Thermal Treatment of PFAS

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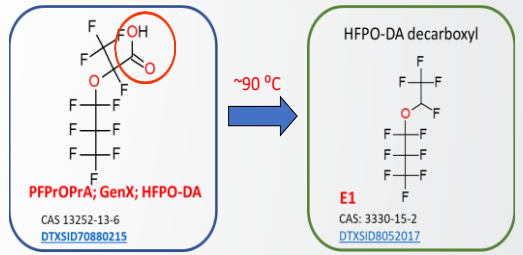
Goals

- Highly electronegative F makes C-F bonds particularly strong, requiring high temperatures for destruction
  - CF4 requires 1,440 °C for >1 sec to achieve 99.99% destruction (Tsang et al., 1998)
  - Information regarding potential products of incomplete combustion (PICs) is lacking
  - Desire to achieve full defluorination and fluorine mineralization (HF)

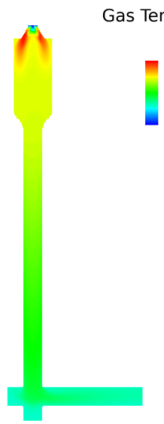
- This research is exploring minimum conditions (temperature, residence time, combustion parameters) necessary for adequate PFAS destruction
  - Different thermal destruction technologies exhibit a large range of temperatures
    - hazardous waste incinerators, municipal waste combustors, sewage sludge incinerators, etc.
  - Halogens inhibit flame propagation
  - PICs from F radicals more likely than for other halogens
    - Stability of CF2 and CF3 radicals suggest the possible reformation of PFAS species
  - Can FTIR detectable surrogate PFAS gases be used to determine destruction behavior of larger PFAS molecules

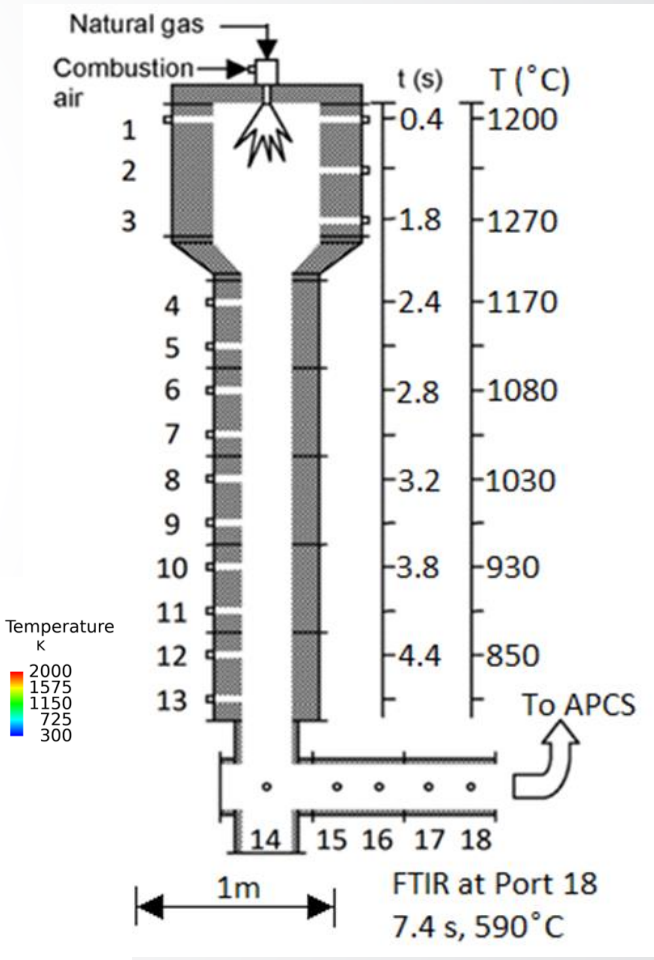


- Inform program offices about the adequacy of different thermal processes to adequately destroy PFAS wastes
  - EPA tasked with developing PFAS thermal treatment guidance (NDAA)
  - Develop a mechanistic understanding of PFAS behavior and help interpret results from full-scale field studies

Approach

- Inhouse experiments supported by fundamental modeling
  - Moderate temperature bench-scale experiments with Ca sorbents and Al catalysts
  - High temperature pilot-scale thermal destruction of C1 and C2 PFAS (gases)
  - High temperature thermal destruction of AFFF (liquids)
- Computational fluid dynamic (CFD) model
  - Developed for DoD for thermal destruction of chemical warfare agents
  - Modified by EPA/HSRP to include three commercial incinerator designs
  - Further modified to include NIST compiled C1-C3 fluorinated kinetics
  - Large molecule fluorine kinetics being developed by DoD (SERDP & DoD Labs) and EPA (NCSU)
- EPA Inhouse pilot-scale combustors include a refractory lined furnace (right) and a rotary kiln with afterburner.
  - Well characterized research combustors able to capture salient features of full-scale units
  - Serve as EPA accessible platforms to address research questions
  - Serve as sources to develop and test PFAS sampling and analytical techniques
- Support full-scale field efforts in a variety of thermal destruction systems





Current Status

- First moderate temperature thermal reaction (FTOHs w/ CaO) paper published - https://doi.org/10.1016/j.chemosphere.2021.129859
  - Fluorine reaction with CaO (forming CaF2) effectively destroyed FTOHs at moderate temperatures (400-900 °C) with non-detectable PICs
  - Encouraging results as a control technology or co-firing PFAS wastes in cement kilns
  - Al catalyst experiments initiated (w/ Guild Associates)
- First high temperature thermal destruction (C1 and C2 PFAS gases) paper submitted to JAWMA
  - CF4, CHF3, and C2F6 destruction efficiencies and PICs measured w/ FTIR
  - PFAS destruction and PIC formation characterized (w/ variable temperatures and residence times) and compared to kinetic model predictions
  - Different PFAS structures (C-H and C-C) examined
  - Surrogate gases amenable to real-time FTIR measurement (useful for field testing)
- High temperature experiments initiated with AFFF (3M Lightwater)
  - Legacy formulation of 3% PFAS in water including C8 PFOS
  - FTIR measurements to be augmented by OTM-45, SUMMA, and sorbent methods to characterize destruction and targeted and non-targeted fluorinated PICs
- C1-C3 fluorinated kinetics are being augmented with C4-C8 kinetics (DoD laboratories and NCSU)
  - Existing CFD combustion model includes three commercial incinerator designs and two pilot-scale units
  - Existing C1-C3 fluorinated kinetics (~1000 reactions) included
  - Expanding the kinetics to include larger PFAS compounds
  - Goal to independently predict PFAS destruction (and PIC formation) in practical full-scale incineration systems

Contributors

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