Destruction of PFAS in concentrated wastes by an innovative advanced reduction process

USWAG PFAS Workshop
21 May 2025

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Acknowledgements

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Overview

In this talk:

- Discuss why we need PFAS destruction technologies
- Discuss what **EradiFluor** is (PFAS destruction system)
- Present results from field demonstrations treating PFAS concentrated waste

Take-home messages:

- Existing technologies produce concentrated PFAS waste
- PFAS treatment system effectively and reliably destroys PFAS

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Existing separation technologies leave behind concentrated waste

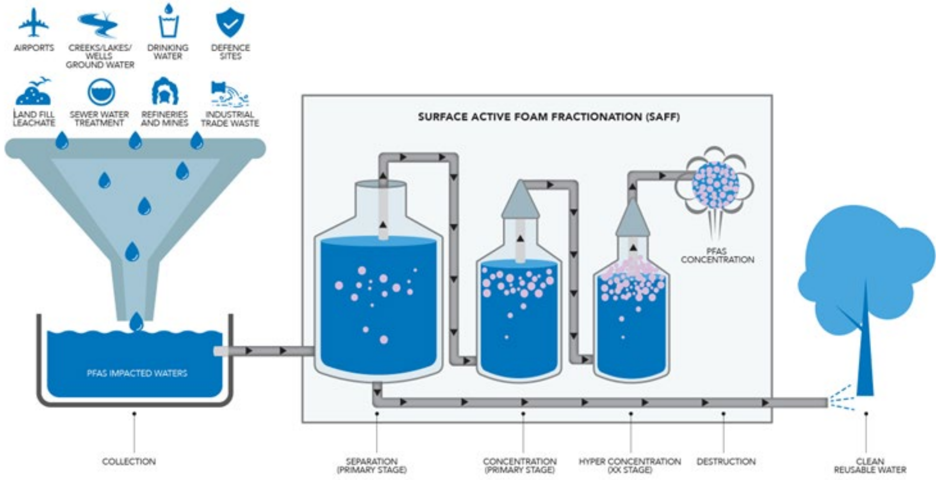
Conventional technology

Granular activated carbon

Membrane filtration

Ion exchange resin

Recent developments



OPEC

Foam fractionation

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There are few options for disposal of PFAS waste

Source: EPA, 2024. Interim guidance on the destruction and disposal of perfluoroalkyl and polyfluoroalkyl substances and materials containing perfluoroalkyl and polyfluoroalkyl substances – Version 2 (2024).

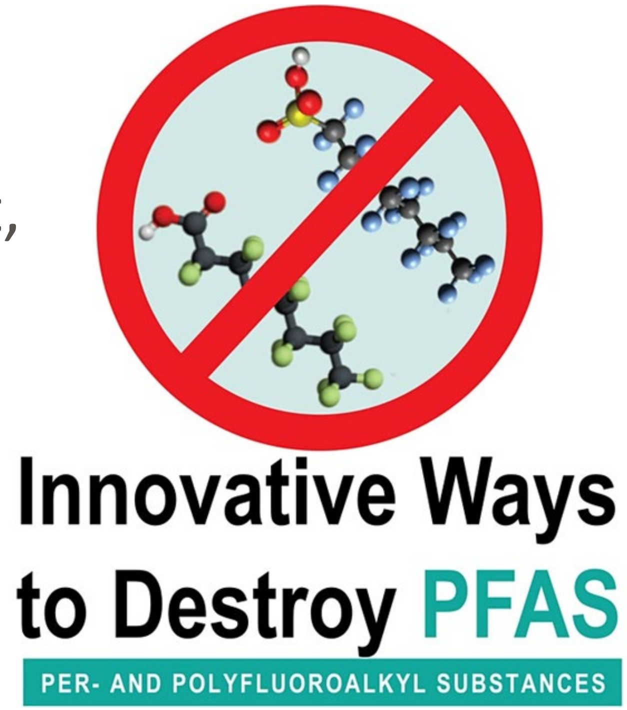
Incineration

Landfill

Deep well injection

There is a growing need for destructive technologies

- Regulations on PFAS are evolving
- Several destructive technologies are under development, and some have moved to commercial application:
  - Supercritical water oxidation
  - Hydrothermal alkaline treatment
  - Electrochemical oxidation
  - Plasma technology
  - Electron beam



EPA launched a technical challenge
for innovative ways to destroy PFAS in 2020

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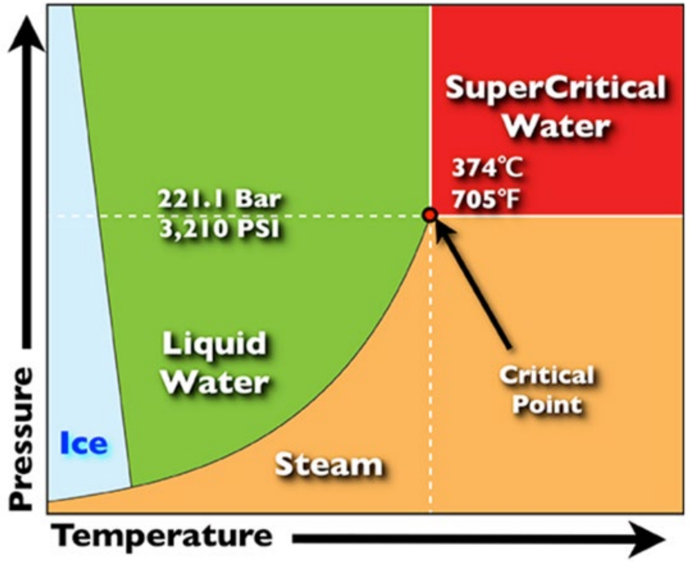
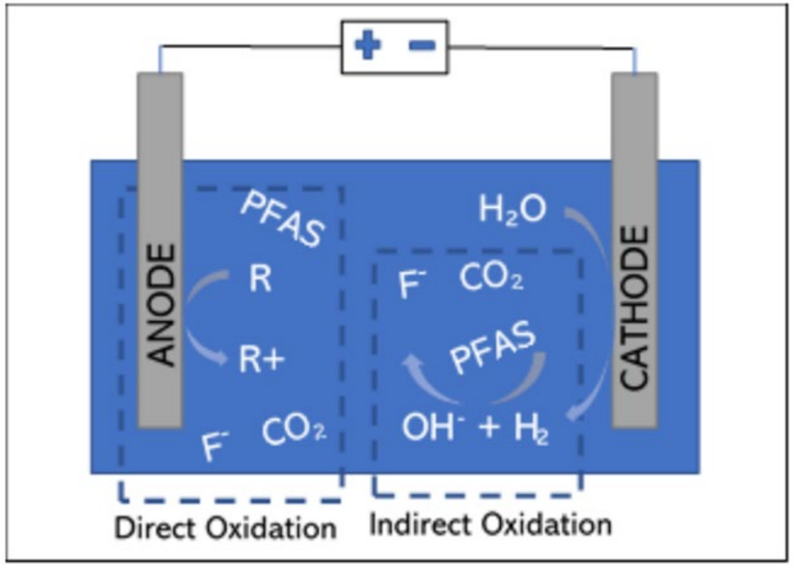
Destructive technologies under development



Supercritical water oxidation

- Chemical oxidation process
- Used to treat other organic waste

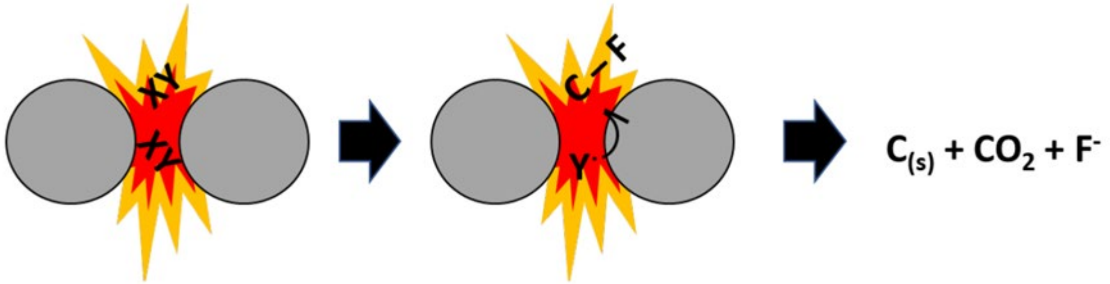


Electrochemical oxidation

- Low energy costs
- No chemical oxidants needed

Source: https://www.epa.gov/chemical-research/pfas-innovative-treatment-team-pitt

Destructive technologies under development (cont'd)



Ball-milling:

- Ball impacts create radicals, heat, and even plasma from co-milling materials and localized high temperatures that mineralize PFAS.

Pyrolysis and gasification:

- Decomposes materials at moderately elevated temperatures in an oxygen-free or low-oxygen condition.
- Treat PFAS-containing sewage and biosolids.

Source: https://www.epa.gov/chemical-research/pfas-innovative-treatment-team-pitt

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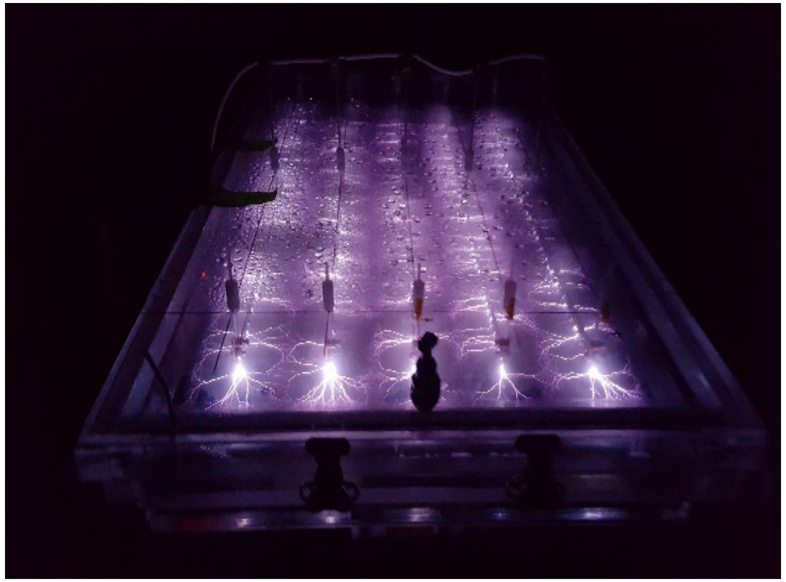
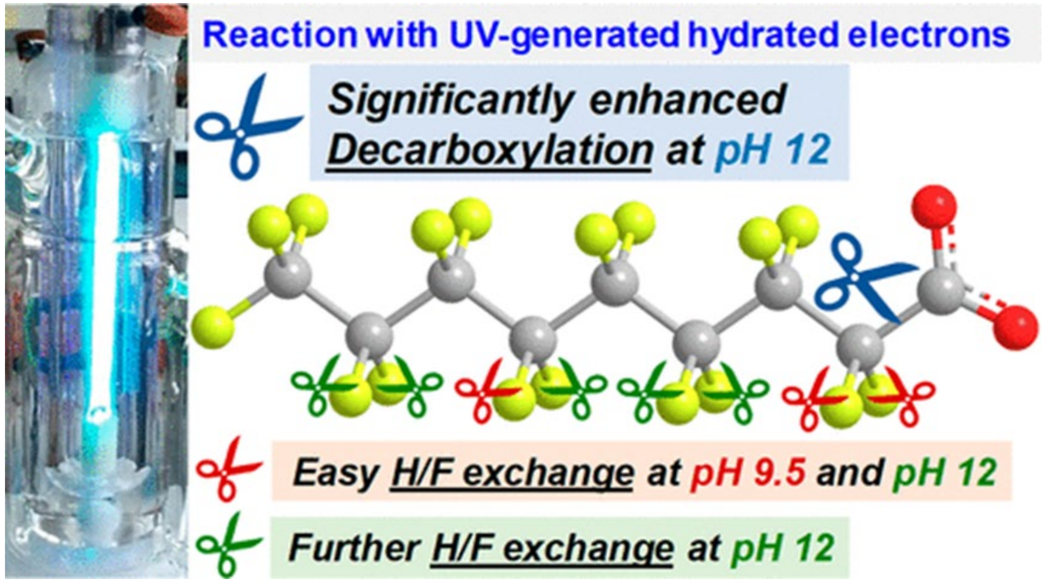
Destructive technologies under development (cont'd)





Plasma technology

- Clarkson University leading this research effort
- Field pilot tests have been conducted
- Promising field data have been collected

Source: Singh et al., ES&T 2019

Hydrated electrons

- UC Riverside leading this research effort
- Near complete defluorination for both long- and short-chain PFAS
- Extensively studied in bench-scale
- Field study to be conducted under an ESTCP-funded project

Source: Bentel et al., ES&T Letter 2020

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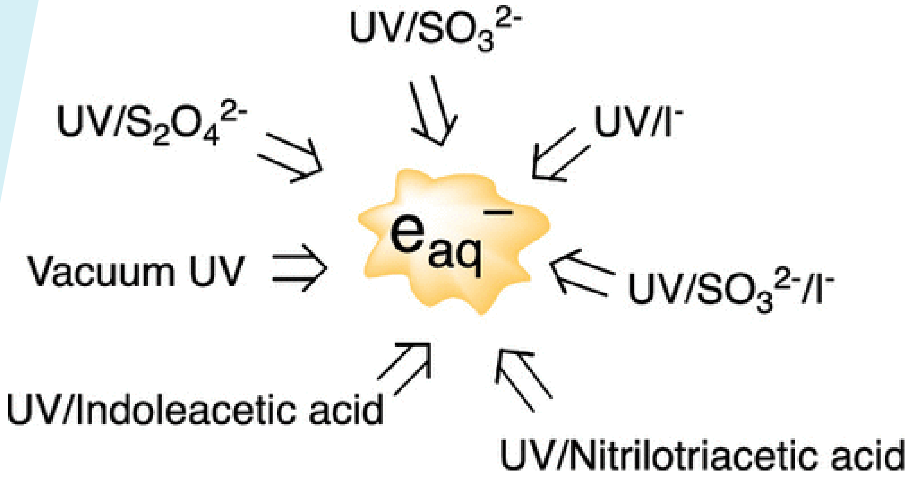
A new approach: UV-based advanced reduction process

- This process is based on the production of highly reducing hydrated electrons, e_{aq}^-
  - Different from UV/H_2O_2 used in water treatment
  - e_{aq}^- is a strong reductant (standard potential = −2.9 V)
  - Key reactant for PFAS destruction by non-thermal plasma and electron beam
- e_{aq}^- can be generated under UV irradiation
  - Several ways to produce e_{aq}^-
  - As shown in the figure on the right



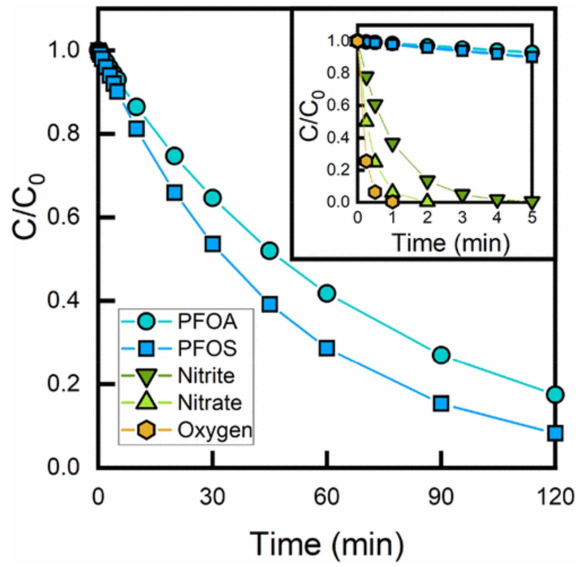
Source: Fennell et al., 2022

A new approach: UV-based advanced reduction process

- e_{aq}^{-} break C-F bond and degrade PFAS compounds
  - Highly effective in PFAS destruction
- e_{aq}^{-} highly effective for treatment
  - Chlorinated solvents, perchlorate, bromate, nitrate, chromium (VI)
- Certain water constituents may scavenge e_{aq}^{-}
  - Oxygen
  - Nitrate/nitrite

$$SO_3^{2-} \xrightarrow{UV} SO_3^{\bullet -} + e_{aq}^{-}$$

NHE = −2.9 V



Source: Fennell et al., 2022

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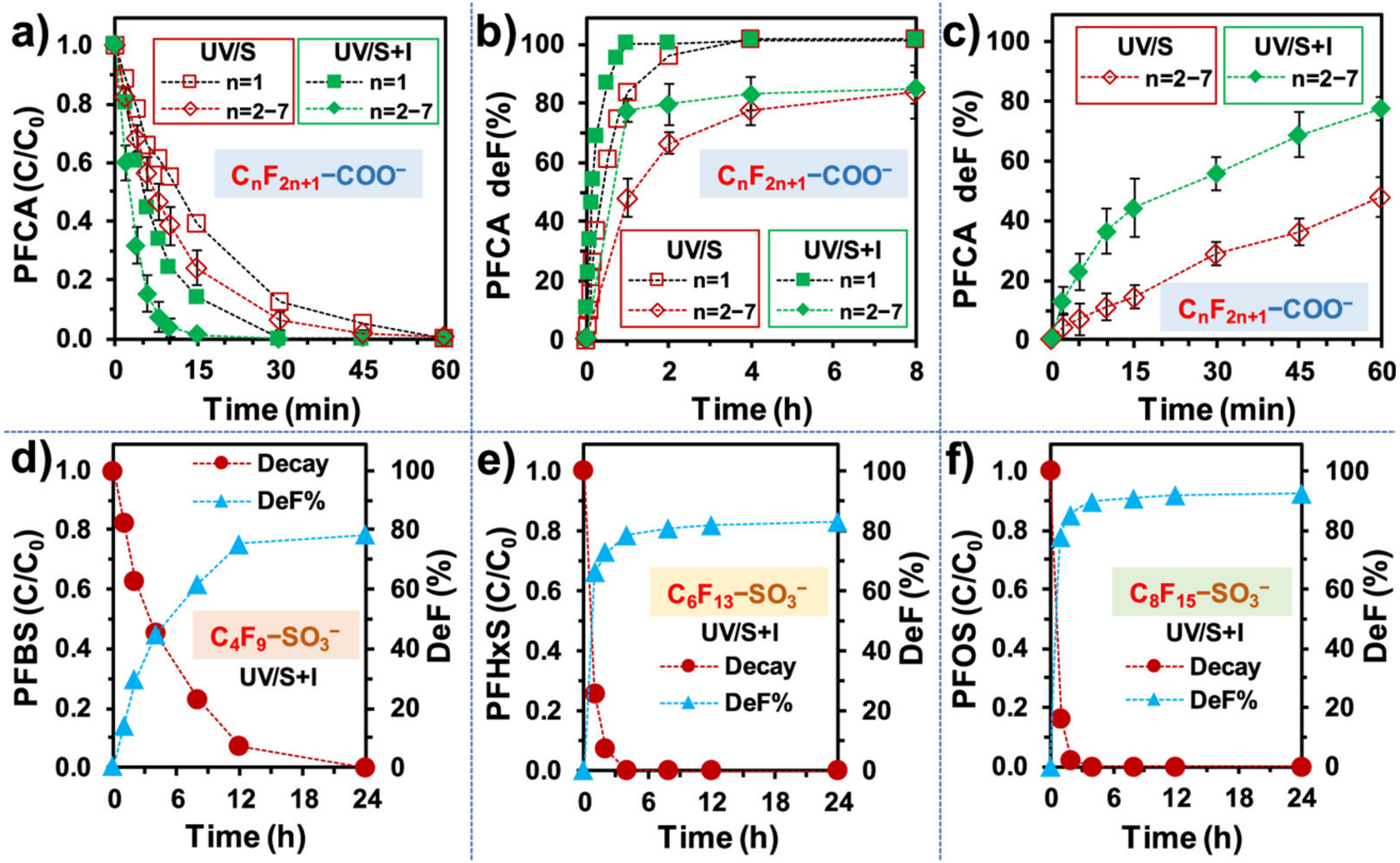
Laboratory study results showed effective destruction of various PFAS

Source: Liu et al., 2022



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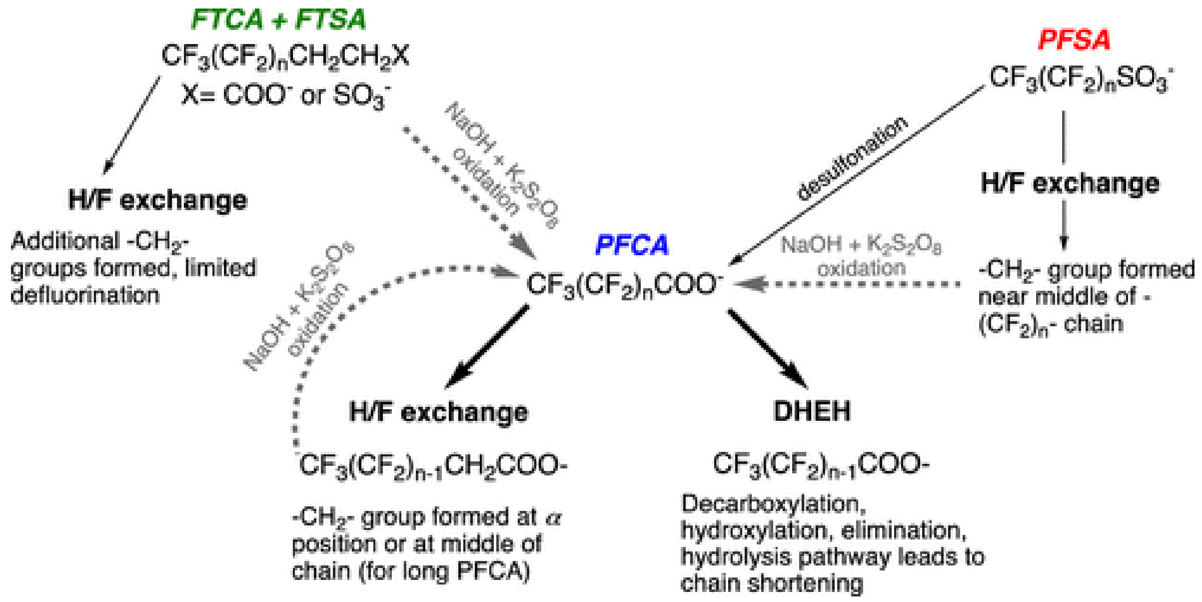
Mechanism of PFAS destruction by hydrated electrons

- Two PFAS defluorination pathways are identified:
  - H/F atom exchange
    - $-CF_2-$ group to $-CH_2-$ group
    - Produces polyfluorinated products
  - DHEH
    - Shorten one $-CF_2-$ group each step
    - Deeper defluorination
    - Mostly occur to PFCAs

DHEH = Decarboxylation, hydroxylation, elimination, hydrolysis



Source: Fennell et al., 2022

Findings from laboratory tests

- Hydrated electrons are highly effective in destroying PFAS
- Near-complete destruction of various short-chain and long-chain PFAS
- No harmful byproducts (e.g., perchlorate, bromate)
- The reactive mechanisms are well understood
- Not affected by high salt concentration
- Mild reaction conditions (e.g., temperature, pressure)

EradiFluor - PFAS destruction system

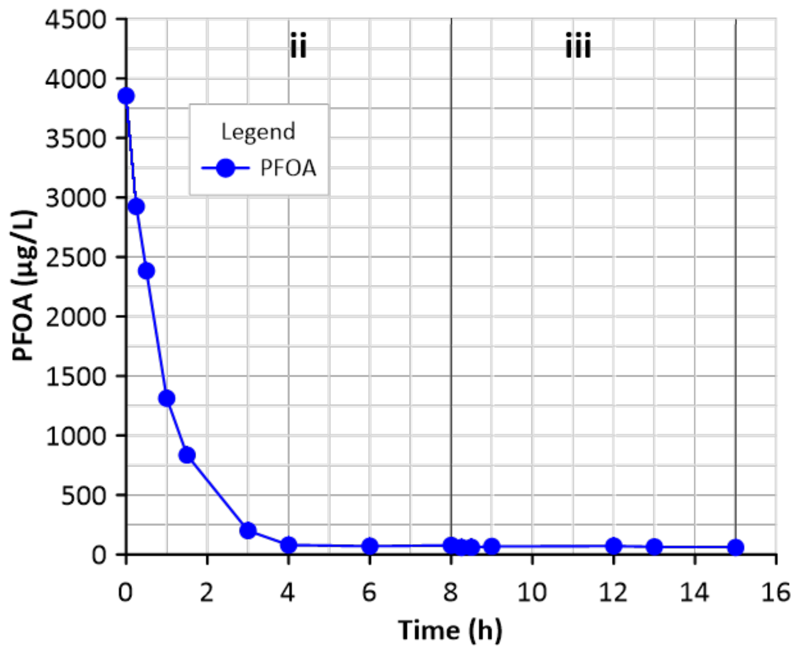
- A PFAS treatment system has recently been designed and constructed
  - UV/sulfite-based treatment process
  - Mobile, on-site treatment unit
  - Ambient reaction conditions
  - Control/monitoring components
- Concentrated PFAS streams to be treated under DoD field conditions

View from the rear of the trailer

Simulated waste test

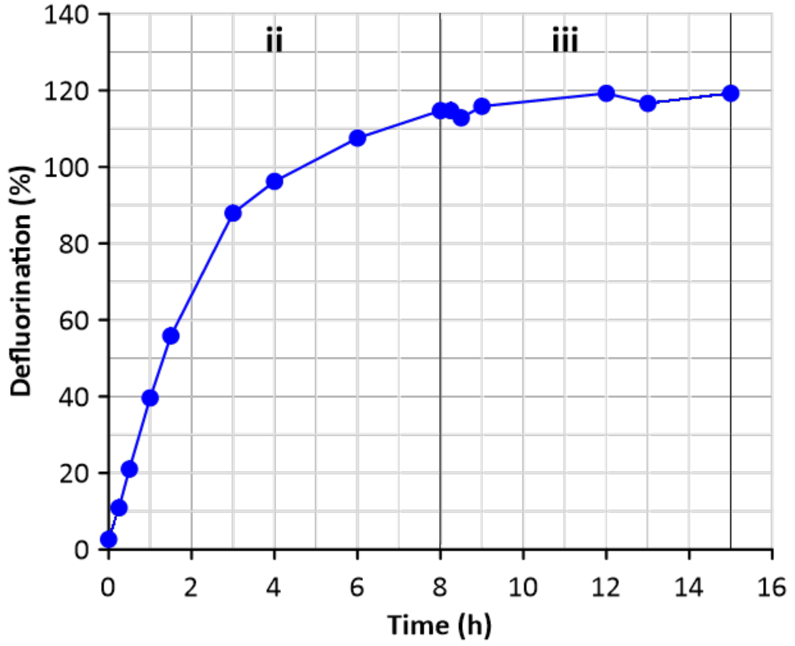
Method:

- **PFOA:** Consumer products, food packaging, firefighting foam, and other industrial processes
- 30-gallon batch liquid waste
- Treatment: (II) reduction, (III) post-oxidation



Results:

- 99% PFOA degradation
- >100% defluorination was achieved
- Post-oxidation didn't improve defluorination efficiency



i = Pre-oxidation **ii** = Reduction **iii** = Post-oxidation

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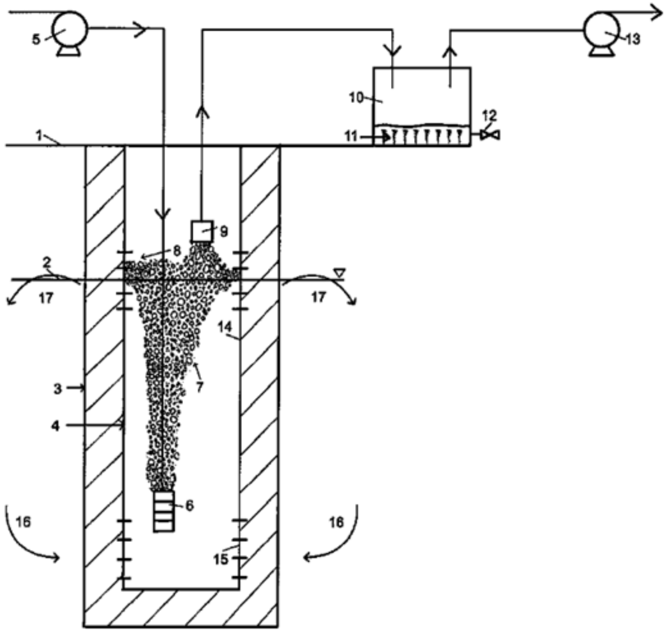
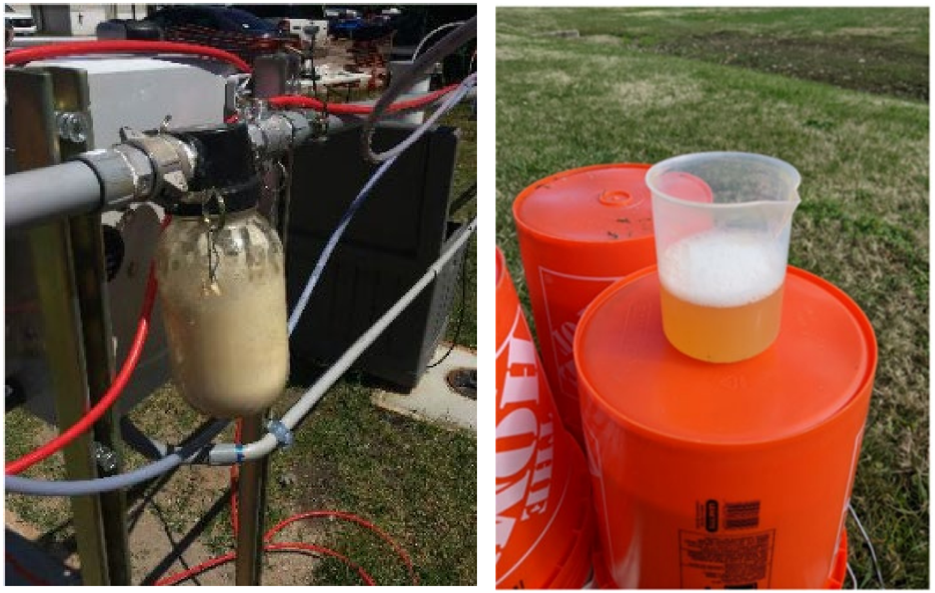
Treatment of waste concentrate: in situ foam fractionation

- Foamate produced from an in situ foam fraction groundwater remediation system from a Navy site
  - Tens of ppm level of PFAS
  - PFOS and 6:2 FTS dominant
  - Low level of TOC and nitrate/nitrite



In situ foam fractionation system for groundwater remediation



PFAS concentrate produced from an in situ foam fractionation system for groundwater remediation (Source: Nelson 2022)

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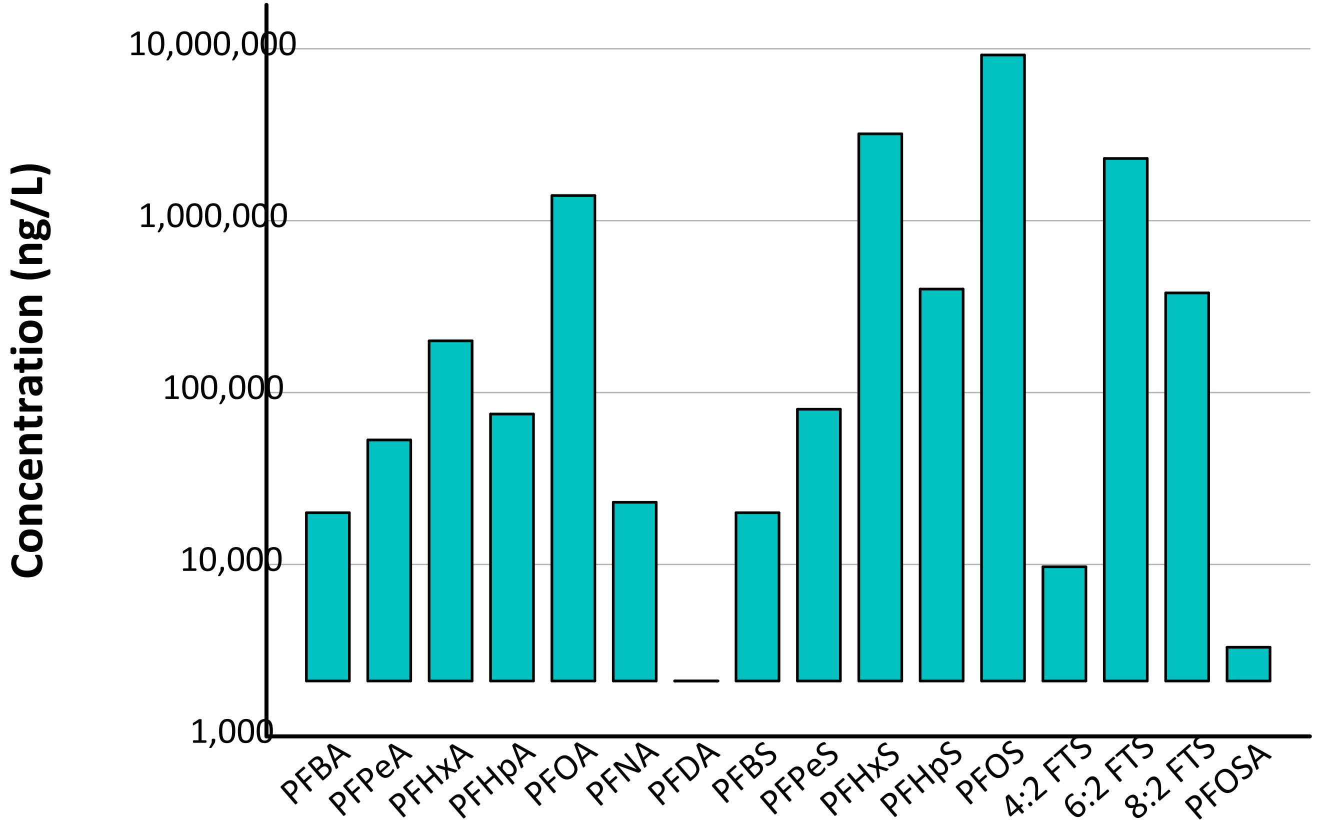
Constituents of the foam fractionate



Parameter	Concentration	Unit
Alkalinity	28.4	mg $CaCO_3$/L
Total Dissolved Solids	92	mg/L
Nitrogen, Nitrite	ND	mg/L
Nitrogen, Nitrate	ND	mg/L
Total Organic Carbon	16	mg/L
Sulfate	34.3	mg/L

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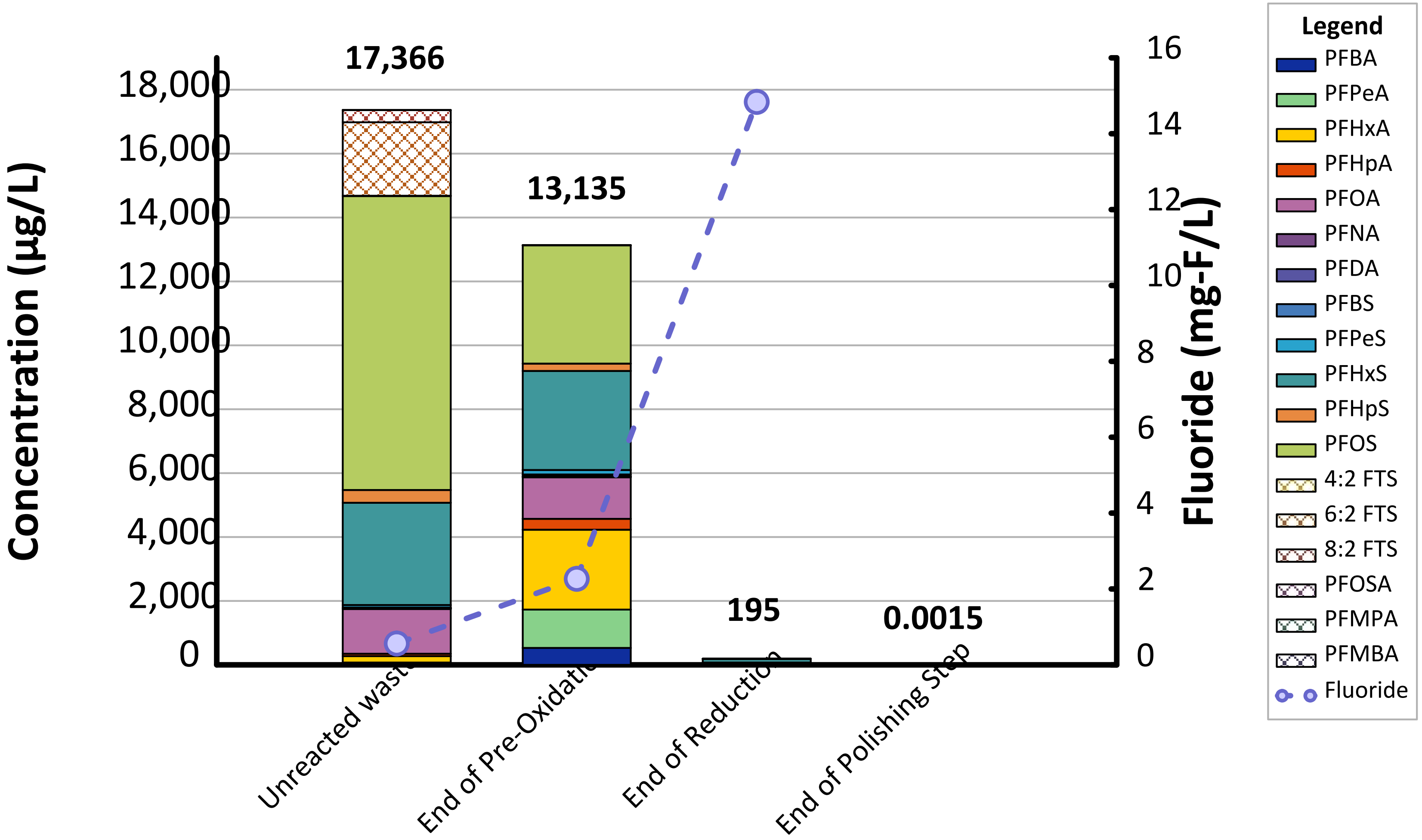
Field demonstration at a Navy site

- Treatment system was mobilized to the site this summer.
  - Simple setup
  - 24/7 operation
  - Ambient conditions
  - Near complete PFAS destruction

PFAS destruction system trailer was transported to the Navy site in the East Coast with a pickup truck.

PFAS destruction system and a temporary tent was set up for the field demonstration

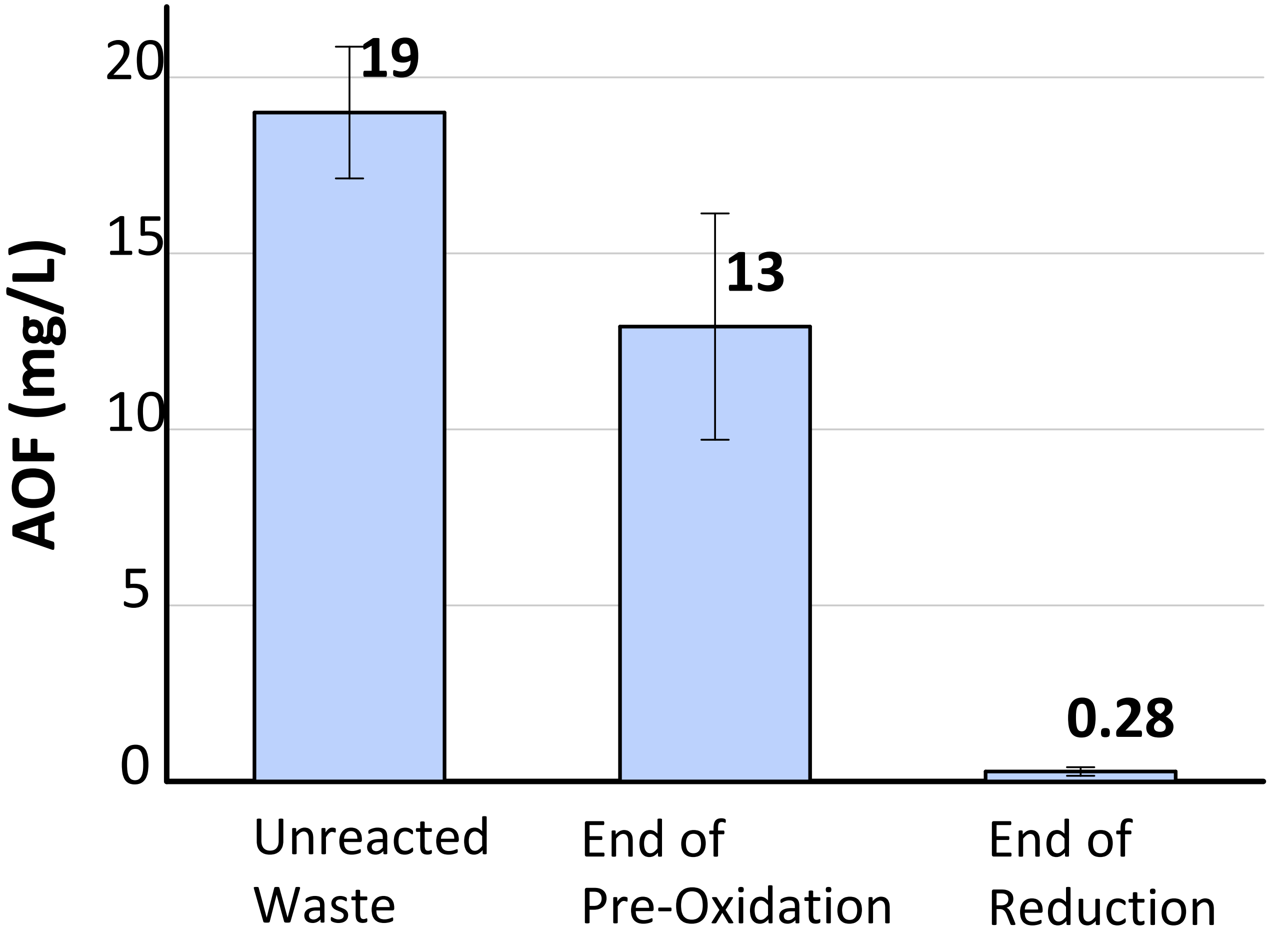
Field results show near-complete destruction of PFAS and removal of all PFAS



About 99 percent of PFAS were destroyed at the end of the reduction step.

After the polishing step, all residual PFAS were removed to the Not-Detect level, except one compound PFOS reported as 1.5 ng/L (below MCL of 4 ng/L).

Adsorbable organic fluorine results provided another line of evidence of PFAS destruction



Average of multiple batches shows 99 percent of adsorbable organic fluorine (AOF) was destroyed after PFAS destruction treatment. AOF combusts and measures carbon-sorbed PFAS and is an estimate of PFAS-associated fluorine mass.

Effective destruction of long- and short-chain PFAS

- Average of multiple batches shows > 99% destruction of most PFAS (short- and long-chain)
- PFBS showed slightly less destruction, but still effectively degraded

Destruction (%) (end of reduction)

Batch	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFBS	PFPeS	PFHxS	PFHpS	PFOS	4:2 FTS	6:2 FTS	8:2 FTS
1	> 99.8	> 99.99	99.96	> 99	> 99.98	> 98	> 99.7	> 99.98	> 99.4	> 99.99	> 97.2	> 99.98	> 99.9
2	99.9	99.8	99.8	> 99.9	99.8	94	99.8	99.8	99.7	99.7	99.6	99.9	99.9
3	**99.98**	99.96	99.99	> 99.6	> 99.998	95	> 99.98	99.99	**99.98**	99.97	99.7	99.99	99.97
4	**99.98**	99.9	99.99	> 99.99	> 99.997	92	> 99.98	99.996	**99.98**	99.97	99.5	99.997	> 99.99
5	99.9	99.95	99.96	> 99.96	99.99	**66**	98.7	99.96	**99.98**	99.9	98	99.99	**99.1**

Notes:
Destruction (%) = 100 x [($C_{max} - C_{end\ of\ reduction}$) / C_{max}]
Calculation uses C_{max} (and not $C_{initial}$) since certain PFAS were generated during pre-oxidation step
Blue = $C_{end\ of\ reduction}$ was above the method detection limit, but below the reporting limit (i.e., J-flag estimated)
Purple = Outlier. Possibly due to operational adjustments in batch 5.

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Effective PFAS destruction at Southern California field demonstration

- Groundwater PFAS remediation using foam fractionation + PFAS destruction
- Secondary foam fractionation (no booster) showed concentration factor ~500x
- Total detected PFAS ~9 mg/L in foamate
- Short- and long-chain PFAS showed >99% destruction

PFAS	GW (ng/L)	Foamate (ng/L)	Destruction Effluent (ng/L)	Destruction (%)
PFBA	690	250,000 U	14	NA
PFPeA	1600	61,000	160 U	>99.7
PFHxA	2100	110,000	160 U	>99.85
PFHpA	720	150,000	160 U	>99.89
PFOA	1300	1,000,000	11	99.9989
PFNA	77	31,000	0.94	99.997
PFBS	460	61,000	14000	77.0
PFPeS	660	81,000	1400	98.3
PFHxS	3600	2,200,000	240	99.989
PFHpS	220	120,000	8.3	99.993
PFOS	10000	3,400,000	91	99.997
4:2 FTS	400 U	250,000 U	11	NA
6:2 FTS	3900	2,000,000	88	99.996
8:2 FTS	170	250,000 U	1.5	NA
HFPO-DA	150 U	94,000 U	120 U	NA
3:3 FTCA	400 U	5,000 U	320 U	NA

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Potential applications of UV/sulfite-based PFAS destruction

- Residue from foam fractionation, ion exchange regeneration, activated carbon regeneration, reverse osmosis/nanofiltration reject
- Industrial wastewater from PFAS manufacturers
- AFFF delivery vehicle cleaning solution
- Soil washing residue
- **Not** designed to treat low-concentration PFAS in groundwater and drinking water

Comparison with other destructive technologies

Strength:

- Does not need special parts
- Low capital cost
- Operate under ambient pressure and temperature (and high pH)
- Low energy use and cost
- Safer operation
- High uptime (rarely shuts down)
- Performance not affected by salt

Limitation:

- Reaction time (to be applied along with concentration technologies)
- Color of liquid waste affects performance (pretreatment is required)

Summary

- Existing technologies produce concentrated PFAS waste
- Growing need for destruction technologies
- Hydrated electrons are effective in destroying various classes of PFAS
- PFAS destruction system field demonstrations showed that near-complete PFAS destruction based on fluorine mass balance was achieved
- Next step: complete field demonstration in SoCal

Questions?

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Take-home messages

- Existing technologies produce concentrated PFAS waste
- PFAS destruction system effectively and reliably destroys PFAS

Find out more at:

https://serdp-estcp.mil/projects/details/4c073623-e73e-4f07-a36d-e35c7acc75b6/er21-5152-project-overview

https://info.haleyaldrich.com/eradifluor

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