CONNECTING THE DOTS TO INNOVATION

PILOT-SCALE PFAS SEPARATIONS AND TRANSFORMATIONS: STATE OF THE SCIENCE AND LESSONS LEARNED

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ADVANCED MATERIALS & SUBSTANCES OF EMERGING ENVIRONMENTAL CONCERN

OVERVIEW

- Problem Statement/Intro
- Destruction State of the Science
- Scalable/ Ready Technologies
- Demonstration Plan
- Demonstration/Validation Effort
- Future Work/Conclusion

Lightwater AFFF


AFFF storage tank

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PROBLEM STATEMENT/ INTRO

- We are confronted with a pressing environmental challenge related to the presence of aqueous film forming foam (AFFF) concentrate, a substance commonly used in firefighting and emergency response activities.
- Legacy AFFF is a significant source of PFAS for the DoD and others. AFFF was used extensively by the DoD as a firefighting tool.
- Conventional Media (GAC, IX) is proven for dilute streams, *but spent media and secondary waste streams require further management.*
- To tackle this complex issue, we are currently leveraging three distinct destructive technologies from four different partners, each with its unique set of advantages and considerations.
  - These technologies include
    - Sonolysis lead by Arcadis
    - Aquagga hydrothermal alkaline treatment (HALT)
    - 374Water super critical water oxidation (AirSCWO)
    - General Atomics (GA) iSCWO.

AFFF Foaming

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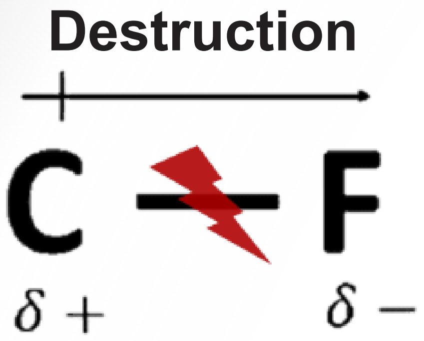
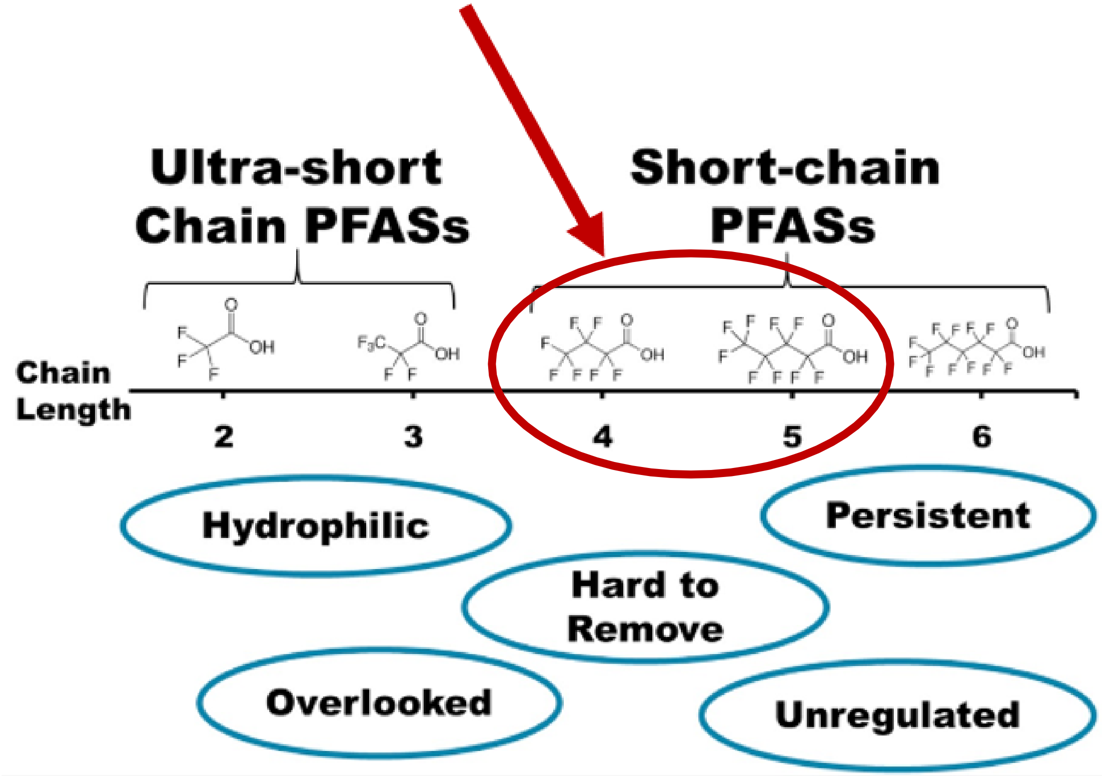
DESTRUCTION STATE OF THE SCIENCE



Transformation ex. (PFBA, PFPeA)



Positive Indicators

- Reduced PFAS concentrations
- Reduced Total Organic Fluorine concentrations
- Fluoride generation

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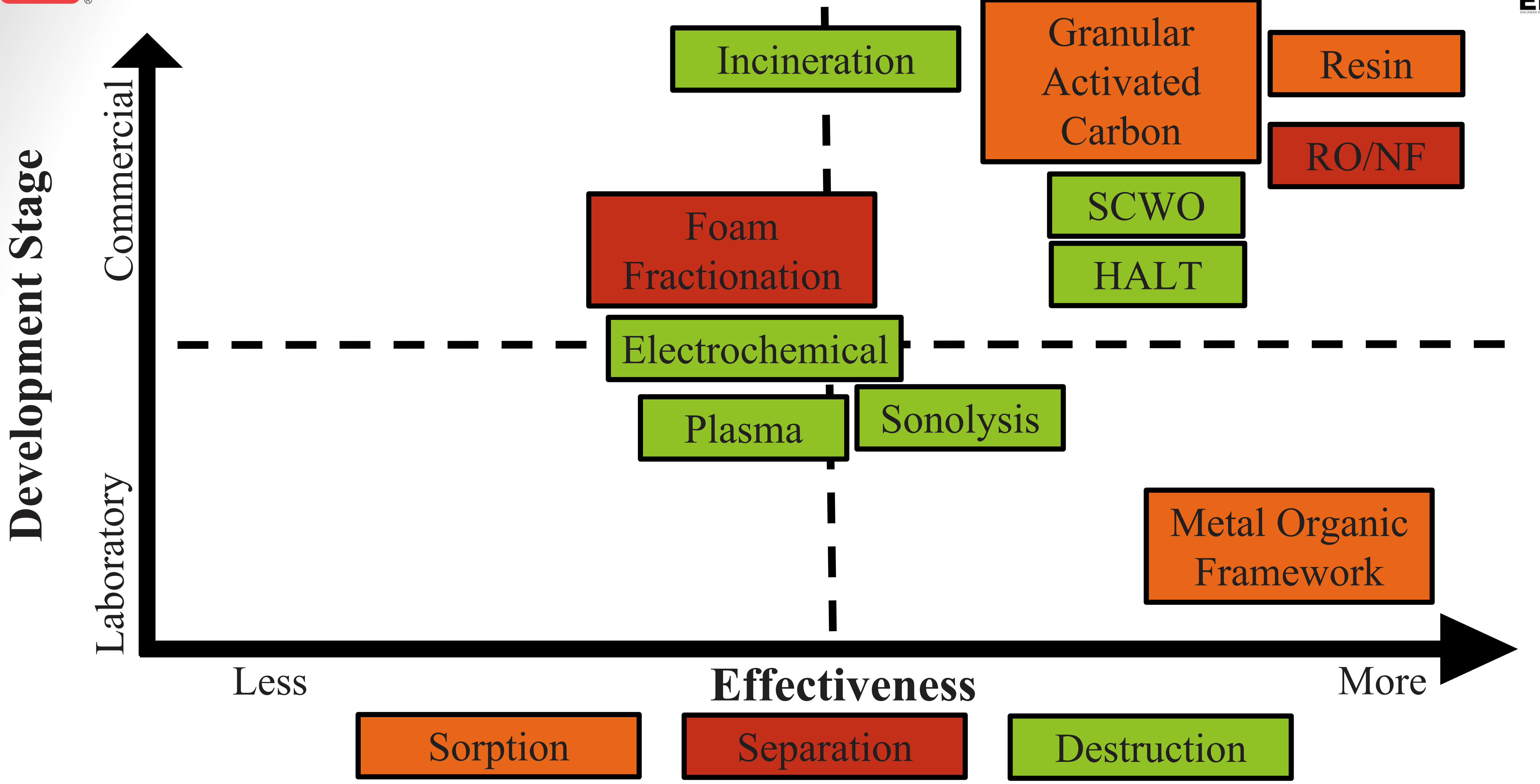
Development Stage
Commercial
Laboratory
Incineration
Granular Activated Carbon
Resin
RO/NF
SCWO
HALT
Foam Fractionation
Electrochemical
Plasma
Sonolysis
Metal Organic Framework
Less
Effectiveness
More
Sorption
Separation
Destruction

SCALABLE/ READY TECHNOLOGIES

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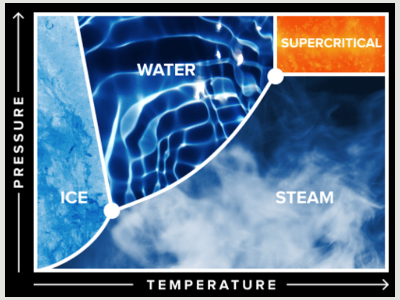
Super Critical Water Oxidation (SCWO)

About

- SCWO relies on the unique reactivity and transport properties of water above its critical point (22.1MPa and 374ºC).
- SCWO process uses supercritical water to quickly and completely oxidize organic and inorganic materials. Water in its supercritical state, maintained at extreme conditions, becomes a potent oxidizing agent.

Advantages

- Nearly complete destruction
- Higher performance with concentrates
- Easily Scalable and commercially available (374Water, General Atomics, Battelle, and Aquarden.)



Hydrothermal Alkaline Treatment (HALT)

About

- HALT is a subcritical water process that leverages an alkaline amendment (typically sodium hydroxide [NaOH]) to break down PFAS under high-pressure (~25 MPa), high-temperature (~350ºC), and high-pH. (Pinkard et al., 2023).

Advantages

- Nearly complete destruction
- Treat high salinity wastewater
- Easily Scalable with many available treatment rate options through Aquagga

AFFF Concentrate

	Untreated (ppm)	HALT Treated (ppm)
PFOS	26,200	0.06
PFOA	268	0.009
PFHxS	4,380	0.5
PFHpS	563	0.006
PFBS	438	0.3
PFHxA	241	0.003
Total PFAS	32,830	1.3

Fire Training Pond

	Untreated (ppb)	HALT Treated (ppb)
PFOS	1,045	1.4
PFOA	414	0.01
PFHxS	240	0.5
PFHpS	19	0.04
PFBS	59	0.1
PFHxA	94	0.015
Total PFAS	2,424	2.3

Landfill Leachate

	Untreated (ppb)	HALT Treated (ppb)
PFOS	8,060	137
PFOA	1,256	7
PFHxS	3,140	22
PFHpS	236	3.6
PFBS	45	2.3
PFHxA	134	1.3
Total PFAS	18,101	182

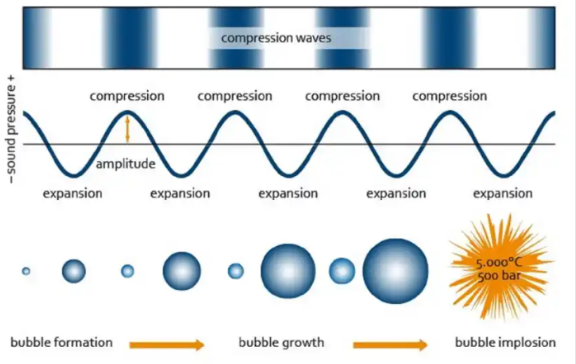
Sonolysis

About

- Sonolysis involves the formation, growth, and subsequent collapse of bubbles (cavitation bubbles) via the application of ultrasonic irradiation to liquids. Cavitation bubble collapse have been reported to reach temperatures as high as 1551 K.
- Sound waves >19kHz create cavities in liquids

Advantages

- >90% destruction of PFAS
- Low cost
- Easily scalable to fit many scenarios
  - Batch or continuous processes
  - In-situ treatment via horizontal well



DEMONSTRATION PLAN

- Each technology will treat 100 gallons of AFFF concentrate collected from North Carolina Army National Guard's Morrisville Army Aviation Support Facility #1 (AASF#1).

Analytical Test	
PFAS Specific	**Destruction/Mass balance/General**
EPA method 1633	Extractable Organofluorine (EOF)
Total oxidizable precursors (TOP) assay	Fluoride Analysis
Non-Target analysis	Total organic Carbon (TOC)
Ultra Short-chain (>C4)	Chemical Oxygen demand (COD)
Other test method (OTM) 45	
OTM 50	

- Gathering over 40 different technology specific operational specs (exp. avg. power, peak power, consumables, mobilization/demobilization, etc.)

- End goal
  - An apples-to-apples comparison of each technologies ability to treat AFFF concentrate.
  - Comprehensive report on cost analysis of technologies treatment of AFFF concentrate.
  - Life-cycle analysis of treatment technology

- Demonstration plan was developed with consultation from tri-services and SERDP/ESTCP

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DEMONSTRATION PLAN

Analytical Demonstrations Plan

- Analysis of treated effluent using field portable nano-spray ion exchange mass spectrometry

Accomplishment

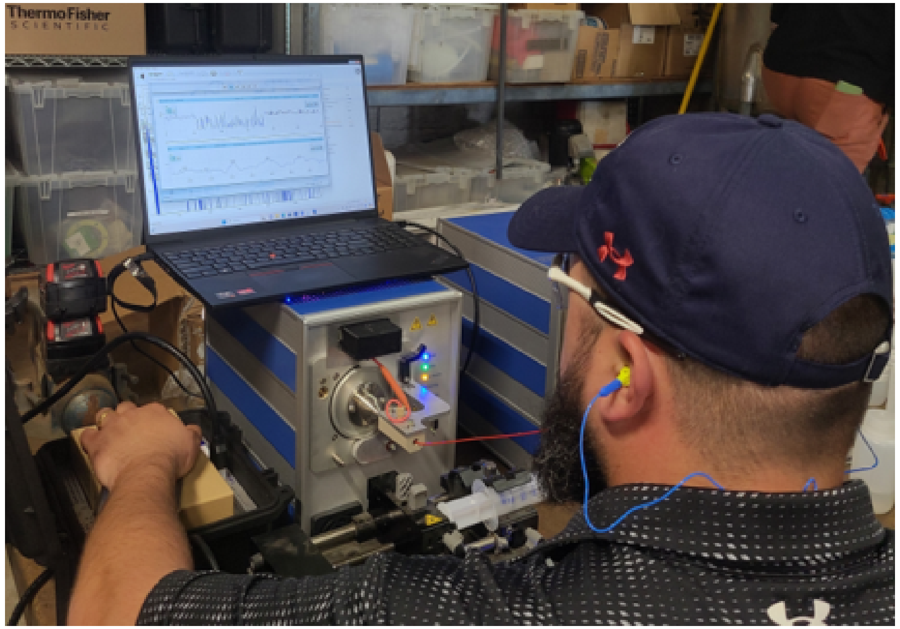
- Initial demonstration of capabilities of in-field technologies for near real time monitoring. Determined short comings of the system (high salt concentrations) and how to overcome them for future demonstrations

Impact

- On site confirmation concerning PFAS destruction

Lead by

- Dr. Patrick Fedrick (Naval Air Warfare Center Weapons Division).



Portable Nano-Spray Ion Trap Mass Spectrometer

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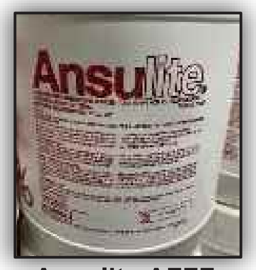
AFFF INITIAL CONCENTRATIONS

Lightwater AFFF

AFFF storage tank



Ansulite AFFF

Target Analysis				
Chain Length	SubClass	Compound	TOP Assay (mg/L)	EPA Method 1633 (mg/L)
N/A	Ether	PFEESA	<LOD	<LOD
N/A	Ether	PFMBA	0.02	<LOD
N/A	Ether	PFMPA	0.03	<LOD
6	FTCA	6:2 FTCA	NR	NR
6	FTCA	6:2 UFTCA	NR	NR
8	FTCA	8:2 UFTCA	NR	NR
4	FTS	4:2 FTS	<LOD	0.180
6	FTS	6:2 FTS	0.22	11.463
8	FTS	8:2 FTS	0.04	2.063
3	PFCA	**PFBA**	**249.67**	**0.214**
4	PFCA	**PFPeA**	**483.33**	**0.304**
5	PFCA	**PFHxA**	**223.67**	**2.703**
6	PFCA	**PFHpA**	**111.67**	**0.053**
7	PFCA	**PFOA**	**37.47**	**0.393**
8	PFCA	PFNA	2.74	0.007
9	PFCA	PFDA	0.86	0.022
10	PFCA	PFUdA	0.30	<LOD
11	PFCA	PFDoA	0.31	0.008
12	PFCA	PFTrDA	0.08	<LOD
13	PFCA	PFTeDA	0.10	0.007
4	PFSA	PFBS	0.15	0.009
5	PFSA	PFPeS	0.29	0.006
6	PFSA	PFHxS	0.05	0.019
7	PFSA	PFHpS	0.05	<LOD
8	PFSA	PFOS	0.14	0.118
		Total	**1111.16**	**17.556**

Non-Target Analysis		
CF2 chain	Compound Name	Concentration (mg/L)
6	6:2 fluorotelomer thia propanoamido dimethyl ethyl sulfonate	415.07
8	8:2 fluorotelomer thia propanoamido dimethyl ethyl sulfonate	218.17
10	10:2 fluorotelomer thia propanoamido dimethyl ethyl sulfonate	42.53
4	4:2 fluorotelomer thia propanoamido dimethyl ethyl sulfonate	18.93
12	12:2 fluorotelomer thia propanoamido dimethyl ethyl sulfonate	2.30
6	6:2 fluorotelomer thia propanoic acid	49.97
8	8:2 fluorotelomer thia propanoic acid	3.60
6	6:2 fluorotelomer thia ammoniohydroxypropyl ethanoic acid	187.07
8	8:2 fluorotelomer thia ammoniohydroxypropyl ethanoic acid	16.37
6	6:2 fluorotelomer thia amido propano amido pentanoic acid	7.47
6	6:2 fluorotelomer thia amido pentanoic acid	19.30
6	6:2 fluorotelomer sulfinyl propanoamido dimethyl ethyl sulfonate	75.23
8	8:2 fluorotelomer sulfinyl propanamido dimethyl ethyl sulfonate	10.73
4	4:2 fluorotelomer sulfinyl propanamido dimethyl ethyl sulfonate	1.83
6	6:2 fluorotelomer sulfonyl propanoamido-dimethylethyl sulfonate	0.70
6	6:2 fluorotelomer sulfinyl propanoic acid	0.40
6	6:2 fluorotelomer sulfinyl ammoniohydroxypropyl ethanoic acid	12.87
6	6:2 fluorotelomersulfonyl propanoic acid	2.27
6	N-dimethylaminohydroxybutyl-perfluorohexanesulfonamidopropylsulfonate	0.20
	Total	**1085.00**

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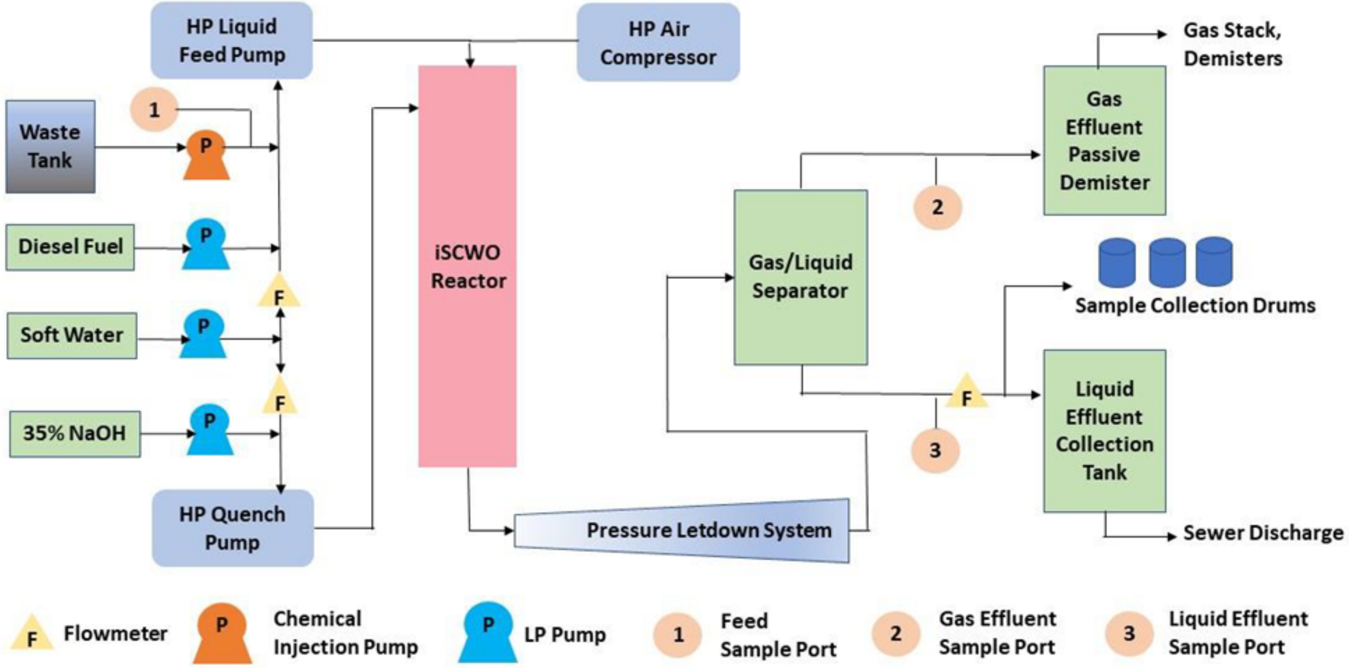
GA iSCWO - DEMO

- GA iSCWO process involves blending organic materials with water, fuel, and air within a continuous flow reactor, operating at an optimal temperature range of 650°C to 700°C, and a pressure of 221 bar (~3,200 psig)

- Demonstration performed on treating 100 gallons of AFFF concentrate completed – pending results

Pilot-Plant iSCWO Main Skid



Pilot-Plant iSCWO Compressor Skid

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GA iSCWO - DEMO

GENERAL ATOMICS ERDC

- Preliminary test performed at similar feed rates of demo showed very little PFAS coming out

Test #1

- AFFF Feed Rate = 0.05 gpm
- Volume AFFF Treated = 15 gal
- Volume of effluent liquid = 770 gal (110 gal during startup and shutdown)

- Process consumables include diesel, softened water, compressed air, and caustic solution.

Test #2

- AFFF Feed Rate = 0.26 gpm
- Volume AFFF Treated = 85 gal
- Volume of effluent liquid = 330 gal

- Process consumables include diesel, softened water, compressed air, and caustic solution.

Test #3

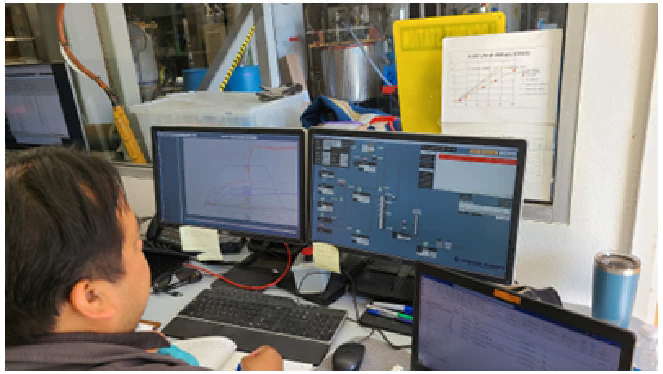
* Treating all effluent produced from test #1 and #2

- Feed Rate = 1.85 to 2 gpm
- Volume Treated = 690 gal (410 gal still to be treated)
- Volume of effluent liquid= 840 gal

- Process consumables include diesel, softened water, compressed air, and caustic solution.

- **Power Consumption** of air compressor was 405 kW
- **Power Consumption** of Reactor was 10 kW

Stack Gas Sampling OTM 45 & 50



Control Room/Operation Monitoring

Stack Gas

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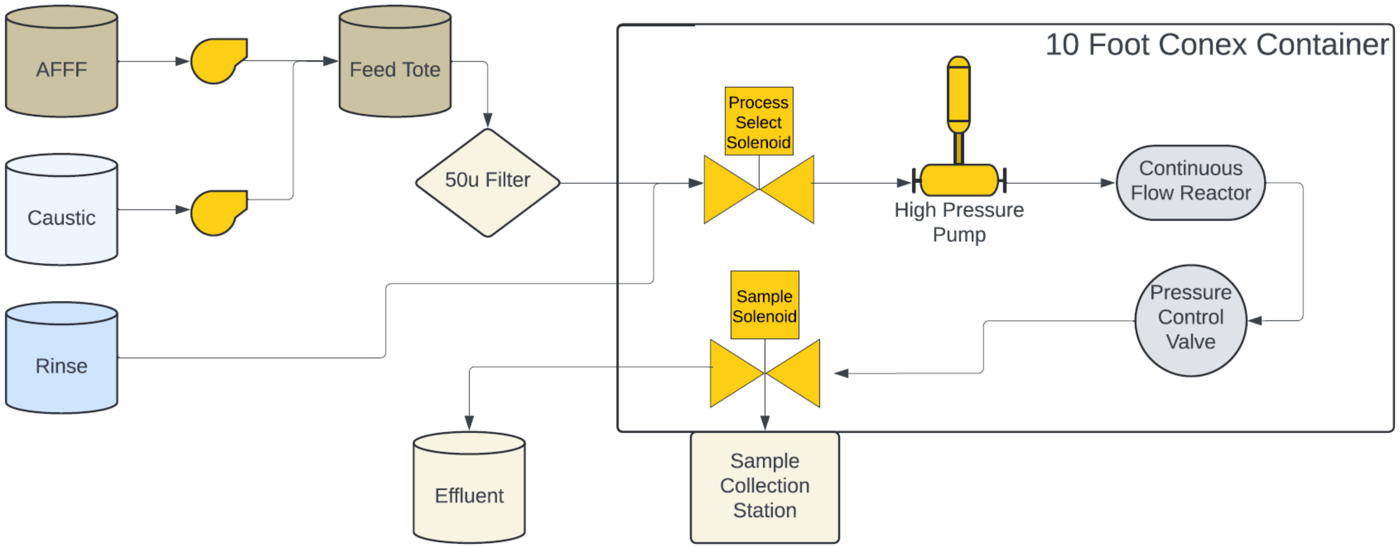
AQUAGGA HALT - DEMO

- HALT is a subcritical reactor operating at elevated pressure, temperature, and alkalinity within the compressed liquid phase of water.

- Demonstration performed on treating 100 gallons of AFFF concentrate completed – pending results



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AQUAGGA HALT - DEMO

Aquagga ERDC

Procedure

- Rinsate fed through reactor during pre-heating
  - Preheating time was 2 hours
- 100 gal of AFFF concentrate was mixed with a caustic amendment and water for a starting volume of 211 gal.
- AFFF solution feed rate = 6 – 6.5 gph
- Total treatment time = 32 hours

Considerations

- Effluent stream may require neutralization depending on discharge requirements
- Effluent liquid from AFFF treatment = 250 gal
  - Total effluent liquid from demo = 375 gal
- Power consumption
  - Startup = 5.7 kW
  - Operation = 4.5 kW

Sample Port

White conex box is the job trailer; Navy conex box is the remote-control station.

OTM 50 sampling setup

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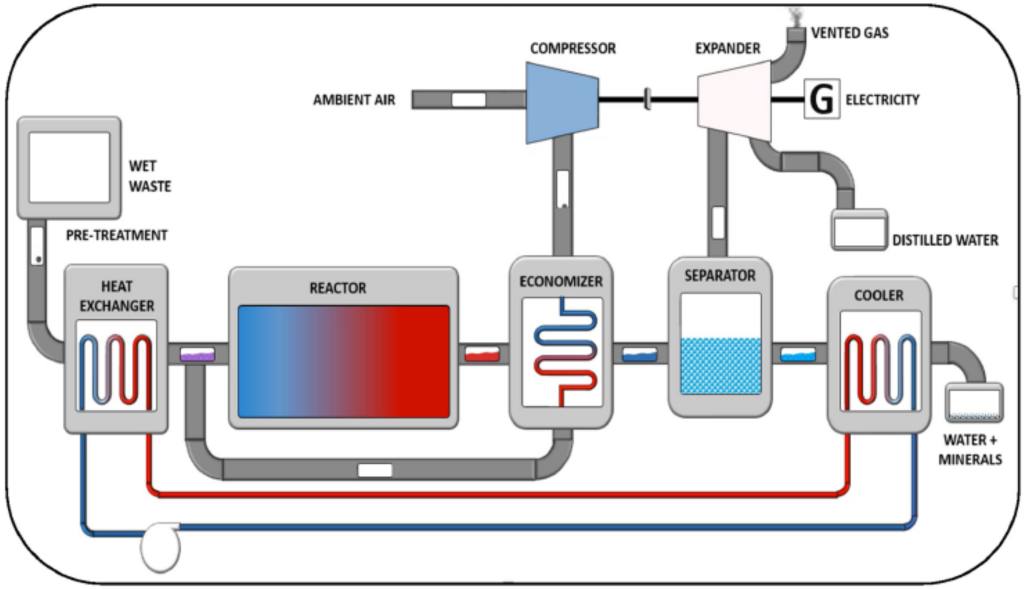
374WATER AirSCWO

- 374Water AirSCWO stands as a cutting-edge oxidation process, boasting vast potential in the remediation of diverse organic wastes such as PFAS.
- Bench Scale AirSCWO system used for a treatability study on a small volume of the AFFF concentrate for tuning system before the100 gal demo.
  - Bench test demonstrated near-complete mineralization of PFAS in AFFF.
  - Capable of up to 9% AFFF concentrate in feed stock

- Full scale 100 gal AFFF concentrate demo planned for July 2024

374Water AirSCWO system (Divine et al., 2023)



374Water AirSCWO process flow diagram (Divine et al., 2023)

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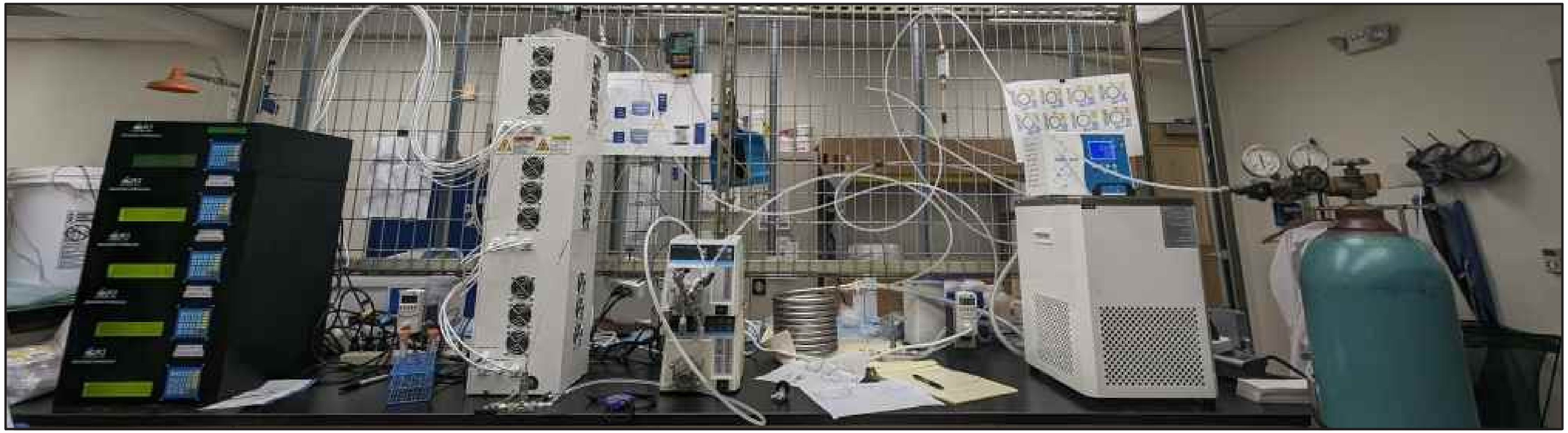
Divine, C., March, L., Kalra, S. S., & Hurst, J. (2023). Sonolysis and Super critical water oxidation (SCWO): development maturity and potential for destroying PFAS. Ground Water Monitoring & Remediation, 43(4), 18–33. https://doi.org/10.1111/gwmr.12619

ARCADIS SONOLYSIS

- Sonolysis is a proven destruction technology for the destruction of PFAS
  - Ultrasonic waves create cavitation bubbles in the liquid medium, leading to localized high temperatures and pressures, which can break down PFAS molecules.
  - It is a relatively environmentally friendly technology, as it does not rely on harsh chemicals or generate harmful by-products.
  - It can be applied to various types of PFAS contaminants and aqueous matrices.



Arcadis sonolysis system

- Optimization is on-going
- Full scale 100 gal AFFF concentrate demo planned for August 2024

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FUTURE WORK/CONCLUSION

Future Work

- 374Water AirSCWO 100 gallon demo of AFFF concentrate to be performed in July 2024
- Arcadis Sonolysis 100 gallon demo of AFFF concentrate to be performed in August 2024

- In FY25 looking to increase the volume of AFFF to treat.
  - Providing a longer duration of treatment time
  - Having systems mobilized/demobilize to treatment location

Conclusion

- Given the estimated 3 million gallons of AFFF concentrate still present at military facilities, it is imperative to prioritize its safe disposal (Roman, 2022).

- GA iSCWO, 374Water AirSCWO, Aquagga HALT, and Arcadis Sonolysis will all be tested on there efficiency to treat 100 gal of AFFF concentrate.

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Roman, J. (2022, July 21). NFPA Journal – The New Foam, Fall 2022. NFPA. Retrieved April 30, 2024, from https://www.nfpa.org/news-blogs-and-articles/nfpa-journal/2022/07/22/the-new-foam

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Questions?

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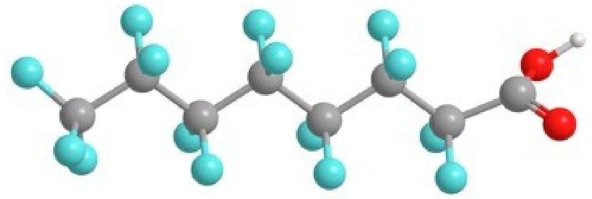
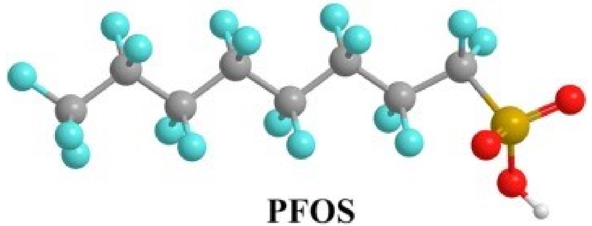
DESTRUCTION STATE OF THE SCIENCE

The challenge (put down the hammer we need a wrecking ball), regardless of matrix

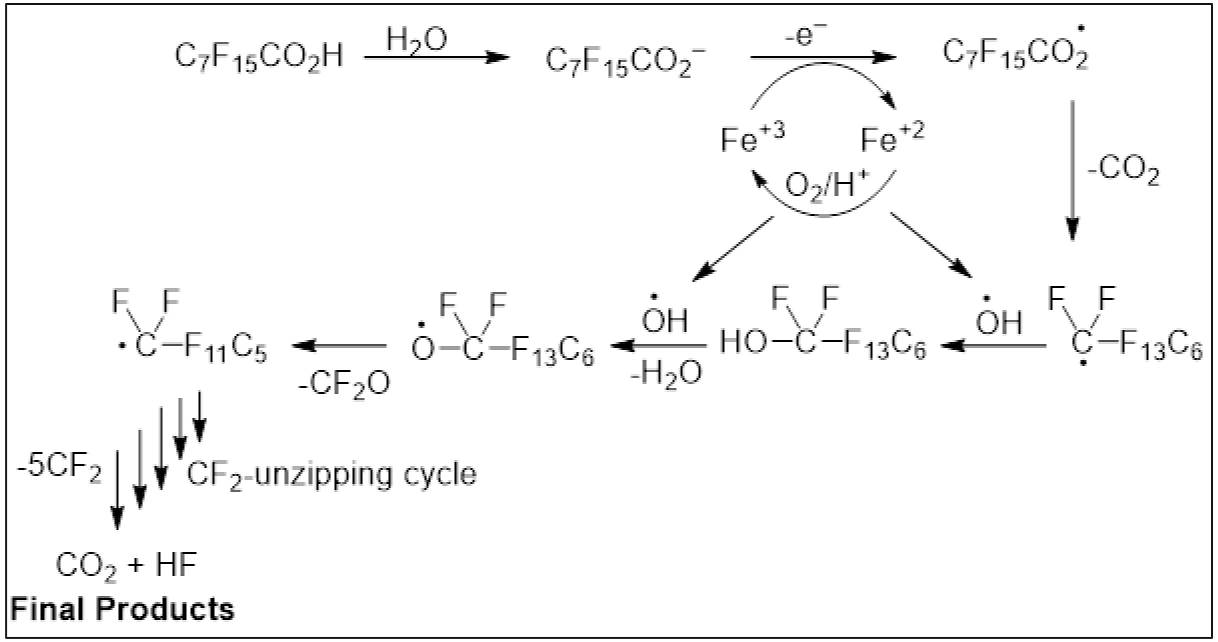
- Unrivalled stability arises because fluorine is the most electronegative element.
- Introduces reinforcing ionic forces through strong polarization of this bond.
- Products can include hydrofluoric acid (HF) and volatile organic fluorine (VOF)
- Dissociation energy of up to 130 kcal/mol



PFOA



PFOS



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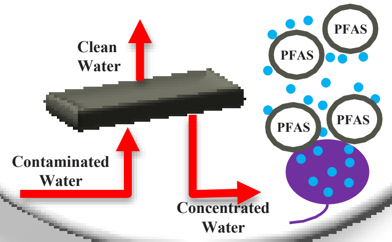
Destruction

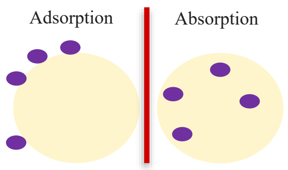
Process of breaking down and eliminating PFAS, a group of persistent synthetic chemicals, from the environment or contaminated materials with the aim of reducing their environmental and health risks.

Separation



It involves the isolation or removal of PFAS from mixtures or contaminated environments. This separation process aims to extract, filter, or otherwise segregate PFAS compounds. Separation is crucial for mitigating the environmental and health impacts of PFAS contamination.

Sorption



Process in which PFAS compounds are physically or chemically attracted and adhered to the surface of a material. PFAS are effectively removed from a contaminated water. Adsorption is a widely used method for reducing PFAS concentrations in water sources and is an essential step in many PFAS remediation processes.

SEPARATION AND ABSORPTION TECHNOLOGIES

Technology	Advantages	Disadvantages	Byproducts	Cost	Potential Usages
Reverse Osmosis and Nanofiltration	Proven technology with great removal of PFAS	Concentrated waste steam still needs to be treated	Concentrated waste stream	High	Develop Concentrate stream for destruction processes
Foam Fractionation	Economical treatment method to make highly concentrated low volume solutions	Short chains need to be addressed and concentrated waste streams	Concentrated waste stream	Low	Develop Concentrate stream for destruction processes
Resin	High adsorption capacity. Many available sources	PFAS sorbed to resin still needs to be destroyed	Solid resin to dispose of	Low	Polishing step post destruction process
GAC	Effective removal of PFAS. Many available sources	Adsorption effected by natural organics. Decrease in effectiveness with decrease in chain length	Solid GAC to dispose of	Low	Polishing step post destruction process

*GAC = Granular Activated Carbon

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ADSORPTION

Granular Activated Carbon (GAC)

About
- Highly porous material made from organic materials, typically coconut shell, wood, or coal, which are heated in the absence of oxygen to create a highly porous carbon material with a large surface area.
  - Coal typically outperforms coconut or wood

Advantages
- Low-cost high removal sorbent material
- Many available providers

Disadvantages
- Performance is best with lower concentrations
- Absorption can be affected by natural organics and other contaminants.
- Effectiveness decreases with chain length.
  - Can be managed by longer EBCT

Resin

About
- Engineered synthetic polymer that is designed to have selective properties for PFAS.

Advantages
- Lower EBCT than GAC allowing for smaller footprint
- Regeneratable resins available but require solvents
  - Often single pass resins are more economical
- Many available providers

Disadvantages
- More expensive than GAC
- Media density could result in higher pumping cost

MEMBRANE SEPARATION

About

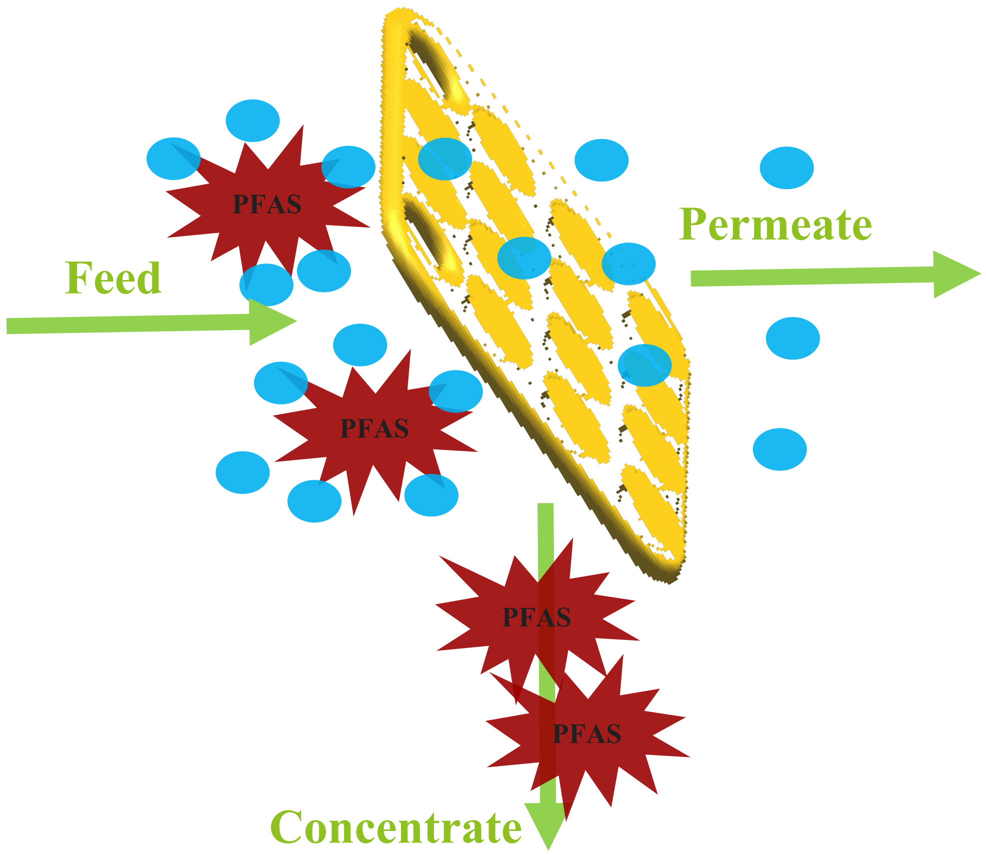
- Reverse Osmosis (RO) and Nanofiltration (NF) are the two most effective membrane processes for PFAS separation processes
  - Main difference in RO and NF is the pore size in the membranes.
  - RO requires higher operating pressure resulting in higher operating cost.

Advantages

- Proven >95% removal from NF and >99% removal from RO
- Capable of providing high-quality effluent
- Effective for point-of-use systems in households
  - Will reduce water pressure

Disadvantages

- Concentrated waste stream produced with PFAS
- Susceptible to fouling thus requiring pretreatment
- Can have high capital and O&M cost.



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DESTRUCTION TECHNOLOGIES

Technology	Average DRE	Cost	Limitations	Throughput	Scalability	Energy Requirements	Temperature	Pressure	Chemical Additives	Pretreatment Requirements	Byproducts
SCWO	High	High-Medium	Corrosions and Salt Deposition	High - Continuous processes available	High	High for startup, lowering during steady state	High	High	Variable, need for neutralization of Effluent	Best performance with concentrates	Without neutralization hydrofluoric acid could become present
HALT	High	High-Medium	Required chemical additives	High - Continuous processes available	High	High-Medium	High	High	NaOH	Best performance with concentrates	High alkaline post-treatment solutions containing residual NaOH and fluoride
EO	Medium	Medium-Low	Short-Chains	Low	Low	Low (Vary from 15-256kWh/m^3)	Low	Low	Electrolytes (Na_2SO_4, $NaClO_4$, and NaCl)	Best performance with concentrates	Hydrogen fluoride gas must be recognized
Plasma	Medium	1000 gal of PFAS-impacted water for $7.30	Short-chains accumulation at bubble-liquid interface	Medium	Medium-Low	Low (294 kWh/m^3)	Low	Low	Argon gas	None	ClO^-_2, ClO^-_3, ClO^-_4, Short-chain PFAS
Sonolysis	High-Medium	Low	Reaction Time/Throughput	Medium	Medium	Medium (Vary from 208 - 3,333 kWh/m^3)	Low	Low	None	None	ClO^-_3, and ClO^-_4 Possible
Incineration	High	Could be as high as $3,600 per metric ton	High energy considerations, Potential for volatiles	High	Achieved	High	High	Low	None	None	If not treated at high enough temperature, then short chains into volatiles and HF.

*DRE = destruction and removal efficiency, SCWO = supercritical water oxidation, HALT = hydrothermal alkaline treatment, EO = electrochemical oxidation, "Throughput may also be thought of as reaction or residence time"

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