Thank you to our Patrons

We will begin our presentation in a few minutes…

Smoldering Treatment of PFAS: Field Demonstration

David Major, Ph.D., BCES

Overview

- Introduction to Smoldering
- Smoldering PFAS
- Lab/Pilot Testing
- Other PFAS Projects

Smoldering Combustion

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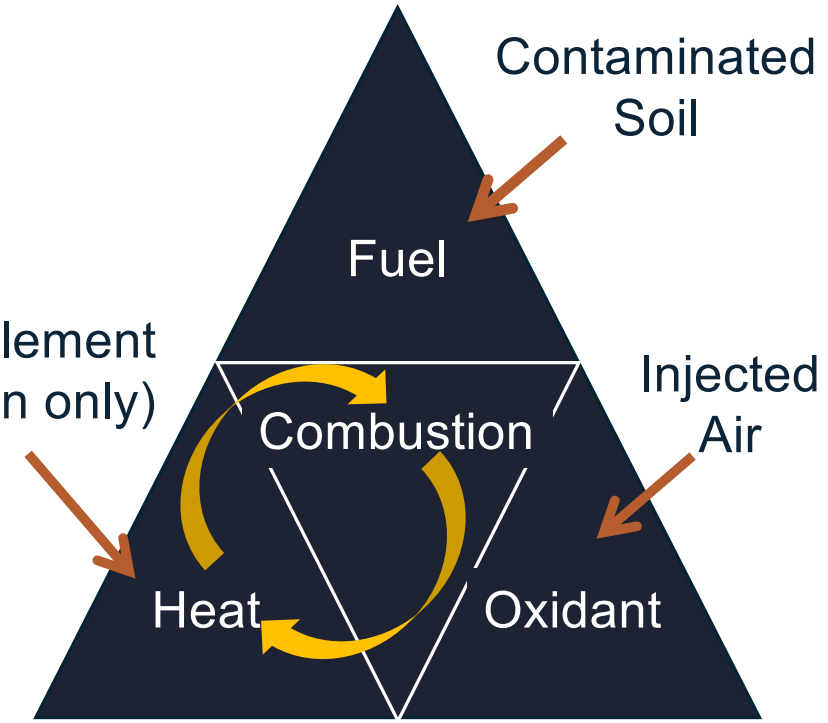


- Behaves like a BBQ

Smoldering Combustion of PFAS

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

Mineralization

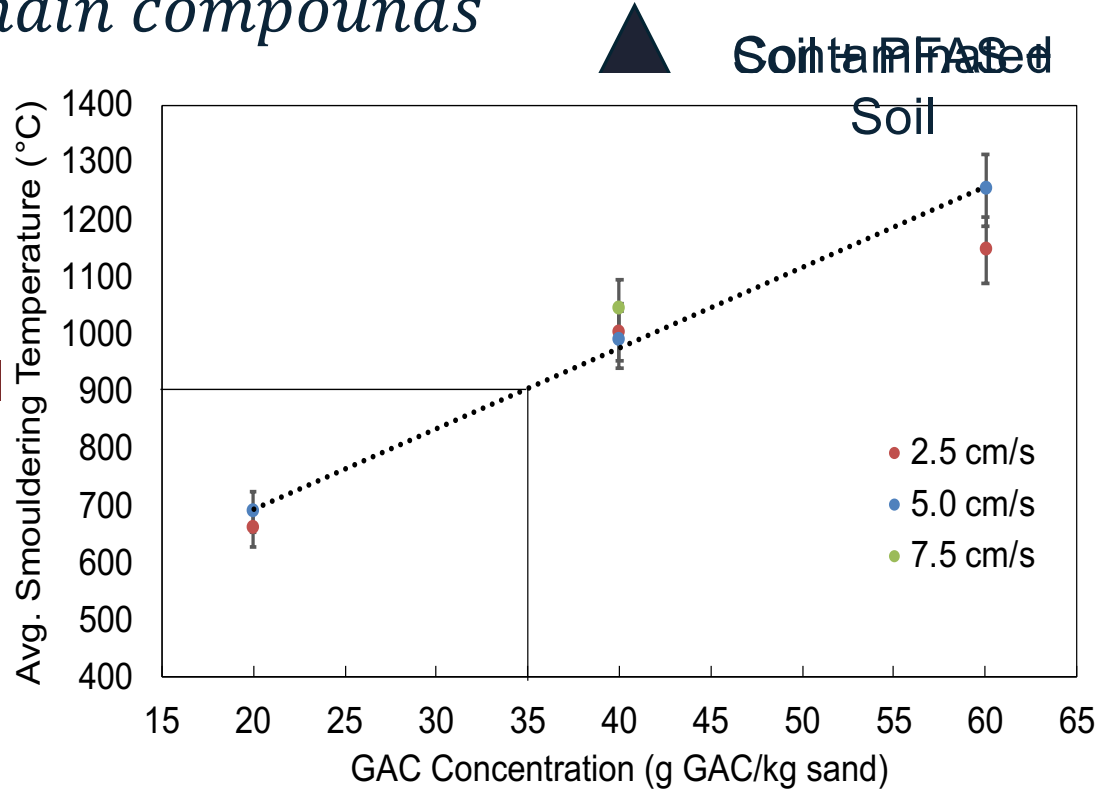
- Increases with Temp > 700°C
- Maximizes at Temp > 900°C

But PFAS not a smolderable fuel

- Need supplemental fuel

Add carbon

- E.g., GAC
- Can contain PFAS
- Temp ∝ [Carbon]



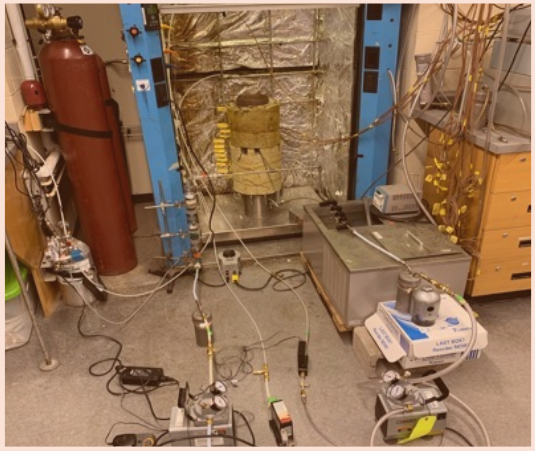
STAR

STARx

Full scale systems implemented at sites around the world for treating hydrocarbon-impacted soils and sludges

SERDP Project

PROJECT OF THE YEAR 2021 SERDP ENVIRONMENTAL RESTORATION



Lab Column Tests

- Fluorine Mass Balance
- CaO Optimization

Pilot Scale Tests

- Scale Up
- Evaluate Field Soils

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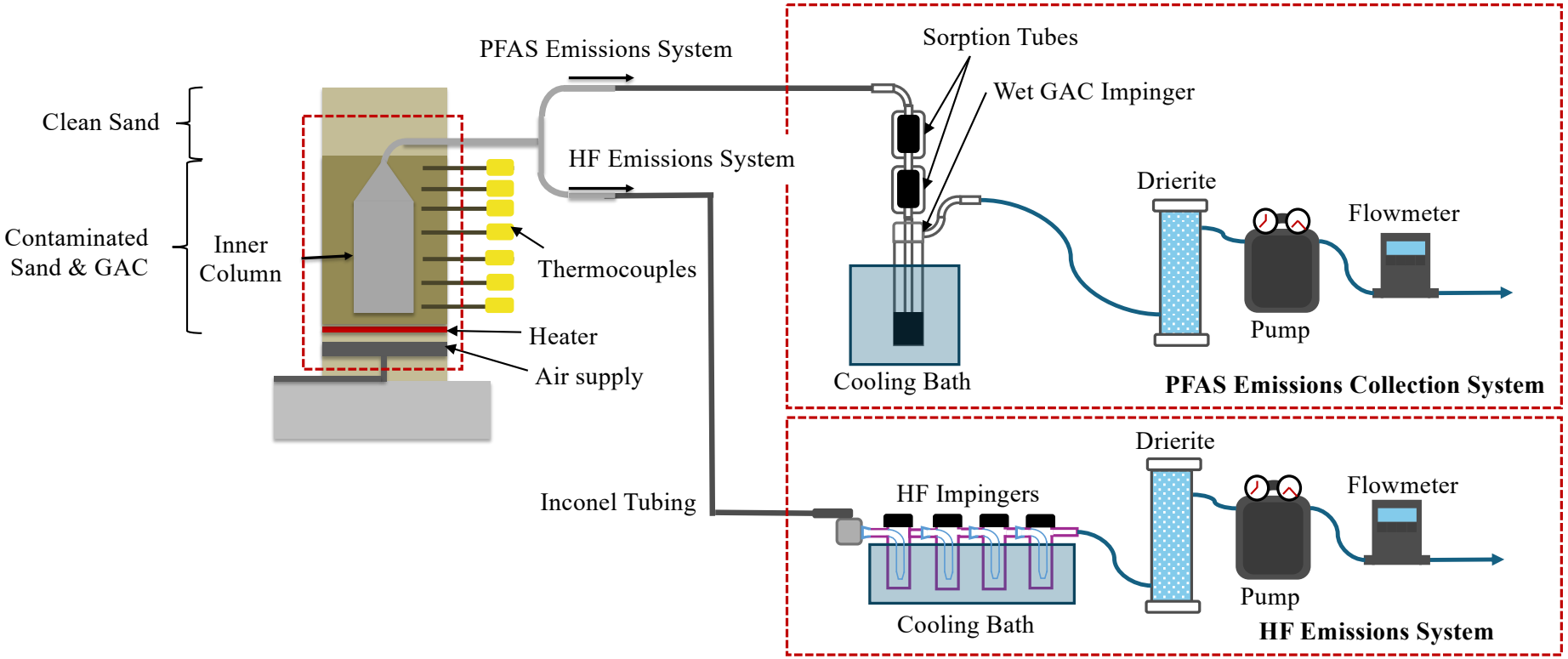
Column Design

Novel experimental design employed for detailed emissions analysis



Lab Column Tests

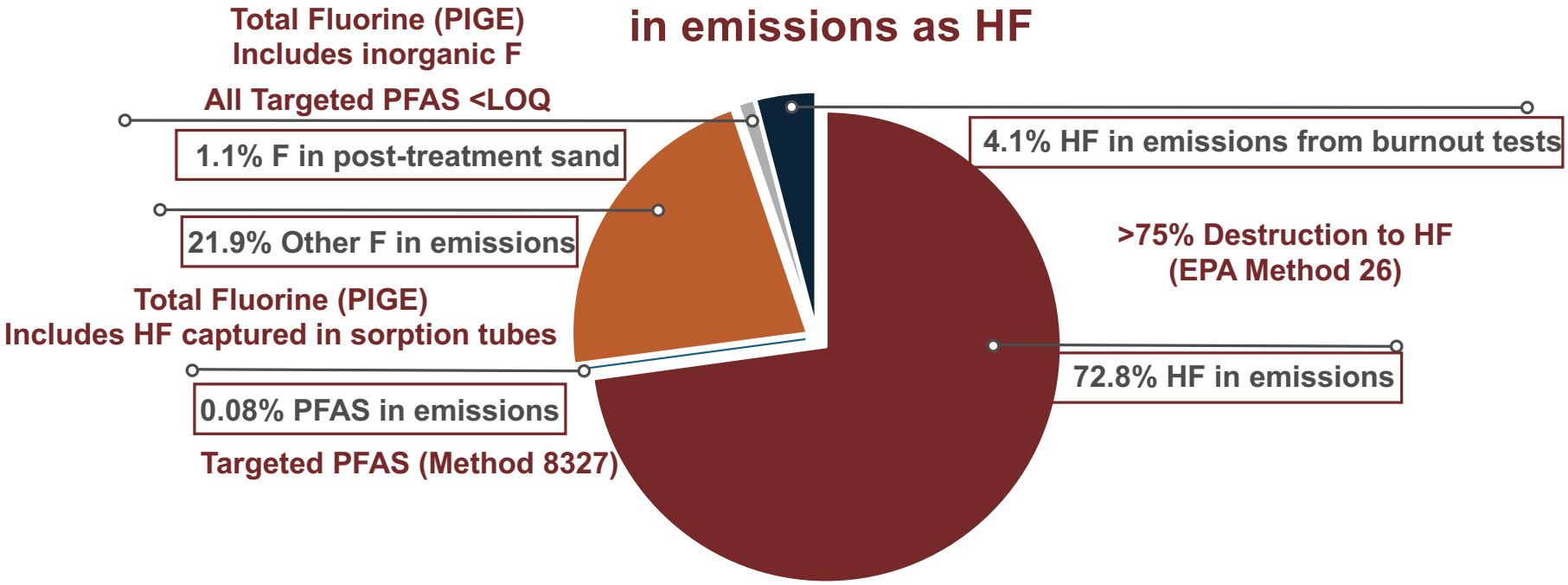
- **8 column tests utilizing PFOS-spiked GAC in Sand (or Sand + CaO)**
- **Self-sustaining smoldering achieved in all experiments**

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	
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	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	
Ca-3	50.0	2.5	10	900 ± 62	0.36 ± 0.03	

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

Flourine Mass Balance – Base Case

Fluorine mass balance for base case tests (50 g/kg GAC) found significant F in emissions as HF



68 – 109% Fluorine Mass Balance

CaO Amendment Optimization

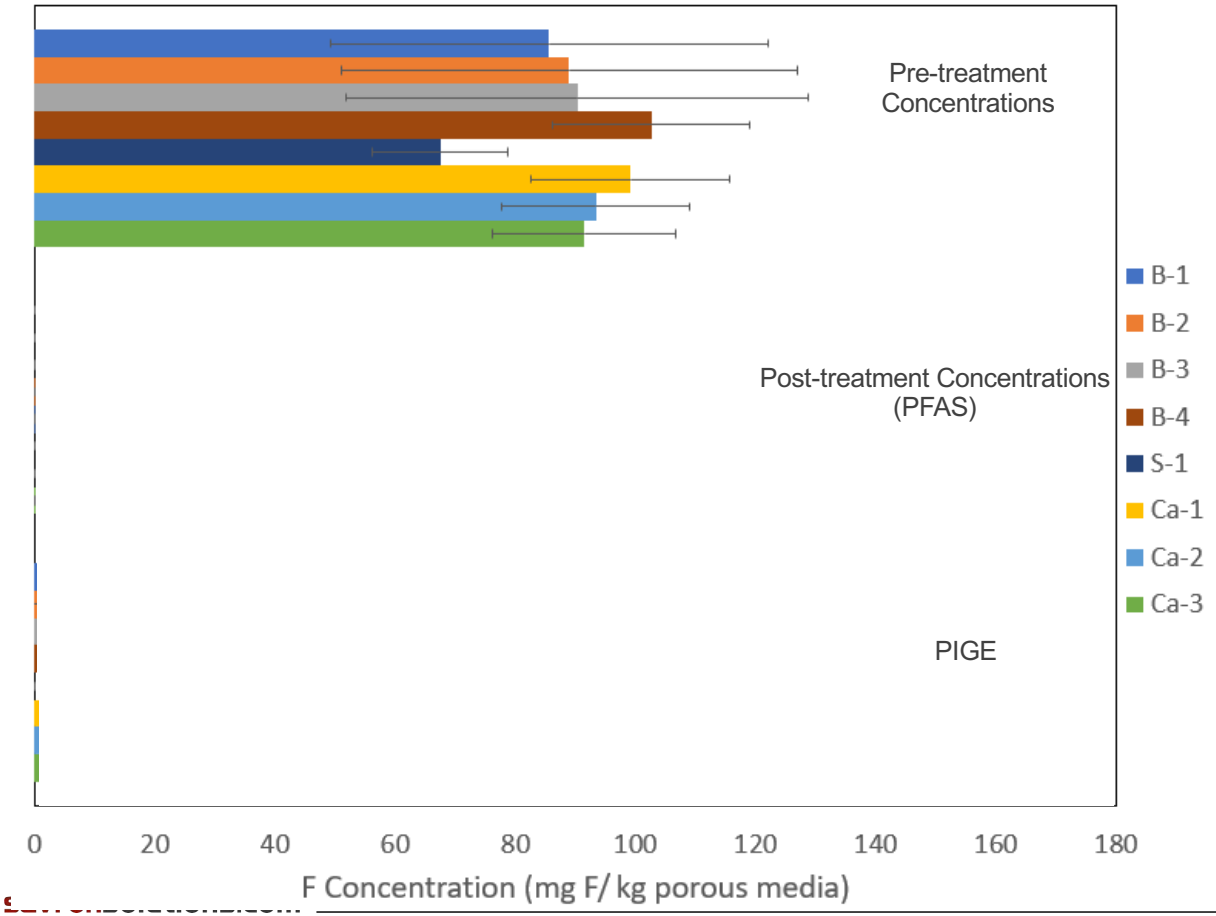
Calcium oxide used to improve PFAS destruction and minimize byproducts in emissions

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

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

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

Lab Column Results

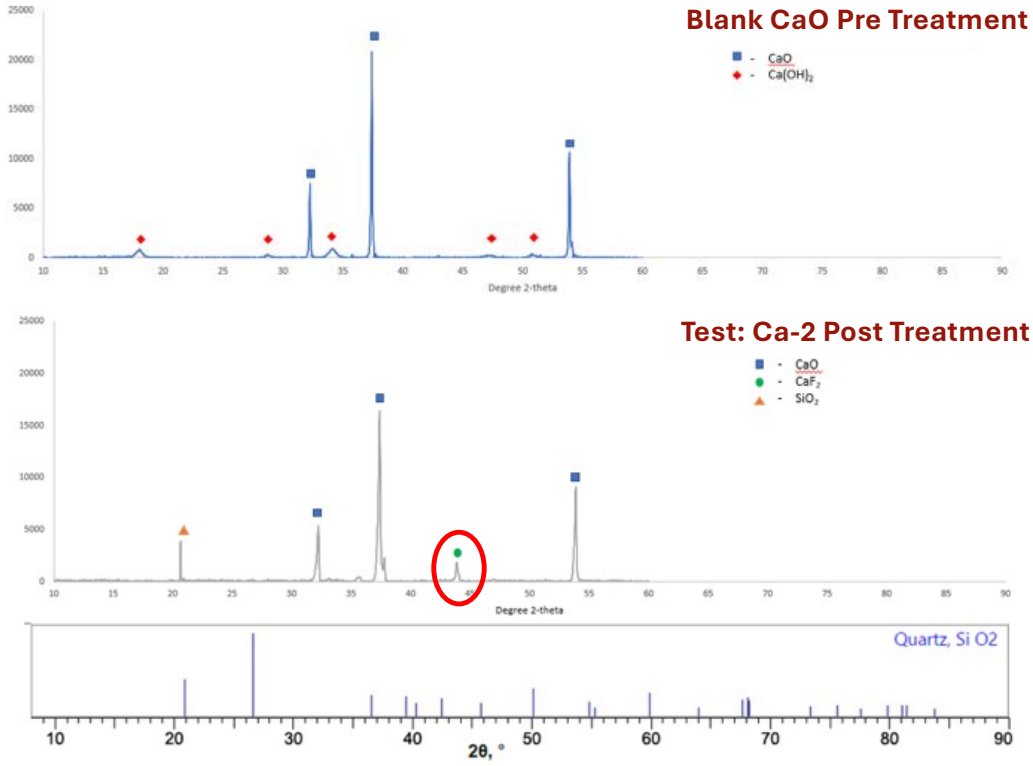


Key Takeaways

- 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

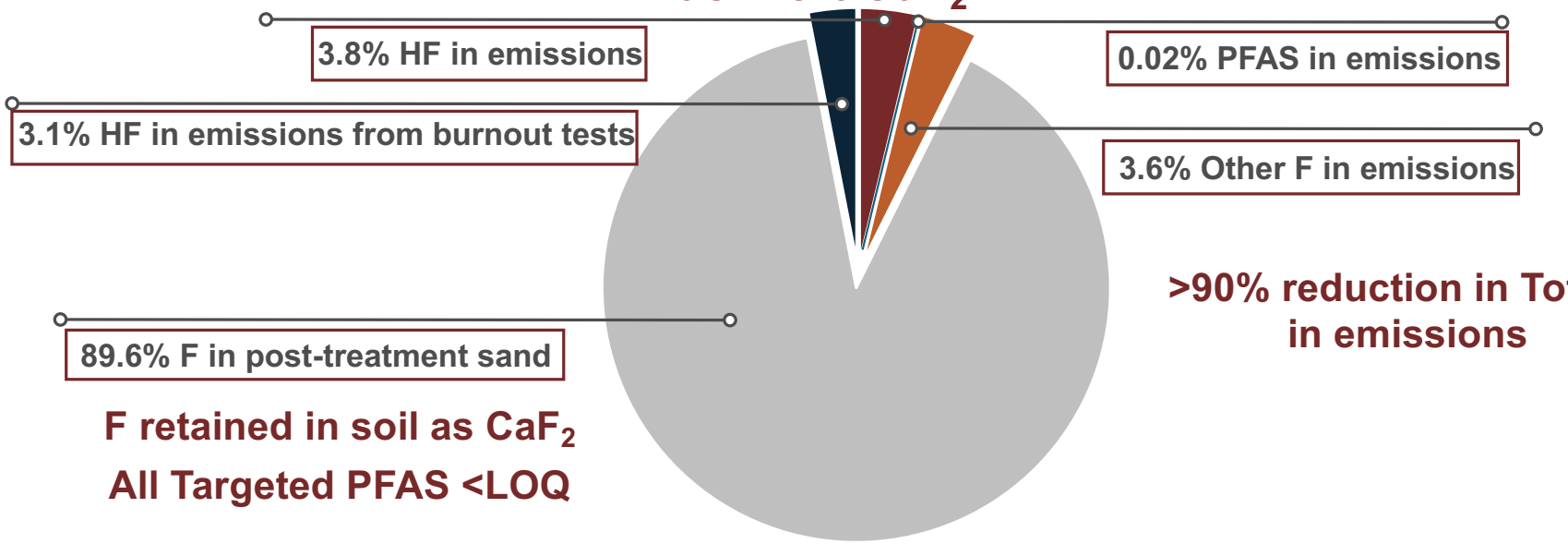
Lab Column XRD Results

XRD Analysis – Tracking CaO Transformation to CaF_2



Flourine Mass Balance- CaO Addition

With the addition of CaO, the majority of F is retained in post-treatment soils as inert CaF_2



>90% reduction in Total F in emissions

F retained in soil as CaF_2

All Targeted PFAS <LOQ

80 – 128% Fluorine Mass Balance

Lab Column Results Key Results

Achieved Smoldering Temperatures

- ***>900°C*** GAC at 40-60 g/kg soil

Targeted PFAS Analytes:

- ***>99.9% reduction***, and **below detectation limits**

PIGE Spectroscopy

- ***95.6 - >99.9% reduction of F mass*** in instances ***without CaO a***mendments
- **No change of F mass *with CaO*** (HF sequestered as CaF_2)

Emissions

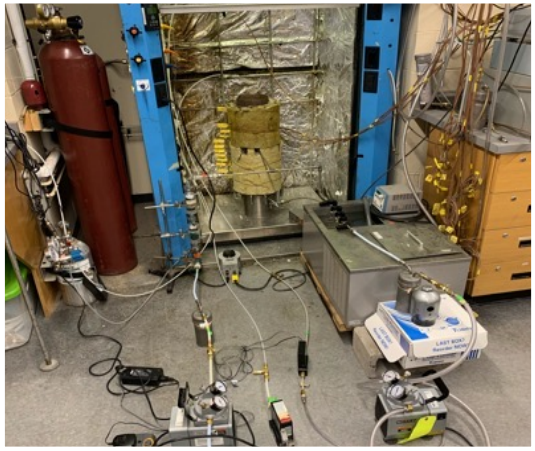
- ***<0.02 – 0.13%*** of initial ***F mass, lower with CaO soil*** amendment
- Consistent with ***less HF and shorter chain compounds*** produced

Mass Balance (F)

- 68-109%, ***without*** CaO
- 80-128% ***with*** CaO

SERDP Project

PROJECT OF THE YEAR 2021 SERDP ENVIRONMENTAL RESTORATION



Lab Column Tests

- Fluorine Mass Balance
- CaO Optimization

Pilot Scale Tests

- Scale Up
- Evaluate Field Soils

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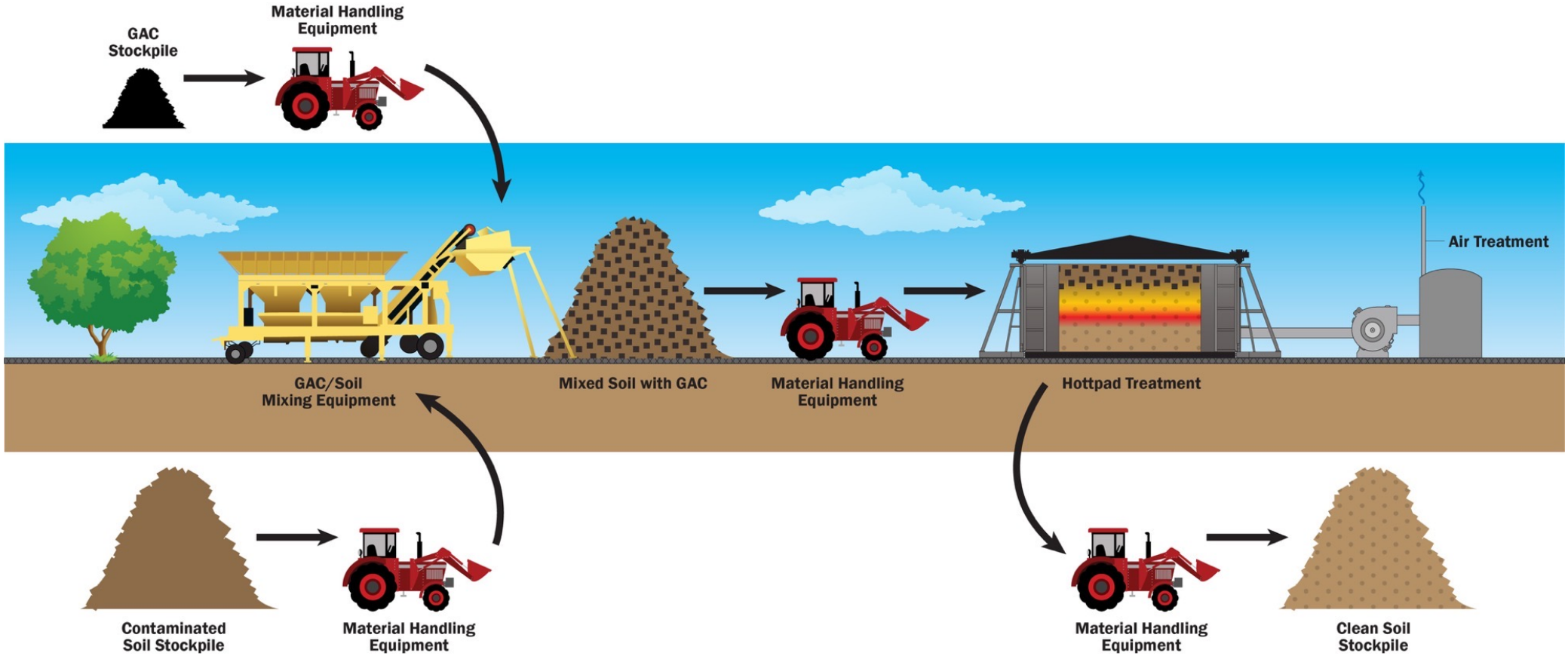
STARx: Soil and/or Waste GAC Treatment

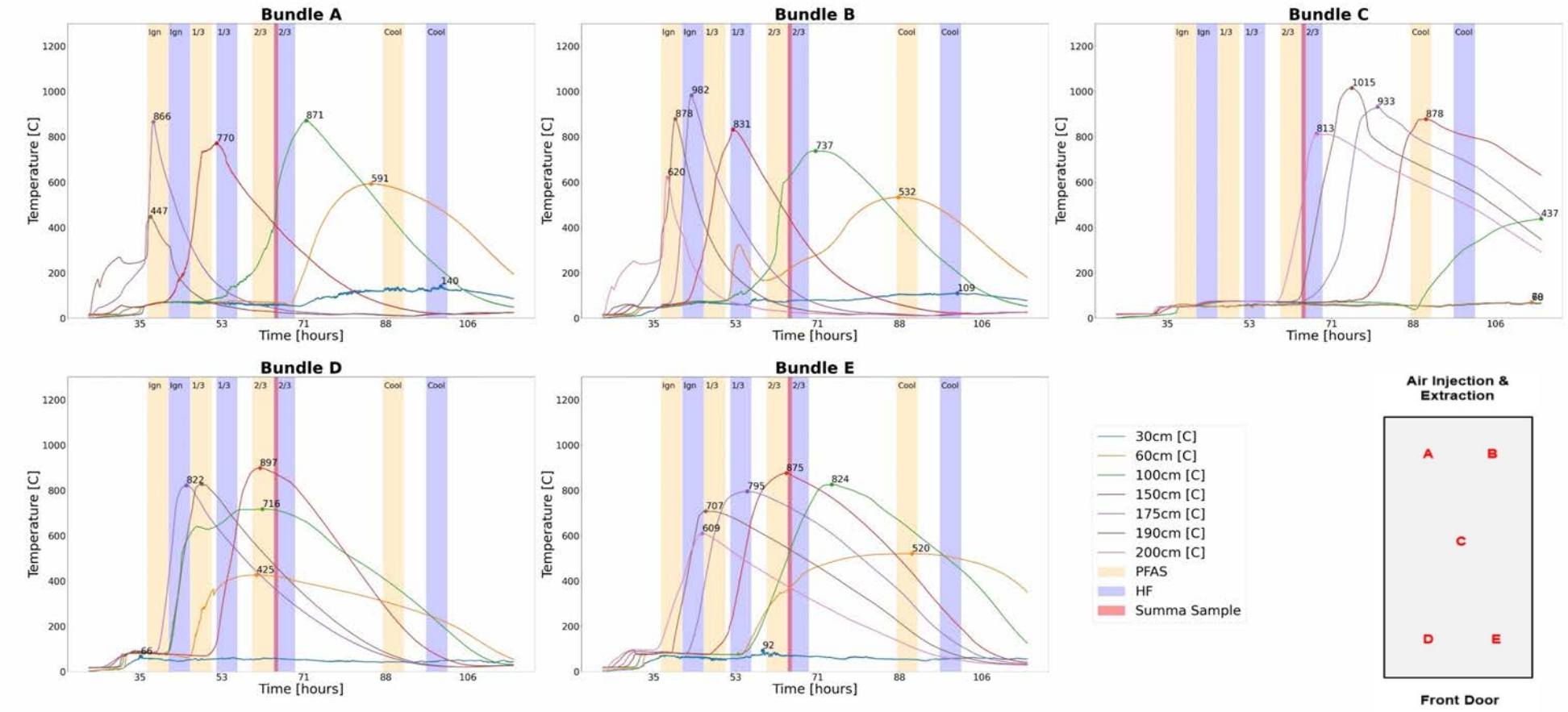


Pilot Test Set Up

Mixing / Loading

Unloading

Air Emission Sampling



Results

Analytical Method	Pilot Test 1					Pilot Test 2				
	Total PFAS Pre-Treatment (ppb)		Total PFAS Post-Treatment (ppb)		% Removed	Total PFAS Pre-Treatment (ppb)		Total PFAS Post-Treatment (ppb)		% Removed
	Average	Std Dev	Average	Std Dev		Average	Std Dev	Average	Std Dev	
LC/MS	2589 (1647)	421 (271)	1.9 (1.2)	4.4 (2.9)	99.915%	2742 (1740)	511 (327)	0.03 (0.02)	0.2 (0.1)	99.999%
TOPA	5230 (3400)	1140 (740)	3.5 (2.3)	1.3 (0.8)	99.933%	9295 (6050)	2599 (1690)	0.5 (0.3)	0.2 (0.1)	99.995%
TOF	2000	283	B.D.L	NA		2300	141	B.D.L	NA	

Soil Results

- Summed PFAS (Bracketed numbers = organic fluorine equivalent)
- PFAS reduced to near or below detection limits
- >99.9% reduction
- Fluorine primarily retained as CaF_2

Emissions Results

- <0.2% of total fluorine emitted as PFAS
- <2% of total fluorine emitted as HF
- Fluorinated breakdown products can be captured via vapor-phase GAC

Suspect Screening Solinite Canister

Compound Name	GC Match	Chemical Formula	Concentration (ng/mL)		
			Lab Air (Blank)	Pilot #1	Pilot #2
3,3,4,4-Tetrafluorohexane	POOR	$C_6H_{10}F_4$	0.03	0.4	0.4
N-Benzamido-2-(heptafluoropropxy)-2,3,3,3-tetrafluoropropionamide	FAIR	$C_{13}H_7F_{11}N_2O_3$	0.03	0.9	0.5
Sebacic Acid, 2-bromo-4-fluorophenyl decyl ester	POOR	$C_{26}H_{40}BrFO_4$		14.6	
Isophthalic acid, 2-fluorophenyl tetradecyl ester	POOR	$C_{28}H_{37}FO_4$		0.1	
Propylphosphonic acid, fluoroanhydride, 4-methylcyclohexyl ester	POOR	$C_{10}H_{20}FO_2P$	0.15	0.3	0.8
2-[(4-Fluorophenyl)methyl]-5-([(3-methoxyphenyl)amino]methyl)-2,3-dihydro-1H-1,2,4-triazol-3-1	POOR	$C_{17}H_{17}FN_4O_2$	1.22	15.2	29.1

- perfluroheptane reference standard
- All POOR or FAIR match
  - Minimum Match Factor (SI) and Reverse Match Factor (RSI) score of 500
- Not detected in GAC sorbent tubes

Pilot Test Key Results

Soil Results

- **>99.9% removal** to near or below detection limits of targeted analytes
- Confirmed **fluorine sequestered** in soil as CaF_2

Emissions Results

- **<0.2% of total fluorine** emitted as PFAS
- **~1%** of total organic fluorine emitted **as HF**
- Air treatment by GAC

Other PFAS Projects

savronsolutions.com

STARxpress System

ESTCP Project Number : ER23-8373

savronsolutions.com

Challenge

Rapid On-Site Treatment

?

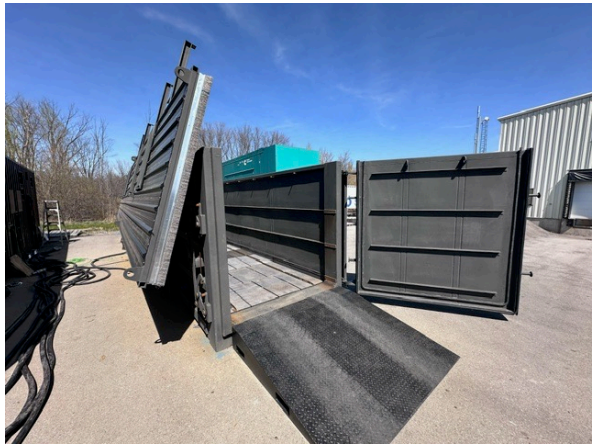
Pilot (10 m^3)

HP-250 (250 m^3)

Scalable Solutions

Challenge

Pilot (10 m^3)



STARxpress (35 m^3)

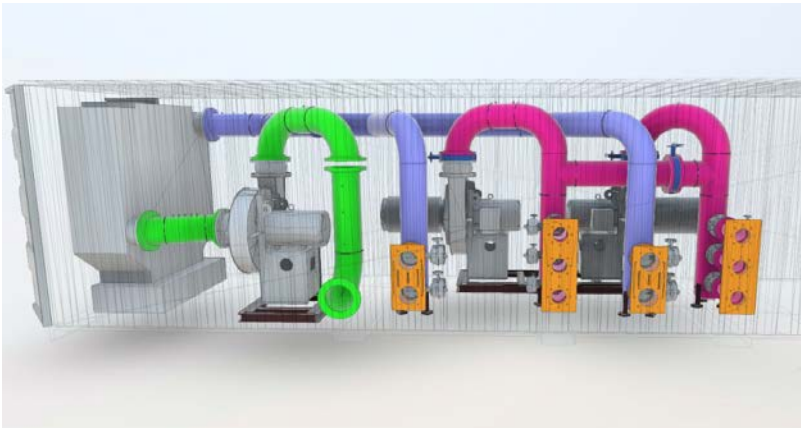
HP-250 (250 m^3)

Scalable Solutions

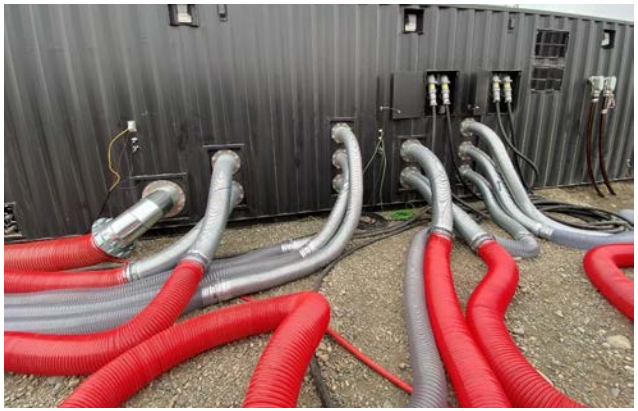
Test Site/Objectives

- Deploy at Joint Base Elmendorf-Richardson (JBER), AK
- Design / fabricate two rapidly deployable 35 m^3 ex situ full scale systems (STARxpress)
- Treat a minimum of 500 yd^3 of PFAS-impacted soil

Fabrication



Field Implementation



Field Implementation

Field Implementation

In Situ Treatment of PFAS and Co-Occurring Chemicals in Source Areas by Smoldering Combustion

ESTCP Project Number : ER22-7470

savronsolutions.com

Objective

- Develop and demonstrate an injectable fuel that supports smoldering combustion and generates sufficient energy to promote the destruction and volatilization of PFAS and co-contaminants

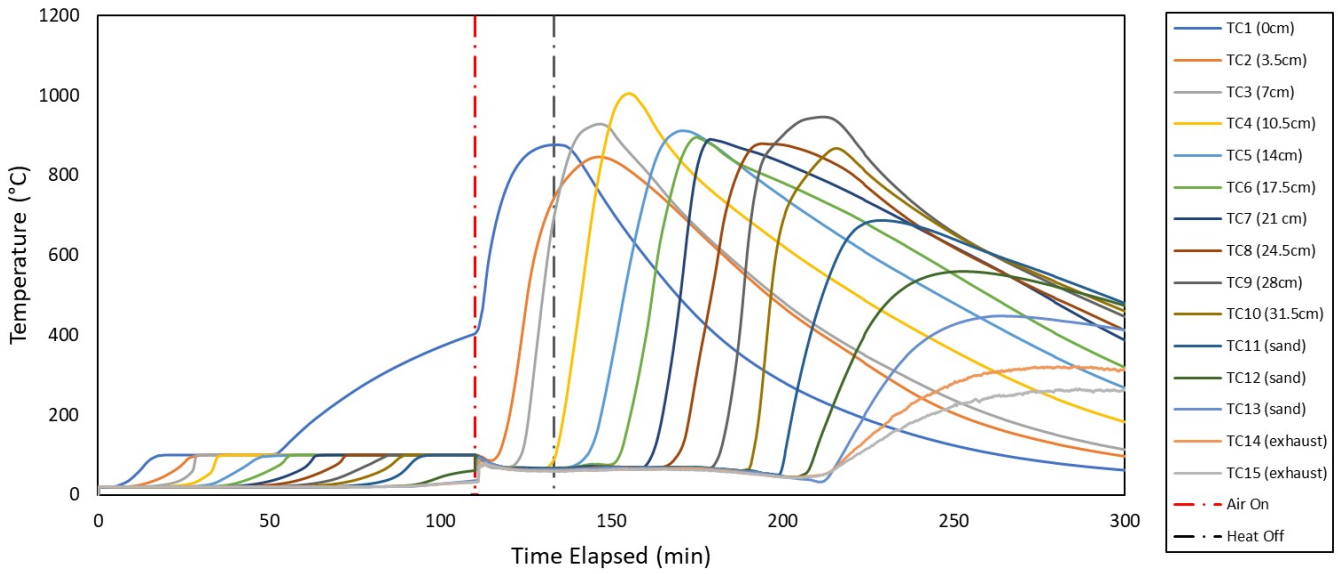
- Conduct field demonstration Joint Base Cape Cod, FTA-1
  - 500 m^3 source area soil volume

Considerations for Carbon Mixtures

- Cost
  - Relative cost of CAC/PAC/EVO products?
- Carbon and calcium content
  - Delivery provides sufficient carbon
- Ease of handling
  - Mixtures must be stable solutions
  - Surfactant cost-benefit
- Viscosity requirements for pumpability
  - <2200 centistokes (cSt mm^2/s)

Fuel Mixture Development/Testing

- CAC/EVO+ $Ca(OH)_2$ challenges
- Fluxsorb™ RP (PAC) + $Ca(OH)_2$ + H_2O

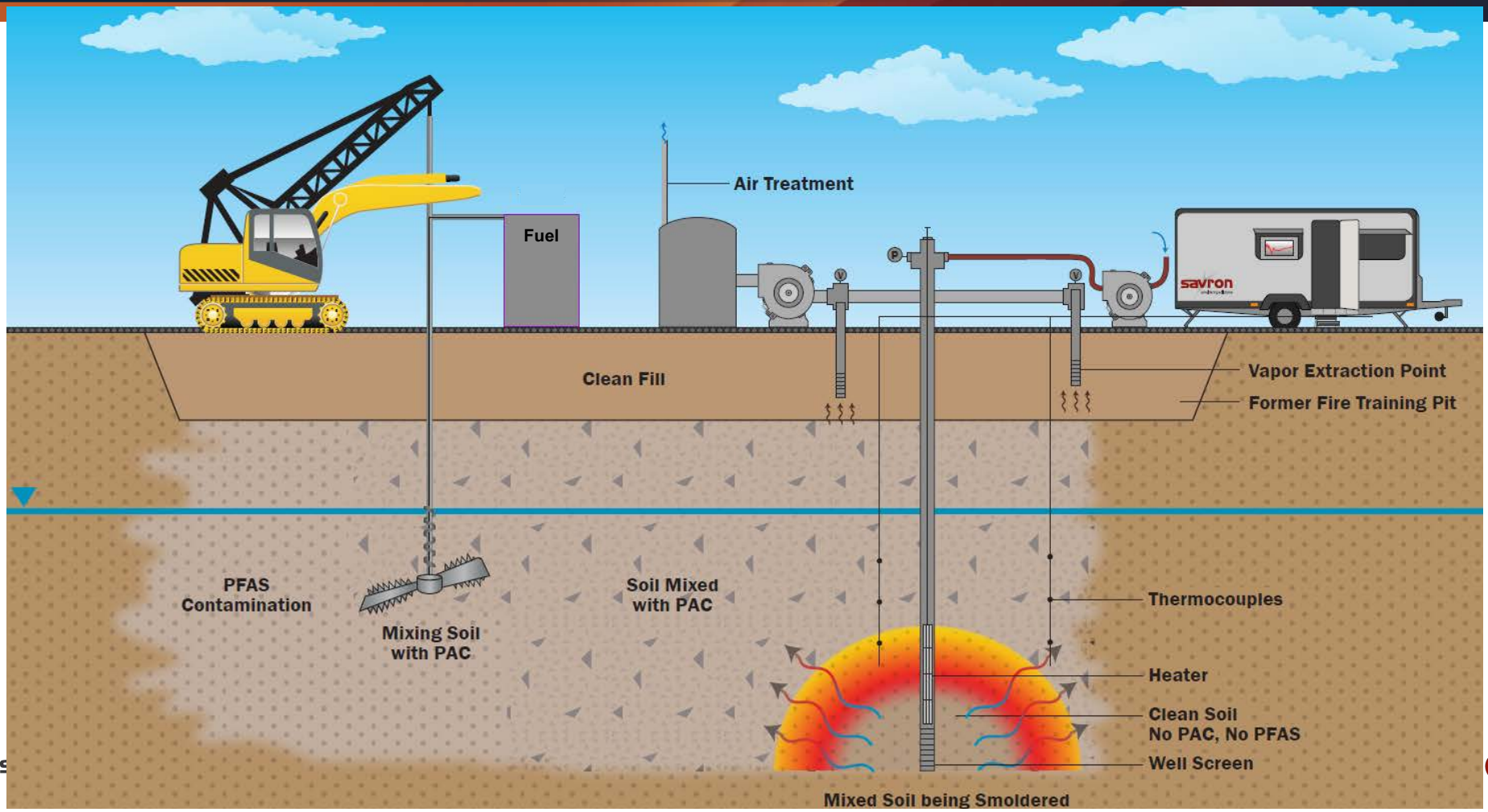


Next Steps

- Intermediate Scale Reactor (ISR) testing
  - Fluoride mass balance
  - Pre-and post treatment soil evaluation
- >99% reduction of PFOS/PFOA
  - Average pre-treatment soil concentration of PFOS and PFOA: 67.7 µg/kg
  - Average post-treatment soil concentrations of PFOS and PFOA: 0.1 µg/kg
- Awaiting analytical for emission samples
- Field demonstration this August

Savron's Intermediate Scale Reactor

Field Demonstration Setup



Summary

- **PFAS can be successfully destroyed using smoldering, leaving minimal treatment residuals**
  - Surrogate fuel is used to achieve high temperatures required for PFAS destruction
  - PFAS in post-treatment soils reduced to below regulatory criteria
  - <1% of total fluorine emitted as PFAS
  - CaO enhances PFAS destruction at lower temperatures and simplifies vapor treatment requirements
- **Co-treatment of contaminated GAC and soils increases net treatment**
- **Additional ex situ and in situ field demonstrations in progress**

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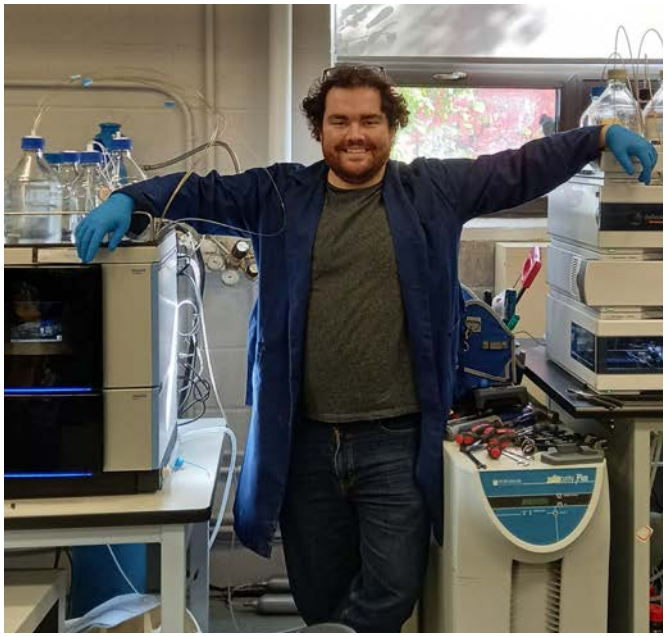

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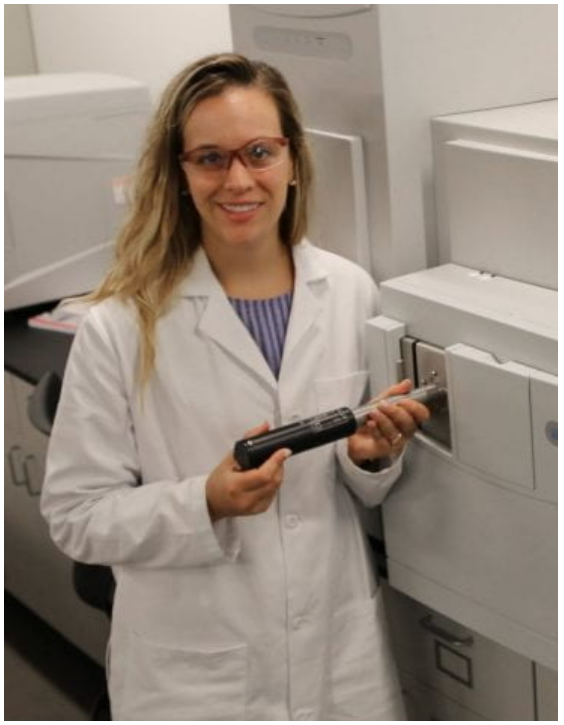

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