Civil & Environmental Consultants, Inc.

Emerging Contaminants– Per and Polyfluoroalkyl (PFAS) Substances

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2023 BISE Conference

Greensboro, NC

September 27, 2023

Agenda

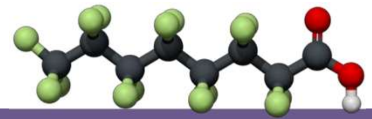
- What are they?
- Where do they come from?
- Why all the fuss?
- What are they (Round 2)?
- How do we measure them?
  - Laboratory Analysis
  - Sampling Methods
- Regulatory issues?
- What do we do about it?
  - Drinking water
  - Groundwater/Surface water
  - Wastewater
  - Remediation
- Summary and Conclusions

Overview - What are PFAS?

Per and Poly-fluoroalkyl substances

- Generic family (over 5000) of chemicals
- Chains of carbon atoms surrounded by fluoride atoms
- Developed in 1940's
- Used to make products that resist heat, oils, grease, stains and water

Most prevalent/researched: PFOS & PFOA (specific compounds: perfluorooctanoic acid (PFOA) and Perfluoroctane sulfuric acid (PFOS)



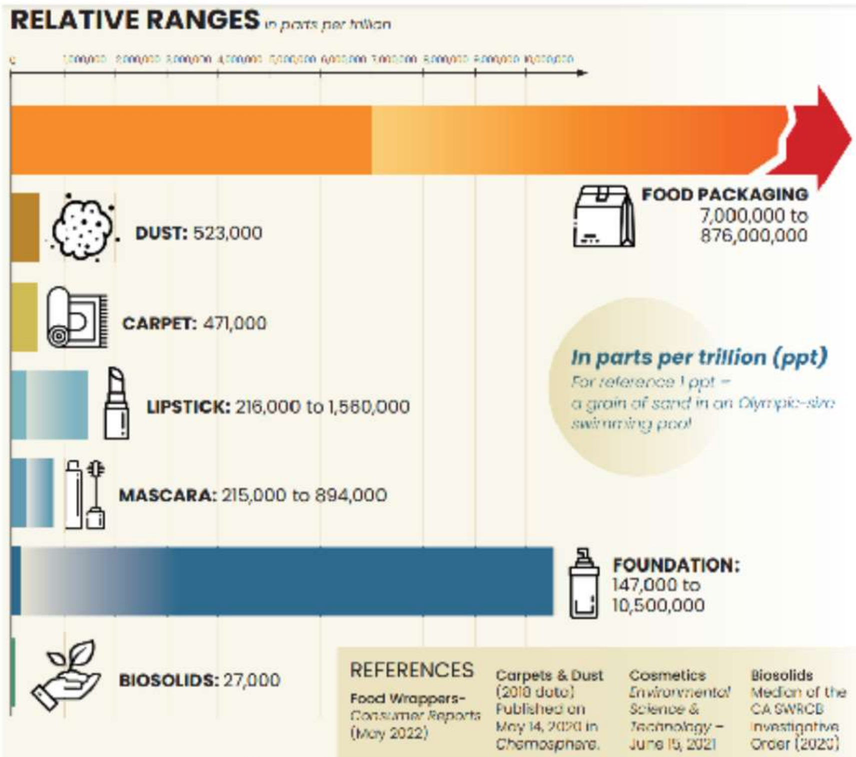
Where Do They Come From?

- Commercial household products, including stain- and water-repellent fabrics, nonstick products (e.g., Teflon), polishes, waxes, paints, cleaning products, and fire-fighting foams (AFFF).

PFAS History Timeline

- **In 1938, Roy J. Plunkett at the DuPont Company's Jackson Laboratory discovered polytetrafluoroethylene (PTFE) researching refrigerants**
- 1940 – Production of PFOA and PFOS begins
- 1949 – Teflon (PTFE) introduced by DuPont
- 1950s – PFOA and PFOS both dominant consumer compounds
- 1951 – Dupont starts C8 (PFOA) in Parkersburg, WV
- 1952 – Scotchguard accidentally invented by Patsy O'Connell Sherman after dropping PFOS on tennis shoes – repelled water

Relative Ranges of PFAS



- PFAS concentrations in biosolids are relatively low compared to other household sources (food packaging, makeup)
- Communication balancing act – land application of biosolids is beneficial
- "Sources" are likely to include everyday consumer products
- Air emissions can affect quality of rainfall and runoff

Source: CASA,
https://static1.squarespace.com/static/54806478e4b0dc44e1698e88/t/63231956ab2d672152b7a5a2/1663244631201/Bar+Chart+PFAS+2022%5B3%5D.pdf

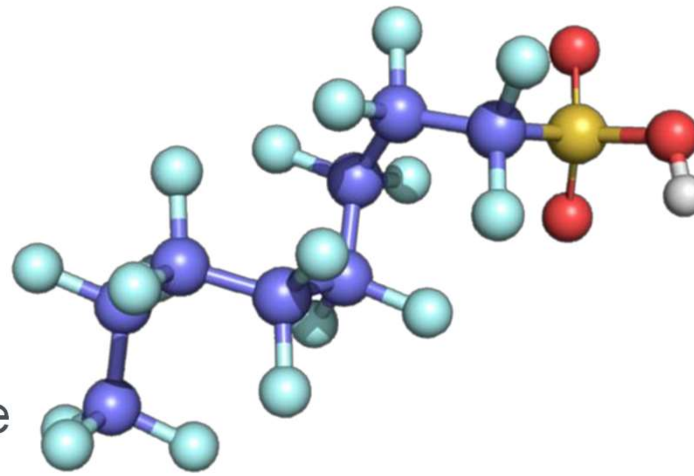
Water Environment Federation

From: WEF Task Force Meeting 9/5/2023

CEC

Why All The Fuss?

- Manmade and do not occur naturally
- PFAS have the ability to buildup and persist overtime
- Pervasive
- Persistent
- Bioaccumulative
- Associated with adverse health effects
- Constantly developing information in scientific literature
- Confusing state standards – EPA proposing



In water, we analyze for PFAS at the parts per trillion level

(1 PPT = 1 grain of sand in Olympic swimming pool)

Why All The Fuss?

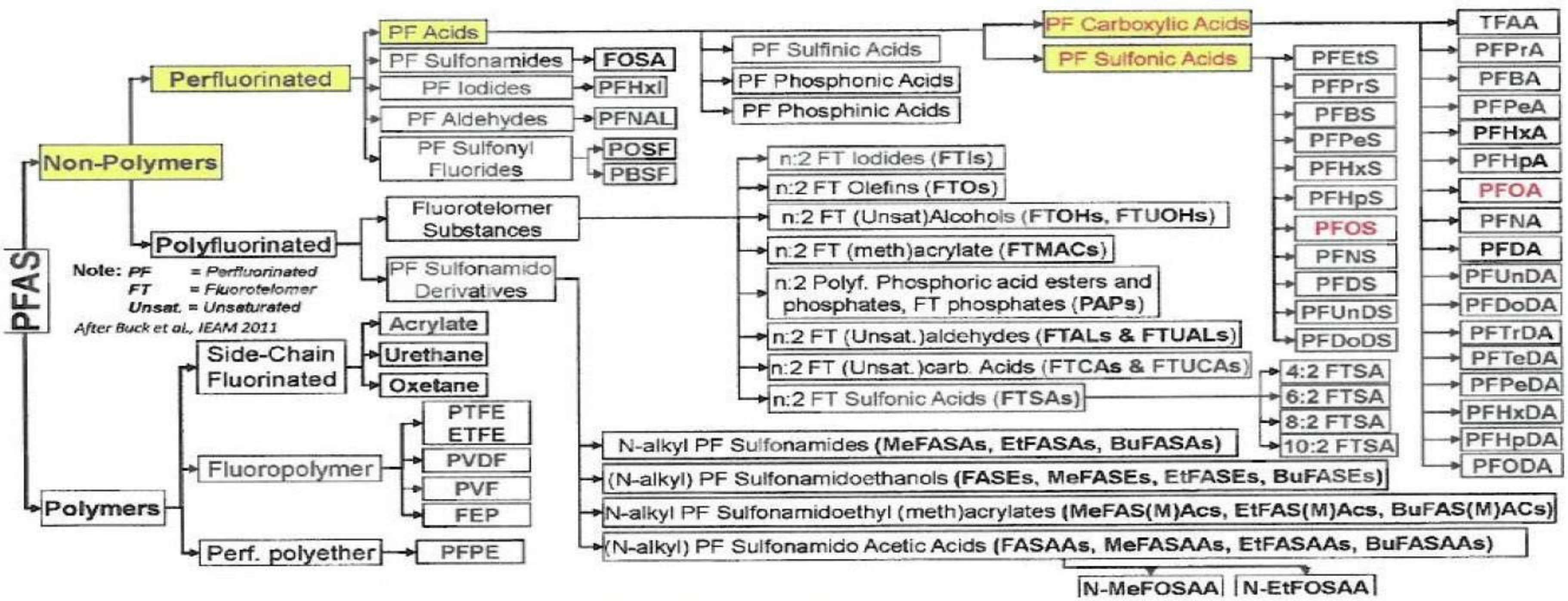
- Associated with adverse health effects
- Various studies, more being done
- Levels bioaccumulate in animals and humans
- ATSDR lists human risks may include:
  - Increased cholesterol levels
  - Liver impact
  - Infant birth weight decrease
  - Decreased vaccine response in children
  - Immune system impacts
  - High blood pressure
  - Increased risk of kidney or testicular cancer
- Most common exposure is through drinking water and food

What are they (Round 2) PFAS Properties and Names

PFAS Types:

- Polymer vs. Non-Polymer PFAS
- Perfluoroalkyl substances
- Polyfluoroalkyl substances
- Naming Conventions
- Long-Chain vs. Short-Chain
- Linear vs. Branched
- Currently short-chain PFAs is being used to replace long chain PFAs
- Types impact chemical characteristics

What are they (Round 2)
PFOS and PFOA are only the tip of the PFAS iceberg



PFAS FAMILY TREE

That is, Alphabet soup

Replacement Chemistry

- Concern regarding the persistence, bioaccumulation, and possible ecological and human health effects of long-chain PFAAs has led manufacturers to develop replacement short-chain PFAS chemistries that should not degrade to long- chain PFAAs
- Still accumulating data on health effects of short chain PFAs

Short Chain versus Long Chain

- Solubility typically increases when the carbon chain number decreases.
- Sorption typically increases when the carbon chain number increases.
- Surfactants can form foam when gas is applied to the water. Foam increases when the carbon chain number increases. Short-chain PFAS are less effective at forming foams.
- Short-chain PFAS can have higher volatility.

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						

How do we measure them? Laboratory Analytical Methods

- **Drinking (Potable) Water** –;
  - Method 537.1 – ***18 PFAS***
    - Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)
  - Method 533: - ***29 PFAS***;
    - Determination of PFAS in Drinking Water by Isotope Dilution Anion Exchange SPE and LC/MS/MS (2019)
- **Non-Potable Water and Other Environmental Media**
  - Method 8327: ***24 PFAS;***
    - Using External Standard Calibration and MRM LC/MS/MS (2019)
  - Draft Method 1633 – ***40 PFAS;***
    - wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue***.***
- **Air –**
  - Other Test Method (OTM)-45 –**50 PFAS +**
- **Total –** Total Organic Fluorine (TOF), Total Oxidizable Precursors (TOP)

Turn Around and other issues

- Currently 2 – 8 weeks Turn Around Time

- Cost - $300 to $500 +per sample

Sampling Methods
PFAS Sampling Dos and Don'ts

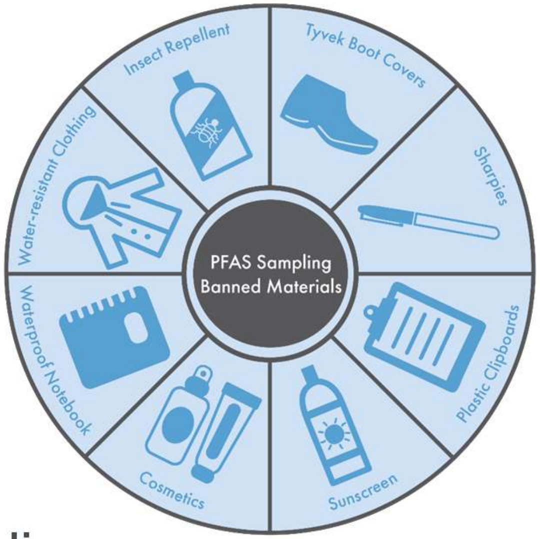
WHAT SHOULD I AVOID?	USE INSTEAD
Passive diffusion bags (PDBs)	
LDPE Hydrasleeves	✓ HDPE Hydrasleeves
Post-It notes during sample handling	
Blue Ice® (chemical ice packs)	✓ Regular ice in Ziploc® bags
Waterproof field books, plastic clipboards and spiral bound notebooks	✓ Field notes recorded on loose paper ✓ Field forms maintained in aluminum or Masonite clipboards
Unnecessary handling of items with nitrile gloves	✓ Personnel collecting and handling samples should wear nitrile gloves at all times while collecting and handling samples or sampling equipment

PFAS Sampling Dos and Don’ts *continued*

WHAT SHOULD I AVOID?	USE INSTEAD
Equipment with **Teflon®** (e.g., bailers, tubing, parts in pump) during sample handling or mobilization/demobilization	✓ High density polyethylene (HDPE) or silicone tubing/materials in lieu of Teflon®
Low-density polyethylene (LDPE) or glass sample containers or containers with Teflon-lined lids	✓ HDPE or polypropylene containers for sample storage ✓ HDPE or polypropylene caps
Tyvek® suits and waterproof boots	✓ Clothing made of cotton preferred ✓ Boots made with polyurethane and polyvinyl chloride (PVC)
Waterproof labels for sample bottles	✓ Paper labels with clear tape
Sunscreens, insect repellants	✓ Products that are 100% natural, DEET
Sharpies	✓ Ballpoint pens
Aluminum foil	✓ Thin HDPE sheeting

Other Special Considerations

- Field QC
- Decontamination of sampling equipment
- No pre-wrapped food or snacks
- Avoid cosmetics, moisturizers, hand creams on day of sampling.
- Do not filter aqueous samples.
- Visitors to site must remain at least 30 feet from sampling area.
- Wash hands with water after leaving vehicle before setting up on a well.
- Field blanks



Equipment Decontamination

Prohibited	Allowable	Needs Screening
Decon 90	Alconox, Liquinox, Citranox	Municipal water
PFAS Treated Paper Towels	Triple rinse with PFAS-free deionized water	Recycled paper towels
	Cotton cloth or untreated paper towels	Chemically treated paper towels

1. Disposal after use – Sample Bottles, tubing
2. Field sampling equipment used at other sites may be highly contaminated- Decontamination to prevent cross-contamination.
3. Sampling equipment scrubbed with polyethylene or PVC brush to remove particulate.
4. No food or beverage consumed in sampling area
5. Only bottled water or Gatorade for hydration OUTSIDE of the sampling area
6. Wash hands and change nitrile gloves frequently.

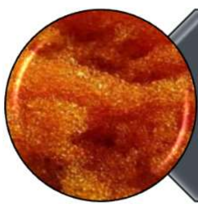
Regulatory Issues

- Toxic release inventory now reporting PFAS
- USEPA developing PFAS emission limit guidelines
- Preliminary Effluent Guidelines Program Plan 15
  - Organic chemicals, plastics and synthetic fibers (OCPSF)
  - Metal finishing
  - Meat and poultry products
  - Steam electric power generating
  - Landfills
  - Textile mills
- Beginning to see effluent limits for discharges
- Develop PFAS as CERCLA hazardous substances and/or RCRA (ongoing)

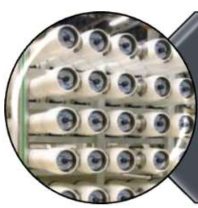
What Do We Do About It?

- Available technologies for PFAS removal:

Granular Activated Carbon (GAC)



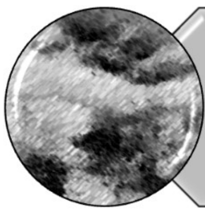
Anion Exchange (AIX)



High Pressure Membranes

What do we do about it?
GAC Treatment Option

Granular Activated Carbon (GAC)



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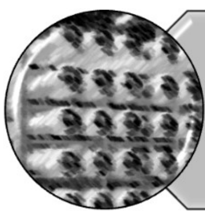
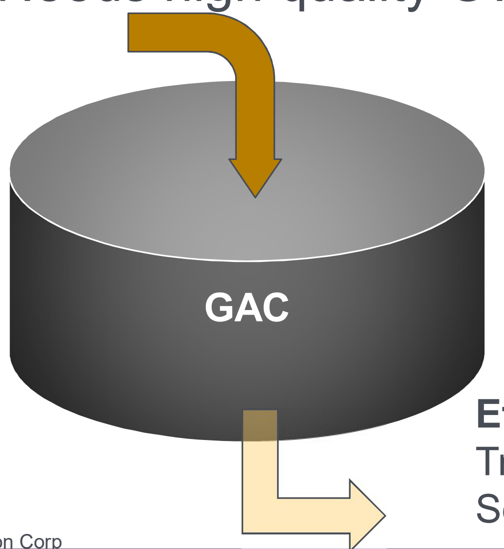


High Pressure Membranes

- ✓ **Water quality (e.g., low organics)**
- ✓ **Compatible with existing treatment**
- ✓ **Low GAC operation tasks**
- ✓ **Exhausted Carbon Management**
- ✓ **Comparatively lower cost (vs. membranes)**

Activated Carbon

- Granular Activated Carbon (GAC) Well Demonstrated
  - Bituminous GAC – increasing full scale installations
  - Competing Organics fill absorption sites
  - Needs high quality GW treatment (Fe, TDS, etc.)



Effluent
Treated
Solution

Courtesy Calgon Corp

- GAC effective for removal of long-chain PFAAs, but not well on short-chain PFAAs
- Removal of precursors less effective;

General Comments:
Typically operate downflow

Typically Empty Bed Contact Time (EBCT) is in **minutes**

Typical Superficial Velocities:
2-5 gpm/ft^2

Isotherm testing initially done for feasibility

Accelerated Column Test (ACT)/Rapid Small Scale Column Test (RSSCT) or pilot performed to validate system design

Some usage rates/performance can be computer modeled in water

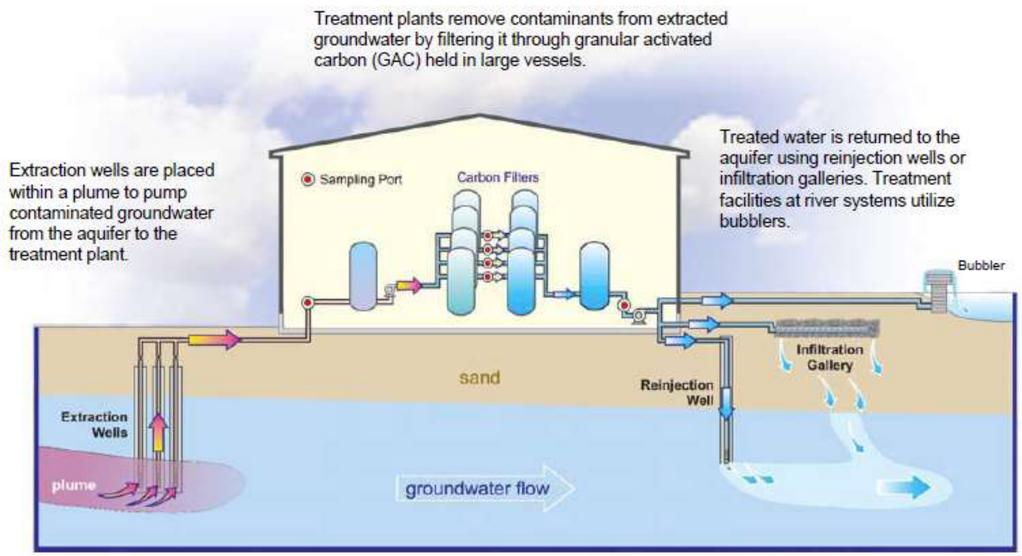
GAC can be reactivated once it has been used

GAC Adsorption

- With GAC, adsorption occurs on the surface of the interior graphite platelets which are the solid part of the porous structure of the granules
- Adsorption is an equilibrium process and capacity is concentration dependent
- Exhausted GAC can often be sent to a reactivation furnace to destroy the adsorbates and produce a reusable product – air emissions?

GAC Perfluorinated Compound Adsorption

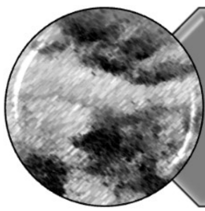
- GAC has been in use at Minnesota sites for groundwater treatment for many years in this service
- Spent GAC can be successfully reactivated from this service for a minimum of waste generation
- As is typical of GAC adsorption, smaller and lower formula weight compounds tend to adsorb less strongly than larger, heavier compounds with similar structures.



Courtesy USAF – Jt. Base Cape Cod

Ion Exchange Treatment Option

Granular Activated Carbon (GAC)



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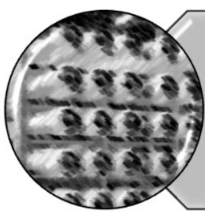
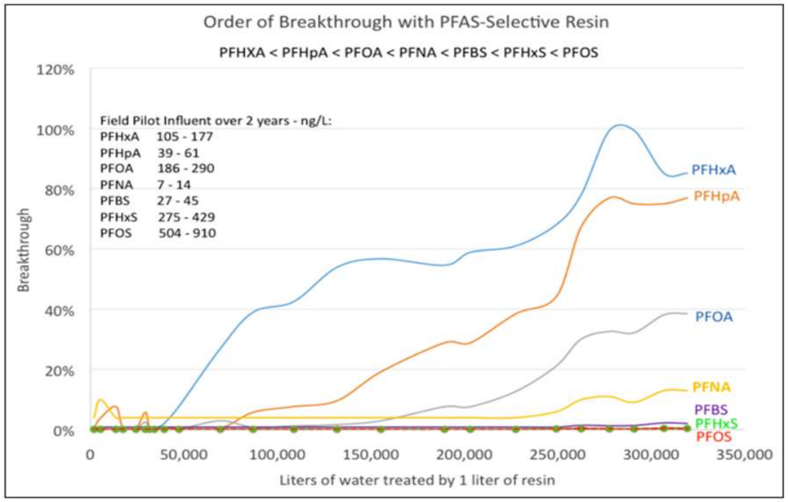


High Pressure Membranes

- ✓ **Water quality (e.g., low organics)**
- ✓ **Compatible with existing treatment**
- ✓ **Smaller footprint than GAC**
- ✓ **Exhausted media management**
- ✓ **Comparatively lower cost (vs. membranes)**

IX - Single-Use Selective Resin or Regenerable Media + Incineration



Courtesy Purolite

Short Contact Time ~3 mins +

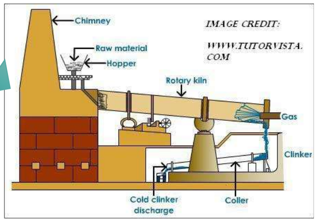
Treated water

Discharge to system

Cement Kiln Incineration 1400°C to 2000°C

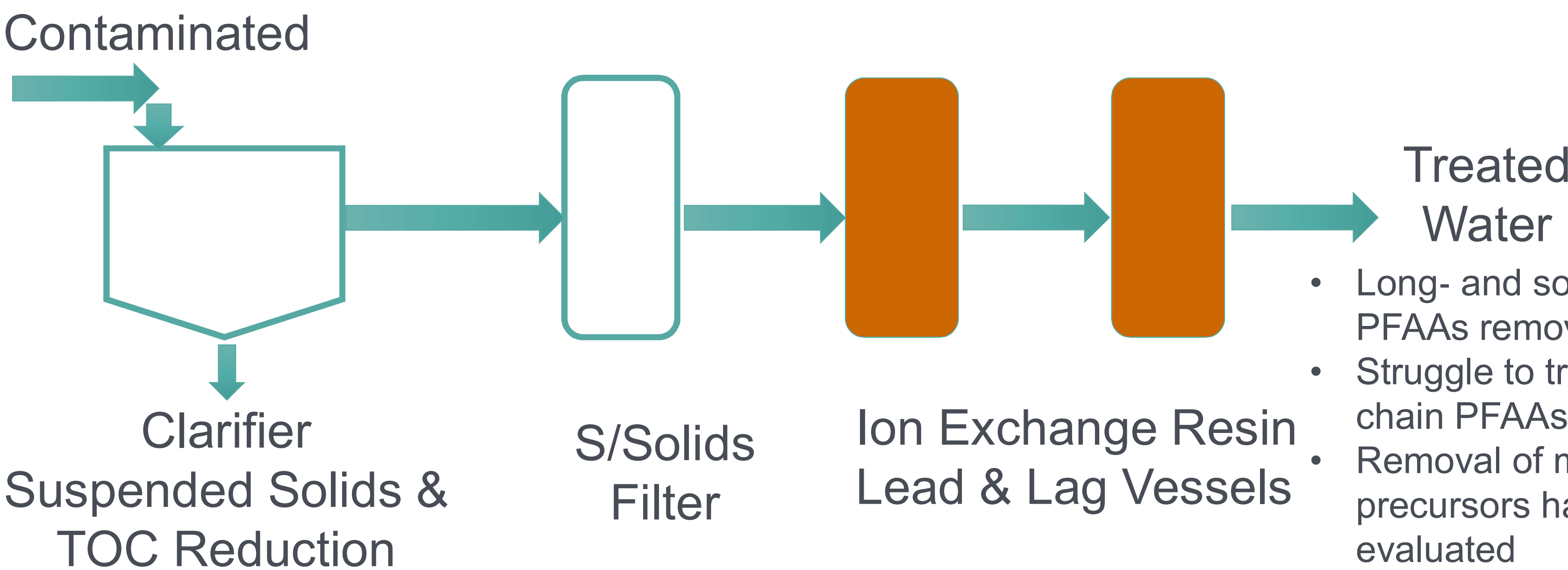
Regeneration or

PFAS loaded resin



Complete Destruction of PFAS ????

General Process Flow Scheme Using Ion Exchange



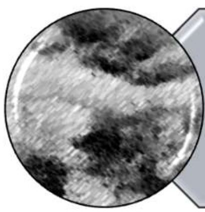
- Long- and some short-chain PFAAs removed
- Struggle to treat the shortest chain PFAAs
- Removal of most PFAA precursors has not been evaluated
- Background organics Anions (chlorides, sulfates)
- Shorter detention time
    - ~3 min Vs. ~15 min for AC

Selective IX Capacity in leachate : Expect 10,000 to 20,000 BV

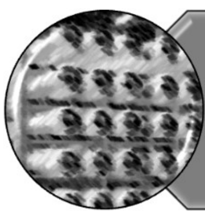
Courtesy Purolite, Inc.

Reverse Osmosis Option

Granular Activated Carbon (GAC)



Anion Exchange (AIX)

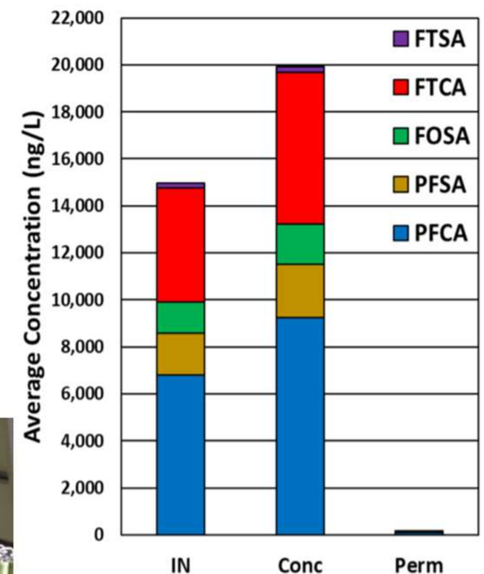


High Pressure Membranes

- ✓ **Water quality (e.g., low organics)**
- ✓ **Compatible with existing treatment**
- ✓ **Removes all contaminants**
- ✓ **Regenerant stream management**
- ✓ **Comparatively lower cost**

Reverse Osmosis Process Flow

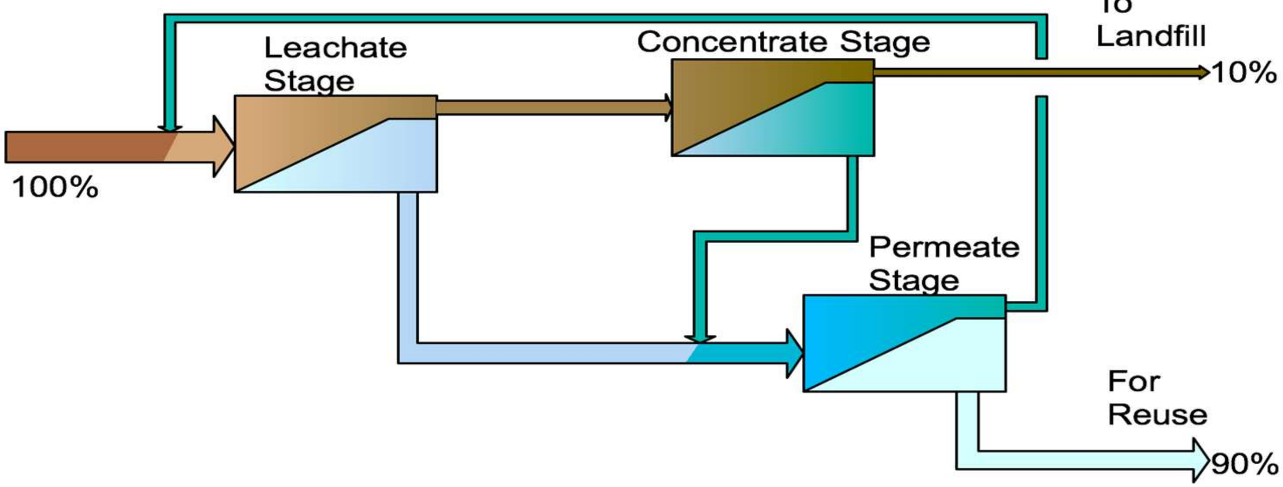
- Membrane Based Separation Process- 99.9% removal +/-
- Separates Water from Organic and Inorganic Compounds.
- Effluent is PFAS free.
- What to do with Reject???
  - Discharge to ocean (depends on location)
  - Solidification
  - Evaporation – Crystallization
    - Heat needed
    - Air Emissions
  - Other –
    - Electrochemical Oxidation
    - Plasma



Courtesy: Rochem Corp

Reverse Osmosis

- Membrane Based Separation Process. 99.9% + removed
- Separates Water from Organic and Inorganic Compounds.
- If recirculation is allowed, returns the contaminants to the landfill where they were originally deposited.
- Effluent for reuse or disposal.



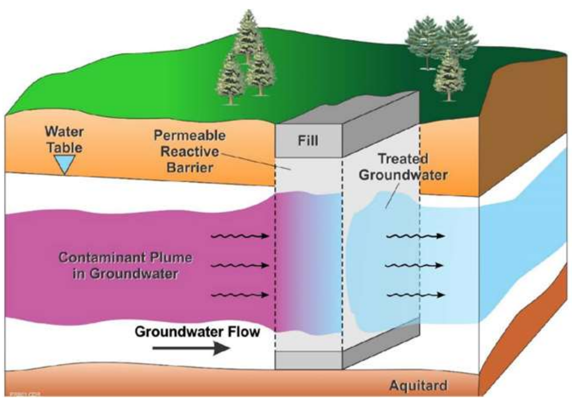
Second Stage to reduce reject volume – or Evaporation

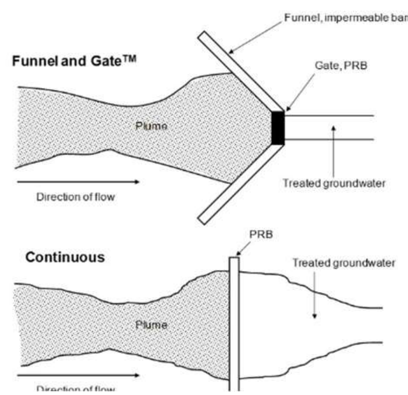
Groundwater Treatment

- Groundwater
  - Ex-Situ
  - In-Situ

In-Situ Groundwater Treatment

- Colloidal GAC
- Injection and stabilize PFAS – Permeable Reactive Barrier (PRB)
- Cut-off wall versus Funnel & Gate





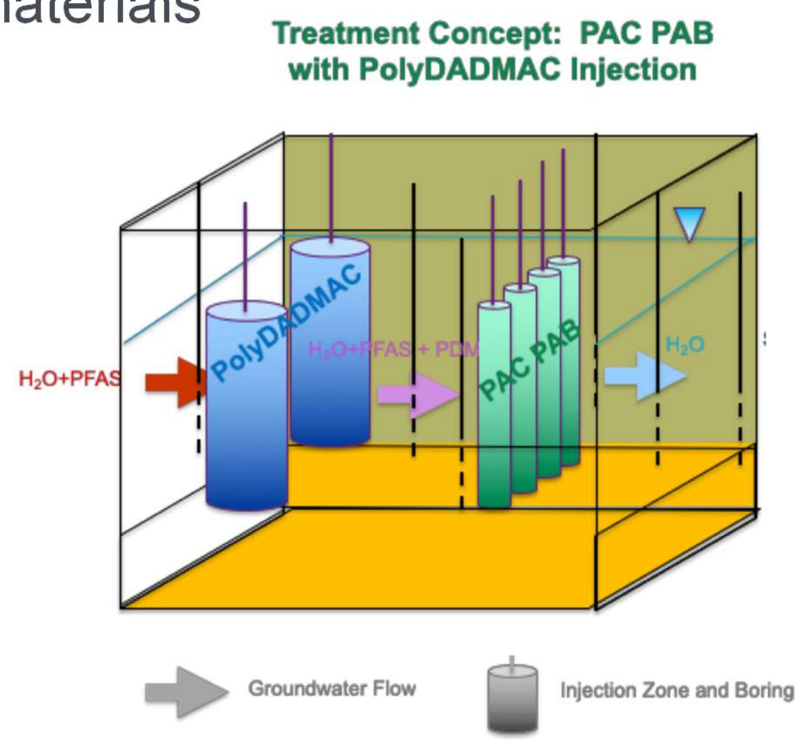
Courtesy REGENESIS: https://clu-in.org/conf/tio/DCHWS10/slides/3Slide_Presentation_for_Ryan_Moore_(YM),_REGENESIS.pdf

Grayling, MI – WWII Army Airfield
130 ng/L PFAS + PCE

CEC

Injectable Liquid Sorbents

- Similar to PlumeStop but non-proprietary materials
- Multiple US DOD research projects:
  - UMN, Tufts, Jacobs
  - UAZ, Jacobs
- US DOD full-scale field pilot test funded
- Multiple polymers have been tested to find optimal one(s):
  – PolyDADMAC (PDM)
  – Polyamine
  – "Designer" polymers
- In combination with powdered activated carbon (PAC) and Permeable Absorptive Barrier (PAB)



Current Ex-Situ Groundwater Technologies and Surface Water

- Similar to Drinking Water Already Presented
- Most Amenable to Ex-situ Treatment
  - Modified Bentonite (Fluorosorb)
  - Carbon
  - Resin
  - RO

Source: NH Business Review 2018v

Source: Australian DOD 2018

Four Adsorbents

FLUORO-SORB®
200 adsorbent

GAC

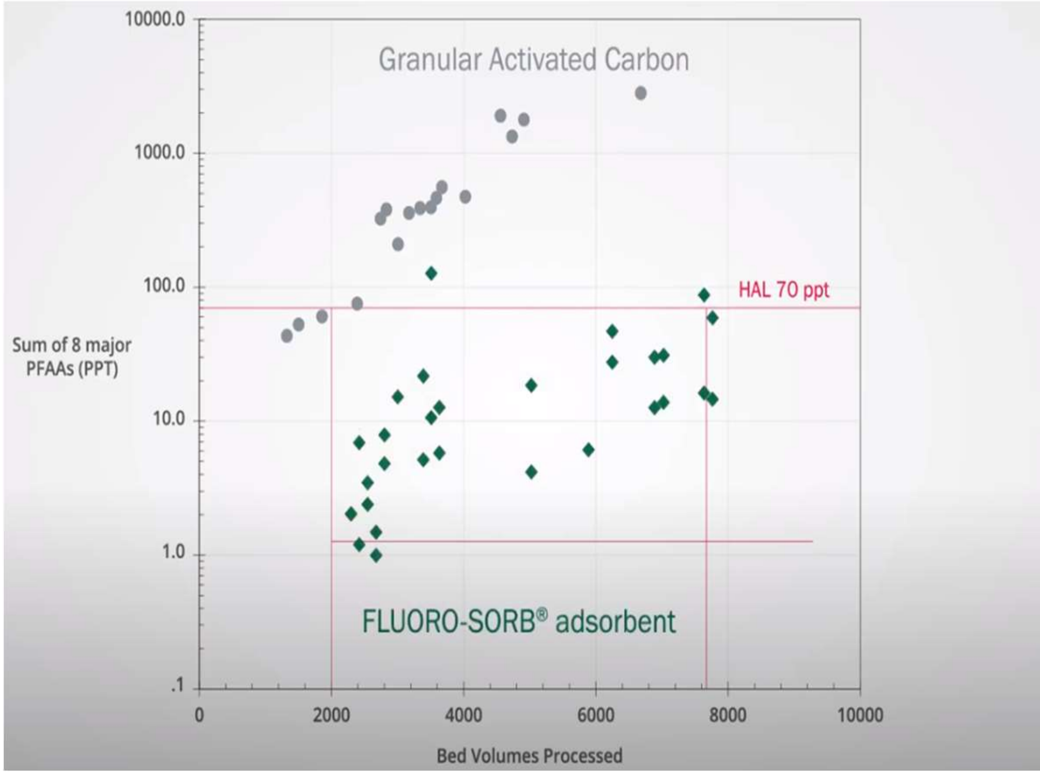
Hardwood Biochar

Ion Exchange Resin

Relative Adsorbance?

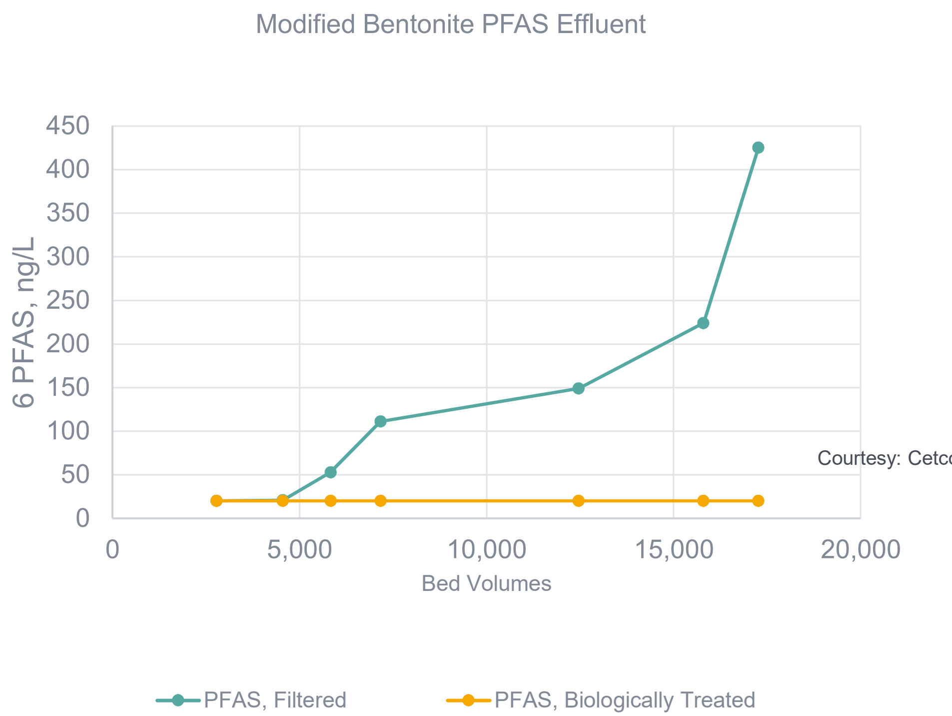
Modified Bentonite
(Adsorbent)

- Effective on groundwater
- Minimal pretreatment
- Unaffected by organic content
- PFOS, PFAS >99% removal
- Longer bed volume than GAC
- Spent media fixation/disposal
- Pilot tests needed



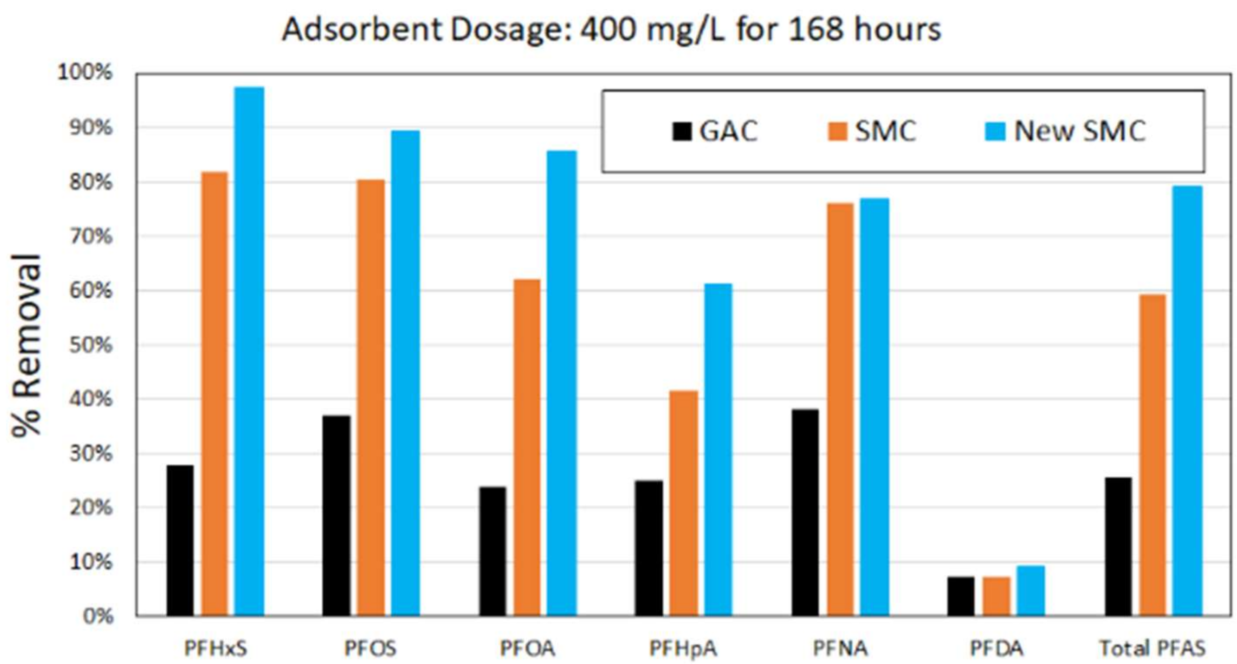
Surface Modified Bentonite
(Adsorbent)

- Bench test on GW, Leachate
- Pretreatment
- PFOS, PFAS >99+% removal
- Longer bed life than GAC
- Spent media fixation/disposal
- **Susceptible to foulants**
- Static Bed versus Fluidized Bed



Surface Modified Clay Performance

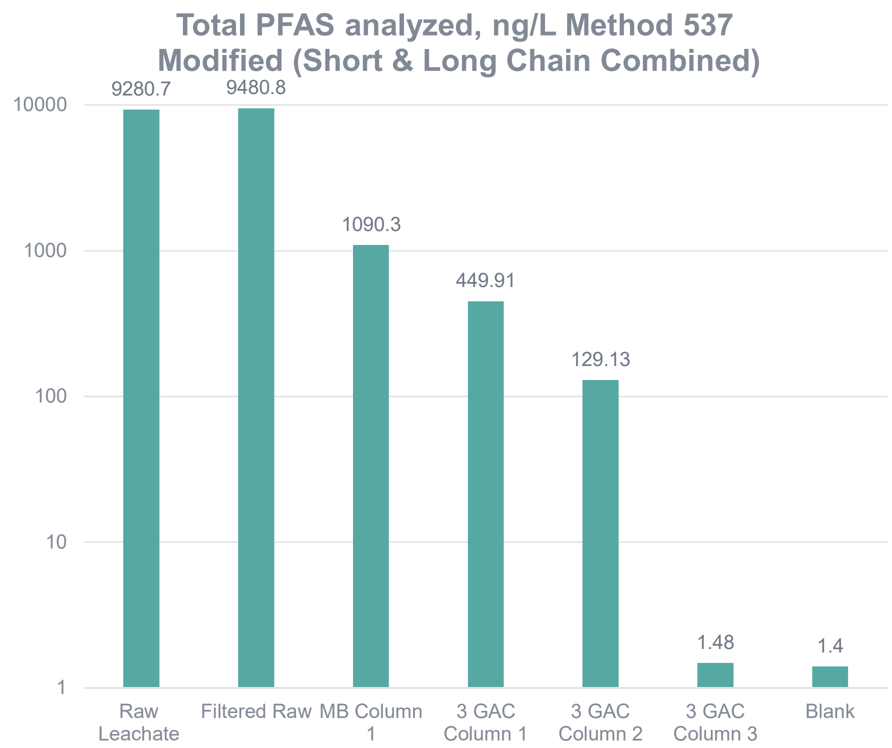
PFAS REMOVAL EFFICIENCY - LANDFILL LEACHATE

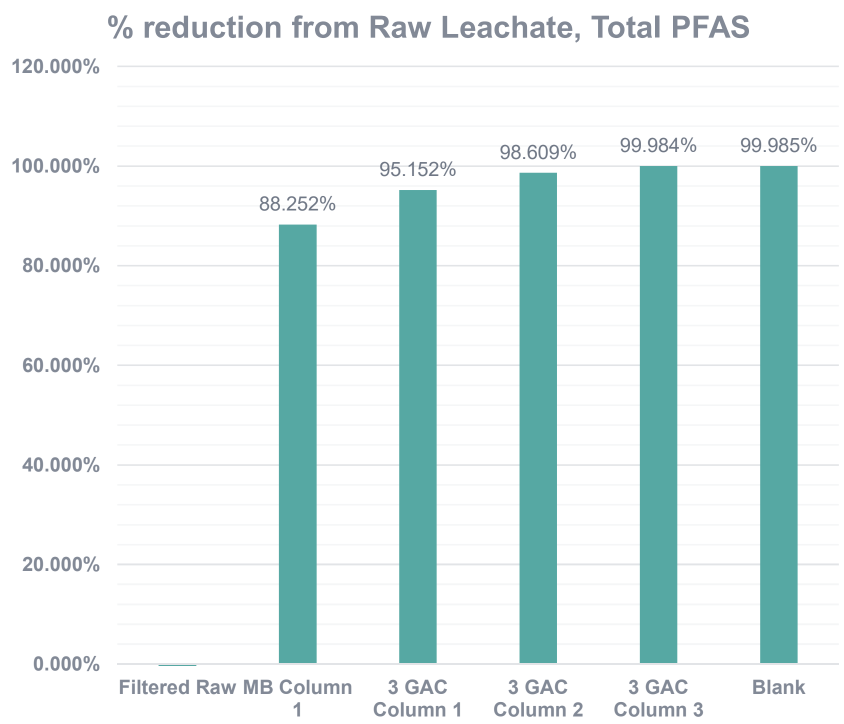


Adsorbents Bench Test System

- 3 stage GAC: 10-minute EBCT (3-GAC)
- Modified Bentonite (MB) adsorbent: 10-minute EBCT
- PFAS Contaminated Pilot Test in Orange County, CA

Granular Activated Carbon
Total PFAS Analyzed, ng/L





Orange County GW Pilot Program

Vendor	Product	Media Material/Type	GAC Pilot	IX Pilot	RSSCT (Lab)
Granular Activated Carbon (GAC)					
Calgon	FILTRASORB 400 (F400)	Bituminous GAC (virgin)	X		X
Calgon	FILTRASORB 400 (F400)	Bituminous GAC (reactivated)	X		X
Calgon	FILTRASORB 400 (F600)	Bituminous GAC	X		X
Cabot	Norit GAC400	Bituminous GAC	X		X
Cabot	Norit HYDRODARCO 4000	Lignite-based GAC	X		X
Evoqua	UltraCarb 1240LD	Sub-Bituminous GAC (low density)	X		X
Evoqua	AquaCarb 1230CX	Enhanced Coconut Shell GAC	X		X
Jacobi	AquaSorb F23	Enhanced Blended GAC	X		

Vendor	Product	Media Material/Type	GAC Pilot	IX Pilot	RSSCT (Lab)
Ion Exchange (IX) Resins					
Purolite	Purofine PFA694E	Single use anion exchange resin		X	
Calgon	CalRes 2301	Single use anion exchange resin		X	
Evoqua	PSR2+	Single use anion exchange resin		X	
ECT2	Sorbix LC4	Single use anion exchange resin		X	
Alternative (Novel) Adsorbents					
CETCO	FLUORO-SORB® 200	Surface modified bentonite clay		X	X
Cyclopure	DEXSORB+®	Cyclodextrin-based adsorbent		X	X

Adsorbent Media	Time (Months) to Reach PFOA Breakthrough	
	Initial Breakthrough Above Detection Limit	Effluent Concentration at ~60% of Influent Concentration[a]
Granular Activated Carbon		
Calgon F400 (Virgin and Reactivated)	5.7 (V), 5.2 (R)	> 13
Calgon F600	2.7	> 13
Cabot Norit GAC 400	3.1	> 13
Evoqua AquaCarb 1230CX	2.7	12.8
Cabot Norit HYDRODARCO 4000	4.3	9.0
Jacobi AquaSorb F23	5.2	8.9
Evoqua UltraCarb 1240LD	3.8	8.7
Ion Exchange (IX) Resins		
Evoqua PSR2+	7.1	> 13
Calgon CalRes 2301	4.3	7.9
Purolite Purofine PFA694E	4.3	7.9
ECT2 Sorbix LC4	3.9	7.1
Alternative (Novel) Adsorbents		
CETCO FLUORO-SORB® 200	8.7	> 11
Cyclopure DEXSORB+®	2.7	5.6

Wastewater PFAS Treatment Processes

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

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

Current Liquids Treatment Technologies
(Usually Treatment Trains)

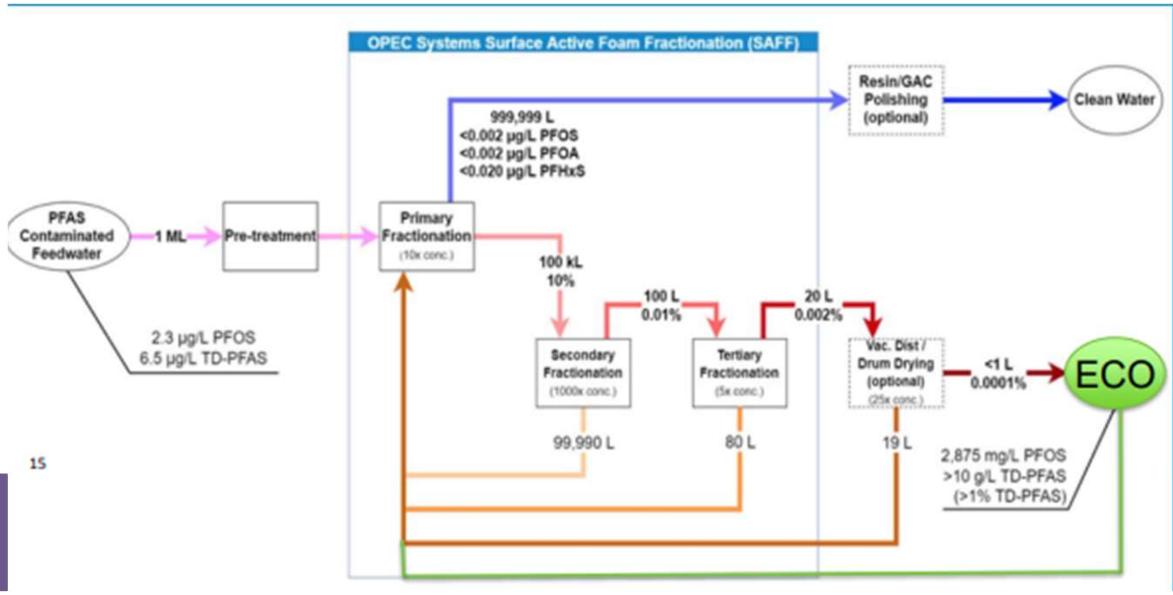
- Separation Technologies
  - Activated Carbon
  - IX Resin
  - Foam Fractionation
  - Deep Well
  - RO
  - Other Adsorbents
- Residuals Management

Source: NH Business Review 2018v

Source: Australian DOD 2018

Foam Fractionation

- Several manufacturers
  - EPOC (Allonia); Montrose; ECT2; Arcadis; Evocra; Sanexen; others
- Air, Nitrogen, Ozone (Ozofractionation) separation on ozone/air microbubbles due to PFAS surfactant properties;
- Polar properties of PFAS attach “head” to bubbles for removal
- Nano-bubbles extracts 95% long & short chain (aphrons).



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First EPOC Foam Fractionation Pilot Test on Leachate in the US!

- Removal of six Massachusetts PFAS to below drinking water standards - < 20 PPT
- Removal efficiencies in excess of 99% or <MDL of 1 PPT

Foam Fractionation

- Takes advantage of foaming capabilities as PFAS attaches to micro or nano sized bubbles
- Better performance on long chain (almost 100% removed)
- Very inexpensive operation
- Small amount of residual concentrated PFAS

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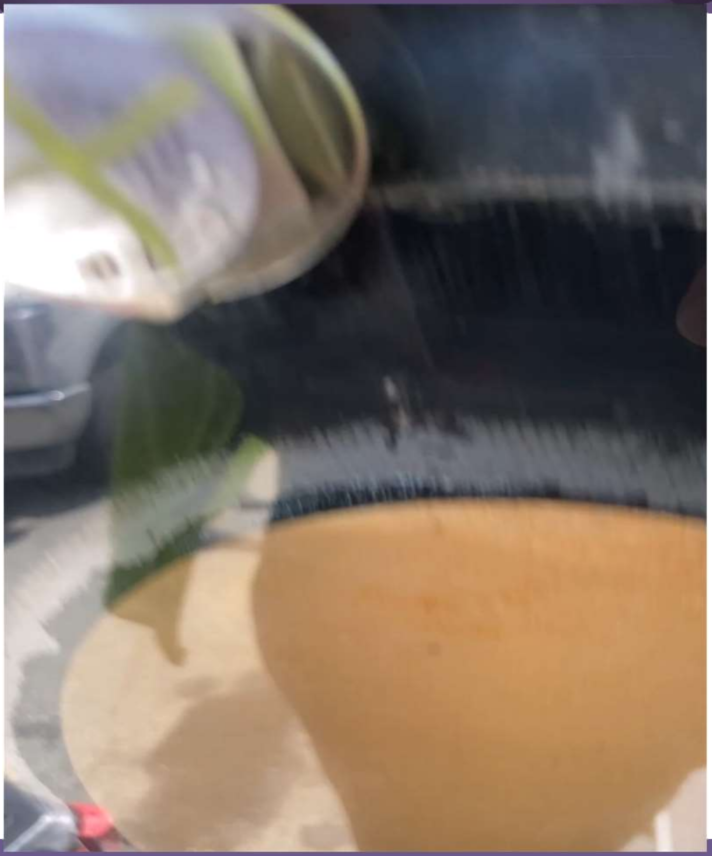
SAFF in Action

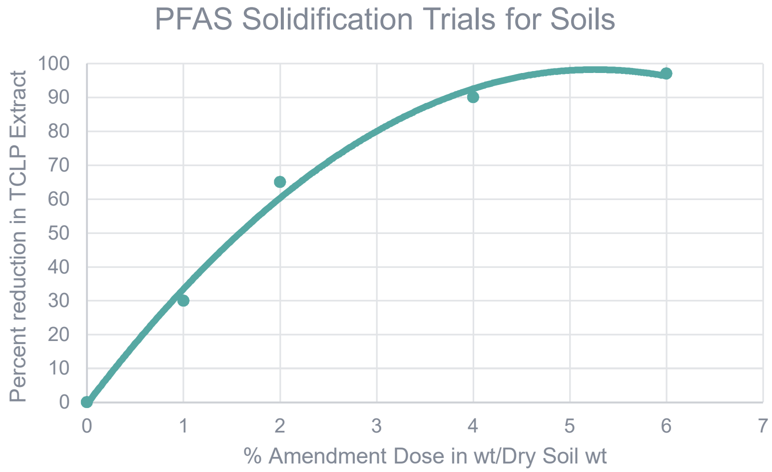


Residual Technologies

- Stabilization/Solidification – Pending regulatory questions (LDRs)
  - Cementitious S/S
    - Encapsulation (In totes or vessels)
    - Holcim/ADC
  - Return to the landfill
  - Hazardous Waste Landfill Haul and Dispose
- Destruction – Similar to S/S on regulatory
  - Incineration – judged to be not viable due PFAS emissions
  - Plasma
  - Supercritical Water Oxidation
  - ElectroChemical Oxidation
  - Reductive Defluorination Technology

Leachate Residuals PFAS Stabilization

- CEC Solidification of SAFF
- 0.6:1 TCLP 99.9% retention all PFAS



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

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

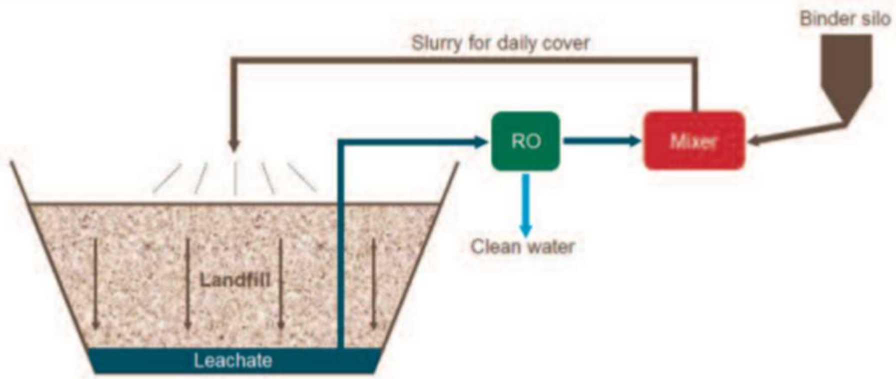
[PFOS] = **14,000 -** 100,000 ng/Kg
[PFAS] = 2,500 – 17,000 ng/Kg

Tested with Fluoro Sorb from Cetco

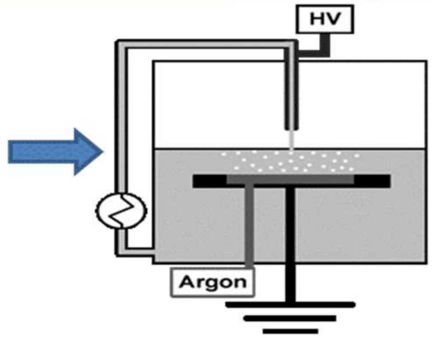
Fixation of Residuals
(Holcim/Lafarge)

- Proprietary cement binder
- No free liquid (Paint Filter Test)
- Friable for use as Alt Daily Cover

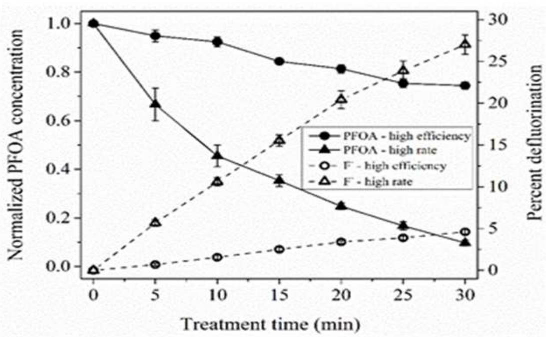
MAR- Enviroset	As Received	SPLP
	Results	Results
Sand	ppt (ng/L)	ppt (ng/L)
PFNA	800	11
PFOS	4,900	63
PFOA	1,500,000	390
NY State- Enviroset		
Sand		
PFNA	500	ND
PFOS	5,900	ND
PFOA	2,400	ND

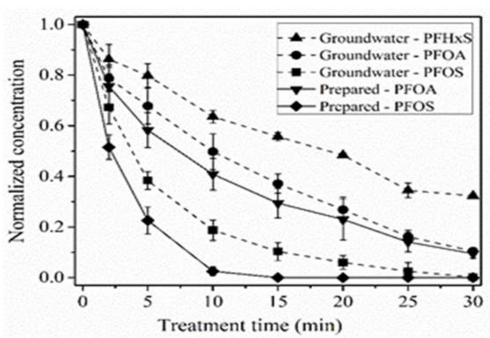


Plasma PFAS Transformation



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.

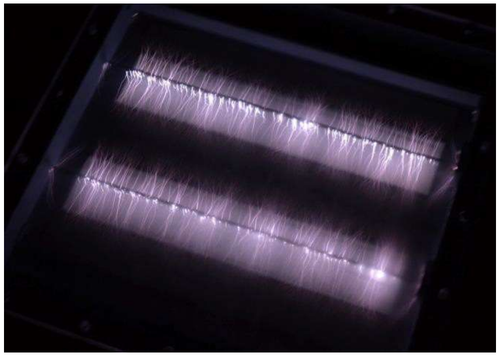




Major byproducts: fluoride ions, fluorinated gases and shorter-chain PFAAs

Courtesy of Selma MededovicThagard, Clarkson University

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.

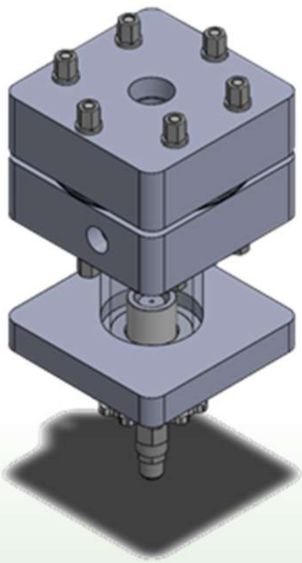
Solid-phase extraction			
Compound	$C_{0\,min}$ (µg/L)	$C_{60\,min}$ (µg/L)	Removal (%)
Perfluorooctanoic acid (PFOA)*	0.89	0.0035	99.6
Perfluorooctane sulfonate (PFOS)*	0.18	0.0026	98.5
Perfluoroheptanoic acid (PFHpA)	0.11	0.0002	99.8
Perfluorohexane sulfonate (PFHxS)	0.32	0.0041	98.7
Perfluorohexanoic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

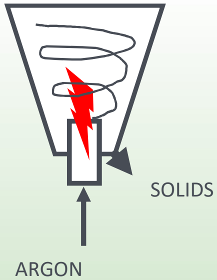
Courtesy of Selma Mededovic Thagard, Clarkson University and John Van Winkle, 88th Air Base Wing Public Affairs

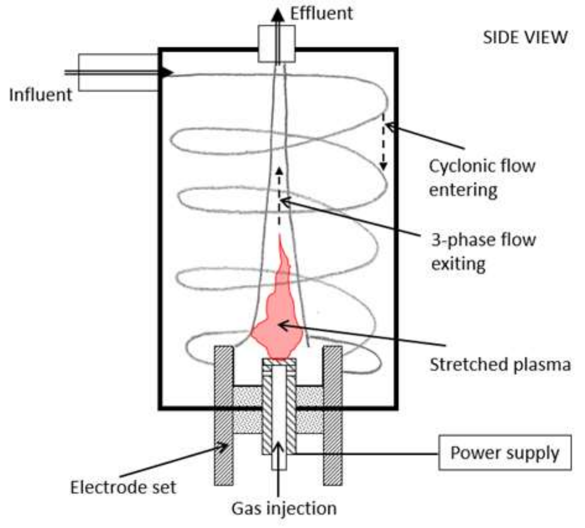
PLASMA VORTEX



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

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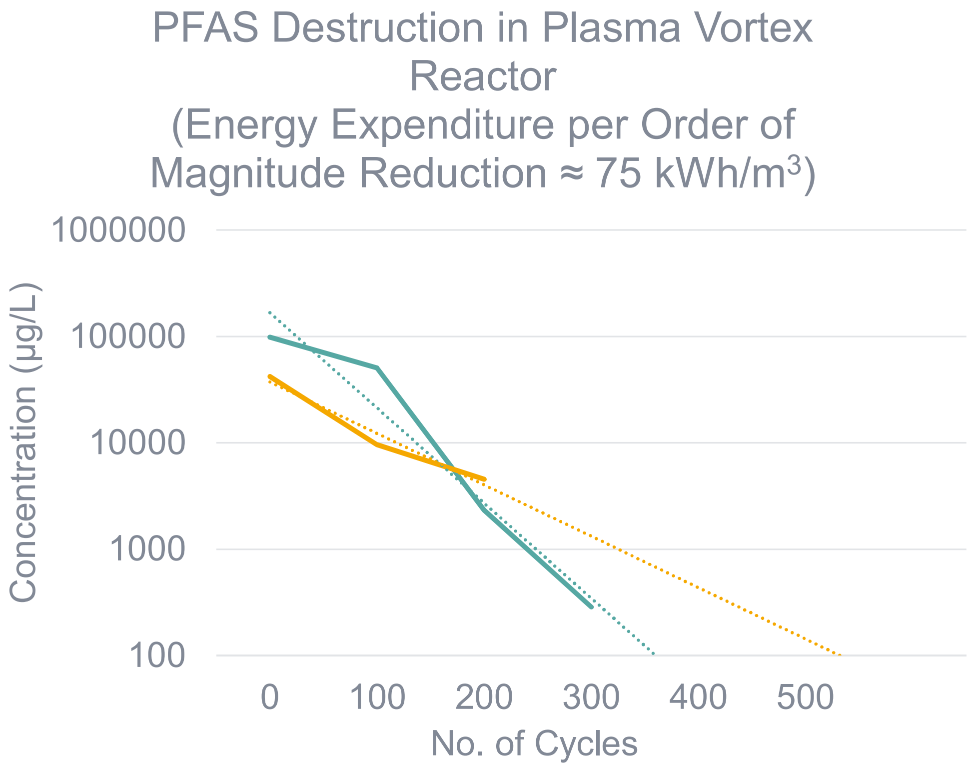
Plasma Vortex

(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

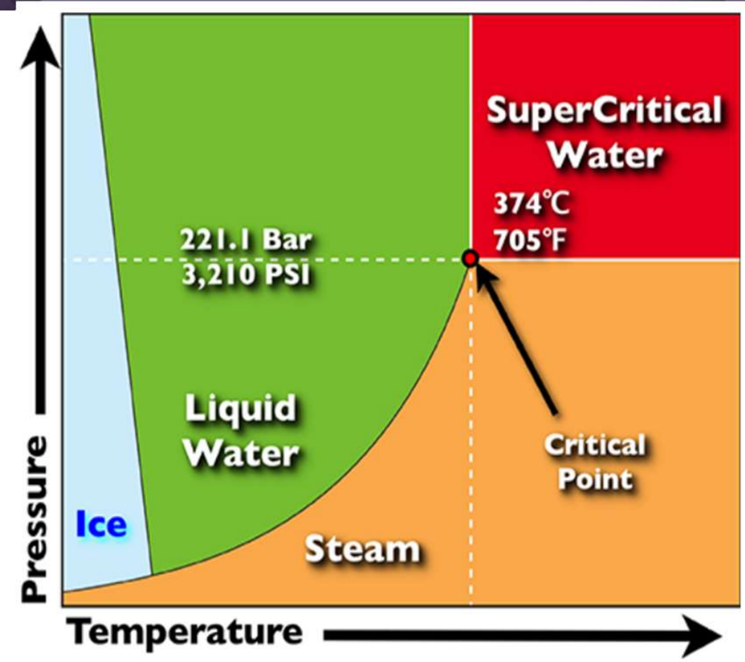
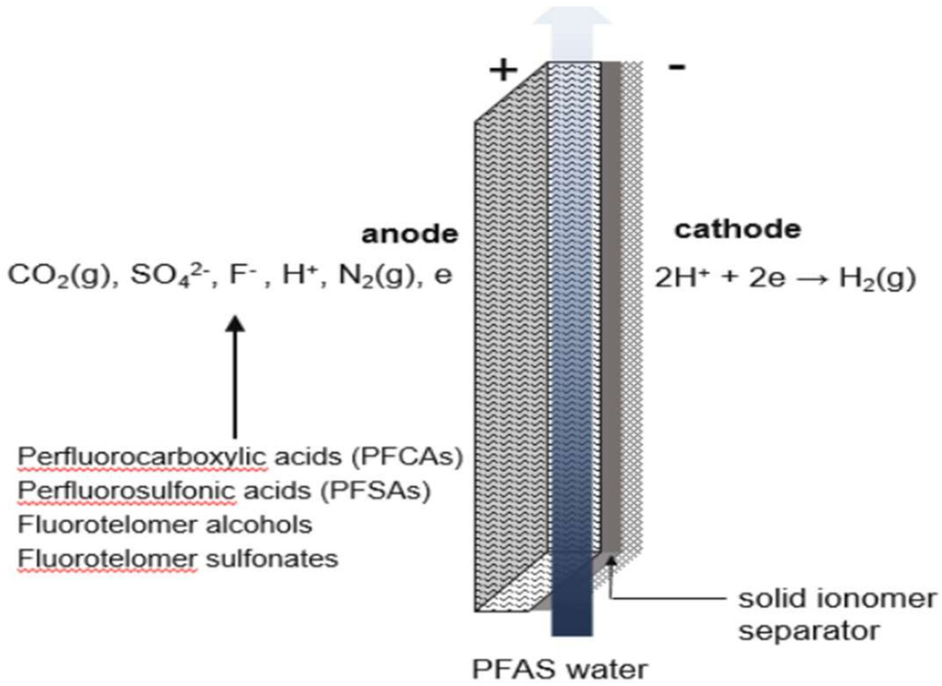


Figure 1. SCWO reactions occur above the critical point of water. Image credit: Jonathan Kamler.

EPA, Jan 2021

Electrochemical Oxidation

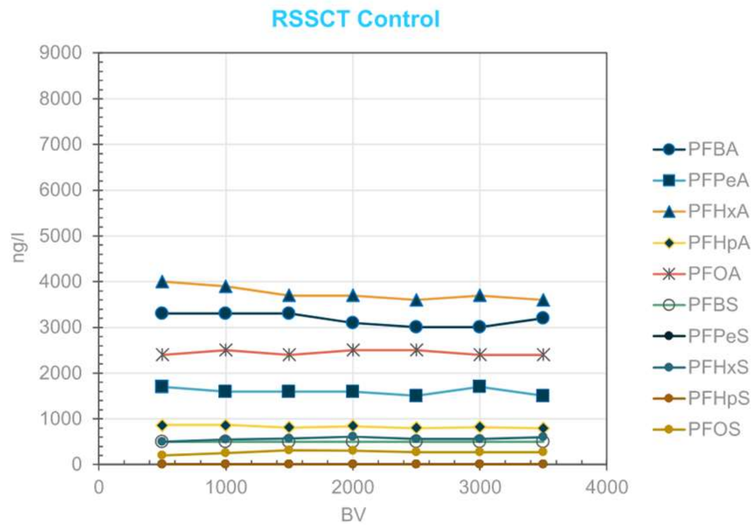
Various Equipment designs



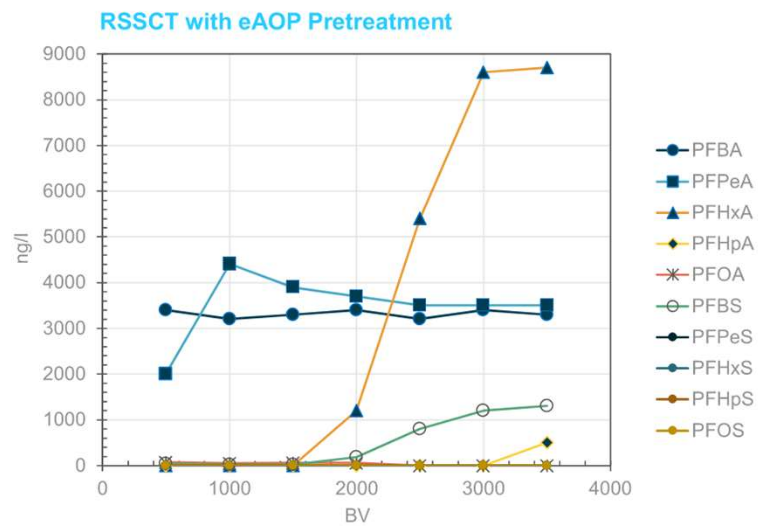
- Several Vendors
  - ECT2; Aclarity; Sanexen; Siemens; OXbyEL; others
- Power Requirements
  - 0.125 - 0.5 kwh/gallon
  - 6 volts produces free electrons
- Electrode materials
  - Titanium; boron doped diamond
- Single pass v. multiple pass
- Destroys ammonia too!

Electrochemical Oxidation

- Landfill Leachate in Bench Test
- Chemical oxidation followed by electrochemical oxidation
- ½ KwH per gallon? Ammonia destruction/PFAS destruction



All PFAS breakthrough from the beginning



Only short chain PFAS materials breakthrough

Comparative Emerging Contaminants Treatment Technologies

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

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

Summary

- PFAS Treatment typically two stage process (concentration to destruction)
  - Alternatives exist for concentration step
    - Technologies are mostly mature with some minor improvements expected
    - Largest unknown – what will be the “allowed” wastewater discharge limit
  - Destruction – Regulatory Questions
    - What will be EPA’s directives/mandates?
    - Approved Destructive Method(s)?
    - Hazardous Waste Status? – Listed or Characteristic or Not?
    - Huge technology advances ongoing for most methods
- Market seems to be creating Hub/Spoke system for PFAS management – on-site concentration step followed by destruction treatment hub

Treatment Challenges

- Carboxylates (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?

Case Study – 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

OHSL – Reverse Osmosis System

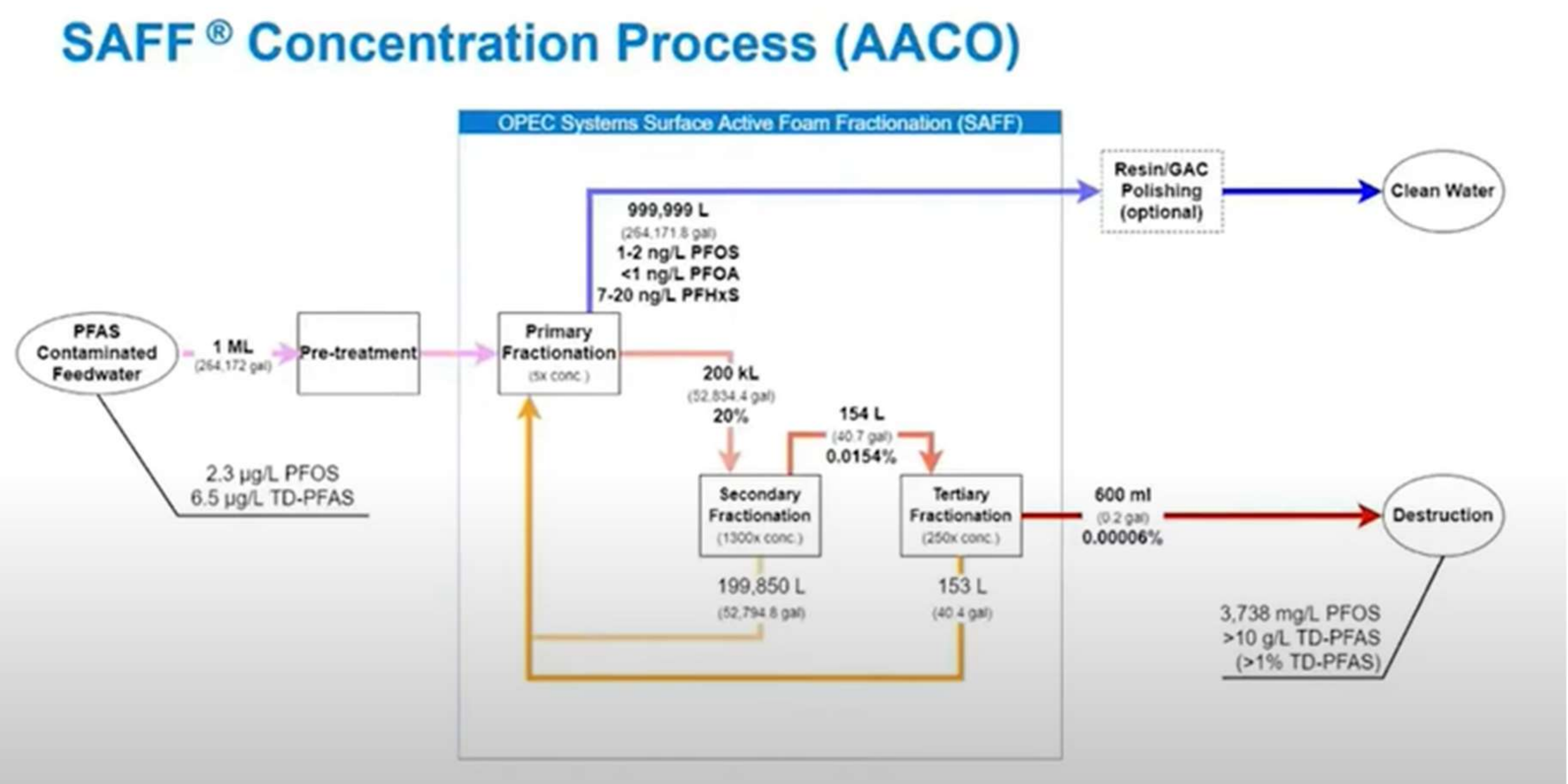
Rochem, EGLE, and MWRA Landfill Leachate PFOA and PFOS Study, March 2019

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 - Foam Fractionation

Courtesy: OPEC

SAFF Process Flow Diagram May 2019 – April 2021



Foam volume reduction by vacuum process

Courtesy:OPEC

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Case Study – 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

Slide 65

CI1 Cooper, Ivan, 6/1/2021

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%

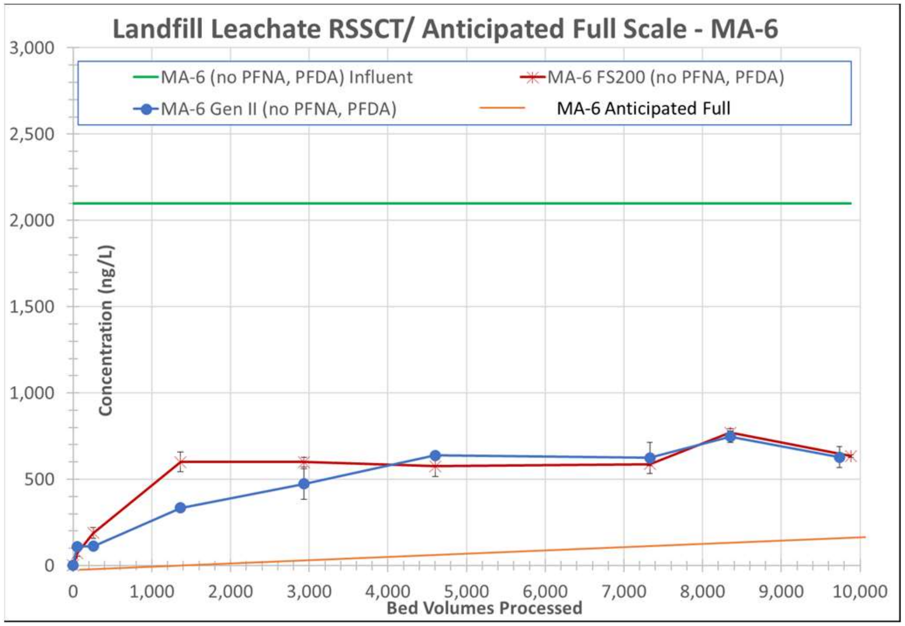
OPEX Costs for Removing PFAS from Landfill Leachate:
SAFF40 case study after two months recycling leachate from a Telge landfill facility in Sweden

- 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 – FluoroSorb

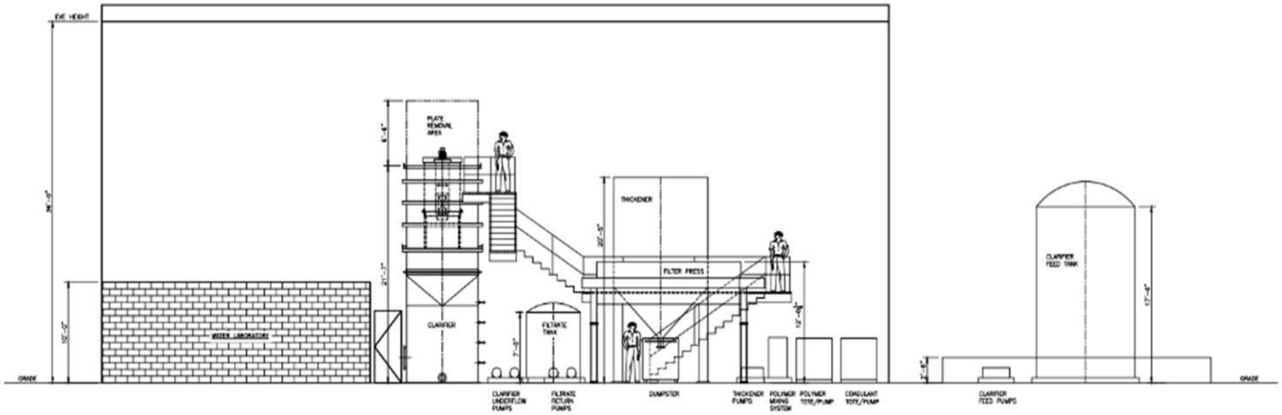
- Bench test
- Pilot Test
- Full Scale Design
  - Polymer/Coagulant – iron/solids removal
  - Inclined plate clarifier
  - Include SAFF?
  - Moving bed media filtration
  - Moving bed Fluoro Sorb media
  - Effluent storage
  - Clarifier solids & backwash concentrated/dewatered
  - Solidification residual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



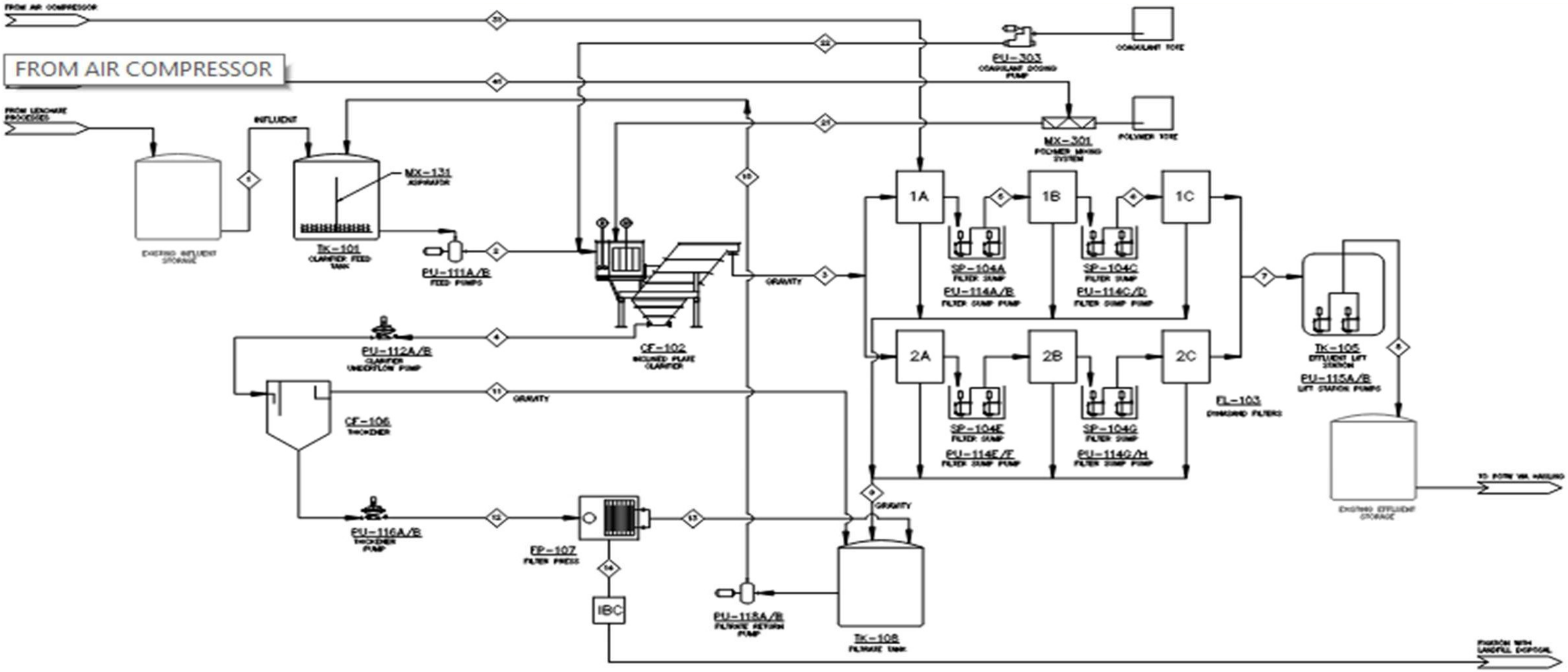
Case Study – FluoroSorb

1st Phase Pilot Study

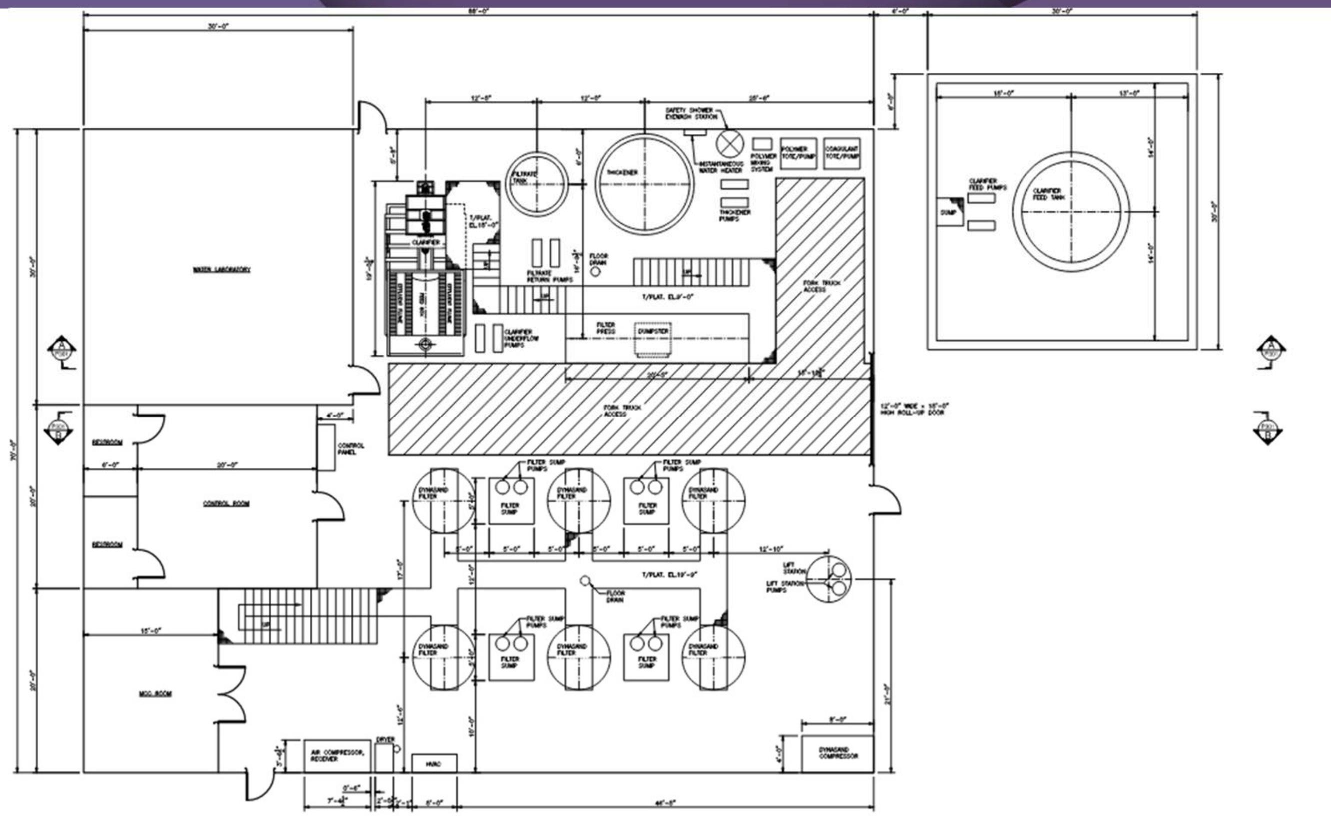
2nd Phase Pilot Study



FluoroSorb Process Flow Diagram



FluoroSorb Plant Layout



Solids Remediation Technologies

What's available now: Field-Demonstrated Technologies

Technology	Description
Sorption and Stabilization	Stabilization involves mixing waste with binding agents like clays, or other proprietary blends to make them less likely to be released into the environment. Questions remain about permanence. Soil (and liability) remains on site in perpetuity.
Excavation and Disposal	Excavation and transport offsite to a permitted landfill. Landfills starting to refuse PFAS wastes. Liability is potentially transferred to landfill. Future regulatory changes (e.g., hazardous substance) may affect options for disposal.
Excavation and Incineration	Incineration is the process of heating PFAS soils to temperatures high enough to destroy contaminants (>1,100 C). Limited facilities available that are permitted for PFAS. Complete destruction not well documented yet.

What's around the corner: Limited Application Technologies

Technology	Description
Thermal Desorption	Thermal desorption utilizes heat to increase the volatility of contaminants such that they can be removed (separated) from the solid matrix (typically soil, sludge or filter cake). Demonstrated in field; offers potential for on-site destruction.
Size Segregation/ Soil Washing	Size segregation can be as simple as dry sieving to separate coarse materials, which does not typically sorb PFAS, from fine material (e.g., clays and organics) which do sorb PFAS. Soil washing is a more involved process through rinsing, chemical separation, etc. Soil washing requires treatment of multiple waste streams to address "end of life" pathway.

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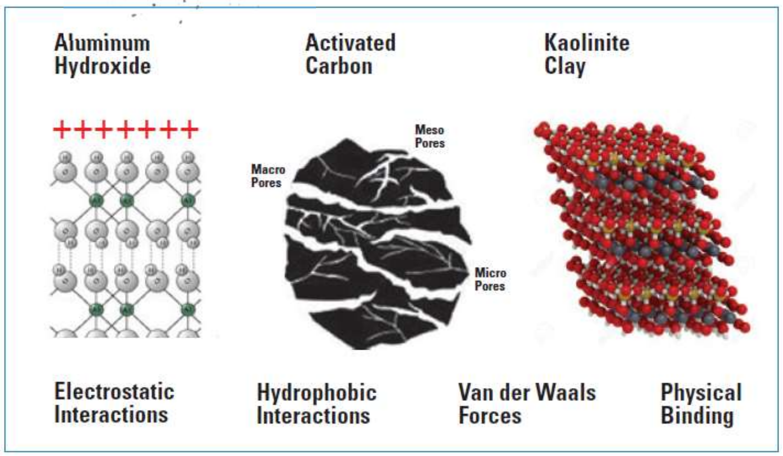
Sorption/Stabilization

- Immobilization via sorption
- Powder-based reagents with high surface area:
  - Example: Powdered activated carbon, aluminum hydroxide, kaolin clay
  - Added from 1-5% by weight to soil
  - Fully commercial & field demonstrated
- In situ with large diameter augers possible

Does not eliminate liability



Images courtesy of Ziltek™ and AquaBlok Ltd.

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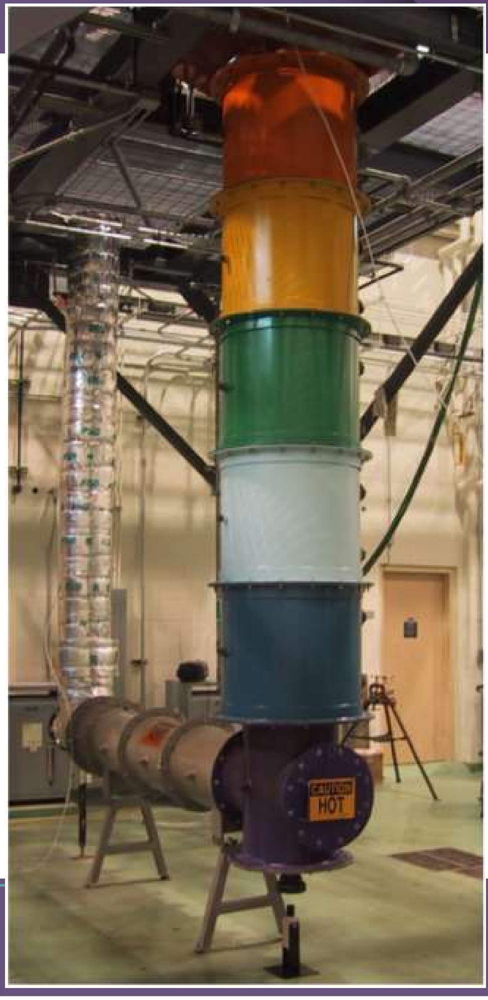
Excavation and Off-Site Disposal

- PFAS non-hazardous at present
- Dispose in Subtitle D permitted facility
- Some landfills not accepting PFAS soils
- Subtitle C permitted (hazardous) disposal 8-10x more expensive
- Future designation may impact options:
  - CERCLA hazardous substance – minimal
  - RCRA hazardous waste – substantial impact

Excavation and Off-Site Incineration

- Must be >1,100°C for PFAS
- Destruction assumed but not well documented
- Sampling methods still being developed
- US EPA, US DOD and other research programs looking closely at destruction in thermal systems
- One thermal facility in the US permitted by state for PFAS soil treatment (Moose Creek, Alaska)
- Hazardous designation could impact cost and availability



PFAS Summary

- Chemistry is important
- Regulations are evolving, Federal, State, Local
- Permitting and treatment are coming
- PFAS has health concerns
- Sampling is costly and time consuming
- Analytical methods still being determined
- Various treatment technologies exist
  - Complicated
  - Ultimate disposal evolving
  - Expensive