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PFAS Degradation and Defluorination of High TDS Wastewater via Continuous Hydrothermal Alkaline Treatment (HALT)

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ABSTRACT

Hydrothermal alkaline treatment (HALT) is an emerging, industry-leading per- and polyfluoroalkyl substances (PFAS) destruction process that is uniquely capable of degrading and defluorinating ultra short-, short- and long-chain PFASs in high total dissolved solids (TDS) wastewaters. HALT operates under subcritical water conditions ($T > 300$ ˚C, $P > 20$ MPa) with the addition of sodium hydroxide (NaOH), which raises the pH and drives PFAS destruction reactions via various reaction mechanisms including thermal decarboxylation and nucleophilic substitution.

Two case studies were performed applying the HALT technology to degrade and defluorinate a range of PFASs within a high total dissolved solids (TDS) wastewater stream. The wastewater was processed under a range of different HALT operating conditions to assess the degradation, defluorination, and F-mass recovery for ultra short- and short-chain PFASs. This was first carried out with synthetic waters processed through a small HALT reactor. This informed, and was followed by, a commercial-scale continuous HALT reactor demonstration at a 3M manufacturing site treating real industrial wastewaters.

Optimized conditions reveal near-quantitative defluorination and F-mass recovery, even at relatively low loadings of NaOH in the HALT reactor. Intensive analytical work for quantitation of total organic fluorine (TOF), inorganic fluoride (IF), and speciated PFAS was supported by LC-MS/MS, ion chromatography (IC), combustion ion chromatography (CIC), ^{19}F NMR spectroscopy, ion selective electrolysis (ISE), Fourier transform infrared spectroscopy (FTIR), and GC-MS analyses. This multiple-lines-of-evidence approach shows good agreement between degradation and defluorination percentages at most HALT treatment conditions, indicating excellent F-mass recovery. Perfluorocarboxylic acids (PFCAs) were highly susceptible to degradation and defluorination via HALT even under relatively mild treatment conditions, while perfluorosulfonic acids (PFSAs) were more recalcitrant.

Overall, these studies demonstrate that a continuous HALT system can be employed to achieve high degradation and defluorination of a myriad of PFASs, including ultra short- short- and long-chain compounds, from high concentration wastewater streams.

INTRODUCTION

3M Company and Aquagga, Inc. established a collaboration in 2022 that has led to extensive development and piloting work related to assessing the hydrothermal alkaline treatment (HALT) technology for applications in the destruction of per- and polyfluoroalkyl substances (PFAS) in challenging liquid matrices.

The term "PFAS" used throughout this work adopts the definition provided by the Organization for Economic Cooperation and Development (OECD, Organization for Economic Cooperation and Development, 2024). Within this definition exists sub-groupings of compositions that vary in organofluorine content. Short- and long-chain designations have been defined by the US Environmental Protection Agency (USEPA, 2009) and the OECD (OECD, 2024). Ultra short-chain is a third class that has been adopted by the technical community with some ambiguity, and is defined as PFASs containing ≤ 3 fully fluorinated carbon atoms. Effective water remediation and mitigation is highly challenging for this third class due to, in part, lower fluorocarbon content which renders PFASs within this category relatively higher in water solubility and lower in surface activity (ITRC, 2024). The work described in this report adopts the PFAS and grouping definitions described above purely on a technical basis, with no intent to suggest grouping or management strategies for regulatory actions.

HALT is a thermochemical process leveraging high pH conditions ($pH > 13$) and elevated temperatures ($T > 300$ ˚C) in subcritical water ($P > P_B$) 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) (Wu, et al., 2019) and trifluoroacetic acid (TFA) (Austin, et al., 2024), AFFF (Hao, et al., 2021), groundwater and soil (Hao, Choi, Deeb, Strathmann, & Higgins, 2022), spent GAC (Soker, Hao, Trewyn, Higgins, & Strathmann, 2023), fire training pond water (Pinkard, Austin, Purohit, Li, & Novosselov, 2023), and foam fractionate (Hao, et al., 2023). 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. 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 as an initial step for perfluorocarboxylic acid (PFCA) degradation (Austin, et al., 2024). Austin et al. also observed that fluoroform (CF_3H) rather than inorganic fluoride 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 fluoroform production, instead promoting fluoride ion production (Austin, et al., 2024).

While HALT has 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, and a wider range of real-world matrices. Herein, we report two destruction studies via HALT focusing on highly challenging salt solutions (3 to 10 wt% total dissolved solids [TDS]) comprising PFASs ranging in chain length and functional group type, with a primary focus on ultra short-chain analogues. A 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 across multiple system scales and liquid matrices.

MATERIALS & METHODS

Two phases of HALT experimental work, with two different HALT systems and two different water matrices, are reported. The first phase of work ("Development Work") involved a small HALT system and a synthetic wastewater matrix. The second phase of work ("Pilot Work") involved a containerized, commercial-scale HALT system, a real wastewater influent, and was performed on-site at an operational manufacturing facility. Further details on the Materials & Methods of each phase of work are described separately. The efficacy of HALT under varying operating conditions was determined by calculating degradation and defluorination and F-mass recovery levels, as described in eqs. 1–3

$$\% \text{ Degradation} = \frac{C}{C_0} \cdot 100 \qquad \textbf{(Eq. 1)}$$

$$\% \text{ Defluorination} = \frac{[\text{IF}]\text{-}[\text{IF}]_0}{[\text{TOF}]_0} \cdot 100 \qquad \textbf{(Eq. 2)}$$

$$\% \text{ F mass recovery} = \frac{[\text{IF}]+[\text{TOF}]}{[\text{IF}]_0+[\text{TOF}]_0} \cdot 100 \qquad \textbf{(Eq. 3)}$$

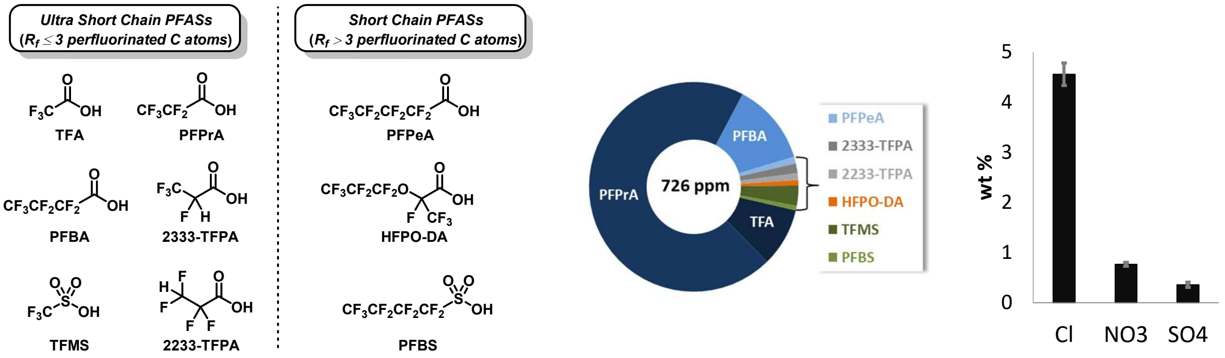
where C_0 is analyte (e.g., PFPrA, TFA, Cl^-, etc.) concentration before the addition of NaOH and HALT. C is analyte concentration following addition of NaOH and HALT. $[TOF]_0$ and $[IF]_0$ are total organic fluorine and inorganic fluoride, respectively, of the initial solution prior to NaOH addition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

Use of analytical techniques including triple quadrupole mass spectrometry (LC-MS/MS), ion chromatography (IC), combustion ion chromatography (CIC), ^{19}F NMR spectroscopy, ion selective electrode (ISE) analysis, and inductively coupled plasma (ICP) spectroscopy were used to determine TOF, IF, PFAS, and non-PFAS concentrations in HALT feed and effluent water streams. For pilot work additional analytical techniques Fourier-transform infrared (FTIR) spectroscopy and gas chromatography-mass spectrometry (GC-MS) were leveraged to track and quantify volatile organofluorine (VOF) by-products in the HALT effluent stream.

DEVELOPMENT WORK. Perfluoroalkyl carboxylic acids (PFCAs), a perfluoroalkyl ether carboxylic acid (PFECA), polyfluoroalkyl carboxylic acids (polyFCAs), and perfluoroalkyl sulfonic acids (PFSAs) highlighted in Figure 1 were included in development work. Compositions within these groupings are highlighted in Figure 1 and span across ultra short- and short-chain homologues. The PFAS-containing solution 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 trifluoroacetic acid (TFA), pentafluoropropionic acid (PFPrA), and heptafluorobutyric acid (PFBA) (a combined ≈92 wt% of total PFAS). 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) studied. Probing HALT destruction efficacy of high TDS solutions was accomplished by also spiking solutions with NaCl, Na_2SO_4, $NaNO_3$, $NaHCO_3$, and

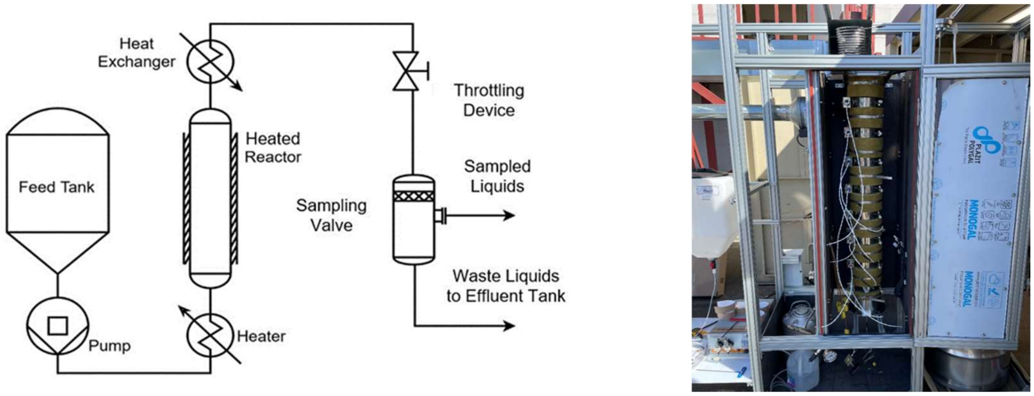
Na_2CO_3 to targeted concentrations of 7.5%, 0.5%, 1.5%, 0.25%, and 0.25%, respectively (Figure 1).

Figure 1. Ultra short- and short-chain PFASs and inorganic anions.



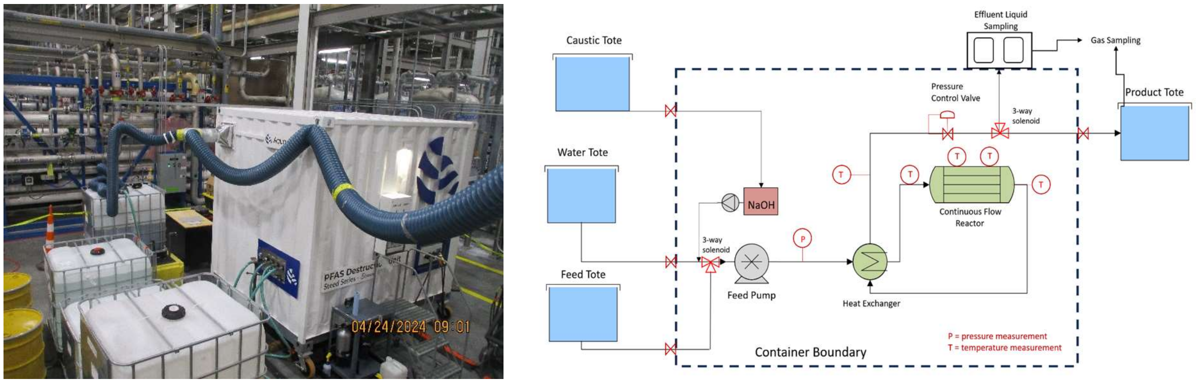
A continuous-flow, small-scale HALT reactor (Figure 2) was used for all Development Work. For every test, solid NaOH was premixed into the individual sample containers to the desired overall NaOH concentration (2 to 16 wt%). Untreated samples were collected before NaOH addition to confirm starting PFAS 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. 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 to 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 datapoints 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.

Figure 2. Process flow diagram (PFD) and picture of small-scale HALT reactor used for Development Work.



PILOT WORK. An actual wastewater stream containing a range of PFASs and concentrations was used to assess the performance of the commercial-scale HALT reactor during the on-site Pilot Work. The commercial-scale HALT reactor was operated for approximately 200 h over the course of two weeks, generating treatment performance data at two temperatures (T1 = lower, T2 = higher), a range of NaOH concentrations (ultra-low to medium), two different bases (NaOH and weaker base Na_2CO_3), and pump flow rates. For each experimental condition tested, liquid NaOH was metered into the wastewater influent to achieve the desired NaOH dosing, and fully pre-mixed before introduction to the HALT reactor. Four treated samples were collected per experimental condition in HDPE sample bottles. For experiments using Na_2CO_3, drums of feed water were pre-dosed with Na_2CO_3 to the desired concentration prior to feeding to the commercial-scale HALT reactor.

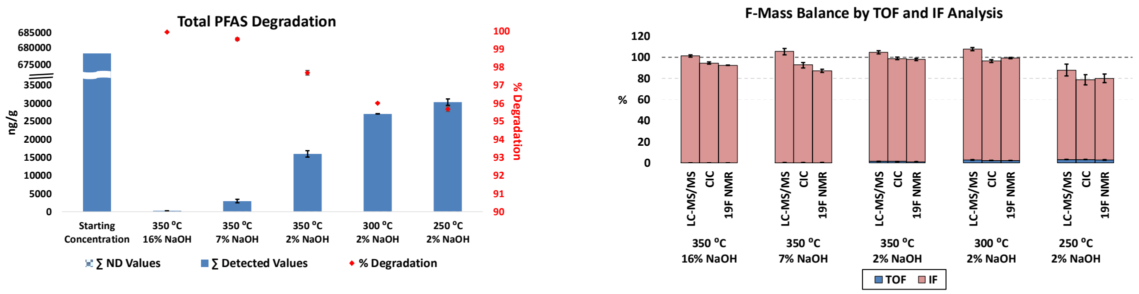
Figure 3. Commercial-scale HALT reactor operating at a water quality building during a 2-week pilot trial (April, 2024) and PFD showing sampling points.



RESULTS – DEVELOPMENT WORK

Figure 4 shows total PFAS concentrations (blue bars) before and after HALT processing at each tested condition and % degradation (red datapoints) for the development work. The most aggressive processing conditions (350 ˚C, 16% 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% and 2% (>99% and 2900 ng/g PFAS, 98% and 16000 ng/g PFAS, respectively). At 2% NaOH loading, lower temperatures of 300 ˚C and 250 ˚C showed further drop in degradation (96%). While not illustrated in Figure 4, the drop in degradation levels at relatively milder conditions is attributed to the recalcitrance of PFSAs TFMS and PFBS.

Figure 4. Targeted and non-targeted analysis of PFAS destruction via HALT.



While the degradation of targeted species is critical in evaluating the efficacy of PFAS degradation, it is also imperative to obtain a complete fluorine mass balance to account for other species formed throughout treatment. Total organic fluorine (TOF) and inorganic fluoride (IF) concentrations in solution were quantified to determine % defluorination as well as % F mass recovery. For each HALT condition, the x-axis indicates the analytical technique used to quantify TOF values. IF was determined by either IC or ^{19}F NMR spectroscopy.

CIC and IC analyses across all NaOH loadings at 350 °C revealed high defluorination and F-mass recovery (92 to 97% and 93 to 99%, respectively). Dropping temperature to 300 °C still resulted in high defluorination and F-mass balance (94% and 97%, respectively). Noticeable drops in defluorination and F-mass recovery were realized when temperature was lowered to 250 °C (75 and 79%, respectively). Given the high degradation under these conditions, it is likely that the F-mass loss is a consequence of VOF losses from solution.

^{19}F NMR spectroscopy and LC-MS/MS analytical techniques also revealed high levels of both defluorination and F-mass recovery, thereby providing validation for IC and CIC analysis. Defluorination and F-mass recovery were generally in excellent agreement (93 to 99% and 92 to 99%, respectively). In all cases, LC-MS/MS showed slightly elevated F-mass recoveries. One potential explanation is slightly depressed $[TOF]_0$ relative to CIC and ^{19}F 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% NaOH at 350 °C and 300 °C (93% and 90%, respectively).

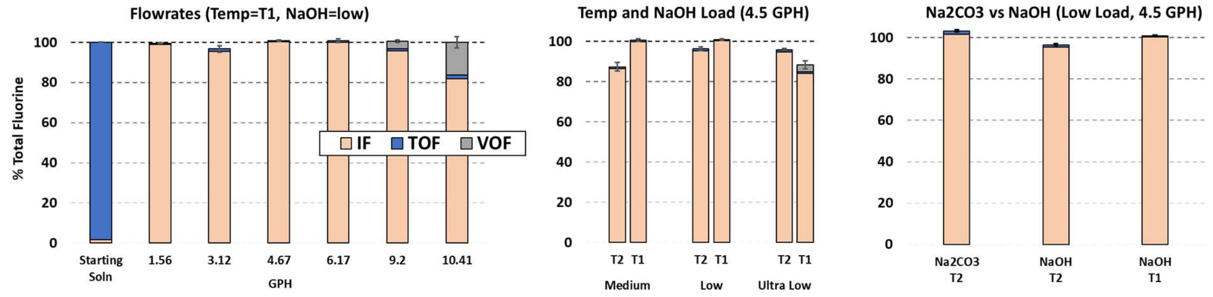
RESULTS – PILOT WORK

Figure 5 summarizes several trends key takeaways from the 2-week pilot trial. The data summarized in Figure 5 is from CIC, IC, and FTIR analytical techniques. Operation of the HALT commercial-scale system under low NaOH loading and temperature set-point T1 showed exceptional degradation and defluorination (>99% and 95 to >99%, respectively) from 1.56 to 6.17 GPH with no observed VOF by FTIR analysis. VOF was observed at higher feed-rates of 9.2 and 10.41 GPH (3.6 and 16% of total F-mass, respectively). VOF generation resulted in lower defluorination rates, which was especially evident at 10.41 GPH feed-rate (81%).

Temperature comparisons at lower and higher setpoint values (T1 and T2, respectively) were also compared at different NaOH loading levels (medium, low, and ultra-low). Surprisingly, better F-mass balance recovery was observed for T1 conditions at both medium and low NaOH loadings. However, the limitations of T1 were realized at ultra-low NaOH loading (VOF = 3.5% of F-mass, 85% aqueous F-mass recovery) while T2 showed no observable VOF by FTIR with approximately 96% F-mass recovery. From a chemical reactivity perspective, the loss of mass balance closure at higher processing temperatures is difficult to explain. However, one potential explanation is that relatively higher precipitation rates of fluoride in conjunction with hard metals, such as calcium or magnesium, occur at higher temperatures. It is also worth noting that degradation is >99% in all cases. Therefore, given that no VOF species are observed at higher temperatures, one could reason that fluoride precipitation accounts for F-mass loss in solution.

The nature of the base is also critical for assessing a full-scale HALT process. While NaOH is highly effective, the resultant pH (>13) could result in elevated corrosion rates. Moving to lower pH levels, such as 10-11, with a milder base such as Na_2CO_3 could prove operationally beneficial. At higher temperature set-point T2, a low loading level of Na_2CO_3 afforded complete F-mass balance closure, and exceptional degradation and defluorination (98 and >99%, respectively).

Figure 5. F-Mass balance trends



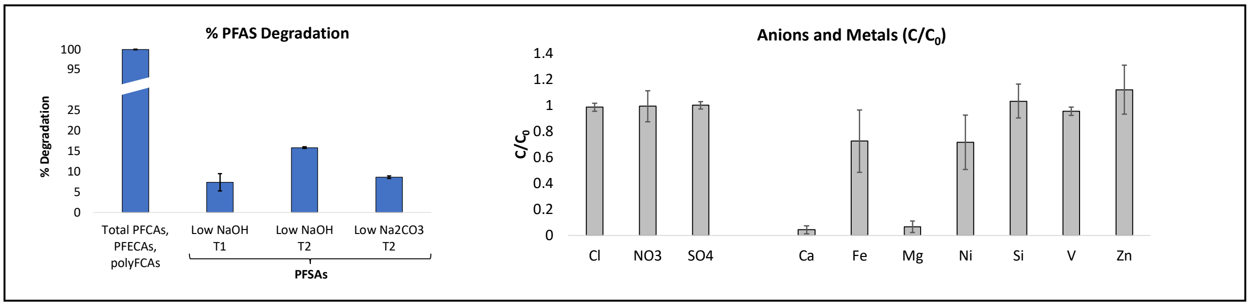
Other analytical techniques for F-quantification were explored to validate some of the experimental runs highlighted in Figure 5, which were determined by IC and CIC analytical techniques. ^{19}F NMR spectroscopy showed very little difference in [TOF] (1 to 4%) and [IF] (4 to 5%). ISE was also in very strong agreement, quantifying minimal difference in [IF] (0.7 to 4.9%).

A majority of the PFASs in the process stream for the 2-week pilot trial comprised PFCAs, which were accompanied by relatively lower concentrations of polyFCAs, PFECAs, and PFSAs. Across all conditions studied, HALT afforded >99% degradation of PFCAs, polyFCAs, and PFECAs (Figure 6). As was observed in our development work, PFSAs underwent significantly lower degradation under the conditions studied. A slight change in PFSA degradation was realized when increasing temperature from T1 to T2 at low NaOH loading (7% and 16% degradation, respectively). Weaker base Na_2CO_3 showed relatively lower degradation (8.6%) at T2 when compared to NaOH. While we are confident that higher base loadings would have likely provided much improved PFSA degradation levels, this was not the objective of the pilot trial.

Other, non-fluorinated analytes were also quantified before and after HALT. Of particular interest were inorganic anions Cl^-, NO_3^-, and SO_4^{2-}, which were the main constituents in these high

TDS streams (Figure 6). It was assumed that these would very likely play a purely spectator role under the treatment conditions assessed. This was confirmed by quantification of initial (C_0) and final (C) concentrations via IC analysis. In all cases, the concentrations for Cl^-, NO_3^-, and SO_4^{2-} remained essentially unchanged (C/C_0 = 0.98, 0.99, and 1.0, respectively). In addition to anions, a wide range of metals were also quantified by ICP analysis for both initial and final concentrations. Those which consistently showed detectable levels on the influent or effluent are highlighted. While Fe, Ni, Si, V, and Zn remained largely unchanged following treatment, Ca and Mg consistently showed a significant drop in concentration following treatment (C/C_0 = 0.043 and 0.067, respectively). This is likely a consequence of precipitation with anions such as SO_4^{2-}, CO_3^{2-}, and even F^-.

Figure 6. PFAS, inorganic anions, and metals analyses



RESULTS – PRACTICAL CONSIDERATIONS

Many other PFAS destruction technologies fail to effectively treat short- and ultra short-chain PFASs, likely due to insufficient surface activity. For example, studies have shown that PFBA and shorter PFASs are not effectively treated by plasma processing (Singh, et al., 2019). Electrochemical oxidation suffers from a similar limitation, where reactions mostly take place near the solid-liquid interface at electrode surfaces. High TDS solutions also create treatment challenges, notably for electrochemical oxidation and supercritical water oxidation (SCWO) destruction processes. Electrochemical oxidation readily generates perchlorates in chloride-rich liquids, which creates subsequent treatment needs (Barisci & Suri, 2022). 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 (Voisin, et al.) (Kritzer & Dinjus, 2001) (Bermejo & Cocero, 2006).

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 PFSAs, milder conditions are sufficient for treating PFCAs, polyFCAs, and PFECAs. For instance, 2 wt% NaOH or lower appears to be sufficient for degrading and defluorinating PFCAs, PFECAs, and polyFCAs; in real treatment scenarios, this drastically reduces the chemical consumption (both alkali and conjugate acid) needed for the HALT process.

The energy cost of HALT processing is low compared to other PFAS destruction processes, when appropriately normalized by order of magnitude (OoM) PFAS destroyed. The commercial-scale HALT reactor draws ~0.9 kWh of power per gallon treated, and reliably achieves >99% total PFAS defluorination, translating to ~0.3 kWh/gal/OoM. For reference, electrochemical oxidation requires ~1.3 to 7.78 kWh/gal/OoM for PFAS destruction in real world samples (McDonough & Houtz, 2024). McDonough et al. reported that SCWO requires ~5.3 kWh/gal of energy to operate, with 4 to 5 OoM of total PFAS reduction, resulting in energy costs of ~1.06 to 1.33 kWh/gal/OoM (McDonough, et al., 2022). McDonough et al. also report that other approaches, such as sonolysis, have even higher energy requirements.

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. As far as the authors are aware, HALT is now the only PFAS destruction process demonstrating the degradation and mineralization of short- and ultra short-chain PFASs in a challenging high TDS matrix with near-stoichiometric fluorine mass-balance closure. A multiple-lines-of-evidence approach by both targeted and non-targeted analytical techniques shows 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, most treatment conditions avoid the production of VOFs, consistent with previous studies. PFCAs, PFECAs, and polyFCAs are significantly more susceptible to degradation via HALT processing compared to PFSAs, suggesting that mild HALT with low NaOH loading can provide efficient and effective treatment of high TDS wastewater streams without significant quantities of PFSAs.

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.

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Prepared Discussion of: PFAS Degradation and Defluorination of High TDS Wastewater via Continuous Hydrothermal Alkaline Treatment (HALT)

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APPROACH

This paper covers results of bench development and site pilot testing to evaluate the application of Hydrothermal Alkaline Treatment (HALT) to degrade and defluorinate a range of per- and polyfluoralkyl substances (PFASs). Subcritical water conditions with the addition of sodium hydroxide (NaOH) to raise the pH drives the HALT destruction of PFASs via decarboxylation and nucleophilic substitution. The focus of treatment for this project is on short-chain and ultra-short chain PFASs in liquid wastes with high total dissolved solids (TDS).

Two phases of experimental work were performed using different HALT systems and feed water matrices. These phases are described as follows:

1. **Development Work** – bench-scale testing using a synthetic feedstock containing primarily PFCAs, with HALT operating temperatures from 250 to 350 degrees Centigrade, and NaOH concentrations 2 wt%, to 16 wt%.

2. **Pilot Work** – operation of a fabricated HALT system at an industrial site using actual wastewater for 2 weeks at two temperatures and a range of NaOH concentrations using two different bases and a range of flow rates.

BACKGROUND DISCUSSION

The application of HALT systems for managing the disposal of PFAS substances is an emerging technology with a developing market capacity to manufacture, install and operate systems.

Because the basis for this project is to evaluate and test the application of HALT systems to manage PFAS disposal, it would be useful to understand the generic capacity and state of the current market to fabricate, install and operate such systems. The basic elements of the treatment system include feed tanks, pumps, valves, a heated reactor vessel, heat exchangers, piping, and instrumentation with sampling and controls. A review of testing research is discussed. It would also be useful to review field experiences with operating systems if applicable.

A physical description of testing equipment with material specifications for the two HALT testing systems installed for use by this project would be useful. Factors such as the use and availability of generic products versus the need for special fabrications or if any proprietary features are included in the test systems deserves consideration. The presentation description of the Pilot Work includes a reference to the manufacturer HALT model system product series installed at the operational facility. Manufacturer product names should be removed.

TECHNICAL CONSIDERATIONS

The need for research and testing of HALT systems for PFAS disposal is presented well including results for this two-phase delivery of treatment test units. This application targets the unique and specific requirements for disposing of short- and ultra-short chain PFAS substances in high TDS liquid wastes. The subcritical water conditions for HALT applications cover temperatures from 200 to 374 degrees Centigrade, pressures from 10 to 30 MPa, pH greater than 14 and water in the liquid phase. The first development of HALT is reported under SERDP ER18-1501 at the Colorado School of Mines cited as Stathmann et al. in the presentation slides, but this reference is missing and not discussed in the paper.

Details of the testing protocol for both Development and Pilot Work deserve additional content to provide actual test information for each run covering items such as the source and chemical content of the feedstock used to formulate synthetic or facility waste feed water, temperatures, pressures, TDS spiking solutions or concentrations, NaOH concentrations, and lab testing methods. A summary table with actual test run details would be appropriate for this information. Was pretreatment provided for feedwater at the site pilot work application? If so, it should be described.

The process flow diagram for the Development Work includes a waste liquids flow path. Does this represent a waste or does the product water become a waste for testing purposes only. The Pilot Work process flow diagram includes a gas sampling point for the product water step. How was gas sampling handled for the Development Work and what are the characteristics of the gas production, volume and constituents for both project phases?

Results of the Developmental Work were used to inform setup and execution of the Pilot Work. The Developmental Work confirmed the ability for HALT to meet targets for the tested feedwater PFAS disposal, while providing criteria for sizing the Pilot System. Some discussion of the lessons learned during the Developmental Work and how this information improved the setup, delivery, and operation of the Pilot Work as appropriate would be useful to include.

IMPLEMENTATION CONSIDERATIONS

Results offer practical information for the design and operation of full-scale HALT applications to effectively treat short- and ultra-short chain PFASs. In addition, the challenges for high TDS wastes were found to be manageable. Of particular interest is the data showing that lower temperatures and pH values using lower NaOH loadings achieved better F-mass balance recovery. In addition, moving to lower pH levels such as 10-11 using sodium carbonate at the higher temperature set-point afforded complete F-mass balance closure with high degradation and defluorination (98 and >99%), respectively resulting in a lower rate of corrosion risk. By optimizing the HALT variables to the waste treatment characteristics, operating conditions can reduce the chemical demands, corrosion risks, and related operating costs. A key variable for achieving optimal performance is the flow rate. Although a range of flows were tested, specific guidance or criteria for setting and managing the flow rate during operations should be discussed.

In addition, the energy demand for HALT processing was found to be lower than other PFAS destruction processes. Energy demands were normalized by estimating the Order of Magnitude energy per gallon treated, with the HALT operating results as several multiples less than published data for other methods including electrochemical oxidation, and super critical water oxidation (SCWO).

The application of HALT at operating facilities will generally require the application of a PFAS separation technology such as RO membranes, foam fractionation, or filtration media such as activated carbon or ion exchange resins, for input to the HALT system prior to destruction and disposal, at near 100% fluorine mass balance. If media is used, additional disposal processing of the spent media would be required to provide complete disposal and complete PFAS destruction. The use of foam fractionation for pretreatment was not mentioned and should be included.

Additional information of interest from the results of this project should expand on the next steps needed for full scale development and delivery. Topics of interest include suggested design standards, regulatory reviews and approvals, system process proving and performance testing, operational controls and testing, and system optimization for corrosion control, chemical use, energy management and compliance reporting.