



PFAS TREATMENT & DESTRUCTION: STATE OF THE PRACTICE

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RECENT PFAS TREATMENT LITERATURE REVIEW

PFAS TRADITIONAL TREATMENT TECHNOLOGIES

US EPA Reported Traditional PFAS Treatment Technologies

- Landfill Storage / Solidification/Disposal of Solid Waste Containing PFAS
- Underground Injection of PFAS Liquid Waste Via UIC Well Systems
- Liquid Phase Sorption by Granular Activated Carbon (GAC) or Ion Exchange (IEX)
- Liquid Phase Membrane Separation - Reverse Osmosis (RO); NanoFiltration Systems
- Chemical Oxidation by Addition of PFAS Treatment Reagents
- Thermal Oxidation, Incineration, Pyrolysis of PFAS Concentrates

PFAS KEYWORD HITS IN LITERATURE REVIEW – 2008 TO 2022

Over 2,470 Literature Papers and Patents Included

Inner ring – reported media

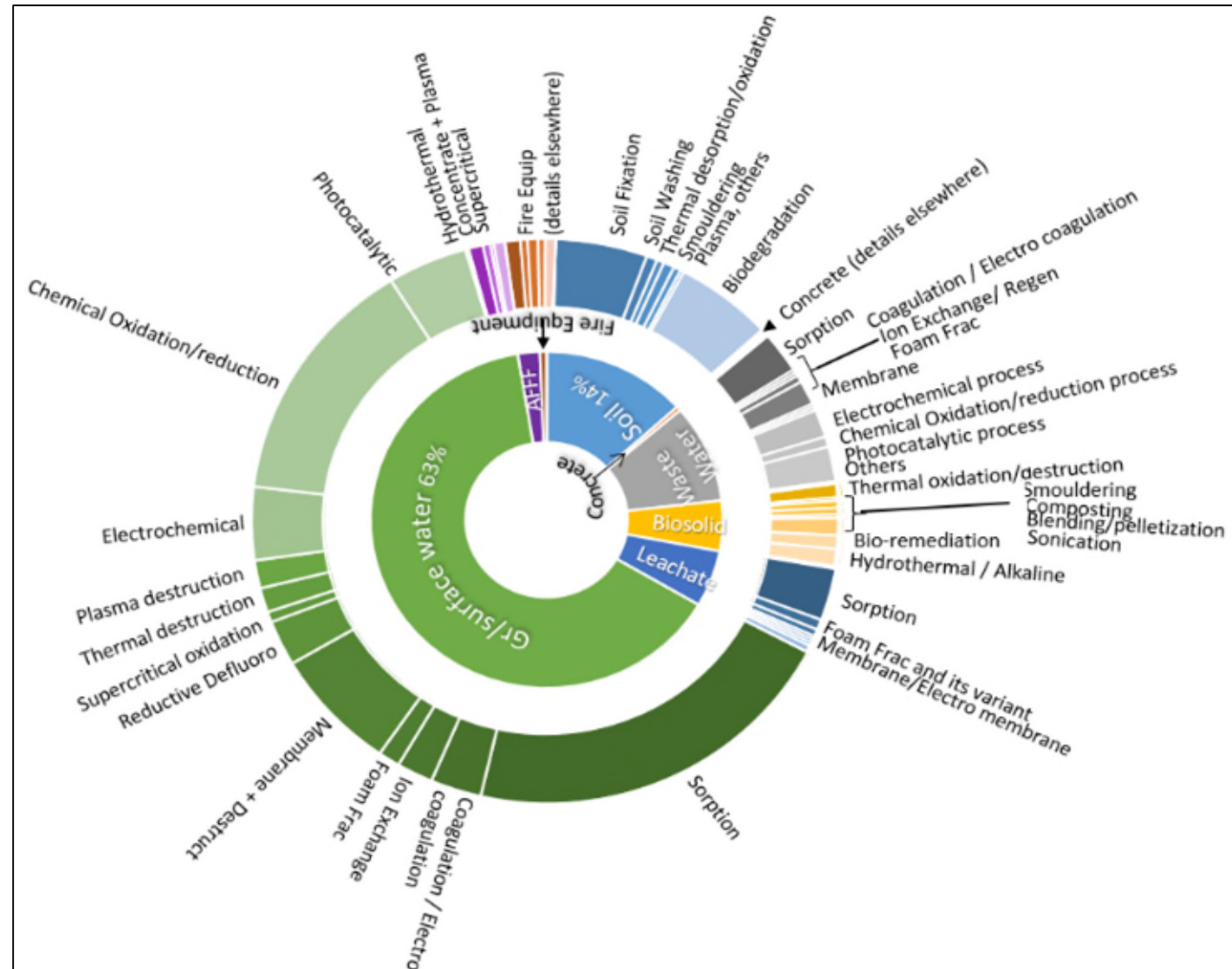
Water/groundwater represented 63% of the returns in the literature search

Soils represented 14%

All other media combined represented 23% of returned results

Outer ring – reported technology

- Sorption
- Chemical oxidation
- Membrane separation
- Electrochemical
- Thermal Oxidation/Incineration



PFAS TECHNOLOGIES REPORTED BY MEDIA (2008-2022)

	Groundwater or Surface Water	Wastewater (municipal or industrial)	Leachates	AFFF Concentrate and Equipment	Soils	Bio-solids	Spent Media	Subtotals
Sorption and Ion Exchange	115	13	15				5	148
Chemical oxidation/degradation	64	3			6			73
Membrane (RO/NF/electro membrane)	35	7	2					44
Microbial Bioremediation (anaerobic/aerobic)	1		1		27	9		38
Electrochemical oxidation (w/wo oxidant)	21	8	2		4			35
Photocatalytic oxidation/degradation	22	10	1					33
Concrete/Soil Fixation/solidification					30			30
Thermal destruction	7		1		5	4	3	20
Phytoremediation	4	1			15			20
Coagulation/Electro-coagulation	14	2		1	1			18
Reductive defluorination	13							13
Other, aqueous technologies	17	4	5	11				37
Other, solid media technologies					24	11	7	42
Subtotals:	313	48	27	12	112	24	15	551

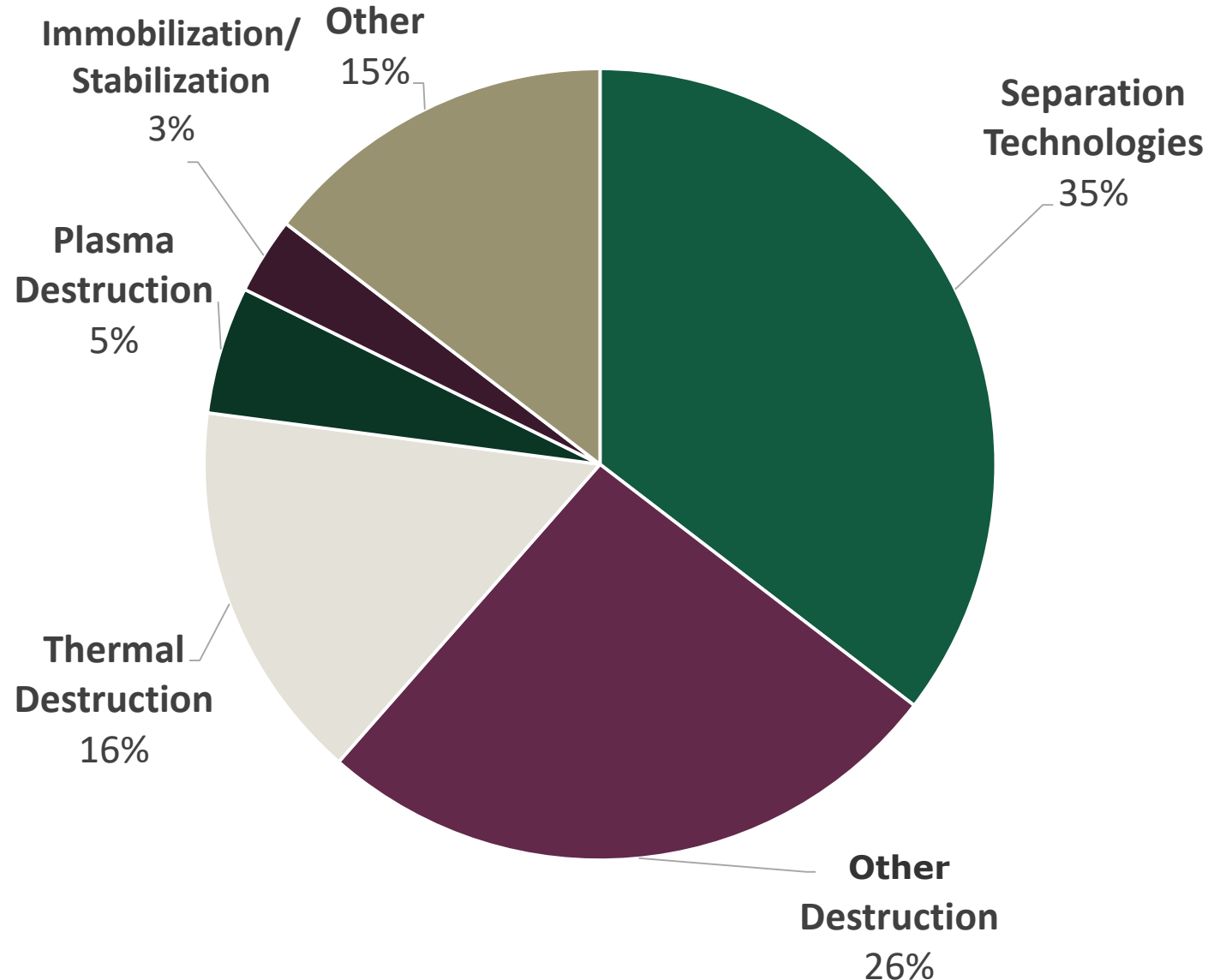
NUMBER OF U.S. PROJECTS BY PFAS REMEDIAL FUNDING

GAC, ion exchange, and membrane separation remain as the default technologies; new separation methods (eg, foam fractionation) are rapidly appearing in full scale projects

Lab-scale PFAS destruction technologies appear in the scientific literature as early as **2003**

Field-scale remediation activities begin appearing in literature around **2017**

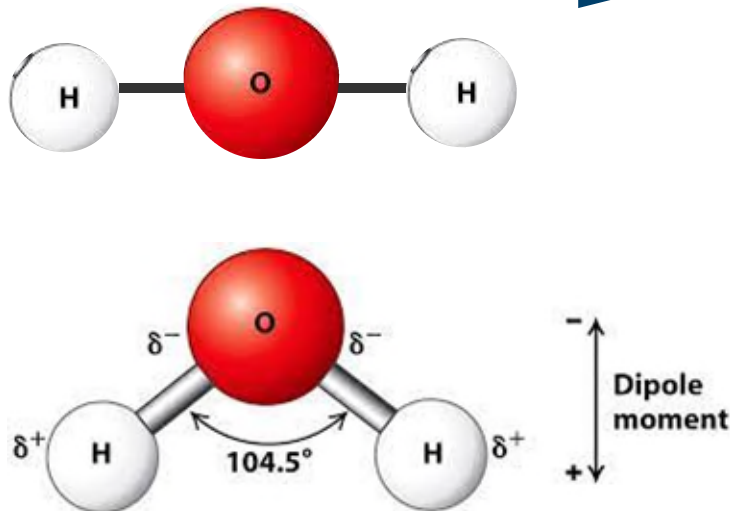
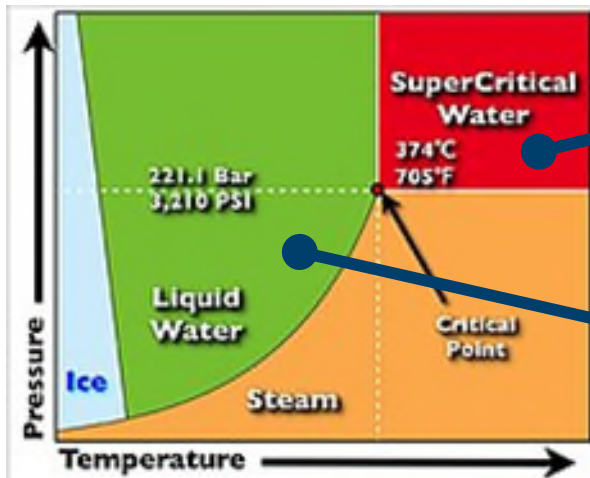
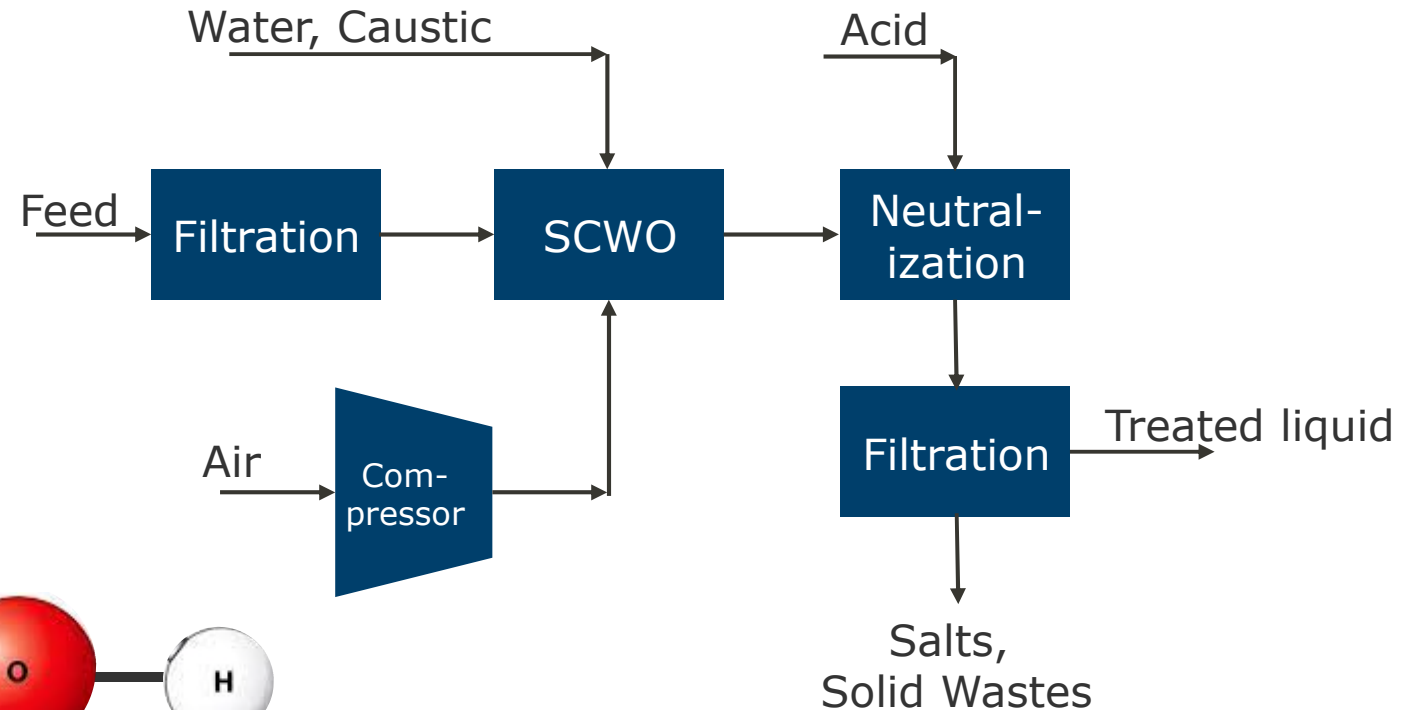
Early work began with chemical and electrochemical destruction; however, hydrothermal, supercritical water oxidation, and plasma processes have more recently entered the market



SELECT RECENT PFAS DESTRUCTION TECHNOLOGY DESCRIPTIONS

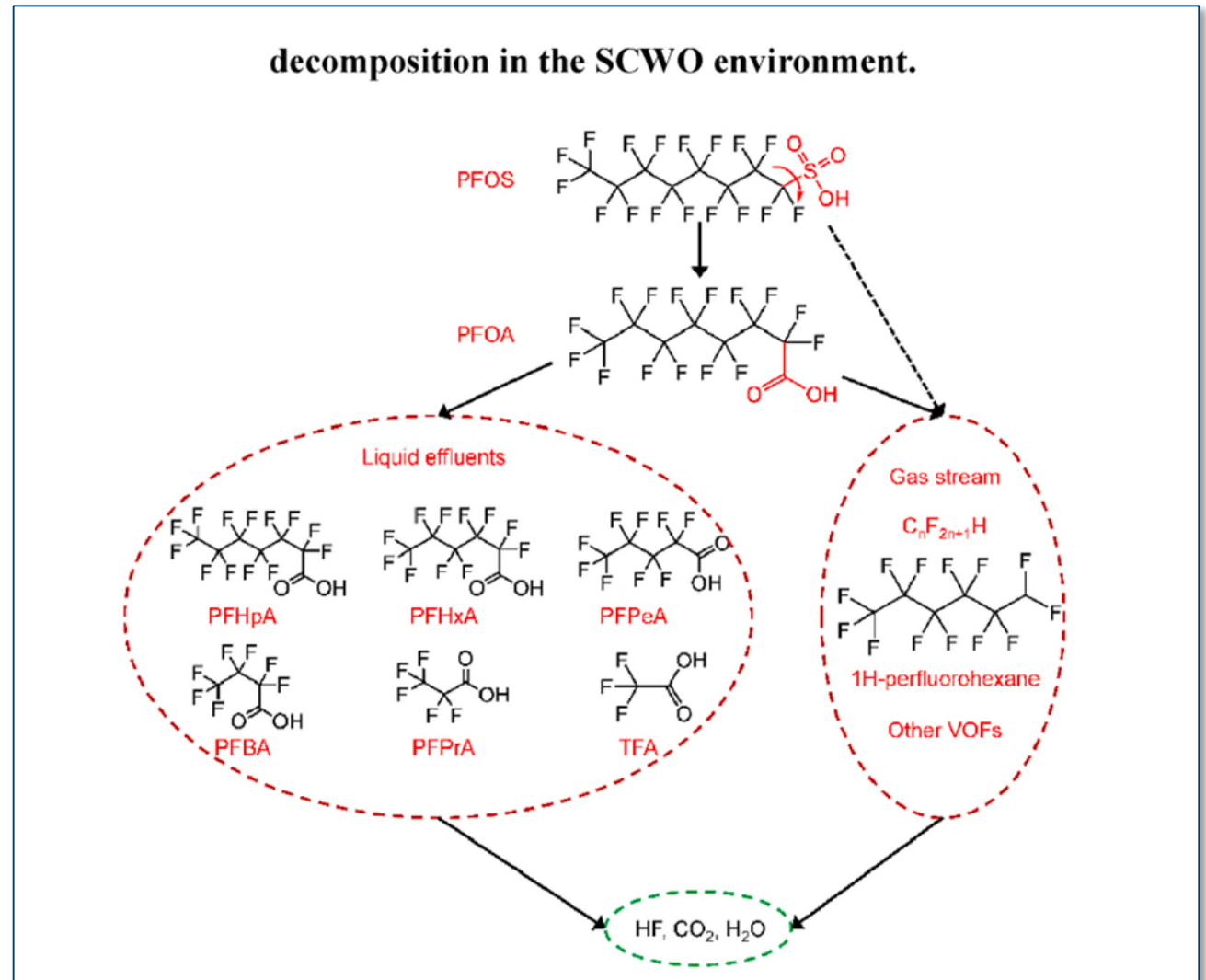
SUPERCritical WATER OXIDATION

- Solution is heated to $>374^{\circ}\text{C}$ (410°C - 600°C) and >221 bar to reach supercritical water condition
- Water becomes non-polar, solubilities invert (salts become insoluble, organics become highly soluble)
- $>95/99\%$ treatment across all PFAS types
- Short residence times/high processing rates
- Above $\sim 600^{\circ}\text{C}$, SO_x and NO_x can be generated
- Requires initial energy input to reach required temperature and pressure, and ongoing energy input to compressor



SUPERCRITICAL WATER OXIDATION (CONT'D)

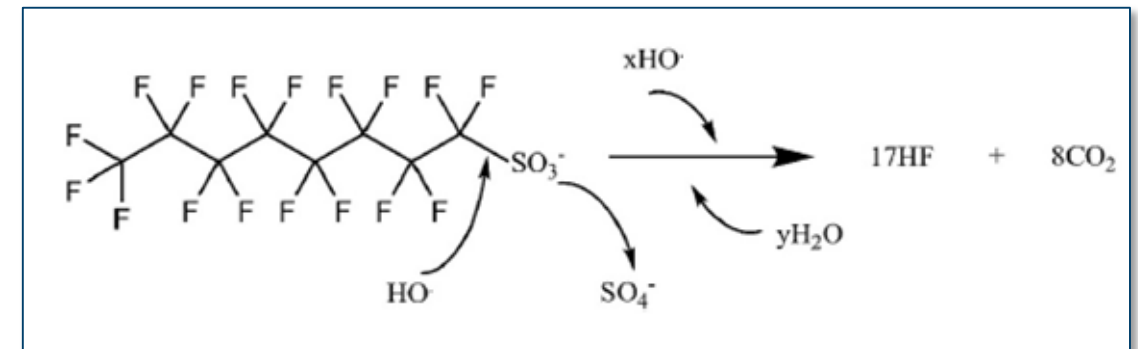
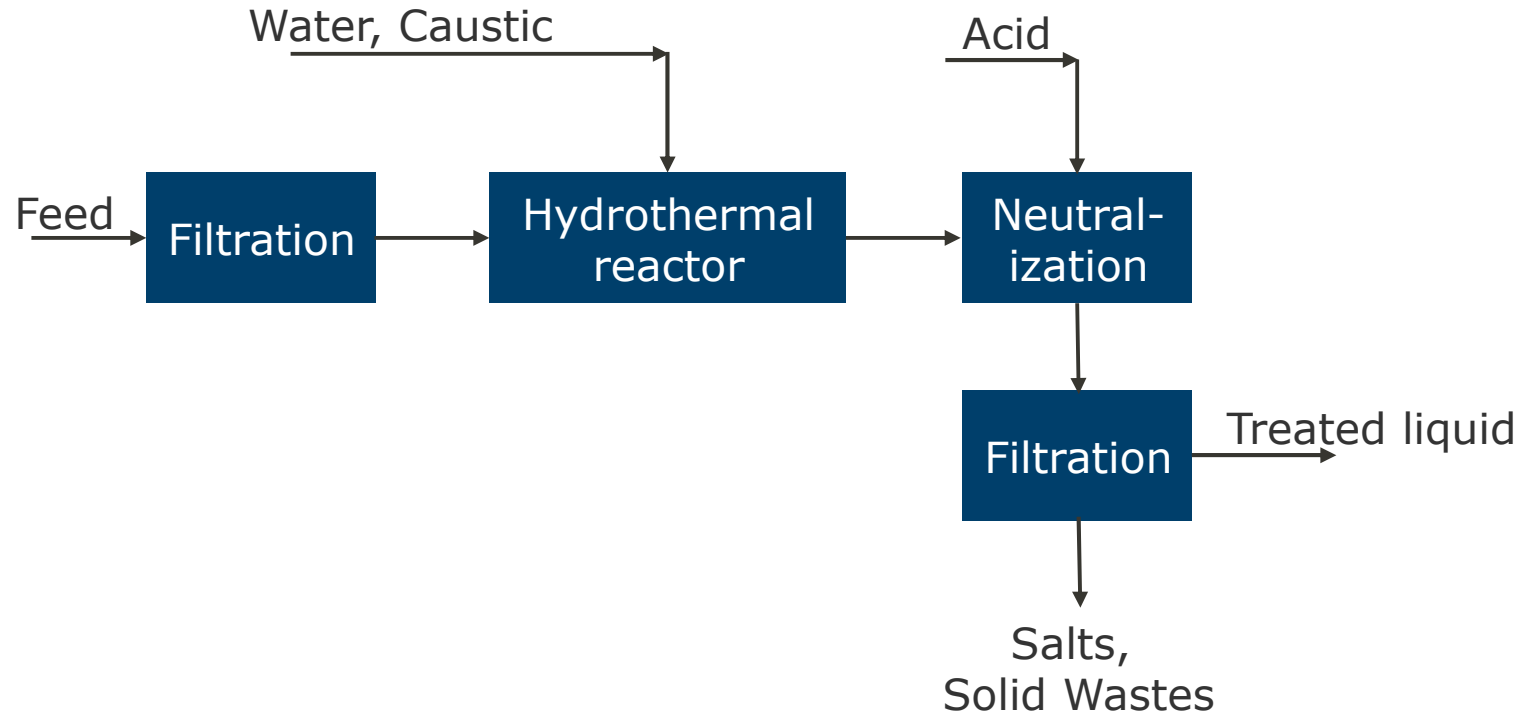
- Feed rate of oxidizable organic molecules must be controlled and moderated; SCWO reactor itself can become self-sustaining with sufficient organics in feed stream
- Produces sulfuric, hydrochloric, and other acidic species; requires addition of alkalinity, which aids overall destruction of PFAS
- End products are treated effluent, off gases, NaF, CaF, and other waste salts, CO₂, and H₂O
- Secondary air treatment technology might be necessary if gaseous PFAS compounds are evolved from the SCWO process.
- Potential for trifluoroacetic acid (TFA) production



From: Li Et Al. (2023), Chem Eng J, Vol. 451(4)
<https://doi.org/10.1016/j.cej.2022.139063>.

HYDROTHERMAL ALKALINE TREATMENT

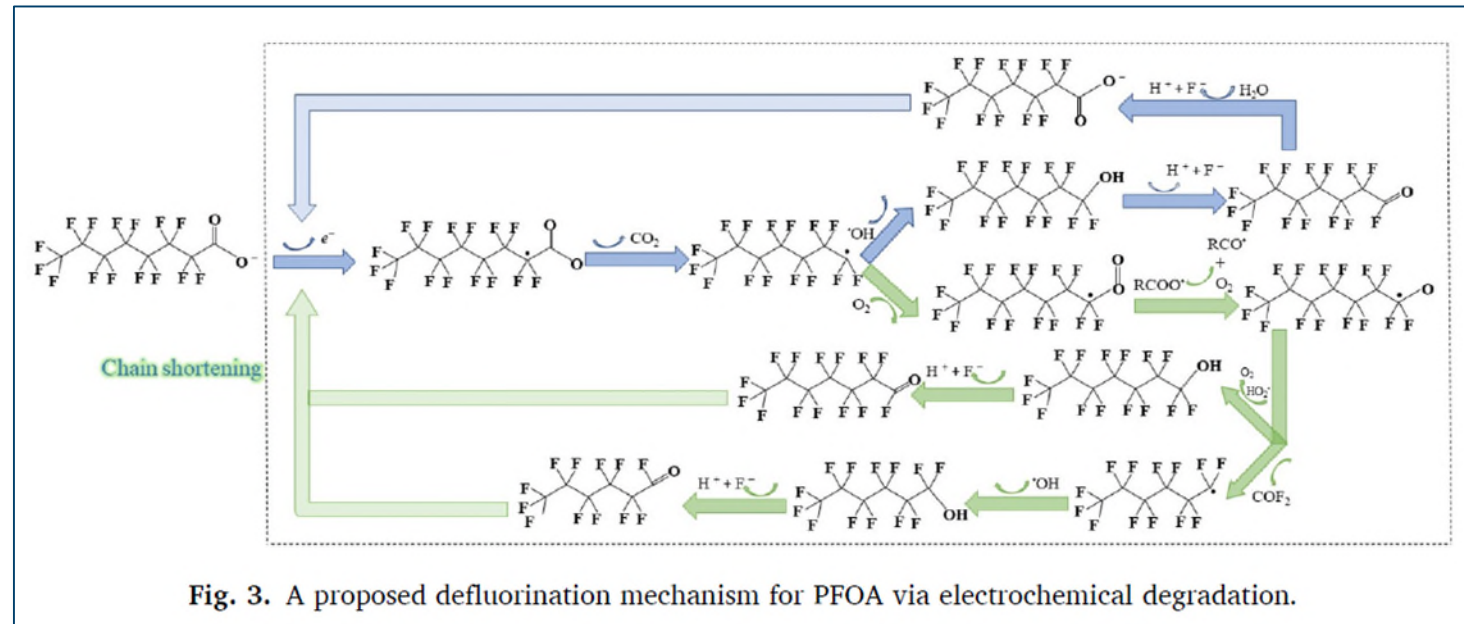
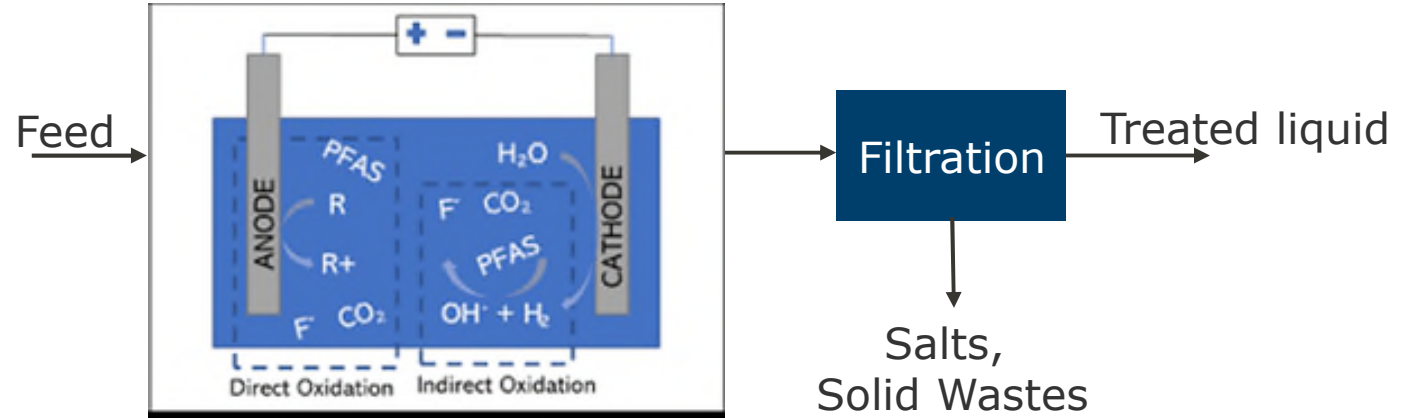
- Solution is heated to 350°C and 160-210 bar, below criticality, with 5 M-NaOH for excess nucleophile
- Operating point (temp, pressure, NaOH feed) is essentially constant regardless of feedstock TDS, organic content, or PFAS loading
- Typically 99.9% destruction, independent of feed strength
- Longer residence time than SCWO, but faster kinetics than plasma or EC Ox
- Elevated TDS can be beneficial (PFAS more hydrophobic)
- Greatest operational efficiency reported ~1 mg/L, however 100s of mg/L have been treated
- Effective destruction of trifluoroacetic acid and trifluoromethane reported



Jianna Et Al.(2022), Chemosphere, Vol 307(2)
<https://doi.org/10.1016/j.chemosphere.2022.135888>

ELECTROCHEMICAL OXIDATION

- Electrical application of sufficient energy density to overcome C-F bond
- Oxidation at anode via direct transfer of electrons, with indirect degradation via electroactive species (i.e., OH^\bullet)
- Can include phased polarity reversal
- Destruction efficiencies of 90 to >99% PFOS and PFOA reported
- Operates at ambient temperature and pressure, but can have extended residence times (hours)
- Key operational parameters are electrode materials, electrolyte composition, and pH
- Treatment rate is dependent on power density and electric current per unit area per unit time – up to break-down limits of electrolyte solution
- Reaction chemistry is diffusion limited and slows as reaction proceeds
- Potential for:
 - Buildup of mineral deposits on anode
 - Formation of perchlorate and other inorganic by-products
 - Generation of O_2 , H_2 , and volatile by-products; can require mist collection and/or GAC for final gas phase polishing



REDUCTIVE PHOTOCHEMICAL DEFLUORINATION

- Production of solvated electrons via UV excitation of organic electron donor
- Solvated electron is one of the strongest nucleophiles in aqueous solution
- Low power requirements, ambient operation conditions
- Destruction of short-chain PFAS in bench and pilot trials
- PFAS feed concentration "sweet spot" is ~0.3-300 mg/L, "too low" matters more to treatment efficiency than "too high"
- Recycle ratio can be varied readily and used to adjust destruction efficiencies to meet treatment goals
- High (%-level) TDS or low UV transparency can decrease overall performance

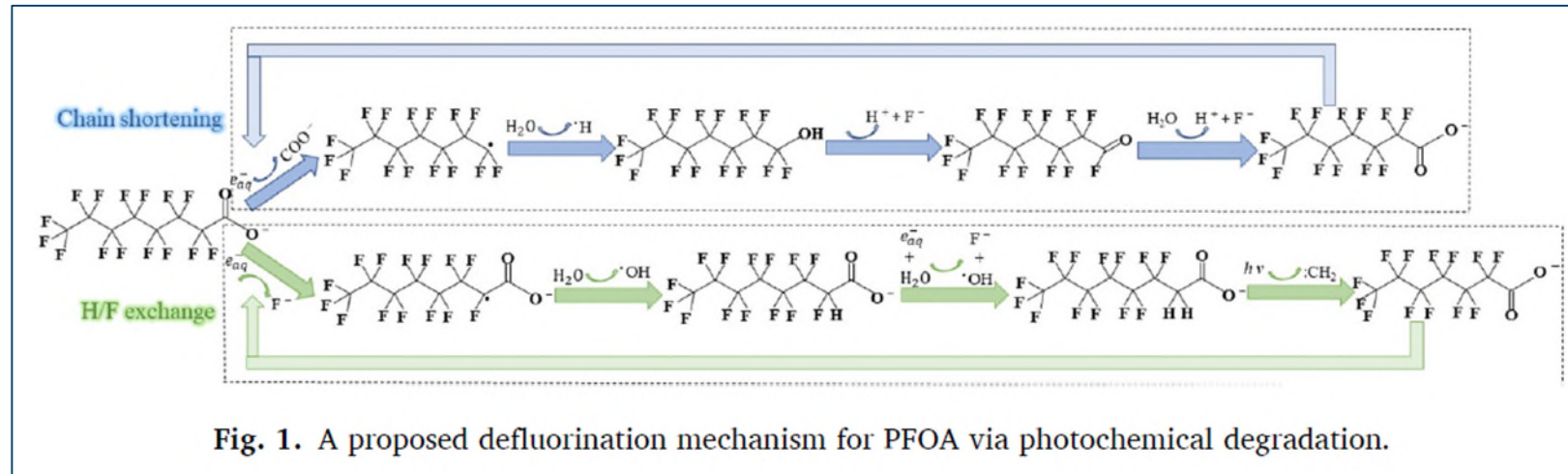
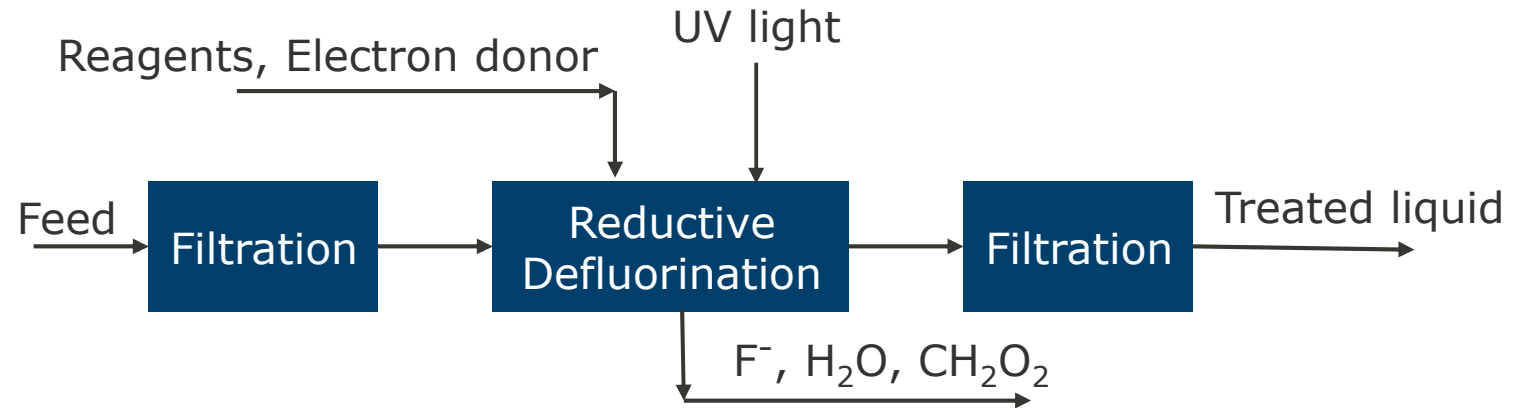
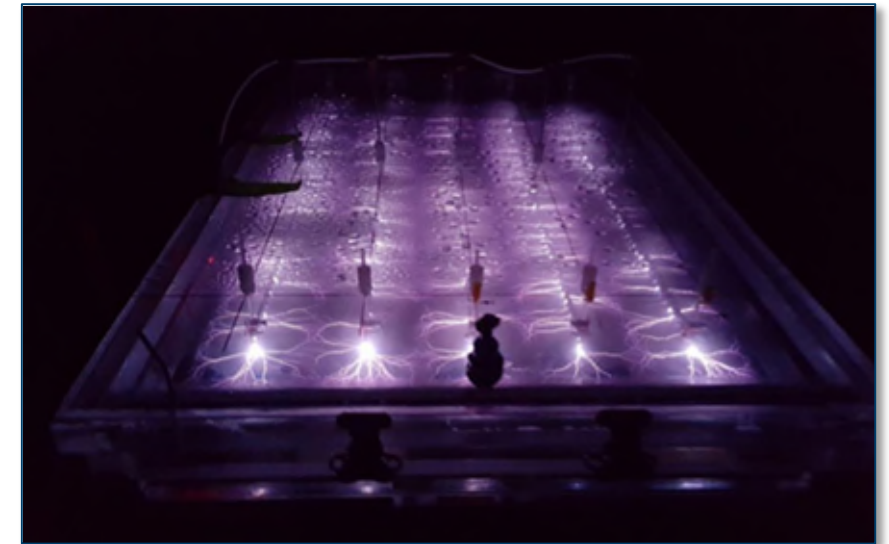
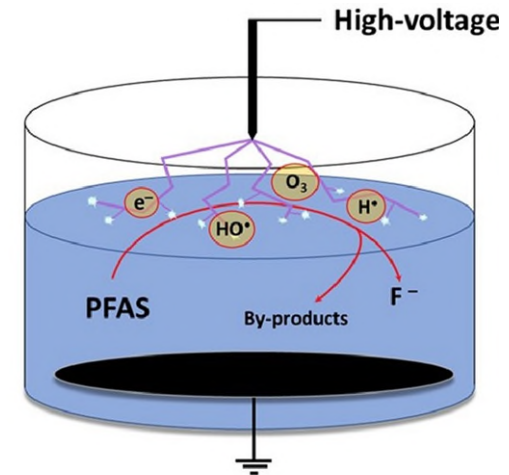


Fig. 1. A proposed defluorination mechanism for PFOA via photochemical degradation.

Deng et al. (2021), Chemosphere, Vol. 283
<https://doi.org/10.1016/j.chemosphere.2021.131168>

NON-THERMAL (ELECTRICAL DISCHARGE) PLASMA

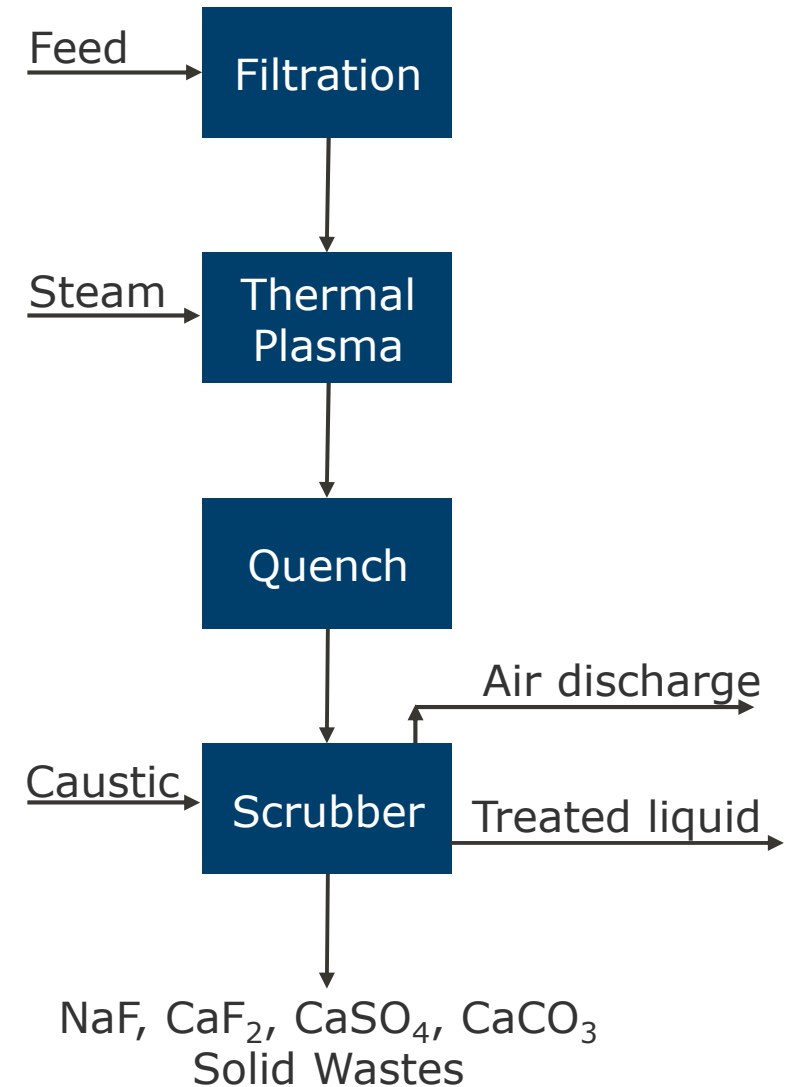
- Electron temperatures reach $>10,000^{\circ}\text{C}$, but bulk temperature and pressure is ambient
- Application of sufficient electrical energy to overcome C-F bond
- Upper electrodes above water surface, submerged lower electrode
- Simultaneous oxidation and reduction reactions via production of hydroxyl radicals and solvated electrons
- Reactions breaking C-F bonds primarily occur at the air-water interface
- TOC and other non-surfactant co-contaminants reported to not influence degradation efficiencies
- Can be used in batch and continuous systems
- Upper concentration limit of about 10,000 ug/L PFAS, above this excessive foaming may occur; lower range of 1 to 50 ug/L
- Limited removal of C_4 and shorter PFAS due to poor air-water adsorption and lower mass concentration at plasma-liquid interface
- Kinetics are relatively slow
- Solution conductivity modulated to ensure effective discharge



Plasma Research Laboratory, Clarkson University

THERMAL PLASMA

- Gases heated such that electrons have sufficient energy to separate from nuclei, leaving bare nuclei (4th state of matter)
- Temperatures >10,000°C in the arc itself, >5,000°C in center of discharge, and ~2,500°C within reaction zone; reactor pressure is 1 atmosphere
- Disintegrates PFAS to F, C, H, O, S atoms, ions, and radicals
- As elemental species move away from arc zone they lose energy and reform to stable compounds
- Steam (2H + O) plasma provides excess of H, favoring production of HF; carbon and sulfur reform to CO₂ and SO_x
- Complete breakdown of short chain PFAS species, precursors, and co-contaminants
- Has been shown to destroy PFAS in presence of other organic and inorganic constituents (up to 5,000 mg/L NaCl); resilience to changes in the feed quality
- Acid gas products (HF, HCl, SO_x) are removed from exit gases by simple lime or caustic scrubbing, generating NaF and/or CaF₂ from liberated fluorine; CaSO₄ and CaCO₃ from excess CO₂



PFAS TECHNOLOGIES REPORTED RECENTLY (2023-2024)

- **PFOS Treatment & Destruction Using Piezocatalytic Decomposition**

Andrea Veciana, et. al., "Breaking the Perfluorooctane Sulfonate Chain: Piezocatalytic Decomposition of PFOS Using BaTiO₃ Nanoparticles"; *Small Science*, 2024-8-28

- **Surface Activated Foam Fractionation for Hi-Volume Liquid Phase Separation (SAFF)**

www.pca.state.mn.us/news-and-stories/mpca-brings-cutting-edge-technology-to-minnesota-to-remove-pfas-from-water/31-October-2022

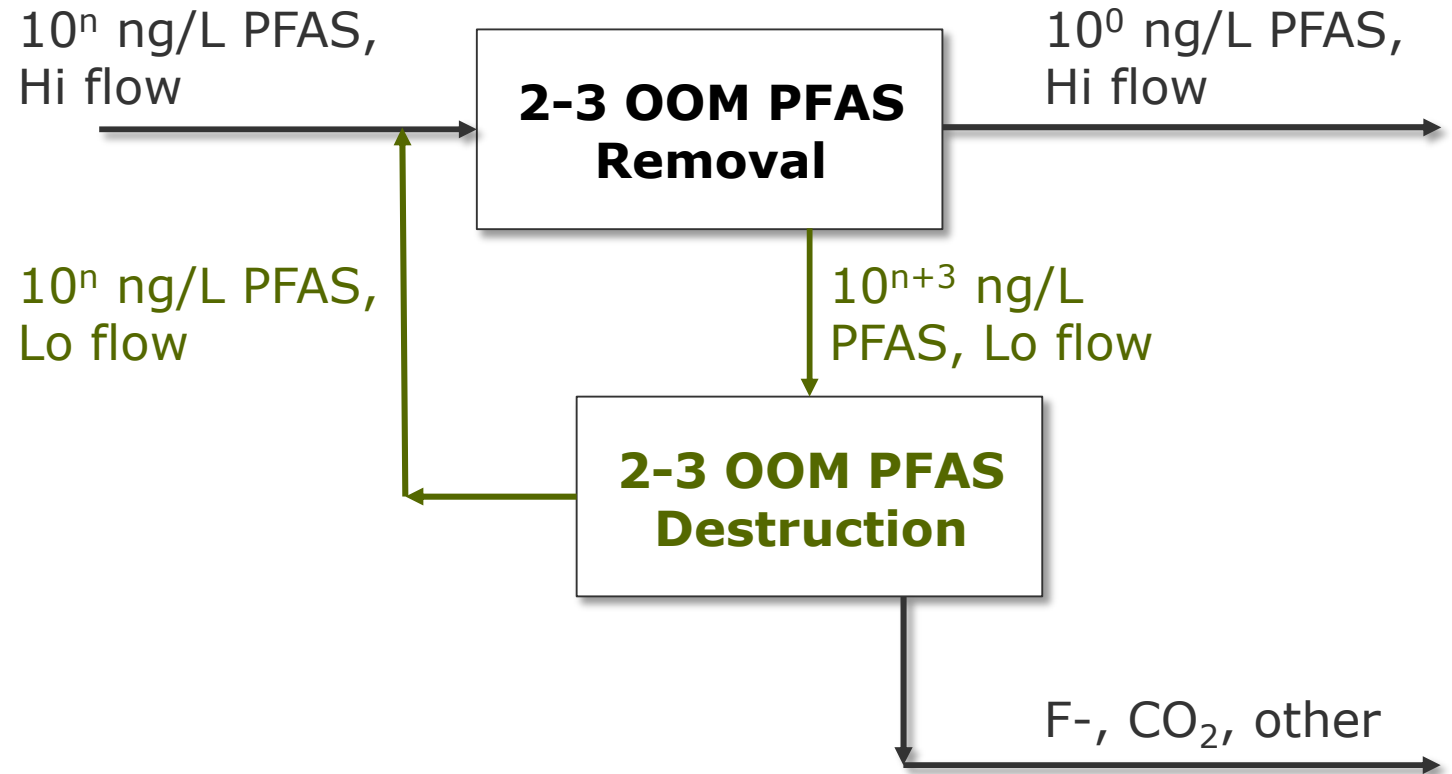
- **Heartland Concentrator (Leachate Treatment for Landfills with PFAS Issues)**

[www.heartlandtech.com/case-studies/Three Rivers Regional Landfill - Pontotoc, Mississippi](http://www.heartlandtech.com/case-studies/Three-Rivers-Regional-Landfill-Pontotoc-Mississippi)
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PFAS TECHNOLOGY IMPLEMENTATION PILOT/DEMONSTRATION/FULL SCALE

PFAS DESTRUCTION WILL REQUIRE A TWO-STEP PROCESS !

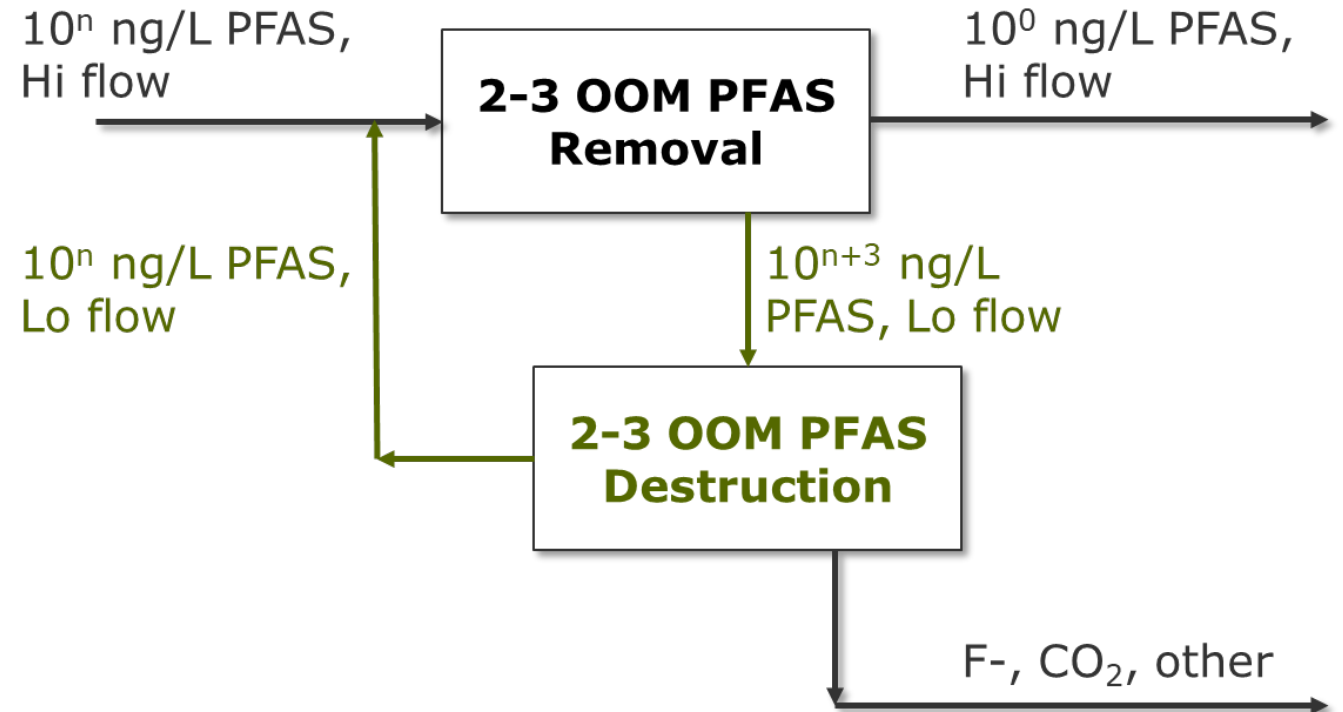
- 100 ng/L
= 2.4×10^{-10} M
= **146×10^{12}** individual molecules per liter
- Very few collisions! Kinetics dictate that reactions will be unrealistically slow
- Therefore a destruction step *must* be preceded by a concentration step
- OOM = Order of Magnitude



TWO THERMODYNAMIC HILLS TO CLIMB

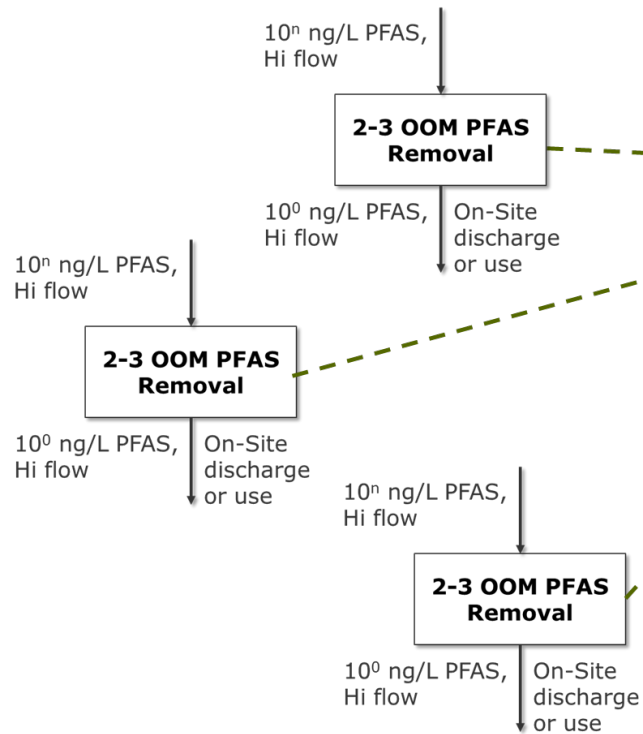
The two hills:

- Reversing the entropy of a very dilute solution
 - $\Delta S = R \cdot \ln(C_1/C_2)$
 - ≈ 33.6 kJ/mol, or \approx **112 kJ/mol** at 293K and 30% thermodynamic efficiency
- Overcoming the Gibbs free energy of the C-F bond
 - $\Delta G = 536$ kJ/mol of C-F bonds, or \approx **9,600 kJ/mol** of PFOA

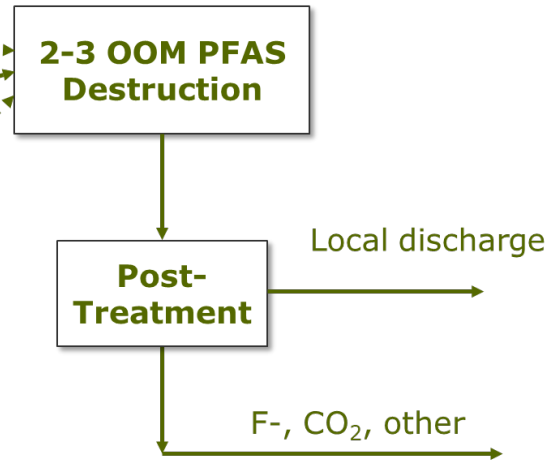


"HUB-AND-SPOKE" BUSINESS MODELS FOR PFAS TREATMENT

On-Site Concentration Step



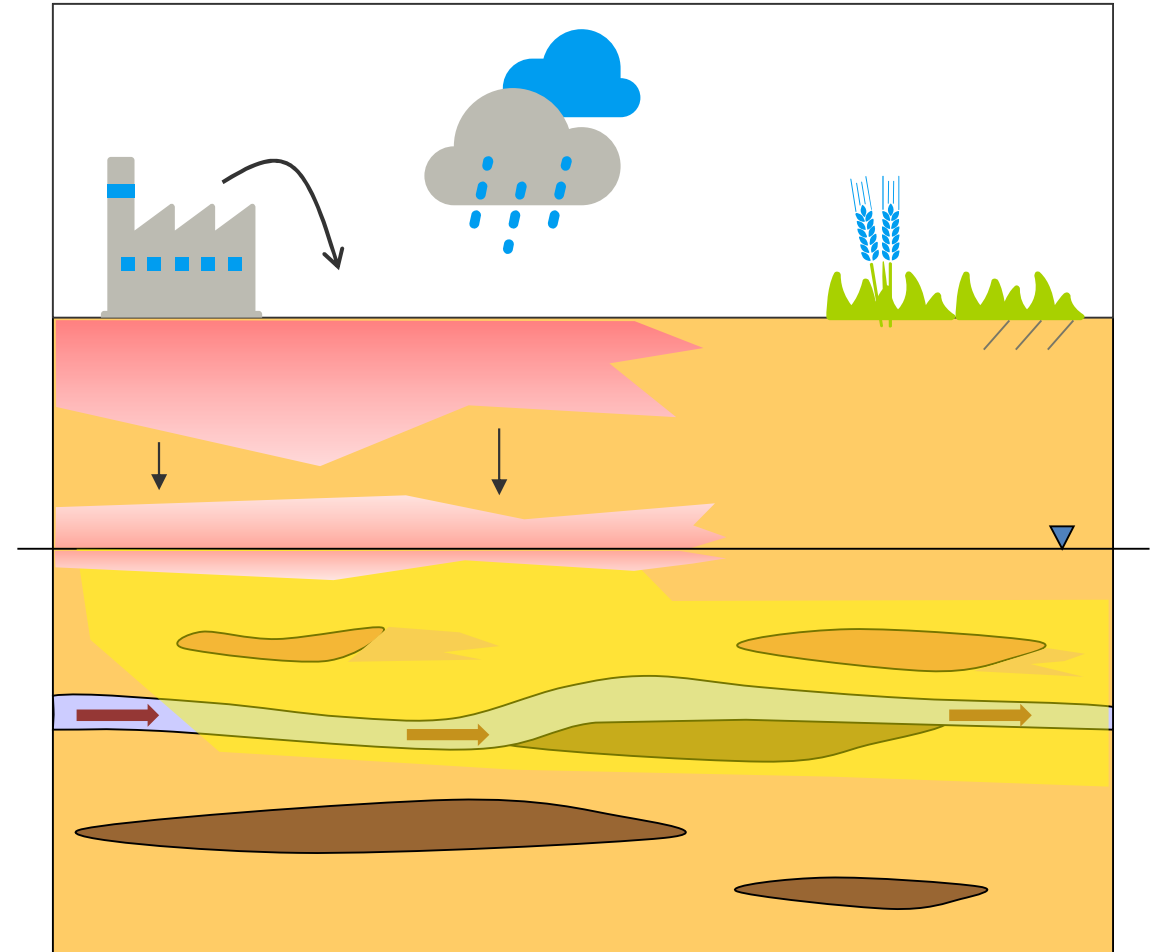
Off-Site Destruction



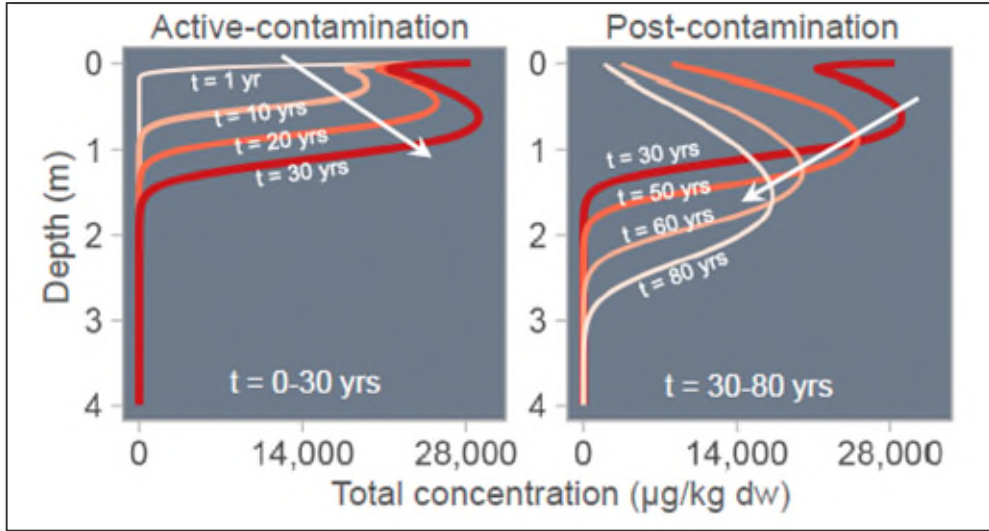
- Existing paradigm for GAC regen and haz waste market
- PFAS as Haz Substances may prohibit on-site treatment
- Very low waste volumes for shipping methods & costs
- On-site concentration units less costly to Own & Operate
- Increase operational demand and efficiency with more expensive destruction units located off-site
- OOS = Order of Magnitude

PFAS SITE REMEDIATION - BACK TO PUMP-AND-TREAT?

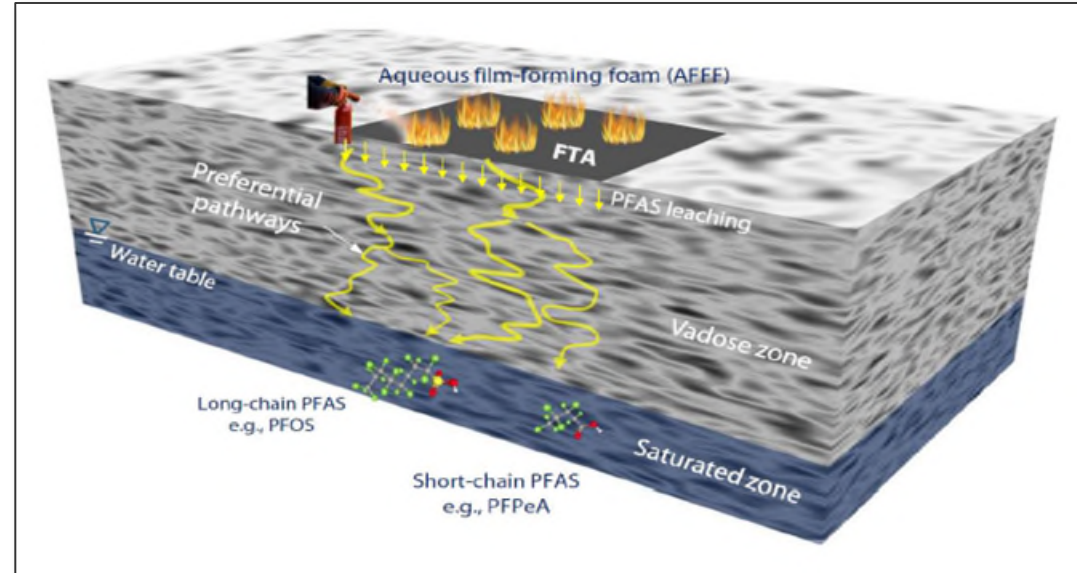
- PFAS release, transport, and fate behaviors differ from classical contaminants in key ways
- Surficial deposition due to stormwater runoff, fire training, and regional-scale impacts via air deposition
- Significant storage in vadose zone
- Self-assembly at air-water interface (capillary zone)
- Multi-component release by definition



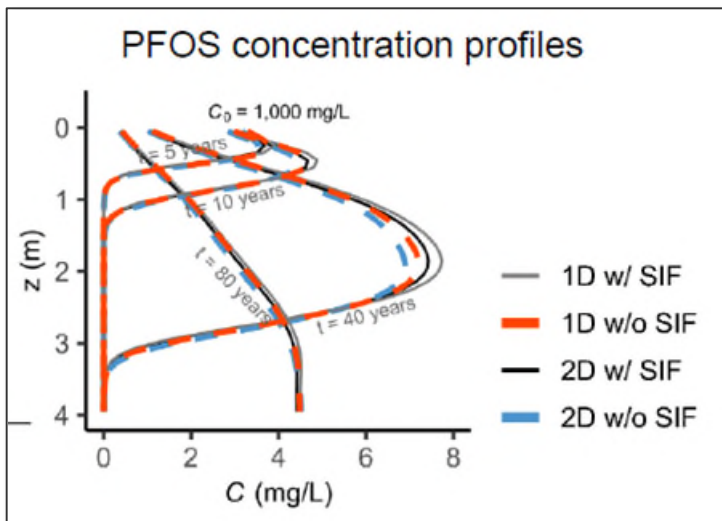
PFAS FATE & TRANSPORT - BACK TO PUMP-AND-TREAT?



Guo Et Al. (2020), *Wat Res Res.* 56(2)
[//doi.org/10.1029/2019WR026667](https://doi.org/10.1029/2019WR026667)



Zeng and Guo (2023), *Geophys Res Letters* 50(8)
[//doi.org/10.1029/2022GL102655](https://doi.org/10.1029/2022GL102655)



Air-water interfacial adsorption leads to strong retention of long-chain PFAS in geological vadose regimes [SIF=Surfactant Induced Flow] Effects in 1D/2D Models

Heterogeneity (=preferential pathways) results in saturation of pore space and “early” PFAS arrival times

KEY TAKE-AWAYS

PFAS Treatment & Destruction: State of the Practice 2024

1. Surface and groundwater represented 63% of the returns in the recent literature search – focus on drinking water PFAS contamination scenarios; AFFF releases
2. 2003: Lab-scale PFAS destruction technologies begin to appear in literature
3. 2017: Field-scale remediation activities begin to appear (eg, AFFF remedial sites)
4. More recently cited projects to 2024 were found to be geared towards destructive technologies, however, most recent demo/full scale projects focused on separation technologies (eg, IEX, GAC, SAFF)
5. SCWO, HALT, ElectroOx, Reductive Defluorination, and Thermal and Non-Thermal Plasma were evaluated further during the literature review as destruction options
6. PFAS destruction will likely require a separation/preconcentration step in most treatment & destruction cases, resulting in two “thermodynamic hills”
7. “Hub-and-Spoke” appears to be favorable business model among treatment suppliers
8. Challenges remain for “PFAS remediation” in the classical sense (ex-situ; in-situ) due to PFAS fate & transport properties in soil & groundwater

KEY RECENT PFAS LITERATURE SOURCES (2023-2024)



PFAS Strategic Roadmap: EPA's Commitments to Action 2021–2024

**US EPA Interim Guidance on the Destruction and Disposal of
Perfluoroalkyl and Polyfluoroalkyl Substances and Materials
Containing Perfluoroalkyl and Polyfluoroalkyl Substances—
Version 2 (2024)**

INTERIM GUIDANCE FOR PUBLIC COMMENT APRIL 8, 2024

KEY RECENT PFAS LITERATURE SOURCES (2023-2024)



Technical/Regulatory Guidance

September 2023

Per- and Polyfluoroalkyl Substances (PFAS)



September 2023

Prepared By

The Interstate Technology & Regulatory Council (ITRC)

Per- and Polyfluoroalkyl Substances Team

THANK YOU !! QUESTIONS ?

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