PFAS TREATMENT OF COMPLEX WASTEWATERS WITH FOAM FRACTIONATION UTILIZING AIR AND OZONE GASSES

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Agenda

1 **PFAS Treatment Background**

2 **Foam Fractionation with Air and Ozone**

3 **Landfill Leachate Case Study**

4 **Future Designs**

PFAS Treatment Approach

- PFAS defy conventional remediation engineering
- Current state of the practice is a **combination** of treatment technologies
- Goal is to **concentrate** PFAS for energy-intensive destruction

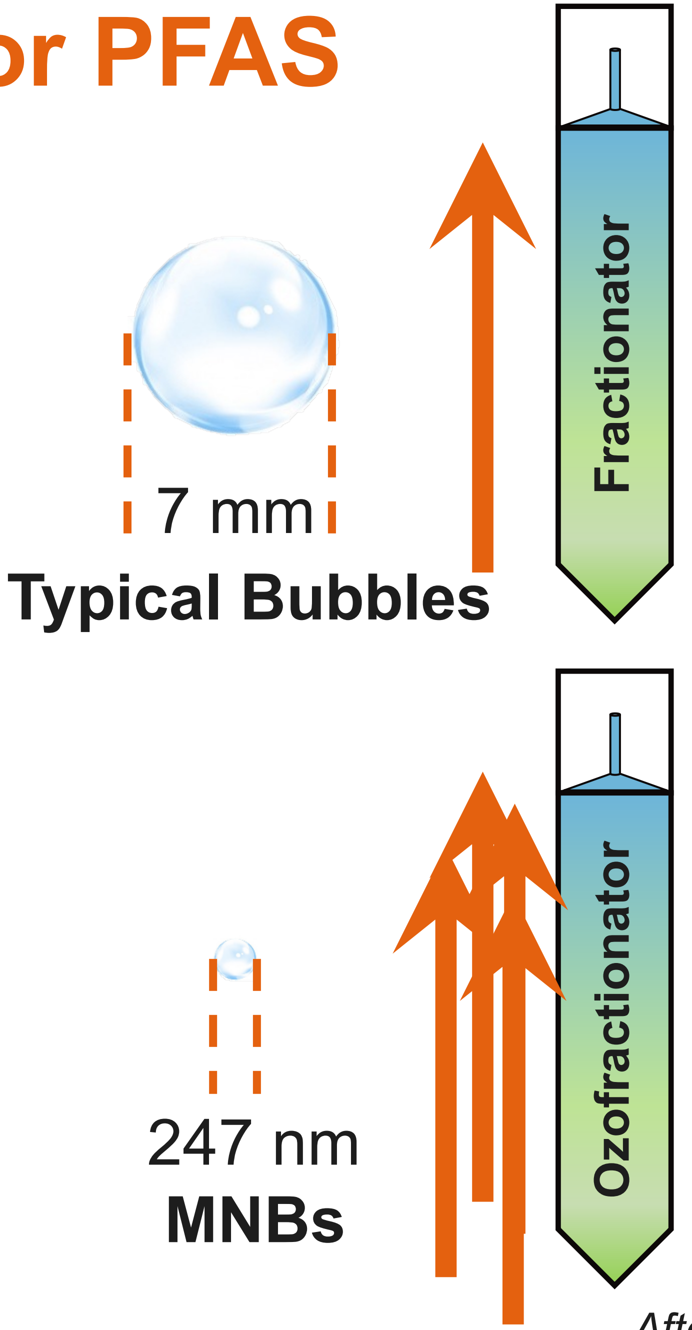
ADSORPTION	SEPARATION/ CONCENTRATION	DESTRUCTION

PFAS Treatment and Destruction Technologies for ***Liquids***

Adsorption	Separation / Concentration	Destruction	
Granular Activated Carbon (GAC)	**Foam Fractionation (FF)**	Incineration	Cement Kilns
Anion Exchange Resin (AIX)	Reverse Osmosis (RO)	Supercritical Water Oxidation (SCWO)	Plasma
Polymeric Adsorbents	Nano Filtration (NF)	Photo/ Electrochemical	Hydrothermal Alkaline Treatment (HALT)
Metal Organic Frameworks	Flocculation	Sonolysis	Advanced Oxidation Processes (AOPs)

Foam Fractionation for PFAS Treatment

- Foam fractionation uses tiny bubbles to separate PFAS from the aqueous solution
- Ozone can create micro-nano-bubbles (MNBs) ranging from 10s nm to 10s µm
- MNBs increase bubble quantity and **available surface area** for treatment
- Ozone bubbles may have a high zeta potential which lessens bubble coalescence and **improves stability**



$2.1x10^6$ bubbles/378 L
316 m^2/378 L

>28,000,000% surface area increase, less incidence of coalescence; more stability

$4.8x10^{22}$ bubbles/378 L
$8.3x10^7$ m^2/378 L

After Hu and Xia 2018

Foam Fractionation for PFAS Treatment

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- Foam Fractionation ≠ Froth Flotation
- Froth Flotation refers more to the removal of particulate materials by bubbling
- Foam fractionation indicates the foaming of dissolved materials by adsorption on the bubble surfaces
- Goal is to increase the available surface area for the PFAS to attract to the bubble interface
- Operating in a continuous stripper mode to minimize foam waste product and optimize operation

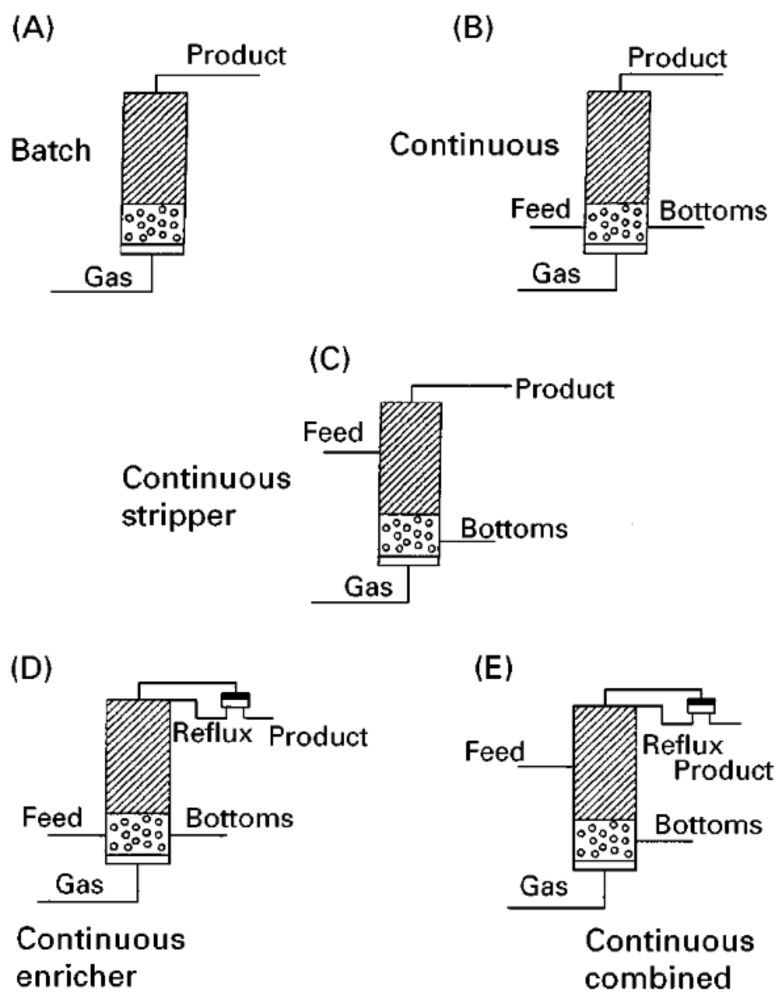

Figure 1 Different modes of operation of a foam fractionation column.

G. Narsimhan, Purdue University, West Lafayette, IN, USA
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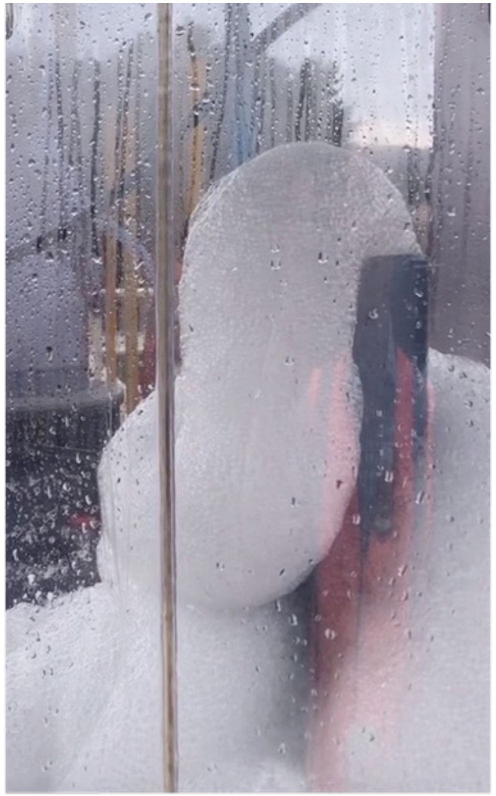
Foam Fractionation PFAS Treatment with Ozone

(OCRA - Ozofractionative Catalyzed Reagent Addition)

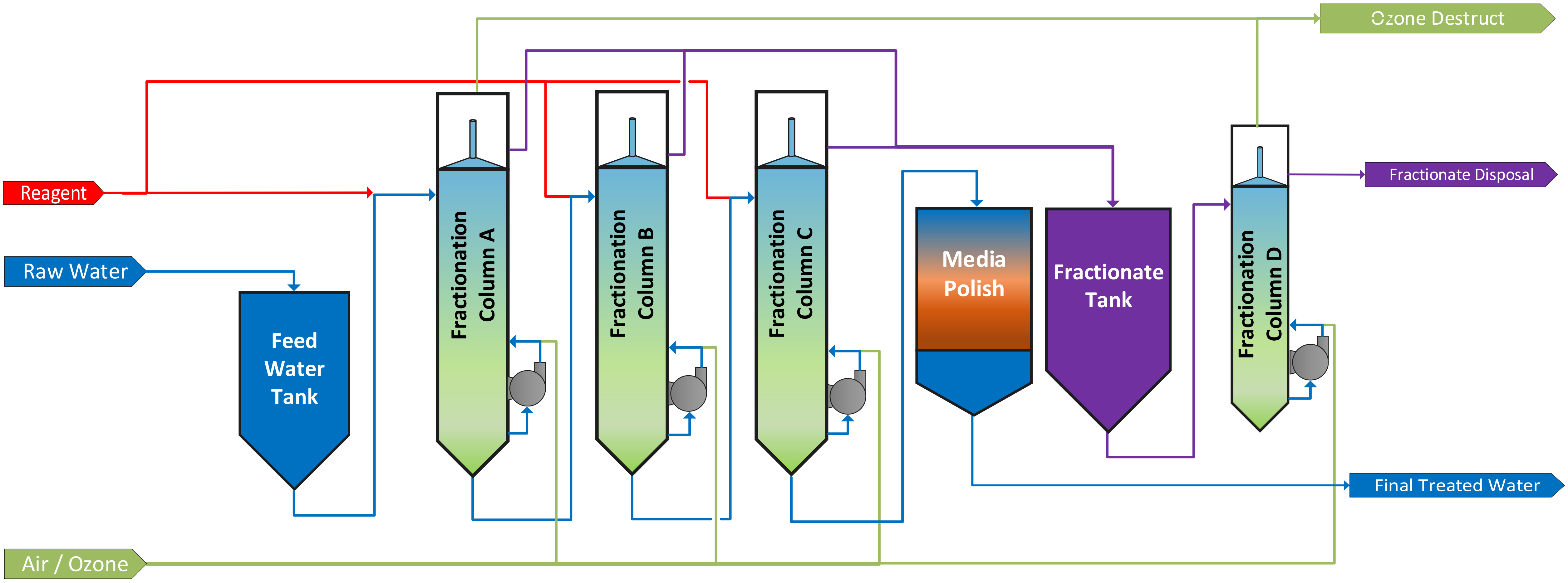
- Patented process by Evocra (Australia)
- Uses ozone bubbles in a multiphase process to extract PFAS
- Reagent can be added to increase efficiency of process
- PFAS removed is collected as a concentrate “foam”
- Volume of foam target is less than 1% of the raw influent (will vary depending upon initial water quality)
- Potential for significant cost savings in disposal volumes
- Additional foam reduction via subsequent processing



Target Structural Collapsing Foam – Optimized Fractionate Flow

(Evocra)

Foam Fractionation Treatment Process



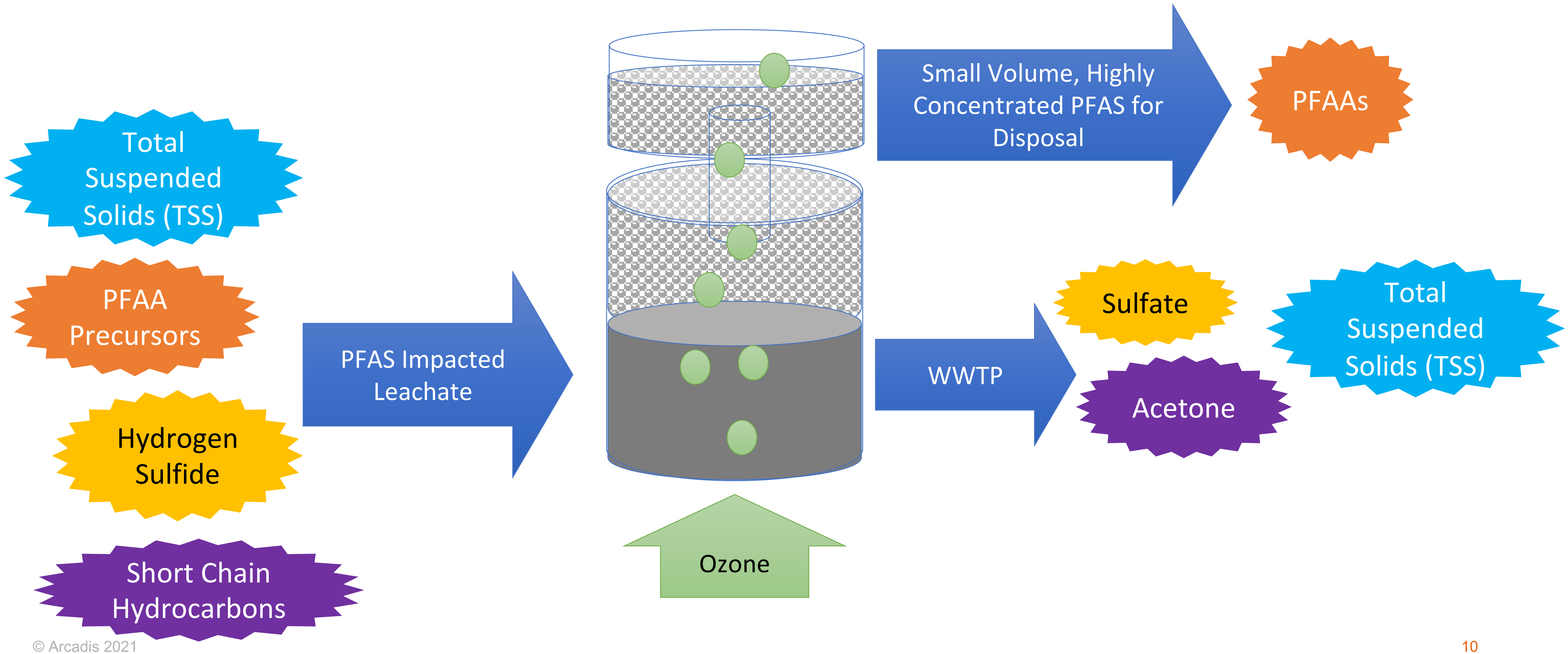
Foam Fractionation and Ozone

- Addressing ozone concern of creating ultra-short chain PFAS
- Optimized concentrations through rigorous testing and trials
- Lower risk of ultra-short chain PFAS
- Maximize waste removal effectiveness with lower volumes
- Zero-waste outcome possible with destruction technologies for foam waste

“Ozonated air fractionation showed the best PFAS removal efficiency, which was more than 95%, as a result of the enriched OH radicals in the gas bubbles.”
Comparative study of PFAS treatment by UV, UV/ozone, and fractionations with air and ozonated air (Dai et. al 2019)

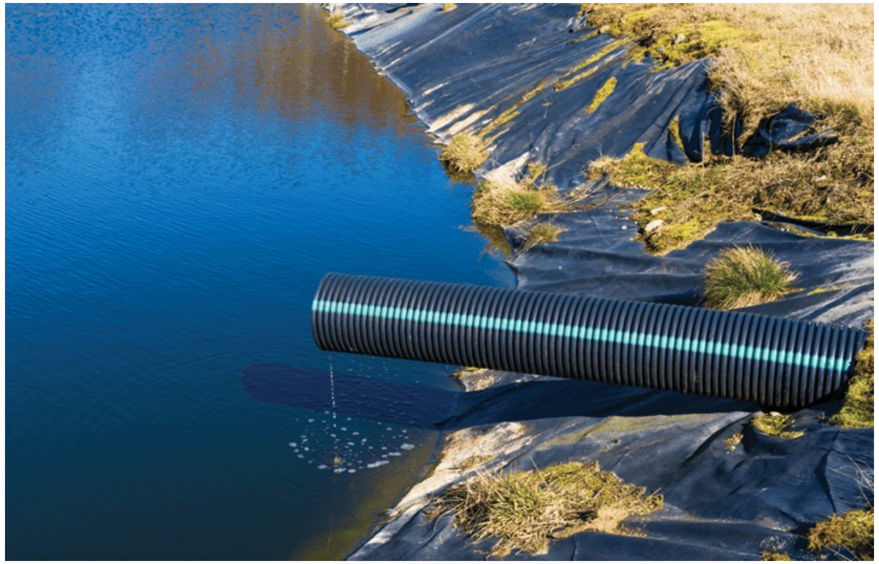
(Arcadis)

Ozone Oxidation During Foam Fractionation



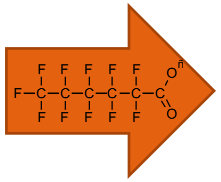
Foam Fractionation Sources

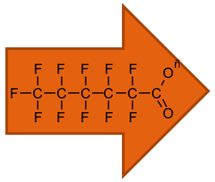
- Targeted high concentration waste streams with high organic co-contaminants
  - Industrial Wastewater
  - Municipal Wastewater Treatment Plants
  - AFFF Impacted Source Zones (spills, groundwater)
  - Landfill Leachate (Robey et. al 2020, McCleaf et. al 2021)
- Applied to groundwater with limited success requiring additional foaming agents or reagents to be added to promote foaming
- Drinking water not targeted

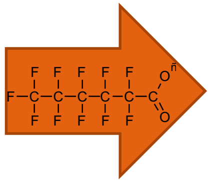


(Adobe Stock Photo)

PFAS in Landfill Leachate







- PFAS are known to be present in landfill leachate from disposal of products containing stain and water repellent coatings
- PFAS are not attenuated in typical biological wastewater treatment processes

PFAS in Landfill Leachate

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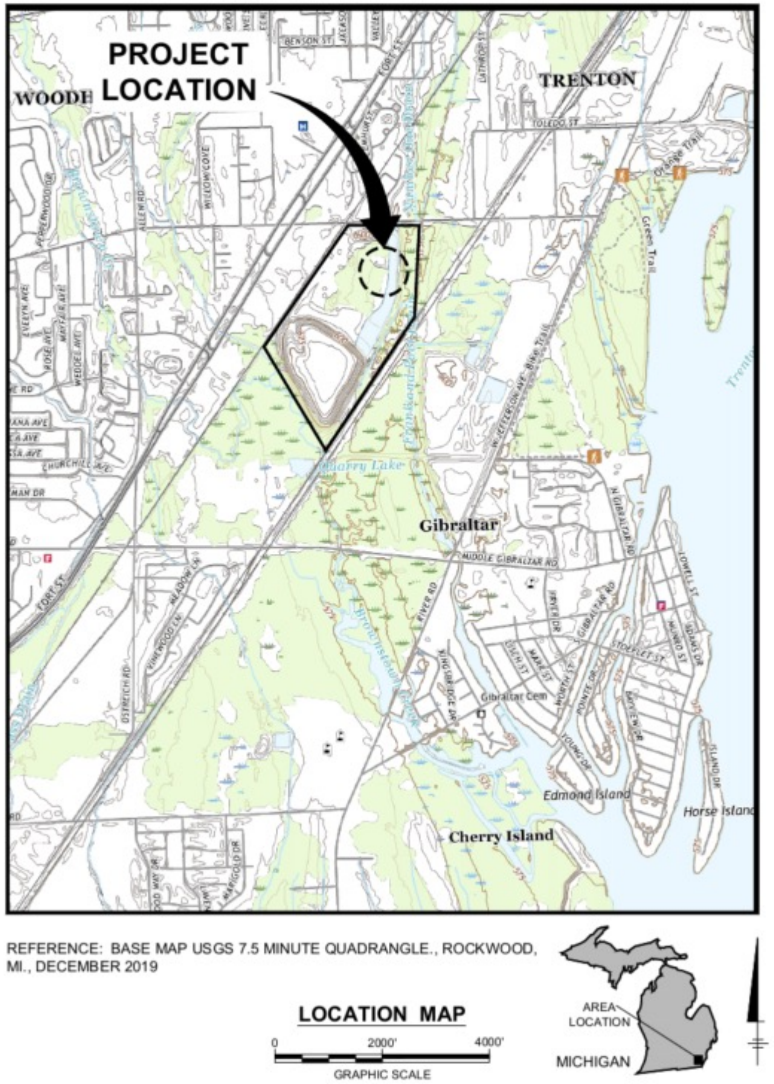
- PFAS WWTP discharge regulations are forcing treatment plants to look upstream at PFAS inputs to their systems

Project Case Study

Site Location and Background

- 330-acre (~136 hectares) site
- Historically operated as steel finishing operation
  - 3 landfills
  - Leachate treatment lagoon system
- Countywide Landfill (CWLF)
  - Steel manufacturing waste (Trenton and Gibraltar McLouth Steel)
  - Construction and demolition debris
- Added to National Priorities List on March 26, 2015
- Discovered PFAS in leachate in 2018
- Leachate collection system along west and south sides of landfill (partially blocked?) – installed by USEPA Contractor in 2011
- 2019 Arcadis contracted for Feasibility Study



Site Conditions

- Current system:
  - EGLE Contract with leachate hauler
  - Off-site treatment and disposal
  - 10,000-20,000 gallons/day
    - (~37,850 – 75,710 Liters /day)
  - Was $0.15 per gallon (~$0.04/ Liter), subject to increase
  - ~$700,000 annual cost
- Electrical power not accessible near sump
- Gravity fed to collection sump

Bench-Scale Testing

ARCADIS

- Landfill leachate samples collected
- Influent
  - **PFOA- 430 ng/L**
  - **PFOS- 190 ng/L**
  - TOC- 74 mg/L
- Target level is for surface water discharge (Rule 57)

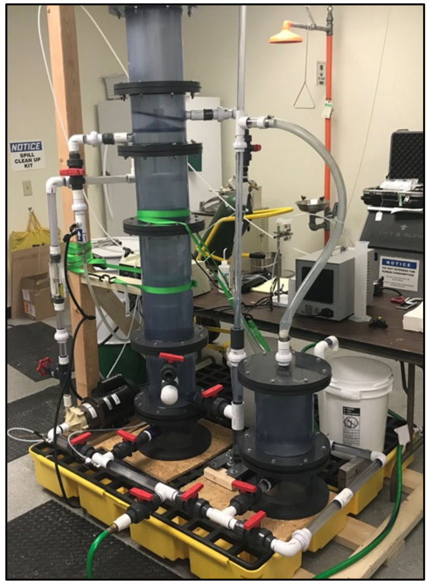
		Influent - Raw Leachate (12/2/2020)
Analyte	**Units**	**Result**
Alkalinity-Total	mg/L	490
Ammonia-N	ug/L	18,000
Chemical Oxygen Demand	mg/L	290
Chloride	mg/L	410
Fluoride	mg/L	0.61
Hexavalent Chromium, Dissolved	ug/L	<50
Nitrate/Nitrite-N	mg/L	<0.2
pH (field)	pH Units	8.7
pH (lab)	pH Units	9.5
Sulfate	mg/L	210
Total Cyanide	ug/L	<0.5
Total Dissolved Solids	mg/L	1,500
Total Organic Carbon	mg/L	74
Total Suspended Solids	mg/L	380

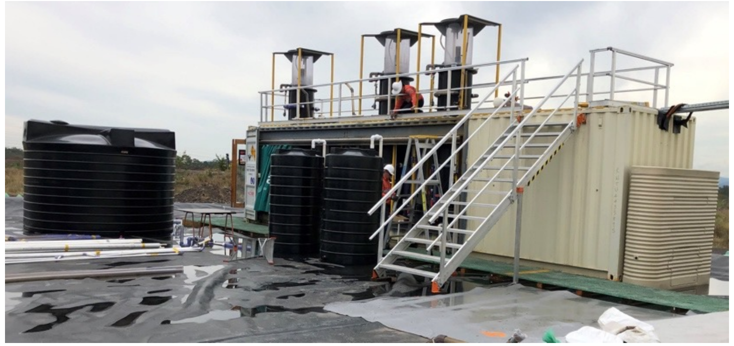
System Design Steps

Bench Scale Testing

Pilot Scale Testing

Full System Installation

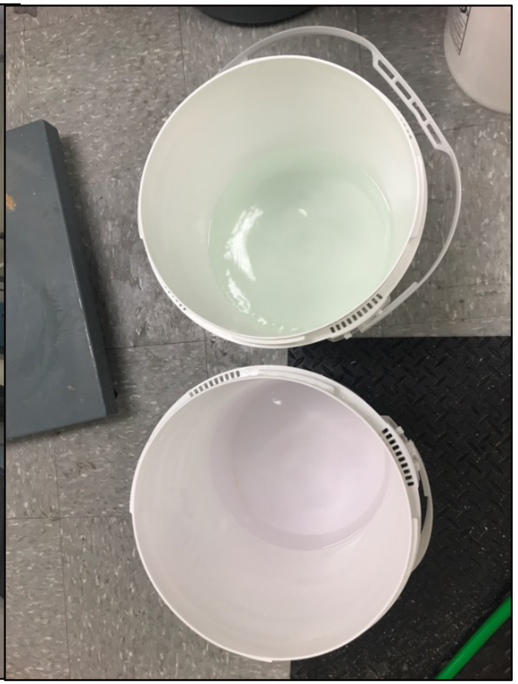




Bench-Scale Testing

- Arcadis Treatability Lab, North Carolina, US
  - Performing fractionation bench-scale studies for over three years
- Providing proof of concept of various waste streams
  - Wastewater, Leachate, AFFF Impacted Streams

Top - Foam Concentrate
Bottom - Treated Effluent



Photos courtesy of Arcadis Treatability Lab

Bench-Scale Testing Summary

Bench Test	PFOA/PFOS Treated <10 ng/L	Concentrated Waste Volume Estimates
Foam Fractionation	Yes	4%
Membrane (UF, NF, RO)	Yes	16%
Coagulation – GAC	No	N/A

Coagulation-GAC Eliminated

Bench-Scale Testing Volume Estimates

Volume Estimates			
Technology	Raw Leachate Influent Volume (MGD) / (MLD)	Treated Effluent Volume Estimate (MGD) / (MLD)	Concentrated Waste Volume Estimate (MGD) / (MLD)
Foam Fractionation (FF)	10 / 37.8	9.6 / 36.4	0.4 / 1.4
Membrane (UF, NF, RO)	10 / 37.8	8.4 / 31.7	1.6 / 6.1

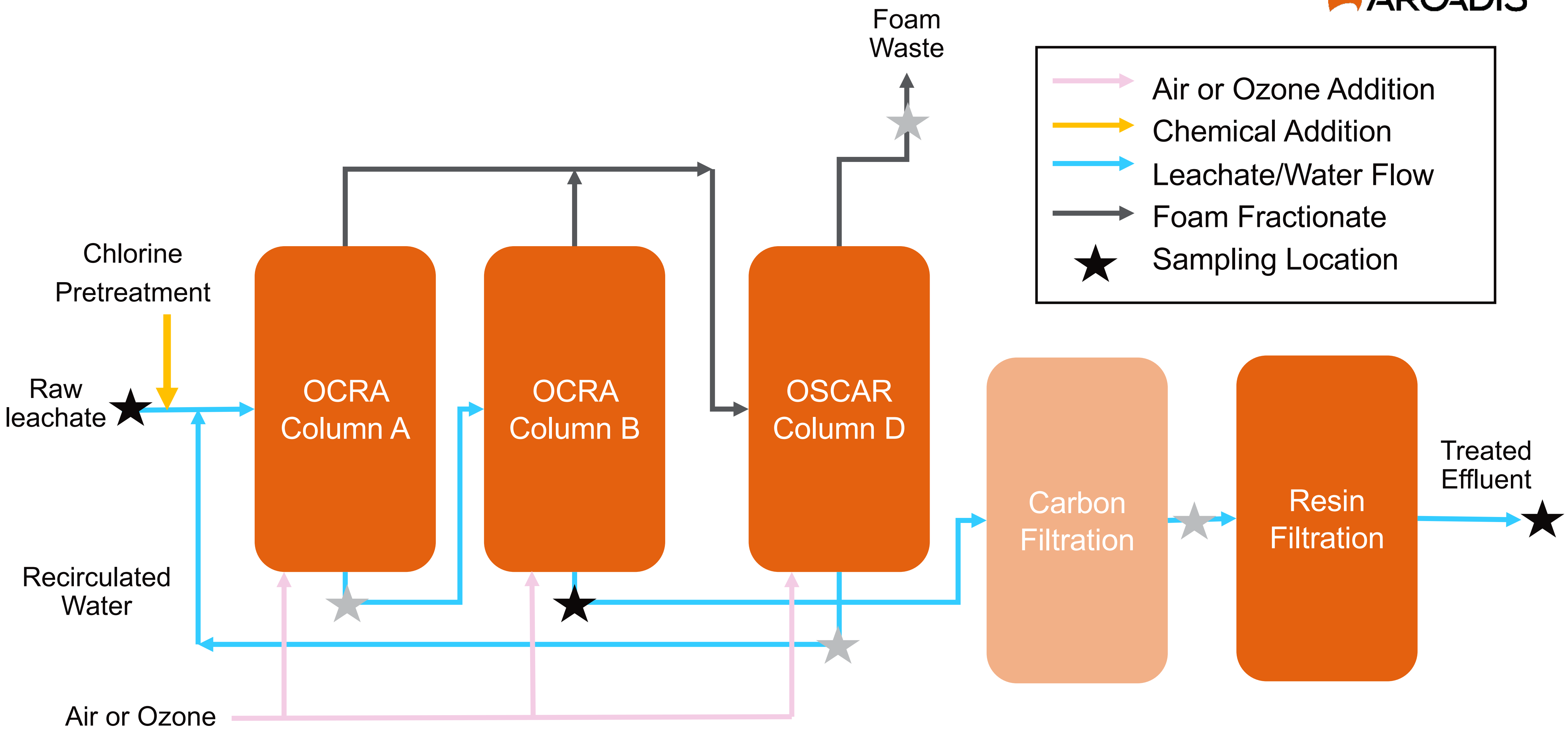
FF Estimated to Produce 4 Times Less Waste than Membrane

Pilot Foam Fractionation Testing – December 2021

- System contains 3 main fractionation columns (OCRA A, B, C); 2 operated for this test
- Column D is concentrating column for further waste reduction (OSCAR)
- Media polish - Purolite PFA694 resin
- Reactivated GAC (TS8X30CPR) was added later during the test in front of the resin
  - Removal of milky coloration from effluent
- Pre-treatment upstream: breakpoint chlorination during select tests
- 4 Scenarios of testing:

Test	Chlorination Pretreatment	Column A	Column B
1	No	Air	Ozone
2	No	Ozone	Ozone
3	Yes	Air	Ozone
4	Yes	Ozone	Ozone

Pilot Test Treatment Train

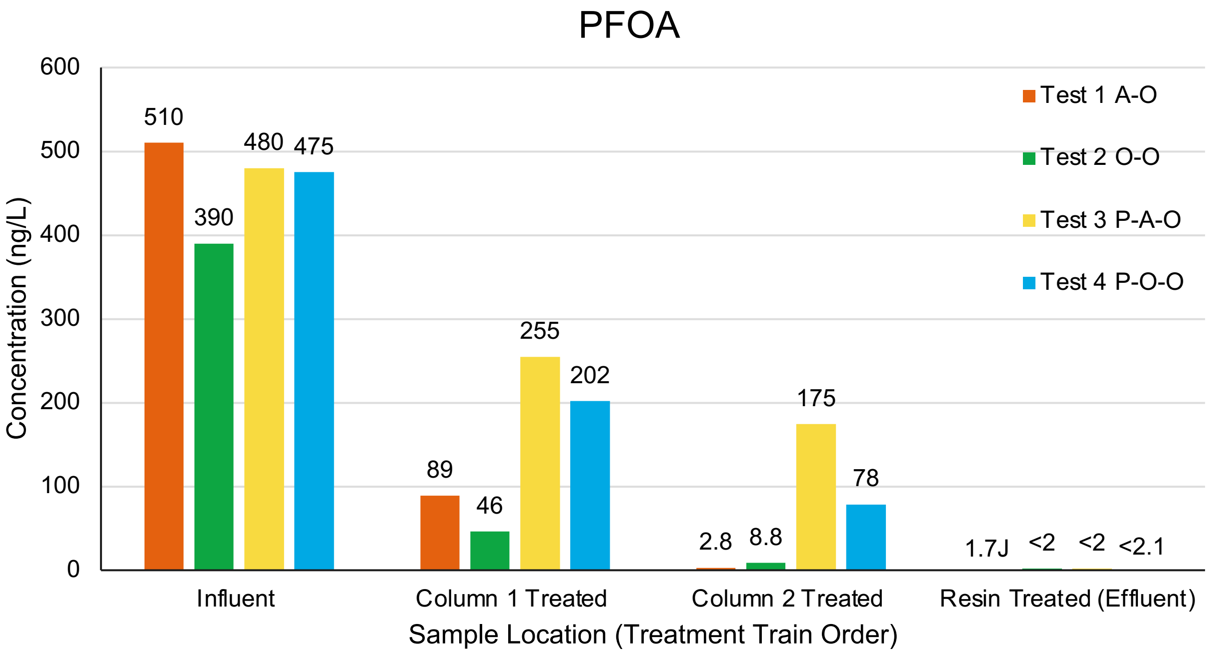


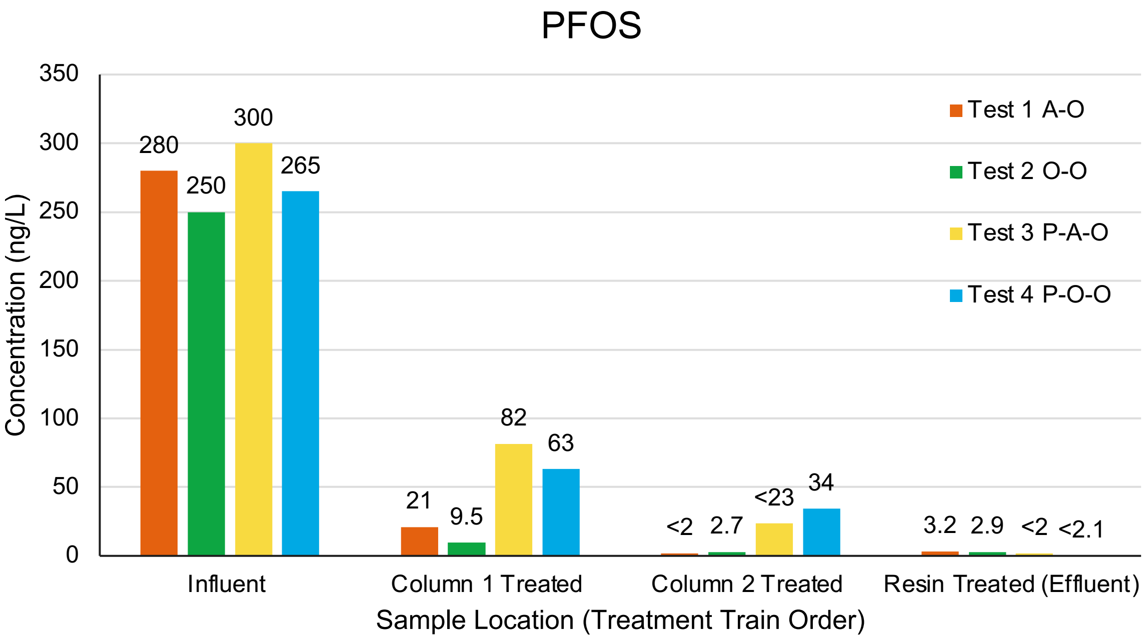
Pilot Test Volumes Summary

- Final concentrated waste to the tote ratios were <5% target range and on target for this test
  - Except Test 1
- Additional volume reduction with concentrating column evident in majority of test days
- 3% to 5% waste volume would be a conservative estimate to use as a basis for full-scale estimates using the concentrating column
- 20,000 gpd influent down to less than 1,000 gpd waste

	Average Influent Flowrate (gpm) / (lpm)	Volume Treated (gal) / (liters)	Final Influent to Waste Ratio (%)
Test 1 – Air - Ozone - No Pretreatment	5 to 8 / 18.9 to 30.3	3,700 / 14,006	3.1 to 7.8
Test 2 – Ozone - Ozone - No Pretreatment		5,848 / 22,137	3.9 to 4.9
Test 3 – Air- Ozone - With Pretreatment		9,282 / 35,136	2.1 to 4.4
Test 4 – Ozone - Ozone - With Pretreatment		8,524 / 32,267	0.7 to 3.3

Pilot Test Results for PFOA and PFOS





- Surface Water Targets, PFOA – 420 ng/L, PFOS – 11 ng/L
- PFOA and PFOS significantly removed through 2 fractionation columns for each test
- Resin polish significantly treated to non-detect levels post-fractionation

Path Forward

Full scale system cost estimates and design	Destruction Testing/Selection for Foam Concentrate
• Pretreatment • Foam Fractionation • Polishing Step	• SCWO • HALT • Plasma

CONCLUSIONS

Foam Fractionation is a viable PFAS treatment technology to be considered as part of a treatment train approach

Ozone can improve treatment and have additional benefits in the foam fractionation PFAS treatment process.

Further optimization to maximize the fractionate-to-treated-water ratio during field pilot applications is possible

Commercialization is increasing in the U.S. and full-scale system construction

Optimization to employ multiple gases (air and ozone) can help to meet increasing demands for comprehensive PFAS treatment.

Thank You!

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