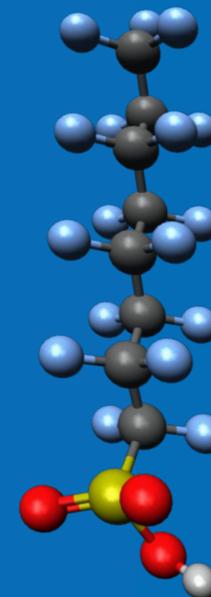
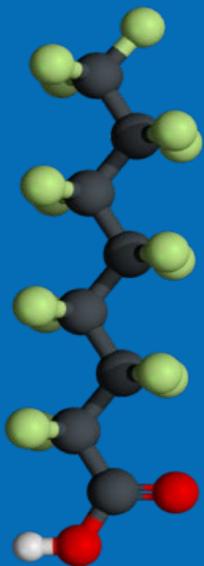


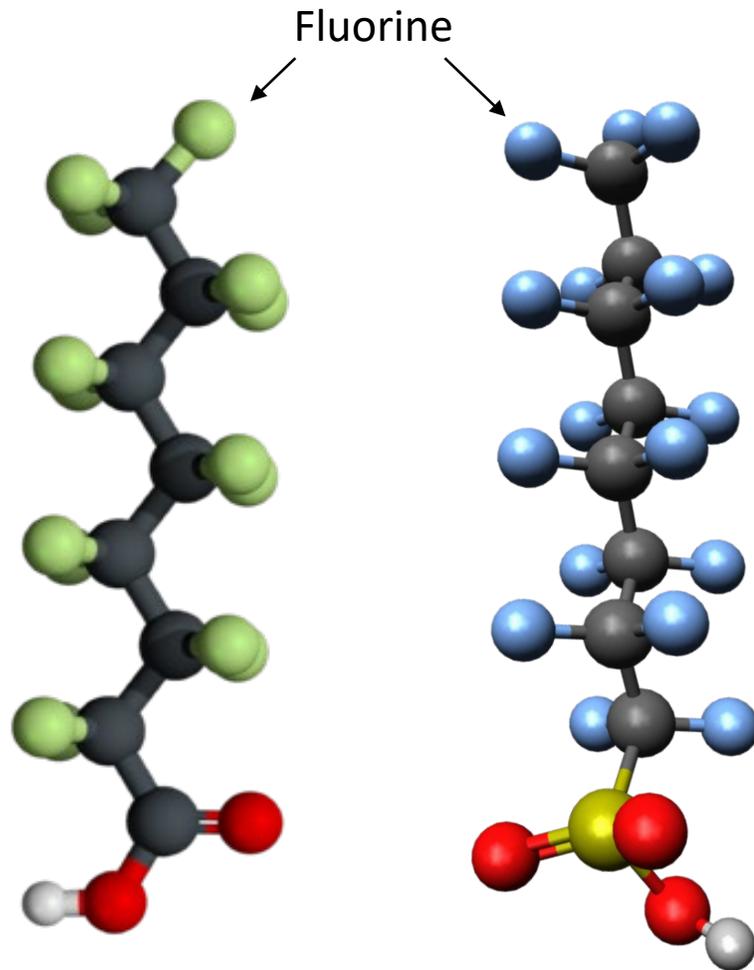
EPA PFAS INNOVATIVE TREATMENT TEAM (PITT) FINDINGS ON PFAS DESTRUCTION TECHNOLOGIES



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

EPA Tools & Resources Webinar
February 17, 2021

Per- & Polyfluoroalkyl Substances (PFAS)



PFOA

PFOS

- **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

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

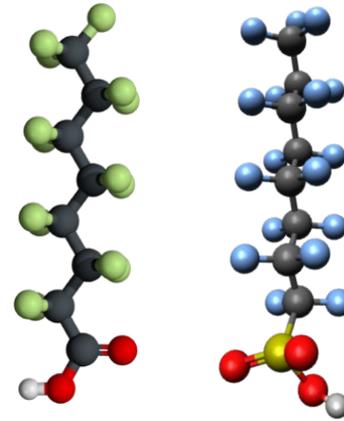
PITT Goals

- 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



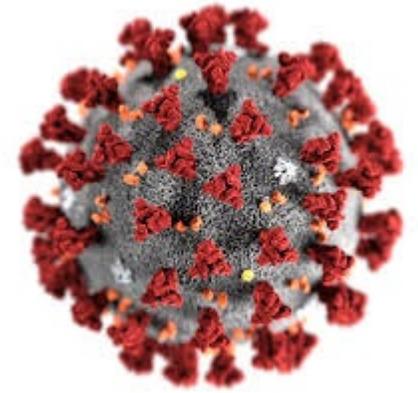
PFAS Sources Considered

- 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





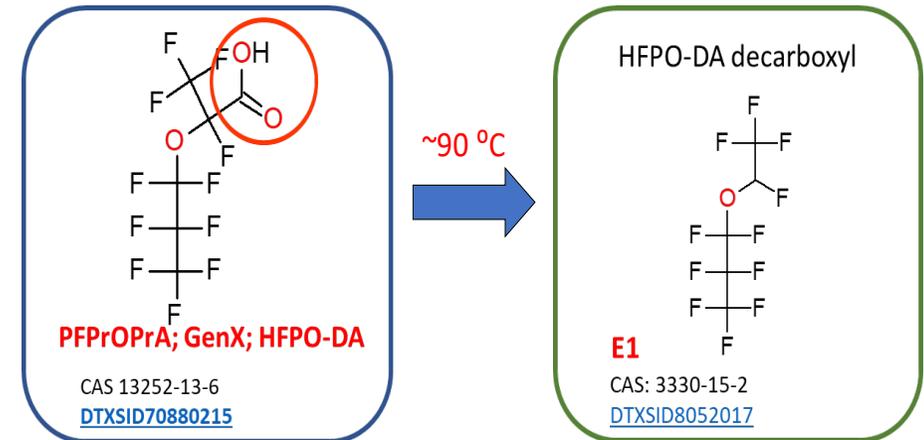
PITT Challenges



- 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

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**

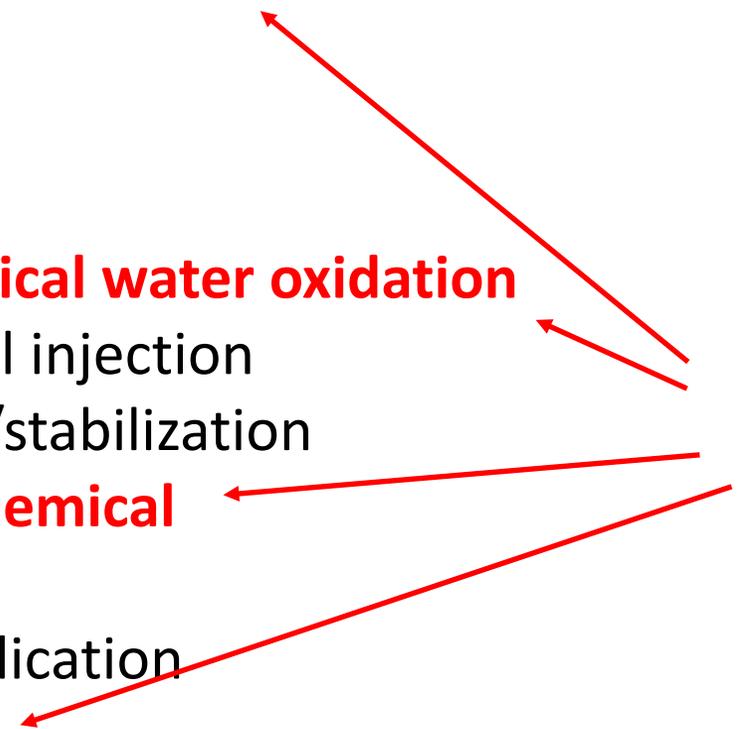
Assessment Factors:

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

Assessment Methods:

- Subject matter expert discussions
- Literature reviews
- PITT discussions

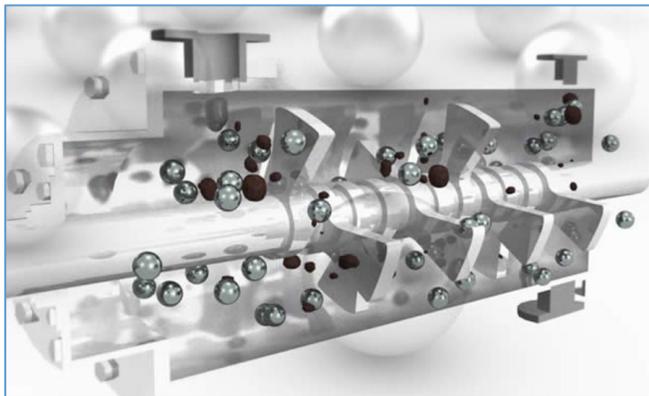
Technologies selected for further investigation



Mechanochemical Treatment

Works by:

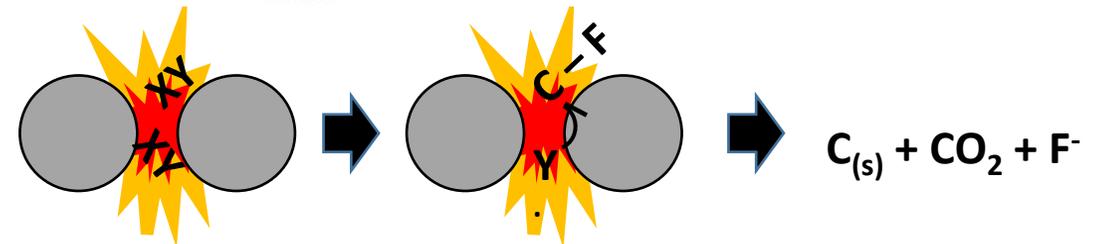
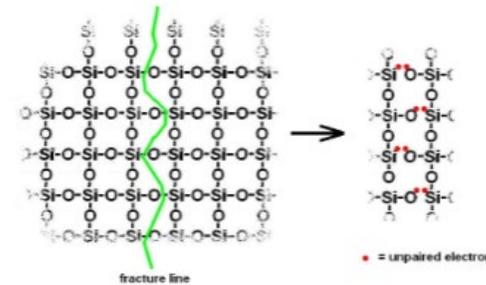
- Introduction of dry solids into a ball mill
- Co-milling reagents: Al, Fe, SiO₂, CaO, MgO, Al₂O₃, KOH, NaOH, MnO₂, TiO₂
- High energy ball impacts fracture solids generating localized high temperatures and radicals that react and breakdown organic molecules
- Technology derived from Persistent Organic Pollutants (POPs)-contaminated soil treatment
 - EDL (NZ) showed >99.8% DRE of PCBs in 45 min (US Navy, Hunters Point, 2006).



Bulley, M.; Black, B. EDL

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



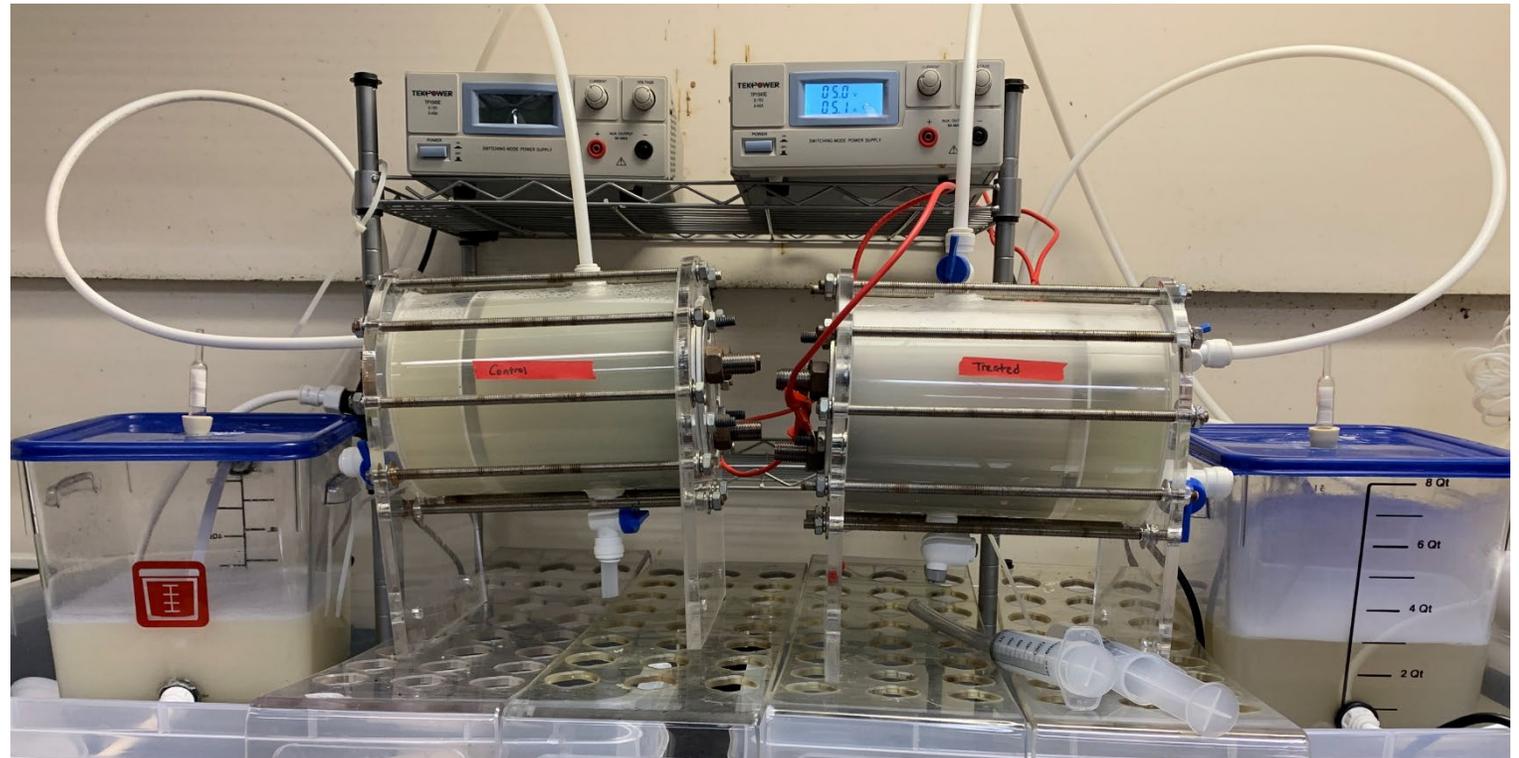
Electrochemical Treatment

Works by:

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

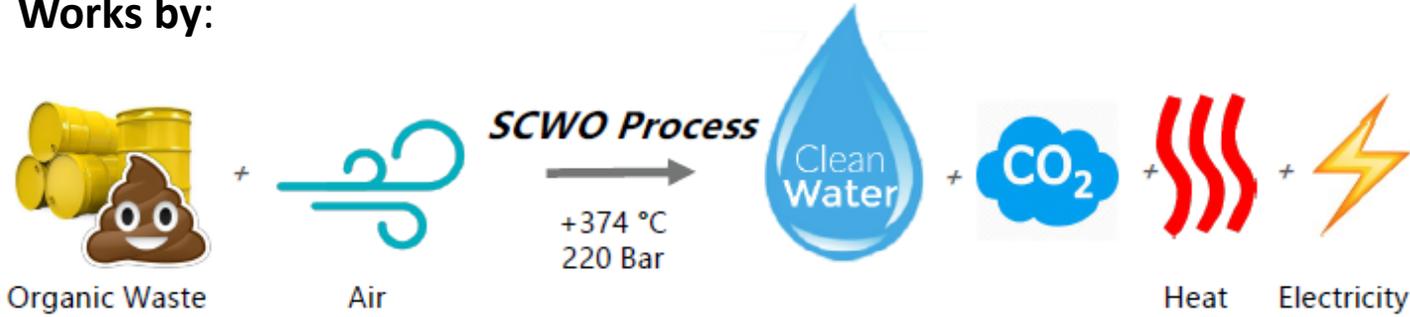
Status:

- 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 $T = 374^{\circ}\text{C}$ and $P = 221 \text{ Bar}$, water becomes supercritical and organics are solubilized and oxidized

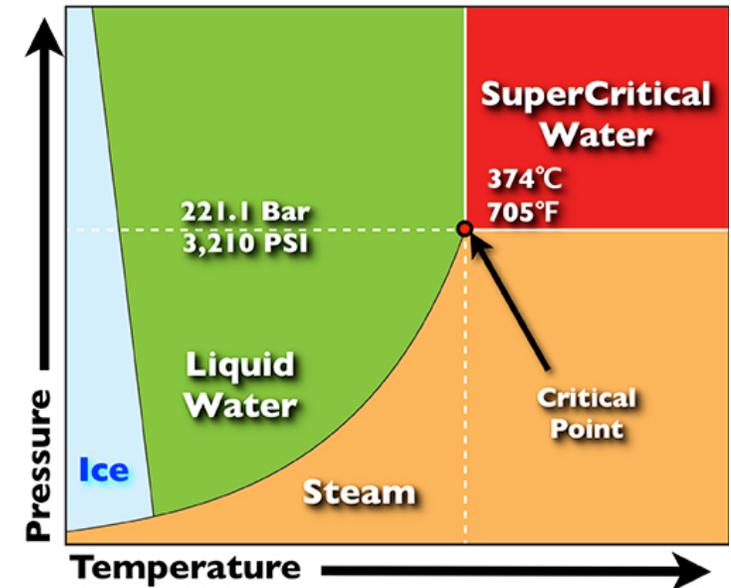


*SCWO converts organic waste into clean water,
heat, electricity and CO₂ in seconds!*

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



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)



MCRADA signed

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



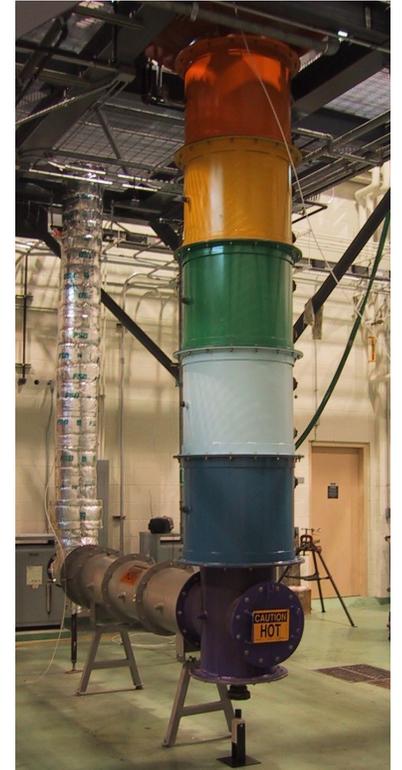
Combustion Technologies

Works by:

- Bond breakage via gas phase oxidation reactions with organic PFAS
- Ideally, formation of CO₂, H₂O and HF
- HF removed in acid gas scrubber

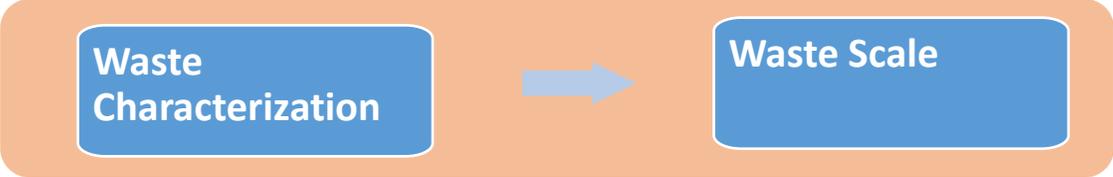
Status

- 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
 - Municipal Waste
 - Wastewater Treatment
 - Rotary Kiln Incineration



Rainbow Furnace
RTP, NC campus

Guide on Waste/Technology Applicability and Design Considerations – 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

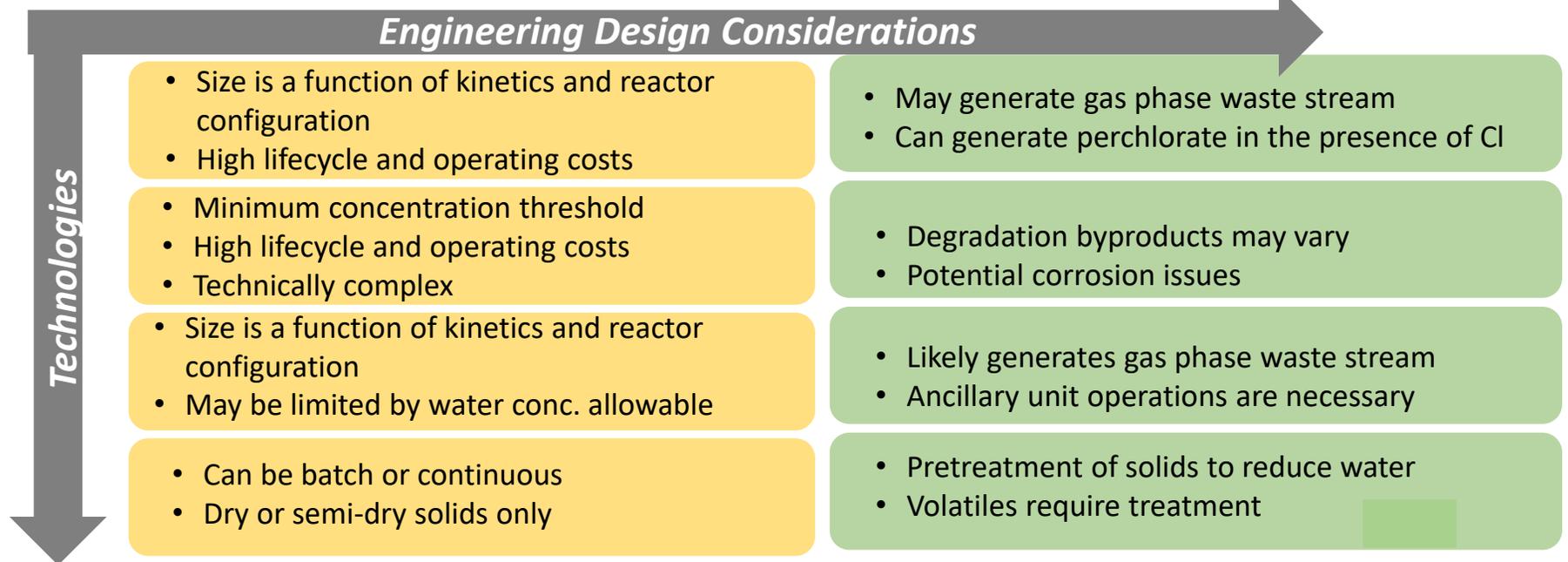
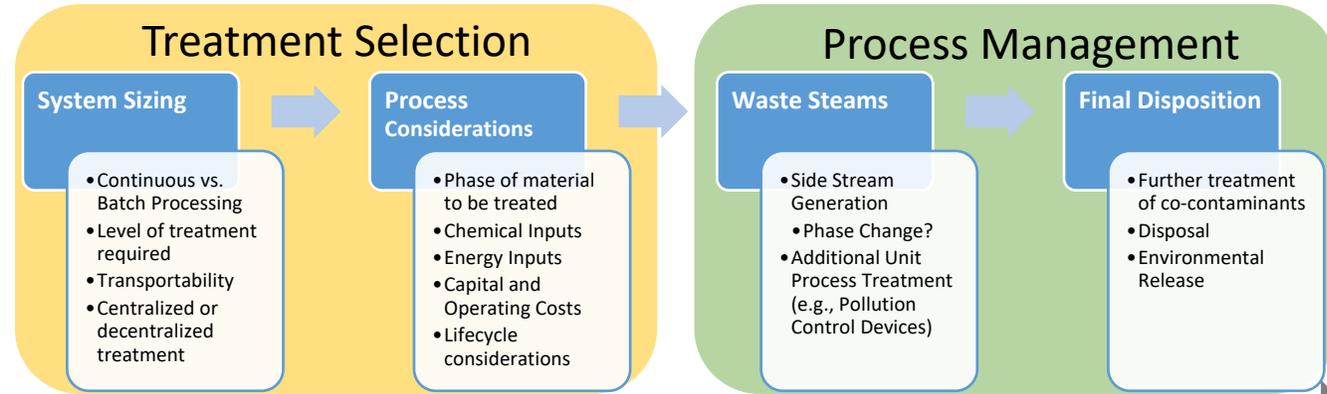
AFFF & Spent AFFF

- Liquid phase, legacy AFFF ~5% PFAS
- Spent AFFF is dilute

Leachate

- Liquid phase with organic co-contaminants

Crosswalk of Wastes and Technologies – Design Issues



PITT Introductory Paper on Four Innovative Technologies Studied

- 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)

Research BRIEF

INNOVATIVE RESEARCH FOR A SUSTAINABLE FUTURE

INNOVATIVE PFAS DESTRUCTION TECHNOLOGY: SUPERCRITICAL WATER OXIDATION

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. The capability to decompose an array of complex molecular structures simultaneously make Supercritical Water Oxidation (SCWO) an ideal candidate for further development.

Supercritical Water Oxidation: Technology Overview

Supercritical water oxidation (SCWO) is a process which can be utilized to destroy hazardous waste compounds. Water above a temperature of 374 °F and pressure of 221.1 bar is considered "supercritical", a special state of water where certain chemical oxidation processes are accelerated. Since the 1980's, SCWO has been used successfully to treat halogenated waste materials (containing fluorine, chlorine, bromine, or iodine) including polychlorinated biphenyls (PCBs) (Lujan et al., 2001; Kim et al., 2010). Organic compounds, usually insoluble in liquid water, are highly soluble in supercritical water. In the presence of an oxidizing agent (such as oxygen), supercritical water dissolves and oxidizes various hazardous organic pollutants. Implementation of SCWO at scale has been limited by several technical challenges

Figure 1. SCWO reactions occur above the critical point of water. Image credit: Jonathan Kopp.

Research Gaps

Technical challenges to implementation of SCWO are presented by the high pressures and temperatures causing potential system degradation and maintenance

U.S. Environmental Protection Agency

November 2020

SCWO

Research BRIEF

INNOVATIVE RESEARCH FOR A SUSTAINABLE FUTURE

INNOVATIVE PFAS DESTRUCTION TECHNOLOGY: ELECTROCHEMICAL OXIDATION

reduced 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. The capability to decompose an array of complex molecular structures simultaneously make Electrochemical Oxidation (EC) an ideal candidate for further development.

Electrochemical Oxidation: Technology Overview

Electrochemical oxidation (EC) is a water treatment technology that currently passes through a number of stages. EC treatment of persistent PFAS has been demonstrated at pilot scale (Nzeribe et al. 2019). Advantages of EC include: (1) operation at ambient temperature and pressure; (2) no need for hazardous oxidants as additives (Garcia et al. 2018). Limitations of this technology include: (1) potential generation of toxic byproducts from the destruction of some PFAS; (2) mineral build up on the anode, high energy consumption (Le et al. 2019; Nzeribe et al. 2019). EC may be a promising technology in certain instances

Figure 1. Mechanisms of EC.

Research Gaps

Technical challenges to implementation of EC are presented by the high pressures and temperatures causing potential system degradation and maintenance

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Electrochemical Oxidation

Research BRIEF

INNOVATIVE RESEARCH FOR A SUSTAINABLE FUTURE

INNOVATIVE PFAS DESTRUCTION TECHNOLOGY: MECHANOCHEMICAL DEGRADATION

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. One potential technology to destroy PFAS-contaminated solid or semi-solid matrices is mechanochemical degradation (MCD).

Mechanochemical Degradation: Technology Overview

MCD describes the mechanism of destruction that persistent organic pollutants undertake in a high-energy ball-milling device (Cagnetta, Huang et al. 2016). Mechanochemical degradation (MCD) does not require reagents or high temperatures to remediate solids and can be considered a "greener" method compared to traditional incineration (Bolan et al. 2020). Co-milling reagents like calcium hydroxide, or calcium oxide are added to react with the fluorine and to produce highly reactive intermediates. The crystalline structures of the co-milling reagents are crushed and sheared by the high energy jets from the stainless-steel milling balls in the rotating vessel (Figure 1). Research has found that these collisions produce radicals, electrons, heat, and even plasma (Kakaya 2010) that react with PFAS to produce

Figure 1. Ball impacts create radicals from co-milling materials and localized high temperatures that mineralize PFAS.

Research Gaps

Further research into the destruction of PFAS with MCD is needed to understand the effects of various matrices, the function of different co-milling reagents, the potential for loss of volatile PFAS, and performance at field application scales. MCD methods for destruction of persistent organic pollutants perform best with dry, sandy soil and the efficiency decreases as the soil becomes more clay-like. Co-milling reagents and other conditions can be modified to provide high efficiencies, but the destruction of PFAS in a variety of soils has not been fully studied yet. A large scale PFAS remediation project has not yet been undertaken, so design

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Ball Milling

Research BRIEF

INNOVATIVE RESEARCH FOR A SUSTAINABLE FUTURE

INNOVATIVE PFAS DESTRUCTION TECHNOLOGY: PYROLYSIS AND GASIFICATION

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 elevated temperatures in an oxygen-free environment. Gasification is similar to pyrolysis but uses quantities of oxygen, taking advantage of the partial oxidation process to provide the heat to operate the process. The oxygen-free environment in pyrolysis and the oxygen environment of gasification distinguish these processes 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). Biochar and syngas can be valuable products. Biochar has many potential applications and is currently used as an 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 expense of air pollution control equipment. PFAS have been found in effluent and solid residual (sewage sludge) streams in wastewater treatment plants (WWTPs), prompting increasing concern over management 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.²⁴ This is done because the nutrients in biosolids deliver nitrogen, phosphorus, and other trace metals that are beneficial for crops and soil (Figure 1).

Research Gaps

Technical challenges to implementation of pyrolysis and gasification are presented by the high pressures and temperatures causing potential system degradation and maintenance

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November 2020

Pyrolysis & Gasification



Innovative Ways to Destroy **PFAS**

PER- AND POLYFLUOROALKYL SUBSTANCES

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>

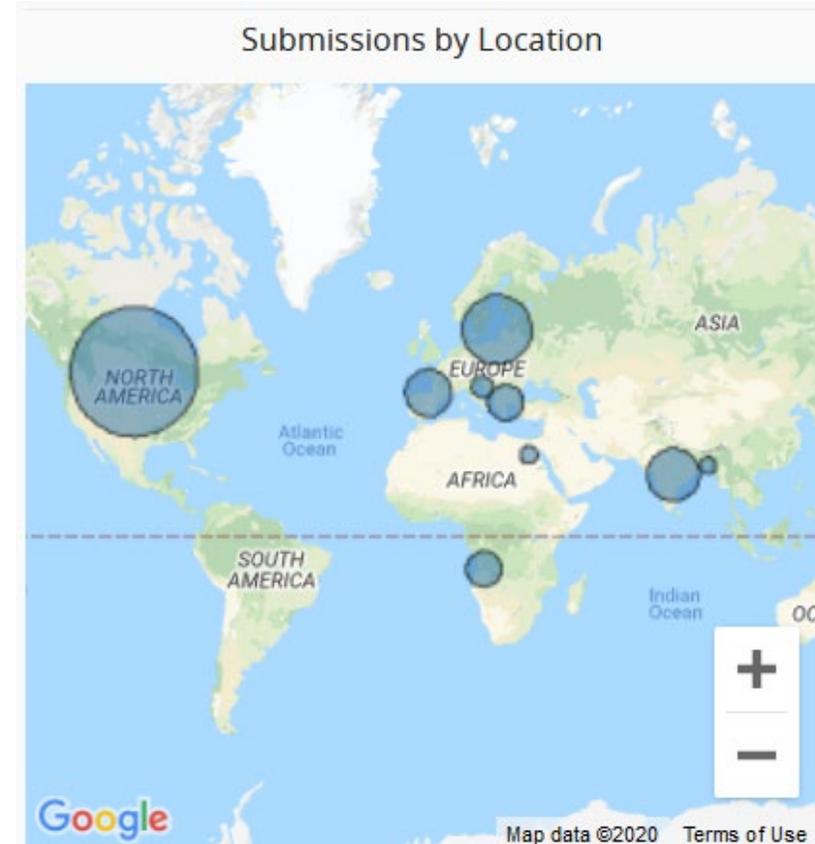
- Goal: Novel, alternative, non-incineration methodologies that offer a pathway to complete destruction of PFAS compounds found in unused PFAS-containing aqueous film forming foam (AFFF), a type of fire suppressant agent, while not creating hazardous byproducts
- Up to \$50K for the best design concept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

Challenge Status



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*

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

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