FINAL REPORT

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

SERDP Project ER18-1593

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Smoldering combustion is a flameless, self-sustaining process that occurs on the surface of a condensed (i.e., solid or liquid-phase) fuel, converting organic material into primarily heat, carbon dioxide, and water. Smoldering has been well documented for solid porous materials and burning charcoal in a barbeque is a familiar example. Smoldering of an organic liquid (i.e., NAPL) embedded within an inert porous matrix is also possible and the reaction continues in a self-sustaining manner (i.e., continue in the absence of external energy input following a onetime, local ignition) and would destroy the NAPL if an oxidant (e.g., oxygen in air) and fuel (NAPL) were in sufficient quantity.

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Table of Contents

List of Figures

List of Tables

List of Acronyms

AFFF	aqueous film forming foams
CO_2	carbon dioxide
CO	carbon monoxide
cm	centimeter
°C	degrees Celsius
DoD	Department of Defense
g	gram
GAC	granular activated carbon
h	hour
IDW	investigation derived wastes
HF	hydrofluoric acid
IP	ignition point
kg	kilogram
L	Liter
ug	microgram
min	minute
mg	milligram
NAPL	non-aqueous phase liquid
N.D.	Not Detected
O_2	oxygen
%	percent
PFAS	per- and polyfluoroalkyl substance
PFDD/F	Perfluorinated dioxins and furans
PFBA	Perflurobutanoic acid
PFBS	Perflurobutanesulfonic acid
PFDA	Perflurodecanonic acid
PFDoA	Perflurododecanoic acid
PFHpA	Perfluroheptanoic acid
PFHxS	Perflurohexanesulfonic acid
PFPeA	Perfluropentanoic acid
PFOA	Perflurooctanoic acid
PFOS	Perflurooctanesulfonic acid
PFOSA	Perfluroflurooactanesulonamide
PFNA	Perflurononanoic acid
PFUnA	Perfluroundecanoic acid
s	second
SERDP	Strategic Environmental Research and Development Program
SON	Statement of Need
TC	thermocouple
XAD	sorbent tube
VOF	volatile organic fluorine

Keywords

PFAS, PFOA, PFOS, smoldering, soil, investigation derived wastes, activated carbon, perfluoroalkyl and polyfluoroalkyl, treatment.

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Abstract

Objective

Smoldering combustion is a flameless, self-sustaining process that occurs on the surface of a condensed (i.e., solid or liquid-phase) fuel, converting organic material into primarily heat, carbon dioxide, and water. Smoldering has been well documented for solid porous materials and burning charcoal in a barbeque is a familiar example. Smoldering of an organic liquid (i.e., NAPL) embedded within an inert porous matrix is also possible and the reaction continues in a self-sustaining manner (i.e., continue in the absence of external energy input following a one-time, local ignition) and would destroy the NAPL if an oxidant (e.g., oxygen in air) and fuel (NAPL) were in sufficient quantity. The self-sustaining nature makes smoldering very energy efficient and therefore cost effective as energy is only added at the start – unlike incineration approaches that require continual energy input.

The temperatures obtained through smoldering can be significant, and exceed temperatures needed to destroy PFAS. However, unlike solid or liquid fuels, PFAS are not contaminants that can support smoldering combustion in of themselves. Therefore, the objective of this study was to evaluate the use of a surrogate fuel that can support the smoldering process that achieves temperatures (greater than 900°C) sufficient to destroy PFAS.

Technical Approach

This study was conducted in two phases. The first phase (Phase I) evaluated if granular activated carbon (GAC) and ground rubber could smolder at required temperatures (greater than 900°C) when mixed with sand. Successful smoldering was assessed through successful ignition, the consumption of oxygen and production of combustion gasses (CO_2 and CO), measuring the average peak temperature and smoldering front velocity, and whether self-sustaining smoldering was observed through either steady or increasing peak temperatures after the heater was turned off.

The second phase (Phase II) examined the treatment of: (1) a PFAS-impacted liquid by absorbing the PFAS to a solid surrogate fuel (e.g., GAC) and subsequently used as the fuel surrogate; and (2) a simulated PFAS-impacted waste soil or drilling waste amended with a surrogate fuel; The degree of PFAS destruction was assessed by measuring: (1) PFAS concentration in soil before and PFAS concentration in soil/ash after treatment; (2) PFAS in emissions; (3) and hydrofluoric acid (HF) concentrations as a measure of total mineralization of PFAS.

All testing was conducted in specialty designed columns used to evaluate smoldering processes.

Results

A total of eight column tests were conducted in Phase I. GAC was found to be the best fuel surrogate and produced temperatures greater than 900°C when mixed with sand or a surrogate soil mixture between 40 and 60 g/kg soil. Crumb rubber also worked but produced undesirable residues. Generally, higher GAC concentration yielded higher average peak temperatures, and higher air flow increased the smoldering front velocity.

The first two Phase II tests (II-1 and II-2) examined treating three PFAS compounds, PFOA, PFOS, and PFHxS, absorbed to GAC. The GAC was mixed with a sand to a target ratio of 40 g GAC/kg sand. The test was completed twice and showed that the average peak temperature exceeded 900ºC, with an average smoldering front velocity of 0.7 cm/min. Prior to smoldering, the calculated concentration in the GAC/Sand mixture for PFOA, PFOS, and PFHxS was 590, 140 and 240 mg/kg in the first test, and 510, 120 and 220 mg/kg in the second test for each respective compound. After smoldering all compounds where ND at a detection limit of 0.4 ug/kg.

Test II-3 and II-4 used a surrogate soil mixture with a known organic fraction on which the PFAS compounds were absorbed. Test II-3 examined the treatment of the same three PFAS compounds used in tests II-1 and II-2, and Test II-4 used six PFAS compounds (PFOA, PFOS, PFHxS, PFNA, PFBS, PFHpA). For both of these tests, a virgin GAC was used as the fuel source which was mixed into the soil mixture.

In test II-3, the PFAS concentration was measured in soil samples before and after smoldering, and HF was measured in the emissions captured from the column. The analysis indicated that all PFAS was removed from the soil (N.D. at a detection limit of 0.5 ug/kg), and that 82% of the available fluorine was captured as HF.

In test II-4 the PFAS concentration was measured in soil samples before and after smoldering. HF was measured in the emissions captured from the column, and XAD tubes containing GAC in series were used to capture any PFAS breakdown products via a separate collection line from the column. Unfortunately, a line leak prevented accurate capture of HF in this test. All of the PFAS added to the soil mixture were not detected in the soil after treatment. Small amounts of PFAS compounds were extracted from the GAC from the XAD tubes, however, the total amount of PFAS emitted cannot be calculated as we estimated that the efficiency of PFAS extraction from GAC was approximately 50%. However, given the adsorption capacity of PFAS onto GAC, and the measured concentrations, it appears that the amount of PFAS emitted during smoldering is small

The observed PFAS compounds in the emission suggests that there may be some conversion of the sulfonates to their carboxylate-versions of PFAS (PFOS → PFOA, PFHxS → PFHxA, PFBS → PFBA). Although PFAS will completely breakdown at high temperatures with sufficient residency time, it is possible that during that during heating, there is sufficient energy to break off the sulfonate headgroup and volatilize a small fraction of PFAS. From a practical consideration, the emitted PFAS could be captured in an off-gas GAC treatment system, and the GAC subsequently used/treated by smoldering.

The successful treatment of PFAS by smoldering was demonstrated. Additional work is recommended to further improve the mass balance of the PFAS destruction, as well as address impacts of heterogeneity on the smoldering process.

Benefits

The results from this study combined with commercially available smoldering remediation technologies suggests two real-world applications: (1) ex situ treatment of PFAS contaminated IDW or excavated soils or spent GAC containing PFAS as shown in Figure A-1; and (2) in situ application to treat PFAS source area or GAC used to create permeable sorbent walls to treat groundwater plumes of PFAS as shown in Figure A-2.

Ex situ treatment would involve placing a soil/GAC mixture on a commercially available engineered system (HottPad). The HottPad is a low-profile platform that supplies the heat and air used to initiate and sustain the smoldering combustion reaction. Soil mixing could simply be done using backhoes or other commercially available methods. The high temperatures that are achieved during smoldering also allows destruction of other co-contaminants and allows treatment of wet soils. Off-gases would be collected and treated by appropriate off the shelf methods.

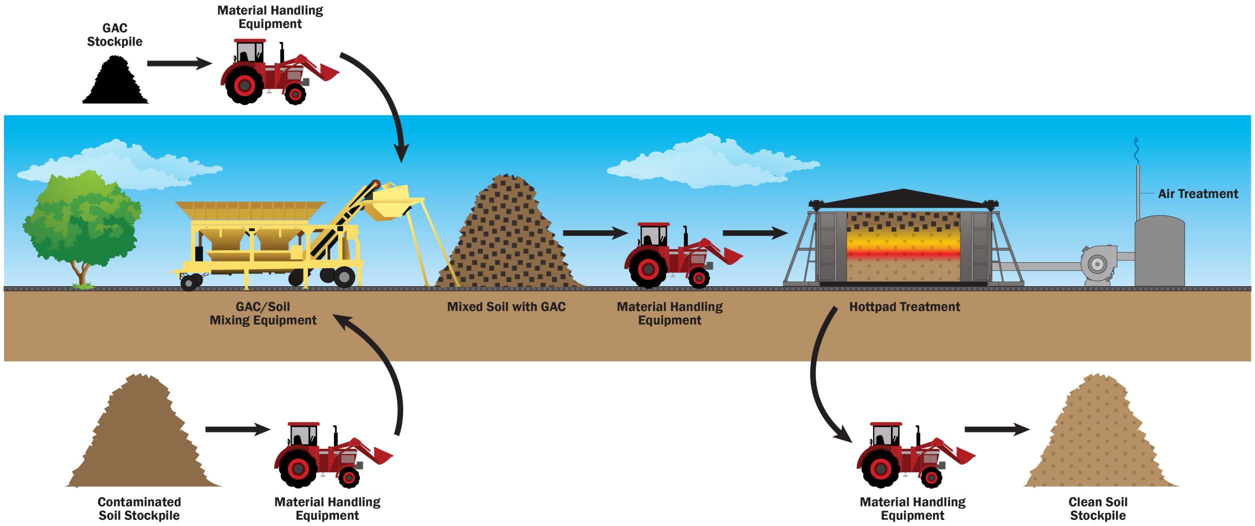

Figure 1: *Ex Situ* Treatment of PFAS Contaminated Materials

I*n situ* treatment requires the mixing of the GAC into the soil using traditional soil mixing technologies (e.g., ten to 12-foot augers). The GAC could be mixed in to a source zone that is located above or below the water table or could also be mixed into soils to form sorbent permeable walls to intersect a PFAS plume. Ignition points (IP) would be installed post soil mixing along with vacuum extraction points and off-gas treatment system. A downhole portable heater inserted into the IP is used to initiate the smoldering process which is maintained by the addition of air through the IP. Application of *in situ* smoldering is commercially available.

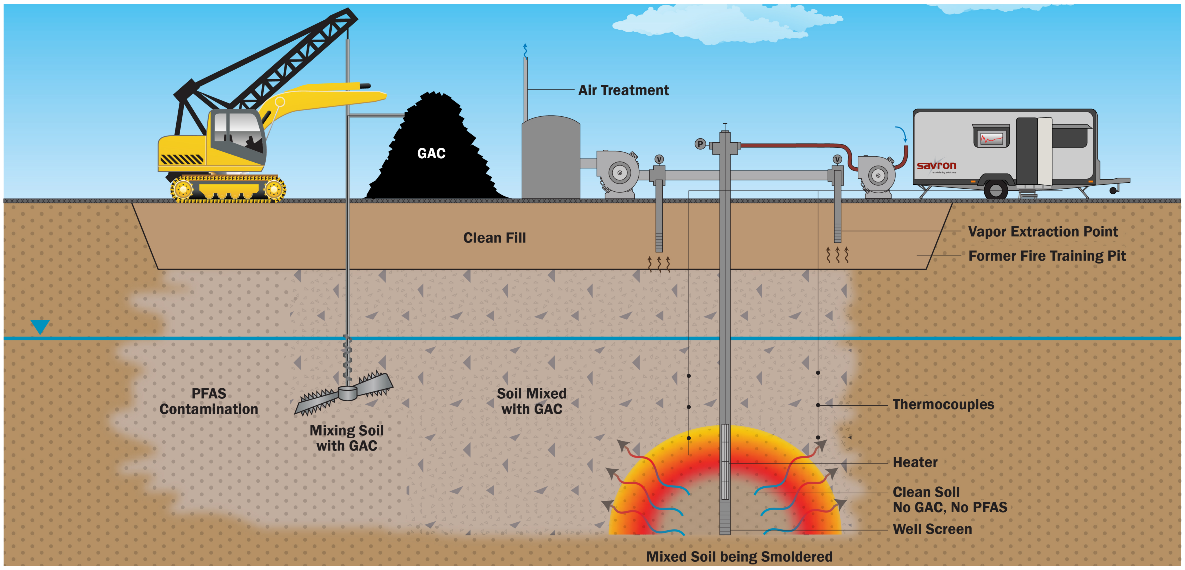

Figure 2: *In Situ* Treatment of PFAS

Regardless of the *in* or *ex* situ application, and although mixing will homogenize soils, the impacts of soil heterogeneity on the performance of smoldering combustion requires further evaluation. The completeness of PFAS combustion also requires further evaluation as it may impact off gas treatment (e.g., removal of partially decomposed PFAS, and the amount of HF produced).

Objective

SERDP's Statement of Need (SON) has a stated goal of fostering the development of innovative destructive approaches to treat investigation-derived waste (IDW) from investigations of per- and polyfluoroalkyl substance (PFAS) contamination in the subsurface. IDW includes excess soil cuttings, purge water from groundwater sampling, and fluids from decontamination of drilling equipment. The desired outcome would be:

1. unrestricted disposal, discharge, and/or reuse of IDW on-site;
2. mobile or temporary treatment systems that can be deployed easily, minimizing the spatial footprint and mobilization time and effort; and
3. cost effective treatment compared to current disposal methods.

The research objective of this project was to demonstrate that smoldering combustion can achieve temperatures needed to treat PFAS to meet the above goal and outcomes. In addition, two secondary objectives included demonstrating:

1. proof-of-concept for the simultaneous treatment of PFAS-impacted IDW and PFAS-impacted granular activated carbon (GAC) historically generated during pump-and-treat management of plumes at PFAS sites, or generated during past management of IDW at PFAS sites; and
2. that smoldering combustion can be used to treat soils.

Smoldering combustion has been successfully developed to treat hydrocarbon impacted soils either in above ground modular treatment systems, or below ground and beneath the water table (www.savronsolutions.com). Therefore, demonstrating the ability of smoldering combustion to treat PFAS-impacted IDW and soils will provide a foundation for the complete, cost-effective, on-site treatment of both liquid and solid IDW and soils at DoD sites.

Background

Per- and poly-fluoroalkyl substances (PFASs) include a wide range of over 3,000 compounds with varying carbon chain lengths, fluorine number and functional groups. They have been used to manufacture a variety of products from different manufacturing sectors including; textiles and leathers, paper products, metal plating and etching, wire manufacture, industrial surfactants, resins, molds, plastics, and semiconductors. PFAS was used to create non-stick, stain and water resistance and flame protective coatings, flame retardant products, insulation, or used in the production as wetting agents, suppression of fumes, or other purposes.

Notably for the United States Department of Defense (DoD), Aqueous Film Forming Foams (AFFF) containing per- and poly-fluoroalkyl substances (PFASs) have been used since the 1970s for fire-training areas and emergency response activities to extinguish hydrocarbon fires. These and other activities, such as spills, releases from automated fire suppression systems at facilities, and equipment calibration, result in the release of PFAS into the environment. It is not surprising therefore that these compounds have been detected in environmental media at hundreds of DoD facilities (Porter, 2014, Anderson et al., 2016) because many PFAS found in AFFF formulations are highly water soluble and can migrate rapidly from their point of release into soil, groundwater and surface water. Furthermore, they become widely distributed because these compounds do not break down easily in the environment and have been found to accumulate.

Investigation derived wastes (IDW) that contain PFAS include water generated from well development and sampling, and from drill soil cuttings. IDW pose a problem for disposal because of the chemical stability of PFAS compounds. Removal of PFAS from water has most commonly been achieved by sorption onto activated carbon or other sorbents (creating a new waste stream); however, soil contamination remains challenging for treatment.

Due to the thermal stability of PFAS, temperatures greater than 800 °C are required to destroy these compounds and temperatures at or above 1000°C are necessary to minimize production of short-chained volatile organic fluorenes (VOFs) and possibly fluorinated dioxins and furans (PFDD/F). A simplified chemical equation for PFAS under combustion conditions is:

$$\text{Organic Fuel} + \text{PFAS} + O_2 \rightarrow CO_2 + CO + H_2O + HF + VOF + PFDD/F$$

Hydrofluoric acid (HF) will be produced in greater abundance, and VOF and PFDD/F in lesser abundance, with increasing completeness of PFAS combustion.

Standard thermal treatment options (incineration) are currently available as an option for achieving substantial destruction of PFAS, however they require transport of the waste off-site or large dedicated equipment to be installed on-site, which is often not cost-effective for the volumes of IDW generated during site investigations

In comparison to incineration, a flaming process that occurs in open air space, smoldering is a flameless heterogenous combustion process that occurs on the surface of a condensed (i.e., solid or liquid-phase) fuel, converting organic material into primarily heat, carbon dioxide, and water (Ohlemiller, 2002). Burning charcoal in a barbeque is a familiar example. Smoldering has been well documented for solid porous materials (e.g., fibrous materials, coal, and polyurethane foam) (Ohlemiller, 2002; Drysdale, 1998; Palmer, 1957; and Rein, 2009).

Laboratory studies first demonstrated that smoldering of an organic liquid (i.e., NAPL) embedded within an inert porous matrix was possible (Switzer et al., 2009; Pironi et al, 2009). That work also demonstrated that the reaction would continue in a self-sustaining manner (i.e., continue in the absence of external energy input following a one-time, local ignition) and would destroy the NAPL if an oxidant (e.g., oxygen in air) and fuel (NAPL) were in sufficient quantity.

The self-sustaining nature makes smoldering very energy efficient (and therefore cost effective) as energy is only added at the start – unlike incineration approaches that require continual energy input. The practical result is a hot, self-sustaining smoldering "wave" that propagates from the ignition point through the contaminated matrix in the direction of air flow. The reaction wave is relatively thin in the direction of travel (i.e., from thicknesses of millimeters to centimeters), and is composed of a complex set of pyrolysis (i.e., endothermic, thermal breakdown) and oxidation (exothermic, converting carbon compounds to CO_2 and H_2O) reactions. The smoldering process is completely controllable and can be terminated at any time by stopping the air flow to the system. Although the majority of fuel is consumed via oxidative destruction, a fraction of the contaminant can be volatilized during pyrolysis reactions and through the heat wave that arrives (via convection and conduction) in advance of the smoldering wave.

As the PFAS are not contaminants that can support smoldering combustion in of themselves, like hydrocarbons and coal tars, a surrogate fuel is required. This study examines treating; (1) a simulated PFAS-impacted waste soil or drilling waste amended with a surrogate fuel; (2) a PFAS-impacted liquid by absorbing the PFAS to a solid surrogate fuel (e.g., GAC) and subsequently used as the fuel surrogate, or added to PFAS contaminated soils to treat both the GAC and soil.

There are two key questions associated with treatment of PFAS using smoldering combustion, which are;

1. Can smoldering combustion achieve the required temperatures for destruction of PFAS using common or waste fuels as surrogate fuels?

Multiple laboratory and field tests have demonstrated that temperatures of over 1000 °C are achievable during smoldering when the contaminant (like coal tar) is the fuel. PFAS destruction occurs at temperatures above 800 °C, with more complete destruction occurring with increasing temperatures above 800 °C. However, to treat PFAS requires using a surrogate fuel source that can support smoldering combustion. The ideal fuel will be either a waste product that itself needs management or destruction (like PFAS-impacted GAC or old tires), or a readily available low-cost substance (like coal).

There are a variety of surrogate fuels that can alone or in combination achieve the required temperatures. Ideally the lowest cost surrogate fuel will be effective. Other variables that affect temperature and processing rate of the treated IDW include the concentration of fuel within a porous matrix and air flux.

2. Does smoldering treatment remove PFAS from a solid matrix?

PFAS present some unique challenges in the potential byproducts and lower than normal environmental criteria for clean-up. The desired endpoint following treatment with smoldering combustion is soil and water that meets environmental criteria, does not require landfill or additional treatment, and can be reused on-site. Off gases may require further treatment before discharge, and therefore an evaluation of the composition of vapors (specifically PFAS and HF) is required.

Two phases of experiments were conducted to address these two technical questions; Phase I - Testing of Surrogate Fuels; and Phase II - Assessment of PFAS Destruction

Materials and Methods

This section outlines the procedures used to prepare the laboratory scale tests.

Table 1 and Table 2 include the materials and equipment used for the Phase I and Phase II tests.

Table 1: Test Materials

Item	Lot, Batch, ASTM No., or Observation	Manufacturer/Supplier Name
Granular activated carbon (GAC)	Bituminous coal	PTI Process Chemicals
Coarse Silica Sand	16 mesh, #12ST size	Bell and Mackenzie Co.
Medium Silica Sand	20-30 mesh, 1240s size	Bell and Mackenzie Co.
Crumb Rubber	10-20 mesh	Emterra
Perfluorooctanoic acid (PFOA)	95% purity, lot # 10199077	VWR International
Heptadecafluorooctanesulfonic acid potassium salt (PFOS)	≥ 98% purity, lot # BCBR8860V	Sigma-Aldrich
Tridecafluorohexane-1-sulfonic acid potassium salt (PFHxS)	≥ 98% purity, lot # BCBT9274	Sigma-Aldrich
Nonafluorobutane-1-sulfonic acid (PFBS)	99% purity, lot # MKCD0791	Sigma-Aldrich
Perfluorononanoic acid (PFNA)	97% purity, lot # MKBZ1794V	Sigma-Aldrich
Perfluoroheptanoic acid (PFHpA)	99% purity, lot # BCBW4625	Sigma-Aldrich
Sulfuric acid	95-98% purity, lot # SHBJ0798	Sigma-Aldrich
Potassium hydroxide pellets	>85% purity, lot # 24699	Caledon Laboratories Ltd.
Topsoil		Fisher’s Landscaping Depot

Table 2: Test Equipment

Item	Lot, Batch ASTM No., or Observation	Manufacturer/ Supplier Name
Stainless Steel Columns	NA	Fabricated at Western University
Thermocouples	Type K	OMEGA
Multi-Gas Analyzer	MGA3000C	ADC Services
Flowmeter	FMA 5400/5500	OMEGA
Nitrogen	Ultra High Purity 5.0 Nitrogen	Praxair
Carbon Dioxide and Carbon Monoxide Span Gas	Y787409303	Praxair
Electric Mixer	Professional 600TM	KitchenAid
Data Logger	34980A	Agilent Technologies
Filter Paper	12.5 cm dia, coarse porosity, 09-790-12E	Fisher Scientific
Silicone Tubing	T4414-25FT	Sigma-Aldrich
500 mL Polypropylene Container	414004-126	VWR International
1 L Polypropylene Container	414004-127	VWR International
Peristaltic Pump	520S	Watson Marlow
5-Gallon Buckets		Lowes
Mechanical Sieve Shaker	HM-300A	Houghton Manufacturing Co.
Nalgene Autoclavable Carboy	20 liters	Life Technologies Inc
Explorer Pro Scale	EP214	Ohaus Corporation
MaxQ 4000 Shaker Table		Thermo Scientific

Phase I: Testing of Surrogate Fuels Methodology

The purpose of Phase I was to determine a fuel and fuel ratio that would achieve temperature sufficient to destroy PFAS. During these tests, fuel, ratio of fuel to sand, and air flux was varied to understand the relationships between these parameters and the resulting temperatures recorded during smoldering tests. For these tests, two potential fuels were identified: granular activated carbon (GAC) and crumb rubber.

Column Test Setup

Laboratory tests used a stainless-steel column that had a diameter of 16 cm and a height of 60 cm. The smoldering column was placed in a walk-in fume hood on a scale which recorded the mass loss in real-time. A coiled resistive heater (450 W, 120 V, Watlow Ltd.) was located at the base of the column and was connected to a single-phase variable power supply (120 V, STACO Energy Products). The air supply was connected at the base of the column; a layer of coarse and medium sand was placed above the air supply to evenly distribute the airflow throughout the cross-section of the column. Thermocouples were inserted horizontally at 3.5 cm increments vertically up the column and measured temperatures at the center of the column. The first and second thermocouples were placed just below and above the heater. The stainless-steel column was wrapped with insulation (5cm thick mineral wool, part number 9364K62, McMaster-Carr, Aurora, OH) to minimize heat losses. Gas emissions were analyzed for volume fractions of oxygen, carbon monoxide, and carbon dioxide using a gas analyzer. During tests, a data logger and personal computer recorded the mass loss, thermocouple, and gas analyzer data. Measurements were taken approximately every two seconds. Figure 3 and Figure 2 is a schematic a picture of the experimental setup, respectively.

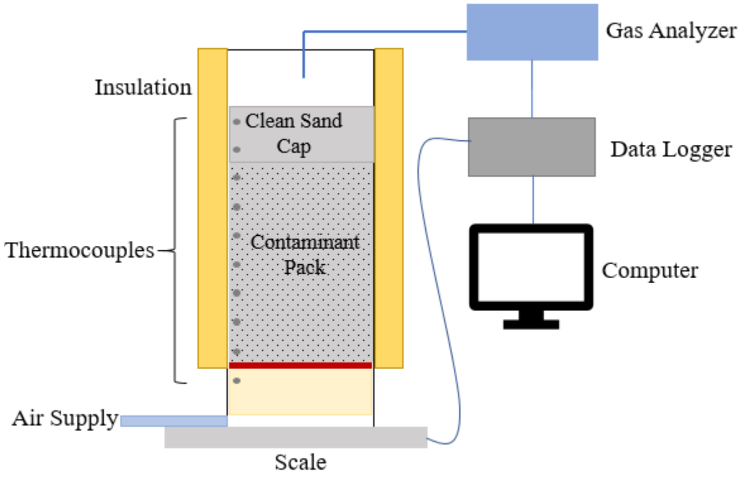

Figure 3: Schematic of Smoldering Experimental Setup

Figure 4: Photo Showing Column Wrapped with Insulation in the Fume Hood

<u>Preparing the Smoldering Fuel & Sand Mixture</u>

The stainless-steel column was packed with approximately 25 cm of coarse silica sand and fuel. The fuel GAC or crumb rubber (mesh 10-20, Emterra) and course silica sand was mixed using the ratio determined for the test. The fuel and sand were mixed using a KitchenAid mixer (Professional 600TM) to create a uniform mixture. Two batches of approximately 4kg each were required to create a 25cm pack height in the smoldering column. 14 cm of coarse sand was added into the column above the fuel and sand mixture to allow for cooling.

Smoldering Procedure

The heater was turned on to begin pre-heating. Once the second thermocouple reached 260 °C, air was introduced into the bottom of the column using a mass flow controller (FMA5400/5500 Series, Omega Ltd.). The heater was turned off when the third thermocouple peaked. Self-sustaining smoldering was then shown by the consecutive consistent peak temperatures exhibited by the thermocouples in the fuel and sand mixture. The self-sustaining smoldering continued until the front reached the clean sand layer; at this time, the temperatures began to decrease.

Figure 3 is an example of the smoldering process. Heater was turned on at time zero. Airflow began at the first dashed and the heater was turned off at the second dashed line. Self-sustaining smoldering was evident by the consecutive, non-diminishing peaks exhibited by the thermocouples. Temperatures decreased once the smoldering front reached the clean sand cap and all reactions ceased. Table 3 summarizes the smoldering tests conducted in Phase I.

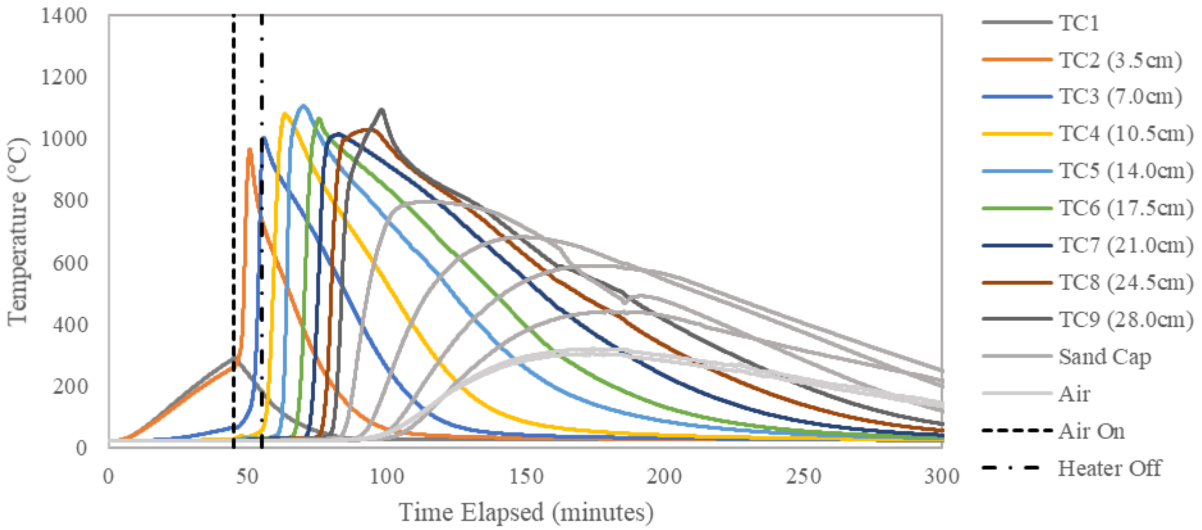

Figure 5: Example of Thermocouple Profiles from a Phase I Test

Table 3: Experimental Parameters for Smoldering Tests Conducted in Phase I

Test Number	**Fuel**	**Ratio (g fuel/kg sand)**	**Air Flux (cm/s)**
I-1	GAC	60	5.0
I-2	Crumb Rubber	60	5.0
I-3	GAC	40	5.0
I-4	GAC	20	5.0
I-5	GAC	40	2.5
I-6	GAC	40	7.5
I-7	GAC	60	2.5
I-8	GAC	20	2.5

Phase II Assessment of PFAS Destruction Methodology

Test results from Phase I indicated GAC would be an ideal fuel to use because it would allow temperatures of over 900 °C to be achieved during self-sustaining smoldering. Phase II tests collected data on the fate of added PFAS during smoldering. This phase is comprised of two tests using PFAS contaminated GAC and two using PFAS contaminated soil.

Preparing Stock Solutions

Stock solutions were prepared for tests II-1 to II-3 that used three PFAS compounds (PFOA, PFOS, PFHxS), and test II-4 used six PFAS compounds (PFOA, PFOS, PFHxS, PFNA, PFBS, and PFHpA). The amounts of PFAS compounds used was determined by using 10-20% of each compound's solubility in order to prevent foam from forming during shaking.

Stock solutions were prepared in 12-1 L polypropylene bottles (for tests II-1 and II-2) or 20 L Nalgene Autoclavable carboy for tests II-3 to II-4. **Error! Reference source not found.** presents the amounts used of each PFAS used to prepare the stock solution. An indirect measurement was used due to some PFAS compounds adhering to the scoopula. After each addition of PFAS, the scoopula was rinsed into the bottle with 250 mL of deionized water and then cleaned before adding the next compound. For tests II-1 and II-2, 200 mL of deionized water was added to each bottle after addition of the PFAS compounds to create 950 mL of stock solution in each bottle. Bottles were placed on a shaker table for 48 hours at an rpm of 170 (to allow the PFAS to dissolve. For tests II-3 to II-4, deionized water was added to the carboy to make a 15L stock solution. The carboy was then agitated periodically over the period of 48 hours to allow the PFAS compounds to dissolve.

Table 4: Amount of PFAS Compound Used for Stock Solutions

Test Number	PFOA (g)	PFOS (g)	PFHxS (g)	PFNA (g)	PFBS (g)	PFHpA (g)
II-1	0.6460	0.0988	0.2660	-	-	-
II-2	0.6460	0.0988	0.2660	-	-	-
II-3	10.2	1.56	4.2	-	-	-
II-4	5.1	0.78	2.1	5.1	0.516	5.1

Adding GAC/Soil to Stock Solution

For tests II-1 and II-2, GAC was added to each of the stock solution bottles. The bottles were placed on the shaker table for an additional four days at 170 rpm. Each bottle was drained under vacuum through a 12.5 cm, coarse filter paper (09-790-12E, Fisher Scientific). The vacuum setup is shown in Figure 6. The GAC was then placed in a covered polypropylene container. This was completed for each of the 12 bottles.

Figure 6: Vacuum Setup Used to Separate the GAC or Soil From the Stock Solution

For tests II-3 to II-4, topsoil was dried in the oven at 105°C for 24 hours, crushed using a mortar and pestle, and then sieved using a standard set of sieves and the mechanical sieve shaker Grains larger than sieve #10 were removed from the soil. Remaining soil was then blended to create a homogenized mixture.

Dried topsoil was added to the stock solution. The carboy was shaken periodically over four days to resuspend the soil and maximize the sorption of PFAS to the soil. Silicone tubing and a peristaltic pump were used to remove the soil and stock solution from the carboy. If drained soil still contained significant free water, it was placed as a thin layer in a tray until the moisture content decreased to less than 20%. After this, the lid was placed on the container to keep residual water in the soil. Moisture content was determined following the ASTM Standard D2974-14, *Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils*.

Smoldering Experiments

The experimental procedure for the smoldering column tests was the same as described for Phase I. Table 5 outlines the experimental parameters for the four Phase II tests.

Table 5: Fuel, Fuel Ratio and Air Flux Used for Phase II

Test Number	Fuel	Porous Media	Ratio (g fuel/kg sand or soil)	Air Flux (cm/s)
II-1	GAC (with 3 PFAS)	Sand	43	5.0
II-2	GAC (with 3 PFAS)	Sand	39	5.0
II-3	GAC	Soil (with 3 PFAS)	48	5.0
II-4	GAC	Soil (with 6 PFAS)	48	5.0

Preparing the Smoldering Fuel & Sand Mixture

For tests II-1 and II-2, the same procedure was followed to prepare the smoldering fuel and sand mixture as described in Phase I. For tests II-3 to II-4 the same procedure was used, however, the coarse silica sand was replaced with a mixture of 28% topsoil, 47% medium sand, and 25% coarse sand. For these measurements, the dry weight of the topsoil was used.

Coarse and medium sand were mixed with the topsoil to achieve the desired grainsize distribution curve and an organic fraction of 1%. These parameters were used to create a soil mixture which would represent common field soils.
Figure 7: Grain Size Distribution Curve for Soil and Sand ***Mixture***
displays the approximate grain size distribution curve.

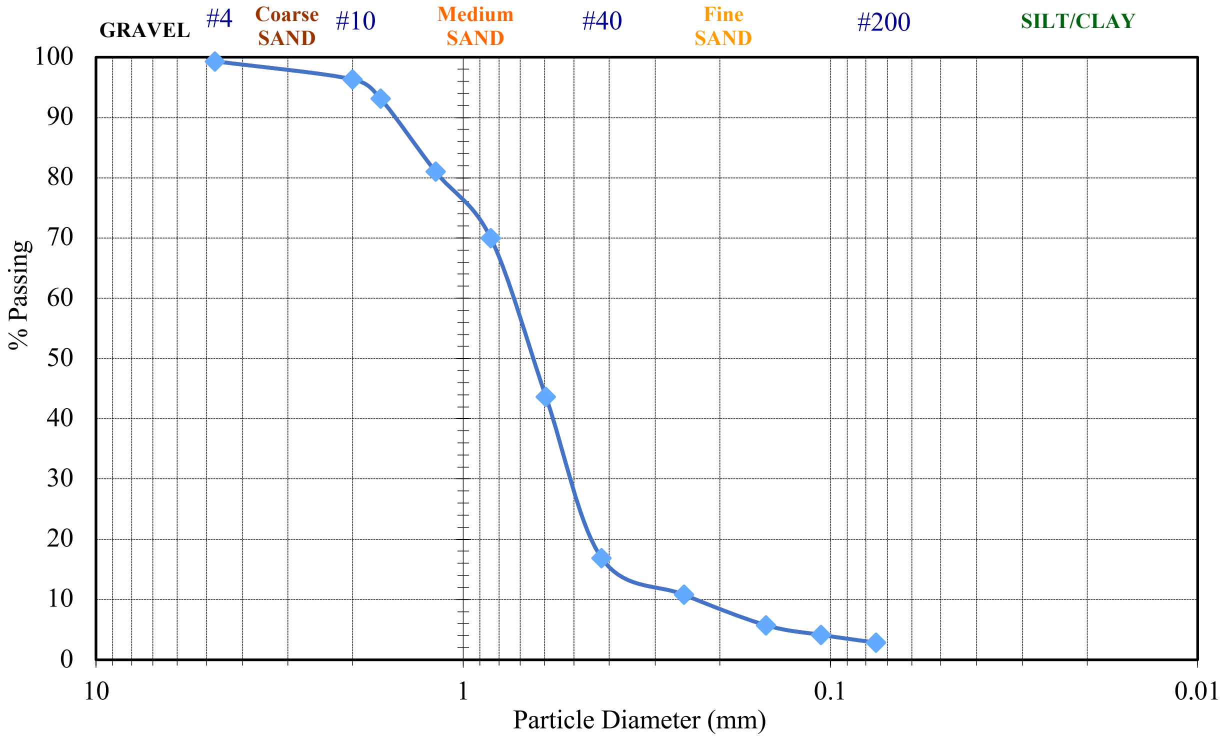

Figure 7: Grain Size Distribution Curve for Soil and Sand Mixture

Smoldering Procedure

The same procedure was used to conduct smoldering tests as described in Phase I. However, for these tests, additional emission collection systems were setup to monitor for hydrogen fluoride (HF) and PFAS emissions. To measure HF, EPA Method 26 - *Determination of Hydrogen Halide, and Halogen Emissions from Stationary Sources Non-Isokinetic Method* (analysis conducted by ALS laboratories, London, Ontario) was used to capture emissions during the smoldering process. 15 mL of sulfuric acid was poured into the second and third impinger in the train of four impingers as described in the method. A schematic showing the HF collection system is in Figure 8. Figure 9 is a photo of the experimental setup. HF was collected from above the contaminant pack.

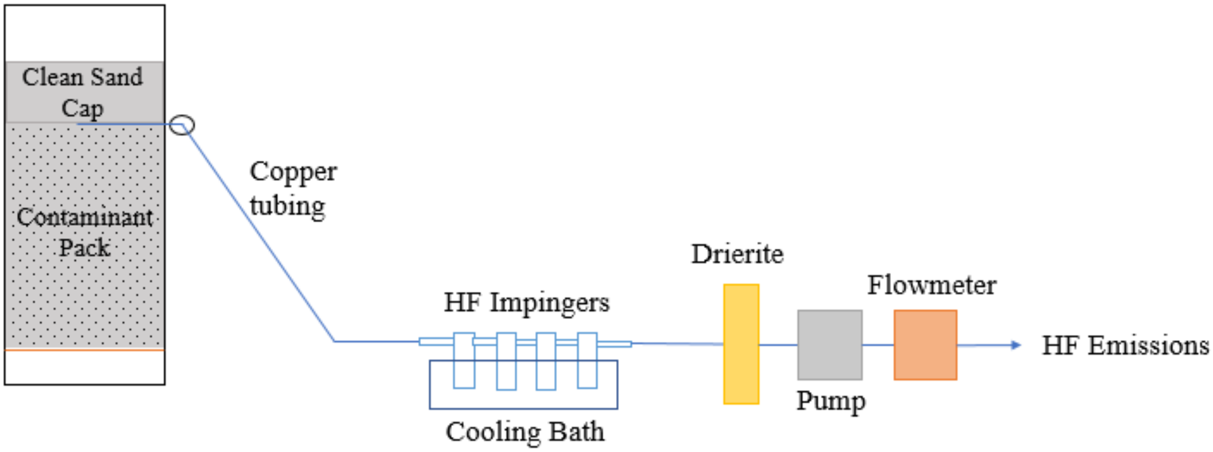

Figure 8: Schematic of HF Collection System

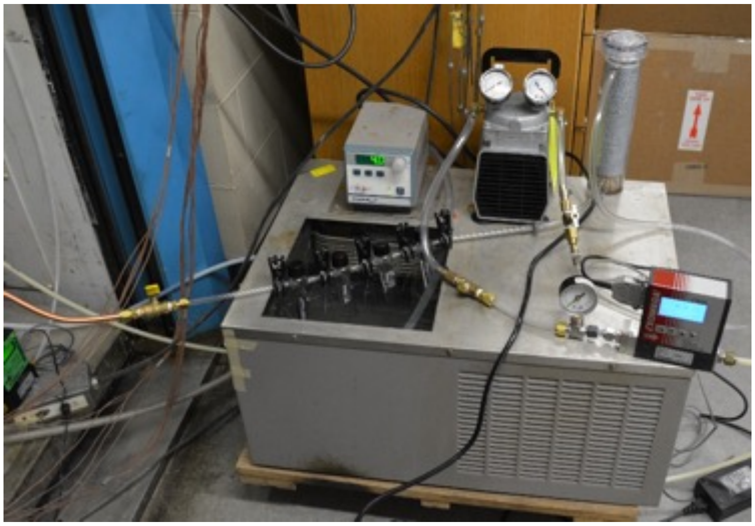

Figure 9: Picture of HF Collection System

Two methods were developed in order to test for PFAS emitted during the smoldering process. For tests II-3 and II-4 an emission collection system was built using two XAD tubes. Each XAD tube was filled with 50 g of GAC and further packed with glass wool. The XAD tubes were placed in series. The XAD tubes were connected to a pump and flowmeter to control the flow and measure the total volume collected during sampling from the top of the column. Figure 8 is a photo of the XAD tubes setup for sampling during the test. Figure 11 includes the emission sampling trains used for tests II-3 and II-4.

The impingers were connected to a pump and flowmeter to control flowrate and measure the total volume of emissions sampled. Flowrates for both PFAS emissions systems were kept between 2-3 L/min.

Figure 10: Picture of the XAD Tubes in Series (Left Side of Column)

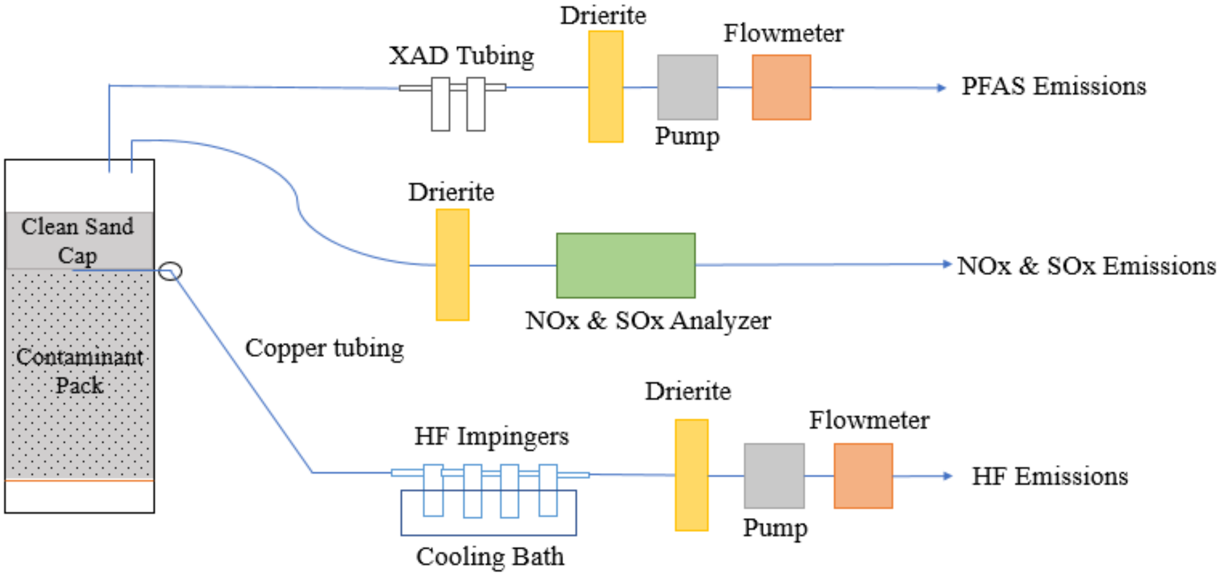

Figure 11: Schematic of Emission Collection Systems Used for Tests II-3 & II-4

Analysis of PFAS

PFAS analysis was conducted by the laboratory of Dr. Kela Weber, Royal Military College of Canada using EPA Method 537 Rev 1. This method was modified for matrices outside the scope of this method. Main modification was a direct injection method following glass fiber filtration. Solids analysis required an organic extraction as follows: two (2) grams of solid material was extracted three (3) times with 4-mL basic methanol (0.1% NaOH). The three extracts were then combined and filtered before direct injection.

Results and Discussion

Phase I: Testing of Surrogate Fuels

Figure 10 presents the thermocouple (TC) temperature data measured over time during test I-1 and represents a typical self-sustaining smoldering reaction TC profile. Each colored line represents the temperature measured over time at a single point along the length of the centerline of the column. TC2 to TC9 are located within the sand mixed with the tested fuel (GAC for this example). TC1 is located near the heater; TC10 to TC13 are within the sand cap, and TC14 is placed in the open-air space above the sand cap.

When TC2 had reached 260°C, the air flow was initiated at 53 minutes and ignition occurred, followed by a self-sustaining smoldering reaction as evident from the both the sharp inflection of temperature to a peak temperature followed by overlapping, non-diminishing profiles from TC2 to TC9. Temperature profiles in the sand gap are consistent with heat transfer through conduction and convection processes.

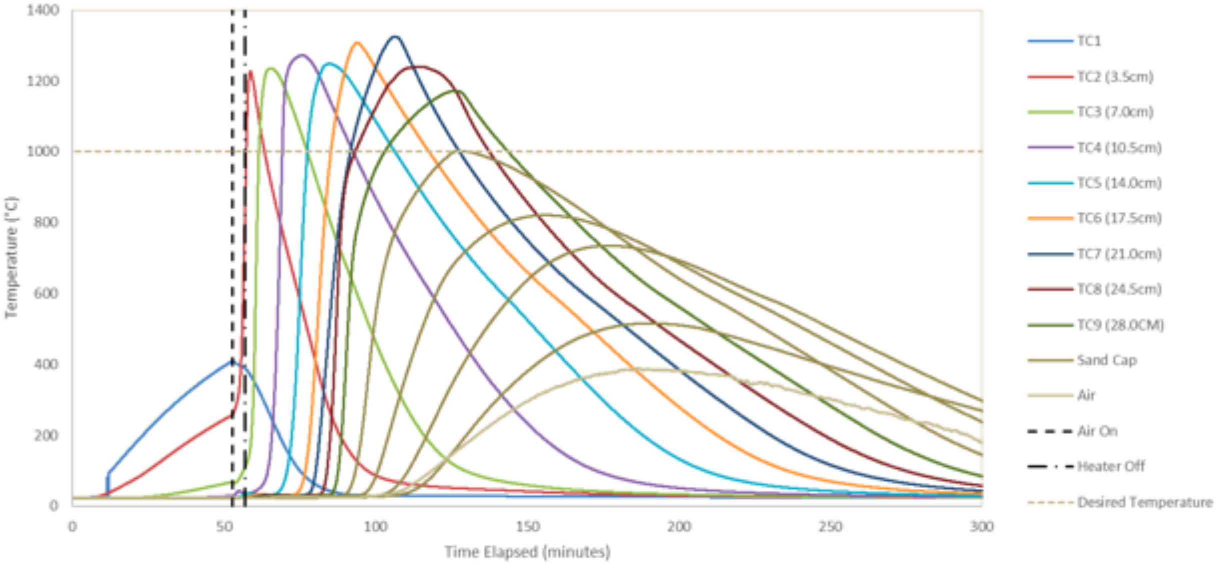

Figure 12: Test I-1 TC profile - 60 g GAC/kg Sand, 5.0 cm/s Air Flux

Examination of the TC temperature profiles in test I-1 shows that average peak temperature was 1253°C, indicating that the high temperatures needed to destroy PFAS is possible by mixing GAC with sand. The smoldering front velocity is estimated by averaging the time between the time of arrival of the front (steep vertical sections) of each temperature profile. In test I-1, this was calculated to be 0.64 cm/min (38 cm/hour). The smoldering front velocity can be used to estimate the time to treat a contaminated soil mixture of different heights.

Figure 11 and Figure 12 presents the TC temperature profile and gas emission profile (CO, CO_2, and O_2), respectively, observed for test I-7 under the same conditions as test I-1 but with a lower air flux (2.5 cm/sec vs 5.0 cm/sec)

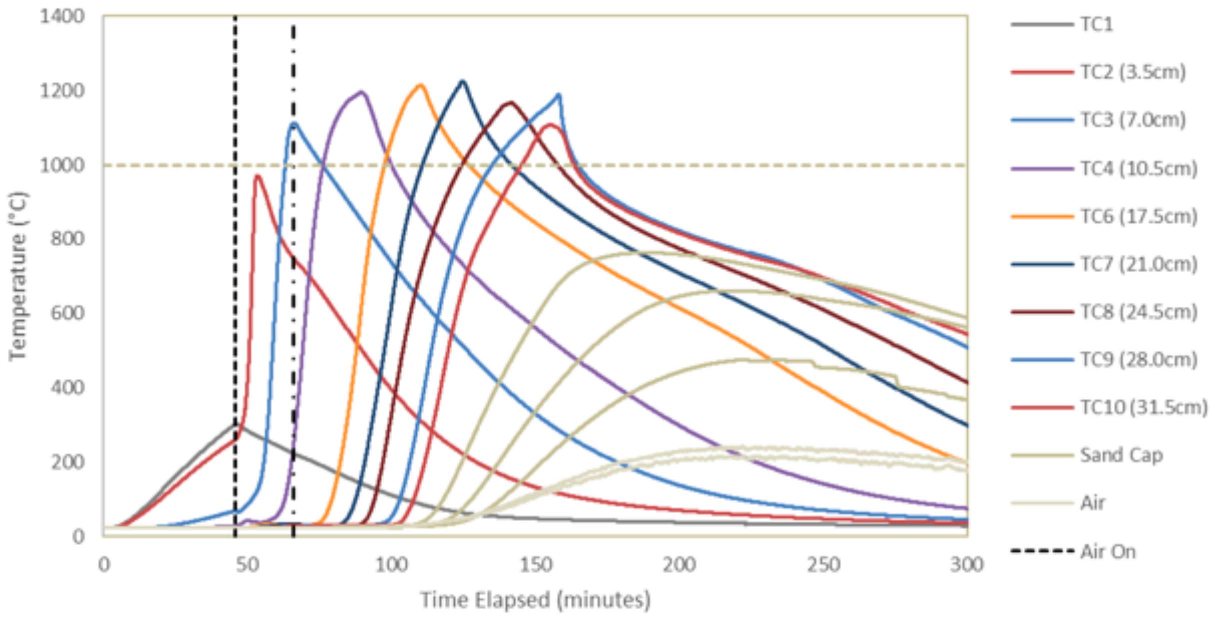

Figure 13: Test I-7 TC profile - 60 g GAC/kg Sand, 2.5 cm/s Air Flux

When TC2 had reached 260°C, the air flow was initiated at 46 minutes and ignition occurred, followed by a self-sustaining smoldering reaction as evident from the both the sharp inflection of temperature to a peak temperature followed by overlapping profiles from TC2 to TC9. In contrast to the test I-1, the average peak temperature was slightly lower at 1153°C, and the smoldering front slower at 0.39 cm/s (23 cm/hour).

Figure 14 shows that combustion gases that were produced and oxygen consumed during the reaction. The CO and CO_2 produced corresponds to the same time interval that self-sustaining smoldering combustion was observed. Note that CO measurement was higher than the calibration of the equipment in this test and plateaued. Oxygen was nearly depleted and led to oxygen starvation of the reaction (reduce heat generation and smoldering front velocity). There was less oxygen depletion observed in other tests with lower GAC concentrations.

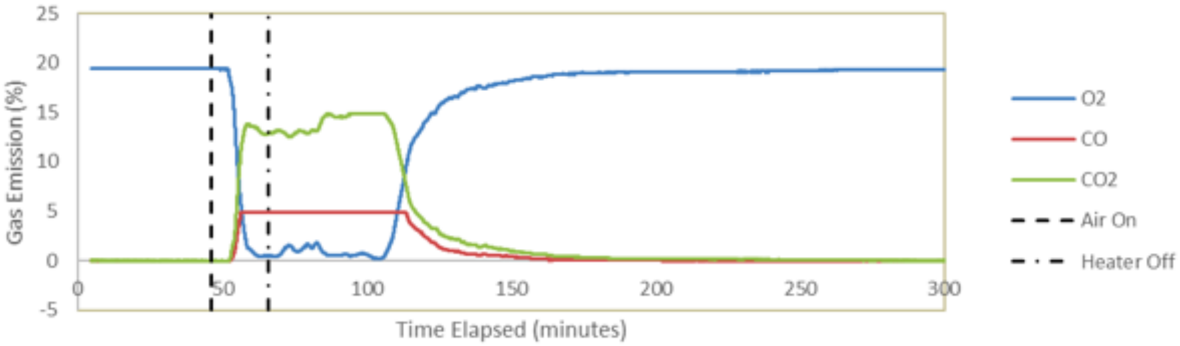

Figure 14: Test I-7 Gas Emissions

Table 6 presents a summary of eight tests conducted with GAC and crumb rubber. Although crumb rubber (test I-2) supported self-sustaining smoldering, it produced emissions with aerosol droplets (condensates) that made it not a suitable candidate for further testing.

Table 6: Test Summary

Test No	Ratio (g fuel /kg sand)	Fuel	Air Flux (cm/ s)	Moisture Content (%)	Average Peak Temp. (°C)	Average Front Velocity (cm/min)	Smoldering Temperature Trend	Self-Sustaining
I-1	60	GAC	5	0	1253	0.64	Steady	Yes
I-2	60	Crumb Rubber	5	0	720	0.64	Increasing	Yes
I-3	40	GAC	5	0	990	0.66	Increasing	Yes
I-4	20	GAC	5	0	690	0.49	Steady	Yes
I-5	40	GAC	2.5	0	1003	0.47	Steady	Yes
I-6	40	GAC	7.5	0	1044	0.7	Steady	Yes
I-7	60	GAC	2.5	0	1153	0.39	Steady	Yes
I-8	20	GAC	2.5	0	661	0.33	Steady	Yes

Figure 13 and 14 plots the relationship between GAC concentration and air flux on the average peak temperature and front velocity.

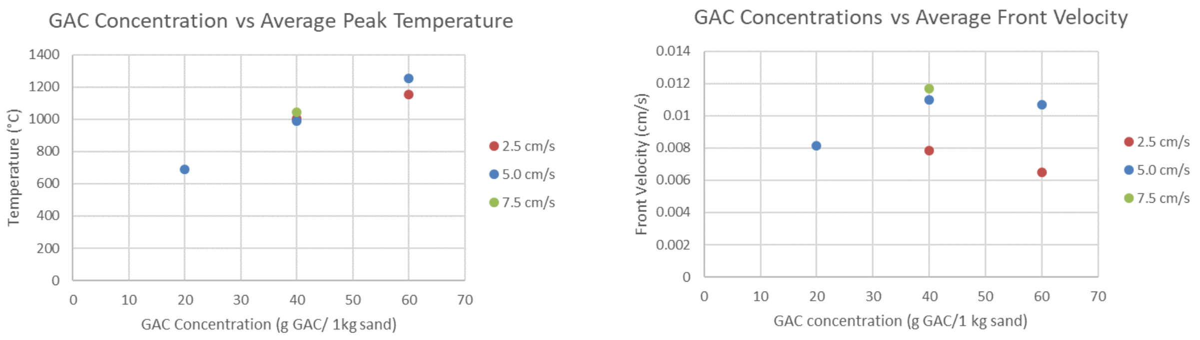

Figure 15: GAC Concentration vs Average Peak Temperature and Front Velocity

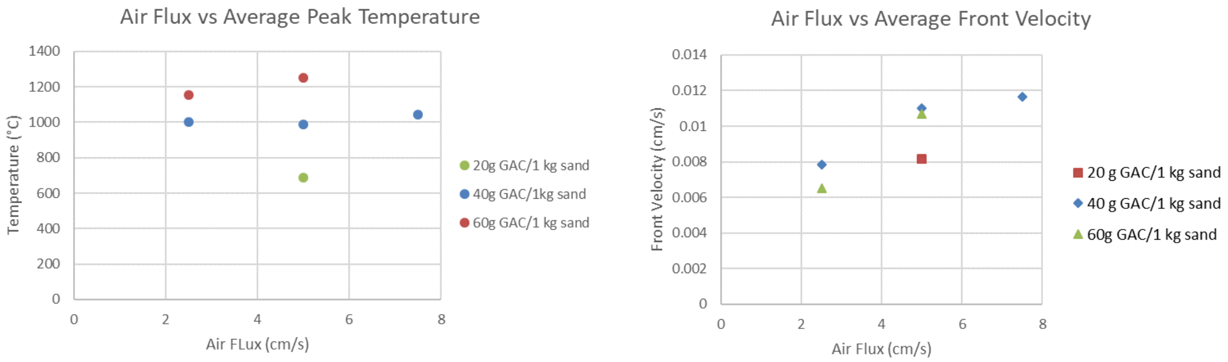

Figure 16: Air Flux vs Average Peak Temperature and Front Velocity

The graphs demonstrate that the peak temperature is controlled (approximate linear relationship) by GAC concentration. There is minimal influence on peak temperature by air flux. Conversely, the front velocity is controlled (linear relationship, matches literature) by air flux.

These results are not surprising as there is an energy balance that is dominated by the rate of oxidation and heat released and heat loss. As the fuel content increases of a given fuel, there is more energy that can be released per unit time if oxygen is in excess to the available fuel. This results in higher average peak temperatures. Increasing the air flux increases the rate of forward convective heat transfer and that results in a faster front velocity (faster mass rate of destruction) at a given GAC concentration

From a practical perspective, the results indicate that:

1. GAC mixed with soil can achieve temperatures greater than 1,000°C;
2. Moderate temperatures (260°C) can be used to initiate the reaction (low energy requirements); and
3. Duration of treatment is relatively short based on achievable front velocity.

Phase II: Assessment of PFAS Destruction

GAC - Loading/Pre-Treatment

The objective of test II-1 and II-2 was to assess if three target PFAS (PFOA, PFOS and PFHxS), could be destroyed when adsorbed onto GAC that is then mixed with a sand. Stock solutions of these three compounds were made for each test and the amount of PFAS absorbed from each stock solution by the GAC is presented in Table 7

Table 7: PFAS Concentration in Stock Solution Before and After GAC Addition

	Test II-1		Test II-2	
PFAS Compound	**Before GAC**	**After GAC**	**Before GAC**	**After GAC**
PFOA	530	<0.2	551	0.083
PFOS	127	<0.2	133	0.046
PFHxS	215	<0.2	241	0.025

All values in mg/L

Note that the detection limit was elevated for test II-1 (0.2 mg/L) but was 0.4 ug/L for test II-2. The samples used to measure PFAS concentrations remaining in the stock solution were from the water that was collected from the GAC under vacuum. The results indicate that GAC removed >99% of the PFAS in the stock solutions. The difference in PFAS concentration in the stock solution before and after GAC addition was used to calculate that total mass absorbed to the GAC and in the columns based on the amount of GAC used. This was done because separate tests demonstrated that extraction of PFAS from GAC has poor efficiency and is thus unreliable.

Vacuum drained GAC were visually dry. Separate tests, where a known amount of water was added, showed that GAC can have up to 26% moisture content and appear dry because the water is adsorbed into the micro-porosity of the GAC (bound water). Oven drying of fresh GAC resulted in 3% mass loss indicating that some water was absorbed even before it was used. This information allowed correction of the GAC concentrations used in further testing. In contrast, the vacuum drained soil did appear to have excess water.

GAC Treatment-Smoldering

Table 8 presents the smoldering summary for both tests. The GAC to sand ratio was adjusted to reflect the moisture content of the GAC.

Table 8: Smoldering Summary for Test II-1 & II-2

Test No.	Ratio (g GAC/kg sand)	Air Flux (cm/s)	Moisture Content (%)	Avg. Peak Temp (°C)	Avg. Front Velocity (cm/min)	Avg. O_2 (%)	Temp. Trend	Self-Sustaining
II-1	43	5	14	908	0.69	5	Steady	Yes
II-2	39	5	21	950	0.68	6	Steady	Yes

The impact of the moisture content on the relationship between GAC concentration and air flux, average peak temperature and front velocity, is shown in Figure 15. In general, the moisture content reduces the average peak temperature slightly, but otherwise little impact on front velocity was observed.

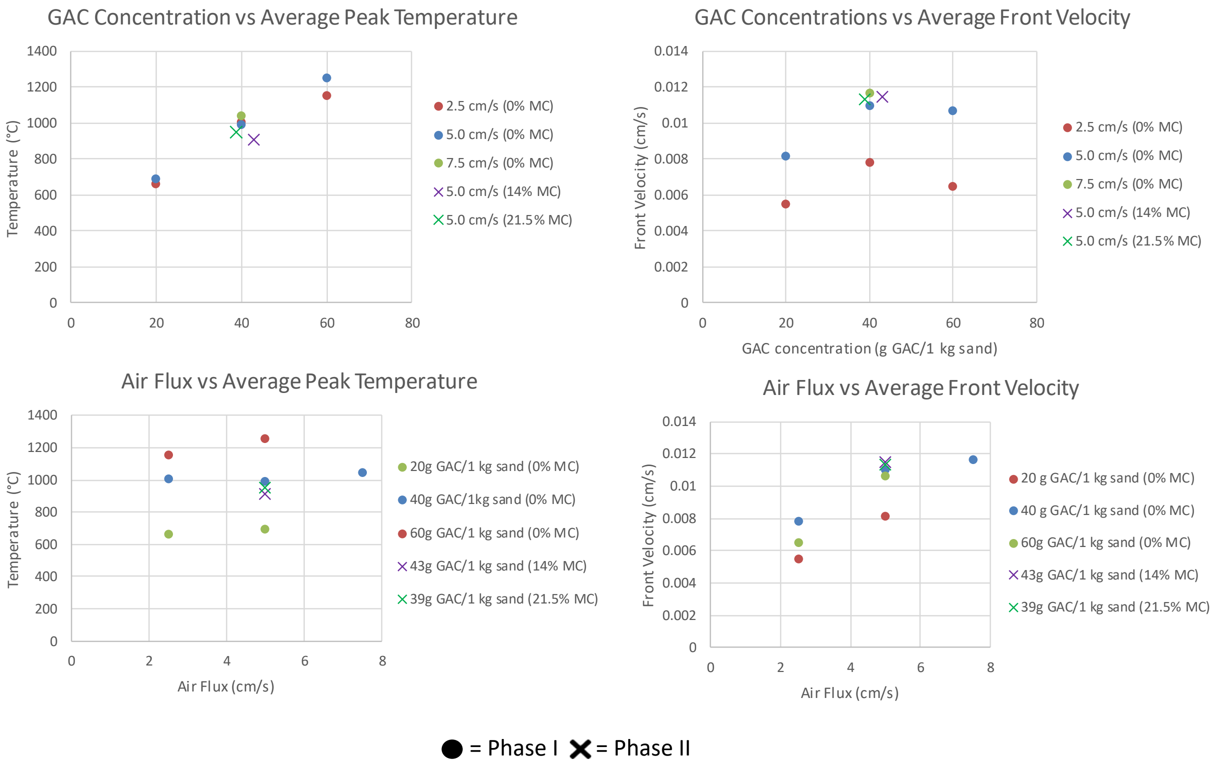

Figure 17: Impact of Moisture Content on Temperature and Front Velocity

GAC Treatment-Post Treatment

Figure 16 shows the sand and GAC mixture before and after smoldering, respectively, and shows how the sand becoming reddish in color, commonly observed from oxidized iron and typical after smoldering.

Figure 18: Pre-Treatment (Left) and Post-Treatment (Right) GAC & Sand Mixture

Table 9 shows the pre and post analytical results and indicates that all PFAS compounds were non-detect in the sand and ash after treatment. Note that PFAS concentration for each test based on the calculated PFAS adsorbed to the GAC (corrected for moisture content).

Table 9:Pre and Post PFAS Concentrations

PFAS	Test II-1		Test II-2	
	Pre	Post	Pre	Post
PFOA	590,000	<0.4	510,000	<0.4
PFOS	140,000	<0.4	120,000	<0.4
PFHxS	240,000	<0.4	220,000	<0.4

All Results in ug/kg
D.L. 0.4 ug/kg

Soil Treatment

The surrogate soil as described in the methods sections was used in two tests: test II-3 using the same three PFAS used in tests II-1 and test II-2, and test 4 that included three additional PFAS: PFNA, PFBS and PFHpA. The objective of these tests was to assess the treatment of PFAS that was adsorbed to the soil, and the use of GAC to create smoldering conditions to support their destruction. In addition, these tests further evaluated gas emissions for breakdown by-products and degree of PFAS destruction. The GAC ratio was targeted at 50 g/kg soil to achieve temperatures greater than 1000°C as observed in Phase I tests.

Table 10 presents a summary of the smoldering data for test II-3 and shows the soil composition, moisture content, and GAC composition. The results indicate that a self-sustaining reaction was obtained with temperatures in excess of 1000°C.

Table 10: Test II-3 Smoldering Summary

Soil Composition (%)										
Top Soil	Med. Sand	Coarse Sand	GAC (g /kg)	Air Flux (cm/s)	M.C. (%)	Avg. Peak Temp. (°C)	Avg. Front Vel. (cm/min)	Avg. O_2 (%)	Temp. Trend	Self-Sustaining
30	45	25	48	5	10.8	1016	0.63	5	Steady	Yes

Table 11 presents the analytical data and shows almost complete removal of all added PFAS.

Table 11: Test II-3 Soil Analytical Results

	PFAS (mg/kg)		
Sample	**PFHxS**	**PFOA**	**PFOS**
Blank Soil	N.D.	N.D.	N.D.
PFAS Loaded Soil	16.86	13.41	23.3
Loaded Soil with Sand & GAC	7.06	6.14	9.54
Post-Treatment Ash/Soil	N.D.	N.D.*	N.D.

Notes
*2 of 3 samples were non-detect for all 3 PFAS compounds. 1 sample had a measured PFOA concentration of 0.0002 mg/kg

N.D. = not detected at Detection Limit of 0.00005 mg/kg

Based on the total mass of PFAS added in the column, 82% of the available fluorine was captured as HF in the impinger tubes.

It is possible that some of the released HF may be reacting with the silica sand used in this study, resulting in a loss of HF as per the following reaction:

$$4HF + SiO_2 \rightarrow 2H_2O + SiF_4$$

The GAC in the XAD tubes was not analyzed because the extraction testing indicated that the mass-balance efficiency of the extraction was approximately 50% without further method modification.

Table 12 presents a summary of the smoldering data for test II-4 and shows the soil composition, moisture content, and GAC composition. The results indicate that a self-sustaining reaction was obtained with temperatures in excess of 1000°C.

Table 12: Test II-4 Smoldering Summary

Soil Composition %)										
Top Soil	**Med. Sand**	**Coarse Sand**	**GAC (g /kg)**	**Air Flux (cm/s)**	**M.C. (%)**	**Avg. Peak Temp. (°C)**	**Avg. Front Vel. (cm/min)**	**Avg. O_2 (%)**	**Temp. Trend**	**Self-Sustaining**
23	47	25	50	5	5.7	1064	0.72	6	Steady	Yes

Table 13 presents the analytical data and shows that all added PFAS was below detection in the ash/soil post-treatment. Note that the total mass loading was three times higher than in test II-3. There was evidence of poor capture in the HF emission line as evident by the lack of condensate suggesting a leak in the line.

Table 13: Test II-4 Soil Analytical Results

	PFAS (mg/kg)					
Sample	**PFBS**	**PFHpA**	**PFHxS**	**PFOA**	**PFNA**	**PFOS**
Blank Soil	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PFAS Loaded Soil	3.19	13.32	10.84	14.91	28.73	10.87
Loaded Soil with Soil & GAC	1.3	9.75	7.21	11.49	25.58	6.67
Post-Treatment Ash/Soil	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

N.D. = not detected at Detection Limit of 0.0005 mg/kg

For this test, we attempted to extract and analyze the PFAS on XAD GAC recognizing the limitation of the mass extraction efficiency and therefore our confidence on total PFAS mass that was emitted. Table 14 shows the analysis of PFAS adsorbed within XAD tubes.

Table 14: XAD Extraction Results

	PFAS Compound (ug/kg of GAC Sorbant)												
No. of Carbons	**- 4 C**	**- 4 C**	**- 5 C**	**- 6 C**	**- 6 C**	**- 7 C**	**- 8 C**	**- 8 C**	**- 8 C**	**- 9 C**	**- 10 C**	**- 11 C**	**- 12 C**
	PFBA	**PFBS**	**PFPeA**	**PFHxA**	**PFHxS**	**PFHpA**	**PFOA**	**PFOS**	**PFOSA**	**PFNA**	**PFDA**	**PFUnA**	**PFDoA**
XAD-First	3.36	0.01J	242.52	264.8	0.14	470.45	535.72	0.47	N.D.	256.91	0.14	0.03J	0.09
XAD-Second	3.09	0.02J	280.56	378.81	0.14	482.68	662.38	0.2	N.D.	277.82	0.13	0.03J	0.15

N.D. Not Detected at Detection Limit of 0.05 ug/kg

J Estimated value, below D.L.

The detection of PFAS compounds in the second XAD tube was expected to be non-detect. The breakthrough is suspected to be due a combination of the short residence time within the XAD tubes and temperature of the effluent gas which would impact adsorption kinetics. Note that the concentrations in the soil reported in Table 13 are in milligrams and in Table 14 in micrograms, suggesting that a very small fraction of PFAS mass was emitted from the column.

The higher carbon number PFAS (greater than 9 carbons) was likely derived from impurities in the stock solutions as the high PFAS compound used in the study was PFNA (9 carbons). The original PFAS carboxylates were detected in the XAD tubes (PFOA, PFHpA, and PFNA), but sulfonates were absent. It is possible that carboxylate-versions of the sulfonates (PFOS → PFOA, PFHxS → PFHxA, PFBS → PFBA) could be breakdown products. Although PFAS will completely breakdown at high temperatures with sufficient residency time, it is possible that during that during heating, there is sufficient energy to break off the sulfonate headgroup and volatilize a small fraction of PFAS. From a practical consideration, the emitted PFAS could be captured in an off-gas GAC treatment system, and the GAC subsequently used/treated by smoldering.

Conclusions and Implications for Future Research

This proof of concept study shows that PFAS adsorbed to GAC (e.g., spent GAC) or to soil can be removed from soil or GAC to below analytical limits using smoldering combustion when GAC, by itself or containing PFAS, is used as a surrogate fuel that is mixed in with soil or suitable porous medium. Extrapolating these results along with knowledge of applying smoldering at full scale with other wastes types, suggests that smoldering can be used to treat IDW.

The overall conclusions of this proof-of-concept research are:

1. GAC can be used to support smoldering combustion to achieve temperatures that destroy PFAS when added to soils at ~40 to 60 g/kg.
2. PFAS absorbed to GAC or soils can be treated via smoldering combustion resulting in non-detectable levels in soils, sand and ash
3. GAC smoldering can be initiated with low heat (260ºC) over short time periods, and the smoldering front velocity is sufficiently fast to be practicable at larger scales (based on full scale experience using smoldering to destroy other hydrocarbons);
4. One test shows that greater than >80% of the PFAS can be recovered as HF suggesting that complete decomposition of PFAS via smoldering combustion is possible; and
5. Some decomposition products may form that can be scrubbed from gas emissions using GAC.

Future recommended work includes:

1. Further work is required to close the mass balance of PFAS destruction and by-product formation (if any)
    a. change method of emission trapping of PFAS (e.g., alkaline traps)
    b. Explore HF fate (e.g., reaction with silica);
2. Test with site soils to assess impact of heterogeneity on performance;
3. Large scale tests to better characterize emissions/ performance; and
4. Test simple soil amendments (e.g., limestone) that can neutralize HF in emissions.

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