PFAS Destruction

A Discussion of Emerging Technologies Aimed at Destroying Fluorinated Organics

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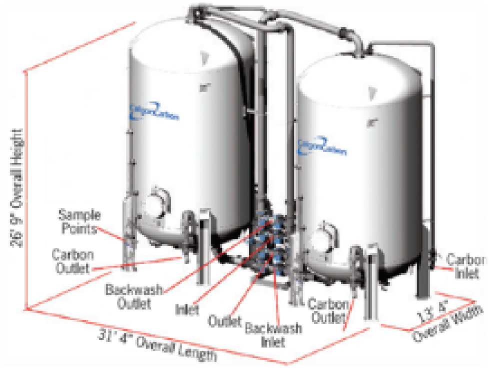
“Demonstrated” PFAS Destruction Technologies

Supercritical Water Oxidation (SCWO)	Photochemical	Hydrothermal Alkaline Treatment (HALT)
Sonolysis	Electrochemical	Plasma

Which one is best?

Concentrate First!

- Necessary for cost efficiency
- Waste Streams are diverse
  - ➢ Investigation or remediation derived waste (IDW), (RDW)
  - ➢ Spent granular activated carbon (GAC), ion exchange resin (IXR), Reverse Osmosis (RO) Reject, Foam Fractionate
  - ➢ AFFF, Rinsates
  - ➢ Landfill Leachates
  - ➢ Biosolids & Sludges
  - ➢ Soils & Sediments



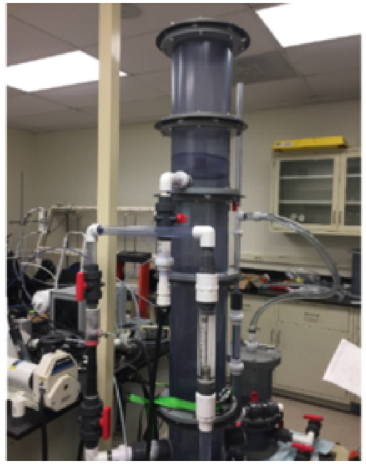
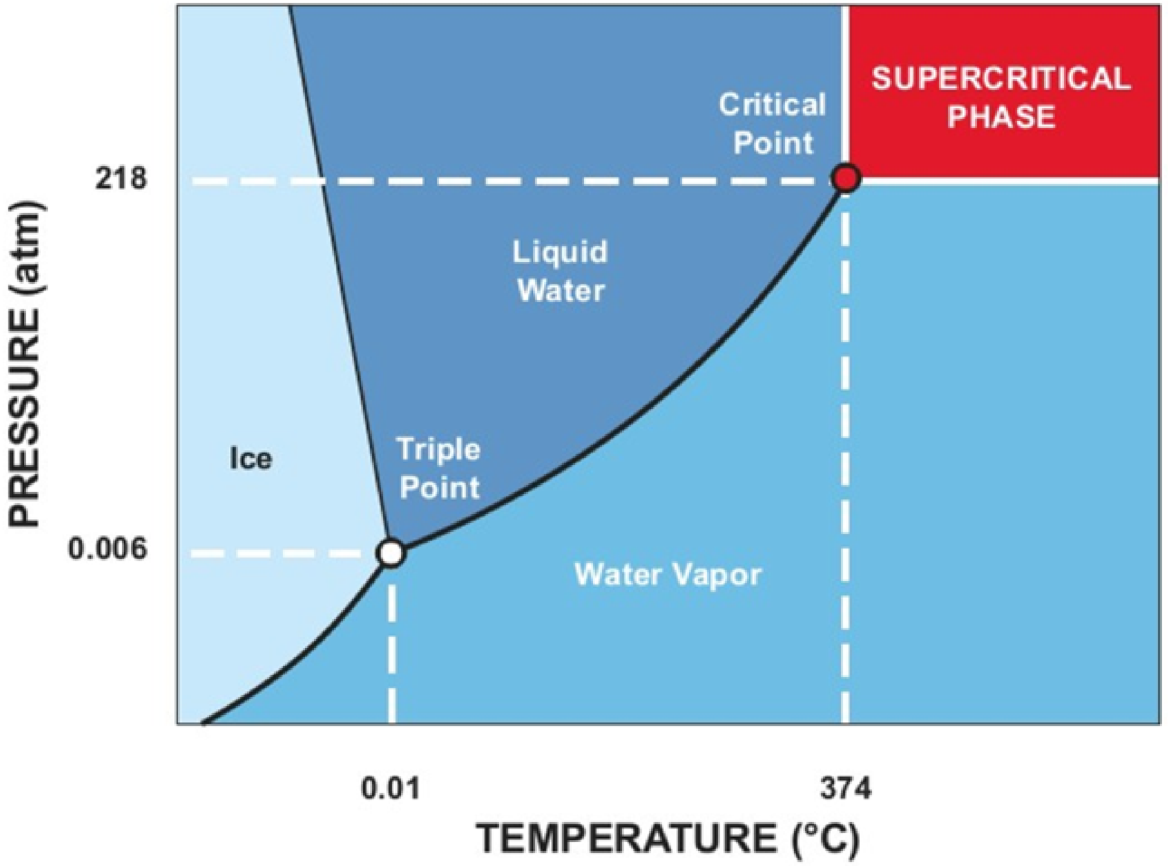


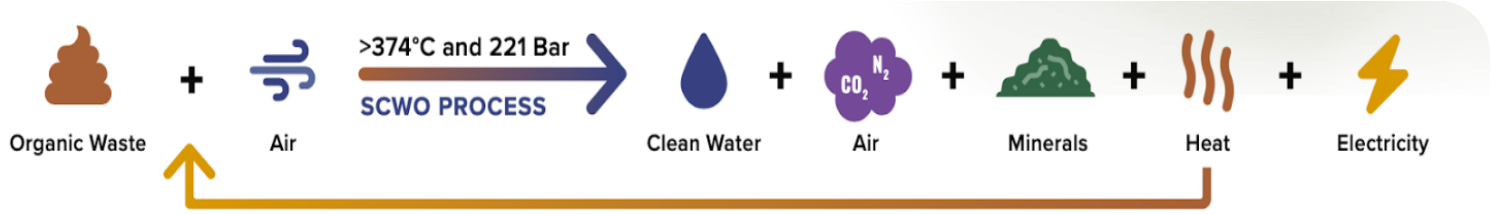
Photo- (top)
Optimized Fractionate Flow

Photo (right)
Single fractionation column set-up

SCWO Overview

- Supercritical phase of water at >374 °C and >218 atm
- Oxygen is fully soluble, rapid and complete oxidation of organics to CO_2, water, and inorganic salts
- When applied to PFAS, organic fluorine is mineralized to inorganic fluoride





SCWO

Advantages

- Current full-scale systems throughput capacity 3 gpm
- Applicable to a wide variety of waste streams
- Ability to destroy lower molecular weight, shorter chain PFAS compounds (<C6) in addition to higher molecular weight, legacy PFAS compounds (≥C8).
- Rapid reaction time (2-10 seconds)
- Absence of harmful reaction byproducts (CO, NOx, SOx)
- Ability to destroy almost all co-organics

Limitations

- High energy requirements (especially during startup)
- Sensitivity to salts
- Solids must be slurried
- Potential for system corrosion
- High level of expertise required for operation
- High capital costs

Source: Steve McKnight, 374Water

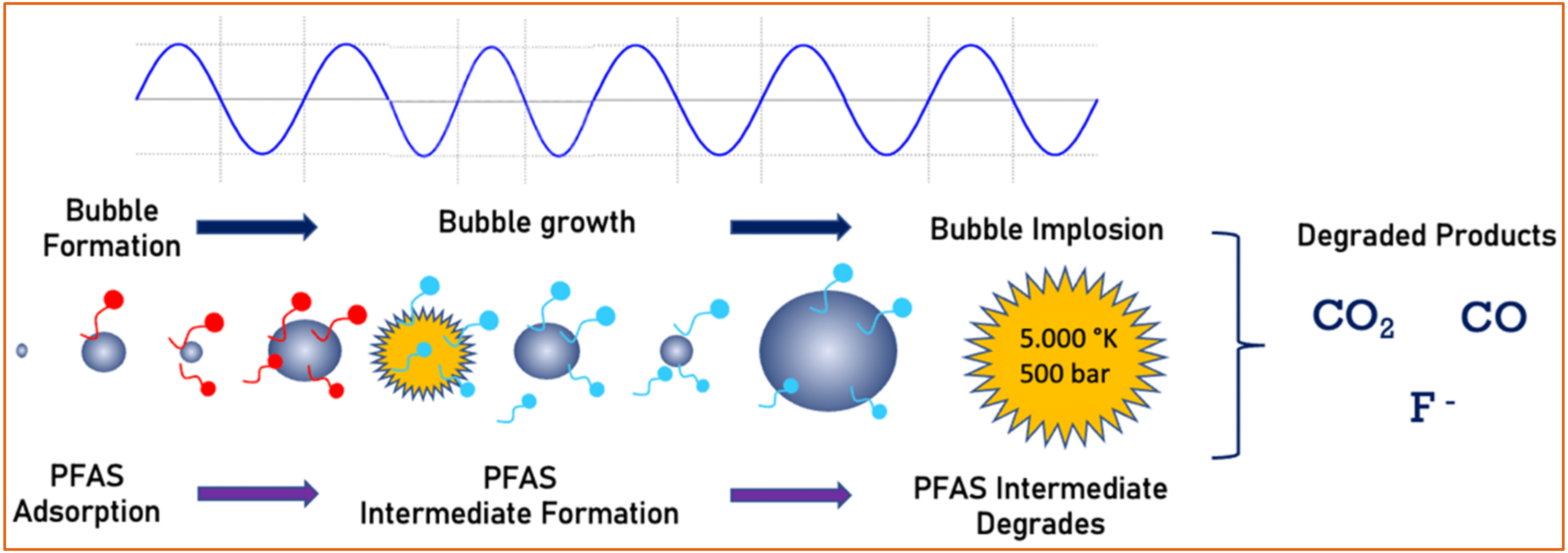
Case Study (374Water)

- GAC sample dried and ground
- AIX did not undergo pretreatment processing
- Total PFAS = 40 compound list of EPA Method 1633
- >99% DRE was achieved for C<6 compounds and total PFAS.
- PFBS in the GAC feedstock had the lowest DRE of 95.88%

Feedstock ID	Analyte	Feedstock (ng/kg)	Effluent (ng/L)	Effluent Blank (ng/L)	DRE Corrected %
WAFB Spent GAC	Short chain (C<6)	41,440	114.7	51.66	99.85%
	Total PFAS	214,400	547.9	305.9	99.89%
WAFB Spent AIX	Short chain (C<6)	84,380	0.97	ND	99.9989%
	Total PFAS	1,386,000	77	104.7	100%
Miramar Spent AIX	Short chain (C<6)	234,100	32.91	ND	99.986%
	Total PFAS	895,200	796	104.7	99.92%

Adapted from "Supercritical Water Oxidation for the Destruction of Spent Media Wastes Generated from PFAS Treatment" (Chiang et al. 2023.) https://doi.org/10.1016/j.jhazmat.2023.132264

Sonolysis Overview



Source: "A Review of PFAS Destruction Technologies" (Meegoda et al.) https://www.mdpi.com/1660-4601/19/24/16397

Sonolysis

Advantages

- Chemical additives/fuels not required for pretreatment
- Near-ambient temperatures and pressures
- Some co-inorganics (e.g., nitrates and chloride) have demonstrated positive effects on destruction results
- Nominal technical expertise required for operation
- Lower capital cost and footprint for full-scale system

Limitations

- Inefficient treatment system design may lead to intermittent increases in short-chain intermediate concentrations.
- Anionic surfactants, bicarbonate, and sulfate shown to reduce PFAS DREs
- Currently, higher residence timed resulting low throughput capacity (0.1 gpm)

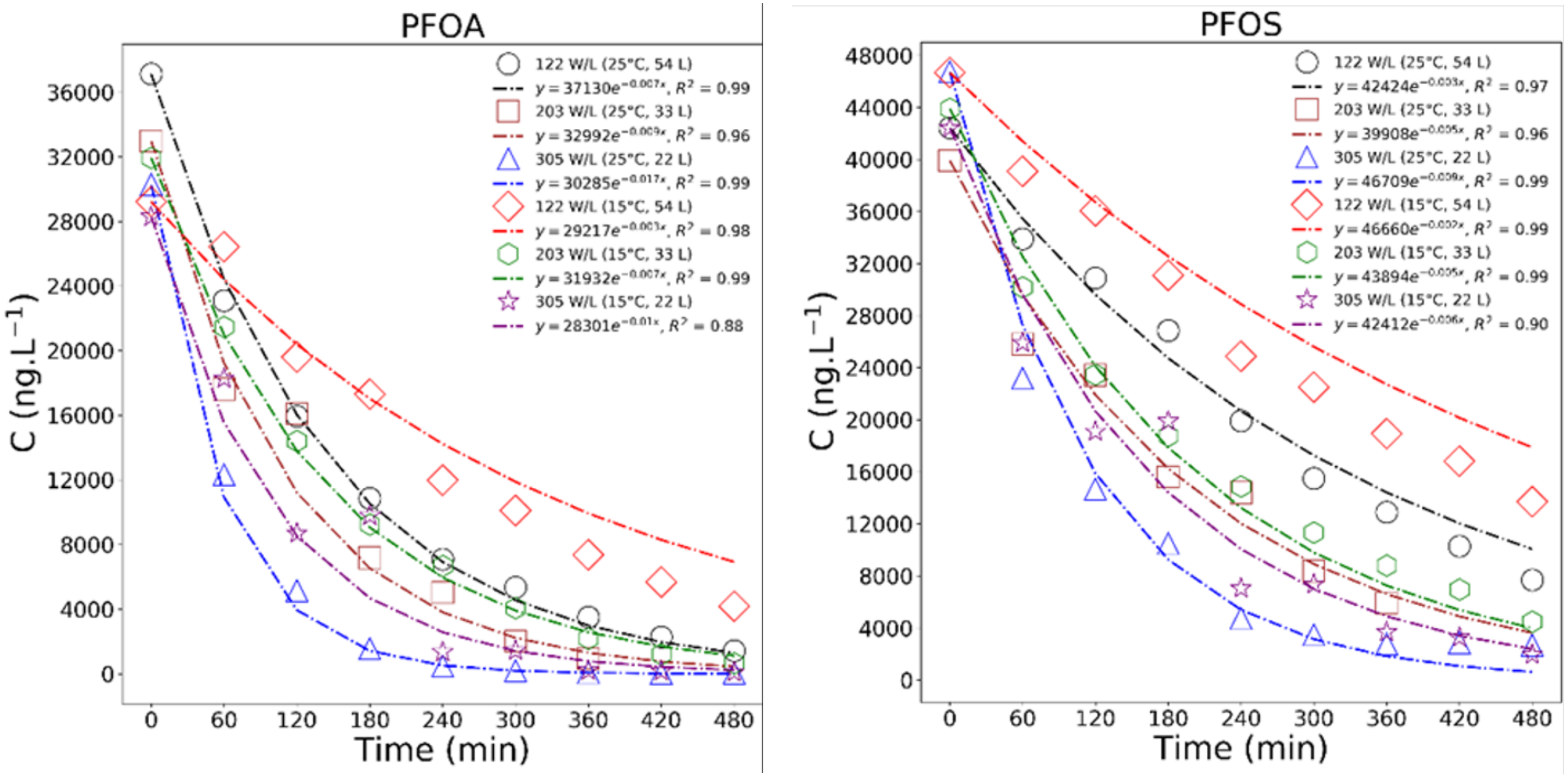
Unknowns

- Optimization of flowthrough conditions and residence times
- R&D stages for solids/slurry testing
- DRE for co-contaminants

Source: "Sonolysis and Super Critical Water Oxidation (SCWO): Development Maturity and Potential for Destroying PFAS" (C. Divine et al.) https://doi.org/10.1111/gwmr.12619

Sonolysis Case Study (GSI, UCLA, CSU)

- A mobile sonolysis reactor was deployed at a California site to treat PFAS-impacted groundwater
- 700 kHz reactor
- Varying temperatures
  - 15 °C
  - 25 °C
- Varying power densities
  - 122 W/L
  - 203 W/L
  - 305 W/L
- Results
  - 93% to 100% removal of 15 PFAS compounds
  - Higher DRE for PFCAs than PFSAs



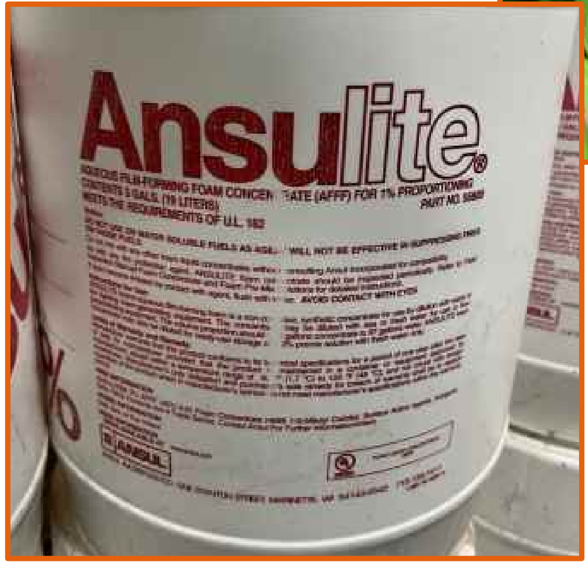
Source: “Field demonstration of a Sonolysis reactor for treatment of PFAS-contaminated groundwater” (R.P. Kulkarni et al.) https://doi.org/10.1061/(ASCE)EE.1943-7870.0002064

USACE ERDC Destruction Demonstration Performers

SCWO	374WATER; GENERAL ATOMICS
Sonolysis	ARCADIS; PCT SYSTEMS; UNIVERSITY OF SURREY
HALT	Aquagga
Program	US Army Corps of Engineers; U.S. ARMY ERDC ENGINEER RESEARCH AND DEVELOPMENT CENTER

Technical Objectives

- Demonstrate destruction of PFAS in AFFF mixture (3M Lightwater and Ansulite)
- Confirm defluorination via fluorine mass balance
- Verify operational requirements and develop cost model
  - Feed flowrate (L/hr)
  - Dilution factor
  - Fresh water influent flowrate (L/hr)
  - Consumables (pH amendment, cofuel, etc.)
  - Peak and average power (kW)
  - System footprint (ft²)
  - Labor (skill level and hours)
  - Maintenance/cleaning



Project Phases

Phase 1

- Bench/initial testing with limited volume of an AFFF mixture (3M Lightwater and Ansulite) at vendor facilities
- Completed March 2024

Phase 2

- Larger-scale testing (100 gal) at vendor facilities
- General Atomics (SCWO) and Aquagga (HALT) demonstrations completed
- 374Water (SCWO) and sonolysis demonstrations to occur Summer 2024

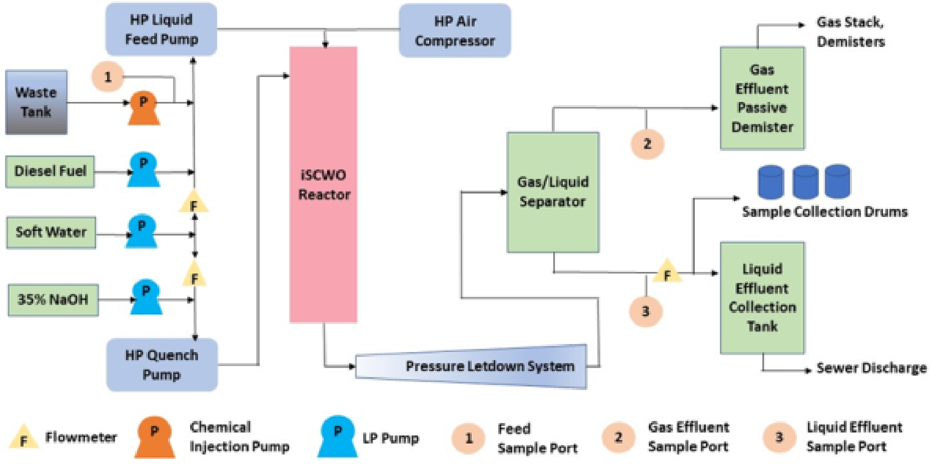
Phase 3

- Onsite testing at ERDC facility in Vicksburg, MS
- Follow-on full scale application at Army installation (TBD)
- 2024-2026?

General Atomics iSCWO Demonstration (Initial Testing)

ARCADIS

- AFFF: 0.19 and 0.48 lpm feed rate
- Preliminary DRE >99.999%
- Testing included reprocessing collected liquid effluent at 2 gpm to demonstrate complete destruction of PFAS before release to sewer



Mixed AFFF Thruput (lpm)	0.19	0.48
PFAS Conc Input (mg/L)	1250	1250
PFAS Mass Input (mg/min)	237.5	600
PFAS Conc Output (mg/L)	0.000117	0.000108
PFAS Mass Output (mg/min)	0.00065403	0.0006048
DE	99.99972%	99.99990%

General Atomics iSCWO Demonstration (Larger Scale Testing)

- Total of ~100 gal AFFF Treated.
  - Day 1 = 0.2 lpm. Day 2 = 1 lpm. Day 3 = reprocessing. Day 1 and Day 2 effluent at 7.5 lpm
- Stack gas sampling (OTM-45, OTM-50)
- Liquid samples collected: 1633, TOP, Non-Target, and TOF/EOF, COD, TOC, and inorganic F (Pace labs)

374Water SCWO Demonstration (Initial Testing)

ARCADIS

SCWO Feedstock Recipes

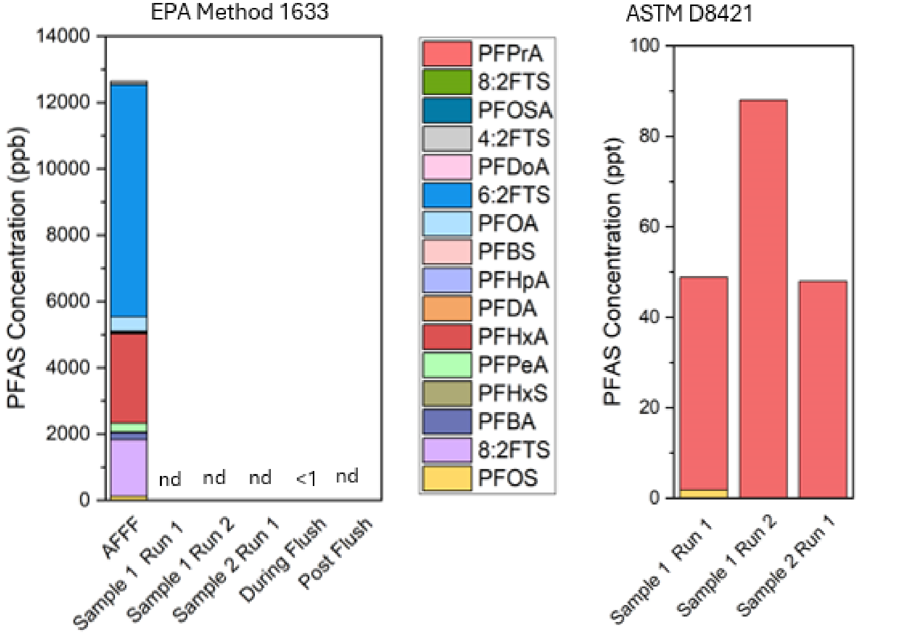
Component (as % by mass)	Feedstock 1 (Sample 1)	Feedstock 2 (Sample 2)
[1]AFFF	6%	9%
[2]IPA	3%	4%
[3]Na_2CO_3	0.5%	0.5%
Water	90.5%	86.5%

[1]Neat AFFF as provided.
[2]IPA = isopropyl alcohol, component was added to increase the calorie content (HHV) from 1.422 or 1.966 MJ/kg to >requirement threshold of ~2.5-3 MJ/kg
[3]Na_2CO_3 = sodium bicarbonate, component was added to prevent the formation of corrosive components (e.g. HF) that may result from the high halogen content of the AFFF

SCWO Operating Conditions

Parameter	Sample 1 Run 1	Sample 1 Run 2	Sample 2 Run 1
Feedstock flow rate	7 mL/min	10 mL/min	10 mL/min
Air flow rate	7 g/min	10 g/min	9.25 g/min
Reactor residence time	27 sec	19 sec	20 sec
Reactor temperature	>374°C	>374°C	>374°C
Pressure	> 221 bar	> 221 bar	> 221 bar

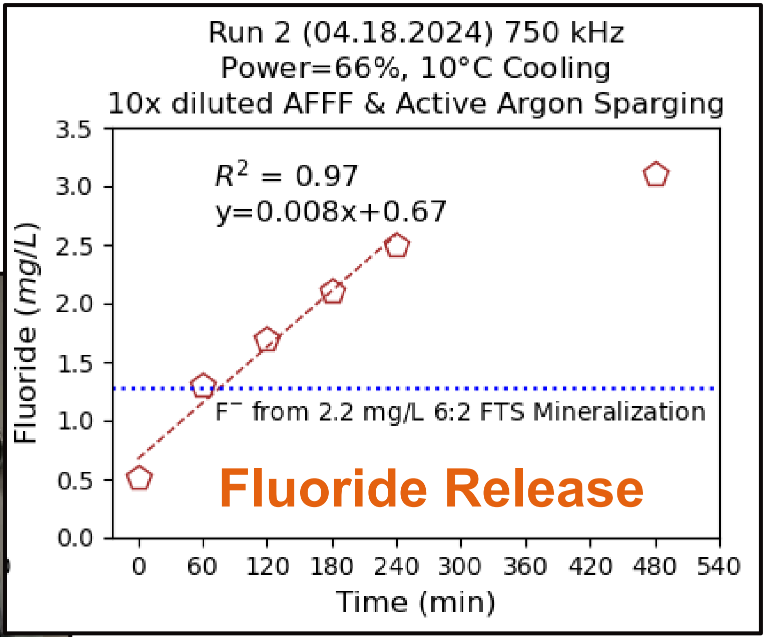
Results

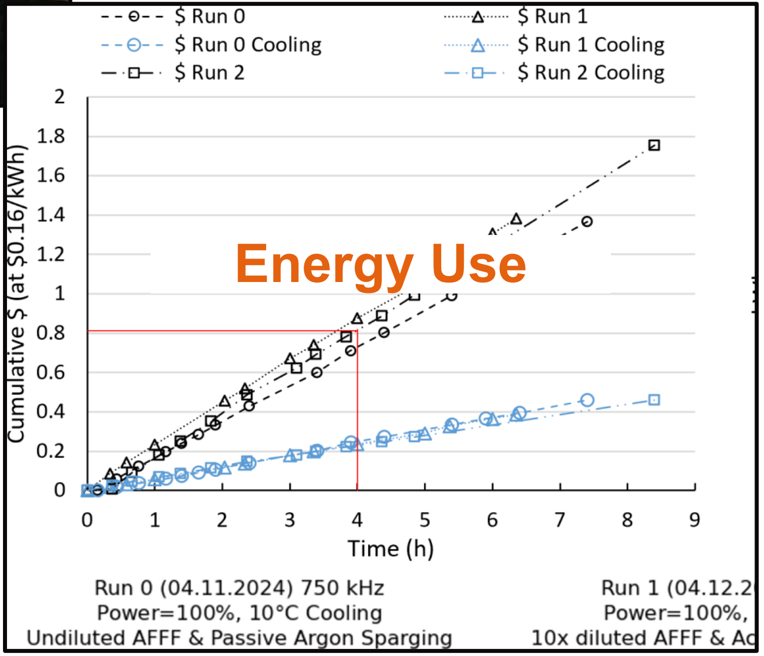


- 13/40 PFAS analytes were detected in the waste (AFFF) pre-SCWO treatment
- The pre-assay TOP concentrations were similar to those measured via EPA Method 1633 (~10,000 ppb) in the neat AFFF
- Major PFAS in the AFFF are 6:2FTS, PFHxA, 8:2FTS, PFOA, PFPeA, and PFBA
- All runs resulted in >**99.99%* PFAS elimination**, as determined by EPA Method 1633analysis
- When tested using ASTM D8421, SCWO effluent from all runs show the presence of PFPrA at levels ranging from 47-88 ppt
- 242.9 ppt of PFAS were washing out during SCWO system flushing

- 1633 results:
  - Non-detect on all treated effluent, DRE>> 99.99%
- 8421 results:
  - Matches 1633 results
  - Presence of 3-carbon PFPrA

Sonolysis (Initial Testing and Optimization)





Operational Parameters Being Optimized

- Frequencies (670 kHz, 750 kHz, 900 kHz)
- Temperature, pressure
- Gas sparging (Ar, N2, none)
- Residence time

DIU/ESTCP Destruction Demonstration

SCWO	374WATER° · BATTELLE · Revive environmental · GENERAL ATOMICS
HALT	Aquagga
Logistics & TSDF	ARCADIS · CleanEarth™
Program Direction	DEFENSE INNOVATION UNIT · ESTCP

Concentrate First

- First phase of project consists of concentration vendors producing wastes to be destroyed by the destruction vendor teams
- Waste concentrates will be transported to and held at the respective Clean Earth facilities for destruction testing

		Allonnia	Cyclopure	ECT2
Waste Type	Spent GAC Spent IX	SAFF40 Foam fractionate	DEXSORB media regenerant	SORBIX RePURE IX regenerant still bottoms

Performance Analyses & Reporting

- Assessment of performance objectives
  - Destruction removal efficiency (DRE)
  - Fluorine mass balance
  - Regulatory limits (MCLs)
  - Clean Earth Detroit facility discharge limits
- Identify optimal operating conditions (flowrate, temperature, chemical dosing, pre/post-treatment, etc.) for each waste stream
- Cost analysis will include:
  - Level of effort (labor)
  - Utilities
  - Consumables
  - Transportation
  - Equipment maintenance/replacement
  - Permitting
  - Decommissioning
- Plan outline for a Phase IV scale-up to other TSDFs

Proposed analyses to assess treatment performance objectives

Analyte	Method
PFAS (liquid)	USEPA Method 1633
TOP Assay	<C10, PFAAs
Inorganic Fluoride	USEPA Method 340.2 or 45000-F
TOC	USEPA Method 9060
SVOCs	USEPA Method 8270C
VOCs	USEPA Method 6200
Metals (RCRA 8)	USEPA Method 200.7
Sulfate	USEPA Method 375.4
BOD	USEPA Method 405.1
COD	USEPA Method 410.4
TSS	USEPA Method 160.2
TDS	USEPA Method 160.1
Air	OTM-45
PFAS (gas)	USEPA Method 1633

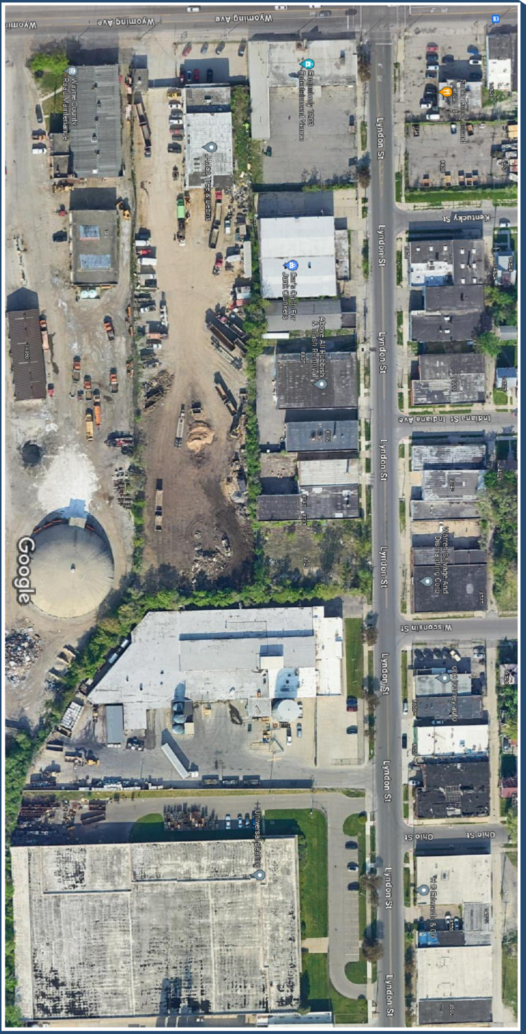
“Hub-and-Spoke” Concept

ARCADIS

- The Hub-and-Spoke Concept aims to provide cost savings by minimizing waste volumes, streamlining waste transportation, and implementing a centralized regional waste receiving and destruction model.

Site 1: Clean Earth Detroit CWT

- Site for 374Water and Battelle/Revive field demos
- The Detroit CWT possesses a PFAS discharge permit, an onsite PFAS testing laboratory, and can accept PFAS-contaminated liquids from anywhere in the US or Canada.



Clean Earth Detroit CWT Aerial (courtesy Rob Martin, Clean Earth)

Site 2: Clean Earth Charlotte

- Site for Aquagga and General Atomics field demos
- PFAS-impacted wastes produced during the demonstrations at the Charlotte facility will be shipped to the Clean Earth Detroit CWT in compliance with the Detroit CWT's PFAS discharge permit.

Clean Earth Charlotte Facility Aerial (courtesy Rob Martin, Clean Earth)

Closing Thoughts

Each technology will have a sweet range and be better suited for specific waste streams, conditions, volumes, or logistical considerations than others.

Concentrating PFAS-contaminated wastes prior to employing destruction technologies will lower costs.

A “Hub-and-spoke” model may be necessary to fully commercialize high-capital technologies

Thank you!

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