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Critical Review

Critical Review of Thermal Decomposition of Per- and Polyfluoroalkyl Substances: Mechanisms and Implications for Thermal Treatment Processes

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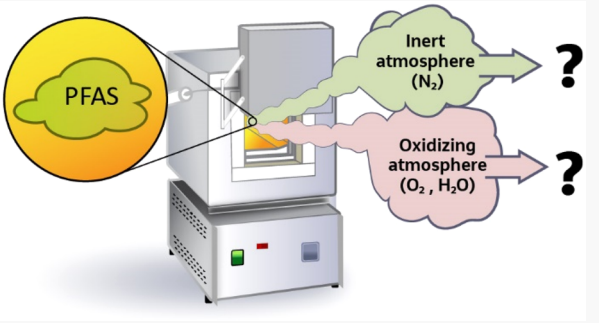
ABSTRACT: Per- and polyfluoroalkyl substances (PFASs) are fluorinated organic chemicals that are concerning due to their environmental persistence and adverse human and ecological effects. Remediation of environmental PFAS contamination and their presence in consumer products have led to the production of solid and liquid waste streams containing high concentrations of PFASs, which require efficient and cost-effective treatment solutions. PFASs are challenging to defluorinate by conventional and advanced destructive treatment processes, and physical separation processes produce waste streams (e.g., membrane concentrate, spent activated carbon) requiring further post-treatment. Incineration and other thermal treatment processes are widely available, but their use in managing PFAS-containing wastes remains poorly understood. Under specific operating conditions, thermal treatment is expected to mineralize PFASs, but the degradation mechanisms and pathways are unknown. In this review, we critically evaluate the thermal decomposition mechanisms, pathways, and byproducts of PFASs that are crucial to the design and operation of thermal treatment processes. We highlight the analytical capabilities and challenges and identify research gaps which limit the current understanding of safely applying thermal treatment to destroy PFASs as a viable end-of-life treatment process.



KEYWORDS: *Thermal treatment, pyrolysis, combustion, incineration, PFAS*

1. INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are synthetic organic chemicals containing a completely or partially fluorinated alkyl chain. Fluorine is strongly electronegative, causing a short bond length between the C and F. While these structures are desirable for the numerous applications of PFASs, C−F bonds are highly stable and thus poorly susceptible to degradation by hydrolysis, oxidation, photolysis, and biological processes.[1]

The unique chemical structures of PFASs make them naturally hydrophobic, oleophobic, and thermodynamically stable. PFASs have been utilized for over 70 years to produce consumer products with water, stain, and chemical repellence, and/or resistance to thermal degradation. PFASs have been used in food packaging, cookware, textiles and carpets, cosmetics, ski wax, building and automotive materials (e.g., wiring, piping, sealants, adhesives, paints, roofing), and mist-suppression in chrome-plating factories.[2−6] They have also been used in aqueous film-forming foams (AFFFs), which represent a significant source of environmental contamination stemming from military and nonmilitary fire training and hydrocarbon fire suppression.[7−13] Approximately 2000 PFASs have been identified in the global market for intentional use, and at least 6000 CAS-indexed PFASs exist with more than 5000 having defined structures.[14] As a result, PFASs are ubiquitous in the environment,[15,16] and they are detectable in wildlife and humans.[17−19] The likelihood of exposure in combination with the potential for adverse ecological and health effects[20−25] has caused tremendous concern.

In the United States (U.S.), the regulatory landscape for PFASs at the state and federal levels is rapidly changing. In 2016, the U.S. Environmental Protection Agency (US EPA) announced a drinking water health advisory limit of 70 ng/L for the sum of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS),[26,27] and some U.S. states have adopted more stringent guidance.[28] As of 2021, no additional federal regulations have been set, but drinking water primary

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standards under the the Safe Drinking Water Act and waste disposal rules under the Resource Conservation and Recovery Act are expected.[29] While replacements for PFOS and PFOA have been developed with increased renal clearance rates and/or biodegradability, for example, shorter-chain perfluorocarboxylic acids (PFCAs), perfluoroether carboxylic acids, and perfluoroosulfonic acids (PFSAs),[30,31] recent toxicological studies have shown they are potentially harmful.[32] For example, in 2021, the US EPA established a chronic oral reference dose for one of the most common PFOA replacements, hexafluoropropylene oxide (i.e., GenX, 3 ng/kg-day), which is ∼10 times lower than for PFOA and PFOS and 100 times lower than for perfluorobutanesulfonate (PFBS).[33]

Various physical and chemical treatment processes have been explored to remove PFASs from environmental media.[34] Physical treatment processes such as adsorption,[35−37] ion exchange,[37−39] and membrane filtration[16,40] are effective for contaminated water or aqueous waste streams (e.g., soil washing[41]), but they produce solid or liquid wastes containing high concentrations of PFASs that still require defluorination to alleviate long-term environmental impacts. While conventional and advanced chemical treatment methods such as oxidation (e.g., ozone, UV/H_2O_2) are largely ineffective for destruction of PFASs, a number of advanced methods are being developed including electrochemical oxidation, sonolysis, bioremediation, advanced reduction, and nonthermal plasma.[42−48] In general, these latter technologies are unproven at scale and/or poorly defluorinate PFASs in time frames that are useful for full-scale application. There is therefore a need for a proven and scalable destruction method for waste streams which contain PFASs.

Thermal treatment processes (e.g., incineration) offer a common, scalable, and widely available approach for managing contaminated solids, liquids, or gases,[49] and many incineration facilities are already knowingly or unknowingly treating PFASs (e.g., consumer products, activated carbon regeneration). Thermal treatment of PFASs has been demonstrated at scale by several commercial interests and is thought to result in mineralization.[50] While thermal treatment processes are generally energy intensive and costly, the technology has already been deployed, and together, these advantages place them as a key solution for managing PFAS-containing wastes.

Many unknowns remain about the thermal behavior of PFASs, despite a growing body of research. In this review, we critically evaluate and summarize the volatility, decomposition mechanisms and pathways, and products of the thermal degradation of PFASs. We further discuss the implications of these mechanisms on thermal degradation of PFASs for industrial-scale thermal treatment systems and highlight analytical methods and needs.

2. SURFACE INTERACTIONS AND VOLATILITY

Thermal decomposition of PFASs sorbed to materials can be initiated via two pathways. First, as the temperature of a solid increases, some PFASs volatilize and undergo gas-phase reactions. Second, some less volatile PFASs undergo thermal degradation in/on the solids. Thus, the extent and type of thermal degradation byproducts are likely to differ based upon the parent PFAS compounds volatility. Aqueous PFASs that are deprotonated or adsorbed to solids via electrostatic or ion exchange interactions have very low propensity to enter the gas phase until the temperature rises above 100 °C, when water evaporates and interactions with the solid weaken. For example, during regeneration of a PFAS containing media, PFOA did not volatilize below 90 °C, then gradually decreased in surface concentration as the temperature increased from 90 to 400 °C.[51]

Vapor pressure describes the equilibrium between a pure liquid and the gas phase in a closed system. This is reflective of the volatility of a pure compound and is useful in understanding thermal treatment processes. In Figure 1a, we show the vapor pressure for different groups of PFASs as a function of chain length. Note that these are computational estimates by the Antoine equation, rather than experimentally derived values. Two other semiempirical models are shown in Figure S1 for comparison, and a comparison of modeled and experimentally measured vapor pressures of fluorotelomer alcohols (FTOHs) is listed in Table S1. Volatility of various structures followed the order of perfluorocarbons (PFCs) > fluorotelomer carboxylic acids (FTCAs) > FTOHs ≈ PFCAs > PFSAs > fluorotelomer sulfonates (FTSAs). Across these same functional groups, vapor pressure increased with decreasing chain length. These modeled trends are further supported by the experimentally derived data shown in Figure 1b and an additional study which reported boiling points of C4−C8 PFCAs and PFSAs increasing from 121 to 192 °C and 210 to 249 °C, respectively.[35] Lower sublimation

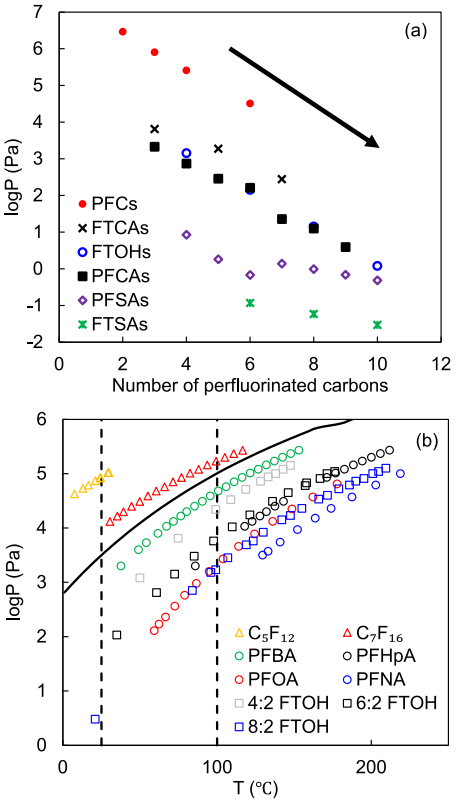

Figure 1. (a) Perfluorocarbon (PFC), fluorotelomer carboxylic acid (FTCA), fluorotelomer alcohol (FTOH), perfluorinated carboxylic acid (PFCA), perfluorinated sulfonic acid (PFSA), and fluorotelomer sulfonate (FTSA) vapor pressures (P) at 25 °C from the semiempirical Antoine method in EPISuite.[57] Arrow indicates a trend of decreasing vapor pressure for longer-chain PFAS. (b) Experimentally determined vapor pressure of specific PFASs over a range of temperatures adapted from Ding and Peijnenburg.[53] Compounds with the same number of fluorinated carbons are shown in the same color, and compounds with similar structures or functional groups have the same marker. The black line shows water vapor pressure. Additional abbreviations are perfluorobutanoic acid (PFBA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), and perfluorononanoic acid (PFNA).

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vapor pressures have been reported for an increasing number of fluorinated carbons,[52] again providing evidence that shorter-chain PFASs are more volatile.

Experimental vapor pressures versus temperature for a limited set of PFASs[53] are shown in Figure 1b. PFCs were more volatile than water, indicating that PFCs are likely to volatilize before water. At temperatures lower than the boiling point of water, some liquid phase water may remain, and this is particularly meaningful for perfluoroalkyl acids (PFAAs). However, very few experimentally determined Henry's Law constants are available in published literature which presents a substantial weakness in the understanding of PFASs' volatilities.[53,54] Further, some PFASs decompose at temperatures lower than the temperature required for vaporization.[55]

However, considerations of pure-phase PFASs, PFASs on surfaces, or even single-solute solutions are probably over-simplifications. The presence of cations in solution can form salts with PFASs that influence the ability to predict volatilization. Also, the composition and heterogeneity of surfaces on which PFASs exist will likely influence the propensity of a PFAS to volatilize from a surface. For example, research on soil demonstrated that volatilization was minimal for both PFCAs and PFSAs at 220 °C over 14 days,[56] despite PFCAs boiling points suggesting they would volatilize at temperatures below 200 °C. The mechanisms and roles of surface hydrophobicity on temperatures at which PFASs volatilize from surfaces remain poorly understood. However, as temperatures increase to far above predicted temperatures for volatilization, the dependence of PFAS volatilization on the PFAS structure decreases.

3. DECOMPOSITION INITIATION, PRODUCTS, MECHANISMS, AND KINETICS

Reported primary thermolytic mechanisms of PFASs include cleavage of intramolecular bonds through transition states (TS), direct homolytic cleavage, radical reactions, hydrolysis, and oxidation. Each mechanism and pathway produce some distinct, but also some overlapping, decomposition products. Temperatures at which PFASs volatilize from surfaces may be higher than temperatures at which thermal decomposition initiates, making it difficult to differentiate between these two different mechanisms.[58,59] While acknowledging the potentially synergistic role of surfaces (see Section 4.2 for more discussion), the temperatures required to initiate PFAS decomposition appear to be related to both the number of perfluorinated carbons and functional groups. Pyrolysis (absence of oxygen) and combustion (presence of oxygen) are influenced by functional groups because pyrolysis is unimolecular and initiates with the decomposition of the least stable group, and combustion is initiated by reactions between O_2 and the most reactive group. A summary of experimentally derived thermal decomposition products of PFASs are provided in Table S2. Various perfluorinated gases and solids such as coke and polymeric materials may be formed during pyrolysis (in dry inert conditions) and may persist even at temperatures above 1000 °C.[60−65] Generally, PFASs are pyrolyzed into other forms of organofluorine, including volatile organofluorine (VOF), especially at temperatures less than 500 °C. The lack of closed mass balances (>90% F accounted for) for nearly all experiments strongly implies that some fluorinated products may escape thermal and post-treatment processes, elude detection, and be released to the environment. Additionally, nearly all studies of thermal decomposition of PFASs are conducted under pyrolytic conditions, and therefore, our discussion primarily focuses on pyrolysis, with combustion discussed where data are available.

3.1. Temperatures Required to Initiate Decomposition.

Temperatures required to initiate decomposition in terms of structure decrease as follows: perfluorocarbons (PFCs) > perfluoroacyl fluorides > PFSAs > PFCAs > perfluoroether carboxylic acids.[66] The order of the decomposition rates of PFCs (C_xF_y) between 1000 °C and 1250 °C was CF_4 < C_2F_6 < cyclo-C_5F_{10} < C_3F_8 < n-C_4F_{10} < n-C_5F_{12},[61] indicating that the temperature required to decompose PFCs decreases with an increasing number of carbons, although isothermal rates (i.e., rates measured at a fixed temperature) may not perfectly represent overall thermal stability. Perfluorohexane (n-C_6F_{14}) did not decompose at temperatures less than 400 °C[67] nor in 450 °C air even in the presence of a palladium catalyst.[68] Pure 2H-heptafluoropropane (HFP, C_3HF_7) did not decompose at temperatures less than 640 °C,[65] and perfluoropentane (n-C_5F_{12}) was not decomposed below 840 °C.[60]

Xiao et al.[66] studied thermal stability of PFASs sorbed to GAC and found that the temperatures needed to degrade PFCAs increased with an increasing number of perfluorinated carbons. The decomposition of PFSAs generally requires higher temperatures (450 °C) than PFCAs (200 °C), and perfluoroether carboxylic acids are more readily decomposed than PFCAs with the same number of fluorinated carbons, demonstrating that ether bonds weaken the molecule.[66] For acids, the counterion may also impact the thermal stability. For example, Lines and Sutcliffe[69] reported that the thermal stability of PFOA salts increased with the following counterions: ammonium < cesium < potassium < silver < lead < sodium < calcium = barium < lithium.

The temperatures required to decompose fluoropolymers are related to monomeric structure, extent of fluorination, and physiochemical conditions (e.g., reactor material, atmosphere).[70−72] Baker and Kasprzak found that $-CF_3$ branching leads to reduced Teflon thermal stability.[73] Overall, polymers of perfluoroethylene are more stable than perfluorophenylene.[74] Fully fluorinated polymers made up of tetrafluoroethylene and/or hexafluoropropylene are the most thermally stable.[71,74] Also, increasing molecular weight tends to reduce thermal stability,[29,30] and some copolymers containing trifluoronitrosomethane (CF_3NO) or (OCF_2) monomers are poorly stable, decomposing at temperatures as low as 200 °C.[71,72]

Reactor materials and reaction conditions (e.g., presence of O_2) also influence the thermal stability of PFASs. For example, heptafluorobutyric anhydride decomposed at as low as 150 °C in a reactor containing alumina but was stable up to 850 °C in a tantalum or silver reactor.[75] Several fluoropolymers such as fluorosilicone B and polyvinylidene fluoride decomposed more rapidly in the presence of O_2 than in a vacuum/inert atmosphere,[71,72] although others have demonstrated that vacuum/inert vs oxidizing atmosphere causes minimal differences in decomposition rates.[70] Even some copolymers (e.g., CF_3NO/C_2F_3H) have been shown to decompose slower in an oxidizing atmosphere than an inert one.[71,72]

Overall, the thermal decomposition initiating temperatures are determined by the least stable part of a molecule, which is typically a nonfluorinated functional group. PFCs, which contain no such functional groups, are thus the most stable, and their stability decreases with increasing perfluoroalkyl chain length. This indicates that at a specific temperature the loss of a longer-chain PFAS should not be interpreted as mineralization,

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as it is possible or likely that it was decomposed to a shorter-chain, more thermally stable, PFC or PFAS.

3.2. Decomposition Products. *3.2.1. Perfluorocarboxylic Acids.* Products of the pyrolysis of PFCA salts include perfluoroacyl fluorides and anhydrides, corresponding acids, and even dimers of the perfluoroalkyl chains (Figure 2).[76,77]

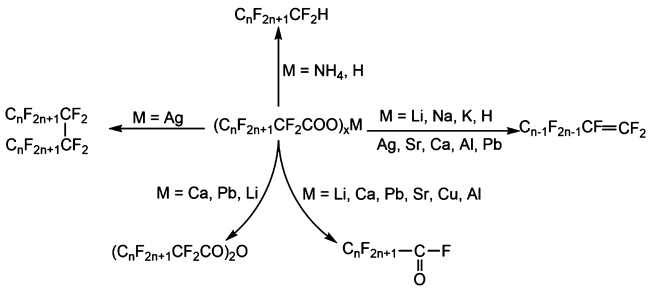

Figure 2. Pathways and products of PFCAs and their salts at temperatures of 200 to 305 °C during pyrolysis. Produced from results presented by LaZerte et al.[76]

Longer-chain PFCA pyrolysis products include shorter-chain PFCAs such as 1*H*-perfluoroalkanes, perfluoro-1-alkenes, and unidentified VOF, CO, CO_2, and HF (Table S2). Perfluoro-1-alkenes are a dominant product of metal salts of PFCAs (except trifluoroacetic acid [TFA] and its salt), and the yield varies with the species of counterion. TFA salts form trifluoroacetyl fluoride and trifluoroacetic anhydride as primary products.[76,78] Sodium or potassium salts of longer-chain PFCAs (C > 3) consistently had the greatest yields of the primary product, perfluoro-1-alkenes, and the yield increased with shortening carbon chain length.[76] Ammonium salts of PFCAs yield neither alkenes nor acetyl-containing compounds but instead almost quantitatively forms 1*H*-perfluoroalkanes.[76,79] Notably, the formation of dimers of the perfluoroalkyl chains was observed for the silver salts of PFCAs. Such detailed observations of varying counterions are not available for PFASs outside of PFCAs during pyrolysis, but given the significant differences between decomposition products and the likelihood of a diversity of counterions present in environmental samples, additional research is warranted, particularly for combustion of soils where PFCAs are likely to be present as salts.[80]

3.2.2. Perfluorosulfonic Acids. PFSAs appear to be thermally defluorinated to a greater extent than PFCAs (i.e., producing stoichiometrically more mineralized fluorine), although the number of investigations available to draw this conclusion is limited.[81−83] Quantification of organic intermediates are rarely presented in these studies, although mass fragments (CF_3^+, $C_2F_3^+$, $C_3F_3^+$, $C_2F_4^+$, $C_2F_5^+$, $C_3F_5^+$, $C_4F_7^+$, $C_5F_9^+$) of some products were observed by GC-MS after thermal decomposition in the presence of lime.[83] The presence of these mass fragments strongly suggests that VOF is a product of thermolysis of PFSAs.[58] Recently, some fluorinated olefins have been identified as thermal decomposition products of PFOS.[84]

3.2.3. Perfluorocarbons. Pyrolysis products of perfluoroalkanes and perfluoroalkenes are similar and include C_2F_6, C_2F_4, C_3F_8, C_3F_6, polymeric compounds, and solid-phase charred residues (Table S2). These products are thought to form as a result of homolysis of C−C bonds (each C retains one electron that formed the bond), forming radicals which in many cases yield stable PFASs such as polymers and cyclo-compounds.[60,64,65] Formation of the products has been shown to be temperature dependent. The thermal decomposition of C_2F_4 was studied from 300 to 800 °C, and the primary product was dimerization to cyclo-C_4F_8 at temperatures below 550 °C. *n*-C_3F_6 and *n*-C_4F_8 were generated between 550 and 700 °C, and C_2F_6, perfluoroisobutene (PFIB, $(CF_3)_2C{=}CF_2$), and other nonvolatiles were formed between 700 and 750 °C.[85,86] In another study, the thermal decomposition of cyclo-C_4F_8 formed *n*-C_3F_6 and C_2F_4 as principal products between 360 and 560 °C.[87] Matula[88] examined *n*-C_3F_6 from 550 to 675 °C and found that perfluoro-2-butene ($CF_3CF{=}CFCF_3$) and PFIB were the primary reaction products.

3.2.4. Fluoropolymers. The thermal decomposition products of fluoropolymers include monomers, dimers, trimers, perfluorocarbons, CO_2, and SiF_4 (when quartz is present).[74,89] C_2F_4 was the primary pyrolysis product of polytetrafluoroethylene (PTFE).[73] The subsequent decomposition of C_2F_4 is discussed in Section 3.2.3.[90] The copolymer-fluorinated ethylene propylene (FEP) more readily forms PFIB than PTFE likely because of the inclusion of a −CF-CF_3− monomer along with −CF_2− in FEP. PFIB is relatively stable and highly toxic.[73,91] Zuev et al.[89] investigated the thermal decomposition of acrylic polymers with fluorinated side chains at 450 to 750 °C and found that the key decomposition pathway of the polymer was scission of the primary polymer carbon bonds. The fluorinated alkyl ester side chains were highly stable and transformed into corresponding fluorinated cycloalkanes.

In the oxidizing atmospheres, carbonyl fluoride (COF_2) is a common gaseous product.[72,73] Defluorination occurs to a greater extent in air (∼60%) than in nitrogen (∼17%).[72,73] TFA and longer-chain perfluoro- and/or polychlorofluoro carboxylic acids (C3−C14) were formed during thermolysis of PTFE and Kel-F at temperatures lower than 500 °C in the presence of O_2 and H_2O.[92] Combustion of fluorinated polymers did not tend to produce PFOA when the temperature was above 1000 °C, similar to municipal and/or medical waste incineration.[50,93] This suggests that the risk of releasing well-known PFASs from incinerators when polymers are combusted may be limited, but there is still the potential to release low molecular weight VOF (Table S2).

Figure 3 is a visual representation of the thermochemical stability and defluorination of PFASs for which there are sufficient data. Although some of the regions are approximate because the experimental data are somewhat coarse, the figure demonstrates overall that mineralization tends to occur above 700 °C in oxidizing atmospheres and that at lower temperatures and in inert atmospheres VOF is formed. This has broad implications for incinerators, which are operated with supplemented air at temperatures greater than 700 °C, potentially limiting the release of VOF. Again, there are few studies of combustion of PFASs, and these studies are limited to select groups of compounds. There is a significant need to study additional PFAS decomposition during combustion to inform treatment approaches of potential gas-phase products. PFAS groups that are not included in this figure have no or too limited published data to make broad conclusions. For example, FTOHs are volatile and thus may escape in the gas phase prior to degradation, but there are limited data available regarding temperatures required to achieve thermal decomposition and/or products.[94] Study of significantly more PFASs (e.g., alcohols, ethers) that are expected to be present in environmental samples and waste streams is warranted to understand the byproducts in relation to the thermolysis temperature.

3.3. Mechanisms and Pathways. *3.3.1. HF Elimination via Transition States. 3.3.1.1. Perfluorocarboxylic Acids.*

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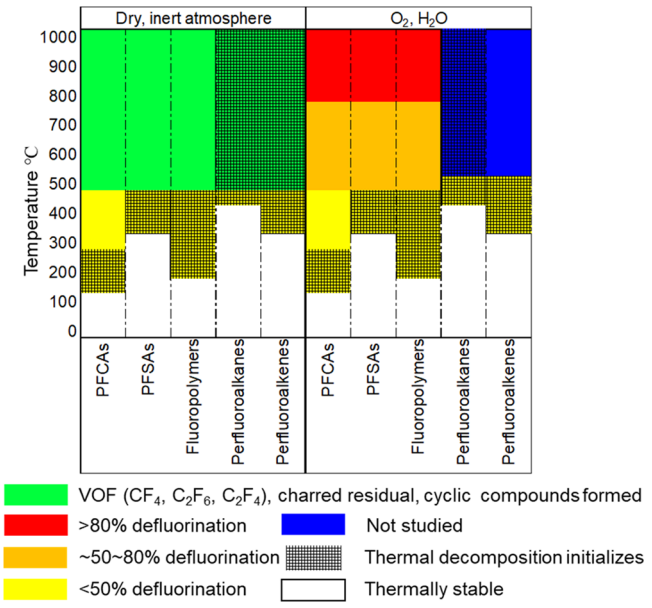

Figure 3. Summary of approximate thermal decomposition in inert and oxidizing atmospheres based on available data provided in Table S2.

Figure 4 illustrates several PFCA decomposition pathways based upon both experimental or computational studies.[95−99] It is worth mentioning that density functional theory calculations are generally carried out at zero Kelvin and that more rigorous ab initio molecular dynamics can simulate thermal effects.[100,101] Pathway 1 depicts the formation of 1*H*-perfluoroalkanes, which begins with HF elimination via a five-membered TS, resulting in the formation of CO_2 and a carbene (C_nF_{2n-1}−:CF). The carbene then reacts with HF to form a 1*H*-perfluoroalkane.[102] 1*H*-Perfluoroalkane formation via pathway 5 has also been proposed.[98] Further, 1*H*-perfluoroalkanes may not be the only products during PFCA pyrolysis. Perfluoro-1-alkenes via a six-membered TS2 may also be possible for long-chain PFCAs (pathway 2), and moderate amounts of perfluoro-1-heptene have been observed during PFOA pyrolysis.[102] Also, through TS2, PFPrA can form perfluoroacetyl fluorides, but this product is specific to PFPrA because it contains only two fluorinated carbons.[66]

Recently, Xiao et al.[66] proposed that thermal decomposition of PFOA on GAC surfaces is initiated by loss of a fluorine atom and −COOH to generate a perfluorocarbon radical (pathway 4), followed by loss of fluorine or CF_2 based on GC-MS identification of the organic fluorine products. There is, however, some debate over the decomposition pathway.[103,104]

Rayne and Forest[77] proposed a terminal perfluoroalkyl carbanion as an intermediate via thermal decarboxylation (pathway 3), yielding 1*H*-perfluoroalkanes by reacting with ambient protons or yielding perfluoroalkenes through loss of a fluorine. However, this pathway is more likely in polar solvents than the gas phase, because the dissociation energy of heterolysis is thought to be greater than homolysis for the same covalent bond in the gas phase.[105]

At least two computational studies of the pyrolysis of PFCAs indicated that direct decarboxylation is not likely to be the main pathway because of the high activation energy.[95,98] The primary decomposition pathway in these studies is HF elimination and the formation of an α-lactone intermediate (M1) via pathway 6, which is not thermally stable and is then degraded to a perfluoroacyl fluoride (M2) and CO at relatively low temperatures (<500 °C).[98] At high temperatures (>1000 °C), M1 tends to be degraded into CO_2 and M3.[98] The formation of M2 is supported by experimental studies of the pyrolysis of the simplest PFCA, TFA (CF_3COOH), which forms COF_2, likely first through the loss of HF and formation of a lactone, followed by loss of CO. This pathway is further supported by the observed

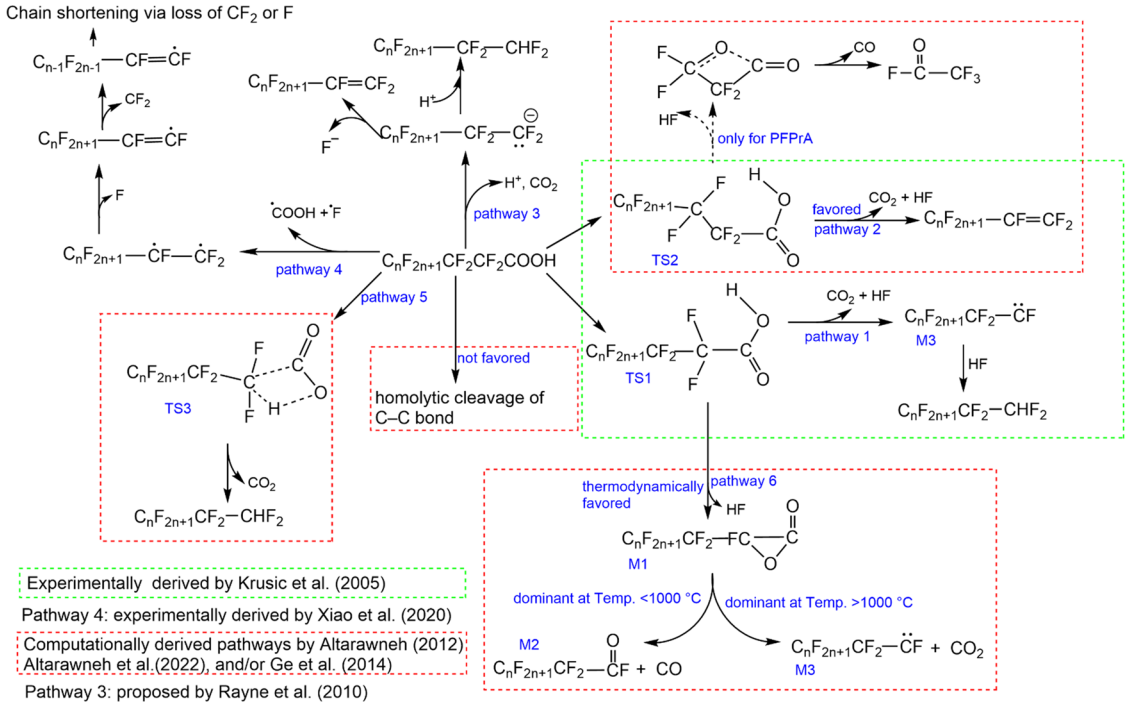

Figure 4. Published experimentally and computationally derived pyrolysis pathways of PFCAs. Dashed boxes indicate the literature source (see bottom left).

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formation of M2 during pyrolysis of PFCA metal salts, both agreeing well with the products in Table S2.

Although M2 has been computationally predicted to be the primary product of PFCAs and has been observed during the thermal decomposition of TFA and PFCA metal salts, M2 was not detected in other experiments of PFCA acids (Table S2). M2 (i.e., CF_3COF) is thermally stable up to ~600 °C (Table S2), and thus, the lack of detection is surprising. The lack of M2 detection may be because either the experimental conditions (e.g., reactor materials) altered the thermal decomposition pathway or because M2 readily reacts with HF and H_2O to form other compounds (Section 3.3.3).

Another poorly understood area of the decomposition of PFCAs is which pathway dominates the formation of the observed intermediates/products (e.g., 1*H*-perfluoroalkanes, perfluoro-1-alkenes). Pathways 1 and 2 support the observed formation of 1*H*-perfluoroalkanes and perfluoro-1-alkenes but fail to explain the traces of short-chained PFBA and perfluoropentanoic acid (PFPeA) present during PFOA pyrolysis.[82] Further, the carbene intermediate in pathway 1 does not explain why water promotes the decomposition of PFOA[77] or how the counterion influences PFCA thermal stability and product formation. Additional products not described well by these pathways have been observed during the pyrolysis of TFA,[106,107] further indicating that the mechanisms may be more complicated than current publications explain.

3.3.1.2. Perfluorosulfonic Acids. For PFSAs, only computationally derived decomposition pathways are available (Figure 5). HF elimination (hydrogen from the sulfonic acid and

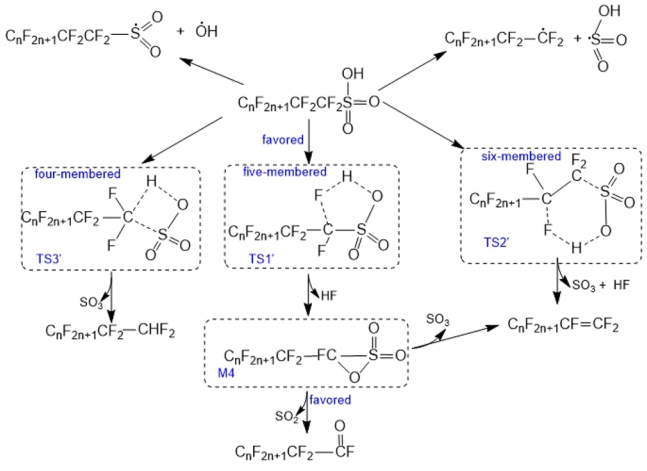

Figure 5. Computationally derived pyrolysis pathways of PFSAs.[96,99]

fluorine from the α carbon) via a five-membered TS1′ is thought to dominate, resulting in formation of an intermediate α-sultone (M4), which is then degraded to a perfluoroacyl fluoride and SO_2 at all studied temperatures.[96,99] Competing pathways include HF elimination leading to the formation of perfluoro-1-ene and SO_3 via six-membered TS2′ and 1*H*-perfluoroalkane formation via TS3′.[96,99]

3.3.1.3. Other Per- and Polyfluoroalkyl Substances. HF elimination is thought to also occur for other PFASs. HF elimination was confirmed experimentally and computationally during the thermal decomposition of 2*H*-heptafluoropropane (R1).[65,108,109] HF elimination was also demonstrated as a pathway for perfluoroalkanol pyrolysis.[110] Thus, HF elimination appears to be a component of multiple pathways of the pyrolysis of PFASs that contain hydrogen in the carbon chain or in a functional group. This is advantageous to incinerators that capture off gases using wet scrubbers, where HF would be captured and retained.

$$CF_3CHFCF_3 \rightarrow CF_3CF = CF_2 + HF \quad \text{(R1)}$$

3.3.2. Direct Cleavage of Intramolecular Bonds. The direct cleavage of intramolecular bonds has been demonstrated to be an initiating mechanism during thermal decomposition of PFASs. During pyrolysis of perfluoropolymers[89,92] and perfluorocarbons,[60,61,64,65,111] intramolecular C−C bond cleavage is dominant in initial reactions. The cleavage proceeds through (1) homolytic cleavage of C−C bonds resulting in the formation of perfluorocarbon radicals[60,61,64] and (2) radical recombination to form relatively thermally stable short-chain VOF or reactions with other matter (e.g., O_2, H_2O, •OH) if available.

One example of the direct cleavage of intermolecular bonds is the decomposition of perfluoroacyl fluorides, which proceeds initially through cleavage of the CF_2−COF bond (R2), leading to a perfluorocarbon radical and •COF.[99] Another example is the cleavage of C−F bonds, which has been observed during thermal decomposition of COF_2 (R3).[112]

$$C_nF_{2n+1}CF_2COF \rightarrow C_nF_{2n+1} - \bullet CF_2 + \bullet COF \quad \text{(R2)}$$

$$COF_2 \rightarrow \bullet COF + \bullet F \quad \text{(R3)}$$

Pyrolysis of perfluorocarbons also proceeds via cleavage of intramolecular bonds and generally yields similar gaseous products independent of the parent structure (Table S2). We summarize the potential pathways for the formation of the most common products (C_2F_6, C_2F_4, C_3F_8, C_3F_6, C_4F_8) with *n*-C_4F_{10} as an example in Figure 6. Additional information related to minor, high activation energy perfluorocarbon radical reactions is available in works by Buravtsev and Kolbanovskii[113] and Yu et al.[64]

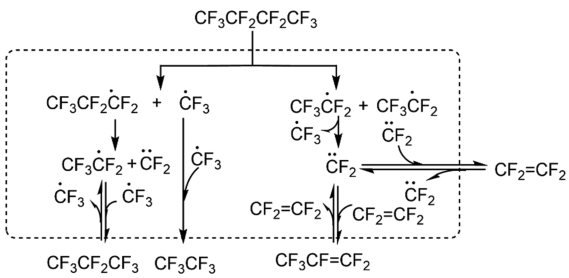

Figure 6. Summarized pyrolysis pathways of perfluorocarbons based on work by Yu et al.[64]

3.3.3. Intermolecular Reactions. 3.3.3.1. Reactions with Radicals and Oxygen. H_2O thermolysis yields •OH and •H at extremely high temperatures (>2000 °C).[114,115] Although the formation of radicals from water thermolysis at typical incinerator temperatures is likely to be low, we discuss their impact on decomposition during thermolysis because they promote decomposition of PFASs by allowing for new decomposition pathways and acting as a source of H for defluorination. In the presence of •OH and •H, abstraction of hydrogen is the dominant reaction pathway for *H*-fluoroalkanes (Figure 7, green box).[116] For sulfonic acids, H abstraction from the sulfonic acid group forms an intermediate M5 which is then decomposed into a corresponding perfluorocarbon radical and

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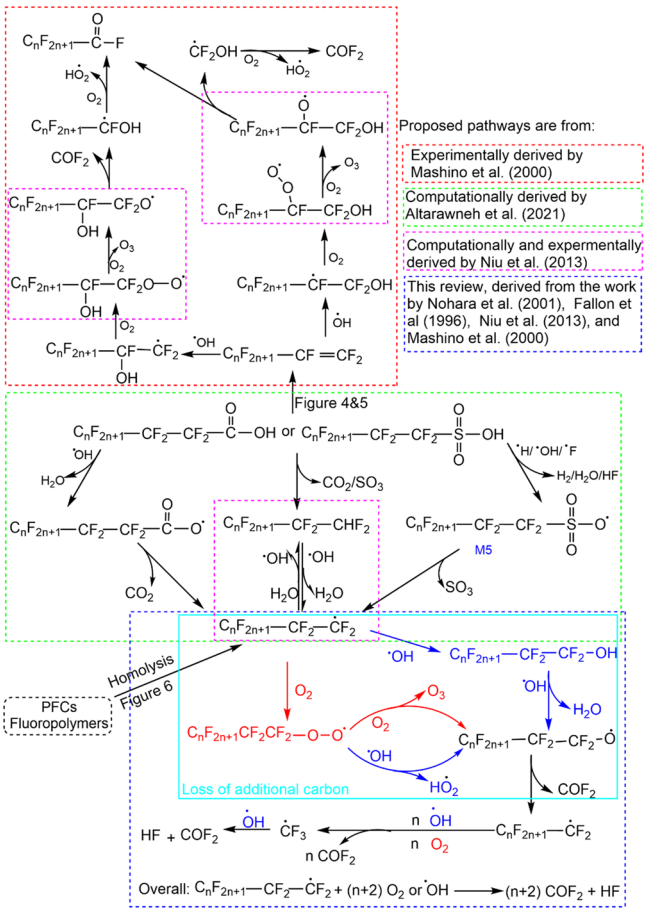

Figure 7. Reactions with •OH and O_2 with PFASs and PFAS decomposition products.[99,117−121] Pathways are generalized regardless of carbon chain length. Dashed boxes indicate literature source (see top right).

SO_3 (Figure 7, green box, right).[99] Similarly, •OH reacts with PFCAs to form a perfluorocarbon radical and CO_2 (Figure 7, green box, left), which has been experimentally observed during drinking water advanced oxidation processes.[117] Although fluorine abstraction is a possible pathway, it is not thermodynamically favored and therefore not illustrated.[116] •OH also attacks carbon−carbon double bonds, initiating the oxidation of perfluoroalkenes in the presence of O_2 to produce corresponding perfluoroacyl fluorides and COF_2 (Figure 7, red box).[118]

On the basis of the mechanisms depicted in the magenta and blue boxes of Figure 7, combined with the appearance of the corresponding expected products in Table S2, we find that the thermal defluorination of PFASs is promoted in the presence of O_2 and H_2O because they participate in reactions with perfluorocarbon radicals. O_2 reacts with perfluorocarbon radicals and the perfluorocarbon chain, and the carbon chain is shortened stepwise through release of COF_2. This has been demonstrated experimentally by the oxidation of PFOA by •OH in an electrochemical system[119] and a photochemical reaction system.[120] The observed formation of COF_2 during thermal decomposition of fluoropolymers provides additional experimental support for this pathway.[72,73]

3.3.3.2. Hydropyrolysis. Water promotes the thermal decomposition of PFASs by hydrolyzing the common intermediate products, perfluoroacyl fluorides (Figure 4, pathway 6; Figure 5, favored pathway; and Figure 7, red box). Perfluoroacyl fluorides are highly thermally stable but react with water to form corresponding PFCAs which are then decomposed to shorter-chain perfluoroacyl fluorides by HF elimination.[122,123] Alternating HF elimination and hydrolysis then occurs, forming shorter and shorter-chain PFCAs (Figure 8).[99,123] An example of such is the formation of PFBA and

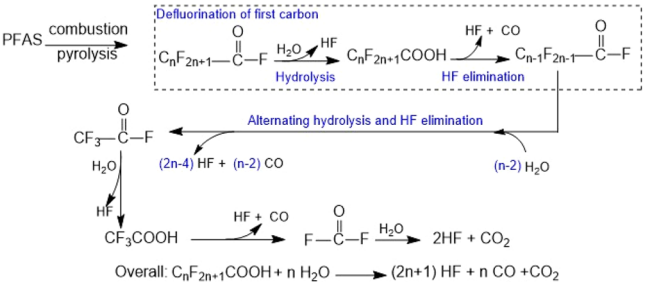

Figure 8. Mineralization of PFASs by alternating hydrolysis and HF elimination during hydropyrolysis.[99,122,123] Combustion and pyrolysis of PFASs to perfluoroacyl fluorides are described in Figures 4, 5, and 7.

PFPeA during PFOA/PFOS hydropyrolysis.[82] The final decomposition product, COF_2, readily reacts with water to produce CO_2 and HF.[124] These reactions have been shown to result in mineralization of F in seconds at temperature as low as 780 °C,[125] but the kinetics at varying temperatures have not been formally measured to our knowledge and are needed to inform hydropyrolytic thermal treatment processes. In the absence of water, the only mechanism which is known to decompose perfluoroacyl fluorides is direct cleavage of intramolecular bonds (Section 3.3.2, R2), resulting in relatively poor defluorination.

At alkaline pH, hydrothermal decomposition of PFOS occurs via OH^- attack of the C alpha to the $-SO_3$, forming a perfluorinated alcohol and SO_3^{2-} (R4).[110,126] The perfluorinated alcohol undergoes HF elimination to form a perfluoroacyl fluoride,[110] which is then hydrolyzed to a corresponding PFCA. The PFCA is ultimately mineralized by decarboxylation and releases F^- (see Figure 8).

$$C_nF_{2n+1} - CF_2 - SO_3^- + OH^- \rightarrow C_nF_{2n+1} - CF_2 - OH + SO_3^{2-} \quad \text{(R4)}$$

3.3.3.3. Reactions with HF. Perfluoroacyl fluorides react with water to form a corresponding PFCA and HF, and this reaction is reversible (R5).[106,127] This mechanism likely competes with those shown in Figure 8, where alternating HF elimination and hydrolysis result in PFAS chain shortening. As an example, perfluoroacyl fluorides have been shown to be formed during pyrolysis of TFA.[106,107,127]

Perfluoroacyl fluorides also react with HF to form perfluoroalkanols by R6.[99] HF may also reversibly react with perfluoroalkenes to form *H*−perfluoroalkanes (R7).[97] Finally, it has been demonstrated that addition of lime to PFAS-containing sludge sequesters F as CaF_2 at temperatures between 300 and 600 °C, but F is released back to the gas phase as HF or SiF_4 at higher temperatures (700−900 °C).[83] These products and decomposition pathways demonstrate that the mechanisms are complex and in many cases lead to the formation of new PFASs which are not part of routine monitoring analyses.

$$C_nF_{2n+1} - COOH + HF \rightleftharpoons C_nF_{2n+1} - COF + H_2O \quad \text{(R5)}$$

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$$C_nF_{2n+1} - COF + HF \rightarrow C_nF_{2n+1} - CF_2 - OH \quad (R6)$$

$$C_nF_{2n+1} - CF = CF_2 + HF \rightleftharpoons C_nF_{2n+1} - CF_2 - CF_2H \quad (R7)$$

3.3.3.4. Surface Catalyzed Reactions. Some oxides (e.g., SiO_2 and Al_2O_3) used as thermolysis reactor materials can participate in the reactions of PFAS thermal decomposition. For example, during pyrolysis of cyclo-C_4F_8 in an inert atmosphere, Butler[87] demonstrated that CO, CO_2, SiF_4, and black solids were produced, and they also noted that the Pyrex reactor was etched. Notably, no oxygen is present in the parent compound, and CO_2 is not a known product of the direct cleavage of fluorocarbon intramolecular bonds (Figure 6). Thus, Butler postulated that R9 and R10 are responsible for the formation of the observed CO, CO_2, and SiF_4. Similarly, CO_2 was formed during the pyrolysis of *n*-C_4F_{10} in an alumina reactor, and once the surface alumina was completely reacted, the formation of CO_2 was significantly reduced.[64]

$$2SiO_2 + \text{cyclo-}C_4F_8 \rightarrow 2SiF_4 + 4CO \quad (R9)$$

$$2SiO_2 + \text{cyclo-}C_4F_8 \rightarrow 2SiF_4 + 2CO_2 + 2C \quad (R10)$$

However, the intermediates during these reactions and reactions of nonfluorocarbon PFASs are not completely resolved. A possible mechanism for fluorocarbons is that some fluoroalkane radicals are formed by direct cleavage of intramolecular bonds (e.g., $\bullet CF_2$, $\bullet CF_3$, and $\bullet C_2F_5$, see Section 3.3.2) which subsequently react with surface oxides.[64,128] This is supported by Ng et al.[129] who found that hydroxyl groups on an Al_2O_3 surface were necessary to degrade a model perfluoroether [$(C_2F_5)_2O$], suggesting that surface hydroxyl groups play a key role in the catalyzed oxidation of PFASs, particularly in inert atmospheres where decomposition of PFASs would typically terminate at the corresponding perfluoroacyl fluoride. This is relevant to incineration of contaminated soils, where surface hydroxyl groups are in abundance but there is a lack of water.

There is also emerging evidence that some metals catalyze thermal PFAS defluorination. For example, nickel catalyzed the decomposition of cyclo-C_4F_8, forming the decomposition product C_3F_8 ~55 times faster than in a Pyrex reactor.[87] Ag and Cu catalyzed the defluorination of perfluoropentacene at ~200 °C.[130] Platinum has been shown in one case to catalyze the pyrolysis of fluorocarbons.[61] Overall, research of catalyzed thermolysis of PFASs is not well studied.

3.4. Thermolysis Kinetics. Published kinetics data are limited, and we are not aware of measured kinetics in the presence O_2 or H_2O. From what has been published, it is evident that thermal unimolecular decomposition of PFASs follows first-order kinetics,[66,87,96] and the relationships between rate and temperature are explained well by the Arrhenius equation.[64,87,95,96,131] Temperature not only has a strong influence on the decomposition rates but also on reaction equilibria.[95] For example, HF elimination (Figure 4, M1) is endothermic, and the equilibrium constant of this reaction increases by approximately 11 orders of magnitude as the temperature is increased from 127 to 727 °C.[95]

Perfluorocarbons are relatively recalcitrant with likely the slowest decomposition rates during pyrolysis. This is evident for perfluoroalkanes (C < 5) which have half-lives greater than 1 h even at temperatures as high as 1000 °C,[61] compared to half-life of PFCAs and PFSAs (<1 s).[96] This is particularly relevant for incinerators because the half-lives of perfluoroalkanes far exceed the typical gas-phase retention time of incinerators (seconds). Perfluoroalkanes may be present in such systems in the feed stream or as decomposition products from other processes.

4. IMPLICATIONS FOR THERMAL TREATMENT PROCESSES

4.1. Treatment Processes. Thermal treatment processes use heat to initiate desorption and degradation of contaminants from a solid or liquid waste. They can be used as a targeted approach to remove PFASs from contaminated matrices such as soil or spent water treatment media (e.g., activated carbon, ion exchange brine), or they can be used as a broad approach to manage mixed municipal solid and hazardous wastes that contain PFASs and are not landfilled.

Thermal decomposition is part of thermal treatment, but thermal treatment encompasses the entire process of thermally treating PFASs, PFAS-containing materials, and the associated products. Thermal treatment processes are often associated generally with the term *incineration*, but incineration is a specific process that is outlined by the US EPA. Title 40 of the Code of Federal Regulations (CFR) Part 260.10 defines an incinerator as any enclosed device that uses controlled flame combustion and is not defined by the CFR as a boiler, sludge dryer, carbon regeneration unit, or industrial furnace, or it is an enclosed device that is operated as an infrared or plasma arc incinerator that has a controlled flame combustion afterburner. Thus, when discussing the thermal treatment of PFASs, one should use the specific terms (i.e., desorption, combustion, pyrolysis) and avoid the use of the term incineration, unless referring to a process described by the CFR.

Thermal desorption uses relatively low temperatures (<600 °C) to separate the contaminant from the solid or liquid waste matrix without the intent to degrade the contaminants, although in some cases they are incidentally decomposed.[132] Thermal desorption includes the energy required to overcome the interaction energy between the PFAS and the solid as well as the energy required to drive the PFAS to the gas phase (volatilization). Thermal desorption can be performed in situ or ex situ. In situ thermal desorption is a widely used method because it eliminates additional costs for transport and/or off-site treatment. It is effective for removing some contaminants at a lower temperature and thus at a lower cost, and those that may form more harmful degradation byproducts at higher temperatures. Although, with thermal desorption, a post-treatment process is always required, which incurs additional costs and complexities to the treatment train. Sörengård et al.[133] demonstrated the use of thermal desorption at temperatures ranging from 150 to 550 °C for a mixture of nine PFASs spiked into two soil types at temperatures ranging from 150 to 550 °C. Greater than 99% desorption of these PFASs from the soil was achieved at 550 °C. The temperature that PFASs desorb can be impacted by the matrix. For example, Crownover et al.[56] showed that desorption was minimal for both PFCAs and PFSAs when the soil was heated to 220 °C for 14 days, despite PFCAs having boiling points below 200 °C.[36] The soil needed to be heated to at least 300 °C to desorb 90% of the PFOA and 60% of the PFOS. Shorter-chain perfluorohexanesulfonic acid desorbed to a lesser extent than PFOS at temperatures below 350 °C. Specific matrix effects that change the required temperature to desorb PFASs are unknown and should be a topic of future studies.

Thermal degradation, which follows or is in conjunction with thermal desorption, is the process of using elevated temperatures (300−1000 °C), often in combination with other

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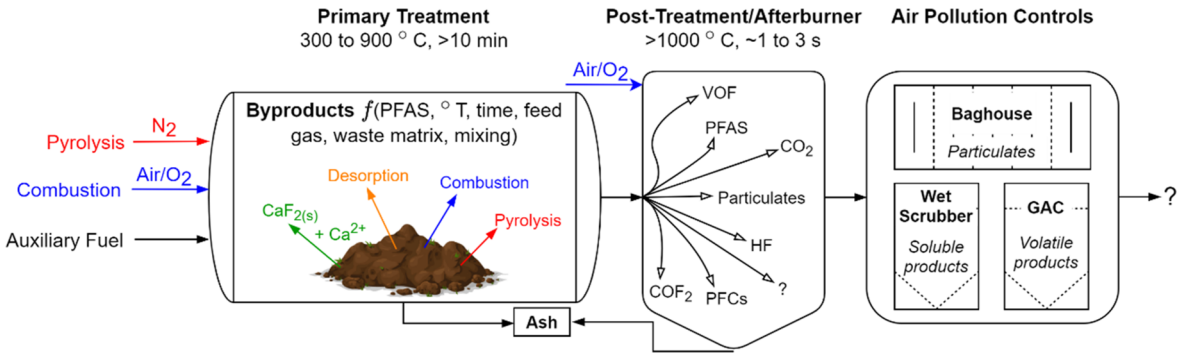

Figure 9. Schematic of a general two-stage thermal treatment system with air pollution control devices installed to treat the produced gases. Potential products and their potential to be captured in typical air pollution control devices are shown. Products formed will depend on temperature, gas mixture (e.g., pyrolysis, combustion), waste components (e.g., calcium), gas turbulence, and residence time.

compounds (e.g., oxygen, catalyst), to bring forth a chemical change in the contaminant. The primary variables that control the efficiency of thermal treatment methods are temperature, gas content, gas- and solid-phase mixing rates, and residence time. For PFASs, thermal degradation has been shown to lead to numerous complete and incomplete combustion products, whose formation depends on the operating conditions and type of PFAS (Table S2).

There are four major thermal degradation technologies: combustion, pyrolysis, gasification, and hydrothermal. Combustion is conducted at stoichiometric or excess oxygen ratios (i.e., excess air). Pyrolysis is performed in the complete absence of oxygen, and gasification is a starved air process performed below stoichiometric oxygen requirements. Hydrothermal treatment processes use water and heat to degrade solid waste at relatively low temperature (<375 °C) but higher pressure (4−22 MPa) and treatment times (>30 min) compared to other thermal processes.[134] It is typically used to treat wastes with a high liquid content, and the temperature and pressure limitations are related to the vapor−liquid critical point of water. Other thermal processes include plasma and microwave treatment. Plasma is an emerging heating technology for extremely high temperature pyrolysis and gasification,[135] but its use has not been specifically applied to PFAS treatment. Microwave heating is an emerging technology for generating rapid temperature changes internally.[136] Gagliano et al. demonstrated that relatively low power microwaves (<500 W) can be used to directly regenerate PFAS-spent GAC, reaching temperatures greater than 600 °C.[137] Combustion is the most commonly used thermal treatment process, and we depict a typical combustion or pyrolysis thermal treatment process treating PFASs in Figure 9, as well as the potential products and the likelihood of products to be captured by typical air pollution control measures.

For PFASs, most of the published combustion studies have involved controlled, laboratory-scale experiments involving the use of simple tube or muffle furnaces.[50,66,81,83,93,138] Lab-scale smoldering has also been investigated. Smoldering, which is a self-sustained combustion, was shown to remove at least 98% of six PFASs from GAC or soil when operated at temperatures above 900 °C.[139] The general consensus across these lab-scale studies is that even the most stable PFASs (e.g., long-chain sulfonates) desorb at temperatures less than 1000 °C, and they are destroyed in the gas phase at temperatures greater than 1000 °C. The critical questions that remain involve the effect of operating parameters (e.g., residence times, oxygen content), the effect of waste type/matrix, the identification of all fluorinated byproducts, and the ability to complete a fluorine mass balance on the system. These questions can be mostly answered at the lab scale with carefully planned experiments, but correlation of the outcomes to a larger scale is also critical. While some studies have confirmed the partial or full removal of PFASs from wastes in a full-scale thermal treatment process,[140−143] there is still a need for more detailed, specific, peer-reviewed studies that probe the impact of operating conditions and completely analyze inorganic and organic volatile fluorine compounds (including PFASs) and HF in the effluent stream.[144]

Further, there are no direct comparative studies on how differing types of full-scale incinerators impact the treatment of PFASs. The incinerator type is defined by the injection, mixing, and heating methods (e.g., fixed or open hearth, rotary film or kiln, fluidized bed, starved air modular). Complete combustion of PFASs will likely be most successful in incinerators that employ a two-stage process. In these, the waste is first fed into the primary combustion chamber where PFASs desorb and partially degrade. The gaseous byproducts are sent to a secondary chamber (the afterburner) that operates in excess air (stoichiometric excess of oxygen) at high temperature (>950 °C) and short residence times (1−3 s). These two-stage incinerators are likely to provide ample residence time to desorb PFASs in the primary chamber and then potentially sufficient temperature and time to mineralize gaseous fluorine products in the secondary chamber.

Although pyrolysis is a common alternative to combustion processes for treating solid waste,[145] there is limited full-scale data on the use of pyrolysis and gasification systems for treating PFASs. Pyrolysis of PFASs forms perfluoroalkanes, olefins, and VOF. Gasification (and combustion) will additionally form oxygenated fluorine compounds (e.g., COF_2). One pilot-plant study treating biosolids containing PFASs confirmed that pyrolysis coupled with combustion was potentially an effective treatment approach, achieving greater than 90% removal of PFOS and PFOA; although, complete defluorination and F mass balance were not achieved.[146]

Hydrothermal treatment is an emerging technology that could be useful for removing PFASs from solid wastes because of the ability of the high-pressure environment to promote defluorination.[134] Yu et al. investigated hydrothermal treatment for destroying PFOA, PFOS, 7:3 FTCA, 8:2 fluorotelomer sulfonate (FTS), and 8:2 fluorotelomer unsaturated carboxylic acid (FTUCA) from wastewater sludge.[147] At a reaction temperature of 350 °C for 90 min, greater than 99% of the carboxylic PFASs were decomposed, but only 34% and 67%

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degradation occurred for PFOS and 8:2 FTS, respectively. Although complete mineralization was not achieved, these results were obtained at a temperature much lower than required for combustion (>700 °C).

One potential solution for the more recalcitrant sulfonates is to amend the liquid phase with acids/bases to catalyze the reactions. Wu et al.[110] showed that conducting hydrothermal treatment at basic conditions at 350 °C for 90 min achieved ∼80% defluorination of PFOS. This approach was confirmed with AFFF waste in a reactor amended with 5 N NaOH.[126] A similar behavior was observed for the hydrothermal treatment of plant biomass. At 300 °C, PFCAs were removed from the biomass to below the detection limit (50% defluorination), and less than 20% removal was observed for PFSAs.[148] The addition of 1 N KOH increased the removal efficiency of PFOS from the biomass beyond 80%, but the shorter-chain PFSAs were less susceptible to destruction (e.g., removal of PFBS was less than 50% observed). This aligns with other destructive technologies, where PFSAs and short-chain PFASs were more recalcitrant.[45,149]

4.2. Co-Occurring Constituents in Wastes. Solid wastes entering thermal treatment systems can be extremely complex, containing myriad co-occurring constituents that may affect the thermal behavior of PFASs. For example, simply changing the PFAS counterion influences both the degradation temperature and the resulting products (Section 3.2.1).[76] The presence of $Ca(OH)_2$ or CaO in the matrix has been shown to affect both the required desorption/degradation temperature and the fate of PFASs during thermal treatment.[83,94,150] In general, for PFAAs, the presence of Ca improved mineralization efficiency and reduced the temperature required for degradation,[83,150] and it prevented the formation of terminal PFAAs when PFAA precursors were treated.[94] In a smoldering column, Duchesne et al.[139] showed that the defluorination efficiency of PFASs was more effective for GAC (44%) compared to a soil (16%). The reason is unknown, but possible mechanisms may be linked to the high specific surface area and porosity of GAC, differing moisture conditions of the solids, differing surface chemistry of the solids, or effects of other constituents in the matrix. Given the complexity of solid waste, attempts to model the thermal behavior PFASs in real systems may prove to be too challenging. Even so, there is a critical need to study the specific effect of co-occurring waste constituents on the thermal behavior of PFASs.

From an operational perspective, the classification of the incinerator will also play a role in deciding what co-occurring constituents will be present during treatment. Municipal, hazardous, and medical waste incinerators are classified as either mass burn or refuse-derived fuel (RDF). For mass burn incinerators, the waste is processed as received, whereas the waste sent to an RDF incinerator is first processed to remove poorly combustible material (e.g., glass, metal), and combustible items are shredded to a uniform size. The removal of glass (i.e., silica) and calcium may alter PFAS degradation pathways because the combustion products (e.g., HF) will react directly with Si and Ca (i.e., Sections 3.3.3.3 and 3.3.3.4).[150] Thus, the thermal behavior of a PFAS is likely to be different in an RDF compared to a mass burn even under similar operating conditions (e.g., temperature).

4.3. Incinerator Solid and Gaseous Byproduct Control Measures. Waste byproducts of incineration include bottom ash, which contain noncombusted products, and gas, containing small particulate and volatile products. Ash, which contains mineralized fluorine but also some PFASs that remain bound to inorganic compounds such as calcium,[150] is typically sent to a landfill or repurposed (e.g., fly ash for concrete). For the gas, there are numerous air pollution control methods available. Particulates that remains in the gas are captured with electrostatic precipitators or baghouses. Numerous methods exist for removing acid gases, including HF that is formed from PFAS thermal conversion. All involve the use of a calcium or sodium salts, such as calcium hydroxide or sodium bicarbonate, forming a corresponding salt (e.g., CaF_2). Escaped HF or volatiles products are presumably captured in the alkaline wet scrubbers, although there is a substantial gap in our understanding of the gas/liquid partitioning (Henry's Law constants) for nearly all PFASs and their combustion products.[53,54] In general, an abundance of information is known about how to capture HF in the gas stream, but very little knowledge exists for removing VOF.

5. IDENTIFYING ANALYTICAL NEEDS TO EVALUATE THERMAL TREATMENT SYSTEMS

The anticipated goal of thermal treatment processes is to completely remove PFASs from the solid/liquid waste and/or mineralize PFASs to CO_2 and inorganic fluorine. Many publications to date report the removal of PFASs from solid or liquid waste matrices but fall short in quantitatively accounting for all fluorine in the system. Reporting a complete F mass balance on thermal treatment systems is important to assess the relative risk of the released products but is challenging because of the following: (1) Numerous fluorinated byproducts are formed (i.e., Table S2). (2) There is no robust analytical method for their quantification. (3) Analysis of multiple phases (gas, surfaces, ash, scrubber liquids) is required.

For targeted PFAS analysis, liquid and gas chromatography−tandem mass spectrometry (LC-MS/MS and GC-MS/MS) can be used to quantify specific PFASs that are present in the produced gas or extractable from the ash.[12,58] However, targeted analysis of PFASs is incapable of quantifying all products, and it has been shown that greater than 50% of postcombustion fluorine is not captured by the sum of LC-MS/MS and HF measurements.[139] Additional compounds can be identified using nontarget analysis, which typically employs high-resolution mass spectrometry (HRMS).[2,151,152] However, this technique is laborious and poorly or not quantitative and does not capture all fluorinated or nonfluorinated products. Achieving a complete mass balance in thermal treatment processes requires total F methods beyond mass spectrometric techniques and measurements of HF.

Common total F analytical approaches include combustion ion chromatography (CIC), particle-induced gamma-ray emission (PIGE), instrumental neutron activation analysis (INAA), and ^{19}F nuclear magnetic resonance (^{19}F-NMR). Schultes et al.[153] showed that CIC, PIGE, and INAA yield similar results when measuring homogeneously packaged samples, but each has advantages and disadvantages. CIC and PIGE have emerged as the most reported methods because of their ease of use, but CIC is more readily available than PIGE.[125] One critical issue for CIC is that it cannot be used to quantify F in solids remaining after combustion (i.e., ash) because CIC requires F to be combusted to HF gas, and ash has already been through a combustion process. PIGE has been used to regularly quantify total F in numerous matrices,[6,153−156] and because it is a direct solid-phase analysis, quantification of total F in all matrices of thermal treatment processes is possible. ^{19}F nuclear magnetic resonance spectroscopy (^{19}F-NMR) has been used to

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measure total F and distinguishes between organofluorine and inorganic F in solids,[157] but poor detection limits (ppm levels) impede its broad application.

Gas-phase compounds may be captured by activated carbon, hydrophobic−lipophilic balance media, or polyurethane foam/XAD samplers[58,158] and then analyzed by LC-MS/MS or GC-MS/MS for targeted compounds or by various total F methods. These methods are validated for well-studied PFASs. However, the capture and recovery of PFAS thermal decomposition products is unknown, and there is a lack of knowledge regarding how sampling procedures may bias the results (i.e., formation of dioxins during cooling of combustion gases).[159] Additionally, GC-MS/MS measurements of gas-phase PFASs using electron impact ionization results in fragmentation spectra that are similar for most PFASs, with prominent product ions representative of the fluoroalkyl chain (e.g., 69 m/z CF_3^+, 119 m/z $CF_2CF_3^+$, 169 m/z $CF_2CF_2CF_3^+$).[58] Chemical ionization reduces fragmentation, but not all GC-MS are equipped with chemical ionization sources.[160,161] Volatile fluorine products can also be measured by Fourier transform infrared spectroscopy (FTIR), and it has been used to quantify COF_2, HF,[162] and CF_4, and C_2F_6.[163] The greatest challenge of employing FTIR to measure such compounds in the gas phase is calibrating the instrument, as pure gas-phase standards used for generating calibration curves are not widely available.

Applying these various capture and analytical schemes is challenging but represents a meaningful first step toward closing the fluorine mass balance. Knowledge of important gaseous products is essential to design and operate next-generation incineration processes that truly achieve complete mineralization of PFASs.

6. KNOWLEDGE GAPS AND RESEARCH NEEDS

The thermal decomposition of only a limited group of mostly pure-phase PFASs under pyrolysis conditions have been thoroughly investigated to date. The implications of such a limited range of studies are relevant to industries, municipalities, and regulators interested in using thermal treatment processes to manage PFAS wastes. Past research focused primarily on determining temperatures that initiate desorption and degradation, as measured by mass loss of the PFASs from the waste. Other studies, to a more limited extent, include measurements or computational predictions of likely decomposition mechanisms and expected products. There are significantly more studies that used computational chemistry to make such conclusions than there are those that used experimental measurements. Some of the coinciding experimental and computational studies do not agree, and several differ significantly. Thus, there is a critical need to conduct studies that incorporate both computation and experimental measures.

A major weakness of existing mechanistic studies is that they do not mimic full-scale thermal treatment systems, which have operational variations that are significantly different than lab-scale systems. There is also a lack of knowledge about the efficiency of full-scale effluent treatment processes for the thermal degradation products of PFASs. While these processes should capture the numerous products, additional studies are required to confirm this hypothesis. Closing the fluorine mass balance on ash, scrubber solutions, and gaseous emissions should be a priority in the near term to understand the fate of PFASs in incinerators having been operated for the past several decades and to understand how to modify incinerator processes in the future.

To adequately assess the fate of PFASs in thermal treatment systems requires analytical techniques that can close the F mass balance. Key to this will be total fluorine measurements because mass spectrometry-based methods do not have readily available standards for the numerous products that may form. Further, measurements of PFASs in the produced ash is a significant challenge, as the detection limits for total fluorine instrumentation (CIC, PIGE, NMR, INAA) are high, and thus, sample preparation and concentration methods are needed if trace levels are to be reached.

To improve upon the understanding of the fate of PFASs during thermal treatment, we propose the following ranked research needs:

(1) Experimental studies of relevant mixtures of PFASs during combustion on different types of surfaces (soils, activated carbon, ion exchange, liquid brines). Although some PFAS decomposition pathways in oxidizing atmospheres are provided in this review, most of the experimental literature focuses on pyrolysis, and therefore, more knowledge relevant to commercial incinerators is needed.
(2) Measurements of Henry's Law constants of organofluorine compounds. Henry's Law constants include interactions with water and better represent environmental systems and incinerator air pollution control measures than vapor pressure (pure compound). These measurements will lead to an understanding of which PFASs are the most likely to elude air pollution control measures. Such constants are not generally available, and combined with the first research need, will provide knowledge of which PFASs are the most likely to be released in flue gases during thermal treatment.
(3) Experimental confirmation of computational studies. Select studies have focused on experimentally derived decomposition, and there is some divergence published between computation and experimental results. Robust studies are needed that incorporate experiments used to validate computational models.
(4) Development and validation of instrumentation and sampling and analytical methods capable of measuring products identified in research needs 1, 2, and 3. These methods will help to close the mass balance on fluorine during thermal treatment and better understand the fate of PFASs.
(5) Experimental research of PFAS decomposition products and temperature-dependent kinetics and pathways of formation of less studied PFASs (e.g., fluorotelomers, iodinated PFASs, PFPAs, perfluorophosphinic acids).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c02251.

Additional figures and a table related to vapor pressure of PFASs and a table containing measured and reported thermal decomposition products from published literature (PDF)

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Notes

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