Incineration of Fluoropolymers Project presentation

[redacted] Karlsruhe Institute of Technology (KIT)
[redacted] SGS Belgium NV
[redacted] P Taylor & Associates, LLC

15th June 2023

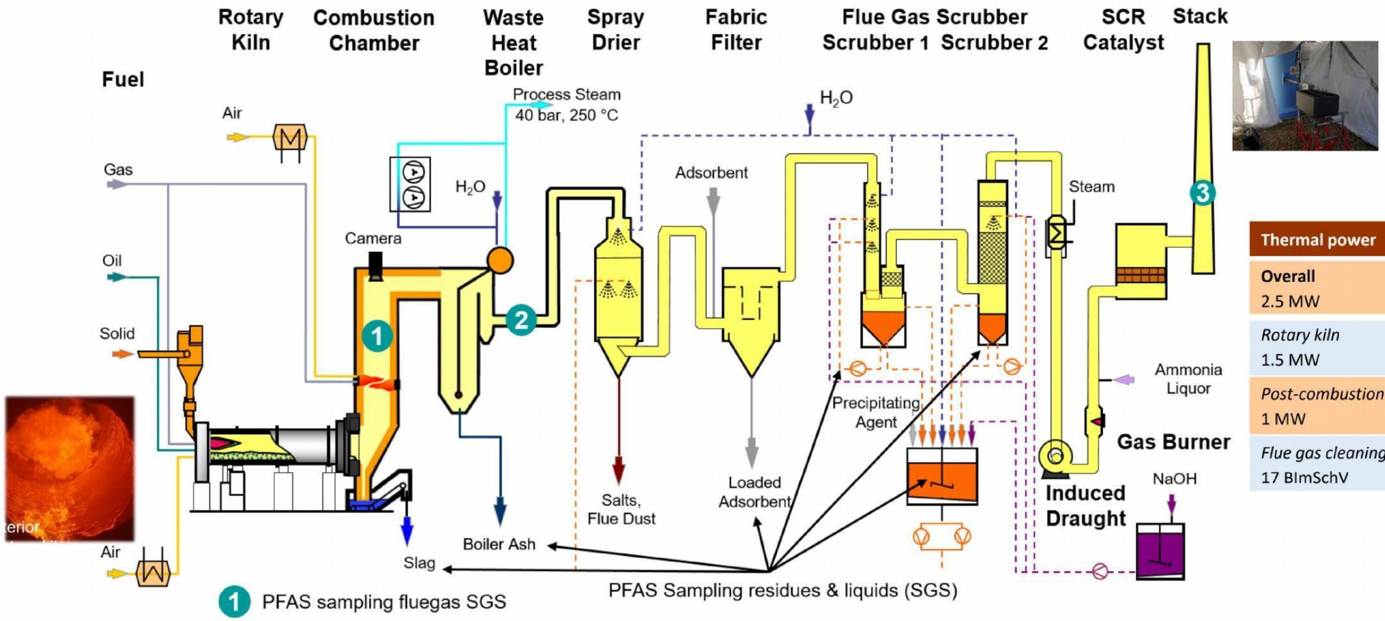
Incineration of fluoropolymers: PFAS analysis along the flue gas pathway

A pilot scale trial at conditions similar to household and industrial waste-to-energy incineration plants that typically burn products containing fluoropolymers was conducted to assess the potential generation of any statistically significant uncontrolled emissions of Per- and Polyfluorinated Alkyl Substances (PFAS) at levels that might present a risk

Project partners

Research partner	Institute for Technical Chemistry (ITC) at Karlsruhe Institute of Technology (KIT)
Sampling partner	SGS Institut Fresenius GmbH, Industries & Environment
Laboratory partner	SGS Belgium NV, Institute for Applied Chromatography
Feed sampling	Pro-K, Fluoropolymer processing and downstream user association, Germany
Incineration Advisor	[redacted] P Taylor & Associates, LLC, USA
Academic Consultant	[redacted] University of Montpellier, France
Data quality review (under process)	Environmental Standards Inc., USA
Observer	UBA, Umweltbundesamt (German Federal Environment Agency)

Test facility BRENDA / Sampling locations

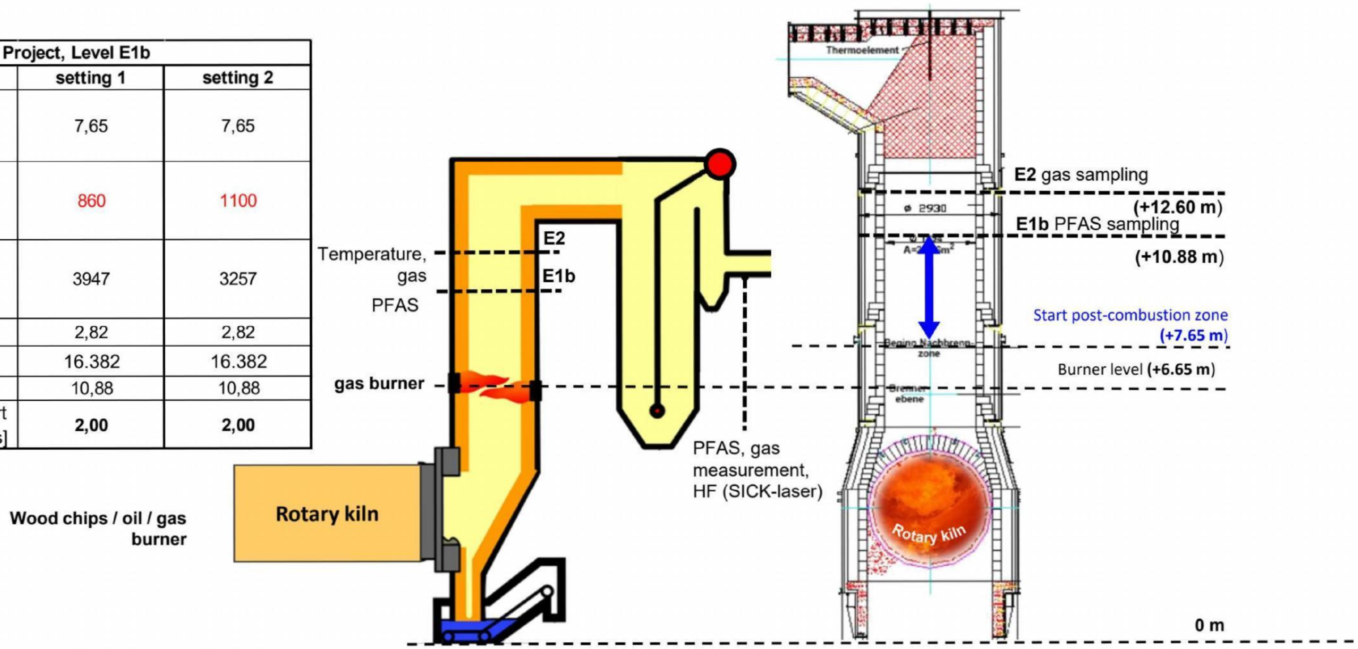


Thermal power
Overall 2.5 MW
Rotary kiln 1.5 MW
Post-combustion chamber 1 MW
Flue gas cleaning 17 BImSchV

The BRENDA plant is a large facility that is a good representation of commercial waste-to-energy plants in Europe

Test facility BRENDA / Post-combustion chamber -Triple T

PFAS Project, Level E1b		
	setting 1	setting 2
Start post combustion zone [m] 1 meter above the burners	7,65	7,65
Temperature in the post combustion chamber (PCC) [°C]	860	1100
Volume flow V_{PCC} [m_N^3/h wet] after boiler	3947	3257
Cross section PCC [m^2]	2,82	2,82
Volume flow V_{PCC} [m^3/h]	16.382	16.382
Height h [m] level E1b	10,88	10,88
Residence time from start PCC zone to level E1b [s]	**2,00**	**2,00**



Experimental Setup

test	parameters	number of HF and PFAS sampling	locations	duration [hrs]	RUN	date / remarks		day
start-up with natural gas and oil				24		25.2.23; 10 a.m.	day 1 and 2	
starting solid feeding (wood chips)				24		26.2.23; 10 a.m.		
background of rotary kiln / combustion chamber with oil, natural gas and 100 kg/h wood chips	T_{PCC}: 860 °C; 2.0 s	3	Top of post-combustion chamber (E1b), after boiler, stack	11	1	27.2.2023; 9 am	day 3	Monday
solid fuel: woodchip (100 kg/h) + 320 g/h FP together with oil and natural gas		no		9		feeding of fluoropolymers over night		
		3		11	2	28.2.2023; 9 am	day 4	Tuesday
background of rotary kiln / combustion chamber with oil, natural gas and 100 kg/h wood chips		no		13		stop feeding flouropolymers in the evening		
		3		11	3	01.03.2023; 9 am	day 5	Wednesday
Change of temperature post combustion chamber				12		over night		
background of rotary kiln / combustion chamber with oil, natural gas and wood chips	T_{PCC}: 1100 °C; 2.0 s	3	Top of post-combustion chamber (E1b), after boiler, stack	11	4	02.03.2023; 9 am	day 6	Thursday
solid fuel: woodchip (100 kg/h) + 320 g/h FP together with oil and natural gas		no		9		feeding of fluoropolymers over night		
		3		11	5	03.03.2023; 9 am	day 7	Friday
background of rotary kiln / combustion chamber with oil, natural gas and 100 kg/h wood chips		no		13		stop feeding flouropolymers in the evening		
		3		11	6	04.03.2023; 9 am	day 8	Saturday
shut down				24			day 9	

Material	Mass fraction [wt.-%]
PTFE tubes	63,00
PTFE tape	7,00
PVDF	18,00
PFA	6,00
FKM rubber	6,00

mass flow = 320 g/h

Basis of fluoropolymer feed mixture:

1. Feed mixture comprises of 4 largest volume fluoropolymers - PTFE, PVDF, PFA, FKM. Together these represent 80% of commercial fluoropolymer production
2. Pro-K supplied fluoropolymer samples of major applications that were grinded and mixed

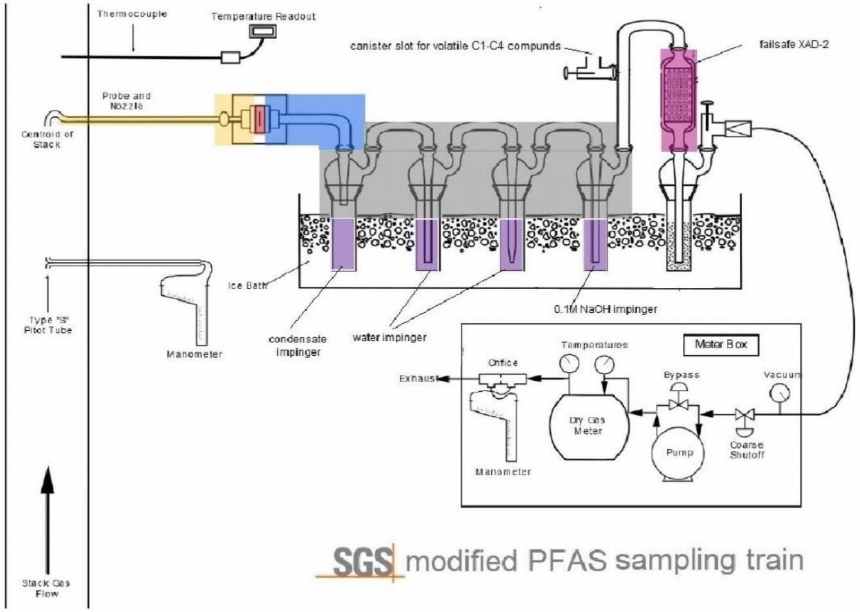
Main Operational Parameters, Setting 1 and 2

		unit	setting S1 RUN 1, 2, 3	setting S2 RUN 4, 5, 6	
Rotary kiln	mass flow wood chips	kg/h	98	98	
	main air	m_N^3/h	418	423	
	mass flow heating oil	kg/h	61	46	
	volume flow natural gas	m_N^3/h	4	4	
	volume flow combustion air	m_N^3/h	872	753	
	inclination	°	2		
	rotation speed	rev p.m.	0.2	0.4	Increase of rotation speed to avoid slagging
	temperature flue gas outlet	°C	800 - 900		
	thermal power	MW	1.1	0.9	- 200 kW, shift thermal power to the PCC
combustion chamber	volume flow natural gas to burner D4.1	m_N^3/h	22	35	
	sum of volume flow combustion air to burner D4.1	m_N^3/h	671	429	
	volume flow natural gas to burner D4.2	m_N^3/h	22	35	
	sum of volume flow combustion air to burner D4.2	m_N^3/h	671	428	
	residence time	s	2		
	temperature flue gas post-combustion chamber outlet (with control)	°C	860	1095	Increase of temperature by reduction of stochiometric ratio
	CO (level E2)	mg/m^3	0.2	1.2	
	O_2 (level E2)	Vol.-% dry	11.2	7.0	
	thermal power	MW	0.46	0.72	+ 260 kW
	total thermal power rotary kiln and post combustion chamber	MW	1.59	1.67	≈ constant
boiler / fluegas	volume flow	m_N^3/h	3958	3238	
	O_2	Vol.-% dry	11.9	9.0	
	CO	mg/m^3	1.35	1.64	
	water vapour	Vol.-% wet	6.20	8.49	

PFAS analysis

1. Modified OTM-45 for sampling train
2. Combustion Ion Chromatography (CIC) for Adsorbable Organic Fluorine (AOF)
3. Ultrahigh-Performance Liquid Chromatography coupled to tandem Mass Spectrometer (UPLC-MS/MS) for targeted long chain PFAS
4. Gas chromatography coupled to mass spectrometry (GC-MS) for volatile Fluorocarbons
5. Ion chromatography (IC) for Trifluoroacetic Acid (TFA)
6. Ion Selective Electrode (ISE) for Inorganic Fluoride
7. Tunable Diode laser for Hydrogen fluoride

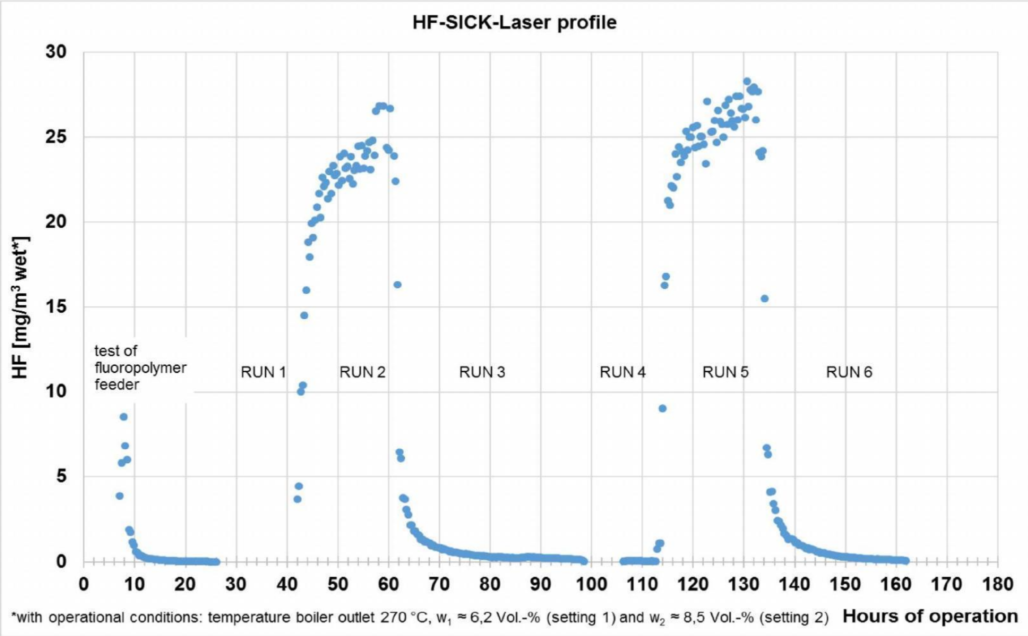
Modified OTM-45 sampling train



Testing methodology

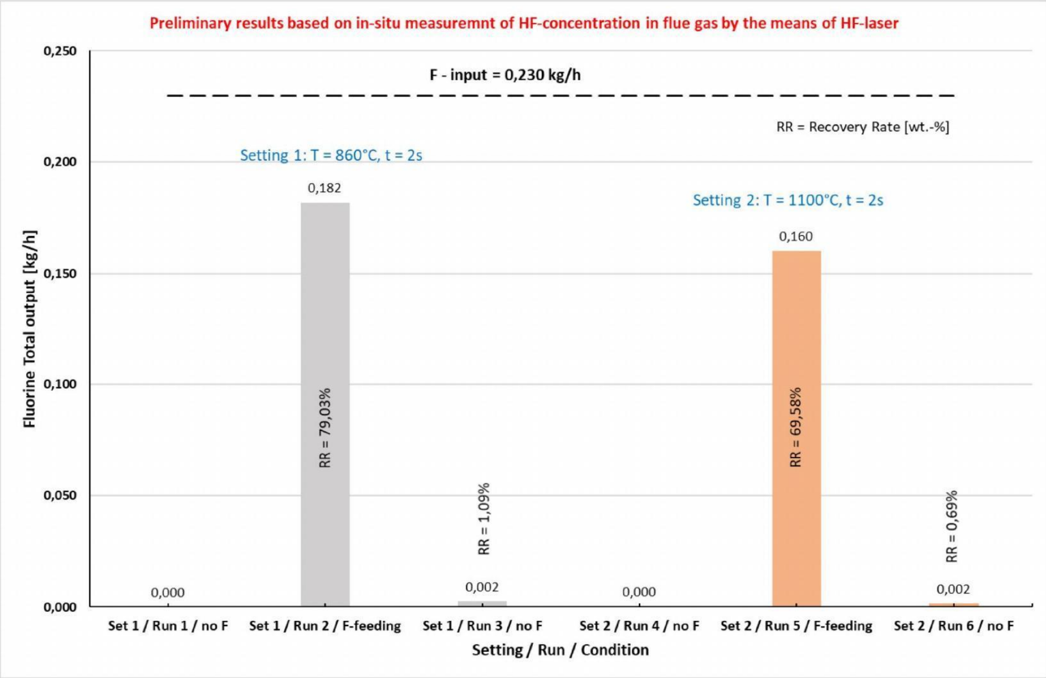
- 24 samples analyzed per setting
- 3 samples were collected and analyzed at each sampling point per setting (triplicate sampling)
- PFAS analyzed at Pre-run, Run and Post-run conditions
- Ash samples were analyzed for target PFAS content
- Blank media and solutions were analyzed for their respective parameters
- Blank sample train were analyzed after every run at relevant sample locations

HF measurement after the boiler (Tunable Diode Laser)



2966620

Fluorine balance (based on HF-Laser)



Summary of analytical results (860°C)

	Avg. Total Fluorine (mg/m^3) (LOQ (gas) – 27 $\mu g/m^3$) (LOQ (part) – 1.7 $\mu g/m^3$)	Avg. AOF (LOQ - 27 $\mu g/m^3$)	Sum of PFAS (ng/m^3)	TFA (LOQ – 14 $\mu g/m^3$)
Post combustion	36.5	31.5	1.5	Non-detectable
After Boiler	17.3	Non-detectable	0.3	Non-detectable
Stack	Non-detectable	Non-detectable	5.1	Non-detectable

Results from GC-MS analysis (50 samples)

Short chain fluorocarbons	LOQ (µg/m³)	Results (Stack)
Tetrafluoromethane	20	Non detectable except 2 values in separate runs near detection limits (20, 27 µg/m³)
Hexafluoroethane	30	Non detectable
Trifluoromethane	20	Non detectable
Hexafluoropropylene	5	Non detectable
Pentafluoroethane	25	Non detectable
Octafluorocyclobutane	25	Non detectable

Total expected PFAS emissions from EU incineration plants

Total waste incinerated in the EU	= 62 million tons per year*
Maximum sum of PFAS released (stack) at 860°C/1100°C with 0.3 % FP feed	= 18.4 $ng/m^3_{N,\ dry}$ assuming PFAS < LOQ = 0
Specific Flue gas amount released per ton of waste**	= 4060 $m^3_{N,\ dry}$
Total load of PFAS emitted in the EU	= 4.63 kilograms per year for 0.3% FP feed
But,	
Actual fluoropolymer waste incinerated (85% of 52,000 tons)	= 44,200 tons per year (0.07% of total waste)

Therefore, total PFAS emissions in the EU should be lower than 4.63 kilograms per year

*https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Municipal_waste_statistics#Municipal_waste_generation
**VDI guideline 3925 "Methods for evaluation of waste treatment processes"

2966620

Results

Fluorine Recovery: Fluorine recoveries ranged from 69 to 84% using Tunable Diode Laser - provides strong evidence for mineralization of the Fluoropolymer feed mixture

Trifluoroacetic acid: TFA was not detected for all samples at a reporting limit of 14 $\mu g/m^3$

Targeted PFAS analysis: A large majority of samples (> 99% of samples associated with 860°C condition and > 98% of samples associated with 1100°C condition) indicated that long-chain PFAS were non-detectable at levels of < 1 ng/m^3

PFAS analysis of wastewater and ash residue: A large majority of the samples were non-detectable with reporting limits of 0.02 µg/l

GC-MS analysis for short chain fluorocarbons: Non-detectable at a reporting limit of 5-30 $\mu g/m^3$ levels

Conclusions

- Fluoropolymers are converted to inorganic fluorides (hydrogen fluoride) and carbon dioxide
- The absence of organic fluorides and PFAS confirms complete mineralization of fluoropolymers
- Therefore, fluoropolymers do not generate any measurable levels of small molecule PFAS of concern
- Standard waste-to-energy incineration operating conditions are sufficient for mineralization of fluoropolymers
- Fluoropolymers pose no risk to human health and the environment at their end of life when incinerated

Thank you