Thank you for signing in early

The webinar will begin promptly at
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Managing AFFF Impacts to Subsurface Environments and Assessment of Commercially Available PFAS-Free Foams (Part 1)

October 8, 2020

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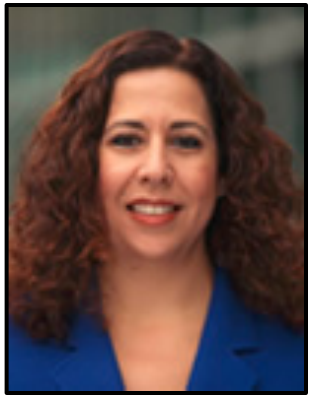
Welcome and Introductions



Rula A. Deeb, Ph.D.
Webinar Coordinator

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Webinar Agenda

- **Webinar Logistics** (5 minutes)
  Dr. Rula A. Deeb, Geosyntec Consultants
- **Overview of SERDP and ESTCP** (5 minutes)
  Dr. Robin Nissan, SERDP and ESTCP
- **Novel Cyclodextrin-Based Adsorbents to Remove PFAS from Water** (25 minutes + Q&A)
  Dr. Damian E. Helbling, Cornell University
- **Assessment of Commercially Available PFAS-Free Foams** (25 minutes + Q&A)
  Dr. Satya P. Chauhan, Battelle
- **Final Q&A session**

Zoom Instructions

- Download Zoom
  - https://zoom.us/download
- If you cannot download Zoom, you can view the slides using an internet browser
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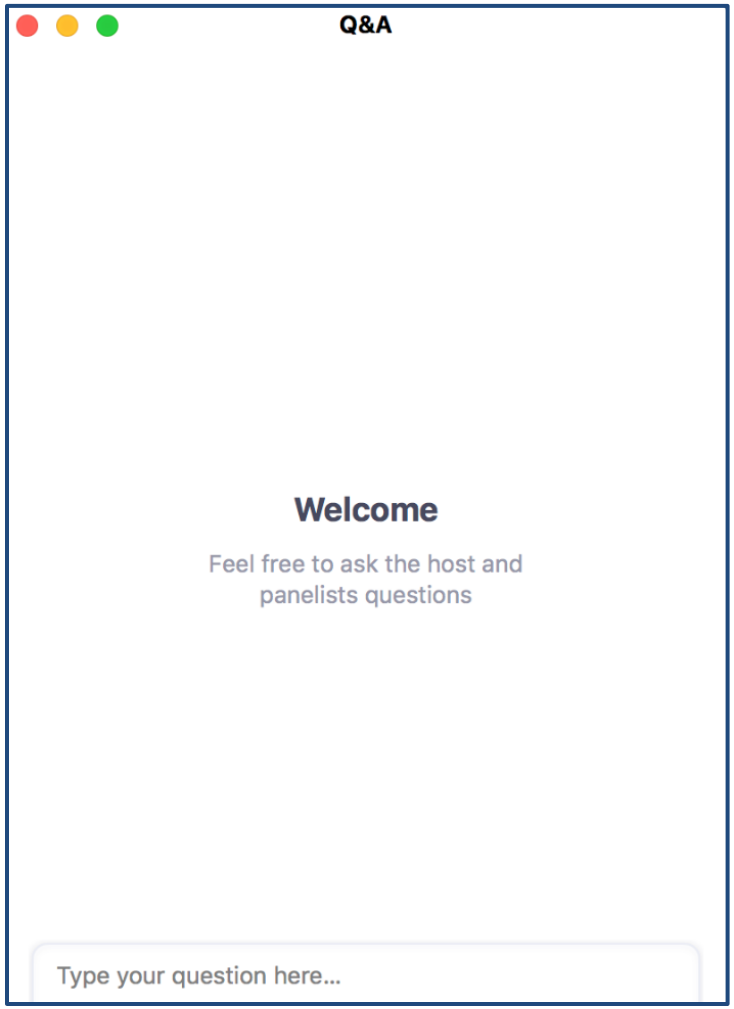
- Find the Q&A button on your control bar and type in your question(s)
- Make sure to add your organization name at the end of your question so that we can identify you during the Q&A sessions



SERDP and ESTCP Overview

Robin Nissan, Ph.D.
SERDP and ESTCP

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SERDP

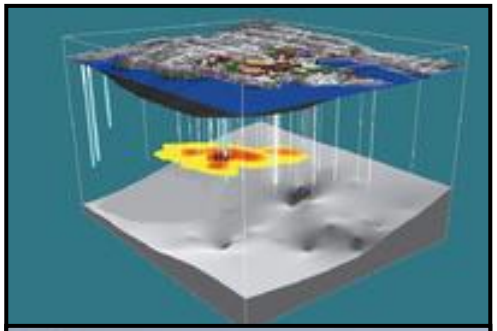
- Strategic Environmental Research and Development Program
- Established by Congress in FY 1991
  - DoD, DOE and EPA partnership
- SERDP is a requirements driven program which identifies high-priority environmental science and technology investment opportunities that address DoD requirements
  - Advanced technology development to address near term needs
  - Fundamental research to impact real world environmental management

ESTCP

- Environmental Security Technology Certification Program
- Demonstrate innovative cost-effective environmental and energy technologies
  - Capitalize on past investments
  - Transition technology out of the lab
- Promote implementation
  - Facilitate regulatory acceptance

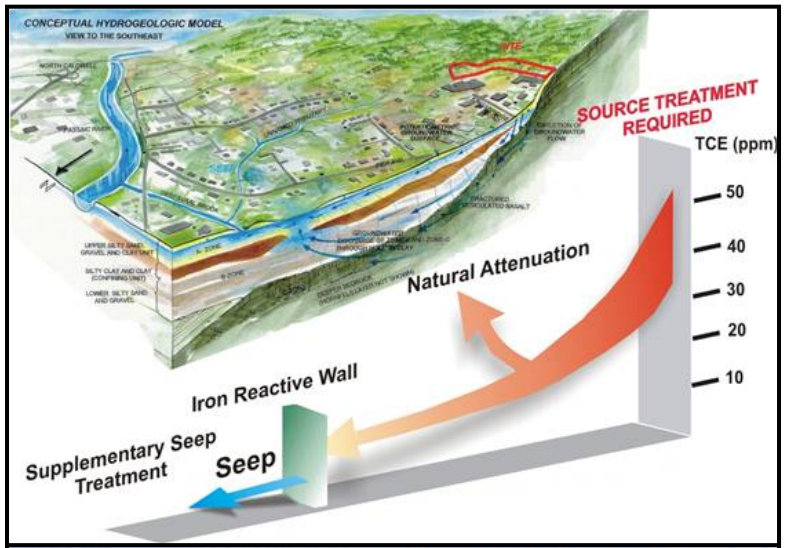
Program Areas

- Environmental Restoration
- Installation Energy and Water
- Munitions Response
- Resource Conservation and Resiliency
- Weapons Systems and Platforms



Environmental Restoration

- Major focus areas
  - Contaminated groundwater
  - Contaminants on ranges
  - Contaminated sediments
  - Wastewater treatment
  - Risk assessment



Weapons Systems and Platforms

- Major focus areas
  - Surface engineering and structural materials
  - Energetic materials and munitions
  - Noise and emissions
  - Waste reduction and treatment in DoD operations
  - Lead free electronics

SERDP and ESTCP PFAS Efforts

https://map.serdp-estcp.org/Featured-Initiatives/Per-and-Polyfluoroalkyl-Substances-PFASs/pfas_efforts.pdf

SERDP and ESTCP Webinar Series

Date	Topic
October 22, 2020	Managing AFFF Impacts to Subsurface Environments and Assessment of Commercially Available PFAS-Free Foams (**Part 2**)
November 5, 2020	Pathways under Non-Stationary Conditions and Their Implications for Wildlife and Human Exposure on Department of Defense Lands
November 19, 2020	Abiotic Degradation of Chlorinated Solvents in Subsurface Environments
December 10, 2020	Approaches for Managing Contaminated Sediments
January 14, 2021	Improving Energy Efficiency through Advanced Building Controls
January 28, 2021	Improved Approaches for PFAS Sampling and Treatment

For upcoming webinars, please visit

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Save the Date

SERDP • ESTCP
SYMPOSIUM

A symposium showcasing the latest technologies that enhance DoD's mission through improved environmental and energy performance

November 30 – December 4, 2020

Registration for the virtual event is open!

Novel Cyclodextrin-Based Adsorbents to Remove PFAS from Water

Damian E. Helbling, Ph.D., P.E.
Cornell University

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Agenda

- Adsorbents for PFAS remediation
- Cyclodextrins and cyclodextrin polymers (CDPs)
- Development of novel CDPs for PFAS
- Preparing CDPs for implementation
- Conclusions
- Benefits to DoD

Conventional Adsorbents for PFAS Remediation

Granular Activated Carbon

Features
- Inexpensive
- Hydrophobic
- Microporous

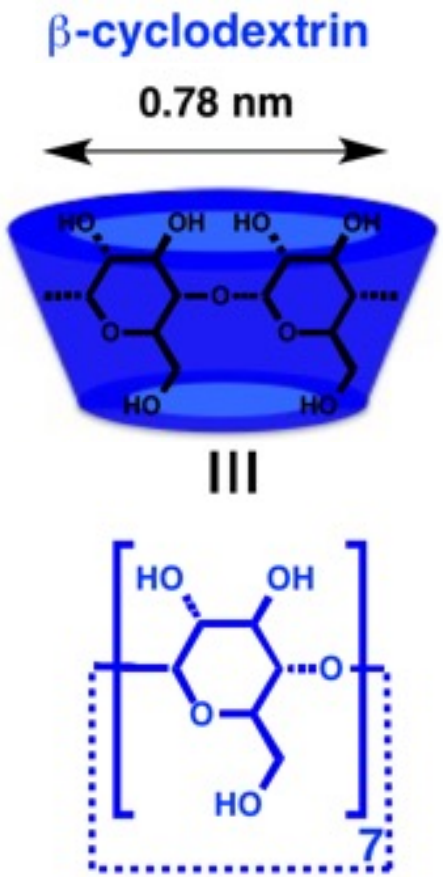
Deficiencies
- Slower kinetics
- Fouled by natural organic matter
- Regeneration

Ion Exchange Resins

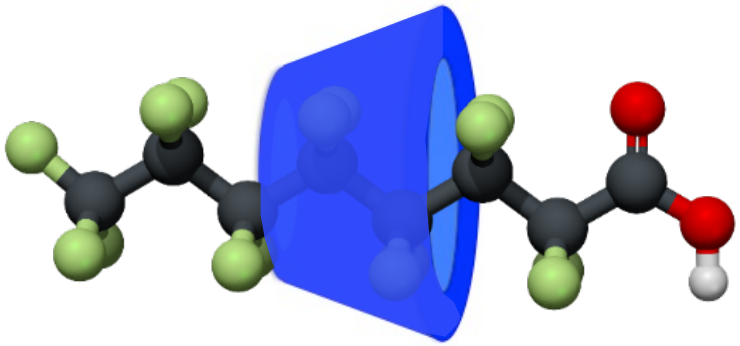
Features
- Selective
- Faster kinetics
- Some regenerable

Deficiencies
- Expensive
- Fouled by ions
- Ionic adsorbates

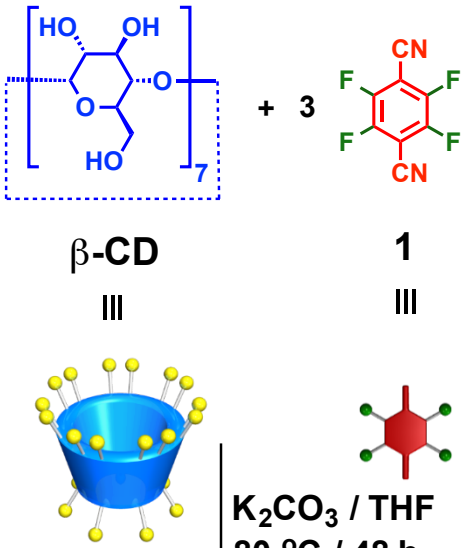
Cyclodextrins Form Host-Guest Complexes with Organic Molecules

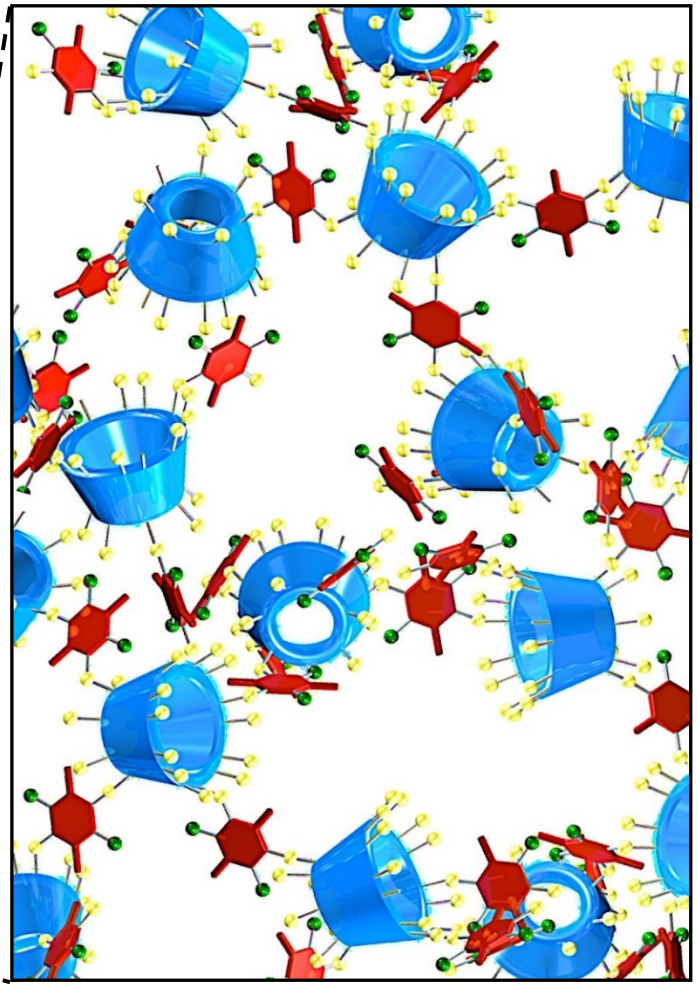


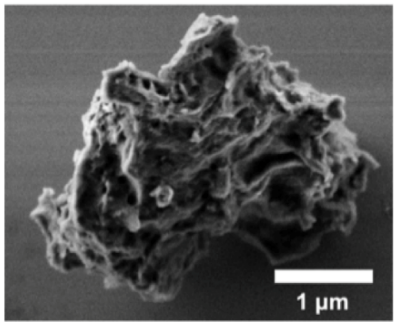
- β-cyclodextrin is an "outstanding complexing agent" for perfluoro carboxylates and sulfonates
  - Demonstrated by detailed nuclear magnetic resonance (NMR) investigations



Porous β-cyclodextrin Polymer (P-CDP) as an Adsorbent for Water Purification

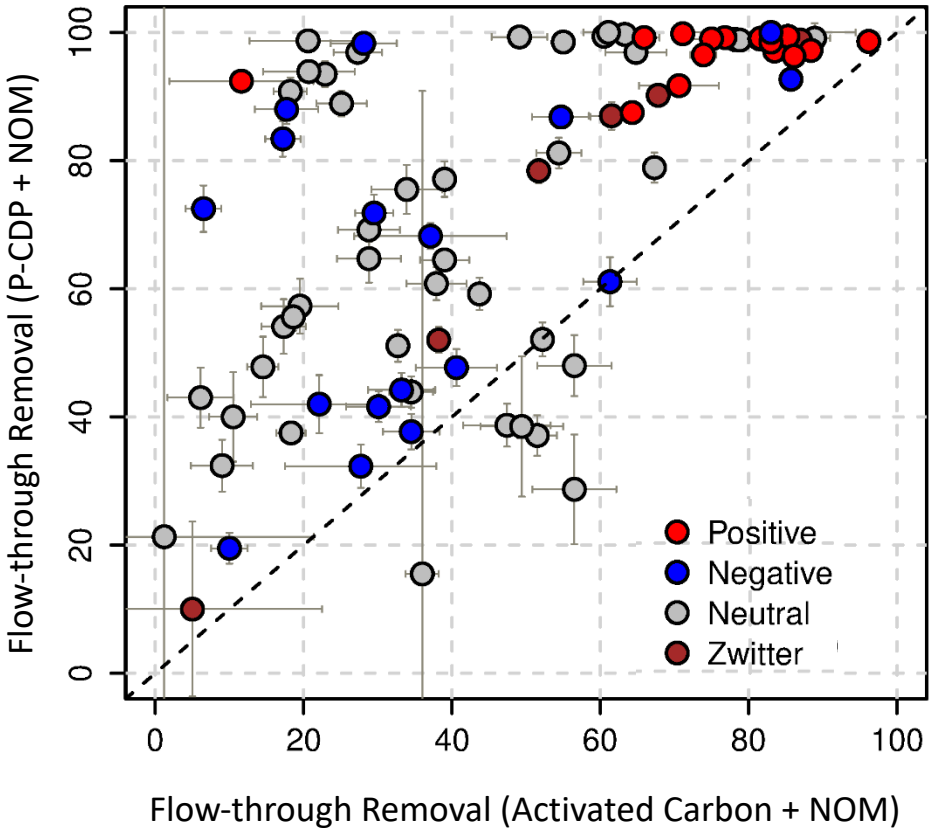






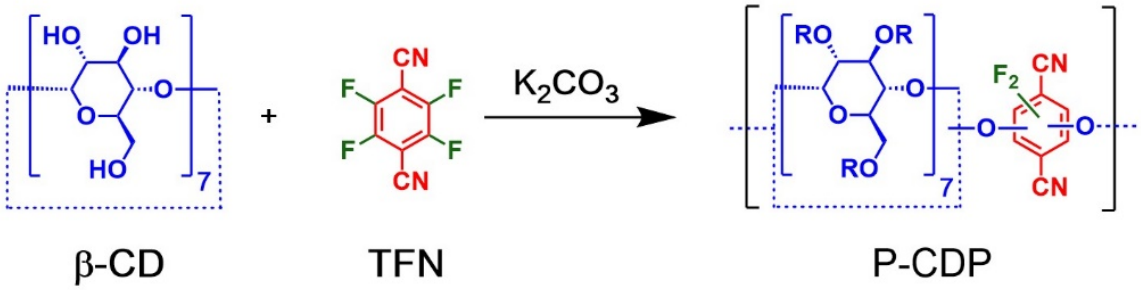
US Patent No. 9,624,314; 9,855,545; 10,086,360

Structure and Morphology of P-CDP Leads to Excellent Performance

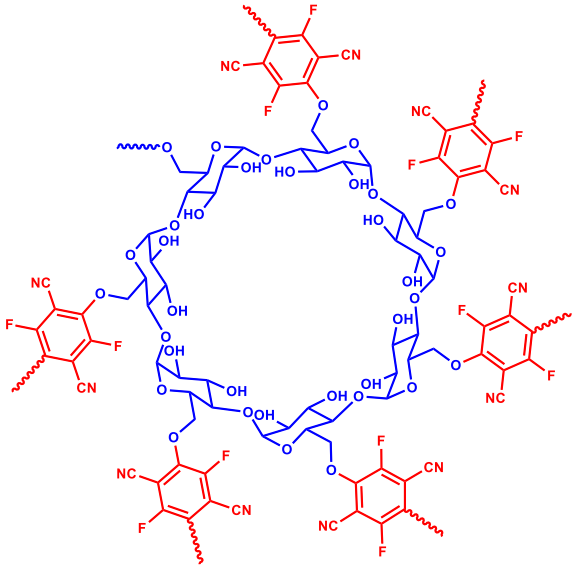


- P-CDP exhibits:
  - Rapid adsorption kinetics
  - Limited adsorption inhibition with natural organic matter (NOM) or inorganic ions
  - Selective uptake of trace organic chemicals
  - Preferred uptake of cationic adsorbates

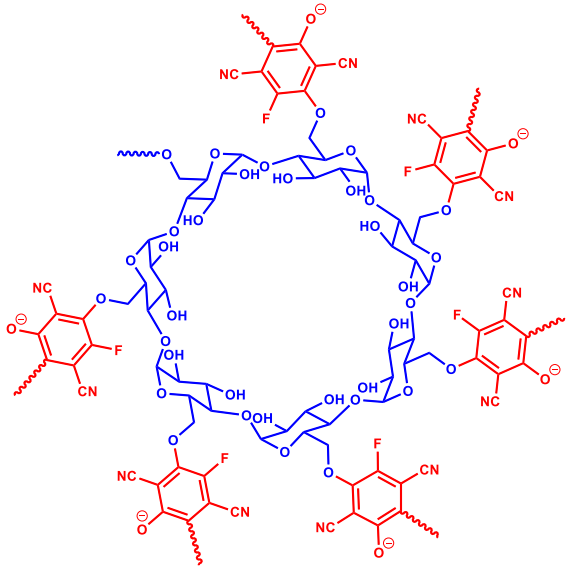
Crosslinker Chemistry Determines Adsorption Affinity



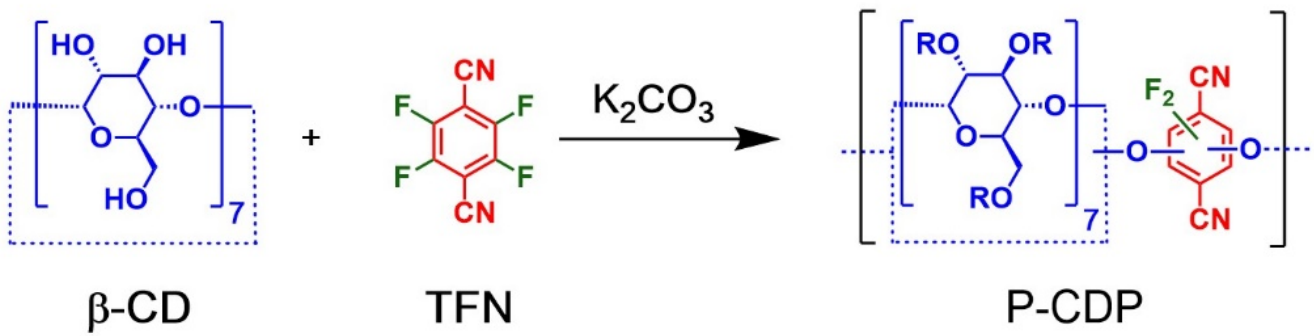
What we thought we made:

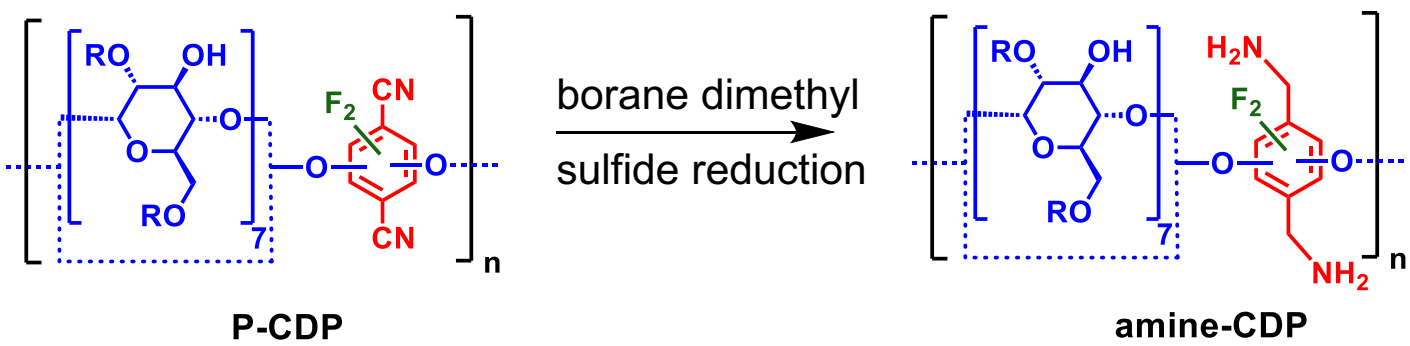


What we really made:

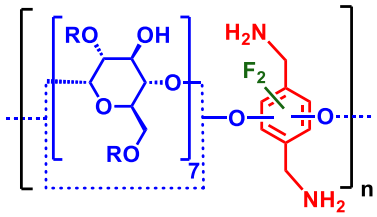


A Postsynthetic Reduction of P-CDP Results in Positive Surface Charge

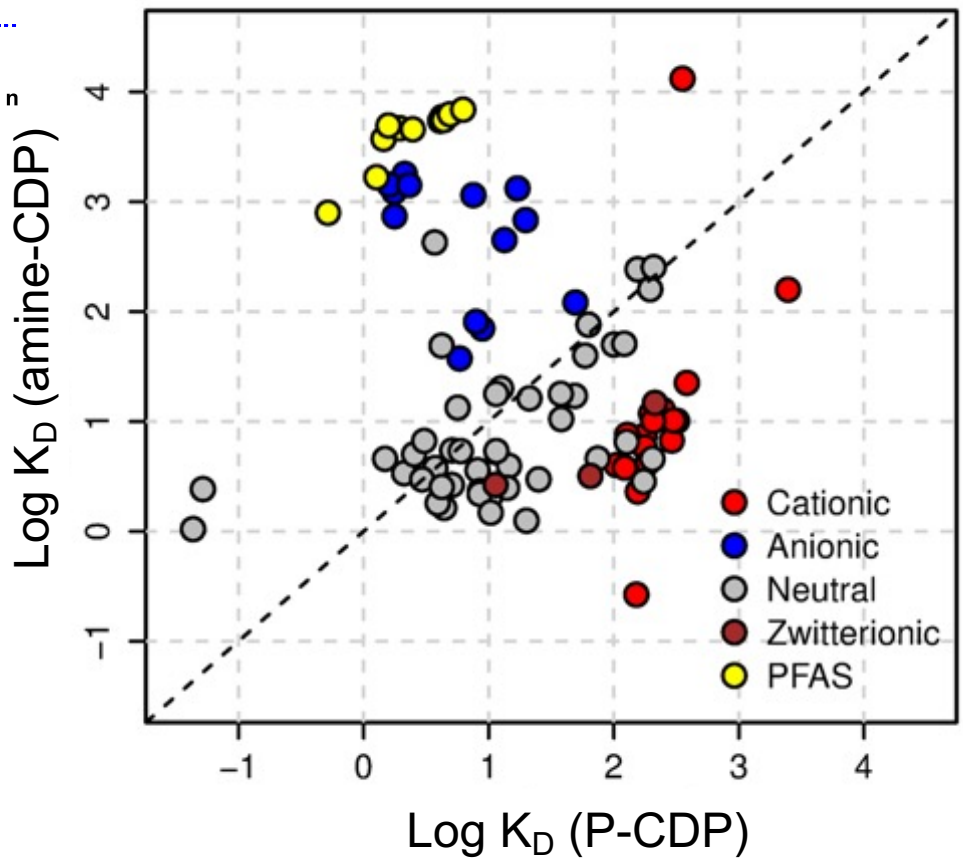




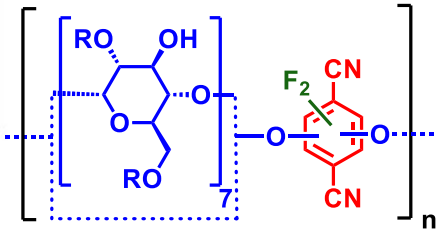
A CDP with a Positive Surface Charge Removes Anionic PFAS from Water



amine-CDP



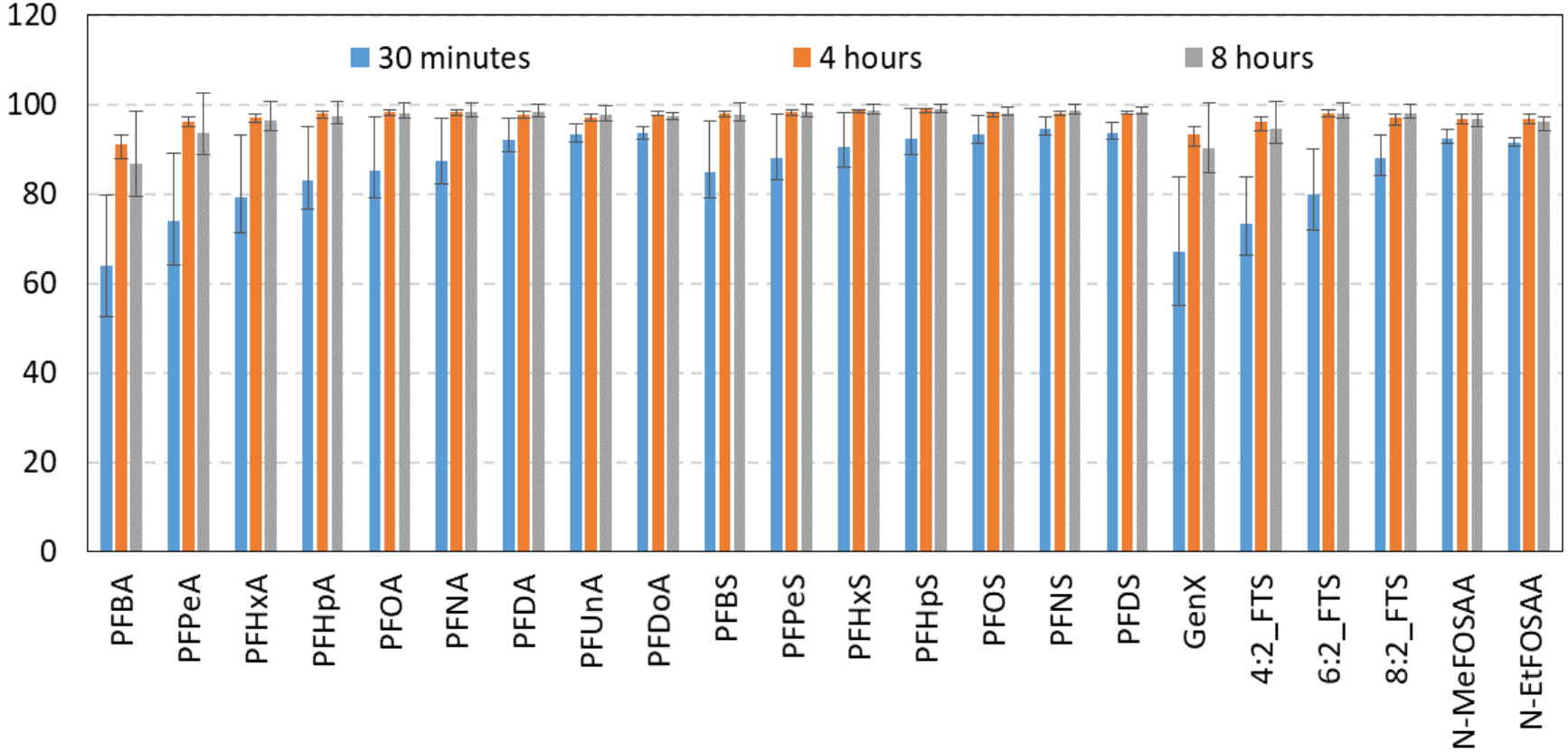
[adsorbent]$_0$ = 10 mg/L
[PFAS]$_0$ = 500 ng/L



P-CDP

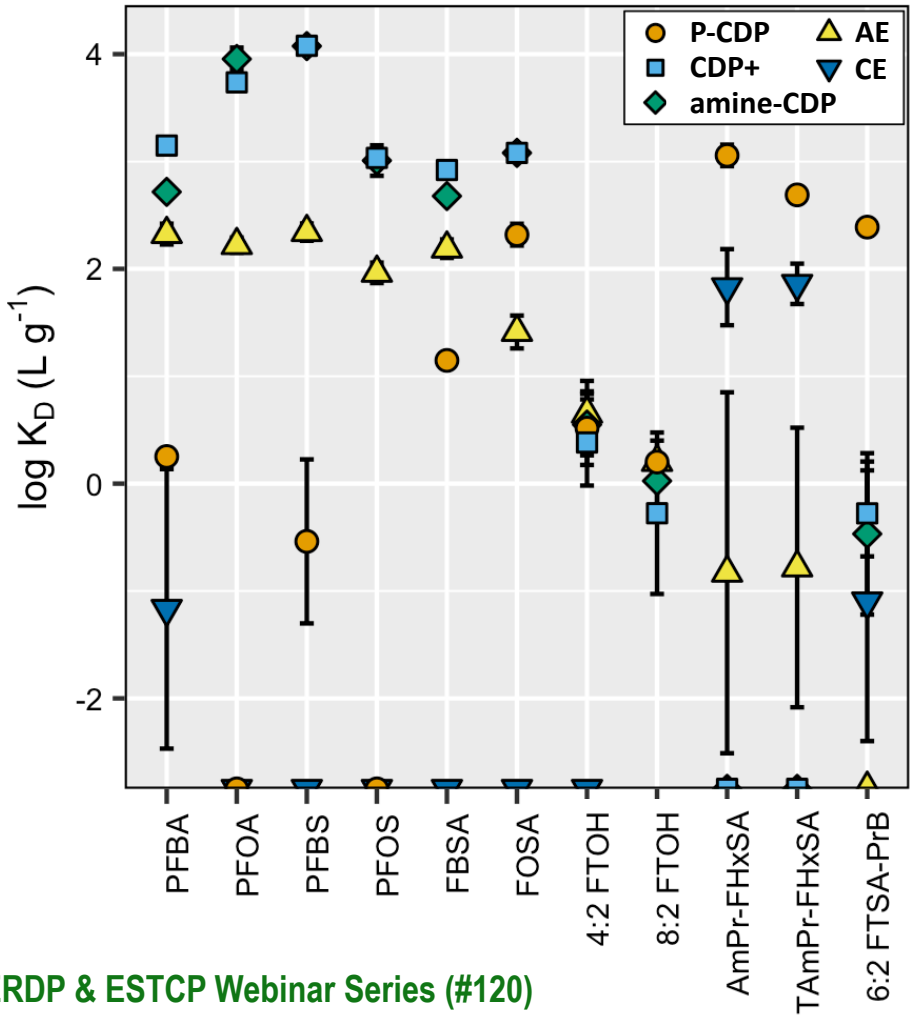
A CDP with a Positive Surface Charge Removes Anionic PFAS from Water (Cont'd)

$[adsorbent]_0$ = 10 mg/L; $[PFAS]_0$ = 500 ng/L

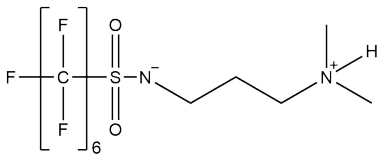


Different CDPs Exhibit Variable Affinity for Different Classes of PFAS

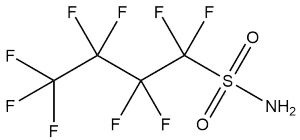
$[adsorbent]_0$ = 10 - 50 mg/L; $[PFAS]_0$ = 1000 - 2000 ng/L



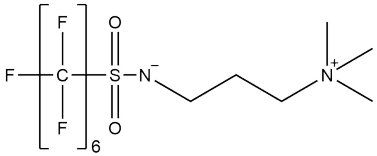
= anion exchange (AE) resin
= cation exchange (CE) resin



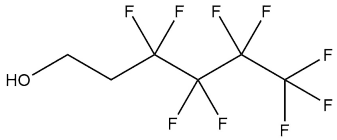
AmPr-FHxSA



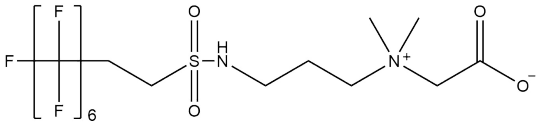
FBSA



TAmPr-FHxSA



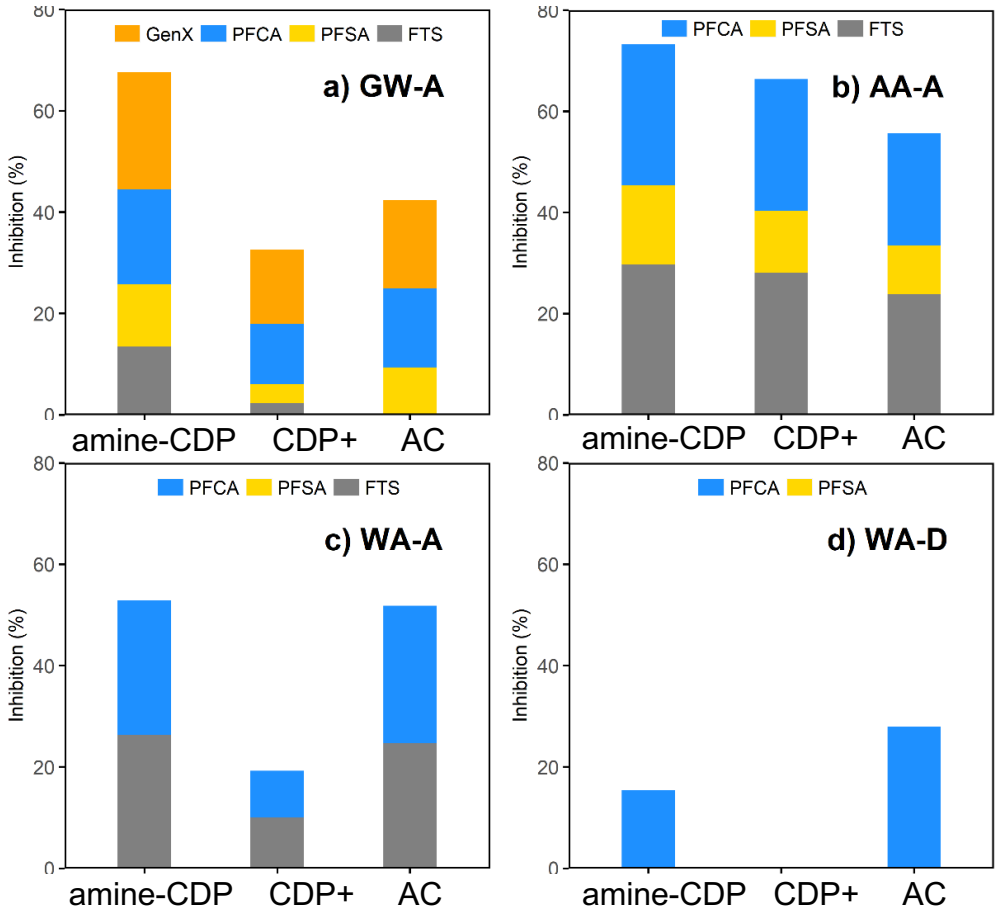
4:2 FTOH



6:2 FTSA-PrB

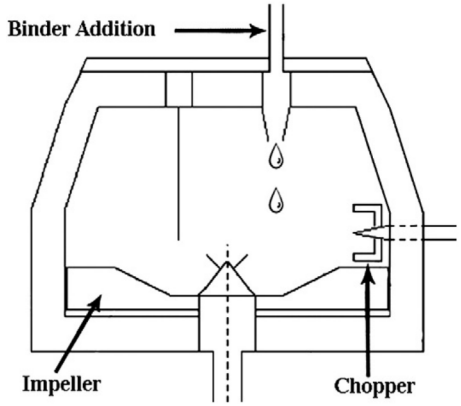
Some Adsorption Inhibition Observed in Experiments with Groundwater

$[\text{adsorbent}]_0$ = 10 mg/L
$[\text{PFAS}]_0$ = 500 ng/L or native conc.

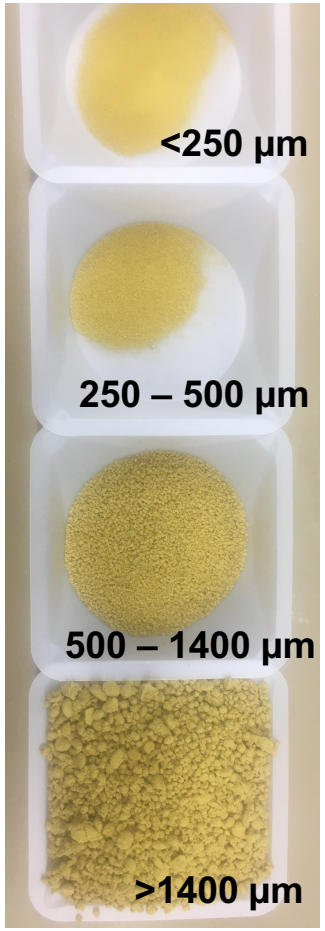


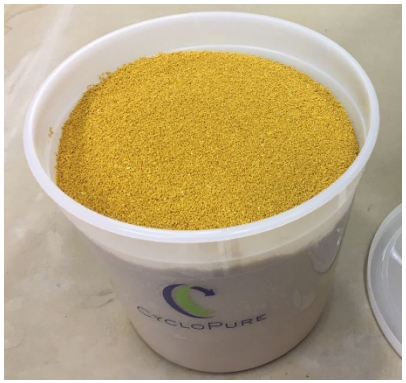
- Experiments
  - 2 CDPs, 1 activated carbon (AC)
  - Four groundwater samples
  - Four classes of PFAS
- Findings
  - Variable adsorption inhibition
  - Inhibition linked to pH and cations

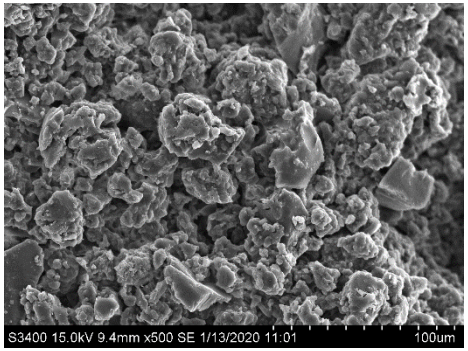
Techniques to Control Cyclodextrin Polymer Particle Size and Morphology



Glatt TMG High Shear Granulator



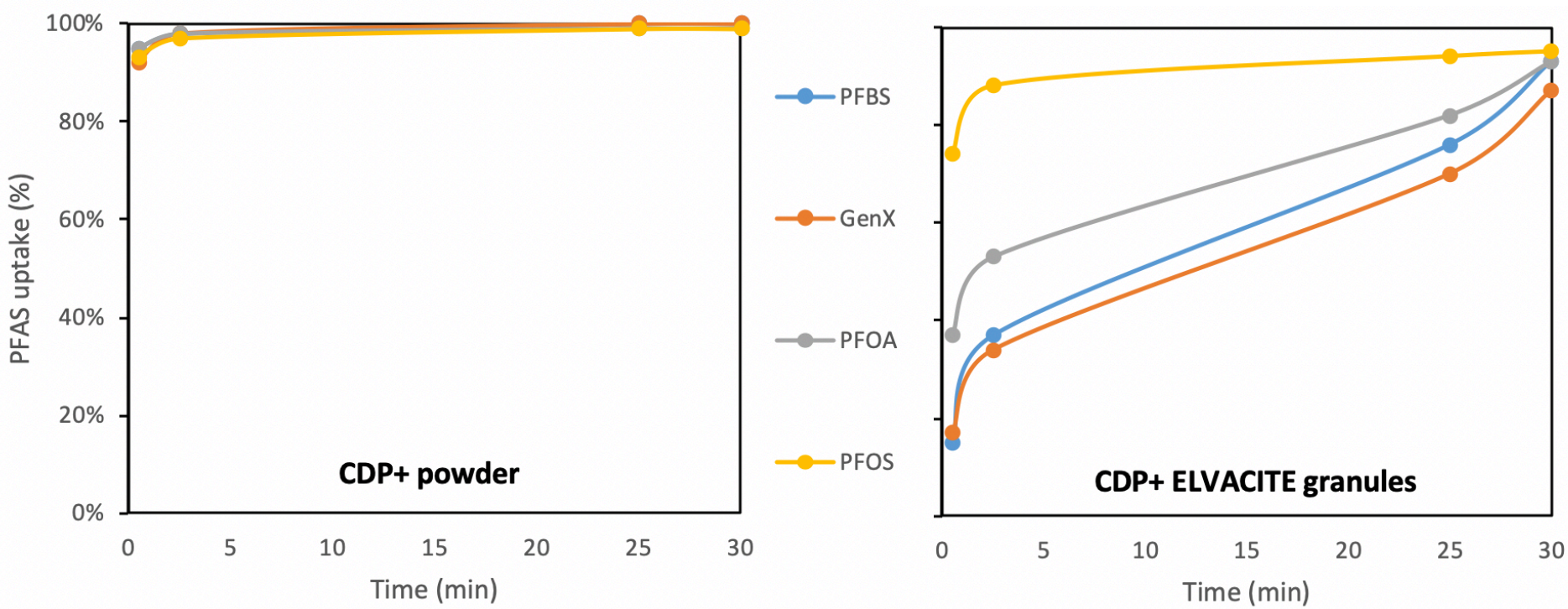




Granule size: 500-850 µm
CDP+ loading: 93%

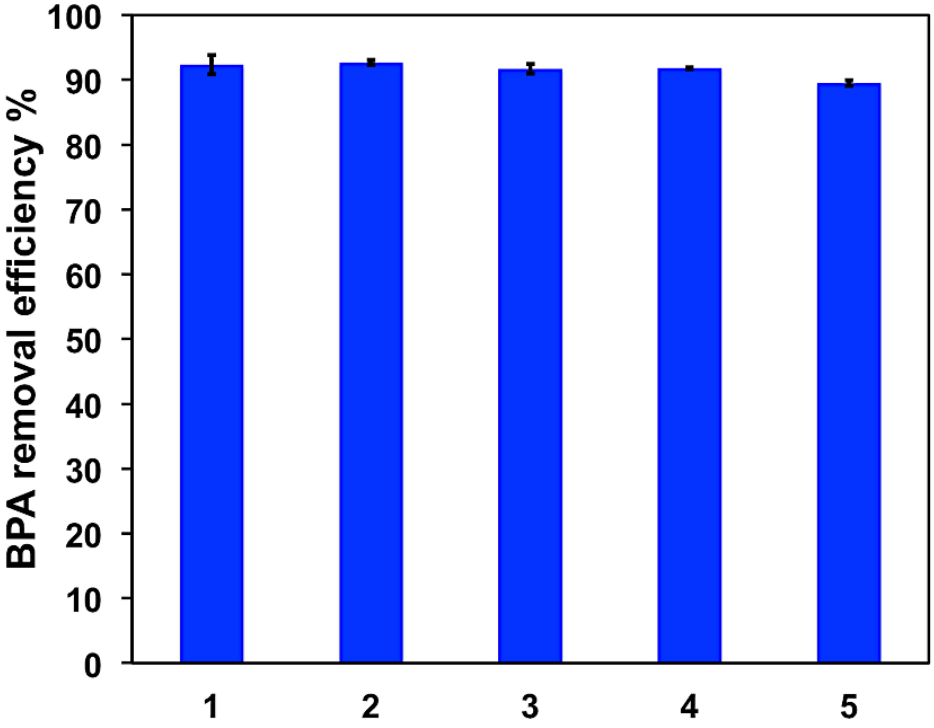
Techniques to Control Cyclodextrin Polymer Particle Size and Morphology

[adsorbent]$_0$ = 1000 mg/L; [PFAS]$_0$ = 100 µg/L

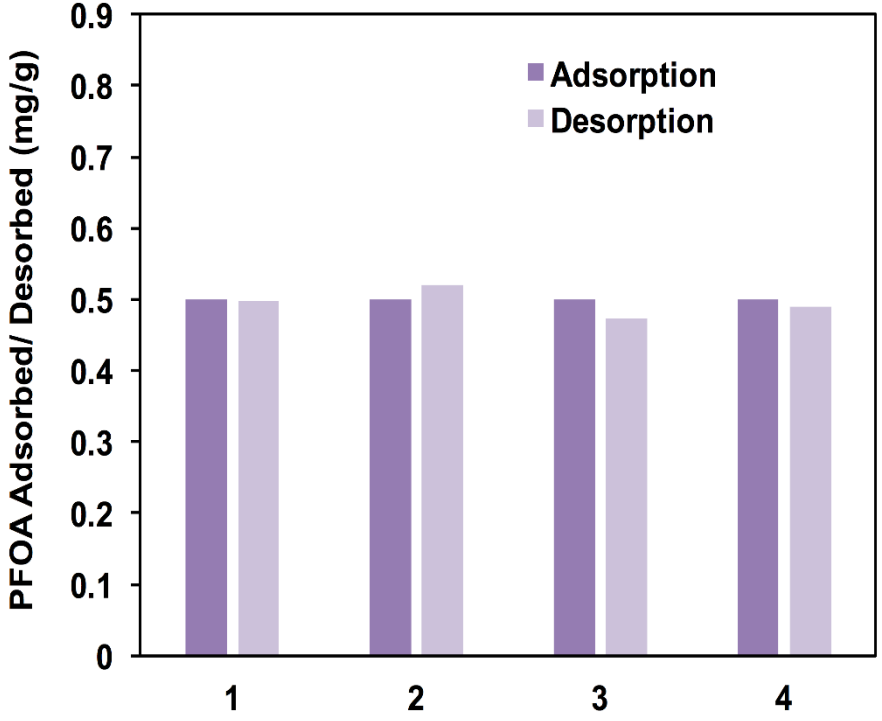


Regeneration Potential of Cyclodextrin-Based Polymer Adsorbents

Bisphenol-A (BPA) removal from CDP



PFOA removal from CDP



Conclusions

- Developed a family of novel adsorbents that target PFAS
- Target specific PFAS by tuning crosslinker chemistry and aim to limit adsorption inhibition
- Control adsorbent morphology
- Demonstrated facile regeneration potential
- Most derivatives incorporate readily available monomers
  - Ideal for scale-up

Benefits to DoD

- Provides RPMs with alternative adsorbents for PFAS remediation processes
- Addressing major deficiencies of conventional adsorbent materials
- Our adsorbents target PFAS of varying charge state and varying chain length
- Demonstrated:
  - Morphological control
  - Facile regeneration
  - Durability

Additional Resources

- Alsbaiee, A., Smith, B., Xiao, L., Ling, Y., Helbling, D.E., and W.R. Dichtel. (**2016**) "Rapid removal of organic micropollutants from water by a porous β-cyclodextrin polymer," *Nature*, 529, 190-194.
- Xiao, L., Ling, Y., Alsbaiee, A., Li, C., Helbling, D.E., and W.R. Dichtel. (**2017**) "A β-cyclodextrin polymer network sequesters PFOA at environmentally relevant concentrations," Journal of the American *Chemical Society*, 139(23), 7689–7692.
- Ling, Y., Klemes, M.J., Xiao, L., Alsbaiee, A., Dichtel, W.R., and D.E. Helbling. (**2017**) "Benchmarking micropollutant removal by activated carbon and porous β-cyclodextrin polymers under environmentally relevant scenarios," *Environmental Science & Technology*, 51(13), 7590–7598.
- Klemes, Ling, Ching, Wu, Xiao, Helbling, Dichtel. (**2019**) "Reduction of a tetrafluoroterephthalonitrile-β-cyclodextrin polymer to remove anionic micropollutants and perfluorinated alkyl substances from water." *Angewandte Chemie*, 58, 12049-12053.
- Wu, C., M.J. Klemes, B. Trang, W.R. Dichtel, and D.E. Helbling. (**2020**) Exploring the factors that influence the adsorption of anionic PFAS on conventional and emerging adsorbents in aquatic matrices. *Water Research*, 182, 115950.
- Ching, C., Klemes, M.J., Trang, B., Dichtel, W.R., and D.E. Helbling. (**2020**) β-cyclodextrin polymers with different crosslinkers and ion exchange resins exhibit variable adsorption of anionic, zwitterionic, and nonionic PFASs," *Environmental Science & Technology*, DOI: 10.1021/acs.est.0c04028.

For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/ER18-1026

Speaker Contact Information

deh262@cornell.edu; 607-255-5146

SERDP DOD • EPA • DOE | ESTCP

Q&A Session 1

Assessment of Commercially Available PFAS-Free Foams

Satya P. Chauhan, Ph.D.
Battelle

SERDP DOD • EPA • DOE | ESTCP

Agenda

- Background and problem
- Project objectives and approach
- Effect of engineering solutions on fire performance
- Benefits to DoD
- Conclusions

Background and Problem

- The Mil-Spec requires the use of aqueous film forming foam (AFFF) products to extinguish flammable liquid (Class B) fires
- Currently approved AFFF formulations contain per- and polyfluoroalkyl substances (PFAS) that are of concern for environment and human health
- AFFF must be phased out of use by October 2024 as per the 2020 National Defense Authorization Act (NDAA)
- Commercially-available PFAS-free foam (PFF) products do not meet the Mil-Spec

Project Objectives

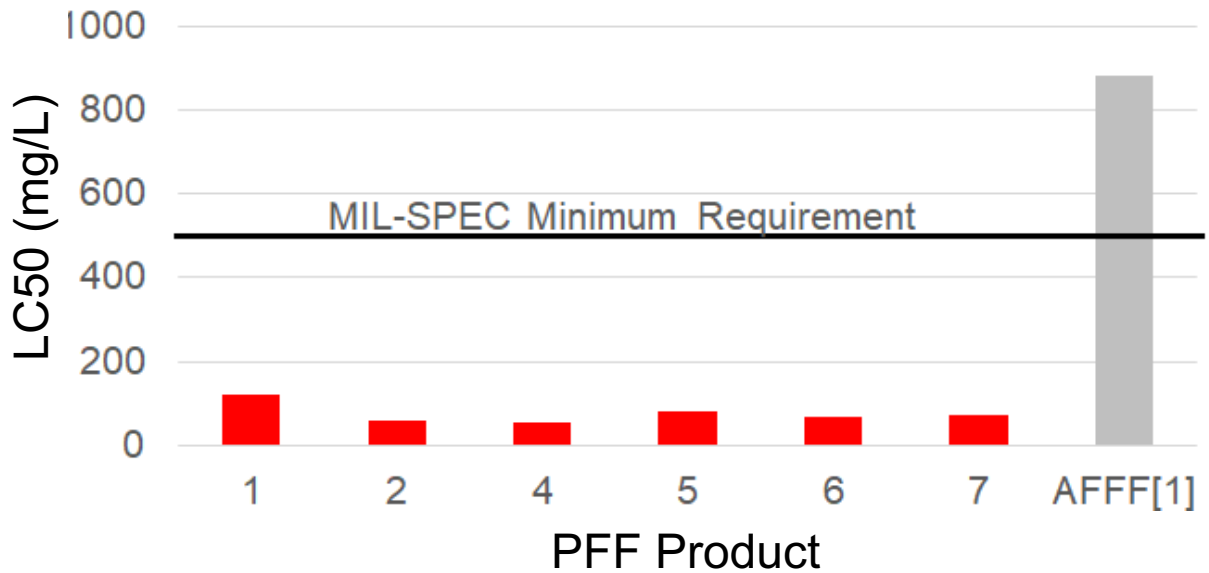
- Assessment, optimization, and demonstration of mature PFFs against MIL-PRF-24385F
- Assessment including:
  - Environmental toxicity
  - Corrosivity
  - Fire performance
- Optimization of fire performance using
  - Compressed Air Foam (CAF)
  - Ultra High Pressure (UHP)
  - Functional additives
- Demonstration/validation against military relevant fire scenario
- Technology transition

Key Requirements of Mil-Spec

- Aquatic toxicity and biodegradability
- Various physical properties
- Corrosion rate for various metals/alloys
- Fire testing at various conditions
  - Extinguishment time
  - Burnback time
  - Standardized test fire
    - 28 ft^2

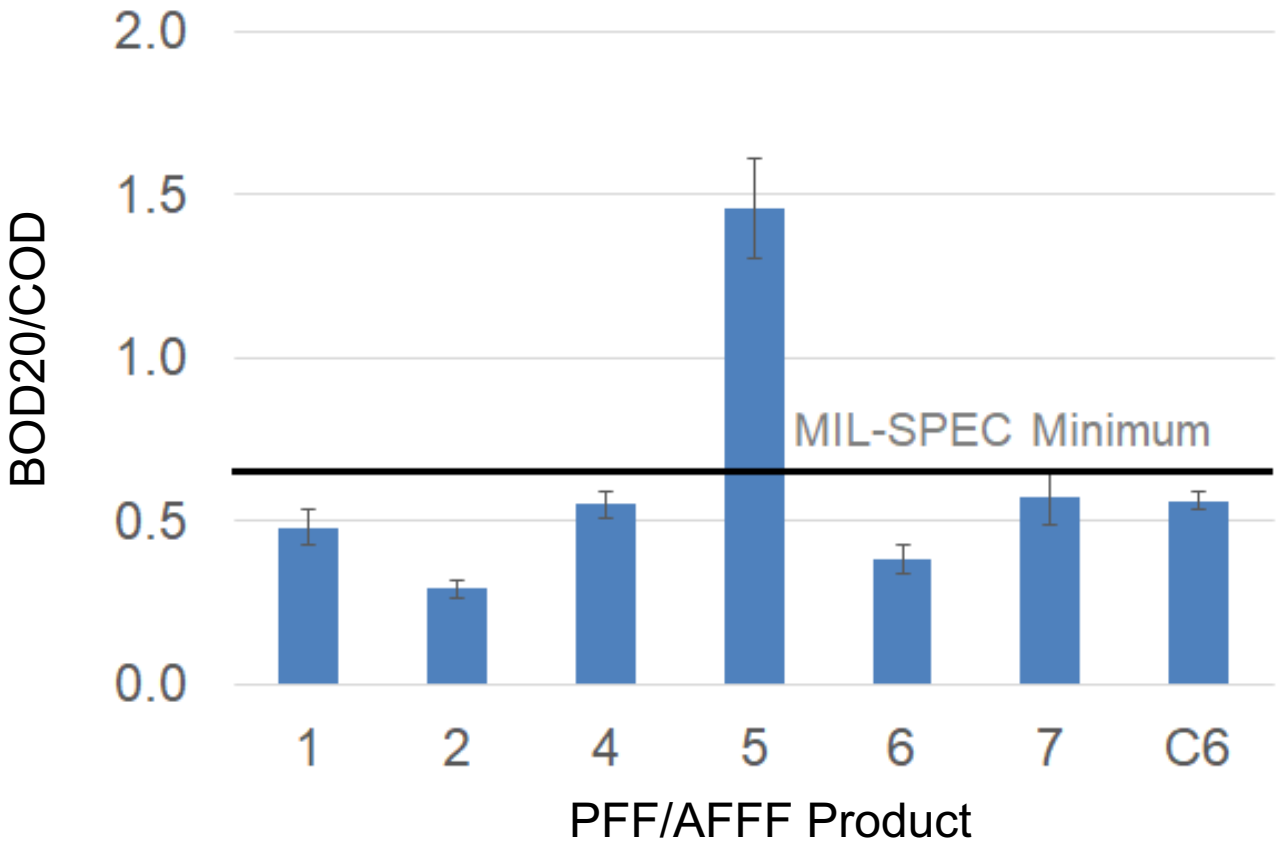
Aquatic Toxicity of PFFs

- LC50 and IC25 data obtained for fathead minnows
- Most products are about an order of magnitude more toxic than C6 AFFF
  - But products are diluted ~30x for foam application



***Notes**: [1] Schaefer, T, 2013; LC50 = concentration lethal for 50% of population; IC25 = concentration which results in 25% reduction in growth*

Biodegradability of PFFs



Most products are less biodegradable than specified in the Mil-Spec

***Notes**: BOD = biological oxidation demand; COD = chemical oxidation demand*

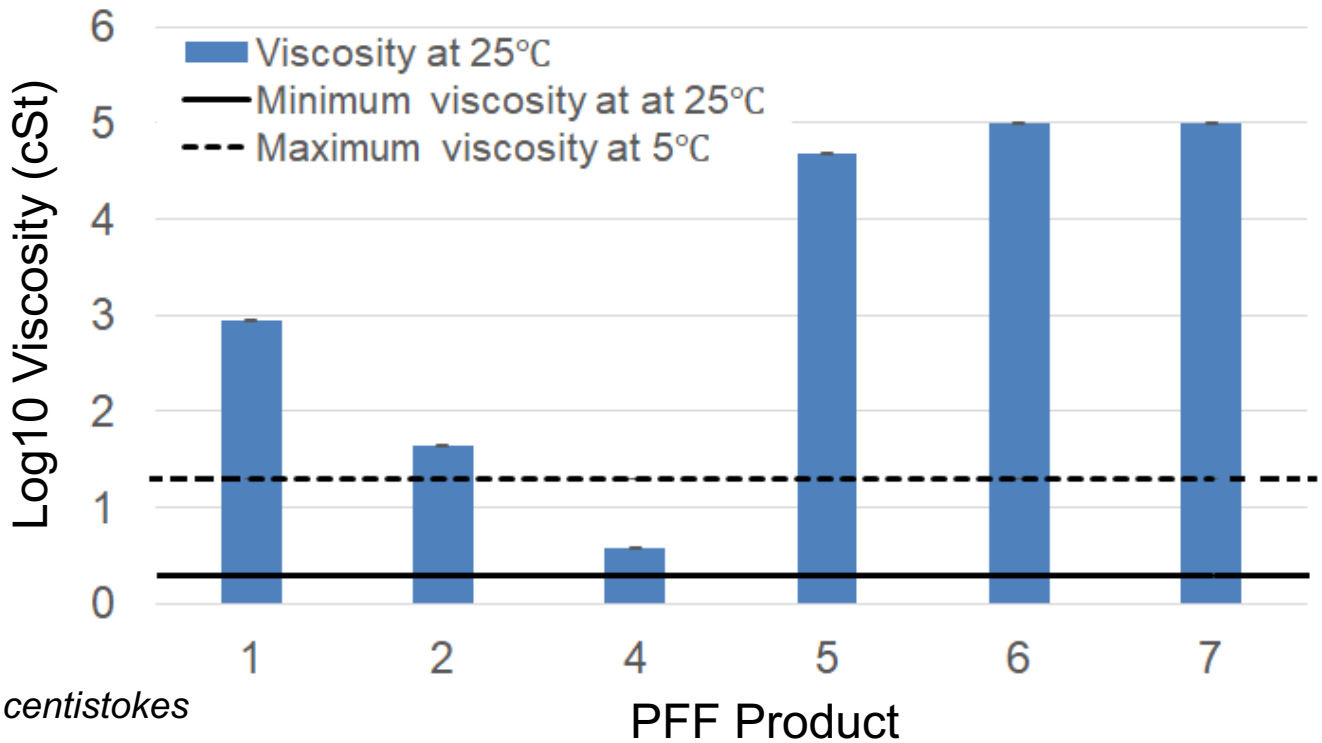
Physical Properties of PFFs

- Green = Complies with Mil-Spec
- Yellow = within 10% variance of Mil-Spec range
- Refractive index and pH have little to no impact on fire performance

Product Code #	pH	Refractive Index
	7-8.5	1.363 (minimum)
1		
2		
4		
5		
6		
7		
8		
9		
10		
11		

Some PFFs are Very Viscous

- All products meet the minimum viscosity of 2 cSt at 25°C; however, span a range of 3 to 90,000 cSt
- There is less variation in the viscosities of the dilute solutions



Notes: *cSt = centistokes*

Corrosion Performance of PFFs

Material Type	mpy	PFF #1	PFF #2	PFF #4	PFF #5	PFF #6	PFF #7	PFF #8	PFF #9
G10100 Steel	1.5	0.89	3.75	2.01	0.11	0.44	0.29	0.59	0.31
C70600 Cu-Ni	1	1.03	6.17	2.44	0.02	0.04	2.10	0.39	0.45
N04400 Ni-Cu	1	0.02	0.30	0.00	0.00	0.04	0.03	0.11	0.01
C90500 Bronze	100 mg gross mass loss	45.66	138.78	85.26	38.74	17.98	68.80	56.14	30.38

***Note**: mpy = milli-inches per year*

Standardized Test Fires

MIL-PRF-24385F

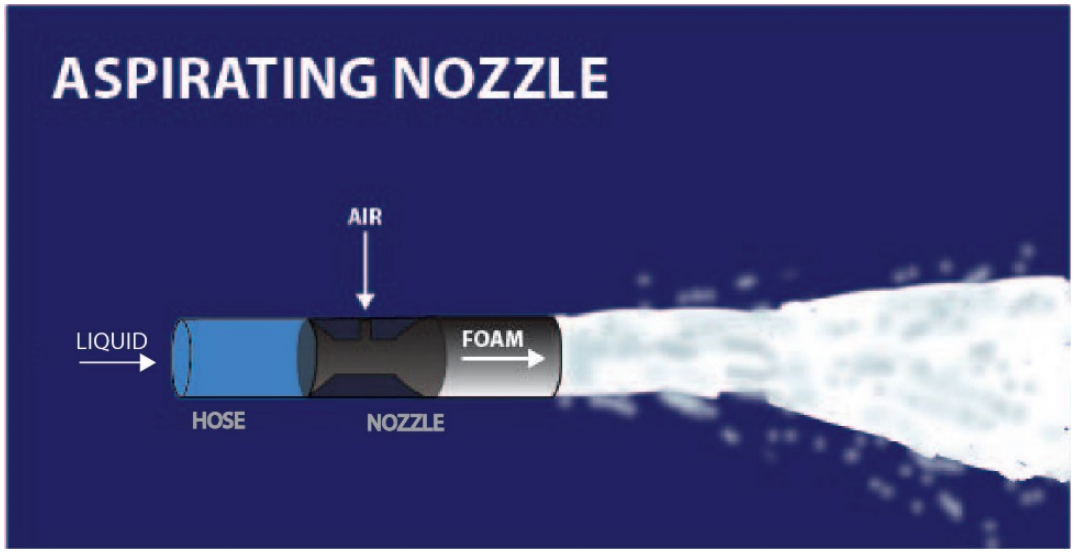
- 28 square feet
- 10 gallons gasoline
- 10 second pre-burn prior to applying foam
  - 30 seconds max to extinguish fire
- Foam is dispensed for 60 additional seconds
- Burnback pan is inserted into foam blanket
  - 360 seconds minimum for 25% of foam blanket to burn away = “Burnback Time”

Enhancing Fire Performance of PFFs

- None of the PFFs tested so far meet Mil-Spec for fire extinguishment time
  - Most meet spec for burnback time, but a few don't
- Employing commonly available engineering solutions to enhance performance
  - Compressed Air Foam (CAF)
  - Ultra High Pressure (UHP)

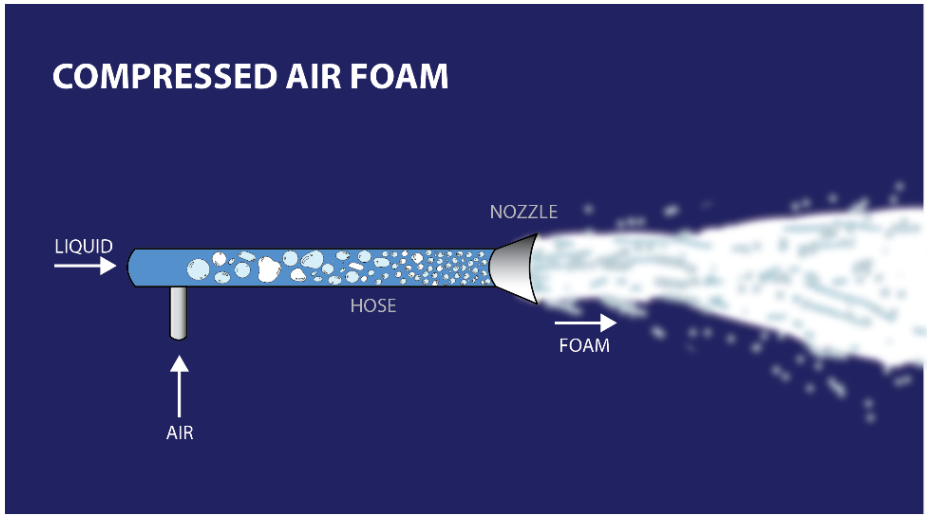
Mil-Spec Nozzle

- Air aspirating nozzle
- Foam is created by air taken in via a venturi at the nozzle
- Specialty nozzle designed specifically for this test



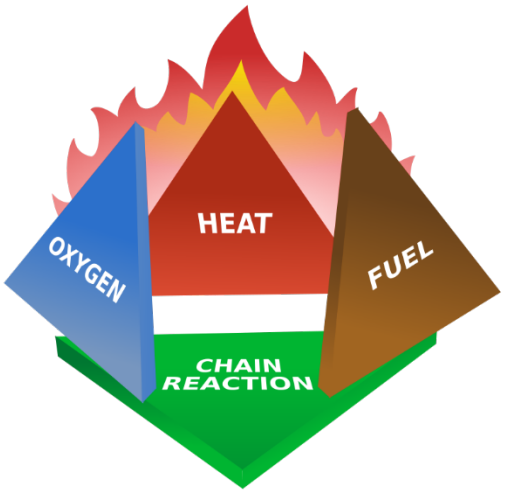
Compressed Air Foam (CAF)

- Compressed (100-200 psi) air is injected into the line
- Produces foam with uniform bubble structure to improve both extinguishment time and burnback time
- Expansion ratio can be manipulated
- Foam expansion occurs before exiting the nozzle



Ultra High Pressure (UHP)

- Truck pressure 1100 - 1400 psi
  - Typically uses aspirating nozzle
- Reduces extinguishment time
- Small droplet size enhances cooling effect
  - Can be combined with dry chemical to take out three sides of the "Fire Tetrahedron" at once to improve firefighting



Mil-Spec Nozzle Foam Properties

- Measured during fire testing
  - Expansion ratio is the foam volume/liquid volume
  - Time for 25% of the liquid to drain from the foam
- Measures of foam quality and stability
  - A key indicator of fire performance

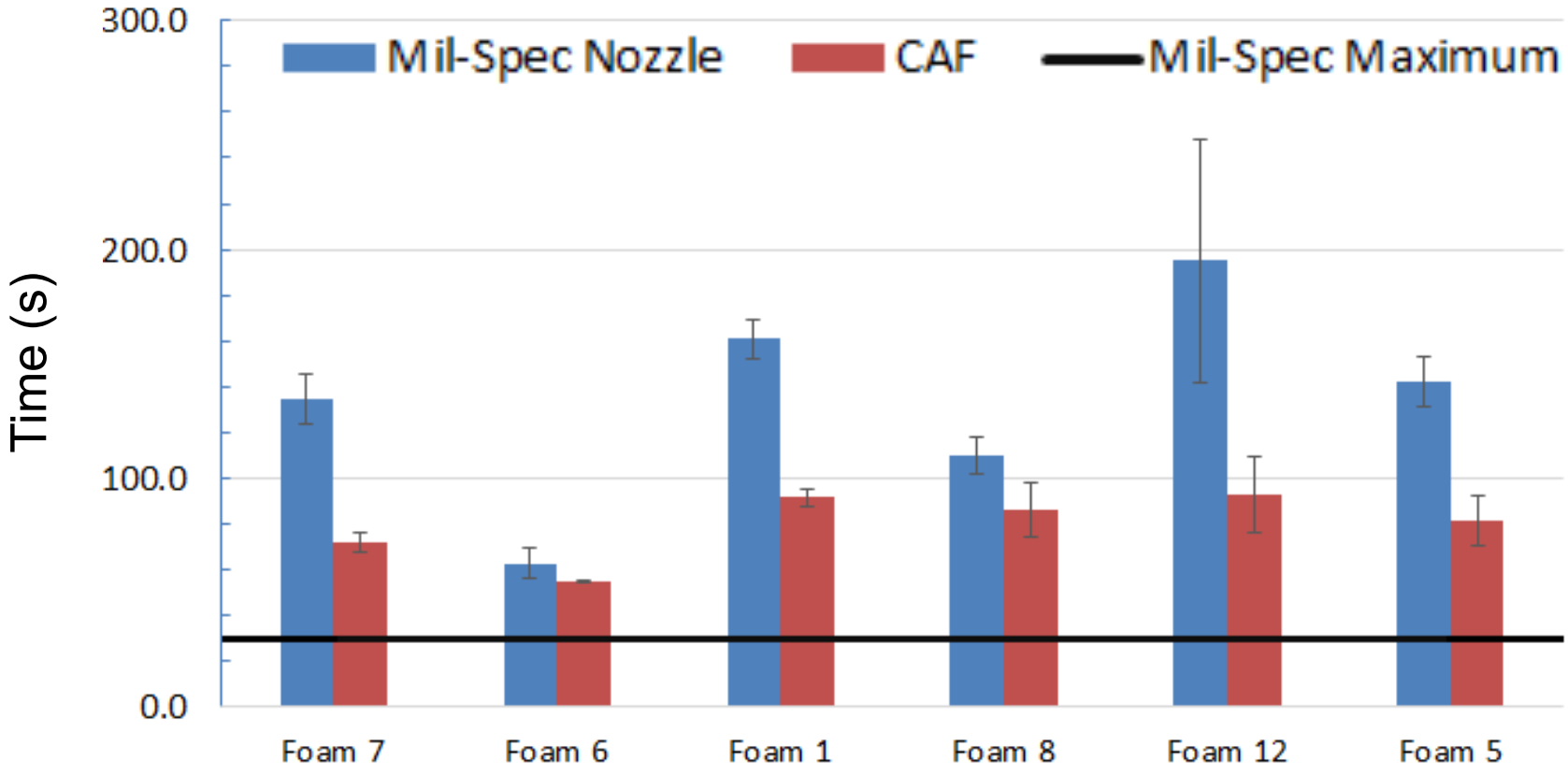
MIL SPEC NOZZLE 4		
PFF Product	Expansion Ratio	25% Drain Time (seconds)
7	6.2	1,380
6	7.1	2,220
10	6.9	>3,600
1	7.7	1,020
8	6.6	165
12	6.4	250
5	6.8	465

CAF Foam Properties

- Air injection is adjusted to achieve an expansion ratio of 10
- Foams 8 and 12 claim to be aqueous film forming foams

COMPRESSED AIR FOAM (CAF)		
PFF Product	Expansion Ratio	25% Drain Time (seconds)
7	10.0	>3,600
6	10.1	>3,600
10	9.9	>>3,600
1	10.2	1,260
8	10.1	910
12	9.9	330
5	10.1	840

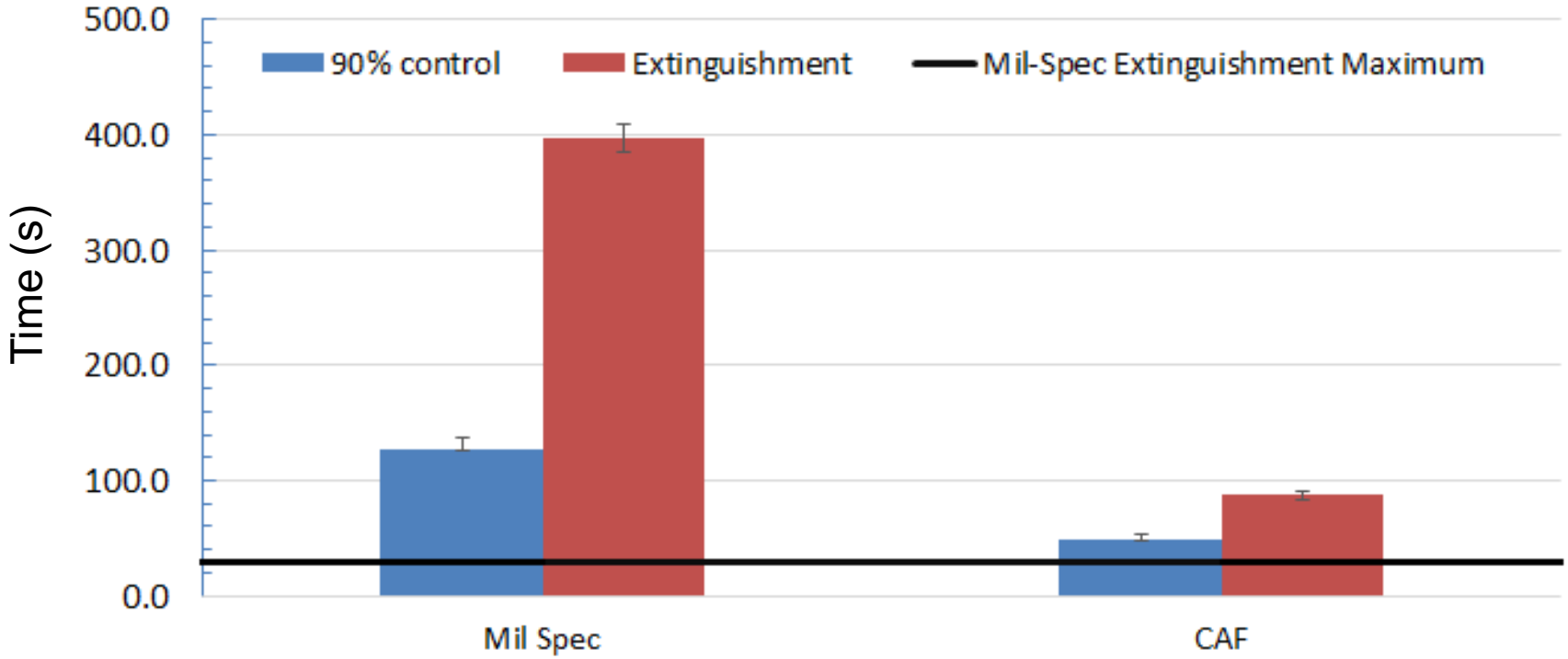
CAF Improved Extinguishment Time



Average reduction of 47% in extinguishment time

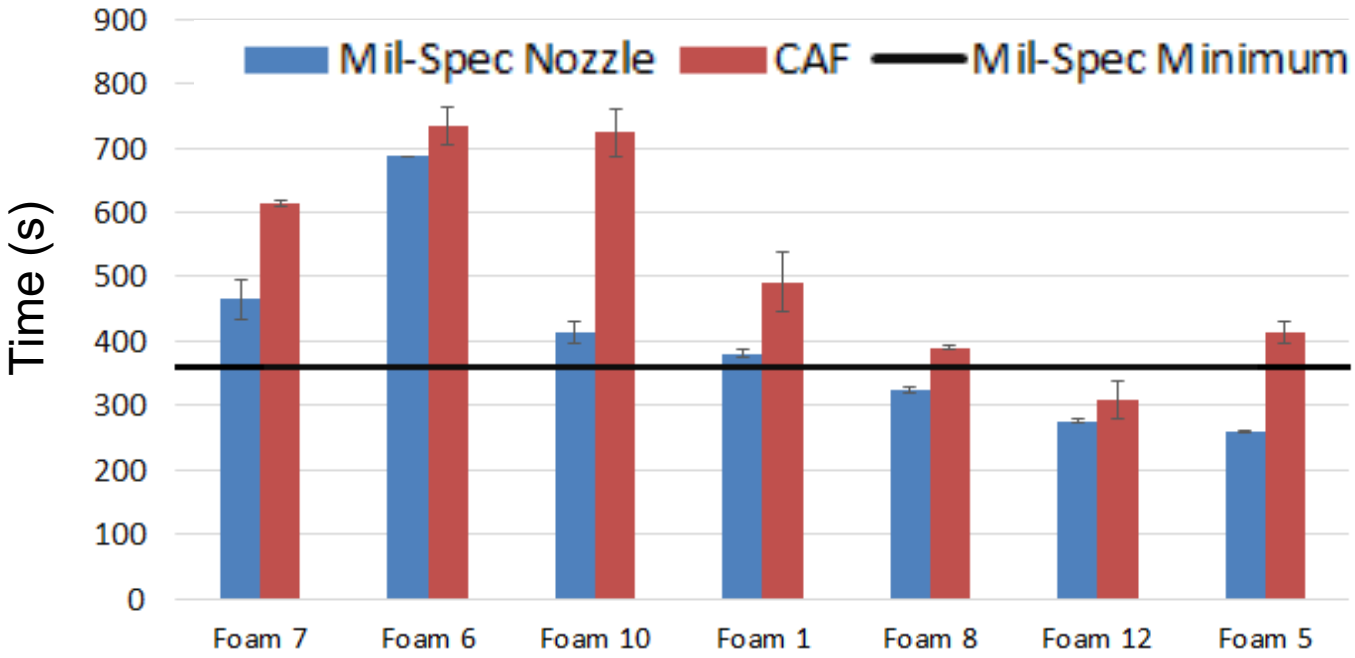
Improved 90% Fire Control

Foam 10



Long time between fire control and complete extinguishment

Burnback Time Improved with CAF



- 2 gallons of foam dispensed onto 10 gallons of unlit fuel
- Mil-Spec burnback procedure conducted
- Burnback time increased by an avg of 34%

Ranking PFF Products

- Fire performance
  - Extinguishment and burnback times
  - Dry chemical compatibility
- Equipment compatibility and ease of use
  - Viscosity, corrosivity
- Environmental impact
  - PFAS-free
  - Biodegradability, LC50, IC25
  - Impact of degradation products

Expected DoD Benefits

- PFAS-containing AFFF cannot be procured by DoD after September 2023
  - FFFs need to be developed, validated, and ready to be procured by October 2024
- Reduction in environmental impact, avoiding future PFAS issues and associated DoD liabilities
  - More than 100 military planes have crashed on U.S. soil in last decade; high clean-up costs
- Cost-effective alternatives likely
  - Some PFFs claim to be cheaper than currently-used C6 AFFF
  - CAF and UHP can significantly reduce amount of foam used; many DoD bases already have CAF/UHP available

Plans for Next Year

Future FFF Testing

- Expand the list of PFFs to be tested with CAF/UHP
- Test selected, commercially-available, functional additives to further improve fire extinguishment
- Conduct large-scale fire testing at Tyndall AFB test site
  - Mil-Spec vs. CAF or UHP foam delivery
  - 100-ft^2 Jet A fire testing

Tyndall AFB Fire Training Facilities

Conclusions

- PFFs tested so far do not meet the Mil-Spec
  - Aquatic, acute toxicity is an order of magnitude higher, but delivered foam toxicity may be acceptable
  - Viscosity of many products is very high; may present handling problems
  - Few products have corrosivity concerns
  - Other physical properties seem acceptable, but compatibility among PFFs is unknown
- CAF improves fire performance
  - Extinguishment times reduced by an average of 47%
  - Burnback times increased by an average of 34%
- Additional improvements in fire performance being explored

References

1. Schaefer, T. (2013). Aquatic Impact of Firefighting Foams [White paper]. Retrieved January 23, 2020 from Solberg Foam: https://www.solbergfoam.com/getattachment/b1698ff8-e0f5-4e09-b3ac-426a59c4bb7e/WP-Aquatic-Impact-of-AFFF-F-2012007.aspx

For additional information, please visit
https://www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Noise-and-Emissions/WP19-5299

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Q&A Session 2

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The next webinar is on October 22, 2020

Managing AFFF Impacts to Subsurface Environments and Assessment of Commercially Available PFAS-Free Foams (Part 2)

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Survey Reminder

Please take a moment to complete the survey that will pop up on your screen when the webinar ends

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