Cost Effective PFAS Leachate Treatment Results from Recent Pilot Testing

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Agenda:

1. What are PFAS ?
2. History of PFAS
3. Health Impacts from PFAS
4. Treatment Options
5. The Path Forward
6. Cumberland NC Pilot Results

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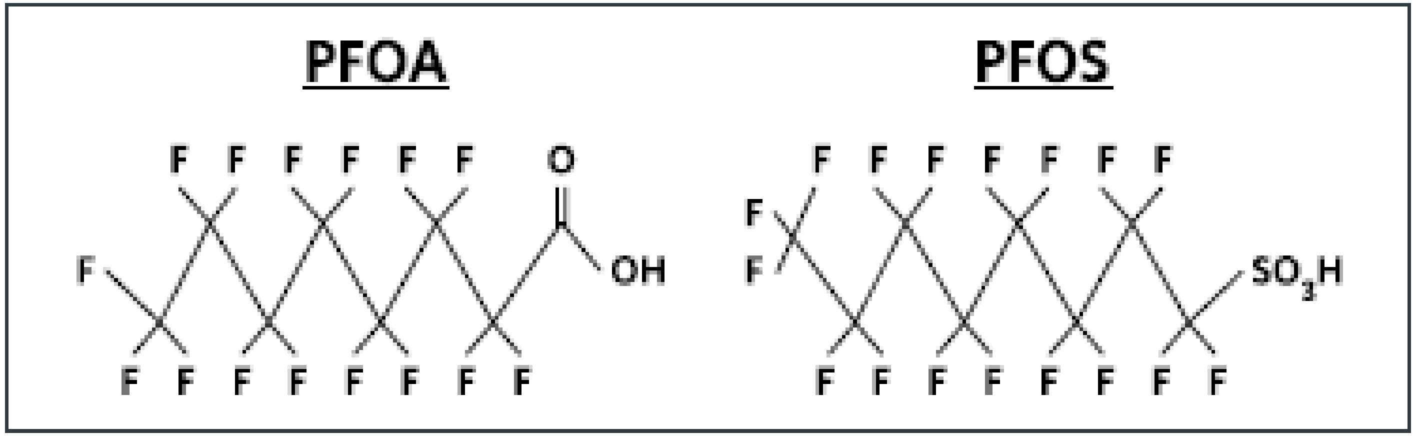
What are PFAS ?

PFAS Defined

- Per- and Poly-Flourinated Alkyl Substances – organic molecules with CF bonds
- Perfluoroalkyl substances – each carbon atom is fully saturated with fluorine, Polyfluoroalkyl substances – mostly saturated CF bonds
- Polymer vs non-polymer PFAS.
- PFAS molecules hydrophobic – soluble molecules have a hydrophilic end.
- Two most commonly cited:

PFOA - $C_8HF_{15}O_2$ or Perfluorooctanoic acid

PFOS - $C_8HF_{17}O_3S$ or Perfluorooctanesulfonic acid



Properties of PFAS

- Carbon-Fluorine bonds = Forever Chemicals
- Hydrophobic end/Hydrophillic end

Parameter	PFOS	PFOA
Molecular Weight	500	414
Solubility at 25^{o}C - mg/L	370 to 570	9500
Melting Point (^{o}C)	>400	45 to 54
Boiling Point (^{o}C)	not measurable	188 to 192
Vapor pressure at 20^{o}C (mmHg)	0.00000248	0.017
Henry's Law constant (atm-m^{3}/mol)	3.1×10^{-9}	not measurable
Half-life - atmospheric	114 days	90 days
Half-life - water	>41 years	>92 years

Some other PFAS

- PFNA - Perfluorononanoic acid ($C_9HF_{17}O_2$)
- PFHpA - Perfluoroheptanoic acid ($C_7HF_{13}O_2$)
- PFHxS - Perfluorohexanesulfonic acid ($C_6HF_{13}O_3S$)
- PFBS - Perfluorobutanesulfonic acid ($C_4HF_9O_3S$)
- Adona- dodecafluoro-3H-4,8-dioxanonanoate ($C_7F_{12}O_4H_5N$)
- GenX - ammonium carboxylate salt of hexafluoropropylene oxide dimer acid (HFPO-DA) ($C_6H_4F_{11}NO_3$)
- Fluorotelomers – straight short-chain compounds

Perspective

- 1 mg/L ~ 1 part/million:
    - 4 drops of ink in a 55 gallon barrel
    - 1 second in 2 weeks
- 0.001 mg/L ~ 1 part/billion
    - one drop of ink in 500 barrels (21,000 gallons) of water,
    - 1 cent out of $10 million or 1 second in 32 years.
- 0.000,001 mg/L ~ part/trillion
    - one drop of ink in 500,000 barrels (21 million gallons) of water
    - traveling 6 inches of a 93 million-mile journey toward the sun

The California Office of Environmental Health Hazard Assessment targets to minimize cancer risk from drinking water of 1 ppt for PFOS and 0.007 ppt for PFOA.

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The History of PFAS

History of PFAS

Based on information from ITRC reports:

Decade	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s
PTFE	Invented	Non-Stick Coatings			Water Proof Fabrics			
PFOS		Initial Production	Stain and Water Resistant Products	Firefighting Foams				US drives reduction of PFOS, PFOA, PFNA and select other PFAS
PFOA		Initial Production	Protective Coatings					
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foam		

before development of chemistry

Initial Chemical Synthesis and Production

Used in Production of Commercial Goods

Big Uses

- Teflon and plastics production
- Aqueous Fire Fighting Foam (AAAF)
- Food Wrappings (fast food wrappers, pizza boxes)
- Water resistant and Flame retardant clothing
- Adhesives
- Cleaning Products
- Paints, Coatings and Waxes
- Textiles and Carpeting
- Cosmetics
- A host of industrial uses in metal plating, electronics, mining, oil and gas, etc.

Current Production and Usage of PFAS in US

- EPA indicates total primary manufacturers reported manufacturing (including importing) about 25,600 metric tons of PFAS at 38 sites in 2015.
- In 2009, an Annex of the Stockholm Convention on Persistent Organic Chemicals was approved which added restriction of PFOS. In 2019, restrictions were placed on PFOA and PFHxS
- World-wide production of PFOS was halted by 3M in 2000. 3M phased out of PFOS, PFOA, PFHxS and related precursers in 2002.
- PFAS are manufactured globally. PFAS production in China started in the 1980s and increased as they were phased out of US production.
- A variety of shorter chain PFAS are currently used as replacements

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Health Impacts of PFAS

Ingestion Pathways

- Drinking Water
- Food
- Ingesting contaminated dust or soil
- Food-wrapping materials
- Contact with materials contaminated with PFAS
- Personal care products
- Airborne PFAS (dust, aerosols or vapor)
- Occupational exposure
- Breast Milk (2021 study) PFOS and PFOA median values 30.4 and 13.0 pg/ml.

Bioaccumulative:

Data shown is from a 2017 FDA study. Later studies show lower levels of PFAS. Contamination amount may vary with proximity to PFAS production facilities and other factors.

Health Risks

- Reproductive effects such as decreased fertility or increased high blood pressure in pregnant women.
- Developmental effects or delays in children, including low birth weight, accelerated puberty, bone variations, or behavioral changes.
- Increased risk of some cancers, including prostate, kidney, and testicular cancers.
- Reduced ability of the body’s immune system to fight infections, including reduced vaccine response.
- Interference with the body’s natural hormones/endocrine distupter
- Increased cholesterol levels and/or risk of obesity.

Current Regulatory Levels

- EPA National Guidance Level: 2016 70 ppt PFOS and PFOA in drinking water
- In 2000, Congress- H.R. 535 directed EPA to promulgate drinking water regulations within two years
- States have taken the lead in the last few years:

		State Action Levels			
Parameter	Units	Washington	Michigan	California	
limit description		action level	MCL	notification	response
PFOA	ppt(ηg/L)	10	8	5.1	10
PFOS	ppt(ηg/L)	15	16	6.5	40
PFNA	ppt(ηg/L)	14	6		
PFHxS	ppt(ηg/L)	70	51		
PFBS	ppt(ηg/L)	860	420	0.5	5
PFHxA	ppt(ηg/L)		400,000		
HFPO-DA	ppt(ηg/L)		370		

Health Criteria for Drinking Water

- California Office of Health Hazard and Assessment (OEHHA) developed PFOA reference levels in drinking water associated with pancreatic and liver tumors. 0.1 parts per trillion (ppt) represents the concentration of PFOA in drinking water that would not pose more than a one in one million cancer risk.
- New Jersey research indicated that based on increased incidence of testicular cancer in rats, the MCL for PFOA was cited as 14 ppt.
- Most PFOS state guidelines are based on non-cancer endpoints -insufficient cancer endpoint data.

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Treatment Options

Wastewater Overview

- Municipal or Industrial Discharge Criteria not established yet
- Water Reuse Facilities
- Landfill Discharges
- Industrial Facilities
- Remediation

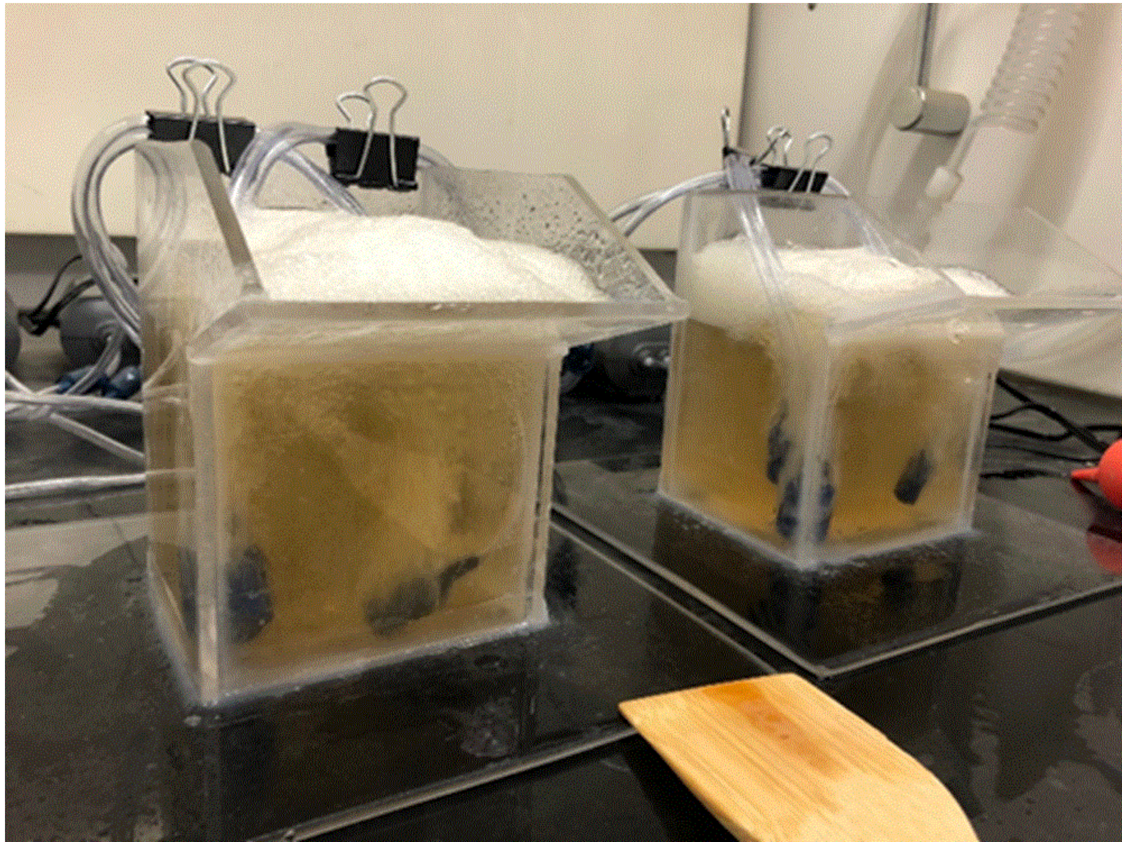
Conventional Approaches for PFAS removal as applied to industrial wastewaters and landfill leachate

- IX – problems with fouling, plugging, cost, media disposal
- GAC – potential short life from organics competition for sites, cost, media disposal
- Membrane processes – concentrate PFAS in reject, but same mass, cost, high reject volume
- HDR started to search for alternative approaches for wastewater

Froth Flotation (1)

- AKA flotation, foam fractionation, and other terms
- Literature showed promise with the appropriate reagents and apparatus
- Initial screening on Phoenix landfill leachate
- Results:

Removal of Measurable PFAS	Reagent
28.6%	Aeration Only
97.5%	Reagent 1
80.1%	Reagent 2
91.2%	Reagent 3 – Dose 1
95.0%	Reagent 3 – Dose 2
94.9%	Reagent 3 – Dose 3

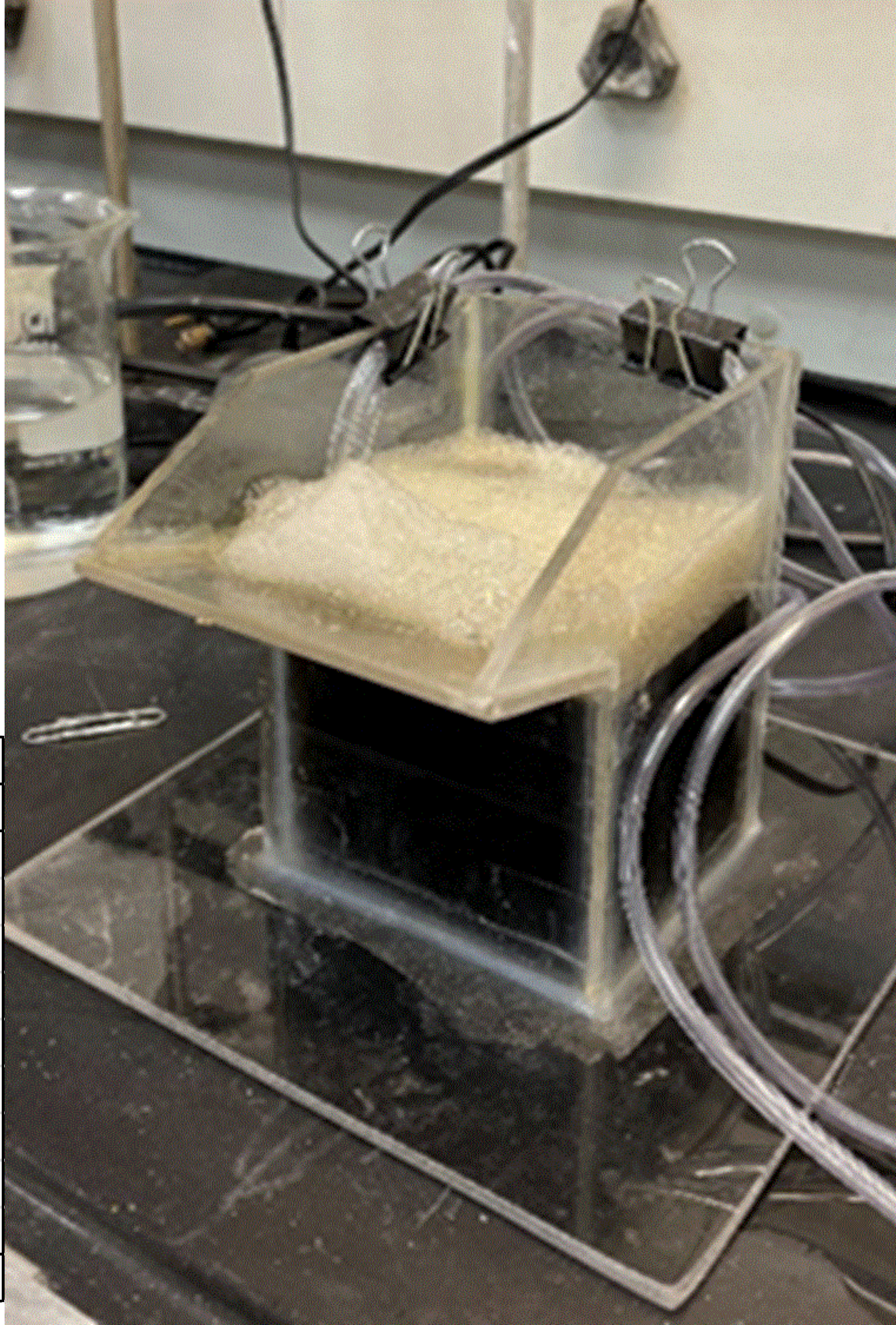


Froth Flotation (2)

- Second Round of Testing-New Jersey Leachate

Raw leachate Characteristics		
Parameter	units	Value
6:2 FTS	ppt	46
PFBS	ppt	397
PFHxS	ppt	195
PFHxA	ppt	741
PFNA	ppt	33.7
PFOS	ppt	93.2
PFOA	ppt	341
NetFOSA	ppt	<14
PFDA	ppt	54.2
sum of measurables		1901.1

Raw RO Reject Characteristics		
Parameter	units	Value
6:2 FTS	ppt	61.1
PFBS	ppt	2530
PFHxS	ppt	533
PFHxA	ppt	3600
PFNA	ppt	180
PFOS	ppt	335
PFOA	ppt	1670
NetFOSA	ppt	<14
PFDA	ppt	204
sum of measurables		9113.1



Froth Flotation Second Round Results

- Effluent – One Stage treating leachate

	Feed Bucket	6:2 FTS	PFBS	PFHxS	PFHxA	PFNA	PFOS	PFOA	PFDA	sum of measurable values	% removal
Raw Leachate		46	397	195	741	33.7	93.2	341	54.2	1901.1	
Reagant 1	1	<15	70.6	<12.4	41.4	<9.8	27.6	<8.4	<14.4	139.6	92.70%
Reagant 2	1	<15	<6.2	<12.4	10.9	<9.8	<7.6	<8.4	<14.4	10.9	99.40%
Reagant 3	1	<15	38.7	<12.4	104	<9.8	11.4	15	<14.4	169.1	91.10%
Reagant 4	1	<15	<6.2	<12.4	<9.4	<9.8	8.1	<8.4	<14.4	8.06	99.60%

- Effluent – One Stage treating RO reject

	Feed Bucket	6:2 FTS	PFBS	PFHxS	PFHxA	PFNA	PFOS	PFOA	PFDA	sum of measurable values	% removal
RO concentrate	RO	61.1	2530	533	3600	180	335	1670	204	9113.1	
Reagant 1	RO	<15	12.2	17.1	<9.4	<9.8	40.4	18.5	<14.4	88.2	99.00%
Reagant 3	RO	<15	59.2	15.8	46.3	<9.8	33.2	17.9	<14.4	172.4	98.10%

- Limited studies - an additional stage was productive,
  - froth collapsed and concentrated further,
  - evaporation had losses to volatization

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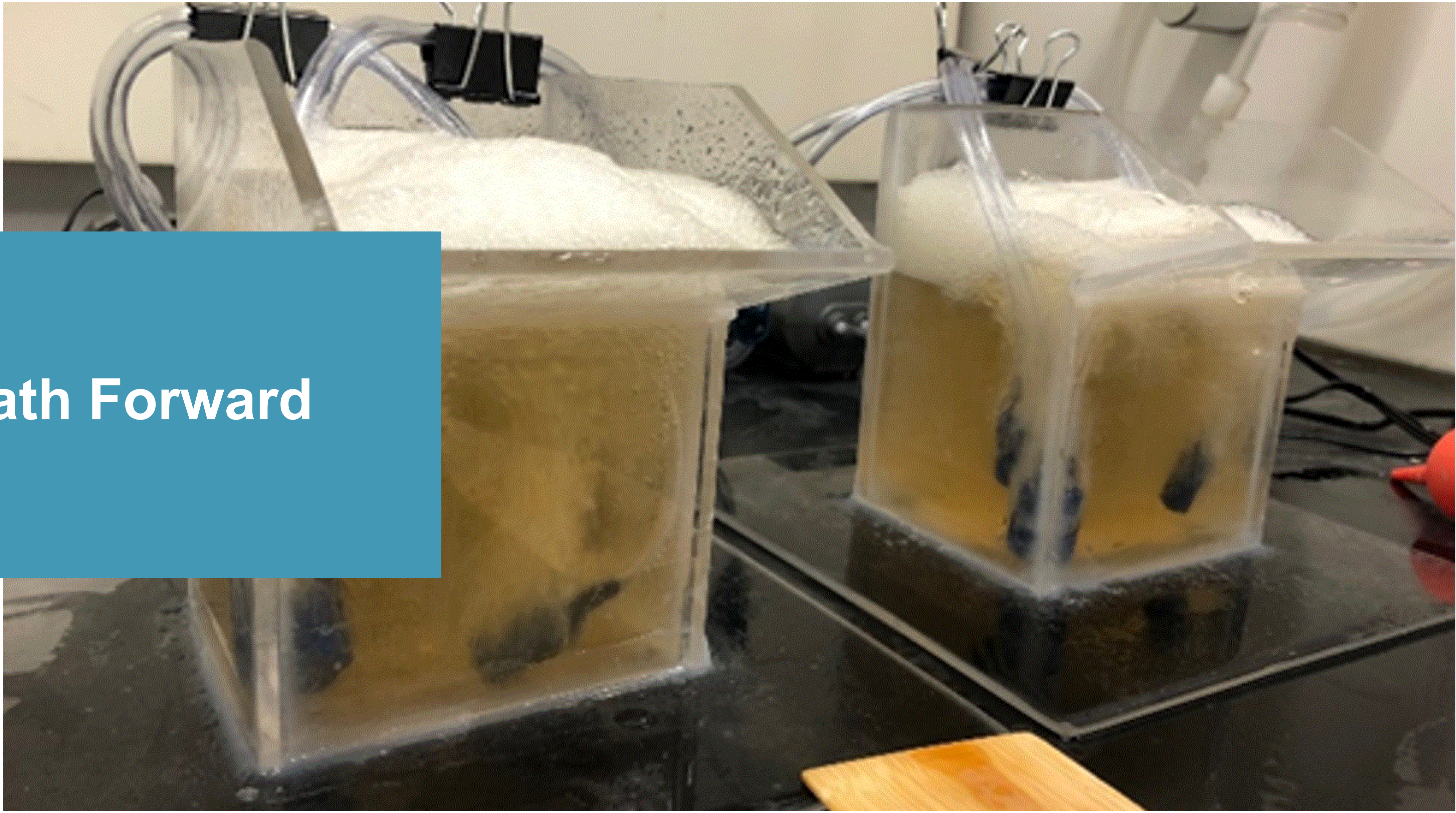
The Path Forward



Going Forward:

- Assemble a Pilot Froth Flotation System (done)
- Pilot Testing for Landfill Leachate (one complete-others scheduled)
- PFAS destruction technologies bench testing (in progress)
- Pilot Testing other streams
  - Metal platers
  - mining operations
  - consumer products companies starting to recognize new limits are coming
- Pilot Testing with destruction technology

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Cumberland County Pilot Results

Cumberland County, NC Pilot

- 200,000 ton per year MSW landfill
- 30,000 gpd leachate
- Gravity connection from leachate lagoon to POTW
- PFAS 2,000 to 7,000 ppt in previous screening
- Located on Cape Fear River – Impacts from Chemours on Surface Water and Ground Water
- Pilot Ran May 18^{th} – May 27^{th}

Pilot Configuration

- Multiple columns
- Scrubber on air used in aeration
- Masterflex pumps for accurate and consistent pumping
- Reagent fed to each column mid-depth
- Run for 5 days at 8 hours/day, sample at end of day
- Not advisable to do this every week in the summertime


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System Performance

		Drinking Water Criteria		Pilot Day 1		Pilot Day 3	
Parameter	Units	Michigan	Washington	Leachate	Effluent	Leachate	Effluent
PFOA	ng/L	8	10	1270	5.86	1170	12.0
PFOS	ng/L	16	15	144	ND	228	ND
PFNA	ng/L	6	14	76.8	ND	92.8	ND
PFHxS	ng/L	51	70	986	ND	948	ND
PFBS	ng/L	430	860	979	558	845	453
PFHxA	ng/L	400,000		3830	1230	3540	1160
HFPO-DA	ng/L	370		125	42.5	92.2	45.6
5:3 FTCA	ng/L			7090	1010	6290	184

Conclusions

- Based on bench and pilot study data, the froth flotation process has merit as a pretreatment process for landfill leachate.
- Preliminary estimates indicate that it is attractive economically compared to conventional water treatment approaches to PFAS removal.
- The performance of the pilot system is expected to improve with additional studies, as there are several tweaks in progress now to refine the operation.

Questions