Civil & Environmental Consultants, Inc.

Innovative Destruction Technologies for PFAS in Leachate

NEWMOA Technical Series

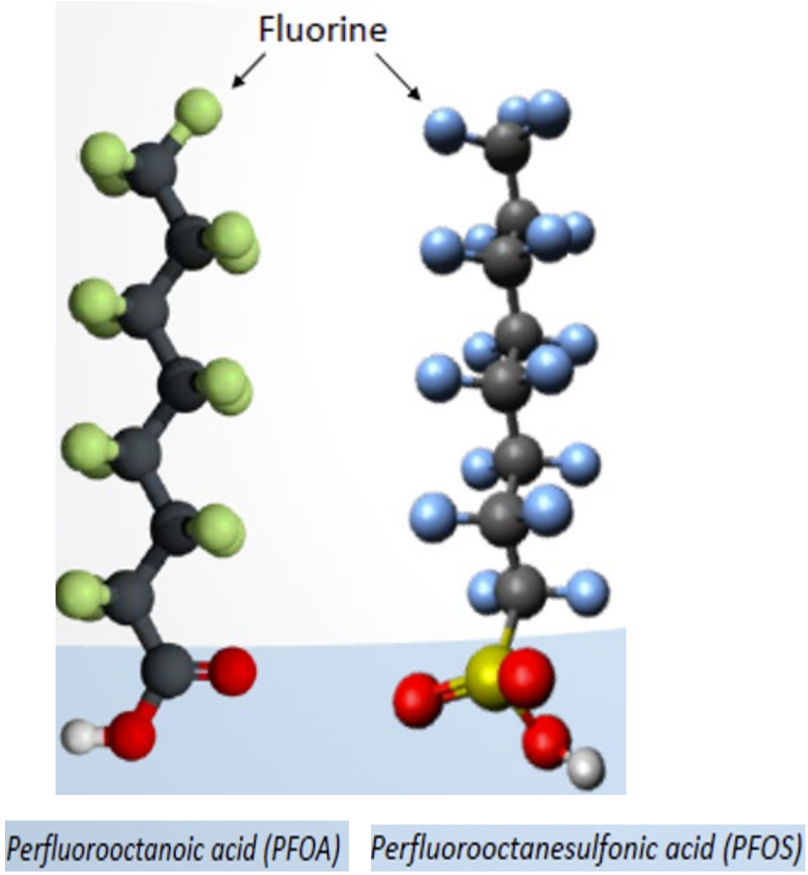
Ivan A. Cooper, PE, BCEE

Practical Implications for Industrial, Municipal, Solid Waste Operations, and Facility Development

April 6, 2022

Agenda

- Treatment Technologies
  - Segregation – Adsorption
  - Segregation – Physical/Chemical
  - Destruction
- Case Studies
- Summary



Ref: EPA

Treatment Technology Status

Field Implemented	Limited Application	Developing
• Full Scale Operation • Multiple Sites • Multiple Designers • Well Document by Peers	• Limited Sites • Limited Number of Designers • No Peer Review Literature	• Laboratory research • Bench Scale Studies • No Field Demonstrations

PFAS Segregation and Destruction

- Few Process are single unit operations
- Commercial Status – **Full Scale** / **Limited** / **Developing or Laboratory**

Segregation – Adsorptive	Segregation- Physical Chemical	Destructive
Activated Carbon	Reverse Osmosis/Nano/Ultra	Plasma
Granular	Foam Fractionation	Thermal
Colloidal	Deep Well Injection	Supercritical Oxidation
Ion Exchange	Cementitious encapsulation	Electrochemical
Polymers	Electrodialysis	Photochemical
Modified bentonite	Electrocoagulation	Oxidation/Reduction
		Persulfate
		Sonolysis
		UV Permutations
		Pyrolysis
		Mechanochemical Degradation

Treatment

- Different approaches for
  - Groundwater (Remediation or for Potable Use)
  - Leachate/Industrial Wastes
  - Residuals
  - Soils/Sludges
- Site Dependent
- Technologies Work on Some of the Compounds
- Long Chain vs. Short Chain PFAS vs. types of PFAS
- May Require Multiple Unit Operations

Current Water Technologies
(Usually Treatment Trains)

- Separation Technologies
- Most Amenable to Leachate Treatment
  - Activated Carbon
  - Resin
  - RO
  - Deep Well
  - Foam Fractionation
  - Thermal Evaporation

Source: NH Business Review 2018v

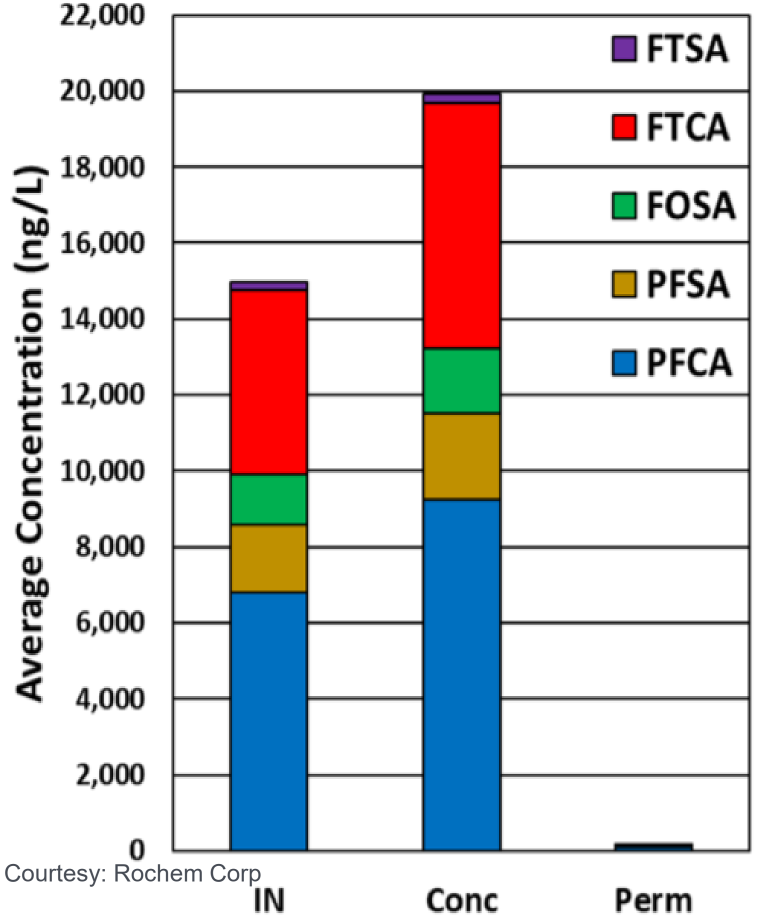
Source: Australian DOD 2018

Adsorbents for Polishing

- Groundwater and Drinking Water Adsorbents require pretreatment and residuals management
- Leachate even more so!
  - Activated Carbon – 15 - 20 minute EBCT – Remove organics, residuals?
  - Ion Exchange – 3 minute EBCT – Impacted by other constituents, residuals?
  - FluoroSorb – 7-10 minute EBCT, impacted by organics, iron, solidification?
- Capacity evaluated by bed volumes until exhaustion, ng/gm absorbent
- Look at individual constituents, some adsorbed better than others!

Reverse Osmosis Leachate Process Flow

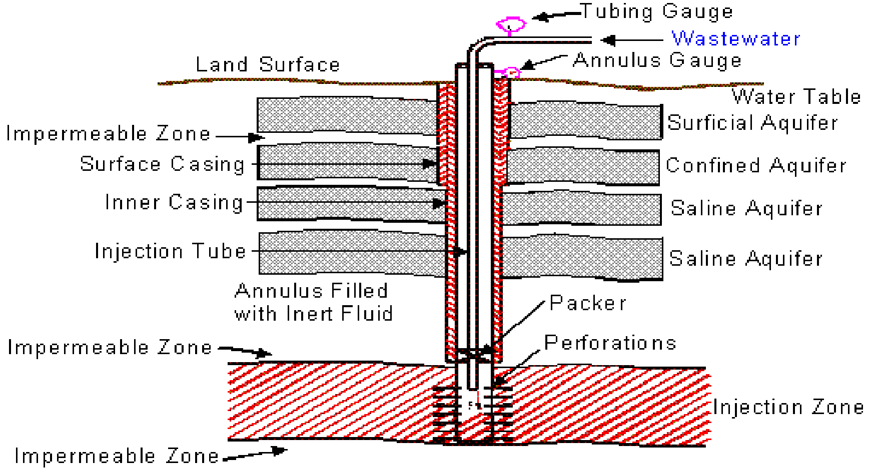
- Membrane Based Separation Process- 99.9% removal +/-
- Separates Water from Organic and Inorganic Compounds.
- Effluent for reuse or disposal.
- What to do with Reject???
  - Recirculation returns the contaminants to the landfill.
  - Solidification
  - Evaporation – Crystallization
    - Heat needed
    - Air Emissions
  - Other –
    - Electrochemical Oxidation
    - Plasma

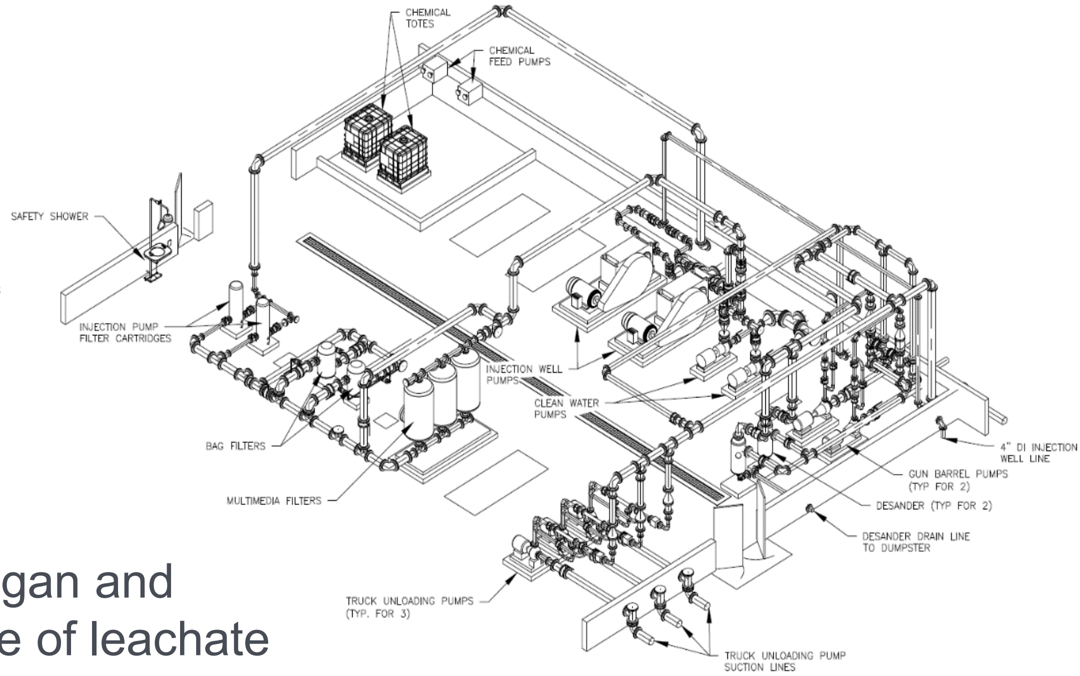


Courtesy: Rochem Corp

Deep Well Injection

- Depends on Geology, Receptors, Seismicity
- Long, Expensive Permit Time
- Pretreatment/Filtration, Ion Removal
- High Pressure Pumps

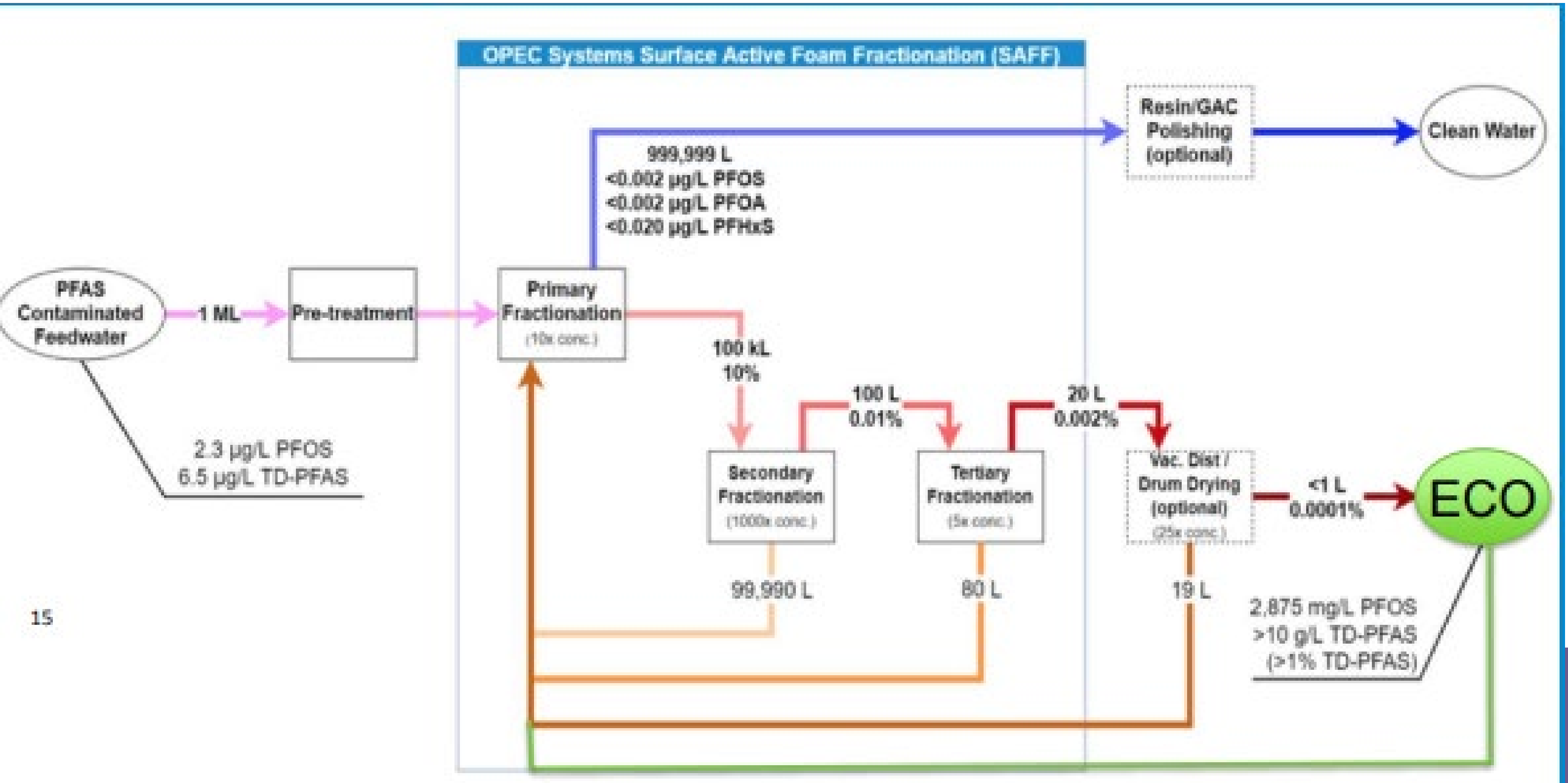




Sites in Michigan and Texas dispose of leachate in deep wells

Foam Fractionation

- Several manufacturers
  - OPEC; Evocra; Sanexen; others
- Air, Nitrogen, Ozone (Ozofractionation) separation on ozone/air microbubbles (as foam) due to PFAS surfactant properties
- Micro-bubbles extracts 95% long & short chain.



Courtesy Arcadis

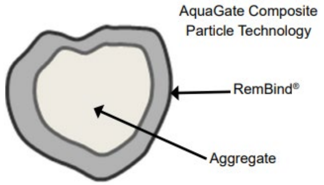
Evaporation/Concentration

- Thermal Evaporator
- ZLD – no discharge?
- Minimal/No odor
- PFAS in Emissions?
- Thermal Oxidizer

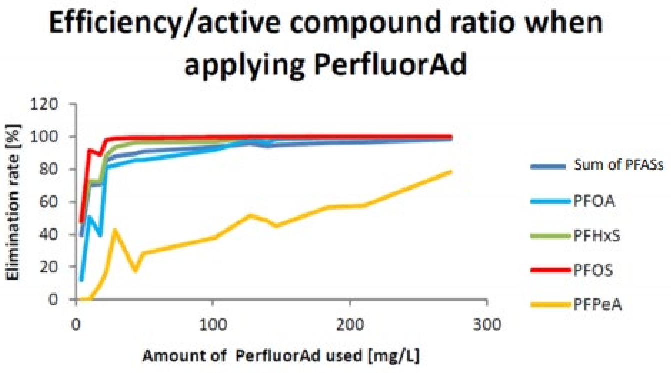
- Air Emissions
- Permitting
- Vapor Cloud

Adsorbents Possible for PFAS in Leachate

- Cetco – Fluoro Sorb – organically modified bentonite clay
- Tsang – Northwestern Univ.
  - Cyclopure – Northwestern Univ. and Purolite - sugar based dextrose molecule that can adsorb PFAS
    - Polymer networks attach to cellulose biocrystals in a packed bed similar to activated carbon. Flushing with chemical rinse results in a concentrated liquid – then disposal.
- Chalkers, Flinders Univ. (Australia)
  - Modified Waste Cooking Oil adsorbent
  - Canola oil polysulfide as support material for powdered activated carbon
  - 150 ppt to 23 ppt in lab test
- Rembind™ – soil & GW (Ziltek)
  - Act Carbon/Al Hydroxide/Organic Matter and additives
  - Short & Long chain removal – 60 min retention time
  - 2,000 ug/g PFOS
  - Remove by precipitation/filtration/act carbon polishing
- MatCare™
  - Blends of modified clay sorbents (CRC Care)
- PLUMESTOP™
  - Colloidal Liquid Activated Carbon (Regenesis)
- Others



Courtesy, Ziltek



Courtesy, Gary M. Birk, Tersus Environmental

Four Adsorbents

FLUORO-SORB®
200 adsorbent

GAC

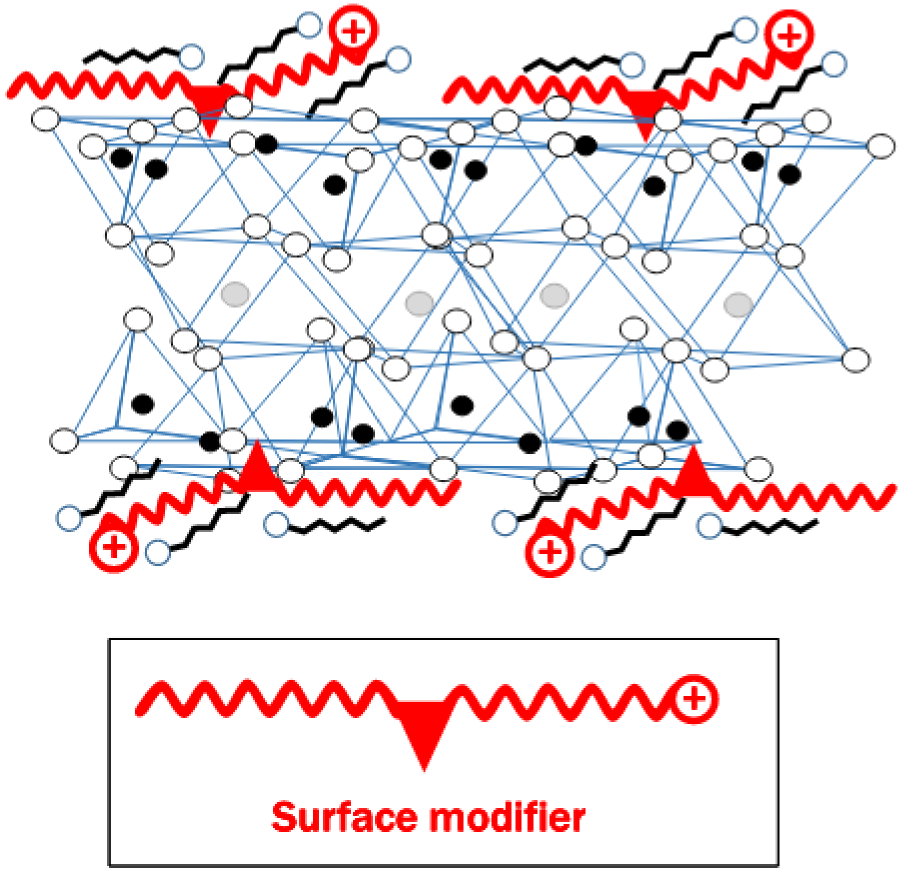
Hardwood Biochar

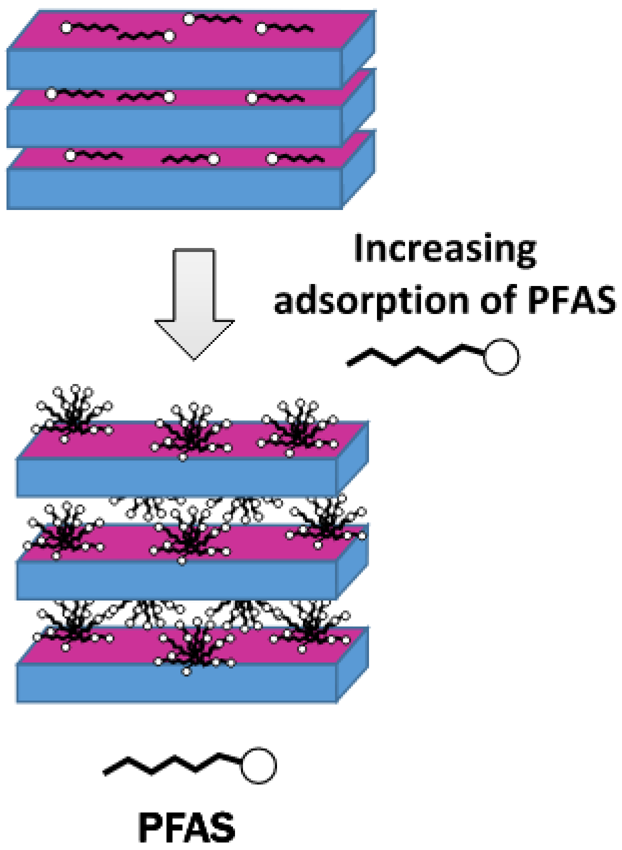
Ion Exchange Resin

Relative Adsorbance?

Courtesy Cetco

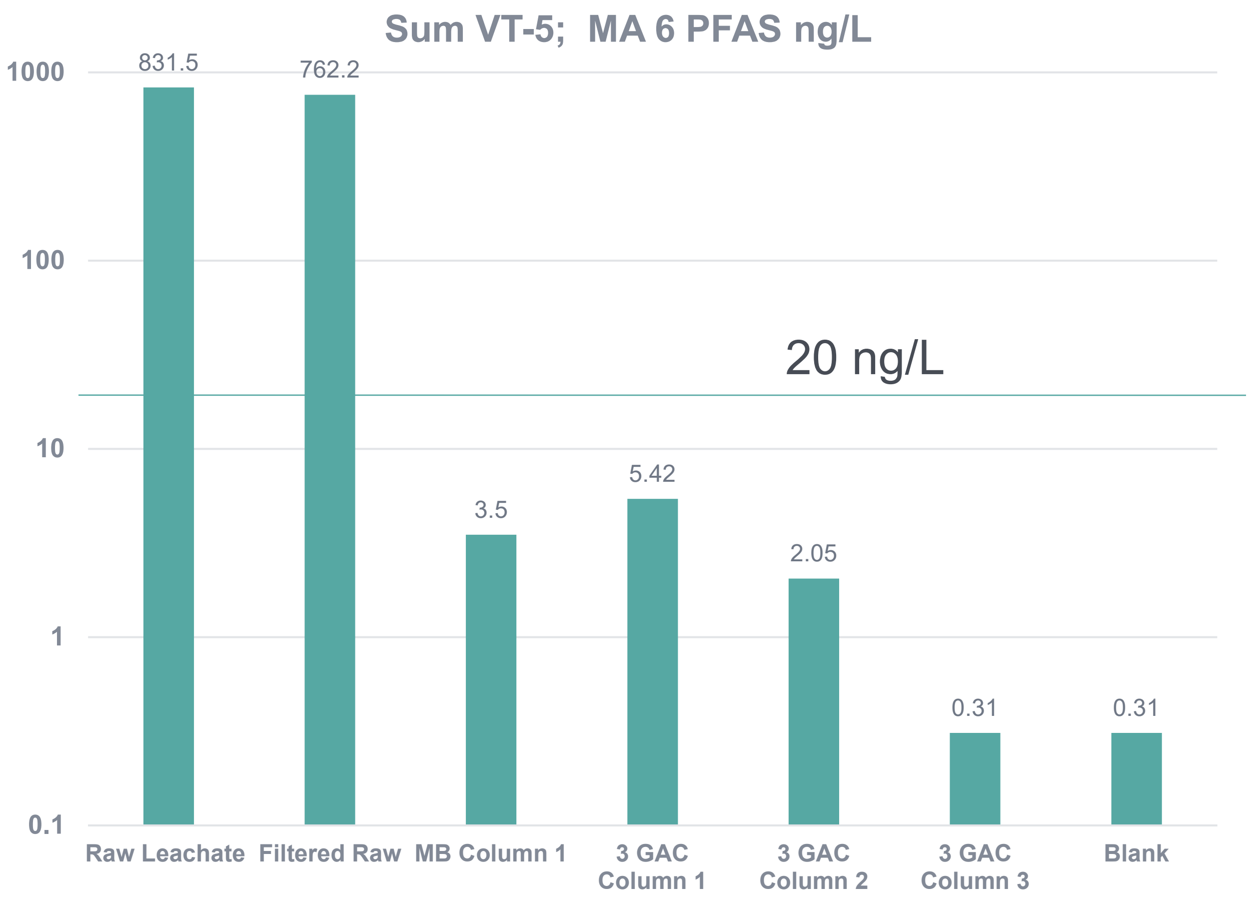
Surface Modified Clay Adsorption

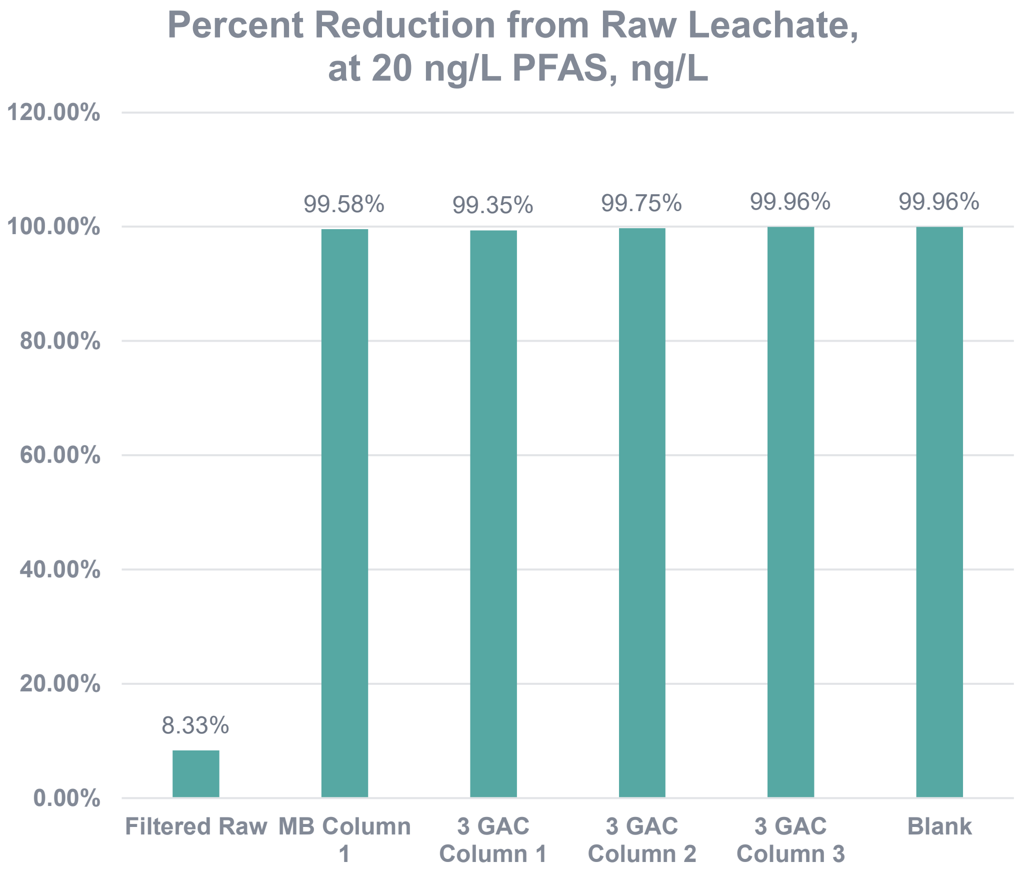




Adsorbents for PFAS Landfill Leachate Removal, ng/L

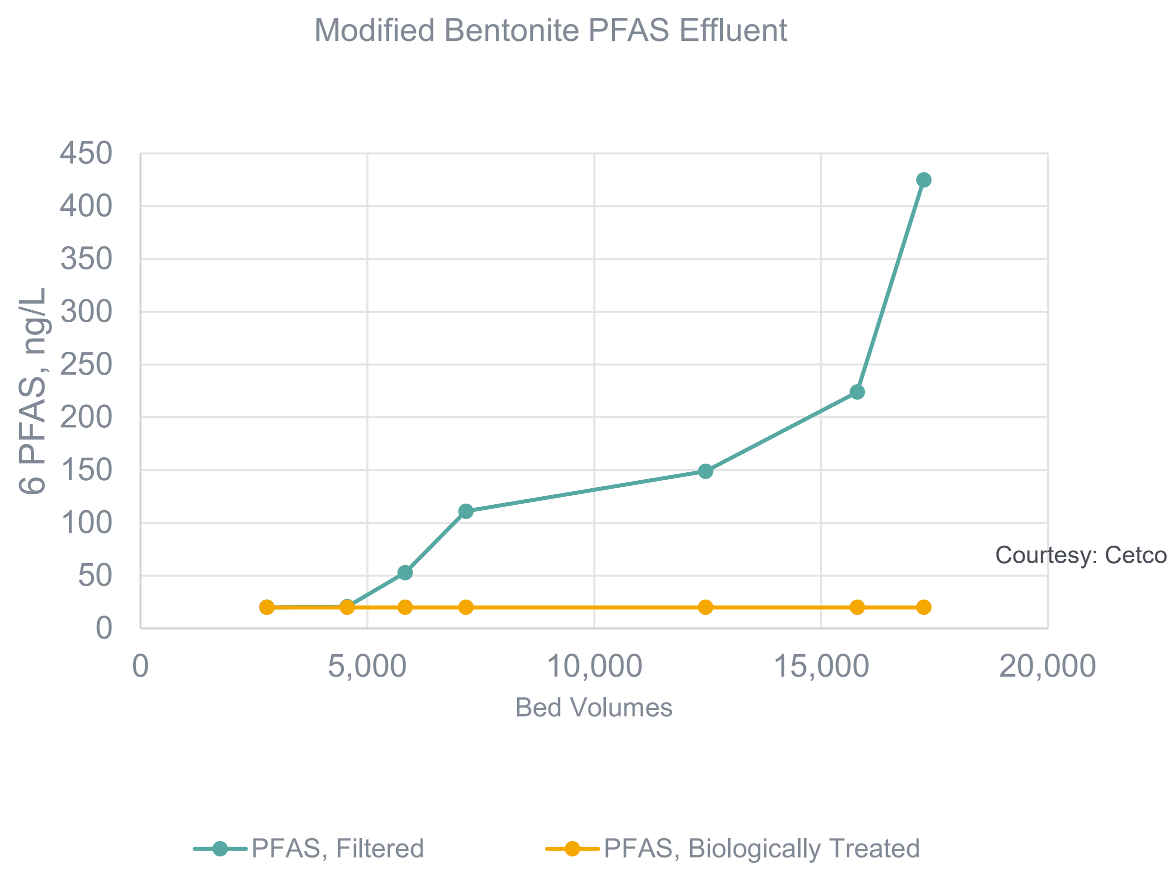
(PFOS; PFOA; PFHxS; PFNA ;PFHpA; PFDA)





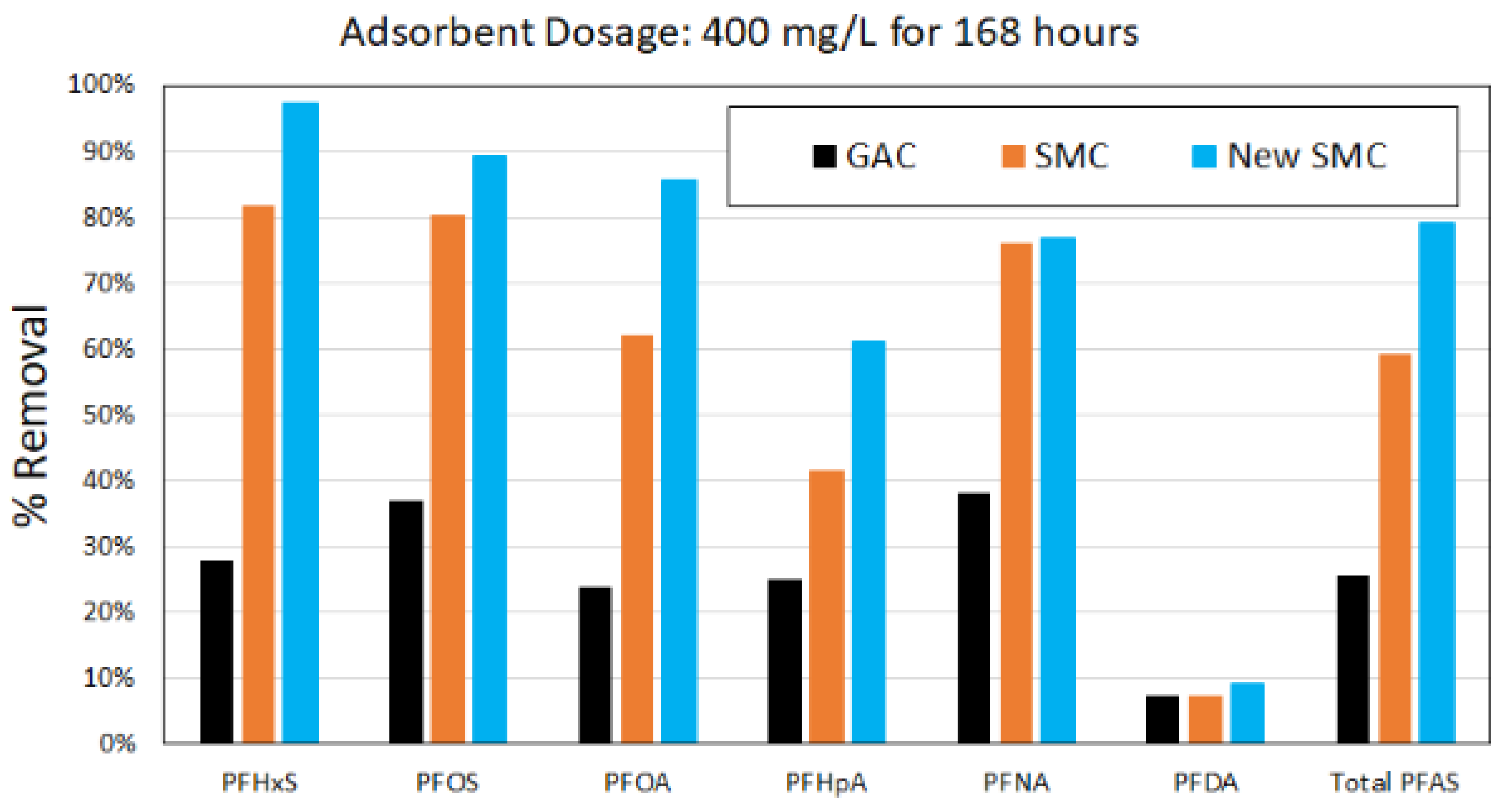
Surface Modified Bentonite Clay
(Adsorbent)

- Effective for Leachate PFAS Adsorption
- Bench test/Pilot test on Leachate
- Pretreatment!!
- PFOS, PFAS >99+% removal, but
  - Short Chain, Oxylates (PFHpA)
- Longer bed volume than GAC
- Spent media fixation/disposal
- Susceptible to foulants
  - NOM, Fe
- Static Bed versus Fluidized Bed



Surface Modified Clay Performance
FluoroSorb 200 vs. FluoroSorb Flex

PFAS REMOVAL EFFICIENCY - LANDFILL LEACHATE



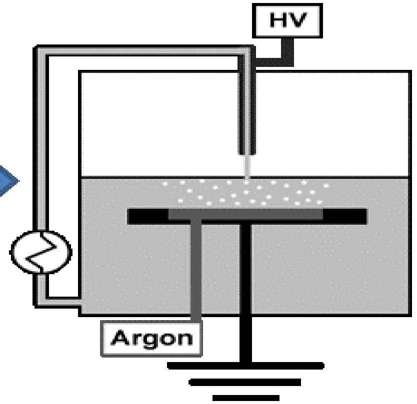
Residuals Technologies

- Destruction
  - Incineration
  - Plasma
  - Supercritical Water Oxidation
  - Electro Chemical Oxidation
  - Reductive Defluorination Technology
- Stabilization/Solidification
  - Cementitious S/S
    - Encapsulation (In totes or vessels)
    - Holcim/ADC
  - Return to the landfill
  - Hazardous Waste Landfill Haul and Dispose

Plasma PFAS Transformation

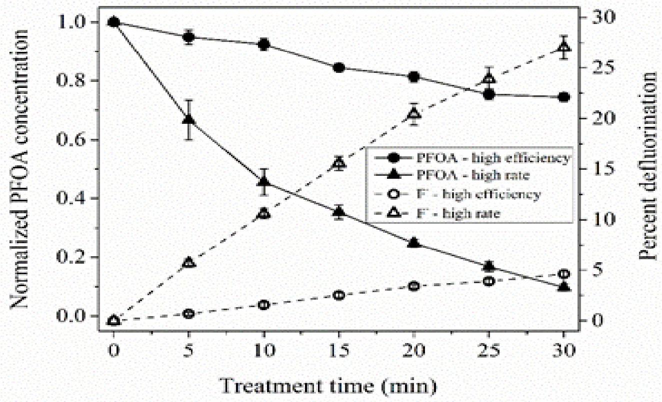
DMAX, ONVECTOR, MSU, Drexel, others

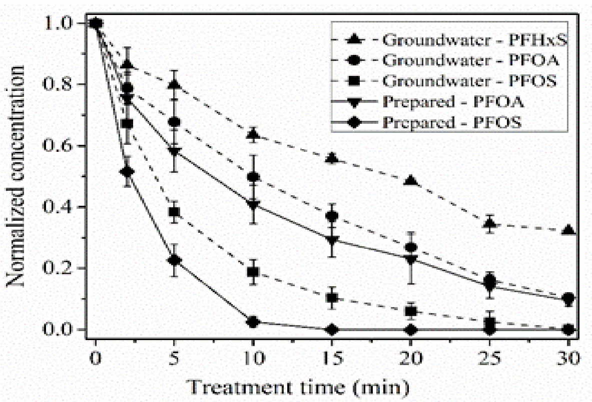
Bench-scale enhanced contact plasma reactor



Plasma produces aqueous electrons and H radicals which are capable of chemically degrading PFASs

Clarkson UNIVERSITY defy convention





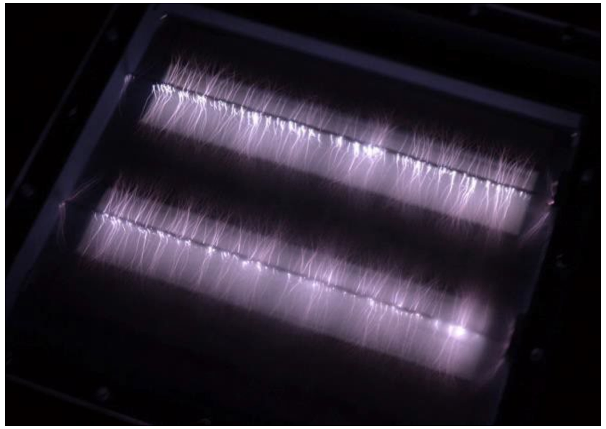
G. R. Stratton, F. Dai, C. L. Bellona, T. M. Holsen, E. R. V. Dickenson and S. Mededovic Thagard, "**Plasma-based water treatment: Demonstration of efficient perfluorooctanoic acid (PFOA) degradation and identification of key reactants**" Environmental Science & Technology, 2016, accepted.

Major byproducts: fluoride ions, fluorinated gases and shorter-chain PFAAs

Courtesy of Selma MededovicThagard, Clarkson University

CEC

Plasma



Treatment efficiency is 15 times greater than in the bench-scale reactor. The overall treatment efficiency is significantly higher compared to leading alternative treatment technologies.

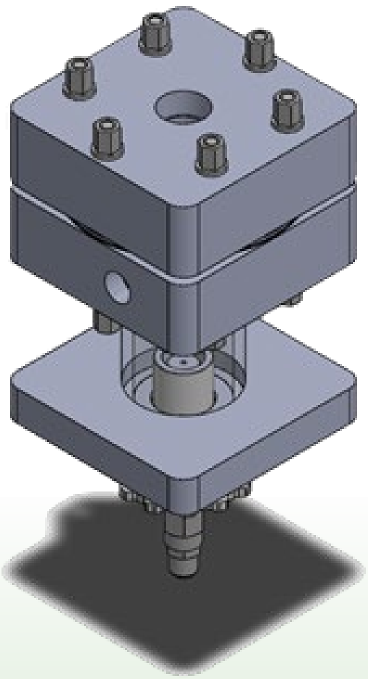
Solid-phase extraction			
Compound	$C_{0\,min}$ (µg/L)	$C_{60\,min}$ (µg/L)	Removal (%)
Perfluorooctanoic acid (PFOA)*	0.89	0.0035	99.6
Perfluorooctane sulfonate (PFOS)*	0.18	0.0026	98.5
Perfluoroheptanoic acid (PFHpA)	0.11	0.0002	99.8
Perfluorohexane sulfonate (PFHxS)	0.32	0.0041	98.7
Perfluorohexanoic acid (PFHxA)	0.27	0.024	91.1
Perfluoropentanoic acid (PFPnA)	0.22	0.16	26.4

Treatment of contaminated groundwater (naval research site, Warminster, PA)

PFOA & PFOS concentration was reduced by at least 75% within one minute of treatment

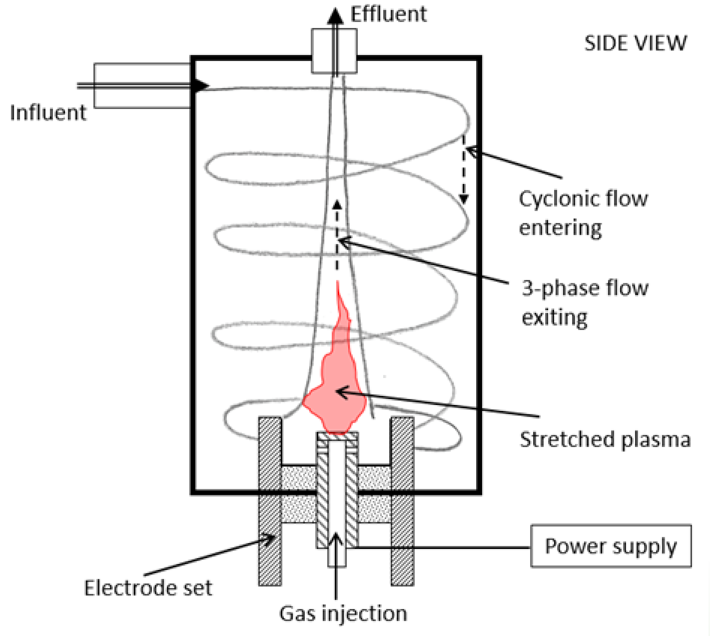
Courtesy of Selma Mededovic Thagard, Clarkson University and John Van Winkle, 88th Air Base Wing Public Affairs

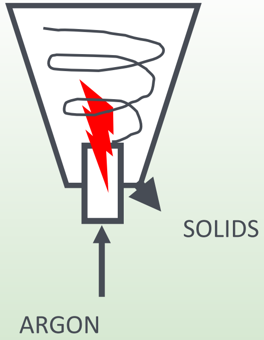
PLASMA VORTEX



Plasma hydrocyclone
Water enters tangentially at the top, spins down, then exits at the center top forming a reverse vortex tornado flow.

Arc generator
Power supply connected to a proprietary electrode set, injecting gas, ignites plasma and stretches plasma through the arc reactor.





Cyclonic separation of solids

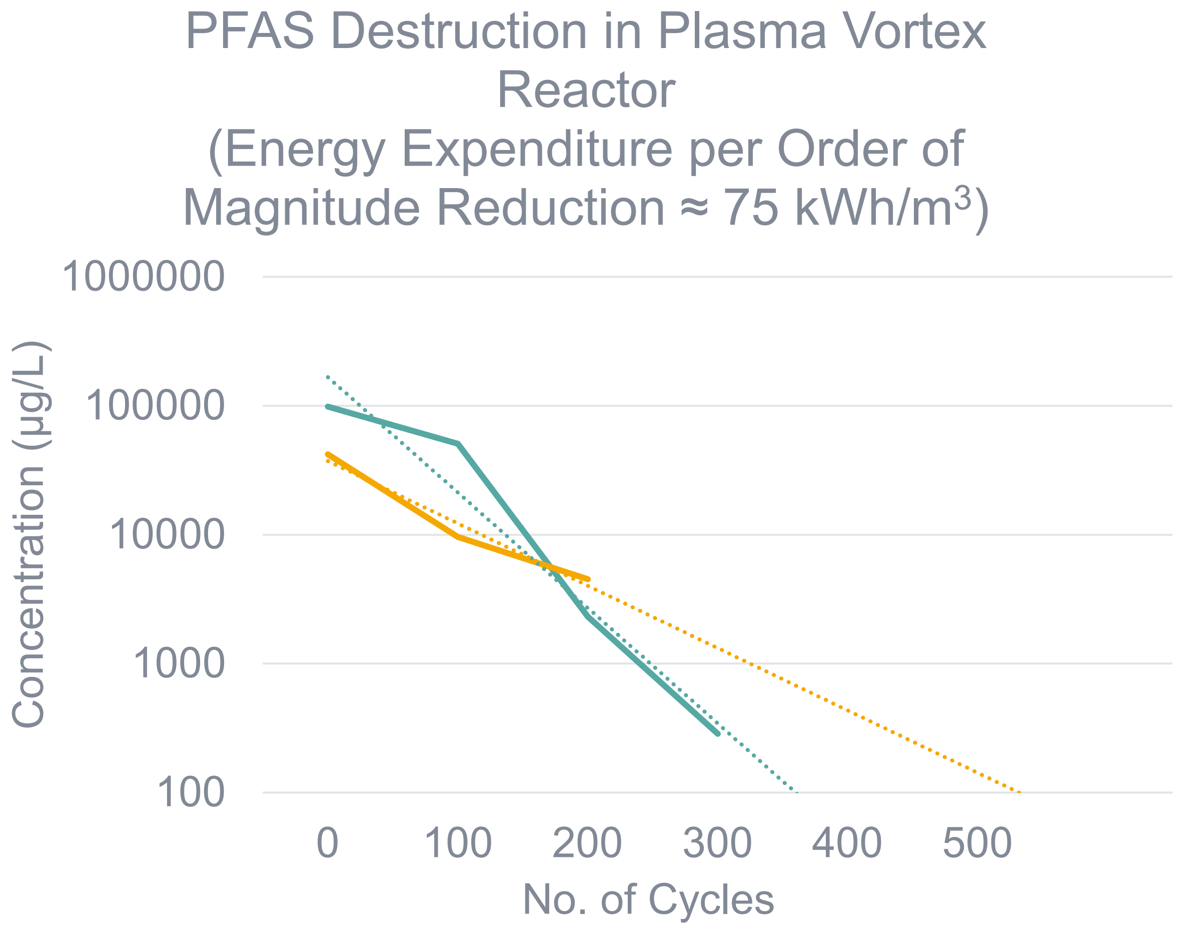
Recirculation of plasma carrier gas (argon)

ONVECTOR

CEC

Plasma Vortex

(Onsite Destruction without Air Emissions)



- Best used for small volumes of concentrated PFAS removed by other processes (i.e., Foam Fractionation)
- Free and hydrated electrons in plasma (reductive reactants) break C-F bonds due to their very high energy (50 to 100 eV) and very low mass
- Reactions are rapid until perfluorobutanoic acid (PFBA) is formed; PFBA degrades more slowly
- Near-complete degradation produces dissolved fluoride anion, small amounts of gaseous fluorocarbons

Supercritical Water Oxidation (SCWO)

- Water above 705°F and 3,200 lbs/in^2 - Rapidly destroys PFAS
- >99.99% removal under 10 seconds or less
- If organics, no additional fuel needed
- Creates HF – needs neutralization
- Tests 99+% reduction in landfill leachate for 12 PFAS : 3,600 ng/L to 36 ng/L (Jama et al 2020)
- Battelle building a mobile trailer for 3,500 gal/day

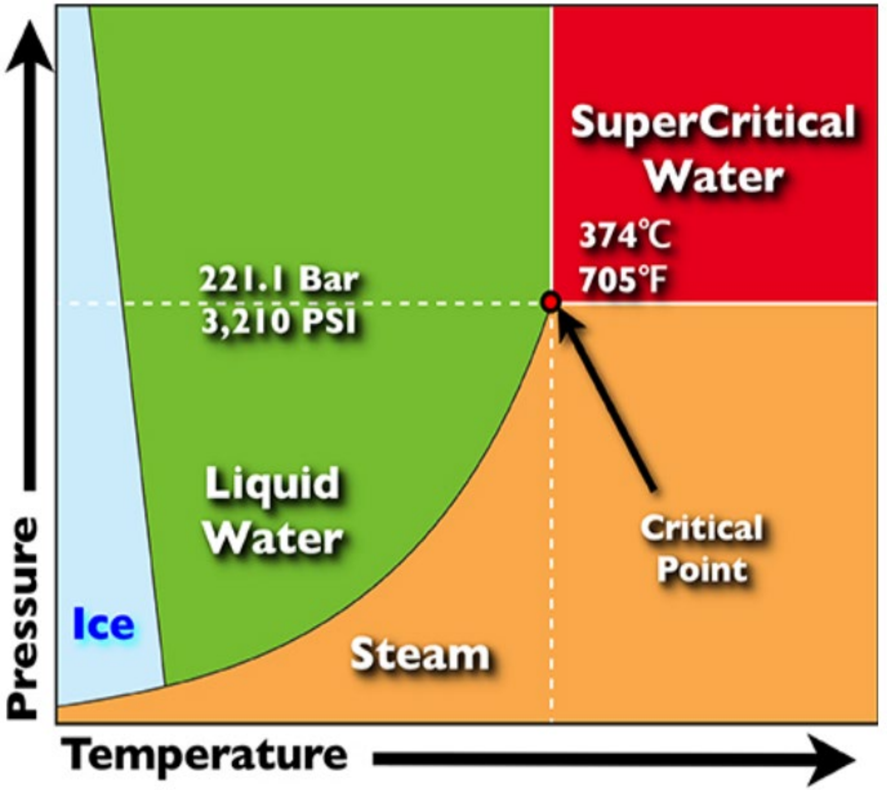
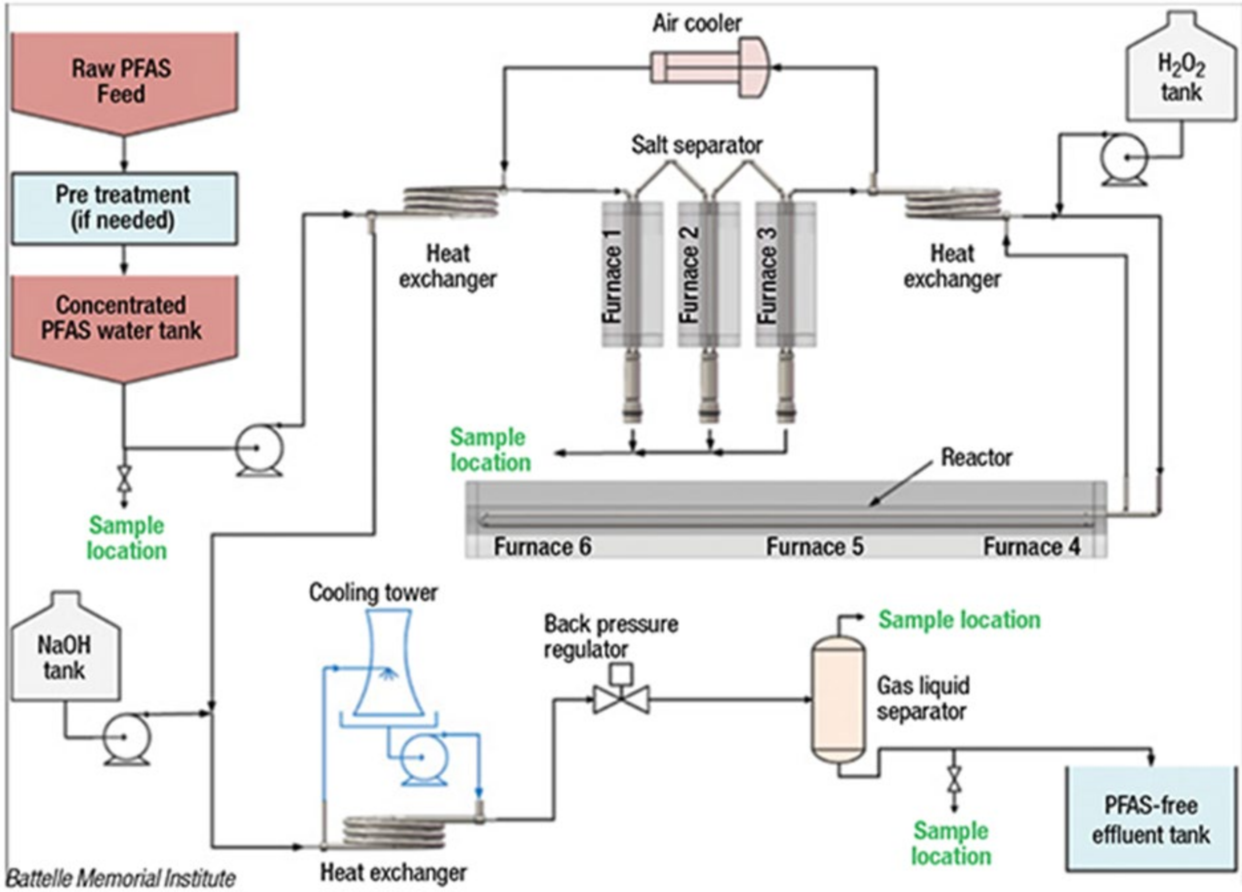


Figure 1. *SCWO reactions occur above the critical point of water. Image credit: Jonathan Kamler.*

EPA, Jan 2021

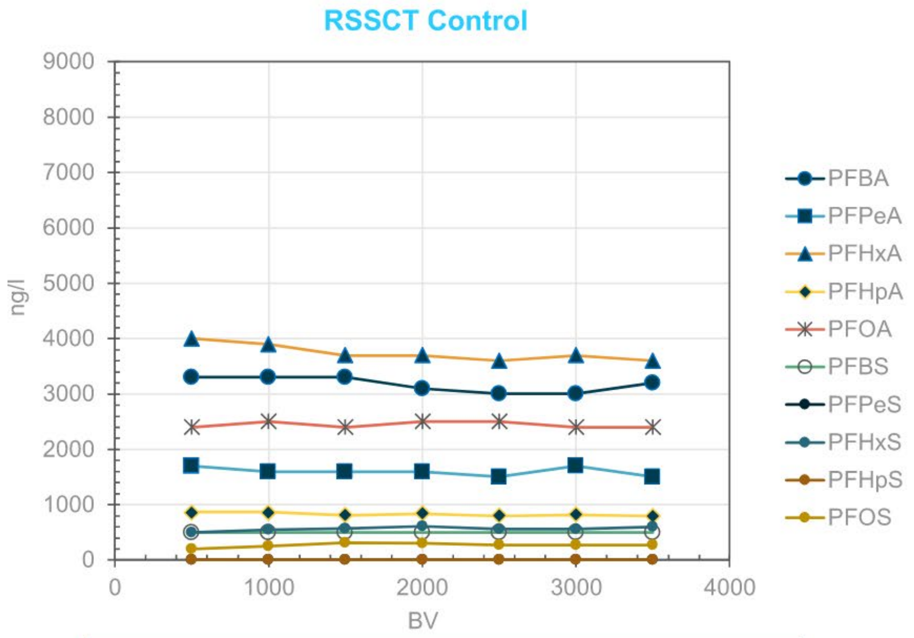
SCWO

- Providers:
  - Battelle "Annihilator"
  - 374Water
  - Aquarden
- Self-sustaining?
- Focus on residuals
- Caustic addition neutralizes HF
- End products – NaF and Na_2SO_4
- Mobile Unit for demonstration
- Leachate, contaminated soil and AFFF stockpiles

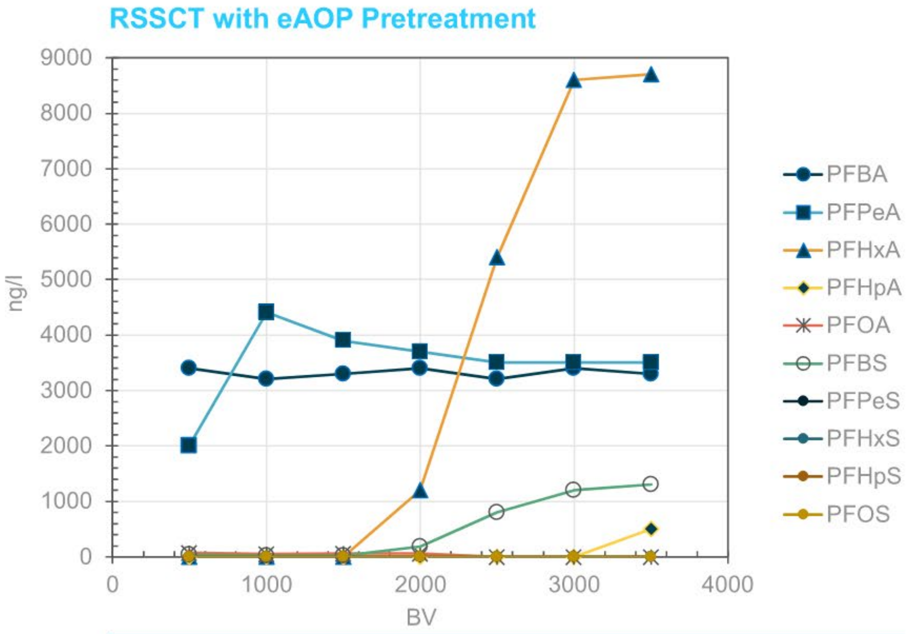


Electrochemical Oxidation

- Landfill Leachate in RSSCT Bench Test
- Chemical oxidation followed by electrochemical oxidation



All PFAS breakthrough from the beginning

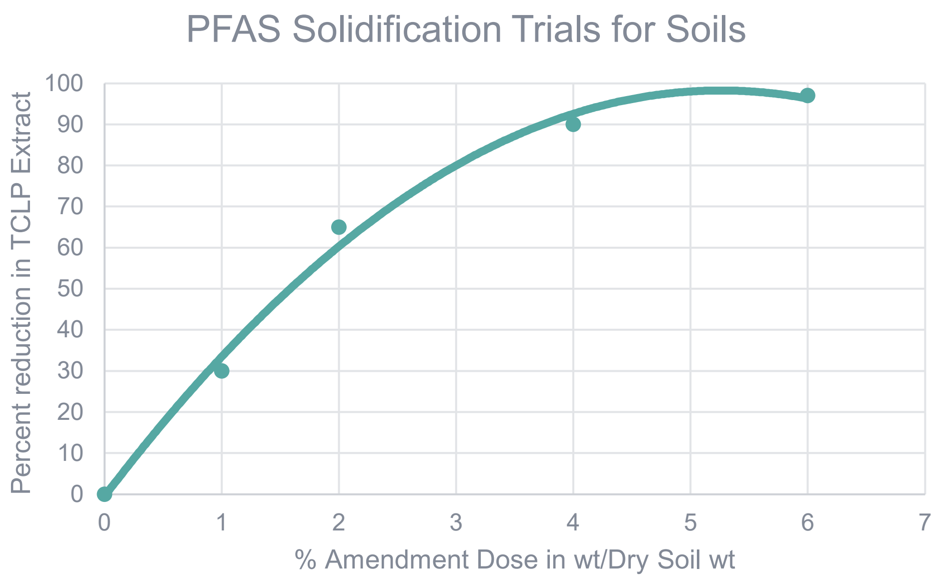


Only short chain PFAS materials breakthrough

S

Leachate Residuals PFAS Stabilization

Tests by Dan Cassidy, Western Michigan University - 6% dose Fluoro Sorb achieved < 70 ppt [PFOA+PFOS] in leachate in all soils using TCLP Test.



https://www.waste360.com/landfill/new-leachate-treatments-tackle-pfas

Techniques:

Mixture of generic S/S amendments known to sorb PFAS*:
Powdered activated carbon (PAC),
Iron oxide (Fe_2O_3) powder,
Montmorillonite clay,
Ground-granulated blast-furnace slag (GGBFS), and
Portland cement (PC)
Fluoro Sorb

Disposal:

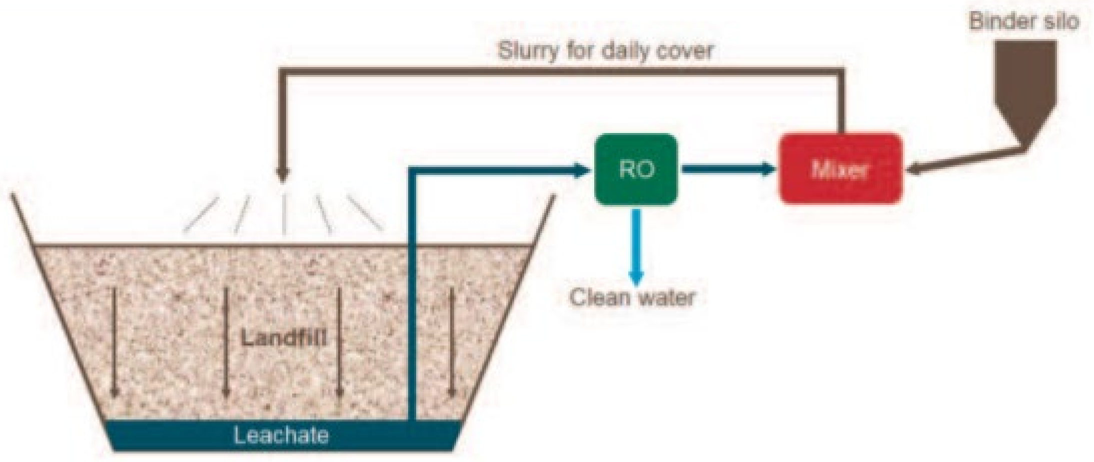
Landfill
Alternate Daily Cover

[PFOS] = **14,000 -** 100,000 ng/Kg
[PFAS] = 2,500 – 17,000 ng/Kg

Tested with Fluoro Sorb from Cetco

Fixation of Residuals
(Holcim/Lafarge)

- Proprietary cement binder
- No free liquid (Paint Filter Test)
- Friable for use as Alt Daily Cover
- SPLP extracts 1.9 – 3.8 ng/L

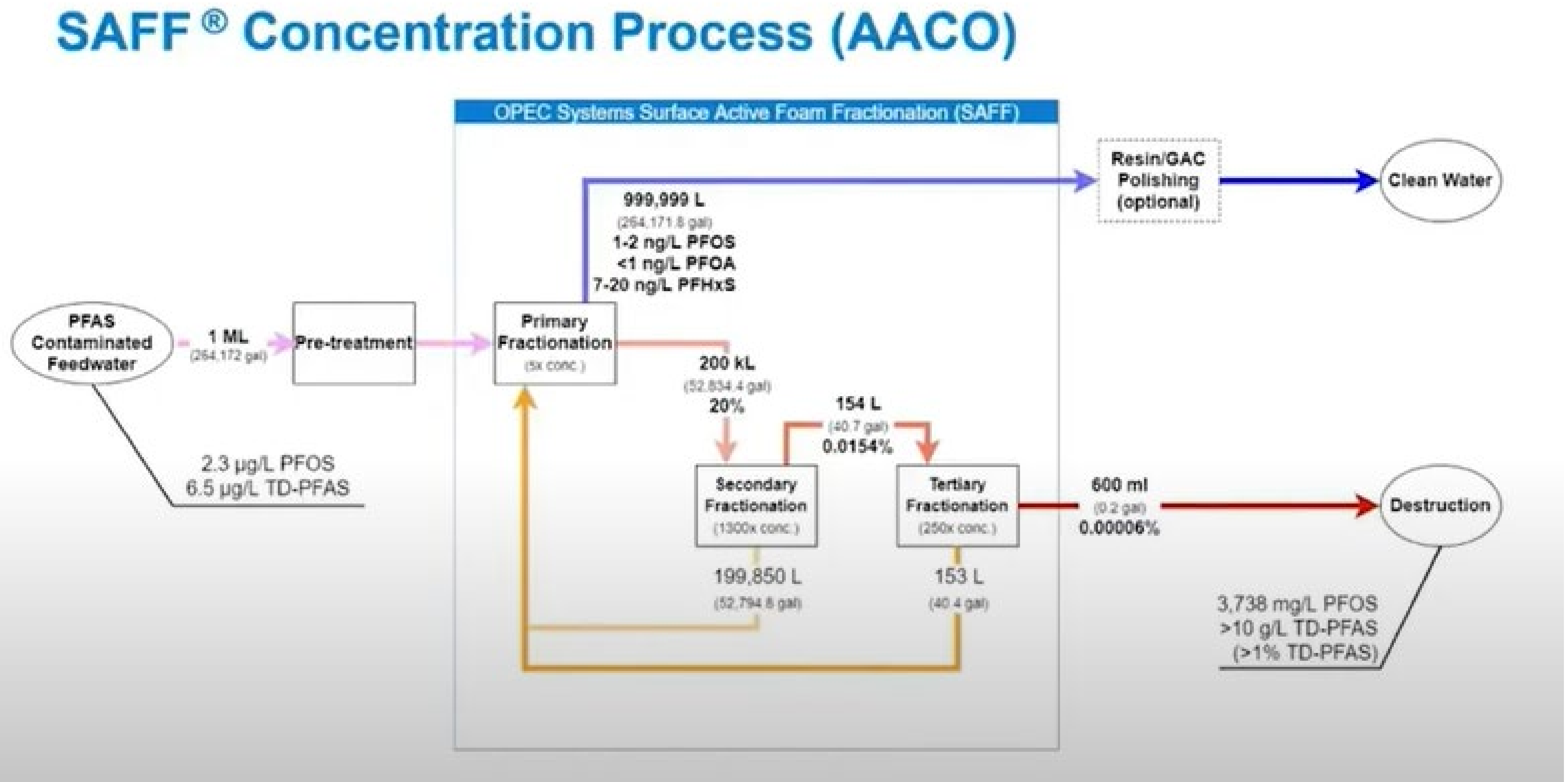


Courtesy: Holcim/Lafarge

Case Study 1 - Foam Fractionation

Courtesy: OPEC

SAFF Process Flow Diagram May 2019 – April 2021



Foam volume reduction by vacuum process

Courtesy:OPEC

Case Study 1 – LF Foam Fractionation

Telge LF- 250,000 L/Day (66,000 gpd)

System inside 40-foot container, Insulated

- Pretreatment and Foam Fractionation combined
- 4 treatment vessels
- Batch operation
- Separation Stage and enrichment stage
- Effluent single ppt
- Concentrate to tote for off-site disposal

HMI controls stage timing, power, cycles, remote operation, reporting

3 stages of Foam Concentration Stage

Courtesy: OPEC

CEC

Foam Fractionation Results
Telge LF (Stockholm, Sweden)

PFAS Compound	Removal Rate % Predictive Model	Removal rate % Telge miniSAFF 15 min	Average Removal rate % Telge SAFF40 19 min (15 000 m3)
PFDA (Perfluordekansyra)	100%	80%	69%
PFNA (Perfluornonansyra)	100%	97%	98%
6:2 FTS (Fluortelomer sulfonat)	100%	73%	98%
PFOA (Perfluoroktansyra)	100%	100%	100%
PFOS (Perfluoroktansulfonsyra)	100%	98%	99%
PFHxS (Perfluorhexansulfonsyra)	97%	99%	98%
PFHpA (Perfluorheptansyra)	67%	95%	94%
PFHxA (Perfluorhexansyra)	20%	8%	44%
PFPeA (Perfluorpentansyra)	24%	0%	11%
PFBA (Perfluorbutansyra)	21%	0%	3%
PFBS (Perfluorbutansulfonsyra)	22%	0%	24%

OPEX Costs for Removing PFAS from Landfill Leachate:
SAFF40 case study after two months recycling leachate from a Telge landfill facility in Sweden

- Labour – AUD $0.08/m^3 (treated)
- Consumables - ZERO
- Energy – AUD $0.084/m^3 (treated)
- Waste – AUD $0.0165/m^3 (treated)

Courtesy: OPEC

Case Study 2 – Reverse Osmosis
Midwest Landfill Leachate

MSW Oct 25, 2018; Pat Stanford, Rochem

Previously:
25,000 gpd to LF gas evaporator
Excess hauled
Excessive costs

Reverse Osmosis:
80,000 gpd 2 Rochem Units
Residuals returned to landfill
Landfill gas now for energy production

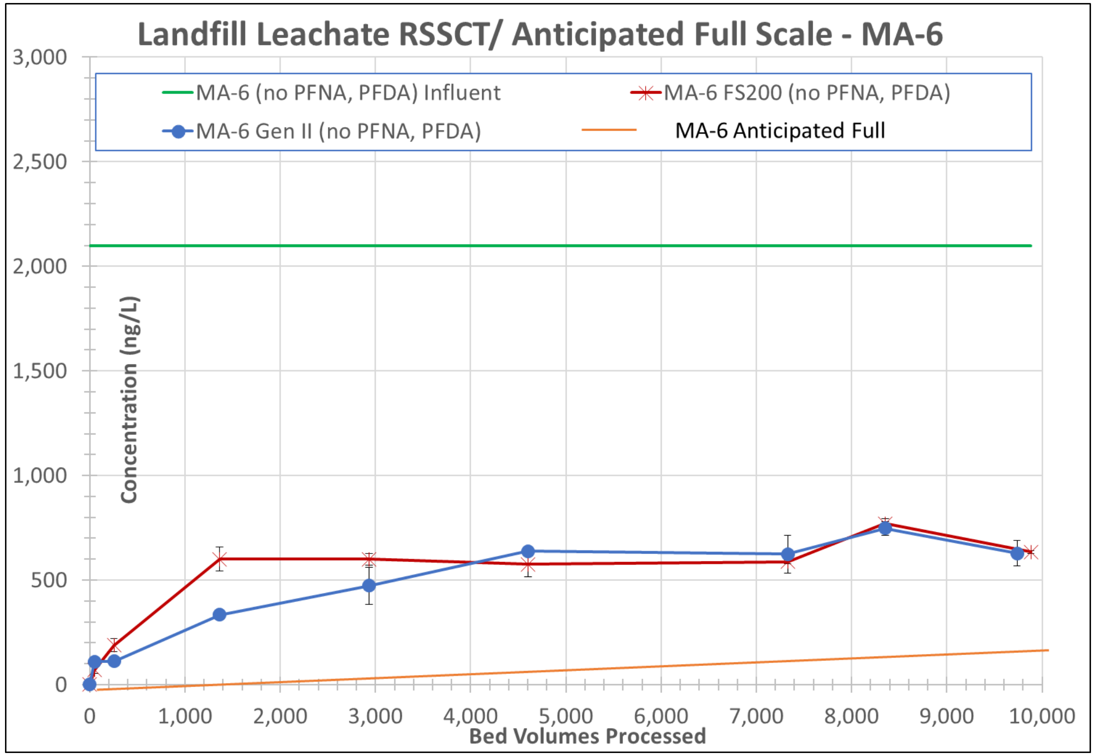
Reverse Osmosis PFAS Removal

Rochem, EGLE, and MWRA Landfill Leachate PFOA and PFOS Study, March 2019

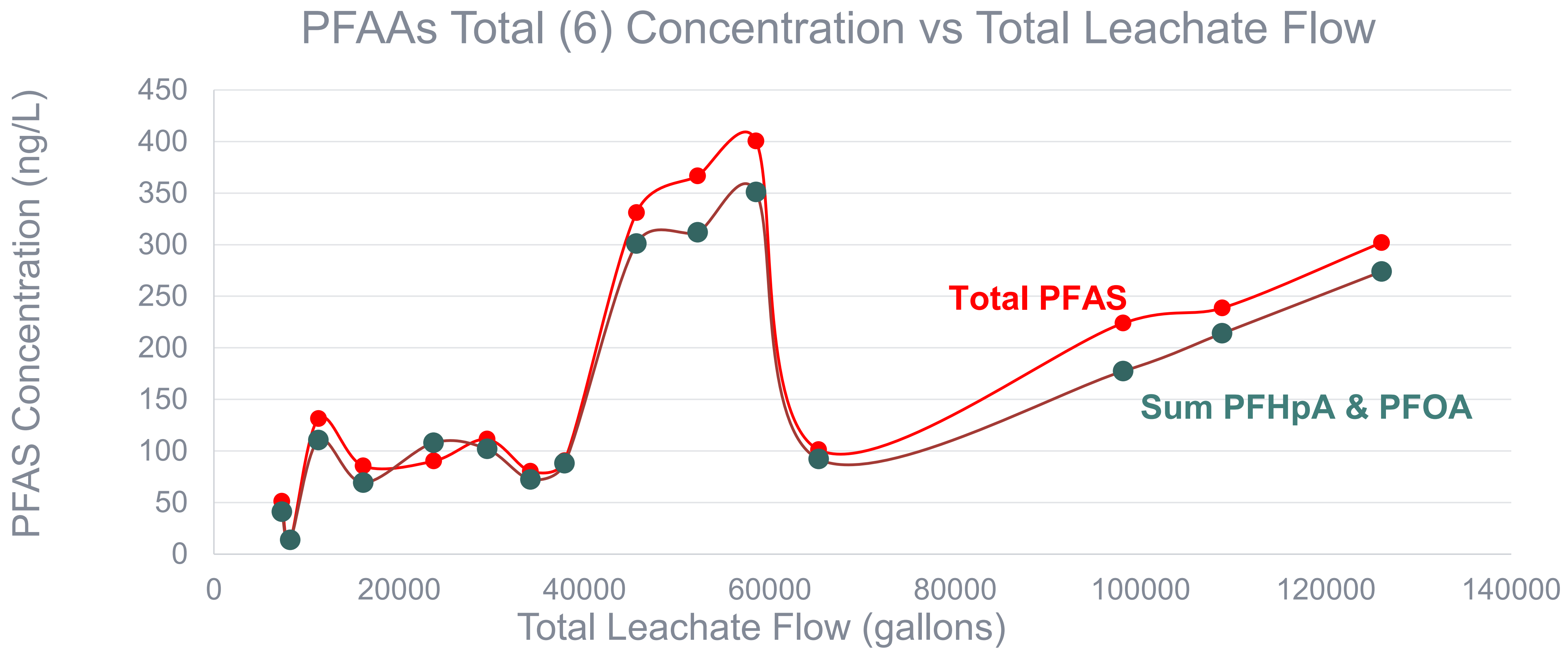
Compound (ng/l)	Leachate	RO 1 Permeate	RO 2 Permeate	Rejection
Perfluorobutanesulfonic acid (PFBS)	280	<2	<1.9	>99.3%
Perfluorobutanoic acid (PFBA)	1100	5	<1.9	>99.8%
Perfluoroheptanoic acid (PFHpA)	480	<2	<1.9	>99.6%
Perfluorohexanesulfonic acid (PFHxS)	690	<2	<1.9	>99.7%
Perfluorohexanoic acid (PFHxA)	2100	7.8	<1.9	>99.9%
Perfluorooctanesulfonic acid (PFOS)	200	<2	<1.9	>99.1%
Perfluorooctanoic acid (PFOA)	820	2.5	<1.9	>99.8%
Perfluoropentanoic acid (PFPeA)	880	2.7	<1.9	>99.8%
Total	6550	18	<1.9	>99.9%

Case Study 3 – FluoroSorb

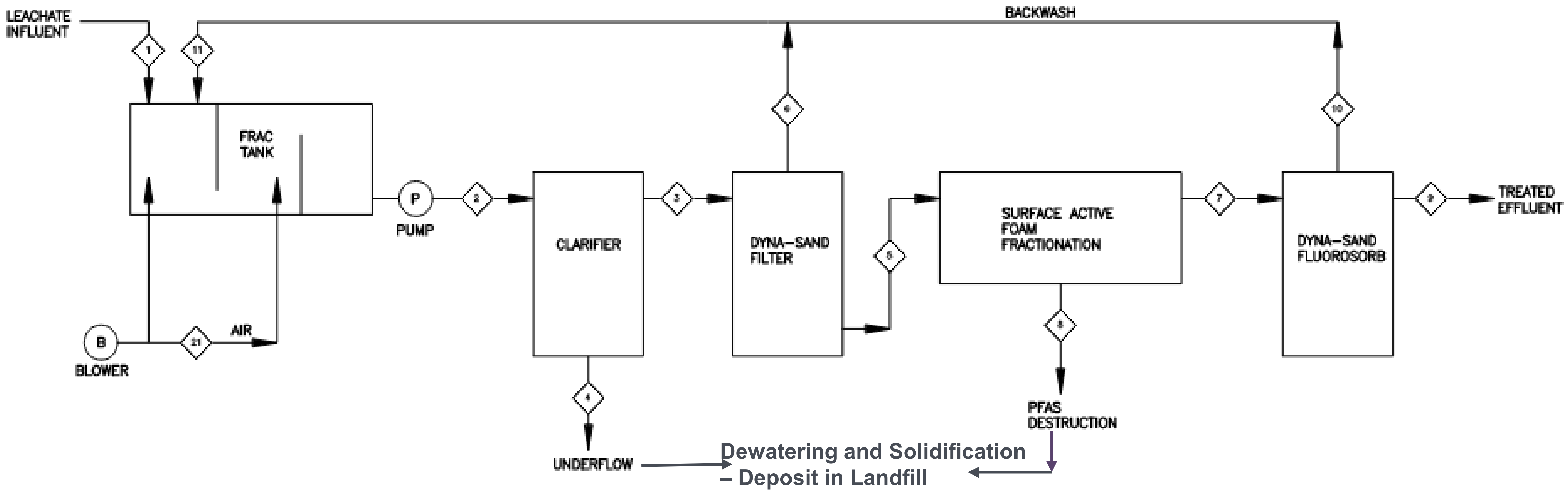
- Bench test
- Pilot Test
- Full Scale Design
  - Polymer/Coagulant – iron/solids removal
  - Inclined plate clarifier
  - Moving bed media filtration
  - SAFF Foam Fractionation
  - Moving bed FluoroSorb Flex media
  - Effluent storage
  - Clarifier solids & backwash concentrated/dewatered
  - Solidification residual solids with cement
  - Landfill disposal
  - Effluent < 20 ppt



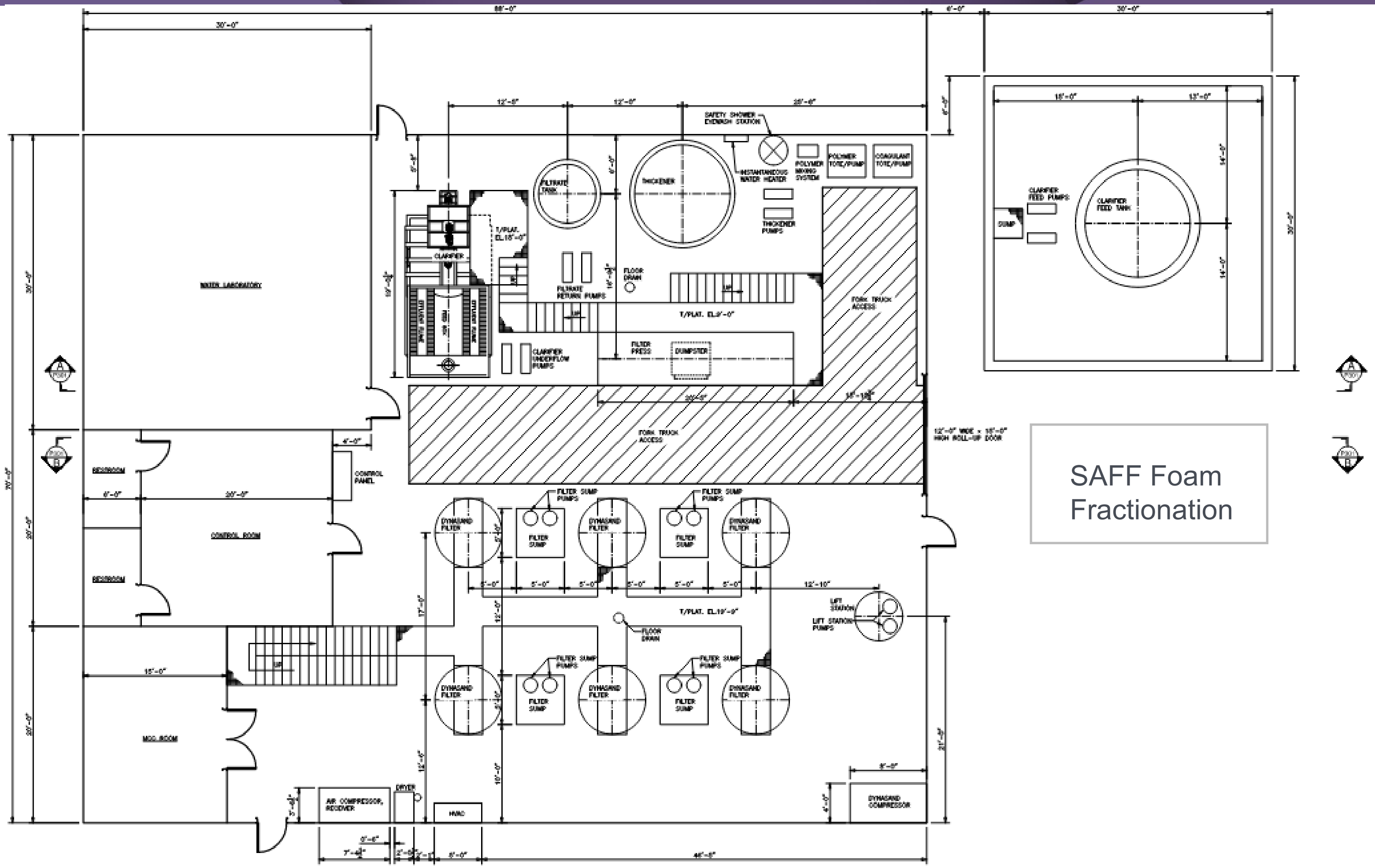
FluoroSorb Pilot Test



Foam Fractionation & FluoroSorb Process Flow Diagram



FluoroSorb Plant Layout



Case Study 4 – Supercritical Water Oxidation

Aquarden, Sweden

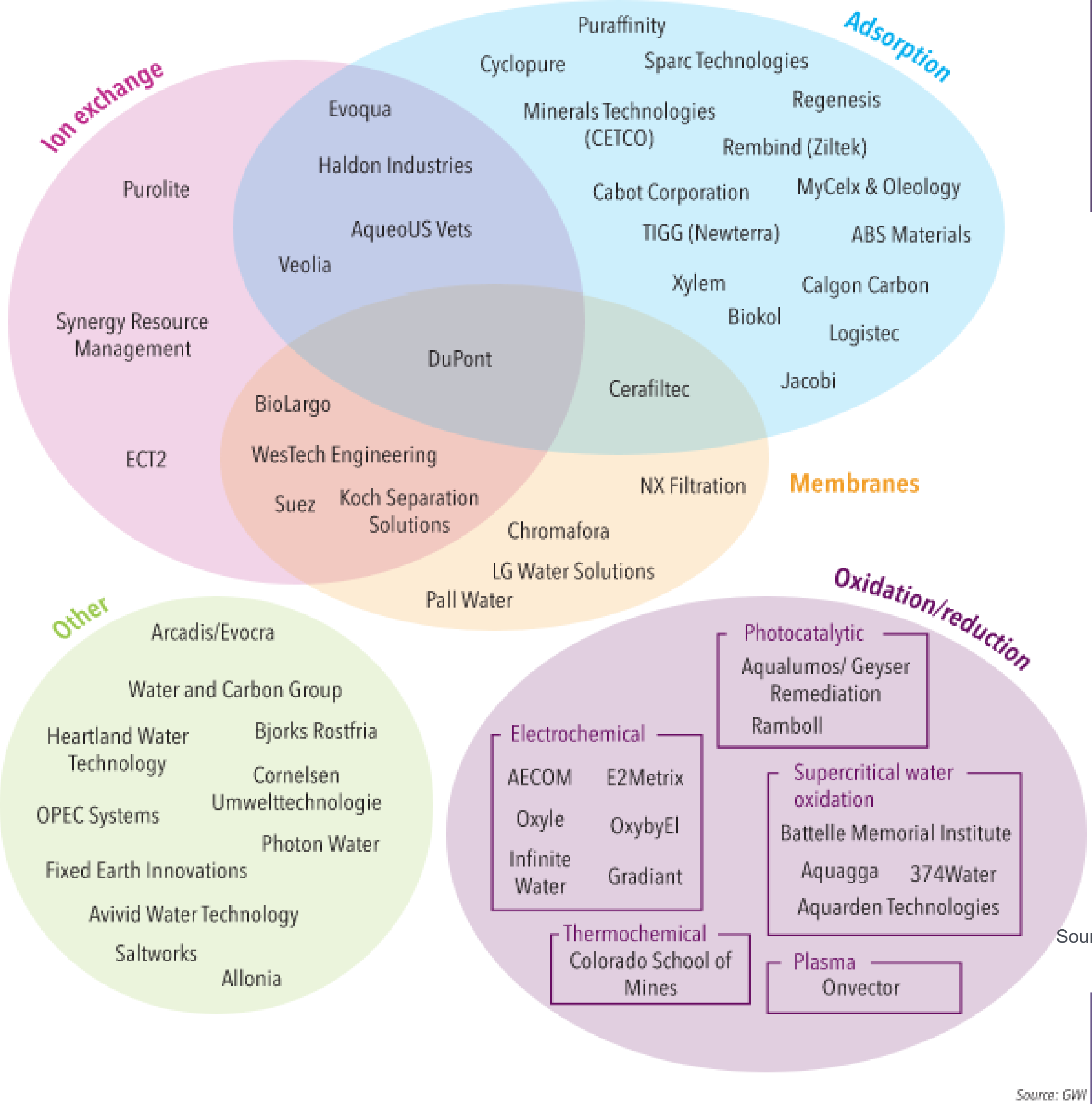
- Sorab LF, Sweden
  - Leachate 3,700 ng/L to 35 ng/L

- Stockholm Arlanda Airport-AFFF
  - 679,000ng/L to 3,400 ng/L

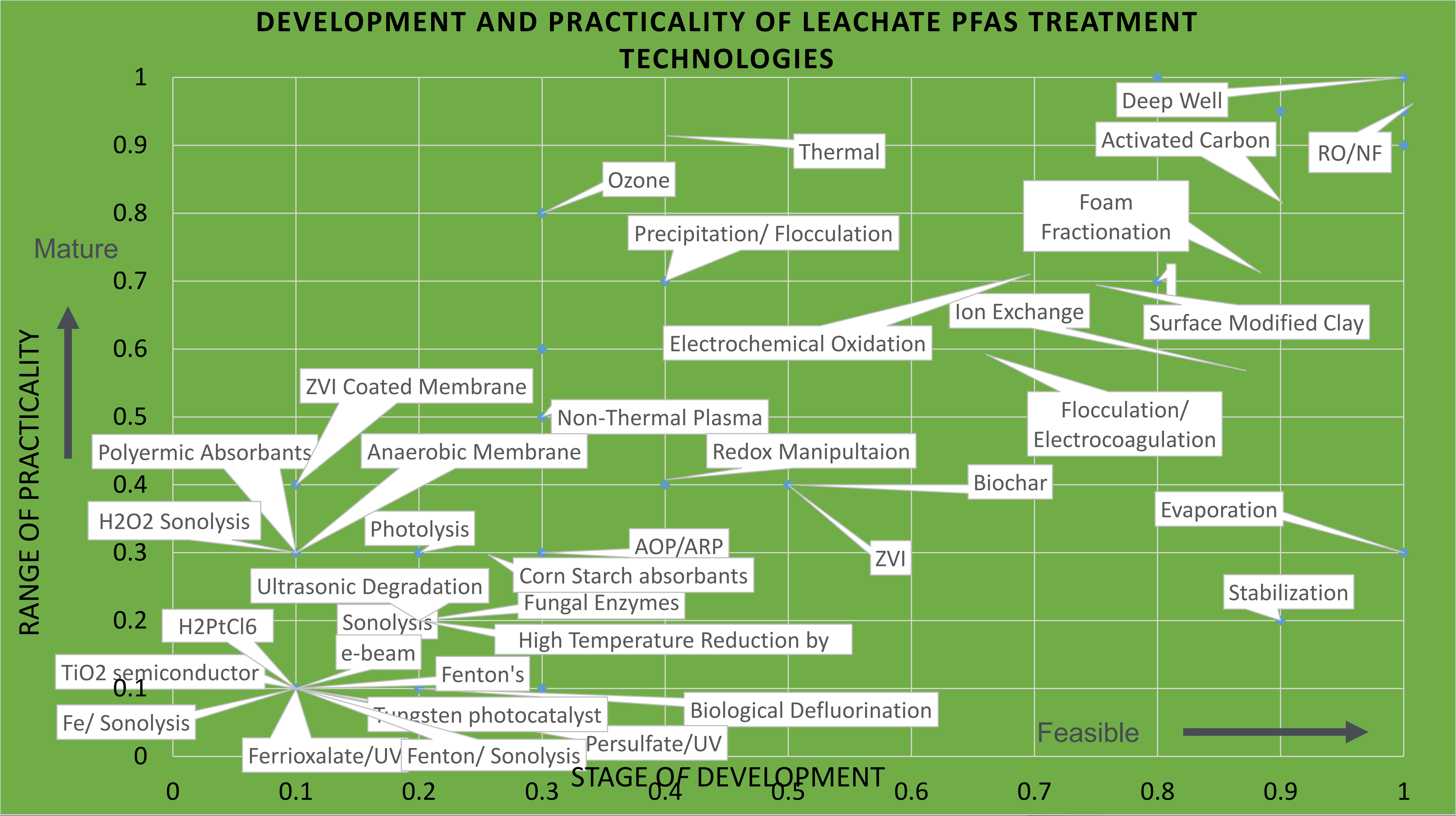
- Perpetuum Waste Management (Norway)
  - Leachate15,000 ng/L to 190 ng/L

Source: Water Online Nov 10, 2020

Current PFAS Market Players



Source: PFAS treatment market concentrates on waste reduction and total destruction, GWI, May 2021


DEVELOPMENT AND PRACTICALITY OF LEACHATE PFAS TREATMENT TECHNOLOGIES
RANGE OF PRACTICALITY
Mature
STAGE OF DEVELOPMENT
Feasible
Deep Well
Activated Carbon
RO/NF
Thermal
Ozone
Precipitation/ Flocculation
Foam Fractionation
Ion Exchange
Surface Modified Clay
Electrochemical Oxidation
ZVI Coated Membrane
Non-Thermal Plasma
Flocculation/ Electrocoagulation
Polyermic Absorbants
Anaerobic Membrane
Redox Manipultaion
Biochar
H2O2 Sonolysis
Photolysis
AOP/ARP
ZVI
Evaporation
Corn Starch absorbants
Ultrasonic Degradation
Fungal Enzymes
Stabilization
Sonolysis
H2PtCl6
High Temperature Reduction by
e-beam
TiO2 semiconductor
Fenton's
Biological Defluorination
Fe/ Sonolysis
Tungsten photocatalyst
Persulfate/UV
Ferrioxalate/UV
Fenton/ Sonolysis
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

Comparative Emerging Contaminants Treatment Technologies

Contaminant	Biological Treatment	Activated Carbon[1]	Ion Exchange[1]	Reverse Osmosis[2]	Chemical Oxidation	Electro Oxidation	AOP	Plasma	Adsorption/ Settle
COD/Ammonia	Yes	Possible	Possible	OK – Reject	Possible	Yes	Possible	Possible	No
I,4 Dioxane	Possible	OK	OK	OK – Reject	Possible	OK	OK	OK	Possible
DON and rDON	Possible	OK	Possible	OK – Reject	NO	Possible	Possible	Possible	No
PPCP	Possible	OK	OK	OK – Reject	Possible	OK	OK	OK	Possible
Nanoparticles /Microplastics	No	No	No	Yes – Reject	No	No	No	No	Possible
UV Absorbing	No	Possible	No	Yes <500 nm, Reject	No	Possible	No	Possible	Possible
PFAS	Combined	OK	OK	OK – Reject	Possible	Possible	Possible	OK	Probable

1. Residuals from spent activated carbon or ion exchange requires replacement and disposal
2. RO reject flow requires management by return to LF, concentration, evaporation, solidification, deep well injection, or other means.

Treatment Challenges

- Oxalates (ex. PFOA) harder to remove than Sulfonates (ex. PFOS)
- Longer chain easier to remove/destroy than shorter chain
- Many technologies focus on longer chain, shorter chain problematic
- Many technologies require multi step processes
- Mixtures, precursors, co-contaminants
- Incomplete mineralization
- Energy intensity
- Peer Reviews for leachate PFAS destruction technologies
- Limited field-scale examples
- Life cycle costs?

Questions?

Ivan A. Cooper, PE, BCEE

Civil & Environmental Consultants, Inc.

3701 Arco Corporate Drive
Charlotte, NC 28273
704-226-8074
icooper@cecinc.com