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A Smoldering Solution to PFAS

David Major, Ph.D., BCES

Managing Director

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25 YEARS OF ESTCP
SYMPOSIUM
2019 | Enhancing DoD's Mission Effectiveness

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Geosyntec consultants

TRUTH · DUTY · VALOUR

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Study Objective and Presentation Outline

- Demonstrate that smoldering combustion of supplementary fuels can destroy PFAS in soils or spent activate carbon (GAC)

- Background on smoldering combustion
- Overview of Testing & Experimental Set Up
- Results
- Potential Applications
- Benefit to DoD
- Summary & Future Work

What is Smoldering Combustion?

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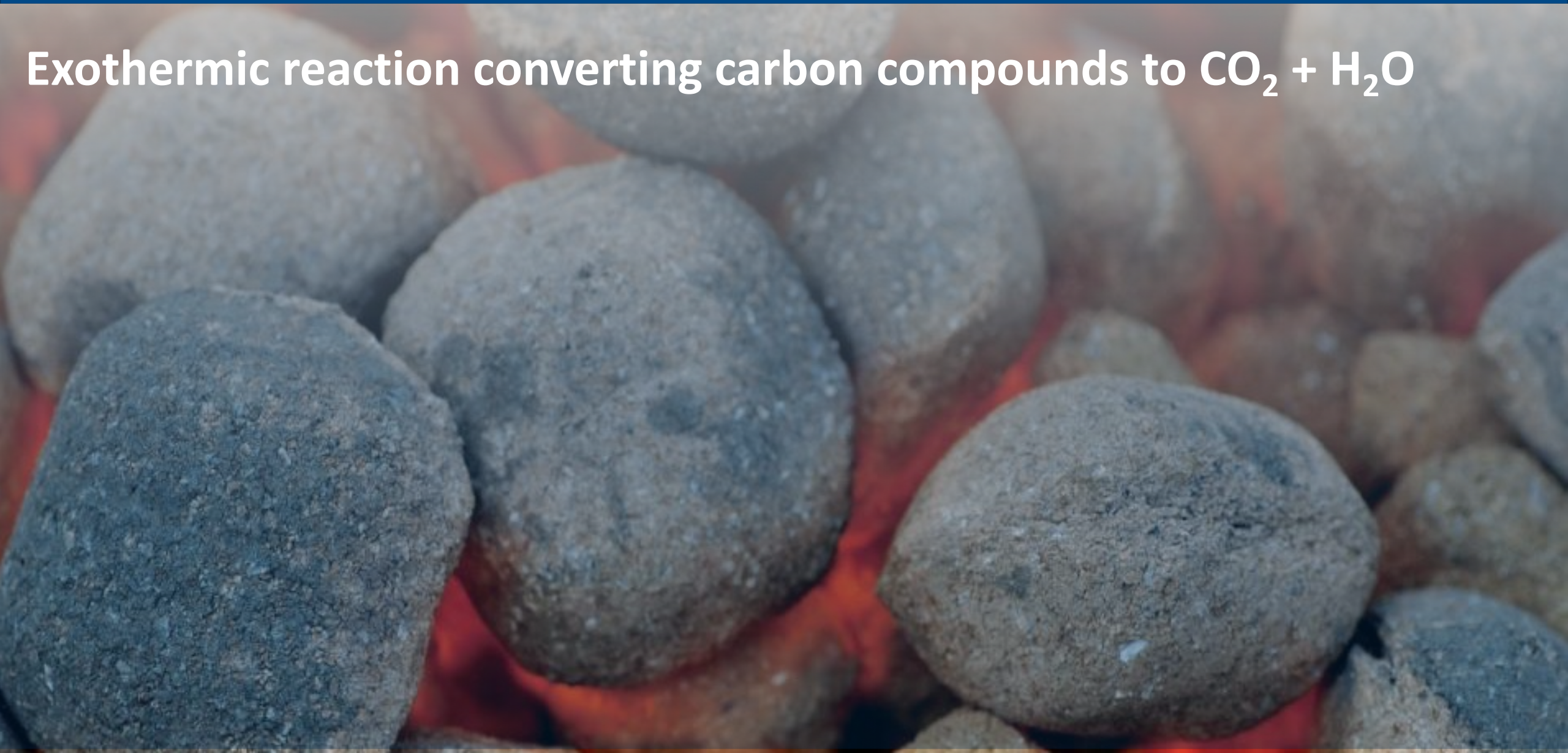

Exothermic reaction converting carbon compounds to $CO_2 + H_2O$

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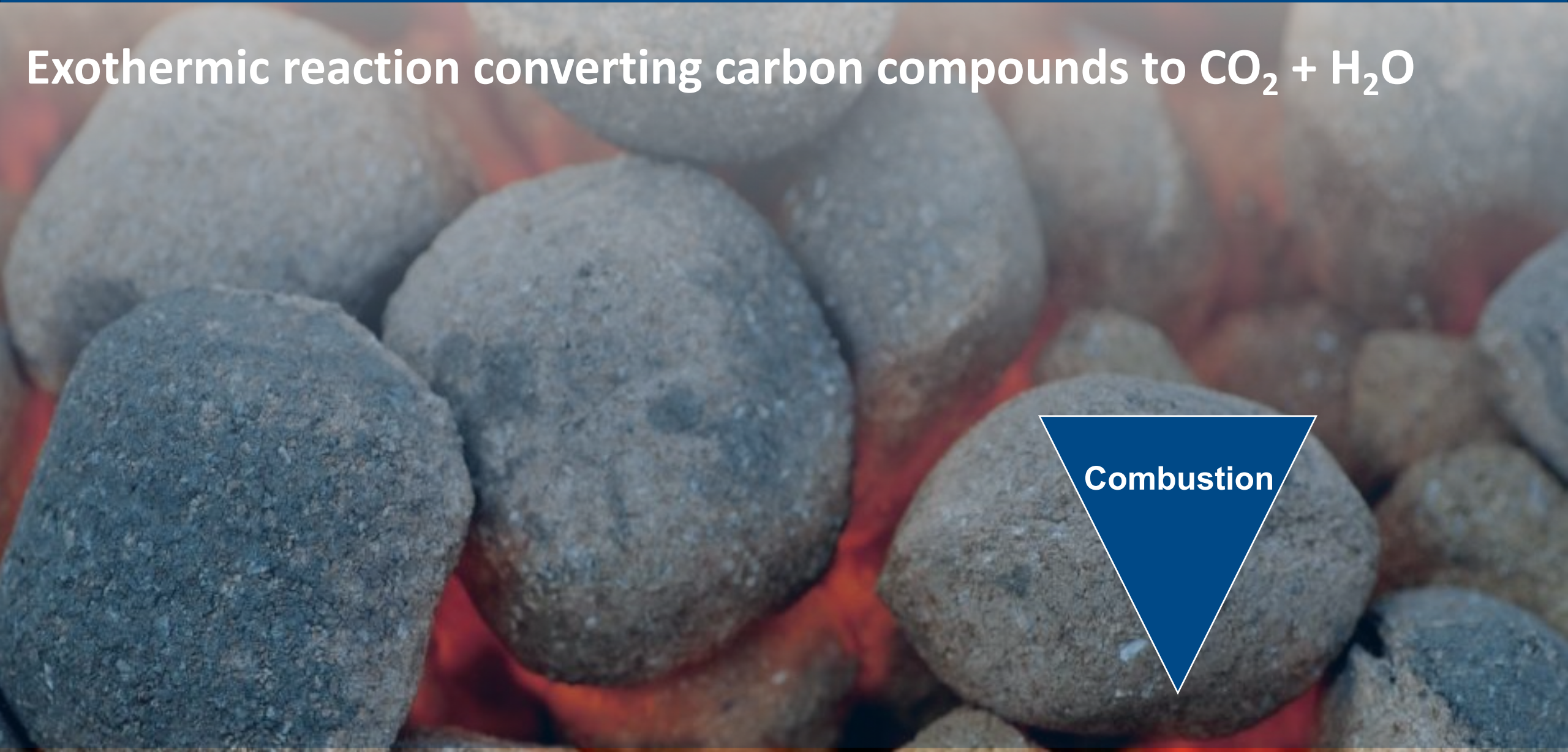

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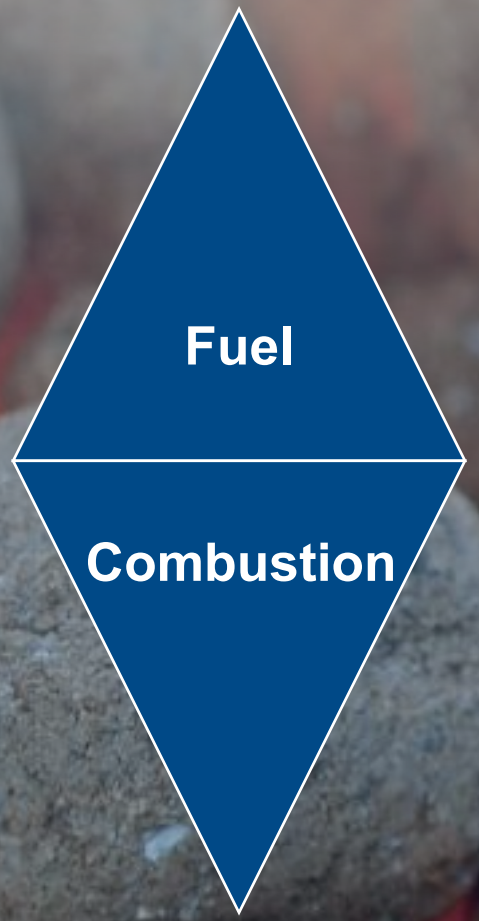

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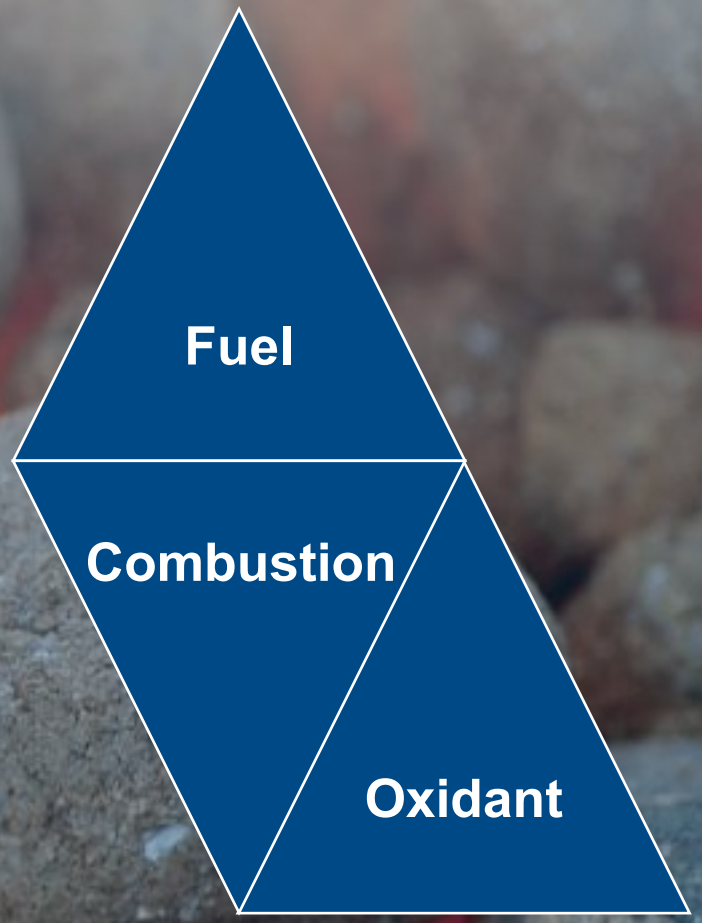

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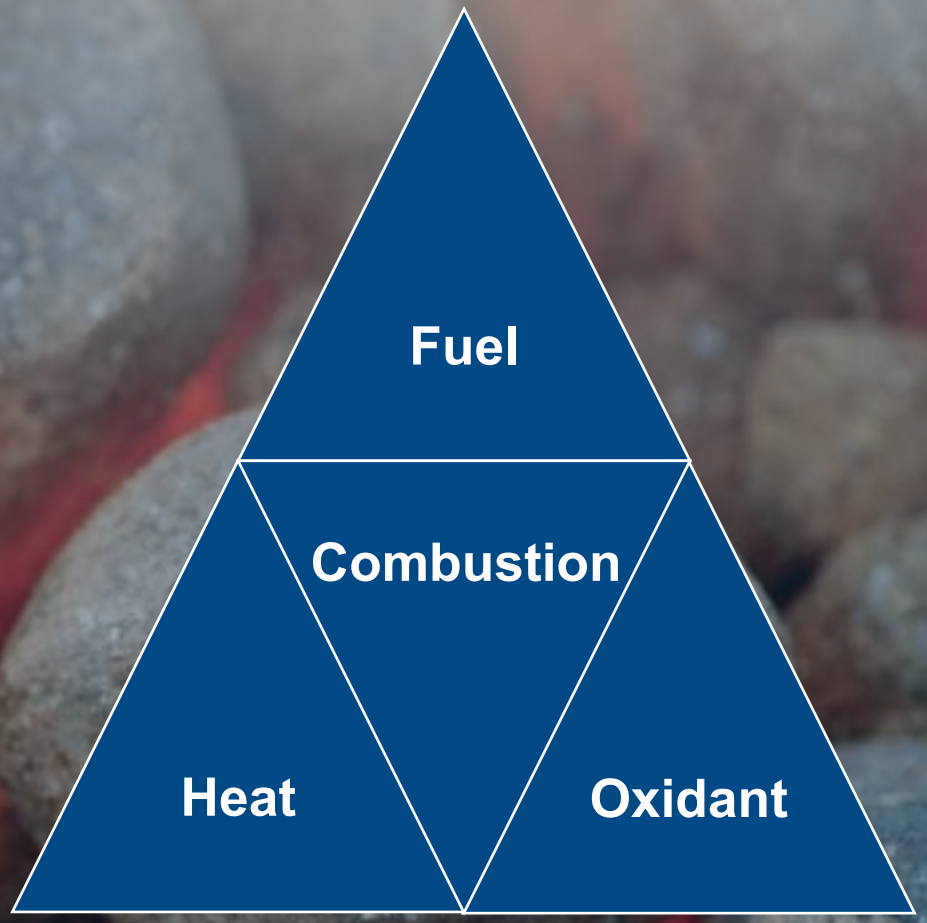

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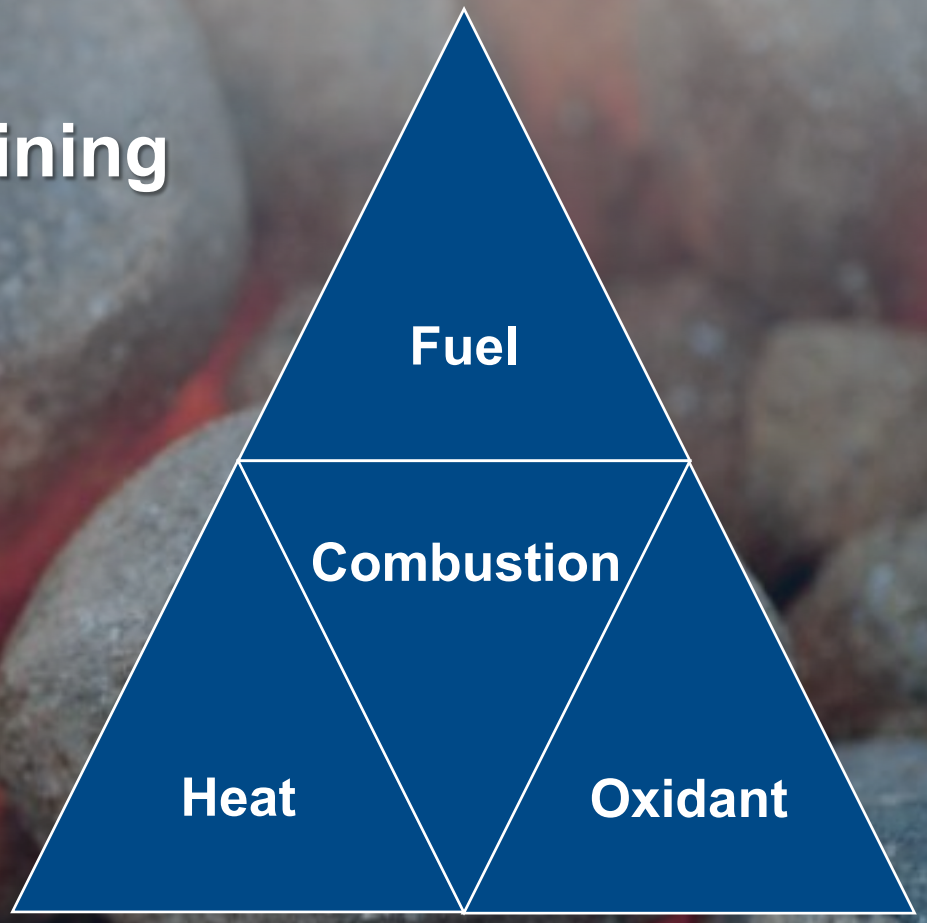
Exothermic reaction converting carbon compounds to $CO_2 + H_2O$

Smoldering Features

- Flameless, energy efficient/self-sustaining

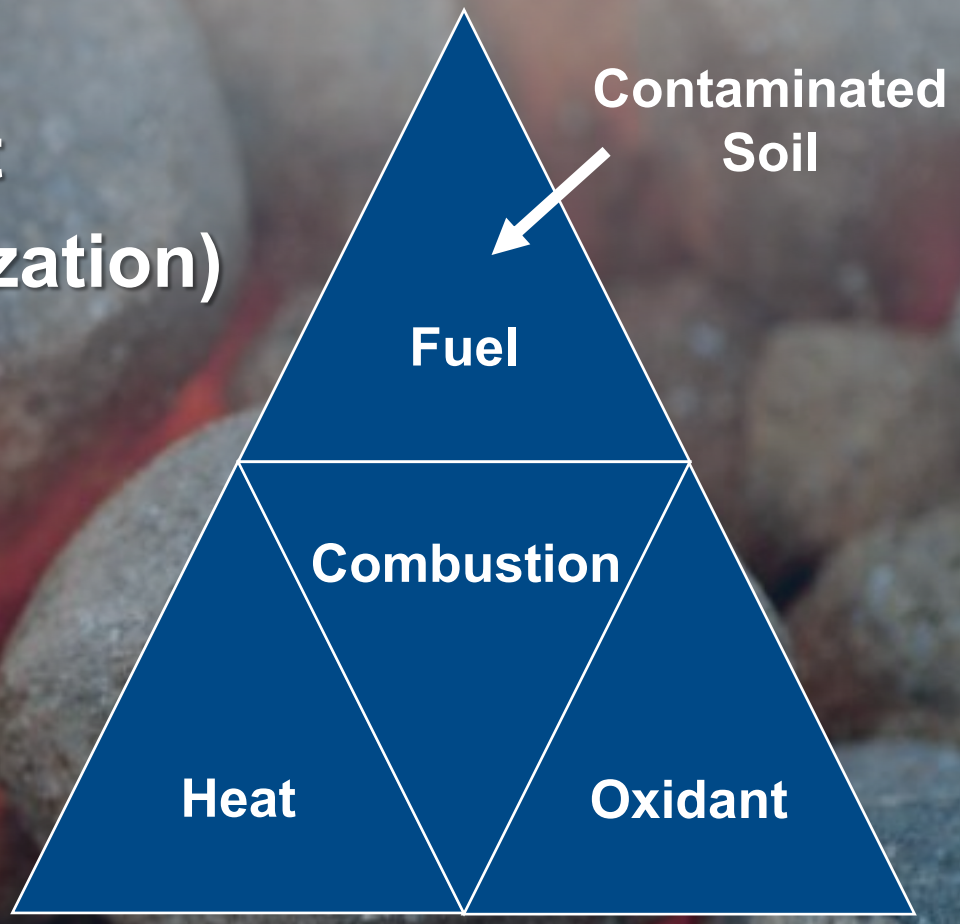


What is Smoldering Combustion?

Exothermic reaction converting carbon compounds to $CO_2 + H_2O$

STAR

- Process "powered" by contaminant
- Complete destruction (i.e., mineralization)



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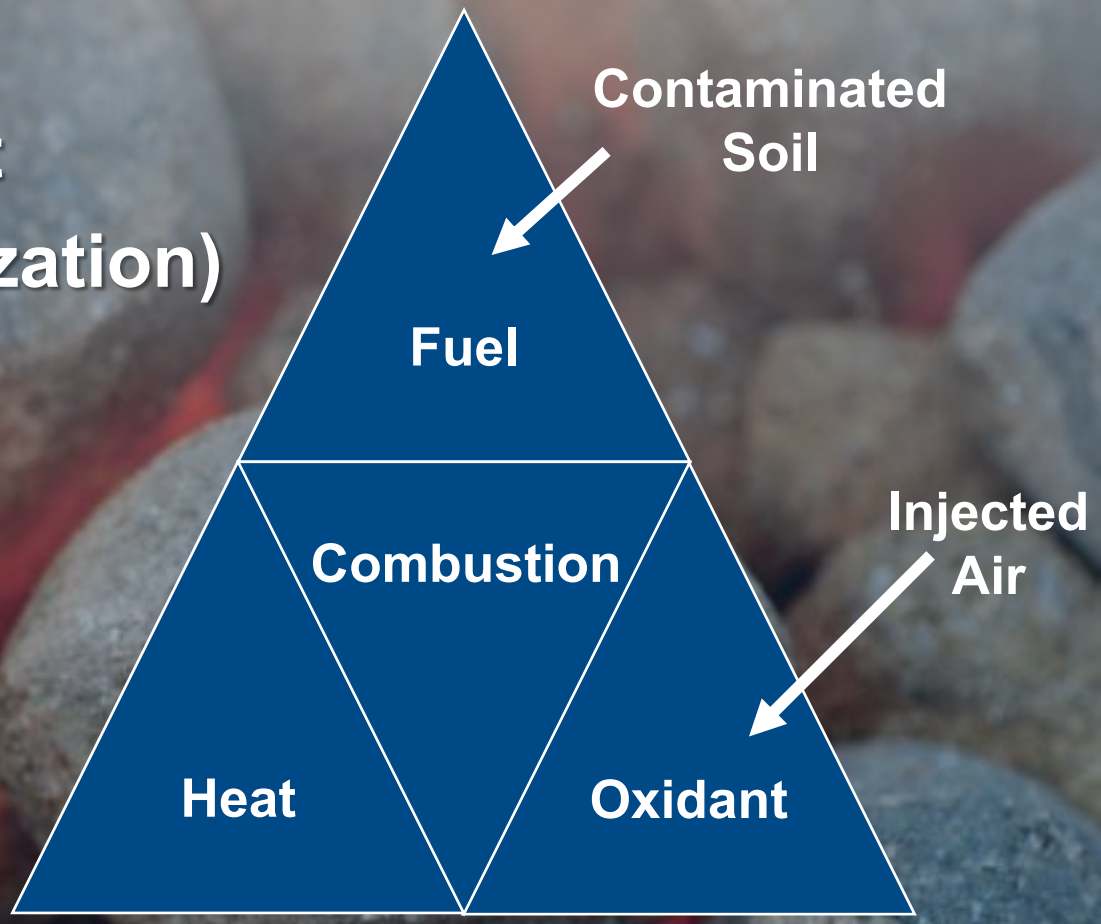

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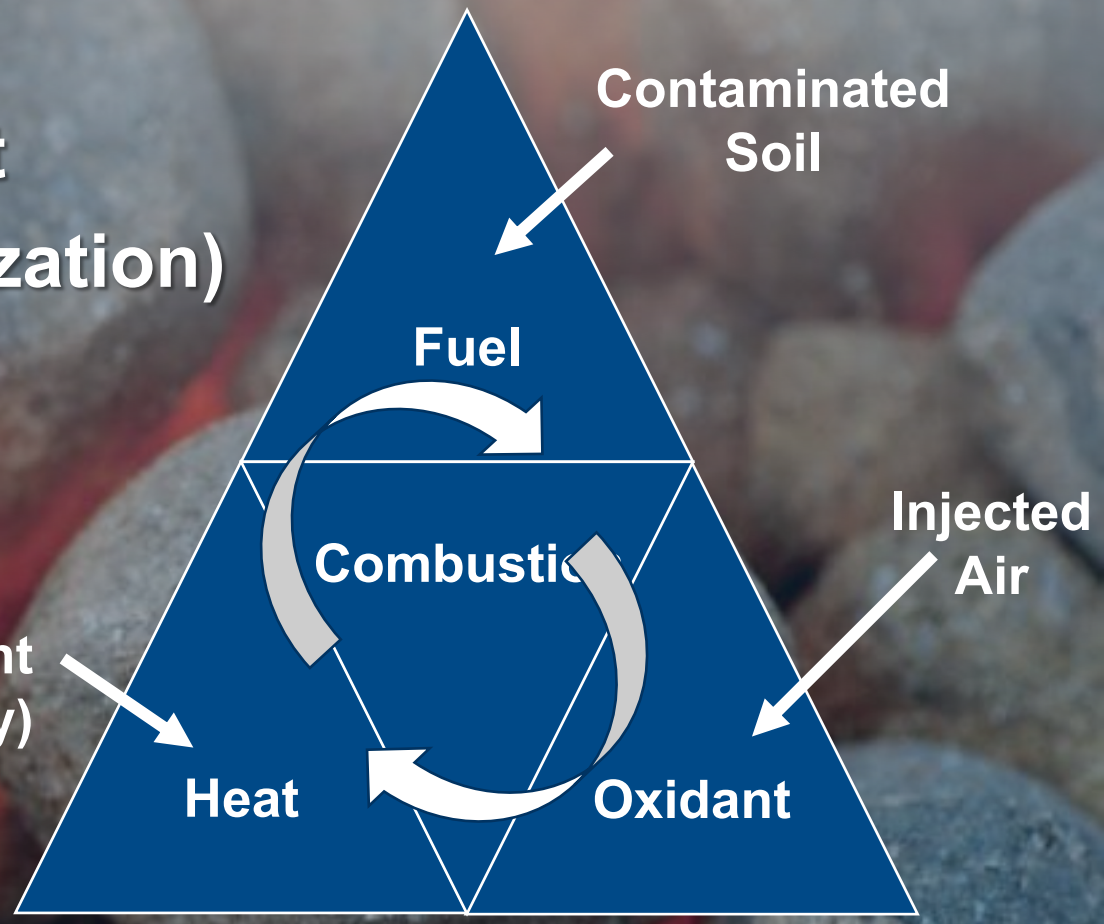
- Small input of energy



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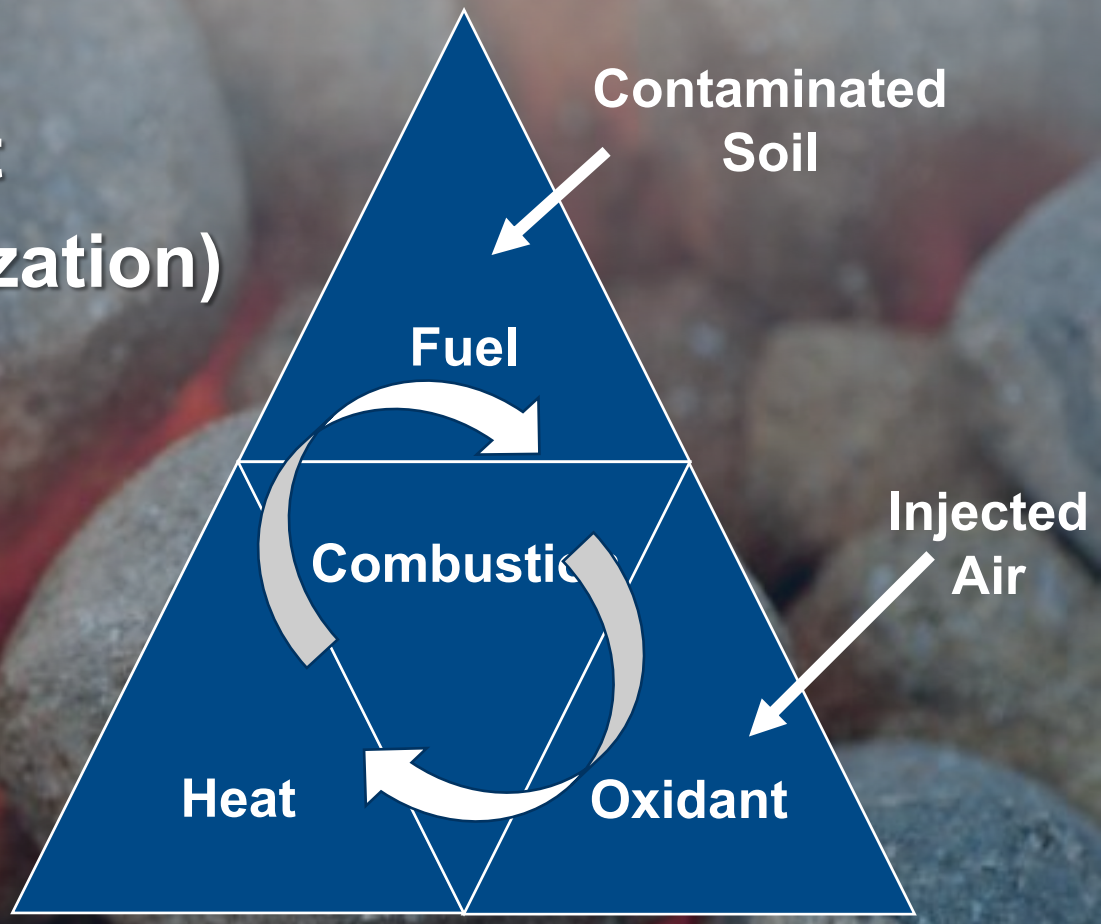
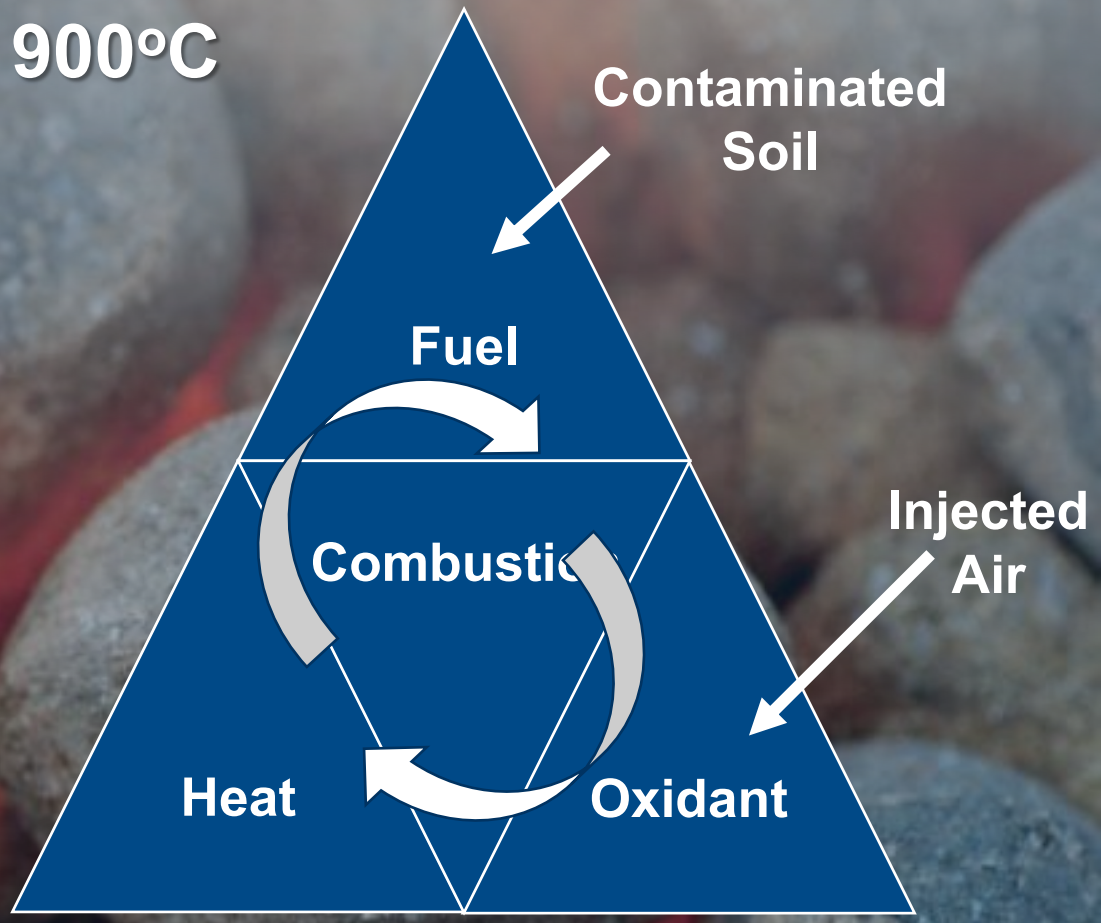
- Process "powered" by contaminant
- Complete destruction (i.e., mineralization)
- Oxidant via supplying air
- Small input of energy
- Self-sustaining



What is Smoldering Combustion?

Smoldering PFAS

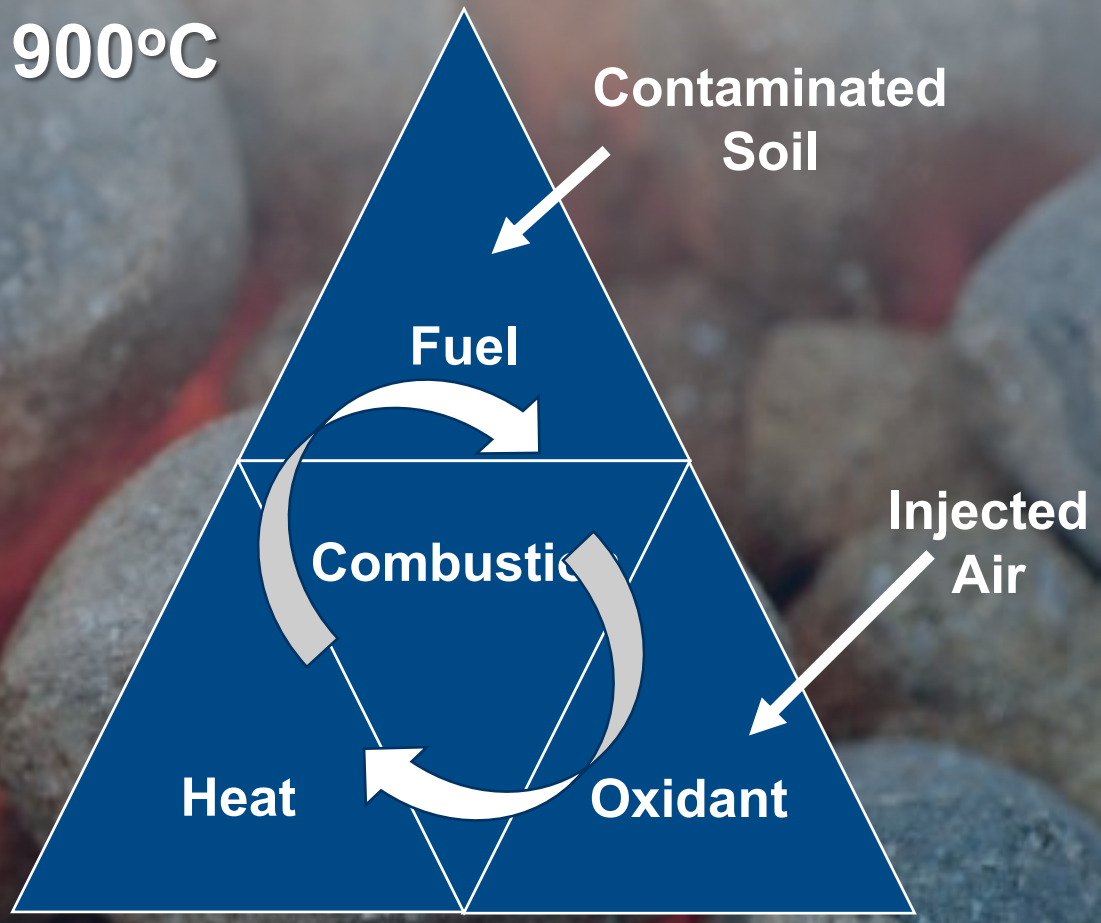
- PFAS mineralization to HF at Temp > 900°C
- PFAS not a smolderable fuel



What is Smoldering Combustion?

Smoldering PFAS

- PFAS mineralization to HF at Temp > 900°C
- PFAS not a smolderable fuel
- Requires a surrogate fuel



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Smoldering PFAS

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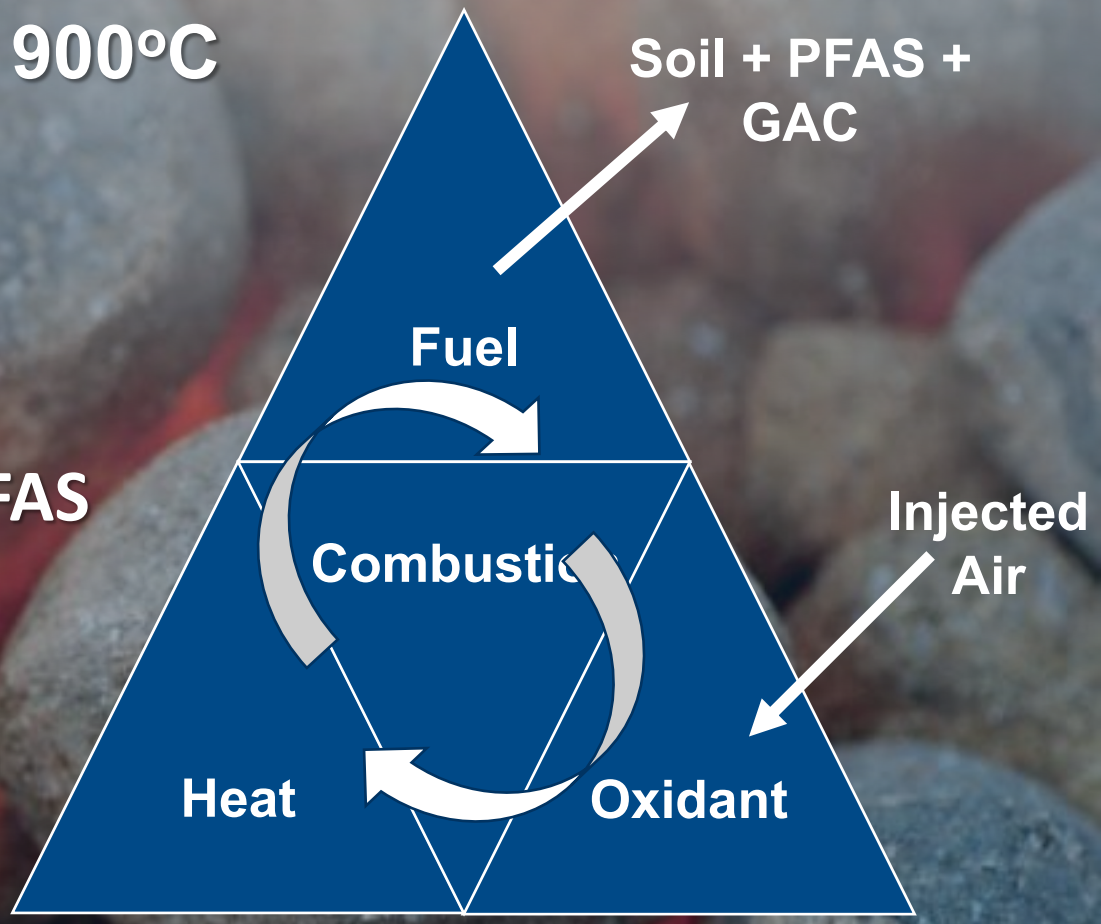
What About GAC?

- A potential waste product that contains PFAS

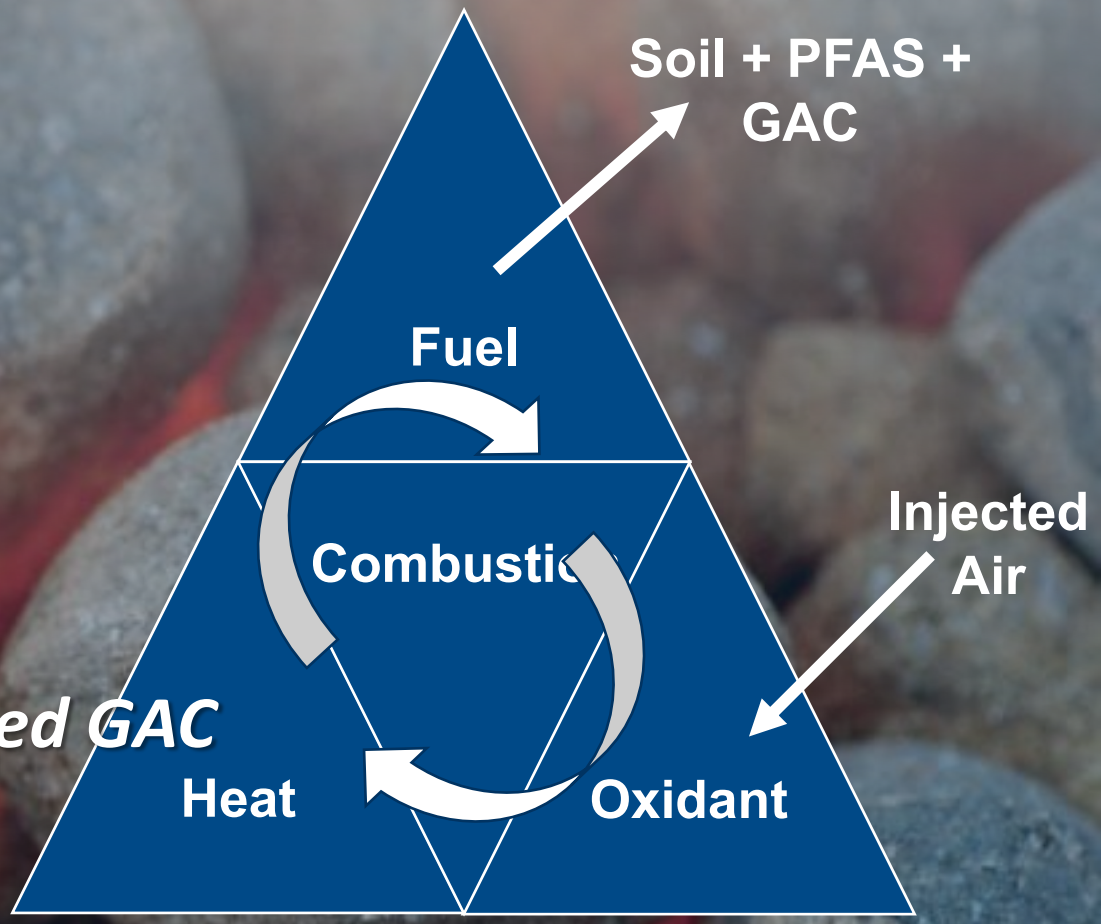


What is Smoldering Combustion?

Smoldering PFAS

Options

- <u>Smolder PFAS-impacted soil</u>
  - *Add GAC as surrogate fuel*
- <u>Smolder PFAS-impacted GAC</u>
  - *Add sand as inert porous matrix*
- <u>Co-treat</u>
  - *Mix PFAS-impacted soil and PFAS-impacted GAC*



Overview of Testing

GAC

Sand

Test 1

- Clean GAC/sand mixture

Key data

- Temperature/combustion gas profile over range of GAC/sand ratios

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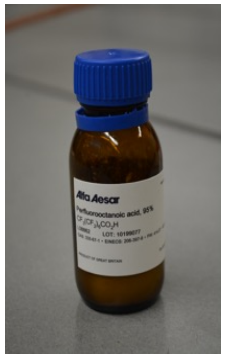
Overview of Testing

GAC

Sand

PFOA



VWR (95%)

PFOS

Sigma (≥ 98%)

PFHxS

Sigma (≥ 98%)

Tests 2 and 3

- PFAS adsorbed to GAG and mixed with clean sand

Key data

- Concentration of PFAS before and after smoldering

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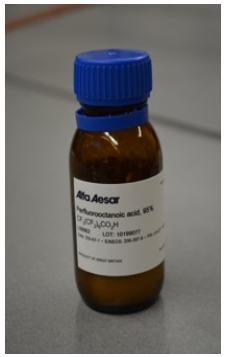
Overview of Testing

PFOA



VWR (95%)

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Sigma (≥ 98%)

PFHxS

Sigma (≥ 98%)

Test 4

- 3 PFAS adsorbed to surrogate soil and mixed with clean GAC

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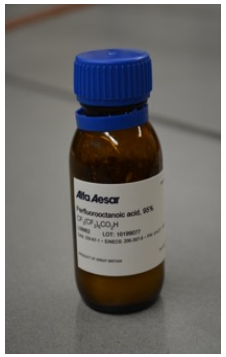
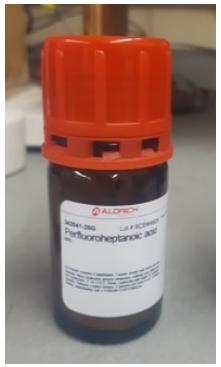
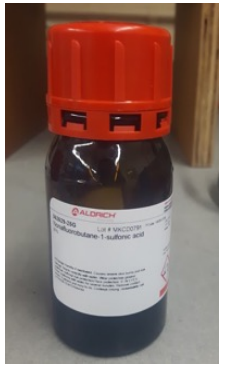
Overview of Testing

PFOA	PFOS	PFHxS
		
VWR (95%)	Sigma (≥ 98%)	Sigma (≥ 98%)
		
Sigma (97%)	Sigma (99%)	Sigma (99%)

Test 4

- 3 PFAS adsorbed to surrogate soil and mixed with clean GAC

Test 5

- PFAS adsorbed to surrogate soil and mixed with clean GAC

Key data

- Concentration of PFAS before and after smoldering
- HF and PFAS in emissions

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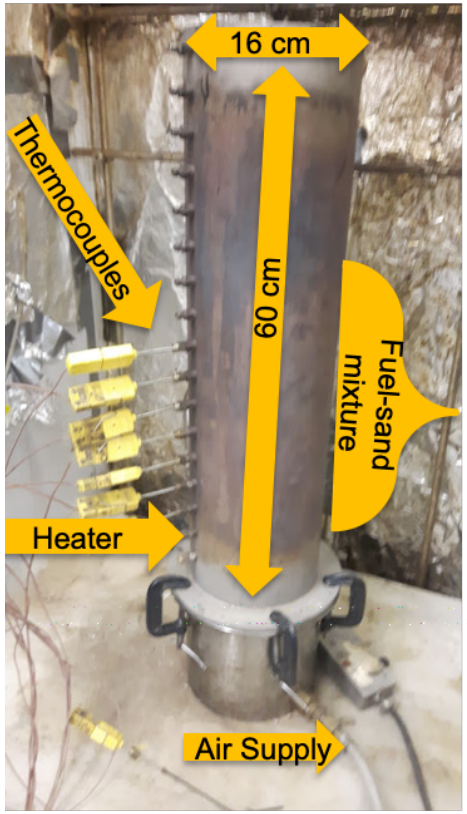
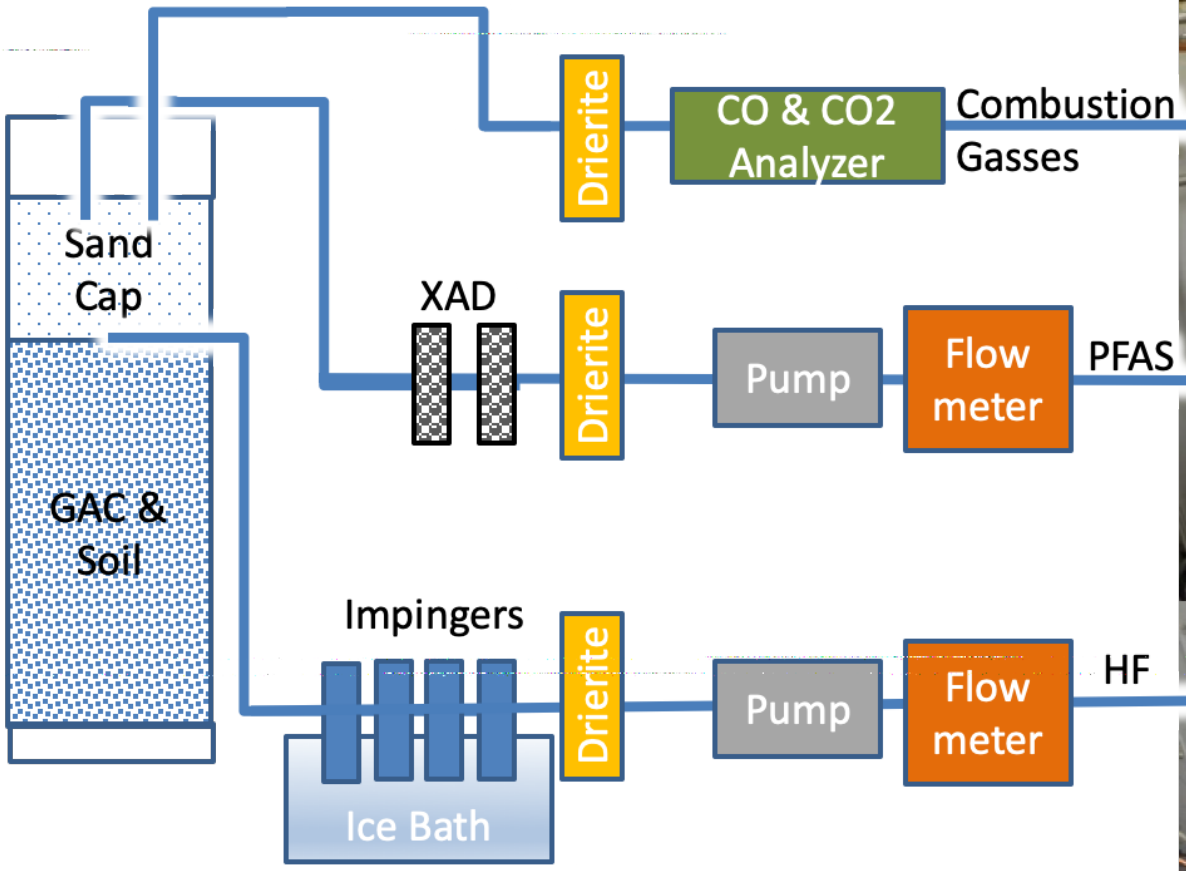
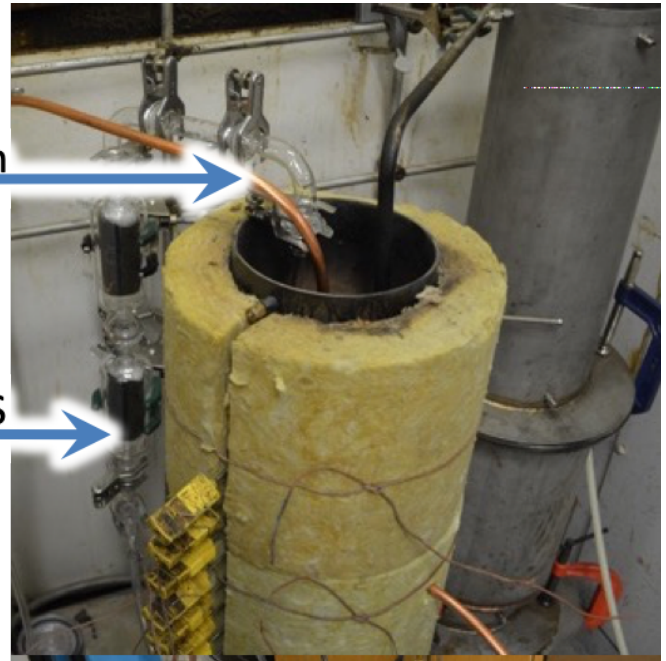
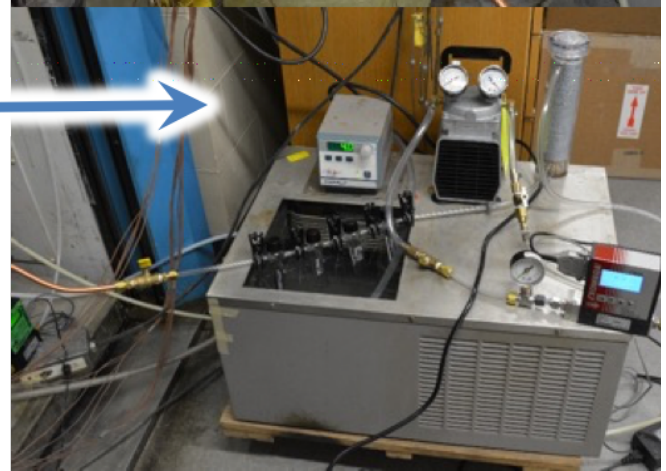
Experimental Setup









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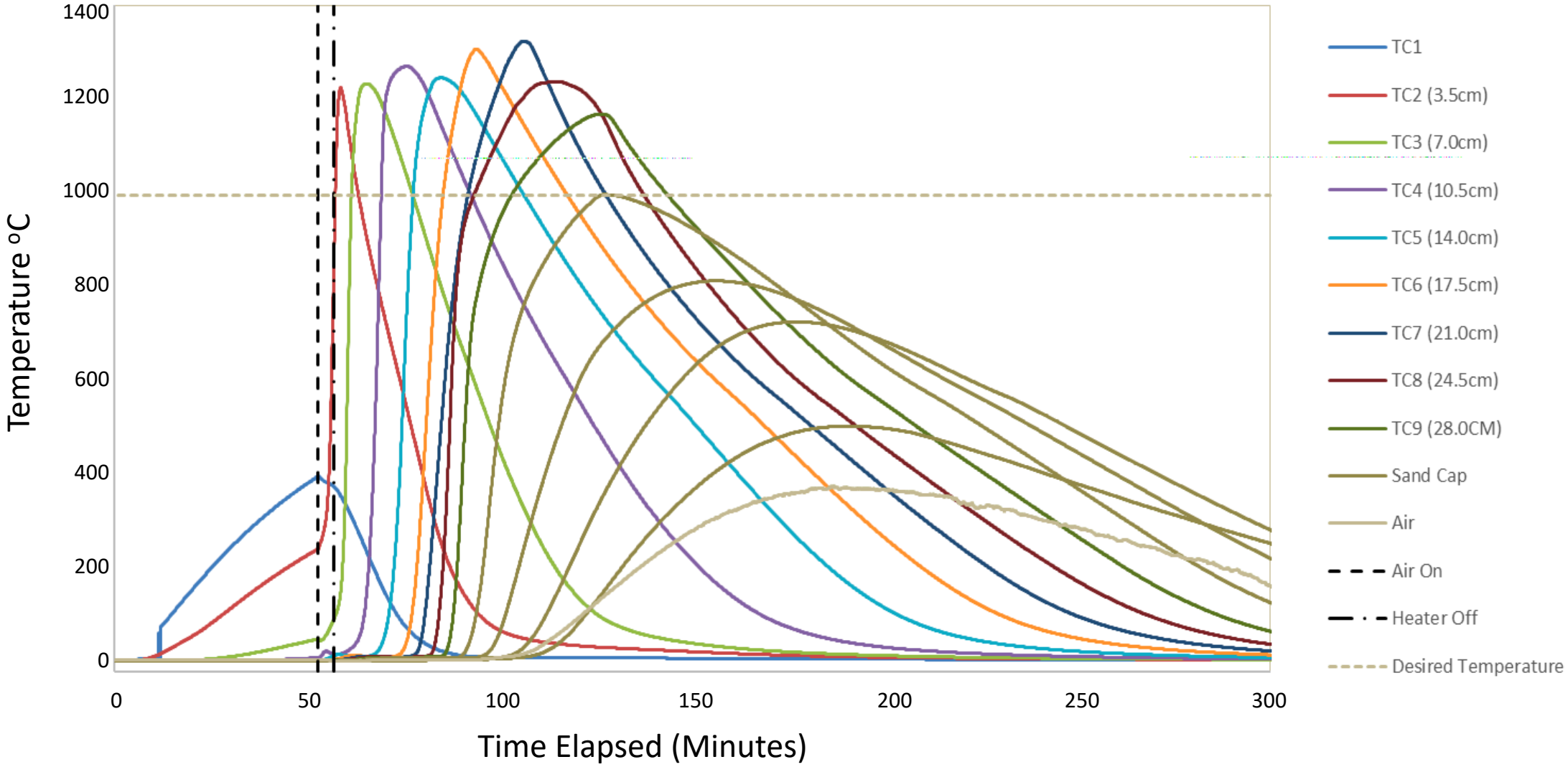
Test 1: Example GAC/Sand Run
60 g GAC/kg Sand, 5.0 cm/s Air Flux



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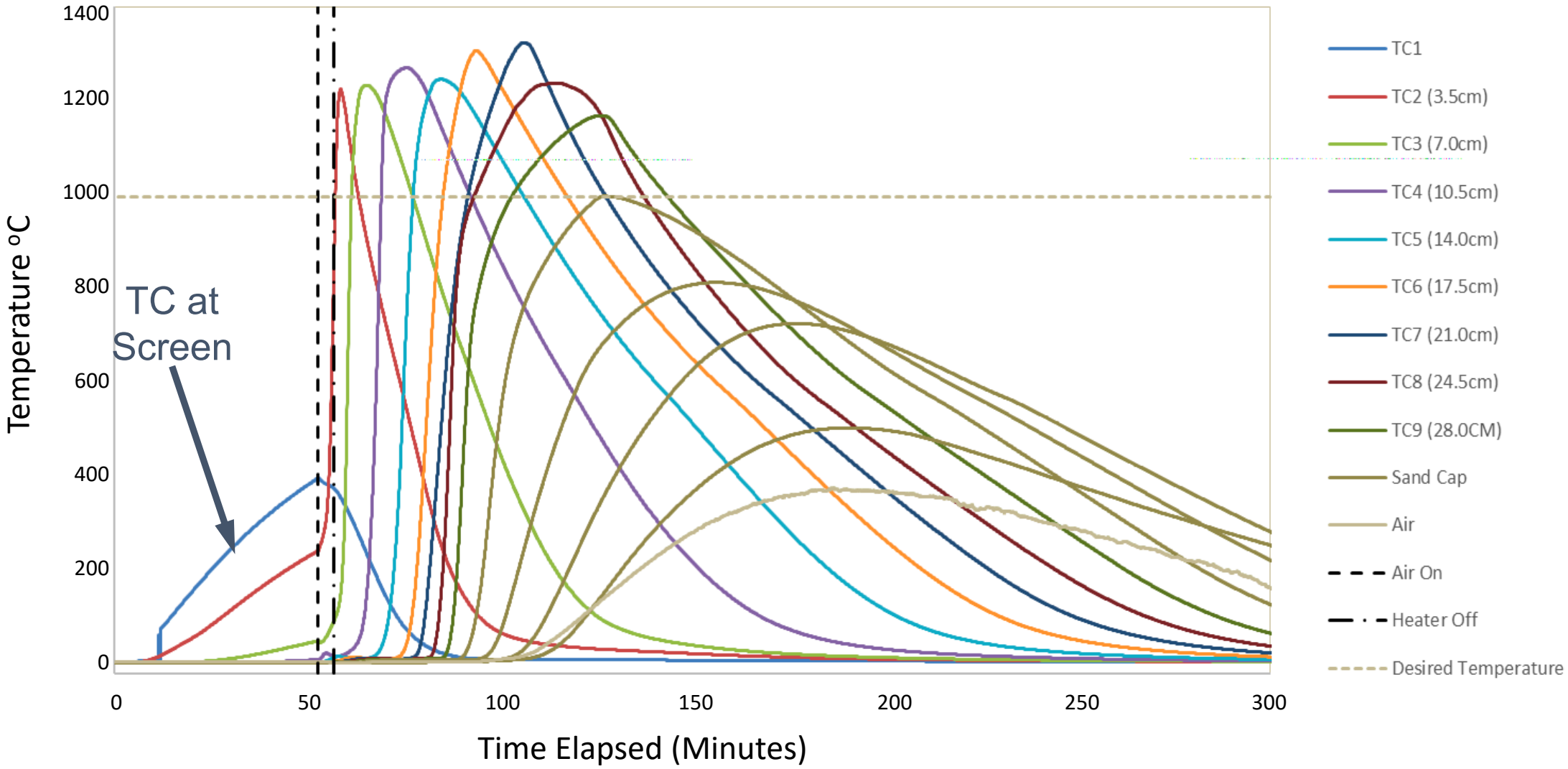

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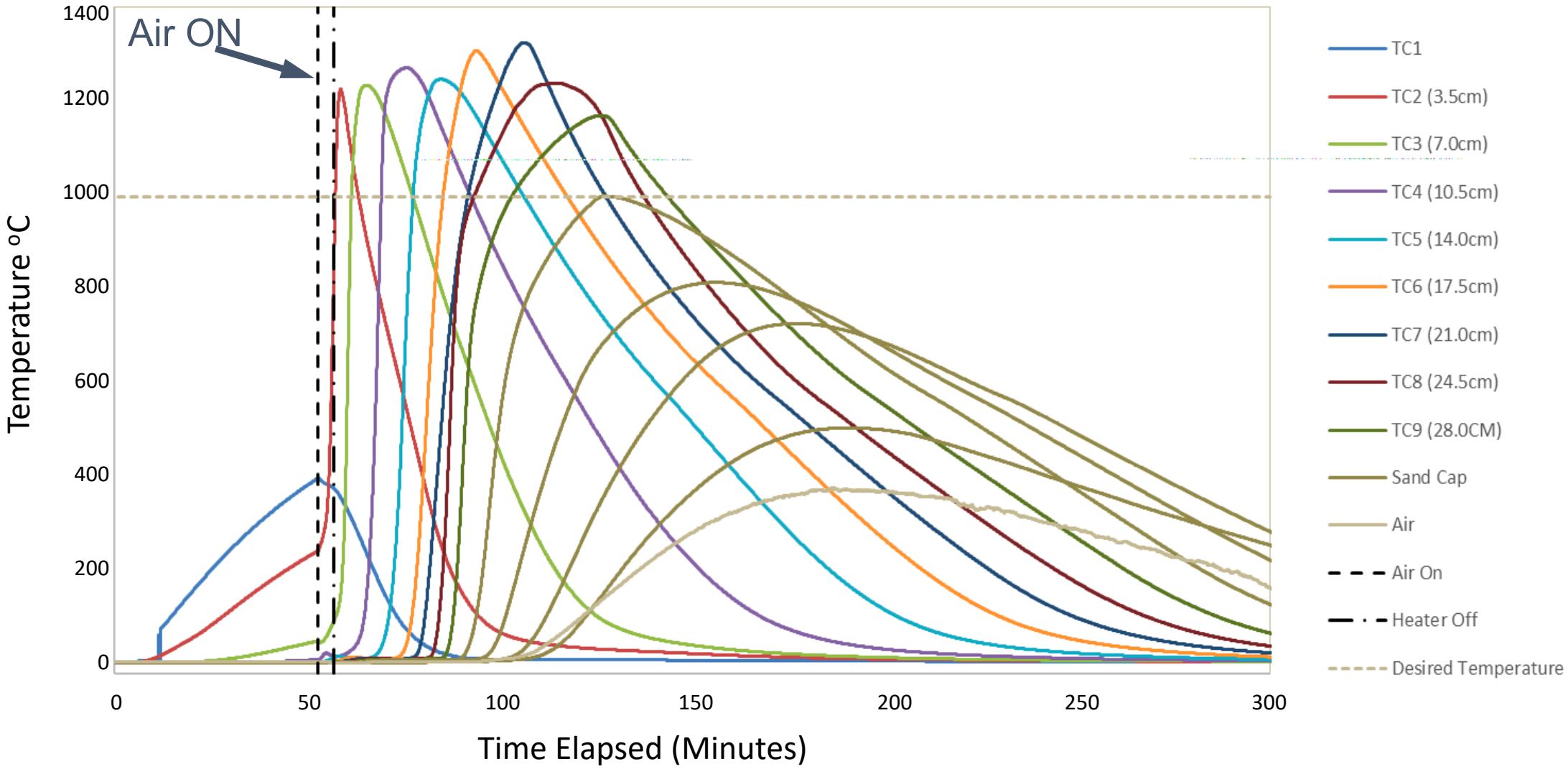

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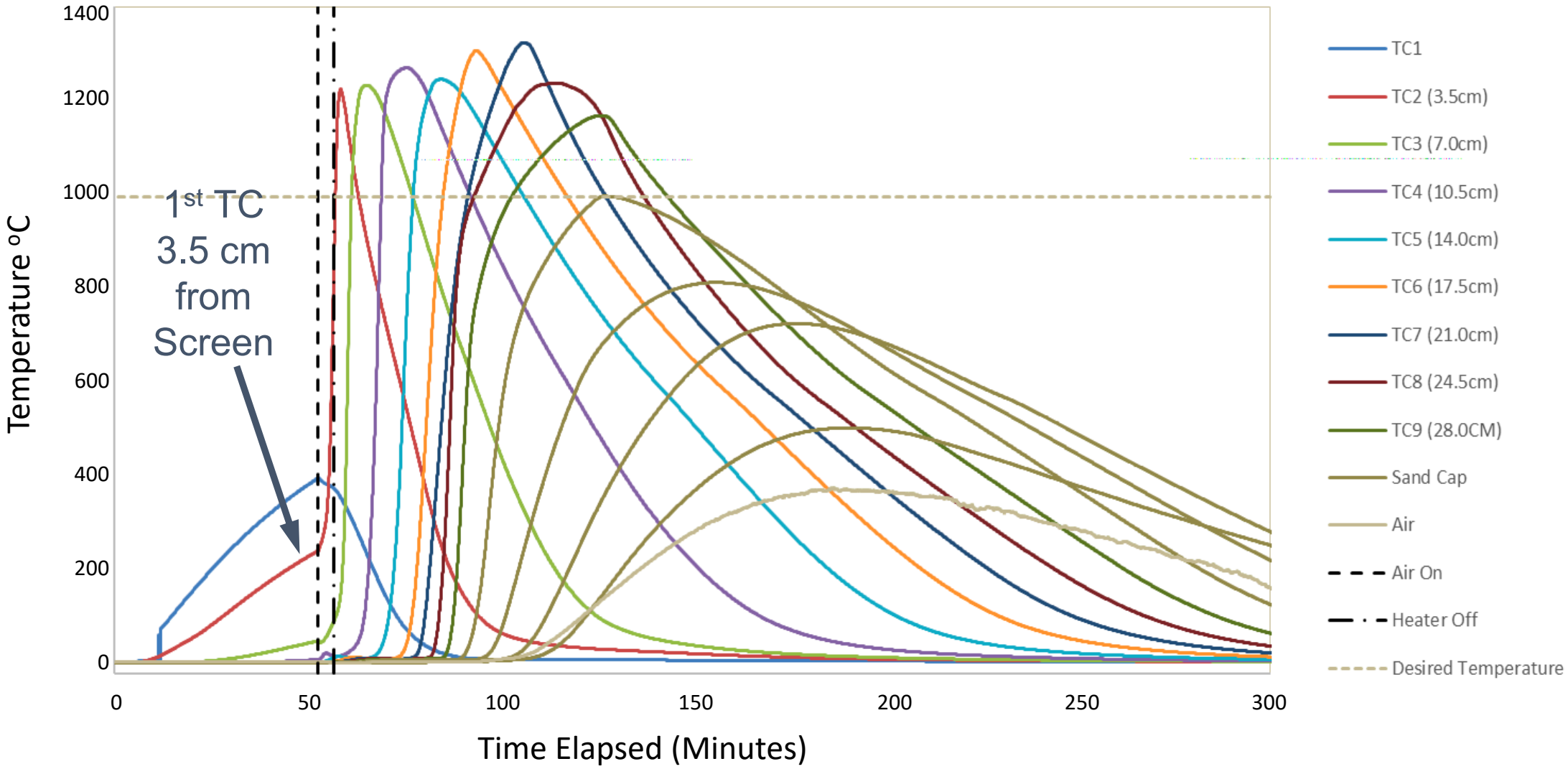

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TCP M

#SerdpEstcp2019

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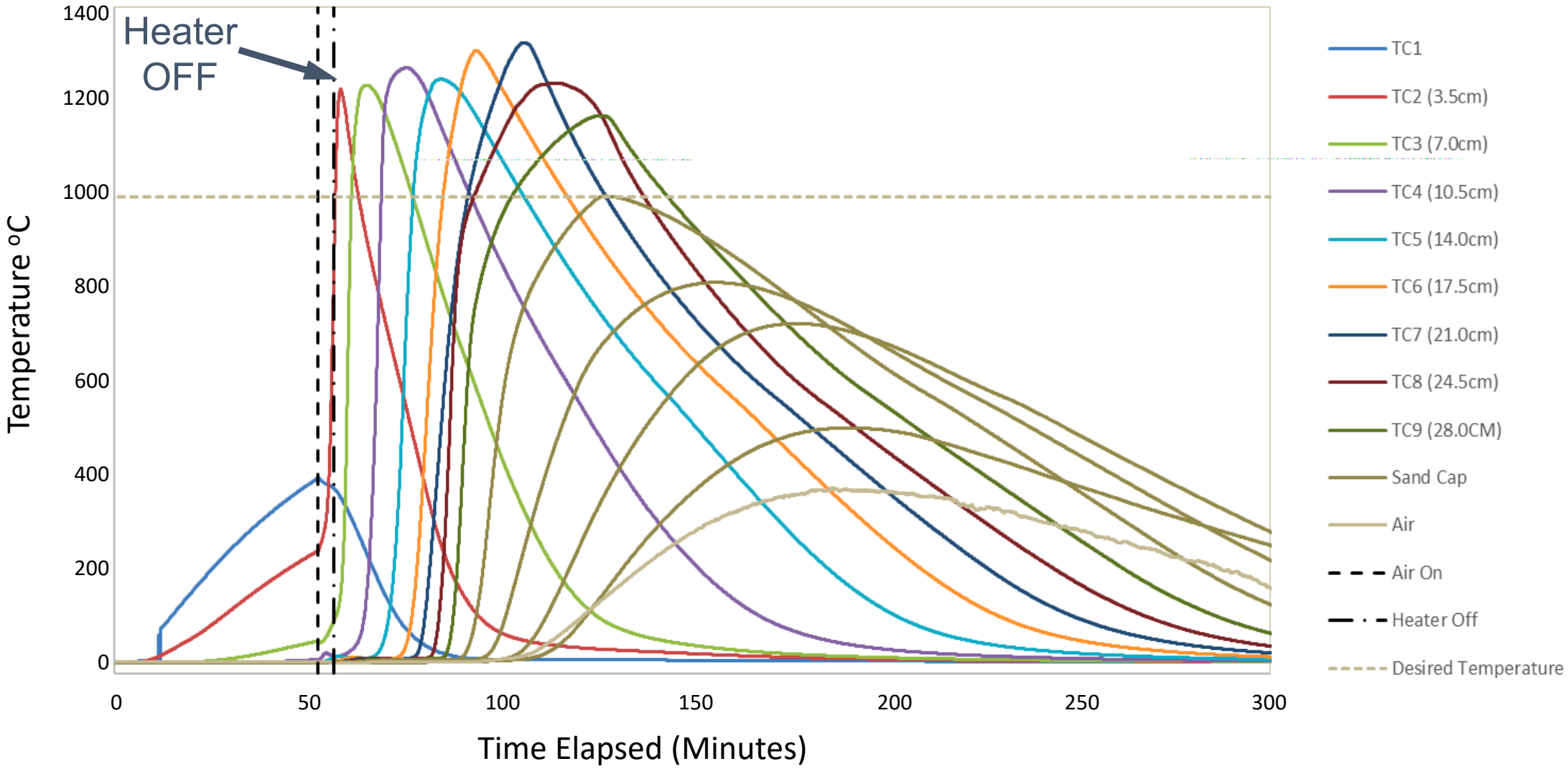

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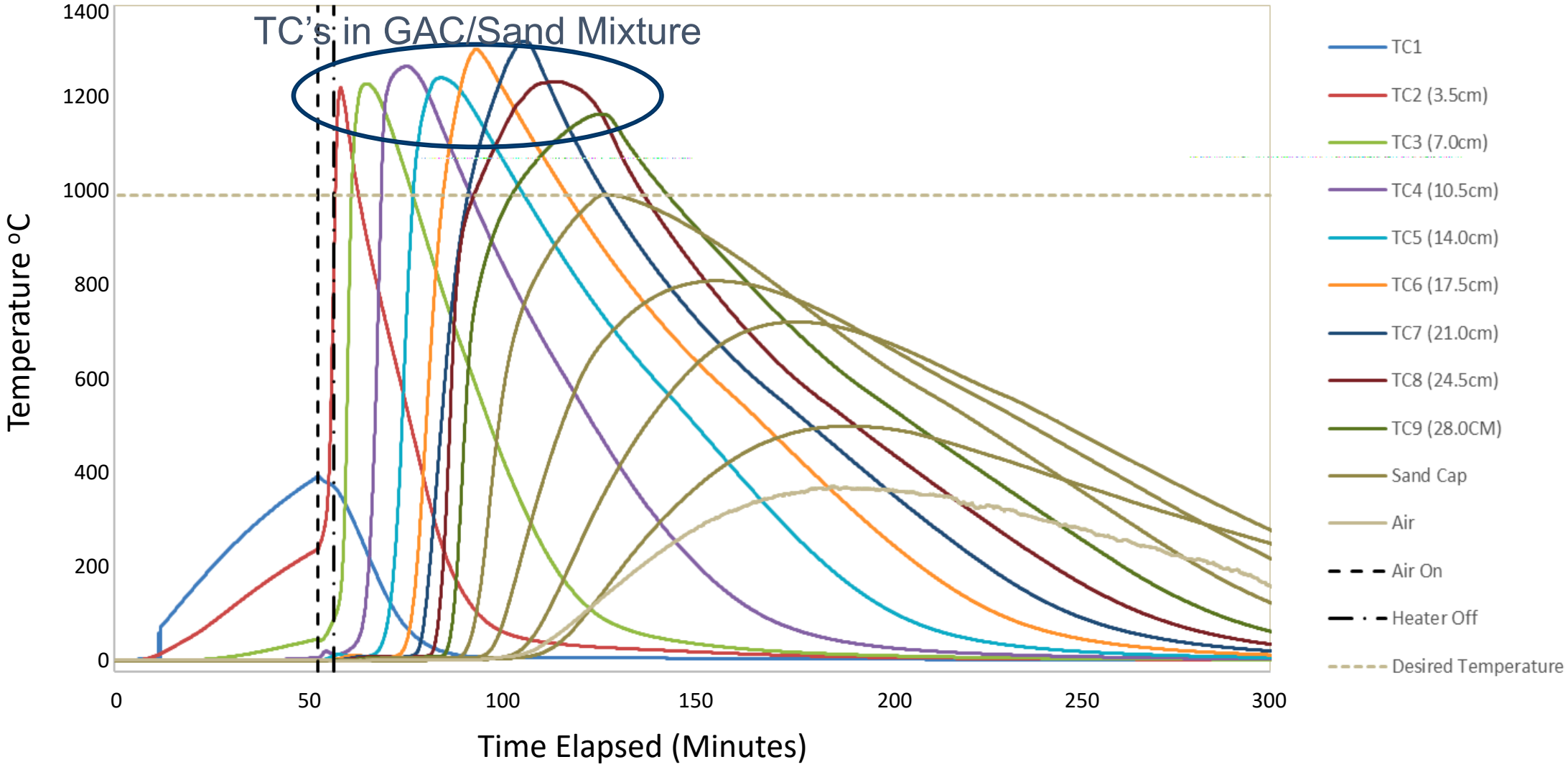

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#SERDP&ESTCP2019

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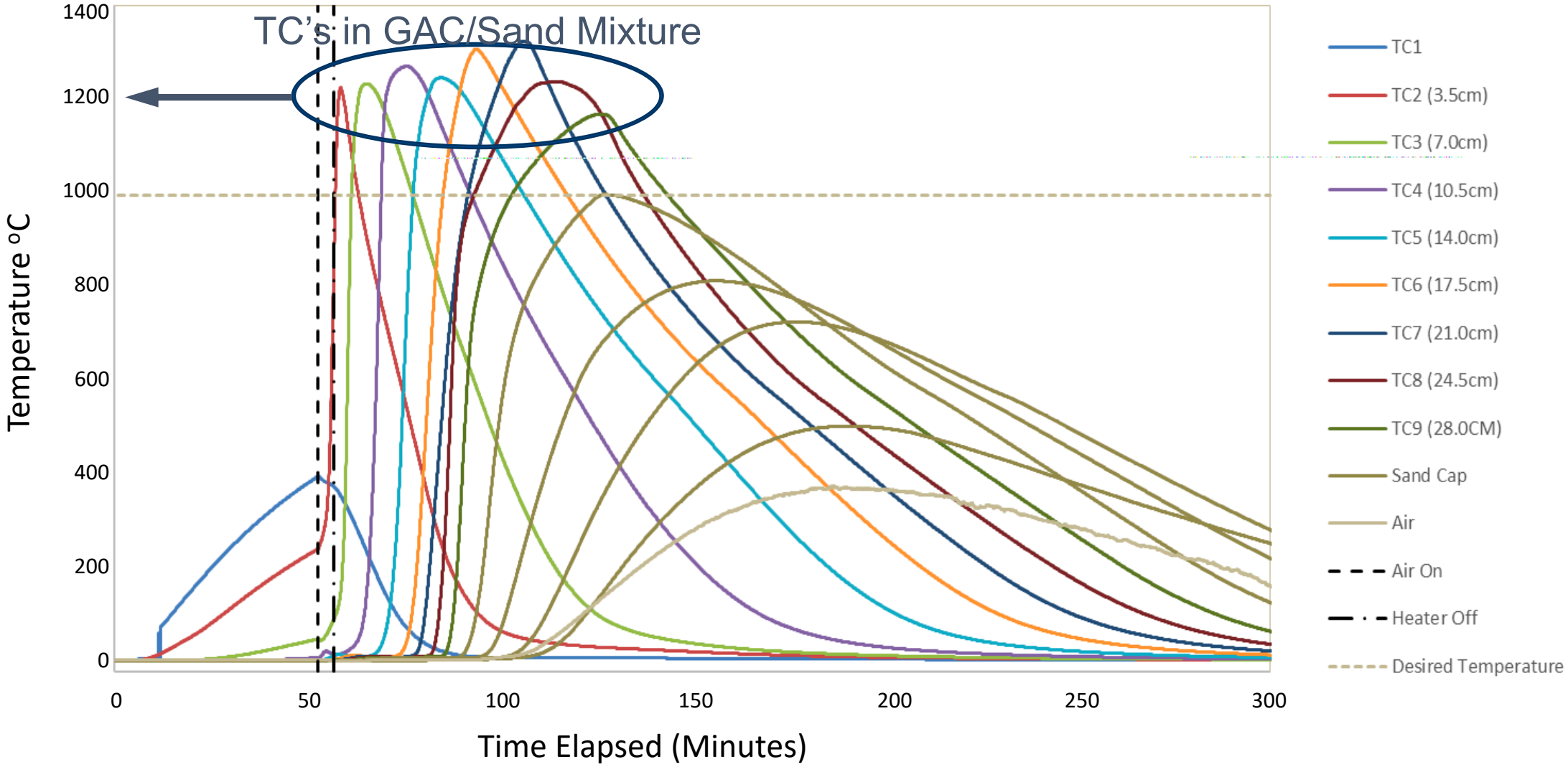

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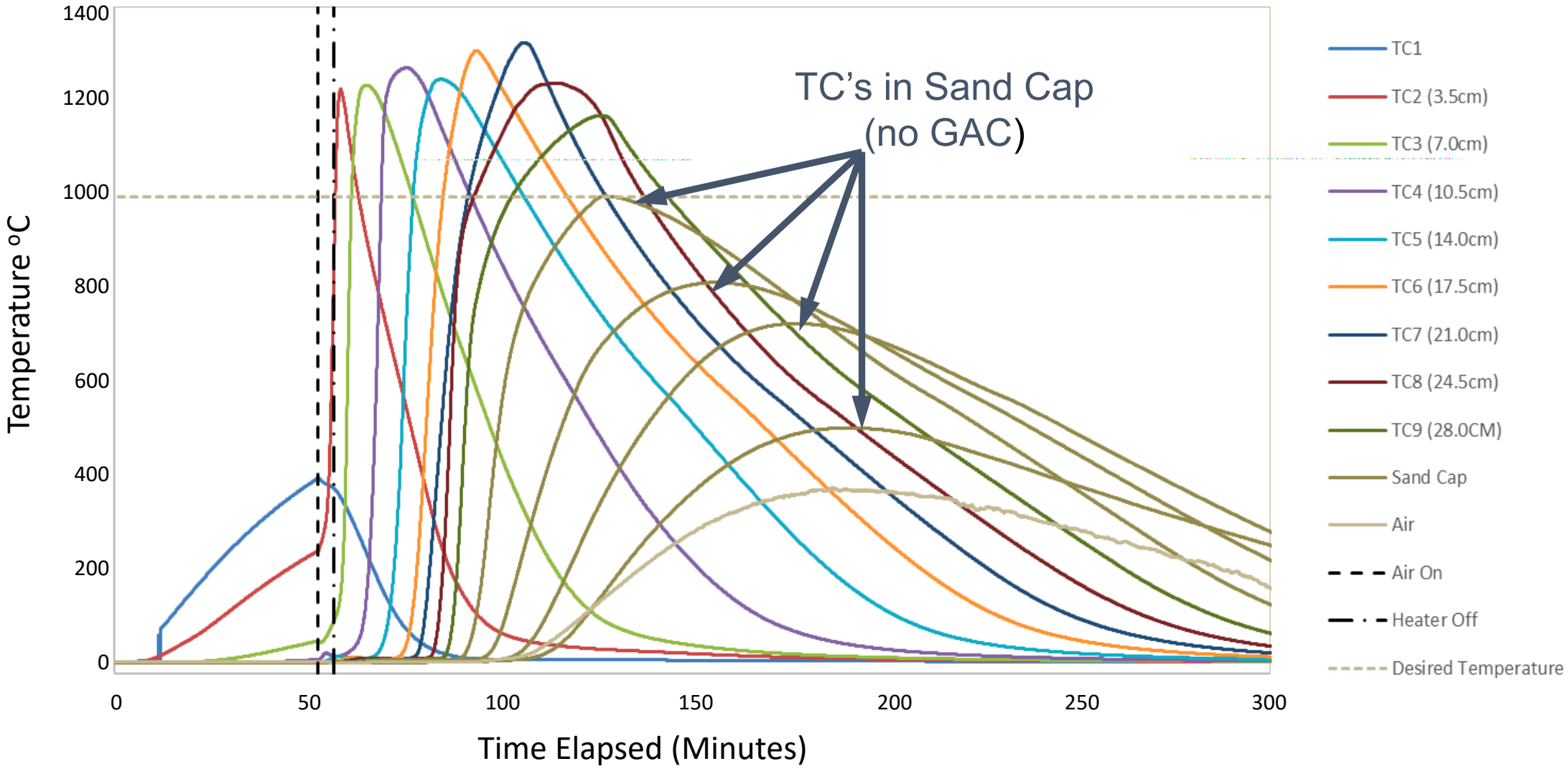

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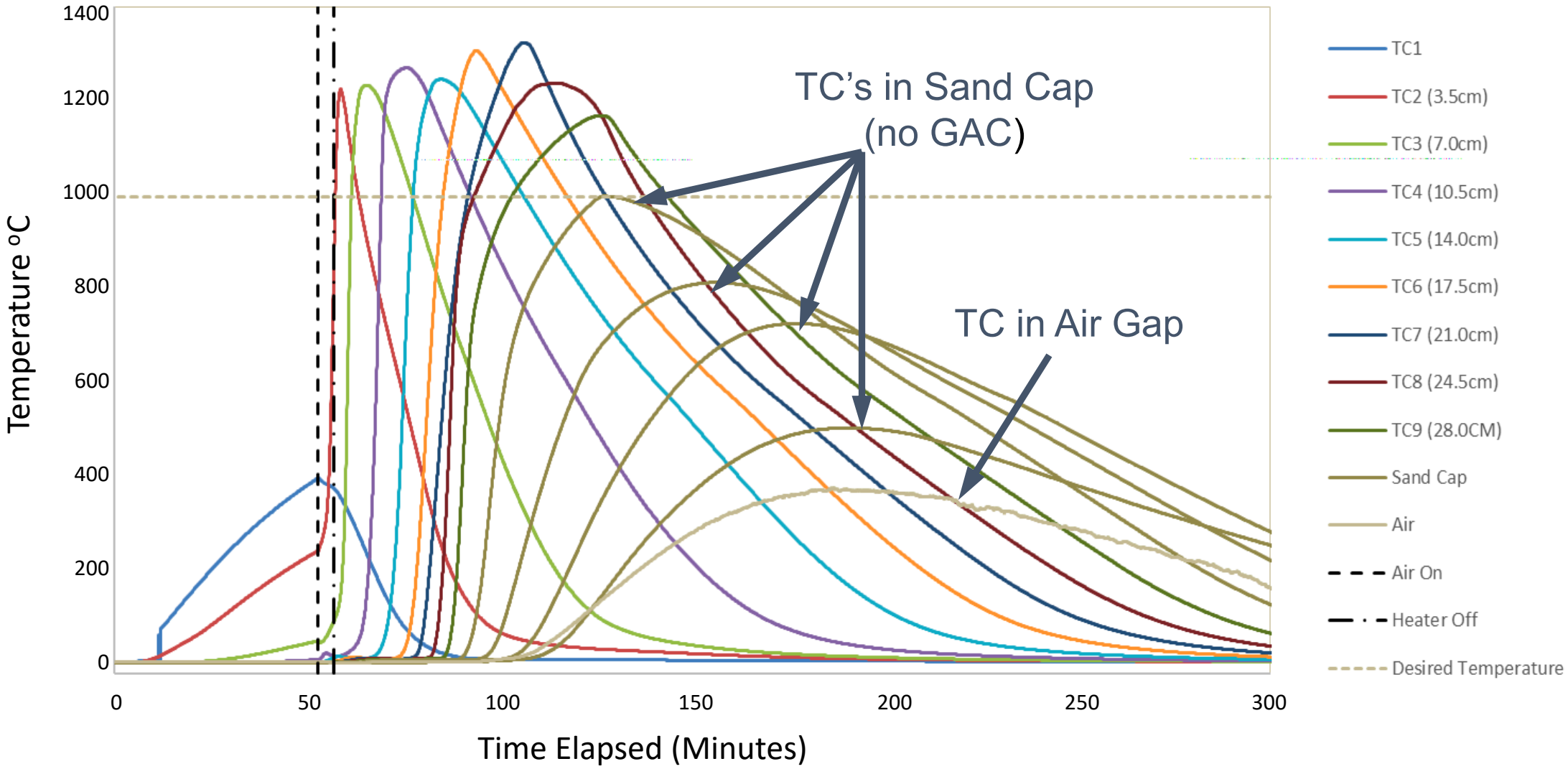

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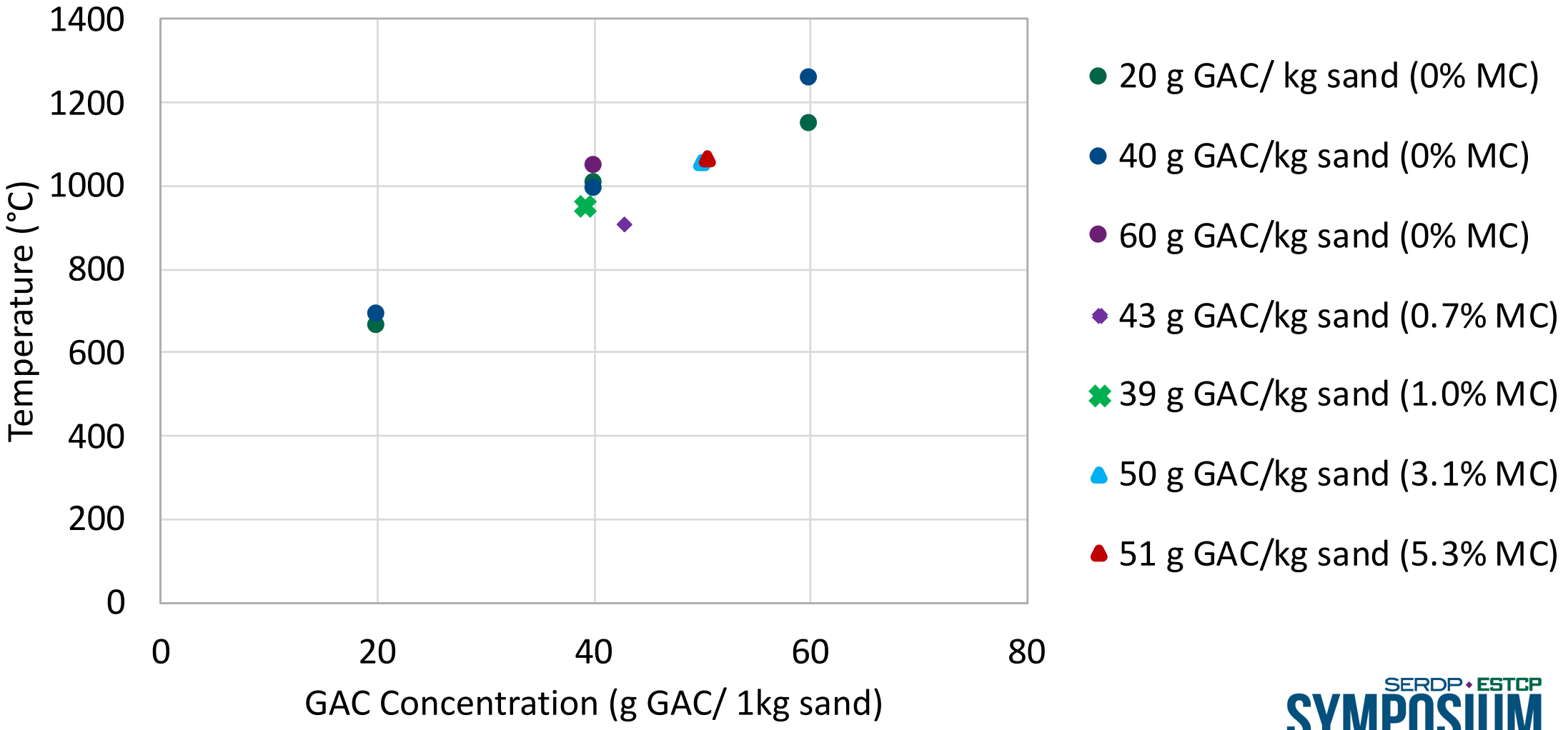
Test 1
Temperature vs. GAC Content/Clean Sand (No PFAS)



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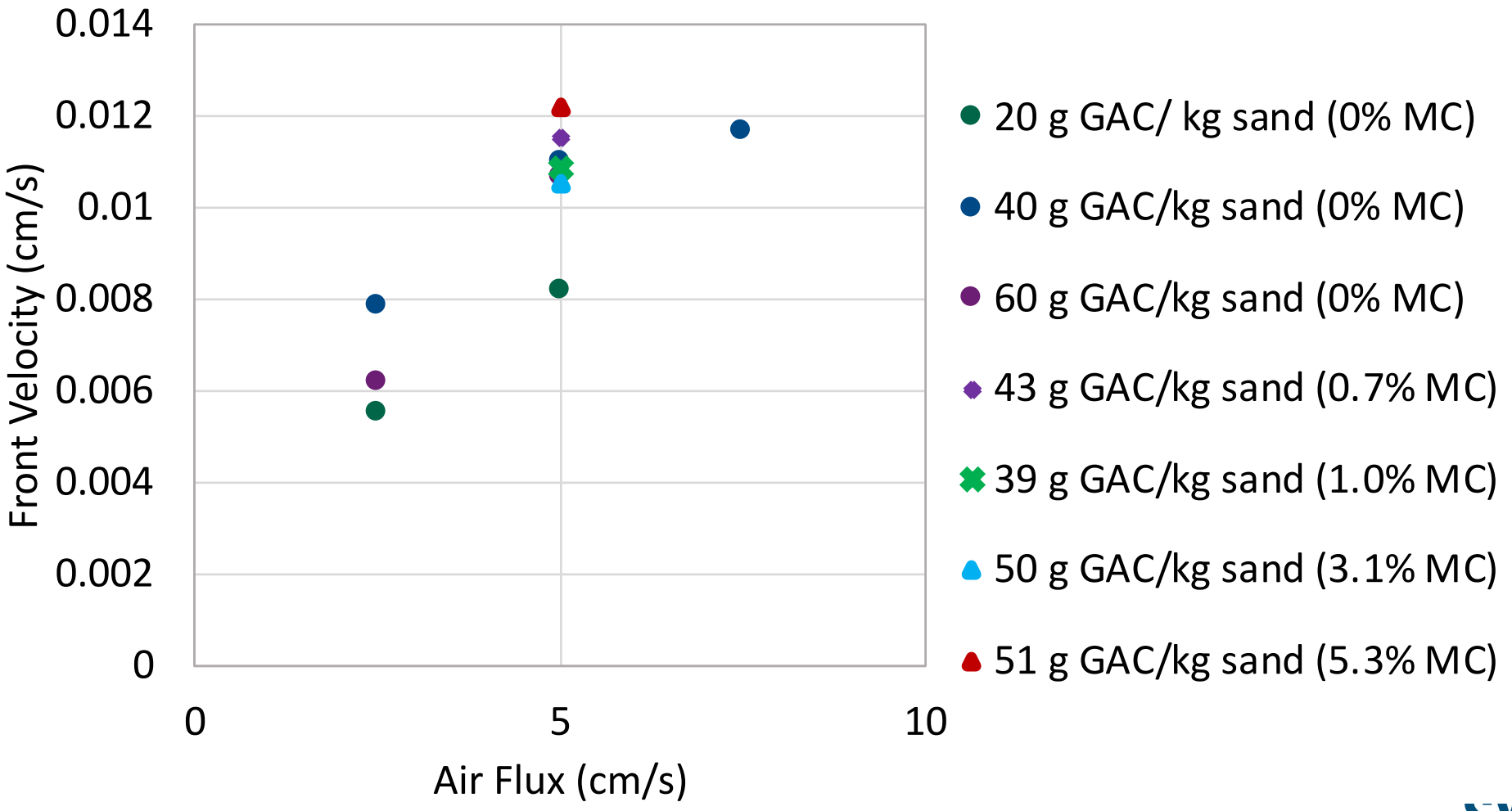
Test 1
Front Velocity vs Air Flux



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Tests 2 and 3
PFAS on GAC/Clean Sand

Test	% GAC (w/w)	MC (%)	Average Peak Temperature (°C)	Compound	Initial Concentration (mg/kg)[1]	Post Treatment Concentration (mg/kg)[2]
2	4.3	14	908	PFOA	591	<0.0004
				PFOS	142	<0.0004
				PFHxS	240	<0.0004
3	3.9	21	950	PFOA	507	<0.0004
				PFOS	122	<0.0004
				PFHxS	221	<0.0004

[1] mg PFAS/kg GAC
[2] mg PFAS/kg ash and sand

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Test 4
PFAS on Soil/Clean GAC (3 Compounds)

Compound	% GAC (w/w)	Avg. Peak Temperature (°C)	Initial Concentration (mg/kg)[1]	Post Treatment Concentration (mg/kg)[1]
PFOA	5.0	1054	13.41	<0.0001[a]
PFOS			23.30	<0.0001
PFHxS			16.86	<0.0001

[1] mg PFAS / kg Soil; average of triplicate sample
[a] PFOA concentration of 0.0005 mg/kg in one (of three) samples
Average temperature > 1000°C

Total fluorine captured as HF in emission ~ 31%(+/-51%)

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Test 5
PFAS on Soil/Clean GAC (6 Compounds)

Compound	% GAC (w/w)	Avg. Peak Temperature (°C)	Initial Concentration (mg/kg)[1]	Post Treatment Concentration (mg/kg)[1]
PFOA	5.1	1064	14.91	<0.0001
PFOS			10.87	<0.0001
PFHxS			10.84	<0.0001
PFBS			3.19	<0.0001
PFHpA			13.32	<0.0001
PFNA			28.73	<0.0001

[1] mg PFAS/kg soil; average of triplicate sample

- Trace carboxylate PFAS detected in XAD tubes (but no sulfonates)
- PFAS could be captured in off gas by GAC that is recycled for treatment

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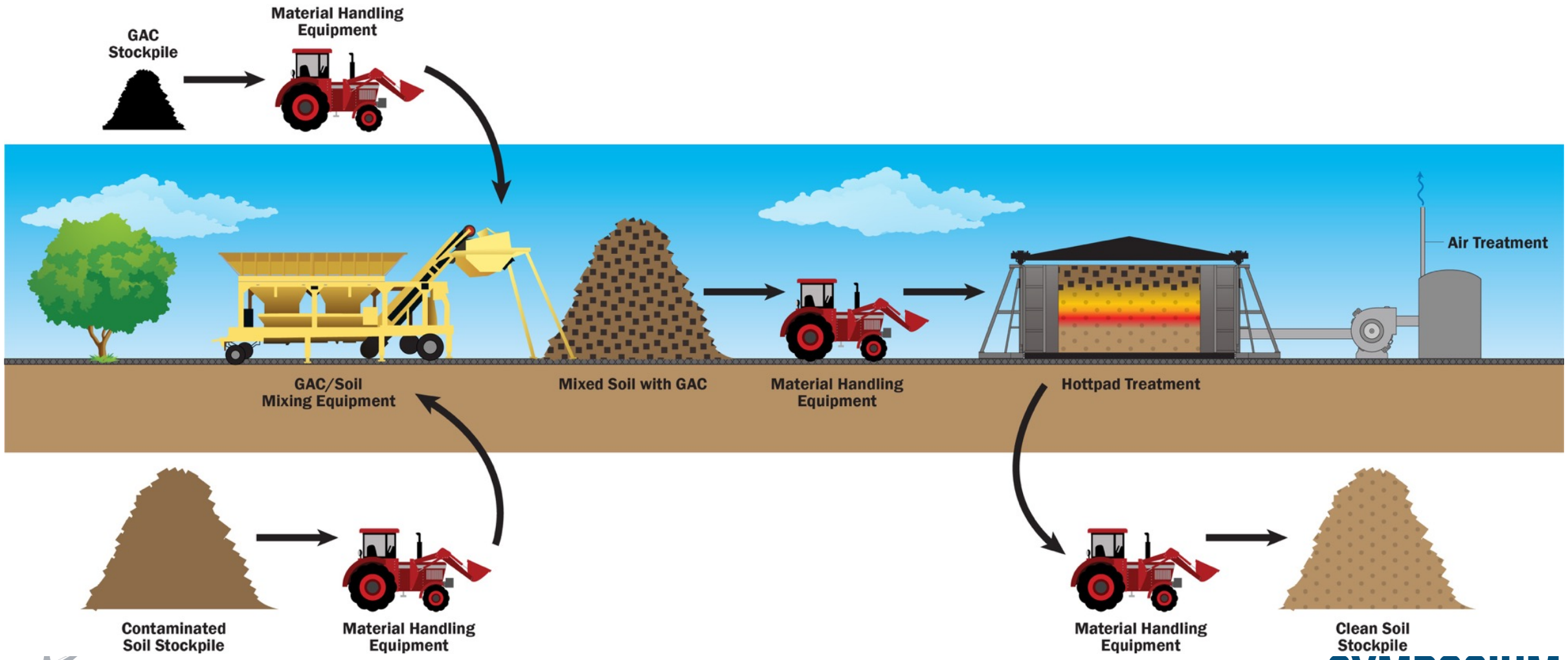
Potential Application
Ex Situ: Soil or Waste GAC Treatment



Potential Application
Ex Situ: Soil or Waste GAC Treatment

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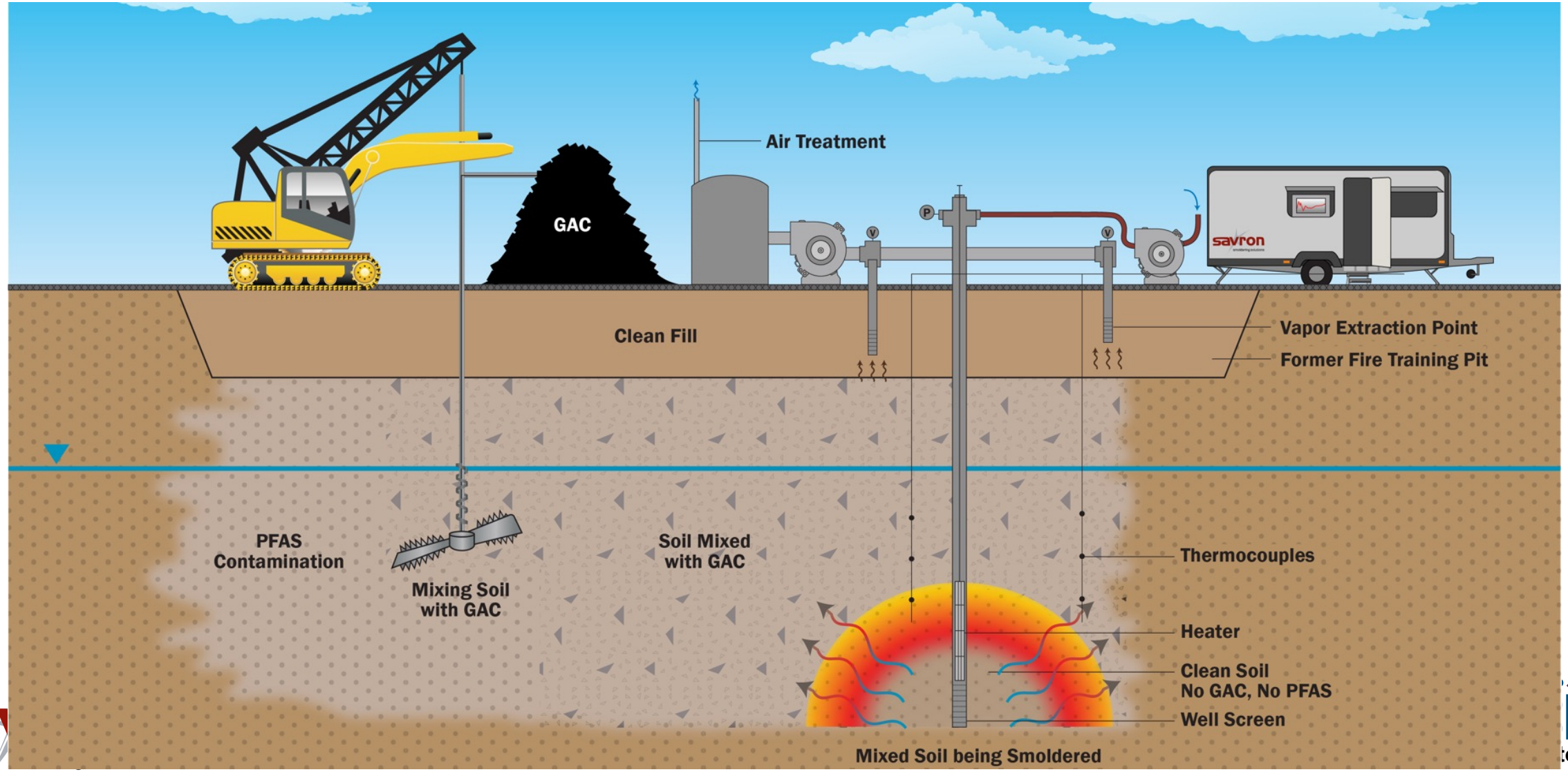
Potential Application
In Situ Source or Sorbant PRB Treatment



Potential Application
In Situ Source or Sorbant PRB Treatment

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Key Takeaways

- Peak temperature is ~ linear with GAC concentration (dial in temp)
- Smoldering front velocity is ~ linear with air flux
- GAC ~ 60 g/kg soil achieved temperatures ~1200°C
- PFAS was below quantification levels in soils, sand and ash
- HF indicates decomposition
- Some PFAS may be present in emissions
  - Capture and re-treat is a viable solution
- In and Ex Situ applications

Future Work

- Improve mass balance
- Characterization of emissions
- Conditions to enhance mineralization to HF
- Impacts of scaling/heterogeneity
- Field demonstration

Benefits to DoD

- Vast amounts of PFAS-contaminated excavated soils and soil cuttings, and GAC from water treatment are being stockpiled
- Currently, only high cost off-site incineration capable to treat PFAS
- Smoldering could provide a low cost and on-site alternative