

Degradation and Defluorination of Ultra Short-, Short-, and Long-Chain PFASs in High Total Dissolved Solids Solutions by Hydrothermal Alkaline Treatment—Closing the Fluorine Mass Balance

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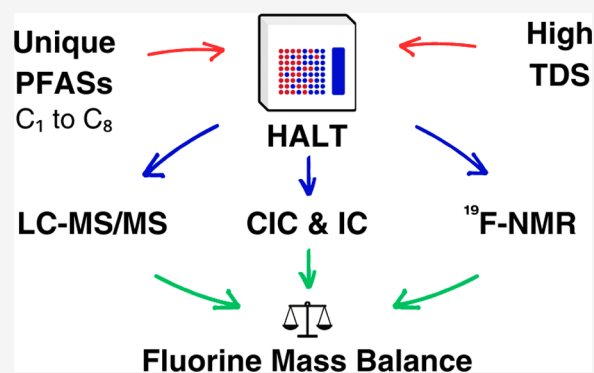
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ABSTRACT: Emerging destructive technologies for per- and polyfluoroalkyl substances (PFASs) are receiving increased attention. To validate these emerging technologies for commercial use, rigorous testing efforts are needed to ensure that all types of PFASs can be degraded with minimal organofluorine byproduct formation. In this effort, a mixture of ultra short-, short-, and long-chain PFASs in an aqueous matrix with high total dissolved solids (TDS) content is processed using hydrothermal alkaline treatment (HALT). Degradation and defluorination are assessed at various HALT operating conditions ($T = 250\text{--}350\text{ }^{\circ}\text{C}$, $\text{NaOH} = 2\text{--}16\text{ wt } \%$). Broadly, perfluoroalkyl sulfonic acids are observed to be more recalcitrant, while PFASs containing a carboxylic acid functional group are readily degraded and defluorinated, even under milder treatment conditions. In all experiments, the fluorine mass balance is near-stoichiometric at optimized conditions, and a “multiple-lines-of-evidence” analytical approach including targeted LC–MS/MS analysis, free fluoride quantification, and total organic fluorine measurements strongly suggests that there is minimal undesired organofluorine byproduct formation. Additionally, the fate of inorganic anions in the aqueous matrix is tracked, evidencing a lack of competing reactions that could afford unwanted byproducts. Overall, this study robustly demonstrates that HALT can facilitate complete degradation and defluorination of ultra short-, short-, and long-chain PFASs in a challenging solution ($\approx 10\text{ wt } \%$ TDS).

KEYWORDS: PFAS, hydrothermal, defluorination, trifluoroacetic acid, ultra short-chain



INTRODUCTION

Per- and polyfluorinated alkyl substances (PFASs) make up a large subclass of organofluorine compounds that has recently encountered regulatory scrutiny.¹ While the unique thermo-physical properties of PFASs offer differentiated performance for many applications, these same properties render some PFASs as highly stable which can lead to persistence in the environment.² Recently, the removal and destruction of PFASs from drinking water, wastewater, and environmental matrices has received increased attention.

Extensive efforts have shed light on the global detection of ultra short-chain PFAS compositions,^{3–5} including compositions such as trifluoroacetic acid (TFA), pentafluoropropionic acid (PFPrA), and heptafluorobutyric acid (PFBA); all of which underwent effective degradation and defluorination in this work. Emerging health advisories for TFA in several European countries, along with evolving global PFAS regulations, highlights that ultra short- and short-chain PFAS treatment in wastewater streams will likely become a focus in coming years.^{6,7}

There has been considerable effort focused on PFAS removal from liquid matrices. Concentration techniques such as adsorption processes using media such as granular activated carbon (GAC)^{8,9} and ion exchange (IEX) resin,¹⁰ and reverse osmosis (RO) membrane filtration¹¹ have been scaled and implemented for treatment. In many cases, spent IEX or GAC media must be replaced in relatively high frequency, and are shipped off-site for incineration or hazardous landfill disposal.¹² Other separation and concentration technologies produce a liquid byproduct, such as foam fractionation,¹³ regenerable IEX,^{14,15} and membrane filtration systems.¹¹ In industrial wastewater treatment settings with high treatment

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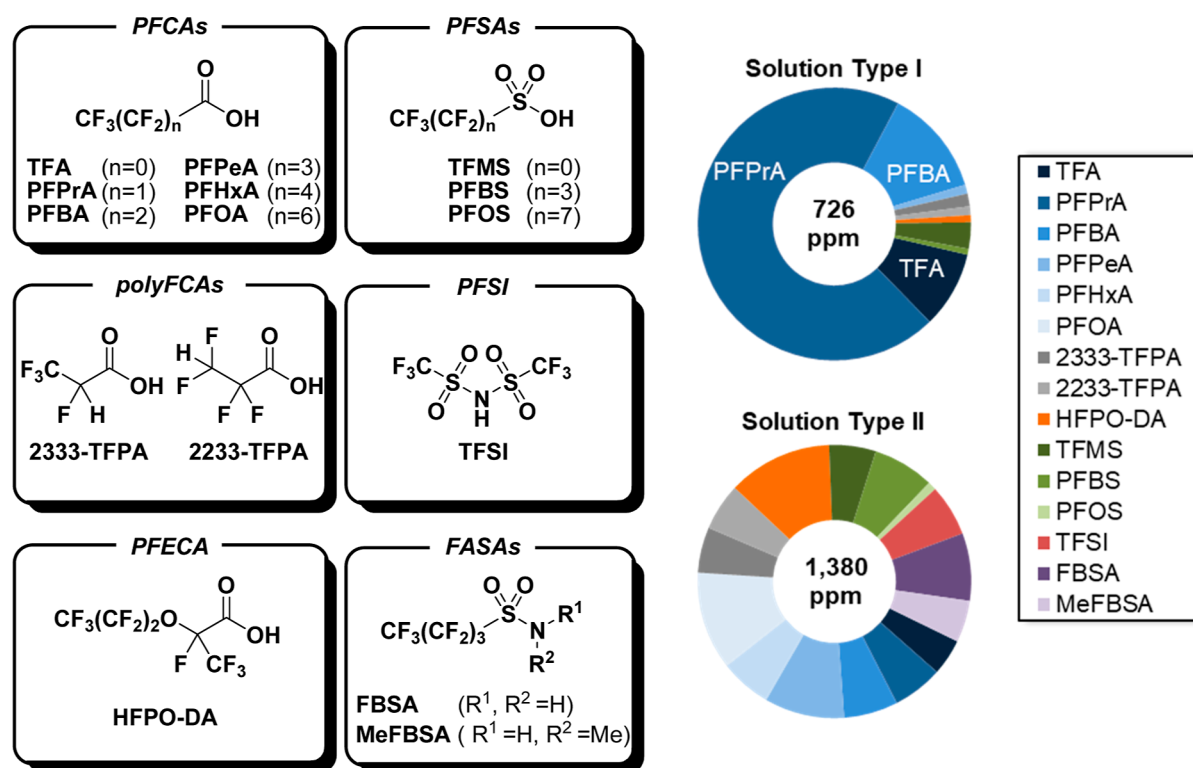


Figure 1. Ultra short-, short-, and long-chain PFASs in solutions type I and type II. Average solution density = 1.07 g/mL.

volumes and where short-chain and/or ultra short-chain PFASs may be present, foam fractionation provides limited efficacy due to the low surface activity of short-chain and ultra short-chain PFAS.¹³ In scenarios with high liquid treatment volumes and high starting PFAS concentrations regenerable IEX resin and/or membrane technologies are more effective and economical.^{16,17} However, these concentration technologies produce PFAS-rich solutions comprising challenging levels of inorganic salts that must be subsequently managed—ideally with destructive treatment.

On-site PFAS destruction methods are now emerging, with an emphasis on removing PFASs from the environment rather than simply concentrating. Some methods have achieved a high degree of PFAS destruction and defluorination even in complex, real-world feedstocks. A coupled photoelectrochemical destructive treatment approach has shown promise in achieving high degrees of destruction and defluorination for a complex AFFF mixture,¹⁸ and supercritical water oxidation (SCWO) systems have also achieved near-stoichiometric levels of PFAS destruction and defluorination in several studies.^{19,20} However, many destruction techniques have primarily focused on long-chain PFASs without attention on the more challenging shorter chain homologues. Some destructive technologies leverage the hydrophobic nature and partitioning behavior of long-chain PFASs to enhance exposure to a localized reacting environment, such as nonthermal plasma-based systems where reactions occur at a gas–liquid interface.^{21,22} Furthermore, water matrix compatibility with selected destruction techniques can significantly limit options for highly challenging PFAS-containing streams and can result in the formation of perchlorate from dissolved chloride in electrochemical systems,²³ the precipitation of inorganic salts (e.g., NaCl, CaCO₃) in supercritical water systems,¹⁹ or

competing reactions and/or transmission challenges in UV-based systems.^{24–26}

Hydrothermal alkaline treatment (HALT) is a thermochemical process leveraging high pH conditions (typically pH > 13) and elevated temperatures ($T = 150$ to 350 °C) in subcritical water ($P > P_{\text{boiling}}$) to degrade halogenated organic compounds. HALT has previously demonstrated effective PFAS degradation and defluorination in a wide range of matrices, including single-compound solutions of perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA),²⁷ TFA,²⁸ AFFF,^{29,30} groundwater and soil,³¹ spent GAC,³² fire training pond water,³³ foam fractionate,³⁴ and plant matter.³⁵ In several previous studies, a high stoichiometric percentage of inorganic fluoride (IF) production was observed, and no known or unknown fluorinated intermediate compounds were observed during HALT processing.^{27,29}

The predominant HALT mechanisms have been hypothesized and characterized in previous studies. In 2021, Hao et al. proposed that nucleophilic substitution is likely to be an active reaction mechanism for defluorination, and both Wu et al. and Hao et al. observed an increase in reaction rates for perfluorosulfonic acid (PFSA) degradation with increasing hydroxide ion concentrations.^{27,29} The current hypothesis is that nucleophilic substitution is the initial reaction step for PFSA degradation, producing an intermediate species which is highly reactive with hydroxide ions. In 2024, Austin et al. observed that TFA degradation occurs at much milder temperatures (150 to 250 °C) with or without the presence of hydroxide, suggesting that a thermal decarboxylation mechanism is active for perfluorocarboxylic acid (PFCA) degradation.²⁸ Austin et al. also observed that fluorocarbon (CF₃H) rather than IF is a stable final product from TFA degradation under hydrothermal conditions without hydroxide ions present, whereas the presence of even small amounts of

hydroxide ions strongly suppressed fluoromethane production, instead promoting fluoride ion production.²⁸ This suggests that fluorocarbon intermediates produced during PFAS degradation are highly reactive with hydroxide ions and suggests that the degradation of the parent PFAS species is the rate-limiting step toward complete defluorination with the HALT process. Overall, PFCA degradation is hypothesized to be a two-step process, the first step involving thermal decarboxylation of the parent compound, followed by hydroxide-driven destruction of an intermediate 1H-perfluoroalkane species (e.g., fluoromethane).

While HALT has clearly been investigated across several specific PFASs and complex matrices, these findings have yet to be generalized to a wider range of PFASs, especially ultra short- and short-chain analogues. The treatment and destruction of ultra short- and short-chain PFAS is a known challenge for many technologies; however, previous HALT studies have shown efficacy in treating ultra short-chain PFASs such as TFA. The objective of this study is to apply the mechanistic insights from previous studies to the treatment of a range of PFASs contained within a synthetic solution representing a real-world feedstock, leveraging a scaled-up HALT system.

Herein, we report a destruction study via HALT focusing on highly challenging salt solutions [$\approx 10\%$ total dissolved solids (TDS)] comprising PFASs ranging in chain length and functional group type, with a primary focus on ultra short-chain analogues (≤ 3 fully fluorinated carbon atoms). The high TDS solution employed in this study is representative of an industrial wastewater stream produced from a treatment train involving regenerable IEX and membrane systems. The regeneration of IEX produces a high TDS brine which is high in PFAS content, and further concentration of this brine is possible via membrane systems. The PFASs present in the mixture are representative of relative hypothetical concentrations in an industrial wastewater stream. The challenge of treating ultra short- and short-chain PFASs in a high TDS matrix is significant, as most PFAS destruction technologies struggle to treat these PFAS species, or struggle to handle high TDS wastewaters. A novel, multiple-lines-of-evidence approach with a suite of analytical techniques is leveraged to track the fluorine mass balance, demonstrating effective degradation and defluorination of PFASs in the HALT environment. Overall, this study is the first-of-its-kind to demonstrate the application of a scaled-up HALT system for the treatment of a range of practically significant PFASs in a high TDS feedstock.

MATERIALS AND METHODS

Reagents. Six groupings of PFASs were tested in this study, including PFCAs, a perfluoroalkyl ether carboxylic acid (PFCEA), polyfluoroalkyl carboxylic acids (polyFCAs), PFASs, fluoroalkane sulfonamides (FASAs), and a bis-(perfluoroalkane sulfonyl)imidic acid (PFSI). Compositions within these groupings are highlighted in Figure 1 and span across ultra short-, short-, and long chain homologues. The term “PFAS” used throughout this work adopts the definition provided by the Organisation for Economic Cooperation and Development (OECD).³⁶ While the “ultra short-chain” PFAS designation remains somewhat ambiguous,^{3,4,37–39} we define PFASs with ≤ 3 fully fluorinated carbon atoms as ultra short. Short- and long-chain designations have been defined by the US Environmental Protection Agency, OECD, and others.^{2,40,41} In the current study, the categorization by chain-length is purely on a technical basis with the sole

motivation of better understanding degradation and defluorination efficacy as a function of PFAS chain length and type. While Figure 1 illustrates all PFASs in their neutral state, the elevated pH (>13) of the current work renders all species shown are in their charged, anionic state.⁴² Additional reagent information is included in the Supporting Information (Table S1).

PFAS-Containing Solutions for HALT. Two solution types were prepared for HALT (Figure 1). Type I was subjected to a range of treatment conditions with an emphasis on understanding the degradation and defluorination levels of relatively understudied ultra short-chain PFCAs TFA, PFPrA, and PFBA (a combined ≈ 92 wt of total PFAS). Other PFASs in type I comprise additional ultra short-chain PFASs 2,3,3,3-tetrafluoropropionic acid (2333-TFPA), 2,2,3,3-tetrafluoropropionic acid (2233-TFPA), trifluoromethanesulfonic acid (TFMS), and short-chain perfluoropentanoic acid (PFPeA), 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid (HFPO-DA), and perfluorobutanesulfonic acid (PFBS). To broaden the spectrum of PFASs studied, solution type II contained the same species as type I in addition to perfluorohexanoic acid (PFHxA), PFOA, PFOS, perfluorobutane sulfonamide (FBSA), *N*-methylperfluorobutane sulfonamide (MeFBSA), and bis(trifluoromethanesulfonyl)imidic acid (TFSI). Both type I and type II solutions were prepared by charging deionized water with NaCl, Na₂SO₄, NaNO₃, NaHCO₃, and Na₂CO₃ to targeted concentrations of 7.5, 0.5, 1.5, 0.25, and 0.25 wt %, respectively. The resultant solution was then spiked to targeted PFAS concentrations. Additional solution preparation details are provided in the Supporting Information.

HALT Experimental Apparatus and Procedures. A continuous-flow, pilot-scale HALT reactor was used for all experiments. A simplified process flow diagram, description of the system, and photos of the system are included in the Supporting Information (Figures S4 and S5).

For every tested solution (type I and type II), solid NaOH was premixed into the individual sample containers to the desired overall NaOH concentration (2–16 wt %). Untreated samples were collected before NaOH addition to confirm starting PFAS concentrations, to assess any degradation due to NaOH at ambient conditions, and to quantify any losses to container surfaces due to changes in the ionic strength of the solution, which is known to affect PFAS solubility. Due to the pH of the prepared solutions, all PFASs will be in a salt form and thus unable to evaporate from solution. Solutions were thoroughly mixed and allowed to cool to ambient temperatures prior to processing through the HALT system.

For each experiment, the HALT system was initialized and brought to the desired experimental temperature (250–350 °C), pressure (~ 25 MPa), and flow rate (63 mL/min [1 gallon per hour]) while processing distilled water. Once the system reached a steady state at the desired temperature, a sample was collected (“system blank”) to quantify any background PFAS concentrations or carryover between experiments. Next, the influent to the HALT system was switched from distilled water to the premixed solution. Individual treated samples were collected after 2, 3, and 4 h of steady-state processing to provide triplicate data points for each condition tested. Error bars in all plots reflect one standard deviation across the three collected samples. All samples were collected in high-density polyethylene (HDPE) sample bottles.

Analytical Materials and Methods. Triple quadrupole mass spectrometry (LC–MS/MS), ion chromatography (IC), combustion ion chromatography (CIC), and ^{19}F NMR spectroscopy are analytical techniques that were used to determine solution concentrations of speciated PFASs, total organic fluorine (TOF), IF, and non-PFAS anions. Detailed summaries of each analytical technique are provided in the [Supporting Information](#).

Data Analysis. Percent PFAS degradation, defluorination, and F-mass recovery were calculated as described in [eqs 1–3](#)

$$\% \text{ degradation} = \frac{C}{C_0} \times 100 \quad (1)$$

$$\% \text{ defluorination} = \frac{[\text{IF}] - [\text{IF}]_0}{[\text{TOF}]_0} \times 100 \quad (2)$$

$$\% \text{ F mass recovery} = \frac{[\text{IF}] + [\text{TOF}]}{[\text{IF}]_0 + [\text{TOF}]_0} \times 100 \quad (3)$$

where C_0 is analyte (e.g., PFPrA, TFA, Cl^- , etc.) concentration before the addition of NaOH and HALT. C is analyte concentration following addition of NaOH and HALT. $[\text{TOF}]_0$ and $[\text{IF}]_0$ are TOF and IF, respectively, of the initial solution prior to NaOH addition and HALT. $[\text{TOF}]$ and $[\text{IF}]$ are TOF and IF concentrations, respectively, of the resultant solution following HALT.

RESULTS AND DISCUSSION

Destruction Performance by PFAS Type. Solution type I was first studied for effective PFAS degradation across a range of temperatures ($T = 250\text{--}350\text{ }^\circ\text{C}$) and NaOH concentrations ($[\text{NaOH}] = 2\text{--}16\text{ wt } \%$). [Figure 2A](#) shows total PFAS concentrations (blue bars) before and after HALT processing at each tested condition and % degradation (red data points). The most aggressive processing conditions ($350\text{ }^\circ\text{C}$, $16\text{ wt } \%$ NaOH) expectedly resulted the highest measured PFAS degradation ($>99\%$), as evidenced by the least total PFAS remaining in solution after treatment (300 ng/g). While holding the same temperature, PFAS degradation remained high at relatively lower NaOH loadings of $7\text{ wt } \%$ and $2\text{ wt } \%$ ($>99\%$ and 2900 ng/g PFAS, 98% and $16,000\text{ ng/g}$ PFAS, respectively). At $2\text{ wt } \%$ NaOH loading, lower temperatures of 300 and $250\text{ }^\circ\text{C}$ showed further drop in degradation (96%).

Carboxylic acid-containing PFCAs, PFECA, and polyFCAs underwent exceptional degradation across all HALT conditions ($>99\%$ removal, [Figure 2B](#)), with only a total of $140\text{--}760\text{ ng/g}$ remaining in solution. Not surprisingly, the mildest HALT conditions ($250\text{ }^\circ\text{C}$, $2\text{ wt } \%$ NaOH) left the highest concentration in solution. It should be noted that even non-detect values (textured bars) were included to calculate final concentrations after HALT. Therefore, remaining concentrations are likely lower than reported. [Figure 2C](#) clearly shows that PFSA are much more recalcitrant in the HALT reaction environment; the reader is directed to the differences in % degradation y-axis scales between graphs B and C. PFSA levels are essentially unchanged after HALT processing at $250\text{ }^\circ\text{C}$ and $2\text{ wt } \%$ NaOH concentration. PFSA degradation is highly sensitive to reaction temperature, as evidenced by the nearly 50% difference in degradation between 300 and $350\text{ }^\circ\text{C}$ at $2\text{ wt } \%$ NaOH concentration, and $>99\%$ difference between 250 and $350\text{ }^\circ\text{C}$. Degradation is also sensitive to $[\text{NaOH}]$, which is clearly shown when evaluating NaOH loadings of 16 , 7 , and 2

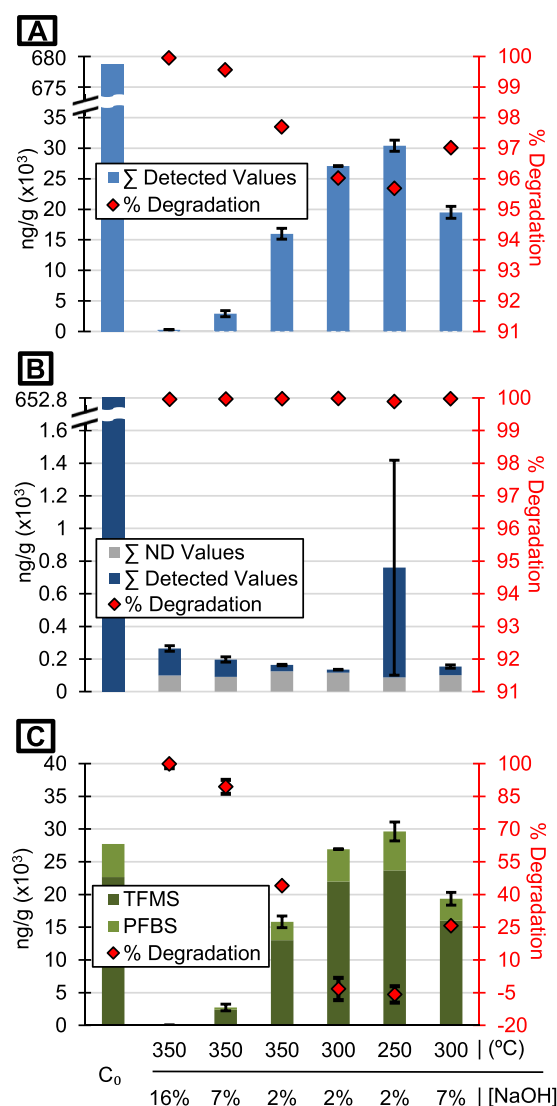


Figure 2. HALT of solution type I. Starting concentration (C_0) is an average across all 6 conditions tested. (A) Total PFAS. (B) Total PFCAs, PFECA, and polyFCAs. (C) Total PFSA. Left y-axes represent the total concentration and the right y-axes are % degradation. Solid bars represent the sum of detected values while textured bars represent the sum of method detection limits (MDLs) for analytes with non-detect values. Red data points represent % degradation. Error bars for both remaining concentrations and % degradation represent one standard deviation of three samples taken throughout each run and only consider detectable values. In cases of relatively lower data spread, error bars may be hidden by data points. Supporting data is provided in the Supporting Information ([Table S3](#)).

wt % at $350\text{ }^\circ\text{C}$ (>99 , 89 , and 44% degradation, respectively). Processing at higher NaOH concentration can achieve near-complete PFSA removal, similar to previous findings.^{27,29}

[Figure 3](#) summarizes a speciated breakdown of the % distribution of residual PFCAs, PFECA, and polyFCAs following HALT across all test conditions. Solid bars represent detected and quantified values while textured portions represent the MDLs of nondetect species. TFA, PFPrA, and 2233-TFPA were most often remaining in solution following HALT, while 2333-TFPA, PFBA, PFPeA, and HFPO–DA were never detected above MDLs. TFA appears to be the most stable PFCA studied, and we hypothesize that the higher

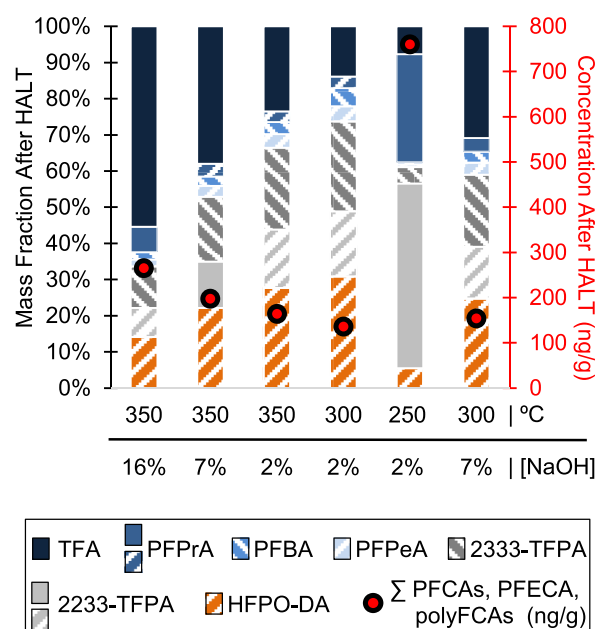


Figure 3. Distribution of PFCAs, PFCEA, and polyFCAs following HALT. The left y-axis corresponds to the stacked bars. Solid bars represent detected values while textured bars represent the MDLs for nondetect values. The right y-axis corresponds to the red data points and represents the sum of PFCA, PFCEA, and polyFCA concentrations following HALT, including MDLs.

quantity of remaining PFPrA at 250 °C and 2 wt % NaOH is a consequence of its relatively higher initial concentration (see Figure 1). Based on previously observed trends in Austin et al., we expect all PFCAs to undergo an initial thermal decarboxylation reaction, and that relatively longer-chain PFCAs (e.g., PFBA) are more susceptible to thermal decarboxylation than TFA.²⁸

The observed difference in concentrations of polyFCAs 2333-TFPA and 2233-TFPA remaining in solution following HALT indicates that the susceptibility of the molecular degradation of partially fluorinated compositions can change as a function of H atom positioning on the fluorinated alkyl tail (see Figure 1 for molecular structures). The disparity between the two TFPA congeners is most apparent under the mildest HALT conditions (250 °C, 2 wt % NaOH), where approximately 390 ng/g 2233-TFPA remains in solution while 2333-TFPA is undetected with an MDL of 34 ng/g. This observed difference could be a consequence of unmatched susceptibility to initial thermal decarboxylation or could be due to degradation via uncommon mechanistic pathways.

Fluorine Mass Balance Closure. While the degradation of targeted species is critical in evaluating the efficacy of PFAS removal, it is also imperative to obtain a complete fluorine mass balance to account for other species formed throughout treatment.⁴³ Two critical components to account for total fluorine (TF) are TOF and IF concentrations in solution, which allow for the quantification of % defluorination (eq 2) as well as % F mass recovery (eq 3). In this pursuit, a multiple-lines-of-evidence approach was taken to quantify both TOF and IF levels before and after HALT by leveraging several analytical techniques (LC–MS/MS, CIC, IC, and ¹⁹F NMR spectroscopy, Figure 4). For each HALT condition, the x-axis

indicates the analytical technique used to quantify TOF values. IF was determined by either IC or ¹⁹F NMR spectroscopy.

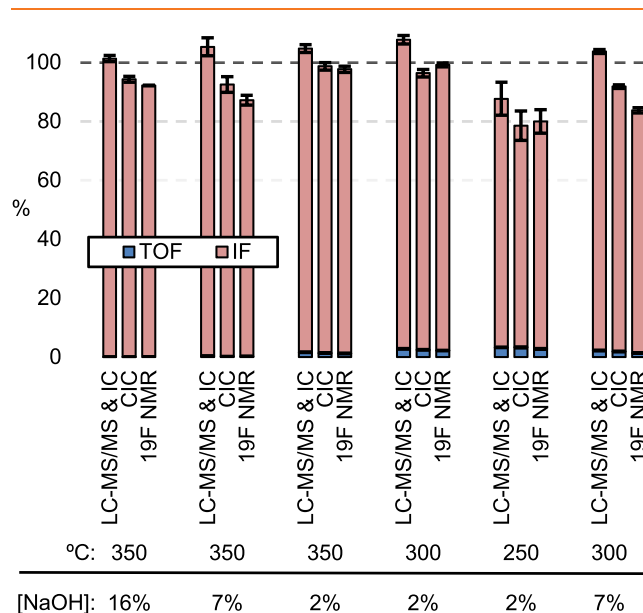


Figure 4. % TOF and IF following HALT of solution type I. Theoretical [TF]₀ was determined by [TOF]₀ + [IF]₀. Analytical methods used for quantification of [TOF]₀ and [TOF] are shown on the x-axis, along with the conditions of each test. For both LC–MS/MS and CIC methods, IC was used for determining [IF]. ¹⁹F NMR quantified both TOF and IF. Error bars represent one standard deviation of three samples taken throughout each experiment. Data supporting this figure can be found in the Supporting Information (Table S7).

First, CIC was evaluated as an analytical technique to quantify % defluorination and % F-mass recovery (eq 3). Across all NaOH loadings at 350 °C, high defluorination (92–97%) and F-mass recovery (93–99%) were realized. Exceptional defluorination levels were also observed at lower temperature. For instance, 2 wt % NaOH loading at 350 and 300 °C afforded 97 and 94% defluorination, respectively, with excellent F-mass recovery (96–99%). However, dropping temperature to 250 °C did show an appreciable decrease in both defluorination (75%) and F-mass recovery (79%). Given the high % degradation levels (96%) under these mildest conditions, it is likely that the gap in F-mass balance is due to volatile organic fluorine generation and losses from solution.

Another effective analytical technique for F-mass tracking is ¹⁹F NMR spectroscopy. Excellent agreement between CIC and ¹⁹F NMR spectroscopy methods for both % defluorination and % F-mass recovery was found (93–99% and 92–99%, respectively). LC–MS/MS analysis can also provide F-mass balance information by conversion of speciated [PFAS] to [TOF]. In all cases, LC–MS/MS showed slightly elevated % F-mass recoveries. One potential explanation is slightly depressed [TOF]₀ relative to CIC and ¹⁹F NMR, which could be a consequence of ion suppression. Despite this, good agreement in % F-mass recovery across all three analytical approaches was realized for optimized cases of 2 wt % NaOH at 350 and 300 °C (93% and 90%, respectively).

Destruction and Defluorination Performance for Solution Type II. To better understand HALT efficacy across a broader library of PFASs, type II solution was processed at

one HALT condition (350 °C and 11 wt % NaOH, Table 1). PFCAs, polyFCAs, and PFECA studied in solution type I were

Table 1. HALT of Solution Type II^a

PFAS type	% degraded ^b	% IF ^c	% TOF ^c
PFCAs	>99	93 ^d	0.30 ^b
PFECA	>99		
polyFCAs	>99	96 ^d	0.31 ^e
PFSA	98		
FASAs	>99	96 ^f	0.15 ^f
PFSI	>99		

^aConditions of HALT: 350 °C, 11% NaOH. ^bDetermined by LC–MS/MS analysis. ^cValues are based on [TF]₀ and the sum of % IF and % TOF is % F mass-balance recovery. ^dDetermined by IC analysis. ^eDetermined by CIC. ^fDetermined by 19F NMR analysis. Supporting data is available in the Supporting Information (Table S8).

included in solution type II, in addition to PFHxA and PFOA. TFMS, PFBS, and PFOS accounted for the PFSA class. The inclusion of fluoroalkyl sulfonamides (FASAs) MeFBSA and FBSA, and perfluorosulfonimide (PFSI) TFSI provided an expansion in PFAS functional groups studied (see Figure 1 for solution type II details). As expected, PFSA were most recalcitrant (≈98% removal) while PFCAs, PFECA, and polyFCAs underwent >99% degradation with analytes measuring nondetect levels with exception to TFA and PFPrA (89 and 13 ng/g, respectively). FASAs MeFBSA and FBSA underwent >99% degradation, indicating facile removal of sulfonamide analytes. Lastly, PFSI (TFSI) showed removal to nondetect levels (MDL = 2.0 ng/g). To the authors' knowledge, the degradation of TFSI has not been reported prior to this work.

The same multiple-lines-of-evidence approach for fluorine mass balance highlighted in Figure 4 was taken for solution type II (Table 1). CIC, ¹⁹F NMR, and LC–MS/MS determined 94–96% F-mass recovery by quantifying TOF and IF concentrations before and after HALT. Exceptional agreement of 97% across all three analytical methods was realized.

Fate of Inorganic Ions. The challenging nature of solution types I and II is, in part, a consequence of high concentrations of inorganic salts NaCl, NaNO₃, Na₂SO₄, and NaHCO₃/Na₂CO₃ buffer (≈10 wt % TDS). Tracking these ion concentrations before and after HALT processing allowed for assessment of any competing reactions, precipitate formation, or production of other reaction byproducts. This is relevant in the context of other PFAS destruction technologies. For example, electrochemical oxidation is known to form perchlorate when chlorides are present,²³ and the presence of inorganic ions can decrease the effectiveness of UV-based processes, presumably as a consequence of lower UV transmission as well as competitive dissolved electron (e_{aq}[−]) scavenging.⁴⁴ In view of these concerns, initial (C₀) and final (C) concentrations were measured and normalized values were compared for SO₄^{2−}, NO₃[−], and Cl[−] anions across all 6 conditions tested for solution type I (Figure 5). For all conditions, anion concentrations before and after processing were nearly equivalent. Under the most aggressive treatment conditions, we surmise that the 16 wt % NaOH load may have contributed to a slight increase in chloride and sulfate levels as a consequence of NaOH impurities. The lack of anion concentration change before and after treatment suggests

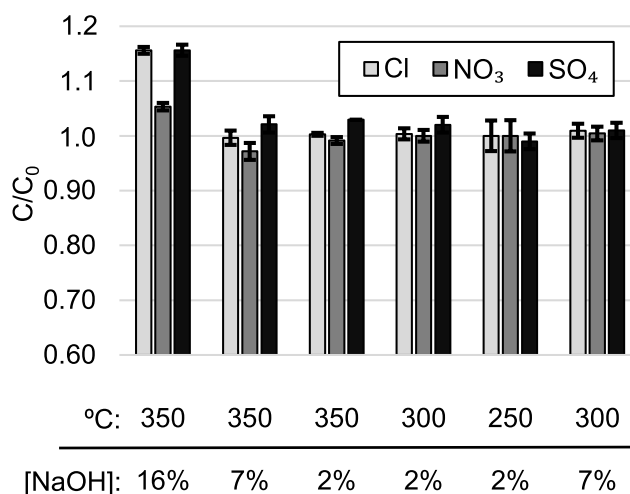


Figure 5. Change in chloride, nitrate, and sulfate concentrations from HALT. Initial (C₀) and final (C) concentrations are an average of three samples taken throughout each run and error bars represent one standard deviation of triplicate data points. Supporting data is provided in the Supporting Information (Table S4).

that dissolved inorganic anions play a purely spectator role during HALT processing.

Practical Implications. Many other PFAS destruction technologies fail to effectively treat short- and ultra short-chain PFASs, in some cases due to insufficient surface activity. For example, plasma destruction relies on PFASs to migrate to a liquid–gas interface at bubble surfaces where plasma is discharged. Studies have shown that PFBA and shorter PFASs are not effectively treated by plasma processing.²¹ Electrochemical oxidation suffers from a similar limitation, where reactions mostly take place near the solid–liquid interface at electrode surfaces. UV-based processes reliant on the formation of micelles will also not effectively address short-chain and ultra short-chain PFASs, as C₄ PFCAs and shorter-chain PFASs will not form micelles or will not effectively migrate to micelles.

High TDS solutions also create treatment challenges, notably for electrochemical oxidation and SCWO destruction processes. Electrochemical oxidation readily generates perchlorates in chloride-rich liquids, which creates subsequent treatment needs.²³ SCWO processing takes place in the supercritical phase of water, where the solubility of polar compounds is very low (e.g., NaCl solubility is ≈0.1 wt %). SCWO processing of salty feedstocks therefore requires excessive dilution, or advanced salt control strategies to prevent salt precipitation and reactor clogging.^{45–47} Many of these other technologies have excellent practical use cases in other scenarios, but the simultaneous treatment of ultra short- and short-chain PFASs in a high TDS solution proves a challenge to most existing technologies.⁴⁸

This study demonstrates that HALT can effectively manage PFAS-rich and high salt solutions, even when short- and ultra short-chain PFASs are present. While more aggressive treatment conditions are needed to effectively degrade and defluorinate PFSA, milder conditions are sufficient for treating PFCAs, polyFCAs, PFECA, FASAs, and PFSIs. For instance, 2 wt % NaOH or lower appears to be sufficient for degrading and defluorinating PFCAs, PFECA, and polyFCAs; in real treatment scenarios, this drastically reduces the chemical

consumption (both alkali and conjugate acid) needed for the HALT process. Overall, this study demonstrates that HALT could be applied to treat IEX regeneration brines and membrane reject streams where both high TDS and high concentrations of ultra short- and short-chain PFASs may be present.

CONCLUSIONS

HALT is one of very few PFAS destruction processes which has now demonstrated the effective degradation and defluorination of short- and ultra short-chain PFASs. A multiple-lines-of-evidence approach by both targeted and nontargeted analytical techniques was leveraged to show complete conversion of PFASs to inorganic dissolved fluoride during HALT treatment. No competing reactions with dissolved ions are observed, and no salt precipitation occurs in the subcritical liquid processing phase. Additionally, near-stoichiometric dissolved fluoride production at optimized conditions strongly indicates that HALT avoids the production of VOFs, as supported by previous studies. PFCAs, PFECAs, and polyFCAs are significantly more susceptible to degradation via HALT processing compared to PFASs, suggesting that mild HALT with low NaOH loading can provide efficient and effective treatment of high TDS wastewater streams without significant quantities of PFASs.

In the practical setting, this study demonstrates that HALT can enable high-volume treatment of industrial wastewater containing short- and ultra short-chain PFASs. Various technologies, including RO membrane separation and regenerable sorbents, can be used to separate and concentrate PFASs from wastewater, and HALT technology can treat the resulting PFAS-rich liquid with no observed deleterious treatment impact imparted by high concentrations of non-fluorinated inorganic salts. Recent trends in PFAS occurrence and an evolving global regulatory environment strongly suggest that effective treatment of ultra short and short-chain PFASs will become a central focus in coming years.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsestengg.4c00378>.

Additional reagent information, analytical information including instrumentation, method descriptions, and validation procedures, experimental procedures, descriptions and figures of the experimental apparatus, and tabulated experimental data on PFAS and ion concentrations (PDF)

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Author Contributions

[†]B. R. Pinkard and S. M. Smith contributed equally to this manuscript. The manuscript was written by contributions of all authors. All authors have given approval to the final version of the manuscript. B. R. Pinkard and S. M. Smith contributed to the conceptualization, project administration, supervision, writing, data curation, and design of methodology employed in this study. P. Vorarath, T. Smrz, S. Schmick, and L. Dressel contributed to the investigation and resources employed in this study. M. Czerski, A. de Marne, A. Halevi, and C. Thomsen contributed to the investigation and resources employed in this study. C. Bryan and C. Woodruff assisted with the supervision and project administration for this study. All experiments were performed by authors affiliated with Aquagga, Inc. All sample and data analyses were performed by authors affiliated with 3M Company.

Notes

The authors declare the following competing financial interest(s): Authors BP, MC, AM, AH, CT, and CW are co-owners and/or employees of Aquagga, Inc., which has a pecuniary interest in the herein described technology. Authors SS, PV, TS, SS, LD, and CB declare no competing financial interests.

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