Resourcing the world VEOLIA

Decoding the fate and transport of PFAS compounds in sludge undergoing thermal oxidation

May 24, 2022 9:00 AM - 9:30 AM | Presented by Sudhakar Viswanathan, Veolia, Cary, NC

Regional Partners

f.r. mahony & associates inc. frma A Division Of CUMMINS-WAGNER 100% Employee Owned

Conference Host

NEWEA WORKING FOR WATER QUALITY

Research Team

Dr. Takahiro Yamada
University of Dayton Research Institute: Power and Energy
Kinetics and Process Engineering - Senior Research Chemist

Dr. Moshan Kahandawala
University of Dayton Research Institute: Power and Energy
Kinetics and Process Engineering - Senior Research Engineer

Dr. Alexander B. Morgan
University of Dayton Research Institute: Power and Energy
Energy and Environmental Sciences - Distinguished Research Scientist

Rich DiMassimo, P.E.
Veolia Water Technologies
Vice President of Engineering

Dr. Hong Zhao, P.E.
Veolia Water Technologies
Process and Technology Leader - Wastewater

Sudhakar Viswanathan
Veolia Water Technologies
National Sales Manager – Biosolids & bioenergy

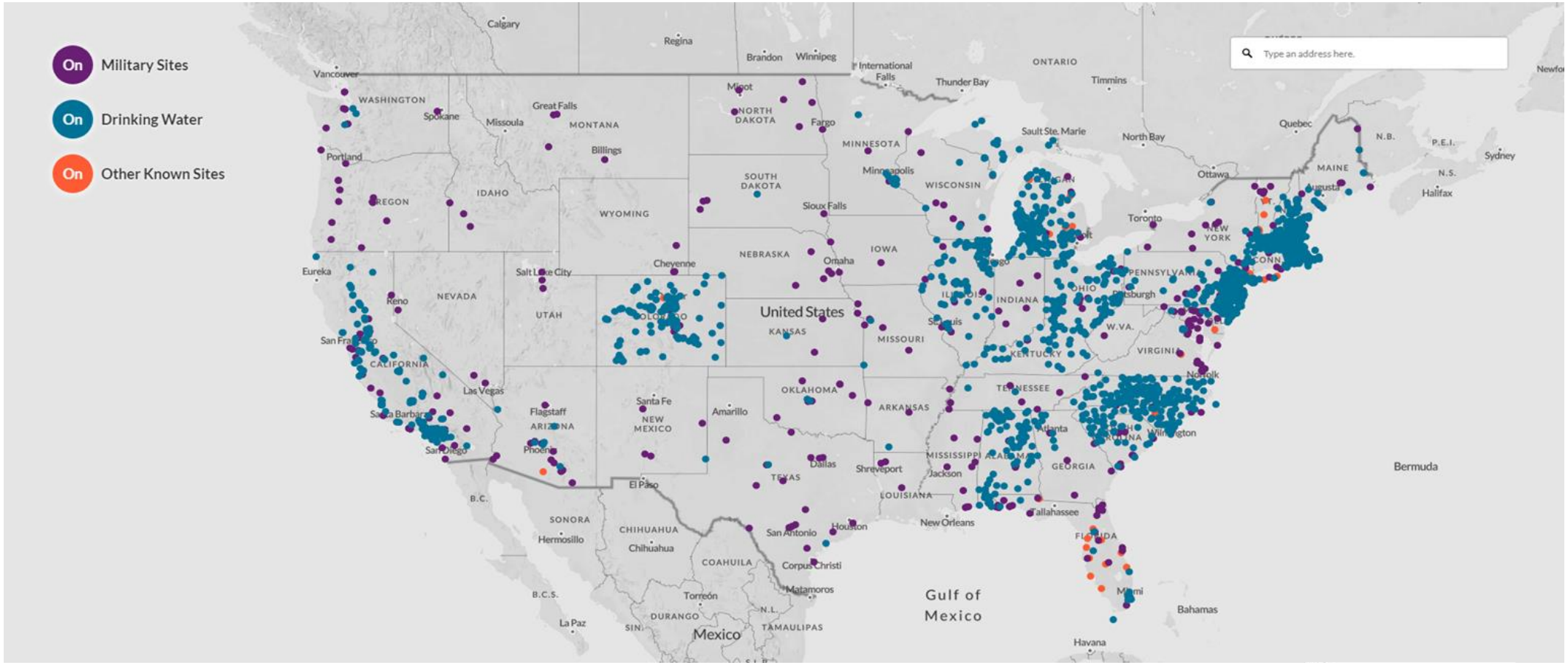
101

What is PFAS?

Source: defence.gov.au

- Family of forever chemicals
  - ~ 4730 compounds
  - PFOA, PFOS, GenX, TEFLON…
  - Aqueous Film Forming Foam (AFFF)
- Persistent
- Toxic
  - ECD
  - Carcinogenic
- Bioaccumulative
  - It's in all our blood ☹

Is PFAS in my sludge?



Source: ewg.org

Local Concerns

ENVIRONMENT

Maine waste handlers eye cost concerns from sludge ban that aims to prevent PFAS contamination

BY ANNIE ROPEIK | MAINE
PUBLISHED 7:00 AM ET MAY. 02, 2022

Maine towns and wastewater plants say they're reeling from the passage of a statewide ban on sludge fertilizer that aims to reduce harmful PFAS chemical contamination in soil and water.

Members of a range of groups that work with these so-called biosolids, from waste management companies to sewage plants and municipalities, met for a forum on the issue hosted by Maine's E2Tech trade group last week.

These solids are left over from wastewater and have historically been treated for use as a nutrient-rich fertilizer instead of being landfilled or incinerated. But they can contain high levels of PFAS due to the chemicals' ubiquity in human bodies and other wastewater sources.

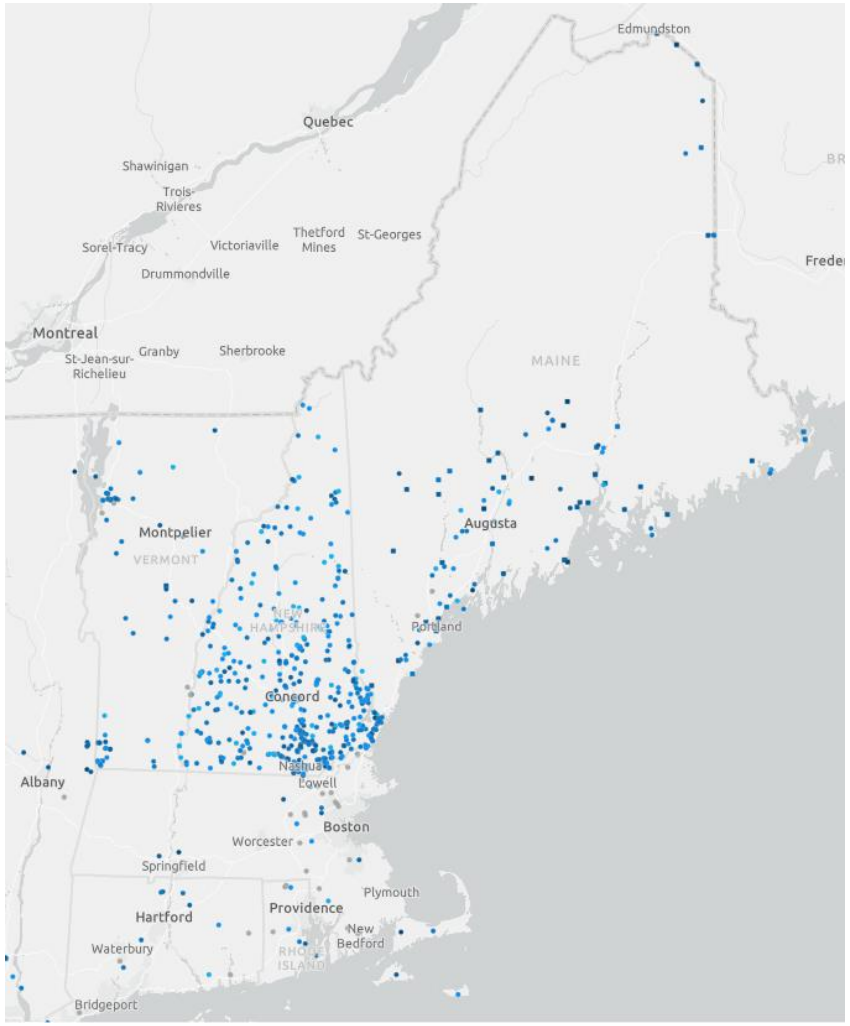
EQUILIBRIUM & SUSTAINABILITY

New England governors approve transformative laws on 'forever chemicals'

State task force recommends Mass. do more to crack down on PFAS

By Dharna Noor Globe Staff, Updated April 20, 2022, 7:10 p.m.

Source: various



Source: northeastern.edu

Legend

Known Contamination

Sites with Water Testing

PFAS Level (ng/L)

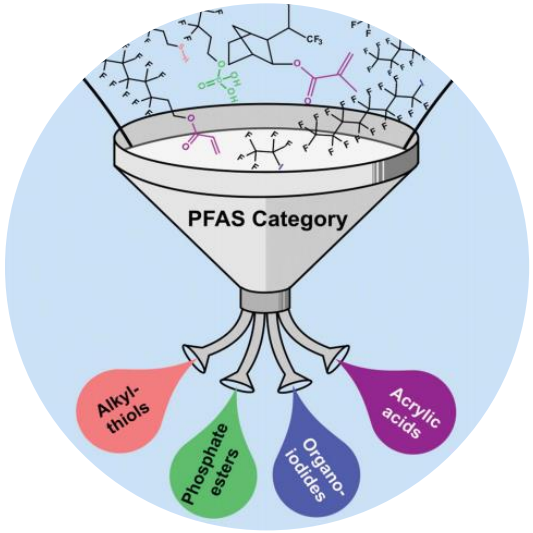
- > 100,000
- > 1,000 - 100,000
- > 70 - 1,000
- > 10 - 70
- 0 - 10
- Unknown

Sites with Solids Testing

PFAS Level (ng/L)

- > 100,000
- > 10,000 - 100,000
- > 100 - 10,000
- 0 - 100
- Unknown

PFAS in wastewater treatment facility



Source: rsc.li/espi

PFASs

- **perfluoroalkyl / per- and polyfluoroalkylether acids (PFAAs)**
  - **perfluoroalkyl carboxylic acids (PFCAs)**, C_nF_{2n+1}-COOH
  - **perfluoroalkane sulfonic acids (PFSAs)**, C_nF_{2n+1}-SO_3H
  - **perfluoroalkyl phosphonic acids (PFPAs)**, C_nF_{2n+1}-PO_3H_2
  - **perfluoroalkyl phosphinic acids (PFPiAs)**, $(C_nF_{2n+1})(C_mF_{2m+1})$-$PO_2H$
  - **per- and polyfluoroether carboxylic acids (PFECAs)**, e.g. $C_2F_5OC_2F_4OCF_2COOH$
  - **per- and polyfluoroether sulfonic acids (PFESAs)**, e.g. $C_6F_{13}OCF_2CF_2SO_3H$
- **PFAA precursors**
  - **perfluoroalkane sulfonyl fluorides (PASFs)** / **perfluoroalkanoyl fluorides (PACFs)** $C_nF_{2n+1}SO_2F$ / $C_nF_{2n+1}CO_2F$ → **PASF/PACF-based substances** $C_nF_{2n+1}SO_2$-R / $C_nF_{2n+1}CO_2$-R
  - **perfluoroalkyl iodides (PFAIs)** $C_nF_{2n+1}I$ → **n:2 fluorotelomer iodides (FTIs)** $C_nF_{2n+1}CH_2CH_2I$ → **n:2 fluorotelomer-based substances** $C_nF_{2n+1}CH_2CH_2$-R
  - **n:1 fluorotelomer alcohols** $C_nF_{2n+1}CH_2OH$ → **n:1 fluorotelomer-based substances** $C_nF_{2n+1}CH_2$-R
  - **Per- and polyfluoroether-based substances**, e.g. $C_4F_9OC_2F_4OC_2F_4OCF_2$-$CH_2OH$ (CAS number 317817-24-6)
- **other PFASs**
  - **fluoropolymers (FPs)** — polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), fluorinated ethylene propylene (FEP), perfluoroalkoxyl polymer (PFA), polyvinyl fluoride (PVF), etc.
  - **perfluoropolyethers (PFPEs)**, e.g. $HOCH_2O$-$(C_mF_{2m}O)_n$-CH_2OH

side-chain fluorinated polymers
e.g. (meth)acrylate, urethane or oxetane polymers

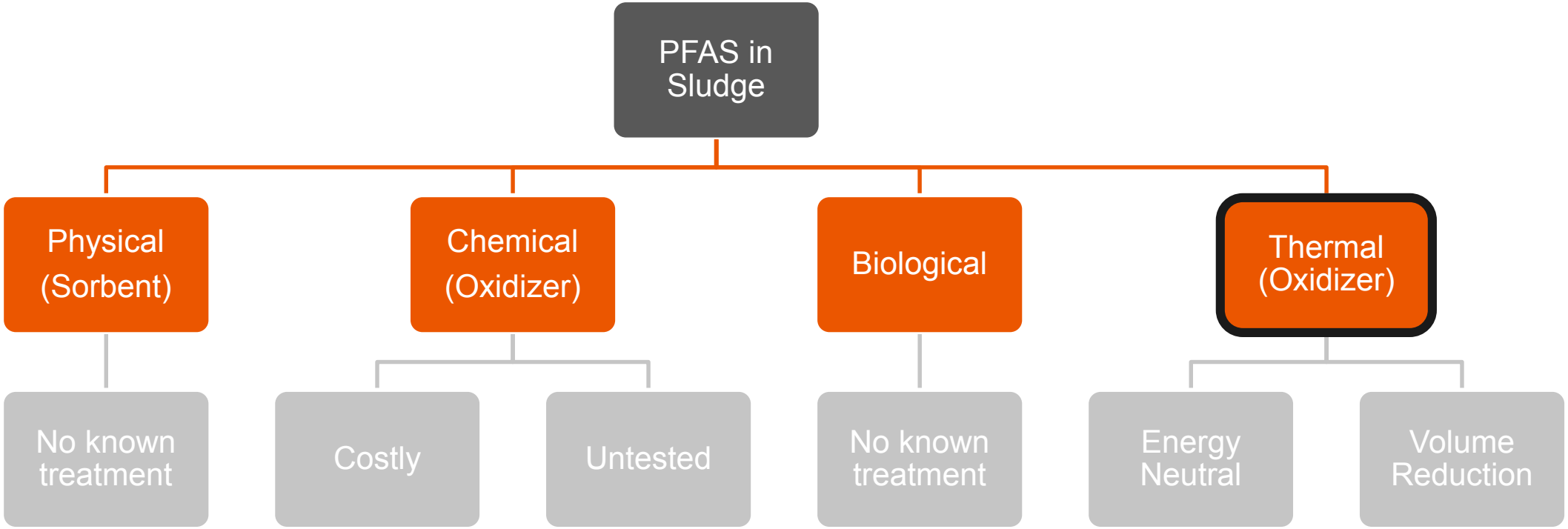
non-polymers
R = NH, $NHCH_2CH_2OH$, etc.

Solids

Liquid

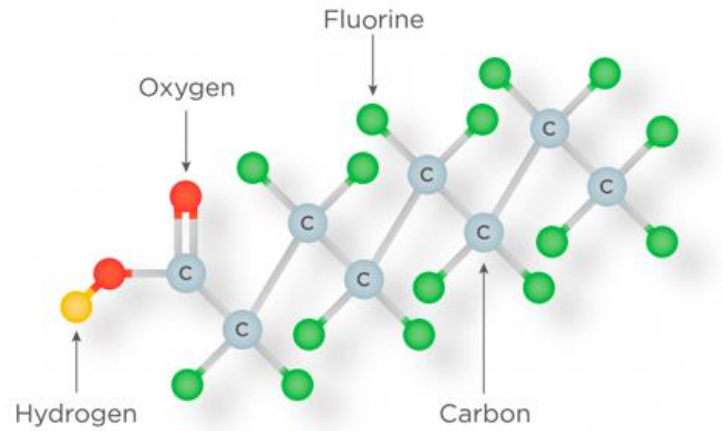
- Laboratory Capabilities
  - ~40 compounds (2021)
  - Total oxidizable precursor (TOP) assay
- Further Reading
  - Dr. Mouser, Univ. of NH

How to treat PFAS laden sludge?



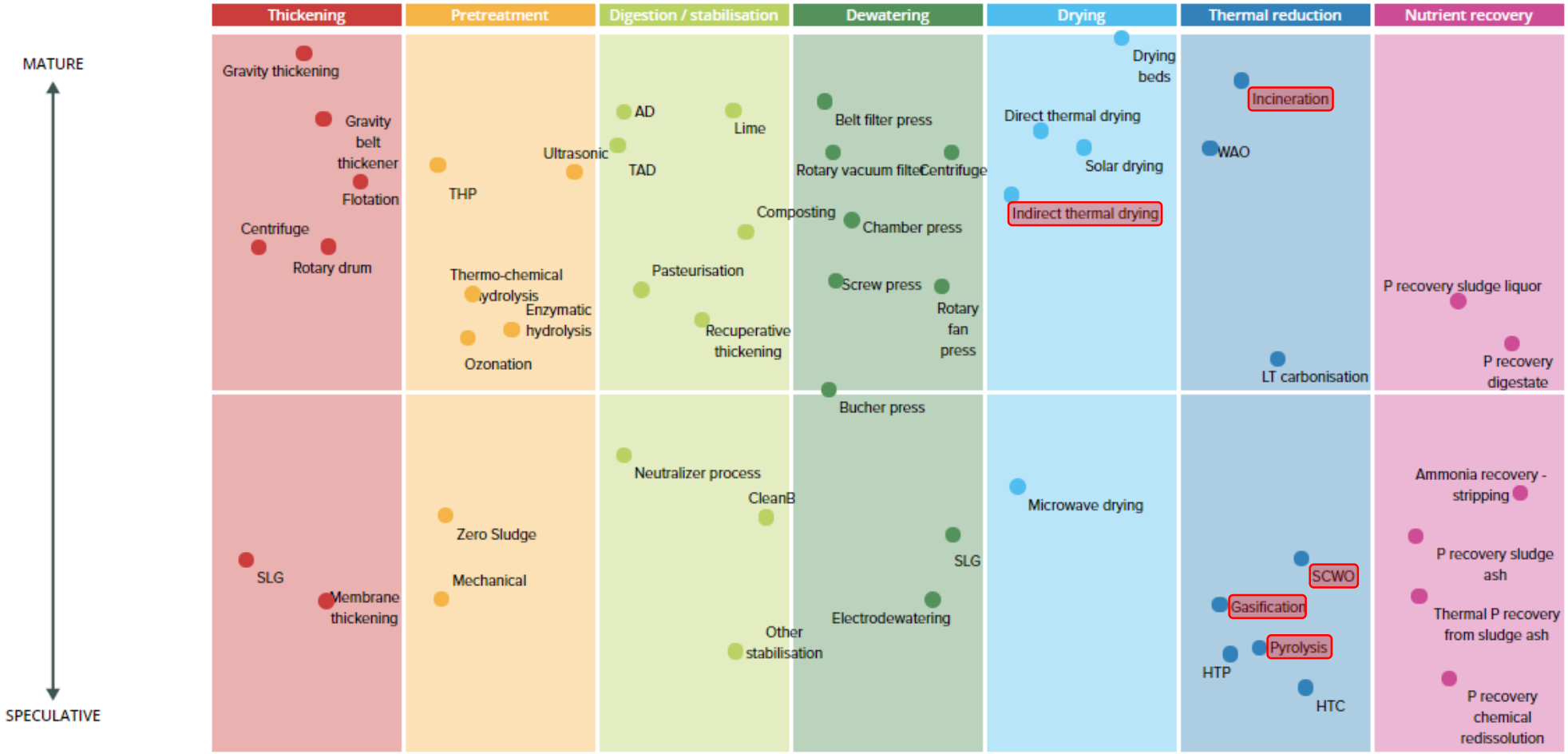
Thermal treatment, in literature!

- Literature review offered limited information on sludge
  - The knowledge on how PFAS behaves in combustion processes is scarce, but consensus in the limited scientific literature is that degradation of PFOS occurs at temperatures above 500°C. However fluorinated by-products are formed, which in themselves may have undesired properties. A study conducted by the United States Environmental Protection Agency and 3M states that degradation of PFOS occurs at temperatures above 600°C, and the main degradation products are the potent greenhouse gases CF_4 and C_2F_6 (***Taylor et al 2003***).
  - Thermally treated PFOS-contaminated sludge with an addition of $Ca(OH)_2$ (***Wang et al 2011; Wang et al. 2013***) has reduced the emissions of CF_4 and C_2F_6 in favor of e.g. CF_3H but, above all, formation of solid CaF_2 and $Ca_5(PO_4)3F$.
  - Most studies pointed to thermal treatment as an effective solution for PFAS waste



Source: pfasfacts.com

Solids Management Options



Source: GWI

Thermal Treatment of Sludge

New and old technologies addressing the PFAS issue

Incineration	Supercritial Water	Pyrolysis/Gasification	BioCon ERS Furnace
900 – 1,600 F	705 – 1,100 F	450 – 1,650 F	800 – 2,100 F
< 6.5 sec (FB), > 10 min (MH) SRT	< 1 min SRT	> 75 min SRT	Adjustable
< 6.5 sec (FB), Varies (MH) gas	?	Syngas combusted	Adjustable
+25% DS	+15% DS	+80% DS	+90% DS
Dewatered Cake	Dewatered Cake	Dried solids	Dried solids
Ash water, wet gas	Water wet gas	Char water, gas	Ash water, gas
Proven	Emerging	Emerging	Proven

What do we know?

- Partial PFAS destruction is possible using thermal treatment above 600^{o} C
  - How do we get complete PFAS destruction via TO?
  - How to quantify PFAS destruction rates in solids, liquids and gases?

Research

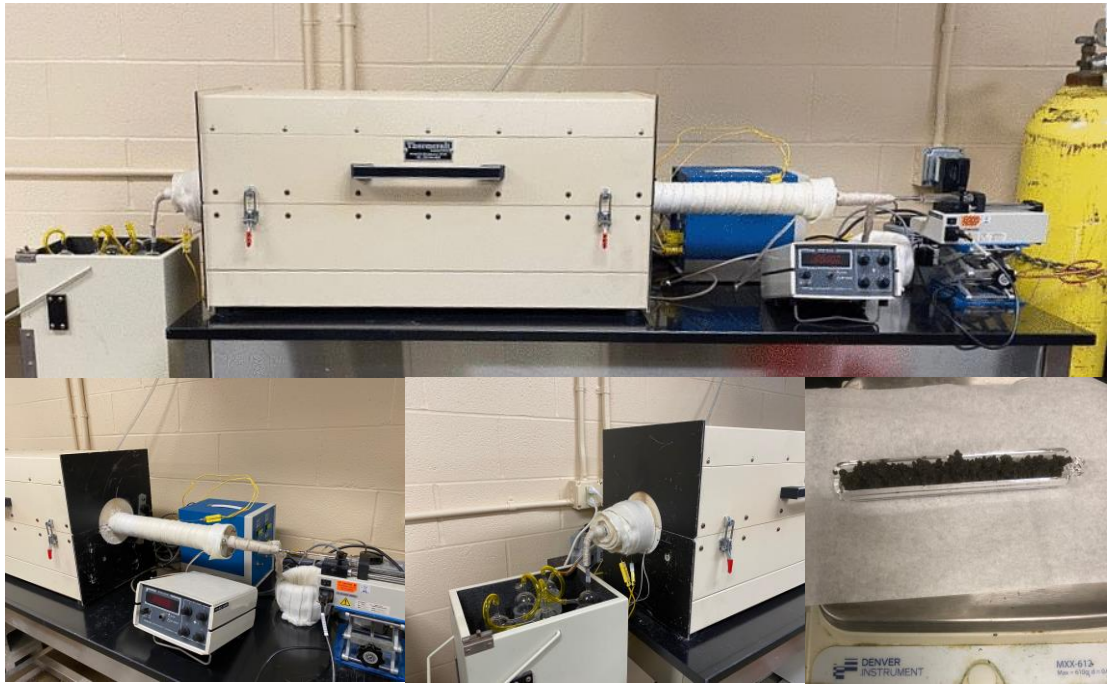
Fate of PFAS in Sludge & Emission

- Laboratory scale test
- Self-funded study
- Phase I: PFAS transport test
- Phase II: Thermal decomposition test
- Phase III: Site specific testing

Study Deliverables

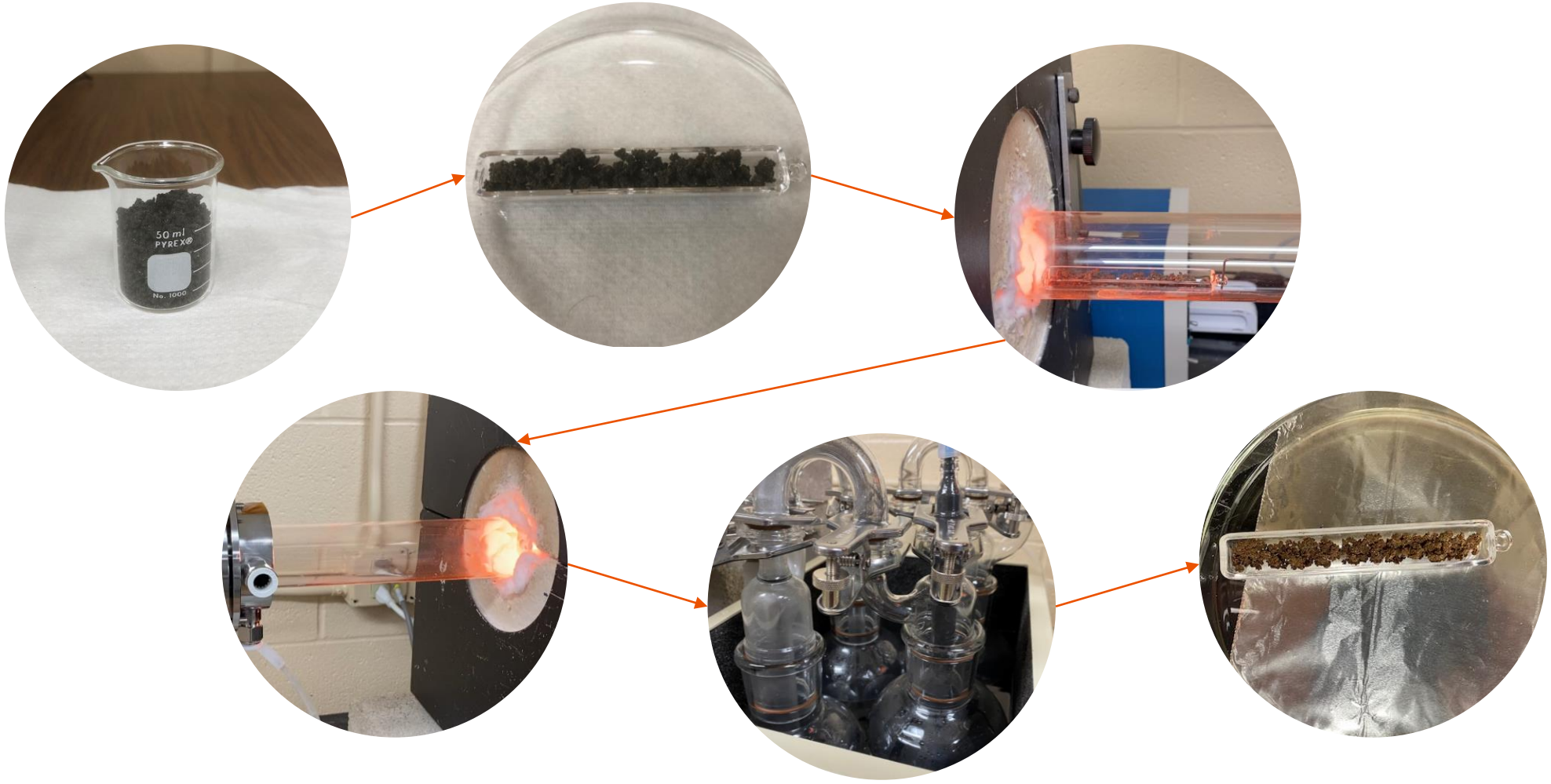
- Verify thermal conditions for destruction of PFAS
  - Develop a Fluoride mass balance
- Identify chemical pre-treatment to reduce regulated emission
  - Acquire knowledge to address this emerging market with data driven design/solutions
- Determine design criteria to fine tune
  - ERS for PFAS destruction
  - APC for emission

Laboratory Scale Simulation of ERS



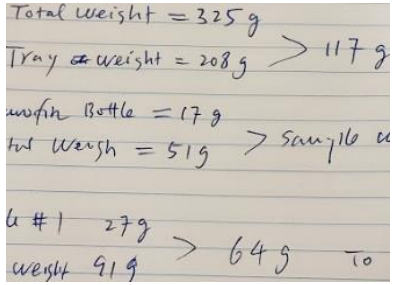
- Phase I
  - GC-MS was not connected to the reactor system
  - No Continuous Gas Analyzer (CGA)
    - Instead we used another CO monitor to check if the incineration goes under stoichiometry.
    - CO is a good indicator to check if enough oxygen is supplied or not.
- Phase II
  - GC-MS to monitor O_2, CO_2, N_2, and H_2O.
  - Supplied gas is only air and N2 and no cal. Gas.
- Phase III
  - Site specific testing
  - Complete HF balance
  - Spiking if/when needed

Solids, liquids and gases



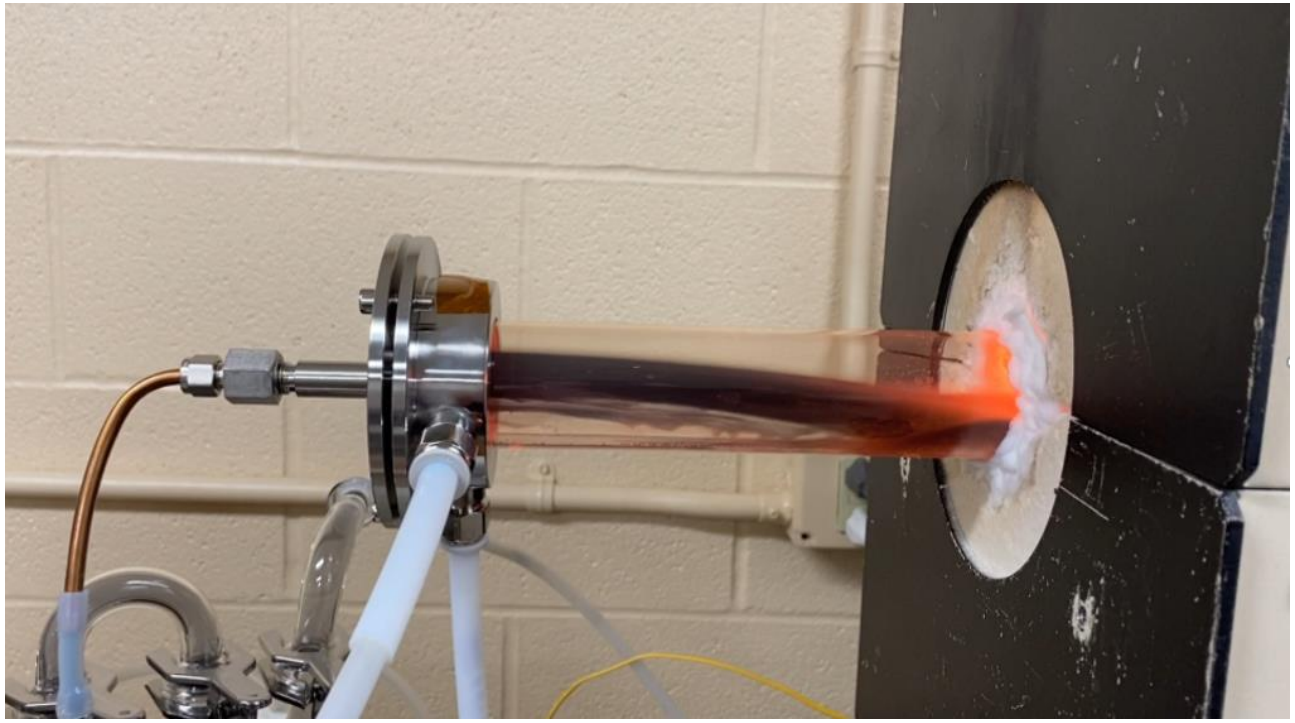
Challenges

- Sites with high concertation of PFAS in sludge (Phase I and II)
  - Extensive search and numerous NDA
  - Sample locations redacted and erased
  - Samples acquired and dried to +90% DS using Veolia laboratory set up to simulate BioCon dryer
- Sample volume vs. ash
  - Limited sample boat size
  - Repetition of test beyond test requirement so collect ash



Challenges

- Combustion air vs. emission capture
  - Air greater than stoichiometry
  - Increasing impinger volume increased capture efficiency
  - Soot formation
- Fluoride balance and need for steam cleaning
  - Flood the reactors and interconnecting tubes to capture any PFAS bound to walls of reactor/tubing



Progress to date

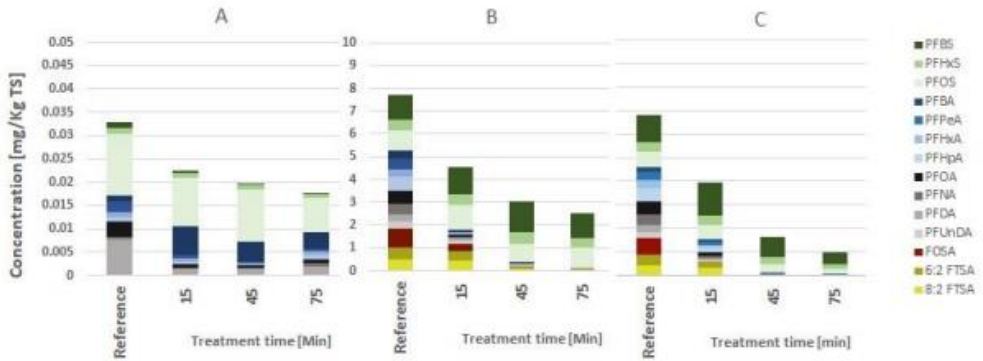
Method: 537 (modified) - Fluorinated Alkyl Substances

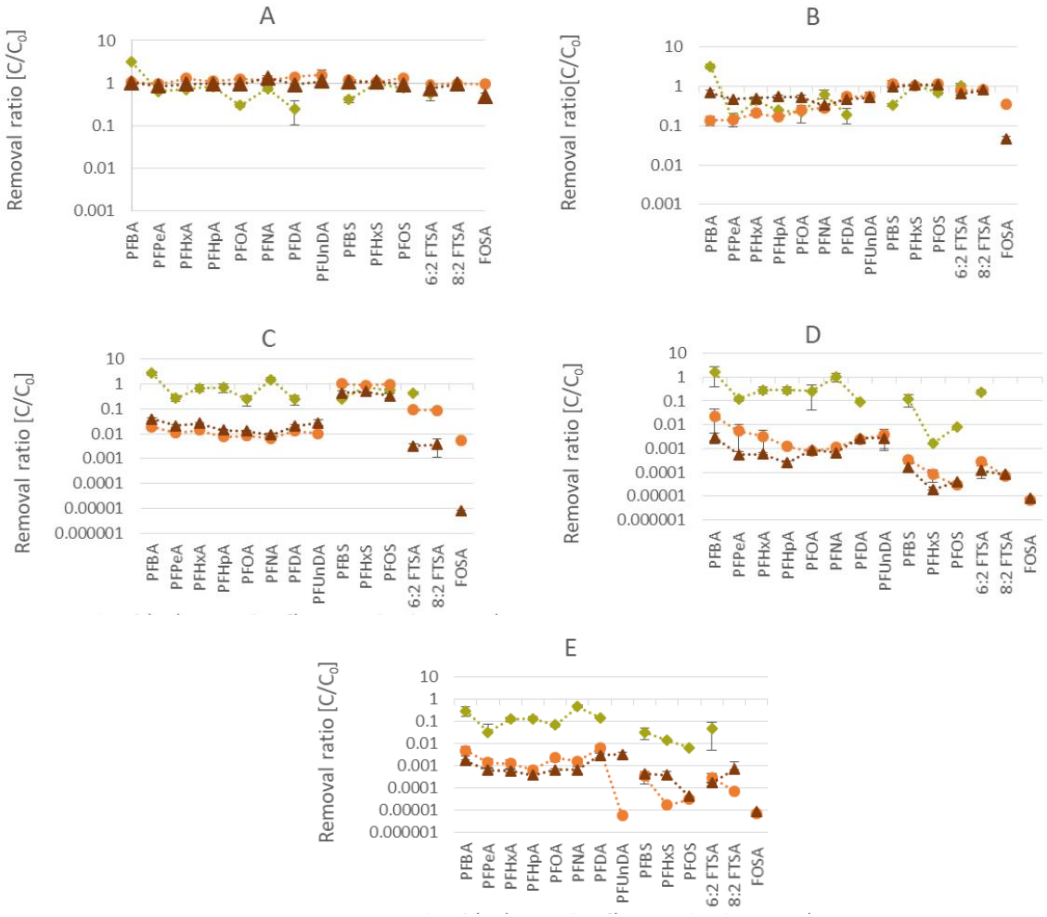
Analyte	Result	Qualifier	RL	MDL	Unit
Perfluorobutanoic acid (PFBA)	**1.7**	**J B**	9.0	1.3	ug/Kg
Perfluoropentanoic acid (PFPeA)	ND	F1	9.0	3.5	ug/Kg
Perfluorohexanoic acid (PFHxA)	**8.8**	**J**	9.0	1.9	ug/Kg
Perfluoroheptanoic acid (PFHpA)	ND		9.0	1.3	ug/Kg
Perfluorooctanoic acid (PFOA)	ND	F1	9.0	3.9	ug/Kg
Perfluorononanoic acid (PFNA)	**2.0**	**J**	9.0	1.6	ug/Kg
Perfluorodecanoic acid (PFDA)	**6.3**	**J F1**	9.0	0.99	ug/Kg
Perfluoroundecanoic acid (PFUnA)	ND	F1	9.0	1.6	ug/Kg
Perfluorododecanoic acid (PFDoA)	ND	F1	9.0	3.0	ug/Kg
Perfluorotridecanoic acid (PFTriA)	ND	F1	9.0	2.3	ug/Kg
Perfluorotetradecanoic acid (PFTeA)	ND		9.0	2.4	ug/Kg
Perfluorobutanesulfonic acid (PFBS)	ND		9.0	1.1	ug/Kg
Perfluoropentanesulfonic acid (PFPeS)	ND		9.0	0.90	ug/Kg
Perfluorohexanesulfonic acid (PFHxS)	**3.1**	**J I F1**	9.0	1.4	ug/Kg
Perfluoroheptanesulfonic Acid (PFHpS)	ND		9.0	1.6	ug/Kg
Perfluorooctanesulfonic acid (PFOS)	**87**		23	9.0	ug/Kg
Perfluorononanesulfonic acid (PFNS)	ND		9.0	0.90	ug/Kg
Perfluorodecanesulfonic acid (PFDS)	ND	F1 F2	9.0	1.8	ug/Kg
Perfluorooctanesulfonamide (FOSA)	ND	F1	9.0	3.7	ug/Kg
N-methylperfluorooctanesulfonamidoacetic acid (NMeFOSAA)	ND		90	18	ug/Kg
N-ethylperfluorooctanesulfonamidoacetic acid (NEtFOSAA)	ND		90	17	ug/Kg
4:2 FTS	ND		90	17	ug/Kg
6:2 FTS	**12**	**J F1**	90	6.8	ug/Kg
8:2 FTS	ND		90	11	ug/Kg

- Phase I
  - Five TE studies completed at various design conditions
  - Emission capture efficiency being fine tuned
- Phase II
  - PFAS volatilization and destruction rates at varying
    - Concentrations
    - Temperature
    - O2 concentration
    - Dwell times - solids and gases
  - TOP Assay to round of F balance
- Phase III
  - In progress
    - Paid feasibility study opportunity

Early Results

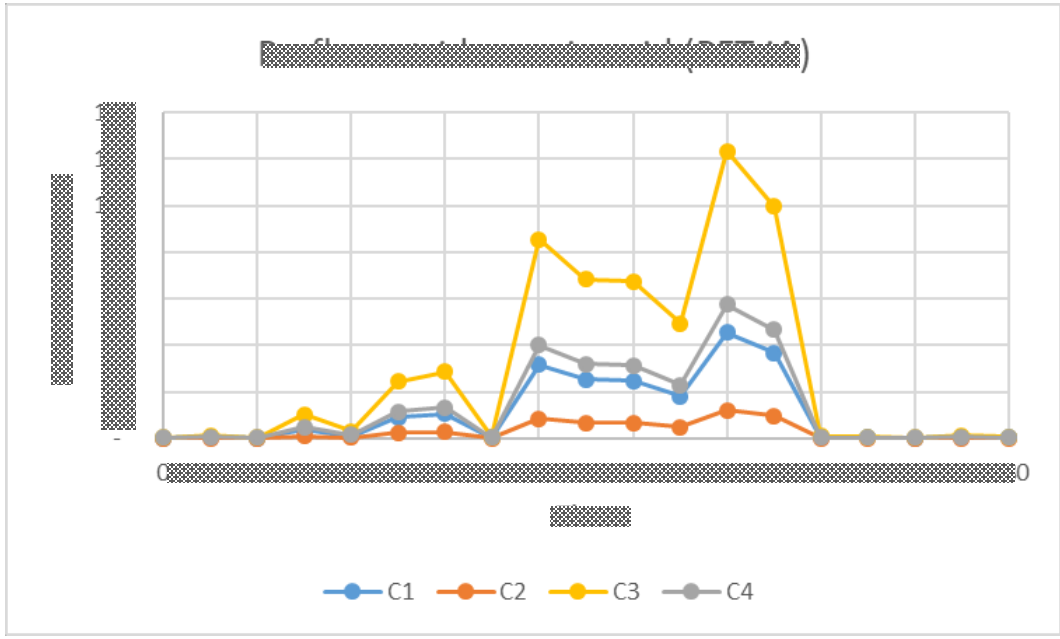
- Verifying Literature Values on Bench Scale
  - Volatilization of PFAS compounds subjected to various thermal oxidative conditions
  - Determine the vapor pressure and desorption potential for each compounds
  - Data used to fine tune dryer model

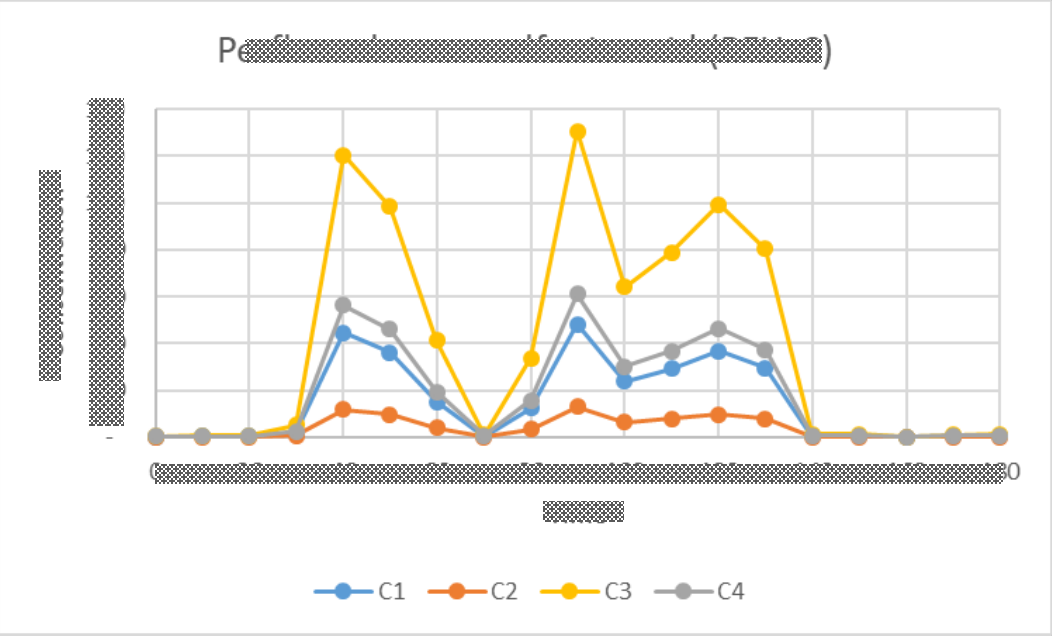




Source: An assessment of thermal desorption as a remediation technique for per- and polyfluoroalkyl substances (PFASs) in contaminated soil - Anna-Stina Lind

Modeling



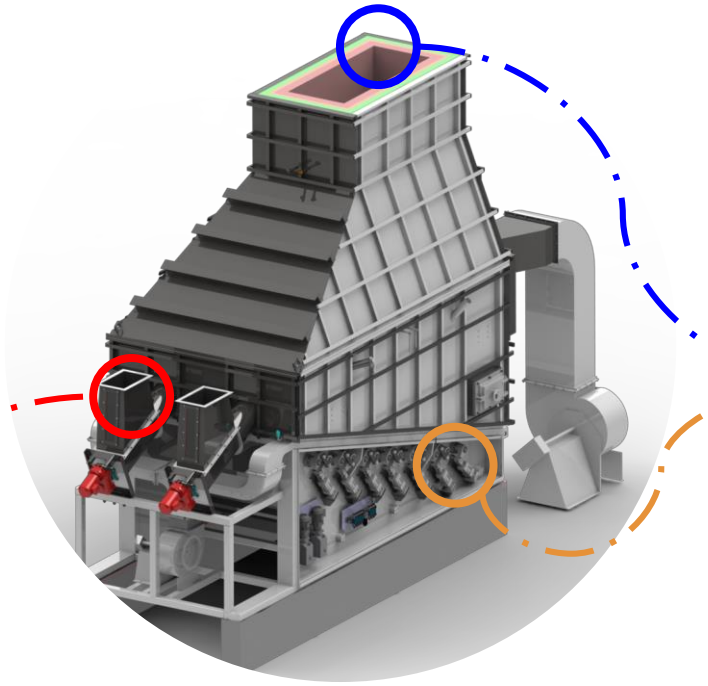


- Calibration
  - T99 identified for various PFAS compounds
  - Determine the minimum temperature for each compounds
  - Data used to fine tune ERS model, update APC efficiencies

Oxidation of PFAS Laden Sludge

36 PFAS Compounds Tested

32 PFAS Compounds Detected



26 PFAS Compounds Destroyed > 4 -log

4 PFAS Compound s Destroyed >2-log

2 PFAS Compound s Destroyed >1.3-log

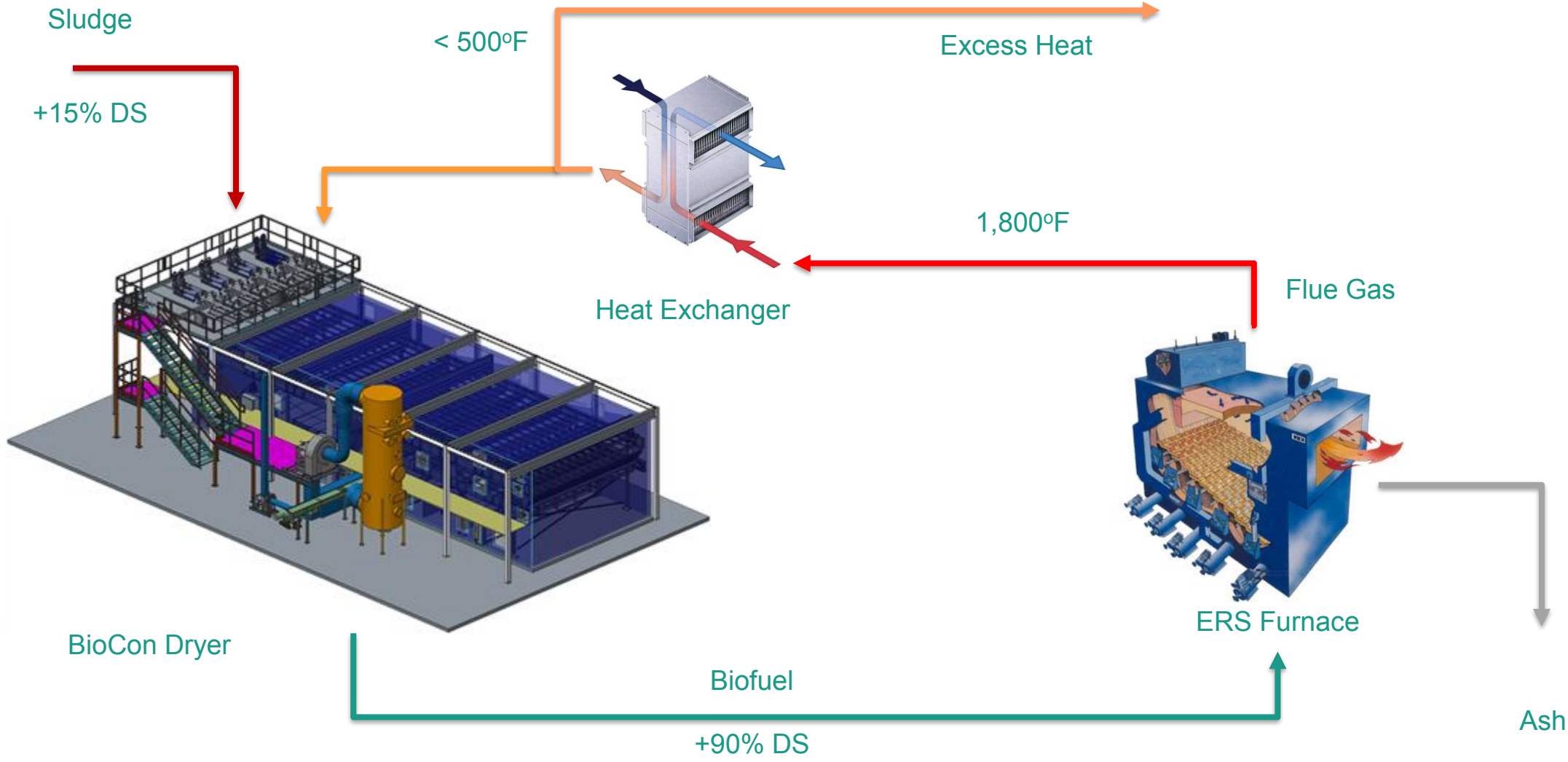
Overall Destruction Rate 4 -log

PFAS laden sludge input

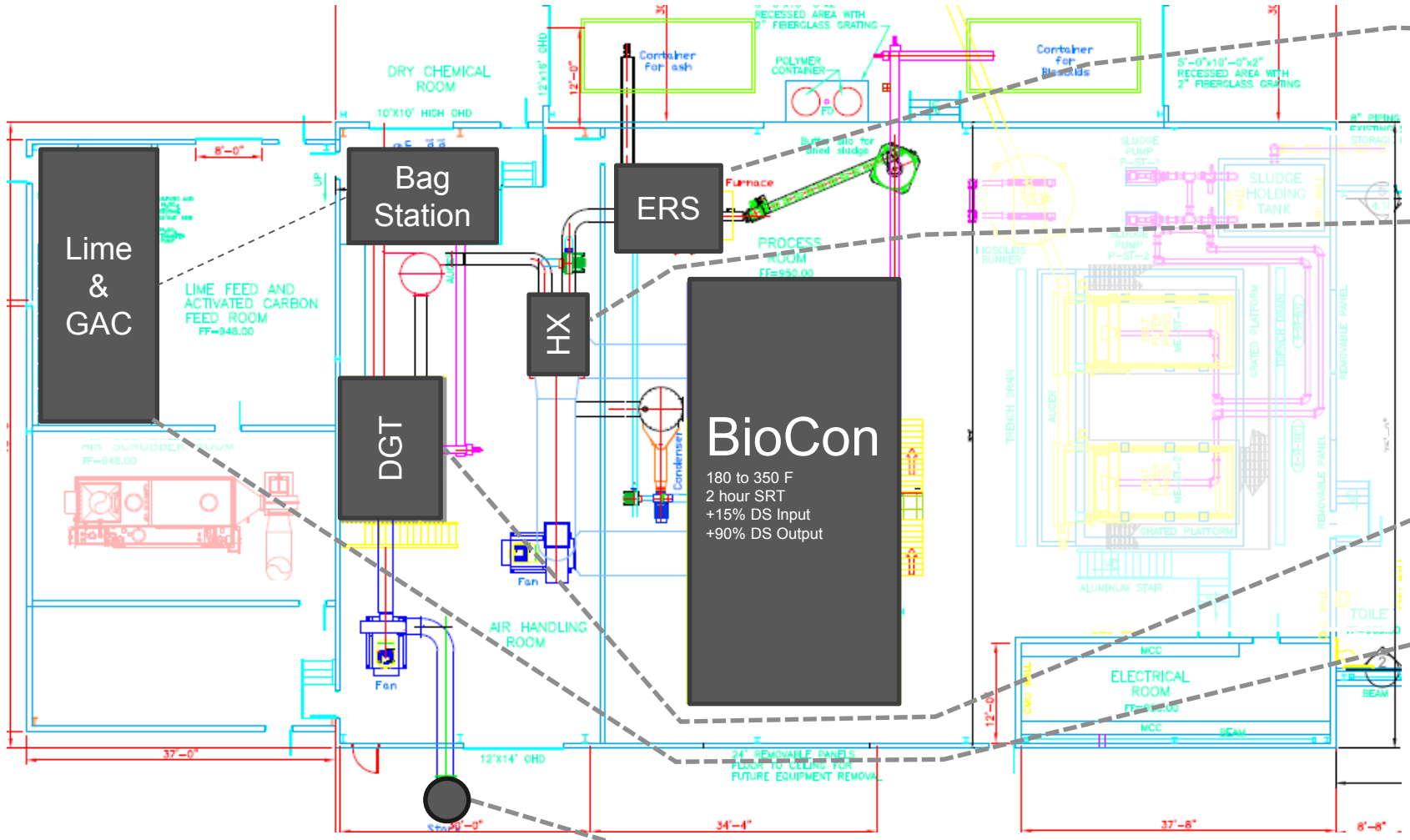
Ash output

Emissions output

BioCon ERS – Highlights



Experience in the US (Buffalo, MN - 2008)



ERS
2000 F, ave 1,800 F
< 1 hour SRT
+90% DS Input
Ash Output

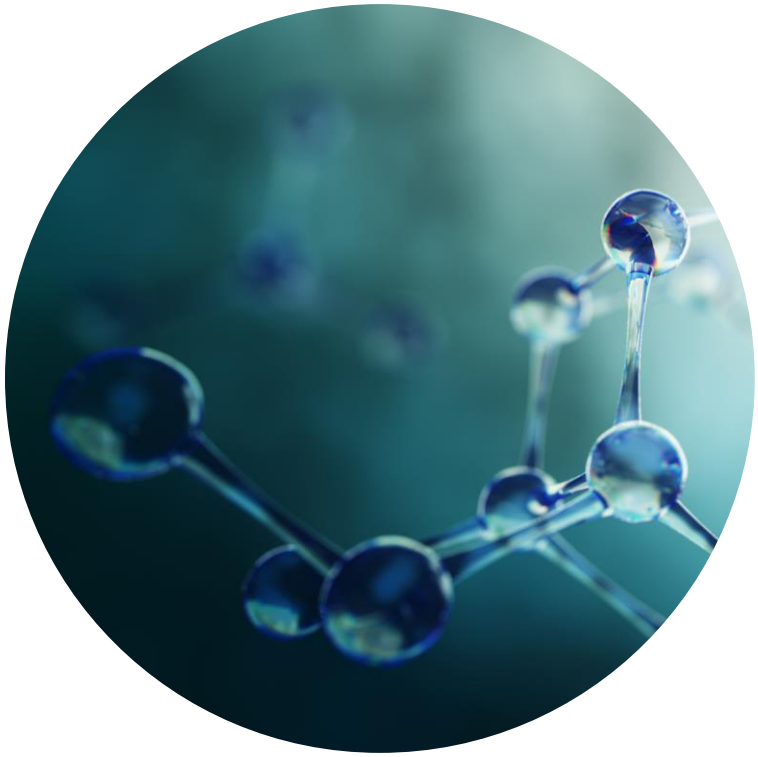
Heat Recovery HX
1800 F Input
550 F Output

Dry Treatment
Bag Filters with GAC for PM, Mercury

Chemicals
Lime and GAC storage and makeup room

Stack
Ensure no PFAS in emission

Summary



Is complete destruction of PFAS in sludge possible?

- ERS and associated APC, at optimized operating conditions, can effectively destroy and remove PFAS from sludge, process liquids and emission
- Longer the chemical chain, the higher the decomposition efficiency
- Short chain compounds can form due to incomplete RT

Other findings

- Emission data is promising, APC impacts project cost
- HF acid management should be integral to the emission control train
- F balance is difficult, but possible with right techniques

Unknowns

- Fate of PFAS subjected to ‘incomplete’ or ‘low temperature’ combustion requires further study, example, PFAS in emissions

Thank you

For PFAS destruction in solids, contact:

- Sudhakar (Sunny) Viswanathan
  sudhakar.viswanathan@veolia.com

Contact our local representatives:

- Daryl Coppola
  dcoppola@frmahony.com