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Graphical Abstract

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Source: *SAE Transactions*, 1999, Vol. 108, Section 5: JOURNAL OF MATERIALS & MANUFACTURING (1999), pp. 442-450

Published by: SAE International

Stable URL: <https://www.jstor.org/stable/44650638>

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THV Fluorothermoplastics in Automotive Fuel Management Systems

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ABSTRACT

THV fluorothermoplastics offer a unique combination of properties, which makes them ideally suited for automotive fuel systems. These properties include low temperature processing, low flex modulus, ease of bonding and excellent permeation resistance to various fuels. Examples of various applications of these fluoropolymers are highlighted and shown in fuel management constructions in combination with both elastomers as well as plastics.

INTRODUCTION

Evaporative emission legislation by the California Air Resource Board (CARB) and by the Environmental Protection Agency (EPA) as well as new proposed emission standards in Europe, has resulted in the increasing use of barrier materials in the fuel systems of vehicles on a global basis. Primary applications have been for fuel fill and vent hose (or tubes), vapor return lines and for high-pressure fuel lines. Also, more recently, the design of vehicles with "On-board Refueling Vapor Recovery" (ORVR) systems has extended the need for barrier materials into these fuel vapor handling systems. Fluoroelastomers have been widely accepted for use in fuel system applications due to their excellent fuel resistance and good fuel permeation barrier properties. However, the recent advent of Dyneon™ THV Fluorothermoplastics, a flexible fluorothermoplastic with very low permeation characteristics, has led to the rapid use of fluorothermoplastics in fuel barrier applications. Their unique combination of fuel resistance, fuel permeation barrier properties, flexibility and ability to form covalent bonds with both elastomers and plastics has often made them the materials of choices where very low fuel evaporative emissions are needed.

This paper will highlight the key properties of Dyneon THV Fluorothermoplastics (hereafter referred to as "THV") and contrast these to other, more traditional, fluorothermoplastics such as ETFE (ethylene-tetrafluoroethylene copolymer), FEP (fluorinated ethylene-propylene)

and PFA (perfluoro-alkoxy polymer). Examples of existing and potential applications for the THV materials will also be covered.

THV PROPERTIES

THV fluorothermoplastics are terpolymers of tetrafluoroethylene (TFE), hexafluoropropylene (HFP), and vinylidene fluoride (VDF). The THV series has been developed with special attention to melt temperature and physical properties as the properties of the polymer can be adjusted by varying the level of incorporation of the three monomers in the terpolymer. Melt temperature, composition, and melt flow index information for selected Dyneon fluorothermoplastics are given in Table 1. Figure 1 contrasts the typical melt temperatures for all THV grades along with those of other Dyneon melt processable fluorothermoplastics. It can be seen that the THV materials provide a range of melting points significantly lower than for other fluorothermoplastics. It will be seen later that this also provides added benefits in flexibility and processing properties.

Of the THV fluorothermoplastics shown, THV 500 has found the most predominant use in automotive fuel applications. The other commercial THV materials and experimental grades of THV are shown for comparison and contrast.

THV PROCESSING – Combining typical processing temperature data with thermo-gravimetric analysis (TGA) data defining the onset for decomposition (under nitrogen @ 10°C/min.), it is possible to develop a rough approximation of the processing window available for a material. An extension of this approach is to deduct 50°C from the temperature for the onset of decomposition and use the result as the upper limit of the processing window. Using these concepts, processing windows for THV and other fluorothermoplastics are shown in Figure 2. As can be seen from the Figure, THV fluorothermoplastics have the widest processing window among all traditional fluorothermoplastics considered here.

Table 1. Dyneon™ Fluorothermoplastic Characteristics

Resin	Composition	Melt Point (°C)	MFI
THV 220	TFE/HFP/VDF	124	20 (265°C/5kg)
THV 310X**	TFE/HFP/VDF	140	10 (265°C/5kg)
THV 410	TFE/HFP/VDF	155	10 (265°C/5kg)
THV 500	TFE/HFP/VDF	165	10 (265°C/5kg)
THV 610X**	TFE/HFP/VDF	185	10 (265°C/5kg)
ETFE 6235	Ethylene/TFE	260	10 (372°C/5kg)
FEP 6307X**	TFE/HFP	260	7 (372°C/5kg)
PFA 6515	TFE/PPVE*	310	15 (372°C/5kg)

* Perfluoropropylvinylether.

** Experimental resins currently being commercialized by Dyneon.

While the above approach represents a reasonable approximation, it is important to remember that the temperature for the onset of decomposition determined by TGA does not reflect a time dimension. Indeed, materials stable to 400°C to 450°C during thermo-gravimetric analysis will, under processing conditions, degrade at lower temperatures when left in processing equipment beyond a certain residence time. Therefore, the practical processing window may be narrower than shown in Figure 2.

Generally, fluorothermoplastics processors manage the corrosion risks associated with the processing of high melting fluorothermoplastics by using corrosion protected equipment. On the other hand, THV resins have a sufficiently wide processing window so as to not require the use of corrosion-protected equipment, thereby eliminating the need for large capital expenditures for such specialized equipment. For example, THV 500, and even THV 610X, can be processed with melt temperatures in the 250 to 260° C range, while ETFE would typically have to be processed at temperatures of 300° C or higher. THV's lower melt temperature also offers advantages in co-extrusion with other plastics, which would typically need a lower melt processing temperature. This will be further highlighted in the applications section below.

MECHANICAL PROPERTIES – The processing advantages of THV resins are complimented by a full range of unique physical properties. THV Fluoropolymers are in general by far the most flexible within the general class of melt processable fluoropolymers as shown in Figure 3. At the same time, these materials also have very good tensile and elongation properties (Figure 4). Furthermore the embrittlement point for all THV grades is in the vicinity of -75°C to -80°C (ASTM D746). These properties make the THV Fluoropolymers particularly attractive in automotive applications requiring cold impact resistance along with good mechanical properties and flexibility. The

excellent fuel resistance of THV 500, and its electrostatic dissipative (ESD) version, to various fuels such as TF-2, Fuel C and sour gas has been previously reported (1).

PRECIPITATES AND EXTRACTABLES – Fuel in contact with elastomeric or plastic surfaces can sometimes lead to the extraction of plasticisers and/or oligomers present in the polymer. These would normally not cause a problem unless this significantly changes the properties of the material or if the extracted material subsequently precipitates, leading to possible clogging in the fuel system. As mentioned before, THV 500 does not show any substantial changes upon extended exposure to various fuels. In an attempt to generate precipitates, THV 500 and its ESD version (THV 510 ESD), along with an automotive fuel line grade of polyamide-12, were soaked in CM15 fuel at 40° C for 1 week and subsequently cooled to 0° C. The THV 500 and THV 510 ESD both showed no precipitates. However, white precipitate crystals were seen, and isolated, for the polyamide-12. This could be a strong reason to put a fluoropolymer barrier as the inside layer of a multilayer fuel-line.

PERMEATION – The unique advantages of THV are not limited to mechanical properties or ease of processing. In fact, THV 500 is one of the best barrier materials available which is the reason it has found wide usage in fuel management applications; especially in low permeation fuel hoses (1). Permeation is one of the key properties used for selecting a material for use in a low permeation hose or tube.

Figure 5 shows a plot of permeation in g/m²-day for THV 500 that was obtained by using a Thwing-Albert cup according to a modified ASTM-D814 method. The plot is clearly non-linear with thickness, but when the permeation is plotted against the *inverse* of thickness (Figure 6) the data now falls on a straight line. The result is a simple

and easy to use linear relationship that obeys Fick's well-known diffusion law (2). In fact, Fick's law has been found to apply to all THV grades and can be used to predict the steady-state permeation (F_{ss}) performance at any given film thickness (L):

$$F_{ss} = P^* / L$$

where P^* is a steady-state permeation constant at a given temperature and for a given permeant. Table 2 below gives P^* for three different THV grades determined for CM15 fuel. CM15 fuel consists of a 50:50 blend of iso-octane and toluene, diluted with 15% methanol and is a commonly used test fuel. The value for THV 500 at 40°C corresponds very well with the value of 3.0 obtained by Nulman *et. al.* (3) using a different technique. This provides an added level of confidence in these difficult to determine values.

Table 2. Steady-state permeation constants with CM15 fuel.

	P^* (g-mm/m ² -day)	
	40°C	60°C
THV 310X	5.0	38
THV 500	3.1	20
THV 610X	2.1	9

The practical use of some P^* values can easily be shown. For instance, if a low-permeation hose is made with a THV 500 layer of 0.01 inches thick, the expected permeation would roughly calculate to 12 g/m²-day at 40°C with CM15 (obtained by converting to a 0.25 mm thickness and dividing this into 3.1). This method has been found to apply relatively well when compared to permeation test results on hose using a canister method. On the other hand, limited permeation results obtained from the SAE J1737 (recirculation method) seem to suggest that numbers from J1737 are usually less than half of that calculated from Equation 1. Factors such as barrier properties of the other layers in the construction, test fuel pressure, processing conditions and the permeation test method may be cause for these differences, and work in this area is continuously evolving.

Table 2 shows the permeation constants for THV 500, and experimental products, THV 610X and THV 310X; the latter two being recent additions to the THV series. Due to its optimized composition, THV 610X exhibits lower permeation characteristics as compared to those of THV 310X and 500. This new material also melts at a higher temperature (185°C) than that for THV 500, thus offering a very good balance between permeation performance, high temperature performance, and flexibility. Flexibility, by comparison is still much better than for most other fluorothermoplastics, including ETFE, FEP, and

PFA (Figure 3). As will be seen later, THV 610X is a good example of the precision with which new THV grades can be designed to meet the technical requirements of specific applications.

BONDABILITY – The chemical composition of THV makes it possible to bond to dissimilar materials such as hydrocarbon-based thermoplastics and elastomers. Contrary to most other bonding methods used for fluoropolymer/hydrocarbon polymer systems, the bond that is developed between THV and hydrocarbon-based substrates is covalent in nature and is, as a result, extremely durable. Therefore, the risks of de-lamination in THV-containing multi-layer co-constructions are considerably lower than with most other systems. Examples of the use of this property of THV in automotive fuel systems will be given in the applications section below.

FUEL MANAGEMENT APPLICATIONS

THV/ELASTOMER CO-CONSTRUCTIONS – Among elastomer systems, Dyneon currently offers commercially proven bonding solutions for THV/fluoroelastomer, THV/poly-epichlorohydrine rubber (ECO), and THV nitrile rubber (NBR) systems. The latter two types of co-constructions, along with a brief schematic of the extrusion process used in their manufacturing, are illustrated in Figures 7 and 8. It is noteworthy that the bonding technologies described here do not involve the use of a tie layer. Both types of co-constructions have found use in large automotive applications such as fill, vent, and vapor line in fuel handling systems. In these particular cases, THV 500's ease of bonding, flexibility, formability, sealability, cold impact resistance, and low permeation characteristics make it a perfect fit in meeting the technical requirements of these applications.

For instance, automotive low permeation elastomeric hoses, including THV/elastomer hoses, are given their final form or shape by placing the hose on a mandrel of a pre-determined shape and subsequently curing the hose in an autoclave. At the end of the cure or forming cycle, the properties of the elastomeric compound are fully developed and the hose assumes its final shape. If the formability of the hose construction is poor, severe bulges can appear at the inner radii of bends during the cure or forming process. Severe bulges in an elastomer/plastic co-construction can ultimately result in the cracking of the barrier material and the ensuing increased permeation levels. But, bulges can be avoided if the bond between the various components of the co-construction is strong and, more importantly, if the elastomeric compound is close in flex properties to that of the barrier material. THV 500 is unique amongst fluorothermoplastics in that it is the only material that combines the good permeation performance and ease of bonding with the flexibility (<35 kpsi) and low modulus of elasticity needed to successfully form a hybrid plastic/elastomer co-construction.

Currently, many North American automobile manufacturers (OEMs) specify that the inner layer of fuel hoses be electrostatic dissipative (ESD). Fortunately, this requirement can be met easily and cost effectively with THV since it can be compounded using standard compounding techniques typical of hydrocarbon-based thermoplastics. Dyneon has been offering its own THV ESD formulation on a commercial basis for the last four years.

ALL-PLASTIC CO-CONSTRUCTIONS – Most traditional fluorothermoplastics melt at high temperatures so that many of these materials require the use of specialized corrosion-protected processing equipment and are generally not suitable for use in more cost-effective multi-layer constructions. Indeed, the wide differences in melt temperatures of ETFE, FEP, and PFA in comparison to those of hydrocarbon-based thermoplastics prevent the use of conventional multi-layer extrusion techniques. Moreover, technologies necessary to adhere these high temperature fluoropolymers to hydrocarbons are very difficult to achieve or cumbersome to apply.

All plastic co-constructions for automotive fuel and vapor hose and tubing are ideally suited for THV. Many of the same THV features that provide benefits in multi-layer rubber hose constructions also apply to multi-layer plastic constructions.

In past studies (43), it was shown that the rheological properties of THV, particularly the 500 grade, are very similar to both PA-12 and polyethylene, whether as linear low density (LLDPE) or high-density (HDPE). A plot of the viscosity as a function of shear rate for THV 500 and polyamide-12 at 220°C is shown in Figure 9. A similar plot for THV and a LLDPE (MFI 0.5) at 240°C is shown in Figure 10. As can be seen, there is a very good match between the flow properties of THV and those of PA-12 and LLDPE. Thus, THV 500 can be readily co-processed with these and other hydrocarbon-based thermoplastics.

North American automotive companies also mandate that the co-construction's inner layer be electrostatic dissipative. The electrostatic dissipative THV ESD does not require any changes in manufacturing process nor does it require that the barrier layer be buried in a 4 or 5 layer co-construction, as is the case for other types of all plastic co-constructions. In addition, as previously mentioned, an inner layer of THV ESD in contact with fuel would not raise concerns with the possibility of extractables.

Stringent North American automotive specifications often cite a cold impact test at -40°C. THV should have no problem passing this requirement since the embrittlement temperature of THV resins is below -75°C. This is contrary to what is observed with certain other types of barrier materials that become brittle at temperatures above -40°C and therefore need to be constrained by an additional layer of hydrocarbon-based thermoplastic.

While this additional layer is successful in meeting the cold impact specification, it can lead to other types of problems, such as the extractables issue mentioned earlier, since it brings a hydrocarbon-based material in contact with the fuel.

CONCLUSION

THV's represent a unique blend of properties which has made the THV 500 often the material of choice in fuel management applications such as fuel fill and vent, and fuel vapor lines. The various grades and the addition of new experimental grades of THV have further opened the application range of the THV materials in automotive applications where low permeation, fuel resistance, bonding and flexibility are desired.

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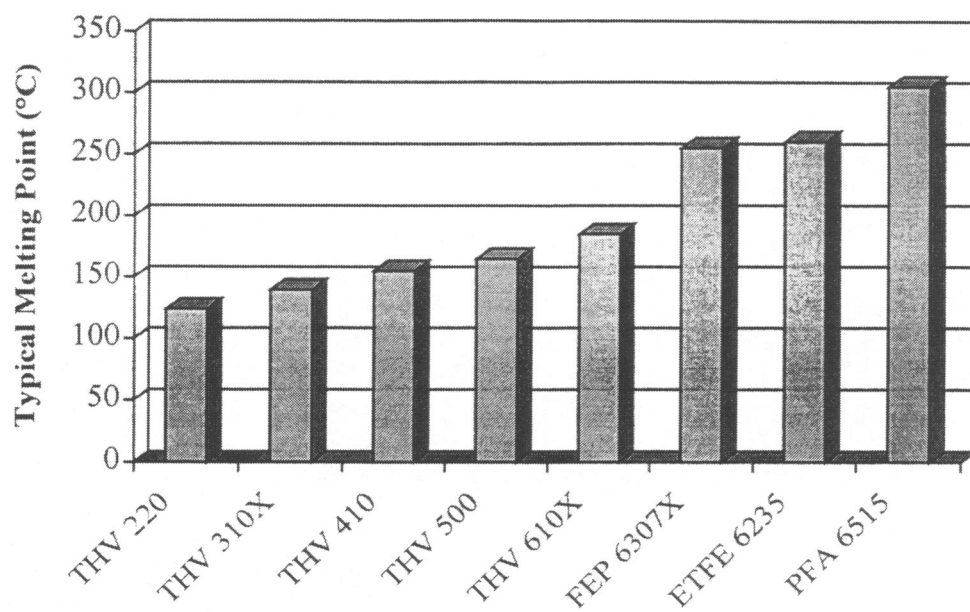


Figure 1. Thermal properties

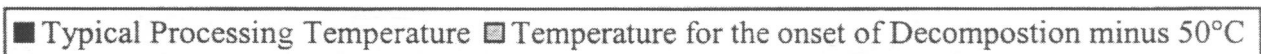
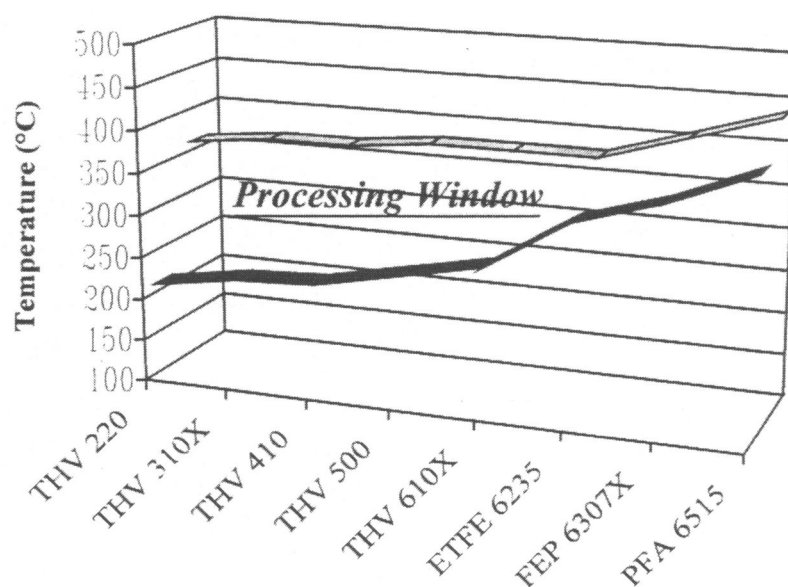


Figure 2. Fluorothermoplastics Processing Window

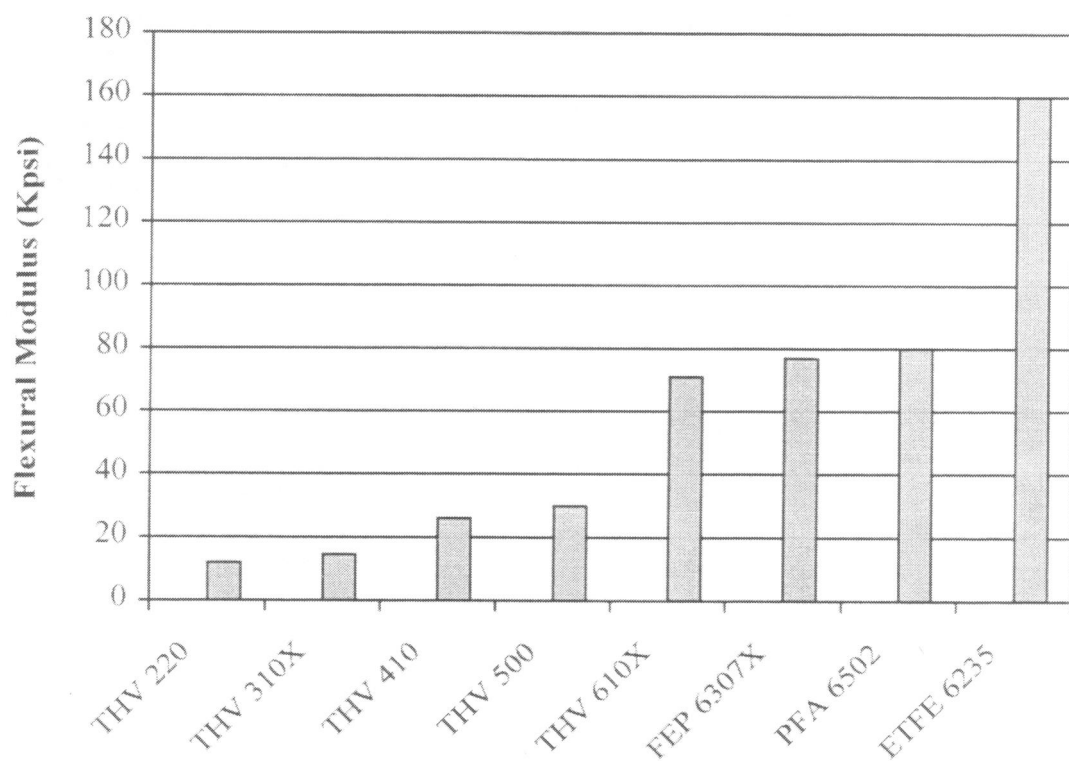


Figure 3. Flexural Modulus (ASTM D 790)

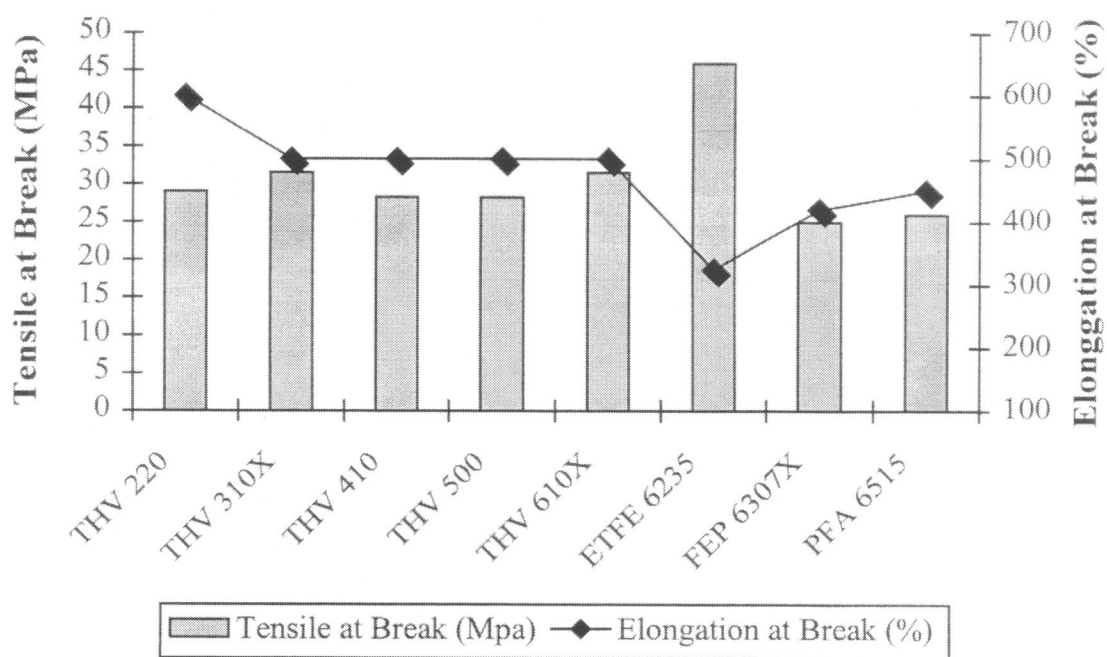


Figure 4. Typical Mechanical Properties

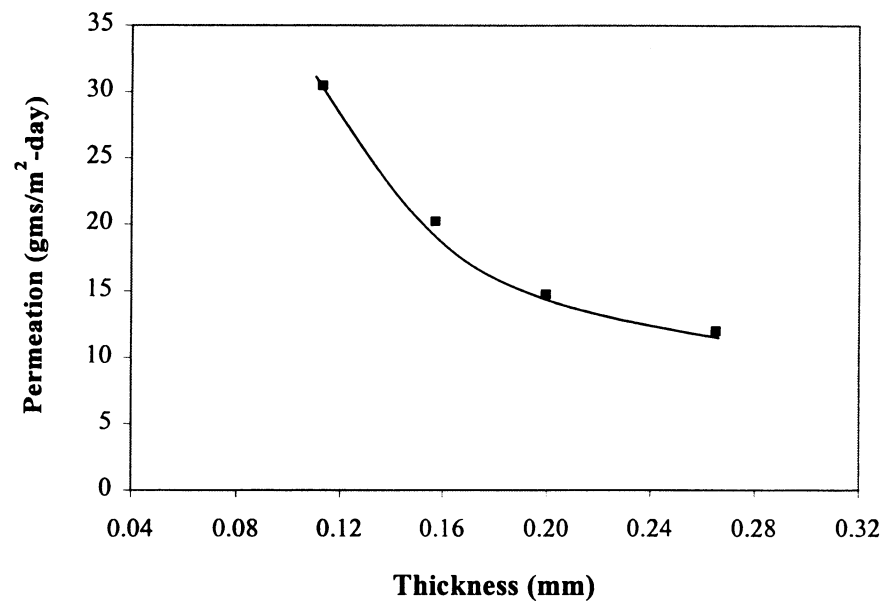


Figure 5. Permeation vs. Thickness – THV-500
(CM15 @ 40° C)

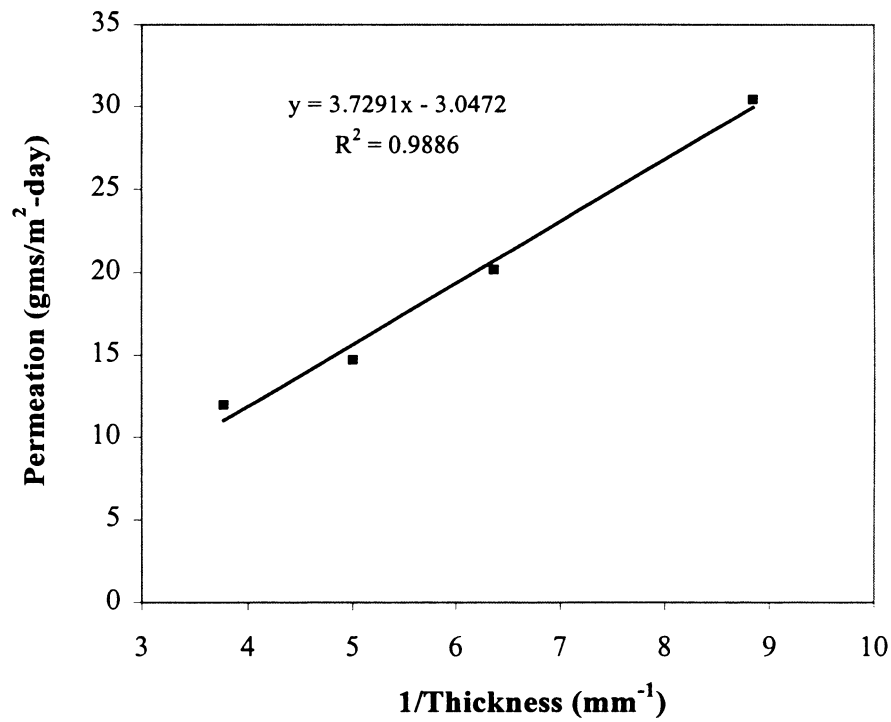


Figure 6. Permeation vs. Inverse of Thickness – THV-500
(CM15 @ 40° C)

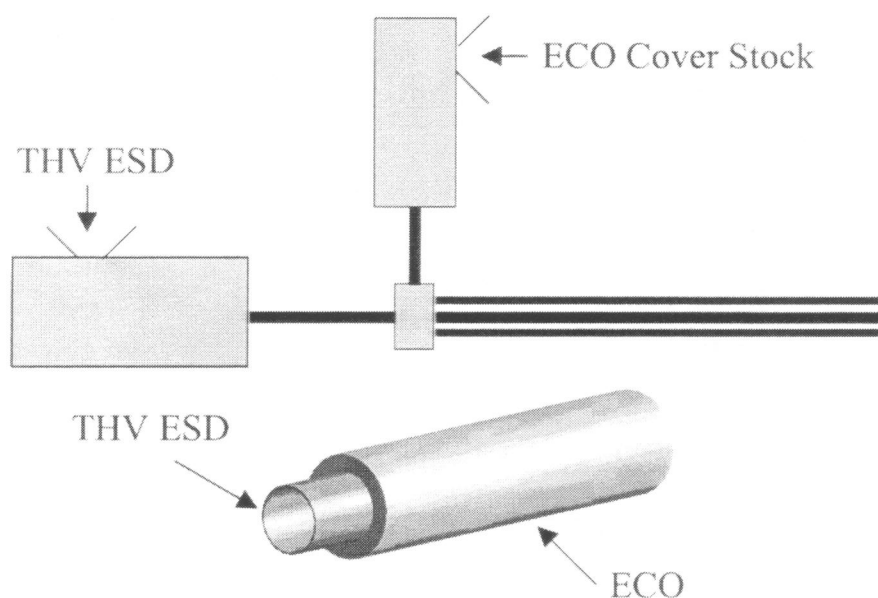


Figure 7. THV/ECO Co-construction

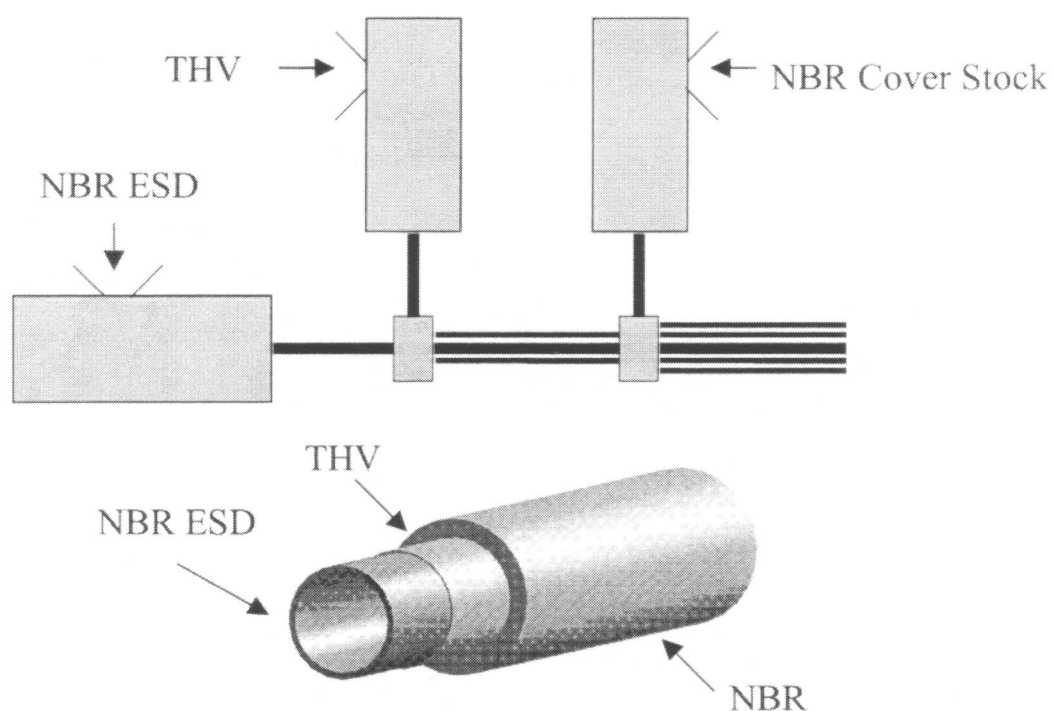


Figure 8. NBR/THV/NBR Co-construction

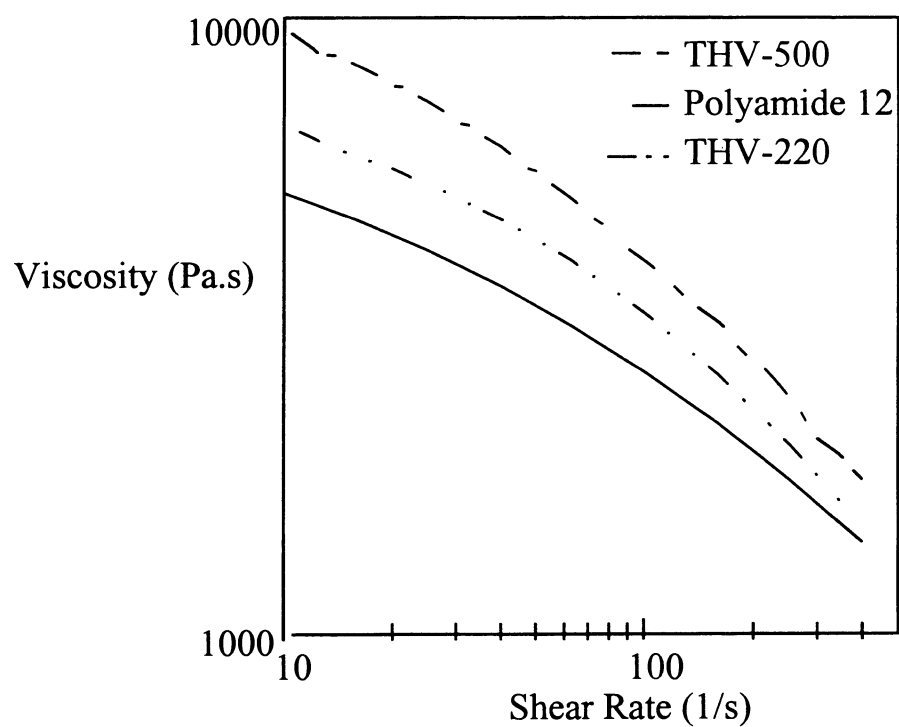


Figure 9. Viscosity vs. Shear Rate at 220° C

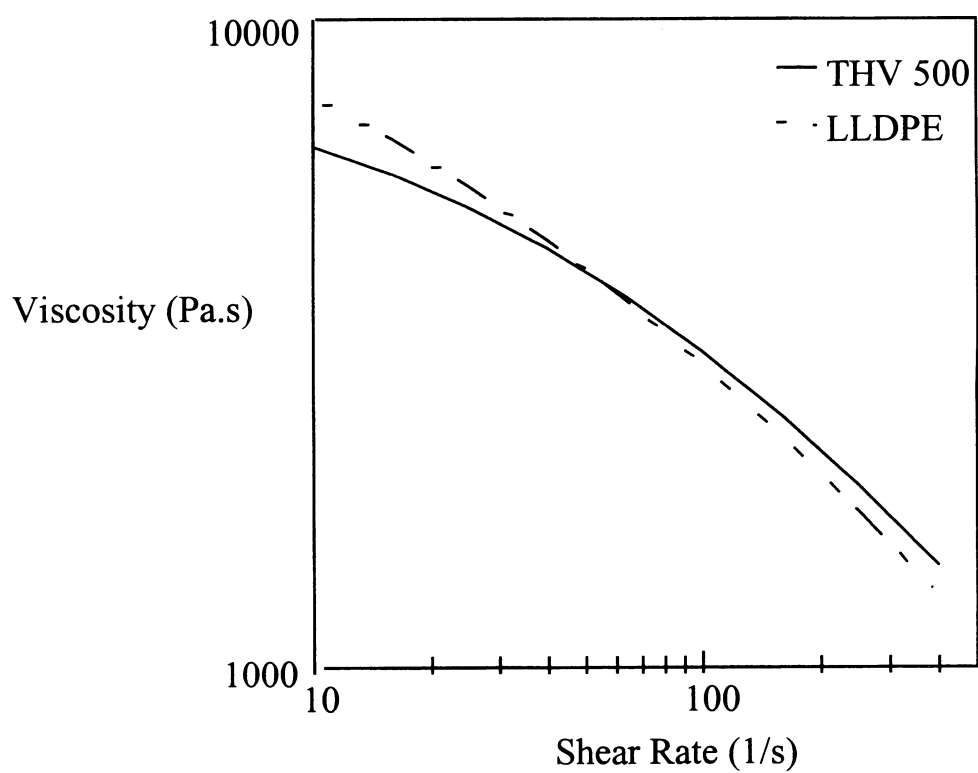
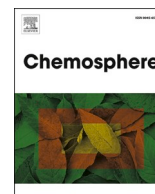


Figure 10. Viscosity vs. Shear Rate at 240° C



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

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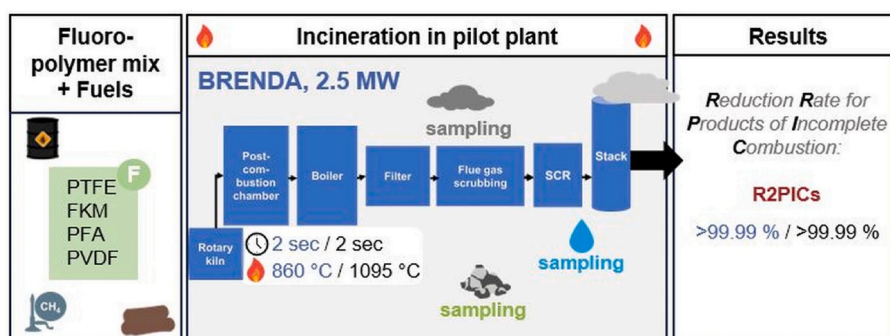
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HIGHLIGHTS

- 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/m³) slightly above the LOQ (0.09 ng/m³).
- External contamination is the likely source of the PFOA detection.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling Editor: Y Yeomin Yoon

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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<https://doi.org/10.1016/j.chemosphere.2024.143403>

Received 14 June 2024; Received in revised form 20 September 2024; Accepted 23 September 2024

Available online 24 September 2024

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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/m³_N (dry, corrected to 7% O₂) 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 CF₄, C₂F₆, and C₃F₈ were reported for fuel-rich (sub-stoichiometric) thermal degradation of PTFE at 850 °C. C₂F₄, 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 µg/m³ 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 CF₂ radicals as reaction intermediates was identified in this review and C₁ and C₂ fluorocarbons (e.g. tetrafluoromethane (CF₄), hexafluoroethane (C₂F₆)) were proposed as stable intermediates at elevated temperatures. The C₂F₄ 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 CF₂ radical (Tsang et al., 1998). CF₄ and C₂F₆ 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 $22\text{ m}^3/\text{h}$ to $35\text{ m}^3/\text{h}$ 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		

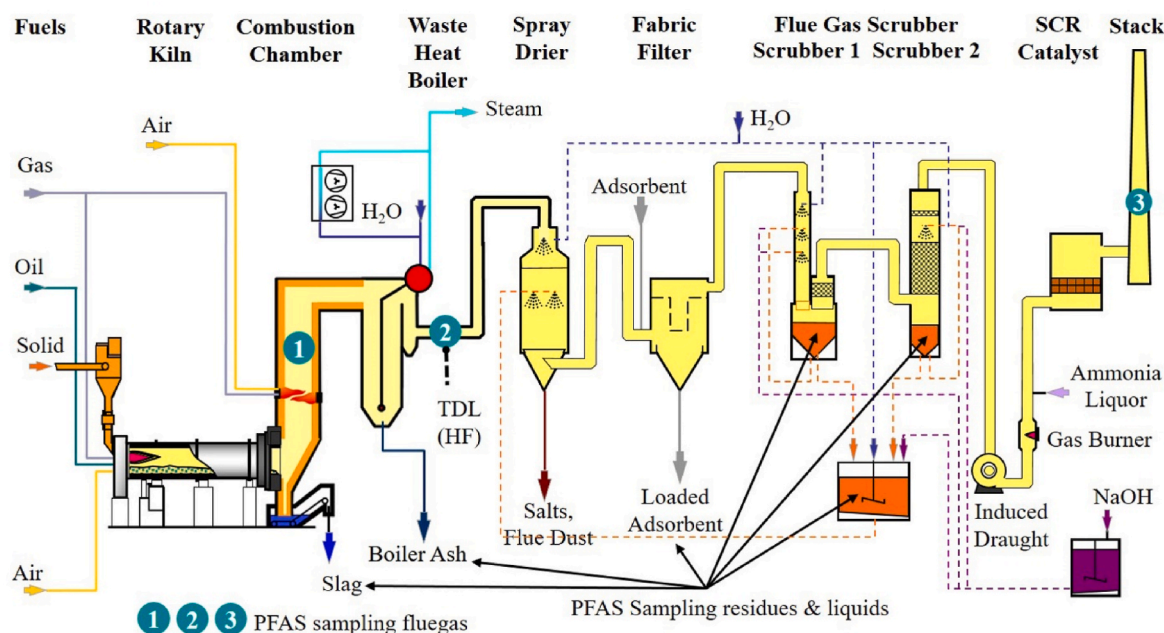


Fig. 1. Layout of BRENDA incineration pilot-plant with PFAS sampling locations.

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 C₁–C₃ PFAS (see Table S5). The C₁–C₃ PFAS measured included CF₄ and C₂F₆ 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 m³. Sampling for the C₁–C₃ 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 C₁–C₃ 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 ₂ F ₄] _n	100.02	76	63	153
PTFE tape	[C ₂ F ₄] _n	100.02	76	7	17
PVDF	[C ₂ H ₂ F ₂] _n	64.04	59	18	34
PFA	[C ₂ F ₄] _n	100.02	76	6	15
FKM rubber	[CF ₂ CH ₂] _m [CF ₂ CH ₂ CF 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	×	×	×	×	
XAD-2			×		
Stack flue gas		×			
Tedlar® bag					×
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/m³) were detected throughout the pre- and post-dosing runs and a low level of AOF (1 µg/m³) 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).

$$R2PIC = 1 - \frac{\sum F_{PFAS,out}}{\sum F_{PFAS,in}} \quad (1)$$

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.

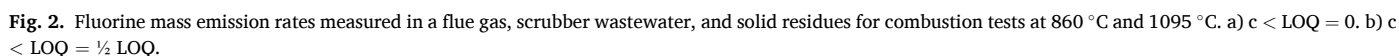
Based on the molar fraction of fluorine for every PFAS measured in the flue gas, liquid and solid residues, a fluorine mass emission flow is calculated and normalized to the input fluorine mass flow, see Eqn. (2). The R2PIC is a value to characterize the effectiveness of combustion as a function of operational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

4. Results

4.1. PFAS emissions

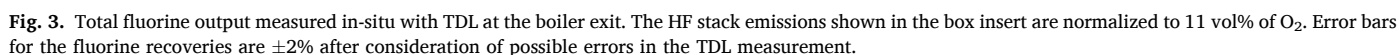
Statistical analysis of the PFAS emissions is presented in Fig. 2. Fig. 2a presents data where non-detects were assigned a concentration equal to zero and Fig. 2b with non-detects assigned a concentration of 50% of the LOQ. Exhaust gas, scrubber water and solid residue measurements are shown from the 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/m³, 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/m³ (0.46 µg/h) with a LOQ of 0.028 ng/m³. 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



The results of these measurements provide an indication of fluorine

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



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 ($\text{PFOA} = 0.26 \text{ ng/m}^3$ or $0.70 \text{ } \mu\text{g/h}$). 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 $\leq 54 \text{ ng/m}^3$ (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 $\text{C}_1\text{--C}_3$ 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 $5 \text{ } \mu\text{g/m}^3$ to $40 \text{ } \mu\text{g/m}^3$. Shields et al. (2023), in a pilot-scale study of AFFF combustion, observed an ~ 1000 increase in $\text{C}_1\text{--C}_3$ PFAS emission concentrations in sampling at $\leq 870 \text{ } ^\circ\text{C}$ compared to sampling at $\geq 970 \text{ } ^\circ\text{C}$. Individual $\text{C}_1\text{--C}_3$ PFAS concentrations were as high as $8950 \text{ } \mu\text{g/m}^3$. 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 ($c < \text{LOQ} = 0$). For the case where $c <$

$\text{LOQ} = \frac{1}{2}$ 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 ($1963 \text{ } ^\circ\text{C}$ and by $1180 \text{ } ^\circ\text{C}$ at a residence time of $\sim 3 \text{ s}$). 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 ($860 \text{ } ^\circ\text{C}$ for 2 s) and industrial ($1095 \text{ } ^\circ\text{C}$ 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 $\text{C}_1\text{--C}_3$ 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 $860 \text{ } ^\circ\text{C}$ versus $1095 \text{ } ^\circ\text{C}$ did not show evidence of an increase in PFAS emissions.

CRedit authorship contribution statement

Hans-Joachim Gehrman: 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 Bologna:** 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

Federal Environment Agency (Umweltbundesamt, UBA), Germany's central environmental authority that evaluates adverse effects on people and environment was involved in this project to identify the standard operating conditions of municipal and hazardous waste-to-energy incineration plants. This project was financially supported by Gujarat Fluorochemicals Limited.

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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