

Per- and Polyfluoroalkyl Substances (PFAS): Incineration to Manage PFAS Waste Streams

Background

Per- and polyfluoroalkyl substances (PFAS) are a very large class of man-made chemicals that include PFOA, PFOS and GenX chemicals. Since the 1940s, PFAS have been manufactured and used in a variety of industries in the United States and around the globe. PFAS are found in everyday items such as food packaging, non-stick stain repellent, and waterproof products, including clothes and other products used by outdoor enthusiasts. PFAS are also widely used in industrial applications and for firefighting. PFAS can enter the environment through production or waste streams and can be very persistent in the environment and the human body. PFAS have many and varied pathways into waste streams, presenting challenges for ultimate disposal. Determining the appropriate method for ultimate disposal of PFAS wastes is a complex issue due to their volatility, solubility, and environmental mobility and persistence. EPA is currently considering multiple disposal techniques, including incineration, to effectively treat and dispose of PFAS waste.

Options and Considerations for the Disposal of PFAS Waste via Incineration

One potential disposal method for PFAS waste is through high temperature chemical breakdown, or incineration. Incineration has been used as a method of destroying related halogenated organic chemicals such as polychlorinated biphenyls (PCBs) and ozone-depleting substances (ODSs), where sufficiently high temperatures and long residence times break the carbon-halogen bond, after which the halogen can be scrubbed from the flue gas, typically as an alkali-halogen. PFAS compounds are difficult to break down due to fluorine's electronegativity and the chemical stability of fluorinated compounds. Incomplete destruction of PFAS compounds can result in the formation of smaller PFAS products, or products of incomplete combustion (PICs), which may not have been researched and thus could be a potential chemical of concern.



Incineration of halogenated organic compounds occurs via unimolecular decomposition and radical reaction. For unimolecular decomposition, fluorinated organic compounds likely require higher temperatures to achieve 99.99% destruction in 1 second residence time than do their chlorinated counterparts. Unimolecular decomposition of highly fluorinated organics most likely occurs through breakage of C-C or C-F bonds (Tsang et al., 1998). The most difficult fluorinated organic compound to decompose is CF_4 , requiring temperatures over $1,400^\circ\text{C}$, but is easily monitored, making it a potential candidate for destructibility trials.

Fluorinated organic compounds can also be degraded via incineration by free radical initiation, propagation, and branching mechanisms. Although hydroxyl radical reaction with hydrocarbons is a common combustion flame-propagating mechanism, the strength of the C-F bond makes this pathway unlikely and would instead leave atomic hydrogen, formed at high temperatures, as the likely radical reacting with the carbon-bonded fluorine.

Radical reactions are more likely for chloroalkanes than fluoroalkanes, due to the lower bond energy of C-Cl (Tsang et al., 1998). If formed, the extremely high electronegativity of fluorine radicals results in their quick combination with other radical species, preventing flame-sustaining free radical propagation and branching processes. This propensity to terminate free radical chemistry make PFAS effective fire suppressants.

The stability of perfluorinated radicals leads to higher concentrations and correspondingly increased propensity to recombine, creating larger molecules that are products of incomplete combustion (PIC) and distinctive from the original fluorinated organics. These reactions are promoted by partial organic combustion resulting from insufficient temperatures, time, and mixing. In addition, the presence of catalytic surfaces, often metals, promotes further reaction and PIC formation in post-combustion regions. This scenario has been most studied related to the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs) in the cool-down regions of waste incinerators.

The effectiveness of incineration to destroy PFAS compounds and the tendency for formation of fluorinated or mixed halogenated organic byproducts is not well understood. Few experiments have been conducted under oxidative and temperature conditions representative of field-scale incineration. Limited studies on the thermal destructibility of fluorotelomer-based polymers found no detectable levels of perfluorooctanoic acid after 2 second residence time and 1,000°C (Yamada et al., 2005; Taylor et al., 2014). Emission studies, particularly for PICs, have been incomplete due to lack of necessary measurement methods suitable for the comprehensive characterization of fluorinated and mixed halogenated organic compounds.

Addressing Gaps in Research for PFAS Waste

The extent to which PFAS-containing waste material in the United States is incinerated is not fully documented or understood. PFAS compounds are not listed as hazardous wastes under the Resource Conservation and Recovery Act (RCRA) nor as hazardous air pollutants under Clean Air Act regulations, so they are not subject to the tracking systems associated with these regulations.

EPA is currently considering multiple disposal techniques, including incineration, to effectively treat and dispose of PFAS wastes. EPA researchers are currently studying PFAS incineration, sampling and analytical methods development, and industrial field sampling. Research on thermal stability of PFAS compounds, the ability to fully

capture and identify PFAS compounds and their thermal decomposition byproducts, and the efficacy of emission control technologies are areas of targeted research. These efforts, in cooperation with states and industries, is aimed at proper disposal of PFAS-laden wastes without media-to-media transfer or environmental release.

References

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Note: This technical brief is a summary of the science and does not necessarily reflect EPA policy.