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

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Overview

- **PFAS Overview**
- **Smouldering Combustion Basics**
  - Hydrocarbon Applications
- **PFAS Smouldering**
  - Lab Study
  - Field Scale Results
- **Summary**

Challenges for PFAS Remediation

Changing and low regulatory levels

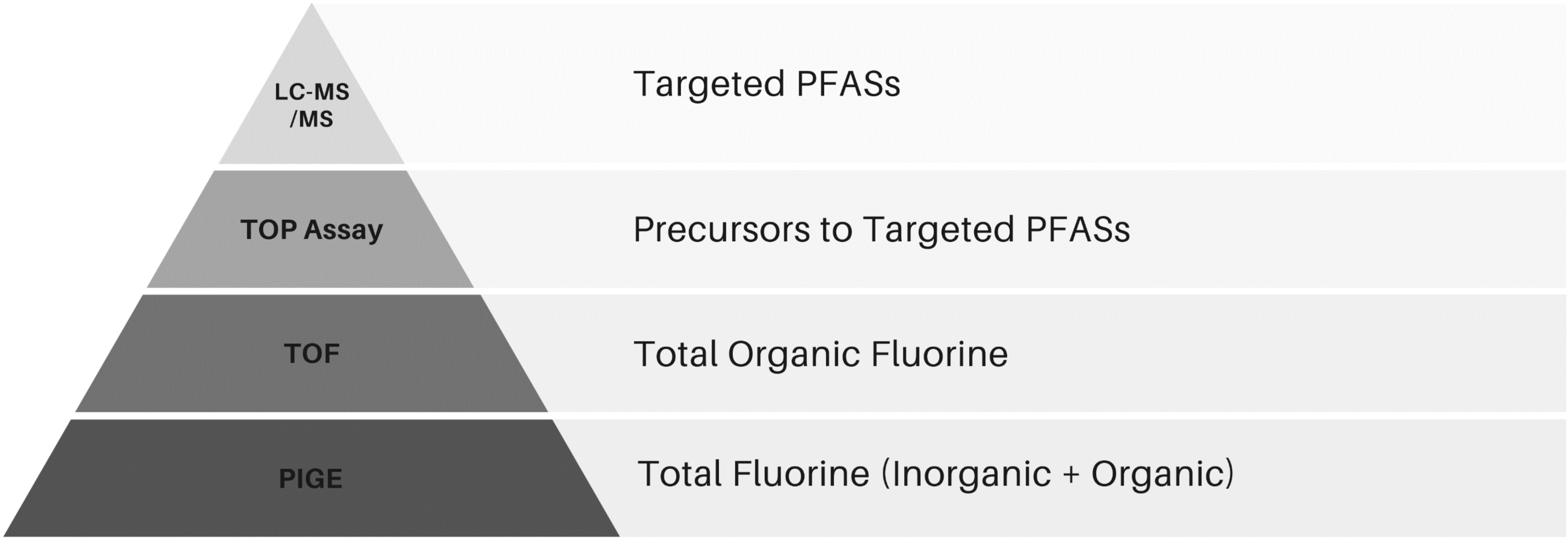
One 20L bucket of some historical AFFF formulations had enough PFOS to contaminate the annual water supply for 94.5 million people to 0.02 ng/L

One Olympic-sized swimming pool filled with this AFFF would have enough PFOS to contaminate ~25,000 years worth of the drinking water supply for the entire U.S. population

(Higgins, 2022)

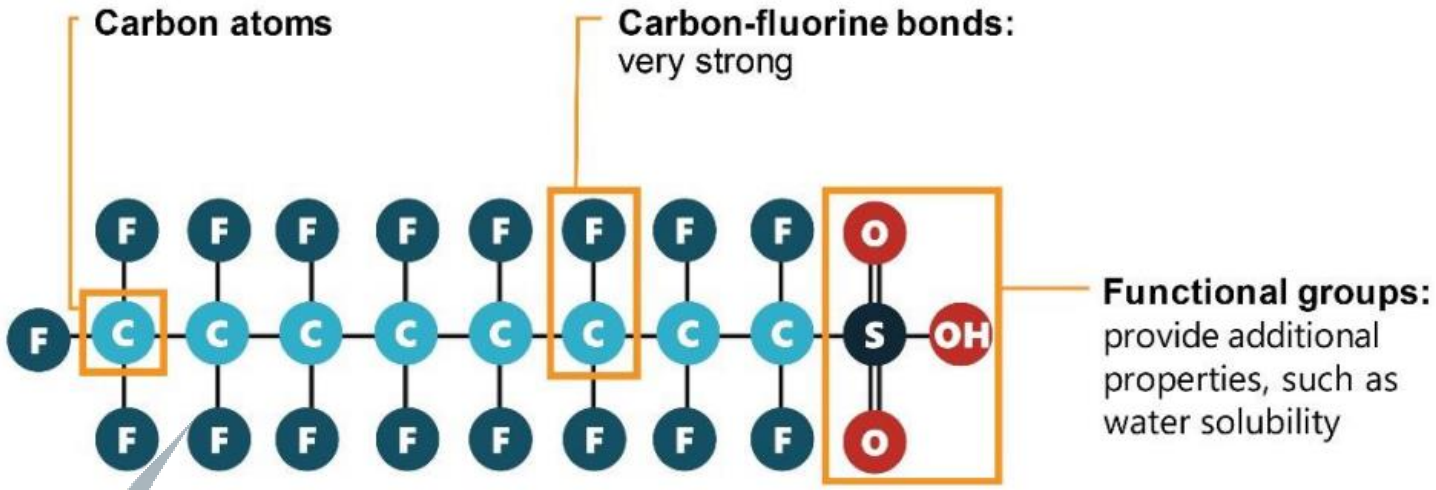
Challenges for PFAS Remediation

Methods for quantifying PFAS



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

Smouldering Combustion

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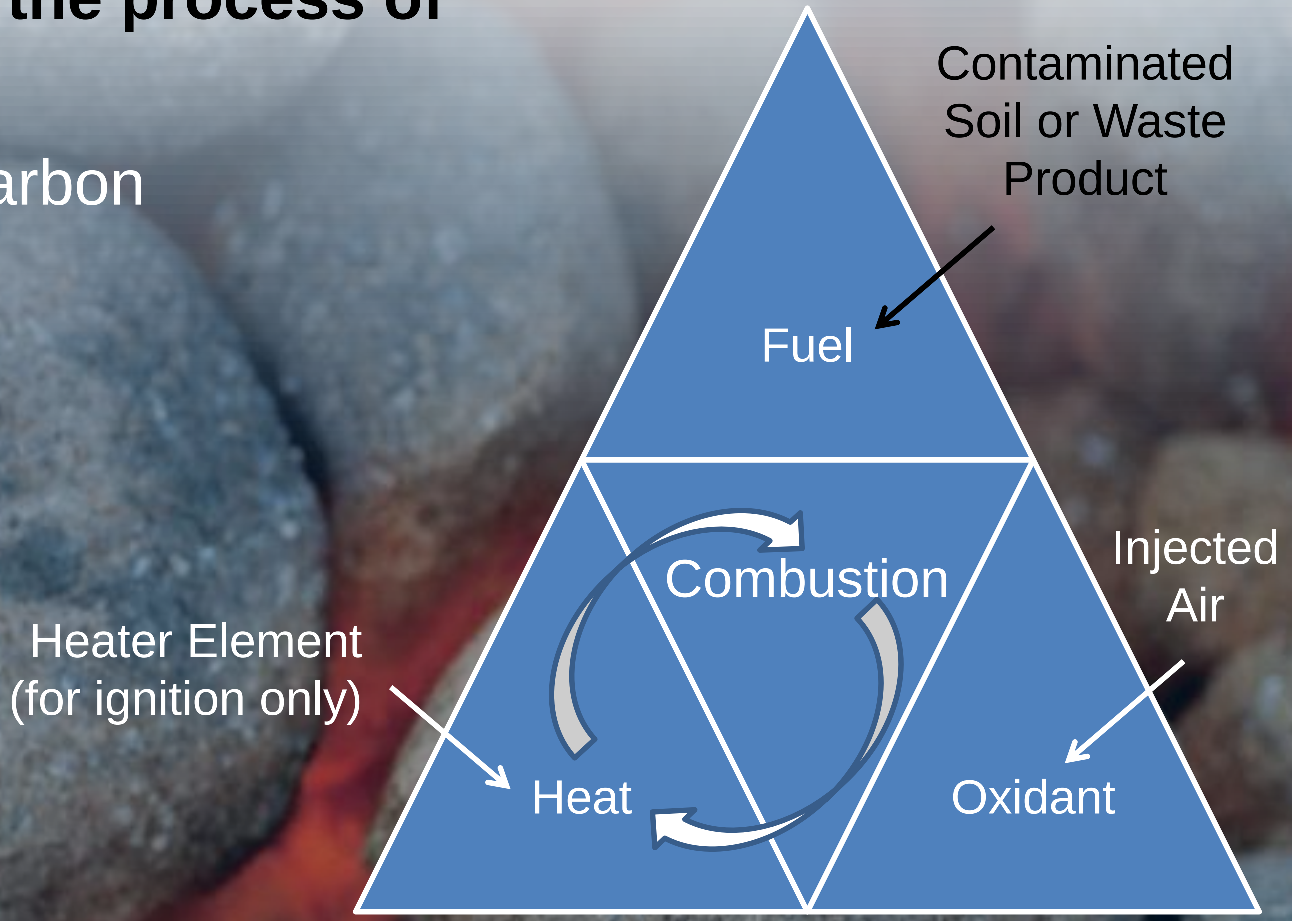
Smouldering Combustion

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

Exothermic reaction converting carbon compounds to CO_2 + H_2O

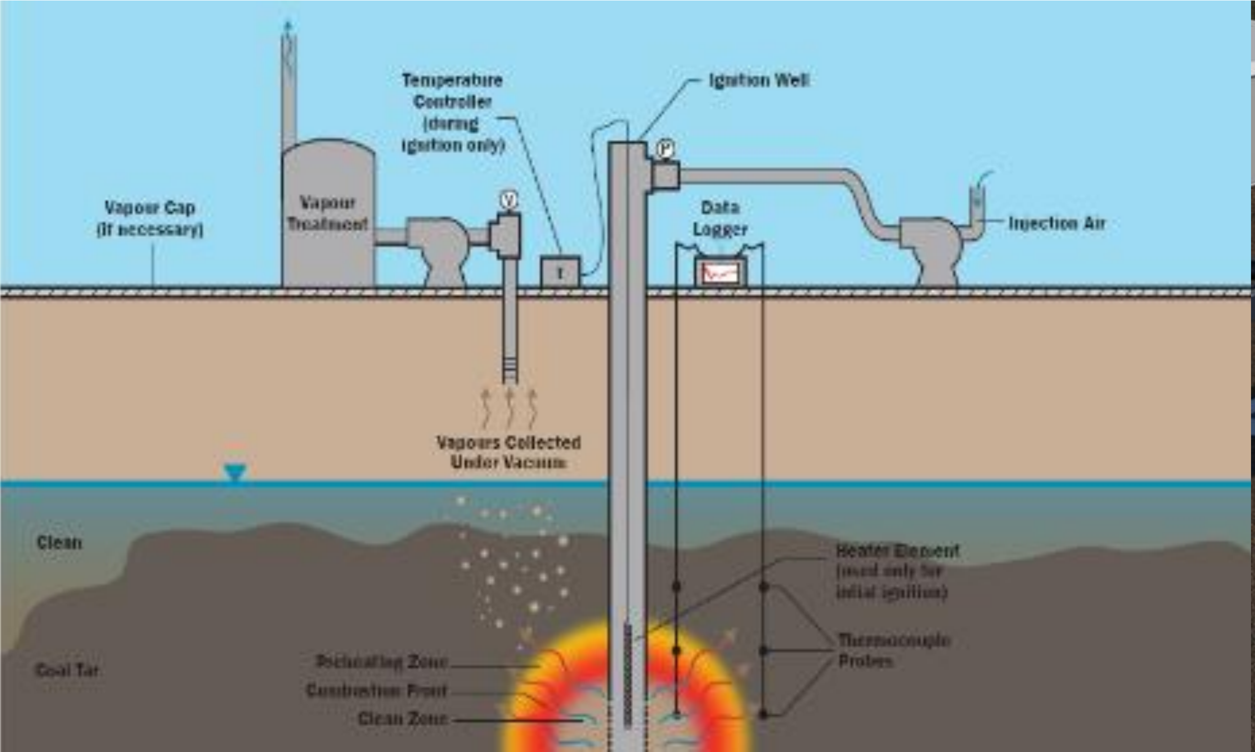


STAR / STARx is a flameless combustion process: only smouldering is possible within a porous matrix (i.e., soil)

Modes of Application

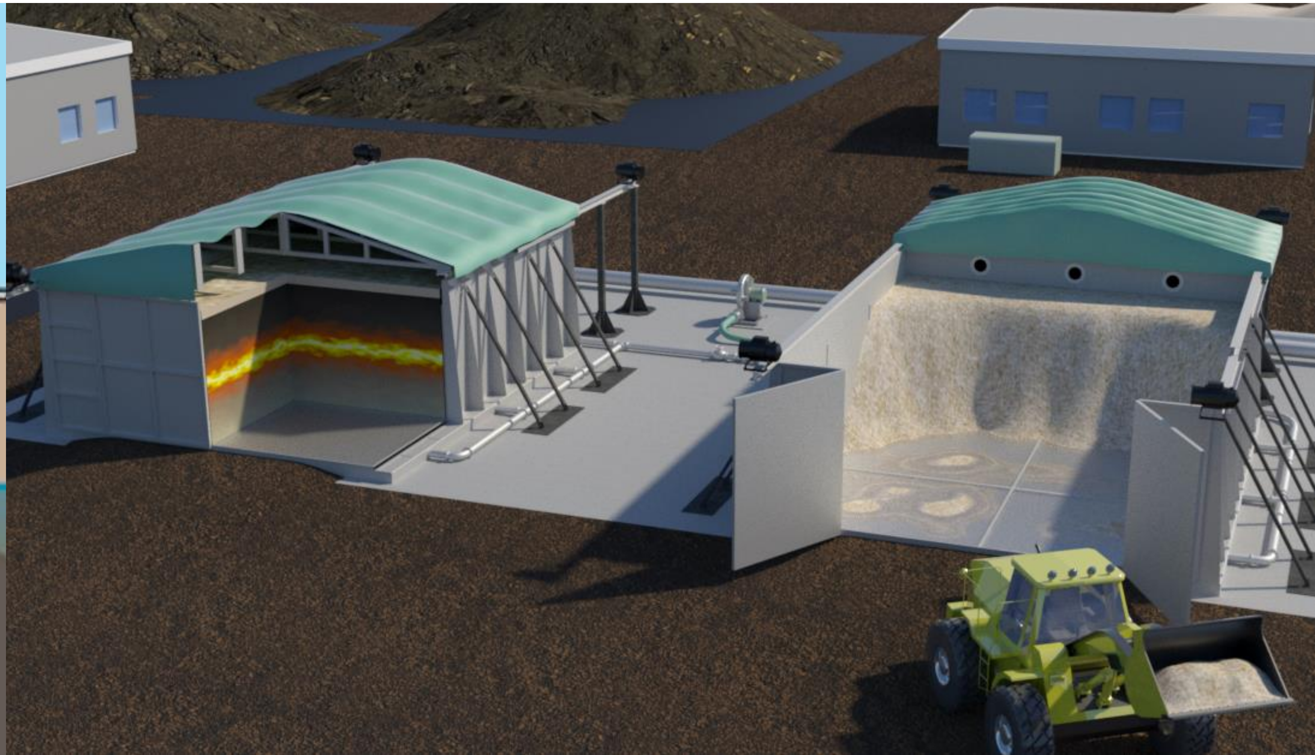
STAR

- **In situ (below water table)**
  - Applied via wells in portable in-well heaters



STARx

- **Ex situ (above ground)**
  - Soil piles placed on “Hottpad” system



STAR Example Project – New Jersey

- **37 acres site**
- **Coal tar mass destroyed = 150,000 lbs (~70,000 kg)**
- **2,200 Ignition Points (IPs)**
  - 1,723 Surficial Fill
  - 482 Deep Sand
- **~1,000 Remedy Verification Samples**
- **200,000 Safe Work Hours**
- **Regulatory Certification for Site Closure – September 2019**

STARx Example Project - Bahamas

Former Oil Terminal

- **11,250 m^3 of consolidated oily sludge from Hurricane Dorian clean up**
- **Turnkey STARx Plant operated by subcontractor**
  - 2 x HP250 systems
- **Operations started August 2022**



PFAS Smouldering

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PFAS Treatment

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

Mineralization

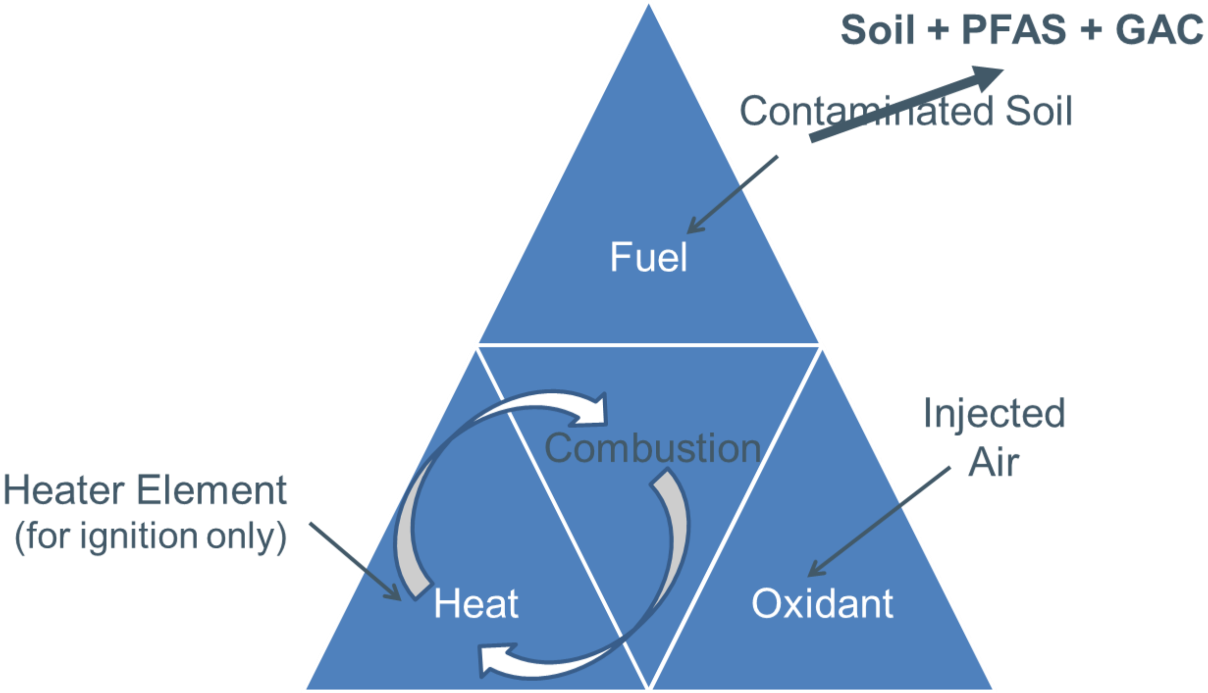
- Increases with Temp > 700°C
- Maximizes at Temp > 900°C

But PFAS not a smoulderable fuel

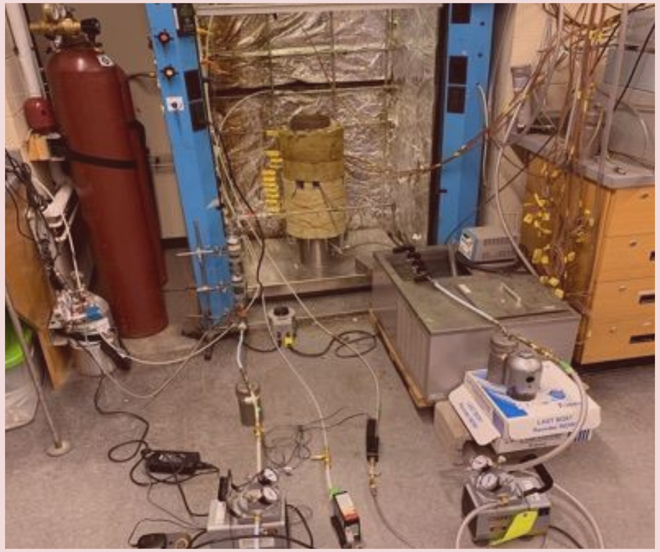
- Requires a surrogate fuel

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

Mass Balance / Optimization

Phase 2:

Pilot Scale Tests

Heterogeneity / Field Deployable

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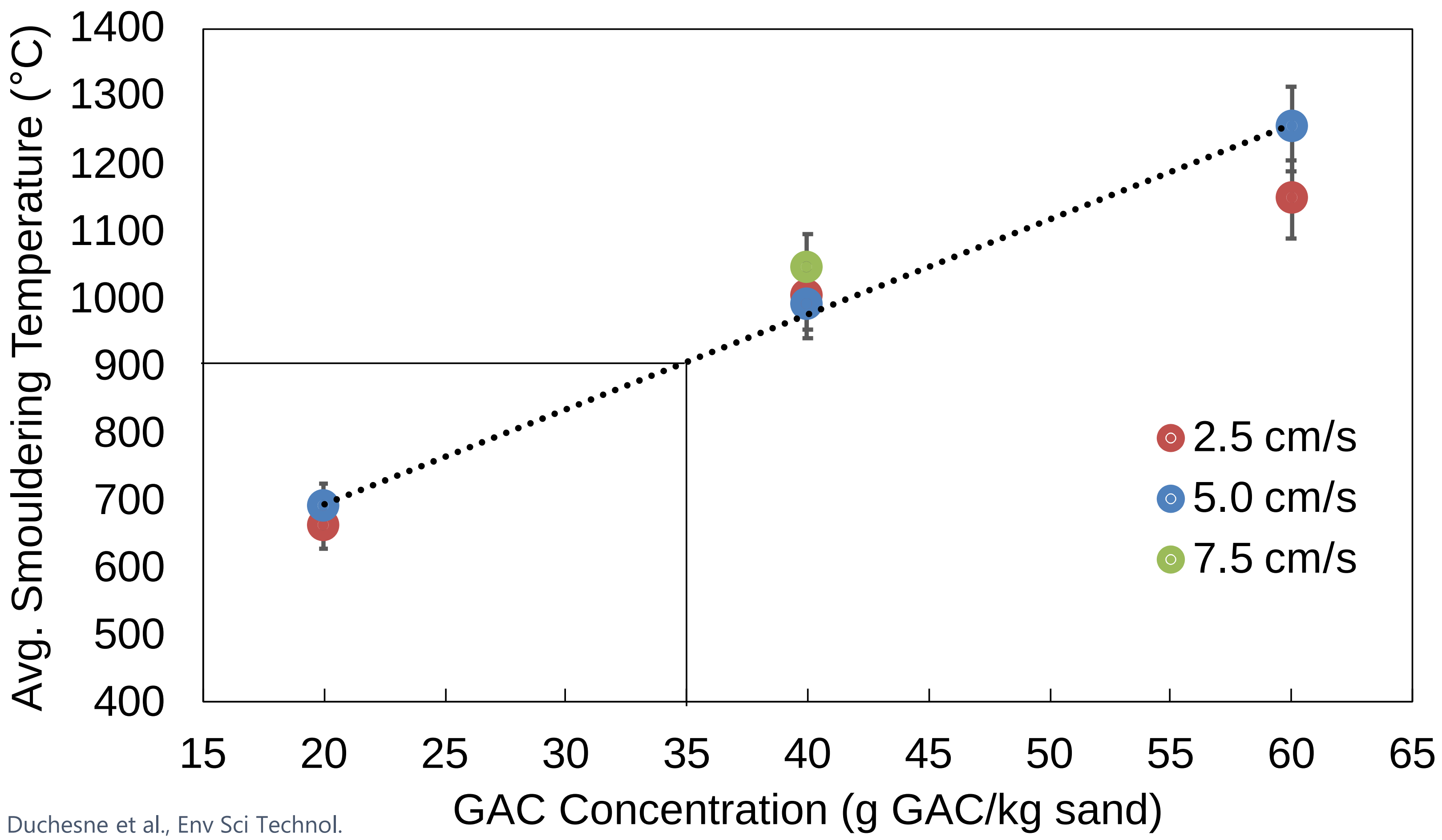
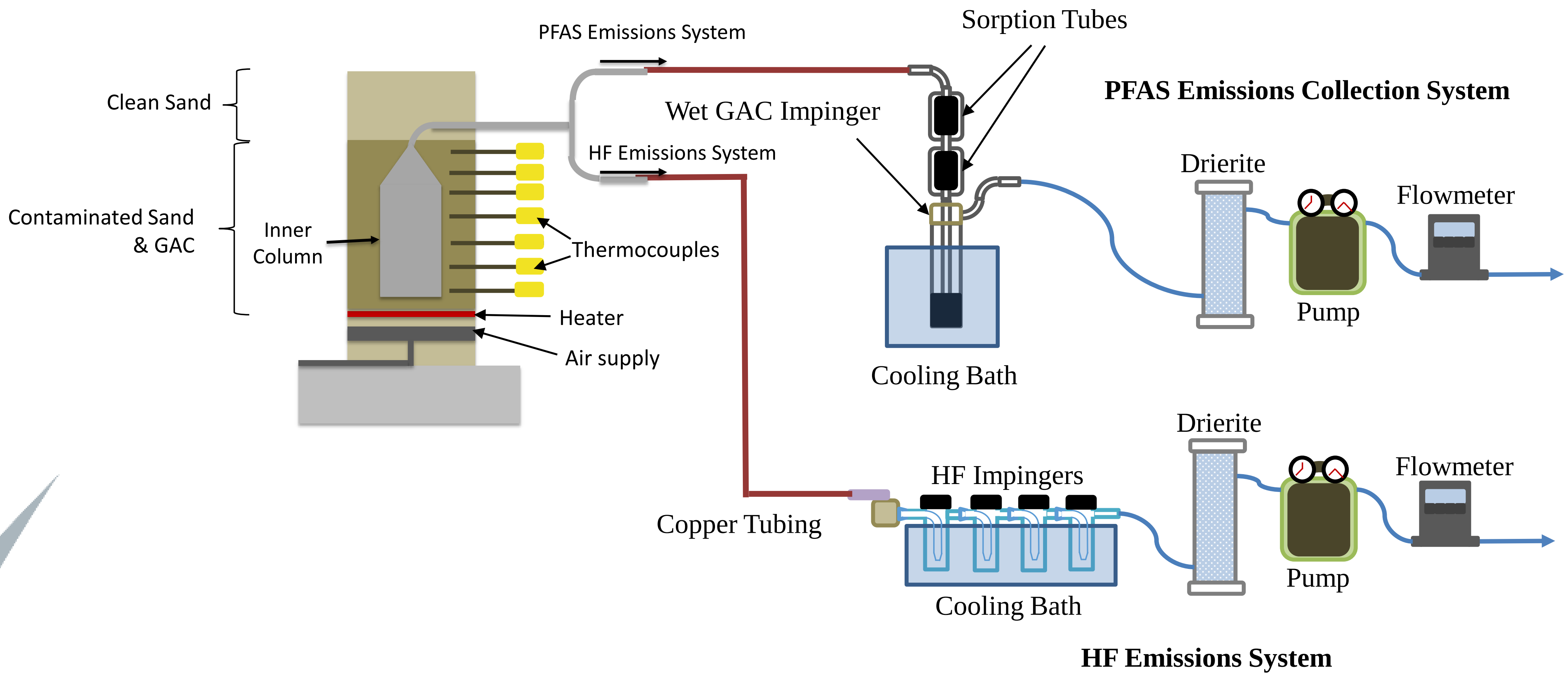
GAC concentration can be selected to target a specific temperature to maximize complete PFAS destruction



Reprinted with permission from Duchesne et al., Env Sci Technol.
dx.doi.org/10.1021/acs.est.0c03058

Objective: Close fluorine mass balance during smouldering



Phase 1 – Amendment Optimization

Objective: Can calcium oxide can be used to enhance destruction and minimize byproducts?

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

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

Phase 1 – Lab Column Tests

- **8 column tests**
  - PFOS-spiked GAC
- **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
B-2	50.0	2.5	-	887 ± 22	0.40 ± 0.04
B-3	50.0	2.5	-	908 ± 34	0.37 ± 0.10
B-4	50.0	2.5	-	834 ± 35*	0.37 ± 0.04
S-1	50.0	2.5	-	935 ± 51	0.37 ± 0.20
Ca-1	50.0	2.5	50	795 ± 37	0.31 ± 0.08
Ca-2	50.0	2.5	20	869 ± 16	0.36 ± 0.07
Ca-3	50.0	2.5	10	900 ± 62	0.36 ± 0.03

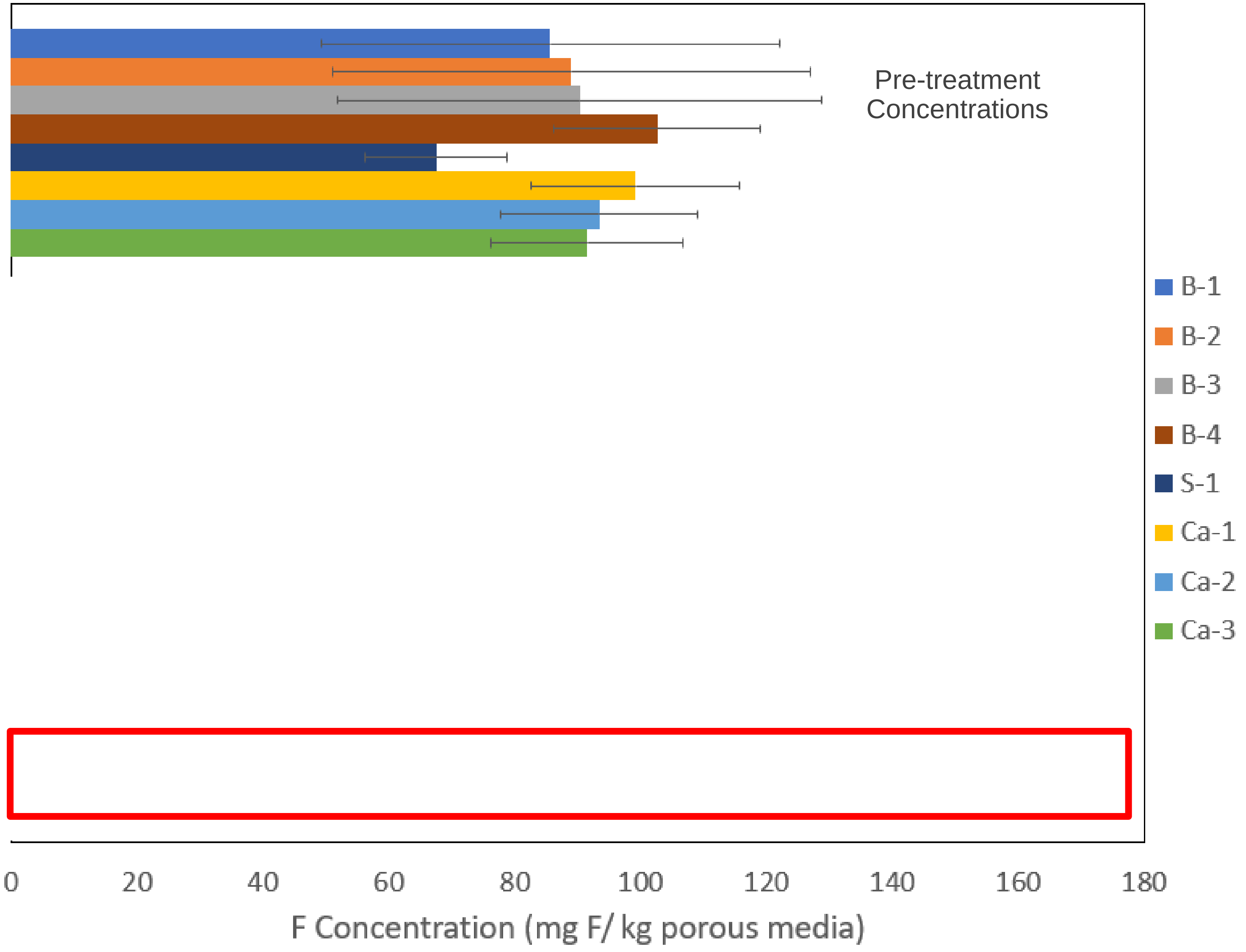
"Base Case" (B-1 to B-4)

Steam Injection (S-1)

Calcium oxide (Ca-1 to Ca-3)

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

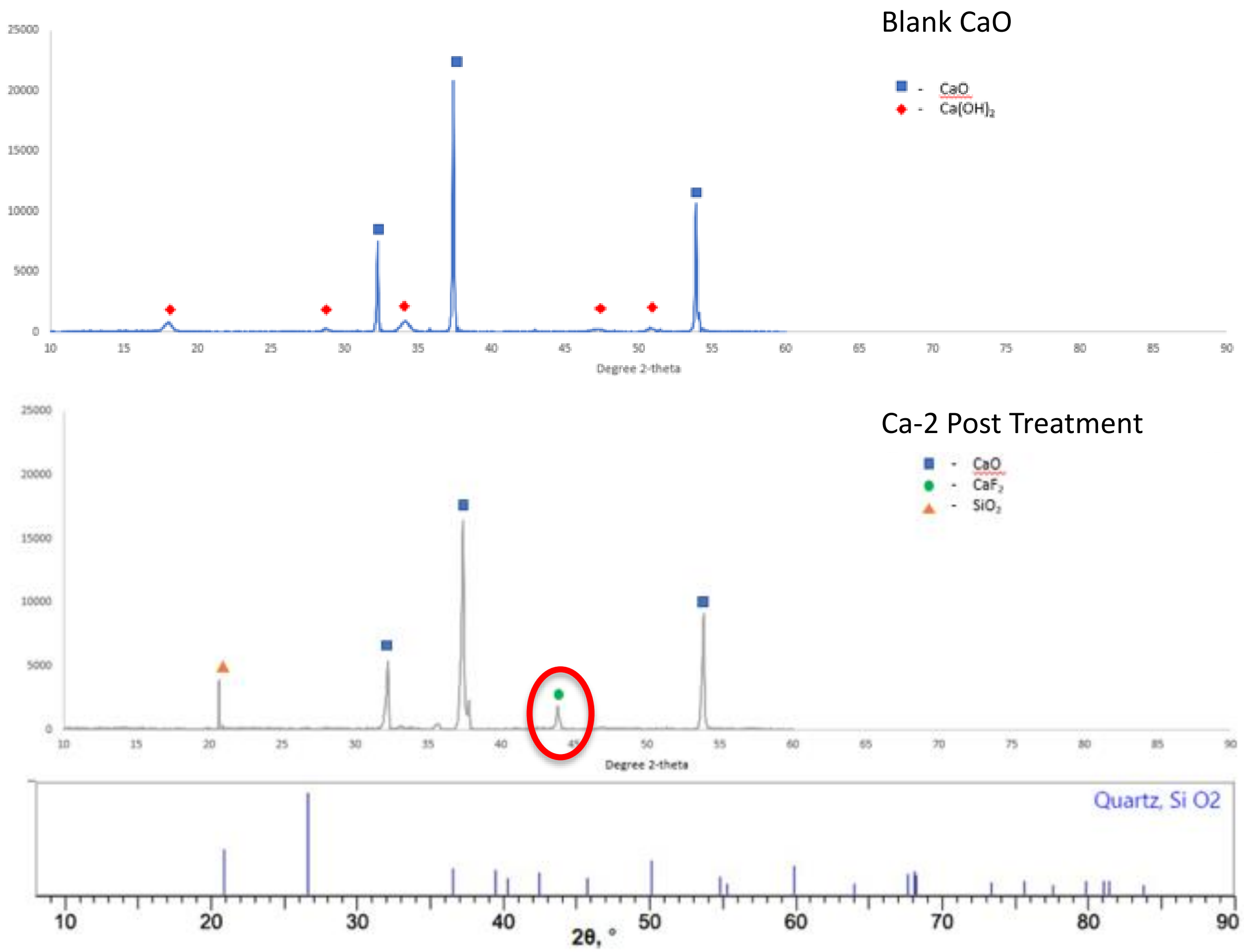
Phase 1 – Lab Column Results



Key Takeaways

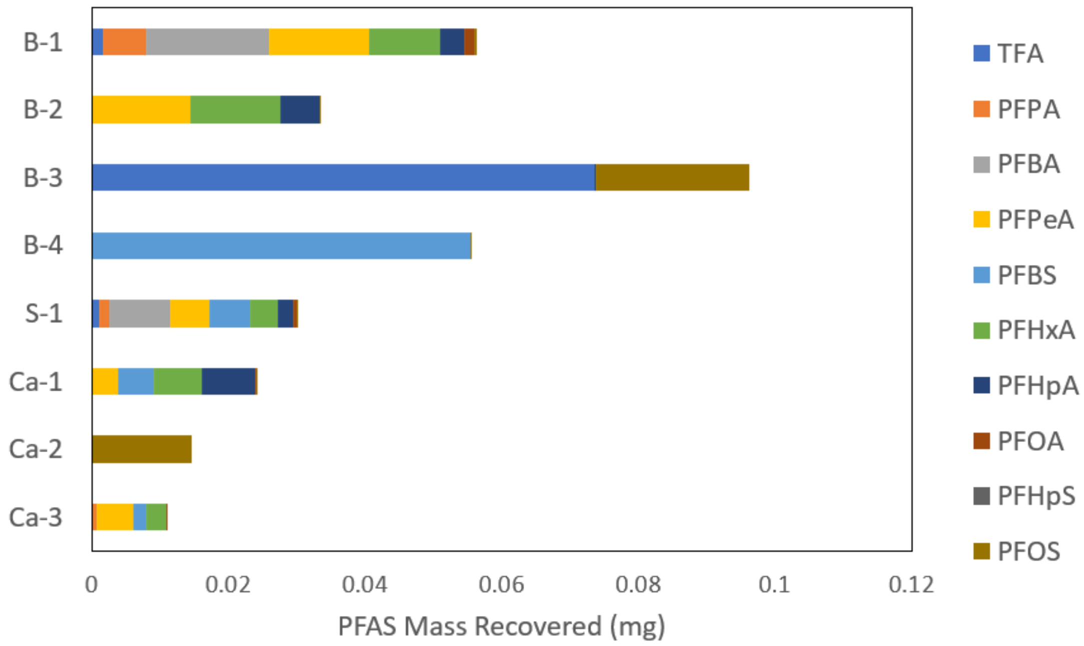
- Targeted PFAS Analytes: >99.9% reduction in detectable PFAS in all instances
- PIGE Spectroscopy
  - 95.6 - >99.9% reduction in instances without CaO amendments
  - No significant change in total F concentration where CaO amendments were employed

XRD Analysis – Tracking CaO Transformation



Phase 1 – Lab Column Results

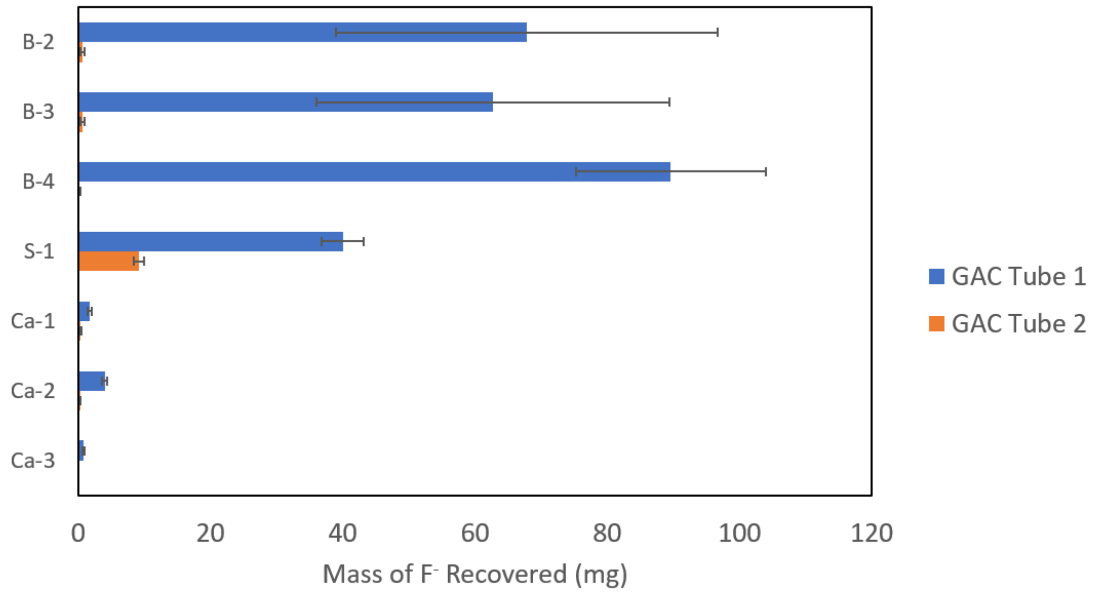
Targeted PFAS in Emissions



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

Total F Recovery in Emissions

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

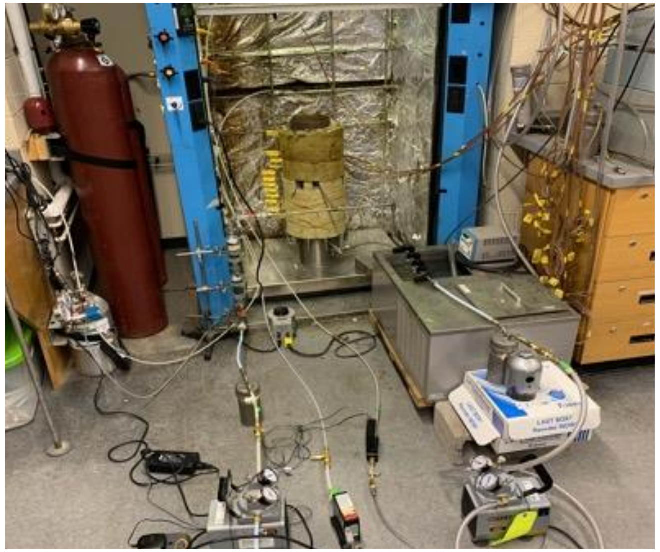


- CaO soil amendment had lower F mass on GAC
  - Consistent with less HF and shorter chain compounds produced

Phase 1 – Summary

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

Mass Balance / Optimization

Phase 2:

Pilot Scale Tests

Heterogeneity / Field Deployable

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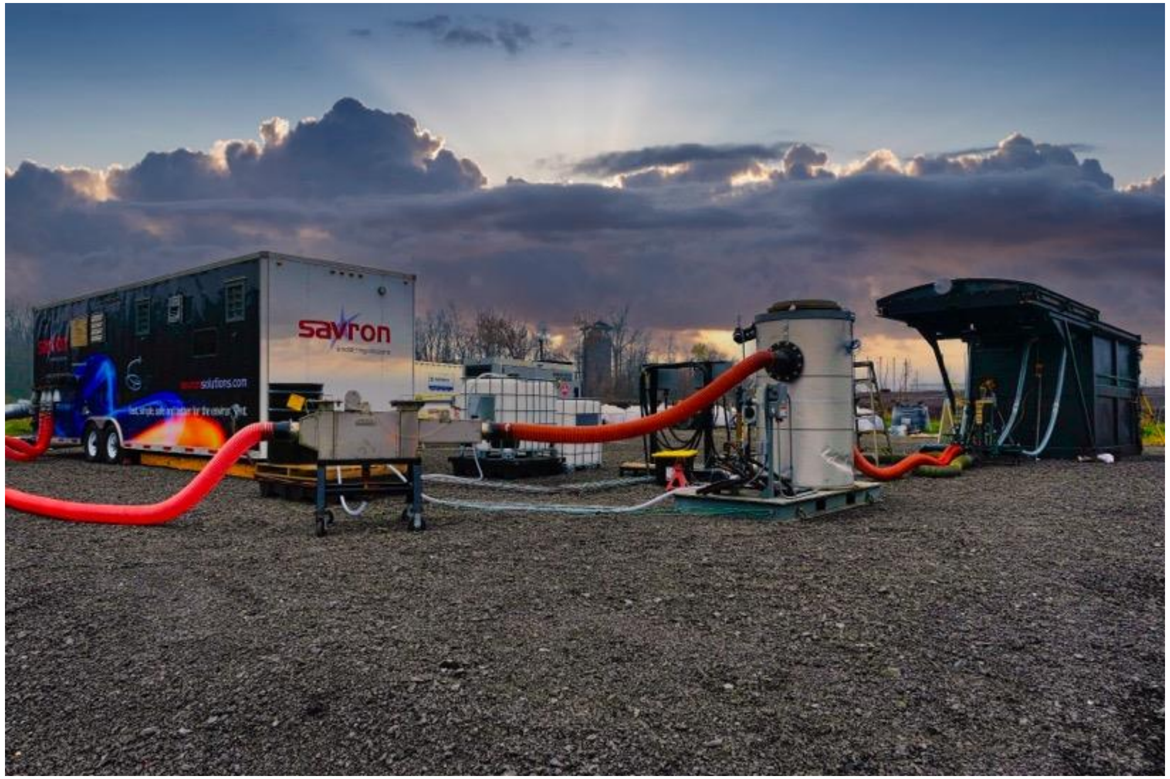
Phase 2 – Pilot Test

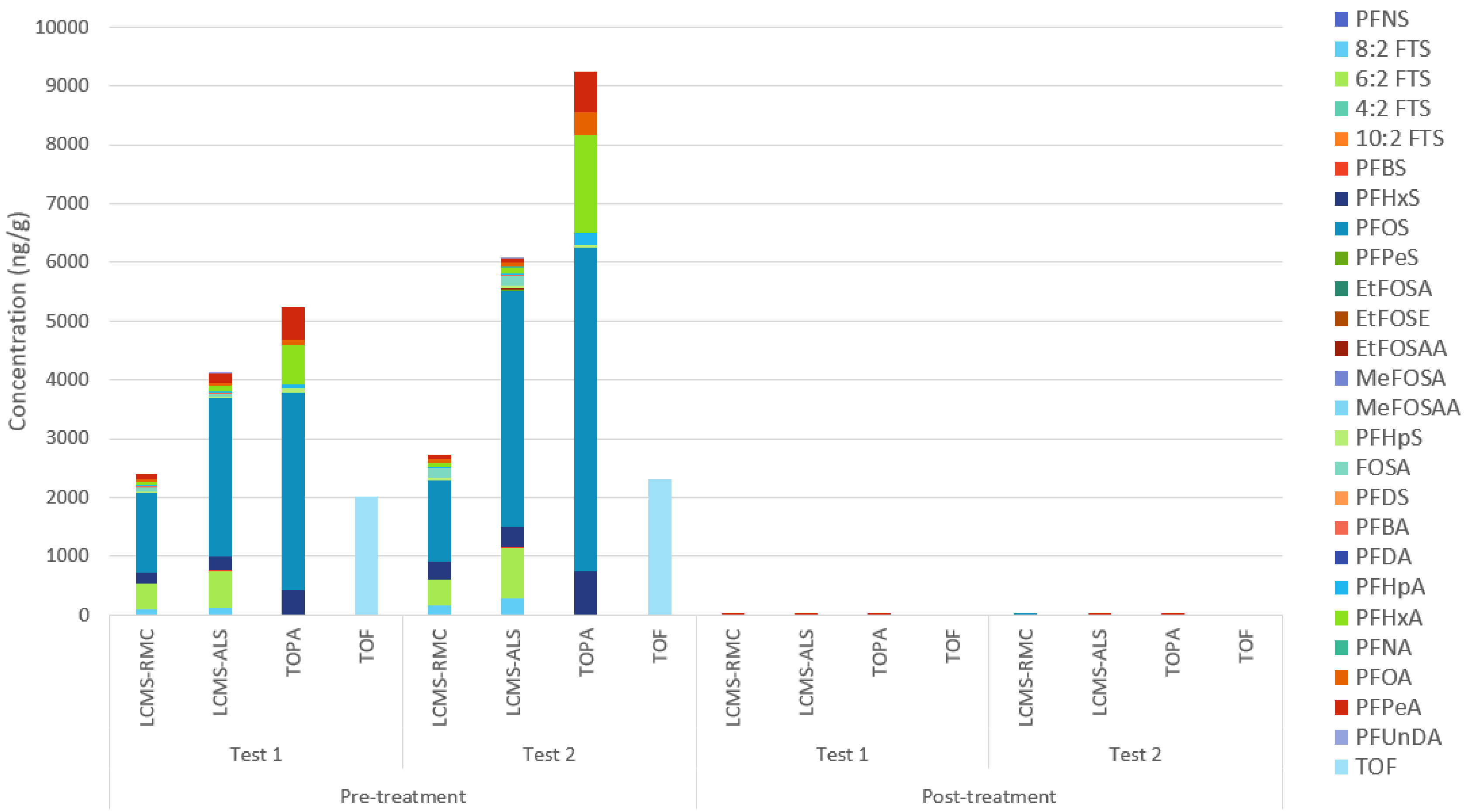
- CFB Trenton
- 2 pilot tests using 10 m^3 Hottpad



Phase 2 – Mixing / Loading

Phase 2 – Unloading

Phase 2 – Results



Soil Results

- PFAS reduced to near or below detection limits
- Awaiting final PIGE / XRD data
- Preliminary PIGE results align with lab study, suggesting that F is converted to 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

Implications / What's Next?

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Implications

- **Smouldering is a promising treatment option for:**
  - PFAS-contaminated soil mixed with clean GAC
  - PFAS-contaminated GAC

- **Potential for low-cost, combined treatment facility**
  - Contaminated GAC and soil can be combined for increased net treatment
  - GAC used in emissions treatment system can be used as fuel once spent

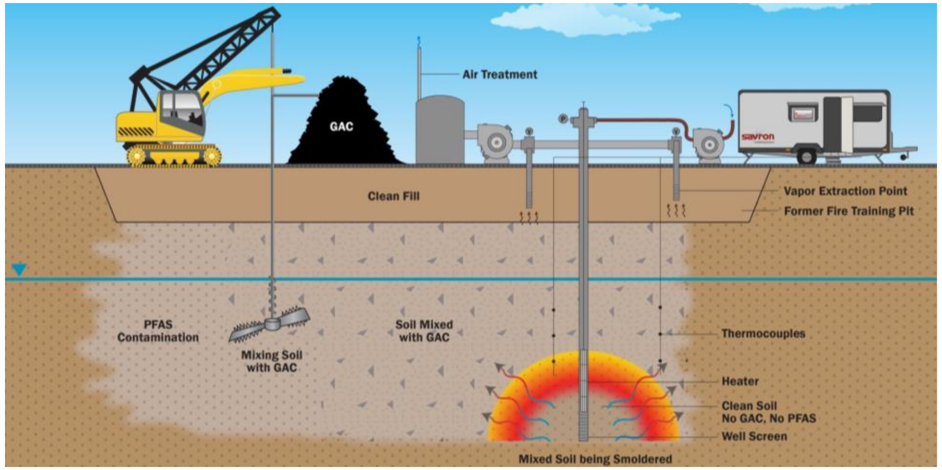
Ex Situ Treatment: Soil or Waste GAC

In Situ Source Treatment

Upcoming PFAS Projects

ESTCP PFAS Study (2023)

- STAR (in-situ) pilot test at US DoD site
- Demonstration of PFAS destruction in source zone
- 4 ignition points, 800 m^3 soil volume
- Carbon injection / in-situ soil mixing



US Air Force STARx (2022/2023)

- STARx extended pilot study at US Air Force site
- Demonstration / validation of STARx in variable conditions (soil type, moisture content, co-contaminants, etc.)
- 10 x 10m^3 pilot tests

Summary

- **STAR / STARx is a rapid, sustainable, and cost-effective method for treatment of coal tar, creosote, and petroleum hydrocarbons**
- **Detailed scale up program demonstrated successful treatment of PFAS**
  - PFAS in soil reduced to below regulatory criteria
  - Majority of PFAS is destroyed (converted to HF or inert CaF_2)
  - CaO can enhance destruction at lower temperatures
- **Full scale ex-situ systems ready for deployment**
- **Pilot testing of in situ smoldering of PFAS scheduled in 2023**

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Questions?

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