State of the Science

Destructive PFAS Technology Application for Water Treatment

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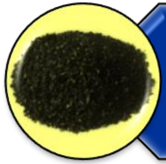
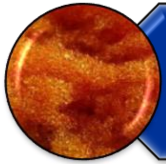
12 November 2021

CDM Smith

Proven Technologies for PFAS Water Treatment



Granular Activated Carbon (GAC)



Anion Exchange (AIX)

NF and RO Membranes

Table 2-1. Summary of PFAS removals for various treatment processes.

Compound	Molecular Weight (g/mol)	Aeration	Coagulation/Dissolved Air Flotation	Coagulation/Flocculation/Sedimentation/Granular Filtration or Microfiltration	Anion Exchange	Granular Activated Carbon Filtration	Nanofiltration	Reverse Osmosis	Permanganate/Ozone/Hypochlorous/Hypochlorite/Chloramination/UV photolysis
PFBA	214	●	●	●	●	●	■	■	●
PFPeA	264	●	●	●	●	▼	■	■	●
PFHxA	314	●	●	●	●	▼	■	■	●
PFHpA	364	●	●	●	▼	■	■	■	●
PFOA	414	●	●	●	▼	■	■	■	●
PFNA	464	●		●	■	■	■	■	●
PFDA	514	●		●	■	■	■	■	●
PFBS	300	●	●	●	▼	■	■	■	●
PFHxS	400	●	●	●	■	■	■	■	●
PFOS	500	●	▼	●	■	■	■	■	●
FOSA	499			●		■		■	
N-MeFOSAA	571	●		●	■	■	■	■	
N-EtFOSAA	585	●		●	■	■	■	■	

From Dickerson & Higgins, 2016 (WRF, #4322)

● Removal <10% ▼ Removal 10-90% ■ Removal >90% □ Unknown □ Assumed

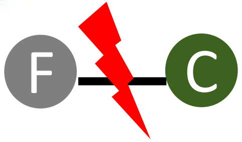
WRF 4322: Treatment Mitigation Strategies for PFCs

Limitations of "Conventional" PFAS Treatment

- High volume of spent media/waste stream requiring waste management
- Significant pretreatment often required to remove competing solutes
- High concentrations of PFAS can lead to inefficient target compound removal
- Overall high costs for removing small mass of contamination (down to trace ppt levels)

PFAS Destruction vs. Transformation

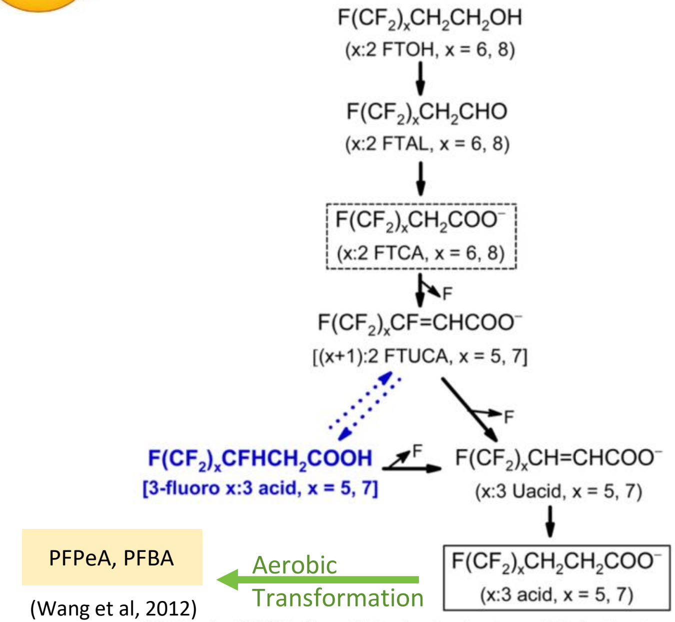
Complete Destruction



Breaking C-F bonds to mineralize PFAS

Three lines of evidence
PFAS disappearance
+
Fluoride generation
+
Total organic fluorine concentration reduction

Incomplete Destruction



6:2 FTOH (x = 6) and 8:2 FTOH (x = 8) anaerobic biotransformation pathways in anaerobic digester sludge under methanogenic conditions. All the polyfluorinated acids are presented in deprotonated forms, which are expected under slightly alkaline pH in digester sludge. The dashed rectangular box represents major intermediate biotransformation product and the solid rectangular box represents the major stable biotransformation product

(Zhang et al, 2013)

PFAS Destructive Technologies

Demonstrated at the Bench: Pilot and Field Scale

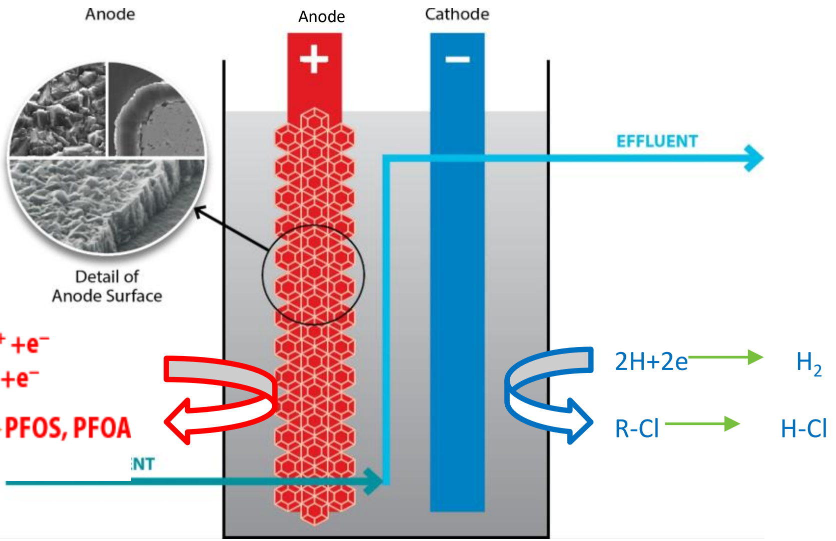
- Electrochemical Oxidation
- Plasma
- UV-Hydrated Electrons
- Hydrothermal
- Supercritical water oxidation

Research and Development: Bench

- Sonochemical
- Photolysis/Photocatalytic
- Mechanochemical (Ball-milling)
- High-energy electron beam
- Radiolytic

Electrochemical Oxidation

- Groundwater, AFFF, AIX or NF reject, IDW
- PFAS are mineralized to F^- and CO_2 in hours
- Generates perchlorate



H_2O + Anode → Anode(OH-) + H^+ + e^-
Anode(OH^-) → Anode + 0.5O_2 + H^+ + e^-
PFAS Precursors + Anode(OH^-) → PFOS, PFOA
PFOS, PFOA + e^- → HF, CO_2

Environmental Science & Technology
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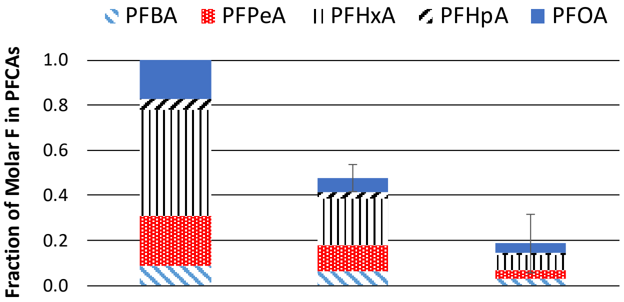
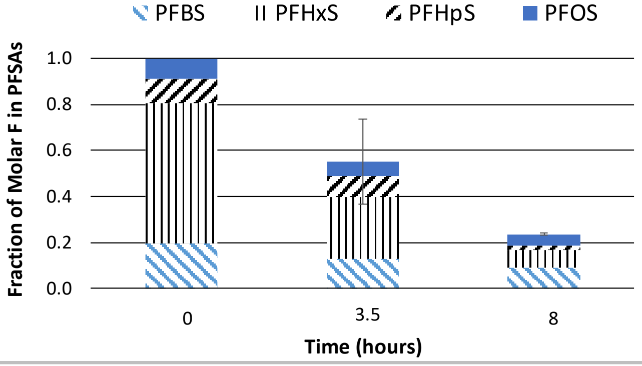
pubs.acs.org/est

Electrochemical Transformations of Perfluoroalkyl Acid (PFAA) Precursors and PFAAs in Groundwater Impacted with Aqueous Film Forming Foams

Charles E. Schaefer,*[†] Sarah Choyke,[‡] P. Lee Ferguson,[‡] Christina Andaya,[§] Aniela Burant,[∥] Andrew Maizel,[∥] Timothy J. Strathmann,[∥] and Christopher P. Higgins[∥]

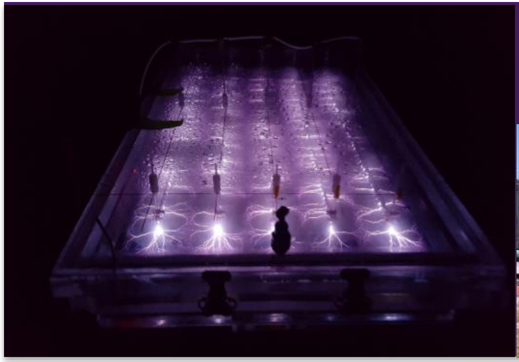




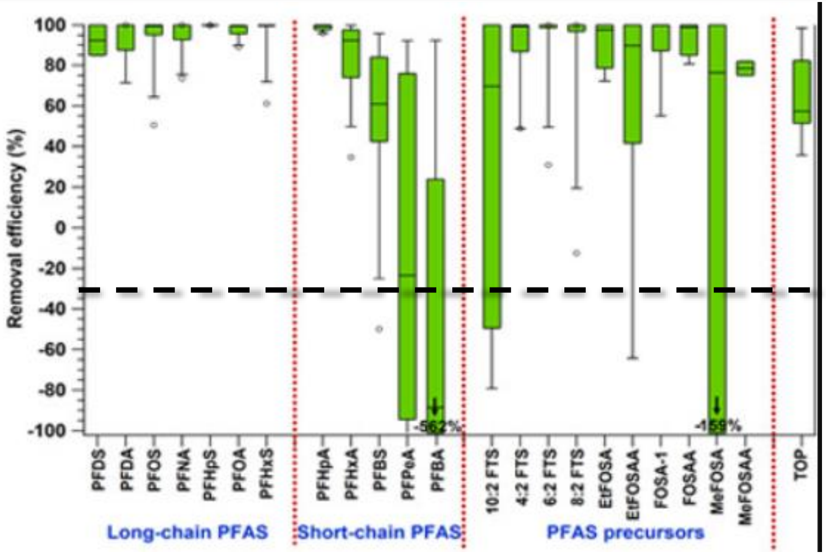
80% reduction of PFCAs and PFSAs after 8-hr treatment

Plasma

- Groundwater; AFFF; AIX and NF reject; IDW
- Less sensitive to co-contaminants
- Shorter (minutes) reaction time
- Less effective for shorter chain PFAS
- Partial destruction leads to accumulation of some PFAS



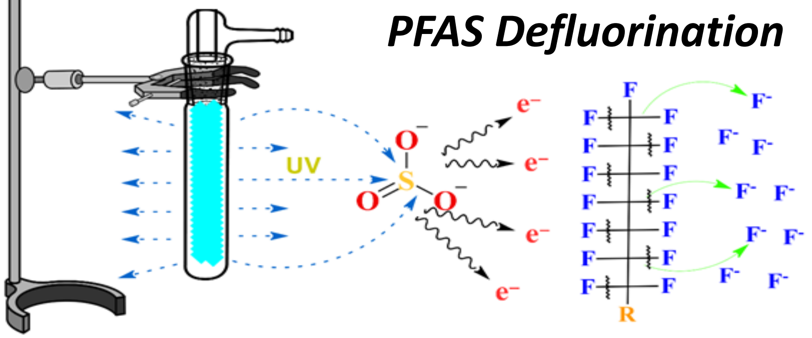
Pilot-scale plasma reactor for IDW treatment
(Singh et al, ES&T, 2019)



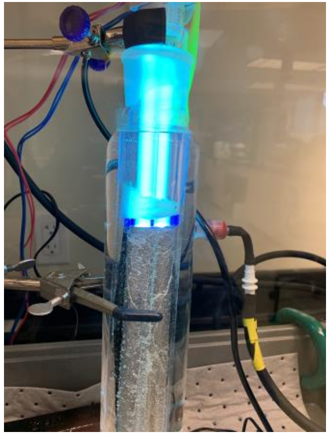
UV-Hydrated Electrons (Sulfite)

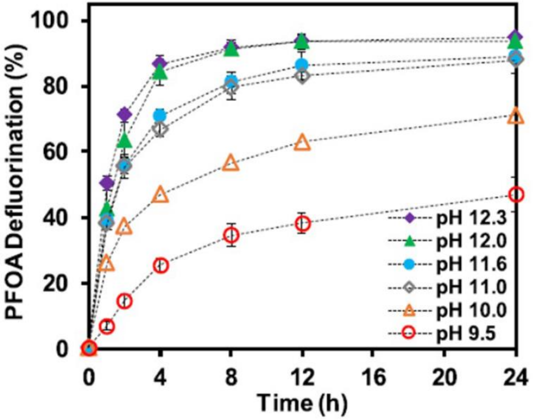
- Groundwater; AFFF; AIX or NF reject; IDW
- Easy to operate and implement in water/wastewater facilities
- PFAS half-lives depend on the PFAS (few hours to days)
- Highly impacted by water and wastewater constitutes including dissolved organic carbon (DOC), alkalinity, nitrate and others which slow PFAS degradation

Low/medium/High Pressure UV Lamp



UV + Sulfite → Hydrated electrons (e_{aq}^{-})+ Sulfate/bisulfate (nontoxic)

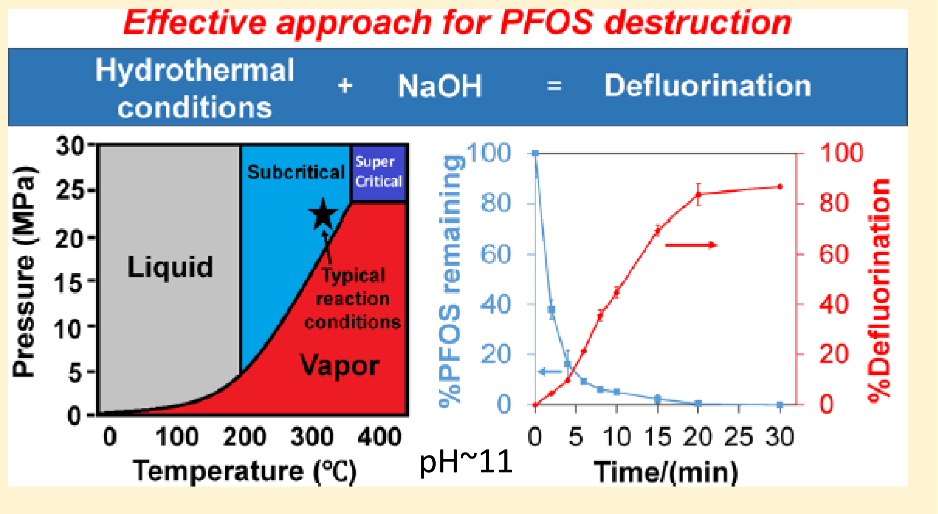




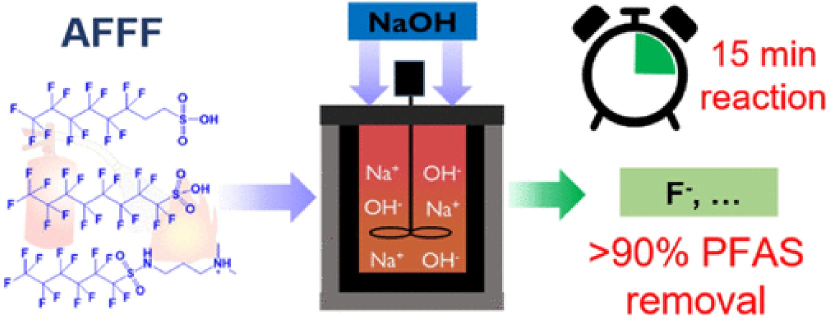
Bentel et al., *ES&T Letters*, 2020

Hydrothermal Alkaline Reaction

- Concentrated wastes, AFFF, IDW, concentrated source materials
- High-temperatures, pressure and caustic conditions, can generate HF
- Near-complete defluorination of PFASs in AFFF mixtures in minutes (e.g., 30) to hours, but mass balance work ongoing



Less than temperatures required for incineration



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Letter
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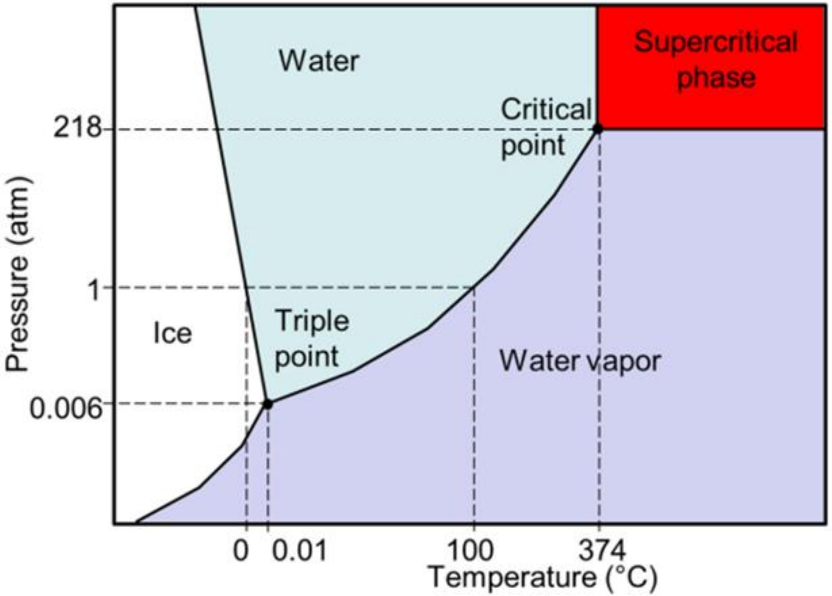
Rapid Destruction and Defluorination of Perfluorooctanesulfonate by Alkaline Hydrothermal Reaction

Boran Wu,[†,‡,§] Shilai Hao,[†] Younjeong Choi,[†] Christopher P. Higgins,[†] Rula Deeb,[‖] and Timothy J. Strathmann[*,†]

Environ. Sci. Technol. 2021, 55, 5, 3283-3295

Supercritical Water Oxidation

- Concentrated wastes, AFFF, IDW, concentrated source including slurries and biosolids
- High-temperatures, pressure, and requires an oxidant (e.g., oxygen, air)
- Corrosive conditions (generate HF) and precipitation of salts
- Near-complete defluorination of PFASs in AFFF mixtures in seconds (e.g., 30), but mass balance work ongoing



ESTCP Project ER20-5350

- Treated 30-300 dilute AFFF
- >95-98% decrease in TOF

$$\textbf{PFAS} + O_2\text{ (air)} \xrightarrow[\sim 240\text{ bars}]{>374\ ^\circ C} CO_2 + \mathbf{F^-} + \underbrace{\mathbf{CaF_2}}_{\text{solid}} + \text{heat}$$

Less than temperatures required for incineration

Treatment Efficiency

where P is the power (kW), t is the treatment time (h), V is the water volume (m^3), and C_0 and C_t are the initial and final concentrations, respectively.

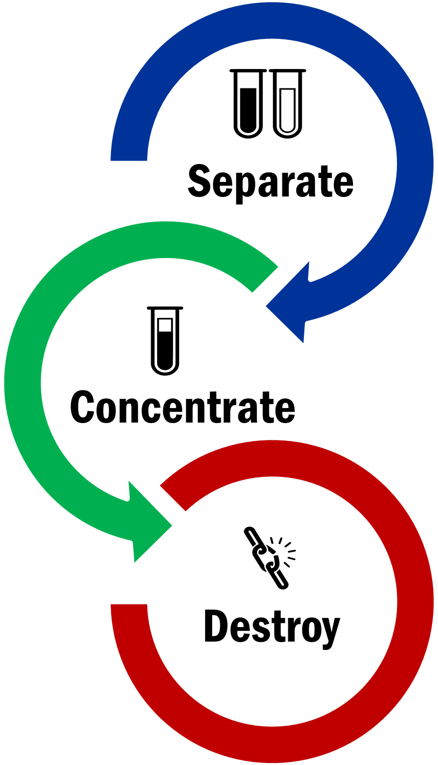
$$E_{EO}\left(\frac{kWh}{m^3}\right) = \frac{P\ t}{V \log\left(\frac{C_0}{C_t}\right)}$$

System	PFAS	Volume (L)	OOM	Time (hr)	E_{EO} (W-h/L)	Defluorination (%)	Source
ECO	PFOS, PFOA, dilute AFFF, RO and NF reject, SAFF concentrate	20	3-5	8	46-100	86-99.9%	Chaplin, 2020, Schaefer, 2017, 2019,2020
Plasma		4	3-5	0.1-1	9-84	~33-133%	Singh et al. 2019
UV-Sulfite		45	3-5	8	15	90%	Jassby, 2020, Rao, 2020, Su 2019
Hydrothermal Alkaline	PFOS, PFOA, Dilute AFFF	0.05	2-5	0.5	127	70-99%	Strathman, 2020
Supercritical Water Oxidation	PFOS, PFOA, Dilute AFFF, Biosolids	1000	2-5	0.003	NA	99.99%	Deshusses, 2020

Takeaways

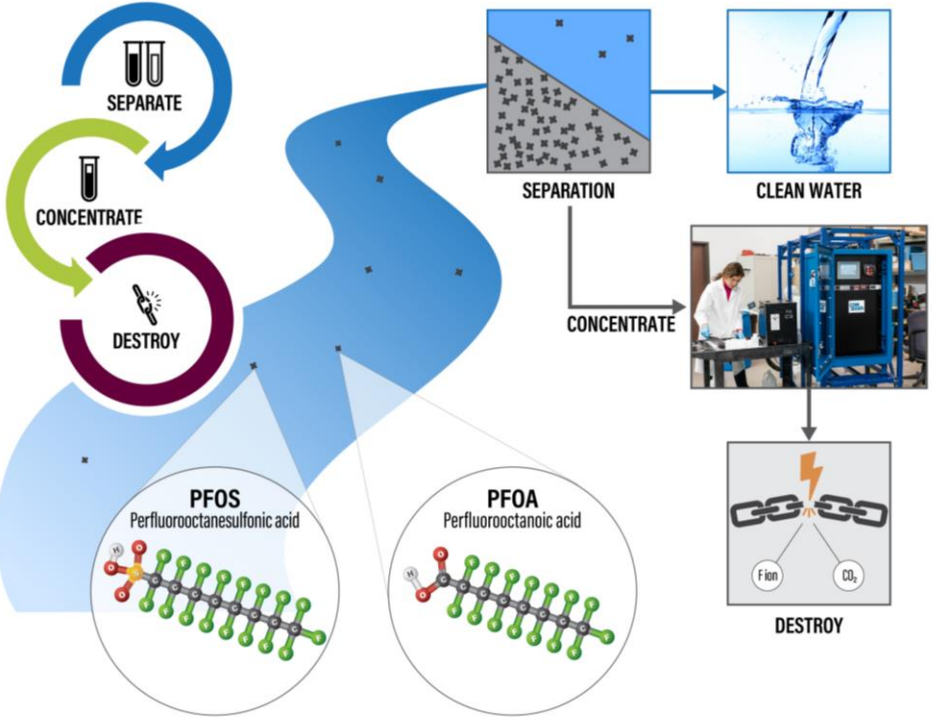
- Future PFAS solutions will focus on PFAS destruction with zero waste discharges
- Most destructive technologies are impractical for dilute streams – best suited for low-volume, high-strength PFAS concentrates
- Effective PFAS destruction that checks all the boxes for full-scale applications is going to be challenging and will take years to develop
- More pilot-scale demonstrations for PFAS destruction in side-by-side comparisons for different treatment streams
- When water matrix is complex, shorter chain PFAS and precursors are present, complete defluorination remain problematic for nearly all destruction technologies

Treatment Trains - PFAS Management Solution

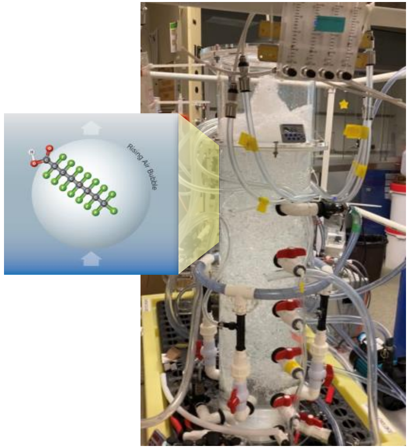


Treatment Goals	Example Technologies
• Protect human health and the environment • Meet safe drinking water and discharge requirements	• GAC, AIX, RO (demonstrated) • NF • Regenerable sorbents • Foam fractionation
• Reduce waste stream volume	• Regenerable media → regenerant waste • Surfactant or coagulant separation → PFAS laden flocs • Foam fractionation → foam concentrate
• Zero PFAS waste discharge	• Electrochemical, plasma, UV-sulfite, Hydrothermal, Supercritical water oxidation

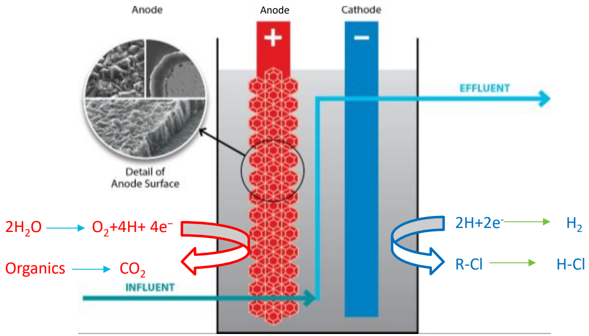
Separate-Concentrate-Destroy



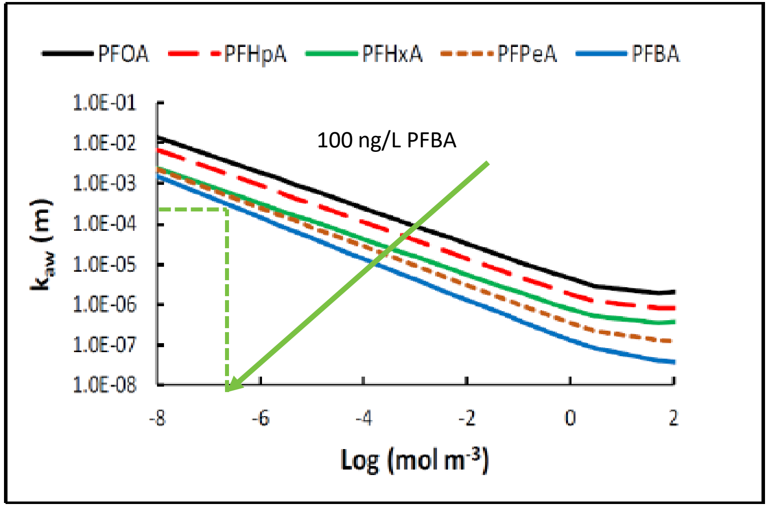
SAFF™



Electrochemical Oxidation



PFAS Removal at the Air-Water Interface



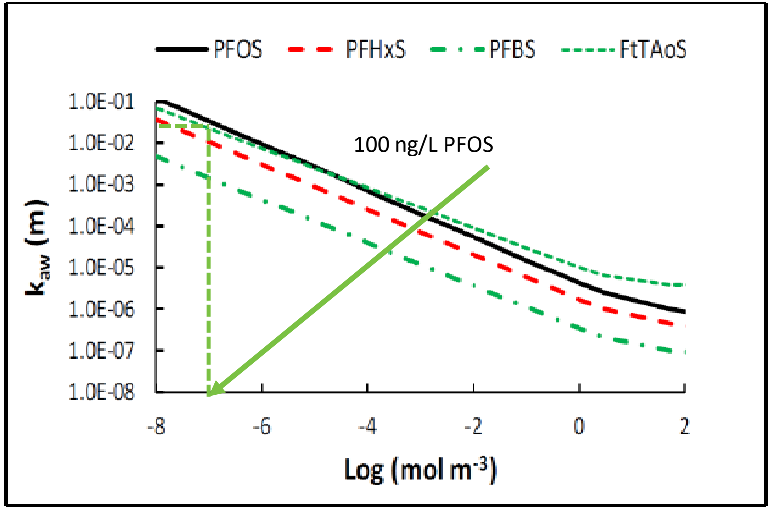
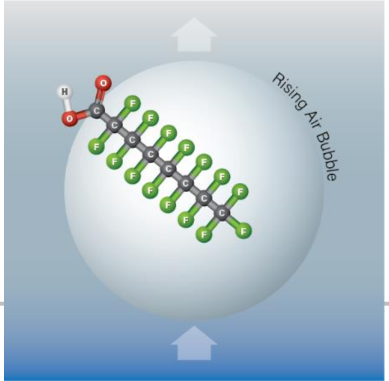
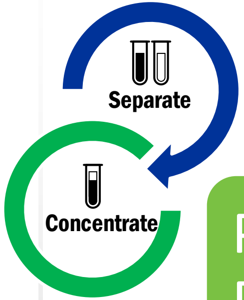


Figure courtesy of Schaefer et al., 2019

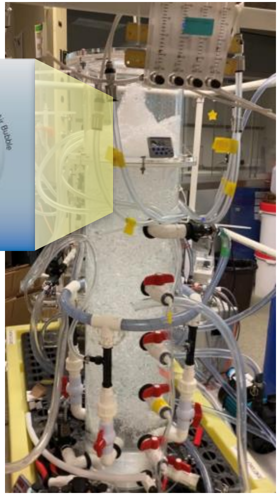




Surface Active Foam Fractionation (SAFF™)

Pilot and Full-Scale Demonstration Ongoing

- Increase air-water interface and separate foam from water phase
- Creates and separates PFAS foam concentrate
- Applicable for:
  - **Groundwater**
  - **Surface water**
  - **Wastewater**
  - **Leachate treatment**



PFAS [3]	Criteria			OPEC Systems AACO Field Trial Data: PFAS Removal Percentages from the AACO Fire Training Area (FTA; GW Extraction Array-1). Performance data derived from 15x consecutive sampling/testing events, collected each Wednesday) 1, 2.			
	Aust. DoH (ADWG, NEPM-2018 drinking Water)	ITRC Standard & Guidance Values (US & International) for PFAS in GW, DW, SW and Waste Water (Table 4.1, August 2019).		Feedwater (GWEW Array) Concentration	SAFF Primary Fractionation (Air Only)		
				Eurofins Data	LEAD Treatment - 18x Week Average Data		
	(μg/l)	Min. (ug/l)	Max. (ug/l)	18x Consecutive Wk Av. (ug/l)	Lab LOR (ug/l)	Av. Treated Water Results (ug/l)	Removal Percentage
PFBA	-	0.1	71	0.23	0.01	<0.15	37%
PFBS	-	0.09	667	0.20	0.001	<0.079	61%
PFPeA	-	0.09	3	0.64	0.001	<0.39	40%
PFPeS	-	-	-	0.15	0.001	<0.051	67%
PFHxA	-	0.09	6	0.80	0.001	<0.38	54%
PFHxS	0.07	0.01	0.1	1.0	0.001	<0.020	98%
PFHpA	-	0.01	300	0.40	0.001	<0.069	83%
PFOA	0.56	0.009	90	0.49	0.001	<0.002	100%
PFOS	0.07	0.00013	300	2.6	0.001	<0.002	100%
PFOSA	-	0.1	0.29	<0.005	0.001	<0.001	100%
PFNA	-	0.009	1	0.047	0.001	<0.001	100%
PFDA	-	0.1	0.37	0.002	0.001	<0.001	100%
6:2-FTS	-	0.1	0.2	0.11	0.005	<0.005	100%
8:2-FTS	-	0.2	0.2	0.020	0.001	<0.001	100%

Criteria Molecules (Australia)

1: New optimisation trials are pending to use surfactant amendments to enhance further removal of short chain PFAS.

2: Data sourced from fifteen continuous sampling/testing weeks (9th Oct 2019 to 5th Feb 2020), Eurofins/ ALS CofA reports, ISO-170125:2015 accredited for PFAS). Laboratory Method modified USEPA 537 (DoD/DoE QSM 5.2/5.3).

3: NATA accredited results (ALS & Eurofins), PFAS compounds presenting 15x compounds of interest .

SAFF™ + AIX

Commissioned 19th May 2019

- 5.3 million gallons treated
- 132 gallons of PFAS waste concentrate
- Concentration factor- 42,000x

Removal

(1) PFHxS 98% RR <0.020 μg/l is less than Michigan HSL 84ppt (0.084 μg/l)

(2) PFBS 59% RR <0.10 μg/l is less than Michigan HSL 1000ppt (1.0 μg/l)

SAFF™ + AIX

- Contract <0.07μg/l
- Aust. DoD website reporting <0.01μg/l

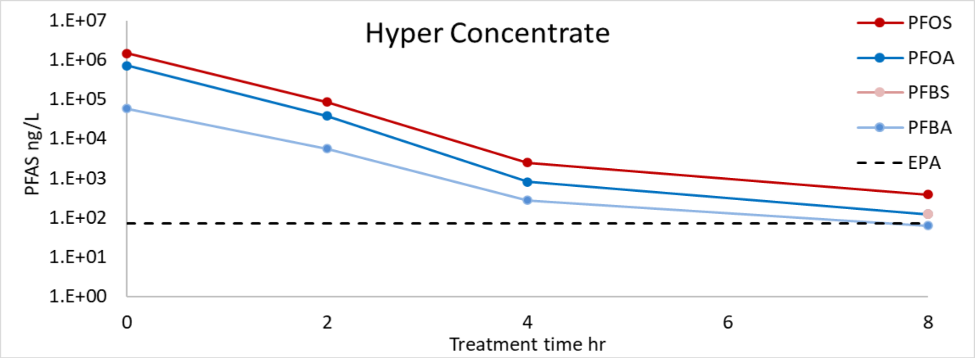
www.opecsystems.com

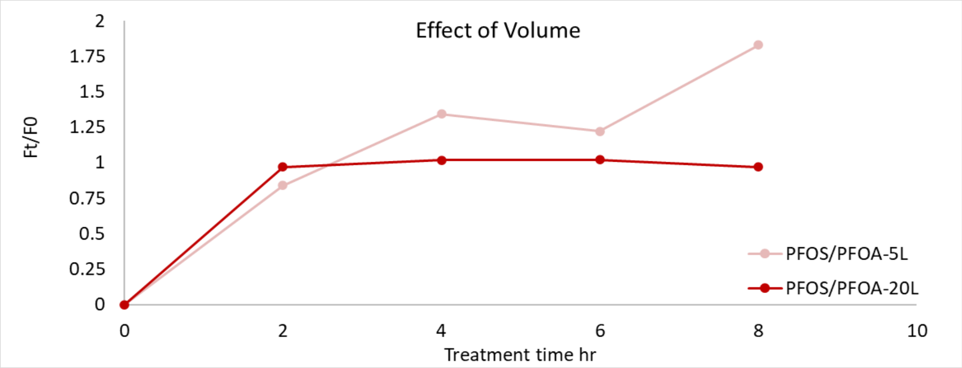
Pilot ECO System

- Proprietary electrodes
- Anti-scaling feature
- 3-8 GPM flow
- Adjustable power
- Gas detection sensor
- Leak detection system

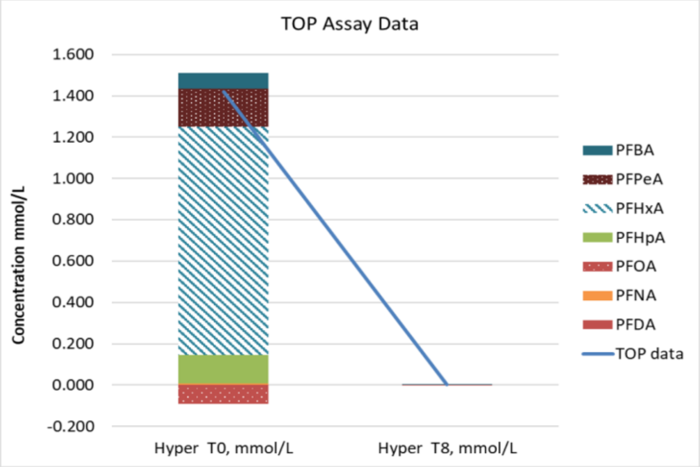
Increases electrode surface area by >100X

Destruction of PFAS in SAFF Foam Concentrates



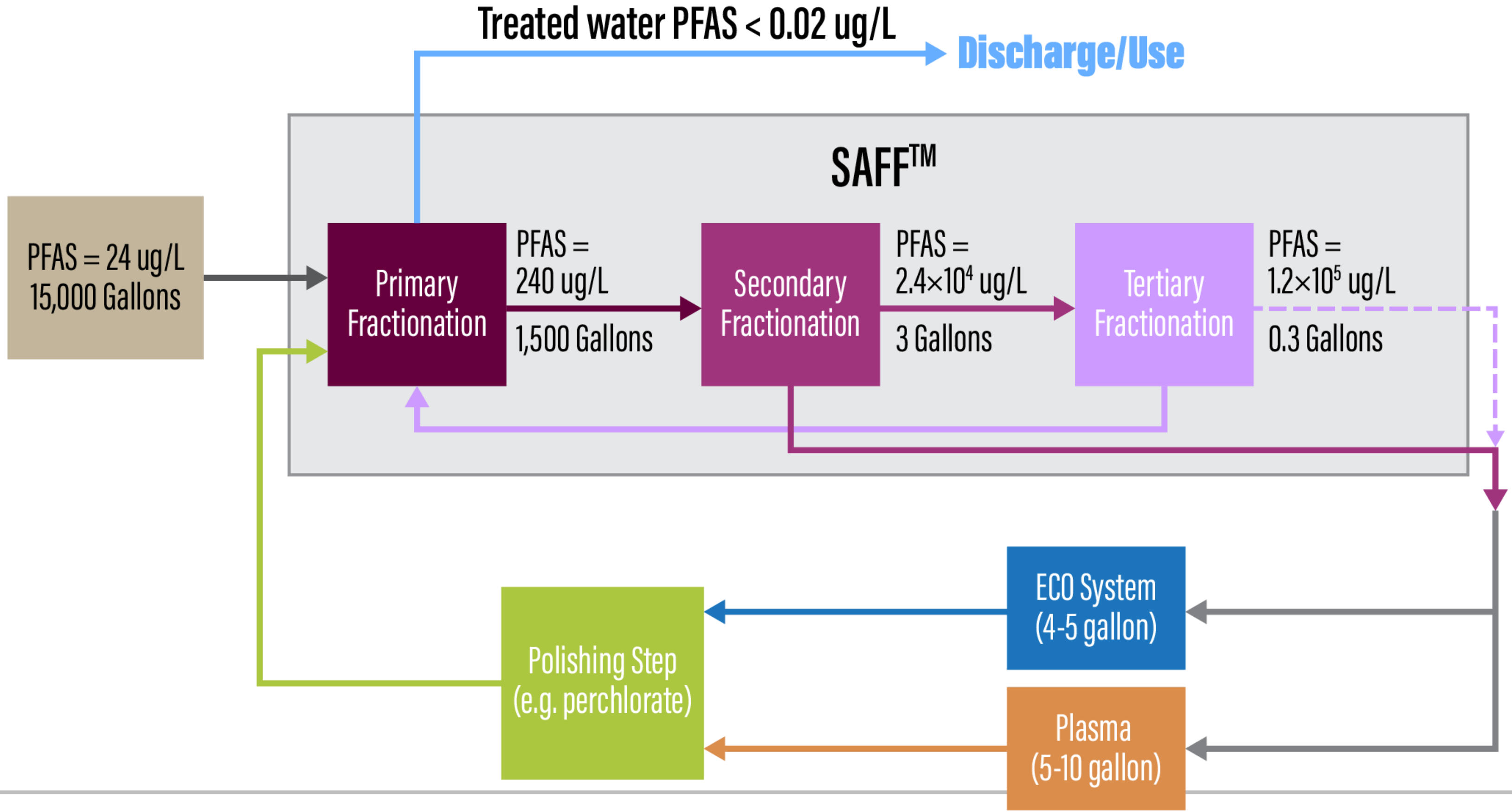


Pilot-Scale Treatment of SAFF concentrate by ECO



- More than 4-5 OoM reduction in PFAS concentration
- More than 98% of total organic fluorine is destroyed/released
- TOP data shows ~ 99.8% removal of precursor compounds

SAFF- ECO or Plasma Treatment Train



Next Steps for Destructive Treatment Trains

- **Demonstrate treatment effectiveness under variable conditions**
- **Obtain data to understand scalability and compatibility**
- **Compare technologies with different treatment streams to understand niches**
- **Develop effective automated controls for continuous operation**
- **Develop parameters to understand operations, maintenance and life-cycle costs**
- **Mitigate or manage undesirable by-products, such as HF, perchlorate and halogenated organics**
- **Optimize processes for a given PFAS stream**

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