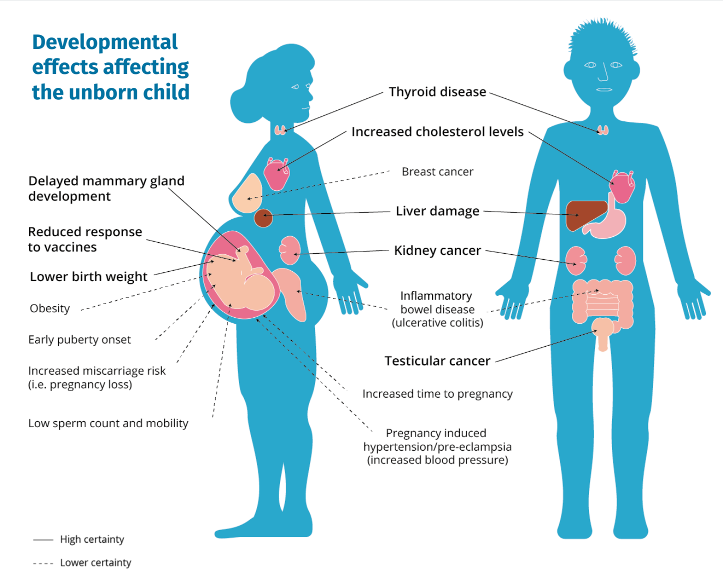
Destroying PFAS: Is Electrochemical Oxidation the Answer?

Anilkumar Krosuri, Ph.D., R & D Engineer

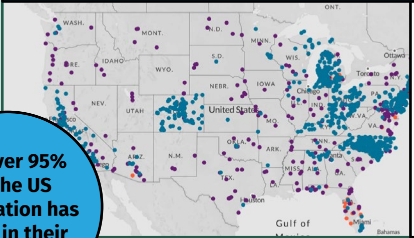
anil.krosuri@aclaritywater.com

PFAS is everywhere, and will be with us a for a long time

Harmful



Widespread



"… over 95% of the US population has PFAS in their bodies."

"Forever Chemicals"

Strong C-F bonds take centuries to break down in nature	Accumulate in the body with half-life of years

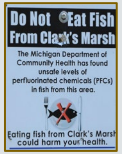
Aclarity

#WeDestroyPFASForever

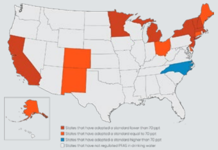
Market is looking for a PFAS destruction solution

Bottom-up public pressure → **Action today at all levels** → **Dwindling disposal options**

Local



State



Federal

- → EPA PFAS Action Act 2022
- → Infrastructure Law: $10B for monitoring and remediation

Industry

- → $1B in RFPs already outstanding
- → 40% CAGR

Corporate

DuPont, Chemours, Corteva to pay Delaware millions over damage from PFAS or 'forever chemicals'

Jeff Neiburg Delaware News Journal

Published 4:32 p.m. ET July 13, 2021 | Updated 7:02 p.m. ET July 13, 2021

Landfill
Raising fees, refusing loads

Wastewater Treatment Plant
Raising fees, refusing loads

Incinerator
Expensive, risk of being disallowed

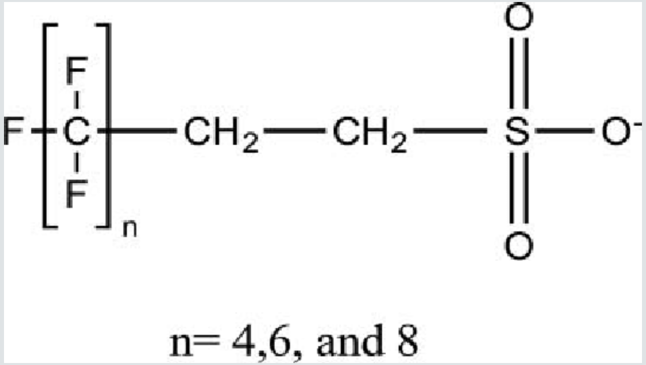
Other destruction technologies
Still in the lab or not economic

PFAS Chemistry

PFAS- Per and Polyfluoroalkyl substances.

Per -fluoroalkyl substances: fully fluorinated tail.

Poly-fluoroalkyl substances: non-fluorine atom attached to one or more carbon.



Perfluoroalkyl sulfonates (or sulfonic acids): **PFSAs**

Tail | Head

Perfluorooctanesulfonic Acid (PFOS)

Perfluoroalkyl carboxylates (or carboxylic acids): **PFCAs**

Tail | Head

Perfluorooctanoic Acid (PFOA)

→ **PFAAs** ←

Fluorotelomer sulfonic acids: **FTSs** → **Precursors**

Chain Length: Long Chain & Short Chain

- **Long chain:**
  - PFCAs with 8 or more carbons
  - PFSAs with six or more carbons
- **Short chain:**
  - PFCAs with seven or fewer carbons
  - PFSAs with five carbons or less

Number of Carbons	4	5	6	7	8	9	10	11	12
PFCAs	Short-chain PFCAs				Long-chain PFCAs				
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
PFSAs	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFUnS	PFDoS
	Short-chain PFSAs		Long-chain PFSAs						

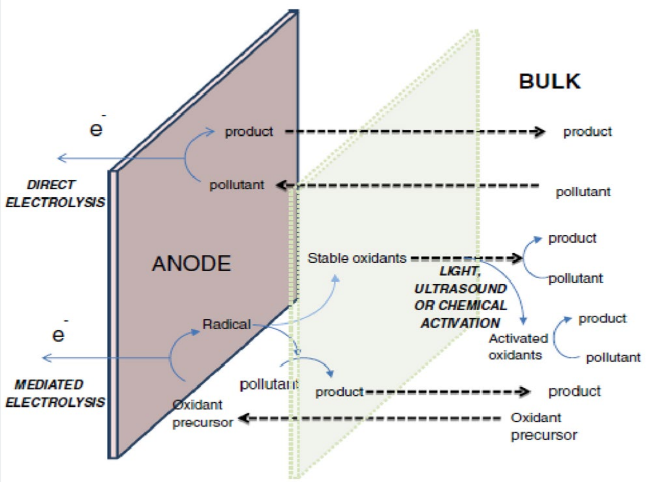
*ITRC, 2019

Electrochemical Oxidation of PFAS

Free electrons **break C-F bonds** resulting in CO_2, HF, F^-

Treats broad range of difficult contaminants at lower cost than current technologies

Simple and rugged enough to deploy on-site

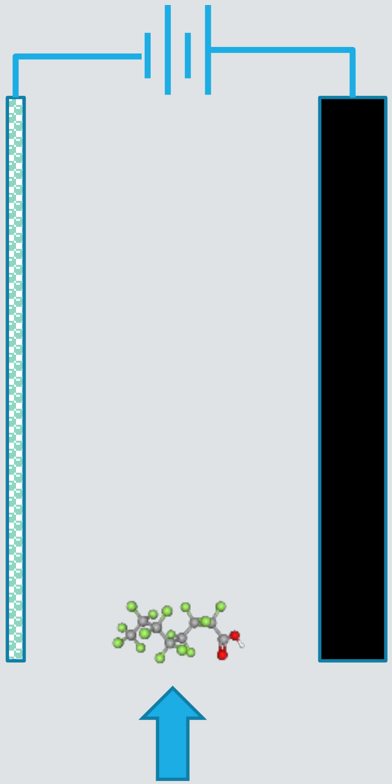


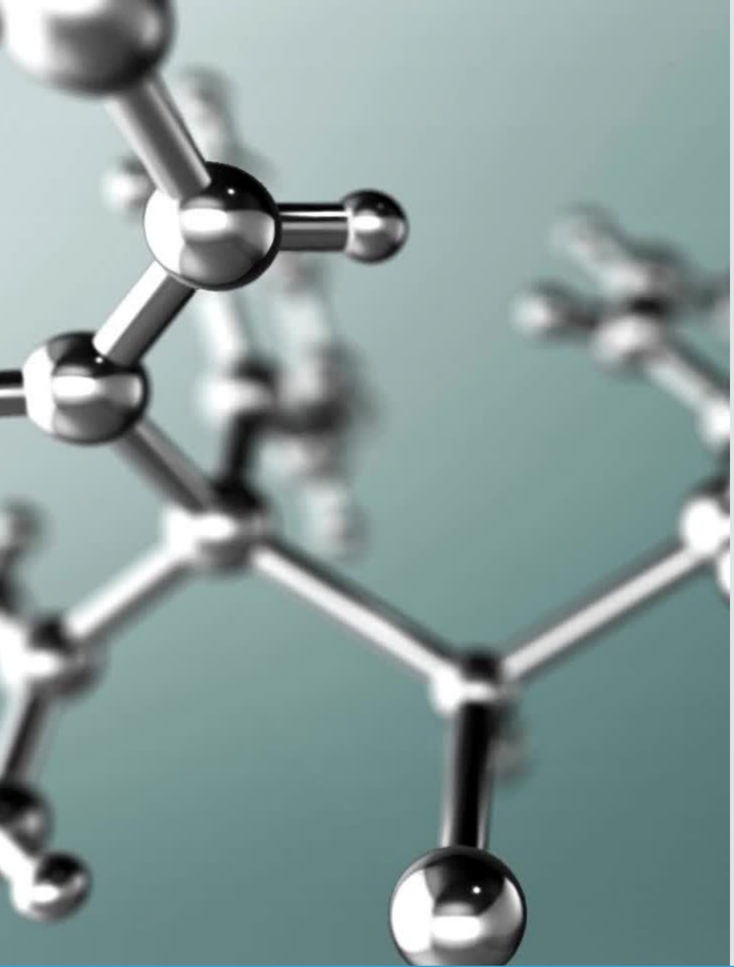
PFAS Destruction Mechanism

Two Step Reaction

1. Convective-Diffusive Transport of PFAS to Anode Surface

2. Direct Electron Transfer Reaction on Electrode Surface





PFAS Destruction Mechanisms

Rate Constant Comparison shows importance of mechanisms

Combination of mass transport and chemical kinetics

- Flow rate/turbulence
  - Too slow and diffuse layer is thick
  - Too high and not enough time to sorb to surface
- Solubility/hydrophobicity
  - Prevents sorption to surface
- Anode Surface Area

Synthetic Water Testing Protocol

Test 1
PFOA = 3,750 ng/L (nominal)
PFOS = 3,750 ng/L (nominal)
Salts = 1,250 mg/L NaCl, 1,250 mg/L CaCl2, 1,250 mg/L MgSO4

Test 2
PFOA = 37,500 ng/L (nominal)
PFOS = 37,500 ng/L (nominal)
Salts = 1,250 mg/L NaCl, 1,250 mg/L CaCl2, 1,250 mg/L MgSO4

Used 16L water, recirculated for 6 hours at 8V. Collected Samples at 2 hr intervals

Test 1 – Current = 61A

Test 2 – Current = 55A

Samples sent to Eurofins (PFAS) and ASU (AOF)

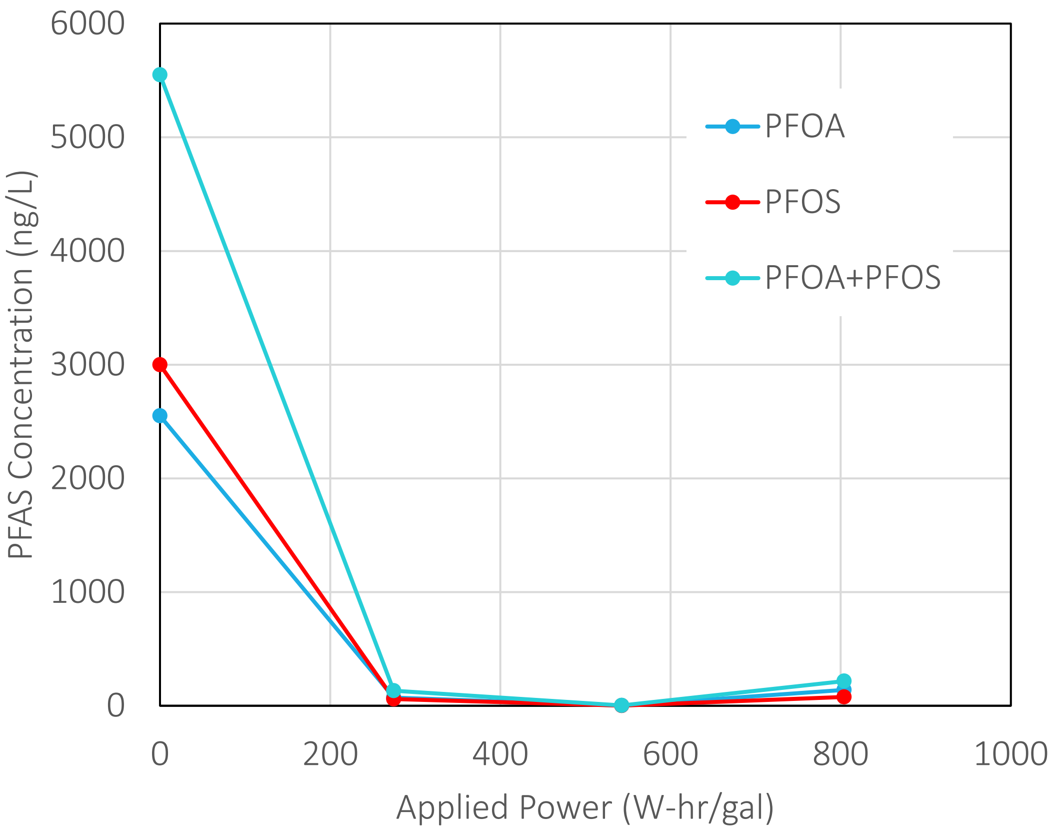
Results

Test 1 (low concentration)

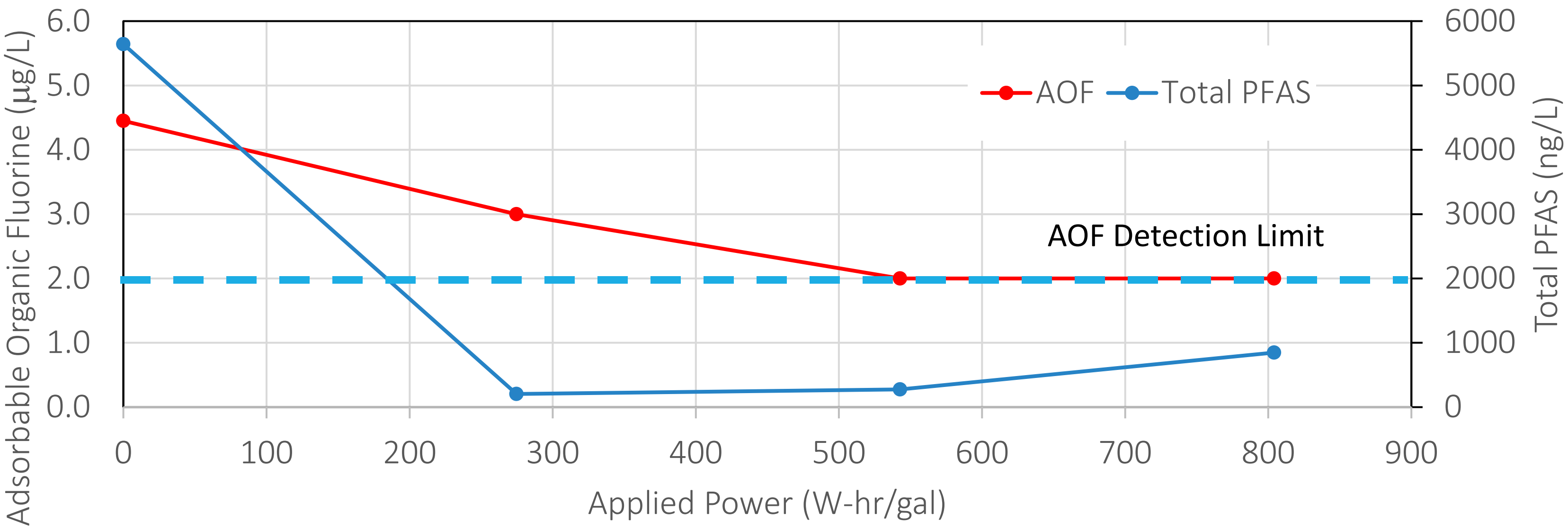
First Order Decay Rates

- PFOA = 2.98×10^{-2}/min
- PFOS = 3.09×10^{-2}/min

Achieved non-detectable concentrations (2 ng/L) of PFOA and PFOS at ~550 W-hr/gal



Adsorbable Organic Fluorine

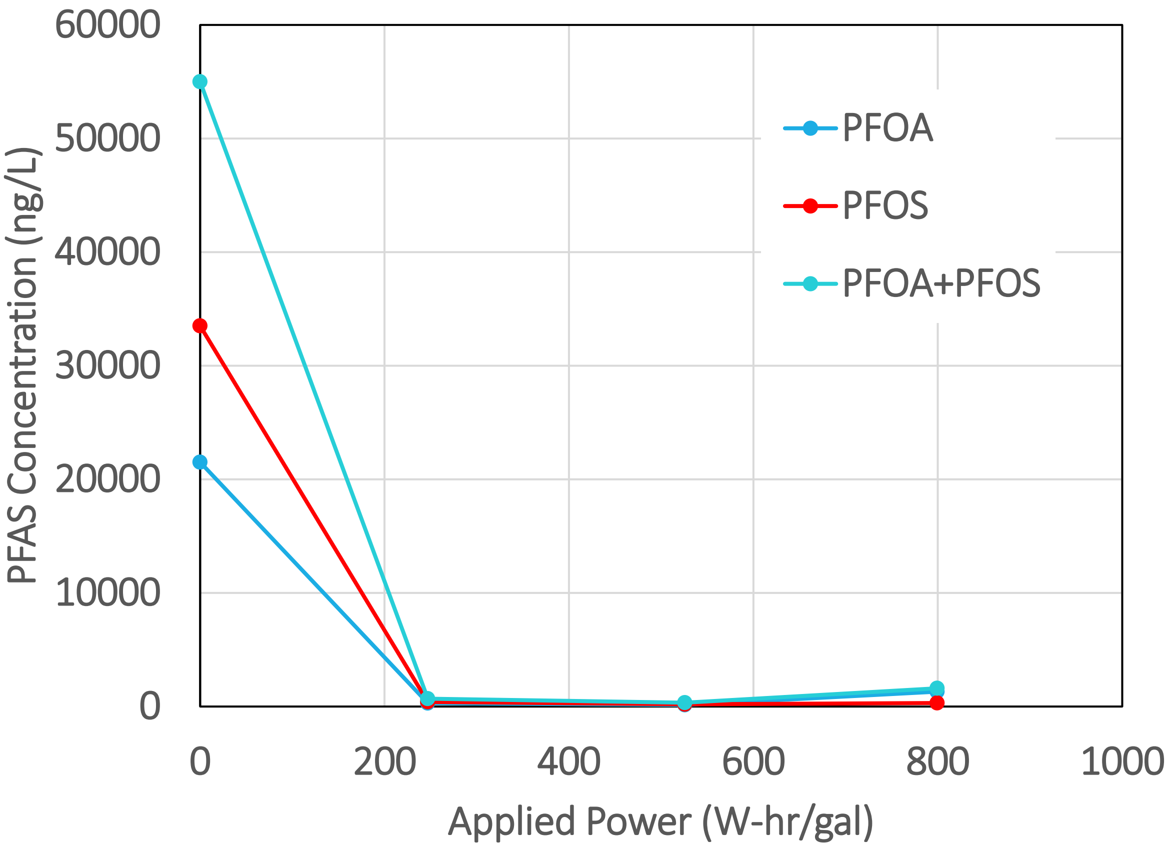


High Concentration PFAS Testing

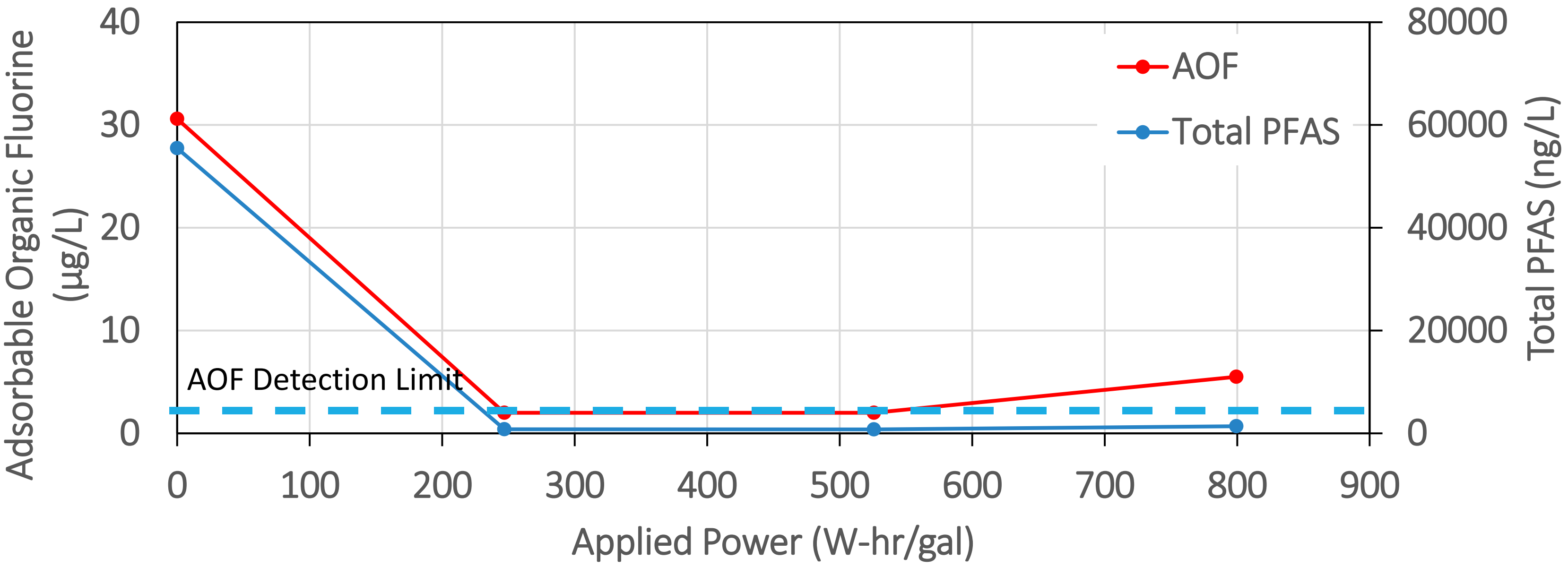
First Order Decay Rates

- PFOA = 2.40 x 10^{-2}/min
- PFOS = 2.46 x 10^{-2}/min

(Simulated RO brine)



Adsorbable Organic Fluorine



By-Product Formation

Small amounts of shorter chain compounds were detected

- PFHxA (C6)
- PFHpA (C7)
- 6:2 FTS

PFOA and PFOS and AOF seemed to reform at end of test after reaching non-detectable levels (2 µg/L).

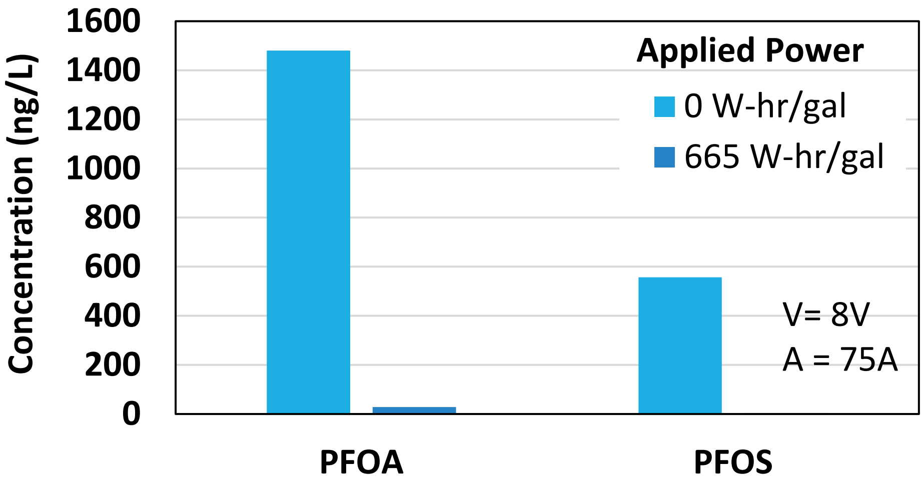
By Product Measurements

	Carboxylic Acids (ng/L)							Sulfonic Acids (ng/L)					Total PFAS (ng/L)
Time (min)	PFPeA [C5]	PFHxA [C6]	PFHpA [C7]	PFOA [C8]	PFNA [C9]	PFDA [C10]	Total	PFHxS [C6]	PFHpS [C7]	6:2FTS [C8]	PFOS [C8]	Total	Total
0	ND	7	4	2550	6	19	2586	5.5	13	38.5	3000	3057	5643
120	ND	ND	ND	73	ND	ND	73	ND	ND	71	60	131	204
240	ND	44	ND	ND	ND	ND	44	ND	ND	230	ND	230	274
360	ND	140	72	140	44	43	439	ND	ND	330	78	408	847
0	2.1	50.5	16	21500	31.5	87	21687	46	180	66	33500	33792	55479
120	ND	61	ND	290	ND	ND	351	ND	ND	56	400	456	807
240	ND	89	ND	140	ND	ND	229	ND	ND	340	190	530	759
360	ND	110	ND	130	55	75	370	ND	ND	700	300	1000	1370

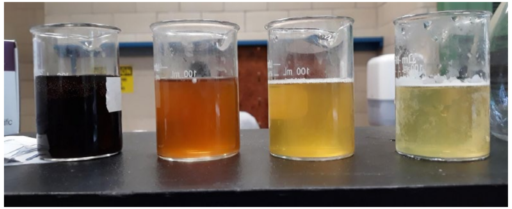
	Initial	Final	Minimum
Day 1	5643	847 (85%)	204 (96.4%)
Day 2	55479	1370 (97.5%)	759 (98.7%)

PFAS in Landfill Leachate

Initial concentration of PFAS: ~2 μg/L
Target concentration of PFOS: 60 ng/L
Target concentration of PFOA: 2,300 ng/L

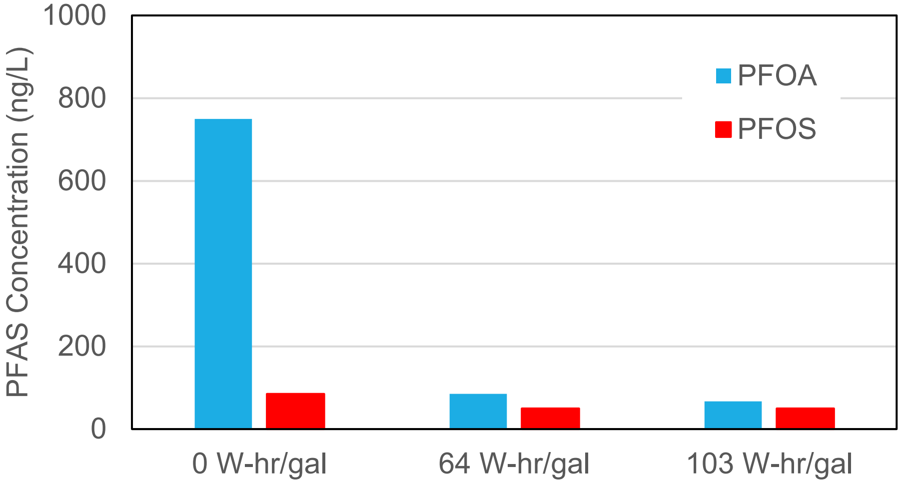


Case	Initial C (ng/L)	Target C (ng/L)	Flow (GPD)	# Reactors	CAPEX ($MM)	OPEX ($/kgal)
PFOS	557	60	180000	67	1.4	6.06
PFOS	557	60	43200	17	0.37	6.48

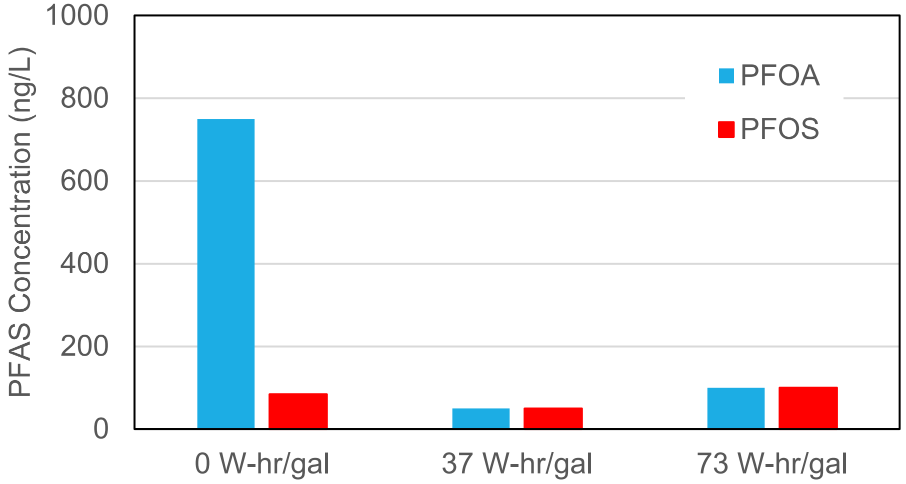


PFAS in Landfill Leachate

Initial concentration of PFOA+PFOS: ~800 ng/L



Raw Leachate



Primary Treated Leachate

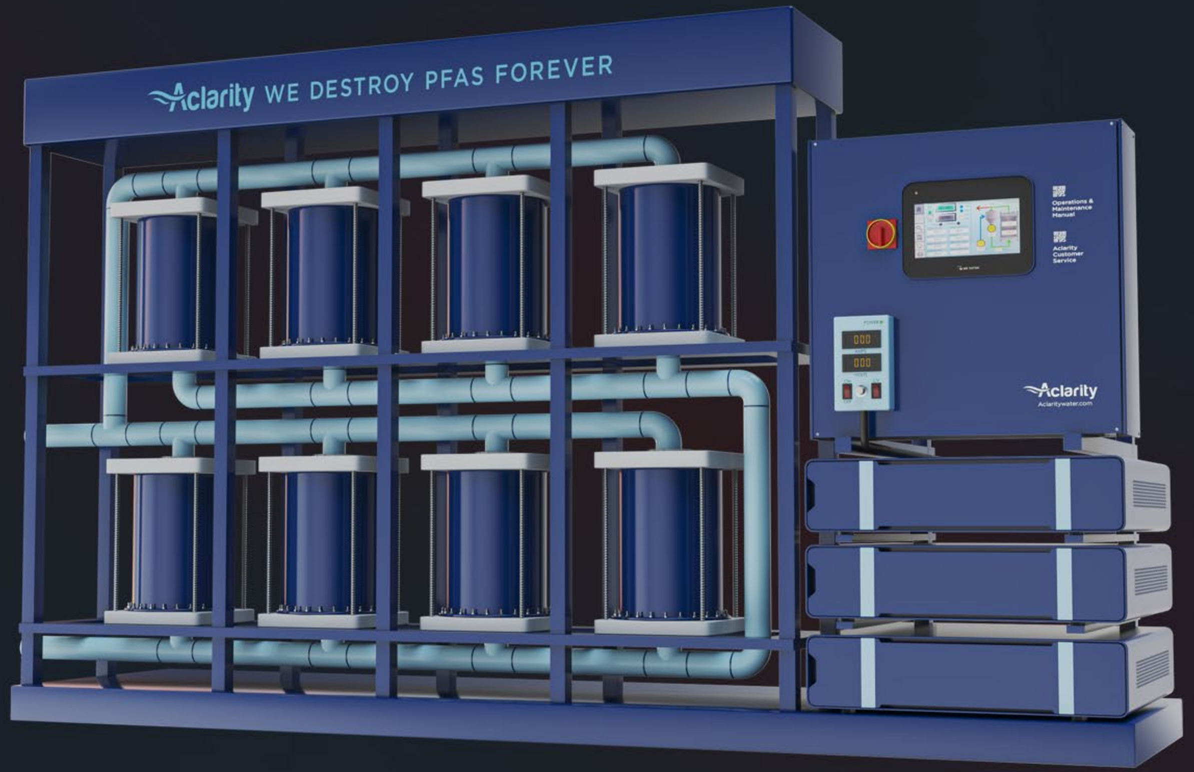
1st Order Kinetic Rate Constants

Case	Condition	Water Matrix	Voltage	Current Density (mA/cm^2)	First Order Rate Constant (min^{-1}) PFOA	PFOS
Synthetic Brine	Low C	Synthetic	8.1 (applied)	71	0.0298	0.0309
	High C	Synthetic	8.0 (applied)	67	0.0240	0.0246
Leachate 1	---	Leachate	7.5 (applied)	87	0.0131	0.0163
Leachate 2	---	Leachate	3.5 (applied)	17	0.0101	>0.00433
Lin et al. 2018	---	20 mM $NaClO_4$	3.7-3.9 (anodic potential)	5	0.034	0.013
Liu et al. 2019	Sulfate	40 mM Na_2SO_4	3-3.5 (anodic potential)	10	0.035	---
	Nitrate	60 mM $NaNO_3$	3-3.5 (anodic potential)	10	0.014	---
Wang et al. 2020	---	100 mM Na2SO4	3-3.5 (anodic potential)	10	---	0.429
Wang et al. 2021	---	IX waste brine	Not reported	10	1.23E-03	1.87E-03

Conclusions

Electrochemical Oxidation:

- Is capable of degrading high levels of PFOA and PFOS to near non-detectable levels
- Does not appear to create significant levels of short-chain byproducts
- Can achieve non-detectable levels of organic fluorine
- Can be a cost-effective destruction technology
- Does not appear to be cost effective for destruction of low concentration PFAS without an upstream concentration technology (IX, RO/NF, FF/SAFF)


Aclarity WE DESTROY PFAS FOREVER
Aclarity

THANK YOU!

www.aclaritywater.com