CleanEarth

Developments in the remediation of PFAS contaminated soil by Thermal Desorption

Rob Martin; Technical Director

Northeast Conference on the Science of PFAS

October 2, 2024

Presentation Outline

- Thermal Desorption Overview
- Clean Earth Research Projects
- Clean Earth Partnership in Research Projects
- Thermal Desorption Industry Data
- Developing PFAS Destruction Science
- Other Thermal Desorption Resources

Thermal Desorption

CleanEarth™

EPA Community Guide to Thermal Desorption

What is Thermal Desorption?

- "Thermal desorption removes contaminants by heating them so that they un-stick (desorb) from soil, sludge or sediment. This heating is done in a machine called a thermal desorber and causes the contaminants to evaporate. Evaporation changes the contaminants into vapors (gases) and separates them from the solid material."
- "Organic vapors are usually destroyed using a thermal oxidizer, which heats the vapors to temperatures high enough to convert them to carbon dioxide and water vapor"
- ""A thermal desorber is not the same as an incinerator."

- The contaminated area is large or deep.
- Contaminant concentrations are high.
- The soil contains a lot of clay or organic material, which causes contaminants to stick to the soil and not evaporate easily.
- A lot of debris must be crushed or removed.
- The capacity of the desorber is small. (Most thermal desorbers can clean over 25 tons of contaminated material per hour.)

Is Thermal Desorption Safe?

A well-designed and operated desorber will safely remove harmful chemicals from contaminated materials. Workers take measures, such as covering loose soil during excavation, to control dust and vapors. Proper temperatures are maintained in the desorber to ensure complete removal of contaminants. If necessary, gases will be collected for treatment.

How Might It Affect Me?

You may notice increased truck traffic when excavation equipment and thermal desorption systems come to the site. You also might hear heavy machinery, such as backhoes and bulldozers, during construction and treatment. If an offsite desorber is used, truckloads of soil must be transported from the site to the desorber.

Why Use Thermal Desorption?

Thermal desorption can be used to clean up soil that has been contaminated with VOCs and SVOCs shallow enough to reach through excavation. Thermal desorption may be faster and provide better cleanup than other methods, particularly at sites that have high concentrations of contaminants. A faster cleanup may be important if a contaminated site poses a threat to the community or needs to be cleaned up quickly so that it can be reused. Thermal desorption has been selected for use at dozens of Superfund sites and other cleanup sites across the country.

Onsite thermal desorber.

Example

Thermal desorption was used to clean up contaminated soil at the Industrial Latex Superfund site in New Jersey. From 1951 to 1983, Industrial Latex manufactured rubber and adhesives, contaminating soil with PCBs and SVOCs.

From April 1999 to June 2000, about 53,600 cubic yards of contaminated material were excavated to depths of up to 14 feet. Materials greater than 2 inches in diameter were removed before placing the soil in the desorber and heating it to 900°F. About 225 tons of contaminated soil were treated each day. A small amount of treated soil had to be placed back in the desorber a second time to meet cleanup goals for PCBs and SVOCs. The cleaned soil was used to backfill the excavated areas.

Vapors from the desorber passed through scrubbers and filters that removed dust particles and contaminant vapors. Air quality was monitored daily to make sure the air released from the desorber met permitted levels. The site was removed from the National Priorities List in 2003.

For More Information

- About this and other technologies in the Community Guide Series, visit: https://clu-in.org/cguides or https://clu-in.org/remediation/About use of
- cleanup technologies at a Superfund site in your community, contact the site's community involvement coordinator or remedial project manager. Select the site name from the list or map at http://www.epa.gov/superfund/sites to view their contact information.

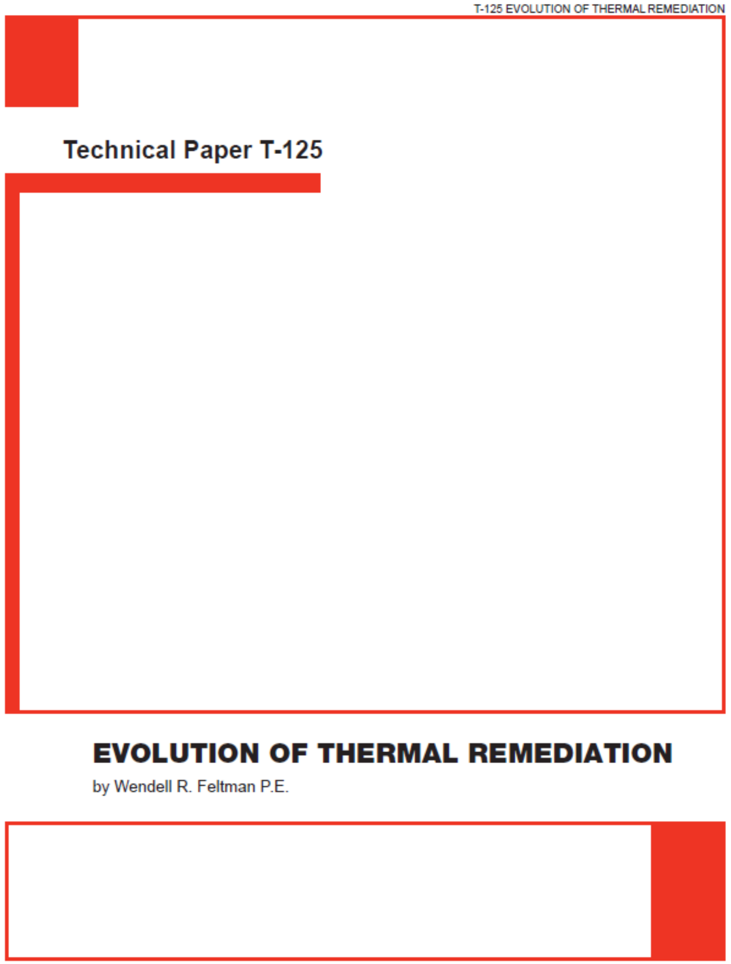
NOTE: This fact sheet is intended solely as general information to the public. It is not intended, nor can it be relied upon, to create any rights enforceable by any party in litigation with the United States, or to endorse the use of products or services provided by specific vendors.

Office of Land and Emergency Management (5203P) | EPA-542-F-21-024 | 2021 | www.clu-in.org

EPA Document Link: https://semspub.epa.gov/work/HQ/401623.pdf

CleanEarth

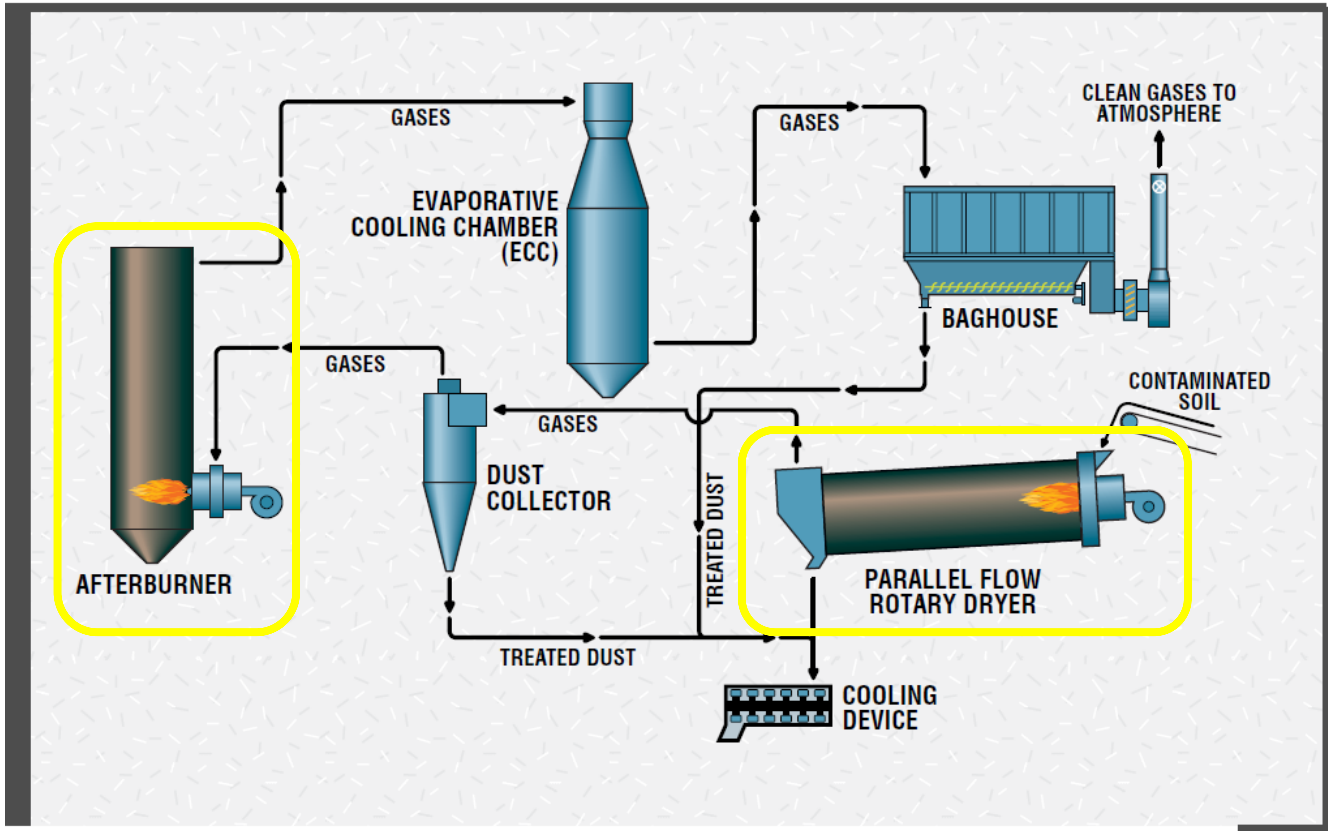
Thermal Desorption Process Flow Diagram


T-125 EVOLUTION OF THERMAL REMEDIATION

Technical Paper T-125

EVOLUTION OF THERMAL REMEDIATION

by Wendell R. Feltman P.E.



PARALLEL-FLOW ROTARY DRUM WITH BAGHOUSE AT END OF PROCESS F4

Source: ASTEC Industries

CleanEarth

Clean Earth Research Projects

Clean Earth PFAS Thermal Desorption Research Project

A Thermal Desorption Solution for Per- and PolyFluoroalkyl Substance (PFAS) in Soils

White Paper Link: https://www.cleanearthinc.com/sites/default/files/file/2022-08/PFAS%20White%20Paper%20-%20Final%20Draft%202.01_logo.pdf

New York State Department of Environmental Conservation (NYSDEC) Research, Development and Demonstration Permit (Year; 2018)

- **Soil Data**
  - 22-Tons Soil
  - Soil Source: Asparagus Farm; 7% to 10.5% Soil Organic Matter
  - 122.91-PPB total PFAS Mass; 807.37-PPT SPLP PFAS Mass
    - PFOA and PFOS Concentrations: 75% of Totals PFAS Mass; 79% SPLP PFAS Mass
- **Permit Criteria; PFOA and PFOS**
  - Soil Total: 72-PPB (additive); Soil SPLP: 10-PPT (each compound)
  - Thermal Oxidation: 1800°F (EPA Technical BRIEF – 2019)

EPA BRIEF: https://www.epa.gov/sites/default/files/2019-09/documents/technical_brief_pfas_incineration_ioaa_approved_final_july_2019.pdf

CleanEarth

Clean Earth PFAS Thermal Desorption Research Project

2018 Treatment Results:

Totals (PPB)	Pre-treatment	Post-treatment	Removal %		SPLP (PPT)	Pre-treatment	Post-treatment	Removal %
PFAS (20)	122.91	7.76	93.7		PFAS (20)	807.37	22.45	97.2
PFOA	4.5	ND	100		PFOA	109.5	0.44	99.6
PFOS	88	7.65	91.3		PFOS	527.5	20.5	96.1

Soil Organic Matter: 1.54%

2019 Treatment Results:

Totals (PPB)	Pre-treatment	Post-treatment	Removal %		SPLP (PPT)	Pre-treatment	Post-treatment	Removal %
Total PFAS	7.76	ND	100		SPLP PFAS	22.45	ND	100
PFOA	-	-	100		PFOA	0.44	ND	100
PFOS	7.65	ND	100		PFOS	20.5	ND	100

Soil Organic Matter: 1.03%

2018 Treatment Results meet the NYSDEC Sampling, Analysis, and Assessment of Per- and Polyfluoroalkyl Substance (PFAS), April 2023, Residential Soil Guidance Values

Document Link: https://extapps.dec.ny.gov/docs/remediation_hudson_pdf/pfassampanaly.pdf

CleanEarth

Clean Earth Future PFAS Technology Research

Stabilization:

- Performing research under a State RD&D permit to evaluate stabilization amendment's ability to control PFAS leachate from contaminated soil

Thermal Desorption:

- Developing opportunities at our fixed and mobile TDU's to perform full-scale research projects on PFAS contaminated soil; Evaluating both Soil and Emissions

Water:

- Partnering with Arcadis and Supporting various technology vendors in a Defense Innovation Unit Demonstration Project
  - Link: https://www.diu.mil/latest/dods-environmental-security-technology-certification-program-diu-partner-to

Regulatory Partnerships and Engagements:

- Engagement with regulatory stakeholders; Federal, State, and Local Agencies

CleanEarth

Clean Earth Partnership in Research Projects

Clean Earth Partnership in Research Projects

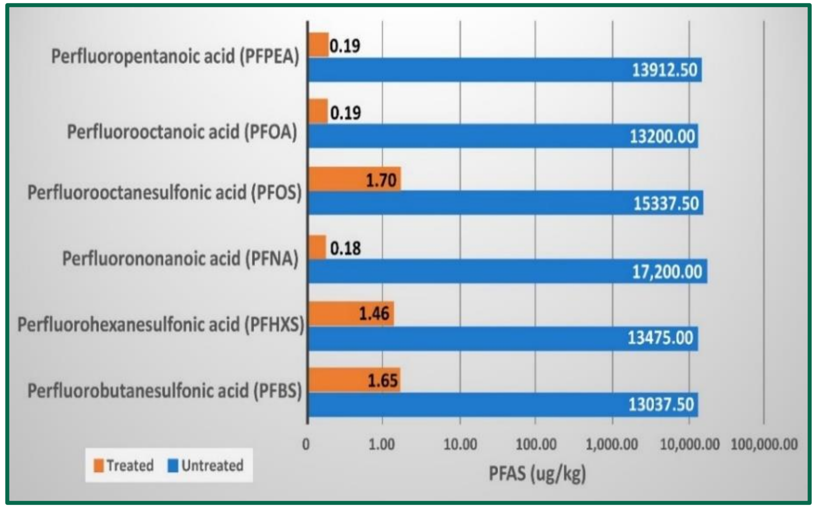
ESTCP Link: https://serdp-estcp.mil/projects/details/02a69957-6c5a-4123-bf5f-49ab4d504826

CleanEarth

SERDP ER18-1572 Results – Indirect Thermal Desorption (ITD) of PFAS-Spiked Soils

Pilot ITD Unit

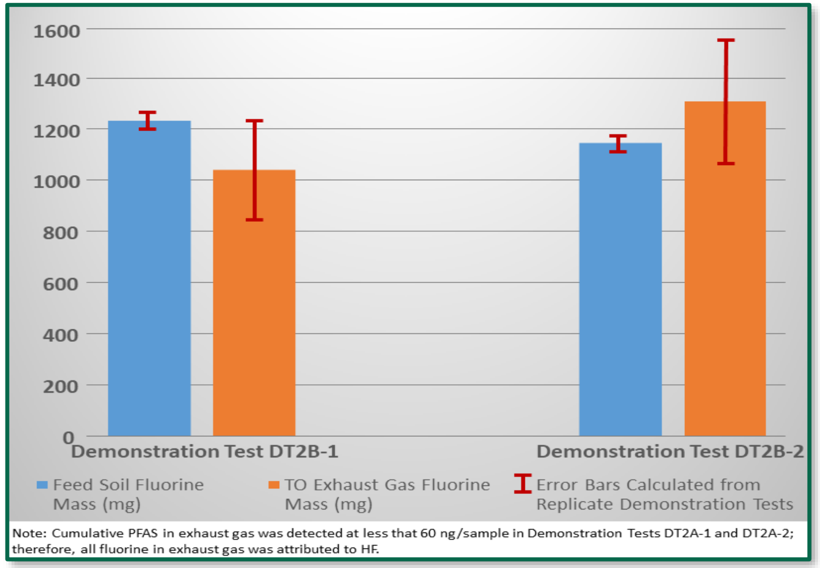
Pilot TO Unit



TDU temperature of 650°C

- PFAS removal efficiency of 99.7% from PFAS spiked soils tested at 650°C
- PFAS results reflect soil treatment to sufficiently low ug/kg levels and capability to meet State soil treatment criteria
- Fluorine balance averaging 99% for two replicate trials with duplicate quality control sampling per test for 6 spiked constituents.
- Experimental error (+/-30%) associated with the measurement and quantification of exhaust gas flux

Source: EA Engineering, Science, and Technology Inc.; Frank Barranco



Fluorine Mass Balance at 650°C

Technical Objectives of ESTCP Demonstration Test

Specific research objectives include:

1) Validate proof-of concept findings of SERDP ER18-1572 as well as to provide evidence of scale-up, can successful results achieve low parts per billion PFAS [and precursor] in treated soil and 99.99 DRE for TO exhaust emissions.

2) Will total organofluorine (TOF) as well as targeted and non-targeted PFAS analyses of exhaust-gas-emissions and improvements in stack testing measurements significantly reduce field/analytical uncertainty (+/-30%) observed with fluorine balance.

3) To what extent do PFAS Products of Incomplete Destruction (PIDs) contribute to PFAS exhaust gas emissions?

4) Can onsite TD/TO be a cost-effective alternative to current costly treatment methods/disposal?

Source: EA Engineering, Science, and Technology Inc.; Frank Barranco

NEWMOA Poll Question

Thermal Desorption Industry Data

ASRC ENERGY

MRS-1 Description and Performance

Informational Slides

CONFIDENTIAL – Property of ASRC Energy

Mobile Remediation System (MRS) - Overview

- **Treats contaminated soil on site**
  - TDU: Thermal desorption leveraging electric induction
  - TOU: High temperature thermal oxidation by fuel or plasma
  - Remediated soil available for re-use
- **Grid connected (or generators)**
- **Modular design for fast deployment**
  - Small footprint
  - Can operate within an enclosed building – year round ops
- **MRS-1 is permitted in Alaska, completed 3 projects**
  - To be deployed on a DoD site in 2024

MRS-1 Results to Date

Remediation

- Pre-treatment samples range from 20 - 1,900 µg/kg (PFOS)
- PFAS ND post-treatment in soils
  - 537M – 0.2 µg/kg RL (18 compounds)
- HF Emissions significantly below HAP limit (0.003 tons/yr on PTE basis)
- PFAS in exhaust is always >1 lb/yr on PTE basis
  - Source testing using OTM-45
- No secondary waste streams

Operational Performance

- Successful connection to 2 utilities
- Operated at private facilities and airports
- Setup in <2 weeks
- 50-80 tons per day reliably achieved, continuing to improve

Developing PFAS Destruction Science

CleanEarth™

Combustion of C_1 and C_2 PFAS: Kinetic modeling and experiments

Jonathan D. Krug, Paul M. Lemieux, Chun-Wai Lee, Jeffrey V. Ryan, Peter H. Kariher, Erin P. Shields, Lindsay C. Wickersham, Martin K. Denison, Kevin A. Davis, David A. Swensen, R. Preston Burnette, Jost O.L. Wendt & William P. Linak

Document Link: https://www.tandfonline.com/doi/full/10.1080/10962247.2021.2021317

PFAS Injection location	CF_4 (ppmv) Exp 1 40 kW	CF_4 (ppmv) Exp 2 45 kW	CF_4 (ppmv) Model 45 kW	CHF_3 (ppmv) Exp 1 40 kW	CHF_3 (ppmv) Exp 2 45 kW	CHF_3 (ppmv) Model 45 kW	C_2F_6 (ppmv) Exp 1 40 kW	C_2F_6 (ppmv) Exp 2 45 kW	C_2F_6 (ppmv) Model 45 kW
Natural gas	CF_4 – 12.53 ± 0.08 HF – 28.73 ± 0.88	CF_4 – 3.57 ± 0.06 HF – 101.72 ± 0.48	CF_4 – 0.80800 HF –134.00 CF_2O – 0.00020	–	CHF_3 – ND HF – 92.79 ± 0.46	CHF_3 – ND HF – 103.00	C_2F_6 – ND HF – 143.99 ± 1.40	C_2F_6 – ND HF – 212.25 ± 0.70	C_2F_6 – ND HF – 205.00 CF_4 – 0.00001 C_3H_6 – 0.00031
Combustion air	–	CF_4 – 5.95 ± 0.04 HF – 88.32 ± 0.34	–	–	CHF_3 – ND HF – 85.90 ± 0.41	–	–	C_2F_6 – ND HF – 196.00 ± 1.51	–
Port 4	–	CF_4 – 29.36 ± 0.28 HF – 2.69 ± 0.01	CF_4 – 34.200 HF – 0.01600 CF_2O – 0.00133	CHF_3 – ND HF – 52.25 ± 0.66	CHF_3 – ND HF – 63.81 ± 0.53 CF_4 – 8.24 ± 0.18	CHF_3 – ND HF – 99.200 CF_2O – 1.7200	C_2F_6 – ND HF – 191.42 ± 0.44 CF_4 – 0.76 ± 0.003	C_2F_6 – ND HF – 84.26 ± 0.24 CF_4 – 30.59 ± 0.18	C_2F_6 – ND HF – 175.00 CF_4 – 0.01150 CF_2O – 14.90
Port 6	–	CF_4 – 29.58 ± 0.15 HF – 2.41 ± 0.01	CF_4 – 34.200 HF – 0.00118 CF_2O – 0.00002	–	CHF_3 – ND HF – 85.09 ± 3.27 CF_4 – 2.82 ± 0.05	CHF_3 – ND HF – 95.500 C_2F_6 – 0.00001 CF_2O – 3.5600	–	C_2F_6 – ND HF – 194.90 ± 0.87 CF_4 – 5.95 ± 0.02	C_2F_6 – 0.15900 HF – 145.00 CHF_3 – 0.00009 CF_4 – 0.01660 CF_2O – 29.900
Port 8 (2070°F)	–	CF_4 – 29.97 ± 0.11 HF – 2.42 ± 0.01	CF_4 – 34.200 HF – 0.00011 CF_2O – 0.00018	–	CHF_3 – ND HF – 96.38 ± 0.69 CF_4 – 0.29 ± 0.001	CHF_3 – ND HF – 91.900 C_2F_6 – 0.00131 CF_2O – 5.3500	C_2F_6 – 6.29 ± 1.20 HF – 114.01 ± 14.59	C_2F_6 – ND HF – 222.88 ± 1.85 CF_4 – 0.93 ± 0.02	C_2F_6 – 12.100 HF – 77.500 CHF_3 – 0.00594 CF_4 – 0.02020 CF_2O – 27.600
Port 10 (1706°F)	–	CF_4 – 29.99 ± 0.24 HF – 2.59 ± 0.005	CF_4 – 34.22 HF – ND	CHF_3 – ND HF – 59.72 ± 4.23 C_2F_6 – 0.93 ± 0.12	CHF_3 – ND HF – 99.58 ± 0.23	CHF_3 – 0.00001 HF – 86.367 CF_4 – 0.00001 CF_2O – 8.0700 C_2F_6 – 0.01990 CF_3COF – 0.00038	C_2F_6 – 21.36 ± 0.21 HF – 25.25 ± 0.16	C_2F_6 – ND HF – 228.11 ± 2.37 CF_4 – 0.21 ± 0.004	C_2F_6 – 30.800 HF – 10.500 CHF_3 – 0.01430 CF_4 – 0.00725 CF_2O – 4.8800

Low temperature thermal treatment of gas-phase fluorotelomer alcohols by calcium oxide

Air Methods and Characterization Division, Center for Environmental Measurement and Modeling, United States Environmental Protection Agency, Research Triangle Park, NC, USA

Link: https://www.sciencedirect.com/science/article/pii/S0045653521003283?via%3Dihub

H I G H L I G H T S

- Fluorotelomer alcohols (FTOHs) are a volatile and commercially useful subset of PFAS.
- Calcium oxide thermal treatment of gas-phase FTOHs was compared to heating alone.
- FTOHs were destroyed more efficiently from thermal treatment with CaO.
- At similar temperatures, CaO reduced secondary PFAS formation relative to thermal only.
- FTOH treatment with CaO effectively reduced gas-phase hydrofluoric acid formation.

4. Conclusions

Extension of CaO treatment could represent an economical solution to waste gas streams containing PFAS like FTOHs. Removal of FTOH vapors and subsequent products of incomplete destruction through CaO thermal treatment requires moderately low temperatures (<800 °C), thus reducing the energy needed to achieve thermal destruction. Stacks that traditionally vent PFAS vapors directly to the atmosphere from drying and sintering processes could efficiently remove such vapors at lower temperatures by incorporating CaO treatment prior to emission. Additionally, use of

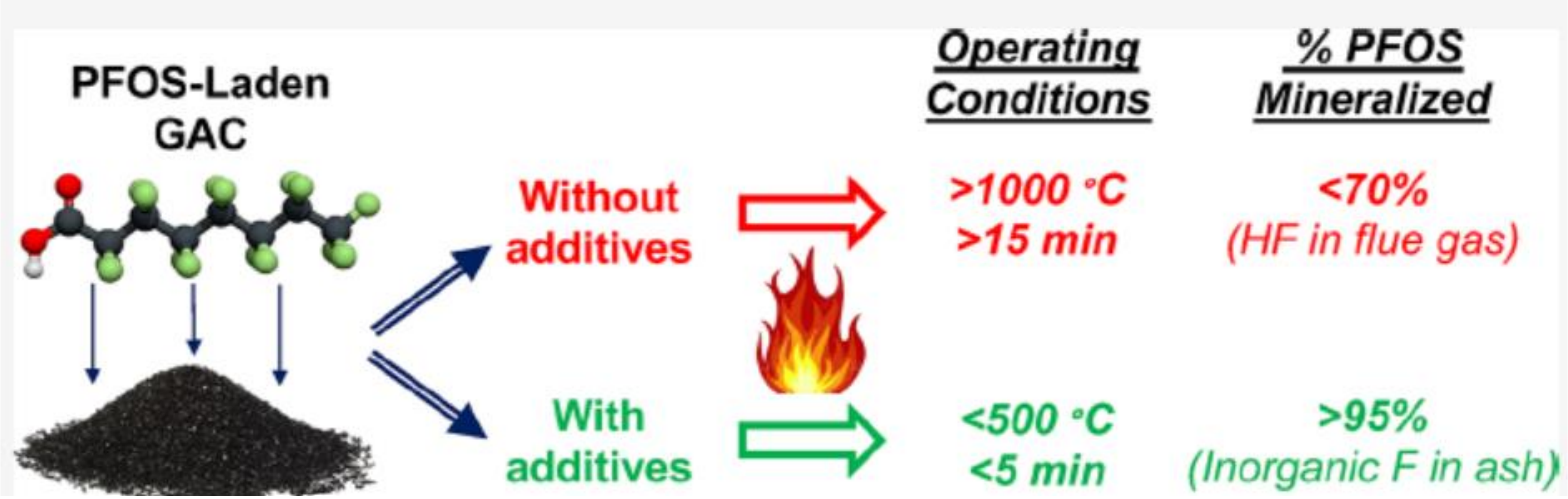
Enhancing the Thermal Mineralization of Perfluorooctanesulfonate on Granular Activated Carbon Using Alkali and Alkaline-Earth Metal Additives; https://pubs.acs.org/doi/10.1021/acs.est.3c09795

CleanEarth

Enhancing the Thermal Mineralization of Perfluorooctanesulfonate on Granular Activated Carbon Using Alkali and Alkaline-Earth Metal Additives

Charbel Abou-Khalil, Liliya Chernysheva, Anthony Miller, Angela Abarca-Perez, Graham Peaslee, Pierre Herckes, Paul Westerhoff, and Kyle Doudrick*

Link: https://pubs.acs.org/doi/10.1021/acs.est.3c09795



"… while CaO effectively enhanced the thermal decomposition of PFOS, its effectiveness on other PFAS variants with differing head groups, tail lengths, and fluorination degrees requires further exploration."

Thermal Mineralization of Perfluorooctanesulfonic Acid (PFOS) to HF, CO2, and SO2

Nathan H. Weber, Cameron S. Delva, Sebastian P. Stockenhuber, Charles C. Grimison, John A. Lucas, John C. Mackie,* Michael Stockenhuber, and Eric M. Kennedy

Link: https://doi.org/10.1021/acs.iecr.2c03197

"Overall, combined air (O2) and excess water vapor and temperatures above 850 °C as reaction conditions provide an inexpensive source of H, OH, and O that can mineralize all PFOS into HF, CO2, and SO2. Hence, this study provides crucial insights into the entire thermal decomposition of PFOS and the role CF2 radicals play in the presence of water vapor and air."

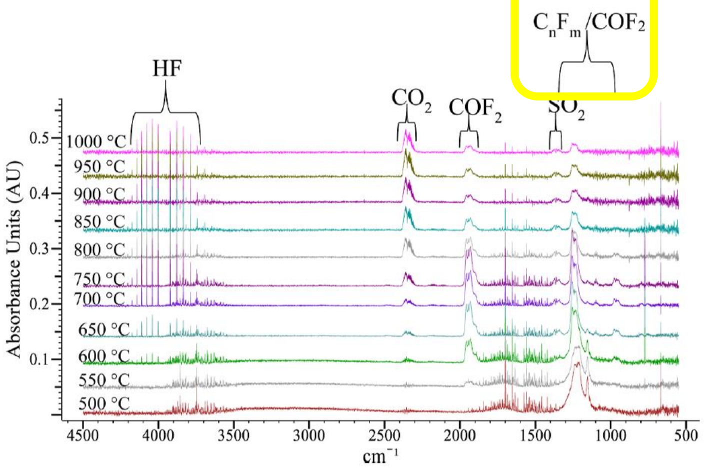


Figure 1. FT-IR spectra of PFOS thermal decomposition in an air bath gas between 500 and 1000 °C at a 150 mL min^{-1} (1.5–0.85 s) in a α-alumina reactor.

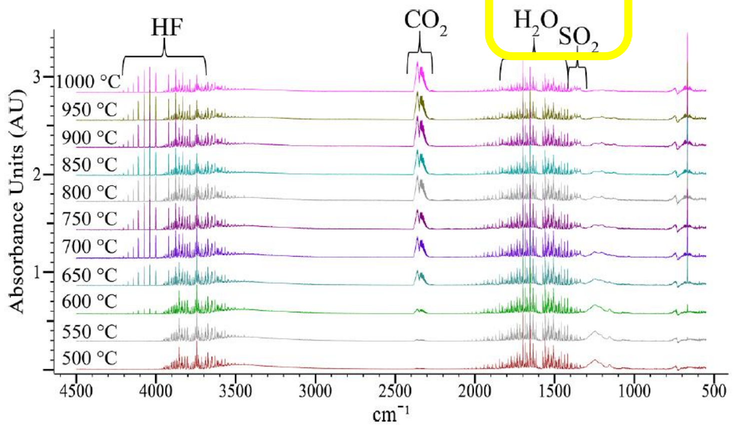


Figure 7. FT-IR spectra of PFOS thermal decomposition in the presence of 20 000 ppmv of $H_2O_{(g)}$ between 500 and 1000 °C using a 150 mL min^{-1} air bath gas giving a residence time of 1.5–0.85 s.

CleanEarth

Reference Sources for Thermal Desorption

Thermal Desorption Sources

- **Interstate Technology Regulatory Council (ITRC)**
  - Thermal Desorption Guidance
    - Mercury, Chlorinated Organics, Petroleum, Coal Tar, Gas Plant Waste
    - https://itrcweb.org/teams/projects/thermal-desorption
- **Contaminated Site Clean Up Information; CLU – IN**
  - https://clu-in.org/remediation/
- **Federal Remediation Technologies Roundtable**
  - https://www.frtr.gov/matrix/default.cfm
- **Clean Earth**
  - www.cleanearthinc.com

Questions

Thank you.

Robert Martin

Technical Director – PFAS

E: rmartin@cleanearthinc.com

O: 518.747.5500

C: 518.681.6759

CleanEarth

CleanEarth