PFAS Technical Group

February 18, 2022

Agenda

- Welcome and Introductions
- Innovative Technologies – Max Krause, EPA
- Conclusions & Next Steps

EPA's Ongoing Research into PFAS Destruction Technologies

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US EPA office of Research & Development Presented to

Wisconsin DNR, PFAS Technical Group

Feb 18, 2022

Office of Research and Development
Center for Environmental Solutions and Emergency Response

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ORD’s Role in Understanding PFAS Destruction & Disposal

Data Gap: Knowledge regarding end-of-life management and ultimate disposal of PFAS-containing materials

Actions:

- Characterize end-of-life PFAS disposal streams
- Evaluate efficacy of disposal/destruction technologies
- Evaluate possibility of products of incomplete combustion/destruction

Research Products:

- PFAS presence in different types of landfills and leachates
- PFAS behavior in incineration environments
- Thermal treatment of PFAS-contaminated biosolids

Impact: Responsible officials will be able to effectively manage end-of-life disposal of PFAS-containing materials

Waste Streams that Contain PFAS

- Aqueous film-forming foam (AFFF)
- Municipal solid waste
- Construction & demolition debris
- Sewage sludge
- Granular activated carbon
- Municipal wastewater
- Investigation-derived wastes
- Contaminated soils
- Street sweepings
- Landfill leachate

- Not all waste streams will have an economically viable, fully destructive treatment
  - Risk management will be required
- In the US, we incinerated
  - 12% of our MSW in 2018
  - 17% of wastewater treatment residuals

EPA is pursuing multiple lines of research into PFAS-destructive technologies

- For the past two years EPA has been conducting a range of lab-, pilot- and field-measurements from
- Conventional technologies:
  - Lab- and pilot scale incinerators
  - Field sampling sewage sludge incinerators
  - Trying to do more field sampling
- Innovative technologies:
  - Pyrolysis
  - Hydrothermal processes
  - Electrochemical
  - Ball milling (Thermomechanochemical treatment)

Source: General Atomics, https://www.ga.com/hazardous-waste-destruction

Highlight a Few Projects

- Incineration
  - Lab
  - Field sampling
- Pyrolysis
  - Field sampling
- Supercritical water oxidation (SCWO)
  - Three lab demonstrations
  - One pilot study
- Electrochemical oxidation (EO)
  - One lab demonstration

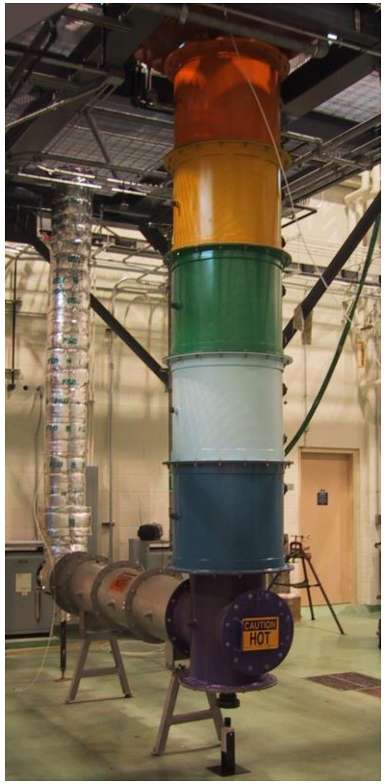
Sewage sludge

AFFF

EPA Incineration Research – Ongoing

- Injection of CF_4, C_2F_6, PFAS compounds and AFFF
- Effect of injection temperature, location, residence time
- Modeling
  - Help understand mechanisms of PFAS destruction
- Analytical method development
  - Fourier transform infrared spectroscopy (FTIR) applicability to PFAS combustion
  - Extractive methods (e.g., OTM-45)

Source: EPA



Source: EPA

Sewage Sludge Incineration

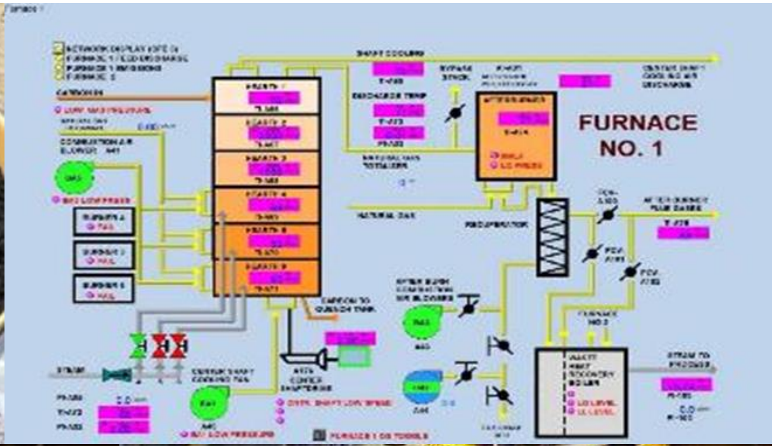
- Site: R7 wastewater treatment plant (WWTP)
  - Full-scale sludge incinerator (details on next slide)
- Site: Pilot-scale research facility
  - Private lab with large-scale incinerators
  - Sampling event in Nov 2021 to evaluate PFAS fate in sewage sludge incineration
- Site: R3 WWTPs
  - Preliminary screening at 5 facilities for 2022 large-scale sampling events

Site: Region 7 WWTP

- Sampling event in Aug 2021
- Sample solids/liquids along treatment process and gas-phase emissions from sludge incineration
  - Targeted analysis for most common PFAS compounds
  - Non-targeted analysis for products of incomplete combustion (PICs)
  - Further develop sampling methods
- Waiting on analytical results, serves as a model for future studies

Granular Activated Carbon (GAC) Reactivation

- Site: Hazen Research Inc.
  - Private lab with large-scale thermal systems
  - Sampling event in Nov 2021 to evaluate PFAS fate during GAC reactivation
- Searching for additional facilities (ideally on-site GAC reactivation at a drinking water treatment plant)

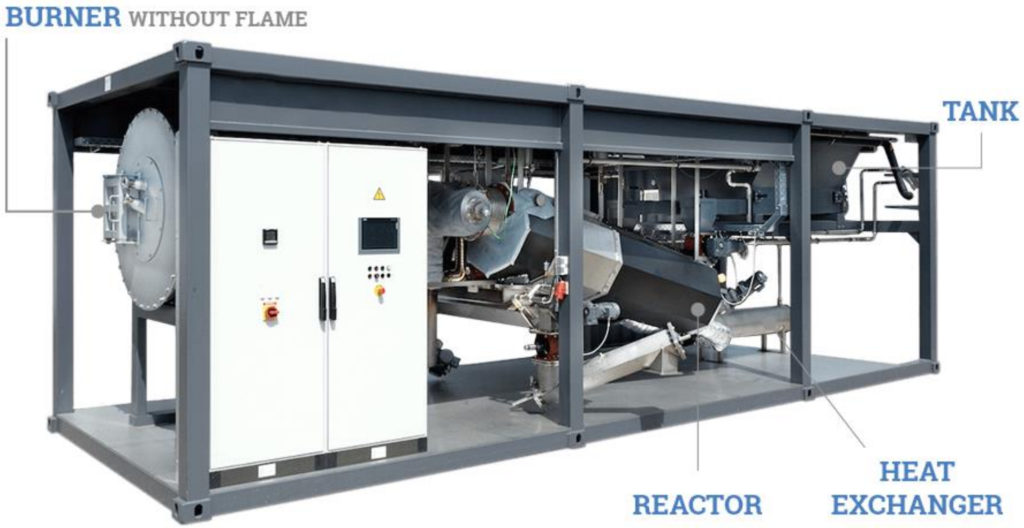




Thermal Desorption (Soil)

- Low temperature treatment to remove volatile species while limiting destruction to the sample matrix
- Site: Moose Creek, AK
  - Develop OTM-45 method for collecting PFAS from gas-phase emissions

Pyrolysis/Gasification

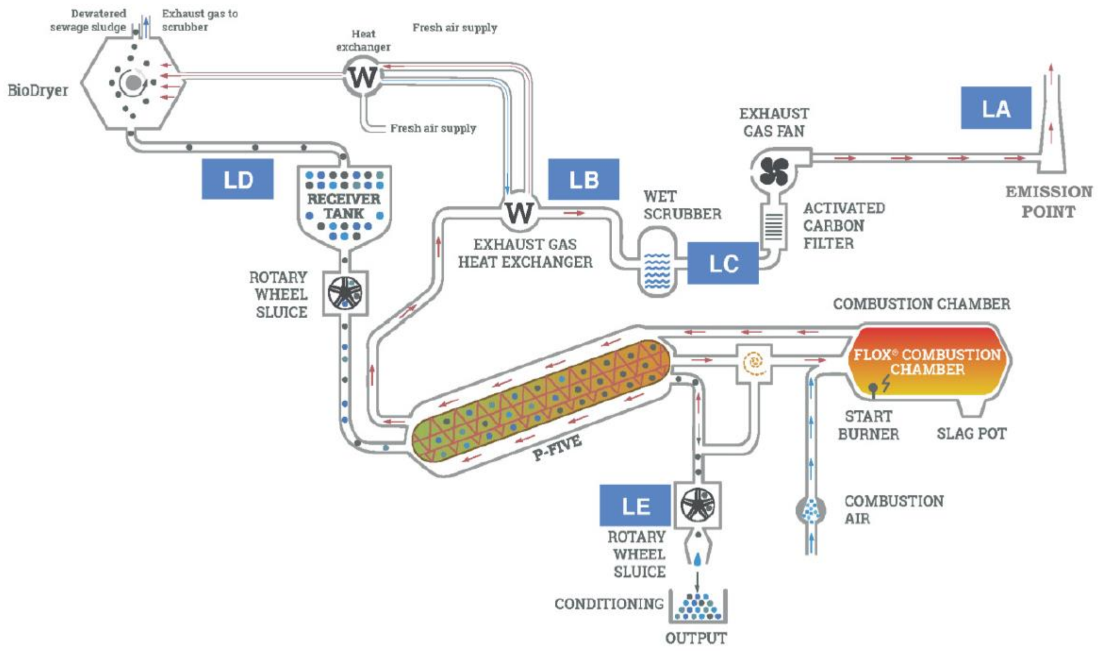
- Treatment at a range of temperatures in the absence of oxygen
- Produces material for beneficial reuse, such as biochar or syngas
- Site: BioForceTech gasification plant in Redwood City, California
  - Preliminary sampling as part of the PFAS Innovative Treatment Team (PITT)
  - https://www.tandfonline.com/doi/full/10.1080/10962247.2021.2009935
- Searching for additional facilities



Source: https://www.bioforcetech.com/

Pyrolysis of Biosolids

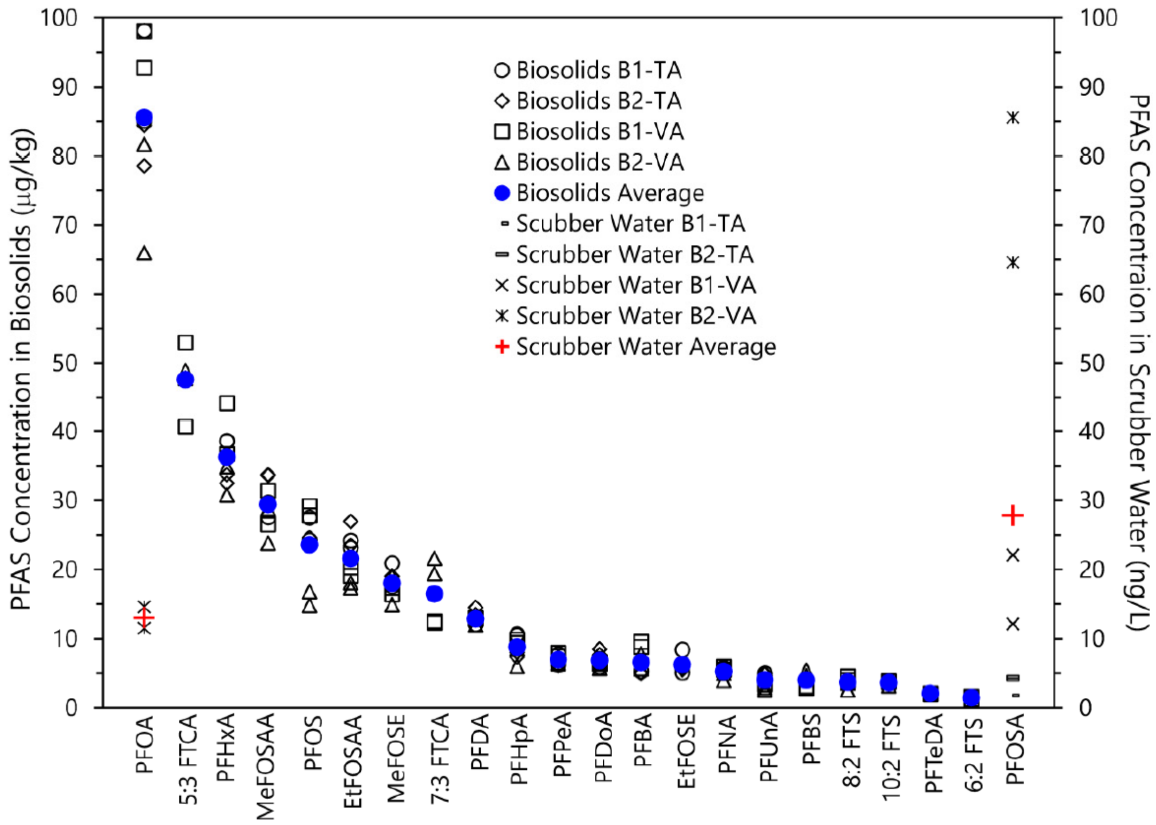
- San Francisco, CA field study with BioForceTech conducted in 2020
- Facility not known to be impacted by PFAS (chosen for operating tech)
- FTIR analysis for fluorine in gas-phase (no tracer used)
- Analyzed PFAS in influent biosolids (LD) and effluent scrubber water (LC)



Source: https://www.bioforcetech.com/

PFAS Sampling of Pyrolysis Biosolids Unit

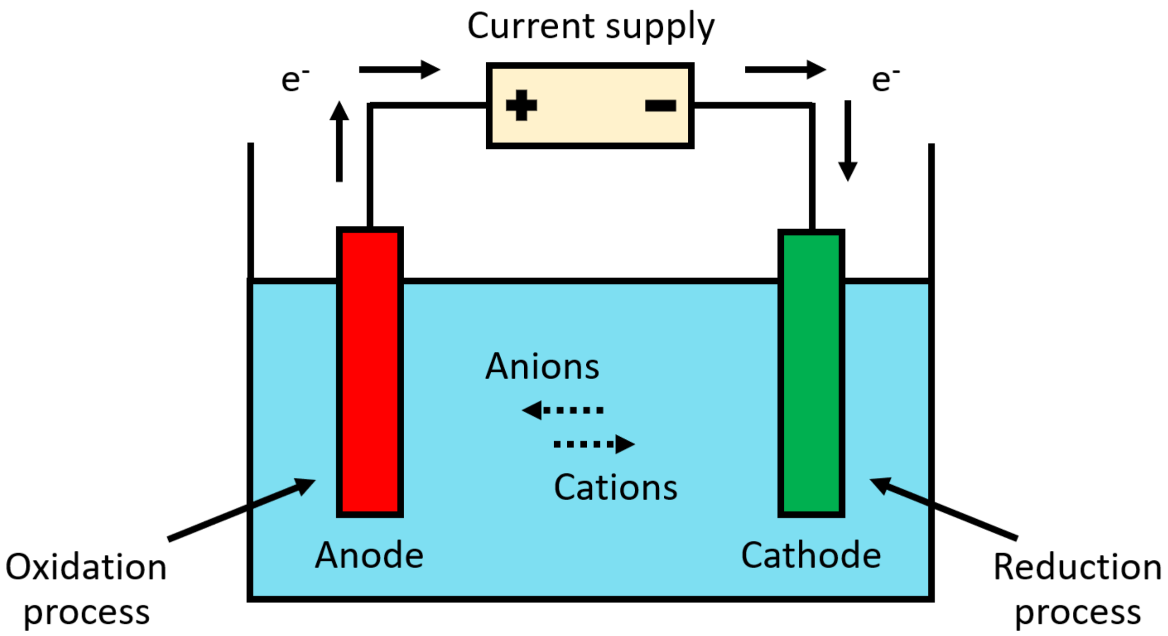
- Analyzed for 24 PFAS
  - Biosolids
  - Scrubber water
  - Biochar
- Biochar was absent of PFAS
- BUT biochar has been proposed as treatment (similar to activated carbon)
  - Unclear if pyrolysis is destroying PFAS or biochar "holds onto it"



Source: Thoma et al. (2021)

Electrochemical Oxidation (EO)

- Advanced oxidation process (AOP)
- Anode and cathode connected to a power source
- Strong oxidizing species are formed
- Interact with the contaminants and degrades them



Source: https://en.wikipedia.org/wiki/Electro-oxidation#/media/File:Electro-oxidation_apparatus.png

EO of PFAS

- Operated at room temperature
- Anode and cathode material can be expensive
- Treatment time is limited by electrode surface area (size)
  - Can arrange in parallel or series
- Potential oxidizer by-product formation
- Co-contaminants can consume the electrode faster
- Right: Still bottom from ion-exchange resin saturated with PFOA and PFOS

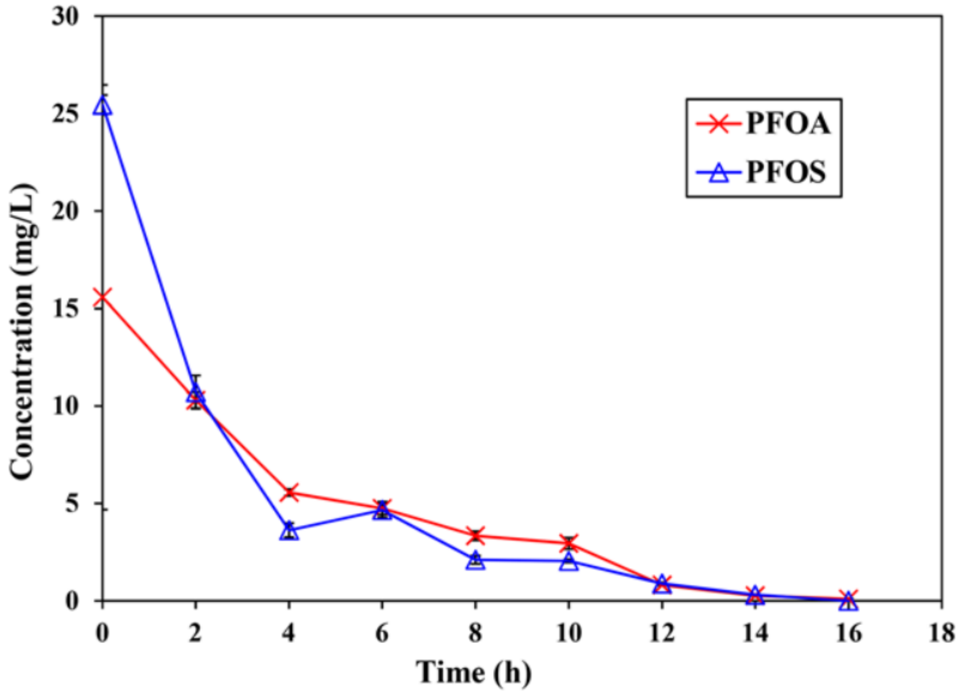
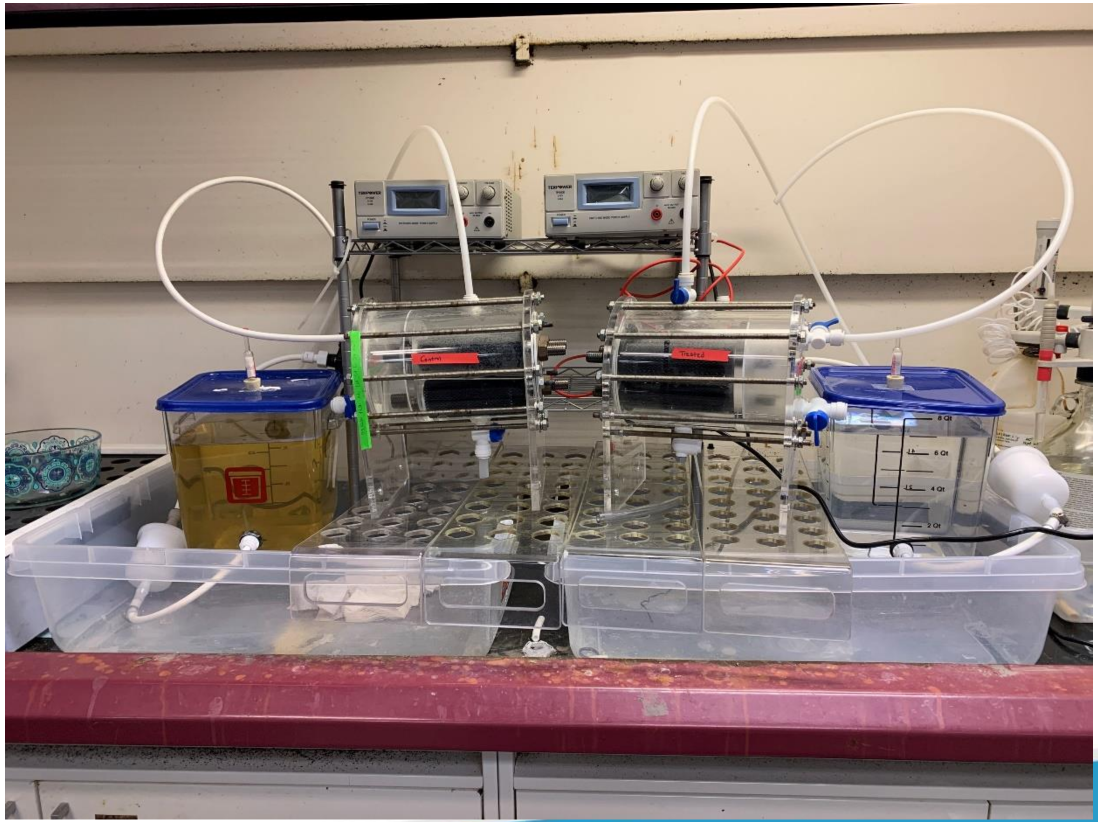


EXHIBIT 6 The degradation of PFOA and PFOS in still bottom sample B during 16-hr electrochemical oxidation treatment

Liang et al. (2018)

EO of PFAS from AFFF

- Collaborator: AECOM
- Site visit and lab-scale experiment in January 2021
- Tested EO on high-PFAS wastewater (AFFF)
- Analyzed for 24 PFAS, Total organofluorine (TOF), fluoride, and chemical oxygen demand (COD)
- Data received being analyzed
- Report in 2022



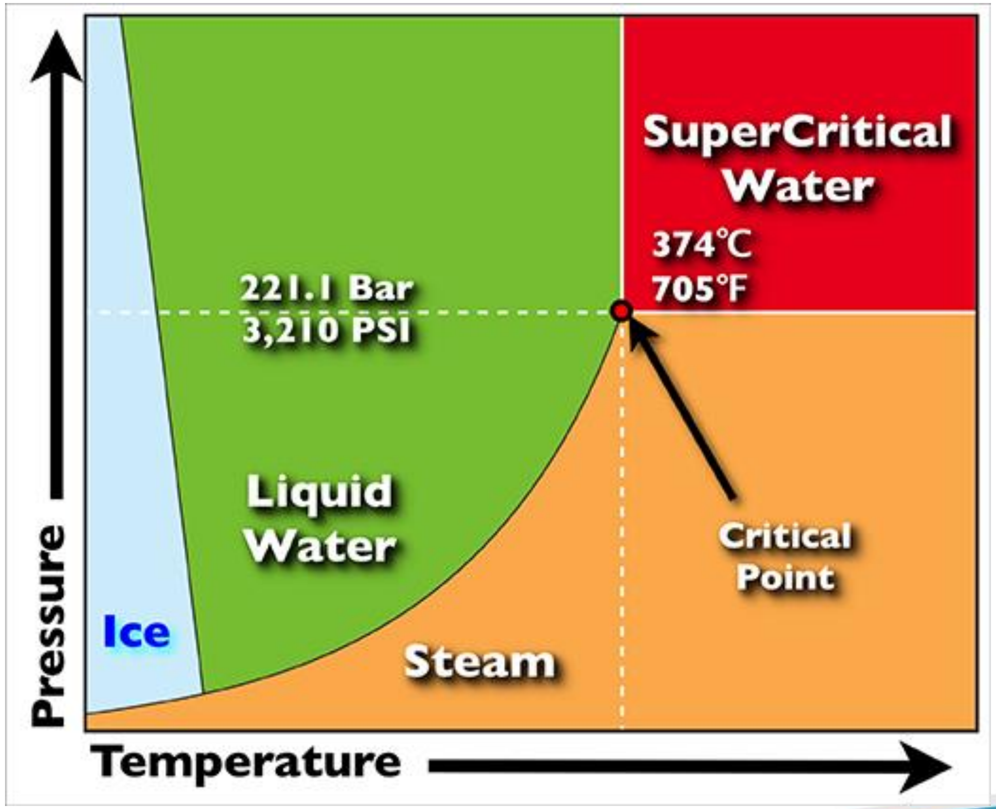
Source: Max Krause (2021)

State of EO Research on PFAS

- Lab-scale
- Different materials for anode, cathode being explored
- Time of treatment investigations
- Impact of co-contaminants

Supercritical Water Oxidation (SCWO)

- Water above 374 °C and 22.1 MPa is considered supercritical, special state of water
- Has properties of liquid and gas-phase
- Beneficial for hazardous waste degradation
  - Halogenated compounds most studied in peer-reviewed literature

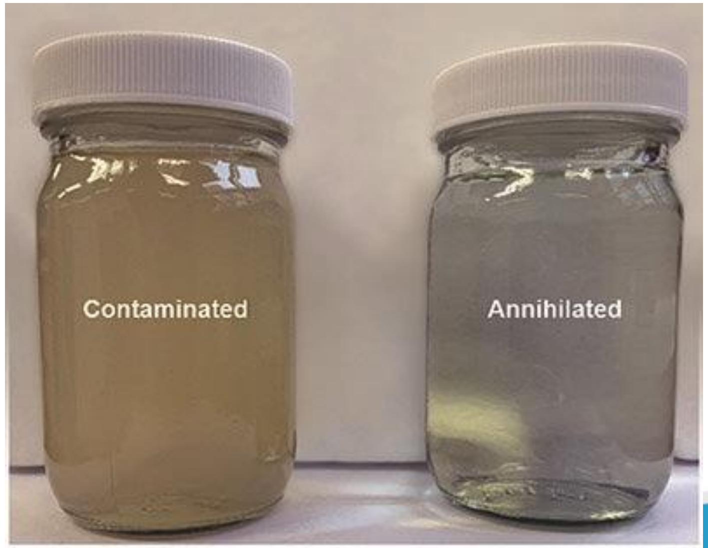


Source: https://en.wikipedia.org/wiki/Supercritical_water_oxidation

SCWO Case Studies

- Case studies performed with four separate SCWO operators
  - Aquarden (Denmark)
  - 374Water (Durham, NC)
  - Battelle (Columbus, OH)
  - General Atomics (San Jose, CA)
- Tested SCWO on dilute AFFF
- Analyzed for PFAS, TOF, fluoride, and COD
  - Some gas-phase PFAS sampled w/General Atomics

Source: https://aquarden.com/



Source: https://www.battelle.org/government-offerings/energy-environment/environmental-services/pfas-assessment-mitigation/pfas-annihilator-destruction-technology

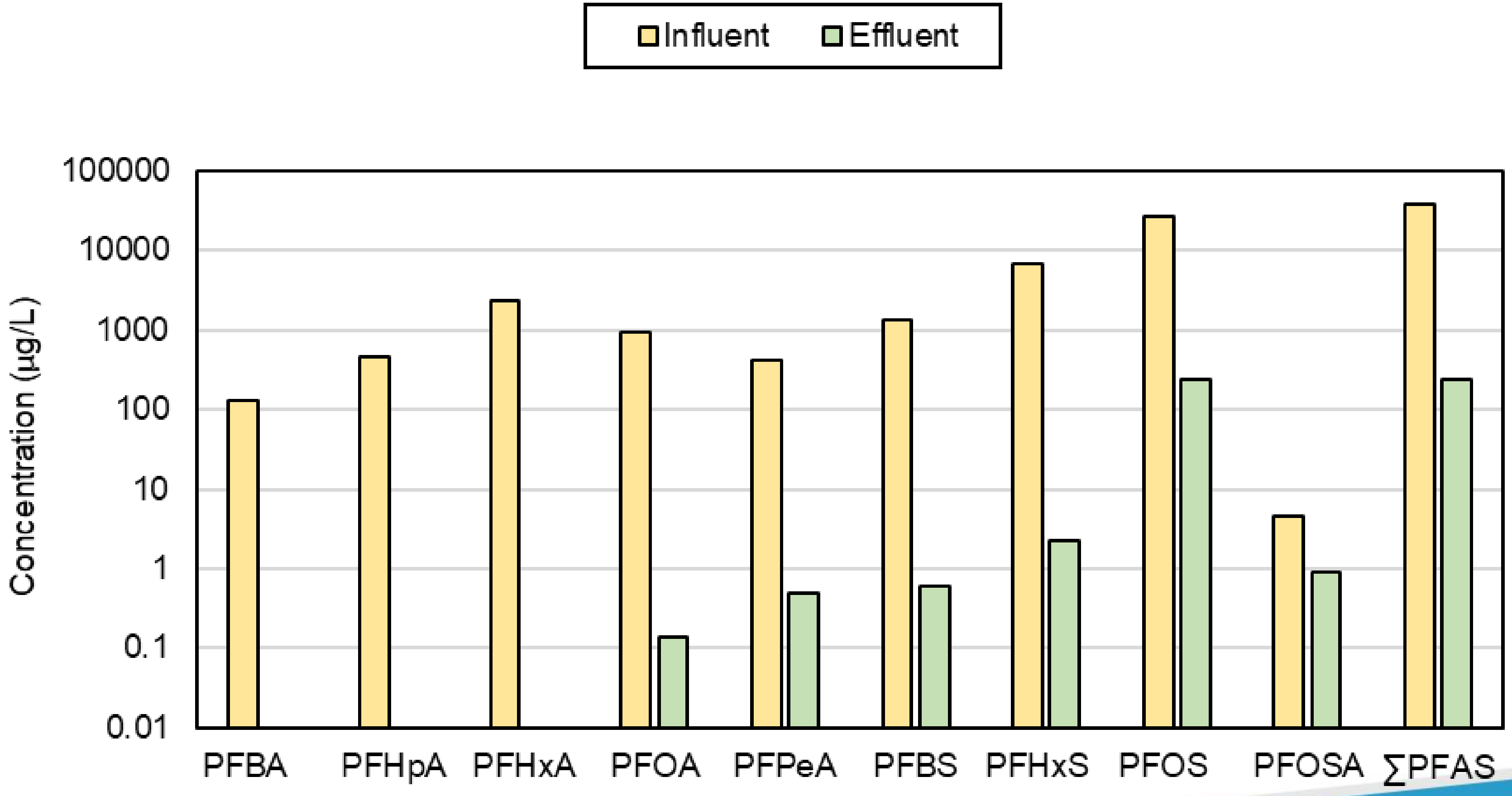
Case Study on SCWO AFFF Destruction

SCWO Providers	Temperature (°C)	Pressure (MPa)	Reaction residence time (s)	Oxidizer	Alkaline treatment type	Alkaline treatment location
374Water	595	CBI	6-8	Air	CBI	Influent
Aquarden	590	24	60	Air	KOH	Influent
Battelle	590	CBI	10	CBI	CBI	Effluent

Source: Krause et al. (2022)

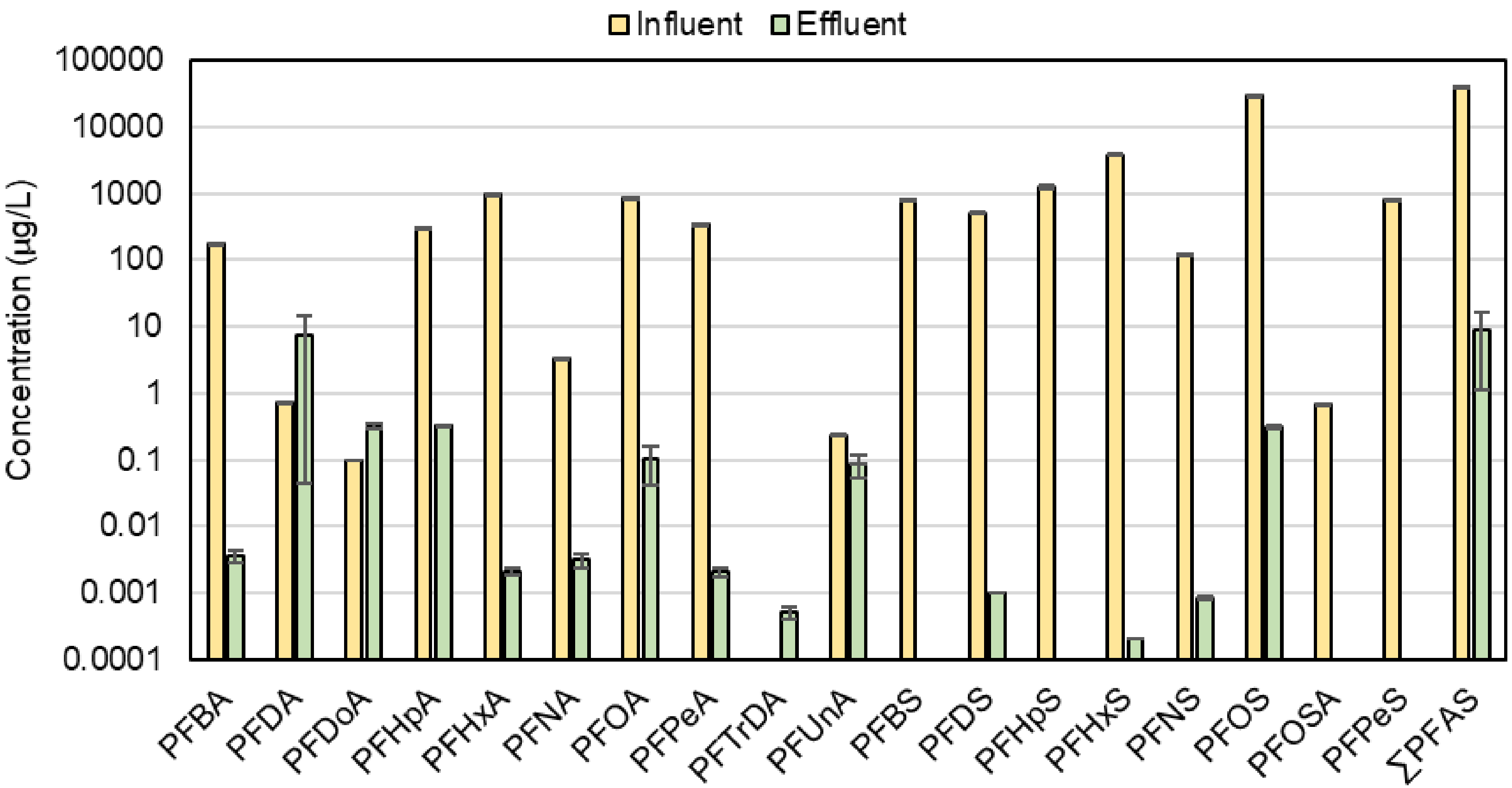
- Testing on PFOS-based AFFF solution (3M Lightwater samples)
- Analysis of 12-28 PFAS influent and effluent

SCWO: Aquarden, 100x dilute AFFF



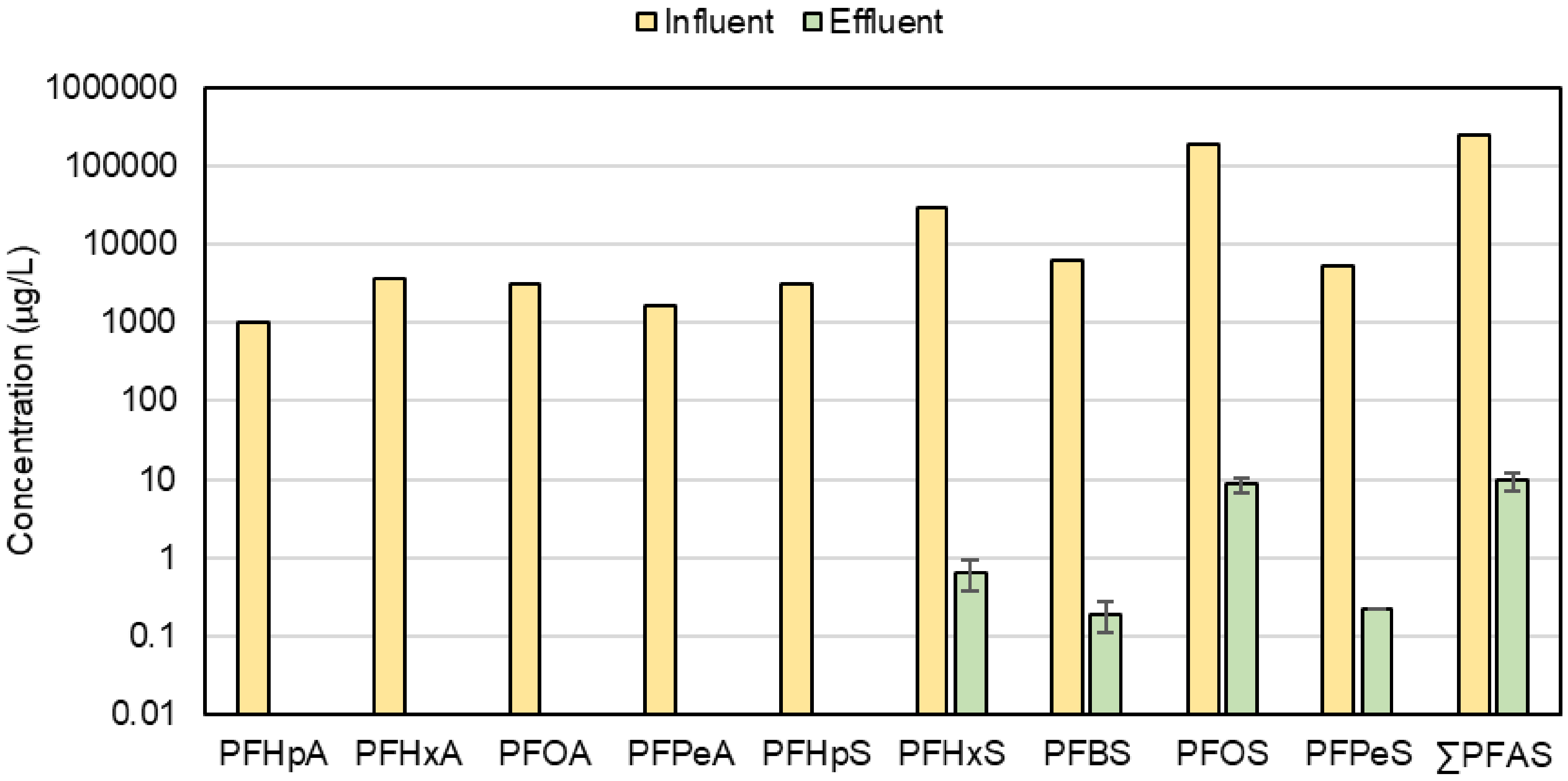
Source: Krause et al. (2022)

SCWO: Battelle, 100x dilute AFFF



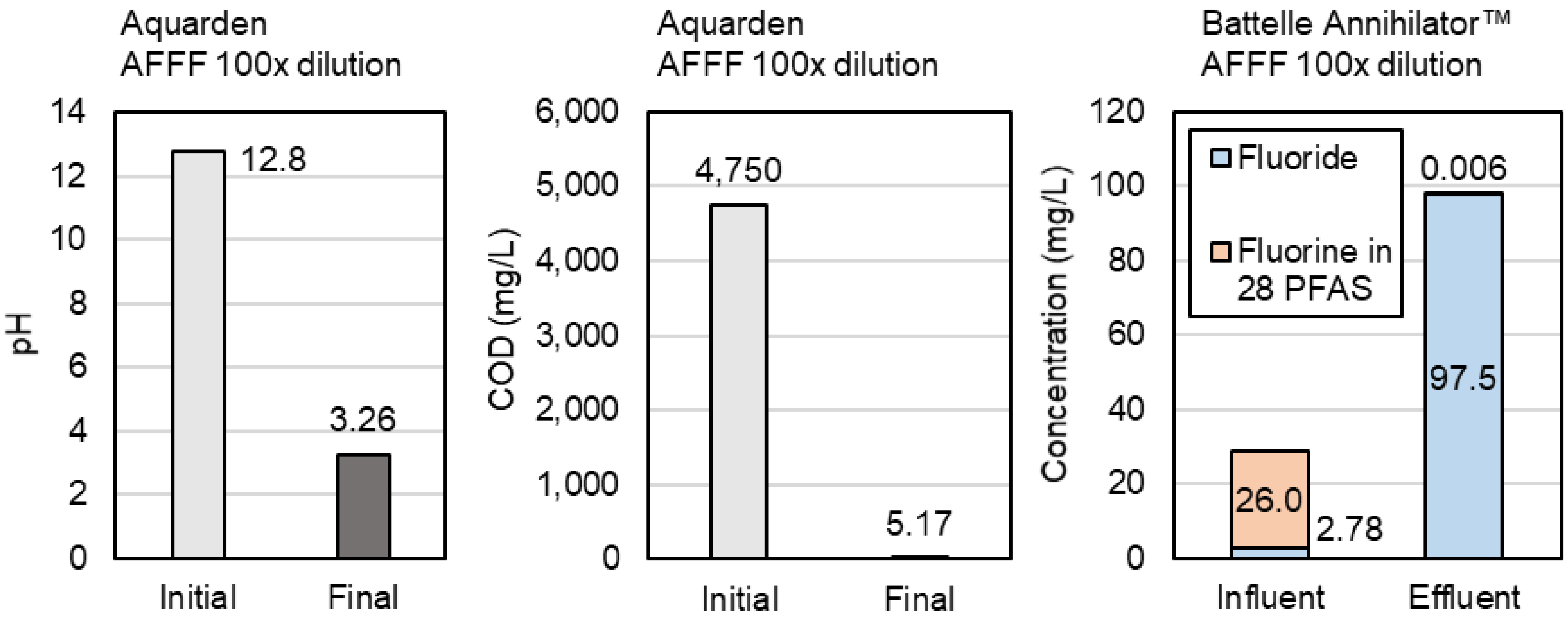
Source: Krause et al. (2022)

SCWO: 374Water, 30x dilute AFFF



Source: Krause et al. (2022)

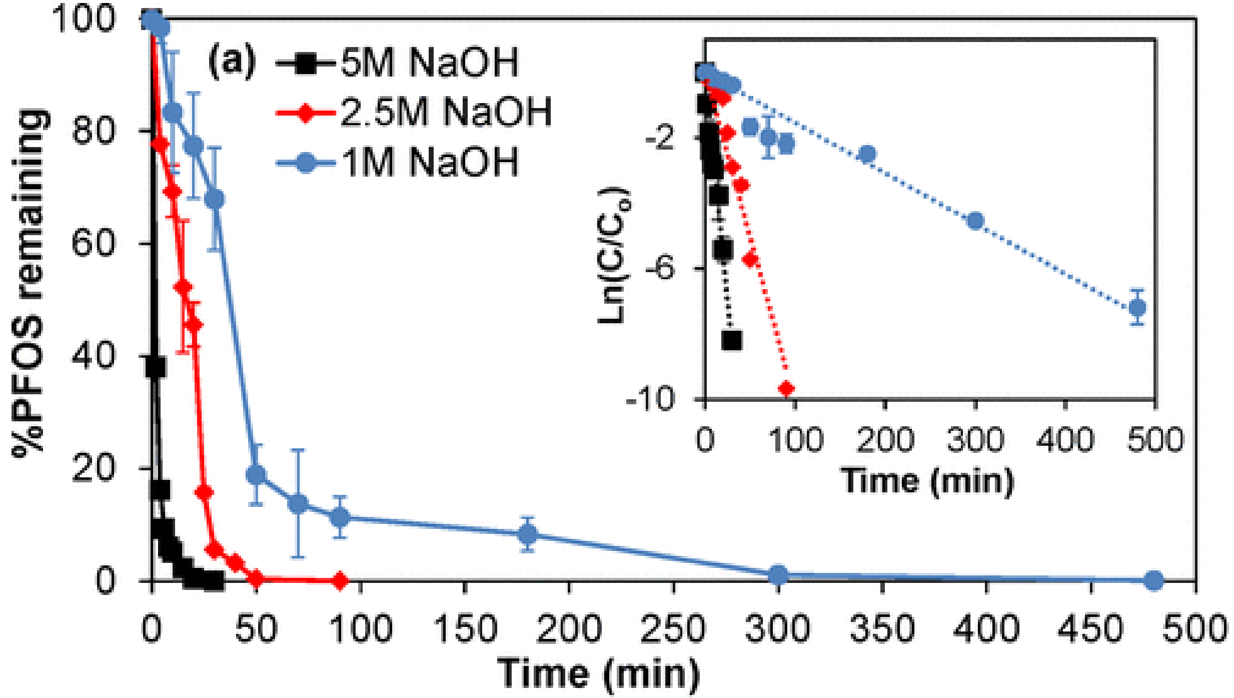
Other Parameters for Consideration



Source: Krause et al. (2022)

Non-EPA Studies on Hydrothermal/Subcritical Processes

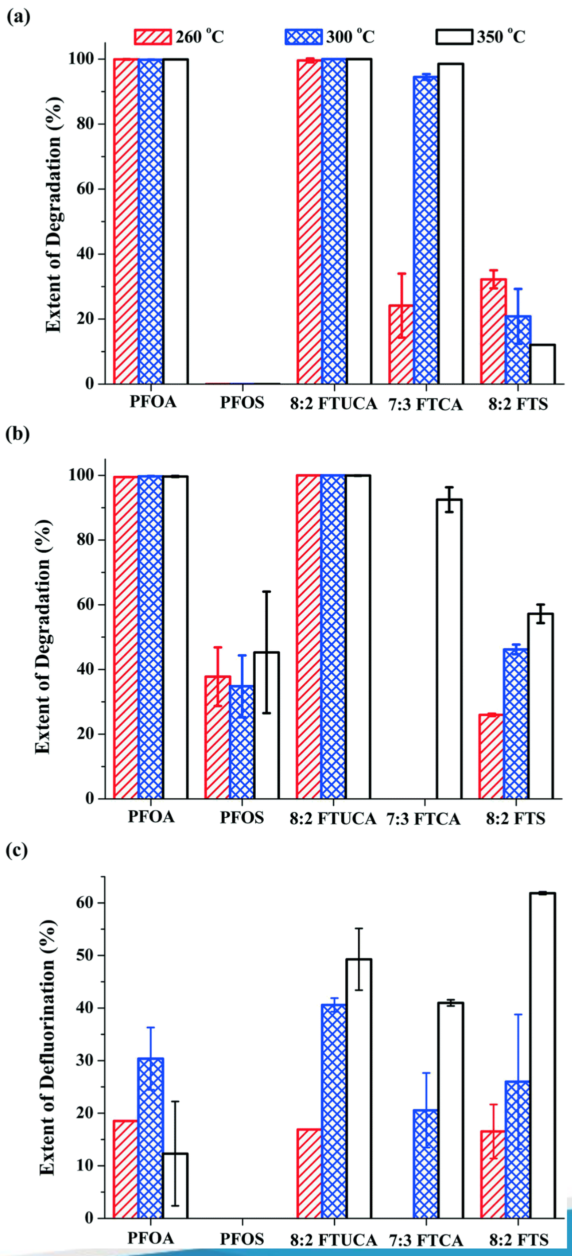
- Subcritical and hydrothermal are synonymous here
  - Temperatures and pressures below supercritical conditions
  - Pressures usually only due to increased temperature in reactor (increased water vapor pressure)
- Alkaline treatments increase rate of PFOS degradation
- Hydrothermal treatments (250 °C) on the order of 50-100 minutes to degrade PFOS



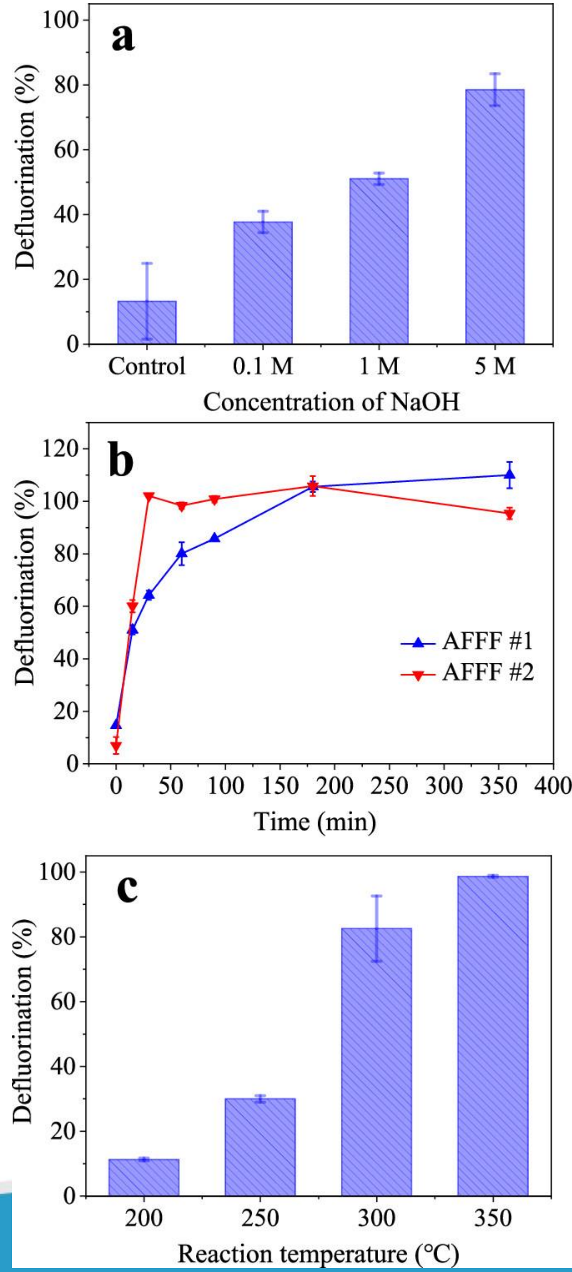
Source: Wu et al. (2019)

Non-EPA Studies on Hydrothermal Processes

- Defluorination (reduction of PFAS) similar after 50-100 minutes treatment
- Increasing temperature increases defluorination
- Very alkaline solutions
- Carboxylic and sulfonic acids, other functional group PFAS have different behavior
  - Important to consider when prioritizing compounds



Source: Yu et al. (2020)



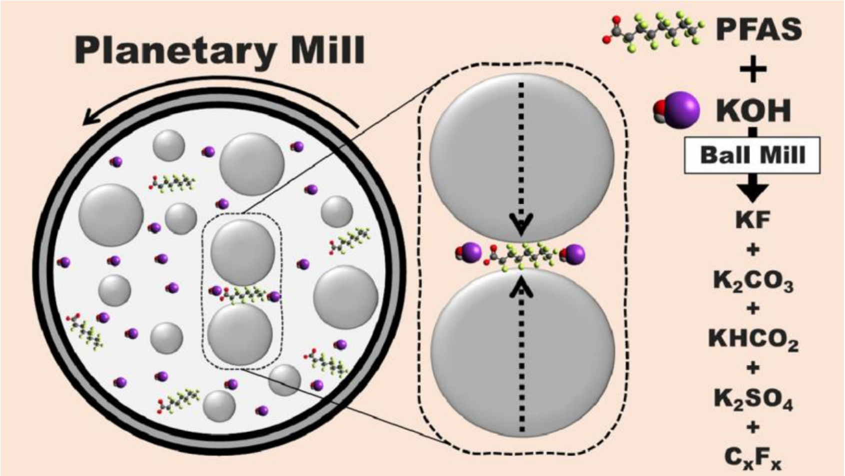
Source: Hao et al. (2021)

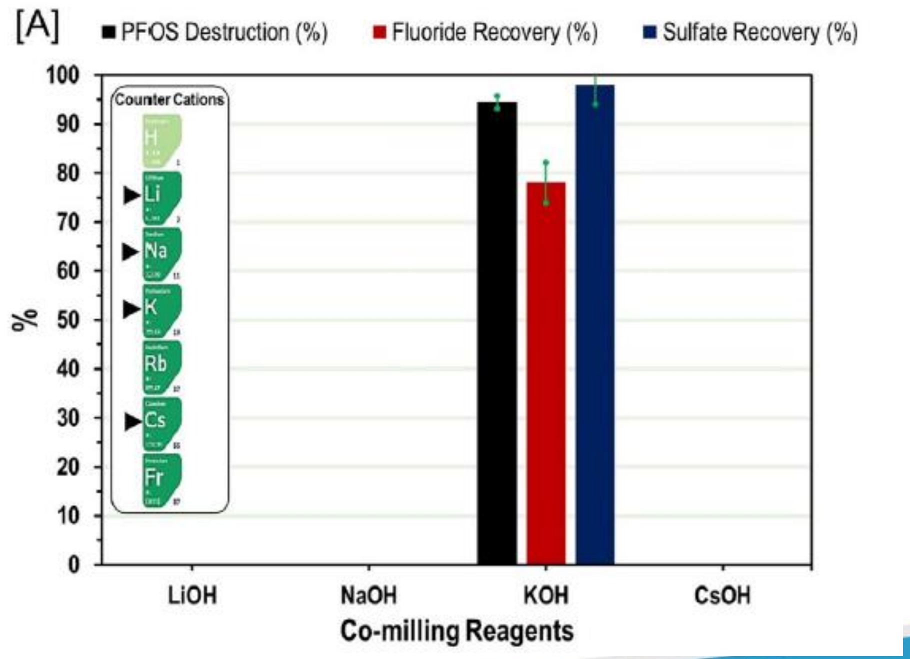
State of Hydrothermal Research

- Called many things, all similar in nature (i.e., pressure-cooking PFAS)
  - Hydrothermal processing (HTP)
  - Hydrothermal liquefaction (HTL)
  - Hydrothermal alkaline treatment (HALT)
  - Supercritical water oxidation (SCWO)
- Consistent findings that high temperature/pressure water can de-fluorinate solutions
  - Combination of targeted analysis and measured fluoride ion (F-) increased in effluent
- Alkaline treatment prevents formation of hydrofluoric acid (HF)
- Pros and cons to operating at sub- or super-critical conditions
  - Salts precipitate but faster destruction times
- Subcritical reaction times are on the order of minutes to hours for sub-critical reactors
  - Seconds for SCWO systems (Krause et al. 2022; Pinkard et al. 2021)
- Supercritical conditions precipitate non-soluble salts

Ball Milling of Soils

- Thermomechanochemical treatment
- Could be used for contaminated soils or other solid matrices
  - Demonstrated with Polycyclic Aromatic Hydrocarbons (PAHs)-contaminated soils
- Collisions of stainless-steel balls are used to create high temperature reactions
  - Pyrolytic
- Addition of alkaline material aids in destruction
- Lab-scale currently
- Patent application filed by EPA/ORD





Source: Ateia et al. (2021)

Technical Readiness Level (TRL) for PFAS

Wastes	EO	SCWO	Mechanochemical	Pyrolysis
Spent GAC/AEX	4	N/A	2	1
Soils	1	N/A	5/6	1
Biosolids/ sludges	N/A	6	1	7
Spent and unused AFFF	4/6	7	3/4	N/A
Landfill leachate	4	4	N/A	N/A

Phase	TRL	Description
Research	1	Basic Principles observed
	2	Technology concept formulated
	3	Experimental proof of concept
Development	4	Technology validated in lab
	5	Technology validated in relevant environment
	6	Technology demonstrated in relevant environment
Deployment	7	System prototype demonstration in operational environment
	8	System complete and qualified
	9	Actual system proven in operational environment

Source: Berg et al. (2021)

Current Status

- Research briefs
  - https://www.epa.gov/chemical-research/pfas-innovative-treatmen team-pitt
- SCWO
  - Manuscript on 3 of 4 case studies:
  - https://ascelibrary.org/doi/full/10.1061/%28ASCE%29EE.1943-7870.0001957
  - 4th case study data being analyzed
- Electrochemical oxidation with AECOM
  - Report being prepared
- Pyrolysis
  - Manuscript on pilot study:
  - https://www.tandfonline.com/doi/pdf/10.1080/10962247.2021.2 9935
  - More detailed sampling plan being coordinated
- Ball milling
  - Data being analyzed

EPA
www.epa.gov/research

Research BRIEF
INNOVATIVE RESEARCH FOR A SUSTAINABLE FUTURE

INNOVATIVE PFAS DESTRUCTION TECHNOLOGY:
PYROLYSIS AND GASIFICATION

Background

Various industries have produced and used PFAS since the mid-20th century. Per- and polyfluoroalkyl substances (PFAS) are found in consumer and industrial products, including non-stick coatings, waterproofing materials, and manufacturing additives. PFAS are stable and resistant to natural destruction in the environment, leading to their pervasive presence in groundwater, surface waters, drinking water and other environmental media (e.g., soil) in some localities. Certain PFAS are also bioaccumulative and the blood of most US citizens contains detectable levels of several PFAS. The toxicity of PFAS is a subject of current study and enough is known to motivate efforts to limit environmental release and human exposure (EPA, 2020). To protect human health and the environment, EPA researchers are identifying technologies that destroy PFAS in liquid and solid waste streams including concentrated and spent (used) fire-fighting foam, biosolids, soils, and landfill leachate. These technologies should be readily available, cost effective, and produce little to no hazardous residuals or byproducts. Pyrolysis and gasification have been identified as promising technologies that may be able to meet these requirements with further development, testing, and demonstrations.

Pyrolysis/Gasification: Technology Overview

Pyrolysis is a process that decomposes materials at moderately elevated temperatures in an oxygen-free environment. Gasification is similar to pyrolysis but uses small quantities of oxygen, taking advantage of the partial combustion process to provide the heat to operate the process. The oxygen-free environment in pyrolysis and the low oxygen environment of gasification distinguish these techniques from incineration. Pyrolysis, and certain forms of gasification, can transform input materials, like biosolids, into a biochar while generating a hydrogen-rich synthetic gas (syngas).

Both biochar and syngas can be valuable products. Biochar has many potential applications and is currently used as a soil amendment that increases the soil's capacity to hold water and nutrients, requiring less irrigation and fertilizer

Figure 1. Biosolids, from wastewater to beneficial use

on crops. Syngas can be used on-site as a supplemental fuel for biosolids drying operations, significantly lowering energy needs. As an additional advantage, pyrolysis and gasification require much lower air flows than incineration, which reduces the size and capital expence of air pollution control equipment.

PFAS have been found in effluent and solid residual (sewage sludge) streams in wastewater treatment plants (WWTPs),[2-6] prompting increasing concern over managment of these materials. In the U.S., WWTP solids have typically been managed in one of three ways: (1) treatment to biosolids followed by land-application; (2) disposal at a lined landfill; or (3) destruction (burning) in a sewage sludge incinerator. WWTP solids are rich in nutrients and the most common U.S. practice is to aerobically or anaerobically digest it to produce a stabilized biosolid product that can be land-applied as fertilizer.[7,8] This is done because the nutrients in biosolids deliver nitrogen, phosphorous, and other trace metals that are beneficial for crops and soil (Figure 1).

Contributors

- Dozens of ORD Research Personnel
- EPA Regions 3 and 7
- Hazen Research
- BioForceTech
- AECOM
- Aquarden
- Battelle
- 374Water
- General Atomics

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DNR Updates, Conclusions & Next Steps