Incineration of Fluoropolymers
Project presentation

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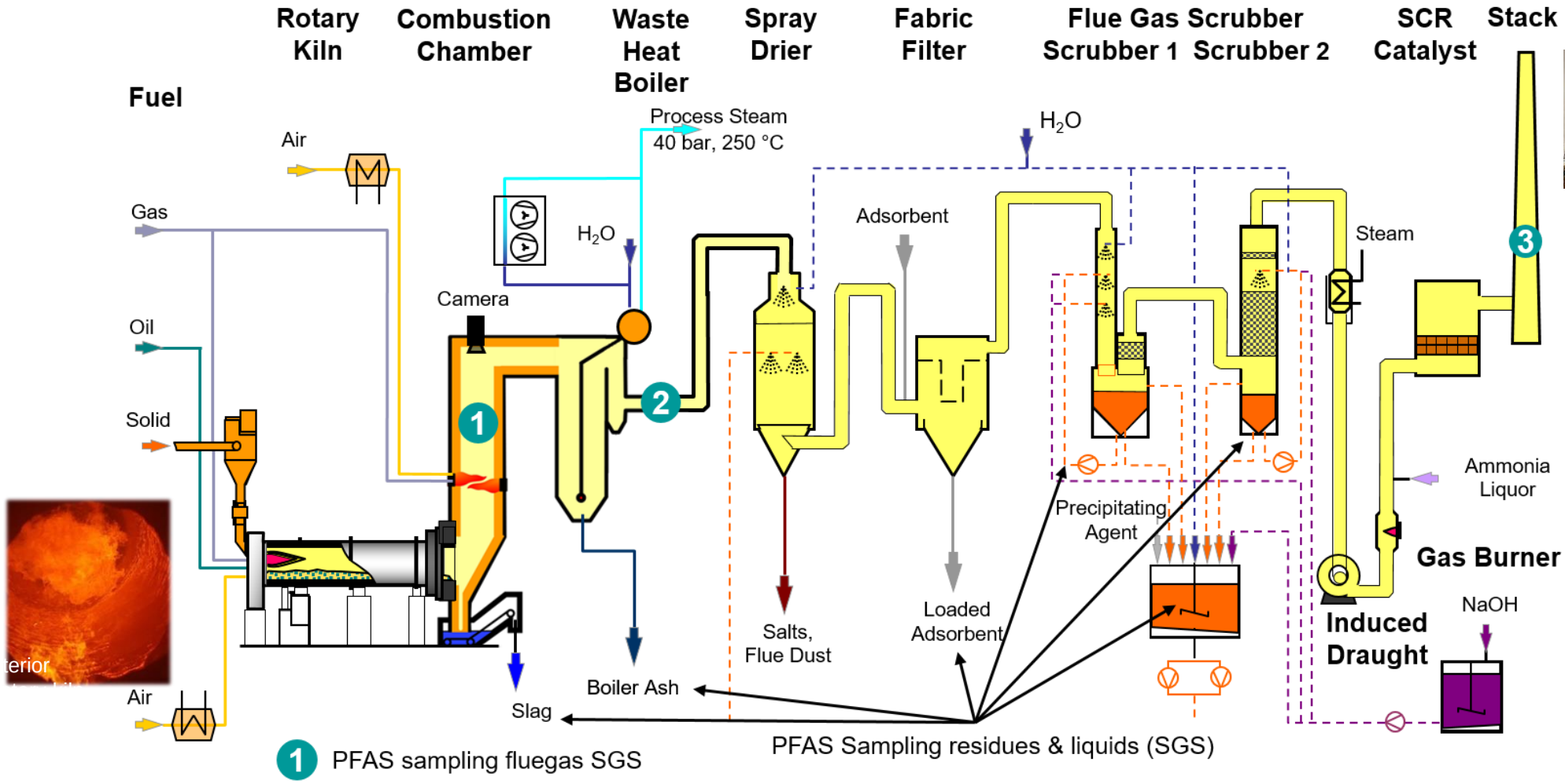
Incineration of fluoropolymers: PFAS analysis along the flue gas pathway

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	Dr. Philip Taylor, P Taylor & Associates, LLC, USA
Academic Consultant	Dr. Bruno Ameduri, Senior Researcher at ICGM, 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

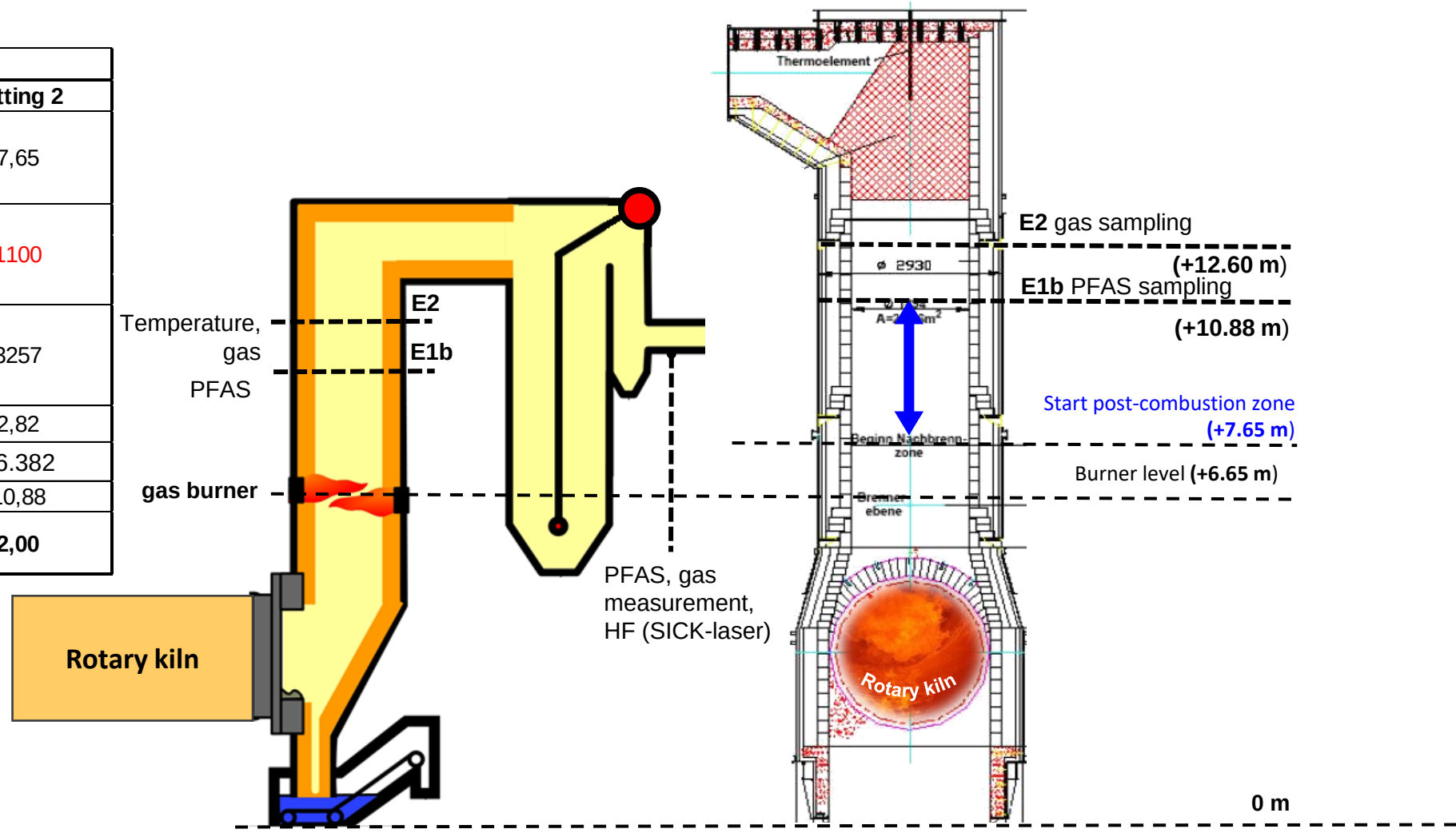


Thermal power
Overall 2.5 MW
Rotary kiln 1.5 MW
Post-combustion chamber 1 MW
Flue gas cleaning 17 BImSchV

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

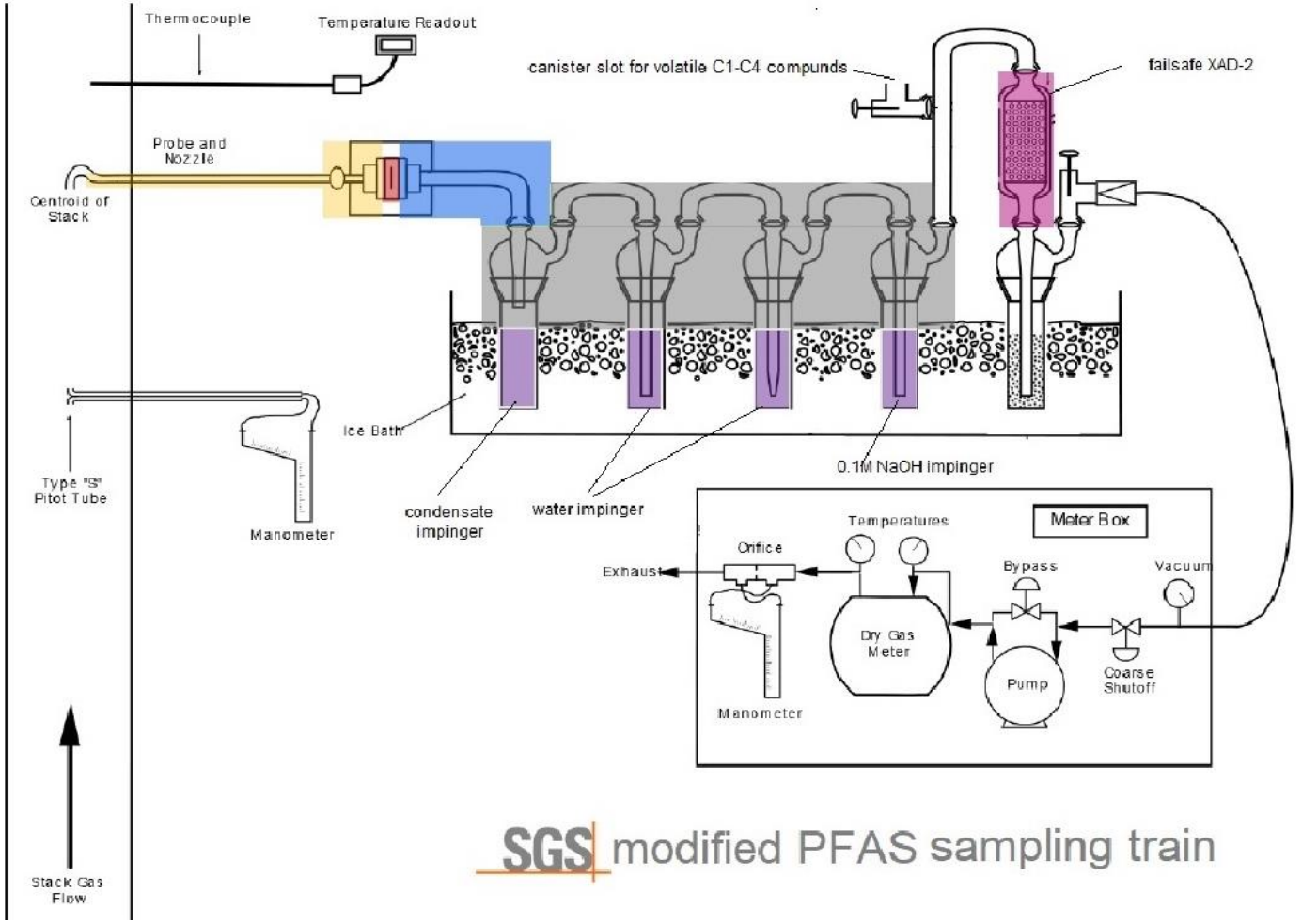
Main Operational Parameters, Setting 1 and 2

			setting S1	setting S2	
		unit	RUN 1, 2, 3	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

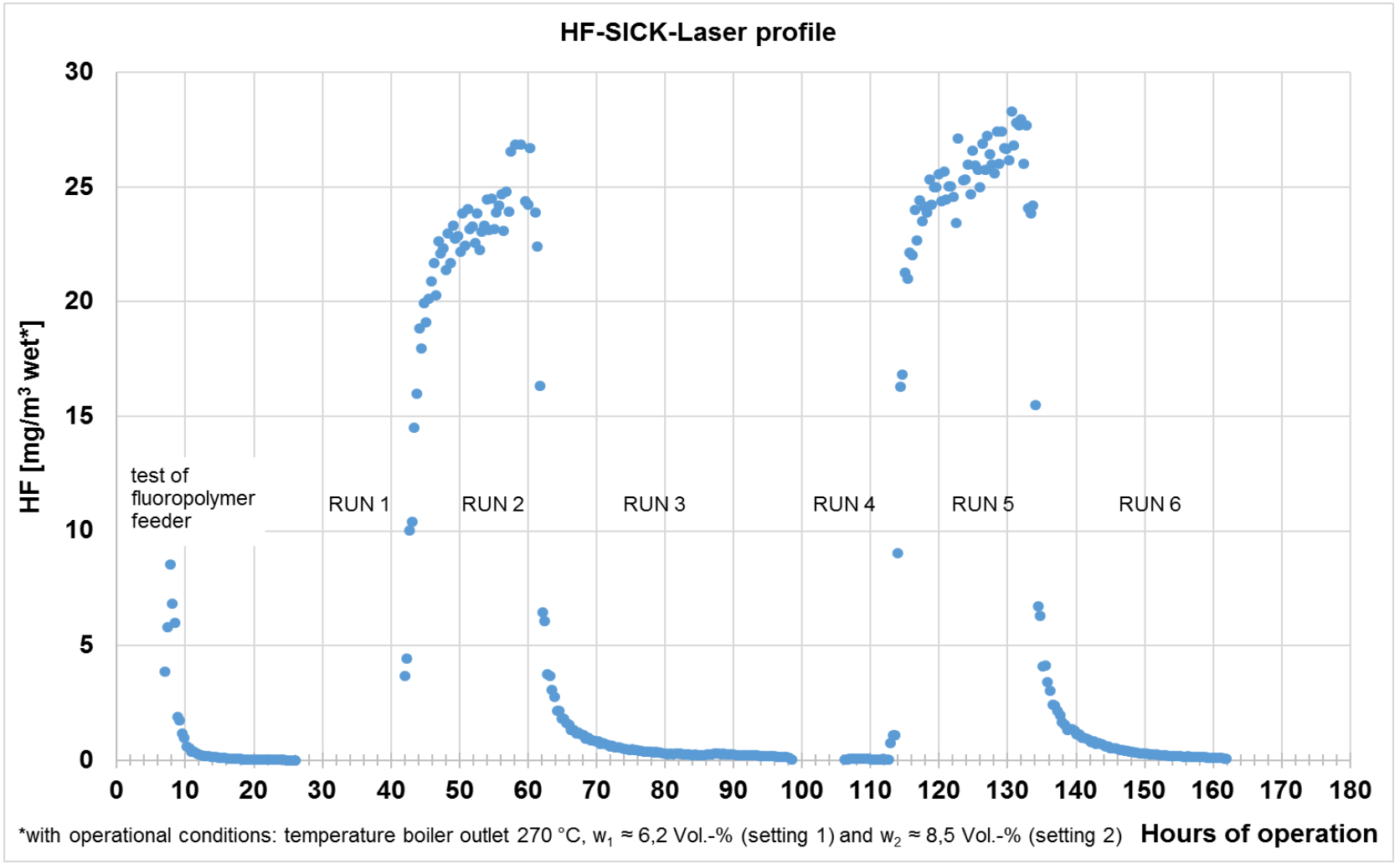
Modified OTM-45 sampling train



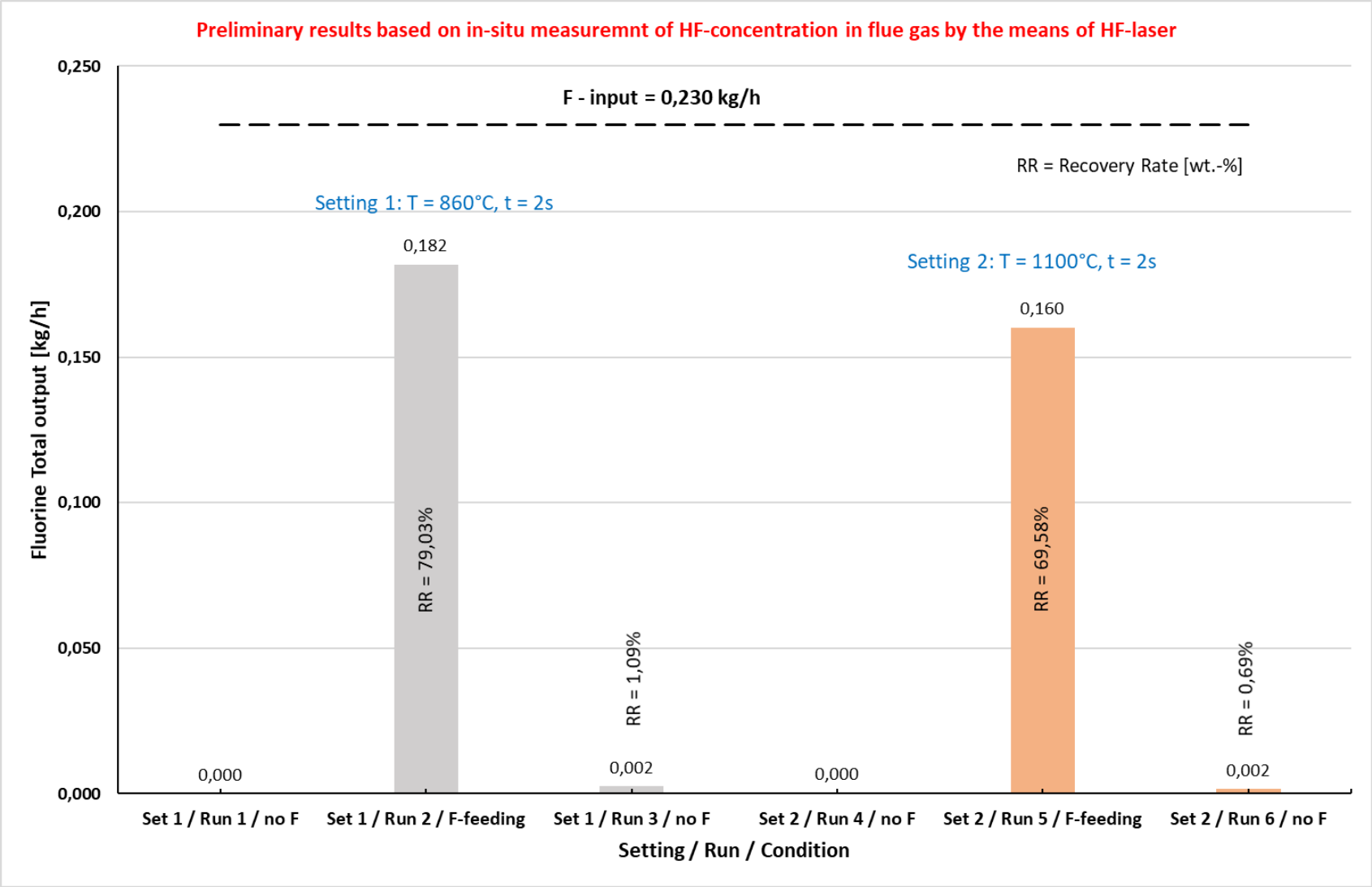
Testing methodology

- 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)



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"

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 µg/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 µg/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