# REMTEC EMERGING CONTAMINANTS SUMMIT

# OCTOBER 3-5, 2023

## Validation of Supercritical Water Oxidation to Destroy Perfluoroalkyl Acids



### Hicks et al., 2019

### **Collaborators:**

- John Kirby
- Chris Bellona
- John Follin
- Ken Liberty



## **Overview**

Plan

Result

- PFAS-concentrated waste actively being generated
- Reliable/practical solutions urgently needed
  - SCWO has decades application in waste disposal; applicable to PFAS
  - Can SCWO destroy PFAS-concentrated waste w/no detectable PFAS in emissions?

- >99.999% reduction of detectable PFAS in <u>liquid</u> and <u>gaseous</u> emissions
- *Limited* defluorination ratio 62.6%



### **Field Validation Test Objectives**

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Effectiveness of SCWO for <u>aqueous</u> & <u>gaseous</u> discharge (gpm flow rate)

Attempt a fluoride mass balance





## Get to Know SCWO

- <u>Water</u> critical point: 374.14<sup>o</sup>C and ~220 bar
- Single-fluid phase
- No incomplete combustion products
- Influent must be pumpable to high pressure (this includes slurries<sup>1</sup>)

<sup>1</sup>Chiang et al 2023

8.0 Density, g/cm<sup>3</sup> CP 20 Vapor-Liquid Region 100 351 Pressura, bar 00 400 300 200 Temperature, oC Ś 500 Tester et al., 1993 OCTOBER 3-5, 2023 NG CONTAMINANTS

### **PFAS-Concentrate Selection (Literature Data\*)**

### **Electrochemical fluorination Aqueous Film Forming Foam (AFFF)**



\*Houtz 2013; Backe et al 2013; Lang and Divine 2020



### **PFAS-Concentrate Selection (Actual)**

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**Influent 1** Influent 2 Diluted 1,000 X  $PFAS_{tot} = 12,176 \ \mu g/L$  $PFAS_{tot} = 14,155 \ \mu g/L$  $PFOS = 10,780 \, \mu g/L$  $PFOS = 12,590 \ \mu g/L$ 89% 90% PFBA PFPeA PFHxA **PFHpA** PFOA PFBS PFPeS **PFHxS** PFOS PFHpS PFNS PFDS REMIEC

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### Field Validation Test Details – San Diego, CA



CompAir

SCWO skid used for validation testing (General Atomics 2021) Two stage air compressor skids (General Atomics 2021)

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### **Field Validation Test Details – Stack Sampling**



Gaseous sampling platform (General Atomics 2021)



OTM-45 sampling train (General Atomics 2021)

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### **Results: Influent, Effluent, Gaseous Flow Rates**

Total DRE<sub>PFOS</sub> (μ; n=2) 99.9999%



### **Results: Destruction & Removal Efficiency (DRE)**

Precursor transformation? Long to short chain PFAA conversion? Reporting limits? Quench water PFAS?



### **Results: Fluoride Considerations**

### Influent mMole F

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Effluent mMole F



## **Energy Considerations**

"It took a lot of energy to make PFAS, and it will take a lot of energy to destroy PFAS." anonymous

PFAS destruction technologies in the literature: ~0.1s to 1,000s kW-hr/m<sup>3</sup> (~\$115/d to \$1,150,000/d)



### 0.08 kW-hr/m<sup>3</sup> (~\$100/d @ \$0.15 USD/kW-hr)

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PFAS-relevant destruction technologies not currently intended for dilute flow through systems

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## **Energy Considerations**



### **Limitations and Future Work**

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Non-target analysis\*,\*\* (\*Weber et al., 2022 & 2023; Krug et al., 2022 \*\*USEPA 2022) Fluoride in gaseous emission

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1,000x dilution of concentrate\*\* (\*\*USEPA 2022)





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### Full Scale Operation of SCWO for Landfill Leachate, Industrial Wastewater and AFFF

Rick Gillespie Chief Commercial Officer

Revive Environmental Columbus, OH





## **Revive Environmental: Overview**

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Water Technology company created in December 2022



Structure: Founded by Battelle and Viking Global Investors



Technology: Global Patents on PFAS Annihilator<sup>®</sup> and GAC Renew<sup>™</sup>



Headquarters: Columbus, OH / CEO: David Trueba



https://revive-environmental.com/



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he forever chemicals are forever gone with the new PFAS Annihilator technolo









# Learning Objectives

Review the capabilities and commercial readiness of SCWO

Provide an overview of the regulatory process - Transparency.

Lessons learned in the deployment, commissioning, and ongoing operation and optimization of a SCWO unit.

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## The PFAS Predicament

Brine Eff

2/23/2

- <u>P</u>ersistent
- <u>A</u>ccumulative
- <u>T</u>oxic

## Not just 'forever' but 'everywhere' chemicals



Source: Presumptive Contamination Sites from PFAS Sites and Community Resources map





## Challenges will differ by application/source



Source: Walnut Valley Water District, <u>https://walnutvalleywater.gov/your-water/your-drinking-water/water-guality/</u>



Landfill Leachate

- High Volume
- Recurring Continuous
- High amount of cocontaminants



- Lower Volume
- Very High PFAS (ppm)
- Concentrate vs Rinsewater



Soil / Ground Water Remediation

- High Volume
- Lower PFAS
  Concentrations
- In-Situ vs Ex-Situ



Drinking Water

- Very High Volume
- Recurring Continuous
- Low PFAS Conc
- Removal via GAC, RO



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### **Current Commercial Application of SCWO**



**Technologies Deployable by Revive** 



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## Process Flow: Landfill Leachate via FF then SCWO



**Chain of Custody** Batch receipt tied to analytical data and operating parameters **Influent, Effluent Testing** Regular sampling of all aqueous and vapor streams to ensure full destruction **PFAS destruction** Full combustion of all organic compounds incl. all PFAS analytes **No Harmful Byproducts** SCWO reaction results in clean water, nominal CO<sub>2</sub>, and inert salts (e.g., NaF)



### **Foam Fractionation**



Source: Allonnia

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## Supercritical Water Oxidation - PFAS Annihilator®



- Fully permitted, commercial operations in Wyoming, MI since March 2023
- 50K-150K gallons per day of raw leachate from 3 landfills, then ran through Foam Fractionation with resulting concentrate destroyed via SCWO
- **Destroyed AFFF concentrate, AFFF rinsate** and other concentrated streams from other sources and applications





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## **Air Permitting**



- EGLE (MI) exemption for air permit
  - PFAS Annihilator emits <5 lbs/day PTE's
- Transparent Monitoring
  - Initial Audit
  - Frequent proactive monitoring and reporting
- Innovation needed to sample air with low flow
- Most important = Execute the monitoring plan
- Communicate diligently



## SCWO: Batch tracking, treatment and annihilation



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#### **PFAS** Destruction

Full mineralization of all organic compounds incl. all PFAS analytes

Influent, Effluent Testing Regular sampling of all aqueous and vapor streams to ensure full destruction **No Harmful Byproducts** SCWO reaction results in clean water, nominal  $CO_2$ , and inert salts (e.g., NaF)



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- Power
- Water
- Shelter
- Footprint





Footprint: 40' x 40' for 2 CONEX boxes + equipment



### **Annihilator Operational Requirements**



Figure 3. Typical M2 System Operational Configuration

- 40 ft x 40 ft x 12 ft
- Electrical 480V, 3-phase, 100 A Service
- On-Site Water 30 gph, >40 psi
- Operational Temp > 35 deg F
- Will require air and liquid discharge permit.
- Pad: Concrete or rock
- Winterization ready



### Lessons Learned from Scaling Technology...

#### Lead with Safety

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- Coordination critical with onsite partners
- Safe handling / Chain of custody •



#### Quality Processes / Scale

Batch tracking

People

- Local regulations compliance
- 500 GPD operational capability

Supply Chain / Manufacturing

Analytical Support Ecosystem

### **Regulatory Transparency**

- Pre-deployment coordination ٠
- Physical audit ٠
- Ongoing sampling
- Water discharge limits



### **Dialing in the Operation**







### Landfill Leacahate – Short and Long Chain



Leachate Feed Cleaned Tote



■ Leachate Feed ■ Cleaned Tote

Destruction Efficiency >99.99% when starting value above 2000 ng/L



## AFF Destruction – Short and Long Chain



Leachate Feed Cleaned Tote

**AFFF** Destruction Short Chain no PFHxA Destruction Efficiency 6,000,000 5,000,000 4,000,000 3,000,000 2,000,000 1,000,000 Ω HFPO-DA PFHpA PFHxS PFHpS PFBA PFPeA PFBS PFPeS Raw AFFF Effluent Sample

Destruction Efficiency >99.99% when starting value above1000 ng/L

ANSULITE 6% AR-AFFF



44 Destruction Efficiency >99.99% when starting value above 2000 ng/L

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## Destroys PFAS Regardless of Chain Length or Functional Groups

### ANSULITE 6% AR-AFFF

			AFFF Production (ng/L)		
	Classification	More Information	Raw AFFF	Effluent Sample	% Destruction
PFBA	Carboxylic Acid	Short Chain	4,880,000	2.41	99.999%
PFPeA	Carboxylic Acid	Short Chain	1,700,000	2.27	99.997%
PFHxA	Carboxylic Acid	Short Chain	75,400,000	3.14	99.9999%
PFHpA	Carboxylic Acid	Short Chain	482,000	0.698	99.997%
PFOA	Carboxylic Acid	Long Chain	7,050	1.17	99.668%
PFNA	Carboxylic Acid	Long Chain	6,080	1.01	99.668%
PFDA	Carboxylic Acid	Long Chain	5,420	0.899	99.668%
PFUnA	Carboxylic Acid	Long Chain	4,930	0.819	99.668%
PFDoA	Carboxylic Acid	Long Chain	7,320	1.21	99.669%
PFBS	Sulfonic Acid	Short Chain	4,300	0.714	99.668%
PFPeS	Sulfonic Acid	Short Chain	13,100	0.52	99.921%
PFHxS	Sulfonic Acid	Short Chain	7,070	1.17	99.669%
PFHpS	Sulfonic Acid	Short Chain	4,960	0.823	99.668%
PFOS	Sulfonic Acid	Long Chain	6,030	1	99.668%
PFNS	Sulfonic Acid	Long Chain	6,050	1	99.669%
8:2FTS	Fluorotelomer	Fluorotelomer	22,300	3.69	99.669%
PFDS	Sulfonic Acid	Long Chain	3,940	0.653	99.669%
PFDoS	Sulfonic Acid	Long Chain	4,380	0.726	99.668%
4:2FTS	Fluorotelomer	Fluorotelomer	1,680,000	5.32	99.994%
6:2FTS	Fluorotelomer	Fluorotelomer	188,000,000	22.4	100.000%
PFTrDA	Carboxylic Acid	Long Chain	8,820	1.46	99.669%
PFTeDA	Carboxylic Acid	Long Chain	10,400	1.73	99.667%
PFOSA	Carboxylic Acid	Fluorotelomer	4,570	0.758	99.668%





- Multiple landfill leachate projects
- Multiple DoD Projects
- AFFF State-Take-Back Programs
- AFFF Foam Transition Projects
  - Oil and Gas
  - Chemical/Mfg Facilities
- Revive's platform delivers consistent, industry leading PFAS Destruction
- Recognize Battelle, Allonnia, HCC, Michigan EGLE, and the City of Wyoming



