UCLA Samueli School of Engineering

# Sonolytic Destruction of PFAS in Groundwater, Aqueous Film-Forming Foam, and Investigation Derived Waste

**Shaily Mahendra, Professor and Samueli Fellow**

UCLA Civil and Environmental Engineering

REMTEC & EMERGING CONTAMINANTS SUMMIT

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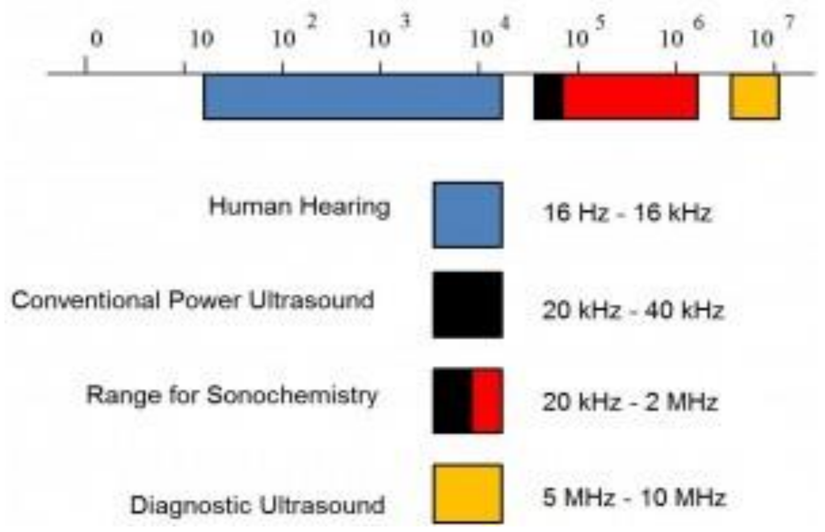
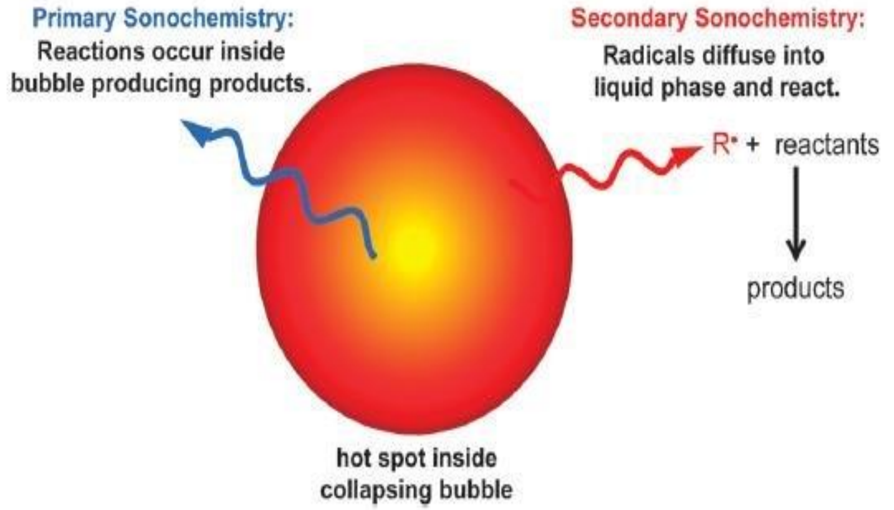
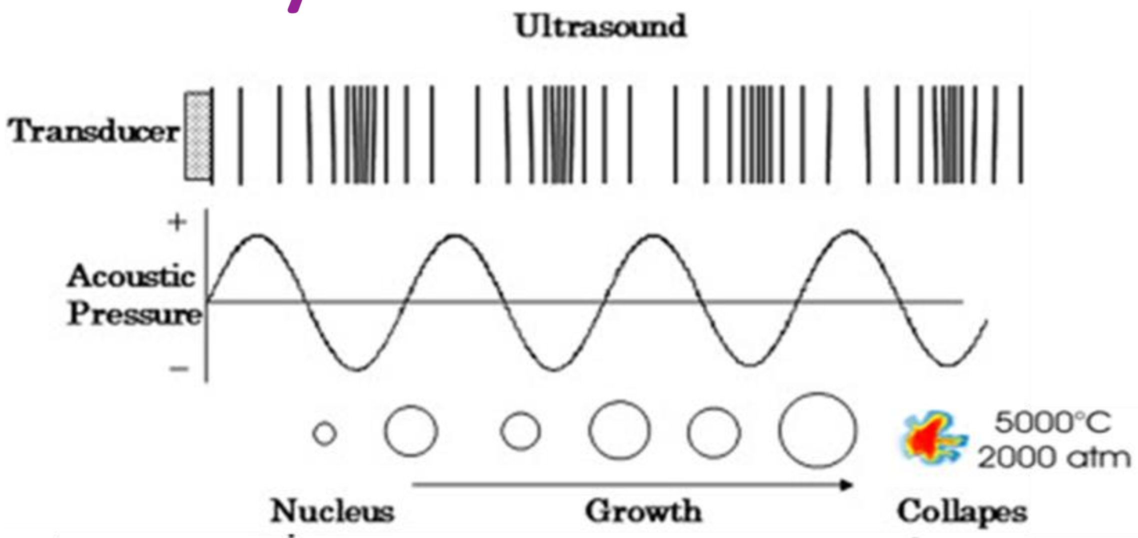
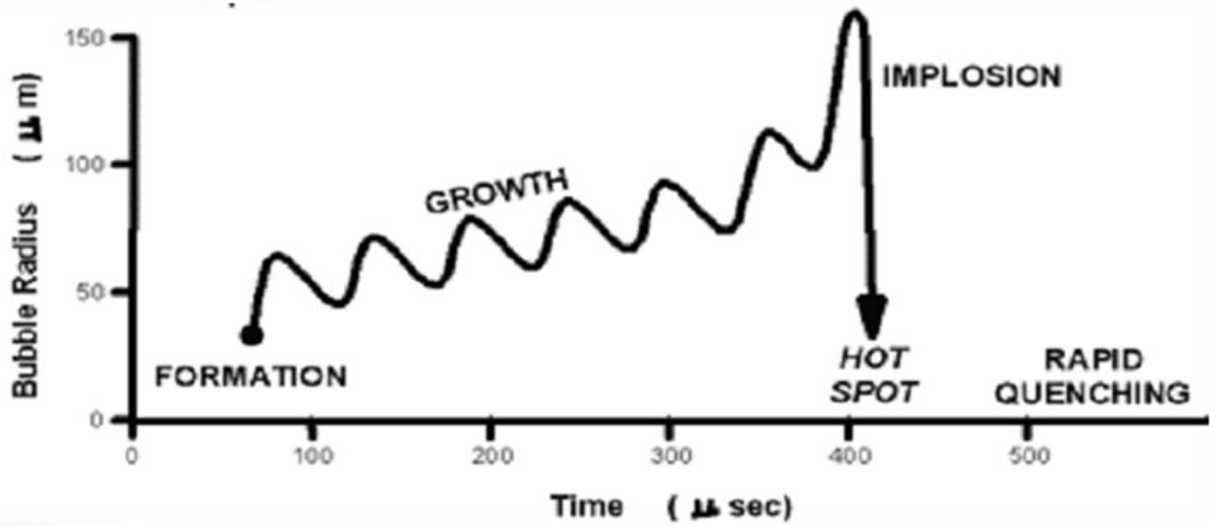
# Principles of Sonochemistry

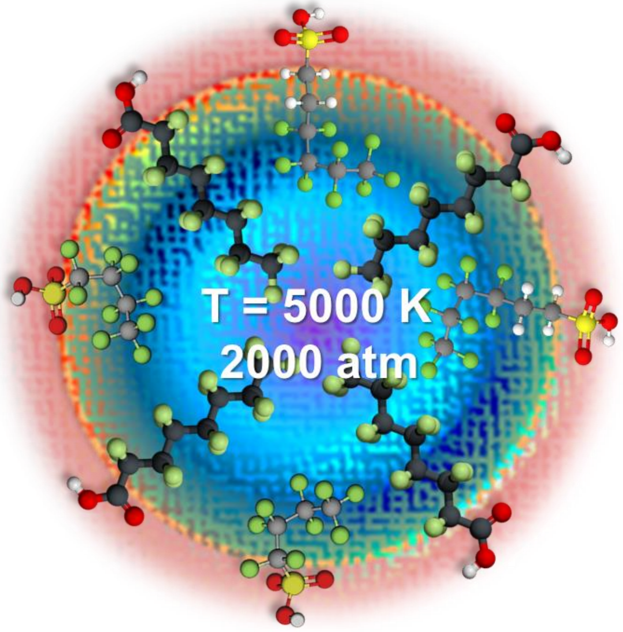


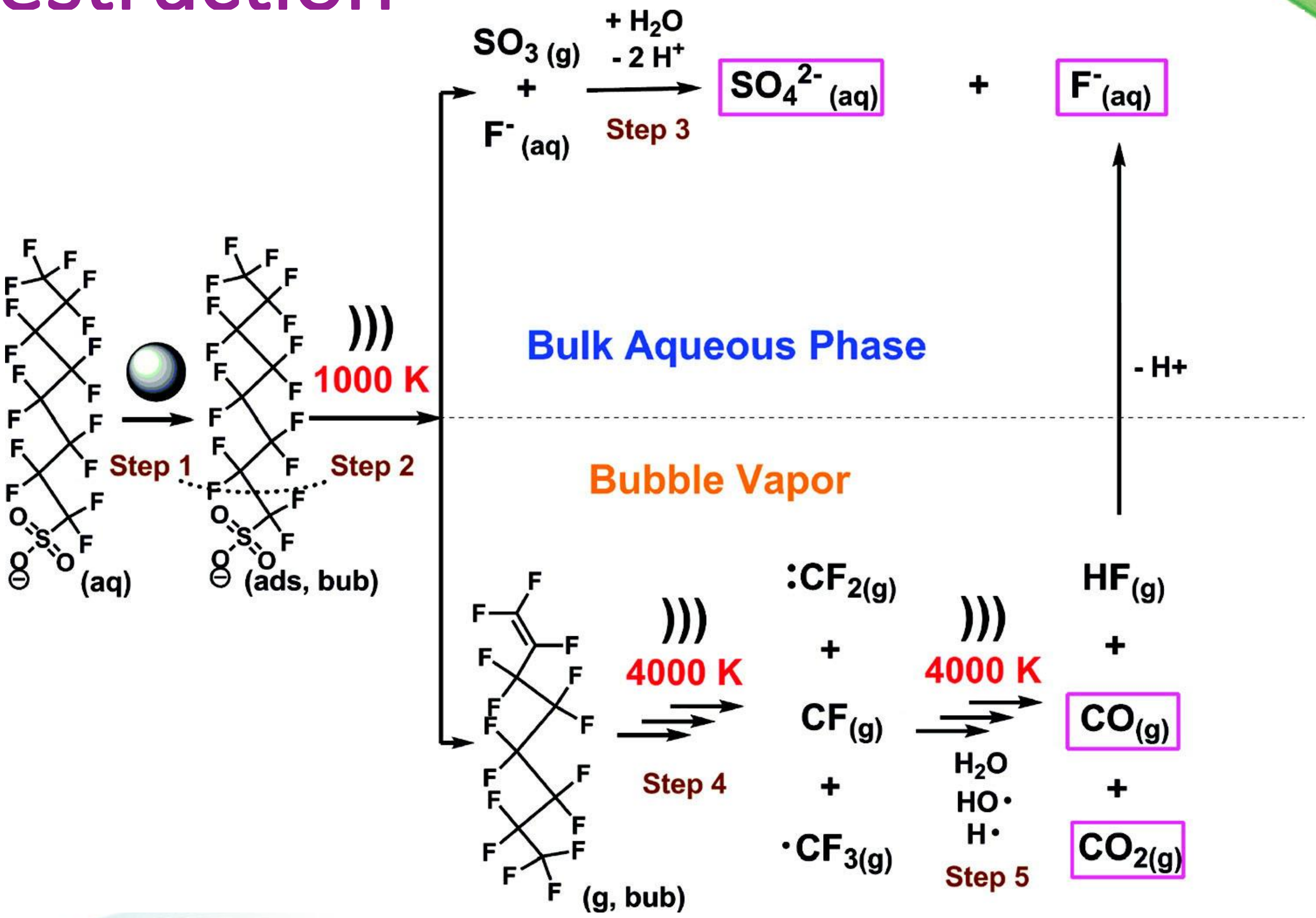



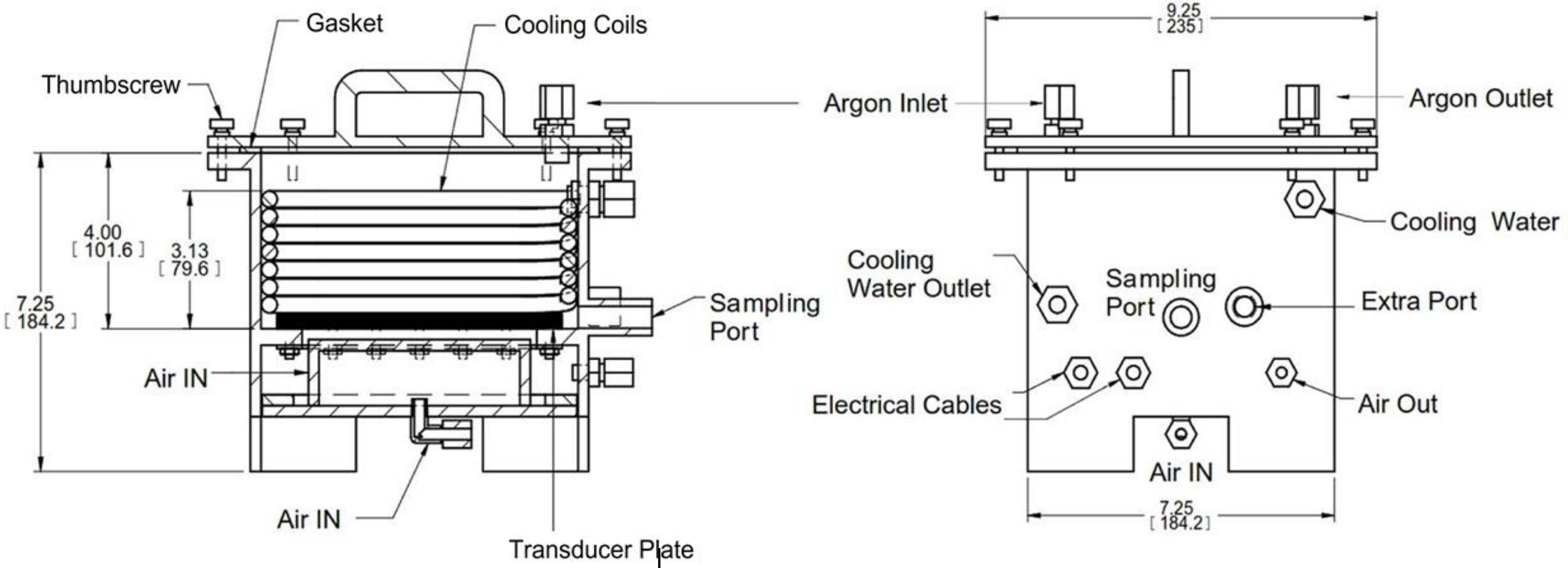
# Mechanism of Destruction

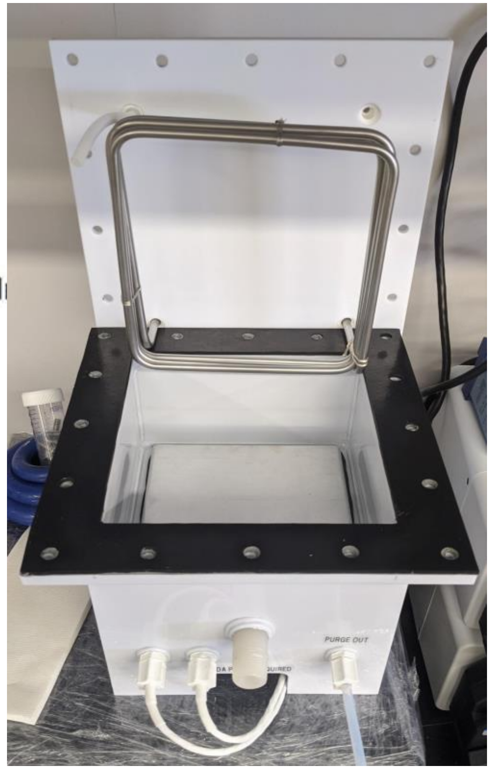



Vecitis et al (2008)

# Laboratory-scale Reactor

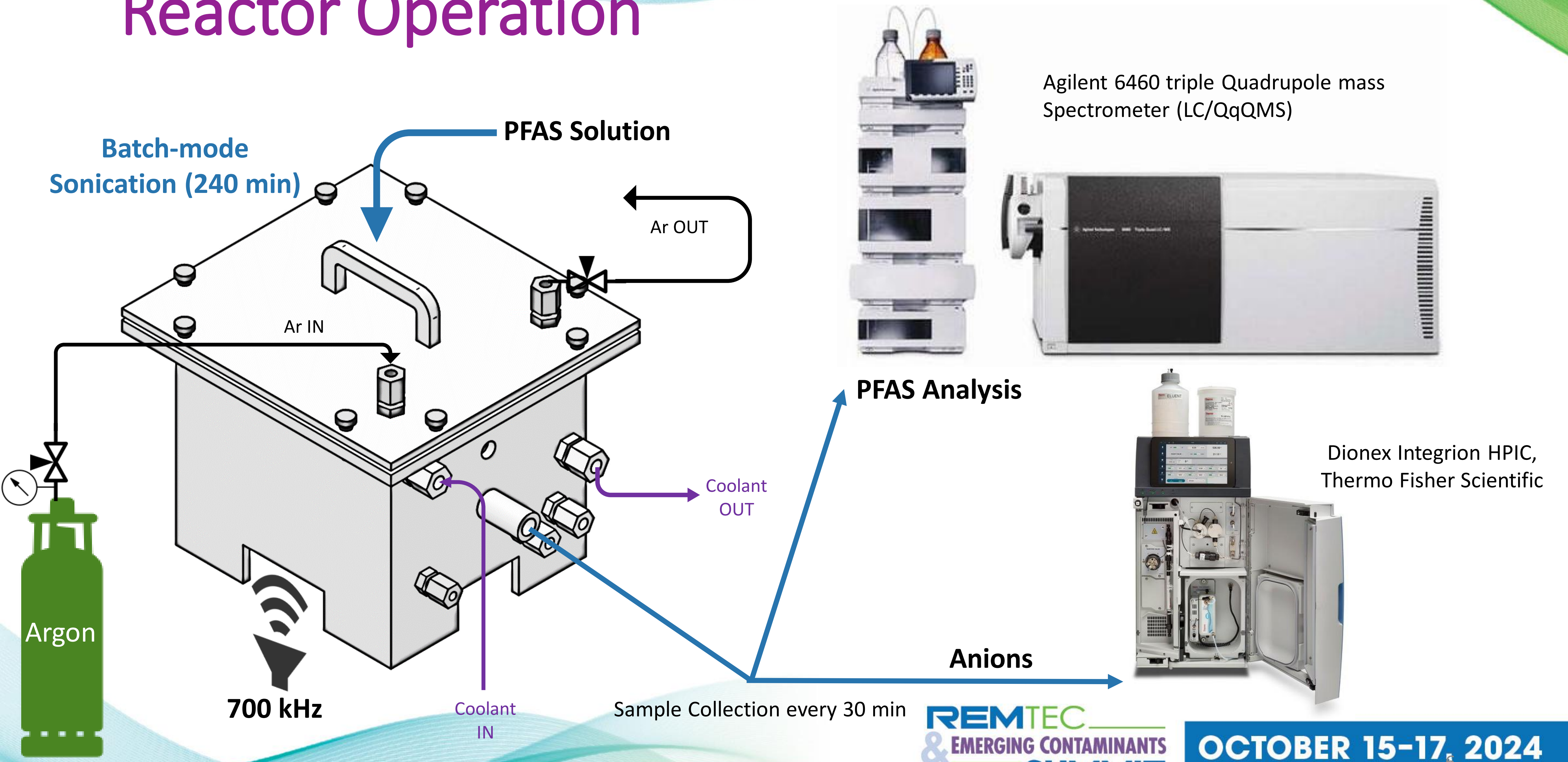


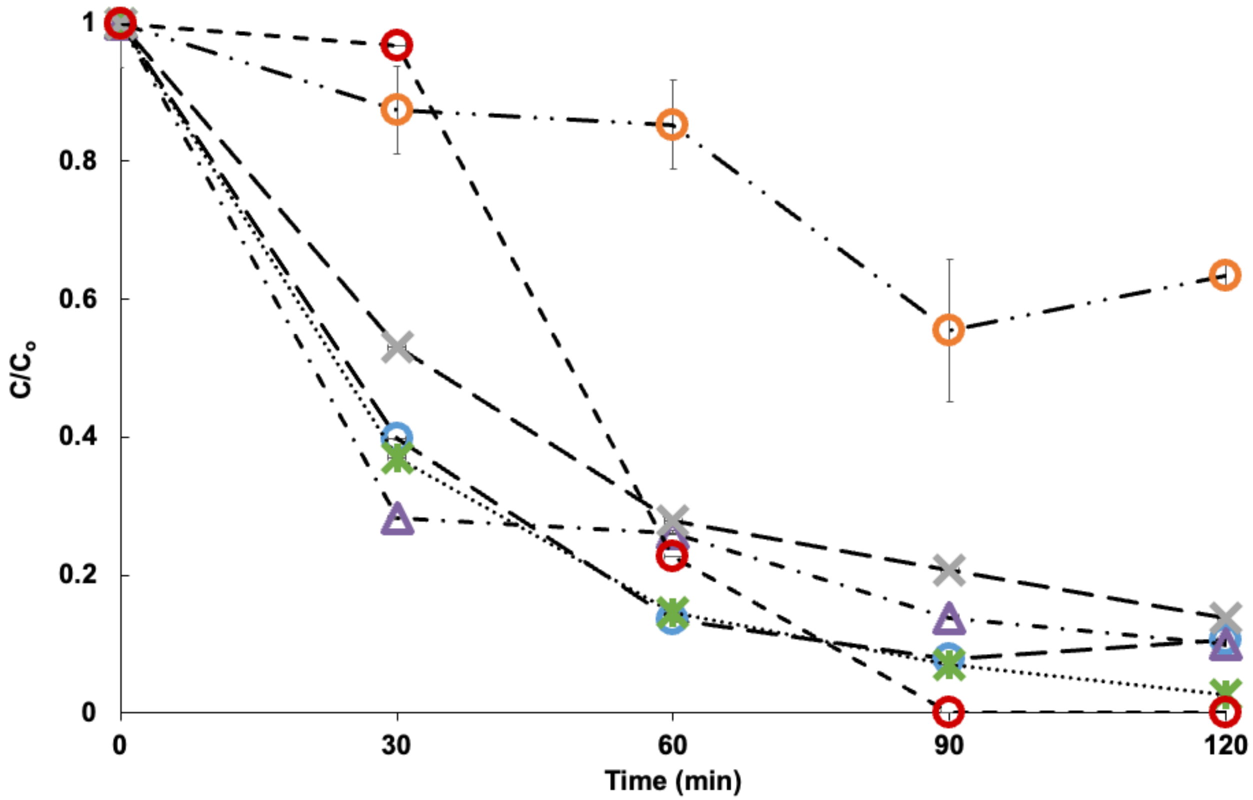
| | |
|---|---|
| Maximum Volume | 2 L |
| Dimensions | 10.1 cm × 18.42 cm × 18.42 cm |
| Rated Power | 250 W |
| Piezo-electric Transducers | 4 |
| Temperature Control | Yes |
| Material | Polypropylene |

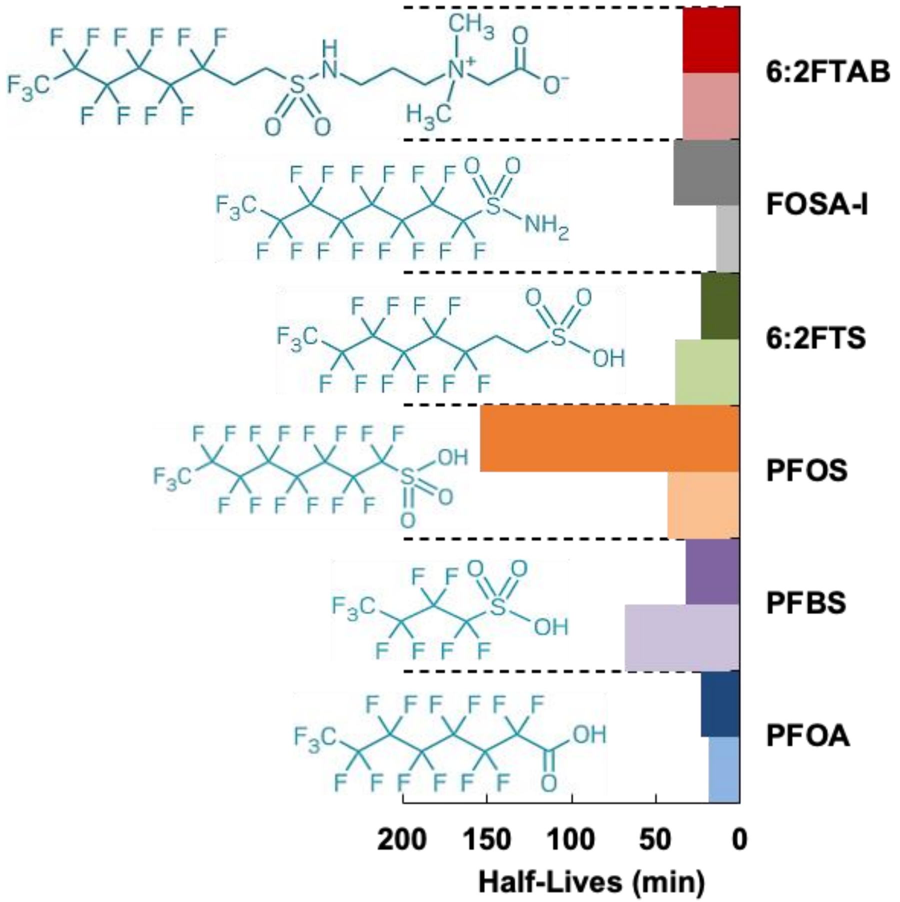
0.4 kWh for 4 h operation
= 5 cents @ $ 0.12/kWh
= $0.18/gal

# Reactor Operation



# Half-lives of Individual PFAS




Kalra et al., Chem Eng J (2021)

# Kinetics of PFAS Sonolytic Degradation

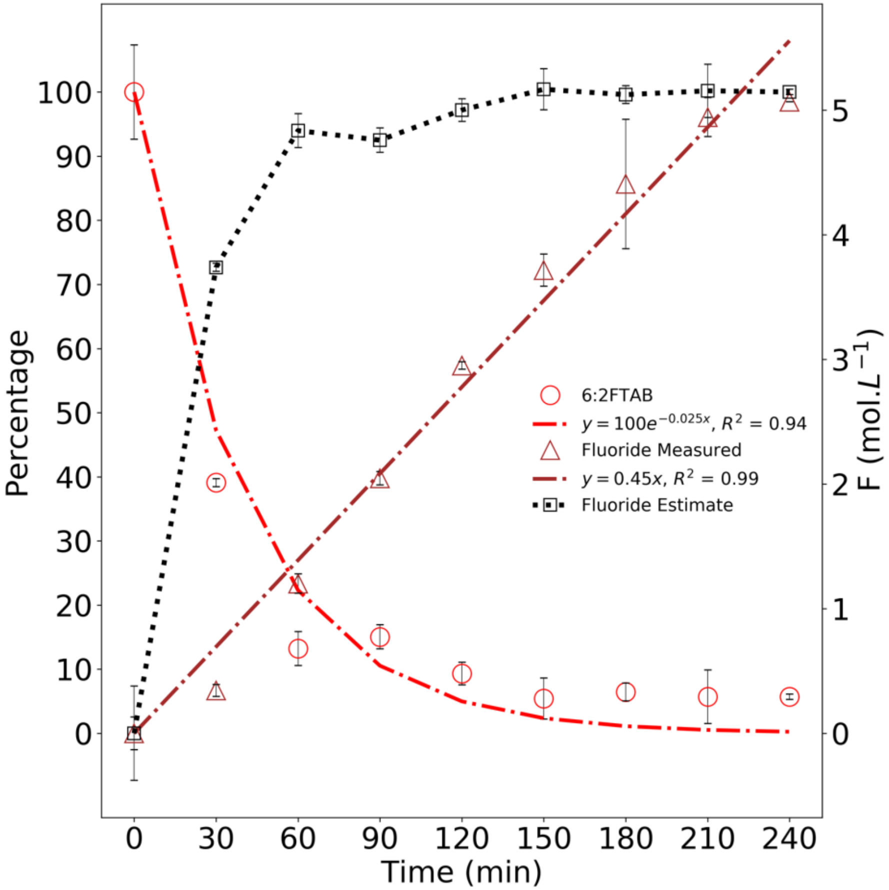
- $k_{\text{sulfonates}} < k_{\text{carboxylates}}$
  - $\text{sulfonates}^{\text{Steric Hindrance \& Surface Activity}}_{\text{C–S Bond Strength}} >$
  
    $\text{carboxylates}^{\text{Steric Hindrance \& Surface Activity}}_{\text{C–C Bond Strength}}$

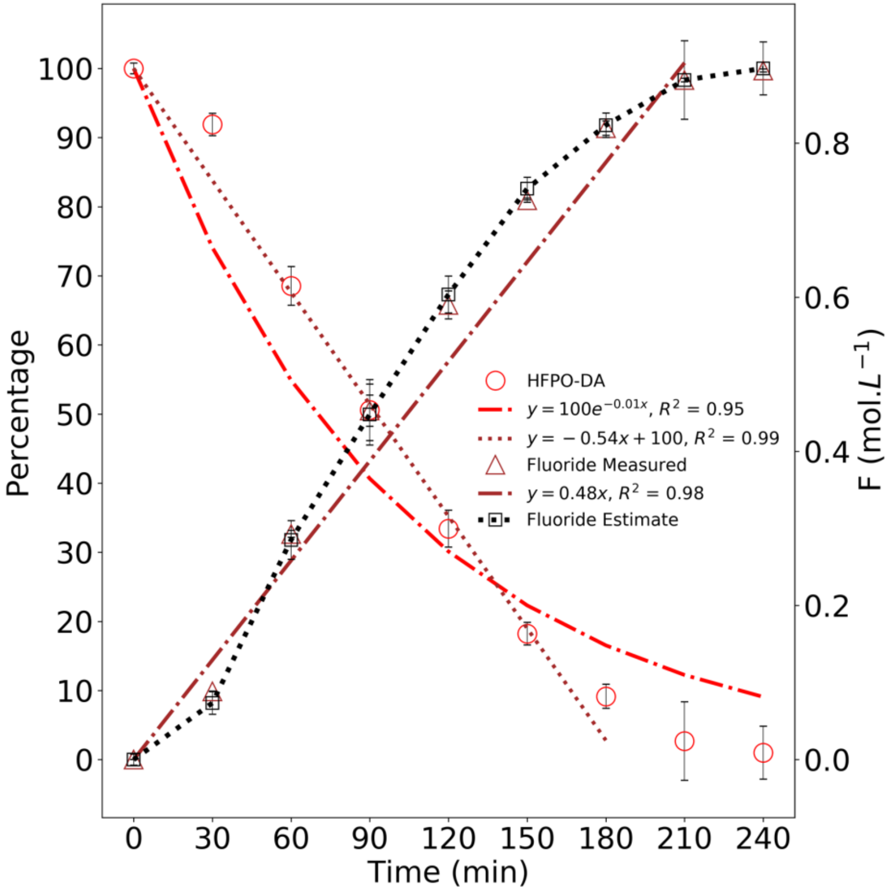
- $k_{\text{long-chain}} > k_{\text{short-chain}}$
  - $\text{long} - \text{chain}^{\text{hydrophobicity}}_{\text{Surface activity}} > \text{short} - \text{chain}^{\text{hydrophobicity}}_{\text{Surface activity}}$

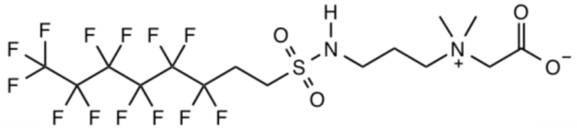
Degradation rates are controlled by the availability of PFAS on/in the ultrasonic cavity

PFOS ($C_8$) > PFOA ($C_7$) > PFBS ($C_4$) > PFBA ($C_3$)

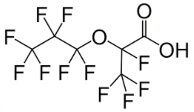
# Stoichiometric Defluorination



**6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB)**

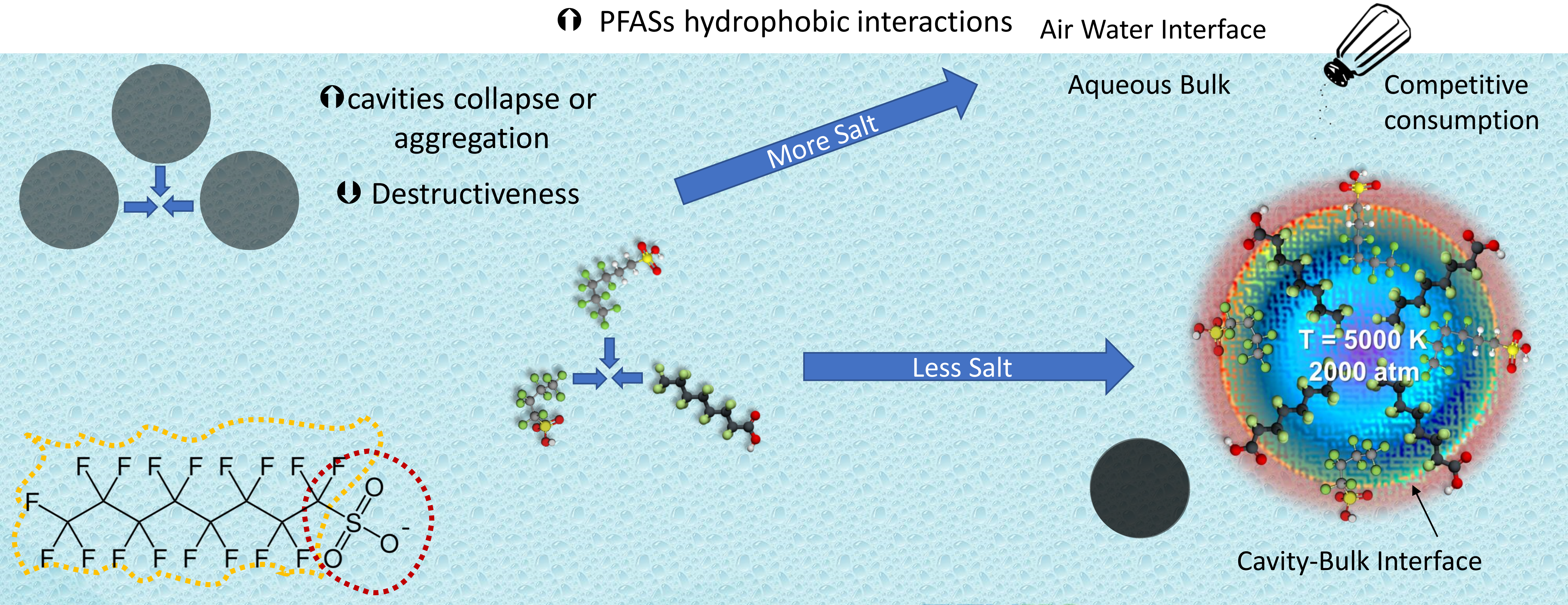


**2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid (HFPO-DA)**

| | 6:2 FTAB | HFPO-DA |
|---|---|---|
| De-F | 98% | 99% |
| $C_i$ | 2 mg/L | 23 mg/L |
| $C_f$ | 0.2 mg/L | 0.2 mg/L |

Kalra et al., Chem Eng J (2021)

# Effect of Salinity



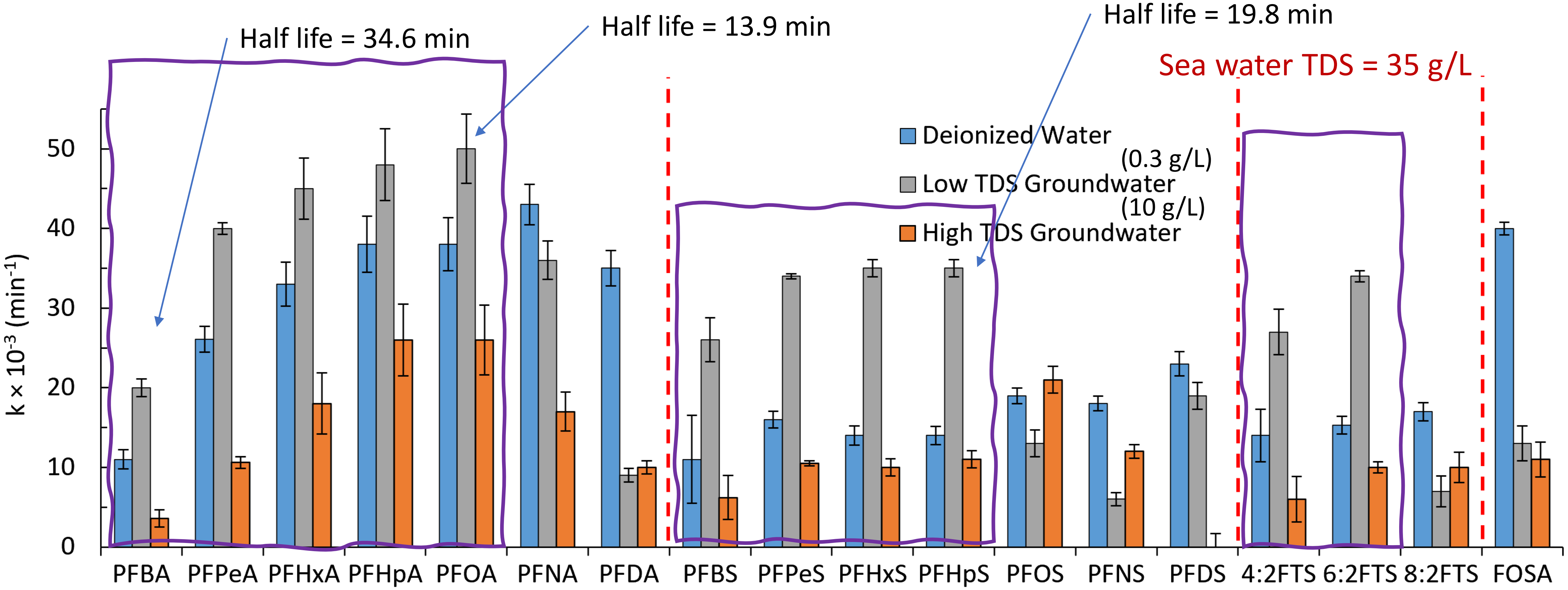

**↑ TDS → ↓ surface tension → ↑ surface excess and phase separation**

# Groundwater Characteristics

| | High TDS | Low TDS |
|---|---|---|
| Fluoride ($mg.L^{-1}$) | N.D. | 3.3 |
| Chloride ($mg.L^{-1}$) | 5283.7 | 55.5 |
| Nitrite ($mg.L^{-1}$) | 15.4 | N.D. |
| Bromide ($mg.L^{-1}$) | 17.4 | N.D. |
| Nitrate ($mg.L^{-1}$) | 11.0 | 4.0 |
| Sulfate ($mg.L^{-1}$) | 1955.5 | 19.7 |
| Sodium ($mg.L^{-1}$) | 3202.9 | 25.13 |
| Aluminum ($mg.L^{-1}$) | N.D. | N.D. |
| Magnesium ($mg.L^{-1}$) | 581.5 | 13.37 |
| Calcium ($mg.L^{-1}$) | 1145.0 | 96.13 |
| Manganese ($mg.L^{-1}$) | 1.71 | 0.02 |
| Iron ($mg.L^{-1}$) | 0.05 | N.D. |
| TDS ($mg.L^{-1}$) | 10200.0 | 388.0 |
| pH | 6.70 | 6.7 |
| Specific Conductance ($\mu S.cm^{-1}$) | 16000.0 | 610.0 |
| TOC ($mg.L^{-1}$) | 6.43 | 4.45 |

Sea water TDS = 35 g/L

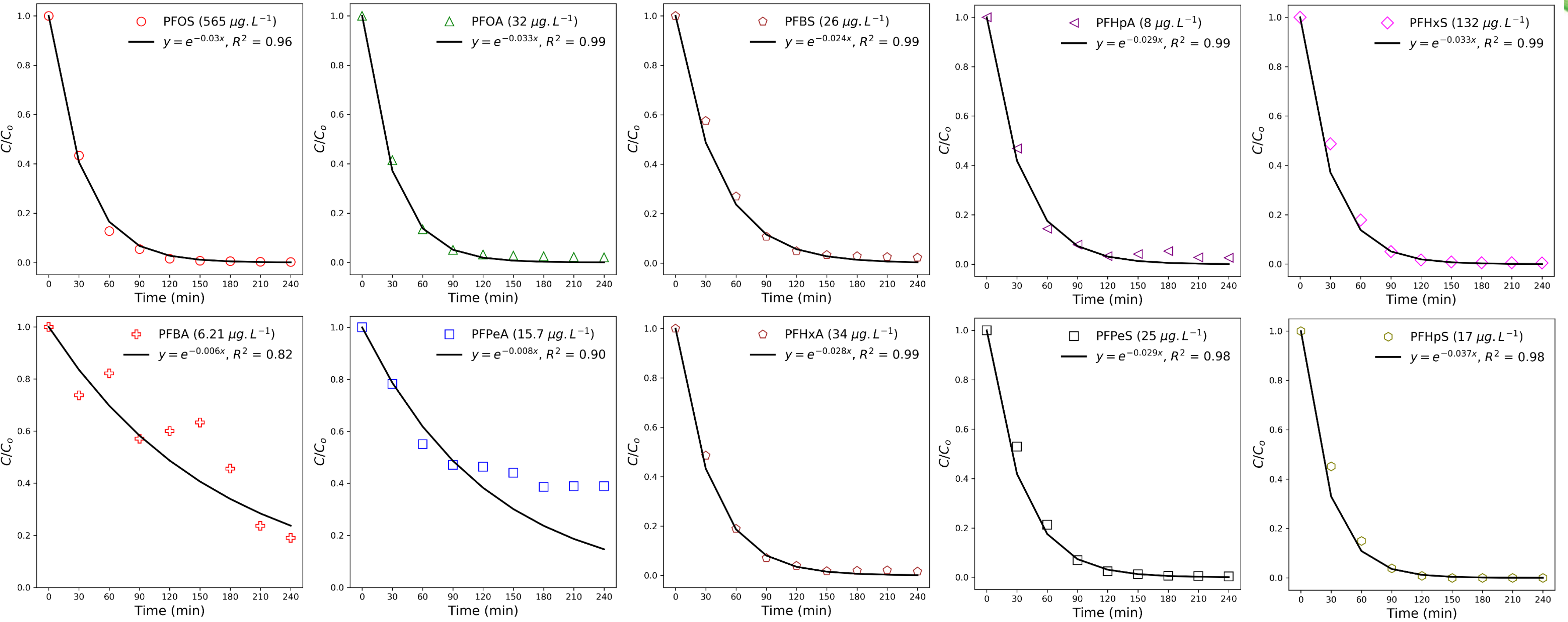
# Pseudo-first-order removal rates of 24Mix




If **multiple species** (24Mix) are competing for the same cavity the **kinetics remain pseudo-first-order**.

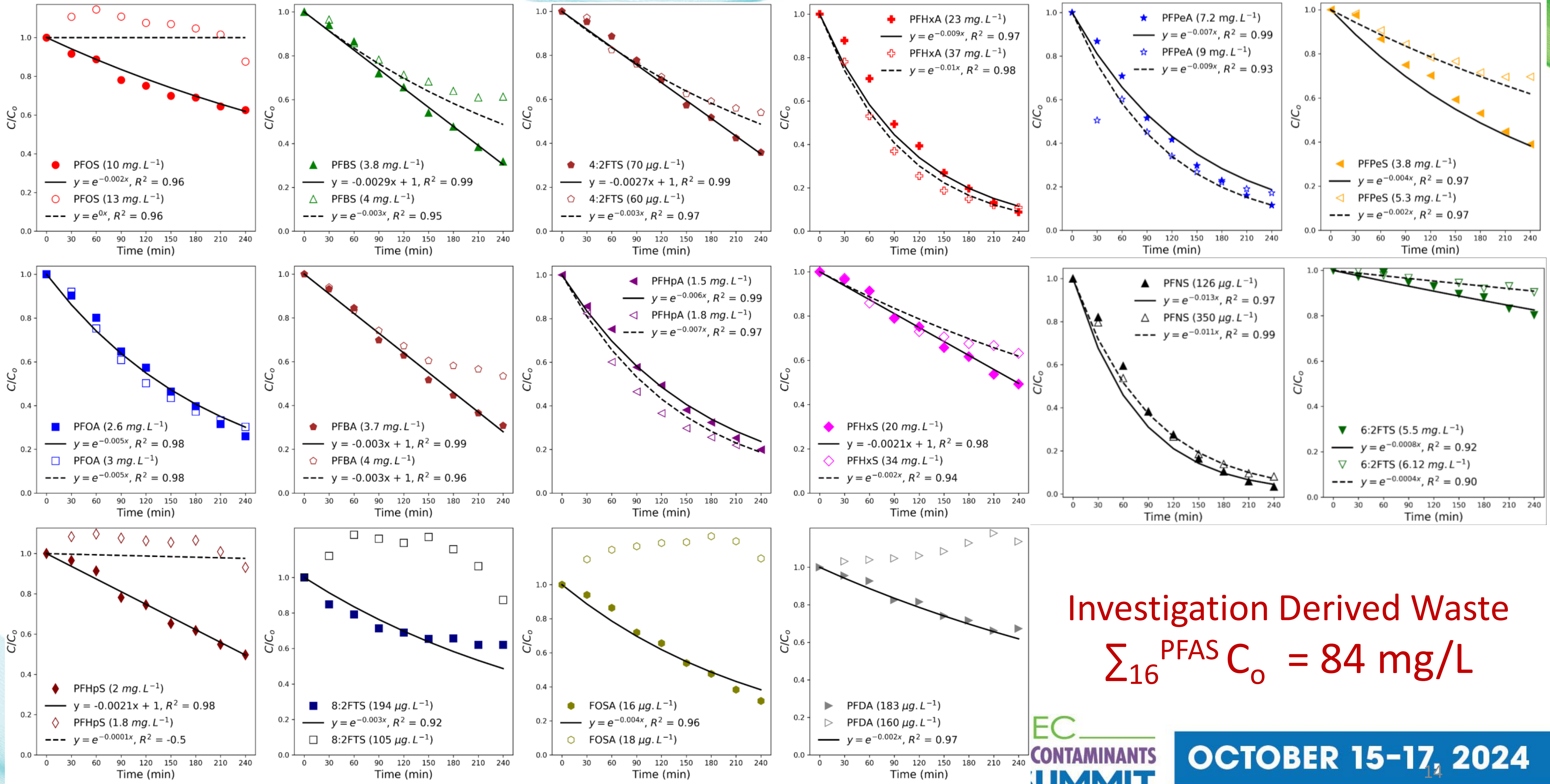
PFASs < 8: $k_{\text{low TDS groundwater}}$ **>** $k_{\text{deionized water}}$

# PFAS Degradation in AFFF sample (1:12500 dilution)




33 PFASs degraded in AFFF including perfluoropropane sulfonate (C=3)

Kalra et al., Chem Eng J (2021)




# Investigation Derived Waste

$\sum_{16}{}^{PFAS} C_o$ = 84 mg/L

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# Defluorination of IDW

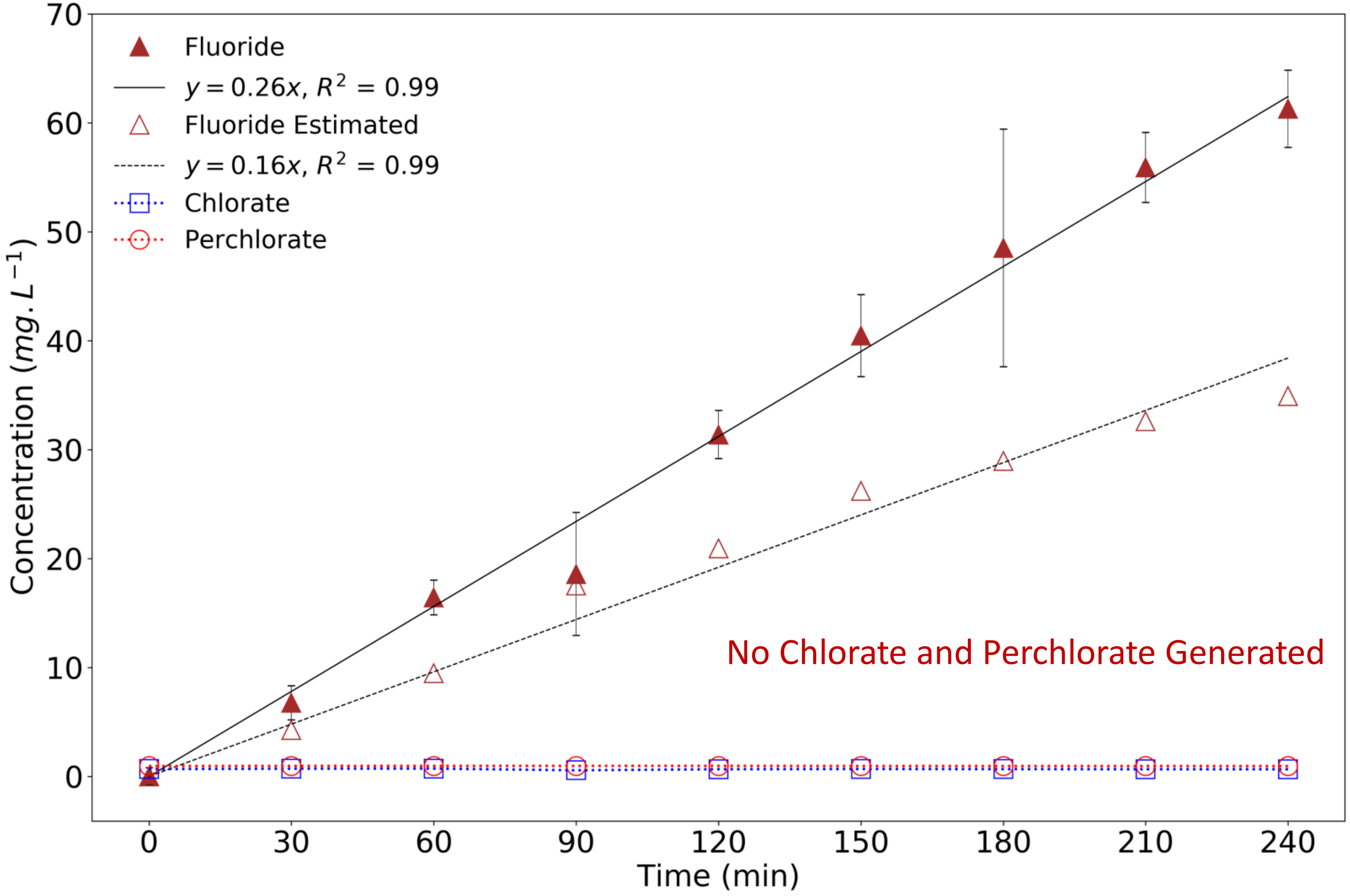
- 41 PFASs degraded in the IDW
- Concentration of PFAS in IDW ranged from 16 µg/L to 37 mg.L$^{-1}$

*i.* $C^{IDW}_{PFOS} = 2.5 \times 10^{5} \times C^{UCMR3}_{PFOS}$

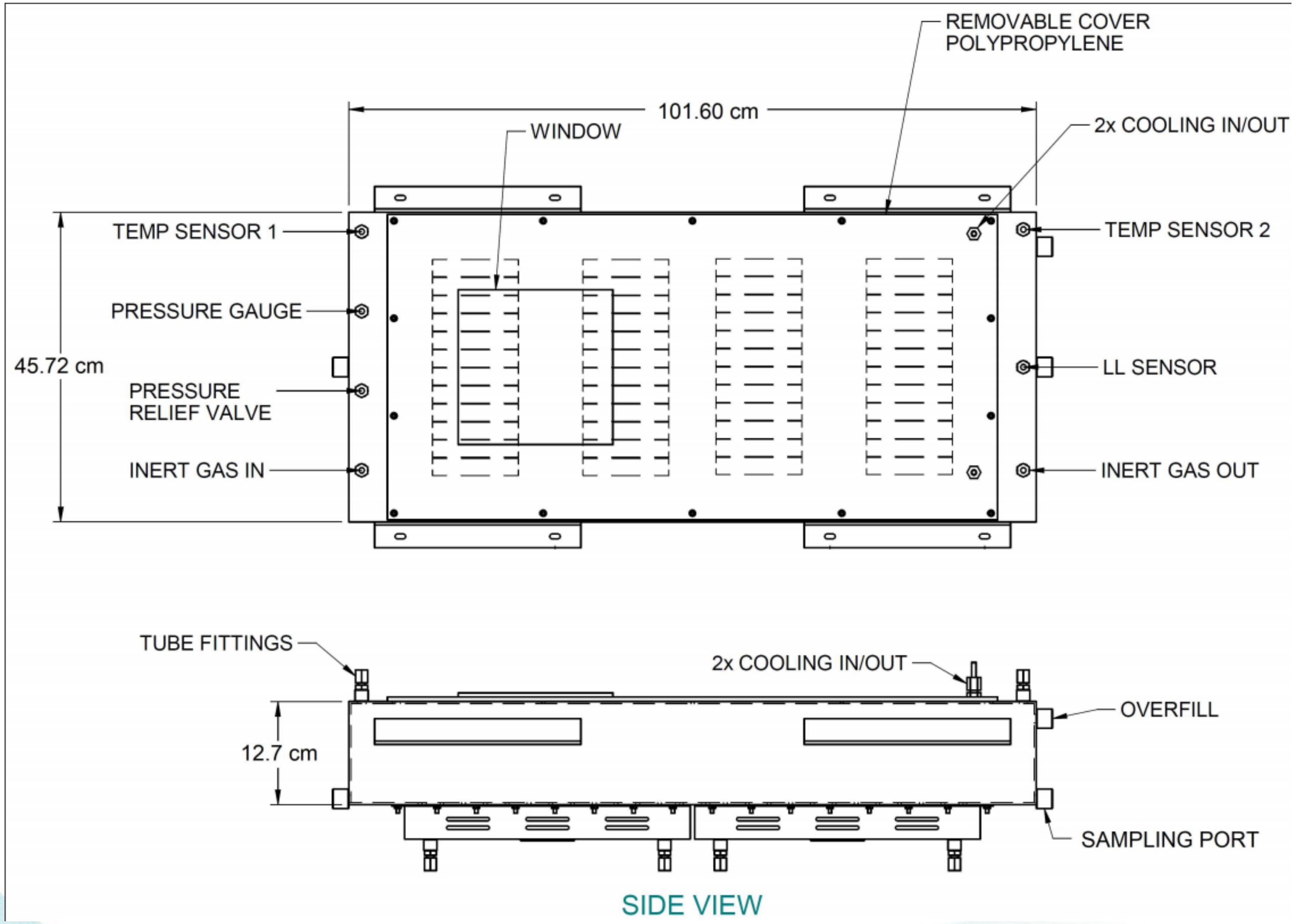
*ii.* $C^{IDW}_{PFHxS} = 6.7 \times 10^{5} \times C^{UCMR3}_{PFHxS}$

*iii.* $C^{IDW}_{PFOA} = 1.3 \times 10^{4} \times C^{UCMR3}_{PFOA}$

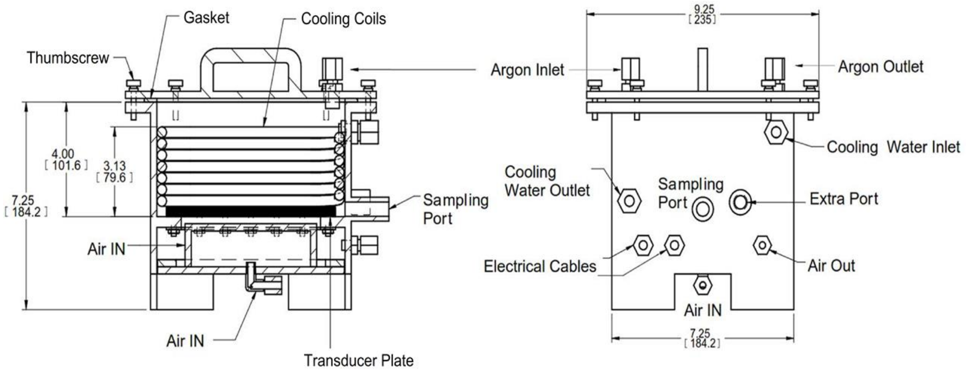
*iv.* $C^{IDW}_{PFBS} = 4.4 \times 10^{4} \times C^{UCMR3}_{PFBS}$



# Large-scale Reactor for Field Demonstration



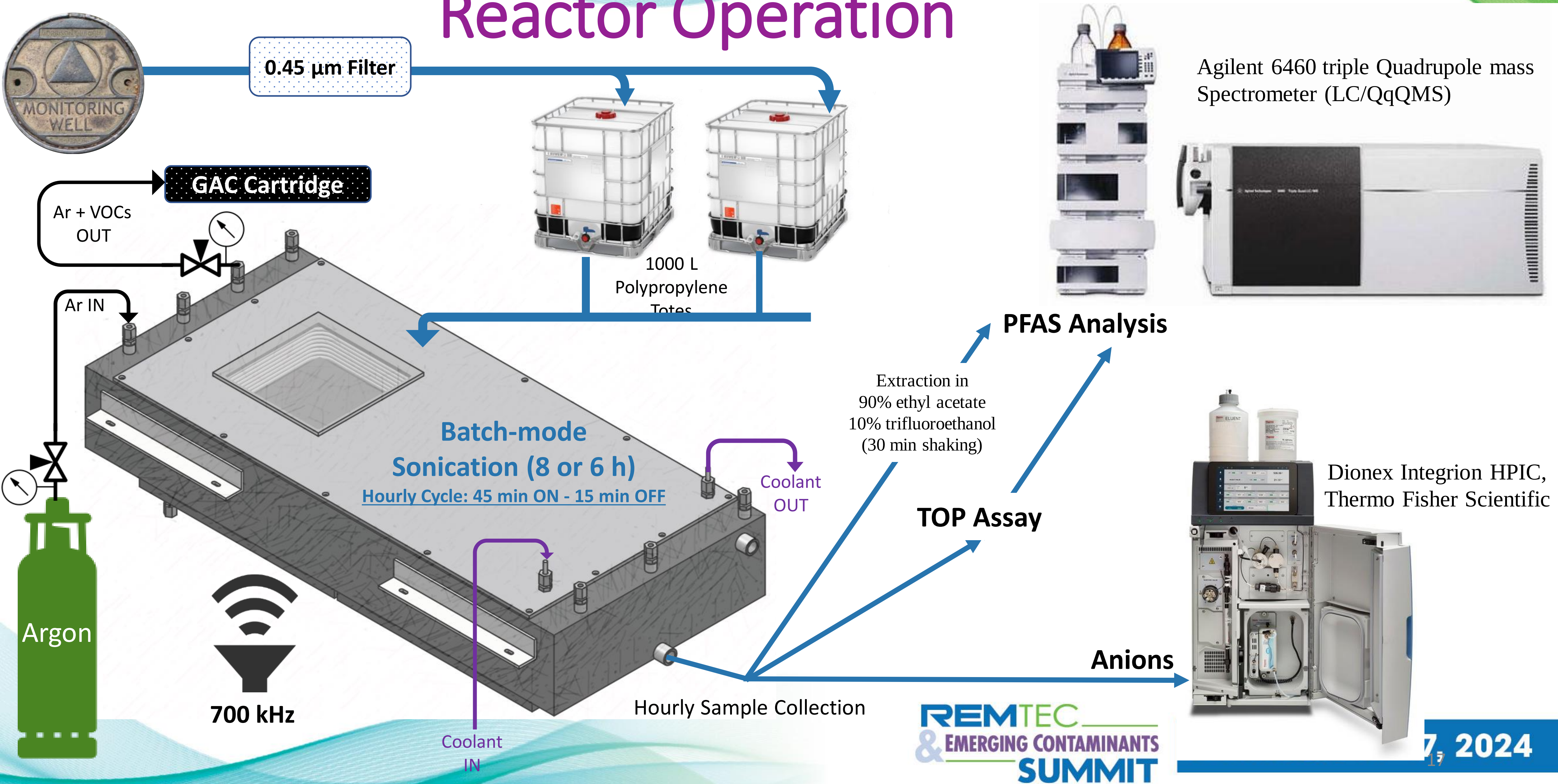

PCT Systems, Inc. (San Jose, CA)




| | Field Reactor | Lab Reactor |
|---|---|---|
| Maximum Volume | 59 L | 2 L |
| Dimensions | 101.60 cm × 45.72 cm × 12.7 cm | 10.1 cm × 18.42 cm × 18.42 cm |
| Rated Power | 7200 W | 250 W |
| Piezo-electric Transducers | 48 | 4 |
| Temperature Control | Yes | Yes |
| Material | Stainless Steel | Polypropylene |

Kulkarni et al., ASCE JEE (2022)

# Reactor Operation

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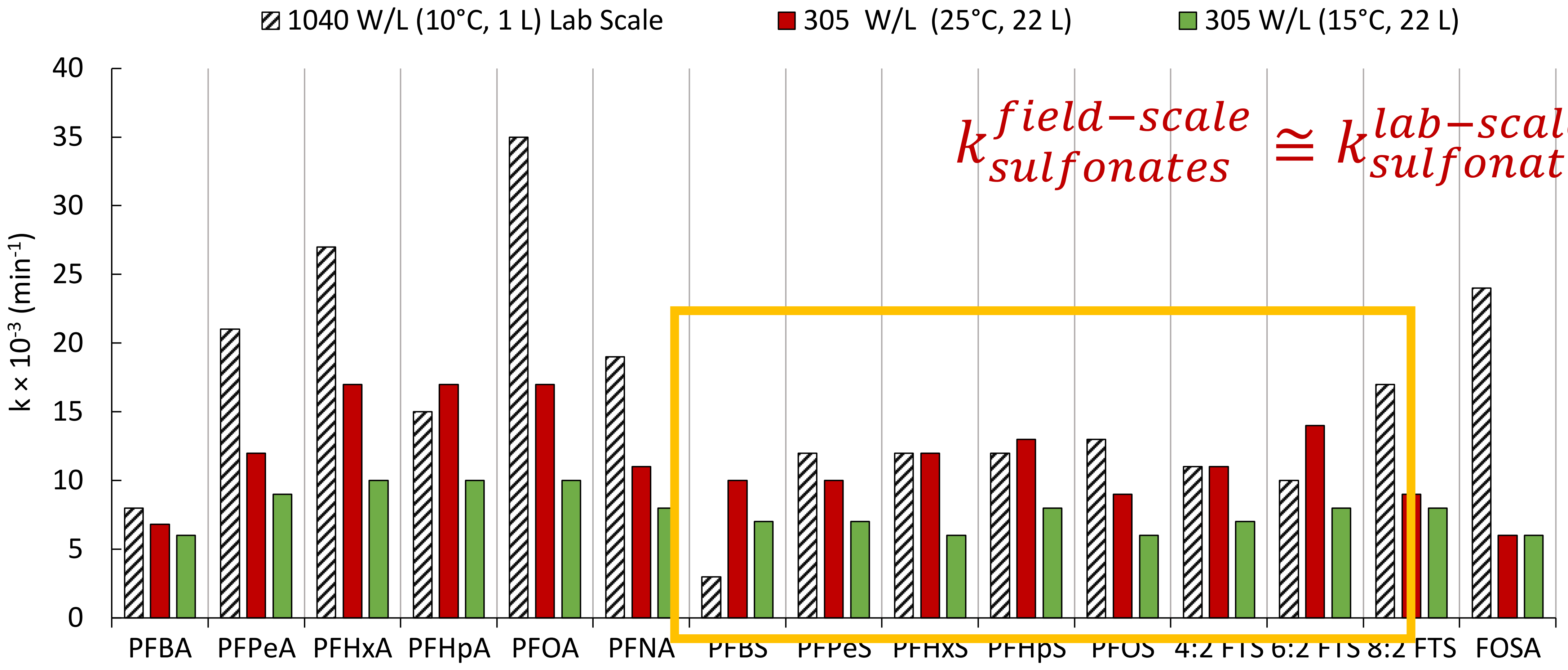
# Rate Comparison: Lab vs. Field

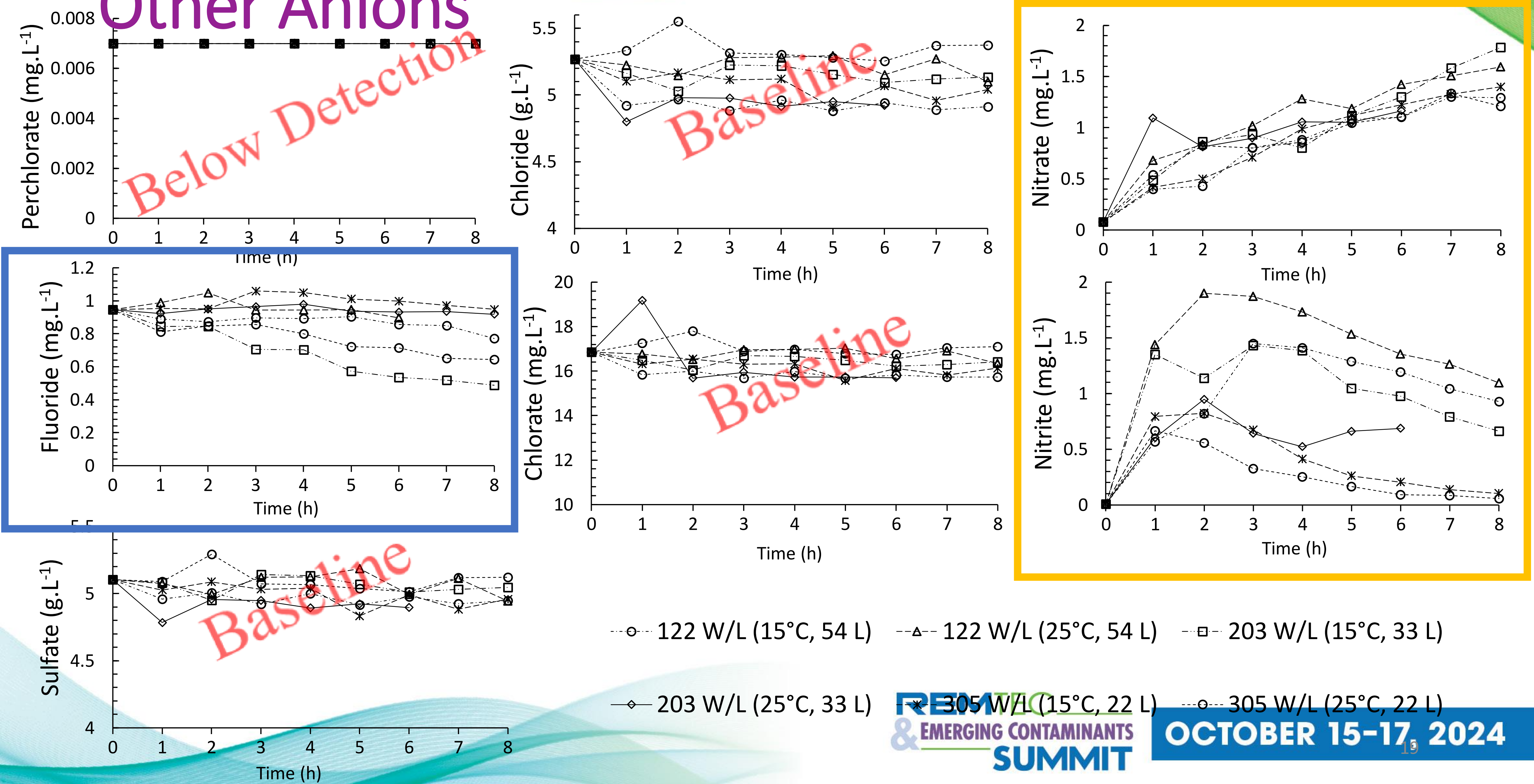



$$k_{sulfonates}^{field-scale} \cong k_{sulfonates}^{lab-scale}$$

$$P_d^{field-scale} = \frac{P_d^{lab-scale}}{3.5}$$

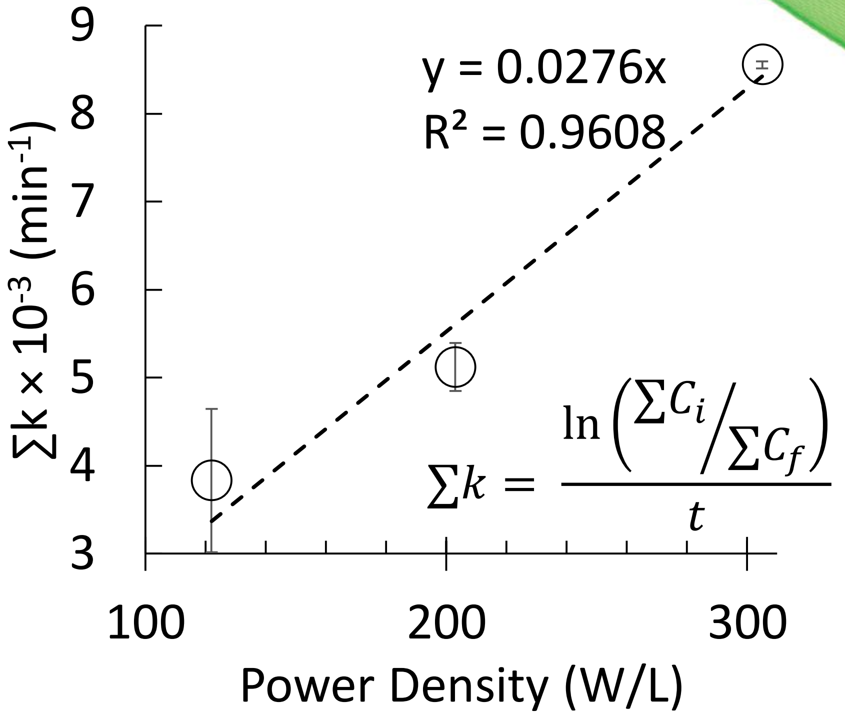
Kulkarni et al., ASCE JEE (2022)

# Other Anions



# Estimated Energy Consumption

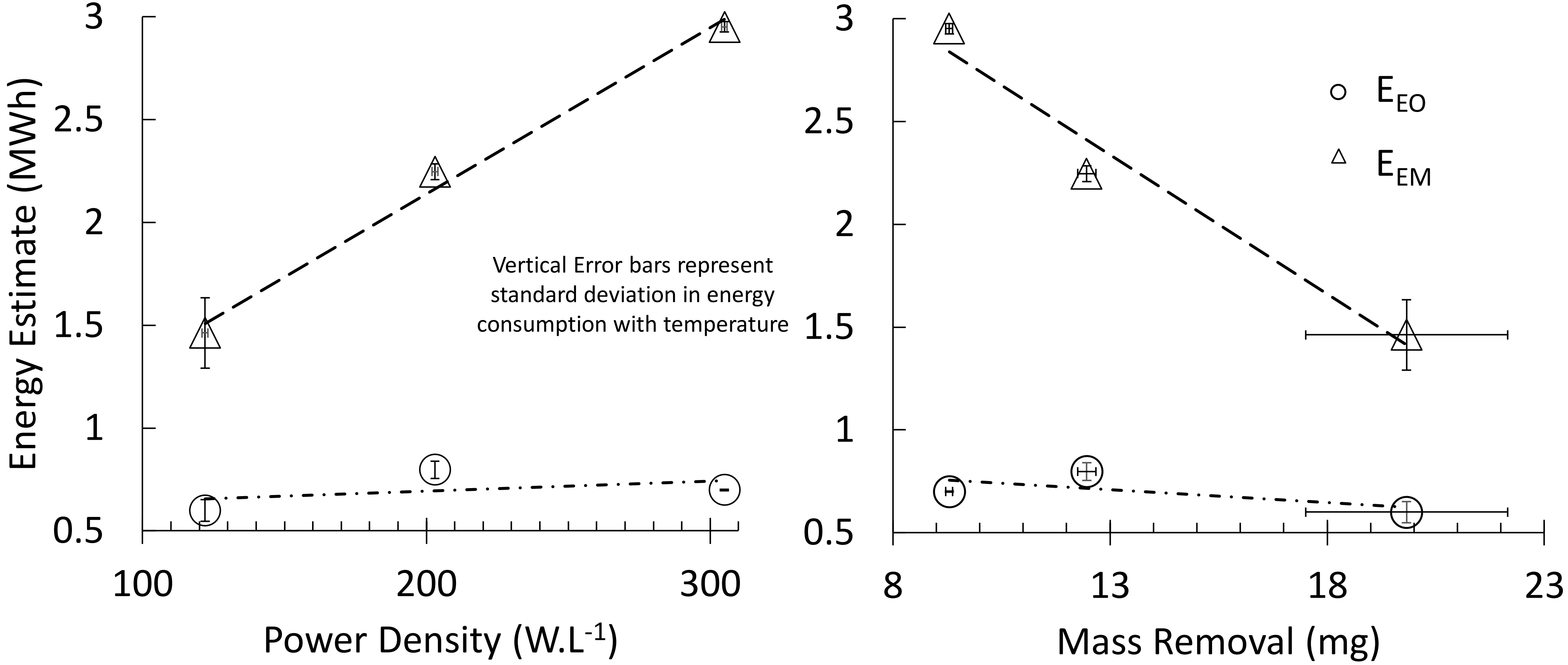
| Power Density ($W.L^{-1}$) | Volume (L) | Performance Characteristics | +TOP T = 25 °C | +TOP T = 15 °C | -TOP T = 25 °C | -TOP T = 15 °C |
|---|---|---|---|---|---|---|
| **122** | 54 | Cumulative k × $10^3$ ($min^{-1}$) | 4.65 | 3.02 | 4.54 | 3.09 |
| | | $E_{EM}$ ($MWh.g^{-1}$) | 1.29 | 1.63 | 2.86 | 3.35 |
| | | $E_{EO}$ ($kWh.m^{-3}.order^{-1}$) | 546.97 | 652.05 | 559.10 | 822.93 |
| | | Energy Consumed (kWh) | 28.60 | | | |
| | | Mass Removed (mg) | 22.15 | 17.50 | 9.99 | 8.54 |
| **203** | 33 | Cumulative k × $10^3$ ($min^{-1}$) | 4.85 | 5.39 | 4.8 | 5.54 |
| | | $E_{EM}$ ($MWh.g^{-1}$) | 2.29 | 2.21 | 4.93 | 4.68 |
| | | $E_{EO}$ ($kWh.m^{-3}.order^{-1}$) | 839.41 | 755.08 | 847.33 | 746.54 |
| | | Energy Consumed (kWh) | 28.00 | | | |
| | | Mass Removed (mg) | 12.25 | 12.68 | 5.68 | 5.99 |
| **305** | 22 | Cumulative k × $10^3$ ($min^{-1}$) | 8.60 | 8.51 | 8.61 | 8.48 |
| | | $E_{EM}$ ($MWh.g^{-1}$) | 2.98 | 2.93 | 6.27 | 6.53 |
| | | $E_{EO}$ ($kWh.m^{-3}.order^{-1}$) | 696.13 | 702.74 | 695.26 | 705.82 |
| | | Energy Consumed (kWh) | 27.44 | | | |
| | | Mass Removed (mg) | 9.22 | 9.38 | 4.38 | 4.20 |




Error bars represent standard deviation in energy consumption with temperature

Only $ 3.14 for 8 h operation @ $ 0.12/kWh = $0.22/gal or **$58/m³**

# $E_{EO}$ for Low PFAS Load & $E_{EM}$ for High PFAS Load




$$E_{EM}(kWh.g^{-1}) = \frac{P \times t \times 10^3}{V(C_i - C_f)}$$

Depends on Mass removal

$$E_{EO}(kWh.m^{-3}.order^{-1}) = \frac{P \times t \times 10^3}{V \times log(C_i/C_f)}$$

Depends on Pseudo-first-order rate

# Key Takeaways

- Ultrasonic irradiation rapidly defluorinates single PFAS and complex mixtures
- Degradation rates are controlled by the availability of PFAS in the ultrasonic cavity
- $k\_carboxylates > k\_sulfonates$
- $k\_(long{-}chain) > k\_(short{-}chain)$
- No short chained terminal PFAS were produced from AFFF or IDW sonolysis.
- Salinity affects PFAS surface activity; consequently degradation rates.
- 600 kWh/order/$m^3$ consumed for 22.15 mg PFAS mass removal @122 W/L
- Ultrasonic treatment can stoichiometrically defluorinate PFAS in mixtures, such as AFFF and IDW → more cost-effective for concentrated wastes, brines; little to no production of disinfection by-products.