United States Environmental Protection Agency

Session 4: PFAS Disposal and Destruction Research

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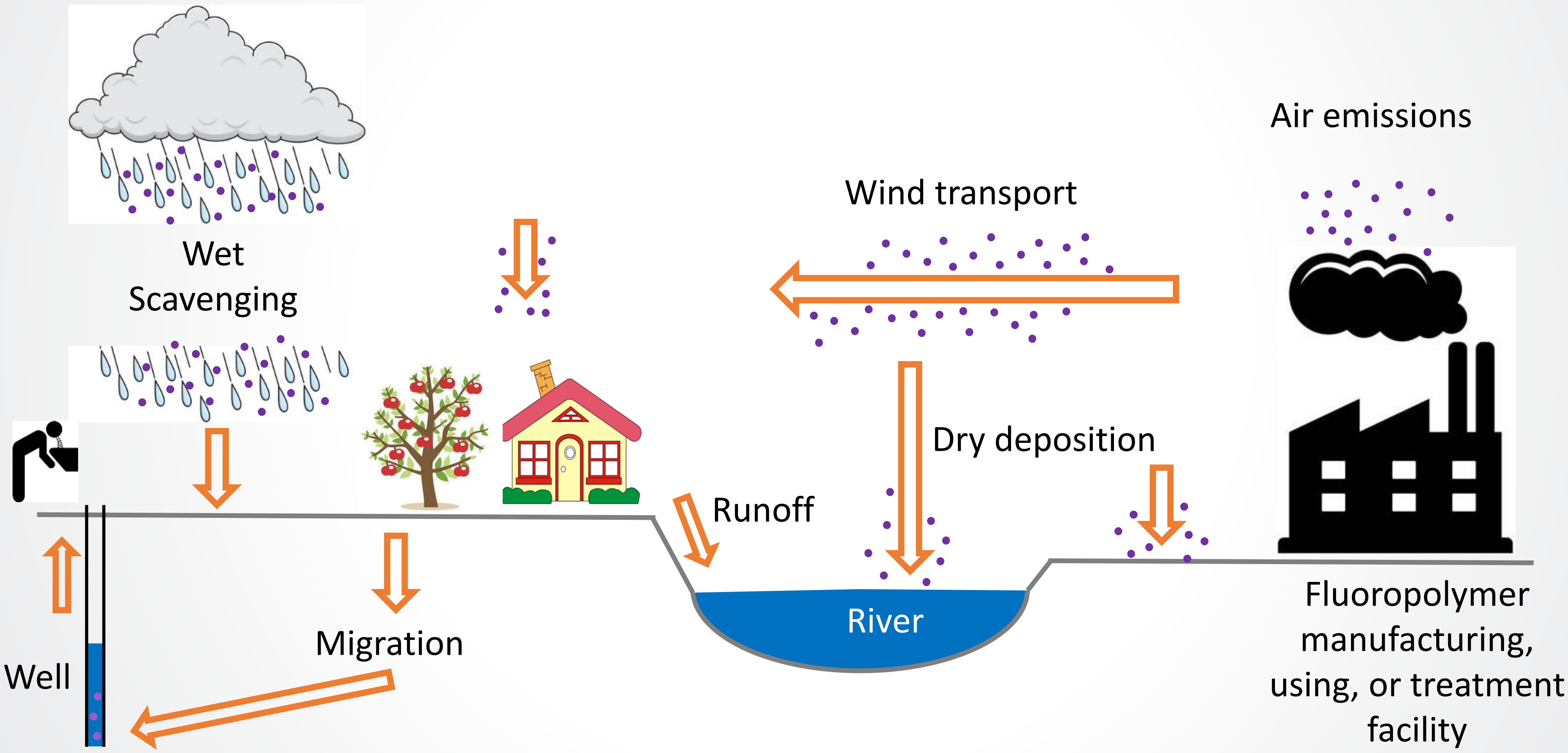
PFAS Science Webinars for Region 1 and New England States & Tribes

September 23, 2020

Potential Sources of PFAS in the Environment

- Direct release of PFAS or PFAS products into the environment
  - Use of aqueous film forming foam (AFFF) in training and emergency response
  - Industrial facilities
  - Incineration/thermal treatment facilities
- Landfills and leachates from disposal of consumer and industrial products containing PFAS
- Wastewater treatment effluent and land application of biosolids

Air Emissions Contribute to PFAS Concentrations



Adapted from:
Davis, K. et al. Chemosphere, 2007.

Thousands of chemicals can potentially become air sources during production, use and disposal of PFAS-contaminated materials

PFAS

- **Non-polymers**
  - **Perfluoroalkyl acids (PFAAs)**
    $C_nF_{2n+1}R$
    - Perfluoroalkyl carboxylic acids (PFCAs)
    - Perfluoroalkane sulfonic acids (PFSAs)
    - Perfluoroalkyl phosphonic acids (PFPAs)
    - Perfluoroalkyl phosphinic acids (PFPIAs)
  - **Perfluoroalkane sulfonyl fluoride (PASF)**
    $C_nF_{2n+1}SO_2F$
    → **PASF-based derivatives**
    $C_nF_{2n+1}SO_2$-R, R = NH, $NHCH_2CH_2OH$, etc.
  - **Perfluoroalkyl iodides (PFAIs)**
    $C_nF_{2n+1}I$
    → **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.
  - **Per- and polyfluoroalkyl ethers (PFPEs)-based derivatives**
    - Polyfluoroalkyl ether carboxylic acids
- **Polymers**
  - **Fluoropolymers**
    - Polytetrafluoroethylene (PTFE)
    - Polyvinylidene fluoride (PVDF)
    - Fluorinated ethylene propylene (FEP)
    - Perfluoroalkoxyl polymer (PFA)
    - Others
  - **Side-chain fluorinated polymers**
    - Fluorinated (meth)acrylate polymers
    - Fluorinated urethane polymers
    - Fluorinated oxetane polymers
  - **Perfluoropolyethers**

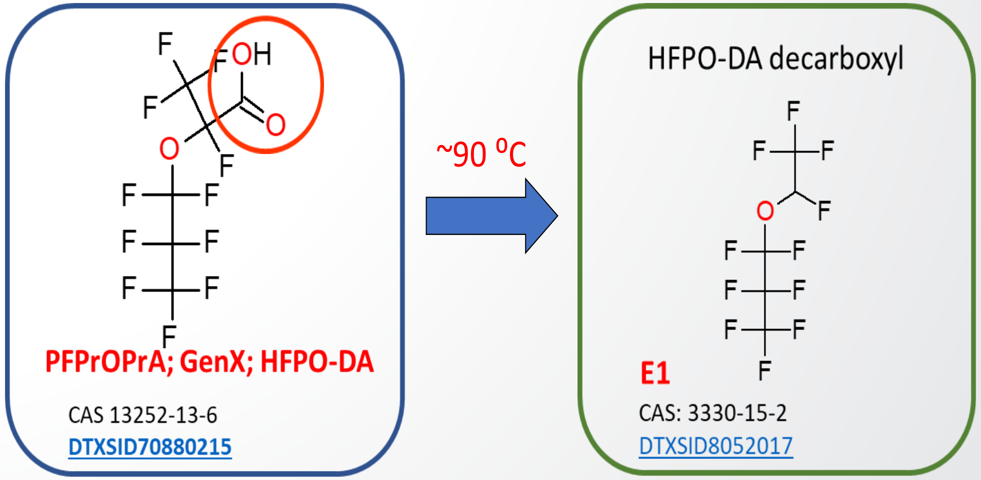
EPA PFAS Air-Related Research

- **Analytical Methods** to detect, identify and quantify PFAS in emissions and ambient air
- **Dispersion Modeling** to predict air transport and deposition associated with air sources
- **Effectiveness of Thermal Treatments** for destroying PFAS materials

Thermal Treatment of PFAS

- Highly electronegative fluorine (F) makes carbon/fluorine (C-F) bonds particularly strong, require high temperatures for destruction
  - Unimolecular thermal destruction calculations suggest that CF_4 requires 1,440 ^{o}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 is an example
  - Information regarding potential products of incomplete combustion (PICs) is lacking



Products of Incomplete Combustion (PICs)

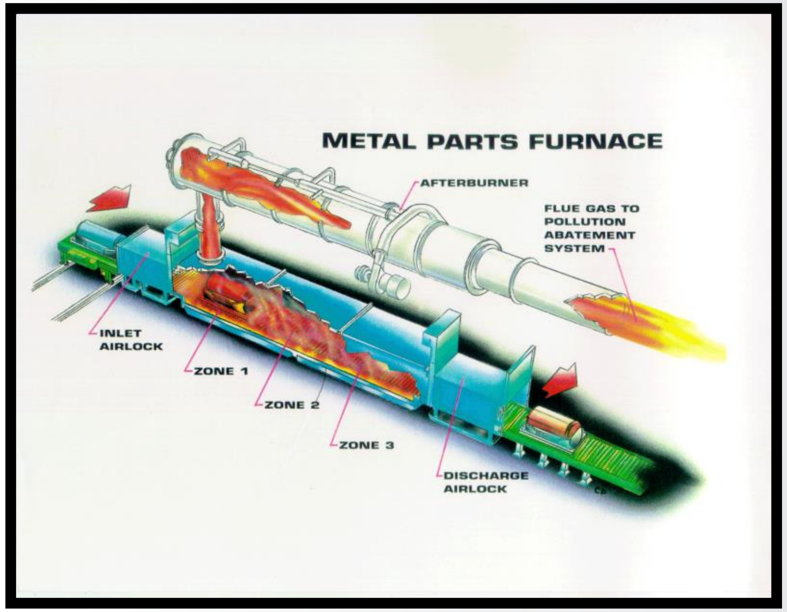
- When formed in flames, F radicals quickly terminate chain branching reactions to act as an extremely efficient flame retardant, inhibiting flame propagation
- PICs are more likely formed with F radicals than other halogens such as chlorine (Cl)
- PICs may be larger or smaller than the original fluorinated 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 minimal with more needed
  - 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 (i.e., lower temperatures)?

Incinerability & Mitigation Research

- Explore minimum conditions (temperature, time, fuel H_2 or hydrogen gas) 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 well studied corresponding chlorinated alkyl species

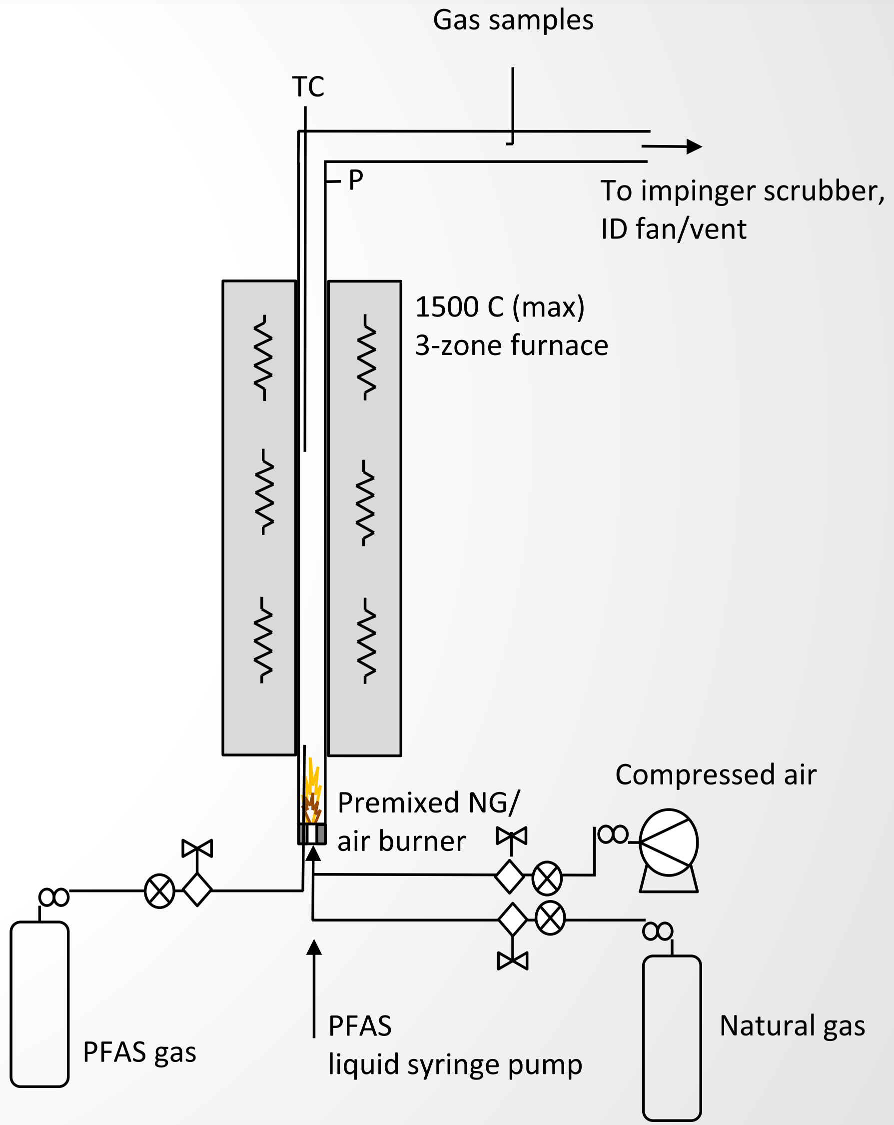
CFS Software for EPA
Reaction Engineering International (REI)

- The **Configured Fireside Simulator (CFS)**
  - Developed for the Department of Defense to evaluate operations of the chemical demilitarization incinerators processing the US chemical warfare agent stockpile
- Destruction kinetics developed
- Adapted to provide for the ability to run "what if" scenarios of waste streams contaminated with chemical and biological warfare agents
  - EPA's pilot-scale Rotary Kiln Incinerator Simulator (RKIS)
  - Three commercial incinerators based on design criteria for actual operating facilities
    - Medical/Pathological Waste Incinerator
    - Hazardous Waste Burning Rotary Kiln
    - Waste-to-Energy Stoker type combustor
- CFS uses chemical kinetic data for destruction derived from bench- and pilot-scale experiments at EPA's Research Triangle Park, NC facility



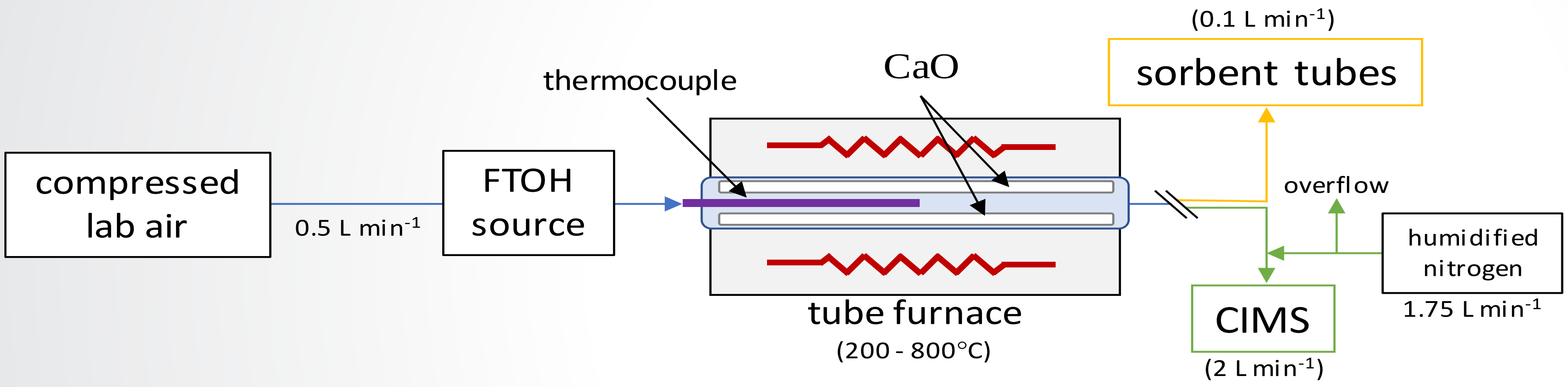
Bench-scale Incineration Experiments

- Repurpose existing equipment (i.e., 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
- Platform for measurement methods development (e.g., SUMMA, sorbent, total F, Gas Chromatography – Electron Capture Detector (GC/ECD), real-time instruments)

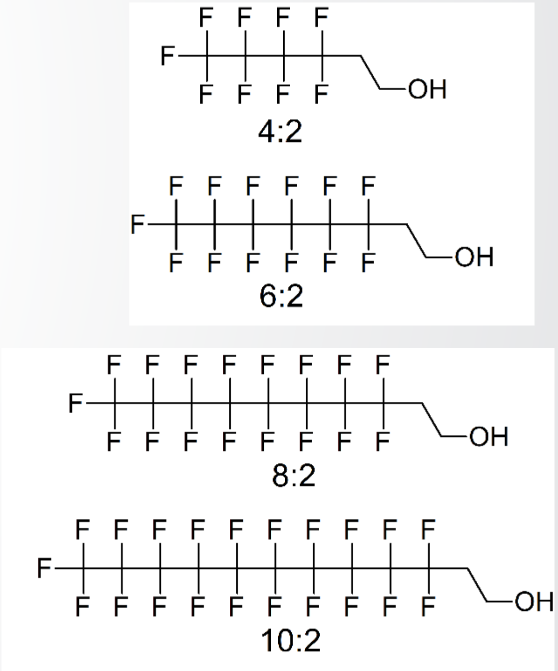


Tube Furnace Experiments

Experimental Setup



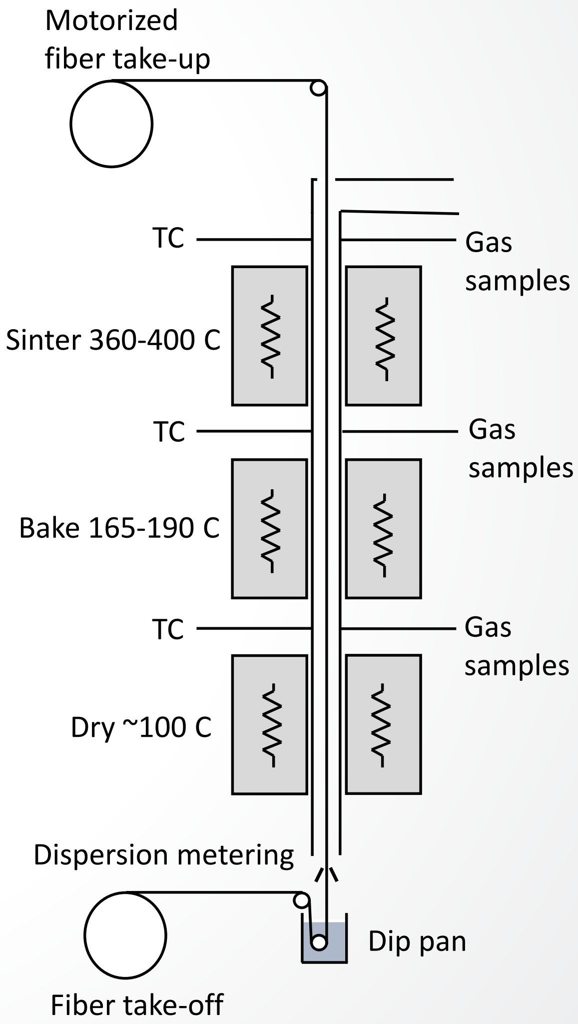
PFAS Fluorotelomer Alcohols Tested:

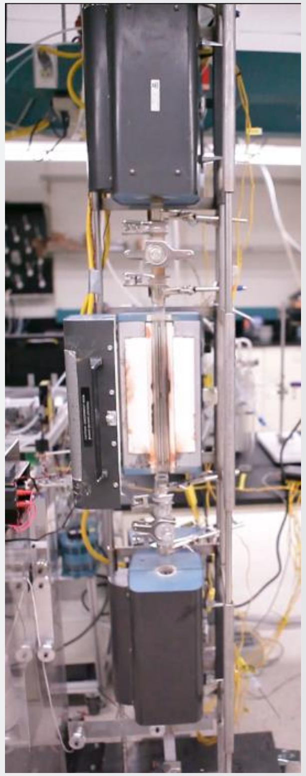


- Thermal treatment with calcium oxide (CaO) from 250 to 800 °C
- Observe destruction of parent compound using two techniques: CIMS and sorbent tube analysis by thermal desorption–gas chromatography–mass spectrometry (TD-GC/MS)
- TD-GC/MS analyses show the presence of degradation products from fluorotelomer alcohols (FTOH) destruction

String Reactor Experiments

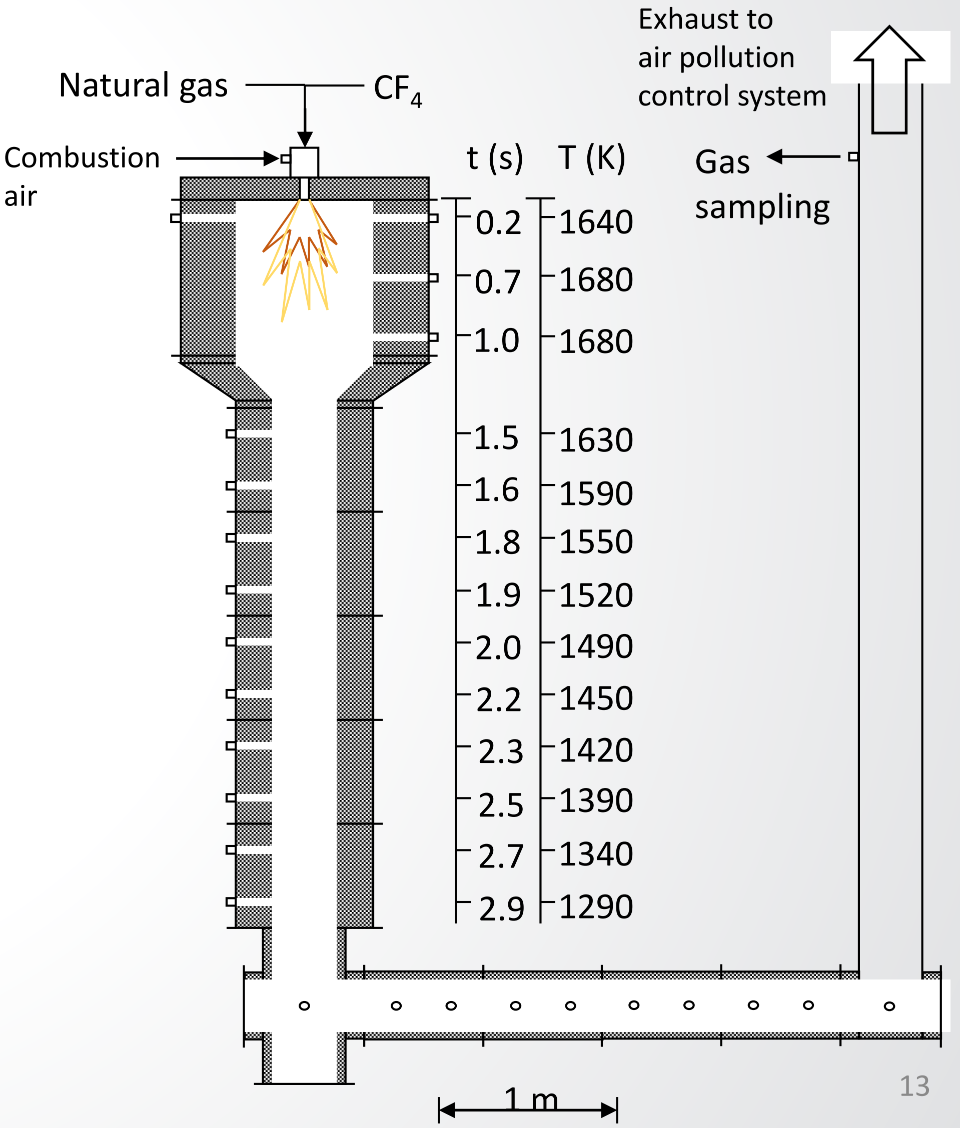
- **New experiment that simulates industrial PFAS coating facilities**
  - Built from 3 existing furnaces
  - Applies commercial dispersions to fiber (string)
  - Full control of flows, times, temperatures, application rates
  - Small scale (L/min & g/min)
  - Located in lab w/ real-time instruments
- **Investigates key research questions:**
  - What PFAS & additives are present in different commercial dispersions?
  - What PFAS (and other species) are vaporized during application processes?
  - How do vapor phase PFAS emissions compare to dispersion compositions?
    - Are surfactants (GenX, telomer alcohols) included in the vapor emissions?
  - Are processing temperatures sufficient to transform PFAS?
    - Cleave functional groups to produce new PFAS?
    - Are processing temperatures sufficient to cleave C-F bonds and produce fluorine (F2) and hydrogen fluoride (HF)?
  - How do processing temperatures and times affect vapor and aerosol emissions (mass and composition)?





Pilot-scale Incineration Experiments

- 65 kW refractory lined furnace (aka Rainbow Furnace) with peak temperatures at ~1400 ºC, and >1000 ºC for ~3 sec
- Combustor connected to facility air pollution controls
  - Afterburner, baghouse, NaOH (sodium hydroxide) scrubber
- Introduce C1 and C2 fluorinated compounds with fuel, air, post flame to measure POHC destruction and PIC formation
  - FTIR (Fourier-transform infrared spectroscopy) and other real-time and extractive methods
- Add modeling component using REI's Configured Fireside Simulator (CFS) CFD/kinetic model to include C1 & C2
  - F chemistry from literature (Burgess et al. [1996])



PFAS Innovative Treatment Team (PITT)

- Full-time team that brings together a multi-disciplined research staff
- Charge: How to remove, destroy and test PFAS-contaminated media and waste
- 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
- Expected Results: States, tribes and local governments will be able to select the approach that best fits their needs, leading to greater confidence in cleanup operations and safer communities
- Deadline: Later this year

Non-Incineration Technologies Reviewed

- Chemical
- Biological
- Plasma
- Mechanochemical
- Sonolysis
- Ebeam
- UV
- Supercritical water oxidation
- Deep well injection
- Sorption/stabilization
- Electrochemical
- Landfill
- Land application

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

Innovative technologies selected for further investigation.

Planned Products

- **ORD Products on Fundamental Understanding of Thermal Treatment**
  - Thermogravimetric Analysis/Mass Spectrometry (TGA/MS)Thermal Destruction Temperature Points with Off Gas Measurements on Potential Defluorination
  - PFAS Model Incorporation of Published C1 and C2 Fluorocarbon Kinetics to Predict Simple PFAS Behavior in Incineration Environments
  - Low Temperature Interactions of PFAS with Sorbents from Bench-Scale Experiments
  - Thermal Destruction of PFAS from Pilot-Scale Experiments

- **ORD Measurement Methods for PFAS**
  - Quantitative Assessment of Modified Method 5 Train for Targeted PFAS
  - PFAS Method OTM 45
  - Total Organic Fluorine Methods
  - Non-targeted Measurement Approaches to Identify PFAS

- **Other Contributions**
  - Supporting Incineration Guidance as part of the National Defense Authorization Act

For More Information

- The research discussed in this presentation is part of EPA's overall efforts to rapidly expand the scientific foundation for understanding and managing risk from PFAS.

- For more information on EPA's efforts to address PFAS, please visit the following websites
  - EPA PFAS Action Plan – https://www.epa.gov/pfas/epas-pfas-action-plan
  - EPA PFAS Research – https://www.epa.gov/chemical-research/research-and-polyfluoroalkyl-substances-pfas

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