PFAS Incineration: EPA Activities and Research

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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

**PFAS**
- **Non-polymers**
  - Perfluoroalkyl acids (PFAAs)
    - $C_nF_{2n+1}R$
  - Perfluoroalkane sulfonic acids (PFSAs)
    - $C_nF_{2n+1}SO_2F$
  - Perfluoroalkyl carboxylic acids (PFCAs)
  - Perfluoroalkyl phosphonic acids (PFPAs)
  - Perfluoroalkyl phosphinic acids (PFPIAs)

**Polymers**
- Fluoropolymers
  - Polytetrafluoroethylene (PTFE)
  - Polyvinylidene fluoride (PVDF)
  - Perfluoroalkoxy polymer (PFA)
  - Fluorinated ethylene propylene (FEP)
  - Others
- Side-chain fluorinated polymers
  - Fluorinated (meth)acrylate polymers
  - Fluorinated urethane polymers
  - Fluorinated oxetane polymers
- Perfluoropolyethers

**Per- and polyfluoroalkyl ethers (PFPEs)-based derivatives**
- Fluorotelomer iodides (FTIs)
  - $C_nF_{2n+1}CH_2CH_2I$
  - FT-based derivatives
  - $C_nF_{2n+1}CH_2CH_2-R, R = NH, NHCH_2CH_2OH, etc.$
  - Polyfluoroalkyl ether carboxylic acids
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 CF$_4$ requires 1,440 °C for greater than 1 second to achieve 99.99% destruction (Tsang et al., 1998)
  - Suggests that CF$_4$ 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-substances-pfas-incineration-manage-pfas-waste
ORD Incineration Research

- 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
ORD Incineration Research

- Examine minimum conditions (temperature, time, fuel H$_2$) for adequate PFAS destruction
- CF$_4$ 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 H$_2$) 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
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
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 non-polar 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
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. C$_3$HF$_5$O$_3$
- Software and fragmentation inform most likely structure
- With mass, formula, structure known, potential identities determined by database search

Source: Strynar et al. 2015; Sun et al. 2016
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
  - Combustion/Ion Chromatography?

C-F bond absorption in IR region?
Questions ...