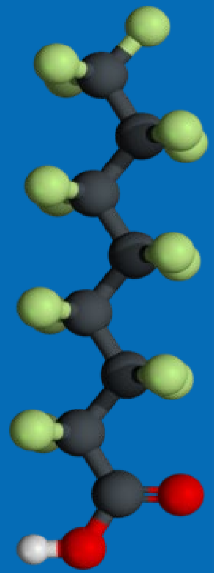
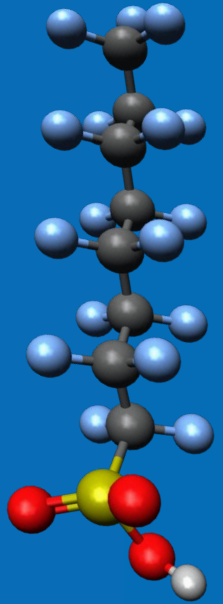
United States Environmental Protection Agency



EPA PFAS INNOVATIVE TREATMENT TEAM (PITT) FINDINGS ON PFAS DESTRUCTION TECHNOLOGIES

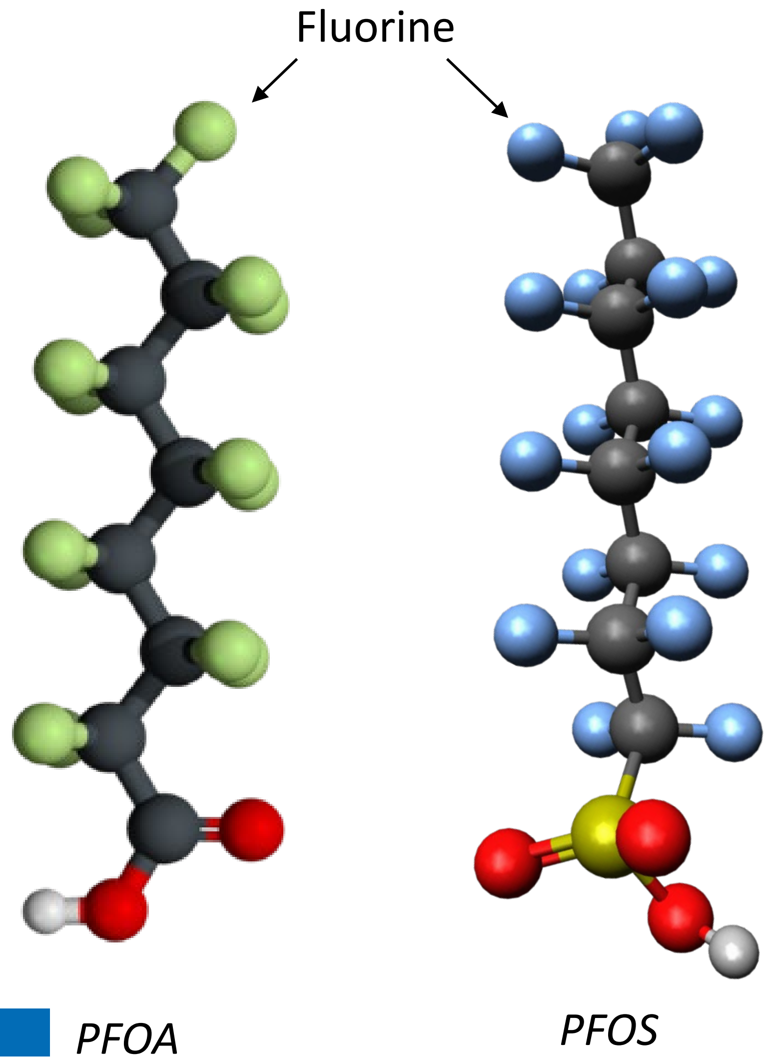


Brian Gullett, PhD
US EPA Office of Research and Development (ORD)

EPA Tools & Resources Webinar
February 17, 2021

Progress for a Stronger Future

Per- & Polyfluoroalkyl Substances (PFAS)



- **A very large class of synthetic chemicals**
  - **Chains** of carbon (C) atoms surrounded by fluorine (F) atoms, with different terminal ends
  - **Complicated chemistry** – thousands of different variations exist in commerce
  - **Widely used** in industrial processes and in consumer products
  - **Mobile** via multiple air, water pathways
  - **Some** PFAS are known to be **PBT:**
    - **Persistent** in the environment
    - **Bioaccumulative** in organisms
    - **Toxic** at relatively low (ppt) levels

Outline

- EPA PFAS Innovative Treatment Team (PITT)
- Goals
- Challenges
- Non-Combustion Technologies
  - Mechanisms
- Combustion Technologies
  - Mechanisms
- Outputs
- Status and PITT Legacy, Next Steps

United States Environmental Protection Agency

PFAS Innovative Treatment Team (PITT)

- Full-time team of multi-disciplined EPA research staff
- Focused efforts and expertise on a single problem: **how to remove, destroy, and test PFAS-contaminated media and waste**
- For 6 months, the PITT worked to achieve the following goals:
  - Assess current and emerging destruction methods being explored by EPA, universities, other research organizations and industry
  - Explore the efficacy of methods while considering byproducts to avoid creating new environmental hazards
  - Evaluate methods' feasibility, performance and costs to validate potential solutions

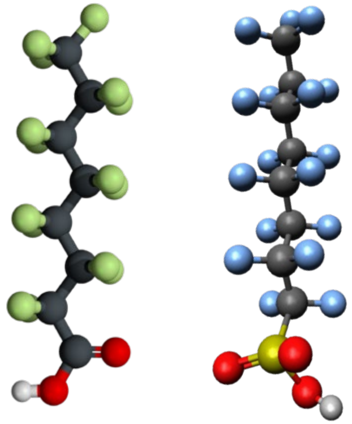
PITT Goals

- Develop a “Toolbox” of reviewed solution(s) for the destruction of PFAS in media and contaminated waste to meet the needs of EPA programs and regions, states and tribes, federal agencies, and industry
  - Traditional (combustion) destruction
    - Temperature and time conditions for C-F bond breakage
    - Performance of flue gas cleaning systems
    - Analysis of byproducts
  - Innovative (high risk), non-traditional approaches
    - Destruction performance
    - Byproducts

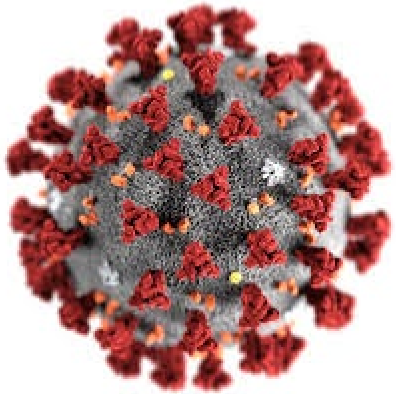
- Provide decision makers with state of the science data on incineration effectiveness enabling them to better manage end-of-life disposal of PFAS-containing materials

PFAS Sources Considered

- Biosolids, sludge
- Aqueous film forming foam (AFFF)-contaminated soils
- AFFF concentrate, spent AFFF
- Municipal Waste Combustors (MWCs), landfills, landfill leachate
- Spent granular activated carbon (GAC), anion exchange resins



PITT Challenges

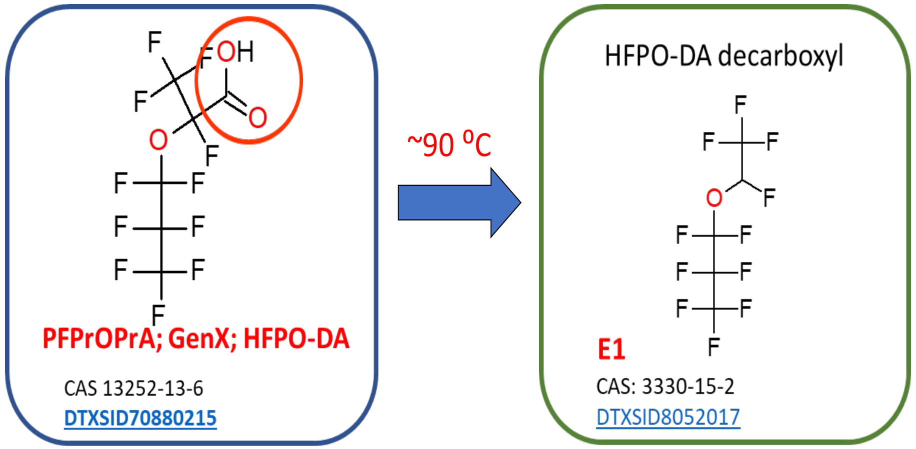


- COVID-19
  - Building closures
  - Lab closures
  - Restricted partner access to labs
  - Closure of suppliers
  - Unavailable instrument repairs
- Finding field test partners
- Concurrent field sampling and sampling methods development

United States Environmental Protection Agency

Challenges of PFAS Destruction

- **Complicated chemistry** – thousands of PFAS exist
- **Widely used** in industrial processes and consumer products
- Efficacy of thermal treatment
  - C-F bond is the strongest bond in organic chemistry
  - Emission sampling and analytical methods are under development
    - Volatile, non-volatile, polar, non-polar
    - Limited number of analytical standards available
  - Field data lacking
  - Historical laboratory research on "destructibility" lacks information about **products of incomplete combustion (PICs)**



Non-Combustion Technologies Selected

- Chemical
- Biological
- Plasma
- **Mechanochemical**
- Sonolysis
- Ebeam
- UV
- **Supercritical water oxidation**
- Deep well injection
- Sorption/stabilization
- **Electrochemical**
- Landfill
- Land application
- **Pyrolysis**

Technologies selected for further investigation

Assessment Factors:

- Technology readiness
- Applicability
- Cost
- Required development remaining
- Risk/reward of technology adoption

Assessment Methods:

- Subject matter expert discussions
- Literature reviews
- PITT discussions

United States Environmental Protection Agency

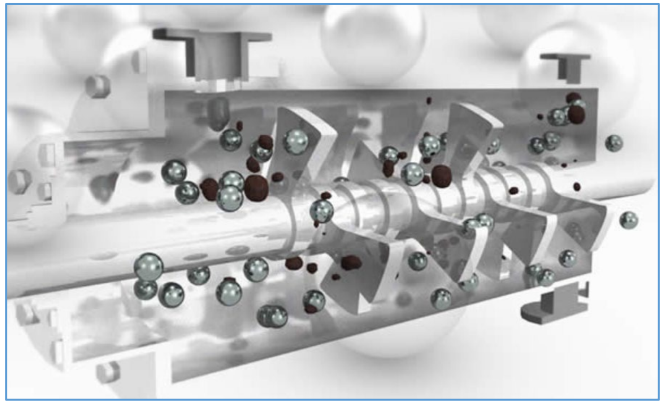
Mechanochemical Treatment

Works by:

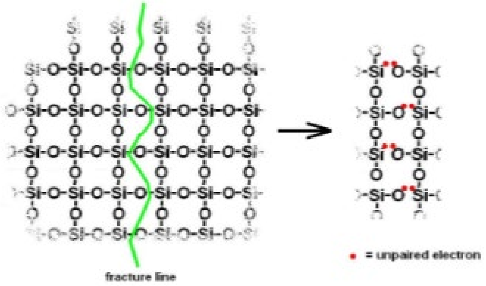
- Introduction of dry solids into a ball mill
- Co-milling reagents: Al, Fe, SiO_2, CaO, MgO, Al_2O_3, KOH, NaOH, MnO_2, TiO_2
- High energy ball impacts fracture solids generating localized high temperatures and radicals that react and breakdown organic molecules
- Technology derived from Persistent Organic Pollutants (POPs)-contaminated soil treatment
  - EDL (NZ) showed >99.8% DRE of PCBs in 45 min (US Navy, Hunters Point, 2006).

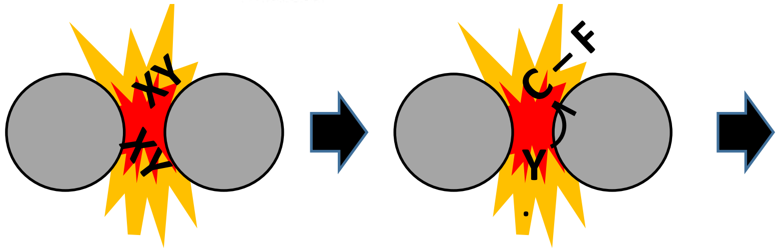
Status:

- Contract with EDL (New Zealand)
  - AFFF impacted soil study
    - >99% destruction of targeted PFAS
  - AFFF destruction study
    - AFFF added to sand
    - >99% destruction of targeted PFAS



Bulley, M.; Black, B. EDL





$C_{(s)} + CO_2 + F^-$

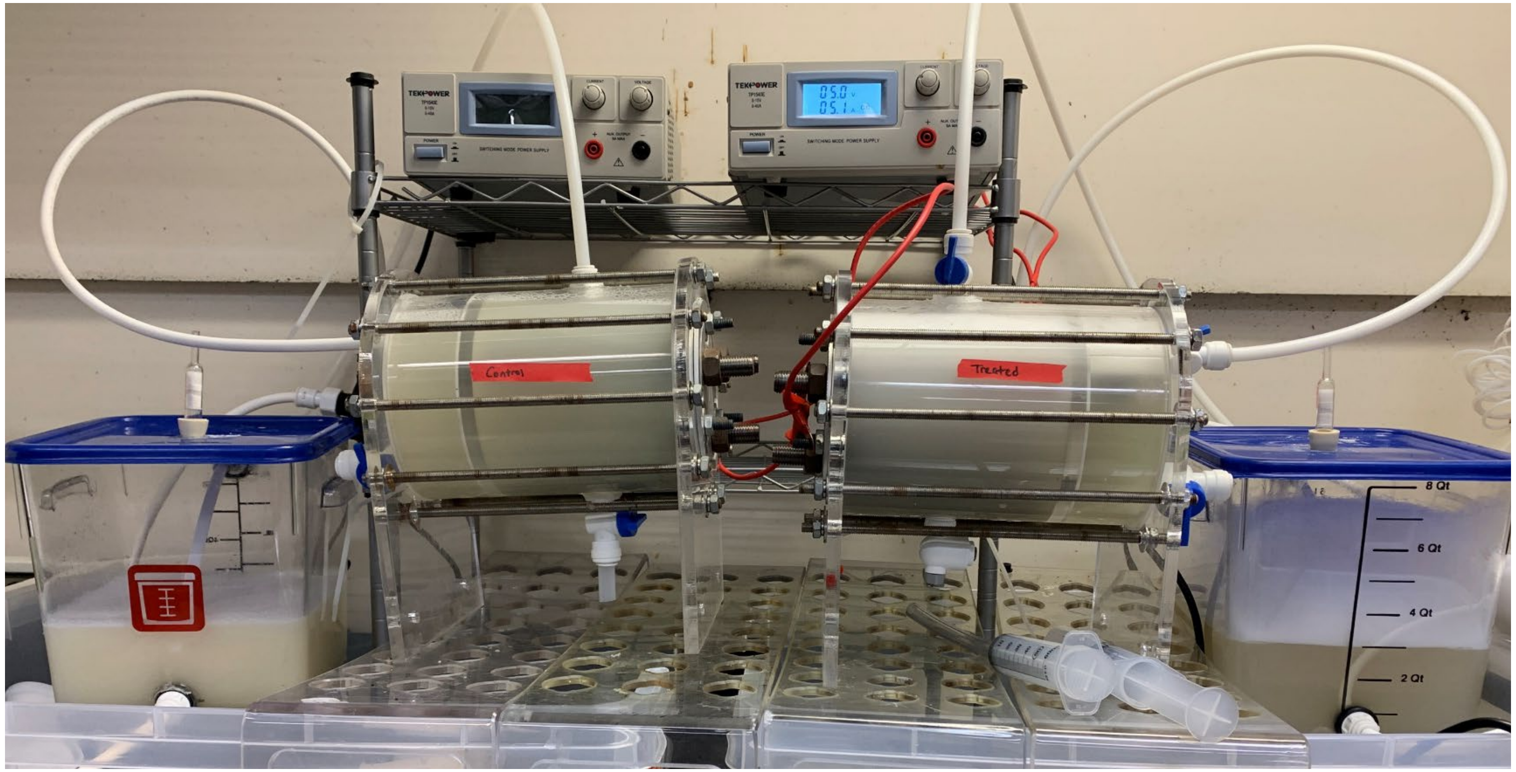
Electrochemical Treatment

Works by:

- A high overpotential (>3 V) is applied to an electrolytic cell
- Stepwise degradation ultimately produces CO_2 and fluoride

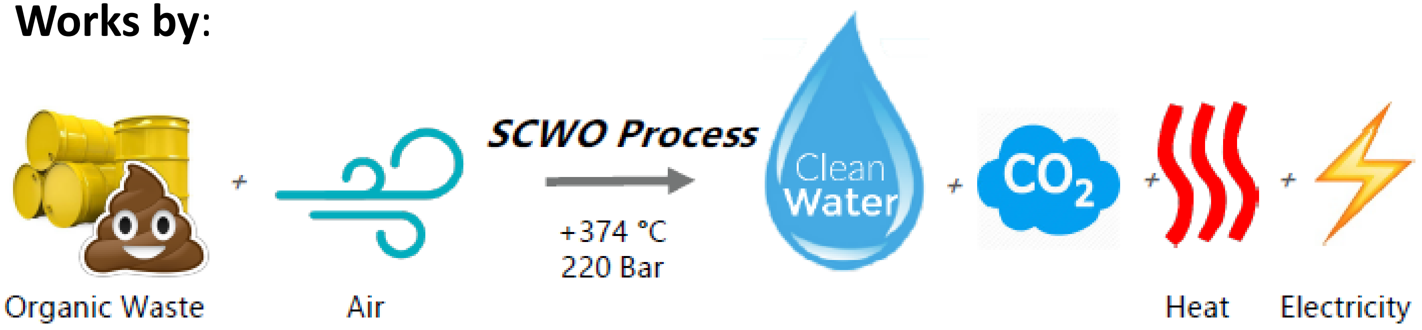
Status:

- Testing AECOM reactors
  - Dilute AFFF
- Data gaps:
  - Uncertain byproducts
  - Volatile loss
  - Matrix effects
- Results expected by May ’21
  - 36 targeted PFAS
  - TOP (precursors assay)
  - TOF (total organic fluorine)



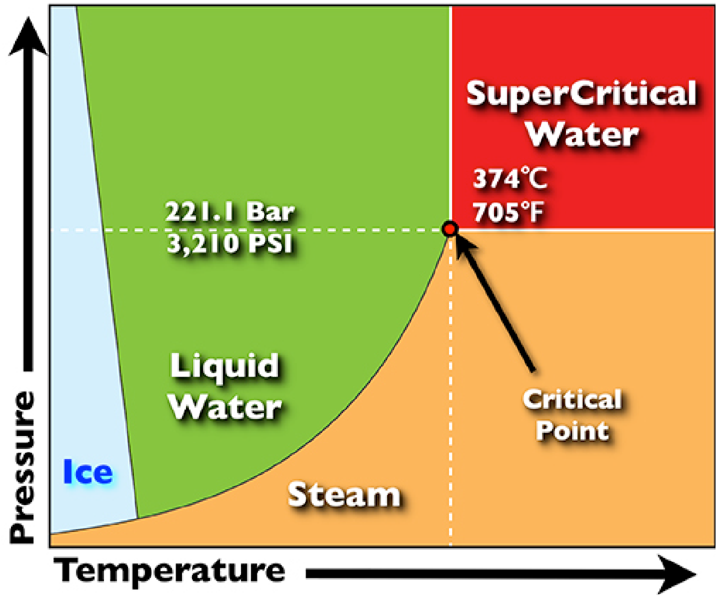
Supercritical Water Oxidation (SCWO)

Works by:



At T = 374°C and P = 221 Bar, water becomes supercritical and organics are solubilized and oxidized

SCWO converts organic waste into clean water, heat, electricity and CO_2 ***in seconds!*** Duke UNIVERSITY



Status:

- **Focus on AFFF concentrate** (*stockpile destruction alternative*)
- In-house lab study on Hydrothermal oxidation
    - Progressing on track
- Experiments complete, chemical analysis complete
- Up to 99% destruction of targeted PFAS seen by 3 vendors
    - Aquarden (Denmark) – Analyzed targeted PFAS
    - Battelle's SCWO "Annihilator" – Analyzed targeted PFAS and fluoride
    - 374Water/Duke – Analyzed targeted PFAS, TOF, and fluoride
- General Atomics MCRADA – Plan under review, experiment in summer '21

EPA United States Environmental Protection Agency

SCWO Status

AFFF Concentrate

Battelle's PFAS Annihilator™

Battelle:
Bench Scale
100x dilute AFFF concentrate
Target PFAS in and out (liquid)
Archived samples (non-target)

Aquarden:
Working unit (pilot test)
100x dilute AFFF concentrate
Target PFAS in and out (liquid)

374Water:
Pilot scale (Test #1: 9/10/20)
4 experiments, varying dilute AFFF
Target PFAS in and out (liquid)
Archived samples (non-target)
Canister and sorbent samples (air)

General Atomics:
Working unit (pilot test)
Varying dilute AFFF
Target PFAS in and out (liquid)
Archived samples (non-target)
Canister and sorbent samples (air)

Biosolids Pyrolysis/Gasification

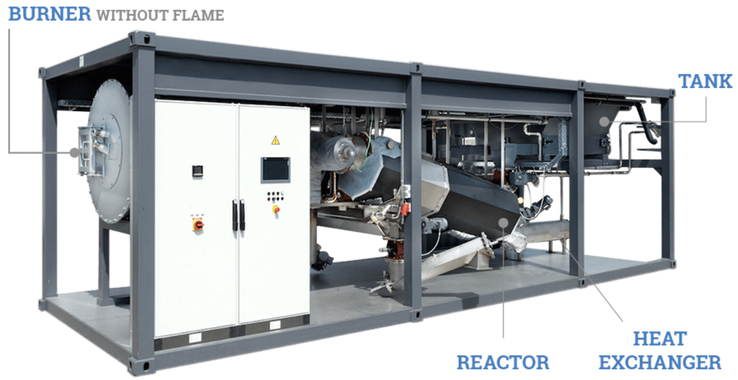
Works by:

- 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).

Status:

- Field test of Pyrolysis unit (with emission controls) that produces Biochar with energy to a biosolids dryer
- Field test completed 2020 and sampled for PFAS in:
  - Input Biosolids
  - Produced Biochar
  - Scrubber Water
  - Multi-position FTIR
- No reportable PFAS found in produced biochar, but additional research needed to understand potential releases to air and water.

BioForceTech
commercial scale



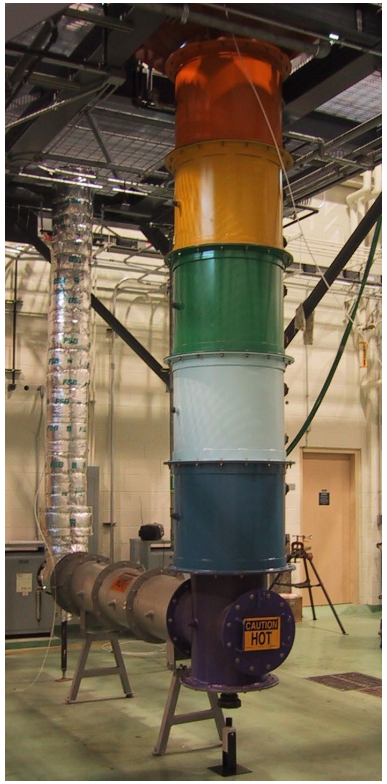
Combustion Technologies

Works by:

- Bond breakage via gas phase oxidation reactions with organic PFAS
- Ideally, formation of CO_2, H_2O and HF
- HF removed in acid gas scrubber

Status

- Laboratory studies
  - At EPA (Rainbow furnace)
    - Indicators for Destruction Removal Efficiency (DRE) and Products of Incomplete Combustion (PICs)
    - FTIR applicability
  - At University of Dayton Research Institute
    - Temperature (T), time (t) effects
    - Byproducts
    - Flame radical studies
    - Spent GAC/Ion Exchange resin
- Pursuing field sampling efforts at facilities with different types of combustion process
  - Muncipal Waste
  - Wastewater Treatment
  - Rotary Kiln Incineration



Rainbow Furnace
RTP, NC campus

Waste Characterization → Waste Scale

Guide on Waste/Technology Applicability and Design Considerations – Waste Characteristics

Waste	Characteristics
Spent GAC/AEX	• Spent GAC & AEX are solids with binding sites saturated with a combination of PFAS and co-contaminants
Soils	• Excavated solids, low PFAS/soil mass ratio, high volumes
Biosolids/ Sludges	• High moisture content, relatively low PFAS concentrations, co-contaminants
AFFF & Spent AFFF	• Liquid phase, legacy AFFF ~5% PFAS • Spent AFFF is dilute
Leachate	• Liquid phase with organic co-contaminants

EPA United States Environmental Protection Agency

Crosswalk of Wastes and Technologies – Design Issues

Treatment Selection

System Sizing
- Continuous vs. Batch Processing
- Level of treatment required
- Transportability
- Centralized or decentralized treatment

Process Considerations
- Phase of material to be treated
- Chemical Inputs
- Energy Inputs
- Capital and Operating Costs
- Lifecycle considerations

Process Management

Waste Steams
- Side Stream Generation
  - Phase Change?
- Additional Unit Process Treatment (e.g., Pollution Control Devices)

Final Disposition
- Further treatment of co-contaminants
- Disposal
- Environmental Release

Engineering Design Considerations

Technologies	Treatment Selection	Process Management
Electrochemical Treatment	• Size is a function of kinetics and reactor configuration • High lifecycle and operating costs	• May generate gas phase waste stream • Can generate perchlorate in the presence of Cl
Supercritical Water Oxidation	• Minimum concentration threshold • High lifecycle and operating costs • Technically complex	• Degradation byproducts may vary • Potential corrosion issues
Mechanochemical Milling	• Size is a function of kinetics and reactor configuration • May be limited by water conc. allowable	• Likely generates gas phase waste stream • Ancillary unit operations are necessary
Pyrolysis	• Can be batch or continuous • Dry or semi-dry solids only	• Pretreatment of solids to reduce water • Volatiles require treatment

PITT Introductory Paper on Four Innovative Technologies Studied

United States Environmental Protection Agency

- PFAS problem
- 5 waste characteristics
- 4 innovative technologies
- Crosswalk of wastes and technologies
- Technology readiness level

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

https://www.twi-global.com/technical-knowledge/faqs/technology-readiness-levels

TRLs of Technology & PFAS Matrices

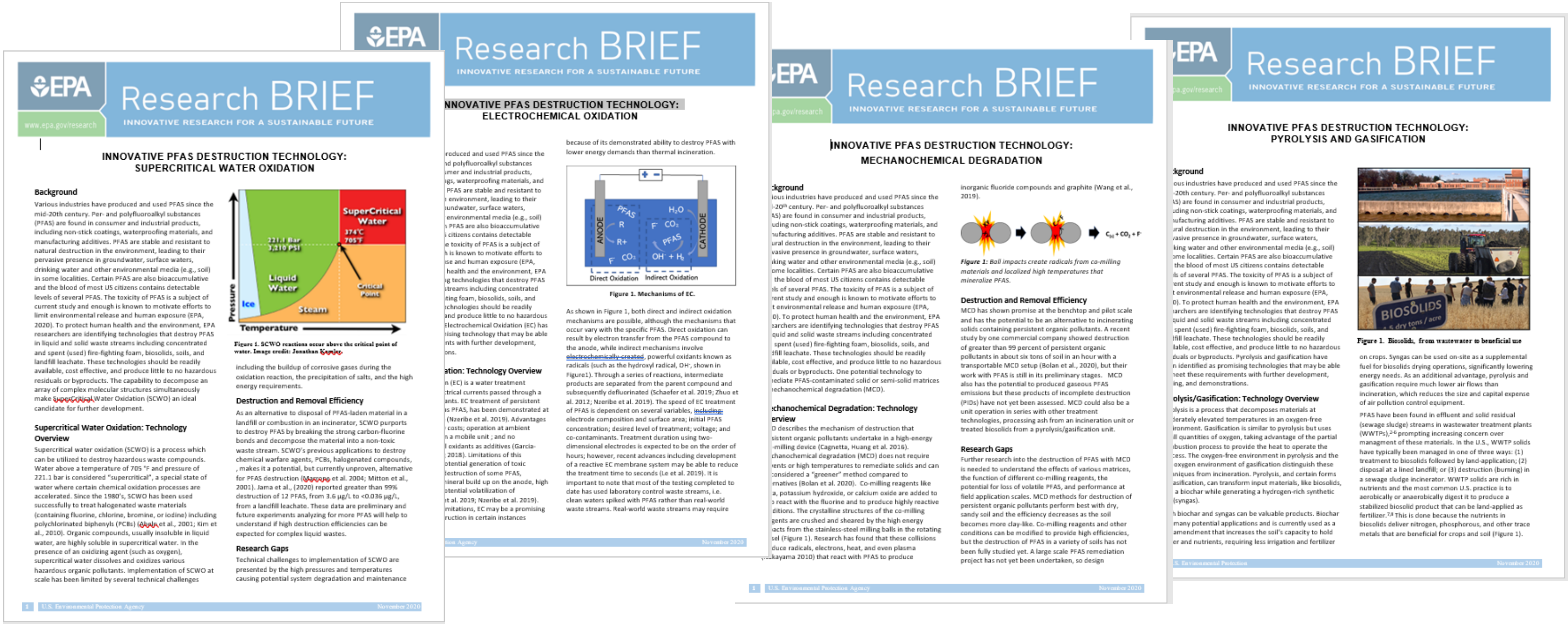
	Electrochemical	SCWO	Mechanochemical Milling	Pyrolysis
Spent GAC/AEX	N/A	N/A	TRL 2[10]	TRL 1
Soils	N/A	N/A	TRL 5[8]	TRL 1
Biosolids/Sludges	N/A	TRL 5[6]	TRL 1	TRL 7[9]
Unused and spent AFFF	TRL 5/6[1,2]	TRL 5[4,5,6,7]	N/A	N/A
Leachate	TRL 4[3]	TRL 4[5]	N/A	N/A

BASIS

[1] (AECOM)
[2](Schaefer et al 2019)
[3] (Pierpaoli et al 2020)
[4] (General Atomics)
[5] (Aquarden)
[6](374Water)
[7](Battelle)
[8](EDL)
[9](BioForceTech)
[10](PITT)

PITT Research Briefs

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



SCWO | **Electrochemical Oxidation** | **Ball Milling** | **Pyrolysis & Gasification**

Challenge Partners

- US Dept. of Defense: Strategic Environmental Research and Development Program (SERDP) & Environmental Security Technology Certification Program (ESTCP)
- Environmental Council of the States (ECOS)/Environmental Research Institute of the States (ERIS)
- Colorado Department of Public Health & Environment
- Michigan Department of Environment, Great Lakes, & Energy

https://www.epa.gov/innovation/innovative-ways-destroy-pfas-challenge

- Goal: Novel, alternative, non-incineration methodologies that offer a pathway to complete destruction of PFAS compounds found in unused PFAS-containing aqueous film forming foam (AFFF), a type of fire suppressant agent, while not creating hazardous byproducts
- Up to $50K for the best design concept for non-thermal technologies

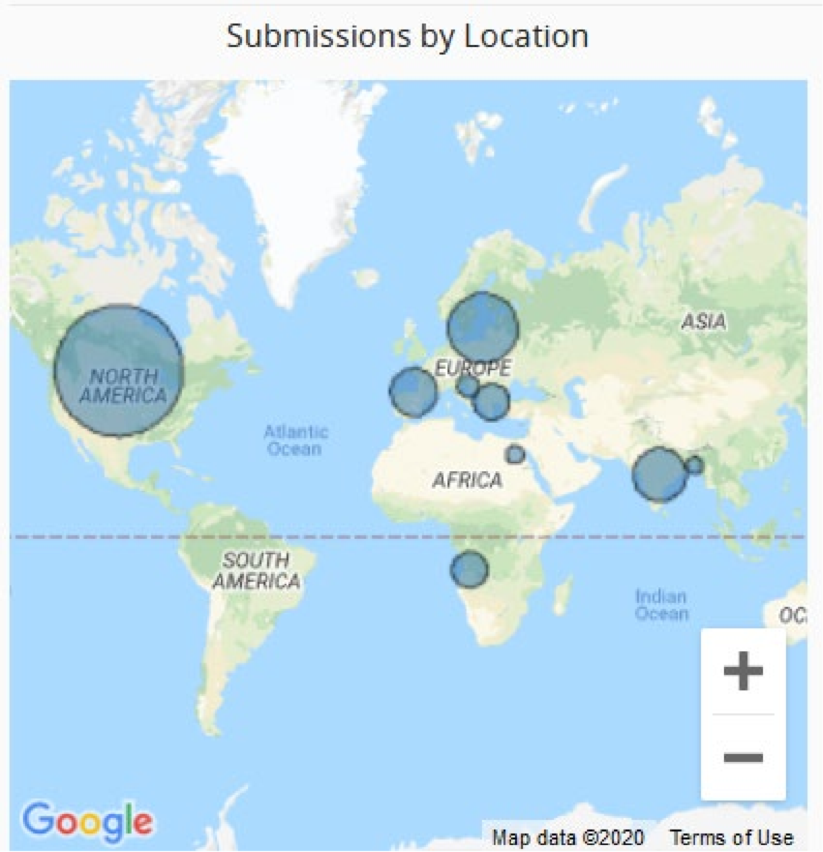
EPA United States Environmental Protection Agency

Challenge Status

- **Aug**
  - 25th Challenge Launched
- **Sept**
  - 16th Public Webinar
    - Est 500 Participants
- **Nov**
  - 23rd Challenge Closed
- **Dec**
  - 18th First round judging complete
    - Some solvers notified of elimination
- **Jan**
  - 18th Judging Panel Selection
  - 25th Propose Winners to Management
- **Feb**
  - Winner Announced

The numbers:

- 212 solvers
- 64 submissions from 18 countries
- 23 solvers met the minimum acceptable criteria



Summary of PITT Findings

- Preliminary results in laboratory and pilot-scale treatment systems demonstrate up to 99% loss of the initial PFAS compounds in the contaminated waste
  - Thermal incineration/combustion
  - Supercritical water oxidation
  - Pyrolysis/gasification
  - Electrochemical oxidation, and
  - Mechanochemical treatment.

- Still unknown, however, is what PFAS byproducts, if any, are formed from each of these technologies.

Next Steps

- Continue laboratory and pilot-scale research and development efforts on:
  - Non-combustion, innovative technologies
    - Thermal catalytic/incineration/combustion,
    - Supercritical water oxidation,
    - Pyrolysis/gasification,
    - Electrochemical oxidation, and
    - Mechanochemical treatment.
  - Thermal/combustion technologies
- Identify potential fluorinated byproducts formed during the application of these treatment approaches (non-target compound analyses)
- Explore opportunities for field sampling, development efforts with industrial and utility facilities
- Summarize efforts on non-combustion, innovative technologies in scientific papers (spring 2021)
- Promote next stage development for winners of the *Innovative Ways to Destroy PFAS* Challenge

Contacts

Brian Gullett
Lead, PITT Team
Center for Environmental Measurement and Modeling
US EPA Office of Research and Development
919-541-1534
Gullett.Brian@epa.gov

Tim Watkins
Director
Center for Environmental Measurement and Modeling
US EPA Office of Research and Development
919-541-5114
Watkins.Tim@epa.gov

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