# Prospects of Complete Mineralization of Per- and Polyfluoroalkyl Substances (PFAS) by Thermal Destruction Methods

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# Keywords:

Per- and polyfluoroalkyl substances, PFAS, Thermal destruction, Active materials, Full mineralization

#### Abstract

Per- and polyfluoroalkyl substances (PFAS) are a class of man-made chemicals found in various consumer goods due to their unique properties. Failing abatement techniques and improper waste management result in the release of these chemicals into the environment (diluted in soil, water and air) causing detrimental effects to human health. Therefore, a variety of novel technologies is currently under development to destroy PFAS. Thermal destruction using active materials has the potential to achieve full mineralization of the fluorine atoms. Nevertheless, two major challenges need to be overcome to remove doubts about the destruction efficiency and enable further optimization: 1) which combination of process conditions/dedicated destruction techniques/active materials can lead to complete mineralization; and 2) incomplete mass balance closure by currently employed analysis techniques.

Due to the complexity of matrices and the myriad of intermediate and incomplete PFAS degradation compounds, a single 'fit-for-all' analytical standard/method likely does not exist. Therefore, a holistic combination of targeted, semi-targeted and non-targeted analyses is required to obtain maximally comprehensive insight into the PFAS degradation compounds. The volatile degradation products can be analyzed via comprehensive two-dimensional gas chromatography (GCxGC) coupled with high-resolution mass spectrometry (HRMS). Non-volatiles can be trapped and analyzed via ultraperformance liquid chromatography (UPLC) coupled with high-resolution mass spectrometry (HRMS) and triple quadrupole mass spectrometry (QqQ), and a myriad of elemental analysis techniques. In addition, also the remaining solid residue needs to be extracted and analyzed via specific methods to quantify the PFAS content in the solid residues.

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## 1. Introduction

Per- and polyfluoroalkyl substances (PFAS) form a large class of thousands of man-made chemicals, with the most important ones being PFOS (perfluorooctanesulfonic acid) and PFOA (perfluorooctanoic acid) [1-3]. These compounds are characterized by stable carbon-fluorine bonds, which are the strongest C-X bonds, with an average dissociation energy of 485 kJ/mol [4]. Due to their unique desirable properties such as their chemical stability, low surface tension and hydrophobicity, PFAS have been manufactured and used in a variety of industries for more than 80 years. They are found in diverse consumer goods, including food packaging, non-stick stain repellent and waterproof products, and are extensively used for industrial applications and firefighting [5]. However, very limited information is available regarding which specific PFAS are used in which applications and at what levels in the European Union [3].

Multiple pathways can lead to PFAS contamination in the environment and human exposure, as depicted in **Figure 1**. Environmental contamination pathways arise from inadequate abatement techniques during production processes and the improper management of waste streams. Similar to other substances that raise environmental concern, the diet is the main pathway for human exposure to PFAS [2]. Additional sources include drinking water and direct contact with PFAS-containing products.



Figure 1. Typical PFAS pathways causing environmental contamination and human exposure. PFAS routes for environmental contamination, or human exposure are represented by red arrows.

As PFAS are persistent in the environment and human body, safe and ultimate disposal is necessary, but highly challenging. In Europe, PFAS have been detected in air, soil, plants, and biota and are meanwhile ubiquitous in the aquatic environment and organisms [6]. In particular, areas around industrial production, manufacturing and application sites have been contaminated with PFAS. According to a report by the Nordic Council of Ministers, it is estimated that more than 100,000 sites in the European Union emit PFAS into the environment [7]. This has led to contaminated surface, ground and drinking water around factories in Belgium, Italy, and the Netherlands, and around airports and military bases in Germany, Sweden and the United Kingdom [4]. The Directive (EU) 2020/2184 sets the thresholds for PFAS contamination in drinking water in the European Union. Currently, the limits for total PFAS and the sum of the 20 PFAS of most concern are set at 0.50  $\mu$ g·L<sup>-1</sup> and 0.10  $\mu$ g·L<sup>-1</sup>, respectively [8]. It is expected that these limits will be lowered once more in the near future. Moreover,

it has been reported that nowadays almost all people have PFAS in their body and 3% of the American population is even exposed to PFAS concentrations above suggested safe threshold values, primarily because of contaminated drinking water [7]. Urgent actions are required as long-term exposure to PFAS would result in human health issues, such as liver damage, thyroid disease, fertility issues and cancer [9].

Selecting the appropriate techniques for ultimate disposal of PFAS is further complicated by their volatility, water solubility, environmental mobility, and persistency [10]. Moreover, the diversity of chemicals within the PFAS class imposes enormous challenges to the detection, characterization and quantification of those molecules via current analytical methodologies [11]. This problem is aggravated by the continuous lack of transparency on the part of industry concerning the types and amounts of PFAS produced and their specific applications [12]. As society accumulates efforts to better regulate the use of PFAS and to minimize its health and environmental impact, two major challenges remain, as depicted in **Figure 2**. Firstly, it is essential to develop cost-efficient methods for the complete destruction and mineralization of PFAS, *i.e.*, complete conversion of organic fluorine-containing molecules into inorganic mineral forms, like HF, CaF<sub>2</sub>, SiF<sub>5</sub><sup>-</sup>, etc. Achieving full mineralization is crucial to prevent the release of toxic PFAS and their persistent decomposition products into the environment, ensuring a secure approach to their management. Secondly, it is necessary to focus on the development of dedicated analytical methods that enable the closure of the fluorine mass balance during the PFAS destruction process and, therefore, allow the comprehensive assessment of PFAS destruction and mineralization increalization increalization increalization increalization increalization fluorine mass balance during the PFAS destruction process and, therefore, allow the comprehensive assessment of PFAS destruction and mineralization increalization increalization increalization increalization increalization increalization increases and their persistent decomposition products into the environment, ensuring a secure approach to their management. Secondly, it is necessary to focus on the development of dedicated analytical methods that enable the closure of the fluorine mass balance during the PFAS destruction proces



Figure 2. The desired way forward with complete degradation of PFAS and the quantification of all the formed destruction products.

#### 2. Technology watch of PFAS destruction techniques

This section gives a brief overview of various thermal and non-thermal methods suitable for destruction of PFAS. To remove concentrated streams of PFAS, thermal operations appear as the mainstream strategy in industry. Waste thermal treatment is favored in land-scarce areas due to its capacity to greatly reduce the waste volume and to generate electricity as valuable by-product [14]. The thermal treatments can be classified based on their oxygen consumption levels. Incineration occurs with the introduction of excess of oxygen in a furnace at temperatures typically above 850°C [15]. For gasification or lean combustion, the waste is in excess compared to oxygen and temperatures above 650°C are used. In the case of pyrolysis, the destruction of chemical waste occurs in the absence of oxygen, starting at temperatures in the range of 500-850°C depending on the waste material [16]. Incineration is currently used for mineralization of PFAS and other harmful chemicals. The type of incinerator depends on the phase of the waste stream. For liquid phases, sewage sludge incineration can be used with either multiple flame or fluidized bed furnaces. In the case of solid waste, moving grate, cement kilns, or liquid injection incinerators are commonly utilized [17]. New scientific insights into emission loads and resulting emission regulations have put strain on industrial incineration, driving the reappearance of pyrolysis and gasification technologies [16,18,19]. Recent studies have demonstrated a significant removal efficiency of 96.9% for PFAS during the pyrolysis of complex matrices, such as sewage sludge and food waste reject [19]. The main advantages of the gasification and pyrolysis processes in comparison to incineration are the generation of reduced flue gas yields and the potential to generate by-products, such as char and hydrogen. However, complex operation and high energy demand remain major challenges [16].

The effectiveness of current state-of-the-art thermal methods to destroy PFAS is still heavily debated. On the one hand, the destruction of chlorofluorocarbons with an efficiency above 99.99% was reported in both waste incinerators and cement kilns [20] and PFOA has not been detected in the gas effluent during the incineration of PFAS containing textile waste [21,22]. On the other hand, during the thermal destruction of PFAS compounds, smaller breakdown products containing still high fluorine content can be formed and emitted. For instance, various short-chain and long-chain PFAS have been detected in the leachates from incineration plants in concentrations ranging from 7.2  $\mu$ g·L<sup>-1</sup> to 16.5  $\mu$ g·L<sup>-1</sup> <sup>1</sup> [23]. It is the incomplete destruction of PFAS by among others thermal treatment that leads to the formation of often undefined shorter-chain PFAS, which are harder to characterize [24]. Only a limited number of studies exist on the production of PFAS and perfluorinated compound (PFC) gases from the waste thermal treatment process. Moreover, the chemical interactions of PFAS with other substances, which can promote or inhibit the reactivity, under thermal operation conditions are currently unknown [14]. Some of the formed by-products are more volatile than their original PFAS resulting in greater airborne dispersion. Formed poly- and, especially, perfluorinated by-products have additionally enormous global warming potentials (GWP) due to their long lifetime and high capacity to absorb heat. GWP is a measure of the global warming impact of a compound relative to  $CO_2$ , which is by definition equal to 1. Considering a time horizon of one hundred years, the GWP of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> are 7380 and 12400, respectively [25].

The formation of by-products is inhibited at higher temperatures. According to the measured yields of fluorine, significant mineralization of PFOA and PFOS requires a heat treatment temperature of minimal 700°C [26]. Studies to understand the thermal stability of PFAS, including nonionic, cationic, and zwitterionic precursor compounds of PFOA and PFOS are still ongoing [27,28]. Thermal treatment is highly attractive because it is an unselective destruction method with applicability to the entire PFAS compound family. However, the pyrolysis and combustion chemistry of fluorine-containing species, *e.g.*, dominant decomposition pathways and important reaction intermediates, is not entirely known, making it difficult to design an appropriate treatment facility and choose appropriate process operation conditions.

Advanced oxidation and reduction defluorination processes are alternative non-thermal technologies that are being studied for PFAS destruction. These processes include electrochemical oxidation, plasma, photocatalysis, sonolysis, subcritical hydrothermal treatment (HT), hydrothermal alkaline treatment (HTAL) and supercritical water oxidation (SCWO) [29-32]. Despite their potential, a destruction method that destroys all PFAS compounds in low concentration samples seems to be lacking. These methods operate under different reaction conditions, ranging from basic chemical treatments to sophisticated electrochemical or photo-oxidation catalysis. Their PFAS destruction efficiencies vary from low percentages to near-complete decomposition and mineralization. For example, a study reported 100% fluoride recovery through SCWO at 610°C and residence times of 30 seconds [33]. Furthermore, a novel method employing polar aprotic solvents and low temperatures within the range of 80 to 120°C led to the fluorine mineralization in perfluoroalkyl carboxylic acids (PFCAs), ranging from 78 to 100% in 24 hours [27]. However, it is clear that these methods do not work for all PFAS compounds and a destruction method in the ideal World should be universal. The effectiveness and degradation pathways of PFAS by advanced oxidation or reduction processes is strongly influenced by the type of reactive species that are formed, *e.g.*, radicals or ions, and the chemical structure of the PFAS substances. This contrasts to non-selective thermal destruction methods such as incineration and pyrolysis [34]. Nevertheless, recent studies have demonstrated remarkable PFAS destruction efficiencies through SCWO. One study reported destruction efficiencies of 99.999%, even with the addition of co-contaminants to simulate matrix effects [35]. Another study presented PFOS destruction efficiencies of 99.9999% at 650°C [36].

The vast majority of photocatalytic oxidation and reduction studies are specifically directed at destruction of PFOA, with only a minority of the studies focusing on sulfonated molecules, or structures of varying chain lengths [37-39]. Sonolysis has presented the most interesting results when considering the complete destruction of PFAS [40]. Furthermore, it has been reported that sonochemistry treatments can achieve complete defluorination without pretreatment and without the need for the addition of chemicals/materials [41]. Catalytic hydrogenative dehalogenation of perfluorinated alkanes is conspicuously absent in the literature. Nevertheless, the different technologies are still in their early phases of development and many other factors need to be taken into account before scaling up those, such as energy consumption, capital and operating expenditures [4,15,29]. Also, the current literature lacks a comprehensive comparison of the various degradation pathways and mechanisms [34].

At the current state, only thermal treatments at very high temperatures, e.g., above 1400°C, with a sufficiently long residence time, e.g., 10 seconds, and without the addition of oxygen, could lead to the complete mineralization of PFAS [42]. However, these conditions would require extremely high energy consumption and are clearly unviable for waste management processes. Moreover, the currently available state-of-the-art analytical techniques for PFAS and PFAS thermal degradation products are unable to fully assess the efficiency of any kind of PFAS treatment. The use of additives as a strategy to enable milder conditions for PFAS mineralization is discussed in Section 3, while the development of a comprehensive analytical toolkit designed to assess PFAS mineralization efficiency is discussed in Section 4.

#### 3. Toward full mineralization by thermal degradation

In the case of complete destruction, so-called mineralization, the entire PFAS molecule (alkyl chain and functional group(s)) must be defluorinated and converted into fluoride salts, hydrogen fluoride (HF) and small hydrocarbons. Formed HF is a corrosive gas and is often neutralized via post-treatment with a base, *e.g.*, milk of lime, Ca(OH)<sub>2</sub>, NaOH or KOH [43]. Additionally, CO and CO<sub>2</sub> can be formed if oxygen is present in the PFAS molecule or if oxygen is added for incineration. However, the

mineralization of fluorine-containing compounds is typically far from complete with the current stateof-the-art destruction methods resulting in an undefined mixture breakdown of PFAS products that are released to soil, water and air around industrial treatment sites [44,45].

Gasification of PFOA and PFOS starts around 200°C and 400-600°C, respectively. They both lead to the formation of short and ultra-short PFAS compounds, such as CF<sub>4</sub>, CHF<sub>3</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>2</sub>F<sub>4</sub>, C<sub>3</sub>F<sub>6</sub>, C<sub>2</sub>HF<sub>3</sub>O<sub>2</sub> and CH<sub>3</sub>F [46-48]. Also COF<sub>2</sub> could be found as a minor product for an operating temperature of 1100°C [49]. Shorter-chained intermediates, derived from the degradation of original PFAS, can be released during the incomplete mineralization, which are stable at high temperatures and can cause secondary contamination. The thermal degradation of three small-chain PFAS compounds, *i.e.*, CF<sub>4</sub>, CHF<sub>3</sub>, and C<sub>2</sub>F<sub>6</sub>, was investigated using a natural gas-fired rainbow furnace with 20% excess of air, which is designed to simulate an industrial incinerator [50]. The PFAS compounds were introduced into the furnace at concentrations ranging from 34 to 203 ppmv. The CHF<sub>3</sub> demonstrated a destruction rate exceeding 99% at temperatures between 850-950°C and a residence time of approximately 1 second. Similarly, C<sub>2</sub>F<sub>6</sub> achieved a destruction rate above 99% when subjected to temperatures ranging from 950 to 1100°C with a residence time of approximately 1.5 seconds. On the other hand, CF<sub>4</sub> exhibited a destruction rate of only 95% when exposed to temperatures ranging from 1590-1650°C with a residence time of approximately 2 seconds. Such conditions are currently not used in industry, which will most certainly lead to incomplete PFAS mineralization.

The addition of low-cost calcium compounds, such as  $Ca(OH)_2$ , CaO, and/or CaCO<sub>3</sub>, provides an opportunity to reduce the temperature conditions for PFAS decomposition. However, it is not clear how these calcium compounds interact with different PFAS compounds, which temperatures are optimal and how other matrices affect the decomposition. What is known is that a minimum temperature of  $350^{\circ}$ C is essential to prevent the decomposition of CaF<sub>2</sub>, which would require additional steps for the treatment of flue gases [14]. In general, CaO and Ca(OH)<sub>2</sub> exhibit higher defluorination capabilities compared to CaCO<sub>3</sub> [51]. While CaO demonstrates the highest mineralization efficiency, Ca(OH)<sub>2</sub> is more effective in promoting defluorination at temperatures below 400°C. Nevertheless, it is important to note that CaO tends to convert into Ca(OH)<sub>2</sub> when in contact with moist waste [14]. Previous studies conducted in a muffle furnace have shown that adding Ca(OH)<sub>2</sub> with a Ca/F molar ratio of 1:1 facilitates fluorine mineralization and reduces the formation of PFCs during the combustion of various PFAS compounds [51-53]. At 400°C and a residence time of 15 minutes, the following fluoride mineralization rates were achieved: 60-75% for PFOS (pure) [51,52], 70% for PFOS (in sludge) [53], 80% for polytetrafluoroethylene (PTFE) [51] and 60% for perfluorohexane sulfonate (PFHxS) [51]. However, the mineralization rates were lower for PFOA and perfluorooctane sulfonamide (FOSA), with only 40% and 20% respectively at these conditions. Even at a higher temperature of 900°C the achieved mineralization for those compounds was only 50% [51]. In another experiment, the impact of a CaO-coated quartz reactor tube with an excess of calcium to fluorine on the destruction efficiency of fluorotelomer alcohol (FTOH) molecules was investigated. FTOH was fed at 50 ppbv in air with a residence time of 20 seconds. At 400°C, the removal efficiency of FTOH 4:2 increased from 25% in a non-coated reactor to 95% in the CaO-coated reactor. However, the efficiency decreased with larger FTOH molecules and the effect of CaO was diminished at higher temperatures [54]. All these aspects indicate the potential of calcium compounds to be added during the decomposition; however, the optimized concentrations and conditions are currently unknown.

Detailed mechanistic studies on degradation of PFAS compounds have shown that additives, including calcium hydroxide, alumina and hematite, can decompose PFAS compounds at temperatures as low as 380°C [49]. While these results demonstrate the great potential of additive materials for PFAS treatment, the complete assessment of PFAS mineralization in those processes is still not possible using the current analytical methods. Furthermore, there is very limited knowledge about the routes of thermal decomposition with active materials and the optimal conditions for mineralization are undefined.

## 4. Data collection and reliability

In order to fully understand chemical processes, each atom and molecule should be accounted for, (at least) from the start to the endpoint of the reaction under study. This principle is known as closing the mass balance. During PFAS degradation studies, new previously unreported reaction intermediates and products will be unavoidably formed. Additionally, each PFAS molecule will break down in a myriad of intermediate and/or end-products leading to a significant dilution of the initially present molecules. While industrial remediation and breakdown processes primarily focus on concentrated PFAS streams, these compounds are often present in the parts-per-trillion (ppt) range, *i.e.*, extremely diluted, in water, soil and air [55]. This combination of complexity and low levels of starting PFAS and breakdown products significantly hampers the ultimate aim of closing the mass balance and thus the unraveling of full reaction mechanisms. Further complicating compounding the mass balance are the diverse chemical characteristics of PFAS, which consist of polar/nonpolar, non-volatile/semivolatile/volatile, and neutral/anionic/cationic/zwitterionic chemicals [56]. And finally, if mineralization is successful, the formed degradation products will consist of a complex mixture of soluble and insoluble inorganic fluorine salts. The analytical challenge of characterizing all the above-mentioned species with a fit-for-purpose measurement uncertainty to close the mass balance is therefore immense. The current state of analytical science for PFAS is focused on so-called target methods for specific PFAS families in a limited number of well-specified matrices. This development was and is mainly driven by regulatory requirements, scientific toxicology and environmental occurrence studies. Holistic analytical workflows encompassing different types of PFAS, related PFAS compounds and media need to be developed first to fully characterize and assess decomposition methods [57].

To study the thermal decomposition of PFAS, optionally with active materials, a more advanced analytical toolkit is needed, especially if the kinetics of solid to gas, or liquid to gas reactions have to be determined as well (see **Figure 3**). It is essential that this comprehensive analysis section allows to maximally close the mass balance with a fit-for-purpose measurement uncertainty between the solid single-phase reactor inlet and the multi-phase, *i.e.*, gas, liquid and solid phases, reactor outlet. In order to achieve this, multi-platform targeted, suspect/non-targeted, and total screening methods need to be combined with adequate sampling procedures to characterize all PFAS degradation products, thus enabling visualization of the reaction pathways from incoming complex matrices to final degradation products. In general, all existing targeted PFAS methods involve liquid or gas chromatography hyphenated to mass spectrometry (LC-MS or GC-MS). Targeted PFAS provides accurate results with very low detection limits, but it requires reference standards and can therefore only be used for certain well-defined PFAS molecules.

Non-targeted analysis (NTA) is used for a broad screening purpose and allows detection and identification of unexpected or previously unknown PFAS compounds. The SI-traceable analytical methods for non-targeted screening includes both liquid chromatography (LC) [58-62] and comprehensive two-dimensional gas chromatography coupled with high-resolution mass spectrometer (GCxGC-HR-MS) [63]. Both one-dimensional gas chromatography (1D-GC) and two-dimensional gas chromatography (2D-GC) can be used depending on the difficulty of separation of reaction products and matrix. The thermal degradation products are captured on a cold trap and then directly transferred to the comprehensive gas chromatography coupled with mass spectrometry, or flame ionization detection (GCxGC-MS/FID). To offset the ionization and response related discrimination in the MS-detector, the FID is a valuable complementary add-on to assign relative amounts to the analytical features identified using MS. In parallel, the degradation products will also be trapped on a comprehensive trapping device based on the US EPA OTM-45 [64] for further analyses on ultra-performance liquid chromatography coupled with high-resolution mass spectrometry (UPLC-HR-MS) and/or EOF/TF/IF and/or Fourier transform infrared spectroscopy (FTIR). This sampling device contains filters, XAD adsorbent cartridges, condenser tubes, polyurethane foam (PUF) and impinger fluids [65].

In addition to SI-traceable methods a wide suit of method-traceable applications, the so-called total organic fluorine methods, can aid in the mass balance closure. These methods are specific for C-F containing molecules and are available for liquids (Adsorbable Organic Fluorine) and solid (Extractable organic Fluorine) samples and yield a method traceable result that is complementary to all other data sets. These techniques can be combined with combustion ion chromatography (CIC) and high-resolution continuum source graphite furnace molecular absorption spectrometry (HR-CS-GFMAS) [66]. Furthermore, particle-induced gamma emission (PIGE), inductively coupled plasma mass spectrometry (ICP MS/MS) [67], instrumental neutron activation analysis (INAA), X-ray photoelectron spectroscopy and optionally total organic precursors analysis (TOP) could also be applied [68,69]. Despite the fact that these techniques allow detection of all types of PFAS, they do not preserve the structural information of the individual compounds. Additional techniques include fluorine-19 nuclear magnetic resonance (<sup>19</sup>F NMR), ion selective electrodes (ISEs) and ion chromatography (IC) [70,71]. In relation

to a PFAS total assessment, a compromise of modifying protocols to capture the largest number of PFAS in different matrices while ensuring good performance for prioritized substances might be required.

Recently, a new infrared spectral database has been created specifically for volatile fluorocarbon compounds generated during the thermal treatment of PFAS. The development of this database followed protocols derived from the Pacific Northwest National Laboratory (PNNL) infrared spectral database. This infrared spectral database plays a crucial role in enhancing the identification, detection, and quantification of fluorine-containing compounds, particularly in applications involving the thermal degradation of PFAS [72]. This suite of on-line and off-line techniques will identify and quantify the pyrolysis products. An important gas-phase reaction product is HF, which is formed during fluorine abstraction reactions. The analysis of HF is performed with FTIR, either independently or in combination with gas chromatography (GC) [19].

Both the PFAS-containing sample and the solid residue produced from the pyrolysis must be analyzed using offline methods. Additionally, the fluorine salts formed as a result of sample mineralization are also subject to analysis via offline methods. The ISO 10359-2 method on the determination of inorganically bound total fluoride can serve as a solid base to further fine-tune methods with the desired performance regarding specificity, sensitivity and limit of detection [73]. Further, fluoride salts such as SiF<sub>5</sub><sup>-</sup> can also be directly characterized using HRMS, albeit with the limitation that SI-traceable quantification might be a challenge [74].

The adsorption or absorption of fluorine compounds on the reactor surface can significantly impact the accuracy of the mass balance calculations. One suitable option for the reactor material is single crystal alumina, which has demonstrated excellent resistance to hydrofluoric acid (HF) [75] and can withstand high temperatures up to 1700°C. Alternatively, the use of alkaline solutions presents another possibility for removing silicon tetrafluoride (SiF<sub>4</sub>) from the system [76].

Using such a wide range of complementary techniques will be essential to cover all reaction products needed to maximally close the mass balance. However, quantification will always remain a challenge because of the lack of authentic reference compounds for calibration.



Figure 3. Schematic of a pyrolysis unit capable to assess the thermal destruction of PFAS.

## 5. Concluding remarks

The thermal destruction with active materials as remediation technology for PFAS pollution is summarized by a SWOT (strengths, weaknesses, opportunities and threats) analysis in **Figure 4**. We consider the main strengths to be the complete destruction above 1400°C and the applicability to all PFAS as thermal decomposition is not selective. The current state-of-the-art technologies should theoretically work well for certain classes of fluor-containing molecules but cannot handle all compounds with the desired conversion yields, as operating temperatures are not sufficiently high. Moreover, the use of cheap active materials, such as Ca(OH)<sub>2</sub>, CaO, and CaCO<sub>3</sub>, as co-reactant provides an advantage compared to competing technologies, which require expensive catalysts or reducing agents. The addition of active materials to efficiently mineralize PFAS during thermal destruction also enables to develop small-scale industrial facilities, which can be operated at reduced reaction temperatures.

However, this destruction technology still has pitfalls as the thermal decomposition of fluorcontaining species has not been completely elucidated. In particular, the following research questions need to be addressed to advance the field of PFAS thermal degradation: 1. How can the destruction efficiency of different thermal destruction technologies for PFAS be effectively investigated and assessed?

2. What are the types of interactions between PFAS and active materials during thermal destruction, and how do they affect the mineralization process?

3. What are the potential limitations and challenges in achieving complete mineralization of PFAS through thermal decomposition?

4. Is the presently used technology for destroying PFAS good enough? Very likely not.

Finally, the current state-of-the-art of the analytical technology poses limitations to the degree of mass balance closure. The lack of molecular specificity on the one hand side and the lack of authentic calibration standards on the other lead to an increased uncertainty of the produced analytical data. We believe however that this uncertainty can decrease to an acceptable level once sufficient degradation can be achieved. Total scientifically sound mass balance closure will probably only be possible for total mineralization to HF, but the comprehensive analytical toolkit available today will certainly be able to unravel pathways and to optimize the process.



Figure 4. SWOT analysis for thermal destruction of PFAS with active materials.

## **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Acknowledgments

We acknowledge financial support from VLAIO (Flemish Agency for Innovation and Entrepreneurship)

via the Flemish spearhead cluster Catalisti. Kevin De Ras acknowledges the Fund for Scientific

Research Flanders (FWO) for financial support via doctoral fellowship grant 3F018119. The research

leading to these results has also received funding from the European Research Council under the

European Union's Horizon 2020 research and innovation program / ERC grant agreement n° 818607.

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\* The authors investigated the thermal degradation of  $CF_4$ ,  $CHF_3$ , and  $C_2F_6$ , in a natural gasfired rainbow furnace that simulates an industrial incinerator. It is shown that the conditions currently applied in industrial incinerators are insufficient to decompose these compounds.

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