

Vertex Environmental Inc.

Treating PFAS: Current In-Situ Remediation Approaches

May 31, 2023 RemTech East Bruce Tunnicliffe, M.A.Sc., P.Eng.



Outline

- About PFAS
 - What is it
 - How is it Made
 - Its Properties
- Remediating PFAS
 - Current State of Affairs
- In-Situ Remediation of PFAS
 - Comparison of 2 Amendments

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Closing

Background



Bruce Tunnicliffe, M.A.Sc., P.Eng.

- Masters U of Waterloo. Remediation
- Founder Vertex Environmental Inc.
- Founder SMART Remediation

Vertex Environmental Inc.

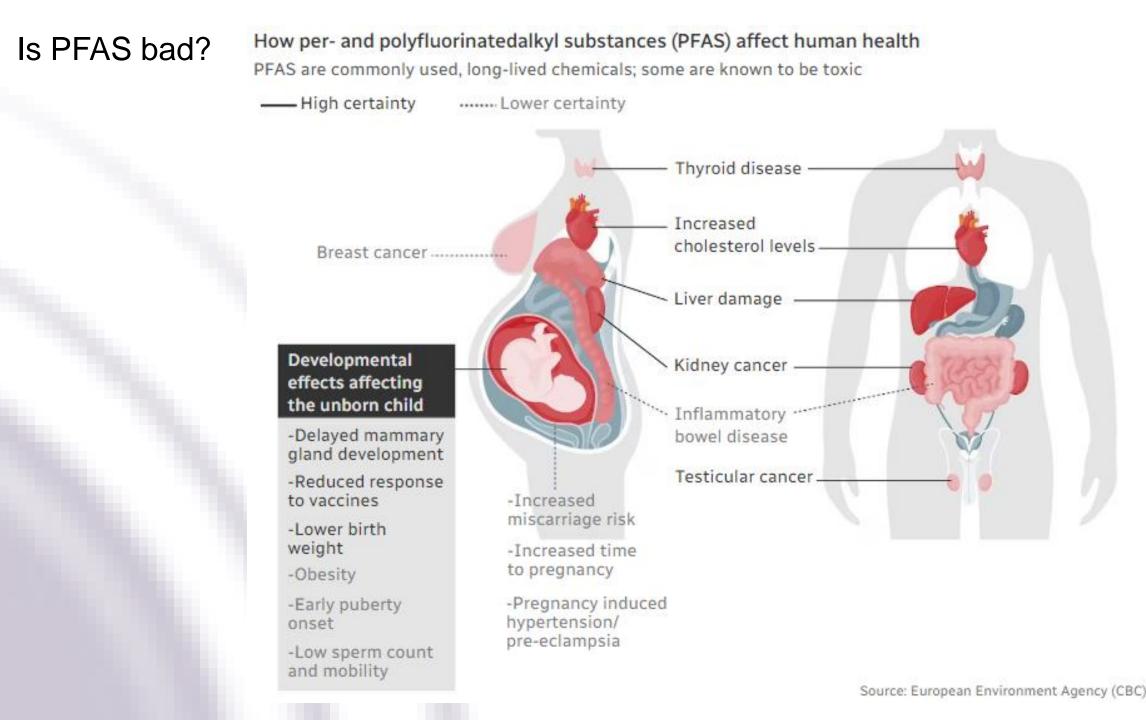
- Started July 2003
- Environmental Contractor



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Are people noticing?



'Forever chemicals' found in Canadians' blood samples: report

Government departments propose listing the <u>chemicals as toxic</u> under Canadian Environmental Protection Act



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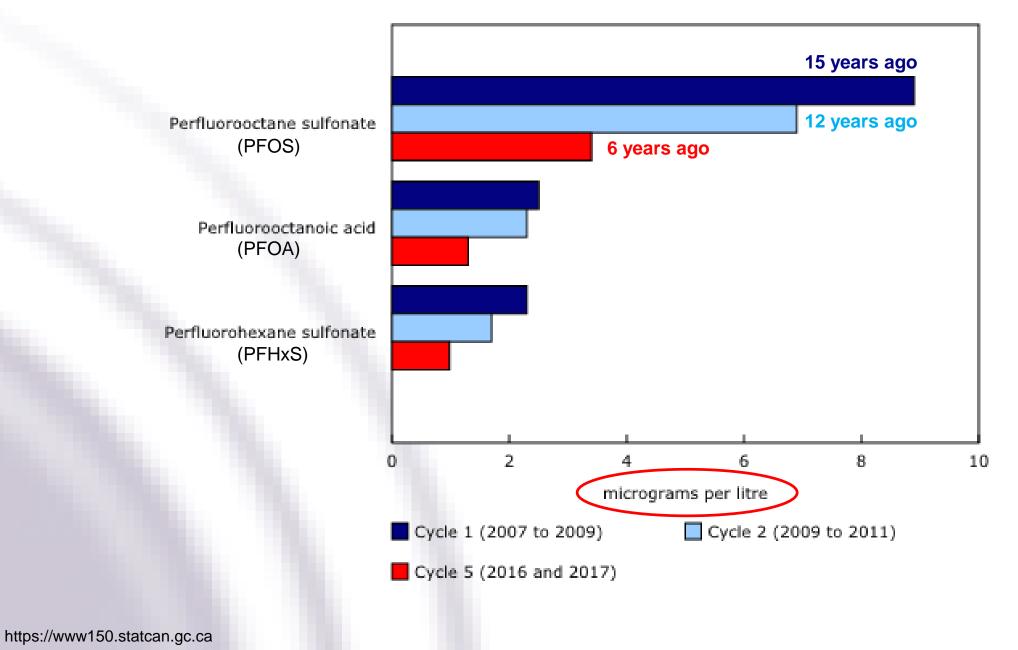
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David Thurton · CBC · Posted: May 20, 2023 2.00 AM EDT | Last Updated: May 20



• ~99% of Canadians have PFAS in their blood:





Is that PFAS concentration in our blood bad?

	EPA Maximum Contaminant Level (ppt)	Canadian's Blood Conc. (2016-2017) (ppt)	Multiple of EPA Maximum
PFOS	4.0*	3,400	850x
PFOA	4.0*	1,300	325x
PFHxS	9.0	980	109x

*limited by detection limits

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EPA, "Proposed PFAS National Primary Drinking Water Regulation" March 29, 2023

How long will PFAS stay in our body?

Contaminant	Half Life in Humans
PFOS	3 – 5 years
PFOA	2 – 4 years
PFHxS	4.5 – 8.5 years

	EPA Maximum	Canadian's	PFOS Time to
	Contaminant Level	Blood Conc.	Reach EPA Level
	(ppt)	(2016-2017) (ppt)	(years)
PFOS	4.0	3,400	40 years*

*assumed 4 year half life



ITRC, "PFAS – Per- and Polyfluoroalkyl Substances" Table 17-7

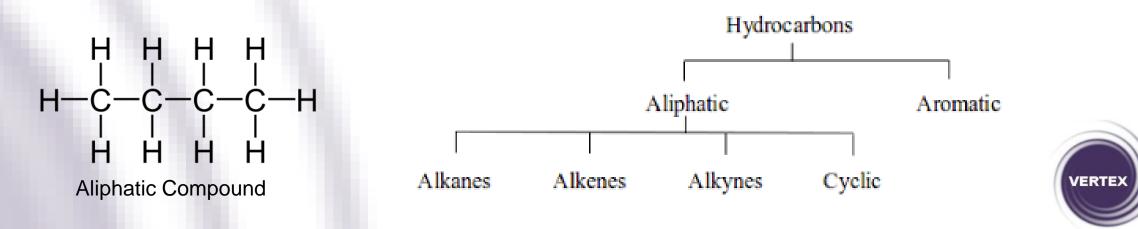
What exactly is PFAS?

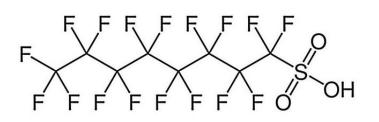
Forever Chemicals

- PFAS is short for <u>Per- and PolyFluoroAlkyl</u> Substances
- A group of chemicals (>4,500). Labs report ~40 PFAS.
 - including PFOS and PFOA

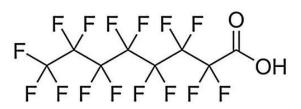
How Are They Made?

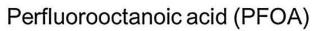
- A fossil fuel derivative
- An organic molecule has bonds of carbon and hydrogen atoms
- To make PFAS, replace the hydrogen with fluorine
- PFAS have chains of carbon-fluorine bonds





Perfluorooctane sulfonic acid (PFOS)





Issues with PFAS, from a Remediation Perspective

PFAS are not natural (its manufactured)

- Unlike PHCs or heavy metals, PFAS does not naturally exist.
- Its in our blood? Its at our client's site? We can't blame natural conditions.

Carbon-Fluorine (C-F) bond

• Strongest covalent bond in organic chemistry

Implications to Remediation

- Low biotic or abiotic degradation under natural conditions
- Thermally degrade at >1,000°C
- Stable, persistent, soluble, mobile and toxic compounds

Issues

- The long-range subsurface transport potential of toxic molecules
- Very challenging to destroy
 - Past attempts to destroy PFAS lead to issues with precursors



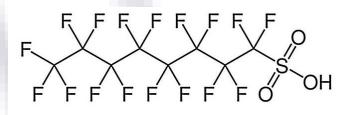
Issues with PFAS, from a Remediation Perspective

Precursors

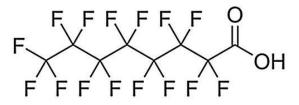
- PFAS is largely unknown mixture of >4,500 compounds... (Dark Matter)
- ...that can degrade to form shorter chain, **regulated** compounds.
- Longer chain PFAS compounds not regulated
- Shorter chain PFAS compounds like PFOS and PFOA are regulated

Documented Treatment Issues

 Waste-water and drinking water treatment plants can increase PFOS and PFOA concentrations due to biological degradation and oxidation of unknown longer chain precursors during the treatment chain



Perfluorooctane sulfonic acid (PFOS)



Perfluorooctanoic acid (PFOA)

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Xiao, F. "An overview of the Formation of PFOA and PFOS in Drinking-Water and Wastewater Treatment Processes", Journal of Environmental Engineering. April 2022

Dealing with PFAS

A Take Away:

Be careful with PFAS Destruction approaches, be sure precursors are considered



Remediating PFAS The Current State of Affairs



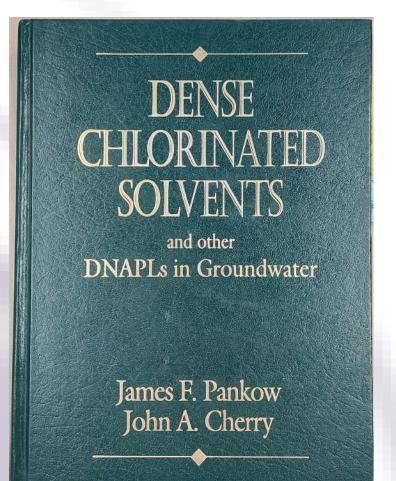
Remediating PFAS Are We In a Unique Situation?



Remediating PFAS

History Repeats Itself

• Similarities: Addressing DNAPL & PFAS?



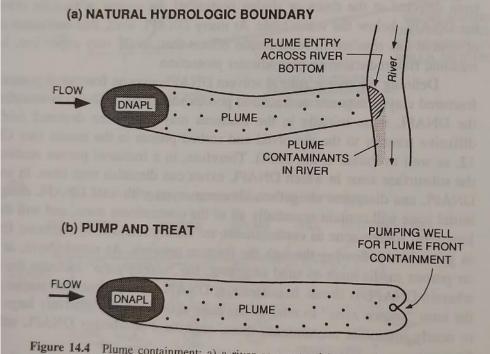
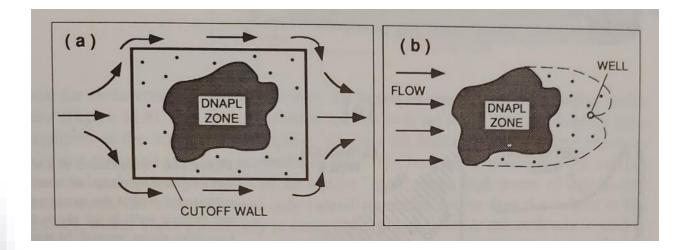
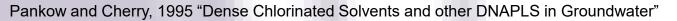


Figure 14.4 Plume containment: a) a river as a natural hydrologic boundary; and b) pump-and-treat captures the front of a plume.

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Remediating PFAS, The Current State of Affairs

Treatment Technologies and Methods for Per- and Polyfluoroalkyl Substances (PFAS)

- Treatment technologies for PFAS are the focus of intense research and are evolving
- The nature of PFAS make many conventional treatment technologies ineffective, including those that rely on:
 - <u>contaminant volatilization</u> at ambient temperature (air stripping, soil vapor extraction)
 - <u>bioremediation</u> (biosparging, biostimulation, bioaugmentation)
- Even aggressive technologies require extreme conditions beyond typical practices:
 - thermal treatment and chemical oxidation
- New technologies or innovative combinations of existing technologies are required



Remediating PFAS, The Current State of Affairs

Treatment Technologies and Methods for Per- and Polyfluoroalkyl Substances (PFAS)

- Commonly field-implemented <u>ex-situ treatment</u> technologies for PFAS treatment include separation/removal using:
 - Stabilization / Adsorption,
 - Granular Activated Carbon (GAC),
 - Ion Exchange Resin (IXR),
 - Reverse Osmosis (RO).
 - Excavation and Disposal in a landfill (soils)

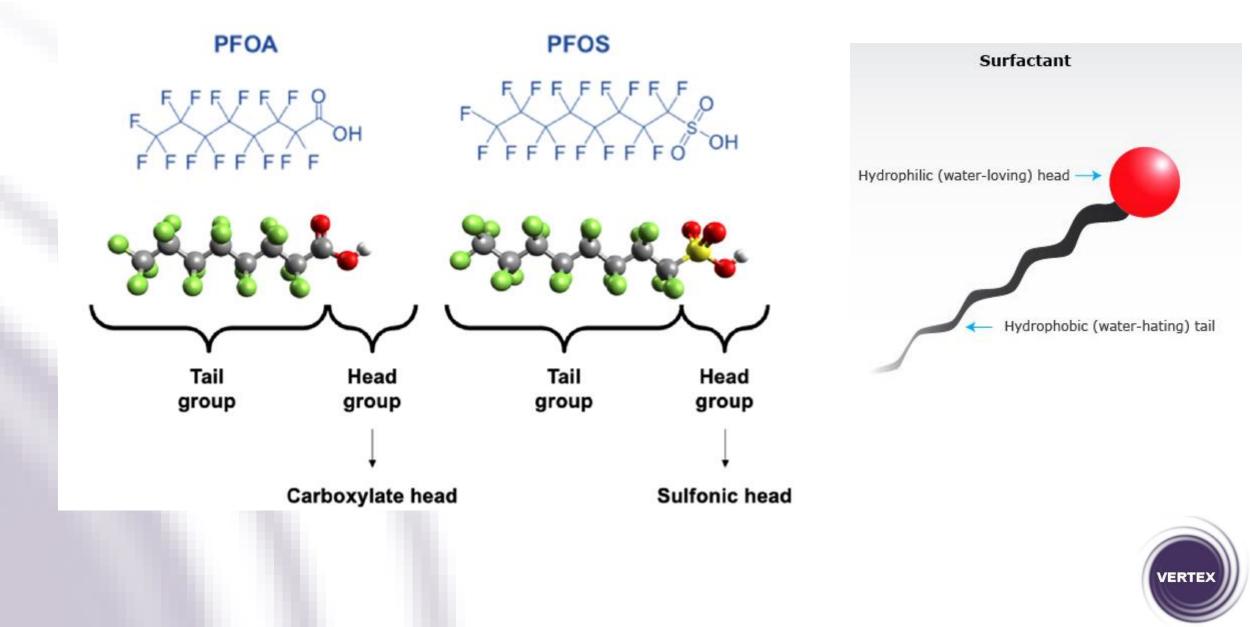


ITRC, July 2022 "Treatment Technologies and Methods for Per- and Polyfluoralkyl Substances (PFAS)"

Remediating PFAS Interesting leading-edge technologies

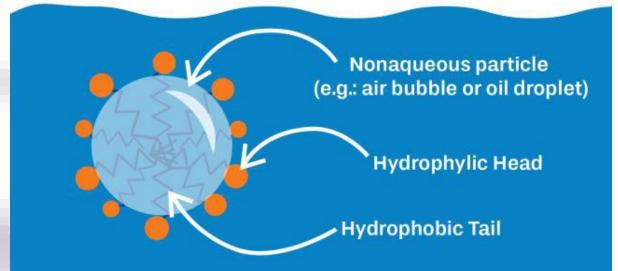


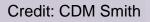
Remediating PFAS, Foam Fractionation

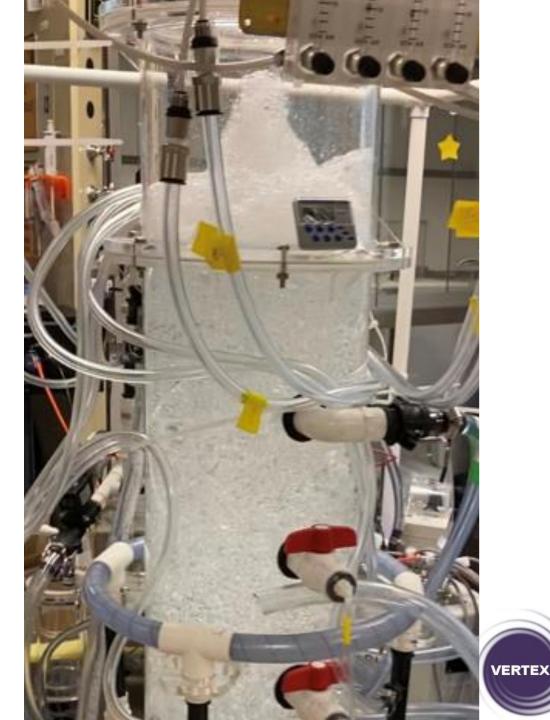


Remediating PFAS, Foam Fractionation

PFAS in an Aqueous Solution







Remediating PFAS, eBeam



Radiation Physics and Chemistry

Volume 189, December 2021, 109705



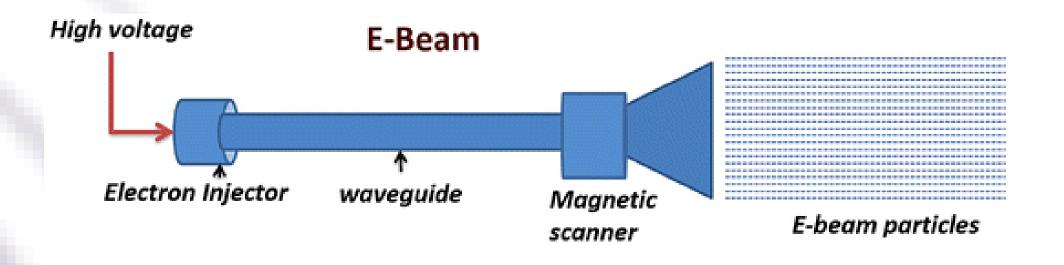
Degradation of PFOS and PFOA in soil and groundwater samples by high dose <u>Electron</u> Beam Technology

John Lassalle^a, Ruilian Gao^a, Robert Rodi^a, Corinne Kowald^b, Mingbao Feng^c, Virender K. Sharma^c, Thomas Hoelen^d, Paul Bireta^d, Erika F. Houtz^e, David Staack^a A 🖾, Suresh D. Pillai^b A 🖾

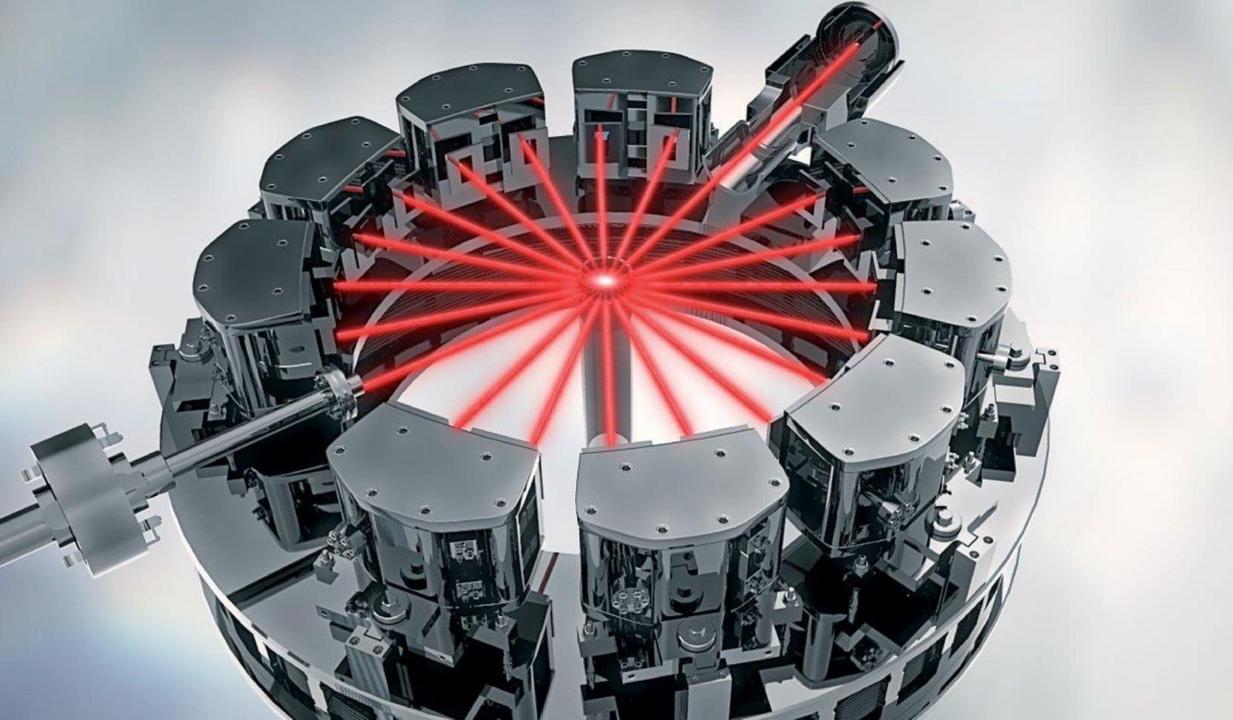


Remediating PFAS, eBeam

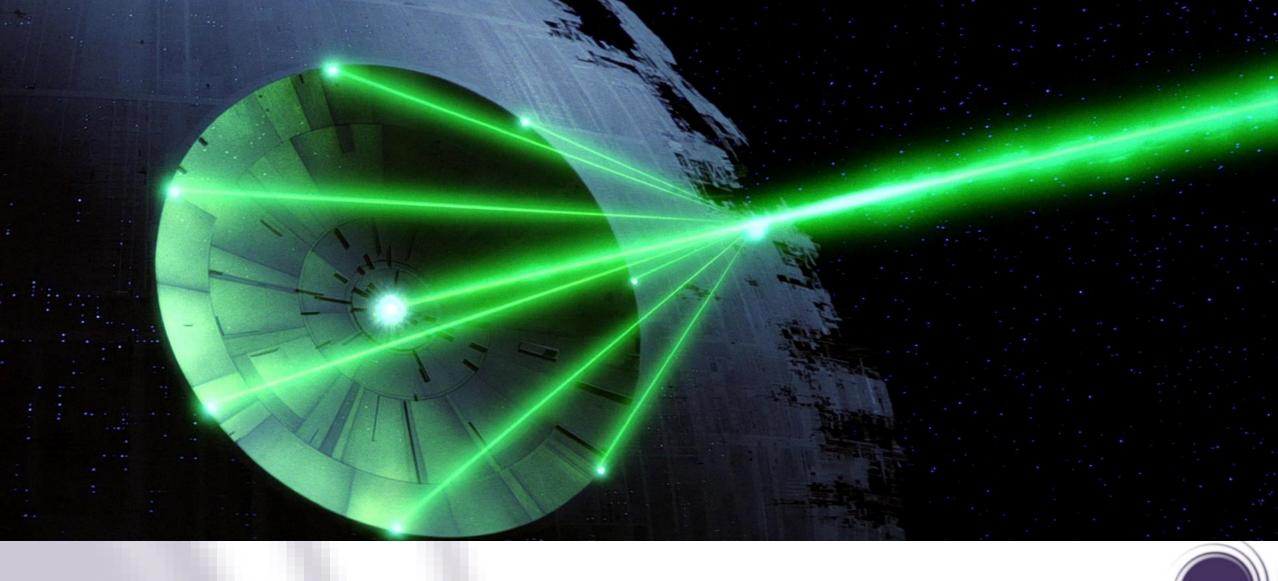
 Electron beam (eBeam) technology utilizes compact electron accelerators to generate large numbers of highly energetic electrons from electricity. The technology is commonplace in the medical device sterilization industry, wire and cable polymer crosslinking and food pasteurization industries.







Remediating PFAS, eBeam



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Remediating PFAS, other Innovative Destruction Technologies

· · · · · · · · · · · · · · · · · · ·	TECHNOLOGY	ADVANTAGES	DISADVANTAGES
PFAS H ₂ O BONNA L R F CO ² R+ PFAS	ELECTROCHEMICAL OXIDATION	 Effective for long-chain PFASs. Efficient for highly concentrated PFASs. Effective for low-volume PFASs. Low environmental impact. Does not require pretreatment. 	 Widescale application. Inefficient for short-chain PFASs. Electrodes are expensive. Reduced electrode lifetime. High energy consumption. Toxic by-products. Forms short-chain PFAS
R+ PFR- A	PLASMA	 Effective for long-chain PFASs. Effective for short-chain PFASs. Low energy consumption. No chemical additives are needed. Short treatment time. Effective for highly concentrated PFASs. Effective against Co-contaminants. 	 Affects water's pH, making it acidic. Forms short-chain PFASs. Its mechanism is not well understood. Longer time for short-chain treatment. The addition of chemicals is required. Nontargeted reactions can result in longer treatment time
SUPERCRITICAL	PHOTOCATALYSIS	 Low energy consumption. Performed at ambient temperatures. Sustainable technology. It can be recycled. 	 Low degradation efficiency. Inefficient for sulfonic groups. Toxic intermediate products. Additional treatment is needed. Affected by co-contaminants.
218 Critical PHASE Point Point PHASE	SONOLYSIS	 Effective for long-chain PFASs. Effective for short-chain PFASs. Effective in soils and liquids. Effective for highly concentrated PFASs. Effective against co-contaminants. No chemical additives are needed. Does not require pretreatment. Efficient for highly concentrated PFASs. 	 Widescale application. High energy consumption. Its mechanism is not well understood. Optimization of ultrasonic and geometric parameters are needed to scaling up of technology
0.006 Water Vapor	SUPERCRITICAL WATER OXIDATION	 Effective for long-chain PFASs. Effective for short-chain PFASs Low environmental impact. Relatively quick treatment time 	 Not economically viable for large volumes. Affects water's pH, making it acidic. Corrosion of the reactor. Precipitation of salts. Toxic intermediate products.
Temperature (°C) "A Review of PFAS Destruction Technologies", Dec 2022, International Journal of Environmental Research and Public Health	THERMAL DEGRADATION/ INCINERATION	 Widescale application. Reduced capital cost. Effective for long-chain PFASs. 	 Toxic intermediate and final products. High environmental impact. Air and soil contamination. Toxic emission. Toxic by-products.

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What Can We Do Right Now?



- In-situ PFAS destruction
 - In general, not feasible at this time
- In-situ: adsorption and stabilization
 - Yes, its feasible to immobilize PFAS in-situ



Treatment Technologies and Methods for Per- and Polyfluoroalkyl Substances (PFAS)

- "It might be reasonable and necessary to implement interim remedial actions...
 - ...to mitigate completed exposure pathways...
 - ... with the intent of applying more robust and permanent solutions as they are developed."
- Now: Adsorption in-situ approaches
- Years, decades, a century later: Apply new technology to destroy PFAS



Adsorption / Stabilization:

- Amendments exist right now that can be injected into the subsurface
 - Activated Carbon
 - Modified Clay (Fluoro-Sorb[®])
- These amendments are proven to effectively adsorb PFAS
- Regarding AC
 - Known individual PFAS AC loading capacities and breakthrough times
 - AC removal capacity for PFOS is greater than PFOA but both can be effectively removed
 - In general, shorter chain PFAS have lower AC loading capacities and faster breakthrough times
- Regarding Modified Clays
 - PFAS treatment demonstrated in both soil and in water
 - Modified nature of the clay prevents swelling
 - Benefit: not negatively affected by some subsurface constituents: TOC, cationic metals, or anions

- Regarding Activated Carbon, one product has been applied numerous times for PFAS
- Colloidal Activated Carbon (PlumeStop)

PFAS Performance Data

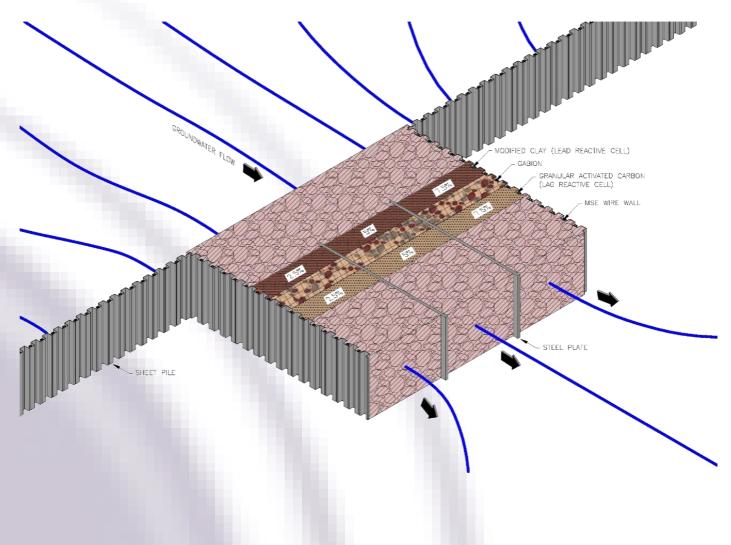
PFAS in Upgradient and Downgradient Well Pairs Following PlumeStop Application





Credit: Regenesis

• Regarding Injectable Modified Clay



Lead Reactive Cells (First 90 days)

	2.5% MC	5% MC	7.5% MC
Vol. of Treated Water (L)	~9,700 L	~9,200 L	~9,050 L
Flux ∑PFAS (µg)	~160,300	~152,900	~149,700
Adsorbed ∑PFAS (µg)	~90,800	~148,200	~149,400
Removal Efficiency (%)	57%	97%	99.8%

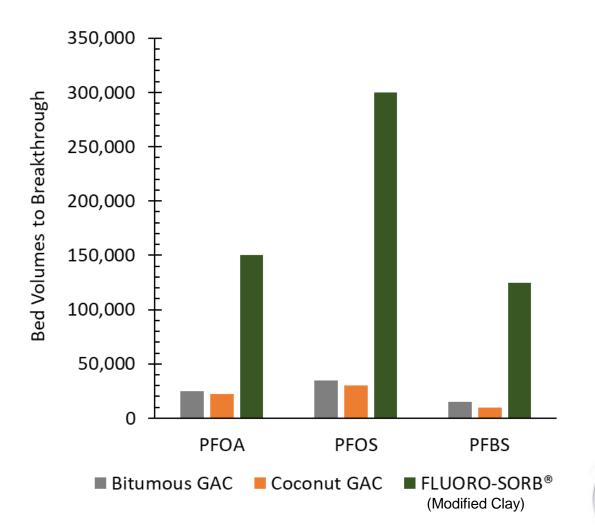
(Second 90 days)

	2.5% MC	5% MC	7.5% MC
Vol. of Treated Water (L)	~9,100 L	~8,250 L	~8,500 L
Flux ∑PFAS (µg)	~236,600	~215,250	~220,040
Adsorbed ∑PFAS (µg)	~235,600	~215,070	~220,020
Removal Efficiency (%)	99.6%	99.9%	100%



- How to select an amendment?
- Capacity of PFAS adsorption (How long will it hold onto the PFAS?)

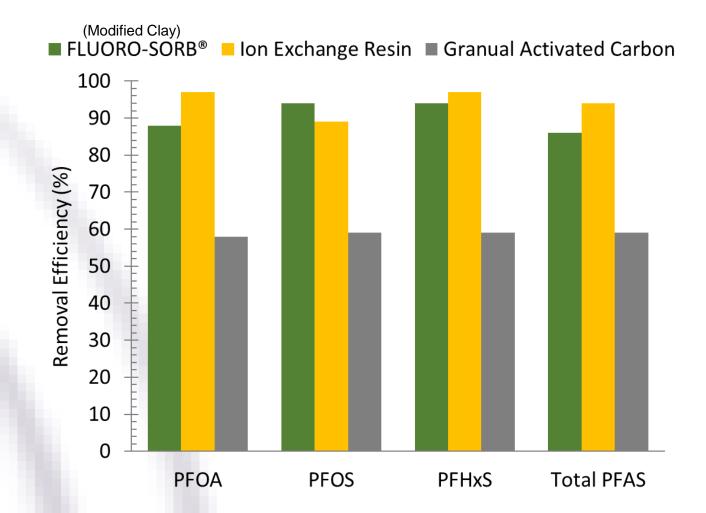




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Orange County Water District (2021). PFAS Phase 1 Pilot Scale Treatment Study Final Report. March 24, 2021.

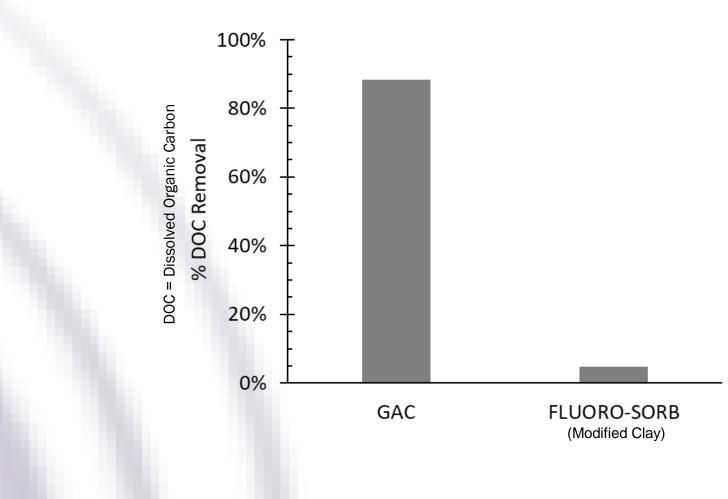
- How to select an amendment?
- Efficiency of PFAS Removal (for same contact time)





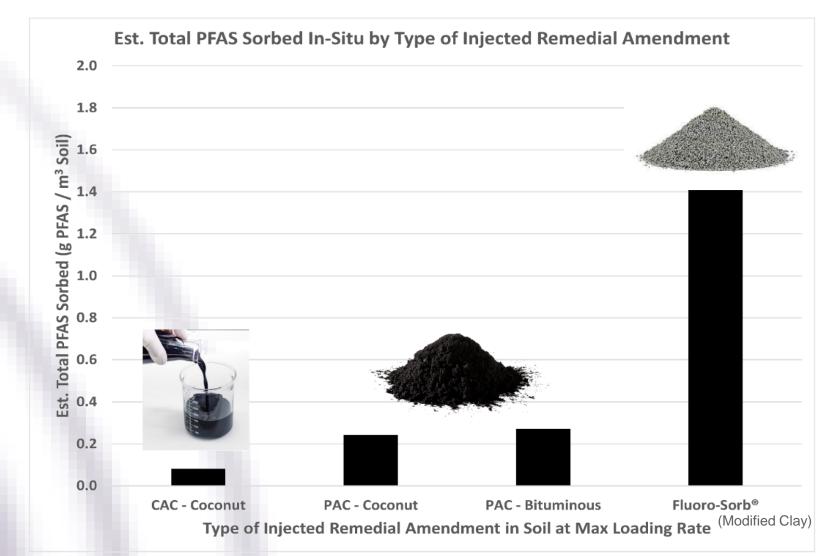
Yan, B., Munoz, G., Sauvé, S., and Liu, J. (2020) "Molecular mechanisms of per- and polyfluoroalkyl substances on a modified clay: a combined experimental and molecular simulation", Water Research, 184, 116166.

- How to select an amendment?
- Impact of non-PFAS groundwater constituents





- How to select an amendment?
- Evaluation of PFAS Mass Adsorption Capacity for a Single Injection





Based upon a one-time injection approach

Thoughts on Modified Clay



Remediating PFAS, in-situ – Using Injectable Modified Clay (Fluoro-Sorb[®])

- Modified Clay, specifically Fluoro-Sorb[®], has some advantages
- Create a suspension with potable water and inject into all geologies
- Will not swell or block formation
- Stays put where placed (non-soluble, non-mobile)
- QA/QC testing





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Closing Thoughts



In-Situ Remediation of PFAS

- PFAS remediation is in a development stage
 - Research, experimentation, pilot tests
 - Very exciting times
- PFAS Destruction is difficult
 - We have to be careful with precursors
- Interim remedial measures are necessary right now
- Two proven in-situ injectable approaches, using:
 - Activated Carbon (specifically, colloidal activated carbon)
 - Modified Clay (specifically, Fluoro-Sorb[®])
- Current Assessment:
 - Activated Carbon In-Situ PFAS Remediation Approach 1.0
 - Modified Clay In-Situ PFAS Remediation Approach 2.0





Questions?

Thank You for Your Time

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