Mineralization of fluoropolymers from combustion in a pilot plant under representative european municipal and hazardous waste combustor conditions

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HIGHLIGHTS

- R2PIC >99.99% demonstrated mineralization of fluoropolymers via incineration.
- Testing conducted under municipal & hazardous waste incineration conditions.
- PFAS, including TFA, were measured at three locations, plus wastewater & residues.
- Only PFOA detected in stack gases (0.20 ng/m^3) slightly above the LOQ (0.09 ng/m^3).
- External contamination is the likely source of the PFOA detection.

GRAPHICAL ABSTRACT
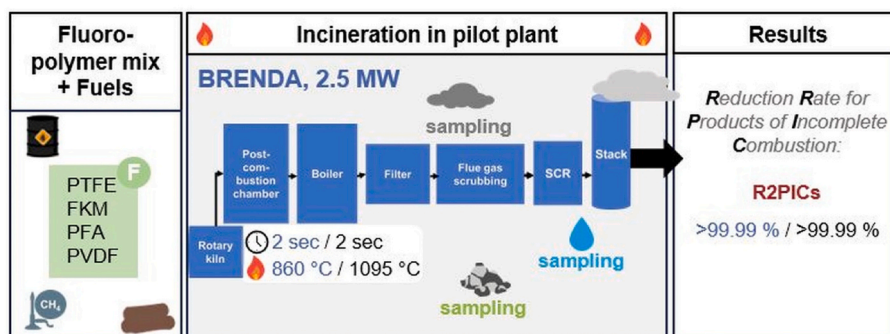
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ABSTRACT

The goal of this study was to provide data to support mineralization of fluoropolymer waste and insignificant generation of PFAS as products of incomplete combustion (PIC) during incineration of fluoropolymer applications at their end-of-life. Destruction efficiency is not an acceptable metric to indicate mineralization and therefore we need to look for and measure products of incomplete destruction. A mixed sample of fluoropolymers

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representing 80% of commercial fluoropolymers was combusted at conditions representative of municipal and industrial waste incinerators operating in EU. State-of-the-art emission sampling and analytical methods (UPLC-MS/MS, GC-MS) were used for identifying and quantifying those PFAS whose standards were available. Statistical analysis of the results confirmed non-detect to negligible levels of PFAS evidencing mineralization of fluoropolymers.

1. Introduction

PFAS (per- and polyfluoroalkyl substances) are a broad group of man-made chemicals that are characterized by strong carbon-fluorine bonds. PFAS are under regulatory scrutiny due to concerns about their presence in the environment and potential adverse effects on human health. PFAS may be mobile, resistant to biodegradation, may accumulate over time in soil, water and living organisms and may be toxic to human health and the environment. However, the broad group of PFAS also includes substances or groups of substances which exhibit different physio-chemical properties, toxicological and environmental profiles. One such unique group is fluoropolymers.

Fluoropolymers are a distinct family of fluorinated polymers, which can be clearly differentiated from other substances typically included in the PFAS group of chemicals. Fluoropolymers are structurally characterized by having fluorine atoms directly attached to their carbon-only backbone. Fluoropolymers are high molecular weight, safe, solid substances that have been proven to be biologically stable and chemically inert in presence of virtually any chemical, insoluble in water, non-bioavailable, non-bioaccumulative, non-toxic and resistant to degradation (Korzeniowski et al., 2023).

Due to their exceptional properties including high thermal stability, chemical resistance, and durability, fluoropolymers are indispensable in many strategic industries like aerospace and automotive, semiconductors and electronics, medical and pharmaceuticals, chemical process, modern architecture, renewable energy, hydrogen economy, electrification of vehicles, electrical and data transmission.

While it has been widely accepted globally that fluoropolymers are safe substances, there is a concern related to their potential degradation to other PFAS of concern. However, the exceptional strength of the C–F bond in fluoropolymers prevents them from degrading to non-polymeric PFAS of concern under intended use and environmental conditions (Danish EPA, 2013). Still there was a concern related to end-of-life disposal of fluoropolymer applications. A study by Conversio (2022), a consultancy based in Germany, has shown that at its end-of-life approximately 84% of all fluoropolymer applications end up in waste to energy recovery incinerators or industrial waste incinerators. A subsequent question of regulators was: do fluoropolymers get fully mineralized without formation of any short-chain or long-chain PFAS? In response, the authors of this publication decided to study the combustion of fluoropolymers at a pilot scale representing European municipal and hazardous waste incineration conditions to analyze emissions for presence of any short-chain and long-chain PFAS compounds.

2. Previous studies

The National Institute for Public Health and the Environment of the Netherlands recently investigated to what extent and under what conditions fluoropolymers are thermally degraded and what kind of incineration byproducts are formed (Bakker and Bokkers, 2021). In this review, polytetrafluoroethylene (PTFE) was found to be the most stable fluorine-containing polymer. For PTFE, it was concluded that complete thermal decomposition is achieved at a temperature of about 800 °C. It was, therefore, assumed that other fluorine-containing polymers also thermally decompose completely at a temperature of 800 °C. Temperatures at the pyrolysis and combustion fronts in the waste-burning bed range from 900 °C to 1100 °C, which is well above 800 °C, the temperature at which the complete thermal decomposition of PTFE is

achieved.

The impact of temperature and residence time on the degradation of fluoropolymers at the pilot-scale were investigated in one prior published study of the combustion of PTFE (see Aleksandrov et al., 2019). Tests were performed at temperature of 870 °C and residence time of 4 s, and at temperature of 1020 °C and residence time of 2.7 s. Statistical evaluation of the results as a function of operational conditions found no significant difference in measured PFAS concentrations. Furthermore, measured PFAS emissions were not found to vary with or without PTFE feeding.

There is one prior bench-scale study of the combustion of fluorotelomer-based polymers (Taylor et al., 2014). This study focused on emissions of PFOA under representative municipal waste combustion conditions. Fluorotelomer-based polymers were incinerated in the presence of methanol fuel. Experiments were carried out at 1000 °C and residence time of 2 s. No PFOA at concentrations above limit of quantitation (LOQ) of 54 ng/m_N^3 (dry, corrected to 7% O_2) were detected.

There are very few prior studies of emission of short-chain PFAS from the combustion of fluorine-containing materials. The only prior bench-scale study of low molecular weight fluorocarbon emissions from combustion of PTFE was reported by Garcia et al. (2007). In this work, percent yields of CF_4, C_2F_6, and C_3F_6 were reported for fuel-rich (sub-stoichiometric) thermal degradation of PTFE at 850 °C. C_2F_4, the monomer of PTFE, was not observed except under oxygen-free conditions.

Shields et al. (2023) presented similar emission measurements in a pilot-scale study of aqueous film forming foam (AFFF) combustion. In that study, emission concentrations were $\mu g/m^3$ or lower for sampling conducted at temperatures of ≥ 970 °C but increased by as much as three orders of magnitude at temperatures of ≤ 870 °C, suggesting that low molecular weight PFAS may form at lower incinerator temperatures.

Puts et al. (2014) has summarized bench-scale thermal decomposition and pyrolysis tests of PTFE. This work is relevant to municipal waste combustion of PTFE in that potential Products of Incomplete Combustion (PIC) formation mechanisms were identified. The importance of CF_2 radicals as reaction intermediates was identified in this review and C_1 and C_2 fluorocarbons (e.g. tetrafluoromethane (CF_4), hexafluoroethane (C_2F_6)) were proposed as stable intermediates at elevated temperatures. The C_2F_4 monomer of PTFE is a significant intermediate at lower temperatures (Puts et al., 2014) but is unlikely to survive combustion conditions due to the stability of the CF_2 radical (Tsang et al., 1998). CF_4 and C_2F_6 are the most stable forms of perfluorocarbons (Tsang et al., 1998) and have been suggested as PFAS surrogates for full-scale incineration (Krug et al., 2022).

The goal of current study was to provide data to support mineralization of fluoropolymer waste and insignificant generation of PFAS as products of incomplete destruction during incineration of fluoropolymer applications at their end-of-life. The testing was conducted at a pilot incineration plant under representative European municipal solid waste and hazardous waste combustor conditions.

3. Materials and methods

3.1. Incineration pilot plant BRENDA

To evaluate the combustion behavior of fluoropolymers the experiments were carried out at the pilot plant BRENnkammer mit DAmpfkessel (BRENDA), which was operated by the Institute of Technical

Chemistry (ITC) at Karlsruhe Institute of Technology (KIT) between February 27 – March 4 of 2023. BRENDA (see Fig. 1) consists of a rotary kiln, a post combustion chamber (PCC), a boiler for heat recovery, and a flue gas cleaning system which complies with German emission regulations (17 BImSchV).

In the rotary kiln, the fuels are converted into a flue gas and ash or slag (depending on the final temperature in the outlet), while the flue gas must be afterburned in the PCC to reach a good burnout and the legal limits. The thermal output of the rotary kiln is 1.5 MW (max) while that of the PCC is ~1 MW. Thus, the overall thermal output of the plant is ~2.5 MW.

The rotary kiln is a steel tube with the inside surfaces covered with two layers of refractory material. The refractory consists predominantly of Al_2O_3 (30–40 wt%) and SiO_2 (30–50 wt%). The remainder are additives such as CaO (13–15 wt%), Fe_2O_3 (~0.5 wt.-%) and alkalis (1–3 wt %). The rotary kiln is equipped with a versatile multi-fuel feeding system able to inject liquid, solid as well as gaseous fuels. The length and inner diameter of the kiln is 8.4 m and 1.4 m, respectively. The inclination of kiln can be adjusted between 0.5° and 3°. With the inclination and the rotation speed the average residence time of the solids in the rotary kiln could be influenced.

Kiln rotation speed can be varied between 0.1 and 3 rpm. From the rotary kiln, the combustion gases flow into the PCC, which contains two natural gas burners, staggered in an opposed manner and slightly shifted to each other (see Fig. 1). Gas temperature and residence time in the PCC were adjusted with the help of the burners and must fulfill the legal requirements according the Industrial and Livestock Rearing Emissions Directive in Europe (2024), respectively the German directive (17 BImSchV). Exiting the post-combustion chamber, the hot exhaust gas enters the boiler where saturated steam at a pressure of 40 bar and temperature of 250 °C is generated. The exhaust gas then cools and enters the flue gas cleaning system, which includes a spray dryer, a baghouse filter, and an acidic and a neutral scrubber to remove e.g., HF, HCl, and SO_2, among other pollutants. In the last stage of the gas cleaning system, nitrogen oxides are removed with a selective catalyst reduction (SCR) catalyst unit. Finally, clean gas is released into the atmosphere through the stack.

The fluoropolymer incineration experiments were planned with two sets of combustion conditions. The first combustion condition called Setting-1 of 860 °C with 2 s residence time represents the minimum temperature condition of municipal waste to energy incineration plants operated in Europe. The second combustion condition called Setting-2 of 1095°C with 2 s residence time represents the minimum temperature condition of hazardous waste incineration plants operated in Europe.

For the Setting-1 (860 °C) tests, (see Table 1 and Table S1, Supplemental Information), the rotary kiln was operated with heating oil, wood chips and a small amount of natural gas, at total thermal power of 1.1 MW. For the Setting-2 (1095 °C) tests, rotary kiln output power was reduced to 0.9 MW and the amount of natural gas in PCC was increased from 22 m^3/h to 35 m^3/h per burner. Simultaneous increase in natural flow rate and reduction of introduced air resulted in decrease in stoichiometry (air ratio). The residual oxygen content in the flue gas at the PCC (location E2 in Fig. S1) decreased from ~11% to ~7% by volume dry (see Table S1). The carbon burnout, measured as CO, was in the low range (see Table S1), in each case based on 11 vol.-% O_2. Good combustion conditions were ensured for all runs, including those with fluoropolymer fed to rotary kiln.

3.2. Feed material

The fluoropolymer mixture comprised materials which are manufactured using different polymerization processes, such as suspension

Table 1
Sequence and designations of tests at BRENDA pilot plant.

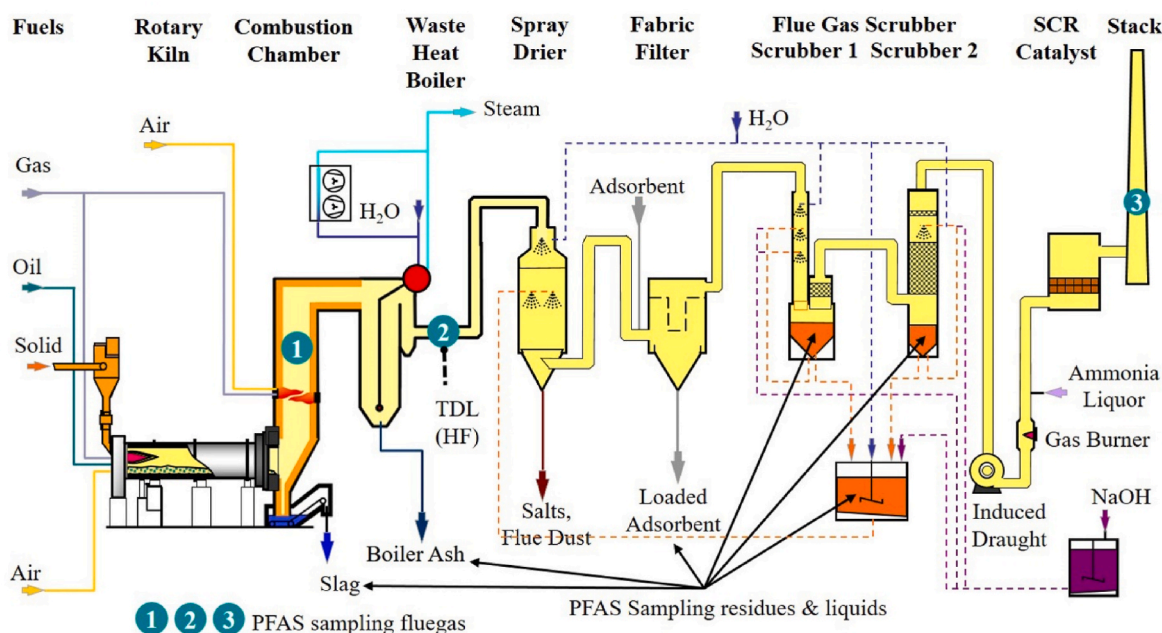| Setting (Temperature)	Test Conditions		
	Background combustion with oil, natural gas and wood chips (without fluoropolymers)	Combustion with oil, natural gas, wood chips and with fluoropolymers	Background combustion with oil, natural gas and wood chips (without fluoropolymers)
	Start-up of pilot plant		
1 (860 °C)	RUN1	RUN2	RUN3
	Change of temperature in post-combustion chamber		
2 (1095 °C)	RUN4	RUN5	RUN6
	Shut down of pilot plant		

Fig. 1. Layout of BRENDA incineration pilot-plant with PFAS sampling locations.

and emulsion polymerization, with and without fluorinated/non-fluorinated polymerization aids. The fluoropolymer feed material consisted of PTFE, polyvinylidene fluoride (PVDF), perfluoro alkoxy alkane (PFA) and fluoroelastomer (FKM), which represent more than 80% of global commercial production of fluoropolymers and also covered fully fluorinated, partially fluorinated, non-melt-processible, melt-processible, plastic and rubber types including homopolymers, copolymers and terpolymers. The fluoropolymer materials and their mass fractions in the fluoropolymer mixture fed into BRENDA during the experimental runs are listed in Table 2.

Each fluoropolymer material was cut into small pieces with a length from 3 mm to 6 mm that allowed their mixing with wood chips before entering the rotary kiln. The wood chips mass flow was kept constant at 100 kg/h and the fluoropolymer mixture was added at a rate of 320 g/h (230 g/h of F, see Table 2) to secure a mass fraction of the fluoropolymer mixture of 0.3 wt%. The elemental composition of the wood chips is given in Table S2. The background level of fluorides in the wood chips was below the detection limit of 0.010 wt.-%, indicating the primary source of fluorine input was from the fluoropolymer feed. The range of fluorine concentration in typical municipal waste is 0.010–0.035 wt% (dry) in Germany (Industrial Emissions Directive, 2019). The fluoropolymer concentration was set at 0.3 wt% to maximize the mass fraction of fluoropolymers to fuel while staying well below the 1% total halogen limit set by regulations (17 BImschV).

3.3. Pilot-plant operational parameters

The incineration of fluoropolymer was studied for two sets of tests Setting-1 (860 °C) and Setting-2 (1095 °C), see Table 2. The purpose was to burn fluoropolymer under conditions relevant to EU municipal and hazardous waste combustors. The BRENDA pilot plant operation parameters are shown in Table S1, including calculations of minimum gas residence time for the operational conditions and PCC pilot plant geometry (see Fig. S1). For Setting-1 (860 °C), a residence time of 2 s was calculated in the PCC. For Setting-2, the higher temperature tests, the temperature in the PCC was increased to 1095 °C while the residence time was maintained at 2 s. Details regarding how the temperatures in the PCC were measured and averaged are given in the Supplemental Information.

The emissions sampling was planned at three stages: pre-dosing, dosing and post-dosing of fluoropolymers for both test conditions (Setting-1 and Setting-2). Table-2 below describes the stage of sampling during dosing of fluoropolymers (Setting-1, RUN2, and Setting-2, RUN5) and without dosing of fluoropolymers (Setting-1, RUN1 and RUN3, and Setting-2, RUN4 and RUN6) at both test conditions. This test sequence provided an assessment of the system background results (PFAS concentrations) for comparison with the results obtained with fluoropolymer combustion.

3.4. Sampling Methods

Three gas sampling locations were chosen to measure PFAS emissions and to determine potential PFAS sources at different stages of the combustion process, see Fig. 1 and Fig. S1, respectively. The first sampling location was the exit of the PCC, the second was downstream of the

boiler, and the third was in the stack. The following analytes were measured: Adsorbable organic fluorine (AOF), inorganic fluorine (IF), long-chain PFAS (see Table S3), trifluoroacetic acid (TFA) (see Table S4), and C_1–C_3 PFAS (see Table S5). The C_1–C_3 PFAS measured included CF_4 and C_2F_6 since these are stable PICs and were observed in the studies of Garcia et al. (2007) and Shields et al. (2023). Sampling was conducted three times at each of the three sampling locations in every run (RUNS1-6). Additional liquid and solid samples that were collected once with each run and analyzed for long-chain PFAS included the following: 1) the gas scrubber water upstream of SCR catalyst (wastewater from Scrubber 1 and from Scrubber 2 and the neutral water fed to these scrubbers), 2) water from the wet deslagger, and 3) the solid residues from the filter and boiler.

Sampling was carried out with a sampling train designed with guidance from OTM-45 (see Fig. S2) that was modified to measure a broader range of analytes. The first XAD-2 cartridge in the OTM-45 sampling train was removed due to low recovery rates for some of long-chain PFAS and the inability to measure TFA and IF on that fraction due to the required ammonia/methanol extraction. The inability to measure TFA and IF on this fraction would create an overall negative bias for these analytes. Instead, the heated dust filter (see Supplemental Information, Fig. S2) was followed by a condenser (only for sampling location 1), a single condensate impinger, two water impingers, and a single 0.1 M NaOH impinger (all impingers contained in an ice bath), followed by a breakthrough XAD-2 cartridge. Further details of the sampling train are given in the Supplemental Information – Sampling Methods.

The sampling time for analysis of AOF, IF, TFA and long-chain PFAS was about 3 h with an average isokinetic volume of 3.2 m_N^3. Sampling for the C_1–C_3 PFAS was done with Tedlar® bags at the locations shown in Fig. S2. The sampling time was 5–10 min. In separate sampling events, the stack gas was passed through a series of impinger bottles over a 24 h sampling time and the water collected in the bottles were analyzed by ion chromatography (IC) to comply with EU regulations for HF emissions. See further details on the sampling methodology in the Supplemental Information - HF stack emissions by IC.

3.5. Analytical methods

The samples fractions were each analyzed for the various analytes given in Table 3.

Ultra-high Pressure Liquid Chromatography coupled with tandem Mass Spectrometry (UPLC-MS/MS) was used to measure the long-chain PFAS and TFA with quantitation utilizing isotopically labeled internal standards. Samples collected in Tedlar® bags were analyzed for C_1–C_3 PFAS by Gas Chromatography coupled with Mass Spectrometry (GC-MS).

Ion selective electrode (ISE) was used to analyze samples for fluoride ion which was converted to HF concentrations (except for the stack flue gas impingers collected to comply with EU regulations for HF emissions that were analyzed by IC). HF was also measured in real time at the boiler exit using Tunable Diode Laser (TDL) spectroscopy (see Fig. 1). The measurements with ISE were biased low at the boiler exit location based on comparison with the TDL HF measurements (see Results - Fluorine Mass Balance).

Table 2
Content and mass fractions of the fluoropolymer mixture.

Fluoropolymer material	Stoichiometric formula	Mol mass [g M^{-1}]	F-content [wt. %]	Mass portion in Fluoropolymer mixture fed at 320 g/h [wt. %]	Mass Flow as F [g h^{-1}]
PTFE tubes	$[C_2F_4]_n$	100.02	76	63	153
PTFE tape	$[C_2F_4]_n$	100.02	76	7	17
PVDF	$[C_2H_2F_2]_n$	64.04	59	18	34
PFA	$[C_2F_4]_n$	100.02	76	6	15
FKM rubber	$[CF_2CH_2]_m$-$[CF_2CH_2CF_2]_n$	178.09	64	6	12

Table 3
Analyses performed on sample fractions collected.

Sample fraction	AOF	IF	Long-chain PFAS	TFA	C_1–C_3 PFAS
Quartz filter		×	×		
Condensate	×[a]	×	×	×	
Water impinger 1	×	×	×	×	
Water impinger 2	×	×	×	×	
0.1 M NaOH impinger	×[a]	×	×	×	
XAD-2			×		
Stack flue gas		x			
Tedlar® bag					×[b]
Scrubber and neutral water			×		
Wet deslagger			×		
Baghouse filter ash			×		
Boiler ash			×		

[a] There was insufficient sample volume to perform the AOF determination in some cases (AOF was measured in 35 of the 54 condensate samples and 45 of the 54 alkaline impingers).

[b] Five of nine samples collected for RUN2 were analyzed.

AOF was analyzed using Combustion Ion Chromatography with Conductivity Detection (C-IC-CD). A high bias for AOF was observed in samples that contained higher levels of IF than could be removed by the analysis performed (US EPA, 2024, Section 1.6), hence the AOF measurements were not considered reliable and are not discussed further. Further details are given in the Supplemental Information – Analytical Techniques.

3.6. Background evaluation

PFAS has been widely used in consumer products which can potentially impact the equipment, supplies, and reagents used for long-chain PFAS sampling. OTM-45 includes the collection of various types of blanks that are to be reported and used to interpret sample results. A summary of collected blanks is given in Table S6. Background contamination was considered in the determination of LOQs. The long-chain PFAS most detected in blank impinger and rinsing solutions and associated reagent blanks were PFBA, 6:2 FTS, and HFPO-DA, with minor detections of PFHxA and PFBS. The long-chain PFAS detected in blank XAD media were PFHxA, PFHxS, 4:2 FTS, and 10:2 FTS. It is pertinent to note that the mentioned PFAS are intentionally produced and used mainly in consumer applications and therefore their cross contamination at such low levels is likely. This background contamination detected in these blanks resulted in elevated LOQs for associated RUN samples.

Rinses of supplies that did not come in direct contact with the samples such as gloves and an Edding® marker indicated the presence of several long-chain PFAS in supplies used at the analytical facility that were not directly related to samples (PFHxA, PFOA, PFUnDA, PFBS, PFOS, 6:2 FTS, and 8:2 DiPAP).

Samples of the scrubber water were also taken during the experimental trials and analyzed for long-chain PFAS by UPLC-MS/MS to verify that it was not a source of PFAS at the stack sampling location (location 3 on Fig. 1). Long-chain PFAS were not detected above the LOQ of 20 ng/l in any of the scrubber water samples collected (see Table S7).

Pre- and post-dosing runs (RUNS 1, 3, 4, and 6) were also evaluated as an indication of potential background contamination. Periodic detections of long-chain PFAS were observed in the individual samples collected. When the median (50th percentile) statistical approach used to evaluate the results (see Statistical Data Analysis and Fluoropolymer Mixture Reduction Rate) was applied to the pre- and post-dosing runs, only one long-chain PFAS, PFOA, was detected in the flue gas in RUN1 (Setting-1, 860 °C). PFBS and PFOS were detected in pre- and post-dosing run samples of the wastewater and solid residues (PFOS was detected in the water from the wet deslagger in RUN1 and RUN4 and PFBS was detected in baghouse filter ash in RUN1 and RUN3). Low

levels of IF (110–4100 µg/m^3) were detected throughout the pre- and post-dosing runs and a low level of AOF (1 µg/m^3) was detected in RUN4 post-PCC when the median (50th percentile) statistical approach used to evaluate the results.

3.7. Statistical analysis of flue gas samples and Fluoropolymer Mixture Reduction Rate for products of incomplete combustion

To prevent "outliers" from distorting the overall results, the median (50th percentile) statistical approach was applied for the flue gas sampling. The mathematical approach is summarized in the Supplemental Information (see Statistical Data Analysis and Figs. S3a and S3b). A sensitivity analysis was performed to show the impact of LOQ on the PFAS measurements. PFAS results reported as "non-detect" were assigned a concentration equal to zero according to the (Compendium of Water Sampling, Measurement and Analysis, 2024). Calculations were also performed where PFAS values were set to 50% of the LOQ (Japan, Manual 2001).

To evaluate the degree of mineralization of PFAS from fluoropolymer combustion the Reduction Rate for Products of Incomplete Combustion (R2PIC) was defined and is calculated from Eqn. (1).

$$R2PIC = 1 - \frac{\sum F_{PFAS,out}}{\sum F_{PFAS,in}} \tag{1}$$

R2PIC circumvents the inability of attaining 100% fluorine mass balance at the pilot-scale given the reactivity of fluorine with refractory surfaces. The sum of PFAS,out ($\sum F_{PFAS,out}$) includes the fluorine content calculated from the individual PFAS concentrations measured in the stack gas and the liquid and the solid residues and excludes the fluorine from HF. The sum of the PFAS,in ($\sum F_{PFAS,in}$) is based on the measured feed rate of each fluoropolymer fed as a mixture and the amount of F in each fluoropolymer mixture component. The sum of PFAS, in ($\sum F_{PFAS,in}$) also assumes that non-polymeric PFAS was not present in the fluoropolymer feed. A schematic describing this calculation is given in Fig. S4 in the Supplemental Information. Taking into consideration the accuracy of analytical data, the mass of each PFAS was determined to two decimal places. The single mass flows are calculated based on the PFAS measurements in the flue gas, the liquid and solid residues according to Eqns. (1)–(6) in the Supplemental Information.

Based on the molar fraction of fluorine for every PFAS measured in the flue gas, liquid and solid residues, a fluorine mass emission flow is calculated and normalized to the input fluorine mass flow, see Eqn. (2). The R2PIC is a value to characterize the effectiveness of combustion as a function of operational conditions such as temperature and residence time.

4. Results

4.1. PFAS emissions

Statistical analysis of the PFAS emissions is presented in Fig. 2. Fig. 2a presents data where non-detects were assigned a concentration equal to zero and Fig. 2b with non-detects assigned a concentration of 50% of the LOQ. Exhaust gas, scrubber water and solid residue measurements are shown from the combustion tests at 860 °C (RUN2) and 1095 °C (RUN5). Because of the different units of the PFAS concentrations in the flue gas and the liquid and solid samples (ng/m^3, ng/l and ng/g respectively), the different concentrations were converted into fluorine mass emission rates (see Supplemental Information - Conversion of PFAS concentrations into a fluorine mass flow).

Fig. 2a and b both show that only one long-chain PFAS, PFOA, was detected in the flue gas in RUN5 (Setting-2, 1095 °C) at a very low concentration of 0.20 ng/m^3 (0.46 µg/h) with a LOQ of 0.028 ng/m^3. Additionally, PFBS in the solid residue and PFOS in the wastewater were detected in RUN2 (Setting-1, 860 °C). Other long-chain PFAS were not
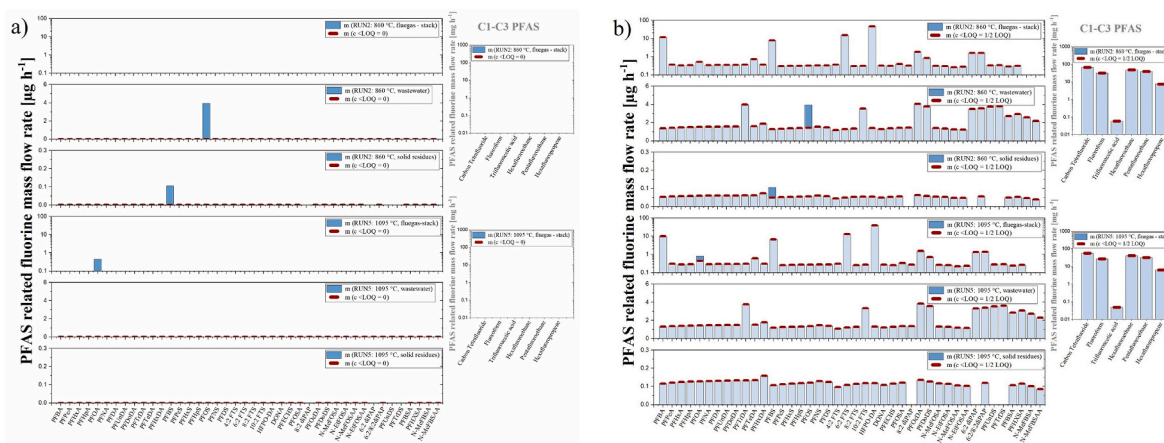
Fig. 2. Fluorine mass emission rates measured in a flue gas, scrubber wastewater, and solid residues for combustion tests at 860 °C and 1095 °C. a) c < LOQ = 0. b) c < LOQ = ½ LOQ.

detected at or above the LOQ which ranged from 0.19 ng/m^3 to 52 ng/m^3 (0.33–130 µg/h) in the flue gas. TFA and other volatile C_1–C_3 PFAS were not detected in either RUN2 or RUN5 (see boxes to the right of Fig. 2). The LOQ for TFA ranged from 30 ng/m^3 to 90 ng/m^3 (49–180 µg/h). LOQ for the C_1–C_3 PFAS ranged from 5000 ng/m^3 to 40,000 ng/m^3 (3800–35,000 µg/h). The PFAS abbreviations and LOQs (in ng/m^3) for individual PFAS are given in the Supplemental Information, Table S3.

4.2. Fluorine mass balance

The feed rate of fluoropolymer mixture was 0.32 kg/h for each test, which corresponds to a fluorine mass flow of 0.23 kg/h (inlet). A TDL was used to measure HF concentrations at the exit of boiler (see Fig. 1, sampling location 2). The HF concentrations were converted to a fluorine mass flow rate exiting the boiler (see Supplemental Information - Conversion of HF boiler exit concentrations into fluorine mass flows). The fluorine recovery rate was then determined by the ratio of fluorine mass flow at the outlet divided by the fluorine mass flow rate at the inlet×100.

The results of these measurements provide an indication of fluorine recovery as HF. This is a reasonable assumption given the large amounts of hydrogen provided during the combustion process (sources of fuel included wood chips and natural gas). As shown in Fig. 3, for Setting-1 (860 °C), RUN2, the fluorine recovery was ~80%. The corresponding fluorine recovery rate for Setting-2 (1095 °C), RUN5 was ~70%. The calculated recoveries are based on the averaged values for HF profile measurements, see Fig. S5. Measurements conducted in the absence of fluoropolymer combustion (RUN1, RUN3, RUN4, and RUN6) indicate less than 0.01 kg/h of fluorine measured. This demonstrates the lack of background contamination or any significant fluorine carryover from the fluoropolymer combustion tests. Fluoride ion measurements at the stack were converted to HF concentrations and were below the maximum limit of 1 mg/m$_N^3$ according to the EU regulations (see Supplemental Information - HF stack emissions by IC and Table S8).

5. Discussion

Statistical analysis of the PFAS emissions measurements confirmed that, out of 40 long-chain PFAS compounds analyzed, PFOA was the only PFAS that was detected in the stack gas sample during the 1095 °C fluoropolymer combustion test – RUN5 (see Fig. 2). This is considered
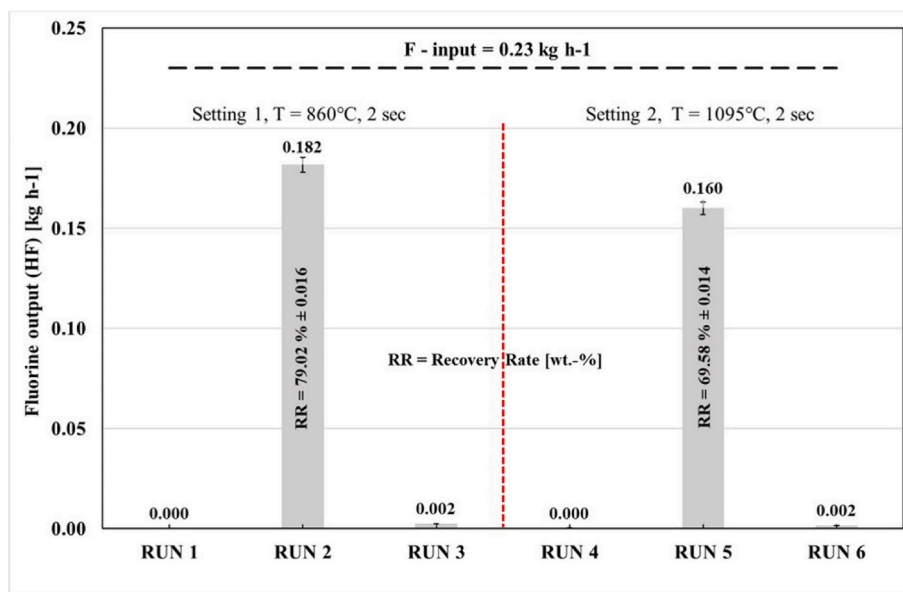

Fig. 3. Total fluorine output measured in-situ with TDL at the boiler exit. The HF stack emissions shown in the box insert are normalized to 11 vol% of O_2. Error bars for the fluorine recoveries are ±2% after consideration of possible errors in the TDL measurement.

external contamination as PFOA was not detected in 860 °C fluoropolymer combustion test - RUN2 (see Fig. 2) where potential PFOA formation from incomplete combustion is even more likely. Further support that the PFOA measurement in the stack gas was external contamination was the detection of PFOA in the stack test samples during a pre-dosing run at the lower temperature setting (RUN1) when the fluoropolymer was not fed (PFOA = 0.26 ng/m^3 or 0.70 μg/h). The wastewater and ash residue samples indicated that PFBS and PFOS, respectively, were detected above the LOQ in RUN2. These detections are also likely due to external contamination since PFBS and PFOS were also detected in pre- and post-dosing run samples (PFOS was detected in wastewater in RUNS 1 and 4 and PFBS were detected in ash residue in RUN1 and RUN3). However, we cannot rule out the combustion process as the source of the PFBS and PFOS given that the wood chips contain trace levels of sulfur (see Table S2).

These results are supported by data published in Taylor et al. (2014), where these authors investigated the release of PFOA emissions to the environment in a bench-scale combustion system. These tests involving the combustion of four different fluorotelomer-based polymer materials indicated PFOA was not formed during the combustion process at a detection limit of ≤54 ng/m^3 (dry and corrected to 7% O_2).

Gaseous PFAS emissions were measured at the PCC exit, the boiler exit, and at the stack. To evaluate possible questions about a "de novo synthesis" mechanism for PFAS like is known for PCDD and PCDF (Vehlow, 2005), the fluorine mass flow of PFAS is presented for each sampling location and RUN number (see Supplemental Information - Effect of Sampling Location on PFAS Emissions). The data in Fig. S6 show a lack of evidence for a "de novo synthesis" mechanism for PFAS.

Gas sampling of the exhaust gas was conducted in this study to evaluate the potential formation of C_1–C_3 PFAS (excluding TFA which was analyzed from the impinger train samples). For both RUN2 and RUN5, none of the targeted PFAS were detected at LOQs ranging from 5 μg/m^3 to 40 μg/m^3. Shields et al. (2023), in a pilot-scale study of AFFF combustion, observed an ~1000 increase in C_1–C_3 PFAS emission concentrations in sampling at ≤870 °C compared to sampling at ≥970 °C. Individual C_1–C_3 PFAS concentrations were as high as 8950 μg/m^3. Pilot-scale combustion systems are complex and reasons for obtaining different results are not always obvious. Potential reasons for the differences in these two studies may be related to temperature variations (or the lack thereof) upstream of the sampling points.

A recent critical review (Longendyke et al., 2022) indicated a lack of data on the closure of the fluorine mass balance as related to the thermal degradation products of PFAS and related waste streams. This work set out to determine if current operation conditions were sufficient to provide complete mineralization of the input fluorine. Ideally, the fluorine added to the fluoropolymer mixture should react with hydrogen from the incinerated biomass and natural gas, forming HF and CO_2. However, it is known that fluorine reacts readily with silica (SiO_2, silica oxide) and alumina (Al_2O_3, alumina oxide). Yamada et al. (2005) found that the use of HF as surrogate for complete PFAS mineralization might be complicated, as HF could react with the reactor tube walls, which contained silica. Yamada et al. observed that the amount of silicon tetrafluoride (SiF_4), measured in fluorotelomer-based (acrylic polymer) combustion tests, increased with temperature. It was concluded that SiF_4 was not formed by sample combustion, but by reaction of HF with fused silica reactor surfaces. As SiO_2 and Al_2O_3 are the constituents of BRENDA pilot plant refractory materials, it was likely that their reaction with fluorine was responsible for reduced fluorine recoveries of 70–80% measured experimentally with TDL. The high reactivity of fluorine with refractory materials, the results of this study, and the results of the prior fluoropolymer combustion study conducted at this facility (Aleksandrov et al., 2019) indicates that fluorine mass balance as a measure of fluoropolymer mineralization is not achievable at the pilot-scale.

Fluoropolymer Reduction Rate for Products of Incomplete Combustion (R2PIC) was determined to be greater than 99.99% for Setting 1–860 °C and Setting 2–1095 °C (c < LOQ = 0). For the case where c <

LOQ = ½ of the LOQ, R2PIC was >99.9 % for both Settings. There was no measurable effect of PCC temperature on fluoropolymer R2PIC. In related work, PFAS destruction efficiencies at the pilot-scale have been recently reported by Shields et al. (2023). In these studies where individual PFAS were fed into the system, the highest decomposition rates (>99.9999%) were achieved by direct injection in the flame (1963 °C and by 1180 °C at a residence time of ~3 s). High destruction rates were reached for PFOS, PFHpS, PFHxS, PFPeS and PFBS, which are comparable with the findings here. All other decomposition rates were in the range 94.03% and 99.9996% for various temperatures and residence time. The R2PIC metric could be calculated in future studies of PFAS thermal destruction if the fluorine content of all feed streams was known. The destruction rate for single PFAS or -in our case-the R2PIC number not only depends on temperature and residence time but additionally on turbulence and geometry of the furnace. Results of different waste streams in different incineration plants may not be directly compared and must be validated in each single plant under their specific operational conditions.

6. Conclusions

The goal of this study was to provide data to support mineralization of fluoropolymer waste and insignificant generation of PFAS as products of incomplete destruction during incineration of fluoropolymer applications at their end-of-life. Destruction efficiency is not an acceptable metric to indicate mineralization and, therefore, we need to look for and measure products of incomplete destruction. A mixed sample of fluoropolymers representing 80% of commercial fluoropolymers was combusted at conditions representative of municipal (860 °C for 2 s) and industrial (1095 °C for 2 s) waste incinerators operating in EU. State-of-the-art emission sampling and analytical methods (UPLC-MS/MS, GC-MS) were used for identifying and quantifying PFAS (35 long chain PFAS, TFA, 5 C_1–C_3 PFAS) whose standards were available. Statistical analysis of the results confirmed non-detect to negligible levels of PFAS evidencing mineralization of fluoropolymers. Inorganic fluorides were detected as hydrogen fluoride (between 70 and 80 wt%). There was no discernible effect of temperature on the mineralization of fluoropolymer and testing at 860 °C versus 1095 °C did not show evidence of an increase in PFAS emissions.

CRediT authorship contribution statement

Hans-Joachim Gehrmann: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Philip Taylor:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis. **Krasimir Aleksandrov:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Philipp Bergdolt:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Andrei Bologa:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **David Blye:** Writing – review & editing, Writing – original draft, Validation. **Priyank Dalal:** Writing – review & editing, Writing – original draft, Investigation. **Priyanga Gunasekar:** Writing – review & editing, Writing – original draft, Resources, Project administration. **Sven Herremanns:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Deepak Kapoor:** Writing – review & editing, Writing – original draft, Funding acquisition,

Conceptualization. **Meg Michell:** Writing – review & editing, Writing – original draft, Validation. **Vanessa Nuredin:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Formal analysis, Data curation. **Michael Schlipf:** Resources. **Dieter Stapf:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Philip H. Taylor reports financial support was provided by Gujarat Fluorochemicals GmbH. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2024.143403.

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