Clean Harbors Aragonite PFAS Test Program Results





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Presentation Overview

- Aragonite facility overview
- Test program overview
- Sampling & analytical program
- QA/QC guidelines
- PFAS spiking protocol
- PFAS mass balance and DRE calculations
- PFAS stack emissions
- Hydrogen fluoride stack emissions
- Fluorine mass balance
- Total organic precursor assay
- Test program summary





Clean Harbors - Aragonite Utah



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Combustion & Emission Control Systems

- Combustion System
 - Slagging rotary kiln (1,893-2009°F/1,034-1,098°C)
 - Afterburner (2,052-2100°F/1,122-1,149°C)
- Emission Control System
 - Spray dryer
 - Baghouse
 - Saturator
 - Wet Scrubber
 - Induced draft fan
 - Stack





Testing Teams

June 2021 Test

- EA Engineering, Science & Technology
- Focus Environmental
- Montrose AQ Services
- Enthalpy Analytical

February 2022 Test

- EA Engineering, Science & Technology
- Focus Environmental
- Alliance Source Testing
- Eurofins





Project Objectives

- Measure destruction and removal efficiency (DRE) for four spiked PFAS compounds (PFOA, PFOS, PFHxS, HFPO-DA)
- Perform PFAS mass balance for waste feed streams, process water, chemical reagents, process residuals, and stack gas
- Measure hydrogen fluoride (HF) stack emissions
- Perform a fluorine mass balance
- Assess "hidden mass" of PFAS in AFFF wastes with total oxidizable precursor assay (TOPA)





Planned Test Conditions - Feed Streams

Test		Test Condition	Normal Waste	Spiked	(2)
Condition	Runs	Description	Feeds	PFAS	AFFF
1	1-3	Baseline	х		
2	4-6	PFAS Spiking	х	Х	
3	7-9	AFFF Feed	Х		Х

(a) AFFF inadvertently fed during Runs 1-8 through sludge port.





Combustion System Sampling Points







Emission Control System Sampling Points



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Process Water



Sampling and Analytical Methods

Stack gas sampling methods

Stack gas PFAS

Stack gas HF

EPA OTM-45 EPA Method 26A

- Analytical methods
 - PFAS Table 5-15 of DoD Quality Systems Manual, Version 5.3 (LC/MS/MS) for 49 target PFAS analytes
 - HF EPA Method 26A (ion chromatography)
 - Total fluoride EPA Method 340.2 (ion selective electrode) on combustate from bomb calorimeter
 - Total oxidizable precursor assay (TOPA) (Houtz et.al.)







PFAS Spiking Material Preparation



Pre-weighed bottles of spiking materials to be bundled in cardboard box



Process for inserting PFAS spiking bottles into numbered cardboard boxes





Mass Balance & DRE Calculation Basis

- PFAS not measured in solid waste feed streams
- PFAS in process water and chemical inputs to the gas cleaning systems were included in mass balances, but not included in DRE calculations (per RCRA definition of DRE)
- PFAS non-detects in waste feed, chemical, process water, and residual streams assumed concentration value of zero
- PFAS non-detects in stack gas assumed to be present at the method detection limit
- PFAS DREs reported are lowest possible values based on conservative assumptions listed above
- Fluorine concentration in waste solids estimated from Clean Harbors' categorical waste profiles





PFAS Mass Balance - Test Condition 1 (Baseline)









PFAS Mass Balance - Test Condition 2 (PFAS Spiking)







PFAS Mass Balance - Test Condition 3 (AFFF Feed Test)







Total Oxidizable Precursor Assay (TOPA) February 2022 Test





Conclusions Salance, DRE, & TOPA

- DRE >99.9999% achieved for all spiked compounds for all three spiking runs
- DRE between 99.99% and 99.999% achieved for FTS compounds for all nine runs. FTS's are key ingredient of AFFF formulations tested.
- Native PFAS concentration in waste feeds too low to demonstrate >99.99% DRE for most compounds
- Roughly half of the PFAS target analytes not detected in waste feeds, input chemicals, or residuals streams
- ~99% of PFAS in liquid waste feeds are from two AFFF streams.
 PFAS contributions from solid feeds unknown.
- PFAS mass in process water, chemicals, and residuals is very small relative to mass in waste feed streams.
- TOPA revealed concentrations 1-3 orders of magnitude higher for some PFAS compounds than target analyses





Stack Gas PFAS Compound Concentrations



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Ambient Air Impacts

Regulation Source	PFAS Compounds Regulated	Ambient Air Limit/ Guideline (ng/m ³)	Modeled ^(a) Ambient Air Conc. (ng/m ³)	Averaging Time	Ratio of Ambient Air Limit to Estimated Concentration
Michigan	PFOA ^(b)	70	5.43E-05	24-hr	1.3E+06
Michigan	PFOS ^(b)	70	3.24E-05	24-hr	2.2E+06
Michigan	PFOA + PFOS ^(b)	70	8.67E-05	24-hr	8.1E+05
Minnesota	PFOA	63	5.43E-05	24-hr	1.2E+06
Minnesota	PFOS	11	3.24E-05	24-hr	3.4E+05
New York	PFOA	5.3	9.05E-06	Annual	5.9E+05
Texas	PFOA	50	9.05E-06	Annual	5.5E+06
Texas	PFOS	100	5.40E-06	Annual	1.9E+07
U.S. EPA	HFPO-DA ^(c,d)	10.5	1.78E-06	Annual	5.9E+06
U.S. EPA	PFOA ^(c)	70	9.05E-06	Annual	7.7E+06
U.S. EPA	PFOS ^(c)	70	5.40E-06	Annual	1.3E+07
U.S. EPA	PFBS ^(c)	1050	1.64E-06	Annual	6.4E+08

(a) Modeled using U.S. EPA AERSCREEN model. Results are likely conservative compared to results that would be produced by a more rigorous model such as AERMOD.

(b) Value applies to PFOA and PFOS individually if only one is present in air, or a combined limit value if both are present in air concurrently.

(c) Ambient concentrations calculated from U.S. EPA Toxicity Assessment Reference Doses (RfD)

(d) https://www.epa.gov/chemical-research/human-health-toxicity-assessment-genx-chemicals





Hydrogen Fluoride Stack Emission Results

Test Condition	Fluoride ^(a) in Liquid Waste Feeds & PFAS Spikes (lb/hr)	HF ^(b) Stack Gas Conc. (ppmvd @7% O ₂)	HF ^(c,d) Emission Rate (Ib/hr)	HF ^(d) Removal Efficiency (%)
TC #1 <mark>(</mark> Baseline)	2.58	0.07	0.006	99.77
TC #2 (PFAS spiking)	2.76	0.10	0.009	99.70
TC #3 (AFFF feed)	2.76	0.11	0.010	99.67
Average	2.70	0.09	0.008	99.72

(a) Excludes estimated fluorine in solid waste streams from Clean Harbors' DSC system.

(b) HWC MACT HCI emission concentration limit (32 ppmvd @7% O2, existing incinerator)

(c) Clean Air Act Hazardous Air Pollutant Emission Limit for HF = 10 tons/yr (2.28 lb/hr)

(d) RCRA HCI emission standard: <4 lb/hr or >99% removal





Fluorine Balance Summary February 2022 Test







Conclusions - Fluorine Balance

- Target analyte PFAS contribute <0.1% of total fluorine measured in waste liquids
- Fluorine in stack gas comprises ~0.02% of the total fluorine mass in all residual streams
- Fluorine mass balance closure was not accurate for short sampling times (individual test runs)
- Fluorine mass balance closure improves as a function of sampling time (average of multiple runs or days)







Overlay of Aragonite Afterburner Temperature with EPA Volatile PFAS and CO Data^(a)



(a) Source: Erin P.Shields et. al, "Pilot-Scale Thermal Destruction of Per- and Polyfluoroalkyl Substances in a Legacy Aqueous Film Forming Foam", ACS ES&T Engineering, May 16, 2023.





Summary of DRE and Emission Results

DRE

- >99.9999% DRE for all spiked PFAS compounds during spiking runs with very conservative assumptions
- 99.99-99.999% DRE for FTS compounds, all runs with very conservative assumptions

PFAS Emissions

 90% of stack gas PFAS analyte concentrations <0.4 ng/dscm @7%O₂ (dioxin/furan TEQ emission standard)

PFAS Modeled Ambient Concentrations

 2-8 orders of magnitude below existing state and EPA air limits/guidelines based on assuming stack NDs = MDL

• HF Emissions

 Average HF emission rate >2 orders of magnitude below Clean Air Act HAP major source threshold (10 tons/yr)





Thank You

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