Final Report

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Appendix F: DE-FLUORO™ PFAS Destruction Pilot Study

Project 1007 Feasibility Study
Minnesota Pollution Control Agency

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Acronyms and Abbreviations

%	Percent
AOF	adsorbable organic fluorine
Cl^-	chloride ion
ClO_4^-	perchlorate ion
Cr	chromium
EO	electrochemical oxidation
F^-	fluoride ion
Fe	iron
FS	feasibility study
GAC	granular activated carbon
HBV	Health-Based Value
hr	hours
HRL	Health Risk Limit
MDH	Minnesota Department of Health
mg/L	milligram per liter
MPCA	Minnesota Pollution Control Agency
mS/cm	milli-Siemens per centimeter
ng/L	nanograms per liter
NS	not sampled
PFAS	per- and polyfluoroalkyl substances
PFBA	perfluorobutanoic acid
PFBS	perfluorobutane sulfonic acid
PFHpS	perfluoroheptane sulfonic acid
PFHxA	perfluorohexanoic acid
PFHxS	perfluorohexane sulfonic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctane sulfonic acid
PFOS	perfluorooctanoic acid
PFOSA	perfluorooctanesulfonamide
PFPeA	perfluoropentanoic acid
PFPeS	perfluoropetane sulfonic acid
PLC	programmable logic controller
QA/QC	quality assurance/quality control
SAFF®	Surface Active Foam Fractionation
SO_4^-	sulfate ion
SVOC	semi-volatile organic compound
TAT	turnaround time
TOC	total organic carbon
TOF	total organo-fluorine
TOP	total oxidizable precursor
µm	micrometer

VOC	volatile organic compound
WCL	Washington County Landfill

F1 Introduction

F1.1 Project Background

As part of the broader Project 1007 Feasibility Study (FS), AECOM was engaged by the Minnesota Pollution Control Agency (MPCA) to undertake a field pilot study to treat per-and polyfluoroalkyl substances (PFAS) impacted liquid wastes utilizing electrochemical oxidation. A Surface Active Foam Fractionation (SAFF®) system, which was also piloted as part of the Project 1007 FS, was used to generate concentrated PFAS waste for the electrochemical oxidation destruction pilot-test. The pairing of these two technologies, in addition to bench-scale testing of other PFAS destruction technologies, was conducted to evaluate a treatment train approach to remove and destroy PFAS in groundwater and surface water within the Project 1007 extent. The results of these studies will inform the selection of technologies in this FS. SAFF® was used to remove and concentrate PFAS from both surface water and groundwater. Results of the SAFF® pilot-study are discussed in Appendix E (Surface Active Foam Fractionation [SAFF®] Pilot Study Report). Several other destructive technologies were tested at the bench-scale using SAFF® concentrate as well. A summary of the results of the bench-scale PFAS destruction testing can be found in Appendix G (PFAS Destruction Technology Bench-Scale Study Summary and Analysis).

This pilot study was designed to evaluate the effectiveness of the DE-FLUORO™ system to electrochemically oxidize PFAS within SAFF® concentrate generated following the SAFF® treatment of PFAS impacted groundwater and surface water. During the treatment of the surface water SAFF® concentrate, the system did not perform as expected. This was found to be a result of improper functioning of the system that was unrelated to the concentrate being tested. As these results are not characteristic of the system, they are not discussed further in this appendix.

The selected DE-FLUORO™ system (internally referred to as “Pike”), housed within a trailer, was transported to Washington County Landfill (WCL) in Lake Elmo, Minnesota near Tablyn Park where the SAFF® was located during the pilot test. WCL and Tablyn Park are shown in Figure 4 in Appendix A. Two experiments were conducted with Pike using SAFF® groundwater concentrate between February 28, 2023, and May 10, 2023.

F1.2 DE-FLUORO™ Background

DE-FLUORO™ uses electrochemical oxidation (EO) to destroy PFAS. EO degrades PFAS through the combination of direct electron transfer and an advanced oxidation process mediated by electrochemically generated hydroxyl radicals (Liang, 2018). Within the electrochemical reactor, electrons cycle through the anode to the cathode under the driving force of an externally applied voltage. During the oxidation process, organic compounds lose electrons and become oxidized. Simultaneously, large amounts of hydroxyl radicals are generated that react with surrounding organic molecules, causing further degradation and ultimately complete mineralization of organic contaminants. For PFAS, the molecule results in the breaking of carbon-fluorine bonds, generating fluoride ions and a degraded PFAS molecule.

F2 Experimental Design

F2.1 Objectives

The primary objectives of this pilot study were to evaluate the ability of DE-FLUORO™ to reduce total PFAS mass in SAFF® concentrate and to determine applicability for a full-scale system as part of a treatment train of technologies treating PFAS-impacted groundwater for Project 1007. Perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA), and perfluorobutanoic acid (PFBA) are the dominant PFAS in groundwater with the reported PFOS and PFOA exceeding the Minnesota Department of Health (MDH) Health-Based Values (HBVs) and Health Risk Limits (HRLs). SAFF® is most effective at concentrating long-chain PFAS, such as PFOS and PFOA, and therefore these compounds represent the largest fraction of PFAS in the SAFF® concentrate. However, the MPCA is concerned about an overall reduction in organo-fluorine and not just the reduction in PFAS exceeding the HBVs/HRLs thus short-chain PFAS were monitored during testing as well.

F2.2 Experimental Overview

Two experiments were conducted with SAFF® concentrate generated from the treatment of groundwater. Experiments using the SAFF® groundwater concentrate were conducted from February 28, 2023, to May 10, 2023. During operation of the DE-FLUORO™ unit, the applied current density was maintained at a constant rate for both experiments. Operational parameters were kept consistent through each experiment with modifications to the system made between the two experiments to improve operations and reduce operator requirements. Approximately one drum of concentrate was used for each experiment with starting volumes of 157 liters in Experiment 1 and 170 liters used in Experiment 2. The system was operated for 123 hours in Experiment 1 and for 125 hours in Experiment 2. As discussed, destruction of SAFF® concentrate generated from the treatment of surface water was also conducted but the results indicated that the system was not operating as intended.

F3 Methods and Materials

F3.1 System Design Overview

The DE-FLUORO™ system utilized for this pilot study is referred to as Pike. The Pike system was designed with a single EO reactor and an air emissions management system. Figure F.1 shows the configuration of Pike, which has a total system capacity of up to 200 gallons (757 liters) of liquid waste went operated in a batch recirculation operation mode.

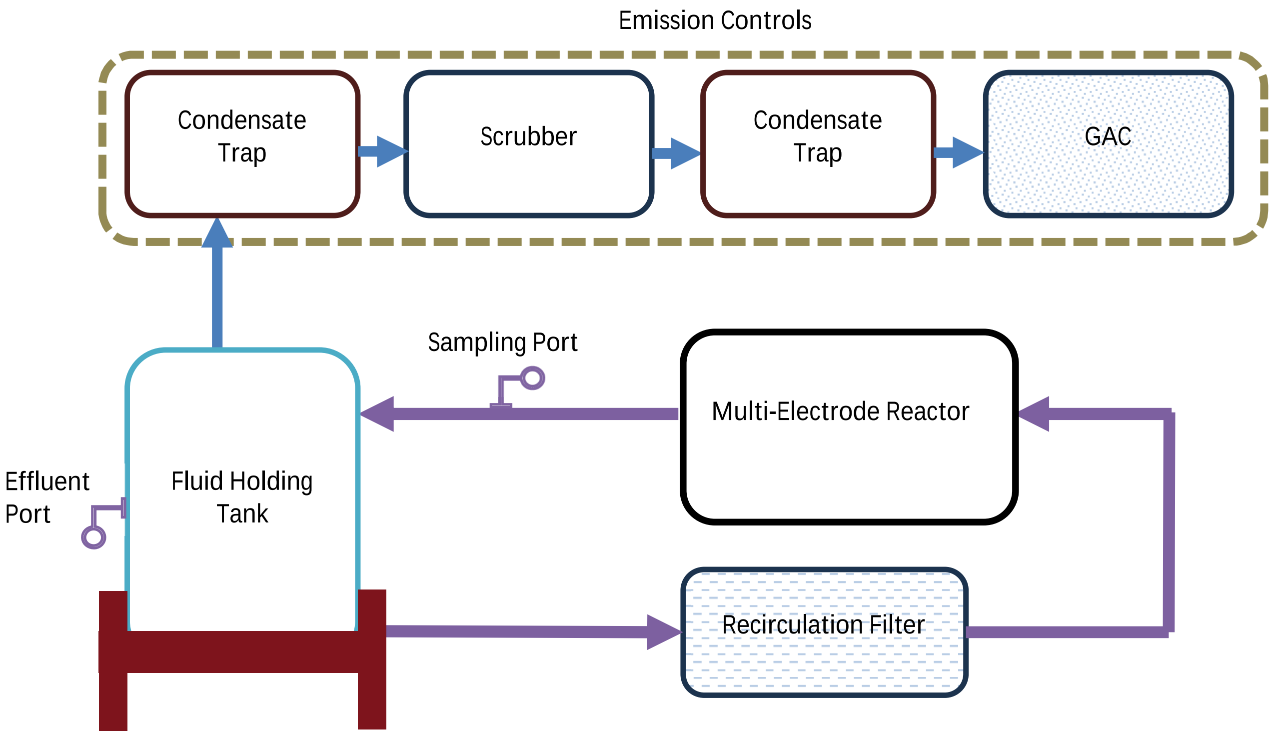

Figure F.1: Conceptual diagram of the Pike system.

F3.2 Key Components of the System

The key components of the DE-FLUORO^{TM} 'Pike' system are summarized below:

- Fluid Holding Tank – A 200-gallon tank was used to store the fluid for treatment. Fluid from the holding tank was recirculated through the reactor during the treatment period. A foam suppression system in the fluid holding tank controlled by an optical sensor was used to reduce foaming.
- Chemical Dosing System - Separate dosing pumps for acid (sulfuric acid) and base (sodium hydroxide) were used to adjust the pH of fluid in the fluid holding tank.
- DE-FLUORO™ Multi-Electrode Reactor - Contains the electrodes. System residence time was controlled by the pumping rate through the reactor. A sample port immediately after the reactor was used for sample collection.
- Emission Control System - Exhaust from the fluid holding tank passes to the emission control system to remove generated hydrogen, hydrofluoric acid, and ensure PFAS is not being released. The air first passes through a condensate trap followed by an alkaline scrubber. A second moisture trap is between the scrubber and the granular activated carbon (GAC) filter.

In addition to the above key components of the system, automated and analog data logging capability was incorporated into the system. Various operational parameters were monitored during experiments such as temperature, pressure, pH, flow rate with inline meters. The DE-FLUORO^{TM} system is controlled by a programmable logic controller (PLC) and is capable of continuously operating 24 hours a day and does not require continuous staffing. The PLC has an internal data-logger to record operating conditions and telemetry allowed operators to remotely monitor status and respond to any process notifications.

F3.3 Consumables

The Pike system utilized several chemicals to maintain optimum treatment conditions. The chemicals were either added to the fluid holding tank prior to the start of treatment or utilizing an in-line chemical feed system if addition was required during treatment. Key chemical consumables and their purposes are outlined below:

- Electrolyte: Sodium sulfate was used as an electrolyte to maintain fluid conductivity above >5 milli-Siemens per centimeter (mS/cm).
- pH: The system pH was maintained throughout treatment between 5 and 7 by dosing acid or alkaline (base) solutions. Electrochemical reactions typically result in increasing hydroxyl ion concentration and increasing pH, however the release of fluoride can result in the formation of hydrofluoric acid, decreasing the pH. Sulfuric acid solution (50%) and sodium hydroxide solution (50%) were variably used to adjust pH at start-up and during treatment.
- Bag filters: A 5 micrometer (µm) bag filter was installed immediately before the reactor to remove particulates in the fluid. The pressure sensor prior to this bag filter was monitored and replaced as needed during treatment.
- Emission scrubber: Diluted potassium hydroxide solution (pH 10) was added to the vapor scrubber solution (approximately 6 liters) for neutralizing acid gases.
- GAC filter: Vapor GAC (approximately 1.4 kilograms) was used to capture vapor from the air-emissions including any potential vaporized or atomized PFAS prior to atmospheric discharge.

F3.4 Site and System Preparation

Prior to the arrival of Pike, a shed was constructed at WCL for the storage of materials and the SAFF® concentrate. An electrical hookup to an existing power drop at the treatment Site was completed. A watertight receptacle was installed for easy connection and disconnection from power.

As Pike arrived in Minnesota in winter, an insulated tarp was installed over the top of the trailer to provide weather protection. Straw bales were placed under the trailer to decrease the loss of heat through the floor. While the trailer came with a heater, a supplemental space heater was also operated as needed inside the trailer to provide additional heat during colder days to maintain temperatures above freezing.

F3.5 Data Collection

F3.5.1 Operational Data Collection and Monitoring

Operation parameters were continuously monitored throughout each experiment. The data were digitally recorded by a datalogger with one minute resolution. Manual inspection and data collection were conducted with analog devices and recorded in daily operational notes.

Monitoring parameters included the following:

- Reactor voltage and current, comprising both the set-point limits and the actual values within the reactor.
- Operation flow rate, pressure, temperature.
- pH and conductivity of fluid.
- Foam (color, volume, structure, stability).

- Hydrogen concentration in air emissions system and inside the trailer.

F3.5.2 Analytical Samples and Data Collection

Samples of the SAFF® concentrate being treated during each experiment were collected prior to the start of treatment and at multiple time increments throughout an experiment. The following analytes were sampled to characterize the SAFF® concentrate during the treatment process:

- PFAS: suite of 40 analytes in full turnaround time (TAT) and 12 analytes in rapid TAT
- Anions: chloride, fluoride, and sulfate
- Perchlorate
- Adsorbable organic fluorine (AOF)
- Total organic carbon (TOC)
- Total oxidizable precursor (TOP) assay
- Volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs)
- Metals: cadmium, chromium, copper, nickel, lead, zinc, and iron

Further sampling of other media involved in the treatment process was also undertaken, including:

- Inline filters in the recirculation line
- Scrubber fluid sampling for emission capture
- Moisture trap for emission capture
- GAC sampling for emission capture

The initial pre-treatment sample was labeled Time-0 (i.e. T0) and subsequent samples were entitled with the 'T' prefix based on the number of elapsed treatment hours incurred prior to sampling. The specific analytes sampled at each time point are shown in Table F.1.

GAC media was sampled after each experiment from both the inlet and outlet of the GAC filter. Approximately 5 grams were collected for each sample. The GAC was changed between each experiment. Additionally, an unused GAC sample was also submitted for analysis. All of the spent inline 5 µm filters were also sampled after use. Prior to submittal, the filter was dried and weighed. The plastic ring around the filter was removed and the sample reweighed for use in the mass balance analysis. Filter samples were cut into pieces and approximately 5 grams were submitted to the lab for analysis.

Table F.1: Sampling Schedule and Analytes.

Target Time (hr)	PFAS	PFAS Rapid TAT	TOF (AOF)	TOP	TOC	Anions (Cl^-, F^-, SO_4^-, ClO_4^-)	VOC/ SVOC	Metals
TREATED FLUID SAMPLES								
T0	1	1	1	1	1	1	1	1
T0 Duplicate	1	1	1					
T2	1	1	1					
T8	1	1	1					
T24	1	1	1					
T24 Duplicate	1	1	1					
T32	1	1	1	1	1	1		
T64	1	1	1					
T100	1	1	1					
T125	1	1	1	1	1	1	1	1
ADDITIONAL MEDIA SAMPLES								
Exhaust Scrubber Water - pre-treatment	1	1						
Exhaust Scrubber Water - end-treatment	1	1	1					
GAC Filter - pre-treatment	1							
GAC Filter - post-treatment GAC Inlet	1		1					
GAC Filter - post-treatment GAC Outlet	1		1					
Pre-Scrubber Condensate_Final	1	1	1					
Pre-GAC Condensate_Final	1	1	1					
5um Filter - end-Treatment	1	1	1					

Legend: Cl^- = chloride ion; ClO_4^- = perchlorate ion; F^- = fluoride ion; hr = hours; SO_4^- = sulfate ion; TOF = total organo- fluorine.

F3.6 Analytical Parameters and Methods

PFAS samples were analyzed by SGS AXYS, perchlorate was analyzed by Eurofins, and all other analytes were analyzed by Pace Analytical. Table F.2 summarizes the analytical parameters, laboratories, and methods.

Table F.2: Analytical Parameters, Laboratories, and Methods.

Analytes	Laboratory	Method
PFAS (40 compounds) Full TAT	SGS Axys	MLA-110
PFAS (12 compounds) Rapid TAT	SGS Axys	Modified EPA 533
AOF	SGS Axys	MLA-119
Total Fluorine	SGS Axys	MLA-119
TOP Assay	SGS Axys	MLA-111
Perchlorate	Eurofins	EPA 331.0
TOC	Pace Analytical	SM5310C-2011
Metals (cadmium, chromium, copper, iron, lead, nickel, zinc)	Pace Analytical	EPA 6010D
SVOCs	Pace Analytical	EPA 8270E
VOCs	Pace Analytical	EPA 8260D
Anions (chloride, fluoride, sulfate)	Pace Analytical	EPA 300.0

AOF was selected for a measure of total organo-fluorine (TOF) of aqueous samples after discussion with the laboratory about appropriate methods. This method is not applicable for solid samples. Total fluorine analysis with samples collected before and after treatment was selected to approximate the change in organo-fluorine on the GAC and filters to reduce biasing the measured concentrations low as not all of the organo-fluorine is removed during the extraction process.

F3.7 Data Validation

Quality assurance and quality control (QA/QC) samples were collected during each experiment comprising of duplicates and matrix spike/matrix spike duplicate samples. QA/QC samples submitted for laboratory analysis showed that the analytical results were accurate and precise.

F3.8 Effluent Management

All DE-FLUORO^{TM} treatment system effluent as well as solutions used during cleaning were containerized in 55-gallon drums for storage prior to disposal via a licensed waste handler. Ultimately, in a full-scale system, the effluent of a DE-FLUORO^{TM} system would likely be recirculated back to the start of the concentration treatment train (e.g. recirculation back to a SAFF® system). Recirculation of the treated DE-FLUORO™ pilot test effluent to the SAFF® pilot unit was not performed due to the potential to release byproducts into the aquatic environment prior to complete evaluation of the data.

F4 Analytical Results

F4.1 Baseline (Pre-Treatment) Analysis

The baseline (T0) samples were collected from the sampling port before providing electrical power to the system. Analytical results of the T0 samples from each experiment are summarized in Table F.3 for total PFAS, PFOA, PFOS, PFBA, perfluorohexane sulfonic acid (PFHxS), perfluorohexanoic acid (PFHxA), AOF, and TOP. Table F.3 includes the combination of the full MLA-110 method and the Rapid TAT method. In the instances where analytes were below detection limit for MLA-110 but detected by the Rapid TAT method, the concentration determined by the Rapid TAT method was used in the analysis.

The primary PFAS detected in the SAFF® concentrate were PFOS followed by PFOA. The reported total PFAS concentration, based on the summation of all compounds analyzed for, was greater than the AOF reported for both experiments. The reported AOF concentrations were approximately 92.2% of the total PFAS in the SAFF® groundwater concentrate.

F4.2 Dissolved Phase PFAS, PFOS, PFOA, PFHxS, PFHxA, AOF, and TOP Concentrations

Due to current limitations of laboratory analytical techniques in measuring all PFAS compounds potentially present, the interpretation of the data focused on total PFAS, PFOS, PFOA, PFHxS, PFHxA, AOF, and TOP. Other PFAS that were detected were PFBA, perfluoropentanoic acid (PFPeA), perfluorononanoic acid (PFNA), perfluorobutane sulfonic acid (PFBS), perfluoropetane sulfonic acid (PFPeS), perfluoroheptane sulfonic acid (PFHpS), and perfluorooctanesulfonamide (PFOSA); however, because of the high detection limits, a subset of these compounds was variably detected. Baseline and post-treatment (T125) concentrations of the selected PFAS compounds, AOF, and TOP for each experiment are summarized in Table F.3. Full results are available upon request.

Experiments 1 and 2 showed destruction efficiencies of 96.4 and 95.3% based on total PFAS, respectively. Notably, the lowest PFAS concentrations were not always observed near the end of each experiment (T125). While water volume did decrease during each experiment (8.0% for Experiment 1 and 12.7% for Experiment 2), the decrease of water volume during each experiment alone does not explain the concentration rebound and it may be a result of desorption from the system components.

Table F.3: Concentrations of Selected PFAS Compounds from Analytical Results.

Experiment Number	Sample	Analyte concentration (ng/L)						
		Total PFAS (1)	PFOS	PFOA	PFHxS	PFHxA	AOF	TOP
Experiment 1 (SAFF® Groundwater Concentrate)	Baseline (T0) (2)	595,929	474,000	100,000	6,420	365	580,000	56,117
	Final (T125)	21,580	10,200	8,050	768	356	24,000	19,458
	% reduction	96.4	97.8	92.0	88.0	2.0	95.9	65.3
	Minimum concentration	7,434 (T102)	1,760 (T66)	2,760 (T102)	427 (T102)	296 (T102)	10,000 (T102)	19,458 (T125)
Experiment 2 (SAFF® Groundwater Concentrate)	Baseline (T0)	562,164	436,000	110,000	6,390	333	490,000	562,370
	Final (T125)	26,680	1,280	18,100	3,330	449	30,000	27,003
	% reduction	95.3	99.7	83.5	47.9	- 35.0	93.9	95.2
	Minimum concentration	26,680 (T125)	1,280 (T125)	18,100 (T125)	3,330 (T125)	333 (T0)	30,000 (T125)	27,003 (T125)

Legend: ng/L = nanograms per liter.

(1) Total PFAS is the sum of detected PFAS by method MLA-110.

(2) T0 samples, collected without power while recirculating through the system.

F4.3 Short-chain PFAS Formation

Analytical results of the four carbon PFAS (PFBS and PFBA) are summarized in Table F.4. The concentrations for both these short-chain PFAS generally increased with treatment time. The increase in concentrations is likely the result of partial defluorination of long-chain PFAS. Increases may also be a result of concentrating the PFAS due to the decrease in water volume.

PFPeA and PFPeS are five carbon PFAS that can also be formed because of the EO. PFPeA was observed to increase over the course of each experiment while PFPeS stayed consistent through each experiment when detection limits were low enough for it to be quantified. If the system were to be operated longer, it is expected that these five carbon PFAS would have begun to undergo defluorination resulting in four carbon PFAS.

Table F.4: Concentrations of PFBS and PFBA from Analytical Results.

Experiment Number	Sample	**Analyte concentration** (ng/L)	
		PFBS	PFBA
Experiment 1 (SAFF® Groundwater Concentrate)	Baseline (T0)	53	568
	Final (T125)	57	869
	% change	+ 7.6	+ 53.0
	Minimum concentration	53 (T0)	568 (T0)
Experiment 2 (SAFF® Groundwater Concentrate)	Baseline (T0)	61	552
	Final (T125)	63	1090
	% change	+ 2.8	+ 97.5
	Minimum concentration	55 (T8)	552 (T0)

F4.4 Anions, Metals, TOC Concentrations

Chloride and perchlorate concentrations were measured throughout the experiments to examine the formation of EO byproducts. In addition, fluoride concentration was monitored as a direct line of evidence for PFAS mineralization. Among the metal species, chromium, cadmium, copper, nickel, and zinc and iron concentrations were monitored. TOC was measured to quantify oxidative competition for the dissolved phase PFAS (i.e. reduction in PFAS treatment efficiency). The concentrations of each of these analytes were measured prior to treatment (T0 baseline), during treatment (T32), and post-treatment (T125); results are summarized in Table F.5.

Perchlorate, a byproduct formed by the oxidation of chloride ions, was observed to increase throughout both experiments. Conversely, concentrations of chloride decreased for both experiments, which is to be expected as chloride undergoes conversion to perchlorate. The baseline perchlorate concentration SAFF® concentrate prior to treatment was less than the method detection limit of 0.5 milligram per liter (mg/L), while the final concentrations were 5.2 mg/L in Experiment 1 and 7.1 mg/L in Experiment 2.

Importantly, fluoride was formed during the treatment of SAFF® groundwater concentrate. The final concentration in the treated water was observed to be 1.4 mg/L and 1.7 mg/L in Experiments 1 and 2, respectfully. The formation of fluoride is a direct line of evidence of PFAS mineralization, as an increase in fluoride concentration indicates breakage of the carbon-fluorine bonds.

Chromium concentrations increased in both experiments while the soluble iron concentration decreased during the experiments. Typically, soluble metal species are precipitated at the cathode as a solid phase. The increase in chromium was unexpected and might be an indication of more complicated oxidation mechanisms within the system. The decrease in iron was predicted because solid iron precipitates were observed to be present on the recirculation filter.

TOC increased in both experiments, with a 319% increase from 2.1 to 8.8 mg/L observed in Experiment 1 and a 180%b increase from 3.0 to 8.4 mg/L observed in Experiment 2. Typically, it would be expected that TOC is oxidized along with PFAS at the anode during EO operation and TOC concentrations would be expected to decrease throughout treatment. It is unclear why this was observed but may have been a result of the breakdown of larger organic complexes that impacted the results.

Table F.5: Anion, Metals, TOC Concentrations.

Experiment Number	Sample	Analyte **concentration** (mg/L)					
		Cl^-	F^-	ClO_4^-	Cr	Fe	TOC
Experiment 1	Baseline (T0)	128	0.074	0.002	<0.0014 (1)	<0.022 (1)	2.1
	Middle (T32)	11.2	0.53	1.20	- (2)	- (2)	6.6
	Final (T125)	<1.2 (1)	1.7	5.20	<0.0014 (1)	<0.022 (1)	8.8
	% change	- (3)	+ 2,197	+ 259,900	- (3)	- (3)	+ 319
Experiment 2	Baseline (T0)	124	0.075	0.50	0.022	<0.022 (1)	3.0
	Middle (T32)	8.6	0.6	1.80	- (2)	- (2)	6.3
	Final (T125)	<0.39 (1)	1.4	7.10	2.33	<0.022 (1)	8.4
	% change	- (3)	+ 1,767	+ 1,320	+ 10,491	- (3)	+ 180

Legend: Cl^- = chloride ion; ClO_4^- = perchlorate ion; Cr = chromium; F^- = fluoride ion; Fe = iron.
(1) Limit of reporting.
(2) Data were not available.
(3) Where the data were not available or below the limit of reporting, the percentage change could not be calculated.

F5 Technical Discussion

F5.1 PFAS Kinetics

The change in concentrations of total PFAS, AOF, and select PFAS are shown in Figure F.3 and Figure F.3. Both experiments showed a decline in PFOS and PFOA concentrations through the treatment period with the largest decrease occurring between two and eight hours. The minimum concentration of PFOS and PFOA in Experiment 1 occurred at 64 and 100 hours, respectively, followed by slight concentration increases, possibly as a combined result of evaporative losses and release of sorbed PFAS from system components. At lower concentrations, PFNA, PFDA, PFHpA, PFHxS, PFHpS, and PFOSA showed similar trends. Concentrations of PFBA and PFPeA were observed to increase over the treatment time. AOF was also detected to decrease until 100 hours in Experiment 1 and 125 hours in Experiment 2 with the largest rate of decrease occurring between two and eight hours of treatment, likely a result of the decrease in PFOS, the dominant PFAS. The observed PFAS degradation trends were less obvious in short-chain PFAS compounds, likely due to short-chain PFAS compounds representing degradation intermediates of the long-chain PFAS. These results show that a treatment time of 125 hours is not needed for destruction of long-chain PFAS. The treatment time could be reduced if effluent targets do not require complete mineralization of short-chain PFAS or if recirculation back to the start of the concentration treatment train is an option. Reconcentrating the effluent by recirculating would allow for DE-FLUORO™ to be operated at the higher PFAS concentrations where destruction occurs more rapidly.

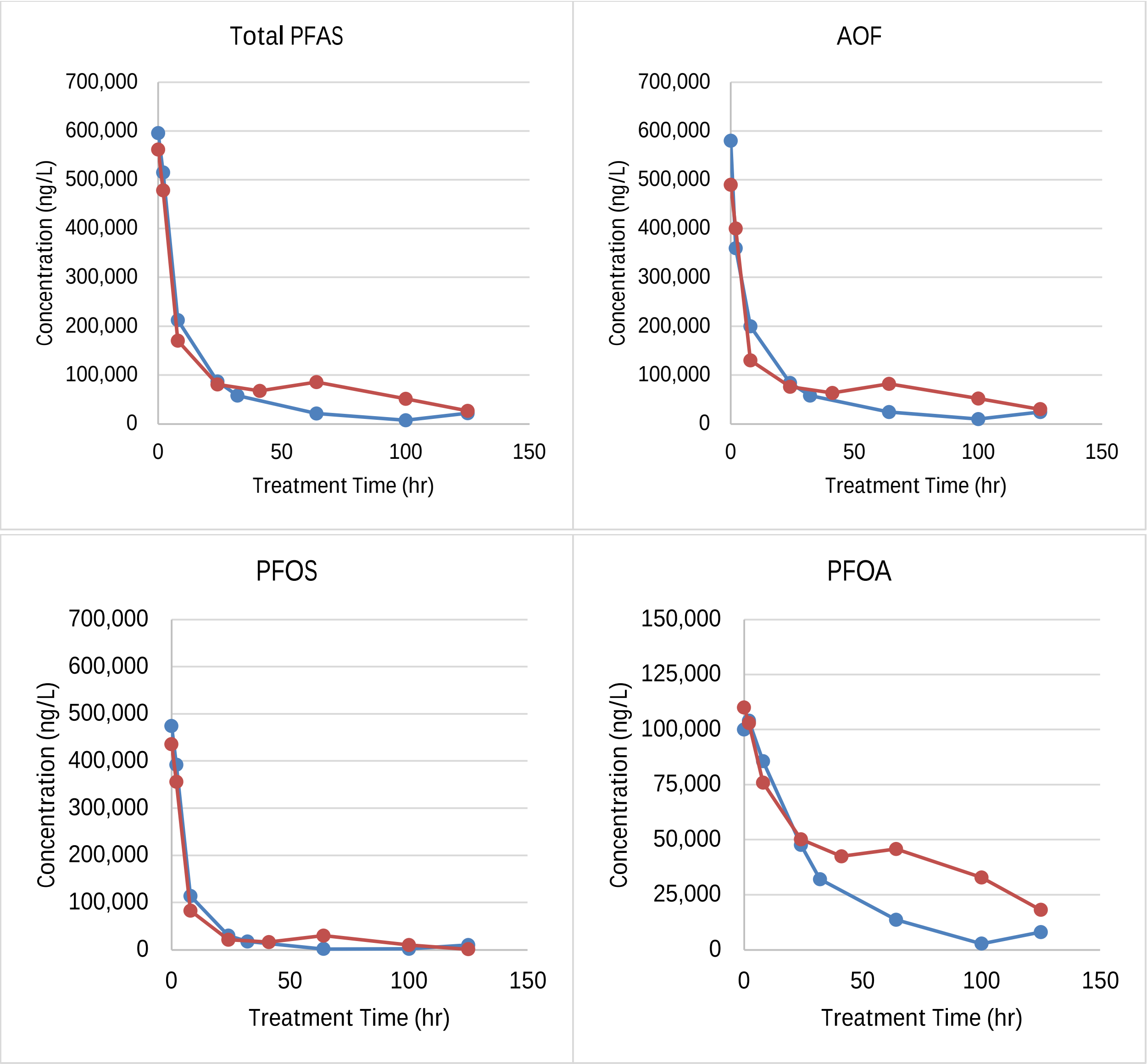

Figure F.2: Concentration of total PFAS (summation of all PFAS detected), AOF, PFOS, and PFOA over time. Blue is Experiment 1, red is Experiment 2.

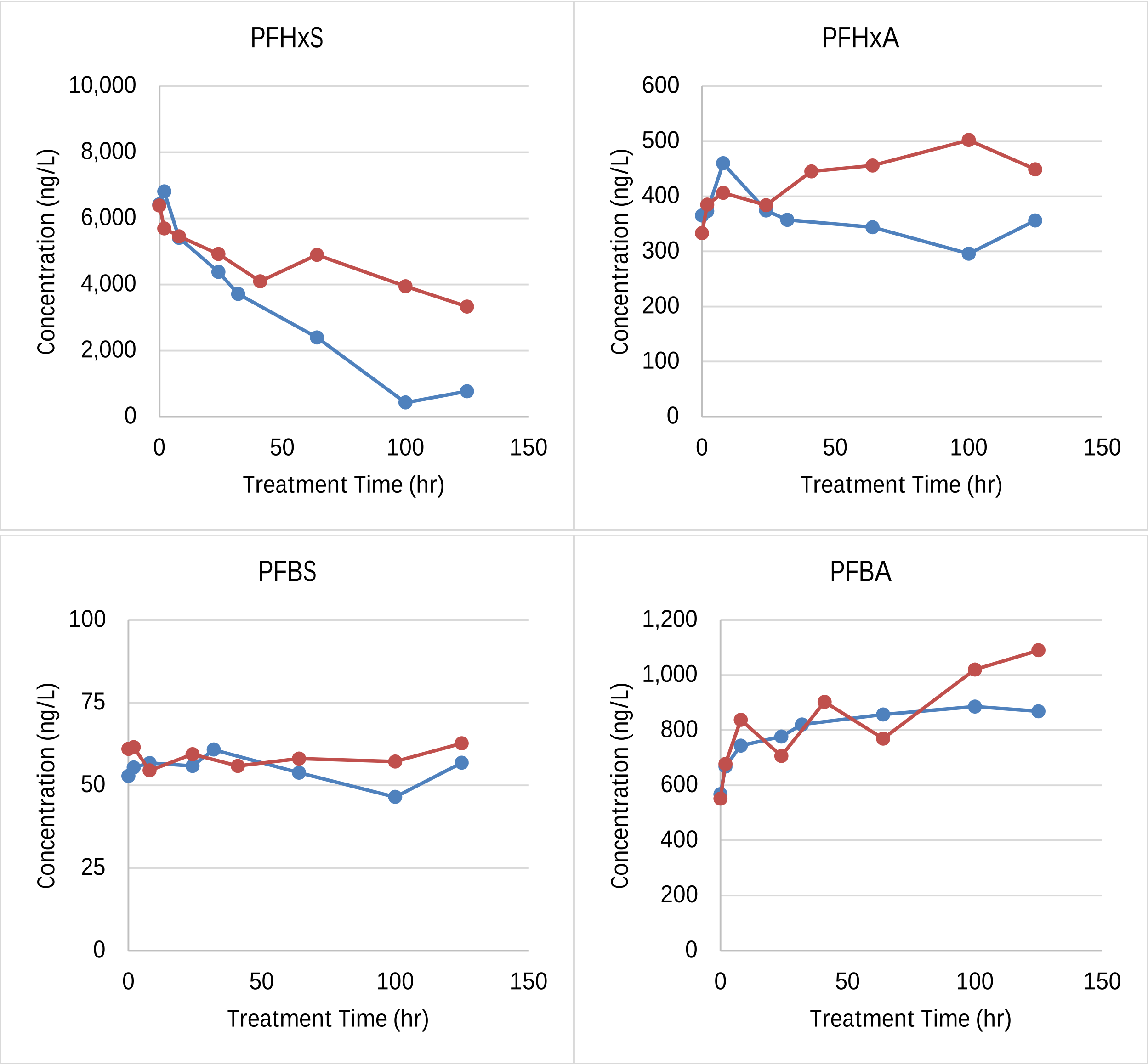

Figure F.3: Concentration of PFHxS, PFHxA, PFBS, and PFBA over time. Blue is Experiment 1, red is Experiment 2.

F5.2 PFAS and AOF Mass Balance

Mass balances for PFAS and AOF were calculated and summarized in Table F.6 for both experiments to determine where PFAS loses may have occurred within the system due to transference and/or destruction. Total PFAS concentrations were based on the summation of all detected PFAS compounds. If a compound was present in the rapid TAT samples but not in the MLA-110 sample, then the rapid TAT data was used. Based on the difference in methods between the rapid TAT and MLA-110, the MLA-110 method tended to have higher detection limits due to the high PFAS concentrations, especially those observed early in the experiments. Analytes at lower concentrations, therefore, are below the detection limit. This is not the case for the rapid TAT.

Mass degradation of AOF of 92.1% and 81.9% were observed in Experiments 1 and 2, respectively. In general, the degradation percentages of total PFAS were higher than those of AOF throughout the experiments. The mass balance calculations showed that PFAS and AOF were transferred to the air emissions system. This emphasizes the need to increase the capabilities of the pre-scrubber condensate trap to ensure PFAS is not migrating into the scrubber. PFAS retained in the pre-scrubber can be transferred back into the tank for destruction as opposed to being trapped within the air emissions system. The highest PFAS percentage in the GAC was observed in Experiment 2 at 1.6%.

The mass balances did not account for PFAS sorbed on the internal surfaces of the DE-FLUORO™ system. The wash and rinse water collected after the completion of the study showed the presence of PFAS. It was uncertain when this PFAS sorption occurred during the experiments. Additionally, negligible amounts of PFAS were found in condensate that collected outside of the condensate traps after Experiment 2. The contribution was too small to include in the mass balance calculations.

Table F.6: Mass Balances of PFAS and AOF results in mg/L.

Experiment No.	Influent	**Analytical samples submitted**	Pre-condensate Trap	Scrubber	Post-condensate Trap	GAC	Recirculation Filter	Effluent	Loss/ Destroyed
Experiment 1 Total PFAS	96.6 (100%)	4.3 (4.5%)	0.6 (0.6%)	1.3 (1.3%)	0.5 (0.5%)	1.2 (1.3%)	0.04 (0.04%)	2.5 (2.6%)	86.2 (89.2%)
Experiment 1 AOF	81.8 (100%)	3.8 (4.6%)	3.07 (3.8%)	2.4 (3.0%)	1.8 (2.2%)	2.1 (2.6%)	0.7 (0.8%)	2.8 (3.4%)	65.1 (79.7%)
Experiment 2 Total PFAS	88.3 (100%)	2.2 (2.4%)	0.21 (0.2%)	0.08 (0.1%)	0.05 (0.1%)	1.4 (1.6%)	0.01 (0.01%)	3.2 (3.5%)	83.3 (92.1%)
Experiment 2 AOF	76.0 (100%)	1.9 (2.7%)	0.2 (0.3%)	0.1 (0.1%)	NS	2.6 (3.7%)	4.4 (6.3%)	3.5 (5.0%)	57.8 (81.9%)

Legend: NS = not sampled for the analysis due to low volume of liquid.

F5.3 Degradation Byproducts

Perchlorate formation from existing chloride in the SAFF® concentrate is unavoidable in EO. During treatment, perchlorate formation was observed as expected. However, the actual molar conversion rate of chloride to perchlorate was less than 2% of the removed chlorine.

Importantly, fluoride formation was confirmed during the system operation, which is the direct line of evidence for the mineralization of PFAS.

Hydrogen is also produced during EO as a result of the hydrolysis of water. Hydrogen concentrations within the system must be maintained below 50% of the lower explosive limit or approximately 2 parts-per-million by volume. This was monitored during operations, and the air emissions blower speed can be adjusted as needed to reduce hydrogen concentrations if needed.

F5.4 Energy Consumption

The energy consumption during each experiment was summarized in Table F.7 as well as the average power consumption of the Site, where the Pike system was located. Additional power consumption outside of the EO reactor was approximately 1.4 – 1.9 times of the power consumption of the EO reactor. This is primarily a result of operation of pumps and heating of the trailer which is dependent on the location of the system.

Table F.7: Energy Consumption Rates.

Experiment #	Power Consumption Rate – Reactor **(kilowatt hours per day)**	Power Consumption Rate – Site **(kilowatt hours per day)**
Experiment 1	32.4	31.7
Experiment 2	27.1	65.8

F6 Conclusion and Recommendations

During this pilot test, the mass of PFAS and AOF from the SAFF® groundwater concentrate was successfully degraded by up to 92.1% and 81.9% respectively. In addition, the mineralization of PFAS was confirmed by fluoride formation during operation of the unit.

Perchlorate was formed as a byproduct of the oxidation of chloride during the operation. Management of perchlorate would be required if EO were to be used for PFAS destruction.

Overall operation of the system went smoothly without major interruptions, indicating that this system can be largely operated unmanned with remote monitoring during the treatment period.

This pilot study showed that electrochemical oxidation can be used to destroy PFAS at the pilot-scale. Future studies which focus on shortening treatment time significantly and evaluating reconcentration of the treated effluent are recommended.

F7 References

Liang S, Pierce D, Lin H, Chiang, D, Huang Q. Electrochemical oxidation of PFOA and PFOS in concentrated waste streams. Remediation. 2018; 28:127–134. https://doi.org/10.1002/rem.21554