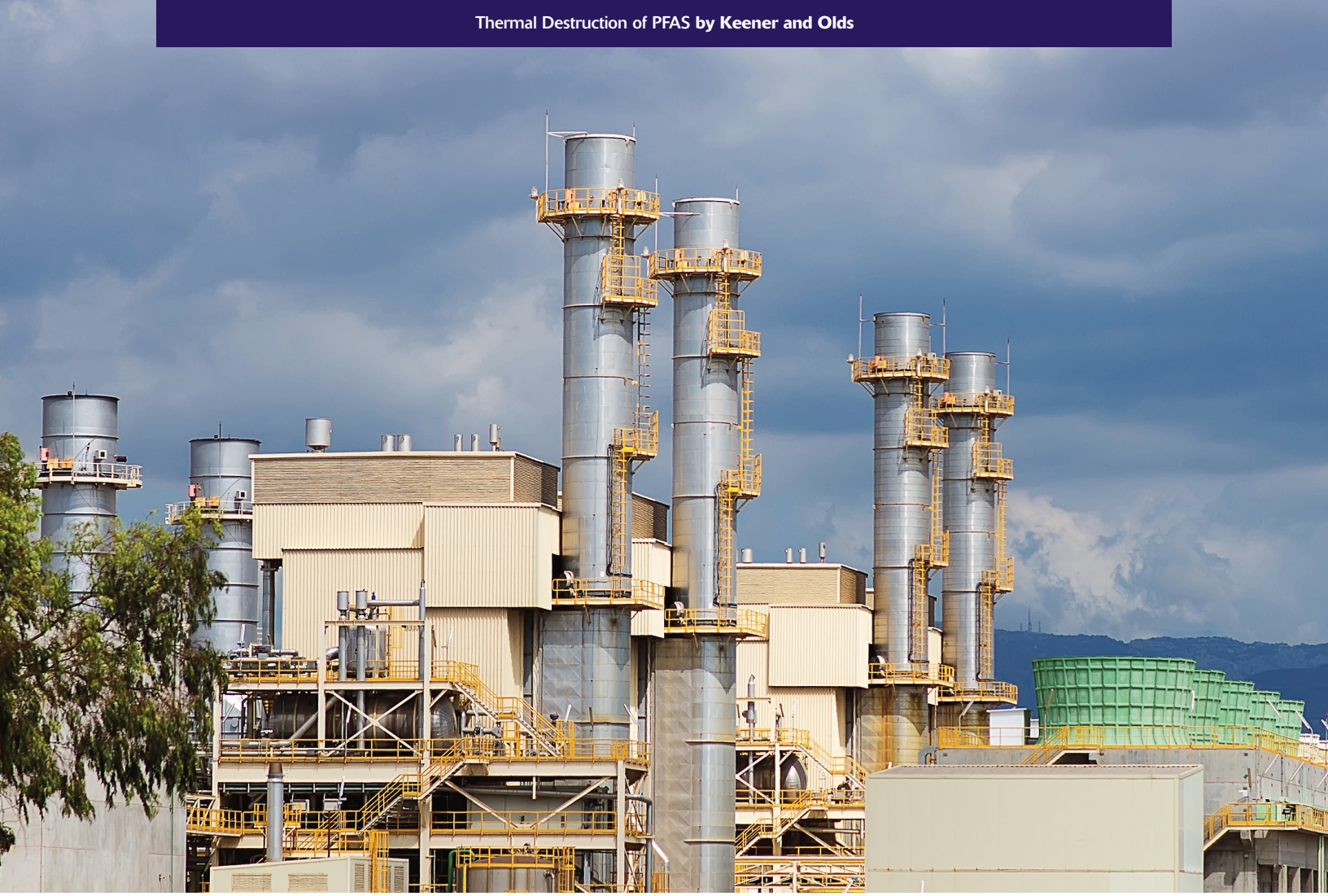

Principles of Thermal Destruction of PFAS

by Melvin Keener and Andy Olds

A look at some of the key issues facing the PFAS destruction industry.

There are four major issues facing the per- and polyfluoroalkyl substances (PFAS) destruction industry. These issues are the same for all destruction techniques. They are not unique to the thermal treatment industry. The issues are destruction of the original compound; the minimization of products of incomplete destruction; control of the acid generated; and test method selection. Each issue is considered in the following discussion.

Destruction of the Original Compound

A method to demonstrate initial destruction of organic chemicals by hazardous waste incinerators has been in place since the promulgation of 40 CFR Part 264 Subpart O in 1981. This method is a destruction and removal efficiency (DRE) test. It has been incorporated into 40 CFR Part 63 Subpart EEE for hazardous waste combustor sources regulated under the U.S. Clean Air Act.

To make this demonstration, the facility must conduct a test proving they can destroy at least 99.99% of an organic compound that is more difficult to destroy than the compounds they would normally treat. In the process of conducting that test, operating parameter limits are established so the facility can demonstrate continuous compliance. In the guidance document for hazardous waste incinerators, the U.S. Environmental Protection Agency (EPA) discusses the concepts for demonstrating DRE for organic hazardous waste. In the opening paragraphs of this guidance document, EPA explains this concept:

"The Subpart O regulations require that POHCs (Principal Organic Hazardous Constituents) be designated for each waste feed. The required DRE must then be demonstrated for the POHCs during the trial burn. Since the POHCs must be representative of the waste feed, they are chosen on factors such as difficulty to incinerate and concentration in the waste feed. The operator is then limited in the permit to burning only waste containing hazardous constituents no more difficult to incinerate than the POHCs for which compliance was demonstrated during the trial burn."[1]

This guidance gives detailed instructions on selecting POHCs and the entire process of demonstrating DRE. Hazardous waste combustion facilities have used this guidance since 1989 to demonstrate the ability to meet these criteria. Appendix VIII of the guidance contains a list of organic compounds ranked on how difficult they are to destroy (thermal stability index). Class 1 chemicals on this list are the most difficult to destroy. For example, chlorobenzene is a Class 1 chemical. When a facility demonstrates a minimum DRE of 99.99% for chlorobenzene, it is inferred that the facility can destroy a similar or greater percentage of any organic chemical ranked lower in Class 1 or any chemical in Classes 2 through 7. This concept has been used by hazardous waste incinerators since 1989 to meet the requirement in the Resource Conservation and Recovery Act (RCRA) and since 1999 to meet the requirements under the Clean Air Act. The same logic can be used to show the destruction of PFAS compounds.

The method for demonstrating the destruction of organic compounds is to conduct a test where the facility selects one or more POHCs that is at least as difficult to destroy as the constituents in waste feed and prove they can destroy at least 99.99% of those POHCs. In the process of conducting a successful DRE test, the facility sets the operating limits that are used to demonstrate continuous compliance with the DRE requirement. While PFAS have some unique properties, in the end, they are organic compounds. Selecting the proper POHC and using the DRE testing process can be used to demonstrate destruction of the original PFAS compounds for any destruction methodology.

The last time the thermal stability index spreadsheet was updated was in 2001 and it did not contain any PFAS compounds. It contained organo-fluoride compounds but no PFAS compounds (as currently defined). Additional research work has developed estimates on where various PFAS compounds fit into this index. Several publications[2-5] have reported either thermal stability rankings or the temperature where thermal destruction of certain PFAS compounds occur. For example, the UDRI study[3] estimated that both perfluorooctanoic acid and perfluorooctane sulfonic acid would be Class 2 compounds. Other examples of Class 2 compounds in the current index are toluene and tetrachloroethene.[1] There are data on other common PFAS compounds in the four publications referenced above.

EPA should update this index to include this new information on PFAS thermal stability. From these data, one can conclude that the destruction of the original PFAS compound is not difficult based on their thermal stability index rankings. This has been shown in the laboratory[6] and in two full-scale hazardous waste incinerator test programs (see accompanying articles in this issue by **Martin, et al.** and **Zemba and Estabrooks**).

Minimization of Products of Incomplete Destruction

Destroying the original PFAS compound does not prove that all carbon-fluoride bonds have been destroyed (mineralization). Several researchers have attempted to develop an organic fluoride measurement method to show there are no carbon-fluoride compounds remaining in the flue gases, but this has been unsuccessful. Research has shown that supplying excess oxygen and hydrogen[7] at the proper temperature and residence time can minimize products of incomplete destruction (PID).

One of the keys to minimizing PID formation is to set the combustion conditions to drive the majority of the free fluoride to form hydrogen fluoride that can be easily scrubbed (more on this later). This can be done with a combination of the three T's of combustion—temperature, time, and turbulence—and making sure there is an excess of oxygen and hydrogen. This has been successfully demonstrated in the laboratory[6] and in the field (two accompanying articles). While it is theoretically and practically impossible to completely demineralize any organo-halide (reduce the PIDs to zero), they can be reduced to a low or non-detectable level.

Acid Gas Control

The final step is to show that the hydrogen fluoride (HF) generated is adequately controlled. The theoretical performance of wet scrubbers for the removal of hydrogen chloride (HCl) and HF is determined by three main factors:

- **Gas-phase resistance:** the device's ability to promote diffusion of the acidic gas to the liquid surface;
- **Gas-liquid equilibrium:** defined by the Henry's Law constant; and
- **Liquid-phase resistance:** the device's ability to diffuse the acid gas away from the liquid surface or promote reactions that reduce its influence at the gas-liquid interface.[8]

The theoretical performance of dry scrubbers for the removal of HF or HCl is driven by:

- **Gas-phase resistance:** the device's ability to promote diffusion of the acidic gas to the liquid or solid surface; and
- **Gas-liquid or gas-solid equilibrium:** for slurries, defined by the Henry's Law constant; for solids, dependent on reaction kinetics.

For both HCl and HF, the properties governing the gas-phase resistance—gas density, viscosity, and diffusivity—are similar. However, the smaller molecular size of HF improves its diffusivity, allowing it to diffuse slightly faster to the absorbent or adsorbent surface. While overall capture depends on the design of the control device, HF should theoretically be captured more efficiently than HCl.

Destroying the original PFAS compound does not prove that all carbon-fluoride bonds have been destroyed.

Henry's Law constant defines the gas-liquid equilibrium. A higher constant implies greater absorption. The constant for HF (130 mol/m3-Pa @ 25°C) is nearly an order of magnitude greater than that for HCl (15 mol/m3-Pa @ 25°C),[9] showing that HF absorbs more rapidly and thoroughly than HCl.

Liquid-phase reactions involving both acids minimize further liquid-phase resistance. HF disassociates and hydrolyzes readily in water, instantly reducing its gas concentration at the interface. It also reacts with alkalis such as sodium and calcium to form stable salts. Likewise, HCl disassociates in water and reacts with alkalis. For either acid, liquid-phase resistance is minimal and insignificant.

Although performance can vary depending on the specific design, operation, and reagent of a dry scrubber, removal efficiencies for HCl and HF are predictable, consistent, and well documented (e.g. approximately 98% of HCl and HF can be removed by injection of trona or sodium bicarbonate[10] and almost all the studied sorbents were allowed to obtain better efficiency of flue gas cleaning from HCl and HF[11]). Thus, HF appears to be easier to control than HCl in a well-designed and operated acid gas air-control system.

Test Methods

EPA developed Other Test Method (OTM) 45 as an air method to measure approximately 50 polar, semi-volatile PFAS compounds. Revision 1[12] was posted in 2025. OTM-50[13] is a canister method designed to measure 30 specific volatile, non-polar fluorinated compounds. OTM-55 is an adaptation of SW-846 Method 0010 that uses methylene chloride and acetone rinses to extract non-polar, semi-volatile PFAS compounds. OTM-55 is expected to be released late in 2026. While these methods measure only a small fraction of the thousands of PFAS compounds, they are adequate to show DRE of the OTM-45 target analyte compounds and measure PIDs. OTM-45 and OTM-50 will need additional work to convert them into EPA reference methods. However, for now, they are adequate to use to show destruction of the original compounds and minimization of PIDs,

Conclusion

As has been demonstrated in the laboratory and the field, hazardous waste combustors can efficiently destroy the original compounds, minimize the emissions of PIDs, and properly capture the acid gases at scale. EPA should update the thermal stability index and allocate resources to convert all three OTMs to reference methods. All destruction technologies should be held to the same standard. **em**

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