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STAR and STARx – A Smouldering Solution to PFAS from Laboratory to Field Scale Applications

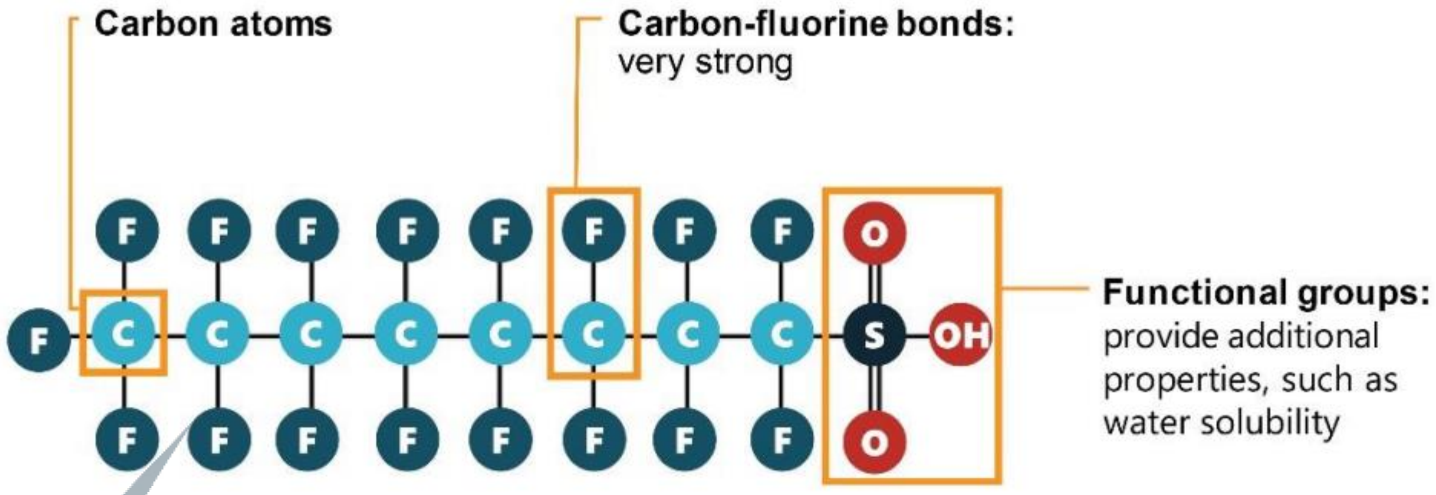
Presented by: Laura Kinsman, M.E.Sc.

Overview

- **Challenges for PFAS Remediation**
- **Smouldering Combustion Basics**
- **PFAS Smouldering**
  - **Ex Situ**
    - SERDP Project (Laboratory and Field Pilot Test)
    - US Air Force Project (Field Pilot Test)
  - **In Situ**
    - US Air Force Project (Field Pilot Test)
- **Summary**

Chemical and thermal stability

$$PFAS \xrightarrow{HEAT} HF + shorter\ chain\ compounds$$



(AAAS, 2021)

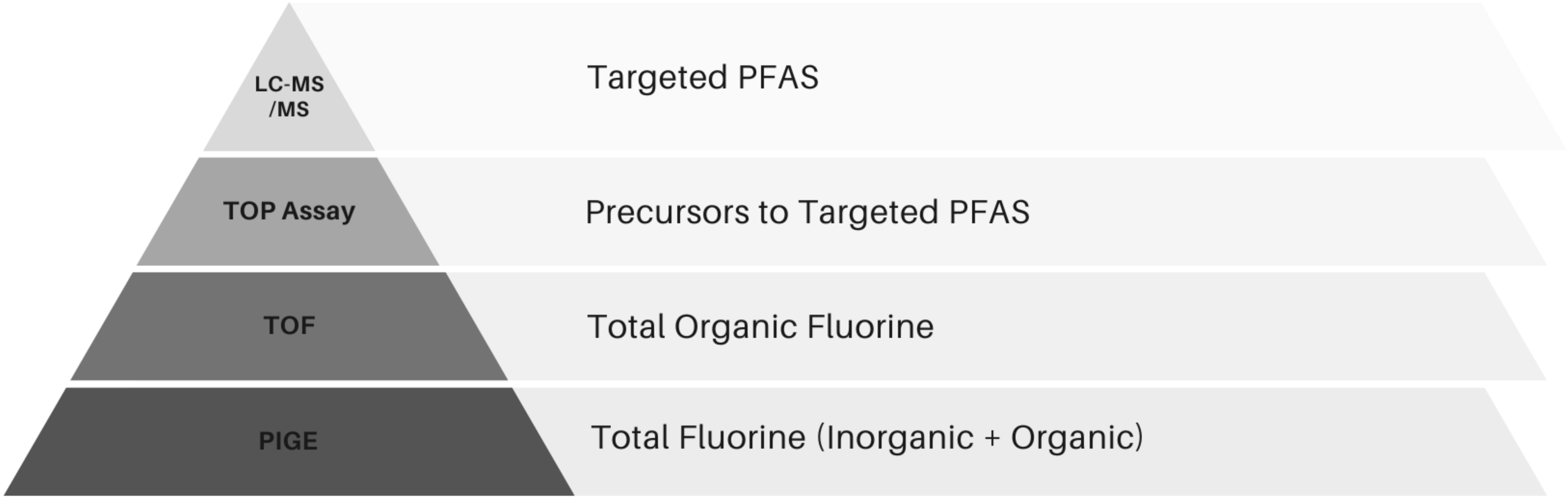
Mineralization

- Increases with Temp > 700°C
- Maximizes at Temp > 900°C

Vecitis et al., 2009; Wang et al., 2011; Watanabe et al., 2015; Yamada et al., 2005

Challenges for PFAS Remediation

Methods for quantifying PFAS



Smouldering Combustion

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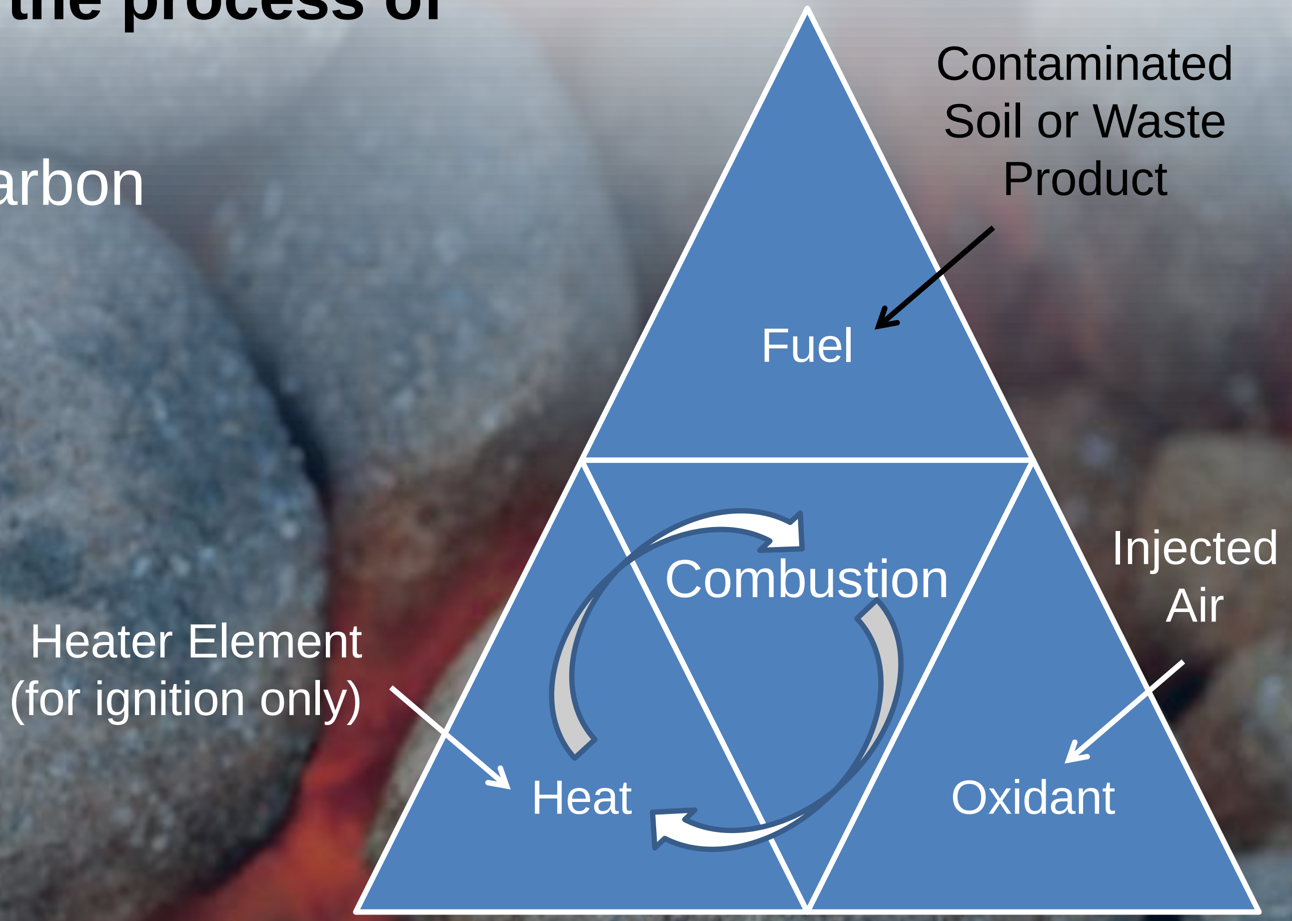
Smoldering Combustion

STAR and STARx are based on the process of smoldering combustion:

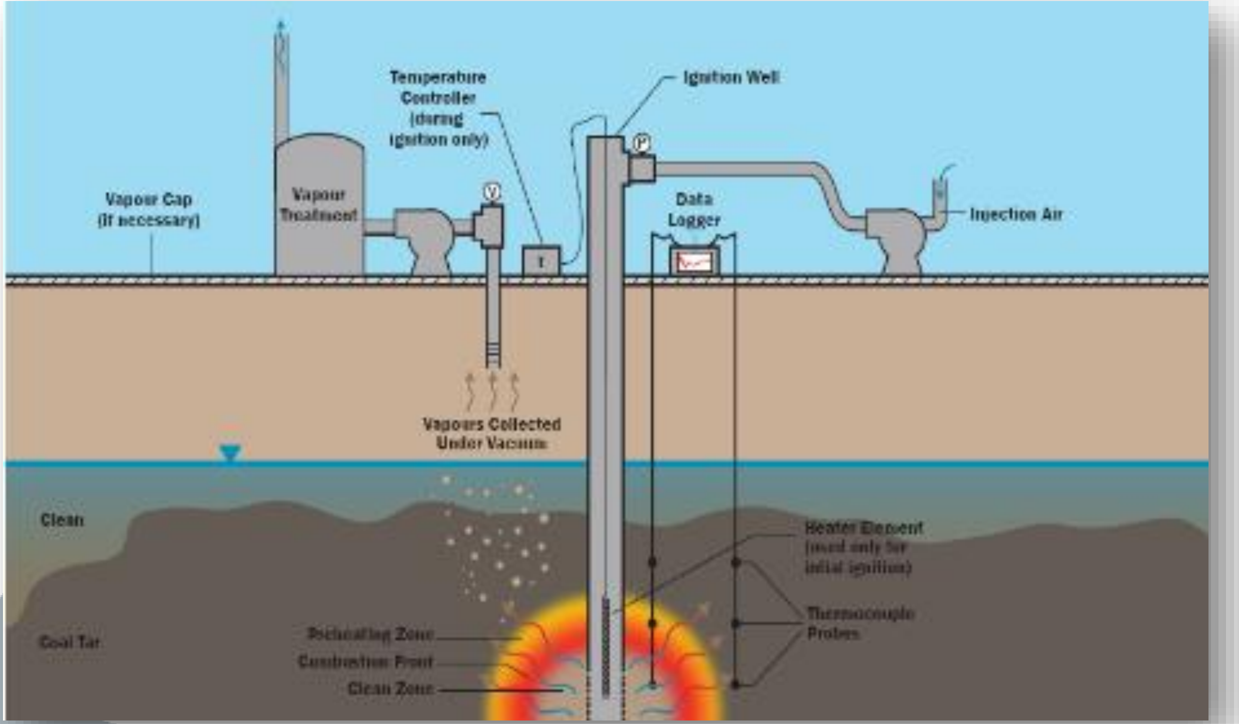
Exothermic reaction converting carbon compounds to CO_2 + H_2O

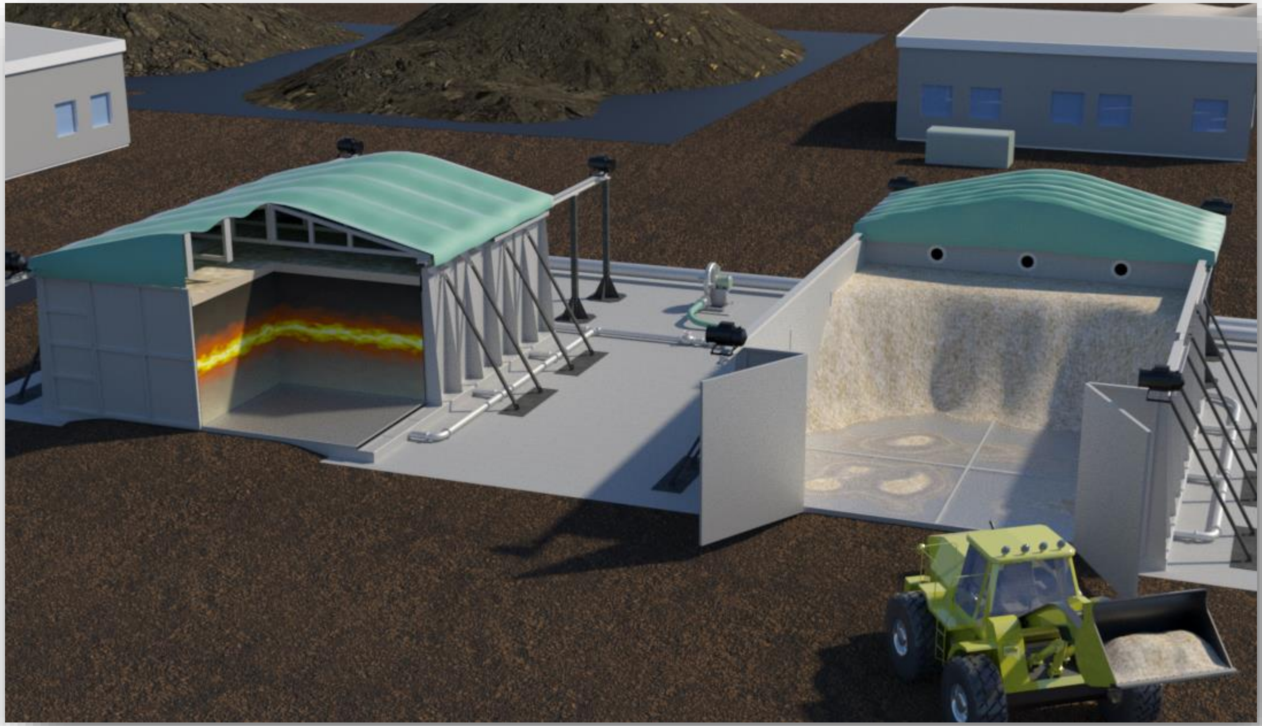


STAR / STARx is a flameless combustion process: only smoldering is possible within a porous matrix (i.e., soil)

Application Methods

- **In situ (vadose zone & below water table)**
  - Applied via ignition points & portable heaters
- **Ex situ (above ground)**
  - Soil piles placed on Hottpad™ system





Ex Situ PFAS Smouldering – SERDP Project

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$$PFAS \xrightarrow{HEAT} HF + shorter\ chain\ compounds$$

Mineralization

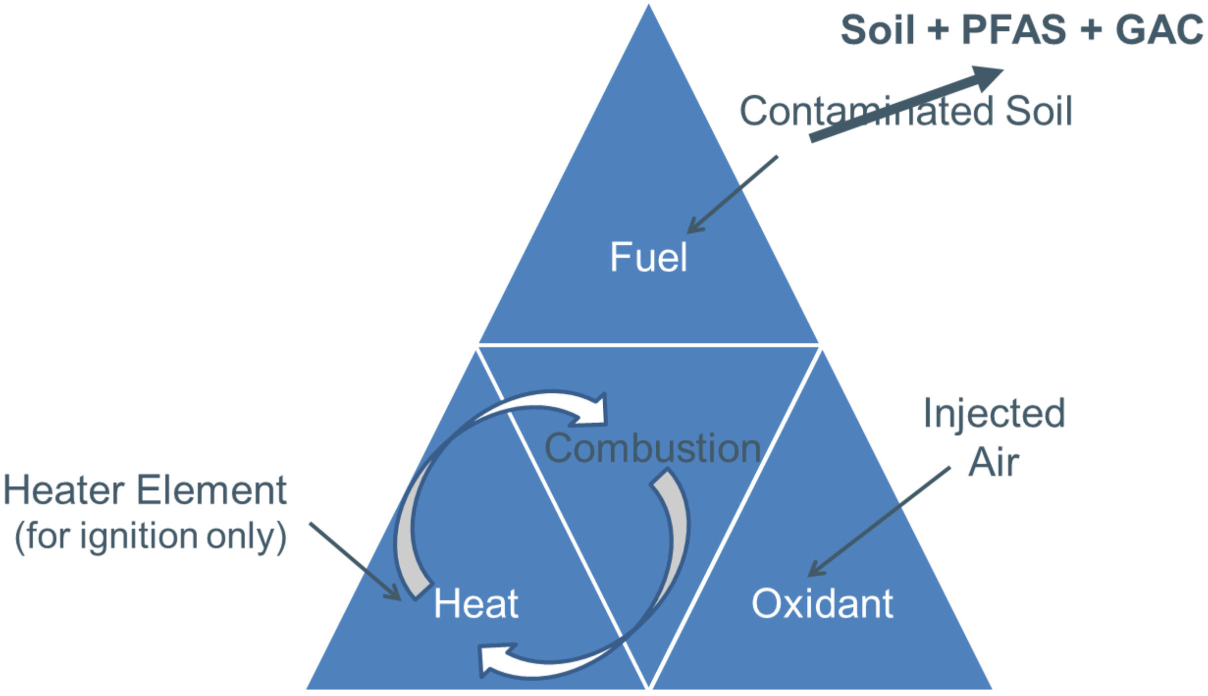
- Increases with Temp > 700°C
- Maximizes at Temp > 900°C

But PFAS not a smoulderable fuel

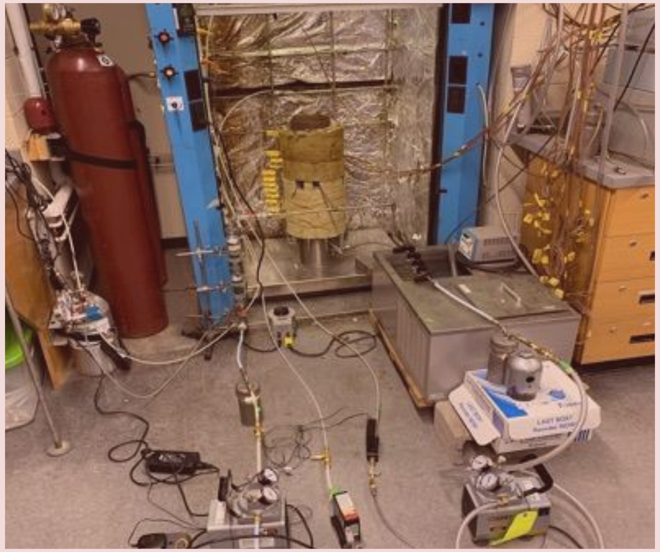
- Requires a surrogate fuel

What About Spent GAC?

- A potential waste product that contains PFAS



Vecitis et al., 2009; Wang et al., 2011; Watanabe et al., 2015; Yamada et al., 2005



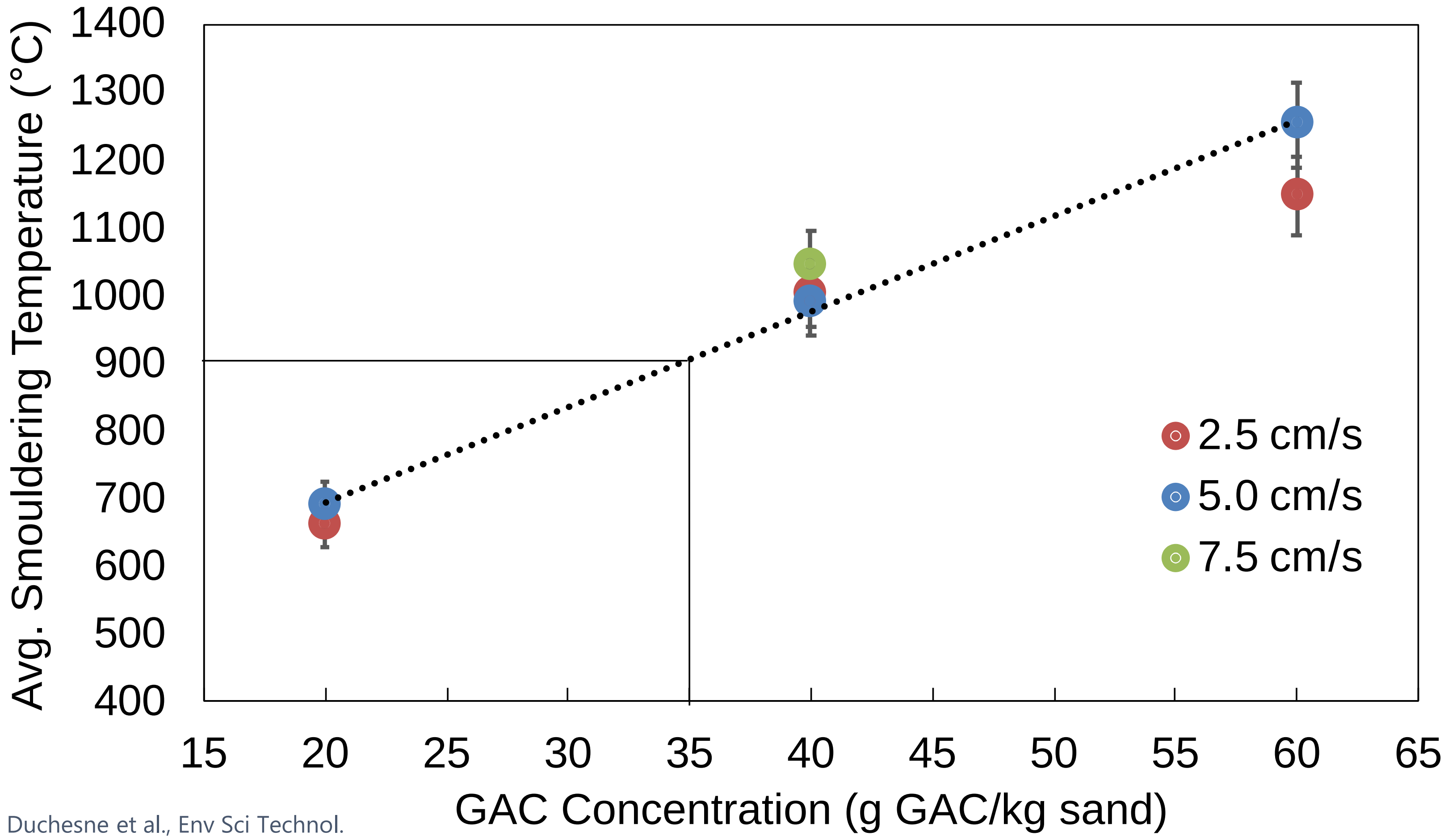
Phase 1:
Lab Column Tests

- Fluorine Mass Balance
- CaO Optimization

Phase 2:
Pilot Scale Tests

- Heterogeneity
- Field Deployable

GAC concentration can be selected to target a specific temperature to maximize complete PFAS destruction



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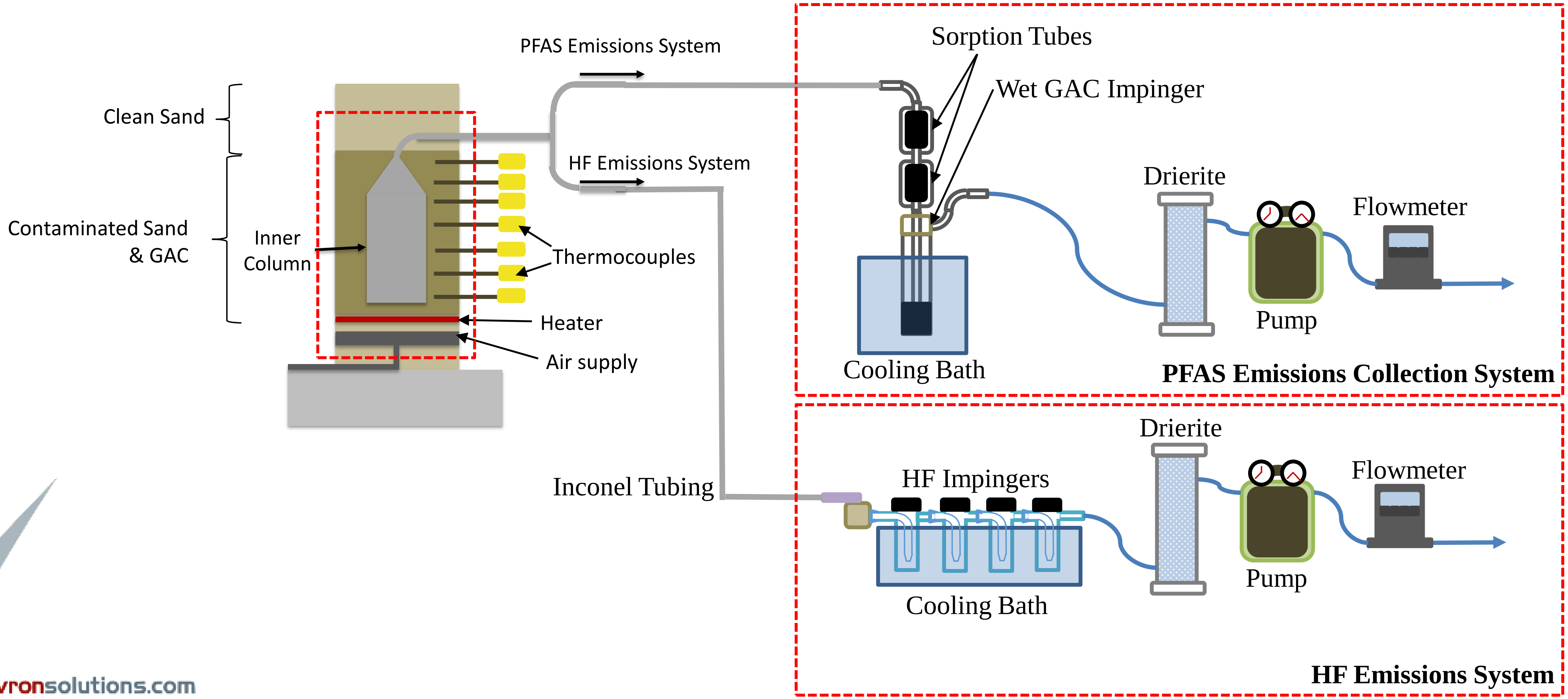
dx.doi.org/10.1021/acs.est.0c03058

Novel experimental design employed for detailed emissions analysis



Phase 1 – CaO Amendment Optimization

Incorporate calcium oxide to improve PFAS destruction and minimize byproducts in emissions

$$PFAS \xrightarrow{HEAT} HF + shorter\ chain\ compounds$$

$$PFAS + CaO \xrightarrow{HEAT} CaF_2 + \downarrow HF + \downarrow shorter\ chain\ compounds$$

(Wang et al., 2011, 2013, 2015)

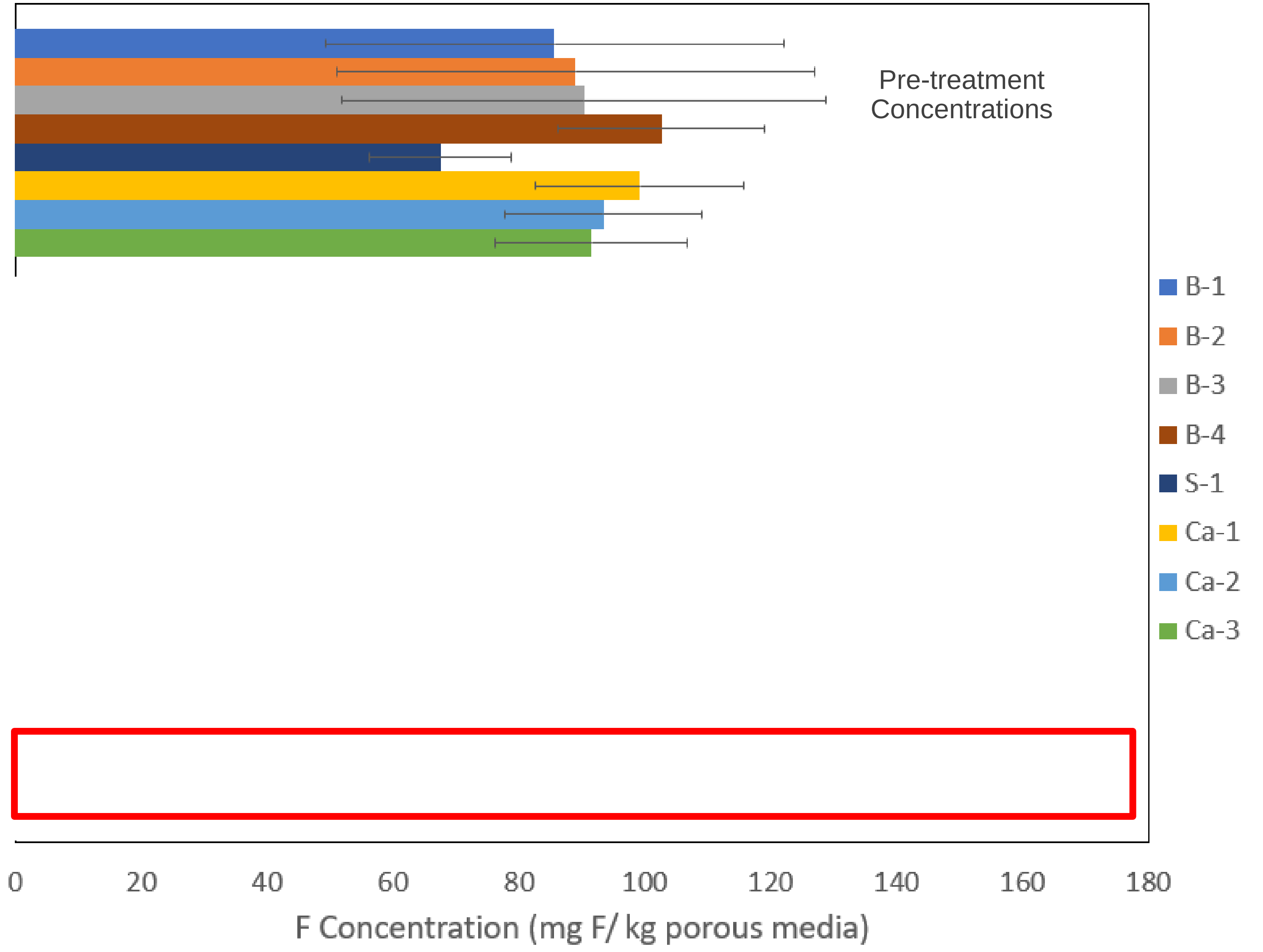
Phase 1 – Lab Column Tests

- **8 column tests utilizing PFOS-spiked GAC in Sand (or Sand + CaO)**
- **Self-sustaining smouldering achieved in all experiments**

Test No.	GAC Concentration (mg GAC/kg sand)	Air Flux (cm/s)	CaO Concentration (g CaO/kg sand)	Average Peak Temperature (˚C)	Smoldering Velocity (cm/min)	
B-1	50.0	2.5	-	940 ± 51	0.33 ± 0.04	Base Cases
B-2	50.0	2.5	-	887 ± 22	0.40 ± 0.04	Base Cases
B-3	50.0	2.5	-	908 ± 34	0.37 ± 0.10	Base Cases
B-4	50.0	2.5	-	834 ± 35*	0.37 ± 0.04	Base Cases
S-1	50.0	2.5	-	935 ± 51	0.37 ± 0.20	Steam Injection
Ca-1	50.0	2.5	50	795 ± 37	0.31 ± 0.08	Calcium Oxide
Ca-2	50.0	2.5	20	869 ± 16	0.36 ± 0.07	Calcium Oxide
Ca-3	50.0	2.5	10	900 ± 62	0.36 ± 0.03	Calcium Oxide

*Lower temperatures in B-4 likely due to deteriorating column insulation

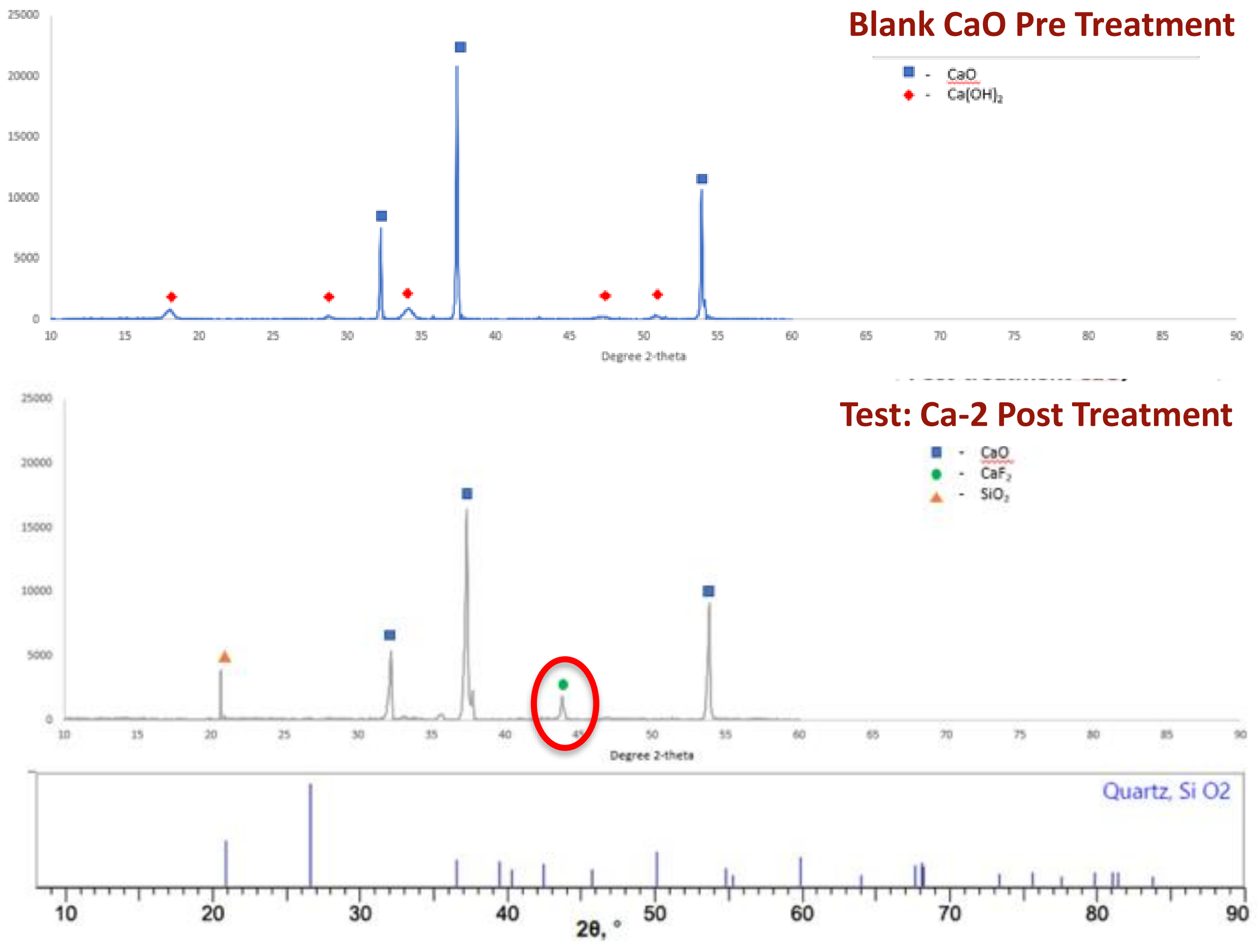
Phase 1 – Lab Column Results



Key Takeaways

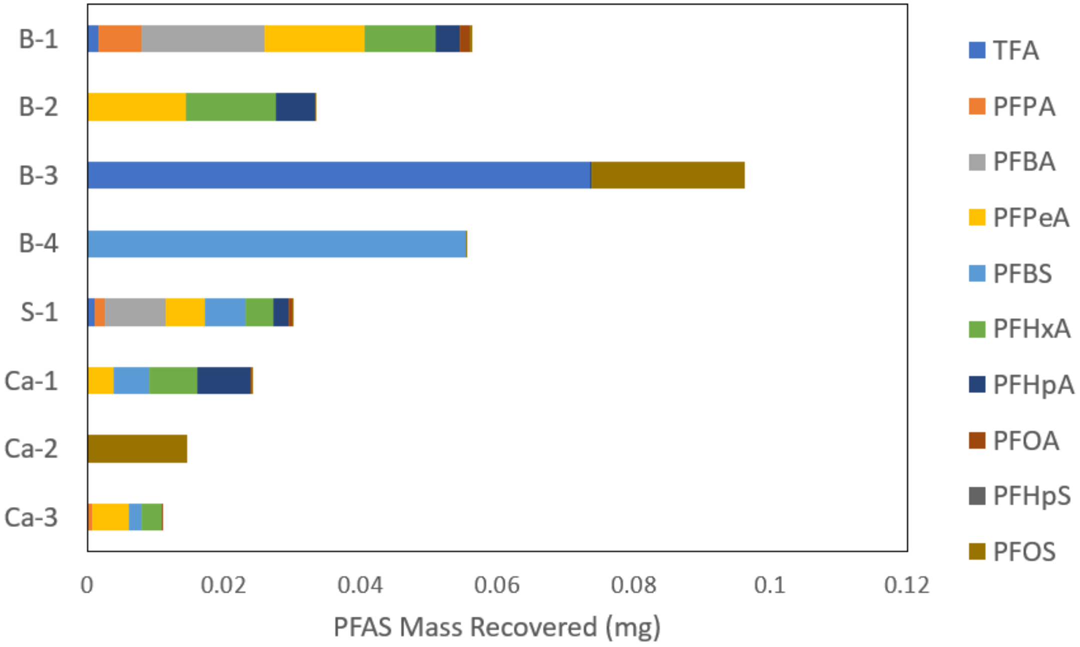
- Targeted PFAS Analytes: >99.9% reduction in detectable PFAS in all instances
- PIGE Spectroscopy
  - 95.6 - >99.9% reduction in instances without CaO amendments
  - No significant change in total F concentration where CaO amendments were employed

XRD Analysis – Tracking CaO Transformation to CaF_2



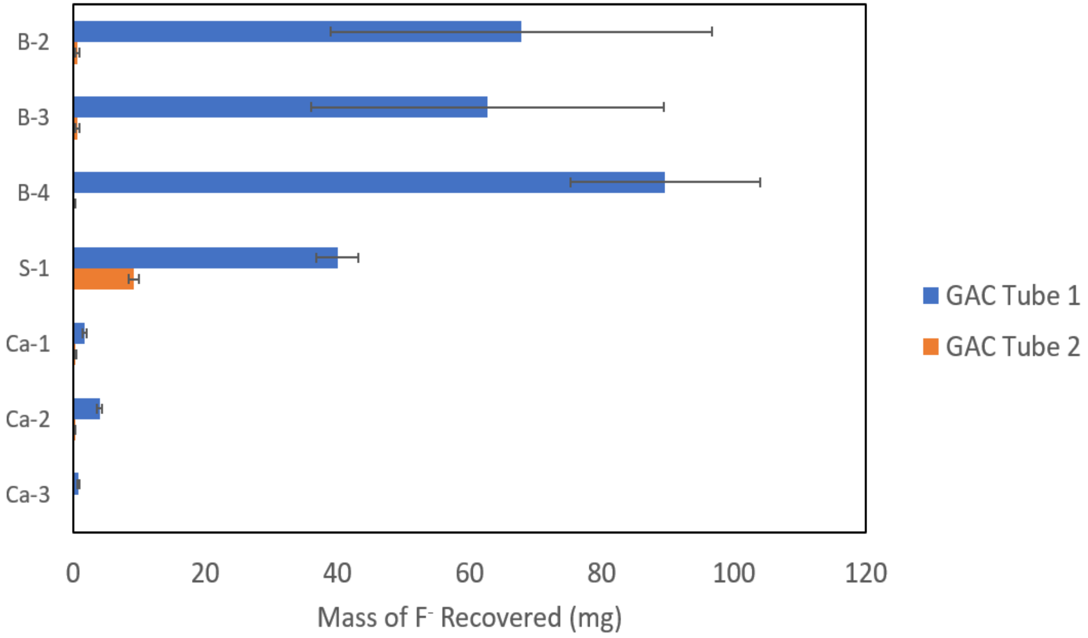
Phase 1 – Lab Column Emission Results

Targeted PFAS



- Little PFAS detected in GAC sorption tubes
  - <0.02 – 0.13% of initial F mass in column

Total F Recovery

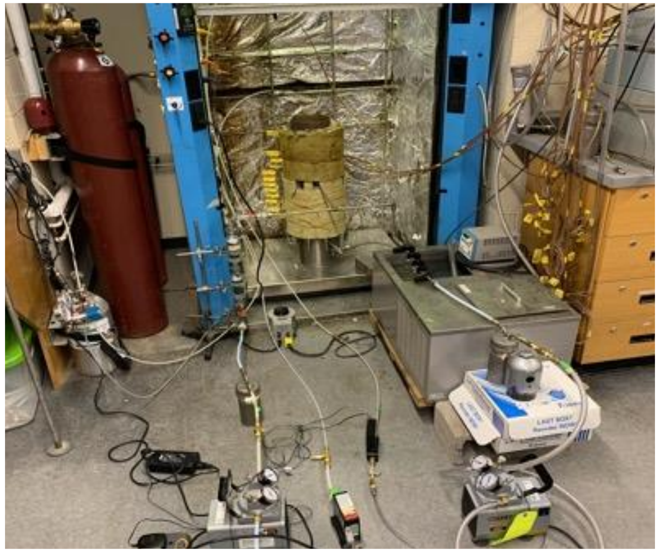


- CaO soil amendment had lower F mass on emissions treatment GAC
  - Consistent with less HF and shorter chain compounds produced

*Emissions train adsorbents for B-1 was not analyzed using PIGE

Key Takeaways

- GAC can be used to achieve high temperatures required for PFAS destruction
- $PFAS_{13}$ reduced to below detection limits in soils
- <1% of $PFAS_{13}$ found in the emissions
- CaO can be used to enhance destruction and reduce formation of HF (converted to CaF_2)
- PIGE data used to obtain >80% mass balance



Phase 1:

Lab Column Tests

- Fluorine Mass Balance
- CaO Optimization

Phase 2:

Pilot Scale Tests

- Heterogeneity
- Field Deployable

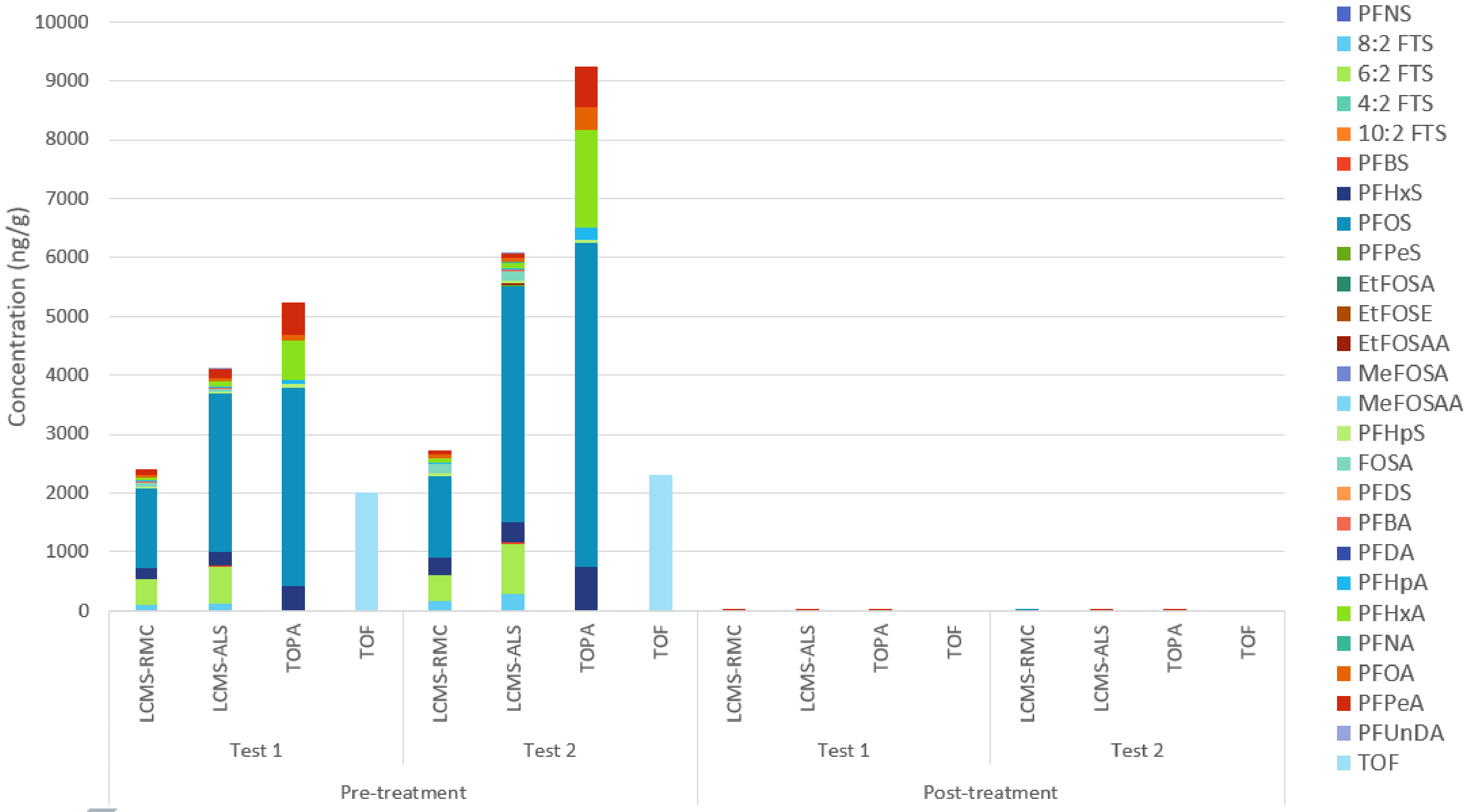
Phase 2 – Pilot Test

- Project Site: CFB Trenton
- Equipment: 10 m^3 Pilot Scale Hottpad™
- Feedstock: PFAS Contaminated Site Soils (20 m^3 total)

Phase 2 – Mixing / Loading

Phase 2 – Unloading

Phase 2 – Pilot Test Results



Soil Results

- PFAS reduced to near or below detection limits
- PIGE confirmed fluorine retained in post-treatment soil
- XRD confirmed fluorine sequestered in soil as CaF_2

Emissions Results

- <0.1% of total fluorine emitted as PFAS
- <4% of total fluorine emitted as HF
- Fluorinated breakdown products can be captured via vapour-phase GAC

Environmental Restoration
Demonstration of Smoldering Combustion Treatment of PFAS-impacted Investigation-Derived Waste

Ex Situ PFAS Smouldering – US Air Force Project

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STARx US Air Force Project

Phase 1: Laboratory Study

- Assess if IX resins and low-cost carbon sources (e.g., anthracite) can serve as a surrogate fuel to support smoldering combustion

Phase 2: Field Demonstration

- Generate performance data on smoldering treatment of PFAS and other co-contaminants in soils and spent GAC
- Assess the impact of soil type, moisture content, and PFAS concentrations on treatment effectiveness
- (10) 10 m^3 batches planned
- Scheduled for Summer 2023

In Situ PFAS Smouldering – ESTCP Project

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STAR ESTCP Project

ESTCP – Location TBD

- STAR (In-Situ) pilot test at DoD Site
- Demonstrate destruction of PFAS and co-contaminants from source area
- 10 m x 10 m x 8 m (800 m^3)
- Four ignition points
- In-situ soil mixing (GAC and CaO) or carbon injection planned
- Lab scale carbon injection completed and published (Wilton et al.)
- Site selection underway
- Field work expected in 2024

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RESEARCH ARTICLE

WILEY

Carbon injection to support in-situ smoldering remediation

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are a group of anthropogenic contaminants that are receiving increasing concern due to their associated negative health effects. The properties of PFAS result in their persistence and stability, which present challenges for remediation. Activated carbon is currently the most widely used method for PFAS treatment since carbon microparticle injection can be used for in-situ treatment; however, this method does not result in PFAS destruction. Thermal treatment is a promising posttreatment method that can be used with activated carbon as long as sufficient PFAS-destroying temperatures are achieved (>900°C). A promising in-situ thermal treatment technology is Self-Sustaining Treatment for Active Remediation (STAR), which uses smoldering combustion to destroy organic contaminants embedded within a porous matrix. This study investigates carbon injection to support STAR for the treatment of PFAS. Four solutions were used (1) 17% colloidal activated carbon (CAC); (2) 23% CAC; (3) 17% powdered activated carbon (PAC); and, (4) 23% PAC. Smoldering temperatures greater than the required PFAS destruction temperature were reached if 50 g carbon/kg sand was achieved for injection and soil-mixing delivery methods. Moreover, emulsified vegetable oil (EVO) was a successful secondary surrogate fuel to enhance smoldering temperatures when supplied at a quantity less than or equal to carbon microparticles. These findings present the necessary intermediate

Summary

- **STARx demonstrated successful destruction of PFAS (converted to HF or inert CaF_2)**
  - PFAS in post treatment soils reduced to below regulatory criteria
  - <1% of of total fluorine emitted as PFAS
  - CaO enhances PFAS destruction at lower temperatures, reduces HF in emissions
- **Co-treatment of contaminated GAC (and/or IX resin) and soils increase net treatment**
- **Further STAR & STARx field testing scheduled for 2023/2024**

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Questions?

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