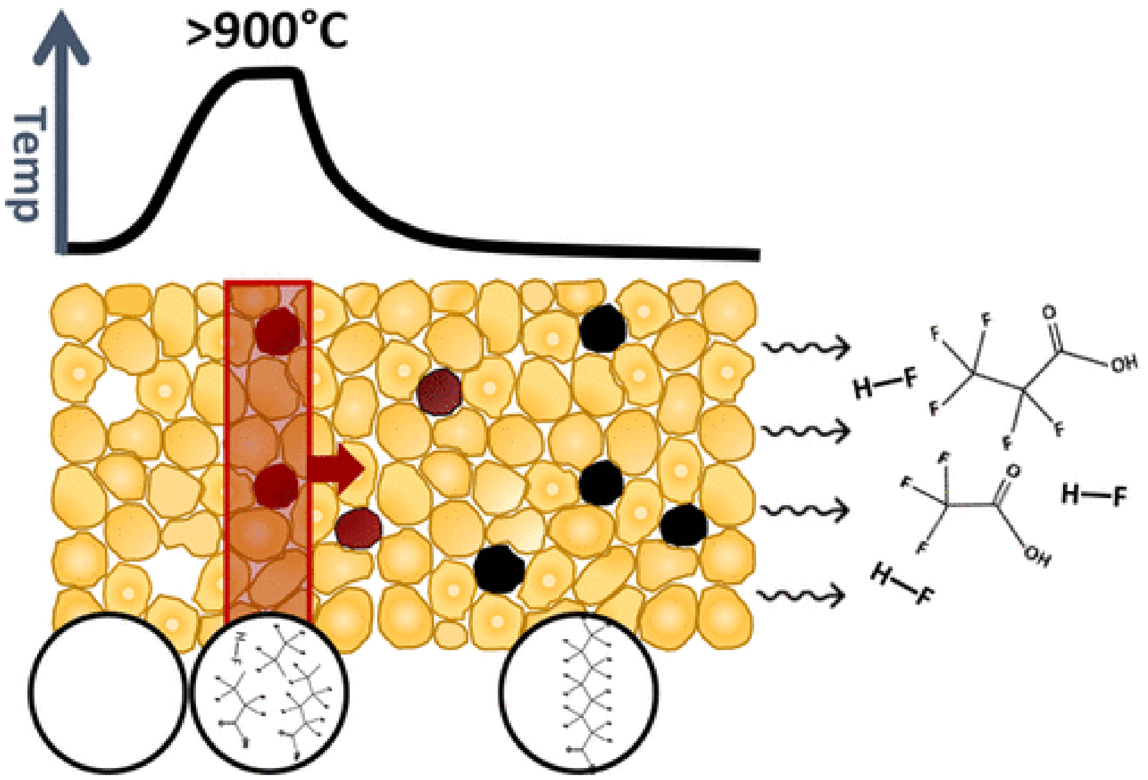
SMOLDERING COMBUSTION

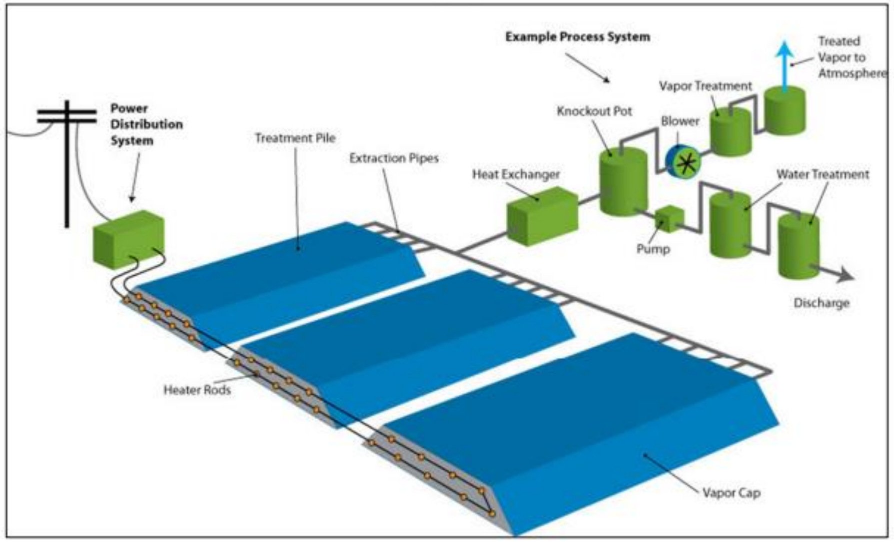


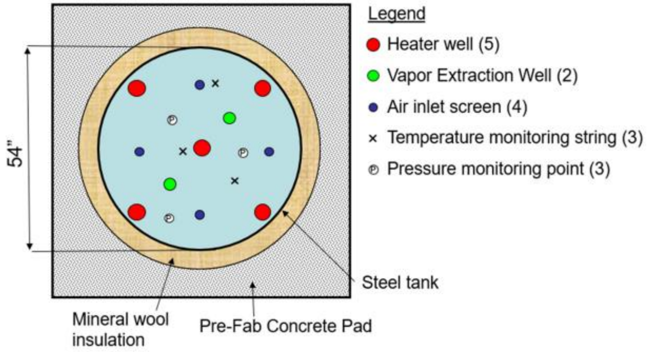
https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/ER18-1593

Duchesne et al., 2020. https://doi.org/10.1021/acs.est.0c03058

- Field-demonstrated technology to destroy PFOS, PFOA, PFHxS, and more to non-detect (<0.4 ug/kg)
- Virgin GAC was used as fuel source
- Temperatures exceeded 900 deg C
- Can be employed in-situ or ex-situ
- Need to assess soil heterogeneity, combustion completeness

THERMAL DESORPTION





Heat and vacuum are applied simultaneously to the material with an array of Thermal Conduction Heating (TCH) wells and vapor collectors, all within an insulated, covered treatment pile and lead to:

1) evaporation;

2) boiling of water and attendant steam distillation;

3) volatilization of the contaminants;

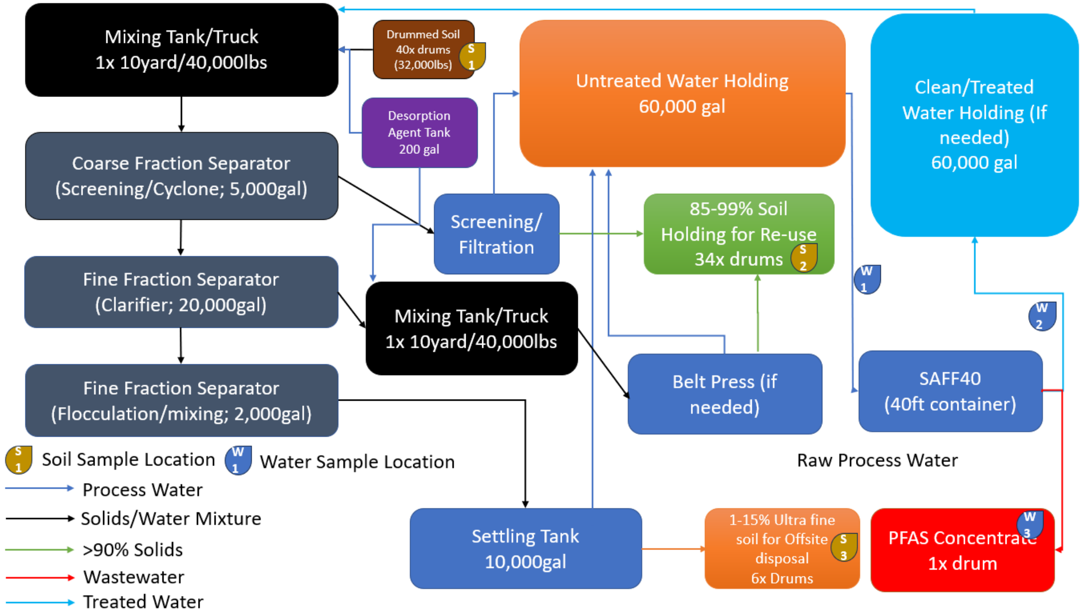
4) oxidation; and

5) pyrolysis

PFAS undergo 30 to 45% mineralization in the soil or sediment at 350-400°C.

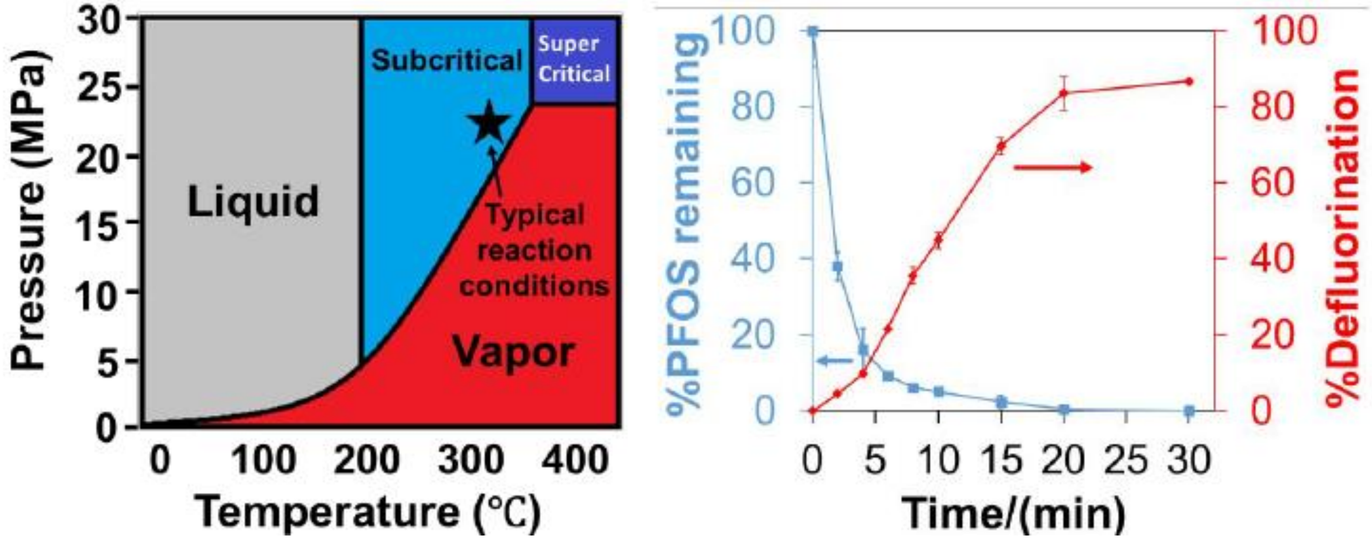
PFAST®/SAFF®

<u>PFAS Foam Assisted Soil Treatment (PFAST®):</u> Uses foam-assisted soil treatment, employing physical agitation to expose and desorb PFAS into process water.

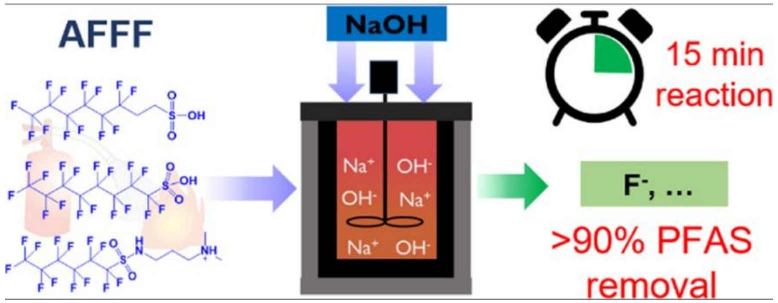


<u>Surface-Active Foam Fractionation (SAFF®):</u> Strips medium to long-chain PFAS from water by leveraging their tendency to partition at the air-water interface. PFAS rise as foam, which is separated and collected. The foam condensates into a PFAS hyper-concentrate.

HYDROTHERMAL ALKALINE TREATMENT

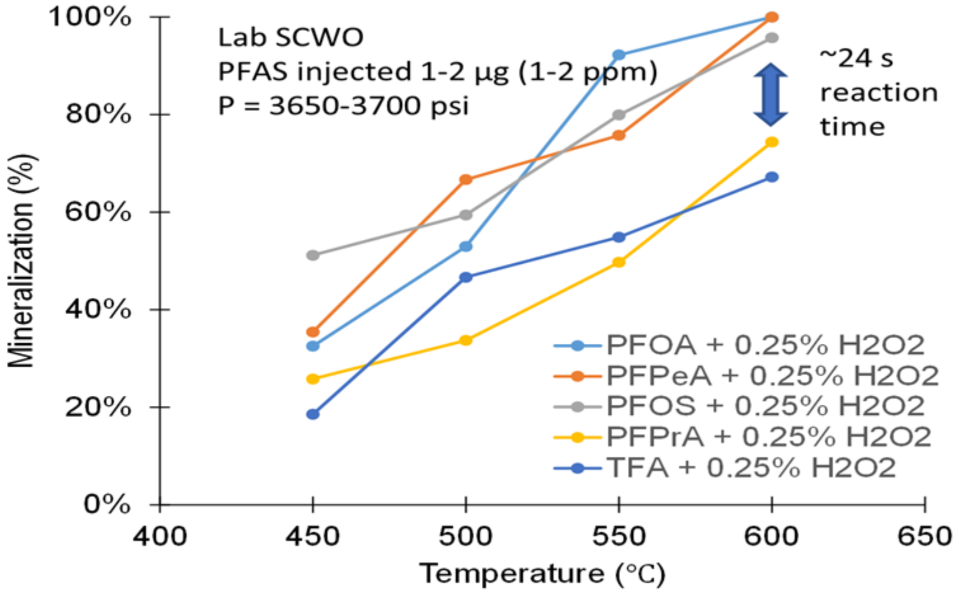


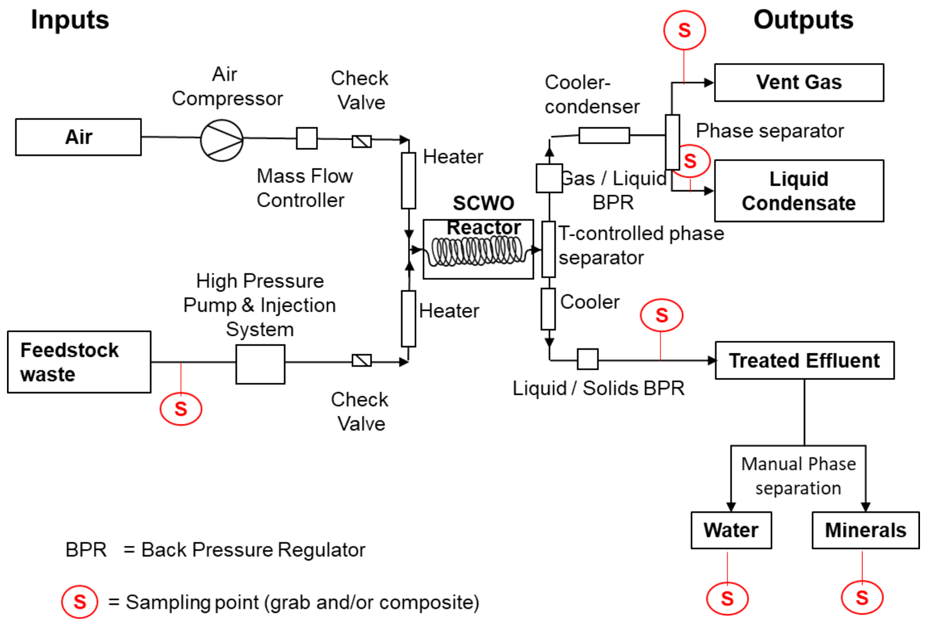
- Alkali amendments promote PFOS destruction
- PFOS destruction rate depends on temperature and alkali concentration
- PFOA destruction occurs rapidly without amendments



SUPER CRITICAL WATER OXIDATION

- **SCWO Process:** Occurs above the supercritical point of water with oxygen, where water becomes compressible, allowing unrestricted mass transfer. PFASs are mineralized to CO2, H2O, HF, and salts by overcoming the C-F bond dissociation energy.
- **AirSCWO Capacity:** Nominal capacity of 14 L per 24 hours.

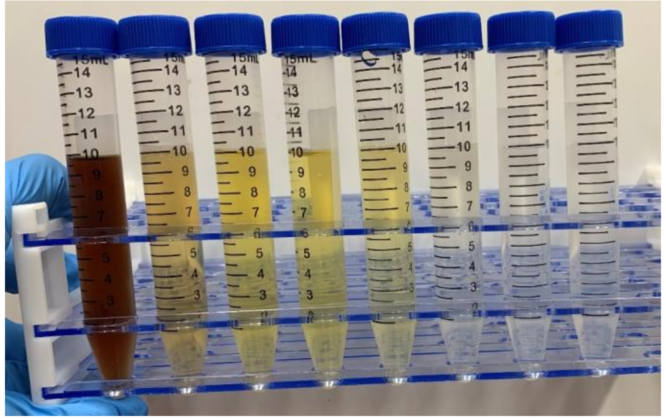


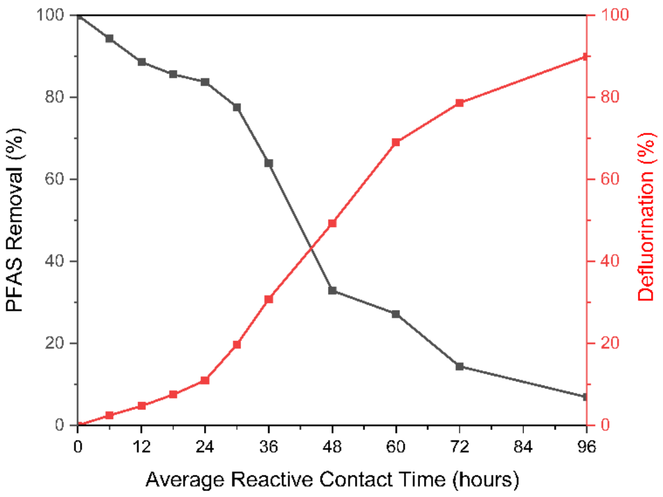


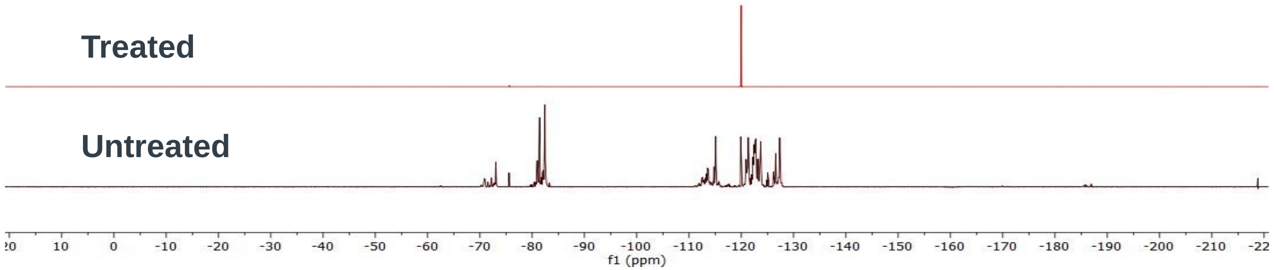
ULTRAVIOLET SILICA-BASED GRANULAR MEDIA

Destruction of Concentrated PFAS Waste Streams Using a Stable Photocatalyst and UV Activation

- Silica-gel based granular media immobilizes photocatalyst within a cross-linked structure
- Relatively low energy, low cost required
- Batch and column test results to optimize media design, validate **destruction** for various PFAS and waste streams
- Applicable for AFFF, stormwater in contact with AFFF area, ion exchange resin still bottoms, and landfill leachate treatment







PFAS NEWSLETTER

EPA Finalizes National Primary Drinking Water Regulation for Six PFAS

On April 10, 2024, the U.S. Environmental Protection Agency (EPA) finalized a National Primary Drinking Water Regulation (NPDWR) for six PFAS:

- Perfluorooctanoic acid (PFOA)
- Perfluorooctane sulfonic acid (PFOS)
- Perfluorohexane sulfonic acid (PFHxS)
- Perfluorononanoic acid (PFNA)
- Hexafluoropropylene oxide dimer acid (HFPO-DA, commonly known as GenX chemicals)
- Perfluorobutane sulfonic acid (PFBS)

geosyntec.com/pfas

CONTACT INFORMATION

Questions?

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