USEPA PFAS THERMAL TREATMENT & METHODS RESEARCH – OPPORTUNITIES FOR COLLABORATIVE INCINERATION FIELD TESTING

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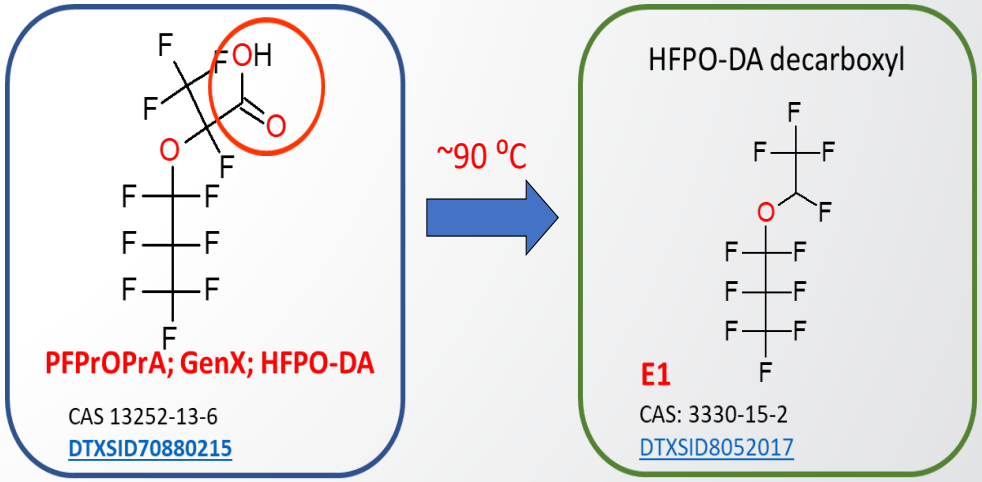
Thermal Treatment of PFAS

- Group of >4000 per- and poly-fluorinated organic compounds
  - PFAS often composed of non-polar fluorinated alkyl chain and polar functional group
  - Used by the military and industry and present in a large variety of consumer products
  - Valued for their hydrophobic and lipophobic properties, thermal and chemical stability
  - Present in many industrial and municipal waste streams including air, water and land discharges
- Highly electronegative fluorine makes C-F bonds particularly strong, require high temperatures for destruction
  - Unimolecular thermal destruction calculations suggest that CF_4 requires 1,440 °C for >1 second to achieve 99.99% destruction (Tsang et al., 1998)
  - Sufficient temperatures, times, and turbulence are required
- Functional group relatively easy to remove/oxidize
  - Low temperature decarboxylation as an example
  - Information regarding potential products of incomplete combustion (PICs) is lacking



Products of Incomplete Combustion (PICs)

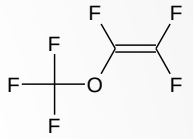
- When formed in flames, F radicals quickly terminate chain branching reactions to act as an extremely efficient flame retardant, inhibiting flame propagation
- PICs are more likely formed with F radicals than other halogens such as Cl
- PICs may be larger or smaller than the original fluorinated Principal Organic Hazardous Constituents (POHC) of concern
  - CF_2 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 destruction but unmeasured and unquantified PICs
- Very little information is published on PFAS destruction
  - Fluorine chemistry sufficiently different than Cl that we cannot extrapolate
  - Analytical methods and PFAS standards are lacking
  - Measurements focusing on POHC destruction may miss the formation of PICs
- Hazardous Waste Incinerators and cement kilns may well be effective, but what about Municipal Waste Combustors and Sewage Sludge Incinerators (lower temperatures)?

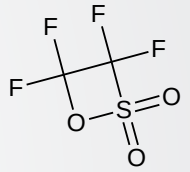
Incinerability & Mitigation Research

- Explore minimum conditions (temperature, time, fuel H_2) for adequate PFAS destruction
- Investigate 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
- Examine relative differences in the incinerability of fluorinated and corresponding chlorinated alkyl species
- Collaborative projects with DoD, universities and industry partners to explore fundamental science questions and evaluate existing technologies
  - Investigate and add PFAS to incinerability index
  - Compare experimental and modeling results for incineration of C1 and C2 fluorinated species
  - Thermal treatment system for PFAS contaminated soils in Alaska
  - Fate of PFAS during Granular Activated Carbon (GAC) reactivation from treatment systems

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 EPA ORD research topic

Near-Term Deliverables

- **Fundamental Understanding of Thermal Treatment**
  - List of Air Relevant PFAS Compounds
  - Data on TGA/MS thermal destruction temperature points with off gas measurements, on potential defluorination, and journal article on thermal destruction temperature points and defluorination derived from report data
  - PFAS Modeling: Report summarizing the feasibility and initial results of incorporating published C1 and C2 fluorocarbon kinetics into existing CFS model to predict simple PFAS behavior in incineration environments
  - Low Temperature Interactions of PFAS with Sorbents: Draft research paper describing results of experimental studies examining PFAS decomposition via heterogeneous reactions with calcium species at low temperature
  - Thermal Destruction of PFAS: Draft research paper describing results of experimental studies examining CF4 incineration in EPA's 65 kW Rainbow Combustor
- **Efficacy of thermal treatment for a variety of contaminated media**
  - Data on efficacy of lime kiln incineration of spent drinking water sorbent materials
- **Measurement methods for PFAS**
  - Quantitative Assessment of Modified Method 5 Train for Targeted PFAS
  - Draft Targeted PFAS Method (OTM 45) for State and source characterization use
  - Development of Total Organic Fluorine methods (e.g., water, air)
  - Non-targeted measurement approaches to identify PFAS compounds and support comprehensive source characterizations

Collaborative Field Opportunities

- EPA ORD is supporting OAQPS and OLEM to provide incineration guidance as part of the National Defense Authorization Act. They have established a list of incineration and thermal treatment sources whose timely field characterization would help inform this process and provide a fundamental opportunity to better understand PFAS thermal treatment behavior in sources of regulatory interest.
- ***Specifically, these tests would seek to:***
  - Investigate how well thermal disposal processes such as hazardous waste and solid waste incinerators work for PFAS waste.
  - What temperature, residence time or other conditions are required for PFAS destruction?
  - Are products of incomplete combustion (PICs) present in process emissions and, if so, do PICs include PFAS compounds and other toxic compounds?
  - Is there a minimum level of destruction of the PFAS compound in the feed (or an appropriate surrogate compound in the feed) that ensures problematic PIC formation can be assumed to be of limited concern?
  - Investigate whether surrogate Principal Organic Hazardous Constituents (e.g. CF4, C2F6) be used in emission tests to ensure PFAS compounds would be adequately destroyed. If so, what demonstrated Destruction and Removal Efficiency would be required?

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