

Breaking Down PFAS @ CDM Smith

By Dora Chiang, CDM Smith Vice President and Remediation Technical Services Leader

January 2019

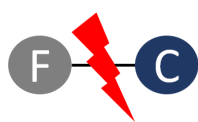


Since 2012 we have been actively developing PFAS destruction technologies. The following highlights the background and concept of PFAS destruction, its need and applicability, and how to confirm that PFAS destruction is occurring.

What is PFAS Destruction? Is it Different from PFAS Transformation?

In our March 2019 PFAS Newsletter, we introduced two treatment technologies—granular activated carbon (GAC) and anion exchange resin (AIX)—for removing PFAS from drinking water and groundwater. Both technologies rely on physical “separation” to remove PFAS molecules with a “sorbent”, like GAC or AIX. PFAS accumulate onto the sorbent until it is spent (with evidence of PFAS breaking through the sorbent). PFAS accumulated on spent sorbent are only destroyed in a high temperature (1000°C) incinerator. However, it is not a standard practice to incinerate spent GAC or AIX around 1000°C, because it is energy intensive and not practical for disposing large quantities of PFAS wastes. Currently, there is no clear guidance on managing PFAS-laden wastes. As such, spent GAC or AIX are often disposed in local landfills or are incinerated at temperature below 1000°C, which removes PFAS from spent sorbent but does not destroy them. In addition, there are concerns about accidental PFAS releases during shipping and handling PFAS-laden wastes off site.

“Recirculating” PFAS in the environment from one media to another without destruction draws significant concern globally. Thus, scientists have invented and developed technologies for permanently destroying PFAS for the benefits of local waste management and for PFAS mass reduction.



So why are PFAS chemicals so hard to destroy? The carbon-fluorine bond is one of the strongest bonds in chemistry. It takes higher energy to break carbon-fluorine bond than any other carbon bond (e.g. carbon-hydrogen bond, carbon-oxygen bond, or carbon-chlorine bond). The high energy requirement to destroy PFAS makes removal of PFAS in large volumes of water (e.g. drinking water treatment systems at scales of millions of gallons per day) infeasible technically and economically.

You may have heard that PFAS precursors can be “transformed” or “converted” into perfluoroalkyl acids (PFAAs) as terminal products. Is this PFAS transformation considered PFAS destruction? If a technology accelerates precursor transformation, is it considered a PFAS destruction technology?

During PFAS transformation, PFAS precursors do change its chemical structure. Some transformation processes do not alter the carbon backbone (the tail with C-F bonds), but some may go through defluorination step (such as dehydrofluorination). But the “transformation” does not break down *all* carbon fluorine bonds. And such transformation process often ends up generating PFAAs as terminal products. **Destruction technology for PFAS is defined as a**

technology that can completely defluorinate PFAAs (such as PFOS and PFOA) to innocuous end products.

[How Do We Confirm PFAS Destruction?](#)

Currently, most PFAS destruction technologies can result in formation of intermediate products, and careful design of treatment systems must include site-specific characteristics to prevent accumulation of persistent, harmful fluorinated chemicals (e.g. PFAAs). A successful destruction technology should ultimately achieve a closed mass balance by measuring the amount of fluoride generated from the complete defluorination process. Our proven approach to conducting treatability testing of PFAS destruction technologies includes the following three lines of evidence to confirm complete PFAS destruction.

1. Disappearance of target PFAAs as the first line of evidence. “Target” PFAAs are defined as those PFAAs that can be quantitatively measured.
2. Accumulation of fluoride as the most direct evidence of defluorination and PFAS destruction. In case of precursor transformation or incomplete destruction, fluoride generation is also possible.
3. Reduction of total organic fluorine concentration. Due to the complex nature of PFAS and relatively small number of target PFAS that can be quantitatively measured with current analytical chemistry, it is highly possible that unmeasurable non-target PFAS are also present in the a treatment system. A good fluorine balance requires the estimate of total organic fluorine in and out of destruction process plus fluoride generation.

Our multiple-lines of evidence approach results in more accurate verification of total fluorine removal within the PFAS destruction treatment system. Analytical methods that can be used to estimate total organic fluorine concentrations include Total Oxidizable Precursor Assay (TOPA, See CDM Smith February 2019 PFAS Newsletter for more information), nontarget PFAS analysis (which semi-quantitatively identify and measure non-target PFAS), and total extractable organic fluorine analysis. Non-target PFAS analysis and total extractable organic fluorine analysis are only available at research laboratories and have not yet been commercialized. Therefore, the next steps in advancing state of the practice of PFAS destruction technologies should also include further development and commercialization of additional analytical tools so these three lines of evidence can be used to verify field-scale treatment performance.

[When Can PFAS Destruction Be Applied?](#)

Because of the energy requirements, feasibility and economics of PFAS destruction technologies, they are considered applicable for high-strength, low volume PFAS concentrates. The following are types of PFAS concentrates for PFAS destruction:

- AFFF concentrates
- Groundwater in the PFAS source areas
- Remediation waste streams (such as wastewater generated from regeneration of GAC or regenerable ion exchange resin, foam fractionation, soil washing, rejected reverse osmosis concentrates, chemical or electro-coagulation)

Often, the destruction technology will be coupled with another treatment technology that will concentrate lower-concentration streams to generate a high-strength, low volume concentrated waste stream.

Types of PFAS Destruction Technologies

There are numerous PFAS destruction technologies under development. The [ITRC PFAS Fact Sheet on remediation technologies](#) summarizes PFAS destruction technologies under development. Ex-situ destruction technologies include several promising options, such as electrochemical (Schaefer et al. 2015; Urriaga et al. 2015), sonolytic (Vecitis et al. 2008; Rodriguez-Freire et al. 2015), plasma (Stratton et al. 2017), and reductive (Arvaniti et al. 2015) technologies. These approaches have successfully degraded an array of high concentration PFAS at the laboratory scale. However, none of these technologies are sufficiently mature yet to assess PFAS treatment costs and overall effectiveness with confidence at the field scale.

In addition to the ex-situ technologies, use of laccase enzymes as catalysts to facilitate humification (“break-down”) of PFOS and PFOA has been demonstrated in laboratory studies and shown effective for both water and soil systems (Luo et al. 2015, Luo et al. 2018). However, slow degradation rates have limited its application to sites where long-treatment timeframes are acceptable. Recent study also shed light that PFOS may be biodegradable when certain geochemical conditions and microbial communities are present at a site (Huang and Jaffe 2019). However, the biodegradation rates are also too slow to be considered effective for field demonstration. As such, in situ treatment of PFAS is an emerging field within research and development.

Is Destructive Technology Ready for Prime Time? What Are the Major Limitations?

There are several ex-situ destructive technologies that have moved from flasks to the field- 1) plasma, 2) sonolysis, 3) electrochemical oxidation and 4) ultraviolet oxidative/reductive destruction. However, because of the potential significant emerging market for destructive PFAS technologies, they are often promoted within industry without fully demonstrating complete defluorination and without confidence the technology can meet stringent effluent discharge requirements. As such, careful consideration of the applicability of these technologies for a specific site and/or application must continue to include treatability and pilot studies to verify technology performance before investment in full-scale treatment systems. Consideration of balanced technology benefits and limitations that should be discussed with technology providers include:

- High energy demand and feasibility of high energy/cost at the scale required for the system.
- Health and safety concerns.
- Feasibility of operating large-scale systems, if required.
- Incomplete PFAS destruction resulting in accumulation of fluorinated intermediates that are generated but not measurable.
- Feasibility of achieving stringent (i.e. very low) treatment requirements, often a treatment train approach (such as use of high capacity AIX) may be needed before effluent discharge.
- Effectiveness in destroying all PFAS chemicals, including short chain PFAS. Typically, destructive technologies are more effective in removing long chain compared to short chain PFAS, which can accumulate during the treatment because of incomplete defluorination and slower destruction rates.

- Generation of non-PFAS toxic byproducts. For instance, perchlorate is known to be formed during electrochemical oxidation treatment due to the aggressive oxidation of chloride in the feedwater. Although perchlorate can be addressed easily, treatment systems must account for, and treat, perchlorate in the process.

Regulatory Acceptance of PFAS Destruction Technologies

In the US, PFAS destruction technologies are currently being field demonstrated at DoD sites with no published data yet. When planning for field demonstration, the following questions may be encountered from the regulators:

- The fate and transport of amendments, parent PFAS, PFAS intermediates and byproducts
- The chemical constituents in the treatment effluent and their impact to water quality
- The feasibility and effectiveness of treatment technology to achieve stringent discharge limits
- The evidence of complete PFAS destruction to innocuous end products

PFAS Destruction Technology Development at CDM Smith

At CDM Smith, our approach to assessing PFAS destructive technologies at a site includes treatability testing at the bench, pilot and full-scale using three lines of evidence to confirm complete PFAS destruction. Our collaboration with universities and research foundations allow us to explore the latest analytical methods for understanding the destructive mechanisms, kinetics, formation of toxic intermediates and end products, and bring the most effective means and methods to our projects. Our Bellevue laboratory specializes in treatability studies for development, design and optimization of PFAS destruction based on direct fluoride measurements in our laboratory. Through our partnerships, we ensure emerging analytical chemistry methods such as target and nontarget PFAS analysis and analysis of total extractable organic fluorine and byproducts (such as perchlorate) are incorporated into our test plans. We have active and ongoing projects evaluating the following destructive technologies funded by multiple federal agencies:

- Electrochemical oxidation using boron-doped diamond (BDD) electrodes as an electrochemical oxidation technology to destroy PFAS (AFCEC BAA Project: completed in 2015, Principal Investigator (PI): Dr. Charles Schaefer at CDM Smith)
- Electrochemical oxidation technology for PFOA and PFOS decomposition in groundwater. The project used BDD and mixed metal oxide anodes to degrade PFAS and confirmed efficient defluorination for PFOS and PFOA, with 98% and 58% recovery as fluoride, respectively (Navy Funded Project: completed in 2015, PI: Dr. Charles Schaefer at CDM Smith)
- Electrocatalytic and catalytic approaches for *in situ* PFAS treatment. Electrocatalytic: ruthenium oxide-coated titanium + mixed metal oxide anodes to oxidize PFAS (SERDP Funded Project, completed in 2018, PI: Dr. Charles Schaefer at CDM Smith)
- A field demonstration of PFAS removal by nanofiltration, then PFAS' destruction by sequential ultraviolet oxidative/reductive in reject water (AFCEC BAA Project; ongoing 2017-2020, PI: Colorado School of Mines, Co-PI: Dr. Charles Schaefer at CDM Smith)
- Evaluate treatment technologies for removing and destroying PFAS at bench and pilot-scale testing levels for potable water production at 39 drinking water utilities. Integrates findings into life cycle cost assessments and utility guidance (Water Research Foundation Project: ongoing 2019-2022, PI: North Carolina State University, Co-PI: Dr. Charles Schaefer at CDM Smith)

- Coupled regenerable ion-exchange resin and destruction (electrochemical and photochemical treatment) technologies for PFAS removal and destruction. Studies the influence of co-contaminants on resin adsorption of PFAS. Uses life-cycle cost analysis and LCA modeling throughout to guide experimental design decisions (SERDP Funded Project: ongoing 2017-2020, PI: Colorado School of Mines, Co-PI: Dr. Charles Schaefer at CDM Smith)
- Coupled electrochemical coagulation with electrochemical oxidation to concentrate, then destroy PFAS in waters (SERDP Funded Project: ongoing 2018-2021, PI: Dr. Dora Chiang at CDM Smith)
- Coupled ion-exchange resin with electrochemical oxidation for complete separation and destruction of PFOS and PFOA in groundwater (AFCEC BAA Project: ongoing 2017-2021, PI: Dr. Dora Chiang at CDM Smith)

CDM Smith has the following publications associated with PFAS destruction technologies:

Charles E. Schaefer, Christina Andaya, Ana Urtiaga, Erica R. McKenzie, Christopher P. Higgins (2015) Electrochemical treatment of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) in groundwater impacted by aqueous film forming foams (AFFFs), Journal of Hazardous Materials, [Volume 295](#), 170-175

Charles E. Schaefer, Christina Andaya, Aniela Burant, Charles W. Condee, Ana Urtiaga, Christopher P. Higgins (2017) Electrochemical treatment of perfluorooctanoic acid and perfluorooctane sulfonate: Insights into mechanisms and application to groundwater treatment. Chemical Engineering Journal, Volume 317, 1 June 2017, Pages 424-432

Charles E. Schaefer, Sarah Choyke, P. Lee Ferguson, Christina Andaya, Aniela Burant, Andrew Maizel, Timothy J. Strathmann, Christopher P. Higgins (2018) Electrochemical Transformations of Perfluoroalkyl Acid (PFAA) Precursors and PFAAs in Groundwater Impacted with Aqueous Film Forming Foams, Environmental Science and Technology, 52(18): 10689-10697

Jinyong Liu, Daniel J. Van Hoomissen, Tianchi Liu, Andrew Maizel, Xiangchen Huo, Seth R. Fernández, Changxu Ren, Xin Xiao, Yida Fang, **Charles E. Schaefer**, Christopher P. Higgins, Shubham Vyas, Timothy J. Strathmann (2018) Reductive Defluorination of Branched Per- and Polyfluoroalkyl Substances with Cobalt Complex Catalysts. Environ. Sci. Technol. Lett. 5(5): 289-294

Charles E. Schaefer, Christina Andaya, Andrew Maizel, and Christopher P. Higgins (2019) Assessing Continued Electrochemical Treatment of Groundwater Impacted by Aqueous Film-Forming Foams. Journal of Environmental Engineering, 145 (12): 06019007

Shangtao Liang, Randall "David" Pierce Jr., Hui Lin, **Sheau-Yun (Dora) Chiang**, Qingguo "Jack" Huang (2018), Electrochemical oxidation of PFOA and PFOS in concentrated waste streams, Volume 28, Issue 2, Pages 127-134

Qi Luo, Junhe Lu, Hao Zhang, Zunyao Wang, Mingbao Feng, **Sheau-Yun Dora Chiang**, David Woodward, Qingguo Huang (2015) Laccase-Catalyzed Degradation of Perfluorooctanoic Acid, Environ. Sci. Technol. Lett. 2 (7): 198-203

Qi Luo, Zunyao Wang, Mingbao Feng, Dora Chiang, David Woodward, Shangtao Liang, Junhe Lu, Qingguo Huang (2017) Factors controlling the rate of perfluorooctanoic acid degradation in laccase-mediator systems: The impact of metal ions, Environmental Pollution, [Volume 224](#), Pages 649-657

CDM Smith believes in the promise of PFAS destruction as one of the future solutions to permanently address PFAS in the environment. Due to the complexity and unique properties of PFAS, the development and commercialization of PFAS destruction technologies will not be easy. Careful consideration and understanding of PFAS transformation and defluorination must be incorporated into the technology evaluation for a particular site/application with thoughtful design of bench and pilot scale systems to demonstrate technology(ies) and incorporate economic feasibility in the selection process. Ultimately, we will leverage our experience to design and build effective large scale systems, that prevent manifestation of unintended consequences, such as discharge of partially degraded PFAS or other byproducts that pose unacceptable risks to human health and the environment.

Since 2012, CDM Smith has developed and demonstrated the latest analytical methods to identify intermediates and end products generated during PFAS destruction. Now that we have the tools to understand PFAS fate and transport, we are confident that we are ready to carefully move to next step in 2020 to continue to develop the most reliable PFAS destruction solution to permanently remove PFAS.