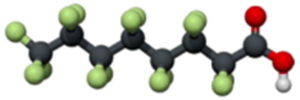
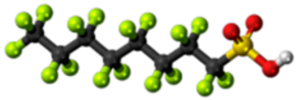
PFAS General Information

PFOA Molecule 

PFOS Molecule 

March 2020

Agenda

- **Per- and Poly-fluorinated Alkyl Substances (PFAS)**
    - General Background
    - Sources
    - Fate & Transport
    - Toxicology
    - Regulatory Status
    - Analytical
    - Treatment Technology Advancements
    - Waste and Wastewater Management

General Background

- **PFAS - one of the most dynamic emerging contaminant classes**
  - Sources - some known sources, many unknown sources
  - Fate and Transport - prevalent in the environment including atmospheric deposition
  - Toxicology - human health and ecological receptors
  - Regulatory Status - Federal and State action levels / criteria / wastewater
  - Analytical Procedures - evolving methodologies and approvals
  - Treatment Technology – proven/mature and experimental/evolving

General Background

- PFAS – in use since the 1940s, US manufacturing reduction/elimination from 2010 to 2015
- PFAS – China, India and Russia manufacturing replaces US manufacturing
- PFAS - studied since the 1990s, gained significant traction when the USEPA published health advisories in 2016
- PFOA/PFOS - in the news in Connecticut and across the US
- Federal - slow to act, States take action
- States – establishing drinking water and remediation criteria, requiring assessment and remedial action

Sources

- **Aqueous Film Forming Foam (AFFF)**
  - Class B Foams: high-hazard flammable liquid fires (more)
- **Metal Plating and Finishing**
  - Surfactant, Wetting Agent and Mist Suppressant (more)
- **Oil and Water Repellant Products**
  - Textiles, Paper and Cardboard Packaging (more)
- **Consumer Products**
  - Cleaning Products, Cosmetics and Personal Care (more)
- **Industrial Products**
  - Paints/Coatings, Plastics, Resins, Adhesives, Antifogging (more)

Sources: Discovery / Manufacturing

PFAS[1]	Development Time Period							
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s
PTFE	Invented	Non-Stick Coatings			Waterproof Fabrics			
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS[2])
PFOA		Initial Production	Protective Coatings					
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foams		Predominant form of firefighting foam
Dominant Process[3]		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)
Pre-Invention of Chemistry /			Initial Chemical Synthesis / Production			Commercial Products Introduced and Used		

Notes:

1. This table includes fluoropolymers, PFAAs, and fluorotelomers. PTFE (polytetrafluoroethylene) is a fluoropolymer. PFOS, PFOA, and PFNA (perfluorononanoic acid) are PFAAs.
2. Refer to Section 3.4.
3. The dominant manufacturing process is shown in the table; note, however, that ECF and fluorotelomerization have both been, and continue to be, used for the production of select PFAS.

Sources: Prevedouros et al. 2006; Concawe 2016; Chemours 2017; Gore-Tex 2017; US Naval Research Academy 2017

History and Use of Per- and Polyfluoroalkyl Substances (PFAS). *Interstate Technology Regulatory Council* **November 2017**.

PFAS Toxicology

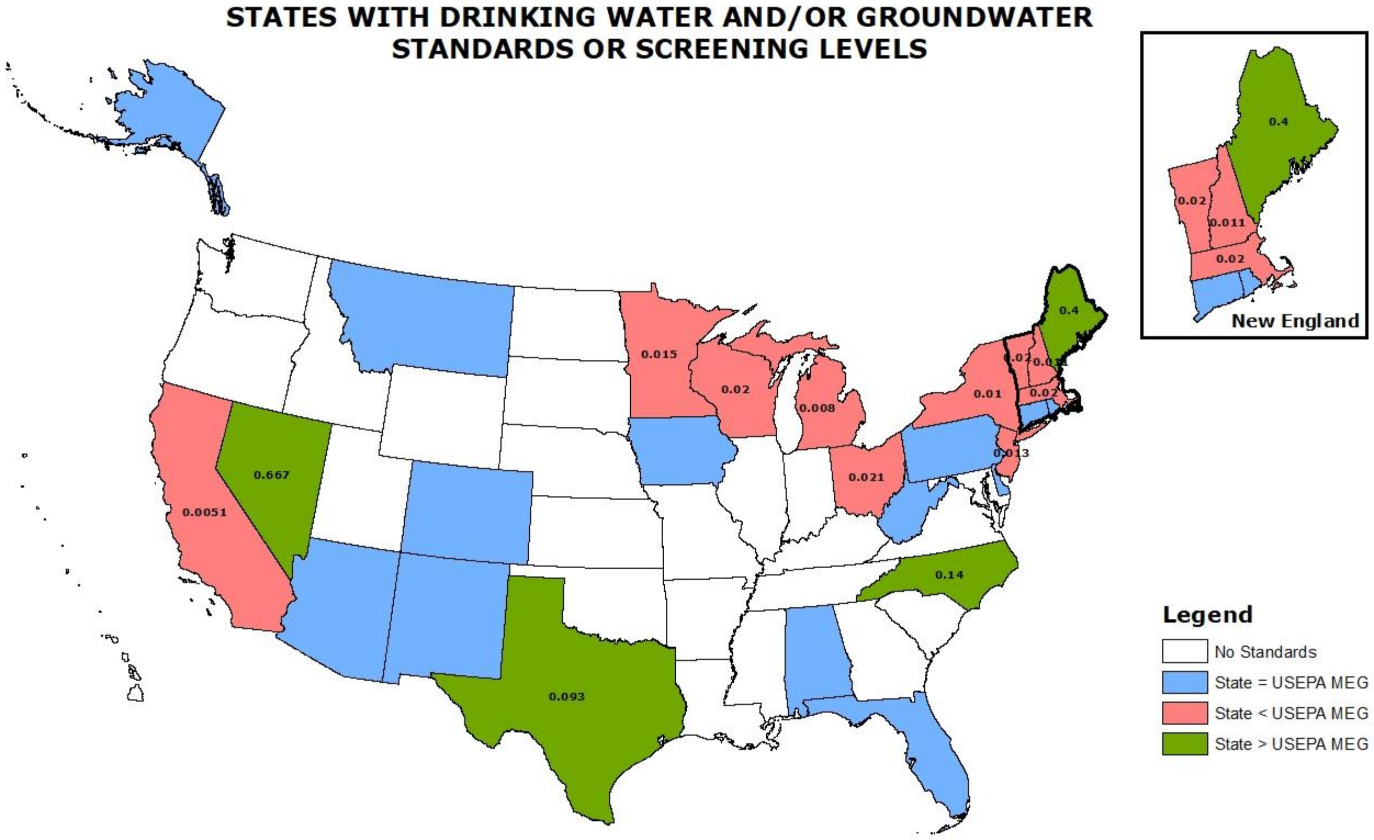
- **Cause of concern:**
  - Liver disease (hepatotoxin)
  - Also linked to kidney disease, developmental toxicity, immunosuppression, elevated cholesterol, thyroid hormone disruption, infertility, and more.
- Wide range of factors (exposure models, references doses, etc…) used by different agencies result in different standards.
- **CT Department of Public Health Action Levels and toxicological evaluation are currently under review and are subject to change.**

PFAS Toxicological Factors Currently Used by Agencies

Agency		ATSDR	US EPA	NY DOH / DWQC	NJ DWQI	NH DES	VT DEC	MI DHHS	MN DOH	TX CEQ
Reference Doses (ng/kg-d)	PFOA	3	20	1.5	2	6.1	20	3.9	18	12
	PFOS	2	20	1.8	1.8	3	20	2.89	3.1	23
	PFNA	3	-	-	4.9 mg/L serum	4.3	-	2.2	-	12
	PFHxS	20	-	-	-	4	-	9.7	9.7	3.8
Relative Source Contribution		100%	20%	60%	20% PFOA & PFOS 50% PFNA	50%	20%	50%	50%	20%
Total Uncertainty Factor	PFOA	300	300	100	300	100	300	300	300	300
	PFOS	300	300	30	30	100	300	300	100	100
	PFNA	300	-	-	1000	100	-	300	-	1000
	PFHxS	300	-	-	-	300	-	300	300	300
Toxological Endpoint	PFOA	Hepatic, Immune, Developmental	Reduced infant body weight	Hepatotoxic response	Increased Liver Weight	Hepatotoxic response	Reduced infant body weight	Developmental	Developmental, Hepatic, Immune, Renal	Developmental
	PFOS	Hepatic, Immune, Developmental	Reduced infant body weight	Hepatotoxic response	Immune Response	Immunotoxic response	Reduced infant body weight	Immunotoxic response	Adrenal, Developmental, Hepatic, Immune, and Thyroid	Developmental
	PFNA	Body Weight	-	-	Increased Liver Weight	Hepatotoxic response	-	Body Weight, Developmental	-	Spleen cell apoptosis
	PFHxS	Hepatic and Thyroid	-	-	-	Reduced infant body weight	-	Thyroid	Hepatic and Thyroid	Hematological
Target Population		Unspecified	Lactating Women	Infant	Adult	Lifetime based on internal serum concentration	Infant (0-1 yr)	Lifetime based on internal serum concentration	Lifetime based on internal serum concentration	Child (0-6 yrs) residential
Water Ingestion Rate (L/kg-day)		Continuous ingestion	0.054	0.151	0.029	95% water intake rates and upper percentile breastmilk intake rates modeled over lifetime.	0.175	95% water intake rates and upper percentile breastmilk intake rates modeled over lifetime.	95% water intake rates and upper percentile breastmilk intake rates modeled over lifetime.	0.043

Note: Underline indicates hyperlink to reference.

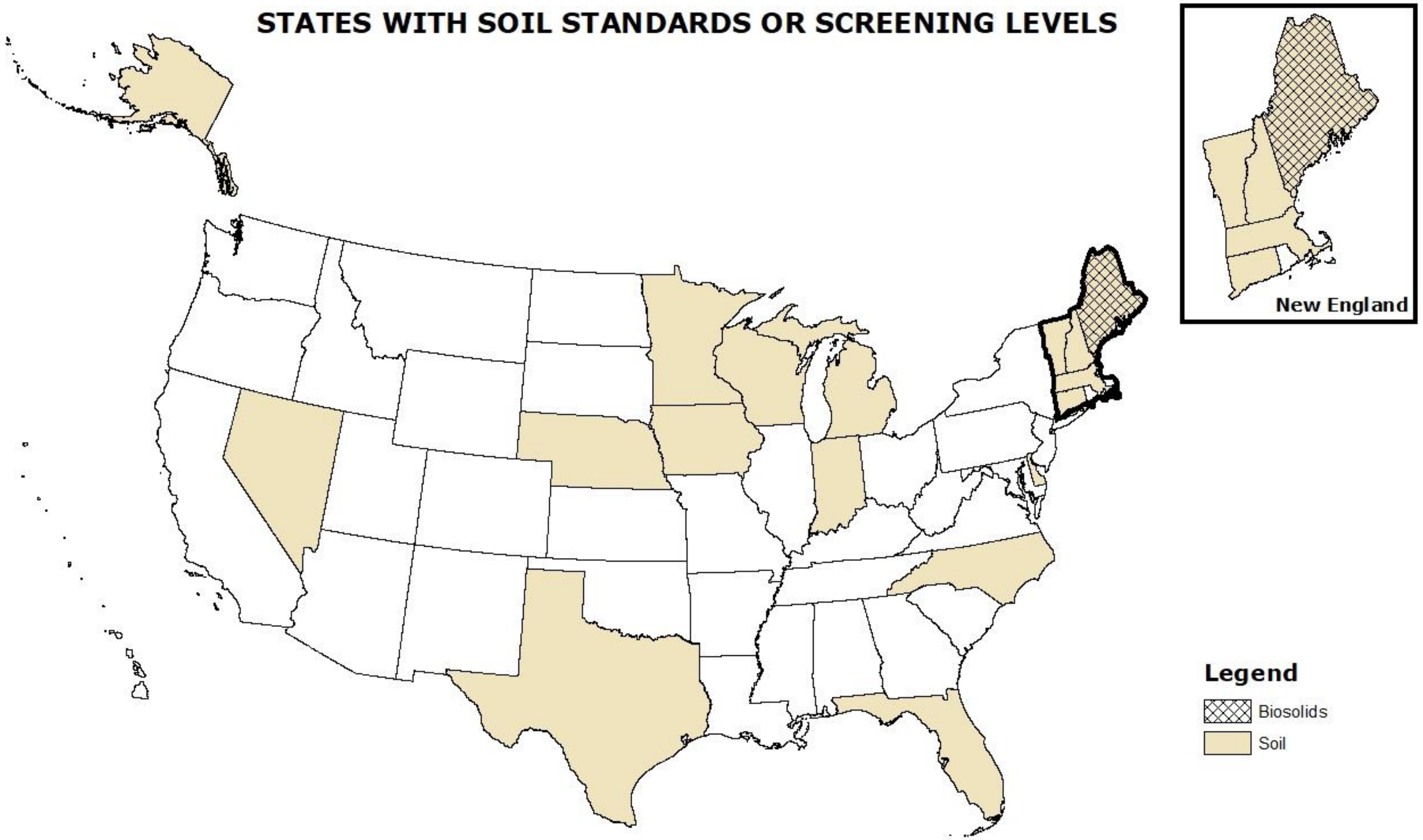
PFAS Regulatory Status



- **US EPA Maximum Exposure Guideline (MEG) 0.070 µg/l**
  - 13 states use EPA MEG
  - 10 states < EPA MEG*
    - Lowest is MI - 0.008 µg/l
  - 4 states > EPA MEG*
    - Highest is NV – 0.667 µg/l

* Based on lowest value for PFAS compound

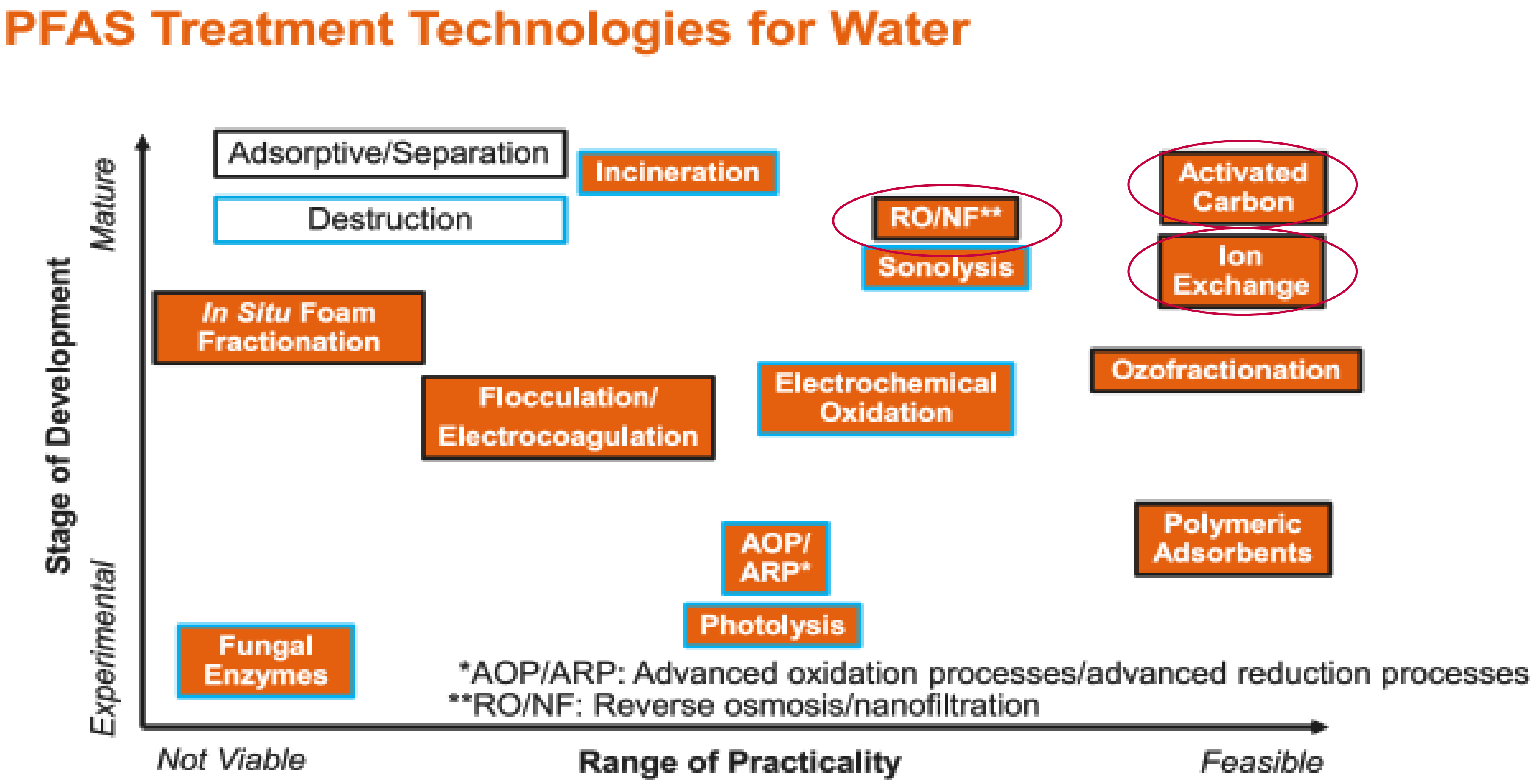
PFAS Regulatory Status



PFAS Regulatory Status
States with Industrial Pretreatment Programs

- **States with Current Wastewater Guidance**
  - Michigan (2016)
    - As of 2018, Michigan DEQ has required wastewater treatment plants with industrial pre-treatment programs to evaluate and investigate potential sources of PFAS and monitor WWTP effluent for PFAS.
    - WWTP effluent must meet promulgated Water Quality Standards: PFOA - 0.420 ug/L; PFOS - 0.011 ug/L
  - Oregon (2017)
    - Initiation level has been identified for 5 PFAS species in Schedule A for NPDES WPCF permits
    - "Initiation level" is the concentration of a persistent pollutant in effluent that requires the preparation of a persistent pollutant reduction plan
  - Wisconsin (2019)
    - In July WI DNR began correspondence with 125 wastewater treatment facilities with industrial pretreatment programs requesting sampling and analysis of influent and effluent for PFAS
    - If results show PFAS at or above 20 ppt DNR recommends *voluntary* sampling and analysis of all industrial users to identify sources
  - New Hampshire (2019)
    - Rulemaking proposal was filed on June 28; new MCL for 4 PFAS species effective October 1, 2019
    - All groundwater discharge sites need to comply with the new rules

Current Stages of Technology Development



Ross, I. T., et al. A Review of Emerging Technologies for Remediation of PFASs. *Remediation Journal* **2018**, *28* (2), 101–126.

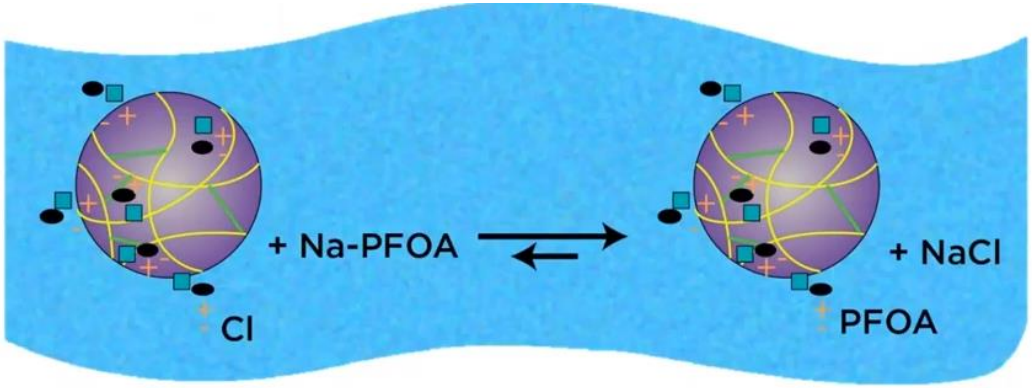
Activated Carbon - Performance

- **Short-chain vs long-chain**
  - PFAS containing five carbon atoms or less with other factors being equal (e.g. influent concentration) breakthrough times are five times quicker than PFAS containing six carbon atoms or more
- **Reported removal efficiencies are between 90% and >99%**
  - Select PFAS reduced to very low/nondetectable concentrations on the order of parts per trillion
  - Lower end of reported efficiencies likely the result of faster breakthrough for short-chain PFAS
- **Re-agglomerated bituminous coal observed to have better removal performance for PFAS than other types of GAC**
- **Column Studies Required to Determine Expected Performance**
- **More Detailed Carbon Information**

Remediation Technologies and Methods for Per- and Polyfluoroalkyl Substances (PFAS). *Interstate Technology Regulatory Council* **2018**. Image from Calgon Carbon

Ion Exchange – Performance

- **Ion exchange resins developed for higher removal of all PFAS contaminants – including short-chain compounds**
- **Resin shown to process higher quantities of contaminants before breakthrough**
  - Resin treated over eight times as many bed volumes of groundwater as GAC for PFOS and six times as many bed volumes for PFOA
  - Mass-to-mass basis, resin removed over four-times as much total PFAS per gram as GAC
  - Ion exchange has a smaller footprint, so may be more viable for sites with space limitations
  - Ion exchange resin tends to cost 3-5x more than GAC per unit volume (purchase and Disposal)
  - More Ion Exchange Information Here



Woodard, S.; Berry, J.; Newman, B. Ion Exchange Resin for PFAS Removal and Pilot Test Comparison to GAC. Remediation Journal **2017**, 27 (3), 19–27. Image from Evoqua Water Technologies

What Next?

- **Race to Zero?**
- **NEWMOA Northeast PFAS Science Conference**
  - Date: TBD
  - Thomas J. Salimeno, PE, LEP will participate in a panel for "Uses & Community-Oriented Solutions" at the NEWMOA Northeast Science of PFAS: Public Health And The Environment Conference.

Questions

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Aqueous Film Forming Foam (AFFF):

- Class A and B foams
- Class A foams are for normal combustibles causes water penetration by reducing surface tension
- Class B foams are for high-hazard flammable liquid fires and often contain PFAS
- Class B foams are synthetic foams – AFFF, alcohol-resistant aqueous film-forming foam (AR-AFFF) or protein foams

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Advisory Information for Aqueous Film Forming Foam *CT Department of Energy and Environmental Protection, CT Department of Emergency Services and Public Protection*, *Commission on Fire Prevention and Control*, **June 2019**

Aqueous Film Forming Foam (AFFF) Class B Foams:

- **Legacy PFOS Foams**
  - Long-carbon-chain fluorinated compounds (C8), PFOS/PFOA
  - Manufactured prior to 2003 by 3M, brand name “Lightwater”
- **Legacy Fluorotelomer Foams**
  - Contain some long-chain PFAS
  - Manufactured from the 1970s until 2016 and include all other brands of AFFF.
  - Contain polyfluorinated precursors that break down to PFOA/PFAS and by-products
- **Modern Fluorotelomer Foams**
  - Short-chain (C6) fluorotelomers or short-carbon-chain fluorinated compounds
  - Manufactured from around 2010 to present
  - May still have trace levels of PFOA and PFOA precursors
- **Flourine Free Foams**

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PFAS Fact Sheet Aqueous Film-Forming Foam, *Interstate Technology Regulatory Council* **October 2018**.

Metal Plating and Finishing:

- **Surfactant, wetting agent and mist suppressant – primarily chromium**
  - Regulatory Requirement from 1995 to
  - Fluorotenside-248, SurTec 960, and Fumetrol 140 (ATOTECH)
- **Electroless plating of copper and depositing nickel-boron layers**
- **Electroplating of copper, nickel, and tin**
- **Zinc electrodeposition**

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History and Use of Per- and Polyfluoroalkyl Substances (PFAS). *Interstate Technology Regulatory Council* **November 2017**.

Oil and Water Repellant Products:

- **Textiles**
  - jackets, shoes, and umbrellas
  - carpets, upholstery, and leather
  - tents and sails
  - Scotchgard (3M) and Zonyl, Foraperle, and Capstone (DuPont)
- **Paper and Cardboard Packaging**
  - plates, popcorn bags, pizza boxes, and food containers and wraps
  - Scotchban (3M), Baysize S (Bayer), Lodyne (Ciba, BASF), Cartafluor (Clariant), and Zonyl (DuPont)

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History and Use of Per- and Polyfluoroalkyl Substances (PFAS). *Interstate Technology Regulatory Council* **November 2017**.

Consumer Products:

- **Cleaning Products**
  - carpet spot cleaners, alkaline cleaners, denture cleaners and shampoos, floor polish, and dishwashing liquids
  - car wash products and automobile waxes
  - Novec (3M) and PolyFox (OMNOVA Solutions)
- **Cosmetics and Personal Care**
  - emulsifiers, lubricants, or oleophobic agents
  - hair-conditioning formulations and hair creams
  - toothpastes, sunscreen, dental floss

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Industrial Products:

- **Paints and Coating**
  - reduce surface tension for substrate wetting, levelling, dispersing agents, and improving gloss and antistatic properties
- **Plastics, resins, and rubbers**
  - polytetrafluoroethylene (PTFE) and polyvinylidine fluoride (PVDF)
- **Adhesives**
- **Antifogging**

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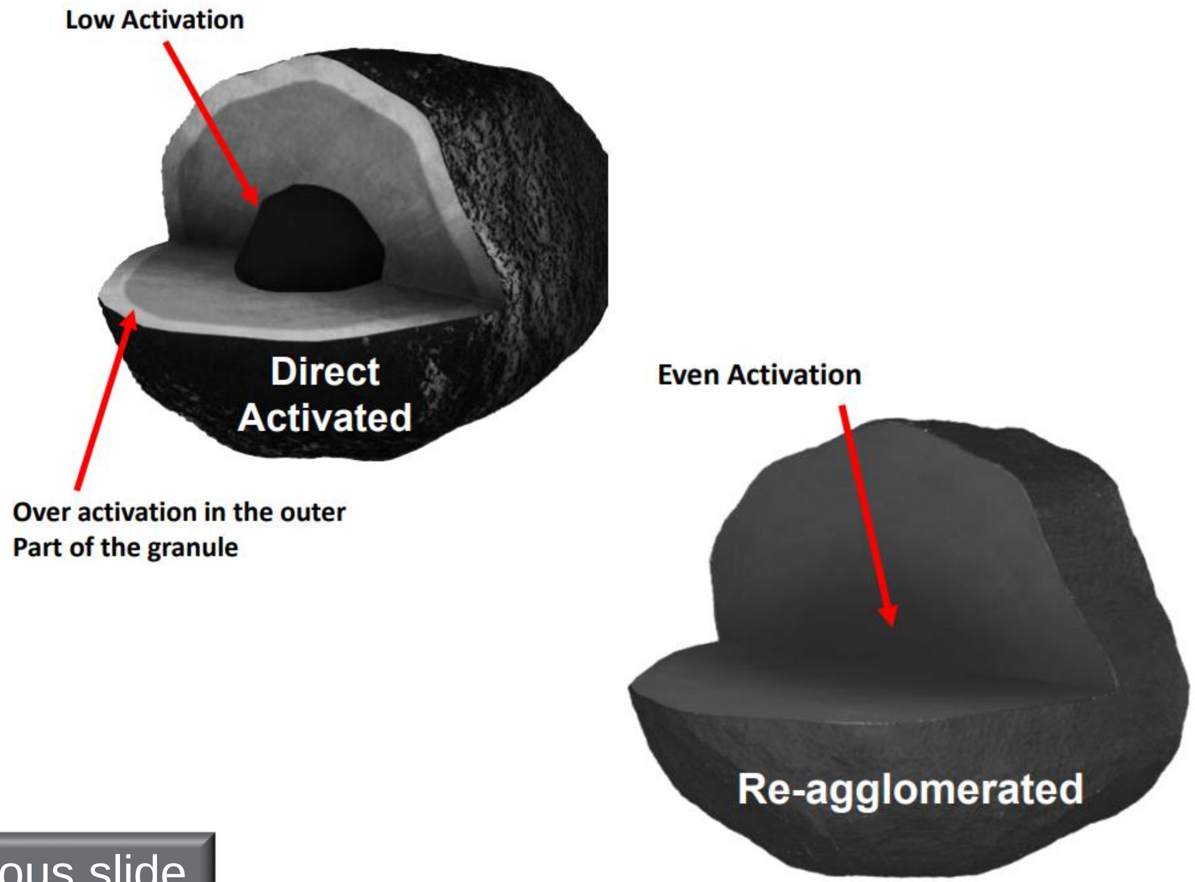
History and Use of Per- and Polyfluoroalkyl Substances (PFAS). *Interstate Technology Regulatory Council* **November 2017**.

Activated Carbon - Implementation

- **Factors affecting changeout frequency**
  - GAC surface area, pore size, and surface chemistry
  - Short-chain vs long-chain PFAS concentrations
  - Co-contaminant concentrations
  - Flowrate
- **Presence of dissolved organic matter can cause inhibitory effect on efficiency removal**
  - Creates competition for adsorption sites
- ***Column studies are the recommended method to predict GAC performance and change-out frequency***



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Ross, I. T., et al. A Review of Emerging Technologies for Remediation of PFASs. *Remediation Journal* **2018**, *28* (2), 101–126. Image from Calgon Carbon

Activated Carbon - Regeneration

- **Spent carbon can be recycled through regeneration**
  - Thermal processing of the activated carbon to destroy the adsorbed components
  - High temperatures to desorb and destruct PFAS from spent GAC
  - Thermal reactivation kilns typically include afterburners for air pollution control at temperatures above 1,100°C – temperature required to destroy volatilized PFAAs
- **Column studies show that virgin GAC and thermally reactivated GAC have similar removal rates and breakthrough times**

Ross, I. T., et al. A Review of Emerging Technologies for Remediation of PFASs. *Remediation Journal* **2018**, *28* (2), 101–126.

Activated Carbon – Advantages vs Disadvantages

Advantages

- Most established technology for PFAS removal
- Removal efficiencies between 90% and >99%
- Removal of co-contaminants
- No concentrated waste stream
- Destruction of volatilized PFAS during carbon regeneration

Disadvantages

- Lower removal efficiency for short-chain PFAS
- Decreased efficiency with presence of dissolved organic matter
- Disposal or reactivation costs of spent carbon
- Potential large footprint
- Less sustainable than an in-situ option

Remediation Technologies and Methods for Per- and Polyfluoroalkyl Substances (PFAS). *Interstate Technology Regulatory Council* **2018**

Ion Exchange – Implementation

- **Ion exchange has a smaller footprint, so may be more viable for sites with space limitations**
- **Less studied and less developed than GAC technology**
- **Ion exchange resin tends to cost 3-5x more than GAC per unit volume**
- **Costly disposal of spent resin**
- **May not prove to be economical for long-term projects (over 15-20 years)**

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