Thermal Treatment of PFAS in Environmental Media: A review of the state-of-the-science

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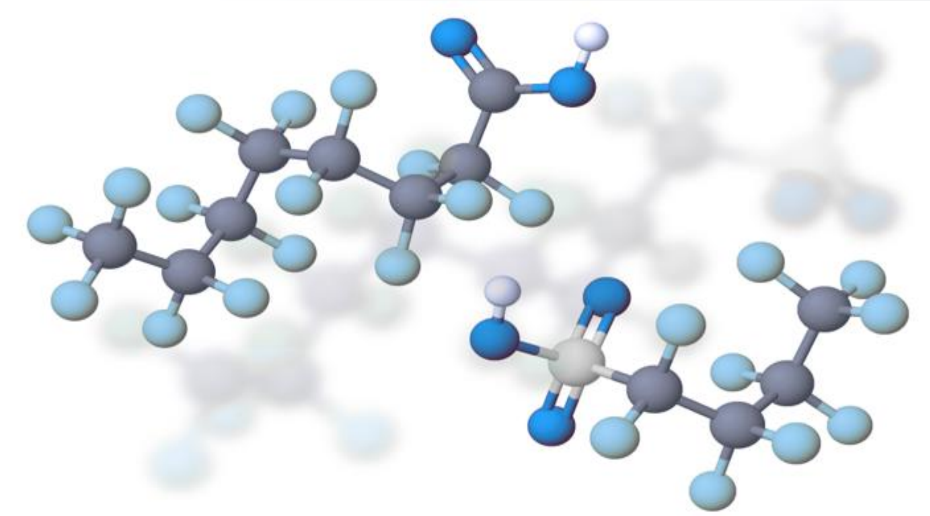
PFAS Background

- Per- and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals that have been in use since the 1940s.
- PFAS are (or have been) found in a wide array of consumer products like cookware, food packaging, and stain and water repellants used in fabrics, carpets and outerwear.
- PFAS can also be found at manufacturing and processing facilities, and airports and military installations that use firefighting foams which contain PFAS.
- Because of their widespread use and environmental persistence, most people have been exposed.
- Some PFAS chemicals can accumulate and can stay in the human body for long periods of time.
- There is evidence that exposure to certain PFAS may lead to adverse health effects.



Purpose of this workshop

- Due to the unique and atypical properties of PFAS, there is a need for research, development, and implementation of existing and innovative technologies to effectively treat PFAS in contaminated media.
- Thermal treatment technologies are common remediation approaches for contaminated media and waste.
- Limited information exists on the efficacy, potential atmospheric emissions, operational conditions, costs, etc. for thermal treatment technologies specifically targeted for PFAS.

- The **purpose** of this workshop is to review the **state-of-the-science** review on thermal treatment technologies for PFAS and to **identify data gaps** to focus further research.

State of the Science – Literature Search Results

- PFAS thermal technologies categorized for specific media/contaminants
- Treatment technologies - scale of the study, media treated, treated contaminants, experimental conditions, achieved results, advantages, and limitations
- Sample collection protocols, characterization techniques, cost analysis, and research needs and recommendations are presented in detailed descriptions based on available information.

PFAS Thermal Technologies

PFAS Thermal Technologies Reported in the Literature

Thermal Destruction Methods

1. Incineration
   - Incineration of Sewage Sludge
2. Cement Kiln Treatment
   - Use of Sewage Sludge as an alternate fuel
3. Pyrolysis/Thermolysis
   - $Ca(OH)_2$ Facilitated Treatment Methods
4. Smoldering

Thermal Desorption Methods

1. Thermal Conduction Heating
2. Infrared Heating

Thermal Desorption Followed By Destruction Methods

1. GAC Reactivation
2. Vapor Energy Generator (VEG)

Off-Gas Treatment Methods

1. Thermal
2. Non-Thermal

Sampling and Analytical Methods

- Sampling:
  - Sampling protocols for emissions are still under development.
  - Solids sampling protocols for PFAS on/out of treatment may be able to “lean on” existing methods for legacy contaminants.
- Analytical methods:
  - Limited lists of targeted PFAS analytes currently measured and a lack of standardized protocols.
  - Lack of analytical methods to identify and quantify PICs
  - Need to understand degradation metabolites formed under operational conditions and allow for a total PFAS mass balance.
  - High-resolution mass spectrometric tools - time of flight mass spectrometry instruments can identify PICs and end products, but the confirmation and quantitation of such identified structures requires analytical standards

Incineration of PFAS

- **Few** studies exist for incineration of PFAS-containing materials
  - Fluoropolymers (e.g. PTFE) and other specific PFAS compounds have been studied.
  - Various PFAAs may be produced as byproducts based on operational conditions.

- Conditions for incineration
  - Typical conditions range between 600-1,000 C with residence times of 2-4 seconds.
  - Incineration used for municipal waste disposal, disposal of production waste, and end-of-life disposal.

- Efficacy in pilot studies for municipal and medical wastes
  - 99.9% destruction for fluoropolymers with HF formation.
  - No detectable known PFAAs in emissions.
- Exhaust gases are filtered in scrubbers, electrostatic precipitators, or baghouses
  - Residual gaseous products are further treated with off-gas treatment technologies.
  - Gaseous products may be suitable for energy recovery.

- Ash produced during the process is disposed in landfills or used for construction
- To date, no full-scale application has been implemented specifically for PFAS.

(Khan, So, and da Silva 2019; Aleksandrov et al. 2019; Taylor et al. 2014; Lemieux et al. 2007; Yamada et al. 2005; Yamada 2003)

Off Gases / Emissions

- Primary end products of PFAS combustion are CO, CO_2, and HF.
- Most thermal treatment systems are equipped with gas emissions controls by using CO_2 scrubbers.
- Low pH environment due to HF production.
- Long-term emission of corrosive HF gas and its effect on the reactors or furnaces is unknown.
- Basic media such as $Ca(OH)_2$, NaOH, and KOH are added to manage the HF generated.
- Due to potential incomplete reactions, there is a need for further treatment methods for PICs.
- NOx/SOx and organic contaminants are common decomposition products.
- In some thermal treatment technologies, syngas (CO and H) is produced and cycled back to use as fuel for the system.
- Need for complete characterization and monitoring of emissions and PICs.

Products of Incomplete Combustion (PICs)

- PICs are generally chemicals beyond the typical list of targeted PFAS analytes
- Shorter chain PFAS, partially fluorinated PFAS, defunctionalized perfluorinated carbon chains, etc.
- Nature and amount of PICs depend on:
  - Temperature
  - Oxygen availability
  - Residence time at higher temperatures
  - Physical state of the product
  - Catalyst
  - Other?

CHF2

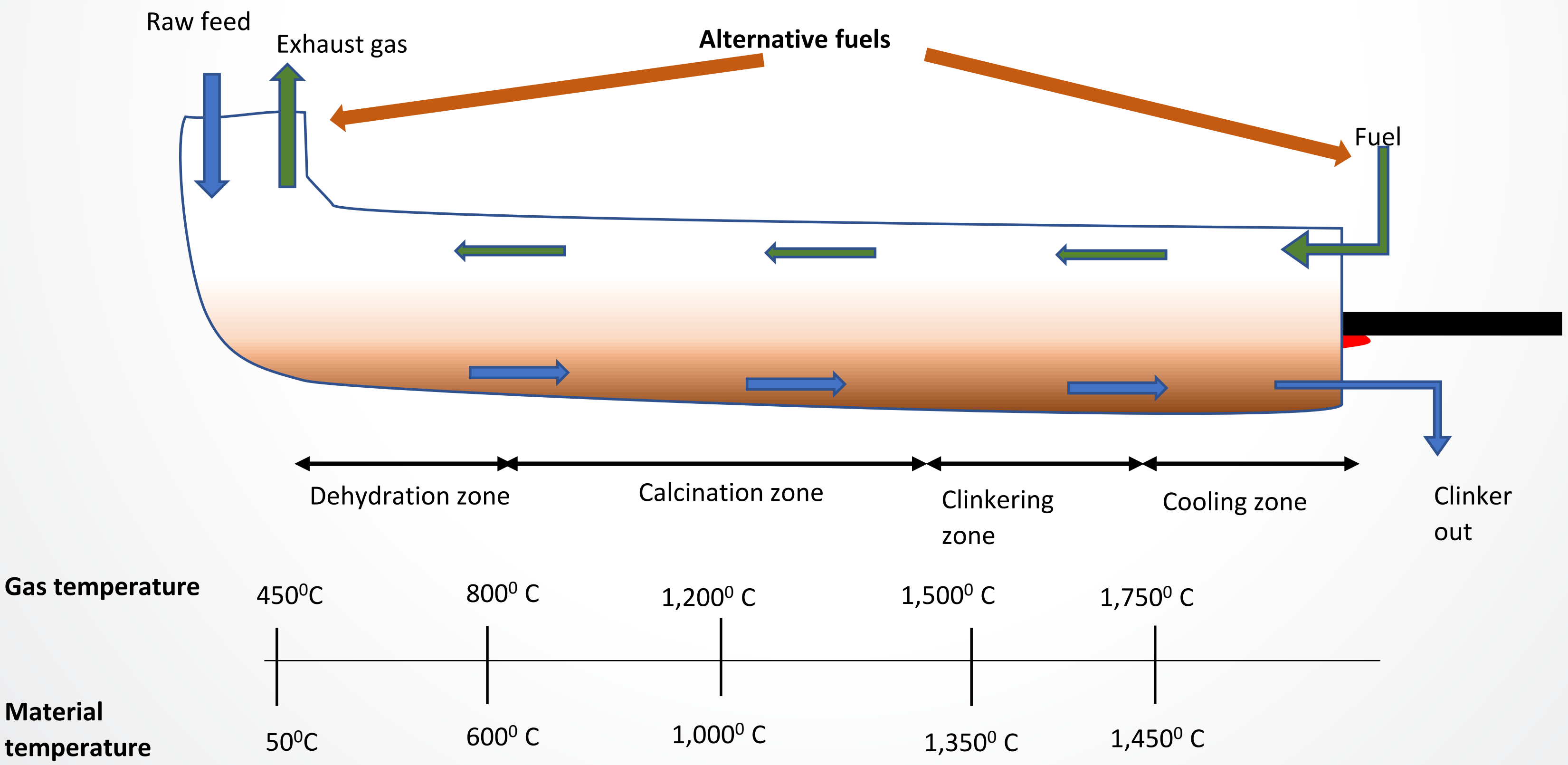
C2F6 CF3

CF3COOH

CH2F

Cement Kiln Systems: Background

Rotary kilns are long, cylindrical and inclined furnaces used for converting raw material to cement. As the material moves down the kiln, it passes different temperature zones.



Cement Kiln Treatment for PFAS

- Few studies have been reported using cement kiln treatment for the destruction of fluoropolymers.
- More research needed to understand the applicability of cement kiln treatment for PFAS-contaminated waste.
- Co-incineration processing of PFAS-contaminated media may be a promising option as it provides the proper conditions for PFAS destruction and potential fuel benefits.
- Typical operating conditions:
  - Temperature > 900°C.
  - Calcium catalyzes the PFAS destruction.
  - Long residence time and quality control of process.

(Ueno et al. 1997; Geocycle 2018, Wang et al. 2011)

Sewage Sludge Treatment using Cement Kilns

- Sewage sludge containing PFAS as a co-fuel for cement kilns is considered as an energetically, economically and environmentally beneficial technology

  - Advantages for using sewage sludge as an alternate fuel:
    - Destruction of toxic organic pollutants,
    - Use of the excess thermal energy,
    - Minimizing sewage odors are advantages.

  - May be a viable option for PFAS treatment if controls for the emissions and other air pollutants can be economically implemented.

(Stasta et al. 2006; Cieślik, Namieśnik, and Konieczka 2015)

Pyrolysis/Thermolysis Treatment Methods

- Pyrolysis is defined as the chemical decomposition of organic materials at high temperatures under inert conditions.
- Pyrolysis has been applied for remediation of soil and requires lower heat/energy requirements compared to incineration.
    - Temperatures range from 400-1,200°C for different contaminants with less than 500°C typically used for the treatment of hydrocarbons.
    - For hydrocarbons, the process involves two steps:
        1. desorption at 150-350°C at their boiling points
        2. followed by pyrolysis at 400-500°C.
    - End products are carbonaceous materials which can be used in agriculture
    - Volatilized contaminants and pyrolyzed products can be incinerated or reused

(Huber et al. 2009, Ding et al. 2019; Vid

$Ca(OH)_2$ Facilitated Treatment Methods

- Fate and transport of PFOS, as a representative PFAS, during thermal treatment in the presence of $Ca(OH)_2$ was investigated through the characterization of reaction products

  - Calcium-based chemicals were added to increase the pH and to control the odor
  - PFOS decomposed at 350°C and the formation of CaF_2 suggests that $Ca(OH)_2$ leads to the decomposition at a temperature lower than its gasification temperature due to solid-state interaction between $Ca(OH)_2$ and PFOS.

Smoldering Background

- Smoldering is a flameless combustion technique that occurs in a condensed fuel surface to produce CO_2, water and energy (heat) in the presence of oxygen.
- The average temperature reported was 500-1,100°C and can reach higher temperatures by providing excess oxygen
- Different mechanisms involved include desorption, exothermic combustion and pyrolysis within different regions
- Further research is required to fully characterize efficacy for PFAS.

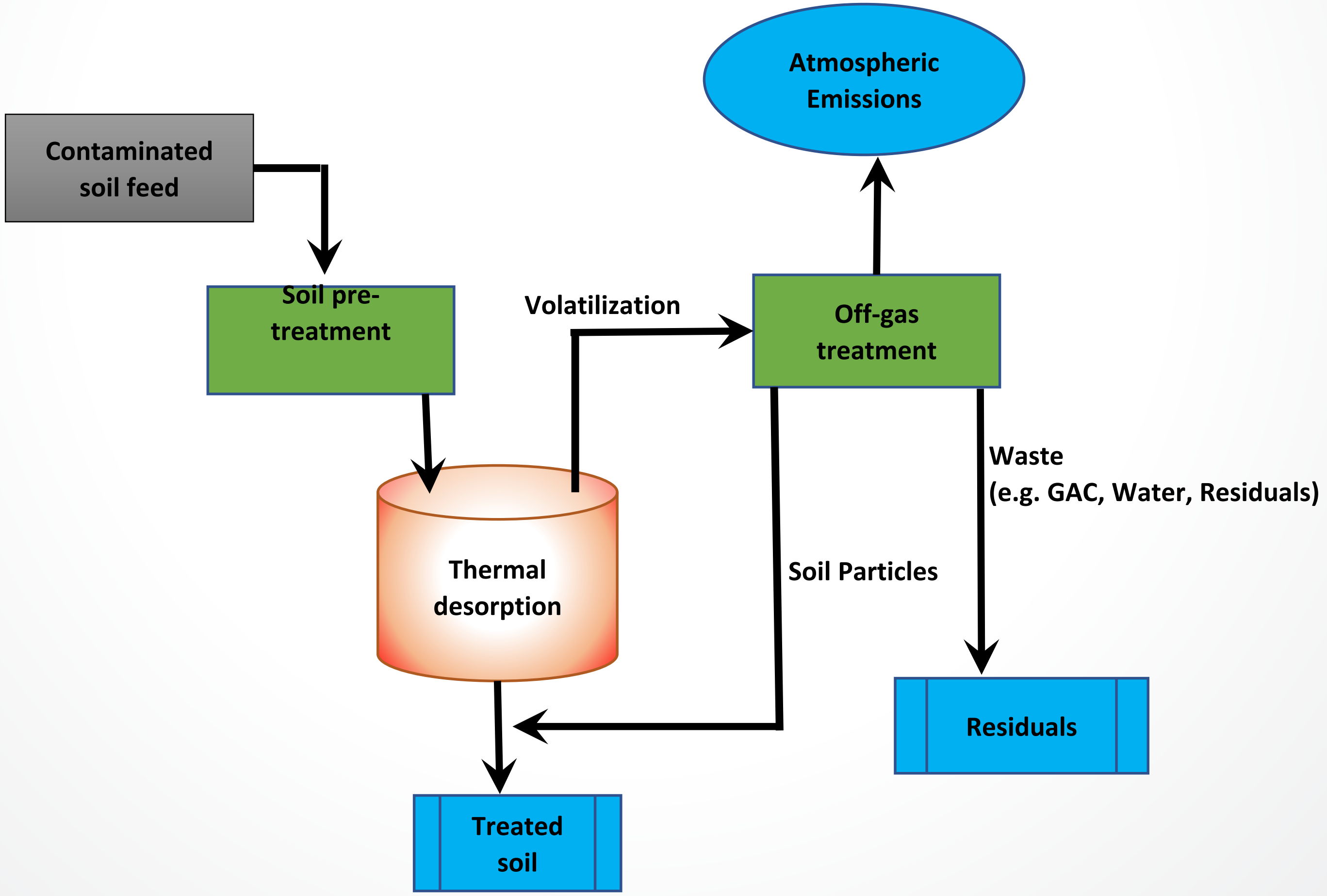
(Ding et al. 2019; Vidonish et al. 2016)

Smoldering Studies

- Energy is added in the initial stage and minimally during the process to support smoldering.
- It can reach the PFAS destruction temperatures when the waste matrix is combined with suitable fuel materials.
- Several limitations:
  - Contaminated media need to be permeable enough to allow sufficient gas flux to complete the destruction in a self-sustaining manner.
  - Sufficient fuel needs to be available in the matrix to maintain combustion.
  - Smoldering performance improves with low volatility contaminants such as coal tar, creosote, and petroleum hydrocarbons.

Thermal Desorption Treatment: Background

Heating to volatilize the contaminant followed by off-gas treatment by either high temperature (900-1,000°C) incineration or carbon adsorption.



Thermal Desorption Methods

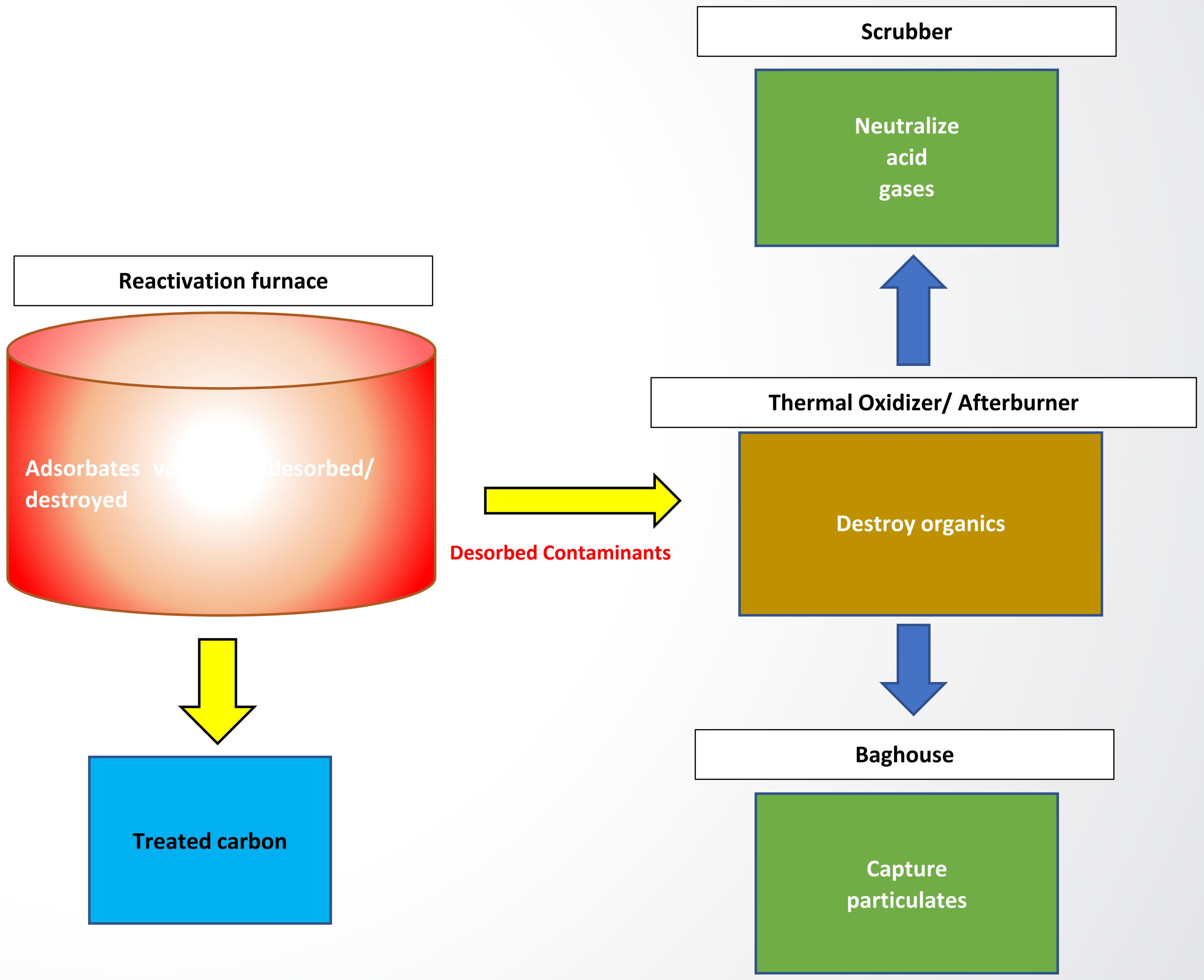
- Thermal Conduction Heating
  - No PFAS removal when soil was heated from 220-400°C.
  - 99.9% of PFAS including PFOA, PFOS, and PFHxS was removed when heating to 350-400°C over a one-week period
  - A proof-of-concept field study demonstrated the capability to heat soil to a desired temperature for thermal desorption of PFAS over time (79 days at 400° C)
- Infrared Heating
  - Infrared heating elements treat contaminated materials (e.g. soil, sludges, solids) at higher temperatures.
  - High thermal efficiency and doesn't use any moving parts compared to other designs which "tumble" the soil and hence lower operating costs.
  - Applied at several PFAS desorption technology pilot tests.

GAC Reactivation Process

GAC reactivation process typically involves two steps

1.) Initially, the adsorbates are volatilized or desorbed from the carbon surface and are destroyed in the reactivation furnace

2.) Contaminants that are not destroyed in the furnace are removed with an adsorbate abatement system. These abatement systems commonly consist of a treatment train with a thermal oxidizer/afterburner to destroy organics, a scrubber to neutralize acid gases, and a baghouse to capture particulates



GAC Reactivation Processes

- Physical and chemical property changes to the GAC surface may affect its performance compared to the virgin GAC.
- Hence, prior to development of a large-scale treatment system, there is a need to optimize certain parameters, such as
  - GAC lifetime after reactivation, and the
  - Number of reactivation cycles without losing the performance of GAC.

Current State of Science

- Limited laboratory scale studies exist with few pilot- and field-scale studies.
- To date, pyrolysis and thermolysis studies have focused on select PFAS and fluoropolymers and are not representative of the wide range of PFAS precursors found at contaminated sites.
- Thermal desorption of soil and sludge at the temperature ranges tested may only volatilize PFAS generating PICs.
- Few studies shown mineralization at higher temperatures with long residence time.
- Need to avoid secondary pollution from emissions.
- Need for a destructive technology to completely destroy desorbed/volatilized PFAS.
- Prior to field scale implementation - Need to optimize parameters for complete volatilization of wide range of PFAS followed by destruction of desorbed contaminants.

Energy consumption and Cost

- Need for energy recovery techniques to reduce energy consumption and cost
  - Some of the self-sustaining techniques via cycling of syngas
  - Alternative fuel in cement kilns – PFAS contaminated IDW
  - Combination of desorption/volatilization and destruction methods, in situ and ex situ methods
- Selection of an appropriate technology is more critical
- Challenges:
  - Implementation at remediation sites
  - Further treatment for short-chain PFAS with unknown toxicity
  - High capital, operational, and maintenance costs
  - Suitability for different site characteristics, environmental matrices, and field conditions based on the soil geochemistry, and environmental and field conditions

Thermal Treatment of PFAS: Costs

Technology	Cost[a]-Vidonish et al. 2016	Cost[b] - Ding et al. 2019 (overall)
Incineration	\$150-2,900/t	\$560-940/t [c]
Thermal Desorption		
a. in situ	\$70-460/t	NA
b. ex situ	\$46-100/t	\$35-200/t [c]
Pyrolysis	NA	\$300/t
Smoldering	\$ 260-330/t	NA

[a]-Vidonish et al. 2016

[b]-Ding et al. 2019

Effectiveness of Field-scale treatment

Factors

- Bench-scale and pilot testing: temperature ranges, reaction time period, and moisture and oxygen conditions
- Field scale: complex mixture of waste, influence of co-contaminants, different geochemical properties and conditions (pH, temperature, organic matter, inorganic ions and metals) and different types of PFAS and precursors to be treated
- Air pollution control, off-gas treatment, and careful analysis for the residuals and emissions must be considered
- More research on laboratory- and pilot-scale studies is needed for the successful field-scale demonstration of PFAS treatment with complete mass balance.

Research Needs for Thermal Treatment

- Sampling protocols and analytical methods to fully characterize the PFAS and related PICs, emissions, and residuals.
- More research on laboratory- and pilot-scale studies for the successful field-scale demonstration of PFAS treatment with complete mass balance.
- Generation of HF during the PFAS treatment and the proper management of the resulting acidic environment in the systems.
- Better characterization and optimization of critical operational parameters for cost-effective treatment of PFAS and resulting residuals and emissions.