

PFAS Separation and Destruction in RO Concentrate

Charlie Liu, PhD
National PFAS Lead



Orange County Water District
GWRS

Agenda

Project Background

WRF 5323

Adsorption of PFAS in ROC

USBR Project

Separation and Destruction of PFAS in ROC



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PFAS Discharge Requirements Are Still Evolving

PFAS is widespread in water and wastewater

-  No national NDPES permits and no ELG's for PFAS
-  Individual states are starting to develop PFAS discharge limits
-  **PFAS treatment is being evaluated in waste streams:**
 - Complex water qualities
 - Planning for potential future PFAS limits

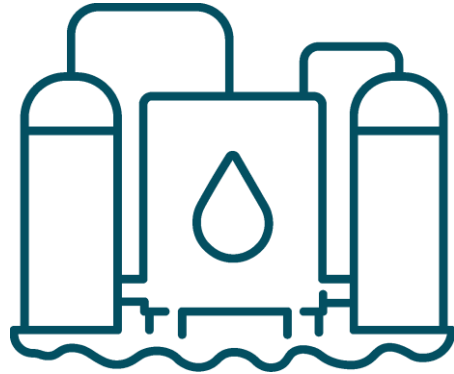
Drinking Water Limits = **Established**
Discharge Requirements = **State Level**

Compound	Drinking Water (MCL)
PFOA	4 ng/L
PFOS	4 ng/L
PFHxS	10 ng/L
PFNA	10 ng/L
GenX	10 ng/L
PFAS Mixtures	1 – Hazard Index

State of Wisconsin Surface Water Limits

PFOA

Surface waters
that supply public
drinking water
20 ng/L



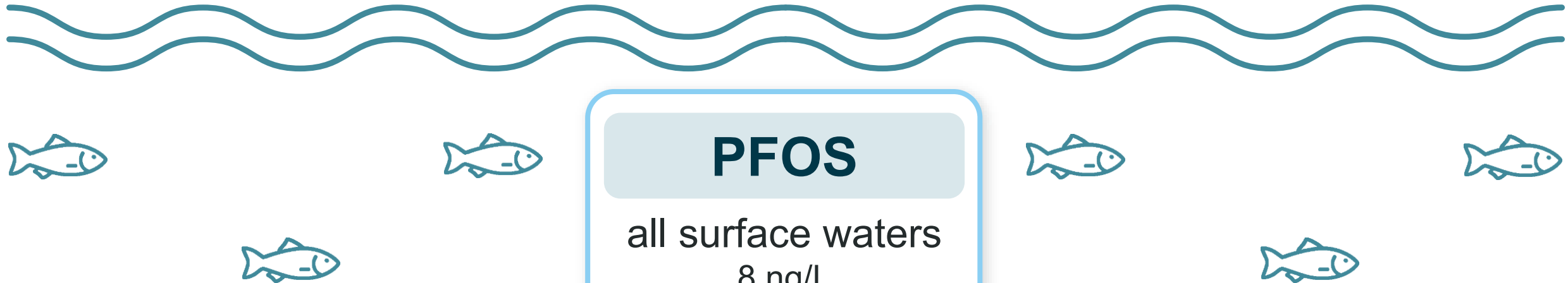
PFOA

Surface waters
that do not
supply public
drinking water
95 ng/L



PFOS

all surface waters
8 ng/L



State of Michigan Surface Water Limits

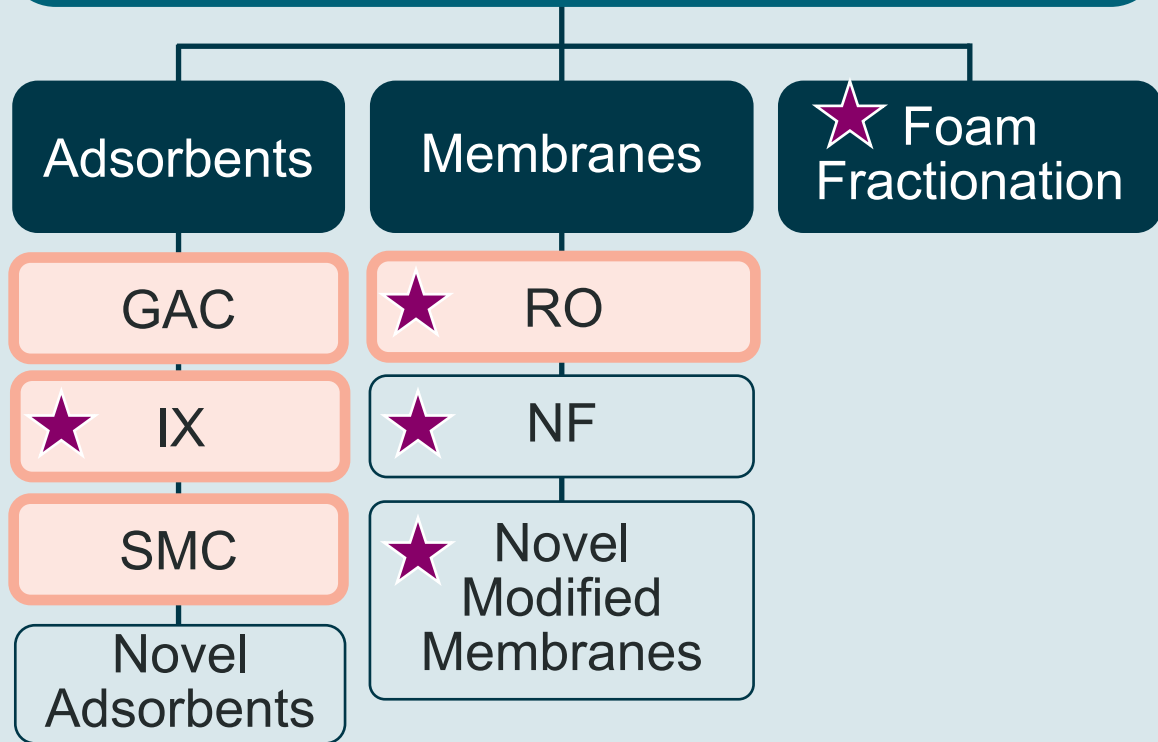
PFAS	Human Noncancer Value Drinking (ng/L)*	Human Noncancer Value Non-Drinking (ng/L)	Final Chronic Value (ng/L)	Aquatic Max Value (ng/L)	Final Acute Value (ng/L)
PFOS	11	12	140K	780K	1.6M
PFOA	66	170	880K	7.7M	15M
PFBS	8,300	670,000	24M	120M	240M
PFHxS	59	210	-	-	-
PFNA	30	30	-	-	-

*nanograms per liter (ng/L) is equivalent to parts per trillion (ppt)

(-) Aquatic Life Values for PFHxS and PFNA are currently under development

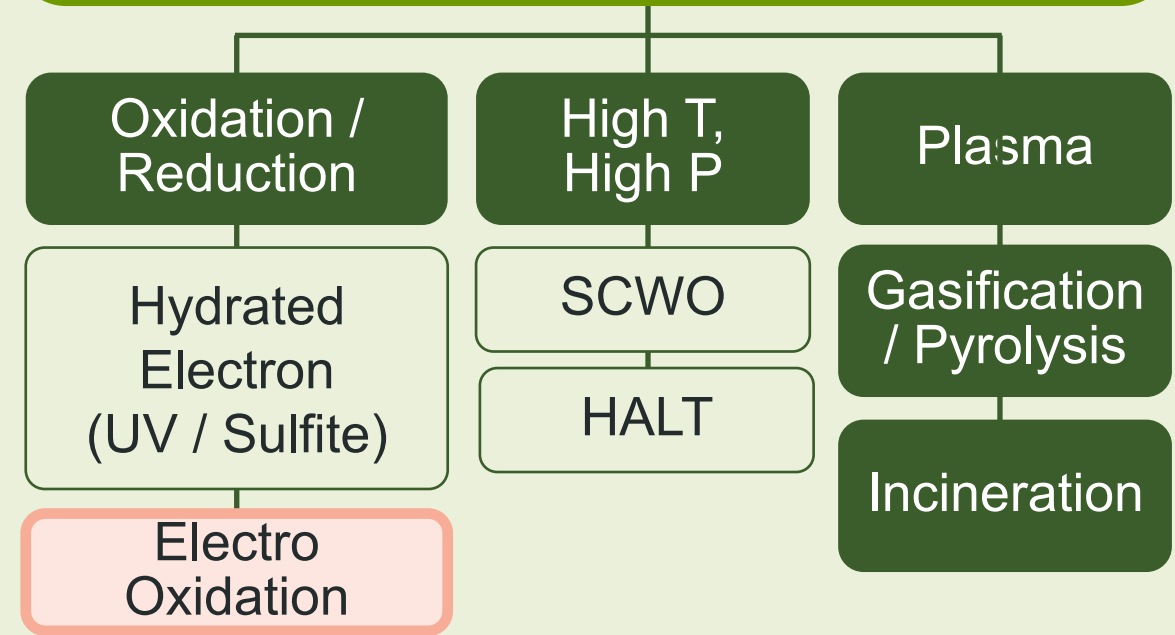
PFAS Separation and Destruction

Separation



★ *Liquid Phase Concentration*

Destruction





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Separation and Destruction of PFAS in ROC

OCWD – GWRS 130 MGD Potable Reuse Facility

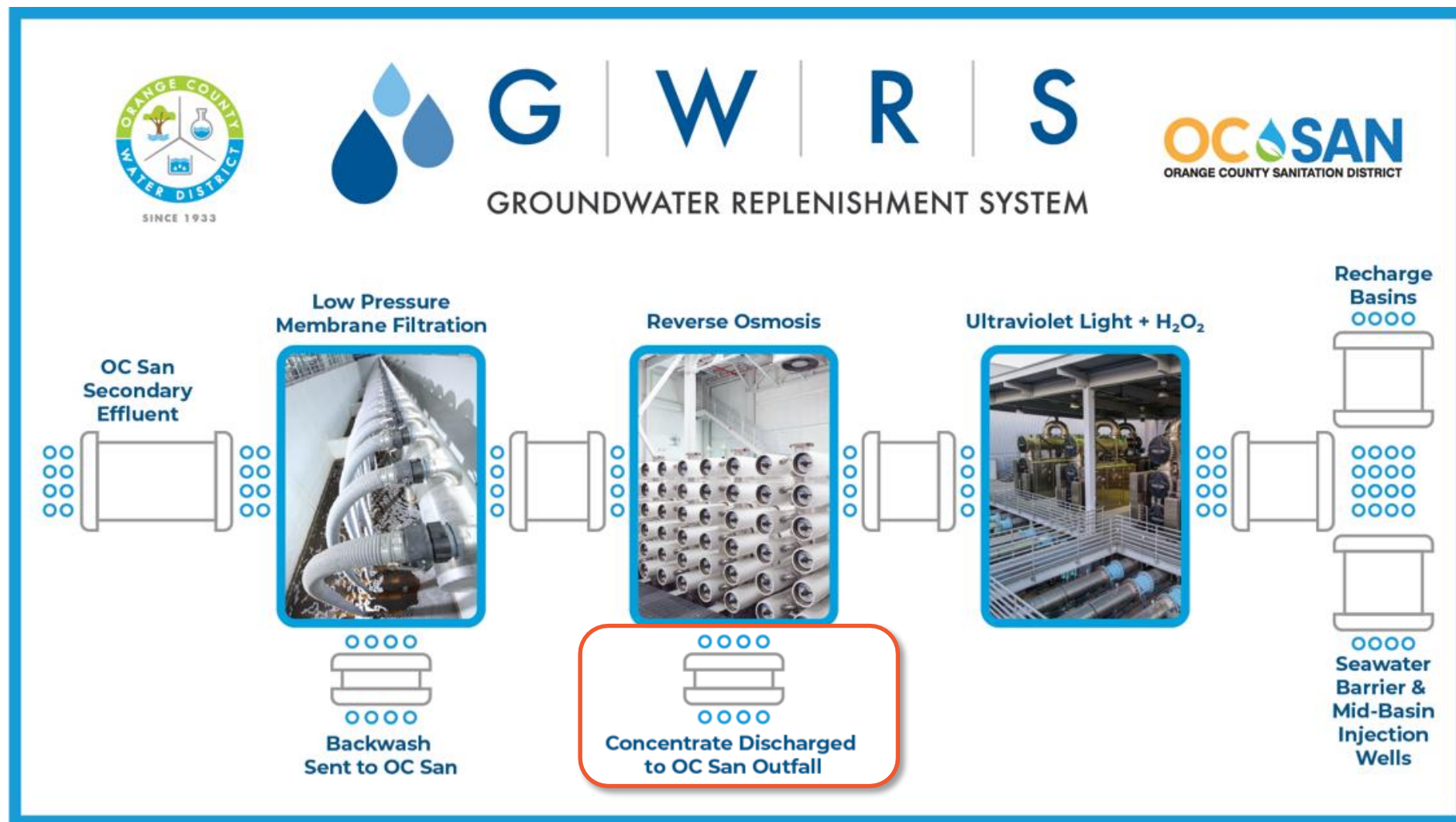
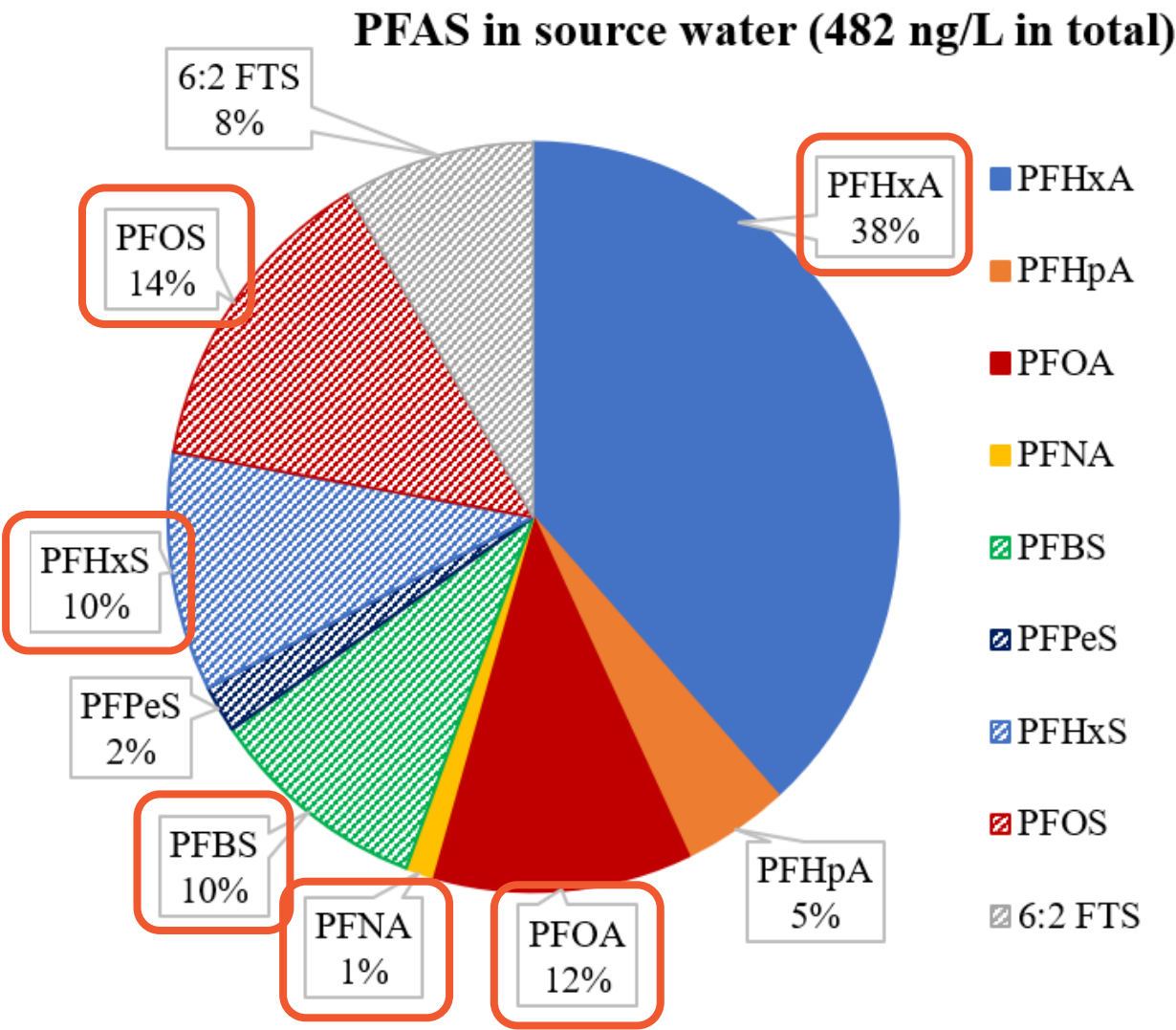


Image Courtesy of OCWD

Municipal Reuse

ROC Water Quality

Analyte	Unit	Average
Cl	mg/L	1673
NO ₃ -N	mg/L	58
Ni	µg/L	33
SO ₄	mg/L	1260
TDS	mg/L	6057
TOC	mg/L	46
Alkalinity	mg/L	1077



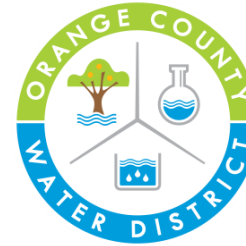
WRF5323 Pilot-Scale Adsorption of PFAS in RO Concentrate from Potable Reuse Systems

Project Team



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WRF Project Manager



Monica Lee-Masi

Project Tasks

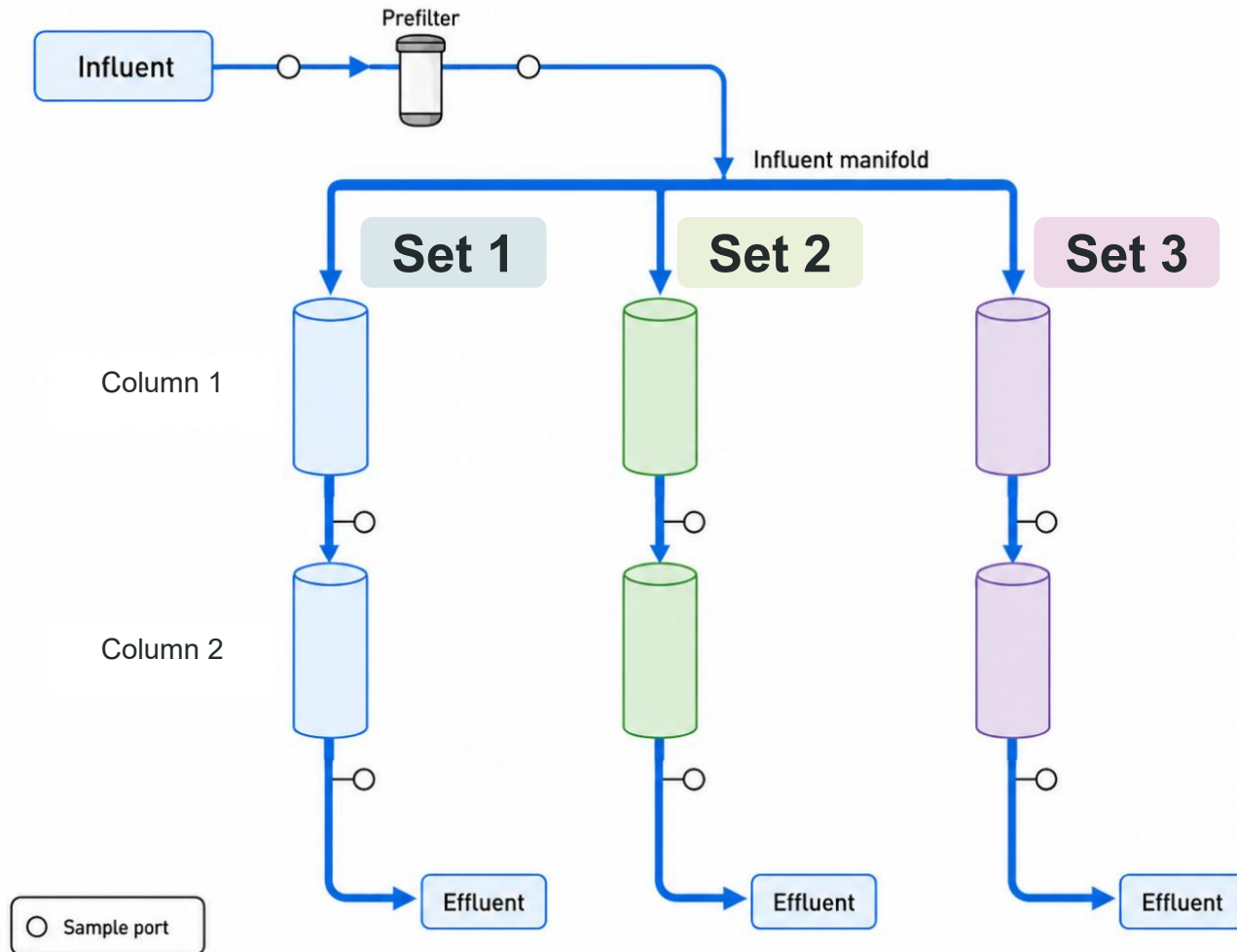
What We Evaluated

PFAS removal using granular activated carbon (GAC), ion exchange (IX), and surface-modified clay (SMC)

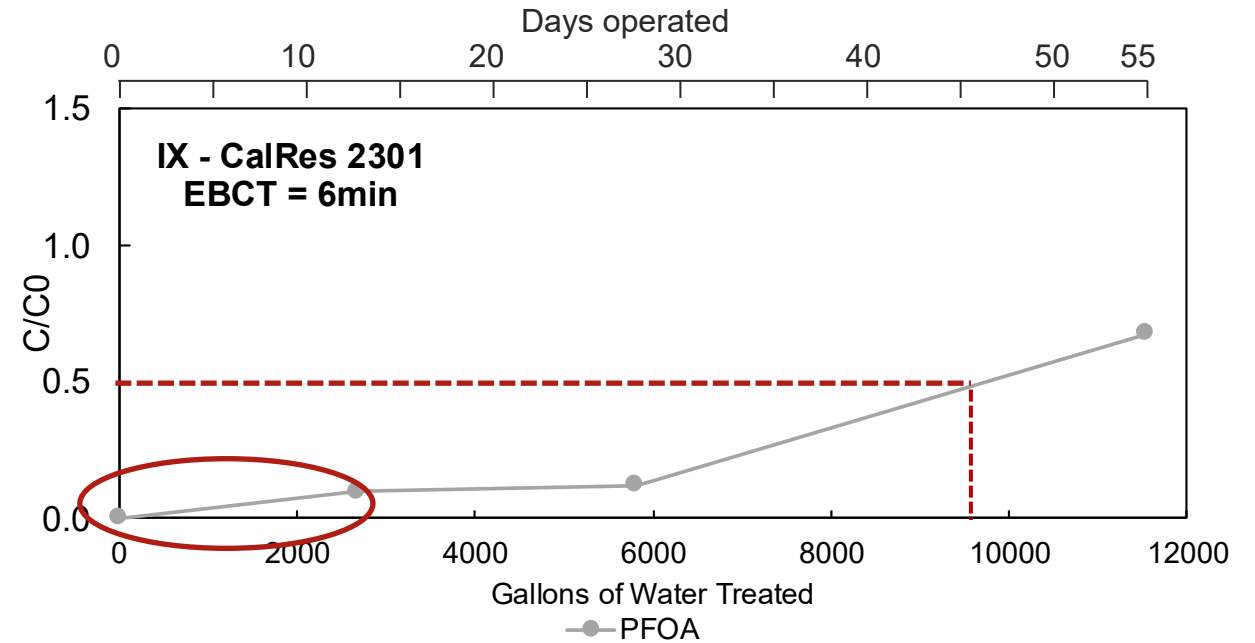
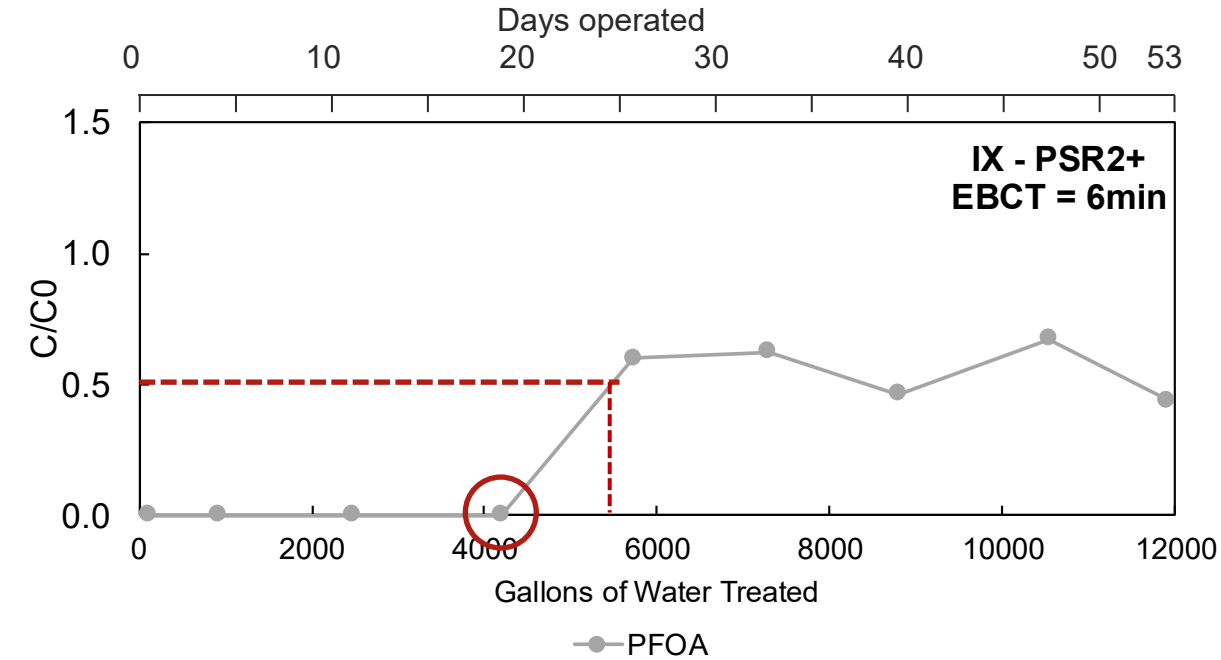
MIEX pretreatment improves adsorption performance

Relative treatment costs and operational considerations

Pilot Configuration

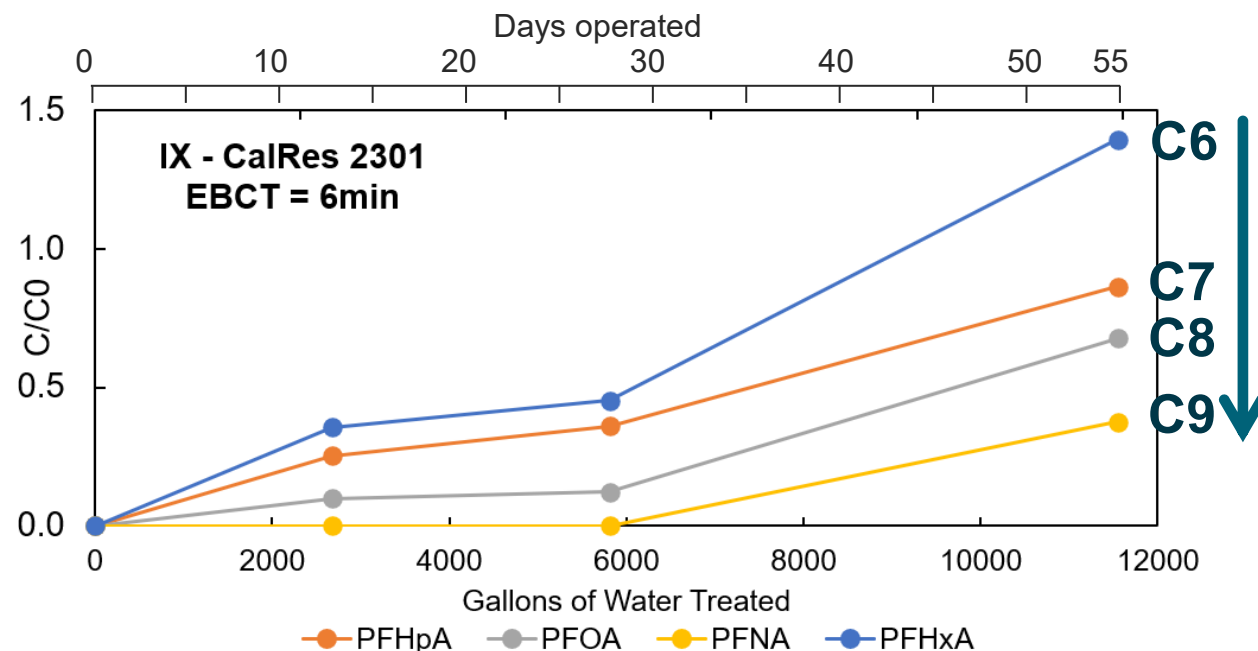
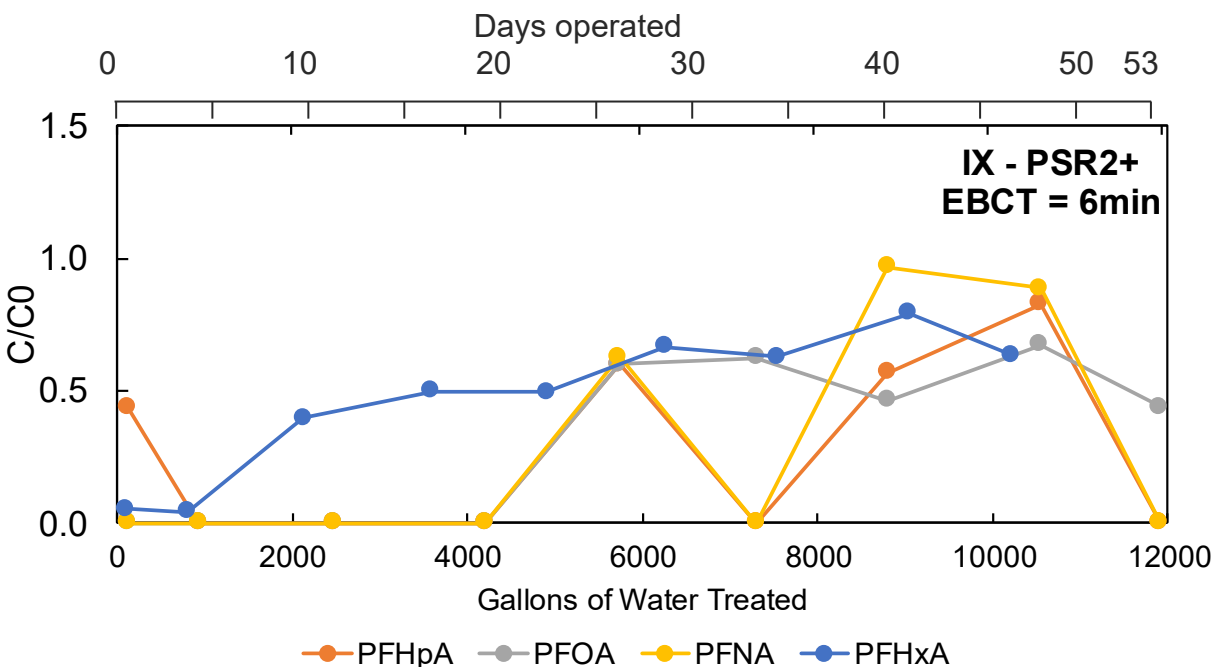


PFCA Breakthrough Curve – IX



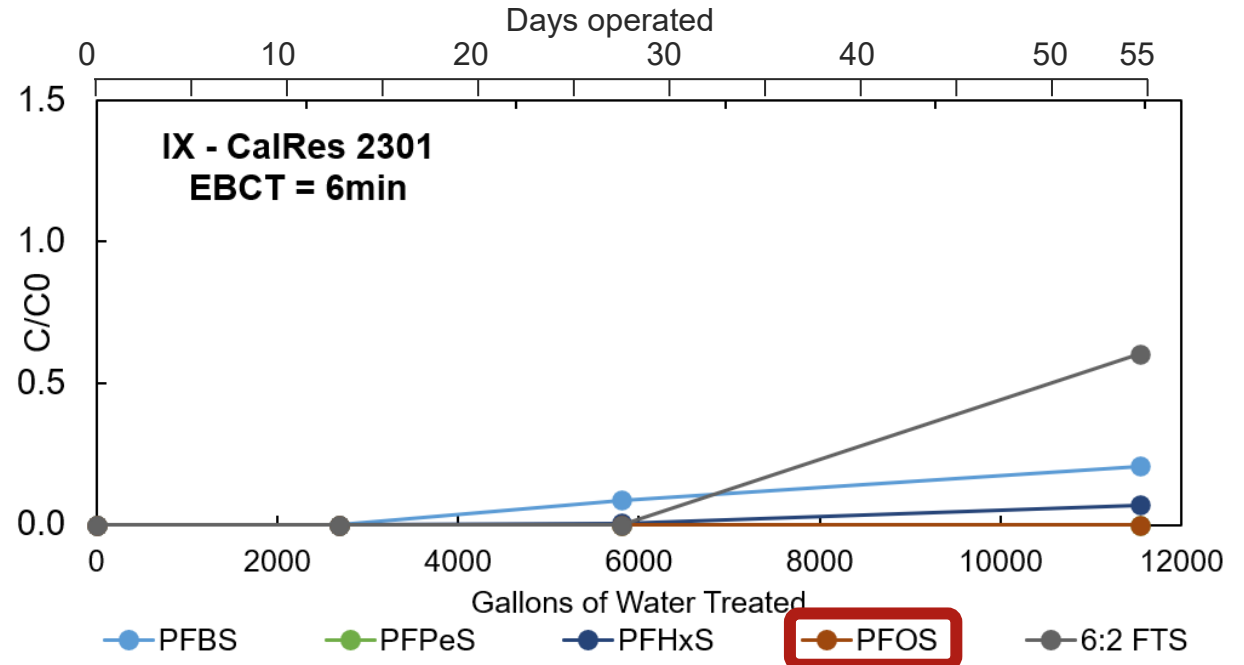
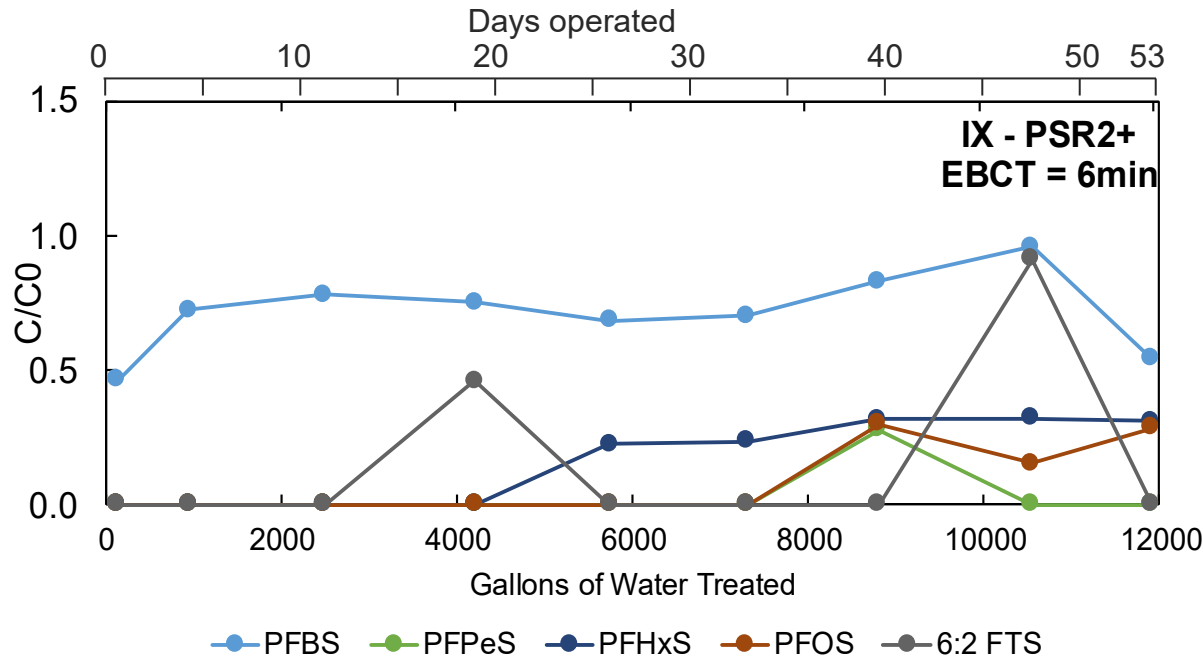
- **PFOA initial breakthrough:** ~20days from PSR2+; immediate from CalRes2301.
- **PFOA 50% breakthrough:** CalRes 2301 later than from PSR2+.

PFCA Breakthrough Curve – IX



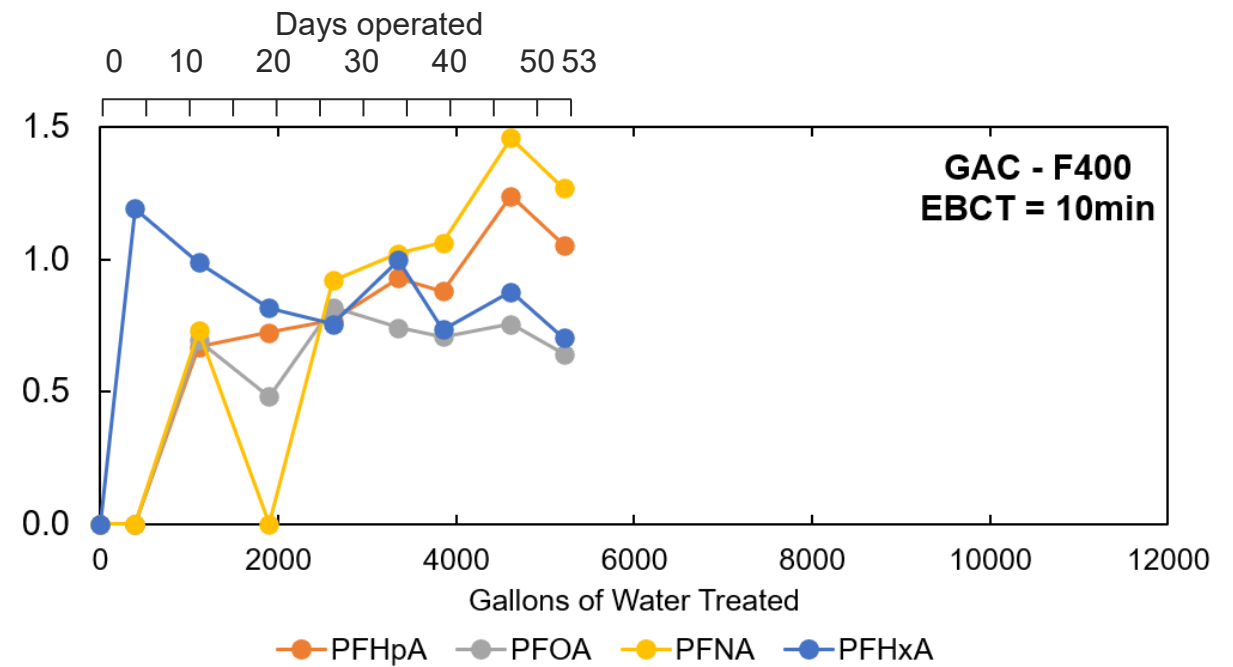
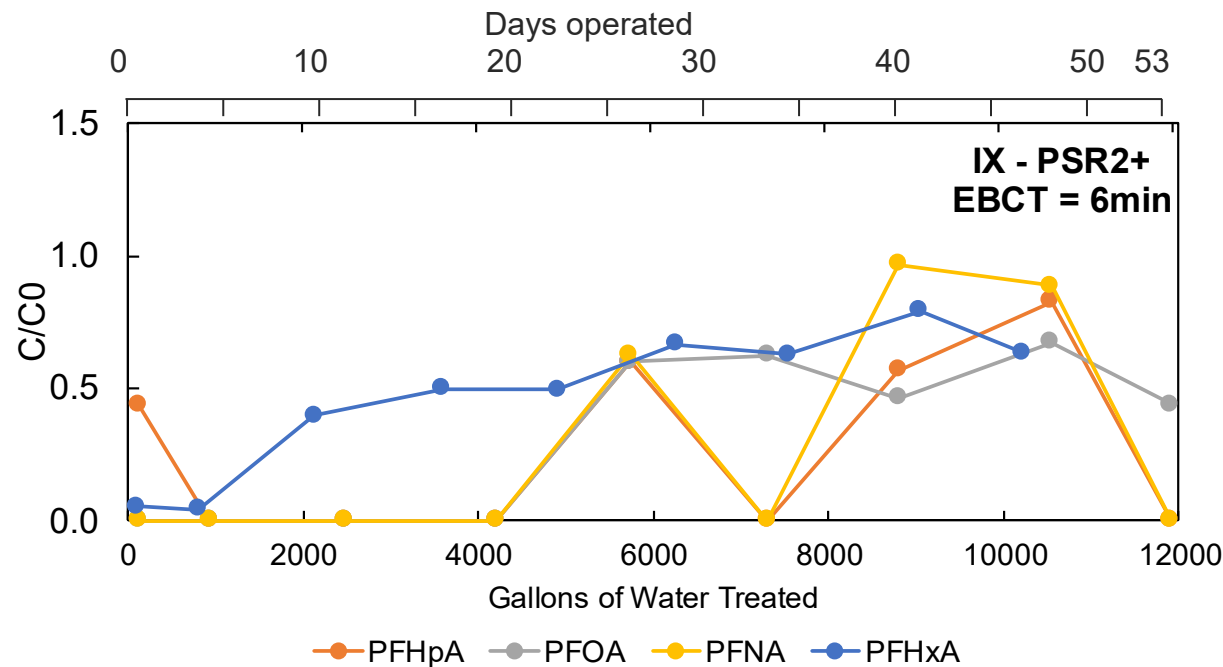
Short chain breakthrough occurred earlier than long chain.

PFCA Breakthrough Curve – IX



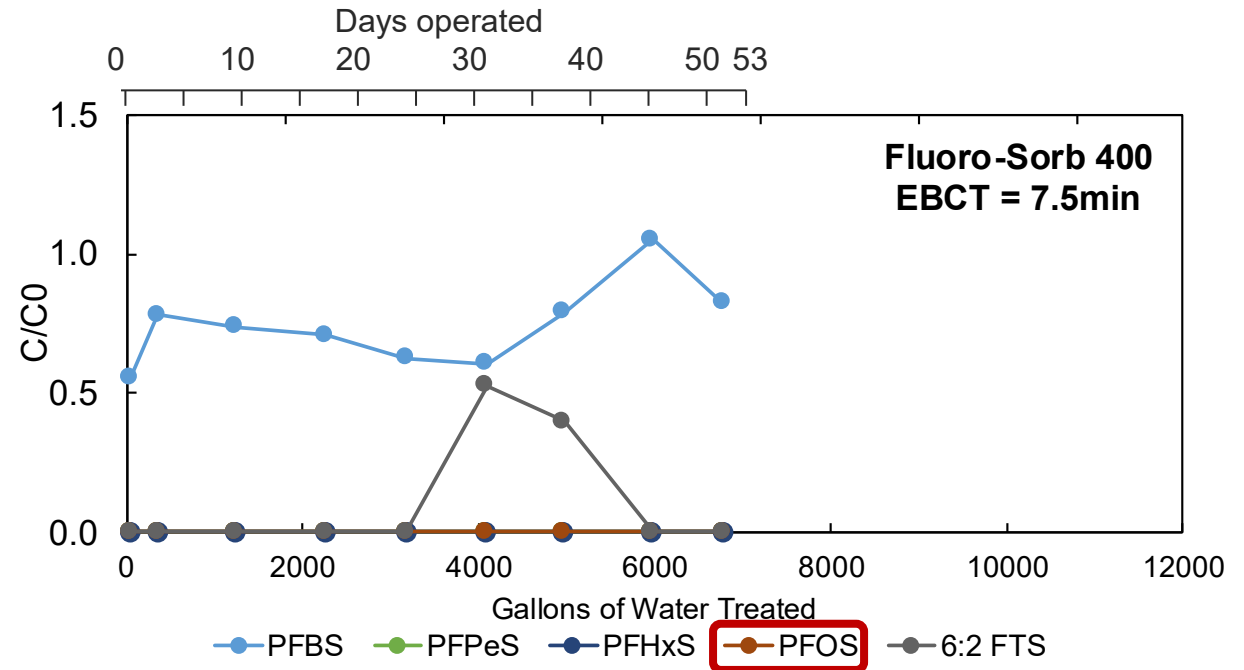
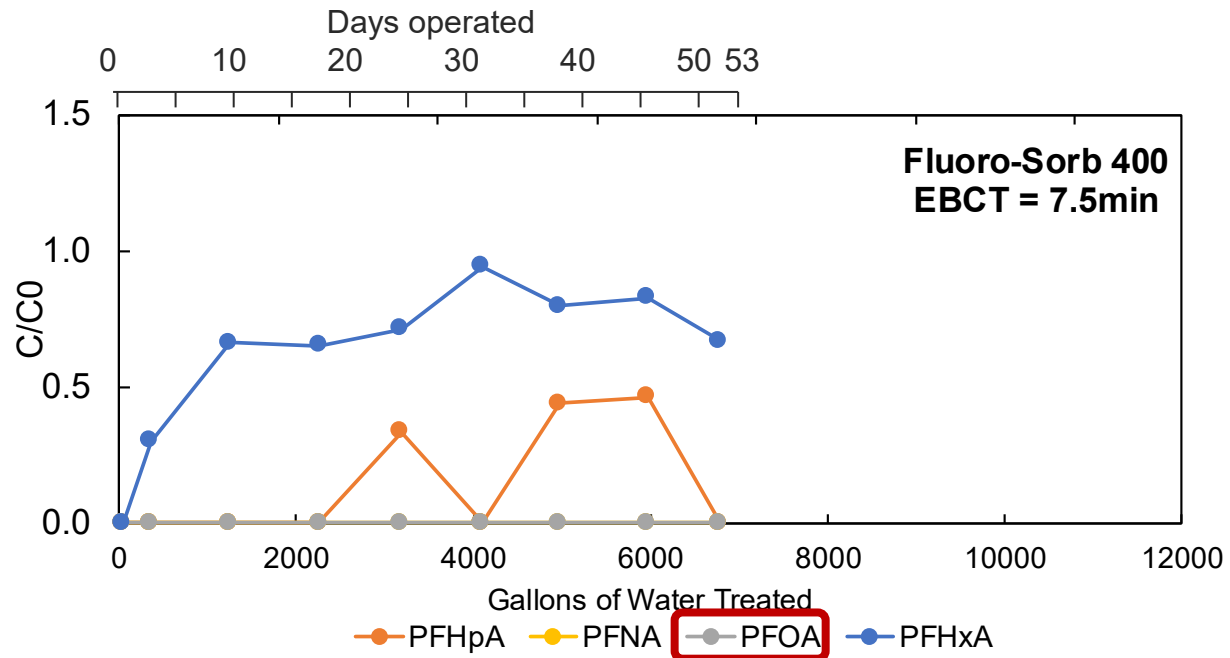
- Short chain breakthrough occurred earlier than long chain.
- **PFOS did not break through from CalRes2301 (55days).**

PFCA Breakthrough Curve – IX vs GAC



- Earlier breakthrough observed in GAC than in IX.
- IX operated a 6 min EBCT; GAC at 10 min EBCT
 - GW/SW design is IX: 2 min EBCT, GAC: 10 min EBCT
 - Evaluating ways to standardize

PFAS Breakthrough Curve – Surface Modified Clay



PFOA and PFOS have not broken through after 7000 gallons (53 days).

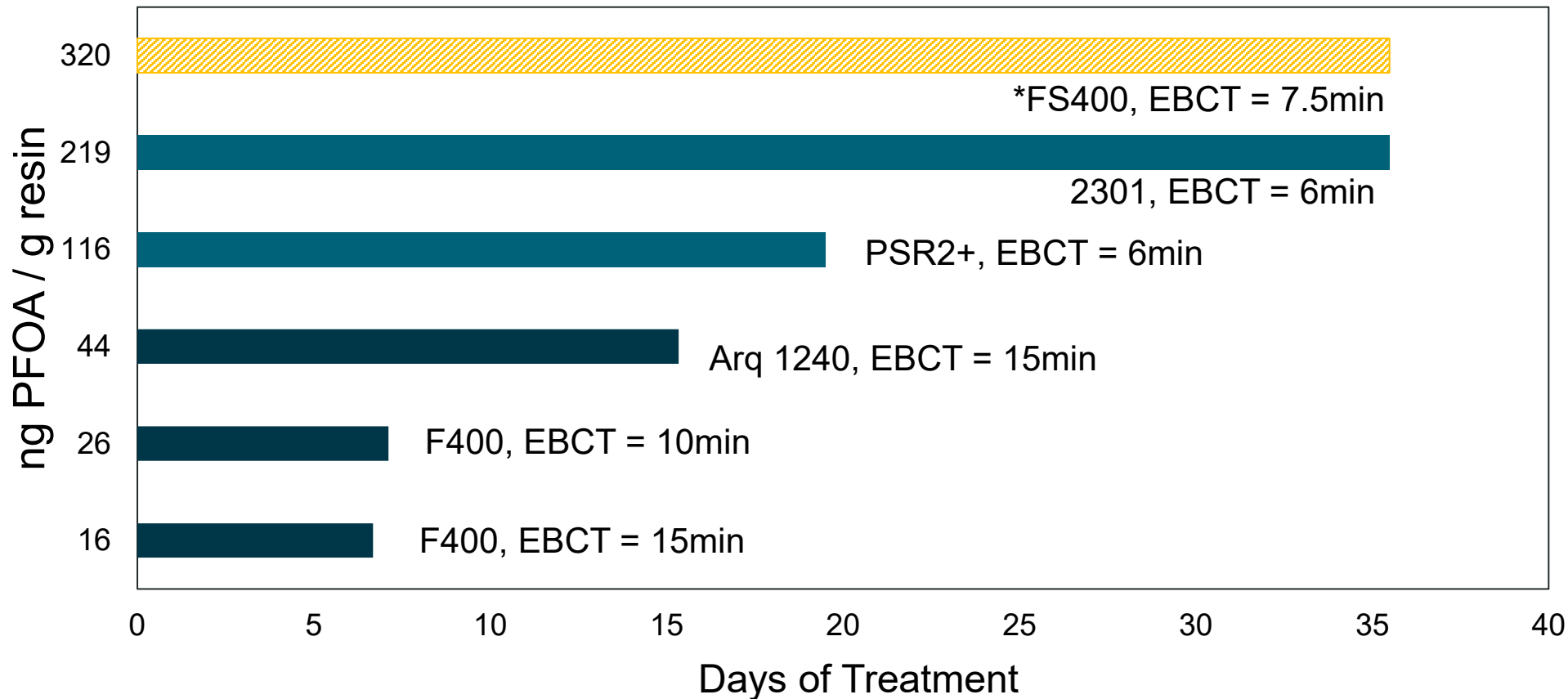
Operational Performance: 50% Breakthrough Within 1 Month?

		PFOA	PFOS	PFHxA	PFHpA	PFNA	PFHxS	PFNS	PFBS
GAC	F400 10min								
	Arq1240 15min								
IX	PSR2+ 6min								
	CalRes 2301 6min								
SMC	FluoroSorb400 7.5min								

Breakthrough < 50% Breakthrough > 50%

How to Quantify Performance Between Media?

PFOA adsorbed per media mass
at 50% breakthrough



IX typically
uses 4-5x
more media
than GAC;

Higher IX
adsorption
capacity is
expected

How to Quantify Performance Between Media?

Media	Media Usage Rate (g media / gal water treated)	\$ / gal of water treated
2301, IX (\$8.7 / lb)	0.31	0.006
PSR2+, IX (\$8.7 / lb)	0.57	0.011
Arq, GAC (\$2.5 / lb)	1.23	0.007
F400, GAC (\$2.5 / lb)	1.99	0.011



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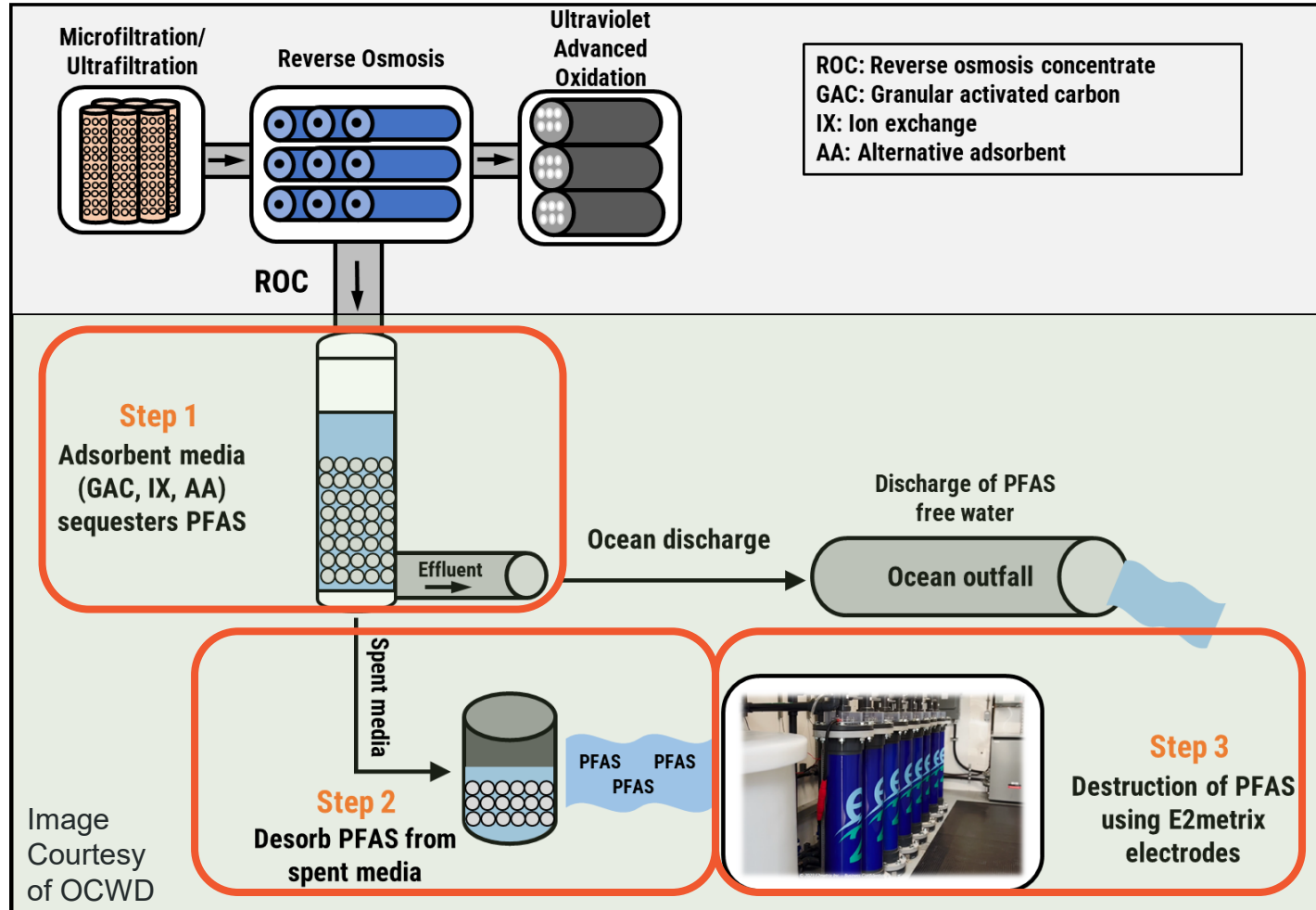
WRF 5323

Adsorption of PFAS in ROC

USBR Project

Separation and Destruction of PFAS in ROC

Novel Approach for ROC Treatment of PFAS



— BUREAU OF —
RECLAMATION



Project Authors

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Ben Salah (E2Metrix)
Charlie Liu (KJ)

Phased Testing

Phase 1: Small 2-inch column pilot

- **Phase 1.1:** Baseline testing of 6 IX supplied by Ovivo/E2METRIX; 2 min EBCT
- **Phase 1.2:** Testing of additional resins + regeneration
- **Phase 1.3:** Destruction of regenerant brine using Obreak® Electro-Oxidation

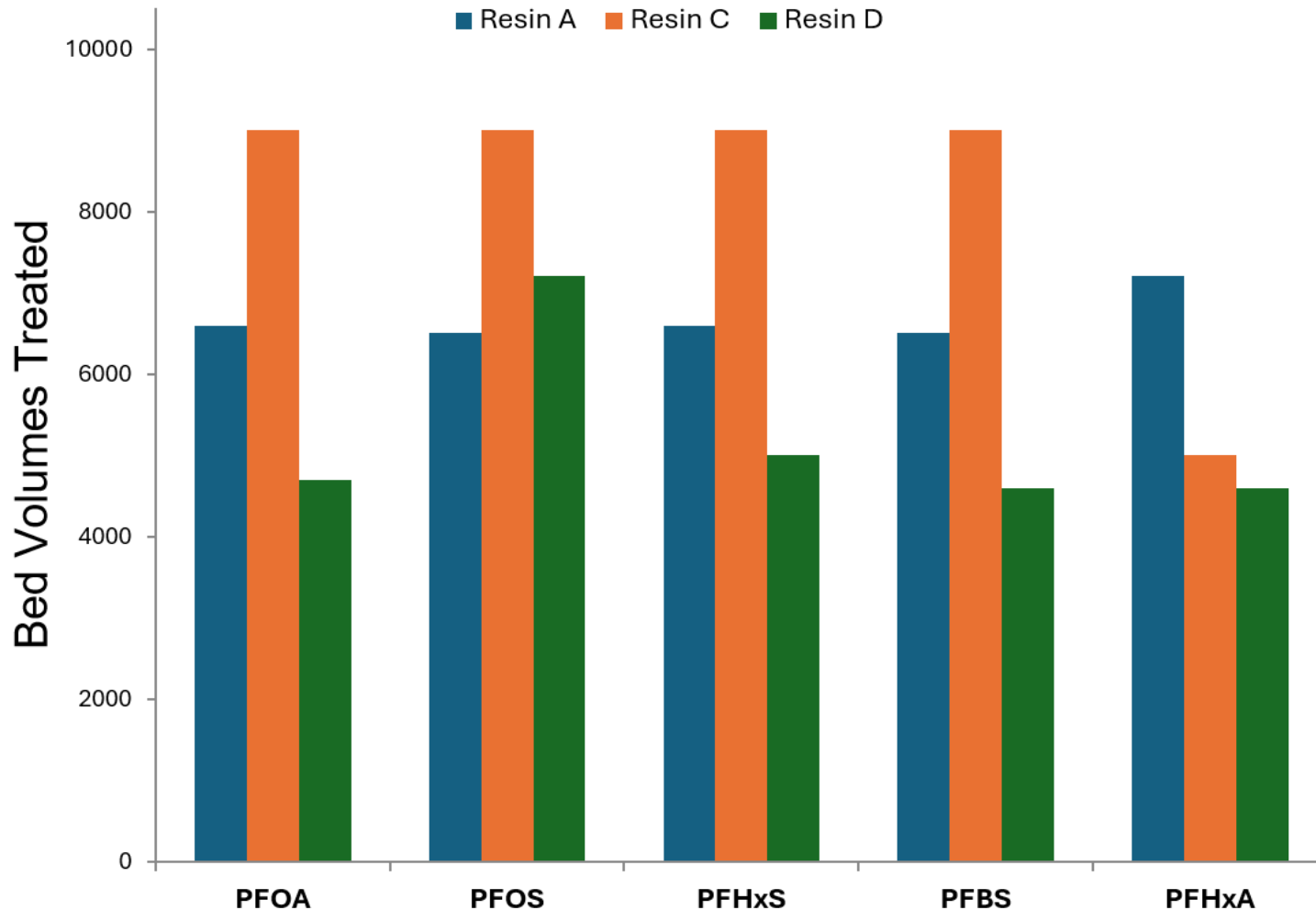


Phase 1.1 – Testing Conditions

	Resin	Resin Type	Configuration	EBCT	HLR	Regen
Column 1	Resin A	Single Use	Single Pass	2.0 min	7.3 gpm/sqft	Alcohol
Column 2	Resin B	Regenerable	Single Pass	2.0 min	7.6 gpm/sqft	Caustic/ Acid
Column 3	Resin C	Regenerable	Single Pass	2.0 min	7.6 gpm/sqft	Caustic/ Acid
Column 4	Resin D	Regenerable	Single Pass	2.0 min	7.6 gpm/sqft	Caustic/ Acid
Column 5	Resin E	Regenerable	Single Pass	2.0 min	6.3 gpm/sqft	Caustic/ Acid
Column 6	Resin F	Regenerable	Single Pass	2.0 min	8.1 gpm/sqft	Caustic/ Acid

Rapid Breakthrough of PFAS by IX

Bed volumes treated to 100% exhaustion

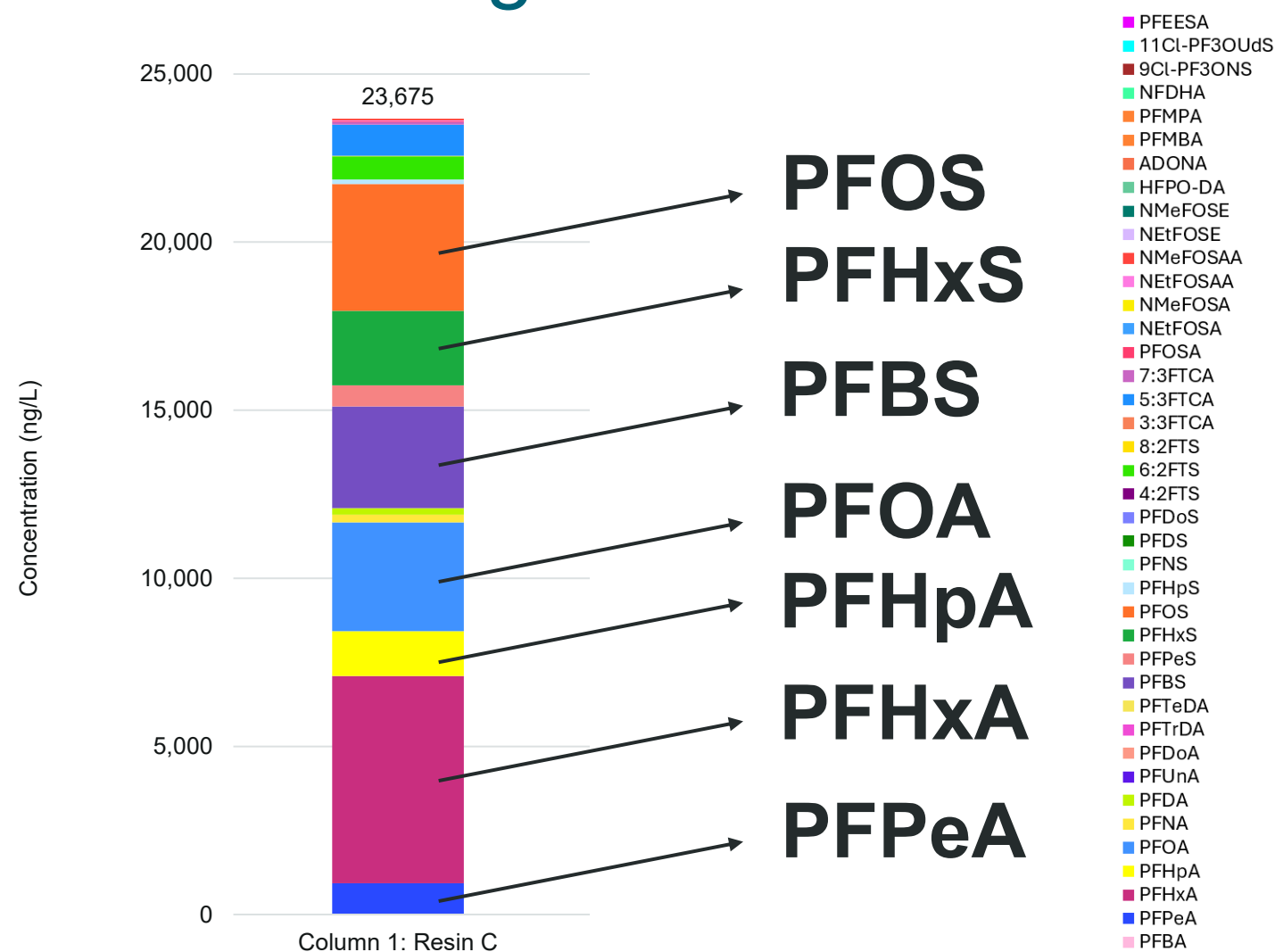


- Six 6 resins were tested at 2 min EBCT
- Rapid breakthrough of long/short chain PFAS
- Resin C > Resin A > Resin D

Phase 1.2 – Testing Conditions

	Resin	Resin Type	Configuration	EBCT	HLR	Regen
Column 1	Resin C	Regenerable	Single Pass	3.0 min	4.5 gpm/sqft	Caustic/ Acid - V1
Column 2	Resin C	Regenerable	Single Pass	3.0 min	4.5 gpm/sqft	Caustic/ Acid - V2
Column 3	Resin C	Regenerable	LEAD	2.0 min	6.7 gpm/sqft	Caustic/ Acid - V3
Column 4	Resin F	Single Use	LAG	2.6 min	6.9 gpm/sqft	NA
Column 5	Resin G	Single Use	Single Pass	3.0 min	4.5 gpm/sqft	Brine
Column 6	Resin C	Regenerable	Single Pass	3.0 min	4.5 gpm/sqft	Caustic/ Acid - V4

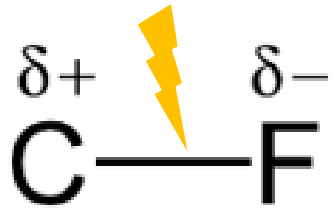
IX Resin Regeneration



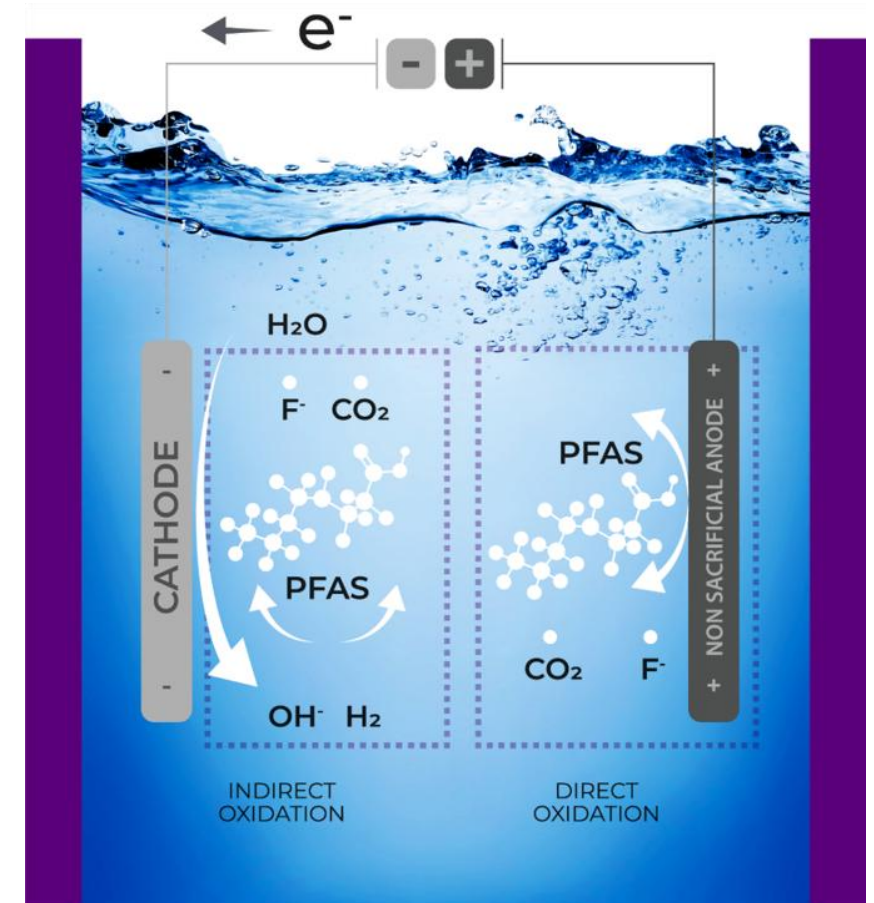
27 PFAS
detected
with PFAS
Method 1633

How Electro-Oxidation Destroys PFAS

- Pass an electrical current through the electrodes submerged in water (anode and cathode)
- **Direct oxidation** happens at the **surface of the anode** that cleaves the C-F bond

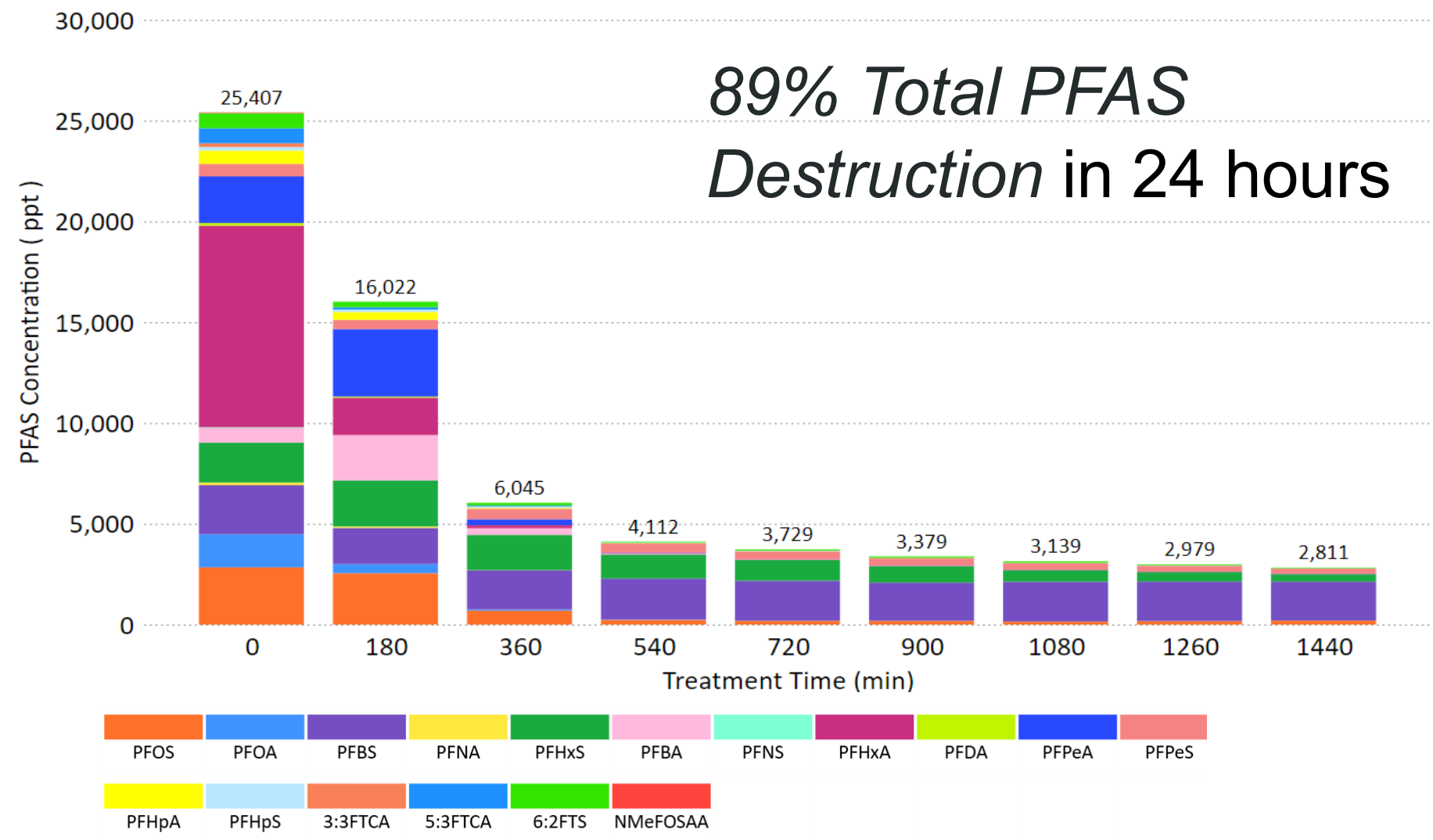


- Cannot handle solids in feed water
- Requires high salt content

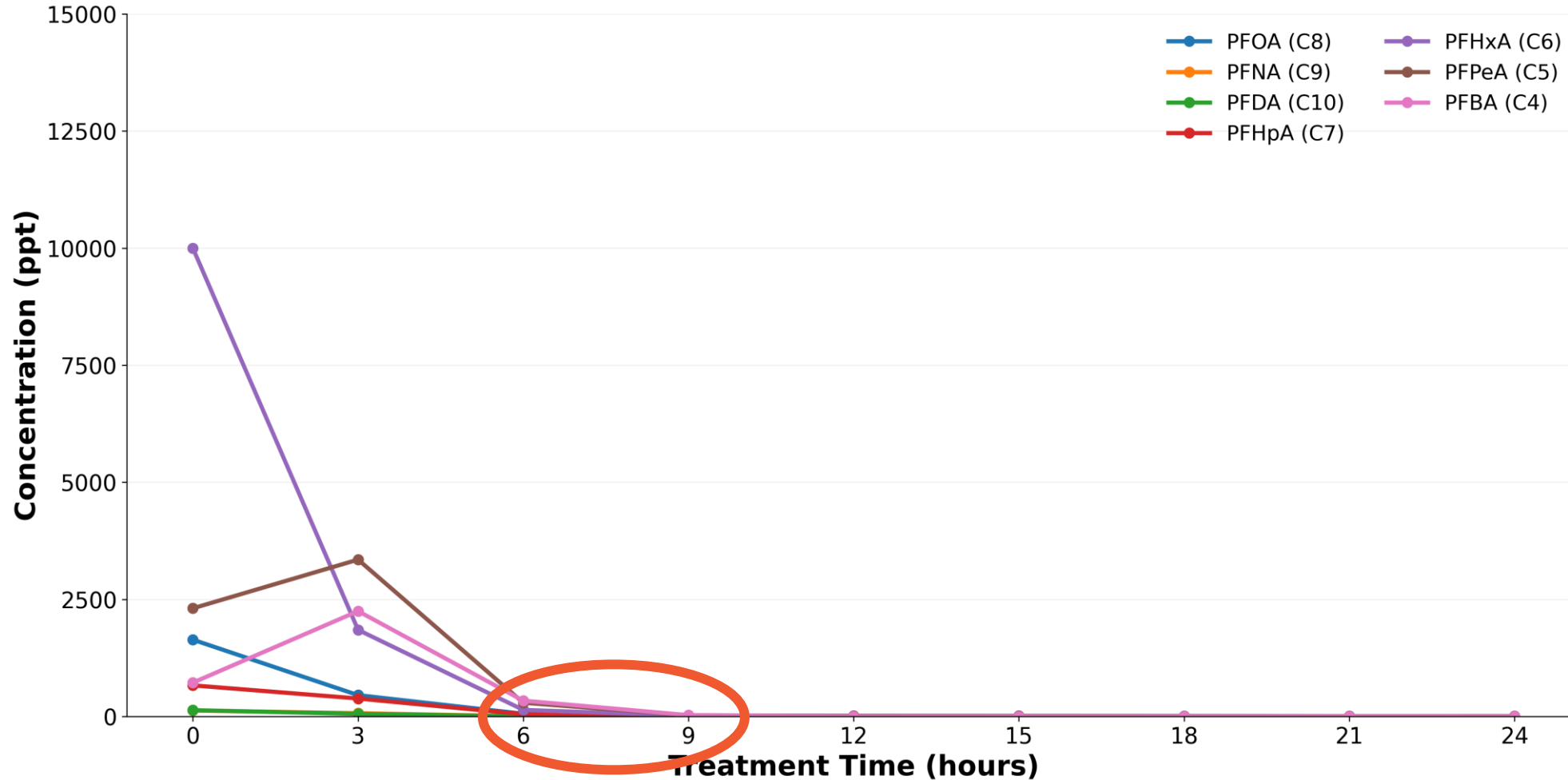


Electro-Oxidation

EO PFAS Destruction



EO PFAS Destruction – Carboxylic Acids



- Long chain PFCAs easily degraded
- Near complete (99.87%) PFCA destruction
- PFCAs degraded in ~6-9 hours

EO PFAS Destruction – Sulfonic Acids



- PFSA's more recalcitrant than PFCAs
- Long chain PFSA's degraded in 6-9 hours
- Short chain PFSA's especially recalcitrant

Phase 2 – Trailer Pilot Testing, Almost Finished!



IX Pilot Unit



EO Pilot Unit

Conclusions

IX and SMC outperformed GAC
under the tested ROC conditions

PFAS adsorption was achievable
despite the challenging water quality
of RO concentrate.

Media life remains the primary
operational challenge, with
breakthrough occurring much faster
than groundwater applications

PFSAs were more difficult to destroy
than **PFC**A's during electro-oxidation
testing

- **Successful separation and destruction of PFAS in ROC is possible**
- **Improving media life and evaluating concentration technologies is critical**

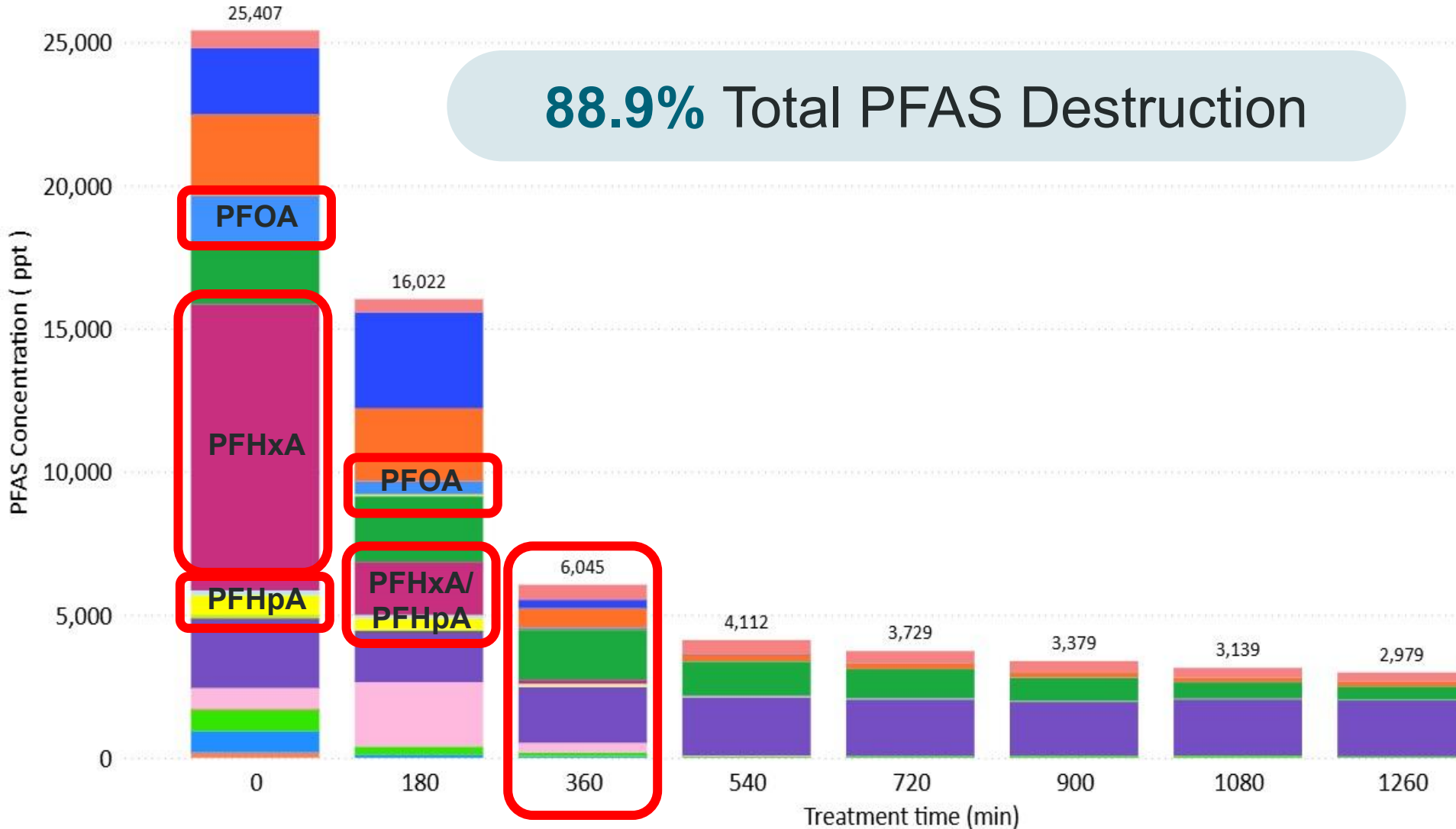
Q&A



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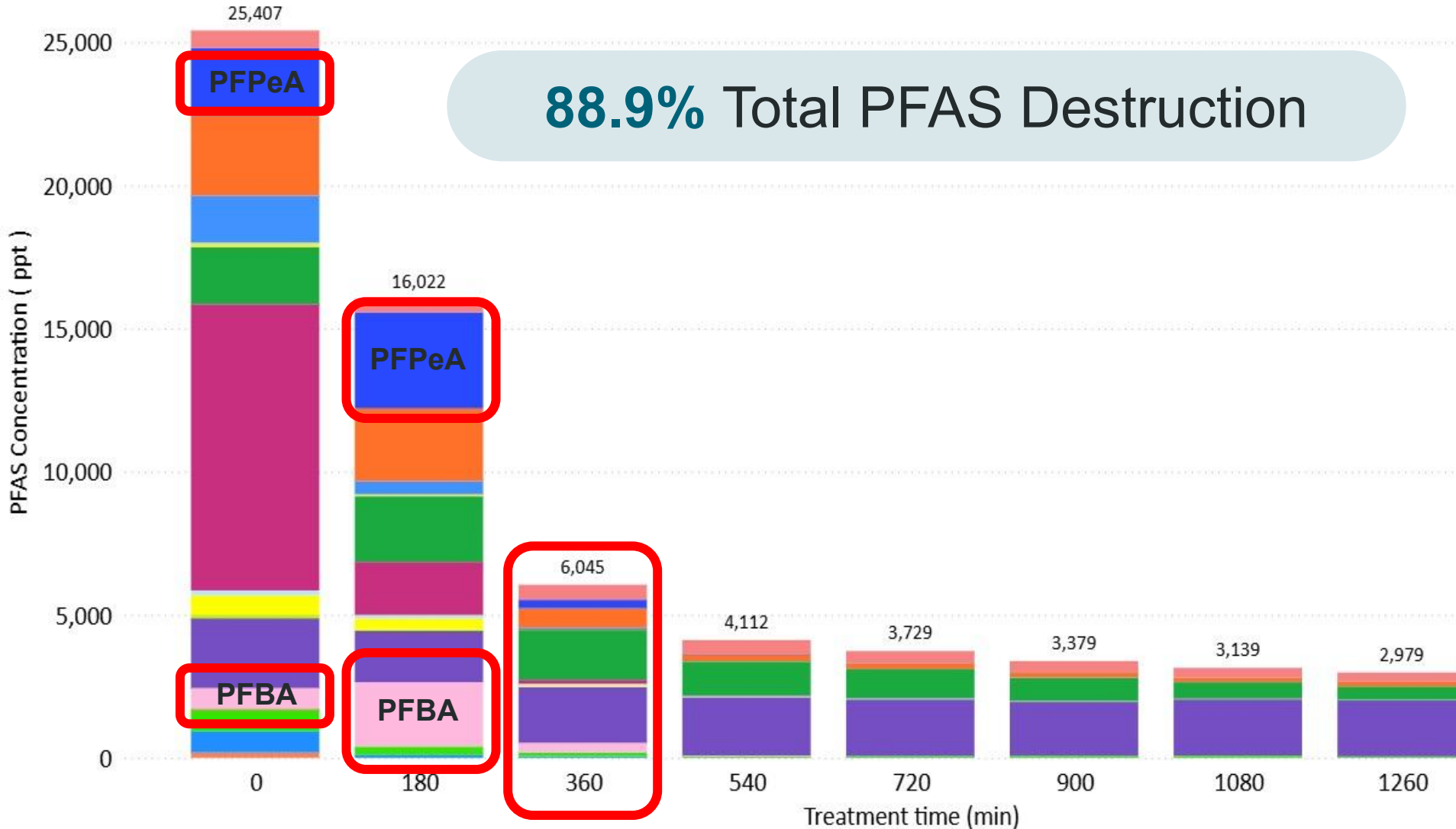


PFAS Destruction by EO – PFCAs



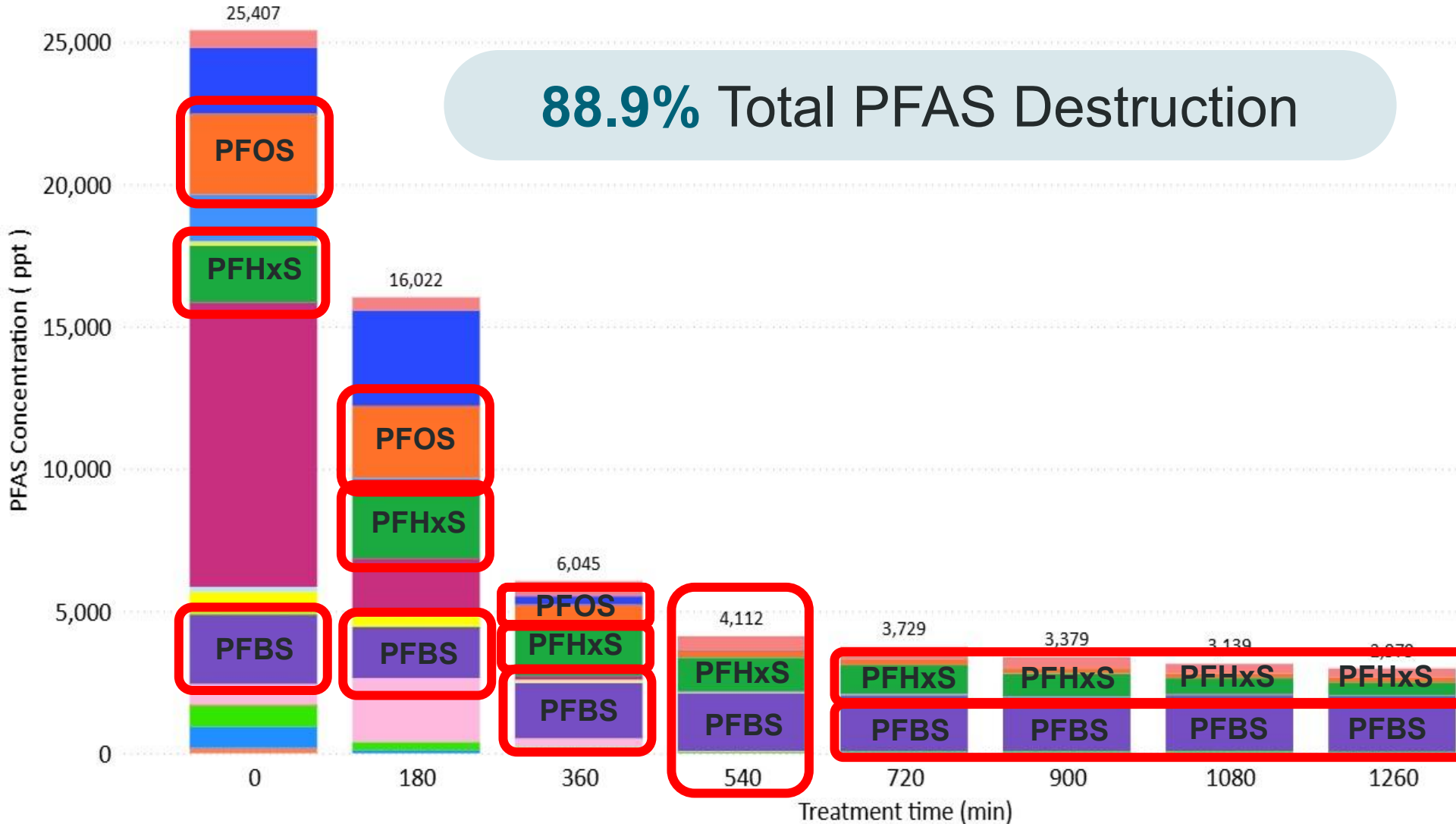
- Long chain PFCAs more easily degraded
- PFCAs degraded in ~6 hours

PFAS Destruction by EO – PFCAs



- Short chains generated as long chains are degraded
- PFCAs degraded in ~6 hours

PFAS Destruction by EO – PFSA



- PFSA more recalcitrant
- PFOS degraded in 9 hours
- PFHxS and PFBS difficult to degrade, even after 21 hours

Project Takeaways

- Destruction of PFAS is possible in ROC
- Consider treatment goals – not feasible to target ***all*** PFAS (e.g., short chain PFASs)
- In order of difficulty to degrade
 - PFCAs < PFSA
 - Long Chain < Short Chain
- Stay tuned for trailer pilot results! Trailer has arrived



Initial Testing and Testing Phases

Phase 1: Preliminary evaluation

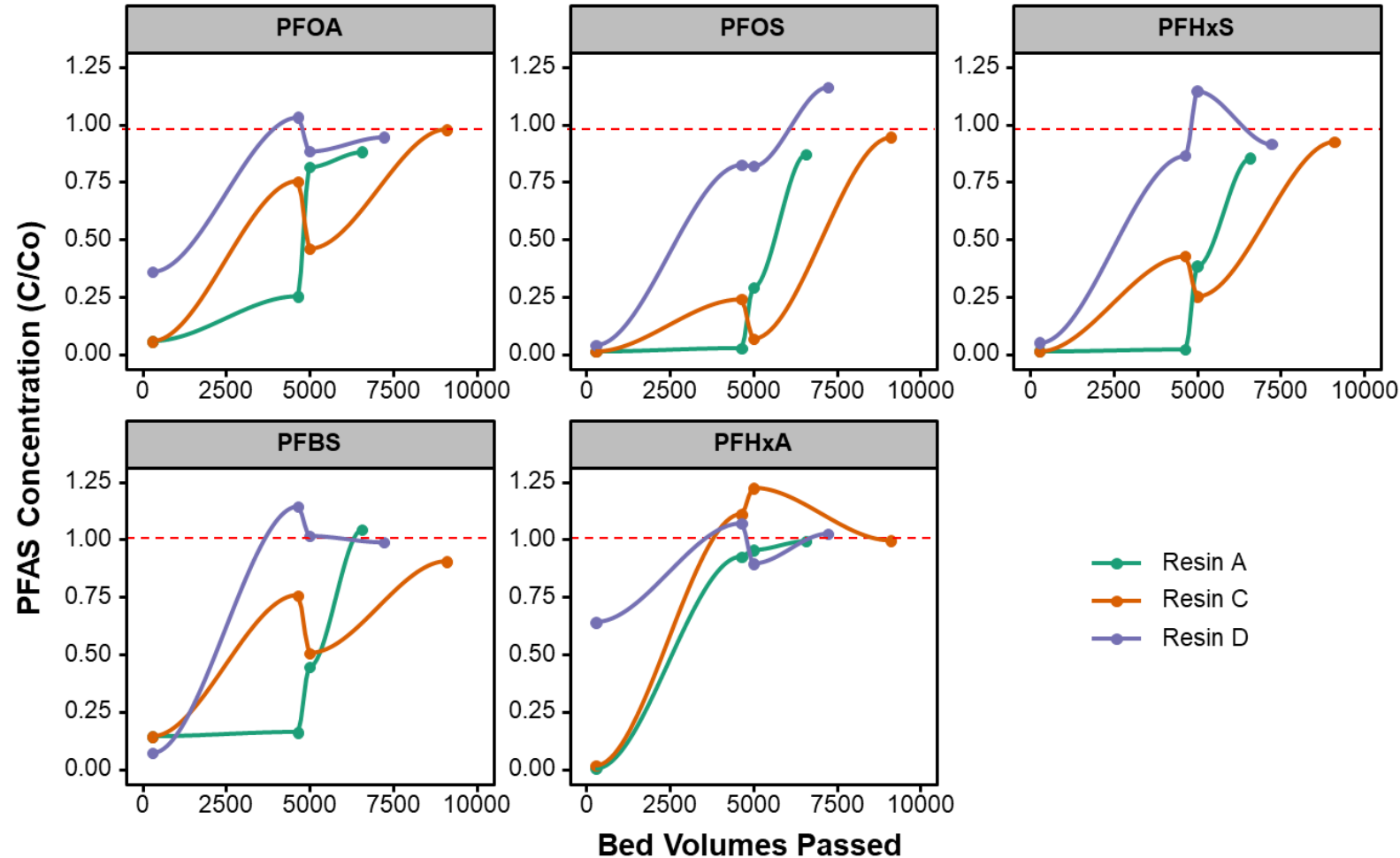
Phase 2: Large-scale trailer pilot!



Phase 1.1 Testing Conditions

	Resin	Resin Type	Configuration	EBCT	HLR	Regen
Column 1	Resin A	Single Use	Single Pass	2.0 min	7.3 gpm/sqft	Alcohol
Column 2	Resin B	Regenerable	Single Pass	2.0 min	7.6 gpm/sqft	Caustic
Column 3	Resin C	Regenerable	Single Pass	2.0 min	7.6 gpm/sqft	Caustic
Column 4	Resin D	Regenerable	Single Pass	2.0 min	7.6 gpm/sqft	Caustic
Column 5	Resin E	Regenerable	Single Pass	2.0 min	6.3 gpm/sqft	Caustic
Column 6	Resin F	Regenerable	Single Pass	2.0 min	8.1 gpm/sqft	Caustic

Phase 1.1 PFAS Breakthrough | Top 3 IX resins

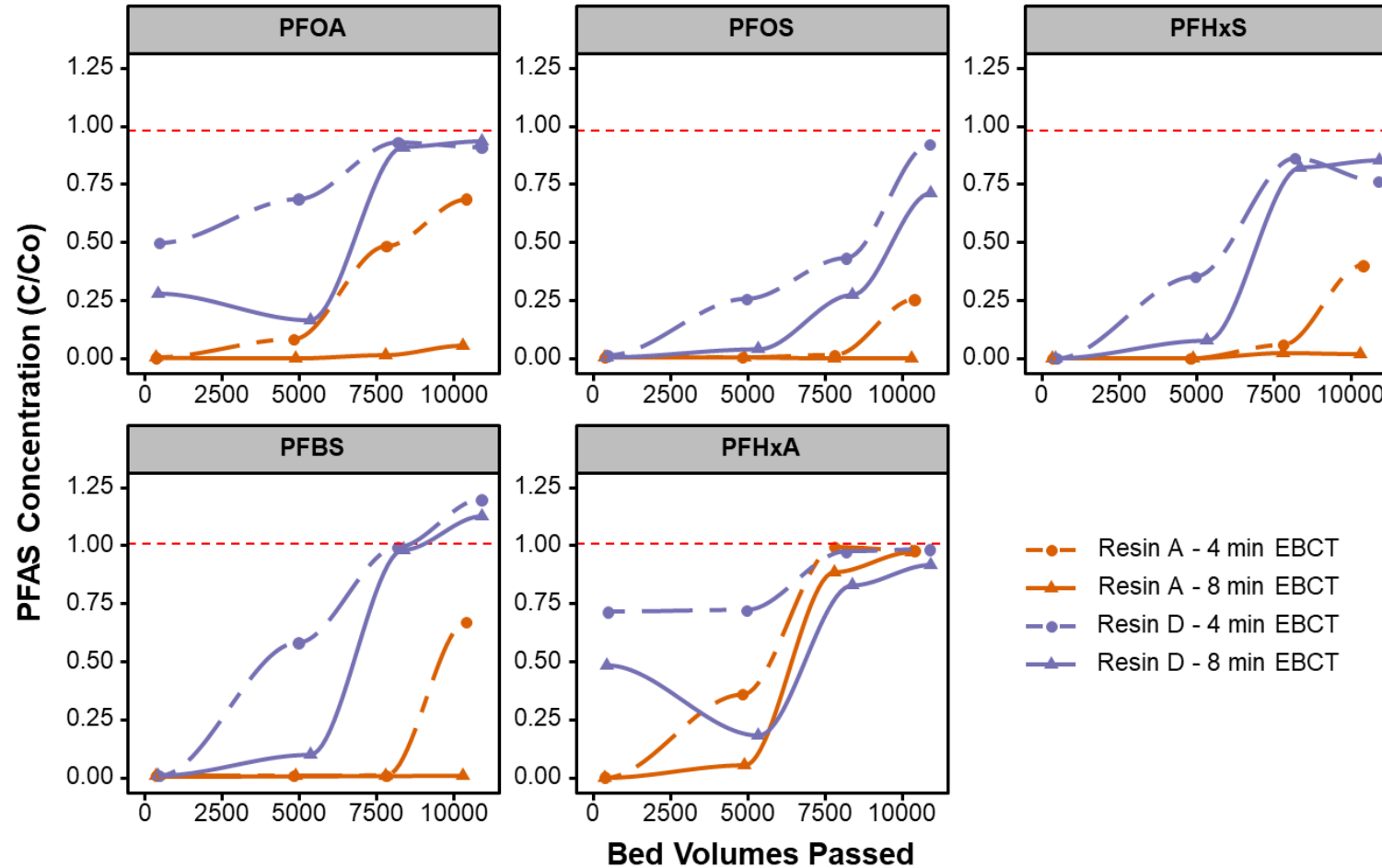


- 6 IX were tested at 2 min Empty Bed Contact time (EBCT)
- Rapid breakthrough of long/short chain PFAS
- Resin A, C, D performed well and further tested in Phase 2

Phase 1.2 Testing Conditions

	Resin	Resin Type	Configuration	EBCT	HLR	Regen
Column 1	Resin C	Regenerable	LEAD	4.0 min	4.5 gpm/sqft	Caustic
Column 2	Resin C		LAG	8.0 min	4.5 gpm/sqft	Caustic
Column 3	Resin A	Single Use	LEAD	4.0 min	4.5 gpm/sqft	NA
Column 4	Resin A		LAG	8.0 min	4.5 gpm/sqft	NA
Column 5	Resin D	Regenerable	LEAD	4.0 min	4.5 gpm/sqft	Caustic
Column 6	Resin D		LAG	8.0 min	4.5 gpm/sqft	Caustic

Phase 1.2 PFAS Breakthrough-Preliminary Data



- Resin C clogged; no data generated
- Greater removal at longer EBCT for both resins A and D

Phase 1.3 Testing Conditions

	Resin	Resin Type	Configuration	EBCT	HLR	Regen
Column 1	Resin C	Regenerable	Single Pass	3.0 min	4.5 gpm/sqft	Caustic 1
Column 2	Resin C	Regenerable	Single Pass	3.0 min	4.5 gpm/sqft	Caustic 2
Column 3	Resin C	Regenerable	LEAD	2.0 min	6.7 gpm/sqft	Caustic 3
Column 4	Resin F	Single Use	LAG	2.6 min	6.9 gpm/sqft	NA
Column 5	Resin G	Single Use	Single Pass	3.0 min	4.5 gpm/sqft	Brine
Column 6	Resin C	Regenerable	Single Pass	3.0 min	4.5 gpm/sqft	Caustic 4

Analyte	Concentration
PFOA	54 ng/L
PFOS	80 ng/L
PFBS	42 ng/L
PFHxA	159 ng/L
PFHxS	33 ng/L
PFHpA	50 ng/L
TDS	6485 mg/L
TOC	24 mg/L
Sulfate	1213 mg/L
Orthophosphate	118 mg/L
Chloride	1800 mg/L

PFAS Treatment Technologies – Separation

Granular
Activated Carbon
(GAC)



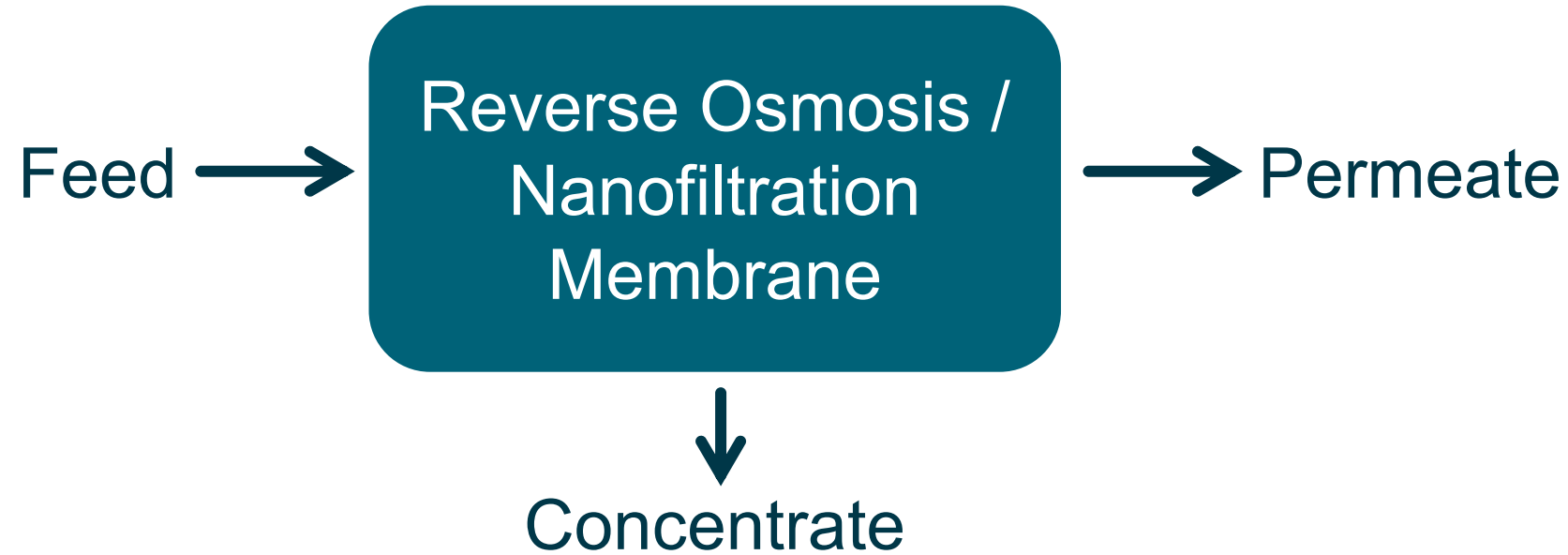
Anion Exchange
Resins (IX)



Surface Modified
Clay (SMC)



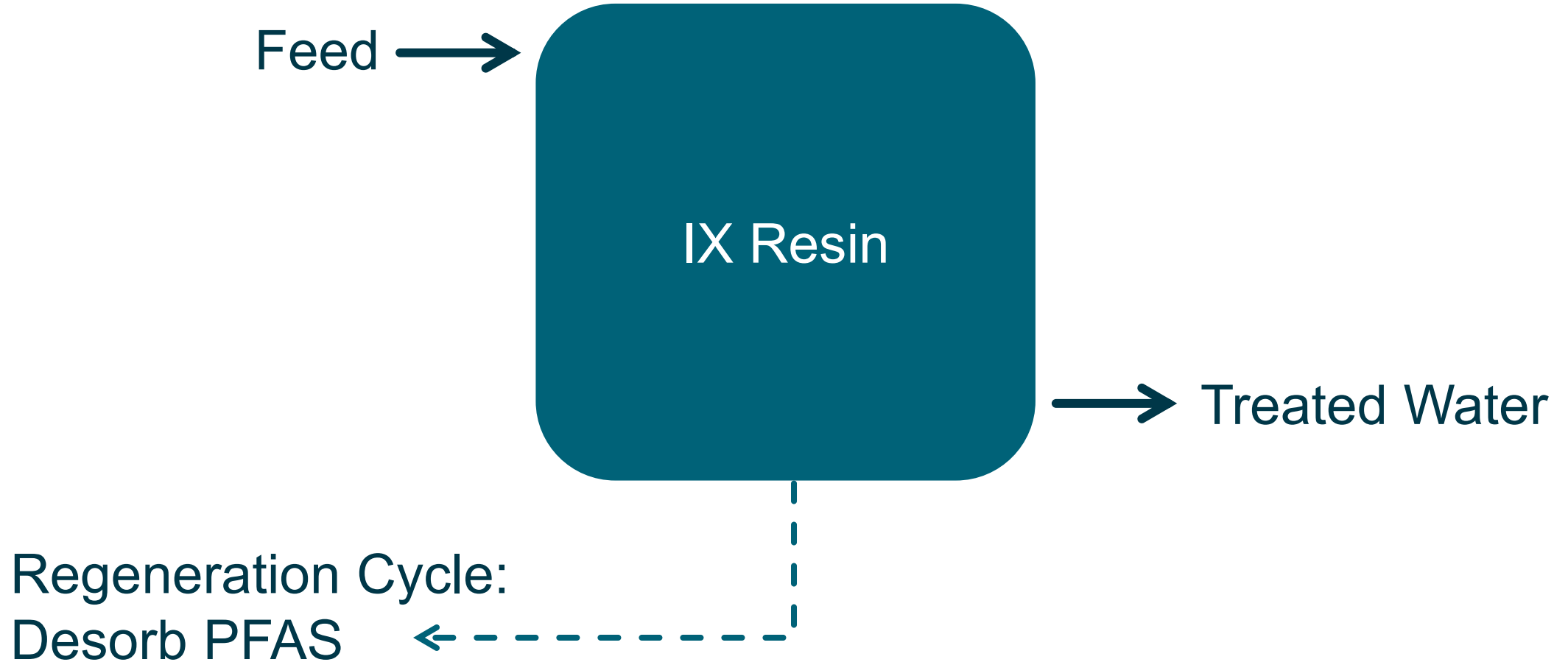
High Pressure Membranes



- 80-90% recovery, depending on RO configuration



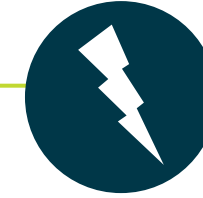
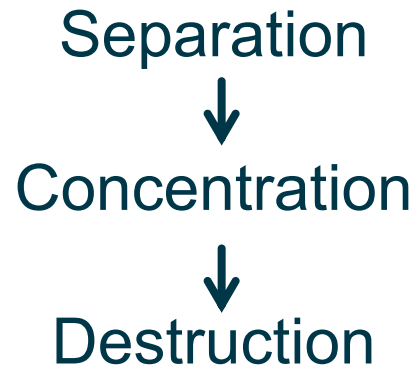
Ion Exchange (IX) Resins



General Destruction Trends



- Not a replacement for separation technologies (e.g., GAC, IX, RO)



- PFSA's (e.g., PFOS) are more recalcitrant than PFCAs (e.g., PFOA)
- Short chains are more recalcitrant than long chains

Emerging PFAS Destruction Technologies

Oxidation and Reduction

Reductive Defluorination

Electrochemical Oxidation

High Temperature High Pressure

Supercritical Water
Oxidation (SCWO)

Hydrothermal Alkaline
Treatment (HALT)

Emerging PFAS Destruction Technologies

Oxidation and Reduction

Reductive Defluorination

Electrochemical Oxidation

High Temperature High Pressure

Supercritical Water
Oxidation (SCWO)

Hydrothermal Alkaline
Treatment (HALT)

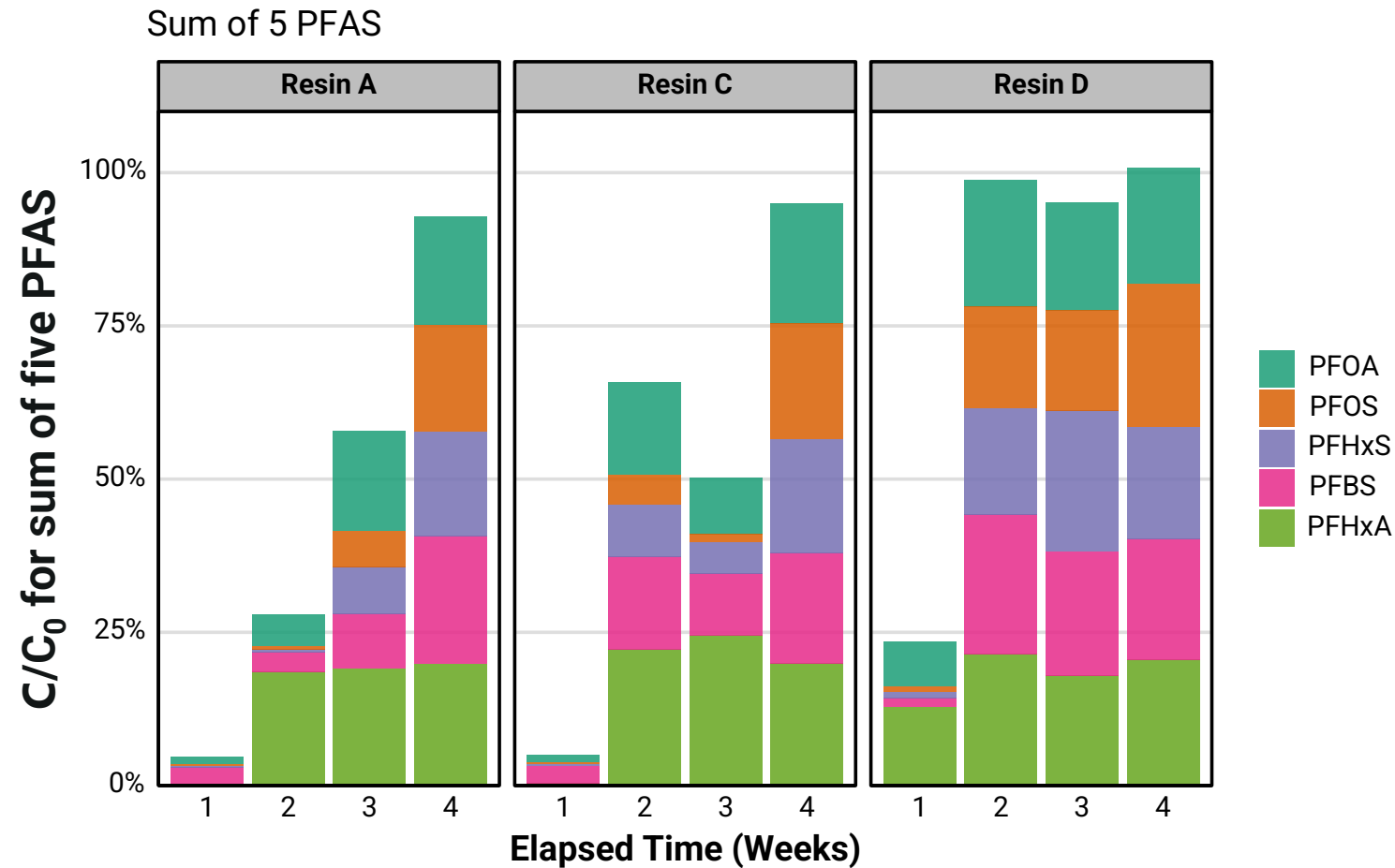
Ambient Conditions for Oxidation and Reduction

Treatment Conditions for PFAS Destruction by Reduction / Oxidation

Technology	Reduction / Oxidation
Temperature / Pressure	Ambient
Residence Time	Hours
Chemical Requirements	• Reduction: alkaline pH adjustment to 11-13; Chemical sensitizer (e.g., sulfite) • Oxidation: potentially salts
Reactor Requirements	• UV 254 lamps and UV reactor • Specialty electrodes; cathodes and anodes
Water Quality Impacts	• Reduction: nitrate, nitrite, DOC, CO_3^{-2}, HCO_3^- • Oxidation: solids

Phase 1 PFAS Breakthrough-Sum of 5 PFAS

- Breakthrough data showing increase in load of total PFAS on the IX resins over time.
- Resin A was best performing.



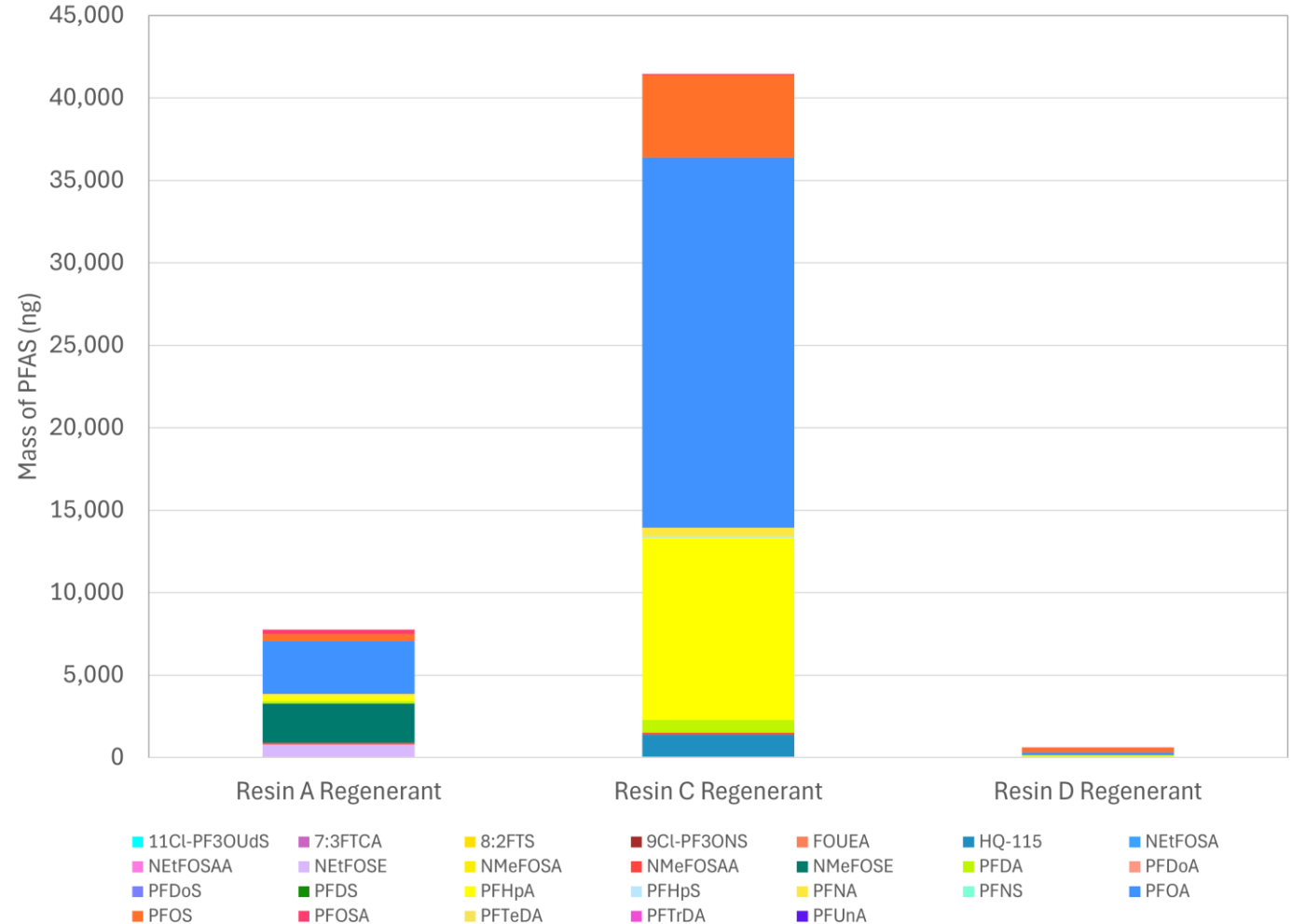
Phase 1 IX Resins Regenerant Tests

- Regeneration solution
 - Resin A - Alcohol based
 - Resin C - Caustic based
 - Resin D - Caustic based



Preliminary Data Mass of Long-Chain PFAS in Regenerant Solution

Resin C recovered the
greatest mass of long-
chain PFAS

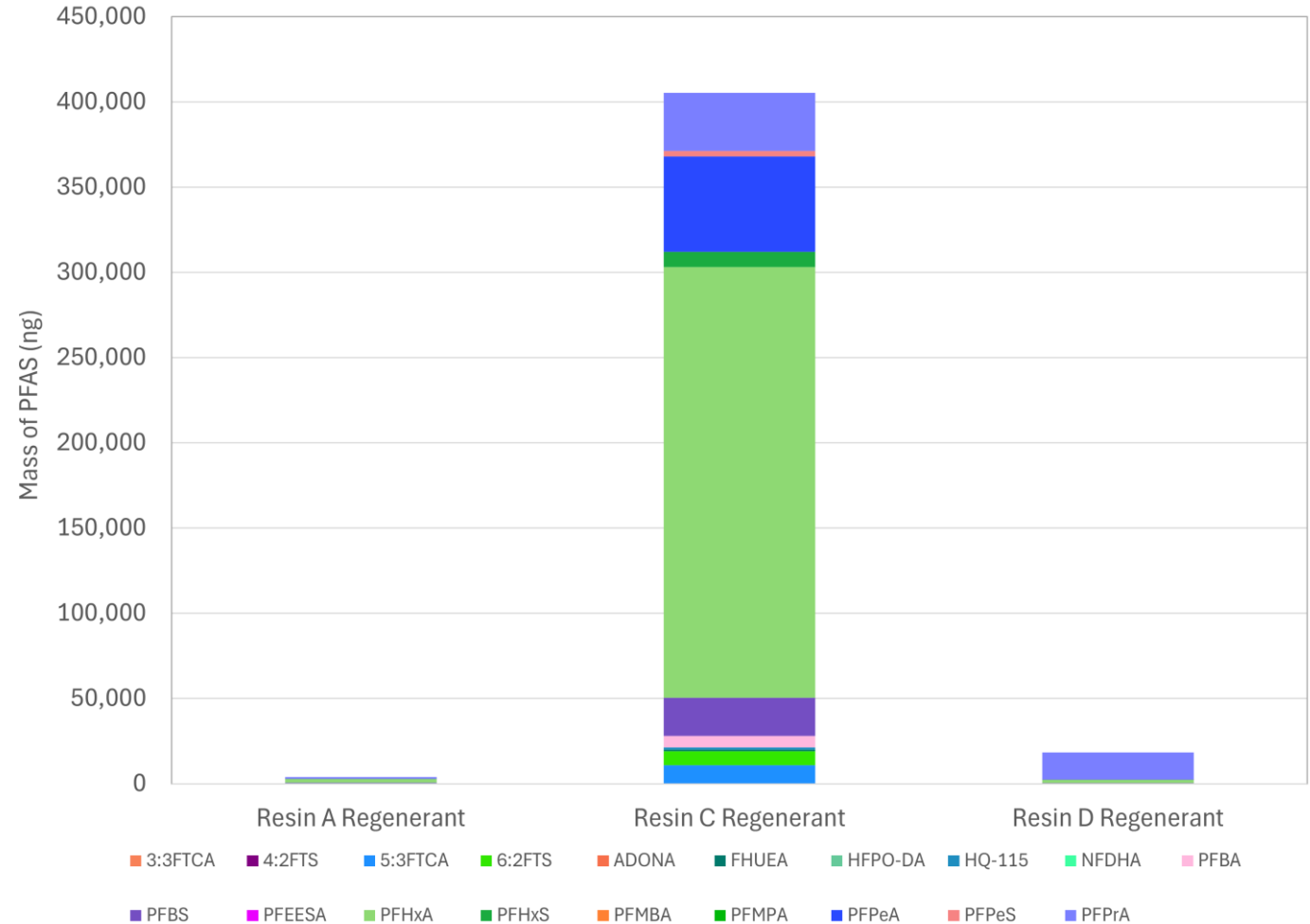


Preliminary Data

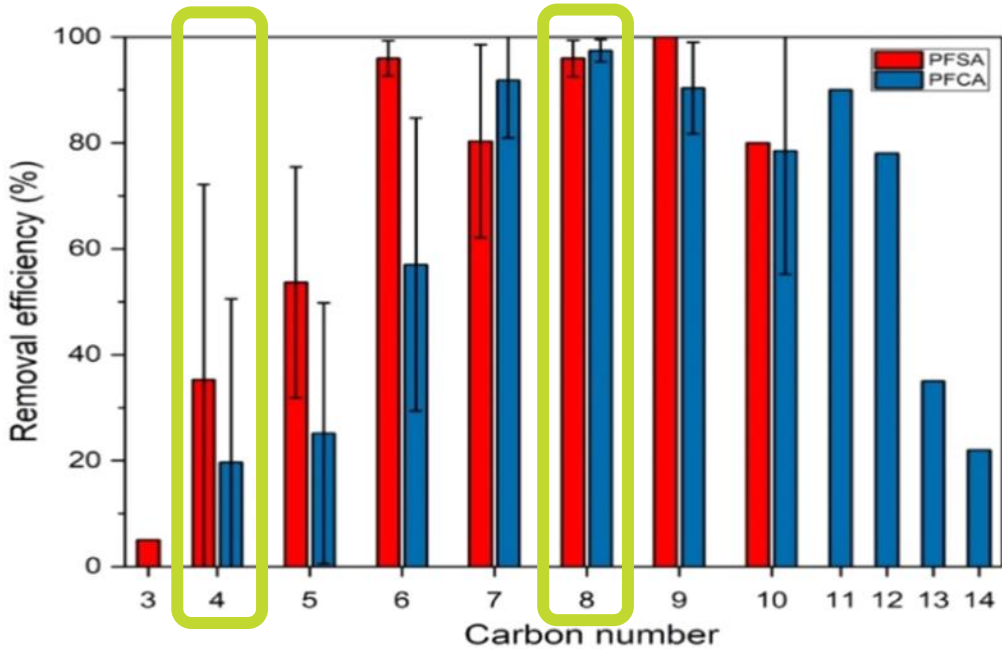
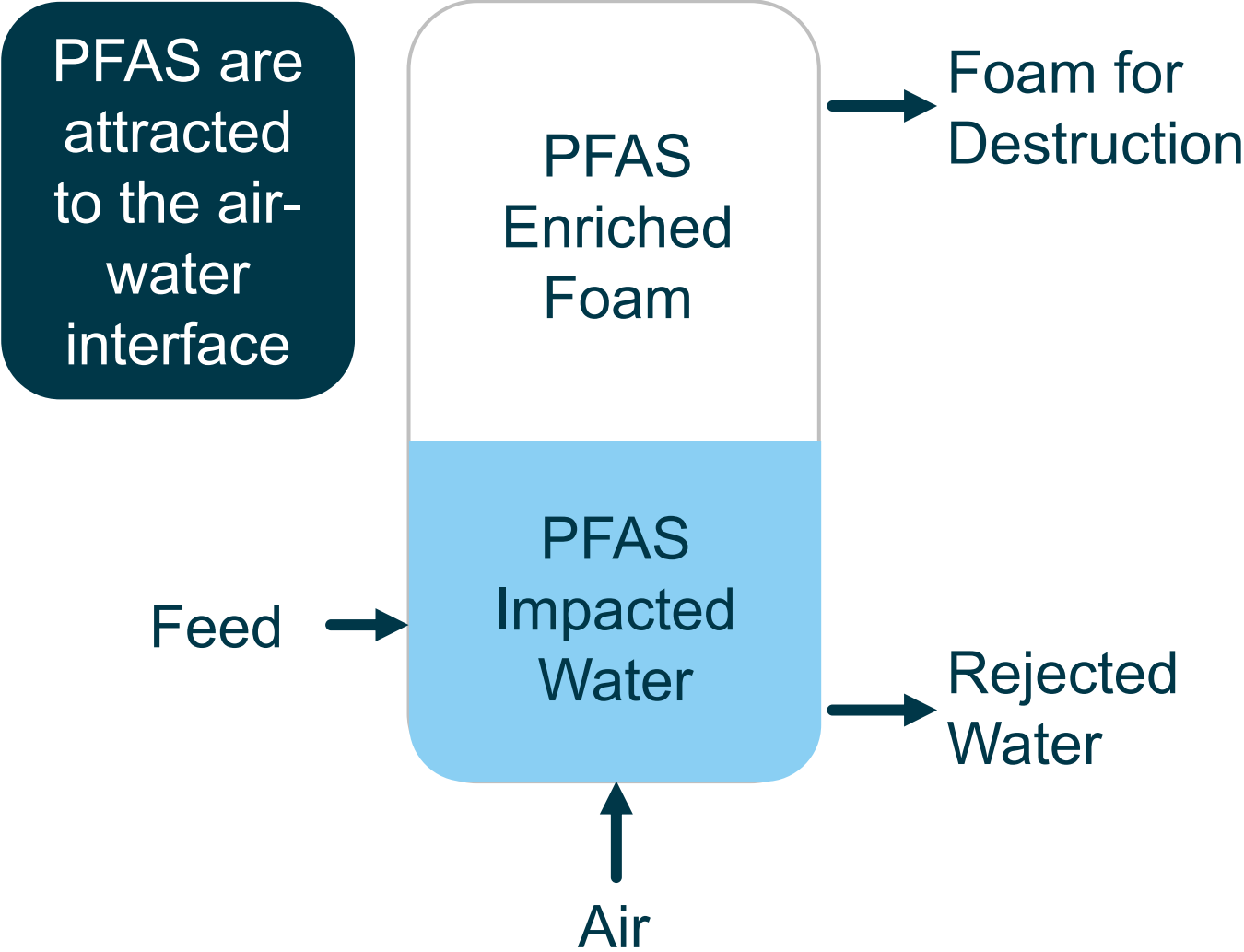
Mass of Short-Chain PFAS in Regenerant Solution

Resin C recovered the greatest mass of short-chain PFAS.

Plan to try Resin A regeneration with alcohol using a longer contact time.



Foam Fractionation



We et al. 2024

Increasing removal efficiencies with increasing chain length

Evaluate Adsorption by GAC, IX, FS200, with and without Pretreatment



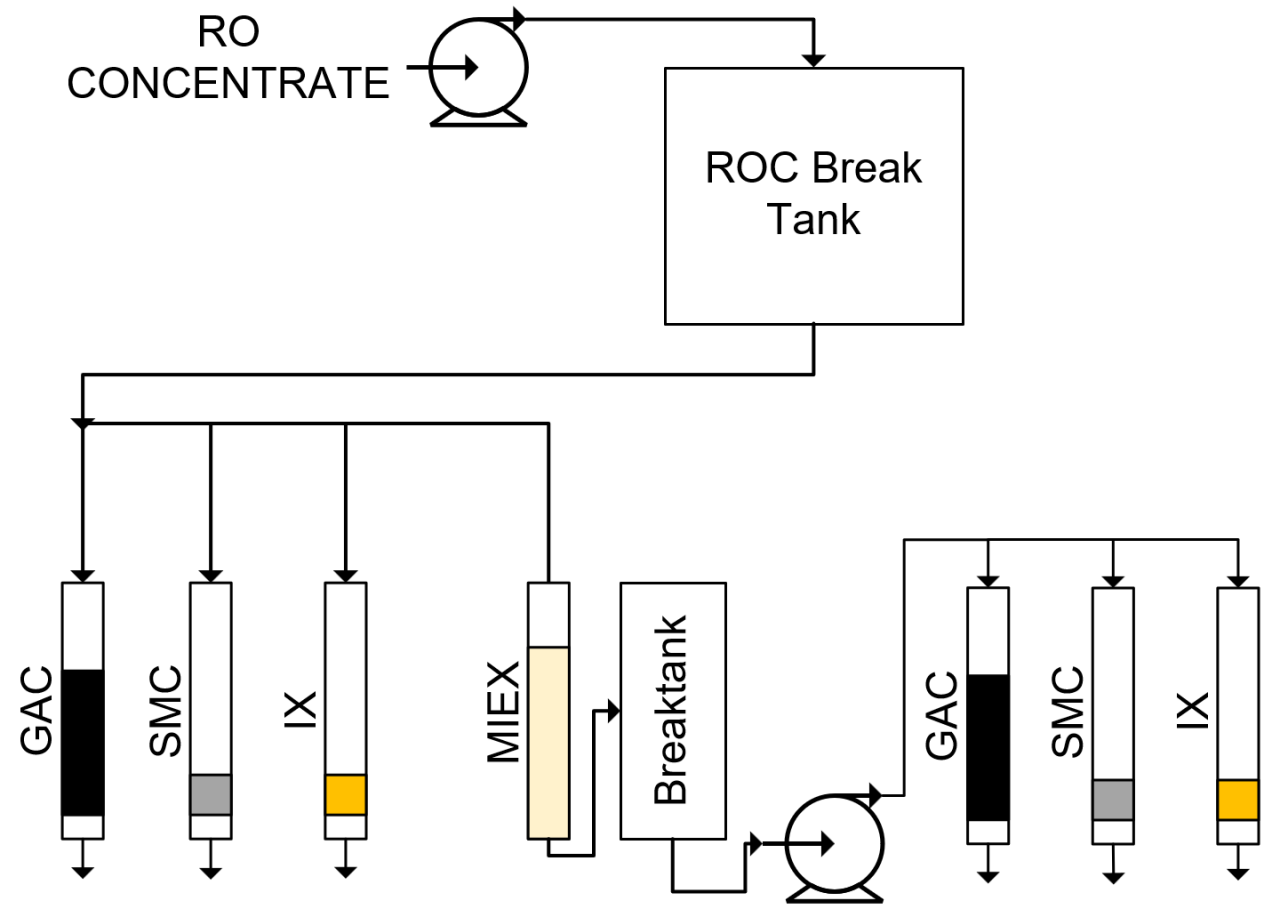
Anion Exchange Resins (IX)



Granular Activated Carbon (GAC)



Surface Modified Clay (SMC)



High Temperature, High Pressure

Treatment Conditions for PFAS Destruction by High Temperature/Pressure

Technology	SCWO / HALT
Temperature (°C)	500°C - 650°C / 250°C - 350°C
Pressure (PSI)	~3500 PSI
Residence Time	10s - 60s
Chemical Requirements	• Addition of oxidant / fuel (e.g., air, H₂O₂) • Addition of pH adjustment chemicals (e.g., NaOH)
Reactor Requirements	• Withstand high temperature/high pressure • Corrosion; salt precipitation

Round 3. Tested a new resin G with a novel brine.

This study looked at new resins, regenerable and single use. G is a single use?

Regenerant: Columns 1, 2, 3, and 6 was with caustic. Column 5 was resin G, single use, that was regen with a brine solution. Very poor regen, as expected. What is regen vs rinse?

Nice graph that shows an average regeneration solution

not enough water for destruction in round 2.

Round 3 – destruction of PFAS.

TOC was oxidized.

Combined the regenerant solution and did destruction testing with BDD. This is one coating

Tested another round with a new electrode. 88.9%. BDD, but with a different coating

Resin C clogged before, but in the new pilot didn't have anymore problems with Resin C with a new screen.

MAKE SURE TO HAVE A TAKEHOME MESSAGE

