

Task 1. Destruction of Per- and Polyfluoroalkyl Substances (PFAS)

Task sponsored by CDM Smith

Task proposed by Brackish Groundwater National Desalination Research Facility/US Bureau of Reclamation

Task Developed by CDM Smith, NM Environment Department, Brackish Groundwater National Desalination Research Facility, Dow Chemical Corporation, and Engineering New Mexico Resource Network

Background

Introduction. Numerous industries and government agencies are faced with remediation of the “forever chemicals” per- and polyfluoroalkyl substances (PFAS). The chemicals have been found most commonly in groundwater, landfill leachate, and surface waters associated with higher-PFAS usage industries such as manufacturing and processing plants, landfill sites, wastewater treatment facilities, and fire-fighting training sites. Researchers have had reasonable success isolating and concentrating the molecules, but the issue of greatest concern is destruction of the concentrated PFAS, once isolated.

PFAS have been prized for their heat-, stain-, and water-resistance, and have been used extensively in fire-fighting foams, water-repellent fabrics, and non-stick products such as Teflon, polishes, waxes, and paints. They owe their unique properties to the carbon-fluorine bond, one of the strongest known chemical bonds. The drawback of this strong bond is that the molecules do not degrade and are highly persistent in the environment. They accumulate in biota, soil, and surface and groundwater, including drinking water sources. Although industrial uses of certain PFAS are in the process of being curtailed in the United States, due to their “forever” nature, PFAS remain a concern to the health of living organisms. In humans, they are linked to a number of serious health issues.

Although there are well over 4,500 known PFAS compounds, this task will focus on perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) because they are the most studied compounds, allowing results obtained from your work to be easily compared to other technologies in the literature.

PFAS remediation research currently focuses on combined technologies: upstream separation, optional midstream concentration, and downstream destruction. This task targets the destruction stage of the treatment process, as it is currently one of the most challenging parts of the PFAS remediation process. To date, there has not been a cost-effective full-scale destruction process capable of completely destroying PFAS.

PFAS Destruction. Recent advancements in destruction techniques include aggressive technologies, such as electrochemical degradation, sonolysis, plasma reactions, thermal treatments, chemical treatments, and UV oxidative/reductive destruction. In addition, slower “green” technologies, such as humification through laccase enzymatic reactions, and biodegradation by microbial communities are being explored. Note that, because of their persistence, PFOS and PFOA resist most conventional treatment technologies such as direct oxidation, biodegradation, air stripping, vapor extraction, and UV photolysis.

The aggressive methods listed above for PFAS destruction each have drawbacks (discussed in Appendix II). In general, they are energy-intensive processes that are not yet economically feasible as downstream treatment technologies. To date, they have required high-strength, low-volume concentrates typically treated through batch processing, but teams are encouraged to explore novel approaches to PFAS destruction and consider continuous processes.

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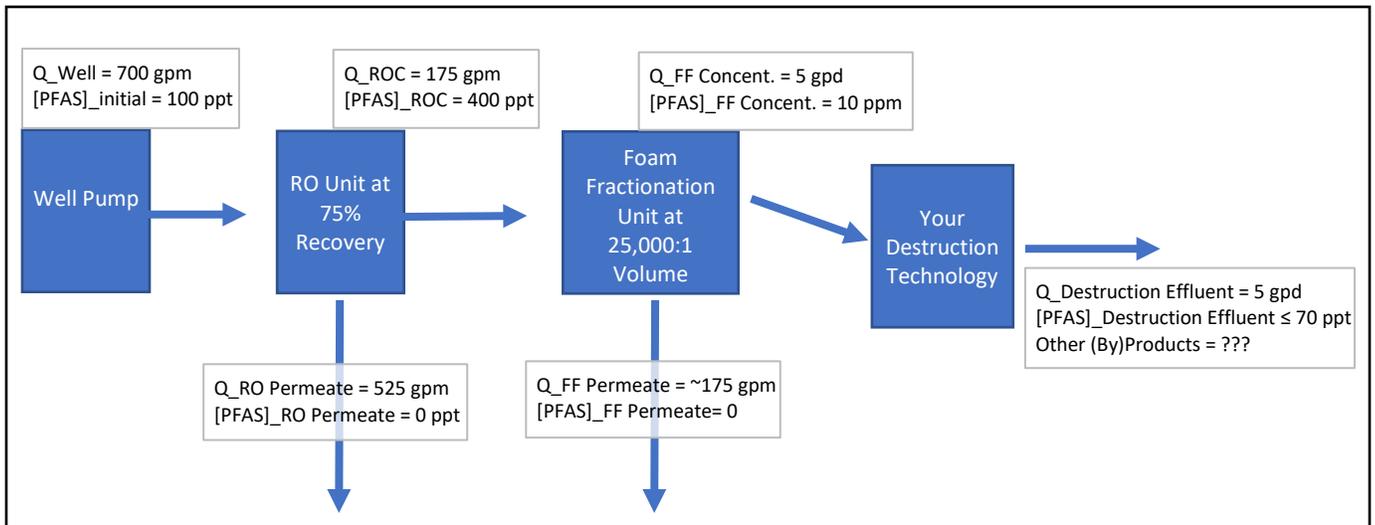


Figure 1. Process flow diagram for field site. Abbreviations: Concent. = concentrate; ppm = parts per million (mg/L); Q = discharge; ROC = reverse osmosis concentrate. All other abbreviations defined in text.

Field Site. The field site of interest for this task is a pump-and-treat system for a groundwater plume containing PFOS and PFOA (see Figure 1). An extraction well pumps groundwater at a flow rate of 700 gallons per minute (gpm). The water is separated onsite through reverse osmosis (RO), reducing the volume of the PFAS solution by 75%. Foam fractionation (FF) is applied to the resulting RO brine to further concentrate the solution (FF is discussed in Appendix I), resulting in a full-scale field treatment rate of 5 gallons of concentrate per day (gpd).

To allow teams to focus on the destruction technology, WERC is assuming upstream RO and FF treatments, as shown in Figure 1. However, teams may consider other upstream separation and/or concentration processes if this will aid the design of the destruction unit. The assumed upstream technologies should result in PFOS and PFOA being in the aqueous phase as it enters the destruction unit.

Problem Statement

Your team will research, evaluate, and design a novel or improved on-site ex-situ PFOS and PFOA destruction technology that can destroy PFOS and PFOA, while in the aqueous phase, for a sample of PFAS concentrate.

Your team should reduce PFAS in the concentrate to the EPA advisory level of 70 ppt (parts per trillion). (Note that many states, including New Mexico, are studying the issue and have not promulgated a final numeric value for safe continuous exposure.)

The destruction treatment technology should scale up to match a rate of 5 gpd, or more for a field site as described above (see “Field Site”). The technology should not introduce harmful byproducts into the environment. All residual waste streams should be safely disposable and accounted for in your final design.

Although your team is not expected to address separation of PFAS from the groundwater in the bench-scale design, for purposes of scale-up, all reports should qualitatively address how your chosen destruction technology fits into a complete on-site PFAS treatment process that includes groundwater pumping, RO separation, and concentration via FF (or other separation/concentration technologies of your team’s choosing) prior to PFAS destruction.

This task’s primary emphasis is improving the cost-effectiveness, energy efficiency, and practicality of on-site PFAS destruction. Teams are encouraged to think out of the box to design a creative treatment system.

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Design Requirements

Your proposed design should provide specific details and outcomes as follows:

- Design an on-site treatment system that will destroy PFOS and PFOA molecules in the aqueous phase.
- Effluent from the destruction process should result in a total combined PFOS and PFOA concentration less than or equal to 70 ppt.
- Include a Process Flow Diagram (PFD) for the selected destruction process. The PFD must include mass and energy balances (input and output rates, reactants, and reaction rates, etc.).
- Estimate the capital costs (CAPEX) of constructing a commercial-size on-site destruction process, assuming a full-scale treatment rate of 5 gpd. This includes, but is not limited to, equipment, buildings, land use, pipes, pumps, construction costs, engineering mark-up, etc.
- Estimate the destruction unit operating cost (OPEX) (calculated as \$/kg of PFAS destroyed) on an annual basis, including, but not limited to, any consumables (chemicals, sacrificial components, etc.) that may be used, energy requirements assuming industrial electricity rates, and labor.
- Document success in improving energy efficiency, pollution prevention, and/or waste minimization, as it applies to your project to qualify for the P2E2 Award. Place this in a separate section of the report.
- Address all wastes, including the fate of all waste products, generated by the PFAS destruction process.
- Discuss any intangible benefits of the selected destruction process.
- Include a Public Involvement Plan, as applicable (See Team Manual).
- Discuss your plan's adherence to appropriate federal (USA), state and local laws and regulations. Attend WERC's webinar for helpful tips for addressing regulatory issues. (See website or email us for webinar info.)
- Address safety aspects of handling the PFAS-laden waters. Safety issues should be addressed in both the written report and the Experimental Safety Plan (ESP). Attend WERC's webinar for helpful tips for addressing health and safety issues. (See website or email us for webinar info.)

Bench Scale Demonstration

Demonstrate the destruction of PFAS contaminants on a bench-scale basis using a concentrated synthetic solution of PFOS and PFOA molecules suspended in DI water (chemistry shown below). The bench-scale demonstration should illustrate the design requirements listed above.

The bench-scale destruction unit should demonstrate a batch or continuous process that can be scaled up to a base-case system that treats a minimum of 5 gpd of PFAS contaminants.

The bench-scale apparatus shall treat water of the following initial chemistry with a total PFOS + PFOA of 10 mg/L.

Analyte	Amount per liter synthetic solution
L-PFOS, Sodium Perfluoro-1-octanesulfonate CAS: 1763-23-1 (Indofine Catalog No: 09-3686) indofinechemical.com	5 mg
PFOA, Perfluoro-n-octanoic acid CAS No. 335-67-1 (Sigma Aldrich Catalog No: #33824) sigmaaldrich.com	5 mg

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Analytical Testing

WERC will employ robust PFAS testing using two analyses:

- PFAS Testing via EPA Method 537 Modified Isotope Dilution, an LC/MS/MS process.
This test determines the concentration of PFAS remaining in your samples after they are processed through your bench-scale apparatus.
- Fluoride detection via Ion Chromatography.
The presence of fluoride in the processed sample is an indication of successful PFAS destruction because F is liberated when the C-F bond is severed. This helps confirm PFAS destruction and rules out the possibility that measured PFAS reduction is merely due to longer-chain PFAS molecules being broken into shorter-chain PFAS molecules.

Team Preliminary Testing

Teams will arrange their own preliminary tests independently and are expected to procure their own PFOA and PFOS analytes for preliminary testing. Take note of published handling and sampling protocols— even the type of collection container is important.

During preliminary testing, and due to the high cost and turnaround times for PFAS testing, WERC recommends that teams use fluoride content as a first-order confirmation that PFAS is being destroyed. The ion-selective electrode fluoride detection method is an inexpensive option.

Contest Synthetic Solution Preparation

During the contest, WERC will provide each team with a minimum of four liters of synthetic solution (chemistry listed in the table) to work with during the bench-scale demonstration. This is likely more than your team will need to run the demonstration. At the end of the treatment process, each team will submit three samples, up to 250 mL in volume, for analysis. Actual volume of samples TBD—watch FAQs for more information.

Contest Testing Procedures

Due to the length of time required for PFAS testing, analytical testing at the contest will be conducted in two phases:

- Phase I—PFAS testing—conducted at each team’s campus laboratory one week prior to the contest date. WERC will arrange for your team’s sample to be sent to an independent lab for testing via Modified Method 537. As always, cost of testing will be funded by the task’s sponsors.
 - Prior to the PFAS test date, WERC will prepare the synthetic solution and ship it to the local judges.
 - Teams will run their bench-scale demonstration at their own campus laboratory, supervised by independent judges who are selected by WERC from the team’s local area.
 - Local judges will hand the team the WERC-prepared synthetic solution, observe the bench-scale demonstration, collect the processed sample, and ship it to the lab for testing.
 - WERC may also conduct fluoride analyses on the samples that are submitted from the team’s home lab
- Phase II—Fluoride testing—conducted in Las Cruces during the officially scheduled contest dates.
 - The bench-scale demonstration will be run at the contest for the same length of time as each team’s run for Phase I testing.
 - Teams will process the WERC-prepared synthetic solution through their bench-scale systems.
 - The results of the bench-scale demonstration will be sent to NMSU laboratories to be analyzed for fluoride content via Ion Chromatography.
 - WERC will compare the results of Phase I fluoride testing and Phase II fluoride testing, if both tests are conducted.

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Optional Bench-scale Demonstration Enhancements.

In addition to the working bench-scale model, the bench-scale demonstration may include video productions, computer simulations, tabletop displays, and scale or architectural models to assist in the presentation. These inclusions can be extremely beneficial to your presentation, but they shall not be substitutes for the bench-scale demonstration.

Technical Report Requirements

The written report should demonstrate your team's insight into the full scope of the issue and include all aspects of the problem and your proposed solution. Process flow diagrams that include all inputs, outputs, and reactions must be included.

The report will be evaluated for writing quality, organization, clarity, reasoning, and coherence. Standards for publications in technical journals apply. In addition to the listed requirements, your report must address in detail the items highlighted in the Problem Statement, Design Considerations, Evaluation Criteria, and the 2021 Team Manual. Note that there are new formatting requirements this year.

Preliminary Report

The preliminary report ensures that your team is heading in a direction that will lead to success, and it helps us prepare for space and power requirements for your bench-scale apparatus. The report should be very brief (1-2 pages). In your preliminary report, outline the planned destruction unit and operating parameters. Include a process-flow diagram showing expected inputs and outputs. Specify the power requirements for the bench-scale apparatus.

Evaluation Criteria

Refer to the 2021 Team Manual for a comprehensive explanation of the evaluation criteria.

The Team Manual and other important resources are on the WERC website (wercdesigncontest.nmsu.edu)

Additionally, your proposed solution will be evaluated on the following:

- Cost, energy use, destruction rate, footprint, and PFAS destruction.
- Discussion of the fate of all waste products generated by your remediation process and the ultimate fate of the PFAS molecules.
- Technical fundamentals, performance, safety, and other issues noted in the problem statement
- Why your design has the best potential for real-life implementation
- Thoroughness and quality of the economic analysis
- Originality, innovation, functionality, ease of use, maintainability, reliability, and affordability of the proposed technology
- How well the bench-scale represents your full-scale design concept
- The quality of your treated media. The bench-scale processed sample will be evaluated for treated media volume, removal efficiency, and time to process
- Other specific evaluation criteria may be provided at a later date (watch the FAQs).

FAQs/Deadlines

- Teams are expected to watch for FAQs online for any updates in the task requirements. (wercdesigncontest.nmsu.edu)
- Due 18 January 2021: Preliminary Report.
- Due 1 February 2021: Experimental Safety Plan (ESP).
- Due 29 March 2021: Written Report.

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Resources

See the Appendices for introductions to foam fractionation and PFAS Destruction Techniques.

References

- [1] Chiang, Dora. 2019. Breaking Down PFAS: What is PFAS destruction? Is it different from PFAS transformation? CDM Smith Newsletter, January 2019.
- [2] Gomez-Ruiz, B., S. Gómez-Lavín, N. Diban, V. Boiteux, A. Colin, X. Dauchy, A. Urtiaga. 2017. Efficient electrochemical degradation of poly- and perfluoroalkyl substances (PFASs) from the effluents of an industrial wastewater treatment plant. *Chemical Engineering Journal*, 322: 196-204.
- [3] Ross I., J. McDonough, J. Miles, P. Storch, P.T. Kochunarayanan, E. Kalve, J. Hurst, S.S. Dasgupta, J. Burdick. 2018. J. A review of emerging technologies for remediation of PFASs. *Remediation Journal*, 28(2): 101-126.
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- [6] _____. 2020. Environmental Fate and Transport for Per- and Polyfluoroalkyl Substances. ITRC Factsheet, April 2020.
- [7] _____. 2020. Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS). ITRC Factsheet, April 2020.
- [8] EPA Technical Brief. February 2020. Per- and Polyfluoroalkyl Substances (PFAS): Incineration to Manage PFAS Waste Streams, <https://www.epa.gov/chemical-research/technical-brief-and-polyfluoroalkyl-substances-pfas-incineration-manage-pfas-waste>

Awards

Each year, the WERC Environmental Design Contest and its sponsors award more than \$25,000 in cash prizes. Successful completion of every stage of the design project qualifies each team for the following awards.

1. Task awards (First, Second, Third Place; minimum amounts: \$2500-\$1000-\$500, respectively).
2. Virtual Desktop Study Awards (awarded independently of the full bench-scale designs). Amounts TBA.
3. WERC Resources Center Pollution Prevention/Energy Efficiency Award (P2E2) (\$500)
4. Judges' Choice Award (\$500)
5. Peer Award (\$250)
6. Terry McManus Outstanding Student Award. (\$500-\$1000, according to funding).
7. Other awards may be announced later.

Award amounts listed are minimum amounts and may increase with available funding.

Detailed criteria for each award:

<https://iee.nmsu.edu/outreach/events/international-environmental-design-contest/guidelines/>

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Appendices

Appendix I–Summary of Foam Fractionation as a midstream PFAS concentration technology

An emerging and promising PFAS concentration technology is foam fractionation (FF). Using only air, with no requirement of sorbents or membranes, the process takes advantage of the surfactant properties of PFAS, which prefer to aggregate at the air-water interface. The FF process works by first creating small air bubbles, which substantially increases the air-water interface surface area, to which the PFAS can adhere. The bubbles containing PFAS then float to the surface where they form a highly concentrated PFAS foam. Preliminary lab experiments have shown that foam fractionation is capable of up to 50,000:1 volume reduction (i.e. FF can reduce the volume of a 50,000-gallon feed source of diluted PFAS to 1 gallon of highly concentrated PFAS). This concentrate is then ready for destruction.

View a video that demonstrates the FF process [NBN News PFAS Solution OPEC Systems](#)

Appendix II–Summary of current knowledge on PFAS Destruction Technologies

PFAS destruction technologies have been in development since the 2010s. PFAS destruction is different from PFAS transformation technologies as the overarching goal of PFAS destruction is to mineralize PFAS by breaking C-F bonds. Here are a few examples of technologies that have been demonstrated at small scales or under laboratory development (ITRC, 2020):

- Electrochemical degradation – Electrochemical treatment occurs via anodic oxidation. It proceeds via direct and indirect anodic oxidation. In direct electrolysis, contaminants are adsorbed onto and degraded directly at the electrode, while in indirect electrolysis, contaminants are degraded in the bulk liquid in reactions with oxidizing agents (that is, hydroxyl radicals) formed by the electrode. Treatment effectiveness can be extremely high; however, the studies have found generation of perchlorate, a highly soluble contaminant, due to oxidation of chloride in water.
- Sonochemical oxidation – The sonochemical process relies on the propagation of acoustic waves in liquids at frequencies ranging between 20 kHz and 1,000 kHz, which results in cavitation. During cavitation, cyclic formation, growth, and collapse of microbubbles result in an intense increase in temperature and pressure (5000 Kelvin (K) and 2000 atmosphere (atm)), along with the generation of free radicals for PFAS destruction.
- Plasma reactions – Plasma is formed as a result of an electrical discharge from the addition of sufficient energy to gas. The main reaction pathway for PFOA by plasma treatment can be by thermal cleavage of the C-C bonds resulting in direct decomposition to gaseous products without formation of shorter chain PFCAs. Others have proposed that PFAS decomposition is due to conversion to unstable radicals during interaction of PFAS with the most energized ions in the plasma, or with positive ion(s) generated by the plasma at the bubble gas-liquid interface.
- Solvated electrons (Advanced reduction processes [ARP]) – ARP involves the combination of activation methods such as ultrasound, ultraviolet, microwaves, and electron beam with reducing agents (reductants) such as ferrous iron, sulfide, sulfite, iodide, and dithionite to generate very reactive reducing radicals and the hydrated electrons ($e^-(aq)$) that mineralize PFAS. The reducing hydrogen radical ($H\bullet$) and the hydrated electron are strong reductants that react easily with halogenated organic compounds.
- Incineration – Requires that PFAS be in the solid phase. This process is usually used with GAC and IX resins. Destruction can be incomplete, resulting in shorter-chain PFAS molecules, rather than destroying them. Alternatively, products of incomplete combustion (PICs) may be chemicals of concern if not properly researched in advance.