

# EXECUTIVE SUMMARY

Hydrothermal Technologies for On-Site Destruction of Site Investigation Wastes Impacted with Per- and Polyfluoroalkyl Substances (PFAS)

SERDP Project ER18-1501

SEPTEMBER 2020

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## ACRONYMS AND ABBREVIATIONS

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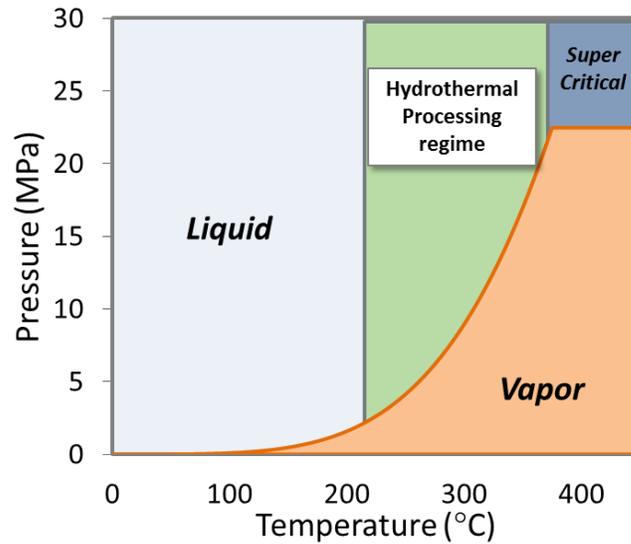
<sup>19</sup> F-NMR	Fluorine-19 nuclear magnetic resonance spectroscopy
°C	Degrees Celsius
AFFF	Aqueous film-forming foam
DGBE	Diethylene glycol monobutyl ether
DoD	U.S. Department of Defense
F <sup>-</sup>	Fluoride
HPLC-DAD	High pressure liquid chromatography with diode array detection
HRMS	High resolution mass spectrometry
IDW	Investigation-derived waste
ISCO	In situ chemical oxidation
ISE	Ion selective electrode
IX	Ion exchange
K <sub>2</sub> FeO <sub>4</sub>	Potassium ferrate
kWh m <sup>-3</sup>	Kilowatt hour per cubic meter
LC	Liquid chromatography
LC-MS/MS	Liquid chromatography tandem mass spectrometry
LC-QToF-MS	Liquid chromatography with quantitative time-of-flight mass spectrometry detection
mg/L	Milligrams per liter
MPa	Megapascal
NaOH	Sodium hydroxide
NaBH <sub>4</sub>	Sodium borohydride
NMR	Nuclear magnetic resonance spectroscopy
OH <sup>-</sup>	Hydroxide
PFAS	Per- and polyfluoroalkyl substances
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
TCE	Trichloroethylene
TOC	Total organic carbon
ZVI	Zerovalent iron

## 1.0 INTRODUCTION

Extensive use of per- and polyfluoroalkyl substances (PFAS) in aqueous film-forming foams (AFFF) has led to significant environmental releases at U.S. Department of Defense (DoD) facilities. As a result, soil and groundwater underlying these sites now represent major source zones for PFAS contamination. To address concerns about PFAS contamination, identify source zones, and prepare for future cleanup efforts, DoD has initiated remedial site investigations nationwide. These activities generate significant liquid and solid waste materials, including soil drilling core materials, well purging water samples, and equipment washing residues. These investigation-derived waste (IDW) materials contain varying levels of contamination by PFAS and other site co-contaminants. Currently, IDW is shipped off site for disposal or incineration, but this is costly and does not completely eliminate liabilities. Incineration can lead to complete PFAS destruction, but this technology is expensive and requires large energy inputs for water samples and soil samples with high moisture content. Ideally, small-scale field-deployable technologies capable of completely destroying PFAS in wet samples would be available to manage these IDW on site.

The fluorinated backbone within PFAS imparts extreme recalcitrance and environmental persistence, and there is only limited evidence for slow biodegradation of these contaminants. As a result, monitored natural attenuation is not a viable remediation strategy for PFAS, and concentrations in groundwater are expected to remain well above action levels indefinitely without active interventions. There is considerable interest in technologies that can not only remove PFAS from environmental media, but also mineralize the chemicals so that they pose no future risk or liability. However, physical-chemical approaches that have been successful for other legacy contaminants, including in situ chemical oxidation (ISCO) and zerovalent iron (ZVI), have shown only limited success in destroying PFAS. Ensuring complete mineralization generally requires incineration or other high temperature thermal treatments. While this may be practical for PFAS-containing solid wastes, incineration of wet wastes and concentrate solutions is inefficient because of the high energy requirements for vaporizing water.

This limited scope project examined the feasibility of applying subcritical hydrothermal processing as an alternative technology for managing wet waste concentrates, including IDW. Hydrothermal technologies apply elevated temperatures and pressures (200-374°C, 2-22 MPa) to water in a sealed environment that prevents vaporization (**Figure ES-1**), leading to a uniquely reactive environment that has been shown to catalyze many chemical transformations that do not occur at lower temperatures. While somewhat counterintuitive, heating compressed water to subcritical hydrothermal conditions consumes much less energy than evaporating water at lower temperatures. As a result, subcritical hydrothermal reactions are currently being heavily exploited for production of biorenewable fuels and chemicals. The same properties responsible for decomposition and transformation of biomass under hydrothermal conditions can potentially be exploited to degrade organic contaminants, including PFAS.



**Figure ES-1. Phase Diagram of Water with Conditions for Subcritical Hydrothermal Reaction Conditions Highlighted**

## 2.0 OBJECTIVES

The overall goal of the proposed work was to evaluate the effectiveness of applying hydrothermal conversion technologies to destroy PFAS and co-contaminants present in liquid and soil wastes. The project team tested a hypothesis that hydrothermal reaction conditions can be coupled with low-cost reactive amendments to effectively degrade and defluorinate the full range of PFAS structures identified at AFFF-impacted sites. High resolution mass spectrometry (HRMS) methods were applied to monitor the transformation of a wide range of PFAS structures, including the most commonly measured perfluoroalkyl acids (i.e., perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA)) and their polyfluorinated precursors, during hydrothermal treatment applications. Experimental work addressed the following specific objectives:

1. Identify hydrothermal reactions conditions (e.g., temperature, reaction time) and reactive amendments (e.g., acids, bases, oxidants, reductants) that promote PFAS degradation and defluorination;
2. Track the fate and decomposition of diverse PFAS identified in AFFF formulations;
3. Evaluate fate and degradation of common co-solvents and co-contaminants (e.g., hydrocarbon fuel compounds, chlorinated solvents) associated with AFFF;
4. Assess treatment of PFAS-contaminated aqueous and soil samples, including IDW;
5. Identify transformation pathways and mechanisms leading to mineralization of PFAS; and
6. Compare energy input requirements for hydrothermal treatment of PFAS-contaminated water with incineration.

### 3.0 TECHNICAL APPROACH

The overall study design included seven related tasks. Task 1 focused on screening a wide range of reaction amendments, including acids, bases, oxidants, reductants, and metallic nanoparticles, for their potential to enhance PFOS and PFOA degradation and defluorination under hydrothermal conditions. Task 2 applied HRMS methods to evaluate degradation of the wider range of PFAS present in AFFF under conditions that were found to be optimal for PFOS degradation. Task 3 then evaluated the stability and degradation of representative AFFF co-solvents and co-contaminants, and Task 4 measured degradations of PFAS present in aqueous and solid IDW samples under the same reaction conditions. Task 5 combined the results of experiments and available literature to provide an initial assessment of the major pathways and mechanisms for hydrothermal decomposition of PFAS, and Task 6 provided an initial assessment of the heat requirements for hydrothermal treatment of wet waste materials in comparison with incineration. Finally, Task 7 included all reporting and technology transfer activities.

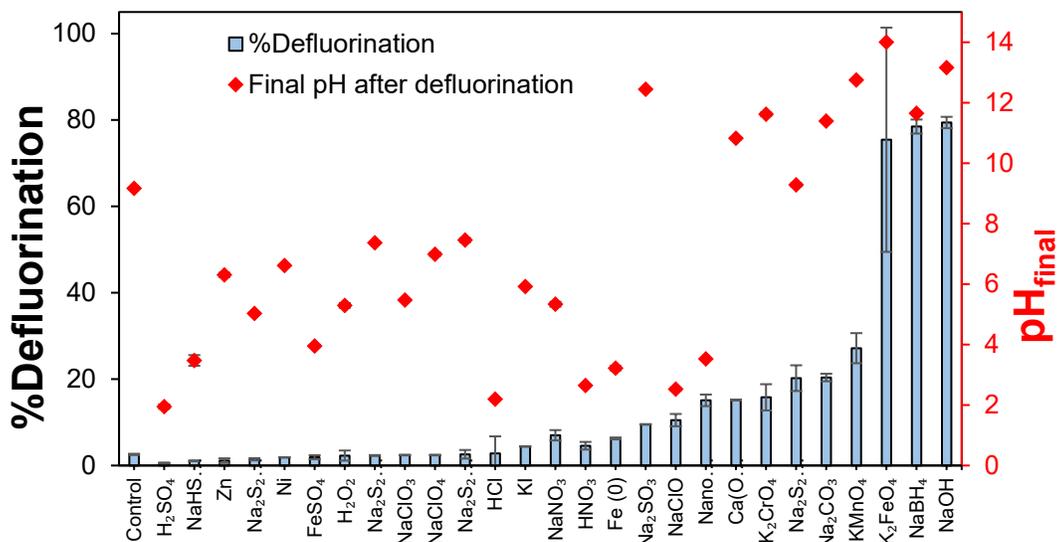
Experiments were conducted using commercial AFFF mixtures and PFAS-contaminated water and soil samples obtained from DoD sites throughout the country. Liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QToF-MS) analysis of samples showed a wide diversity of PFAS, spanning the full range of structures identified at contaminated sites.

Hydrothermal reactions of PFAS were evaluated in laboratory batch reactor systems. PFAS-containing solutions and soil suspensions were added to reactors together with water and the appropriate reactive amendments before sealing and heating to the desired temperature. After completion of reactions, contents were collected for analysis of residual PFAS, fluoride, and other selected analytes. PFAS concentrations were measured by LC-QToF-MS and LC with tandem mass spectrometry (LC-MS/MS). Fluoride ion released upon degradation of PFAS was measured by ion selective electrode (ISE) analysis. Gas chromatography methods were applied to evaluate gas-phase reaction products. Co-solvent and co-contaminant concentrations were measured by total organic carbon (TOC) and high pressure liquid chromatography with diode array detection (HPLC-DAD).

## 4.0 RESULTS AND DISCUSSION

### 4.1 DEGRADATION AND DEFLUORINATION OF PFOS

Initially, a series of amendments, including acids, bases, salts, oxidants, reductants, and metal nanoparticles, were screened for their potential to promote defluorination of PFOS under near-critical hydrothermal conditions (350°C, 16.5 MPa autogenous pressure). **Figure ES-2** shows that the extent of F<sup>-</sup> release varied widely, ranging from near 0% (for the unamended control and roughly half the screened amendments) to 80% fluoride release.



**Figure ES-2. Screening of the Potential of Different Reactive Amendments**

*Screening of the potential of different reactive amendments for defluorination of PFOS under hydrothermal reaction conditions: 50 mg/L PFOS, 1 M reactive amendment, 350°C, 90 minute reaction. Solution pH value after reaction shown on right axis.*

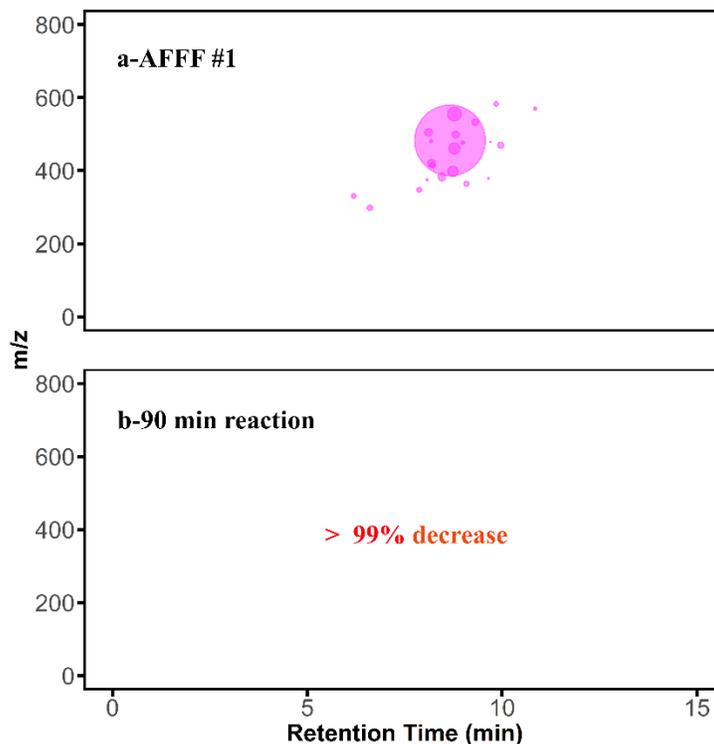
The most effective reagents, yielding >70% defluorination, include sodium hydroxide (NaOH), sodium borohydride (NaBH<sub>4</sub>), and potassium ferrate (K<sub>2</sub>FeO<sub>4</sub>). Although the most effective amendments belong to different classes of reagents, subsequent tests strongly suggest that their effectiveness was related to the increase in solution pH caused by their addition to solution. As a result, further investigation focused on hydrothermal reactions in solutions amended with NaOH, a low-cost alkali.

An analysis of PFOS degradation showed that reaction kinetics follow a generalized second-order rate law, where rates were proportional to both PFOS and hydroxide ion (OH<sup>-</sup>) concentrations. Tests also showed that reaction rates increase with increasing reaction temperature. Together, these findings provide for model predictions that can be applied to design reactor process conditions to ensure treatment goals are met. Analysis of reaction solutions confirms formation of some fluorinated organic intermediates, albeit at very low concentrations, indicating conversion of PFOS to shorter-chain carboxylate intermediates that rapidly degrade and release fluoride. Mineralization of PFOS and conversion of organic C-F bonds to fluoride ion were further confirmed by application of nuclear magnetic resonance spectroscopy (<sup>19</sup>F-NMR).

## 4.2 DEGRADATION AND DEFLUORINATION OF AFFF

Experiments conducted with two AFFF mixtures (one dominated by perfluoroalkyl sulfonates and one dominated by fluorotelomer acids) demonstrated that the same alkali-inducing amendments that were effective for degrading PFOS also were efficient in promoting destruction and defluorination of the wider suite of PFAS identified in AFFF mixtures. Through LC-QToF-MS targeted and suspect screening analysis as well as <sup>19</sup>F-NMR analysis, degradation of the full suite of structures was confirmed. **Figure ES-3** shows “bubble plots” tracking the estimated concentrations of PFAS in one of the AFFF mixtures before and after hydrothermal reaction.

In these plots, individual bubbles represent different PFAS structures detected in the AFFF arranged according to their chromatographic retention times (x-axis) and mass-to-charge ratio (m/z; y-axis), and the diameters of the individual bubbles are proportional to chromatographic peak area. More than 99% of the PFAS identified through suspect screening analysis of AFFF were degraded within 90 minutes.



**Figure ES-3. Bubble Plots Summarizing the Removal of PFAS**

*Bubble plots summarizing the removal of PFAS identified in AFFF by LC-QToF-MS analysis. Reaction conditions: AFFF diluted 1-to-1000, 350 °C, 5 M NaOH.*

Analysis of fluorine by  $^{19}\text{F}$ -NMR and ISE analysis confirmed near-complete mineralization and release of fluoride ion from PFAS present in the AFFF. Furthermore, analysis of volatile products by gas chromatography methods showed principally carbon dioxide, with smaller amounts of hydrocarbon products (butene isomers, ethane); and no organofluorine products were detected.

Results are consistent with a tentative mechanism for PFAS transformation wherein  $\text{OH}^-$  catalyzes a series of nucleophilic substitution and decarboxylation reactions that defluorinate PFOS/PFOA and perfluorocarboxylate intermediates. For PFOS, an initial  $\text{OH}^-$  substitution reaction with the sulfonate headgroup leads to a series of unstable intermediates that hydrolyze to form PFOA, and further decarboxylation then converts PFOA sequentially to increasingly short-chain perfluorocarboxylates, releasing  $2\text{F}^-$  ions with each reaction.

### **4.3 REACTIVITY OF AFFF CO-SOLVENTS AND CO-CONTAMINANTS**

Tests showed that two co-solvents, diethylene glycol monobutyl ether (DGBE) and methanol, are minimally affected by exposure to alkaline hydrothermal conditions found to degrade PFAS, whereas several model co-contaminants, including trichloroethylene (TCE) (a model chlorinated solvent) and aromatic hydrocarbon contaminants (benzene, toluene, ethylbenzene, and m-xylene), are completely degraded under the same conditions. Degradation of TCE suggests common nucleophilic attack mechanisms that might be applicable to halogenated organic contaminants in general. The mechanisms for degradation of the aromatic hydrocarbons is unclear, but it is possible that the same reactive nucleophiles responsible for PFAS decomposition attack the electron-rich aromatic bonds in these structures. Nonetheless, findings suggest that this technology may be broadly applicable for many of the contaminants detected at these locations.

### **4.4 REACTIVITY OF PFAS IN AFFF-IMPACTED WATER AND SOIL**

Tests of hydrothermal reactions were conducted with two PFAS-contaminated IDW aqueous samples and three PFAS-contaminated soil samples collected from DoD sites. These tests confirmed that PFAS in contaminated matrices can be destroyed by alkaline hydrothermal treatment. Greater than 99% removal of the PFAS detected in the original aqueous IDW samples was measured following hydrothermal treatment, and >90% removal was observed following treatment of the three PFAS-contaminated soil samples. Follow-up studies are recommended to characterize these treatments in greater detail and identify the influences of important soil and water conditions to reaction rates.

### **4.5 ASSESSMENT OF ENERGY INPUT REQUIREMENTS**

A preliminary analysis of energy input requirements for alkaline hydrothermal treatment indicate significant potential for energy savings compared to incineration processes for PFAS-contaminated water and sediment samples. Avoiding vaporization of water through hydrothermal reactions in compressed water at subcritical conditions yields expected energy requirements of 110-127 kWh m<sup>-3</sup> for hydrothermal treatment at 300 - 350°C with integrated heat recovery, much lower than estimates for incineration of the same samples (534 kWh m<sup>-3</sup> for incineration in a circulating fluidized bed combustion chamber at 1,100°C with integrated heat recovery; 1,336 kWh m<sup>-3</sup> for incineration in a cement kiln with 1,100°C afterburner and no heat recovery). While these estimates are necessarily rough, they support further development of alkaline hydrothermal treatment technologies.

## **5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS**

Findings from this limited scope project demonstrate a promising new strategy for achieving complete destruction and defluorination of PFAS present in IDW as well as other concentrate streams. To the project team's knowledge, this is the first effort demonstrating that subcritical hydrothermal reaction conditions can be combined with low-cost alkali amendments to achieve complete degradation and defluorination of PFAS, both individual solutes and complex mixtures of PFAS (e.g., AFFF). These findings indicate a very promising technology pathway for treatment of PFAS-contamination that can achieve complete destruction of the PFAS, thereby eliminating future liabilities associated with contamination at DoD facilities. The broad efficacy and lower heat requirements compared to conventional hazardous waste incineration is suggestive of an alternative technology for managing a variety of high moisture content PFAS wastes and concentrates, including:

- Aqueous and soil IDWs;
- Unused stockpiles of AFFF containing legacy PFAS requiring disposal;
- PFAS-contaminated source zone soils, sediments, and concentrated solutions;
- Waste ion exchange (IX) concentrate management, including PFAS-contaminated still bottoms and aqueous/co-solvent mixtures;
- High pressure membrane reject streams with elevated PFAS concentrations;
- Accident site wastes collected following application of AFFF;
- PFAS-contaminated wastewater sludge and biosolids;
- Rinse solutions from AFFF spray equipment; and
- Manufacturing wastewater with elevated PFAS concentrations where adsorption/membranes are not practical for direct treatment.

For dilute contaminated water, it is recommended that alkaline hydrothermal treatment be combined into hybrid treatment systems where physical separation processes (e.g., IX, nanofiltration) are applied to concentrate the PFAS in a low-volume secondary stream (e.g., waste IX regenerant brine) that would then be subjected to hydrothermal treatment and destruction.

While incineration is a mature technology, public acceptance of incineration of PFAS-containing wastes is low, and some incinerators are reluctant to accept PFAS-containing wastes due to concerns about generation of corrosive hydrofluoric acid and impending regulations on PFAS-associated emissions. Transportation of PFAS-contaminated wastes off site to centralized incineration facilities also raises serious concerns about accidental releases. Hydrothermal destruction technologies are conducive to application of mobile treatment units for small scale treatment needs (e.g., treatment of IDW samples generated on site). Still, further research is needed to address a number of important issues related to the underlying mechanisms of hydrothermal destruction processes, application to important PFAS-contaminated matrices (including those listed above), translation of the technology to continuous-flow reactors systems, and scale-up and demonstration at DoD facilities.