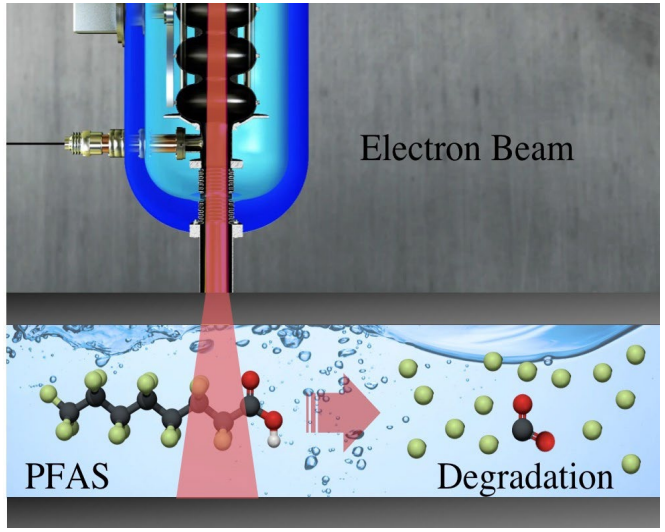
Electron beam destruction of PFAS

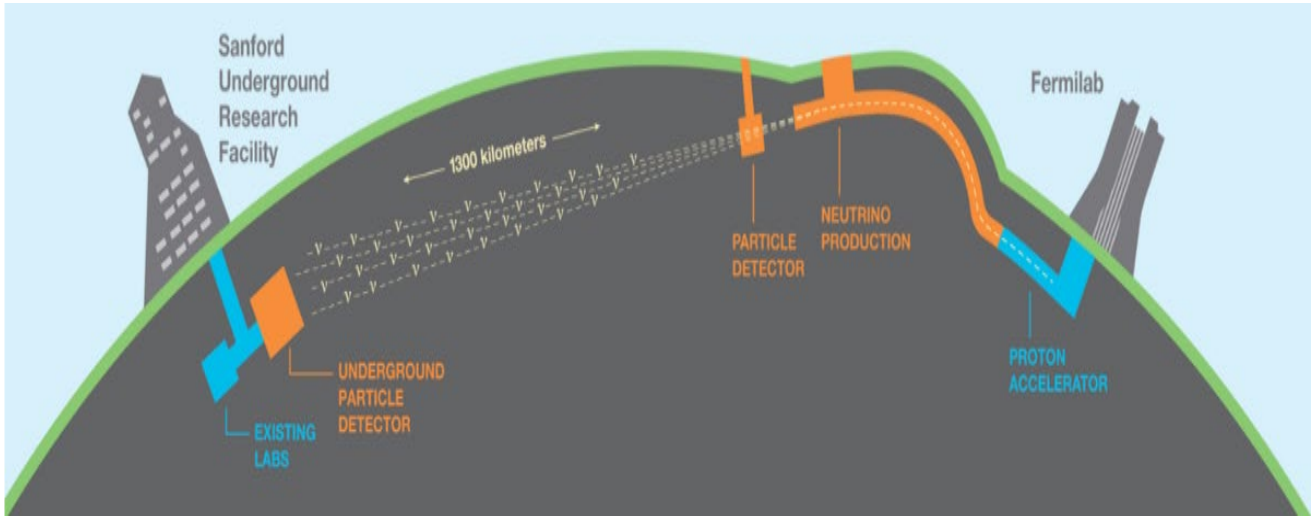
Charlie Cooper
Slavica Grdanovska
Illinois Accelerator Research Center, Fermi National Accelerator Laboratory
2024



Fermi National Accelerator Laboratory

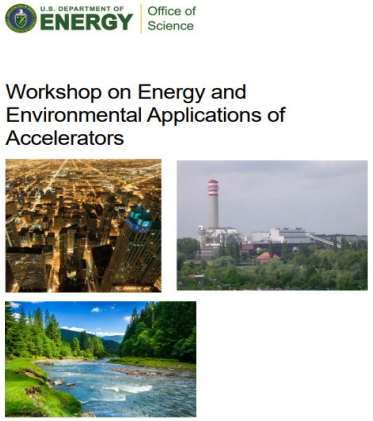
- Basic science DOE lab founded in 1967 studying the smallest building blocks of matter to see what the universe is made of.

- Discover what happened after the big bang: Are neutrinos the reason the universe is made of matter?

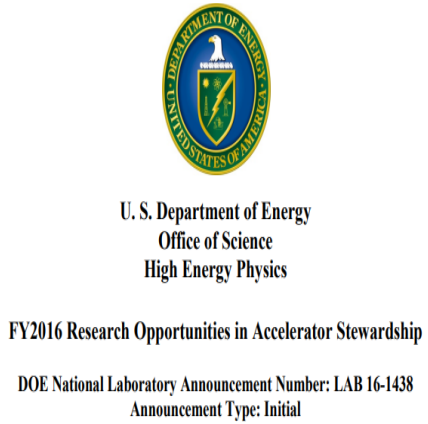


History of IARC

2010 10-year strategic plan for accelerator technology research and development



2015 - DOE Basic Research Needs Workshop on Energy & Environmental Applications of Accelerators



2016 Research Opportunities in Accelerator Stewardship


FINAL REPORT: CONCEPTUAL DESIGN OF AN ELECTRON ACCELERATOR FOR BIO-SOLID WASTE TREATMENT

Fermi National Accelerator Laboratory
Kirk and Pine Street / P.O. Box 500 / Batavia, IL 60510

Managed by Fermi Research Alliance, LLC for the U.S. Department of Energy Office of Science
DOE National Laboratory Announcement Number: LAB 16-1438

DOE / Office of Science Program Office: High Energy Physics

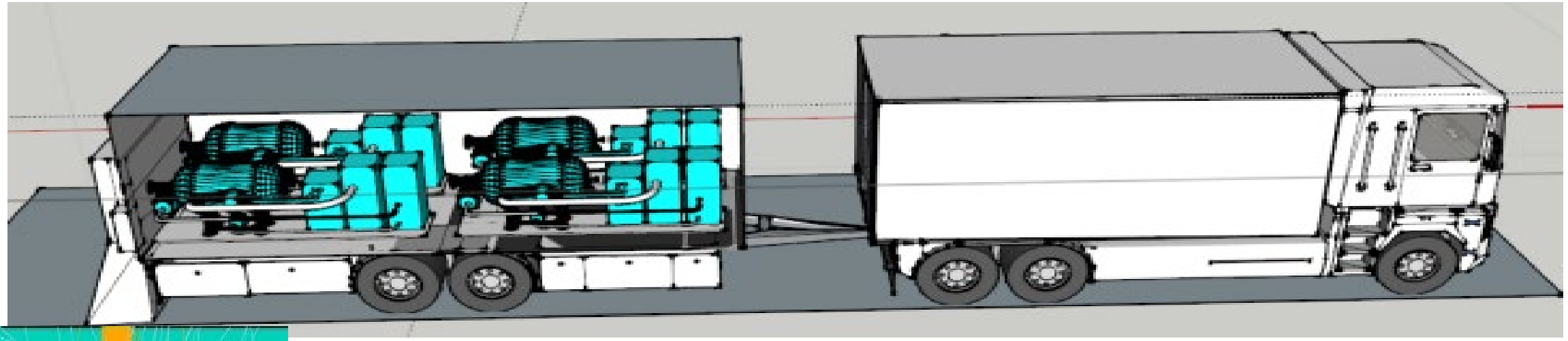
PAMS Pre-Proposal Tracking Number: PRE-0000008407

Research Track and Topic: 1.3 Accelerator R&D Stewardship / Energy and Environmental Applications of Accelerators

September 20, 2017
Fermi National Accelerator Laboratory
Metropolitan Water Reclamation District of Chicago
FERMILAB-FN-1055-DI

2017 – FINAL REPORT: CONCEPTUAL DESIGN OF AN ELECTRON ACCELERATOR FOR BIOSOLID WASTE TREATMENT

Compact Accelerator for Pavement



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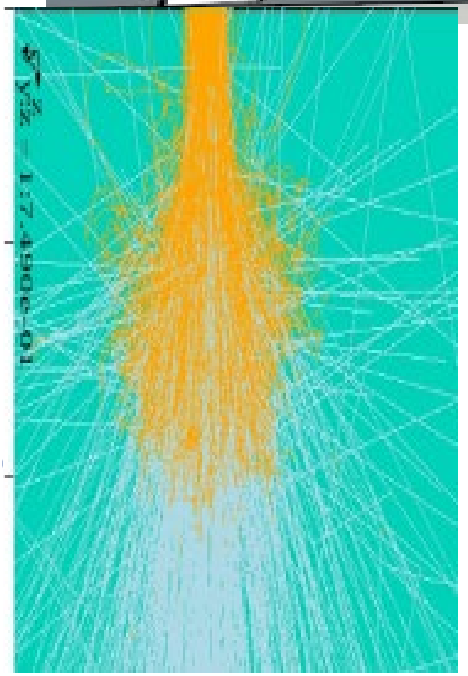

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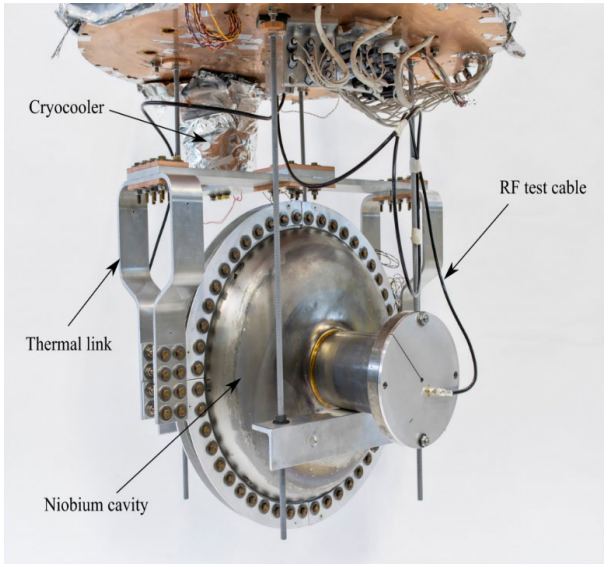
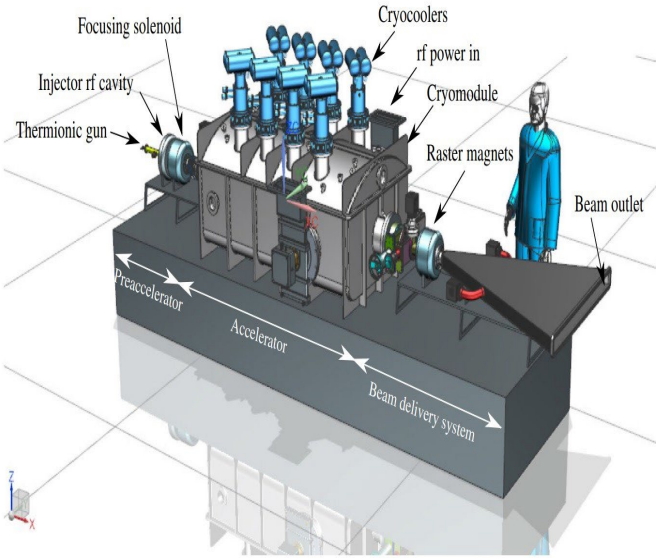




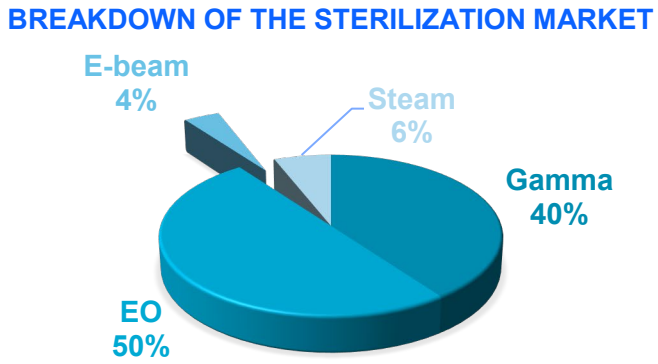
Accelerator for Medical Sterilization – X-ray

- **Current Sterilization Options**

  Steam – incompatible with most polymers

  Ethylene oxide gas – explosive, toxic and harmful to the environment

  ^{60}Co irradiators – require radioactive sources to operate, associated with secure transportation and disposal concerns as well as annual regulatory requalification.



- **E-beam**

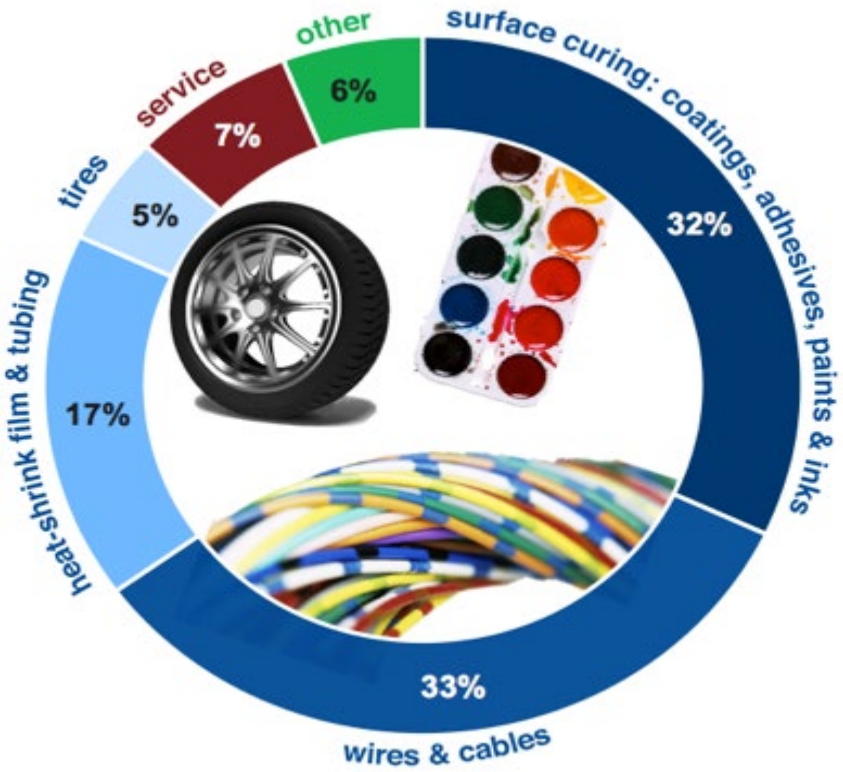
  Directed radiation → Efficient use

  Lowest cost of sterilization for large capacities

  Can be turned OFF → safer

E-Beam Applications – Why do I care about E-beam?

Today



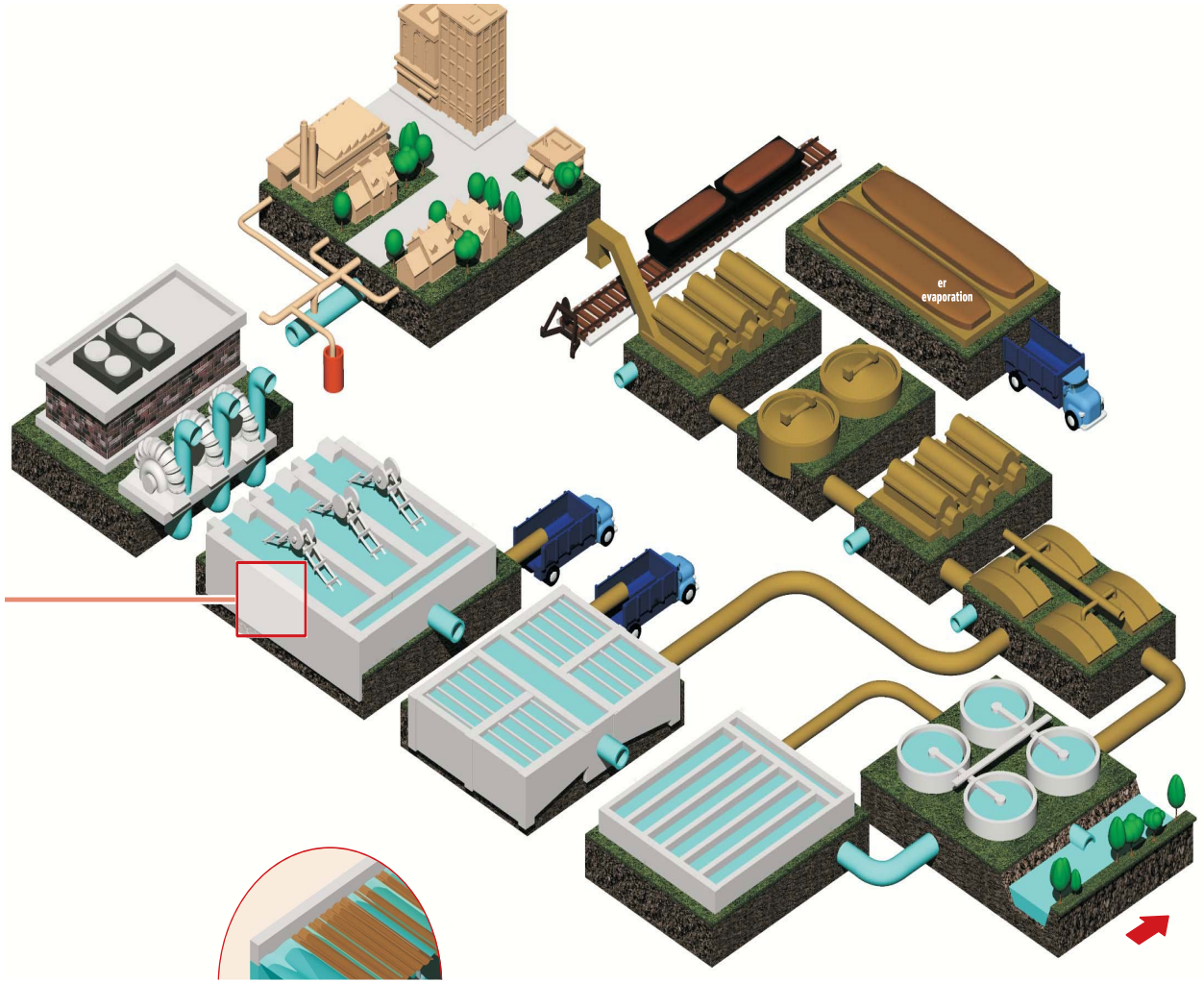
Tomorrow

Electron beam currently touches many industries

With Fermi tech poised to touch more

E-Beam Treatment of Biosolids – Fermi & MWRD of Chicago

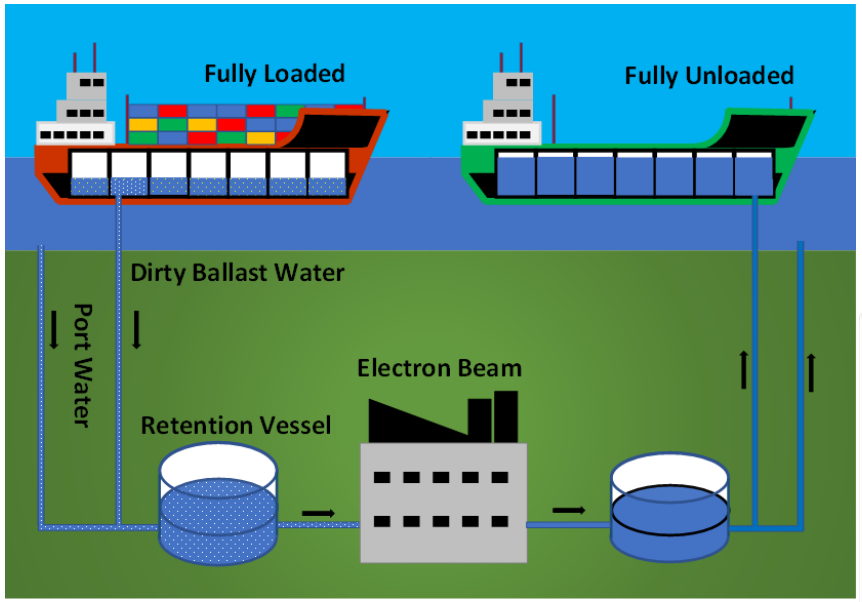
- Complete kill of fecal coliform
- Increased recovery of phosphorous in Ostara process
- Double energy recovery
- Reduce/eliminate smell

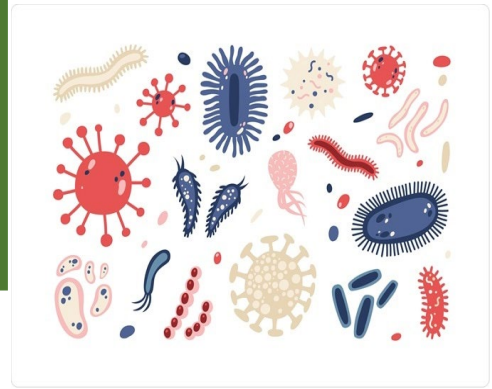


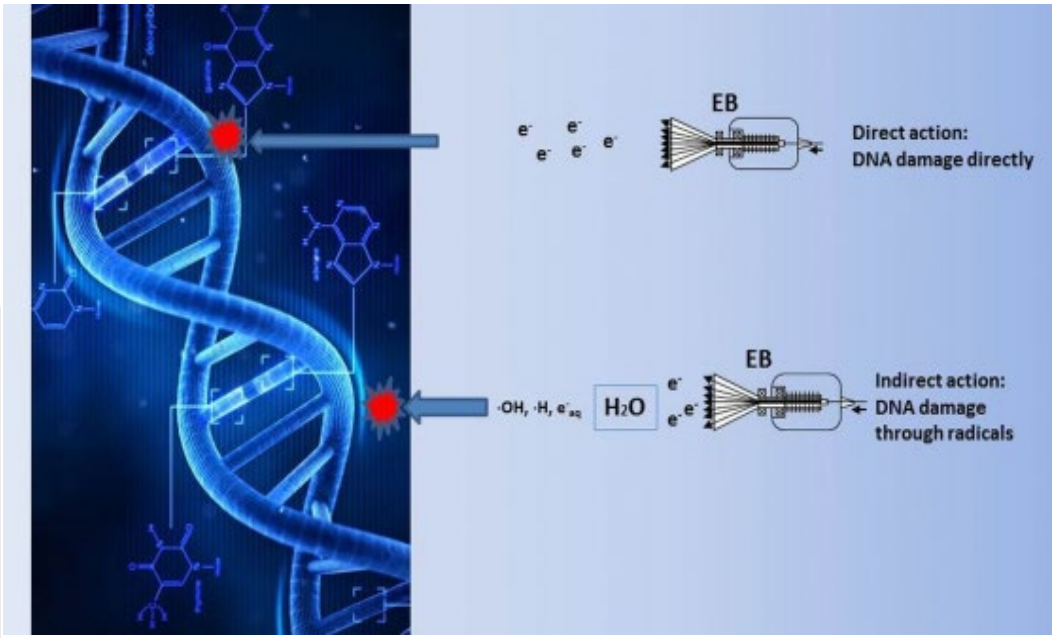
- Estimates operating cost 30% higher(CFR) & High Capital Cost

Management of Ballast Water – UW Superior

- 1 Billion $ a year problem - biological invasion throughout the world
- Electron beams rapidly damage and destroy the cells of harmful marine organisms, including viruses, bacteria and algae
- Common resource issue

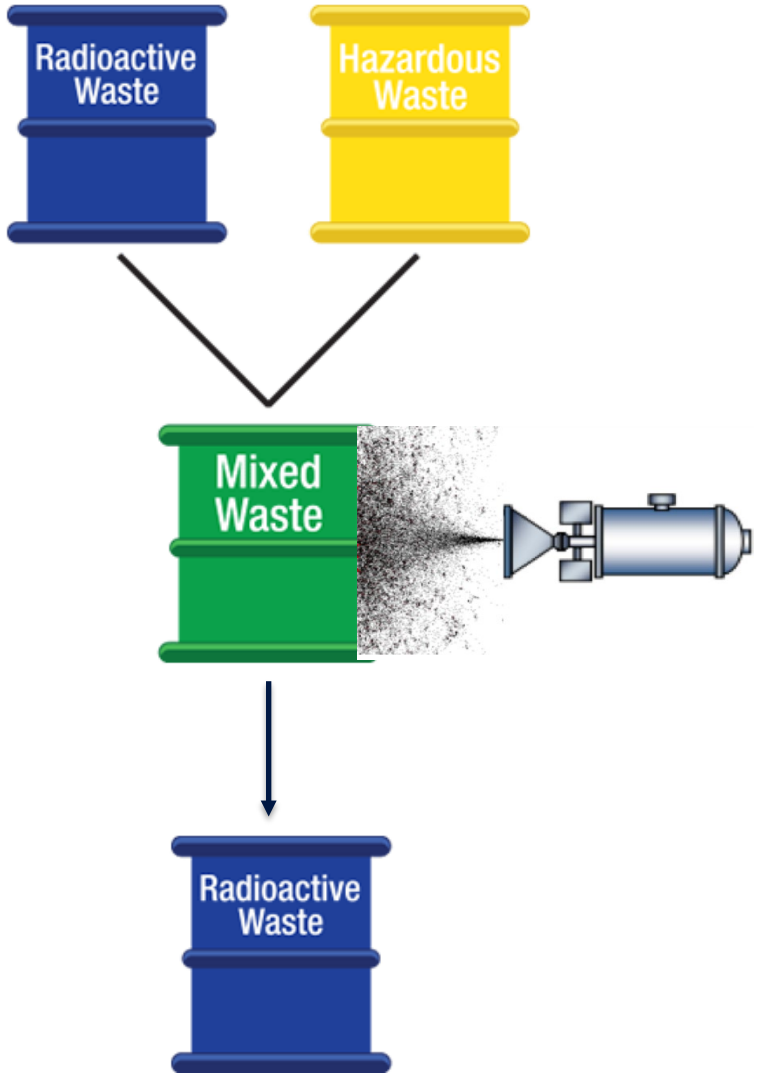






Treatment of Mixed Waste – FUSRAP (DOE/DOD)

- U.S. government has a large stockpile of mixed waste
- No viable solutions so far – Billions Spent
- Storage is current solution (turn into glass)

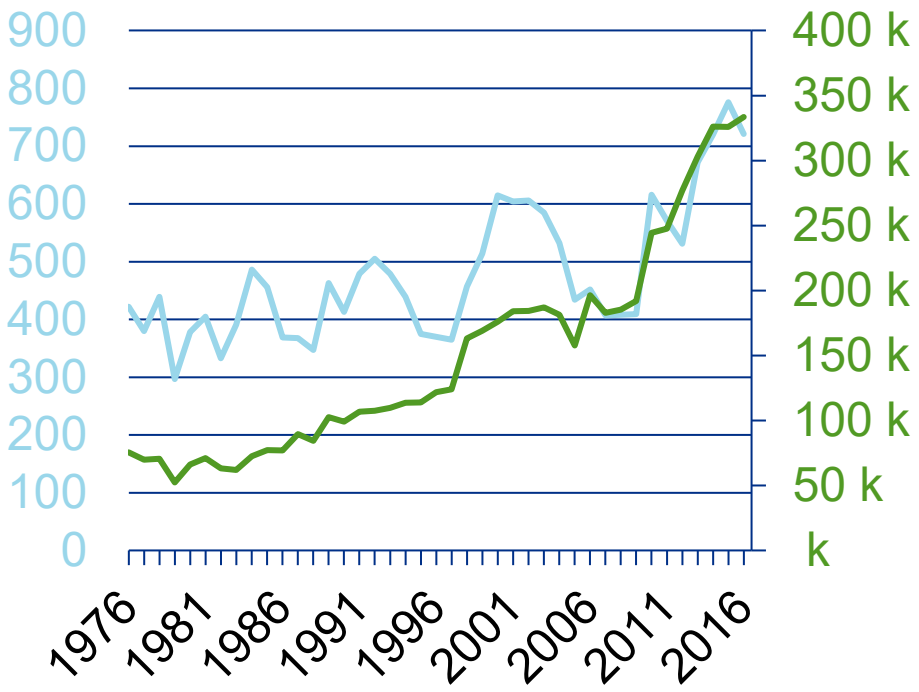


E-beam can

- Destroy toxics, leaving it only radioactive.
- Reduced cost and regulation and simplify transport of the waste
- Improve safety of handling waste

Compact Accelerator for Driving Chemistry

- In the U.S. Industry consumes ~32% of end use sector
  - 27% of that is used in the Chemical Sector (www.eia.gov) ~17 quads



Total # US Original Catalyst Patents
Total # US Original Patents
patft.uspto.gov

Electron beam adds a 4th lever to driving chemical reactions in addition to temperature, pressure and catalyst.

- Demonstrated industrial effort to develop catalyst to increase efficiency
- Electron beam driven chemistry largely unexplored
- More efficient that direct heating
  - Rubber Industry
- Can remove need for some toxic initiators, cross linkers

Info on PFAS - Sources

- Used in many important products and processes
- Release to the environment in some uses (AFFF)

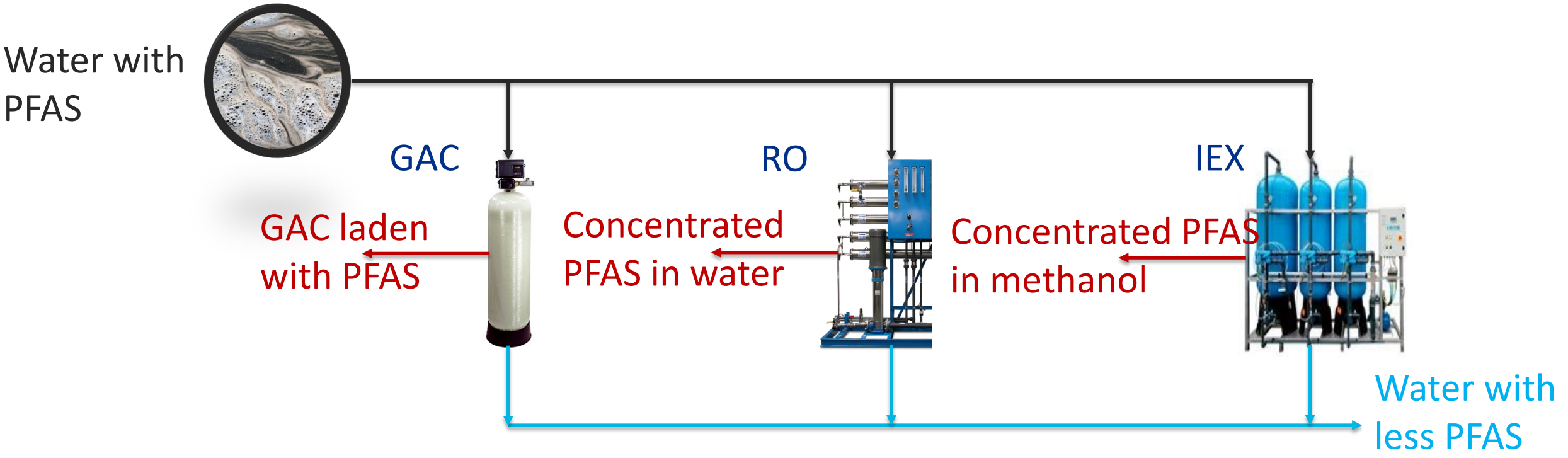
Food Packaging, Personnel Care Products, Stain Resistant Fabrics

Aqueous Film Forming Foam – Airports & Tank Farms

PTFE

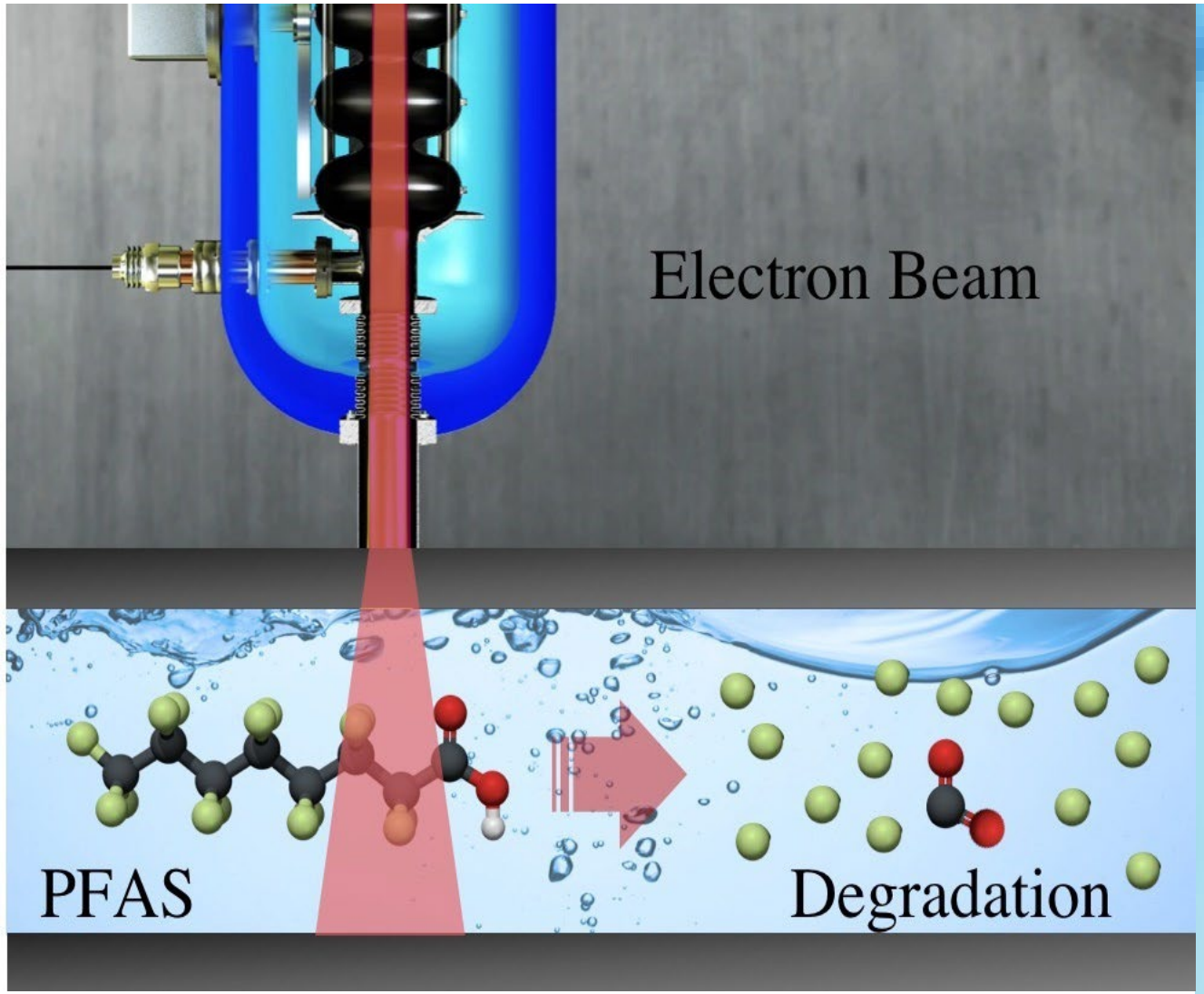
Info on PFAS – Conventional Treatment

- **Conventional water treatment technologies** don't fully meet needs of PFAS remediation – short chain PFAS problematic, biofouling
- **Concentrate PFAS into another state - does not destroy PFAS**

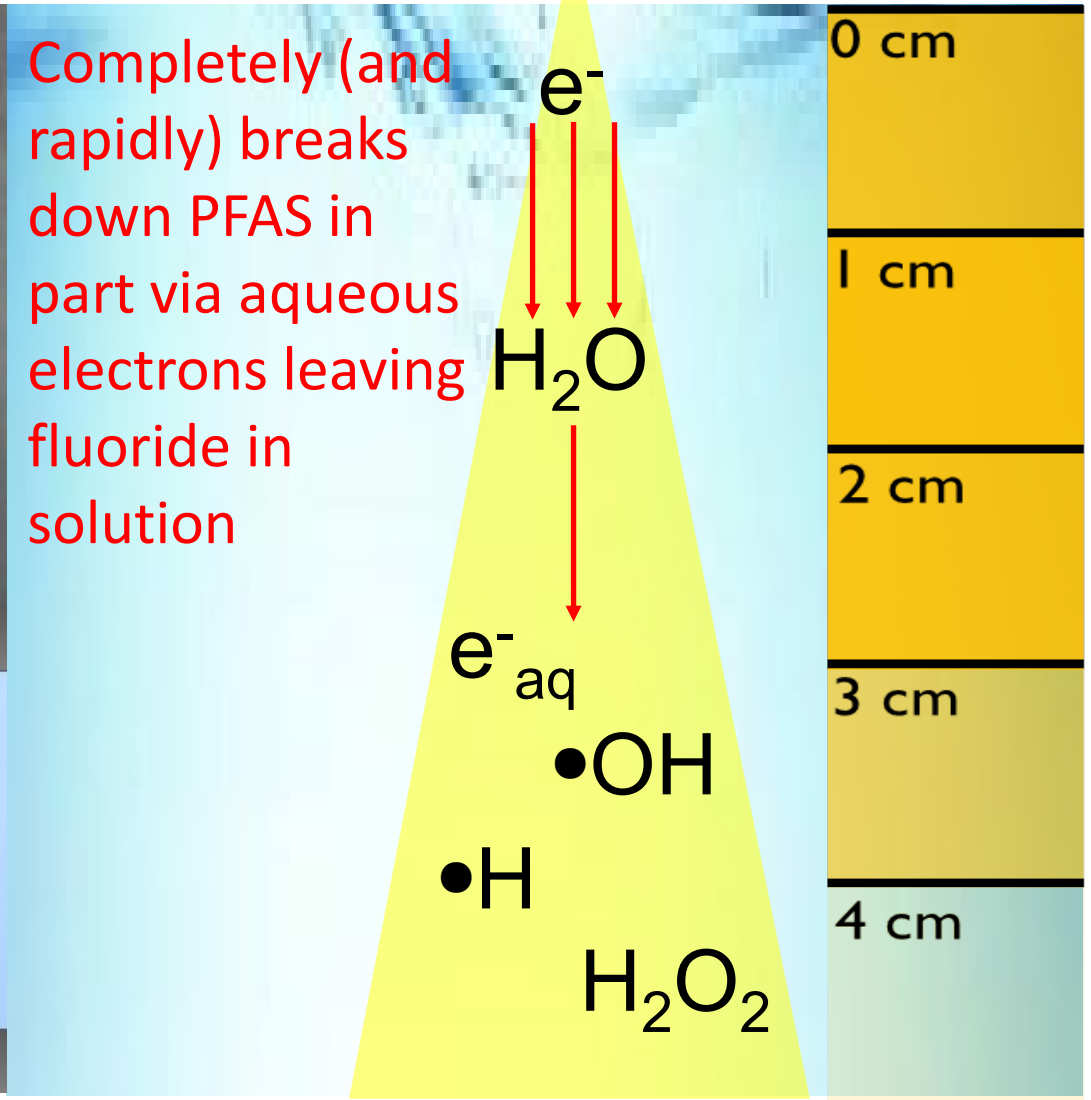


E-beam destroys PFAS, conventional water treatment technology doesn't

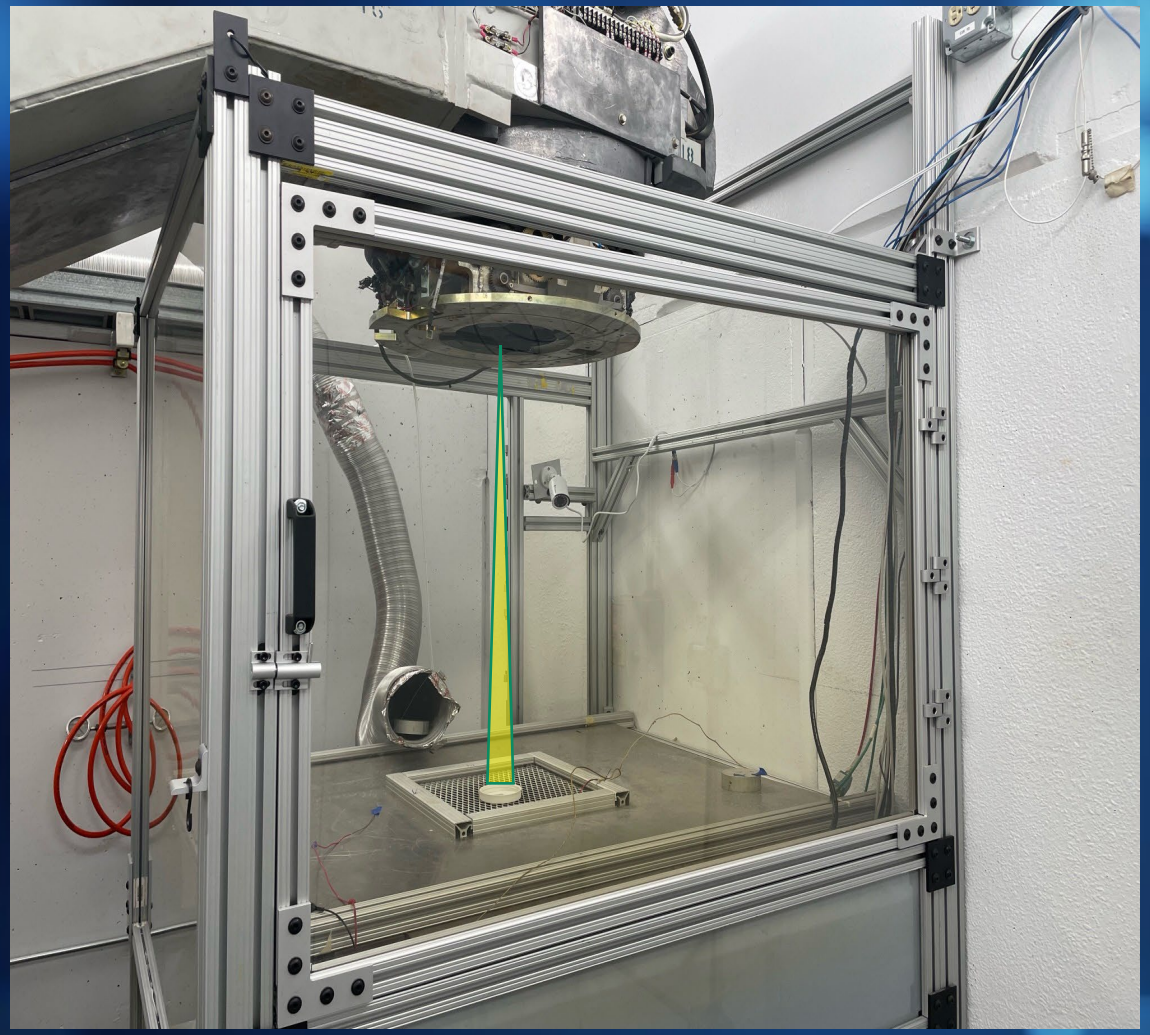
Electron beam destruction of PFAS



Completely (and rapidly) breaks down PFAS in part via aqueous electrons leaving fluoride in solution



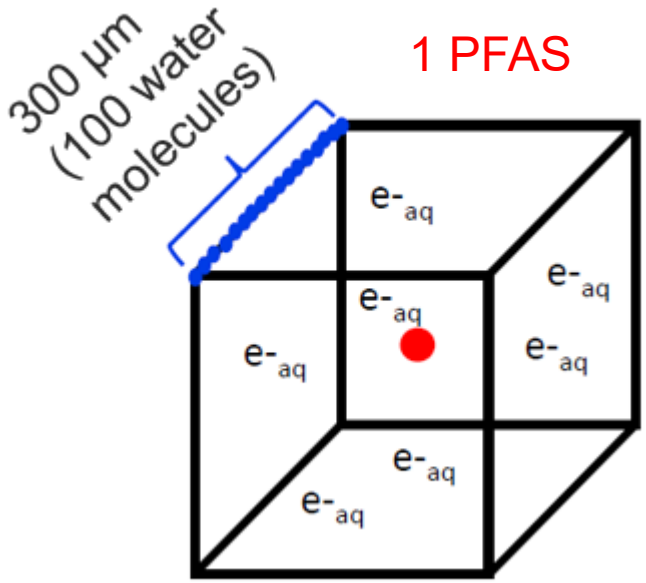
How Work was Carried Out



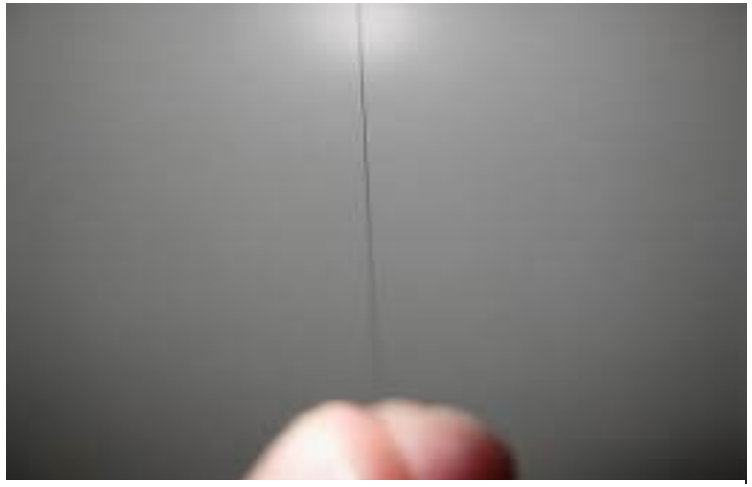
- Samples prepared in borosilicate glass vials with butyl rubber septum and crimped aluminum lids
- Samples irradiated in A2D2 shown on left
- Samples analyzed using many techniques but mainly LC/MS/MS

- Total dose - the main operating cost
- Dose rate - affects water breakdown products
- Dissolved oxygen concentration – electron scavenger
- PFAS concentration
- Effect of additives

H_2O —Electron Beam→ OH-, H+, e^-_{aq}, H_2, H_2O_2



- One electron from accelerator has 200,000 interaction
- Creates 10's of thousands of aqueous electrons



300 µm = 3 human hairs

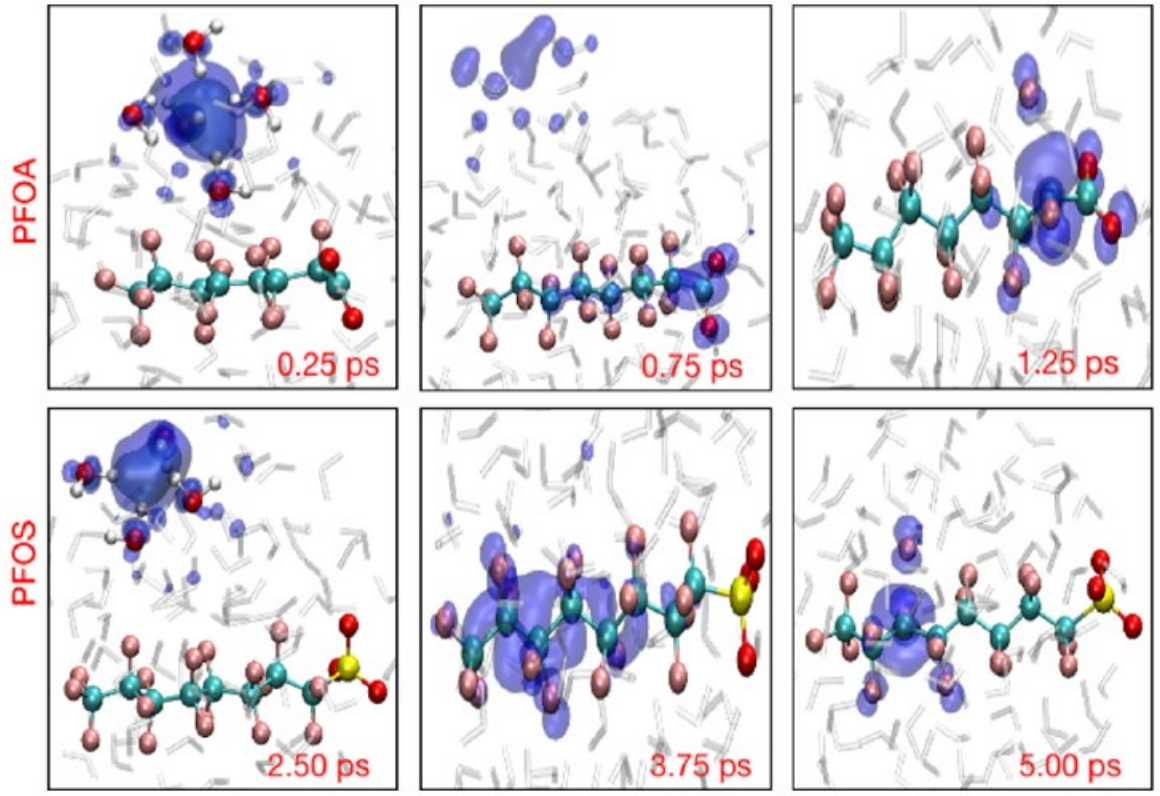
- Diffusion limited process can be improved when scaling up

Electron Beam Treatment of Water

- Kinetics suggest pseudo first order and not dependent on PFAS concentration.
- Suggests diffusion limited

Breakdown Mechanism

Literature

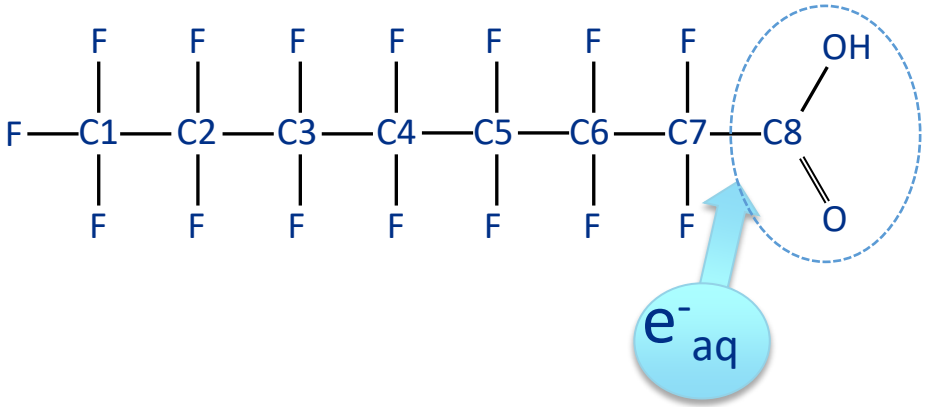


Degradation of Per- and Polyfluoroalkyl Substances with Hydrated Electrons: A New Mechanism from First-Principles Calculations

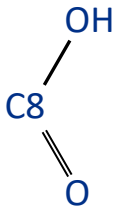
Sohag Biswas, Sharma S. R. K. C. Yamijala, and Bryan M. Wong*

- Modeling is one PFAS molecule in solution with one aqueous electron, showing removal of fluorine as first step
- Experiment suggests first step is removal of functional group followed by unzipping of C-F chain by hydrolysis

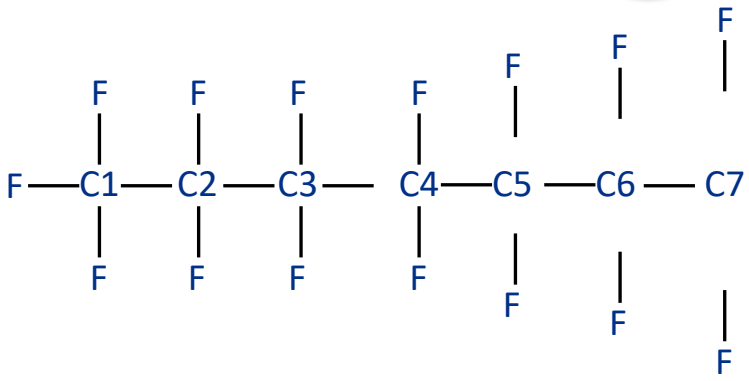
Degradation of PFOA Homologs

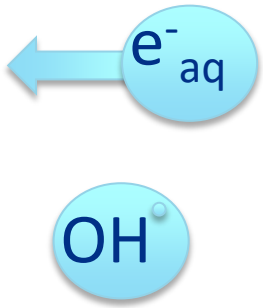


Faster on branched chain



1. Remove Carboxylic Acid Head Group (1.2 ps)



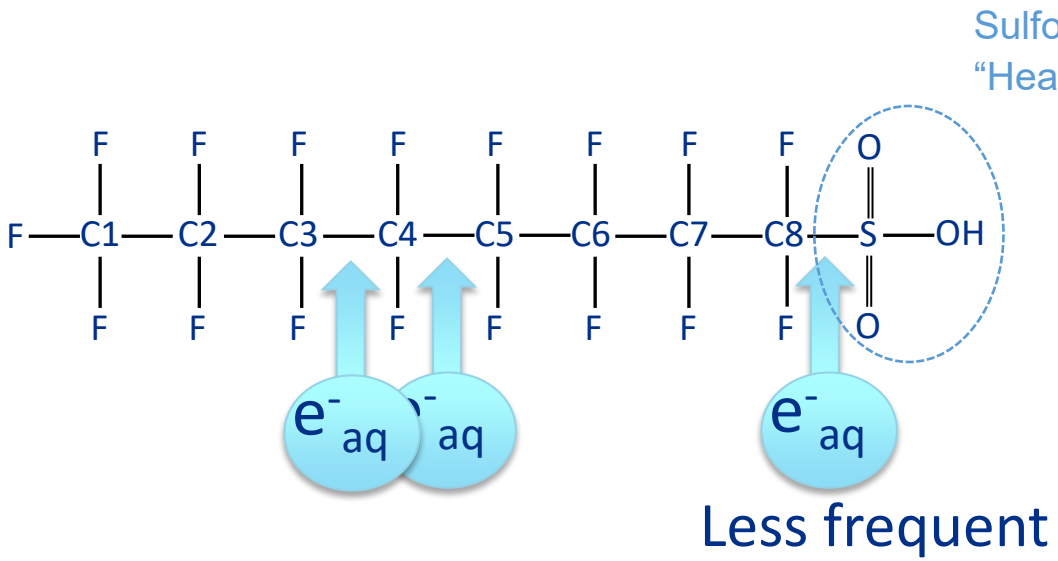


1. Stepwise unzipping of PFAS chain

DHEH pathway (decarboxylation-hydroxylation-elimination-hydrolysis)

100% Destruction of PFOA Homologs with half-life times of minutes to seconds.
Fluorine in the form of free fluoride.

Degradation of PFOS Homologs



C-F bond dissociation energy via aqueous electron is three times higher in PFOS when compared to PFOA(4ps)

- 99%+ Destruction of 20 ppm PFOS in 4 mins.
- No intermediate breakdown products under optimal conditions.
- Fluorine in the form of free fluoride.
- Destruction efficiency of PFOS homolog depends on chain length.

Electron Beams Can Destroy PFAS

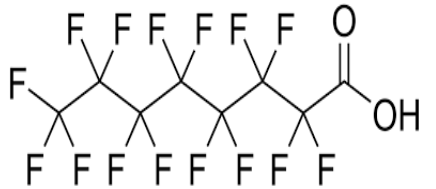
EPA has proposed a National Primary Drinking Water Regulation (NPDWR) to establish legally enforceable levels, called Maximum Contaminant Levels (MCLs), for six PFAS in drinking water.

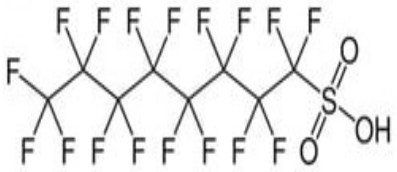
- 4 PPT PFOA MCL
- 4 PPT PFOS MCL

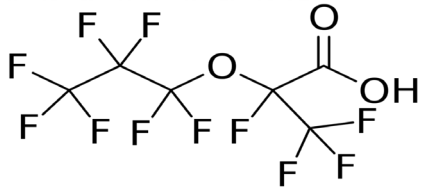
} 4-5 yr clearance half life in people

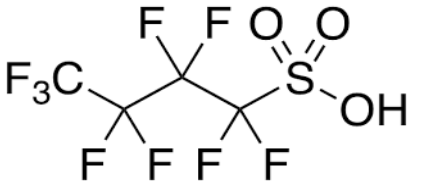
$$\frac{GenX}{10} + \frac{PFBS}{2000} + \frac{PFNA}{10} + \frac{PFHxS}{9} = 1$$

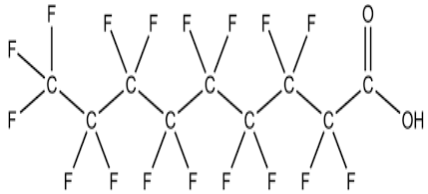
- Electron Beam Can Destroy all these PFAS

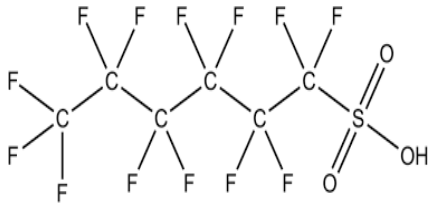

PFOA


PFOS


GenX


PFBS

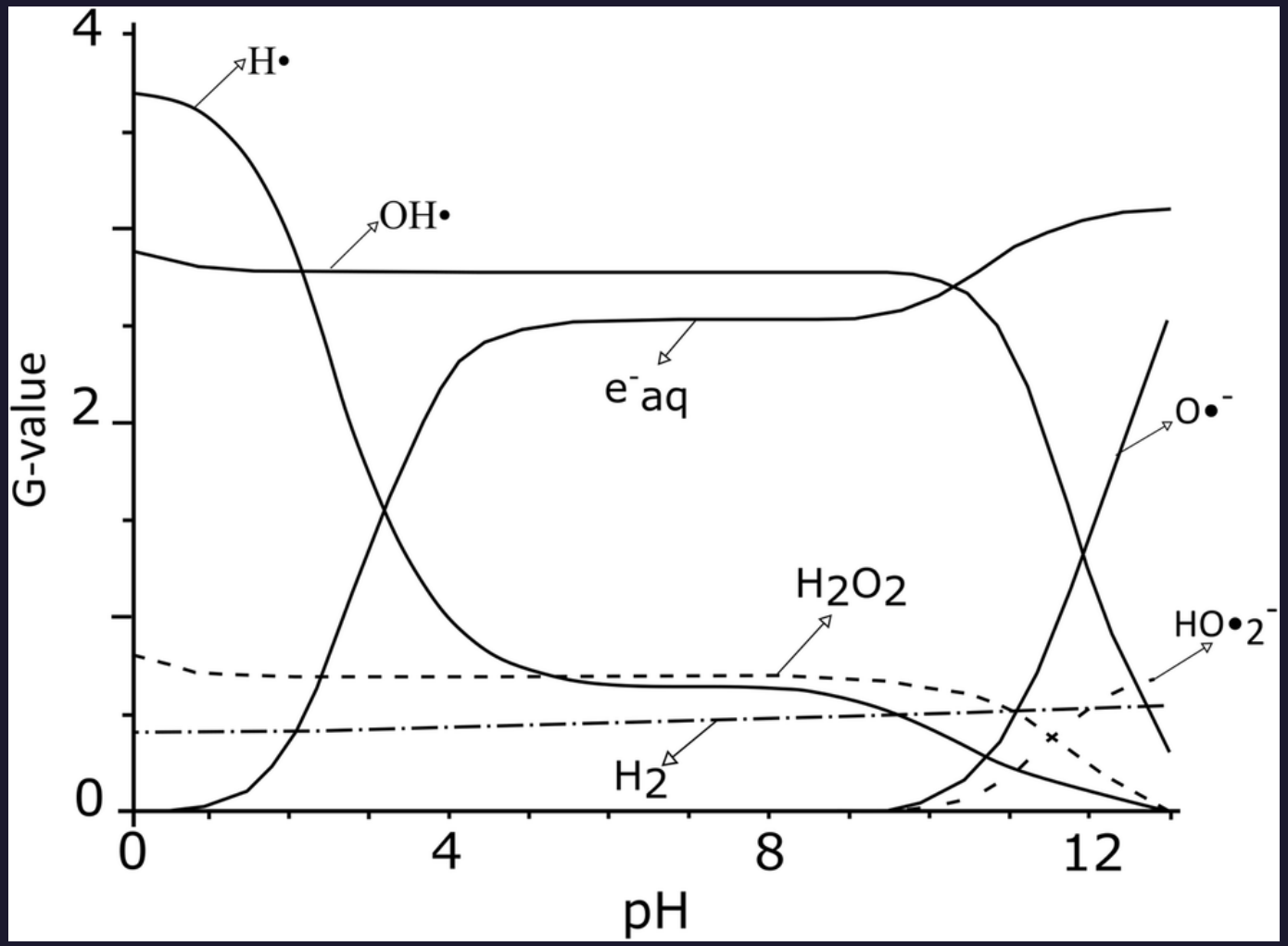

PFNA

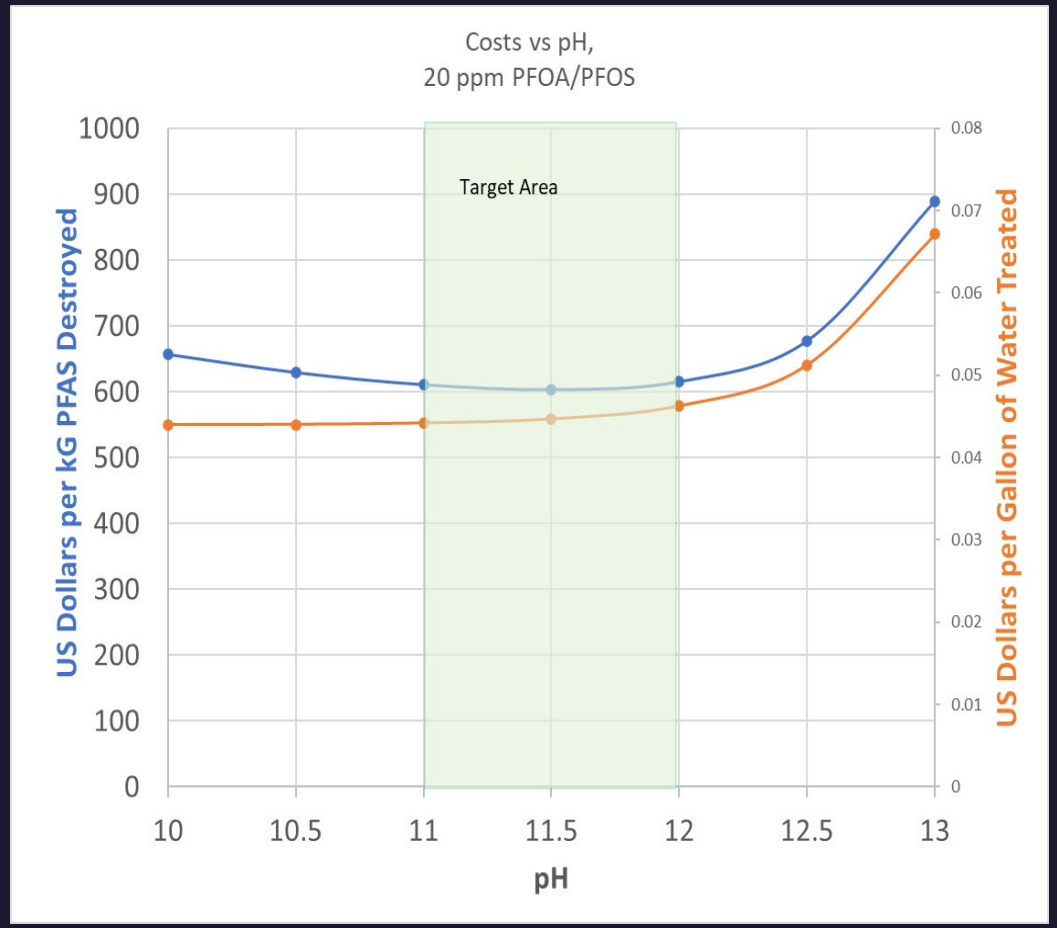

PFHxS

pH impacts the ratio of water radiolysis products - dose rate as well

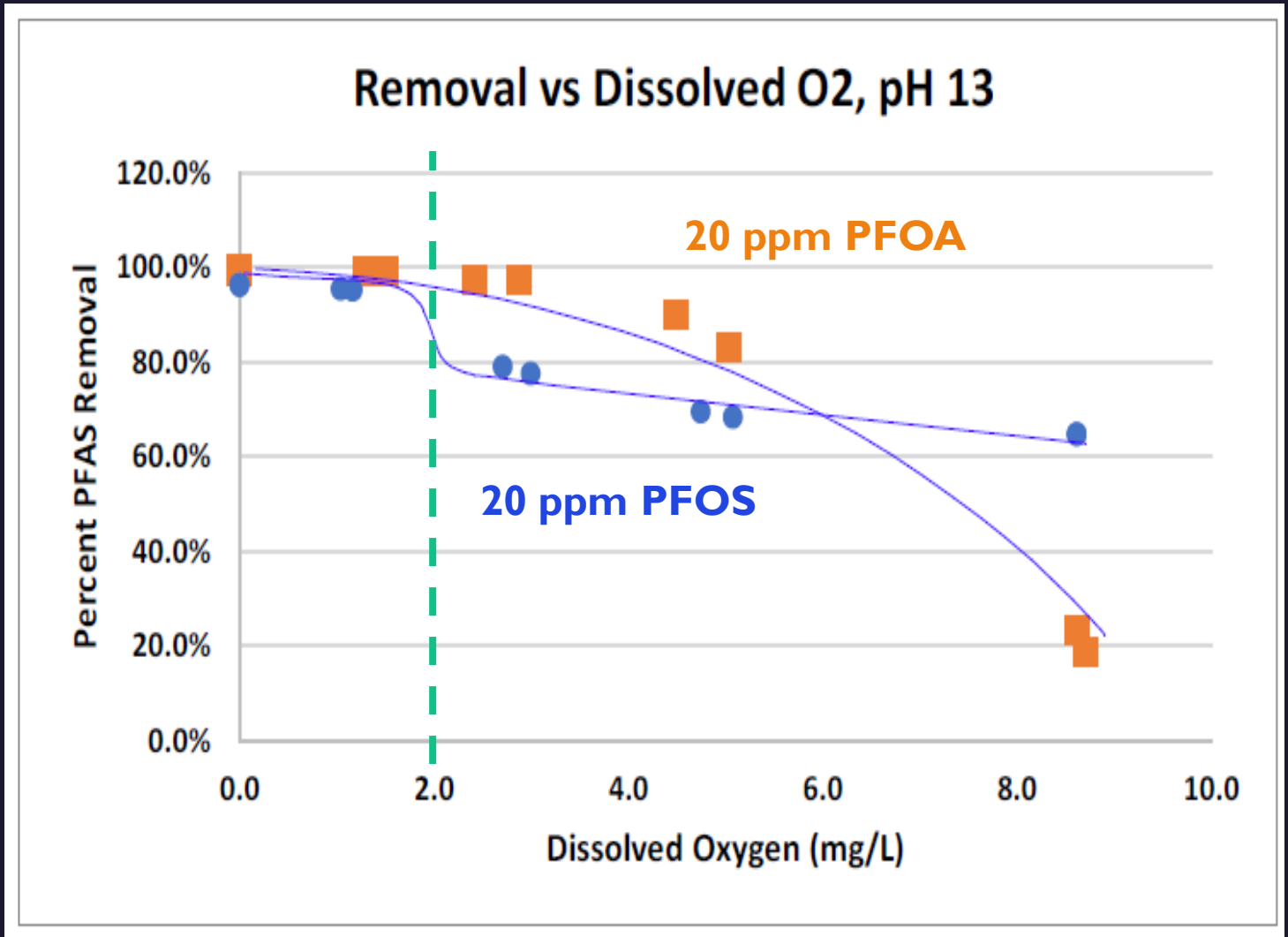
G-value is number of species created per 100 eV

We are at 9 M eV





Effect of dissolved Oxygen on PFAS destruction



- Dissolved oxygen effective at aqueous electron uptake
- Can remove dissolved oxygen with a nitrogen purge
- Removal of oxygen below 2 ppm "not" beneficial
- Shows that aqueous electron important in PFOA destruction
- For PFOS destruction likely aqueous electron and hydroxyl radical important

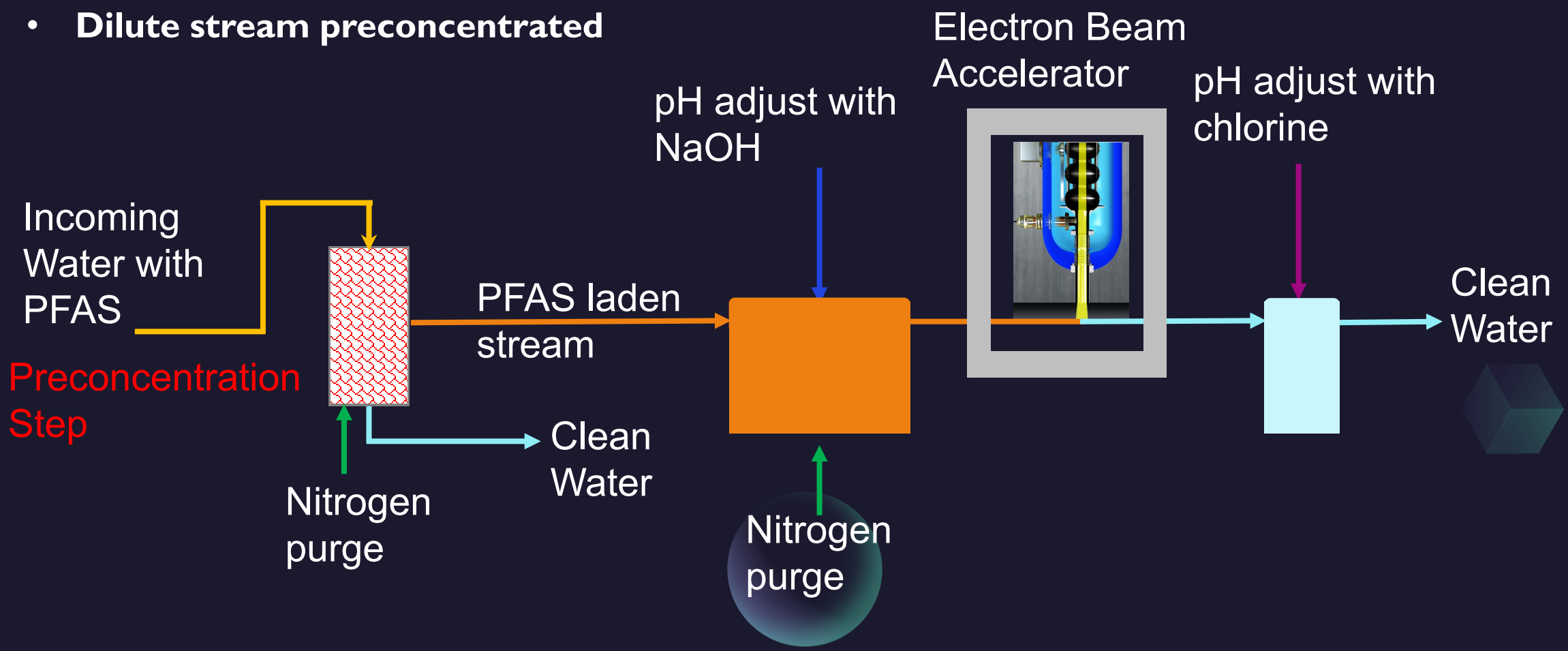
Preliminary Results

E-Beam in Water Treatment System

Best to treat concentrated stream – Approximate 1000 gal/hr (20 ppm PFAS) – 500 kW WPP

From the results so far can be applied to:

- **Industrial stream**
- **Dilute stream preconcentrated**

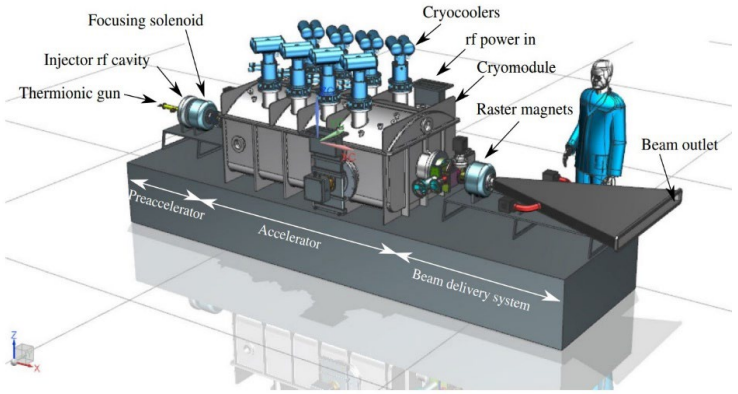


Capital Costs versus GAC?

Purchase Today 300kW, 10 MeV IBA Rhodotron

~3 x cost of GAC

Future Fermilab Technology



$7.8 M Ver 1 ($15M)

$5.5 M Ver 2 ($11M)

Conventional GAC (Granular Activated Carbon)

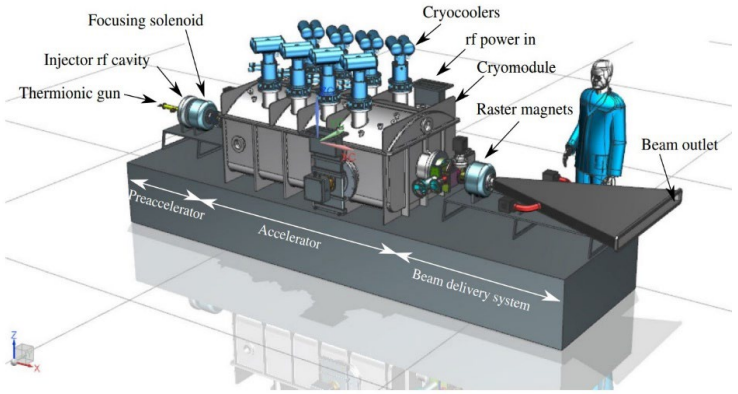
$3.3 M

Economies of scale can provide cost savings for e-beam

Operating Costs versus GAC?

Purchase Today 300kW,
10 MeV IBA Rhodotron

Future Fermilab
Technology



Conventional GAC
(Granular Activated Carbon)

$2.5k/kG PFAS

$2-1.3k/kG PFAS

$34k/kG PFAS

¢/gallon

¢/gallon
Room for improvement

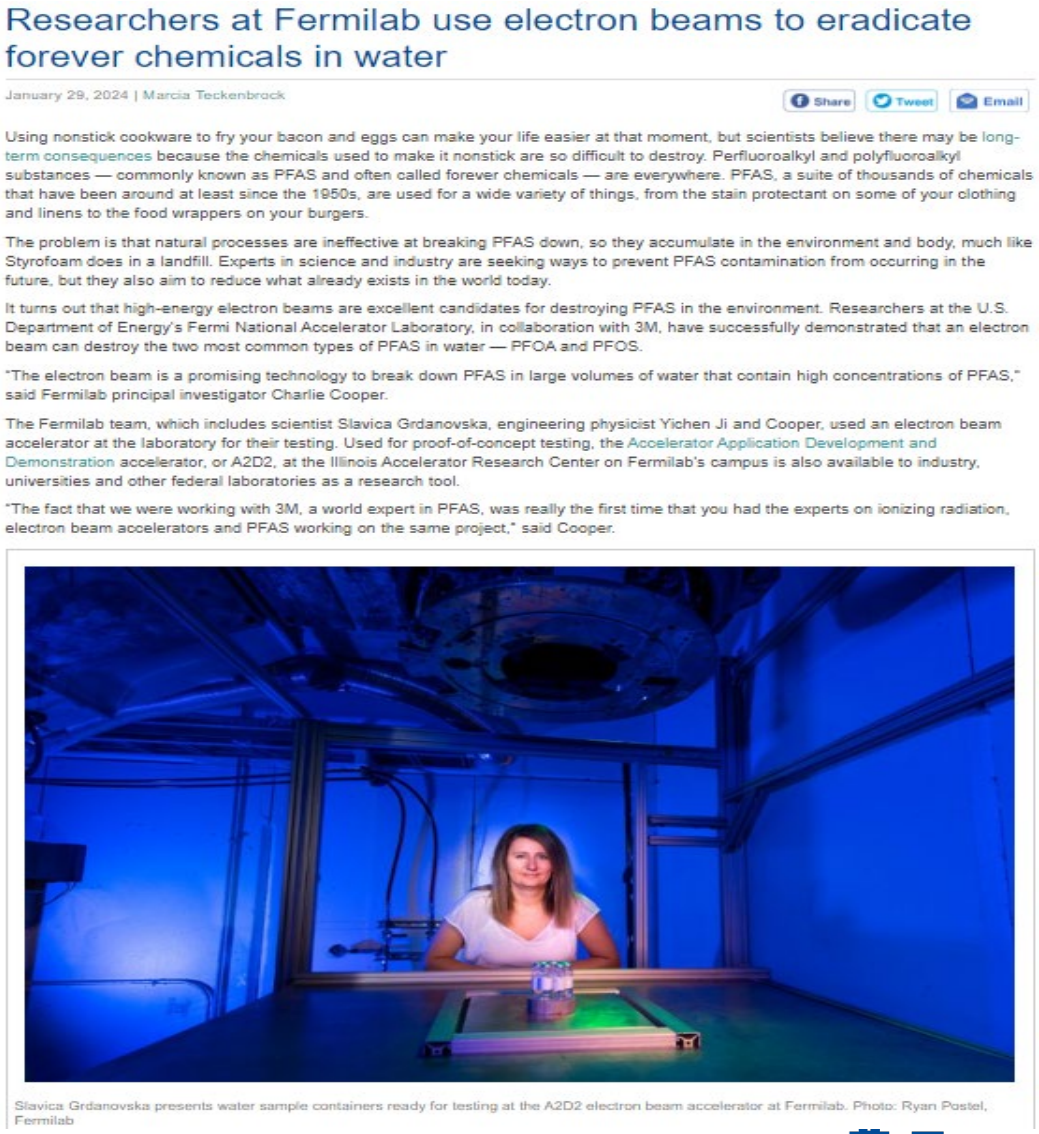
¢/1000 gallon

Operating cost cheaper when comparing cost per mass PFAS destroyed

Fermilab

Recent Attention

- Fermi Today
https://news.fnal.gov/2024/01/researchers-at-fermilab-use-electron-beams-to-eradicate-forever-chemicals-in-water/
- Instagram
https://www.instagram.com/reel/C25X4ZePGn6/?utm_source=ig_web_copy_link
- Water Online
https://www.wateronline.com/search?keyword=fermi
- Smart Water Magazine
https://smartwatermagazine.com/news/fermilab/researchers-fermilab-use-electron-beams-eradicate-forever-chemicals-water
- Social Bites
https://socialbites.ca/latest-news/497284.html
- BNN
https://bnnbreaking.com/world/us/fermilab-and-3m-unleash-electron-beams-to-eradicate-forever-chemicals-a-leap-forward-in-environmental-protection
- Today's Chronic
https://todayschronic.com/researchers-use-electron-beams-to-eradicate-forever-chemicals-in-water/#more-229485
- Phys.org
https://phys.org/news/2024-02-electron-eradicate-chemicals.html



Researchers at Fermilab use electron beams to eradicate forever chemicals in water

January 29, 2024 | Marcia Teckenbrock

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Using nonstick cookware to fry your bacon and eggs can make your life easier at that moment, but scientists believe there may be long-term consequences because the chemicals used to make it nonstick are so difficult to destroy. Perfluoroalkyl and polyfluoroalkyl substances — commonly known as PFAS and often called forever chemicals — are everywhere. PFAS, a suite of thousands of chemicals that have been around at least since the 1950s, are used for a wide variety of things, from the stain protectant on some of your clothing and linens to the food wrappers on your burgers.

The problem is that natural processes are ineffective at breaking PFAS down, so they accumulate in the environment and body, much like Styrofoam does in a landfill. Experts in science and industry are seeking ways to prevent PFAS contamination from occurring in the future, but they also aim to reduce what already exists in the world today.

It turns out that high-energy electron beams are excellent candidates for destroying PFAS in the environment. Researchers at the U.S. Department of Energy's Fermi National Accelerator Laboratory, in collaboration with 3M, have successfully demonstrated that an electron beam can destroy the two most common types of PFAS in water — PFOA and PFOS.

"The electron beam is a promising technology to break down PFAS in large volumes of water that contain high concentrations of PFAS," said Fermilab principal investigator Charlie Cooper.

The Fermilab team, which includes scientist Slavica Grdanovska, engineering physicist Yichen Ji and Cooper, used an electron beam accelerator at the laboratory for their testing. Used for proof-of-concept testing, the Accelerator Application Development and Demonstration accelerator, or A2D2, at the Illinois Accelerator Research Center on Fermilab's campus is also available to industry, universities and other federal laboratories as a research tool.

"The fact that we were working with 3M, a world expert in PFAS, was really the first time that you had the experts on ionizing radiation, electron beam accelerators and PFAS working on the same project," said Cooper.

Slavica Grdanovska presents water sample containers ready for testing at the A2D2 electron beam accelerator at Fermilab. Photo: Ryan Postel, Fermilab

Thanks for your attention