

PFAS Incineration: EPA Activities and Research

Jeff Ryan

US EPA – Office of Research and Development Center for Environmental Measurements and Modeling

State/USEPA Region 5 Air Toxics Risk Assessment Meeting November 13, 2019 • Chicago, Illinois

Per- and Polyfluoroalkyl Substances (PFAS)



A class of man-made chemicals used for multiple purposes

- Chains of carbon (C) atoms surrounded by fluorine (F) atoms
 - Stable C-F bond
 - Many include a polar end

Some are persistent, bioaccumulative, and toxic

Perfluorooctanoic acid (PFOA)

Perfluorooctanesulfonic acid (PFOS)

Thousands of chemicals that can become air sources during production and use of products



Thermal Treatment of PFAS

- PFAS often composed of non-polar fluorinated alkyl chain and polar functional group
- Highly electronegative fluorine makes C-F bonds particularly strong, require high temperatures for destruction
 - Calculated unimolecular reaction rates suggest that CF₄ requires 1,440 °C for greater than 1 second to achieve 99.99% destruction (Tsang et al., 1998)
 - Suggests that CF₄ may be a good surrogate for destruction removal efficiency (DRE) testing
 - Sufficient temperatures, times, and turbulence are required
- Polar functional group relatively easy to remove/oxidize
 - Low temperature decarboxylation as an example
 - Information regarding potential products of incomplete combustion (PIC) is lacking



Products of Incomplete Combustion (PICs)

- When formed in flames, F radicals quickly terminate chain branching reactions to act as an extremely efficient flame retardant, inhibiting flame propagation
- PICs are more likely formed with F radicals than other halogens such as Cl
- PICs may be larger or smaller than the original fluorinated compound of concern
 - CF₂ radicals preferred and relatively stable, suggesting the possibility of reforming fluorinated alkyl chains
 - Remaining C-F fragments may recombine to produce a wide variety of fluorinated PICs with no analytical method or calibration standards
 - May result in adequate PFAS compound destruction but unmeasured and unquantified PICs
- See also: "Technical Brief on Per- and Polyfluoroalkyl Substances (PFAS): Incineration to Manage PFAS Waste Streams"
 - https://www.epa.gov/chemical-research/technical-brief-and-polyfluoroalkyl-substancespfas-incineration-manage-pfas-waste

- There are many sources of PFAS materials that may need to be incinerated/treated
 - Manufacturing wastes
 - Biosolid sludges
 - Municipal waste
 - Obsolete flame retardants
 - Spent water treatment sorbents (resins/activated carbon)

Objective: What minimum conditions (temperature, time) are needed to adequately destroy PFAS and what are the products of incomplete combustion?

Action: Conduct bench- and full-scale field incineration studies to evaluate:

- Impact of source material
- Impact of temperature on degree of destruction
- Impact of calcium
- PFAS releases from incineration systems

- Examine minimum conditions (temperature, time, fuel H₂) for adequate PFAS destruction
- CF₄ as a complete thermal destruction surrogate
- Fluorine incineration chemistry modeling
- Relative difficulties in removing PFAS functional groups (POHC destruction) vs full defluorination (PIC destruction)
- Effects of incineration conditions (temperature, time, and H₂) on PIC emissions
- Relative differences in the incinerability of fluorinated and related chlorinated alkyl species
- Collaborative projects with DoD and industry partners to evaluate existing technologies
 - Thermal treatment system for PFAS contaminated soils in Alaska
 - Fate of PFAS during granular activated carbon (GAC) reactivation from treatment systems

Direct- and Indirect-fired Thermal Oxidation Mitigation Experiment

- Existing equipment (formerly used for oxy-coal)
- Small scale (L/min & g/min)
- Full control of post-flame temperature & time (2-3 sec)
- Able to add either gas or liquid PFAS through or bypassing flame
- Premixed or diffusion flames possible



Packed Bed Reactor Experiment

- Small scale (L/min & g/min)
- Control of temperature & time (2-3 sec)
- Methane added below flammability limit as a source of hydrogen
- CaF₂ formation eliminates the need for a scrubber
- Platform for measurement methods development
 - SUMMA, sorbent, total organic fluorine (TOF)
 - real-time instruments



Future work: Activated Carbon Reactivation

- Problem: There is a liability concern regarding the reactivation of spent granular activated carbon
 - What percentage of the adsorbed PFAS are released from the carbon and how much remains after reactivation
 - What conditions are optimal for reactivation (temperature, time, reactor configuration)?
 - What impact does reactivation have on the performance of off-gas incineration treatment?
 - Are PFAS released after reactivation with incineration off-gas treatment?
- Action: Conduct bench- and full-scale research on reactivation processes
 - Impact of time and temperature
 - PFAS reactions during reactivation
 - Impact of post incineration
 - Post GAC evaluations to determine PFAS remaining on carbon (fate)



Thermal Treatment at Moose Creek

• Objectives: Improve understanding of incinerability of PFAS compounds

- Evaluate several candidate PFAS-specific emissions sampling and measurement methods
- Conduct a comprehensive PFAS emissions characterization from a representative thermal treatment process

Collaborators:

- National Response Corporation Alaska, LLC (NRC), formerly Organic Incineration Technology Incorporated (OIT) – facility operator
- EPA Office of Research and Development (ORD) and contractors
- Department of Defense (DoD) Strategic Environmental Research and Development Program (SERDP)

Thermal Treatment at Moose Creek

• Facility: Two-Stage Thermal Treatment Operation

- In operation since early 1990s for treating petroleum-contaminated soils
- Rotary kiln system in two stages:
 - Initial temperature up to 1,500 F to treat soil, volatilize contaminants
 - Secondary chamber up to 2,100 F to burn the off gas
 - Treated materials are ready for reuse
- Following some preliminary testing, facility was permitted in 2019 to treat certain PFAS contaminated wastes

Thermal Treatment at Moose Creek

Sampling and Analytical Testing Approaches

- Testing done at a facility licensed for thermal treatment of PFAS-contaminated media (NRC/OIT), operating on a representative load of contaminated soils
- Collection of replicate samples using different systems
 - Modified SW-846 Method 0010 Train (MM5) to collect polar and nonpolar, semivolatile and nonvolatile PFAS compounds
 - Modified Method 18 PFAS sampling train developed by Test America to collect polar, volatile PFAS
 - EPA-ORD's SUMMA canister sampling method to collect nonpolar, volatile PFAS
 - Collection of adjacent soil and water samples for background analysis
- Analysis will include targeted (known analytes) and nontargeted (high resolution mass) spectrometry for unknown PFAS), and a proof-of-concept test for a Total Organic Fluorine (TOF) method 13

PFAS Emissions Measurement Considerations

- PFAS emission measurement methods are needed to inform regulatory decisions
 - Comprehensive emissions characterizations
 - Technology evaluations
 - What methods are available and appropriate?
- What kind of PFAS measurement methods are needed?
 - Ability to measure volatile/semivolatile/nonvolatile and polar/nonpolar PFAS compounds
 - Ability to measure targeted PFAS compounds and identify nontargeted PFAS compounds
- What PFAS to measure?
 - Targeted compounds?
 - Legacy (537) compounds
 - What about PFAS wastes (e.g., AFFF) constituents?
 - What about Products of Incomplete Combustion (PICs)?
- What about measurement data quality?
- Accepted emissions measurement methods for PFAS do NOT exist but are a core ORD research topic





ORD Emissions Methods Development Research

- Semivolatile/Nonvolatile:
 - Focusing on modified SW-846 Method 0010 (MM5) Train-based approaches that are amenable to performance-based measurements and suitable for nonpolar and polar PFAS compounds
 - Extra XAD-2 trap for breakthrough
 - Use of internal and pre-sampling surrogate standards (limited by availability of labeled standards)
 - Solvent extractions for polar and nonpolar compounds
 - Primary approach for targeted and non-targeted analyses
 - Isotope dilution for targeted analyses
 - High resolution mass spec nontargeted analyses
 - Looking at legacy PFAS to start, but also examining functional group properties for potential surrogates representative of multiple PFAS compounds



Modified MM5 Train

ORD Emissions Methods Development Research

- Volatiles:
 - Modified TO-15 for targeted and non-targeted compounds
 - Using SUMMA canisters
 - Limiting sample volume to avoid moisture condensation
 - Primarily non-polar, volatile compounds
 - GC/MS analysis for targeted and non-targeted compounds
 - TO-15 targets
 - Additional targeted compounds of interest:
 - Tetrafluoroethylene (TFE)
 - Hexafluoropropylene (HFP)
 - E1
 - E2
 - Non-targeted analyses
 - Sorbent traps (suitable for polars and non-polars)





Non-Targeted Analysis

- High resolution mass spectrometry
- Software calculates exact number and type of atoms needed to achieve measured mass, e.g. C₃HF₅O₃
- Software and fragmentation inform most likely structure
- With mass, formula, structure known, potential identities determined by database search









 Molecular Formula:
 C₃HF₅O₃

 Monoisotopic Mass:
 179.984585 Da

 [M-H]-:
 178.977308 Da



Innovative Measurements Research



Field Deployable, Time of Flight - Chemical Ionization Mass Spectrometer (ToF–CIMS)

- Real-time measurement of polyfluorinated carboxylic acids (PFAS) and fluorotelomer alcohols (FTOHs)
- Super sensitive (ppt measurement levels)
- Currently being evaluated as a process emissions analyzer

Surrogate measurements

- Total Organic Fluorine
 - o Combustion/Ion Chromatography?





18

C-F bond absorption in IR region?







The views expressed in this presentation are those of the author and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency. Any mention of trade names, products, or services does not imply an endorsement by the US Government or the United States Environmental Protection Agency. EPA does not endorse any commercial products, services, or enterprises.