

Civil & Environmental Consultants, Inc.

Destroying PFAS in Groundwater & Landfill Leachate

NEWMOA Technical Series

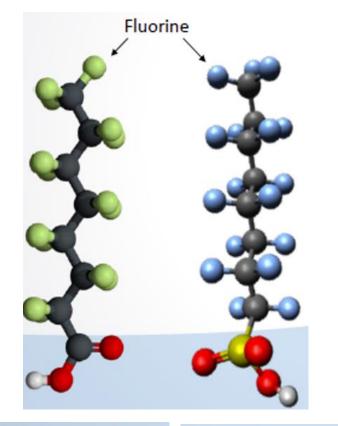
Ivan A. Cooper, PE, BCEE

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

May 25, 2021

Agenda

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



Perfluorooctanoic acid (PFOA) Perfluorooc

) Perfluorooctanesulfonic acid (PFOS)

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 Granular Colloidal Ion Exchange Polymers Modified bentonite	Reverse Osmosis/Nano/Ultra Foam Fractionation Deep Well Injection Cementitious encapsulation Electrodialysis Electrocoagulation	Plasma Thermal Supercritical Oxidation Electrochemical Photochemical 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



- Technologies Work on Some of the Compounds
- Site Dependent
- 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 Ex-situ Treatment
 - Activated Carbon
 - Resin
 - RO
 - Deep Well





Source: Australian DOD 2018

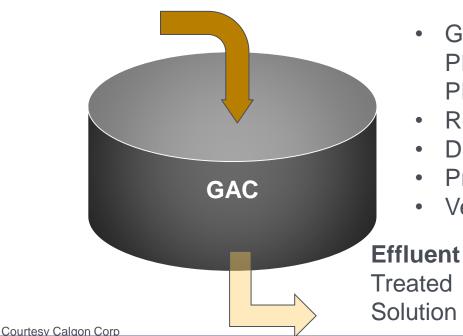


Source: NH Business Review 2018v



Activated Carbon

- Granular Activated Carbon (GAC) Well Demonstrated
 - Bituminous GAC increasing full scale installations
 - Competing Organics fill absorption sites



- GAC effective for removal of long-chain PFAAs, but not well on short-chain PFAAs
- Removal of precursors less effective;
- Drinking Water/Groundwater ok
- Pretreatment needed for leachate
- Very Short Bed Volume Life for Leachate

General Comments: Typically operate downflow

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

Typical Superficial Velocities: 2-5 gpm/ft²

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
- Exhausted GAC reactivated in a furnace destroys the adsorbents produces a reusable product but, air emissions?
- Blunt Hammer Adsorption
 - PFAS/VOC/Organics/etc.
 - Long Chain better than short chain (sometimes)

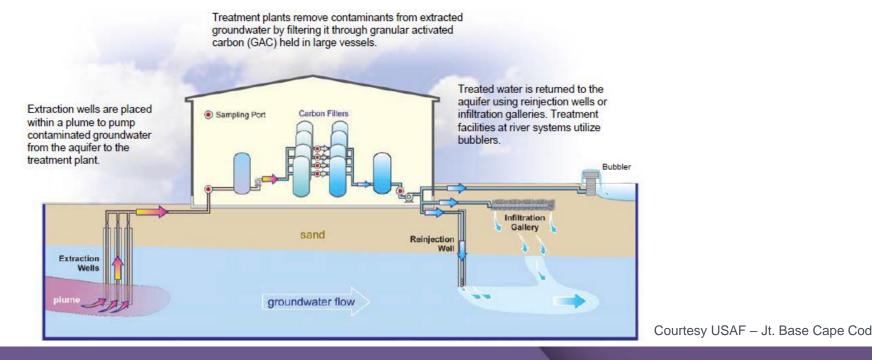


Courtesy: Calgon Corp



GAC PFAS Adsorption

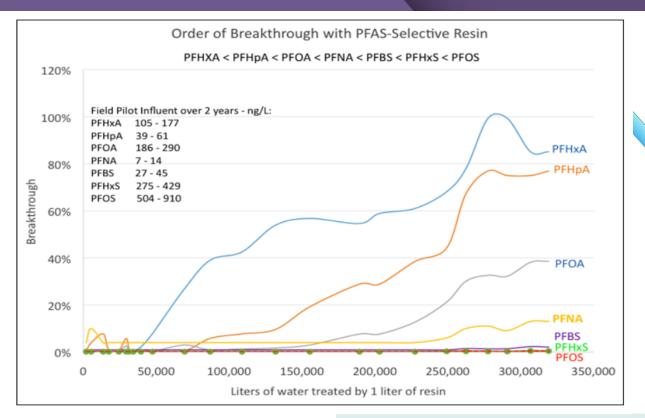
- GAC has been in use at sites for groundwater treatment for many years
- Spent GAC can be successfully reactivated from this service for a minimum of waste generation
- As is typical of GAC adsorption, smaller and lower formula weight compounds tend to adsorb less strongly than larger, heavier compounds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





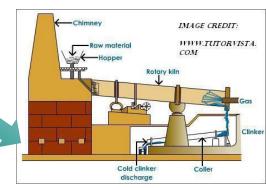
IX - Single-Use Selective Resin or Regenerable Media + Incineration

PFAS in water



Courtesy Purolite

Short Contact Time ~3 mins + Simple & Effective - Operator Preferred. PFAS –free water Cement Kiln Incineration 1400°C to 2000°C



Complete Destruction of PFAS ????

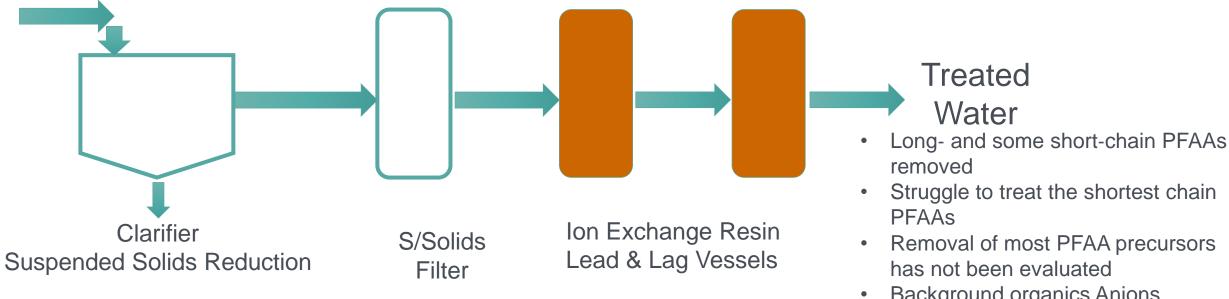
PFAS loaded resin

Regeneration or



Groundwater Process Flow Scheme Using Ion Exchange

Contaminated Groundwater



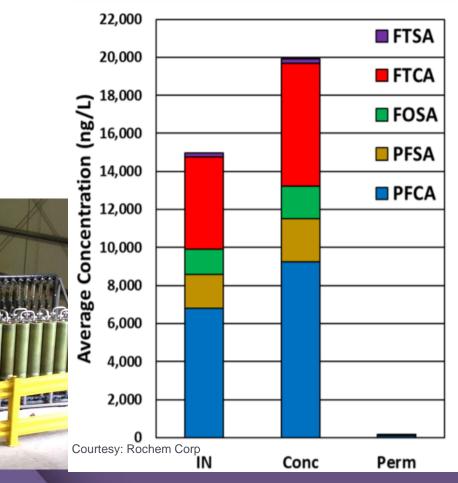
- Background organics Anions (chlorides, sulfates)
- Shorter detention time
 - ~3 min Vs. ~15 min for AC

EEE/

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

Reverse Osmosis

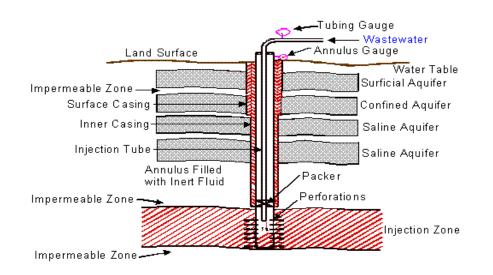
- Membrane Based Separation Process. 99.9% removal +/-
- Separates Water from Organic and Inorganic Compounds.
- Effluent for reuse or disposal.
- What to do with Reject???
 - Recirculation returns the contaminants to the landfill.
 - Solidification –
 - Evaporation Crystallization
 - Heat needed
 -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

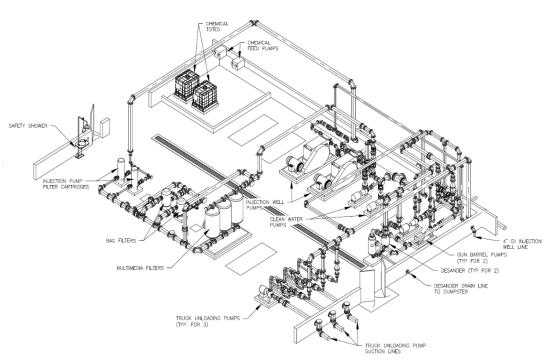




Deep Well Injection

- Depends on Geology, Receptors, Seismicity
- Long, Expensive Permit Time
- Filtration, Ions, High Pressure Pumps







Electrocoagulation Leachate Solution

- HTX Solutions Service Proposed at cost per gallon
- Patented Electrocoagulation Technology
- Combined pre and post treatment
- Removes most PFAS as concentrated PFAS liquid
- Final polishing of PFAS to non-detect levels with GAC or IX resins
- <u>Produces >90 gallons effluent per 100 gallons of leachate processed</u>
- Includes Sequestration Technology transforms residuals to a <u>solid</u>, <u>non-leachable form</u> for permanent disposal into landfill

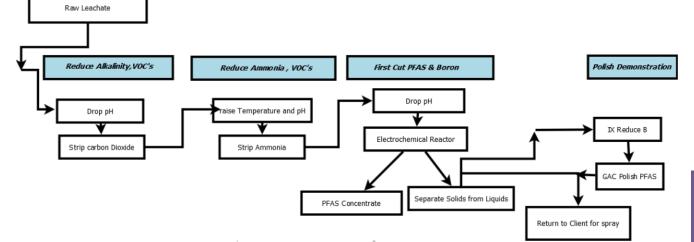






Courtesy HTX Corp.



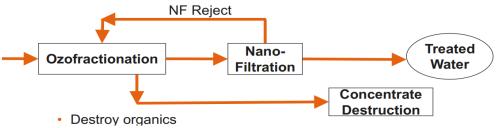


Ozofractionation – Separation Techniques

- Ozofractionation full scale to separate and concentrate PFASs
 - OPEC
 - Evocra ozofractionation
- Ozofractionation separation on ozone / air microbubbles (as foam) due to PFAS surfactant properties
- Micro-bubbles of ozone extracts 95% long & short chain
 - Degrade hydrocarbons.
 - Ozone may treat co-contaminants



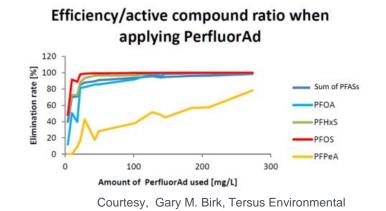
Courtesy Arcadis





Adsorbents Exsitu and Insitu

- Cetco Fluoro Sorb organically modified Bentonite
- 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)



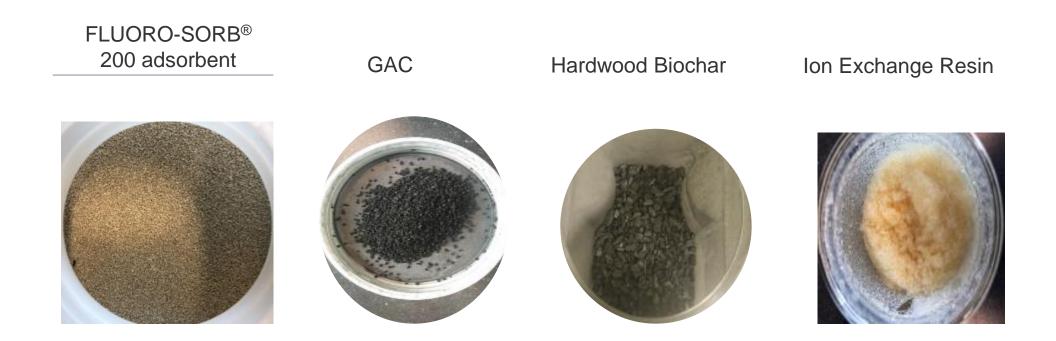


AquaGate Composite Particle Technology RemBind® Aggregate



Courtesy, Ziltek

Four Adsorbents



Relative Adsorbance?

Courtesy Cetco



Modified Bentonite (Adsorbent)

- Effective on groundwater
- Bench test on Groundwater
- Minimal pretreatment
- PFOS, PFAS >99% removal
- Longer bed volume than GAC
- Spent media fixation/disposal
- Pilot tests on leachate
- Susceptible to foulants





Supercritical Water Oxidation

- Water above 705°F and 3,200 lbs/in² -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

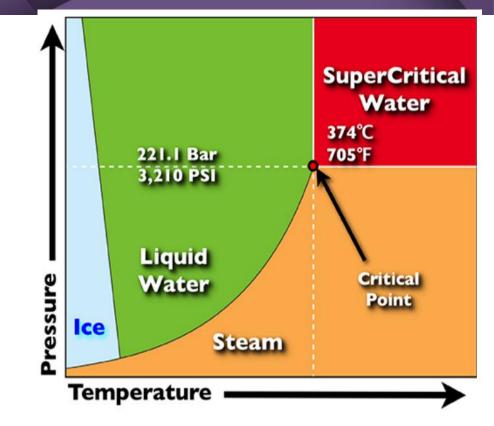
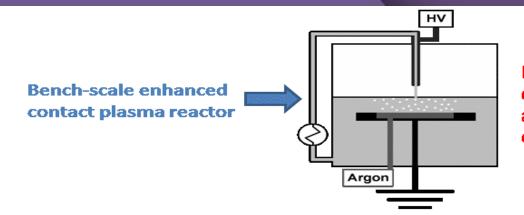


Figure 1. SCWO reactions occur above the critical point of water. Image credit: Jonathan Kamler.

EPA, Jan 2021

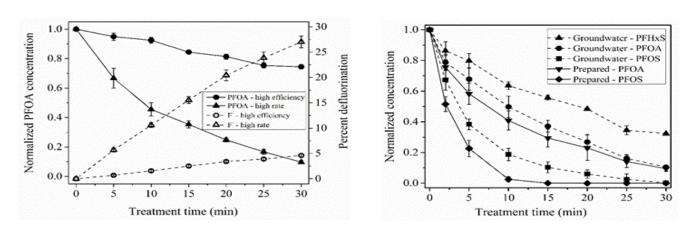


Plasma PFAS Transformation



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





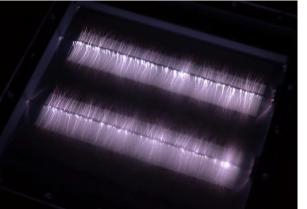
G. R. Stratton, F. Dai, C. L. Bellona, T. M. Holsen, E. R. V. Dickenson and S. Mededovic Thagard, "**Plasma-based water treatment: Demonstration of efficient perfluorooctanoic acid (PFOA) degradation and identification of key reactants**" Environmental Science & Technology, 2016, accepted.

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



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)

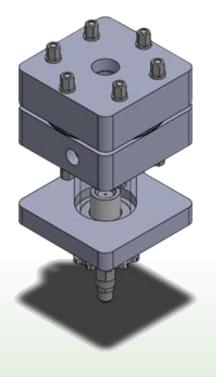


PFOA & PFOS concentration was reduced by at least 75% within one minute of treatment

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



PLASMA VORTEX



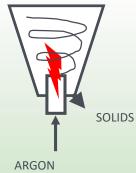
PLASMA HYDROCYCLONE

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.





Influent SIDE VIEW Cyclonic flow entering 3-phase flow exiting Stretched plasma Electrode set Gas injection

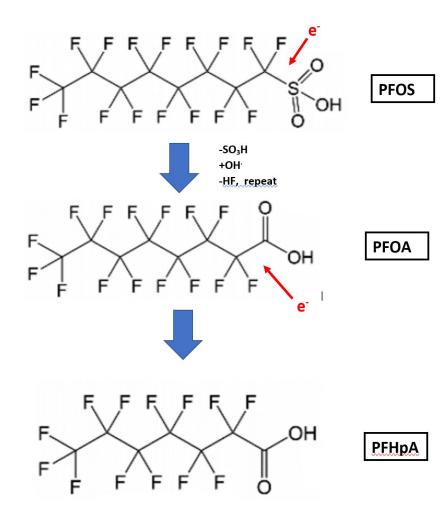
CYCLONIC SEPARATION OF SOLIDS

RECIRCULATION OF PLASMA CARRIER GAS (ARGON)

 \land ONVECTOR



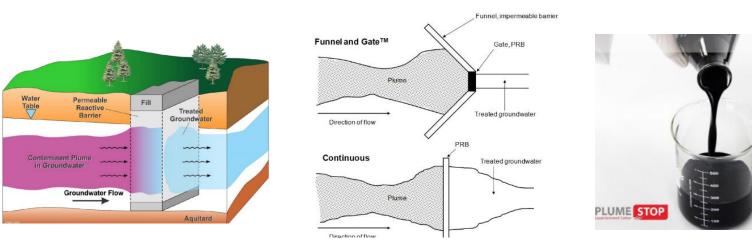
Possible PFAS Degradation by Non-Thermal Plasma

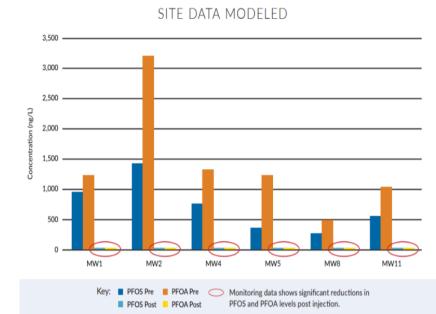


- Free and hydrated electrons in plasma (reductive reactants) can break C-F bonds due to their very high energy and very low mass
- Typical degradation pathway: sulfonates convert to carboxylic acid forms, carboxylic acids break down "one carbon atom at a time"
- Degradation pathways suggested by Onvector; possibly resultants of precursor conversions?
- 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, trifluoroacetate ion (TFA)

In-Situ Groundwater Treatment

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





Grayling, MI – WWII Army Airfield

130 ng/L PFAS + PCE

EE

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

Residuals Technologies

- Liquid Destruction / Disposal
 - Incineration
 - Supercritical Oxidation
 - Electro Chemical Oxidation
 - Reductive Defluorination Technology
 - Plasma
 - Hazardous Waste Landfill
- Adsorptive Media
 - Cementitious S/S (In Landfills or Holcim/ADC)
 - Incineration
 - Hazardous Waste Landfill



PFAS Contaminated Media and Wastes

Fixation

- Incineration
- Electrochemical oxidation
- Pyrolysis and gasification
- Supercritical Water Oxidation
- Mechanochemical Degradation



Works by:

- · Introduction of dry solids into a ball mill
- Co-milling reagents: Al, Fe, SiO₂, CaO, MgO, Al₂O₃, KOH, NaOH, MnO₂, TiO₂
- High energy ball impacts fracture solids generating localized high temperatures and radicals that react and breakdown organic molecules
- Technology derived from Persistent Organic Pollutants (POPs)-contaminated soil treatment
 - EDL (NZ) showed >99.8% DRE of PCBs in 45 min (US Navy, Hunters Point, 2006).

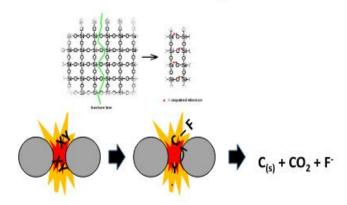


Bulley, M.; Black, B. EDL



Status:

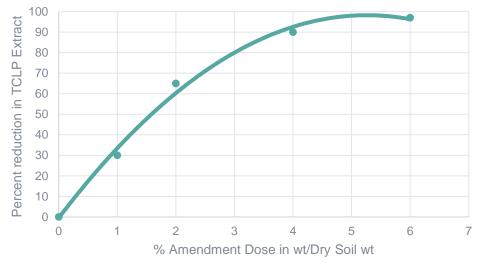
- Contract with EDL (New Zealand)
 - AFFF impacted soil study
 - >99% destruction of targeted PFAS
 - AFFF destruction study
 - AFFF added to sand
 - >99% destruction of targeted PFAS





Soil and Sludges 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.



PFAS Solidification Trials for Soils

Techniques:

Mixture of generic S/S amendments known to sorb PFAS*: Powdered activated carbon (PAC), Iron oxide (Fe2O3) 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



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

In-Situ Stabilization of PFAS Soils

- Solidification/Stabilization (S/S) used at a number of Superfund sites
- Immobilizes and encapsulates contaminants
- May be beneficially used when cement is used as S/S agent
- Low Porosity in matrix keeps PFAS out of Surface and Groundwater
- EPA Testing 5 sorbents
 - GAC
 - Biochar
 - Fe amended biochar
 - 2 mineral binders

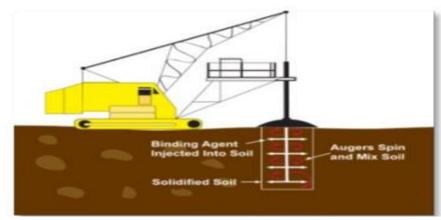


5 sorbents selected

https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=538693

Installation Technologies:

- Trencher
- Excavators
- Soil Mixing
- Injection
- Lesser means vibrating beam; hydraulic/pneumatic fracturing



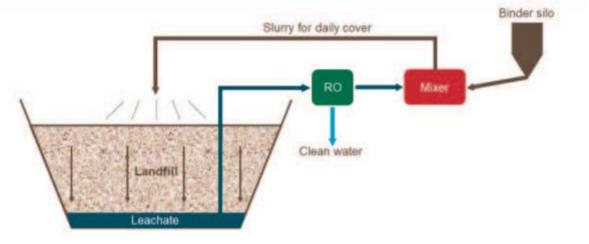
EPA Testing at Superfund Sites



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



AFFF Groundwater Contamination

Oakey Army Air Force Base SAFF Removal System – Queensland, Australia

Courtesy: OPEC



Oakey SAFF Performance – Groundwater Oct 2019 – Oct 2020

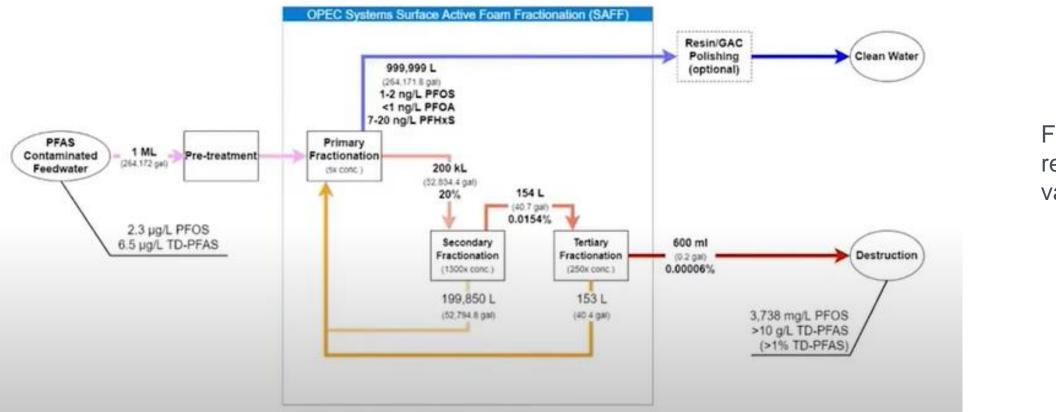
Aust. & NZ NEMP	Remov	al Percentage	es (%R)	Treatment Results (Field Trial)			
(2020) PFAS Suite ⁽³⁾	Predictive Desktop Audit ⁽¹⁾	15L Bench- Scale Testing (1,4)	Full-Scale Field Trial Removal Results (4)	Feedwater Conc. ⁽²⁾ (ng/l)	Criteria (ng/l)	Treated Water Results (ng/l)	
PFOS	98-99%	98% (4)	99.8% ⁽⁴⁾	2,790	70	<4	
PFOA	98-99%	98% (4)	99.8% (4)	480	560	< 1	
PFHxS	95-97%	97% (4)	98.4% (4)	1,030	70	< 17	
Combined PFOS + PFHxS	96-98%	97-98% (4)	99.1% ⁽⁴⁾	3,810	70	< 11	
8:2-FTS	100%	98% (4)	100% (4)	32	•	< 1	
PFDA	100%	98% (4)	98.8% (4)	156		< 3	
PFNA	100%	98% (4)	100% (4)	116	-	< 1	
6:2-FTS	100%	98% (4)	100% (4)	100		< 6	
PFHpS	95%	75% (4)	80.8% (4)	104	-	< 20	
PFHpA	95%	70% (4)	81.5% (4)	367		68	
PFHxA	<50%	51% (4)	46.7% (4)	755		402	

Courtesy: OPEC



Oakey Field Test May 2019 – April 2021

SAFF[®] Concentration Process (AACO)



Foam volume reduction by vacuum process

Courtesy:OPEC



Case Study 2 – LF Foam Fractionation Telge LF- 250,000 L/Day (66,000 gpd)

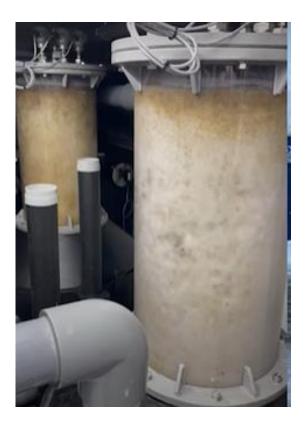
System inside 40-foot container, Insulated

- 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



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

Consumables - ZERO	
Energy – AUD \$0.084/m ³ (treated)	_

Courtesy: OPEC



Case Study 3 – Reverse Osmosis Orchard Hills 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 4 – Modified Bentonite Comox, BC/ Civilian Regional Airport and Wing 19 Canadian Air Force

Military Installation and FFTA



Project Objectives: Remove/Stabilize source zone PFAS contaminated soil; Rebuild the FFTA



Source: Comox FFTA Source Control Project; www.pspc-spac.gc.ca



Comox Project Scope

MAJOR SCOPE ITEMS

PFAS STABILIZATION

- Excavation
- Transportation
- Destruction and Disposal
- Stabilization
- Backfill
- FFTA Design/Construction
- Bioswale Design/Construction
- Water Treatment

- Objective: reduce PFAS mobility in the environment and by binding contaminants in place reduce groundwater and surface water concentrations.
- The Work includes stabilization to meet PFAS Stabilization Efficacy Target (SET) by mixing site soil with approved Amendment(s).
 - Fluorosorb 200 [a Cetco Product] at a 1% minimum dosage rate by weight,
 - RemBind Plus [A Ziltek Product] at a 4% minimum dosage rate by weight, or
 - Equivalent via Amendment Equivalency Proposal and Documentation;
- Be compacted to density of not less than 90% modified maximum proctor dry density test in accordance with ASTM D1557;

Soil for Destruction PFOS >0.54 mg/kg Soil for Stabilization and Reuse PFOS >0.14 mg/kg and <0.54 mg/kg Fluoro Sorb@ 1%; Rembind @ 4%

Source: Comox FFTA Source Control Project; www.pspc-spac.gc.ca



Comox CFB Unit Price Proposal

		BAS	E WORK (A)			
ltem	Class of Labour, Plant or Material	Specification Section	Unit of Measure	Estimated Quantity (EQ)	Price per Unit (PU) applicable taxes extra	Extended amount (EQ x PU) applicable taxes extra
15	Backfill Material - 100 mm Pit Run Gravel	32 11 16	Tonnes	17,800		
16	PFAS Contaminated Soil for Destruction	02 61 00.04	Tonnes	12,500		
17	PFAS Contaminated Soil for Stabilization	02 61 00.05	Tonnes	15,500		
18	PFAS Stabilization Amendment	02 61 00.05	Lump Sum	1		
19	Concrete Disposal	02 61 00.06	Lump Sum	1		
20	Site Restoration and Bioswale	01 25 20	Lump Sum	1		
21	New FFTA Design and Construction	01 25 20	Lump Sum	1		

Bids March 2, 2021 Not Yet Awarded

Substantial Completion Nov 1, 2021 Final Completion Feb 28, 2022

Source: Comox FFTA Source Control Project; www.pspc-spac.gc.ca



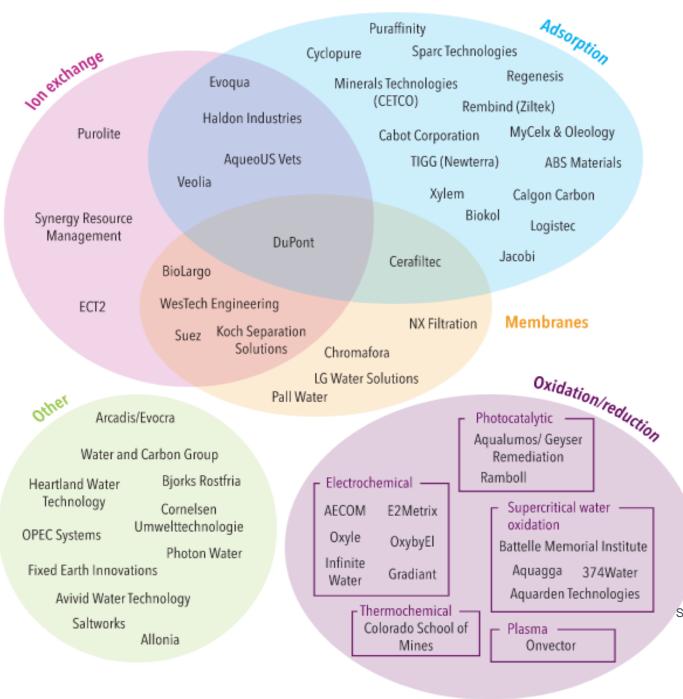
Case Study 5 – Supercritical Water Oxidation

- 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



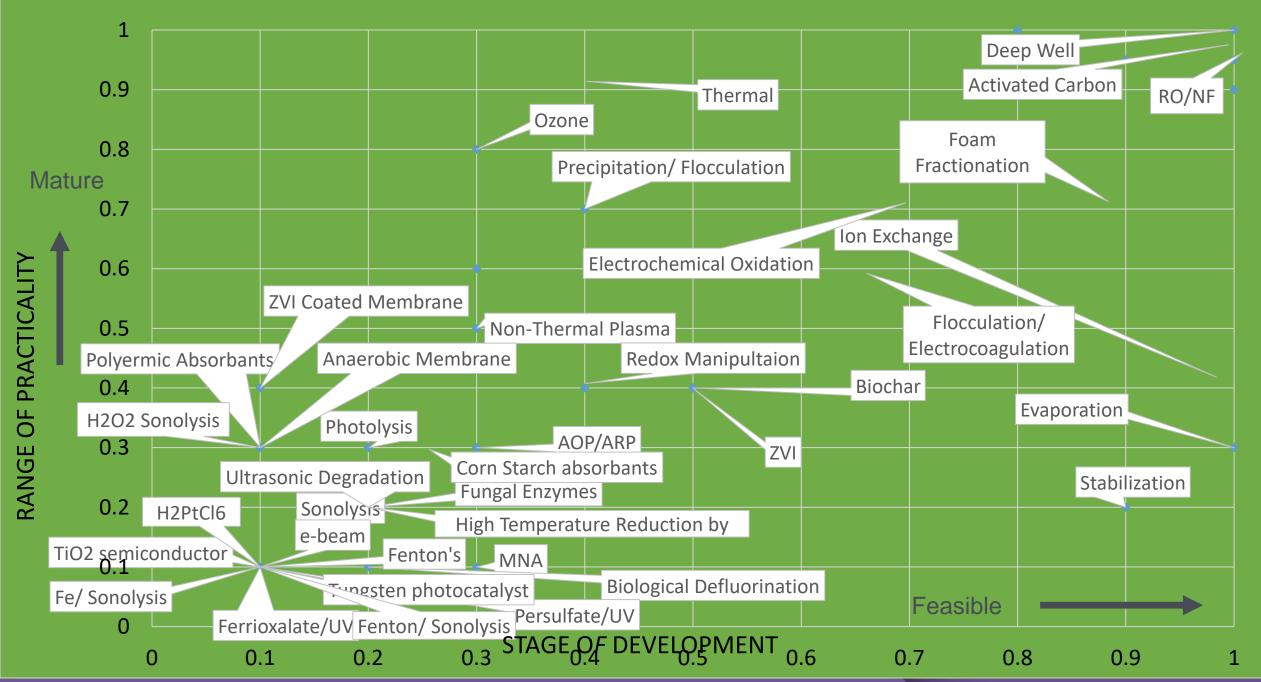


Current PFAS Market Players

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



DEVELOPMENT AND PRACTICALITY OF TREATMENT TECHNOLOGIES



Comparative Emerging Contaminants Treatment Technologies

Contaminant	Biological Treatment	Activated Carbon ¹	lon Exchange 1	Reverse Osmosis ²	Chemical Oxidation	Electro Oxidation	ΑΟΡ	Plasma	Adsorption/ Settle
COD/Ammoni a	Yes	Possible	Possible	OK – Reject	Possible	Yes	Possible	Possible	No
I,4 Dioxane	Possible	OK	OK	OK – Reject	Possible	ОК	OK	OK	Possible
DON and rDON	Possible	OK	Possible	OK – Reject	NO	Possible	Possible	Possible	No
PPCP	Possible	OK	OK	OK – Reject	Possible	ОК	OK	OK	Possible
Nanoparticles /Microplastic s	Νο	No	No	Yes – Reject	No	No	Νο	Νο	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 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?





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