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Recent Developments In Alternatives For PFAS Groundwater Treatment Including An Emerging On-Site Destruction Technology

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Introduction

Per- and polyfluoroalkyl substances (PFAS) are carbon-chain based organo-fluorine compounds containing stable C-F bonds. The most commonly encountered PFAS are perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA), perfluorohexanesulfonic acid PFHxS) were widely used in many commercial and industrial applications. The production and discharge of industrial and municipal wastewater, and the use of aqueous film forming foam (AFFF) in fire fighting has resulted in widespread PFAS contamination of surface waters and groundwater including many drinking water supplies. Because current heath advisory levels for PFAS are orders of magnitude lower than concentrations measured to date at many impacted sites, cost effective surface- and groundwater treatment approaches are needed that consider the unique chemical properties of PFAS such as high solubility, low volatility, emulsification behavior and recalcitrance.

Conventional water treatment processes are not effective for the removal of perfluoroalkyl acids (PFAAs, e.g., PFOA, PFOS). Past research has also demonstrated that commonly used advanced oxidation processes (AOPs) such as ultraviolet light or ozone with peroxide are not effective for PFAA degradation, due to the stability of the carbon-fluorine bond. As a result, a number of emerging advanced oxidation and reduction processes including electrochemistry, heat-activated persulfate, and sonolysis have been evaluated for the degradation of PFAAs and, to a lesser extent, additional PFAS, even though these methods typically require significant chemical and/or energy additions for decomposition reactions to proceed. Activated persulfate has shown promise for the oxidation of perfluorinated carboxylic acids (e.g., PFOA) but is ineffective at removing sulfonates such as PFOS and also can produce perchlorate (regulated by the United States Environmental Protection Agency, U.S. EPA) at significant quantities depending on the chloride concentration.

Current remediation practices for the treatment of PFAS-contaminated water thus rely on sorption and disposal and include granulated activated carbon (GAC) and to a lesser extent, nanofiltration and reverse osmosis. However, relatively short breakthrough times have been reported for GAC certain PFAAs, and all of these processes produce a residual requiring disposal or further – mostly off-site – treatment or destruction. There is thus a clear need to develop and validate technologies capable of overcoming the limitations of currently practiced remediation methods for PFAS. The proposed and validated electrical discharge plasma technology addresses this need by providing the stakeholders with the most effective and efficient destructive technology available today for degrading PFAS.

Strategic Environmental Research and Development Program (SERDP)
U.S. DoD Basic and Applied Research Program

Awarded: "Removal and Destruction of PFAS and Co-contaminants from Groundwater via Groundwater Extraction and Treatment with Ion-exchange Media, and On-site Regeneration, Distillation, and Plasma Destruction"

Environmental Security Technology Certification Program (ESTCP)
U.S. DoD Technology Demonstration and Validation

Awarded: "Removal and Destruction of PFAS and Co-Contaminants from Groundwater"

Research Team:

Clarkson
ect$_2$
NAVFAC
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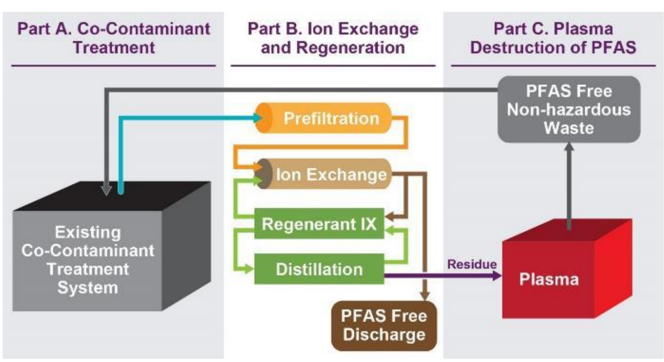
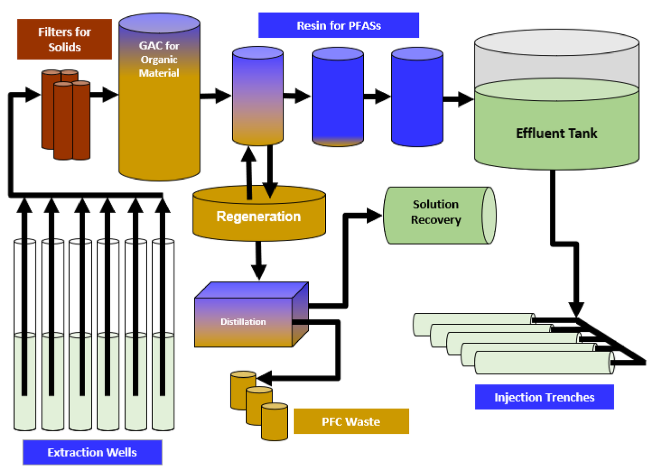
Two research projects were awarded to further investigate and develop the treatment train principle for PFAS-impacted groundwater utilizing a regenerable ion exchange (IX) resin, a resin regeneration step followed by up-concentrating of the regenerate by distillation, and on-site destruction of PFAS in the concentrated brine employing a plasma destruction technology.

Objectives

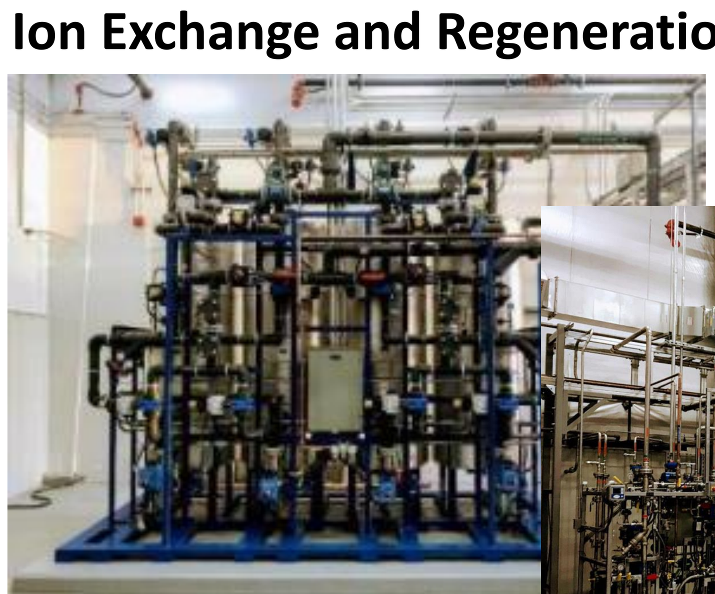
- Removal of PFAS from contaminated groundwater by Ion Exchange (IX)
- Regeneration of IX media
- Destruction of high concentration PFAS waste stream from distilled regenerant still bottoms

Technical Approach





Ion Exchange and Regeneration



IX Resin System

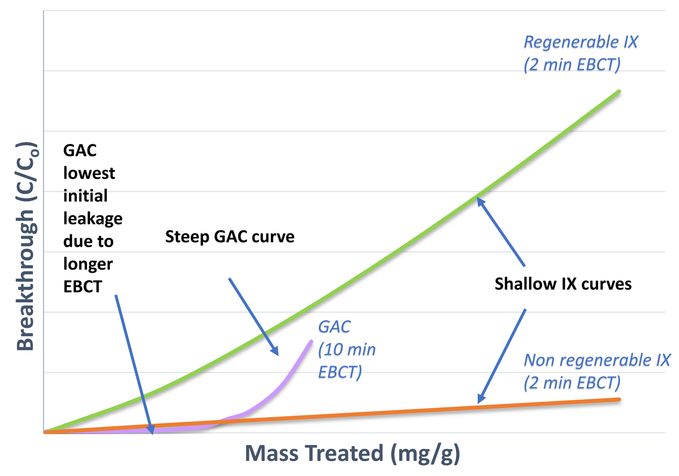
In-vessel IX Resin Regeneration System

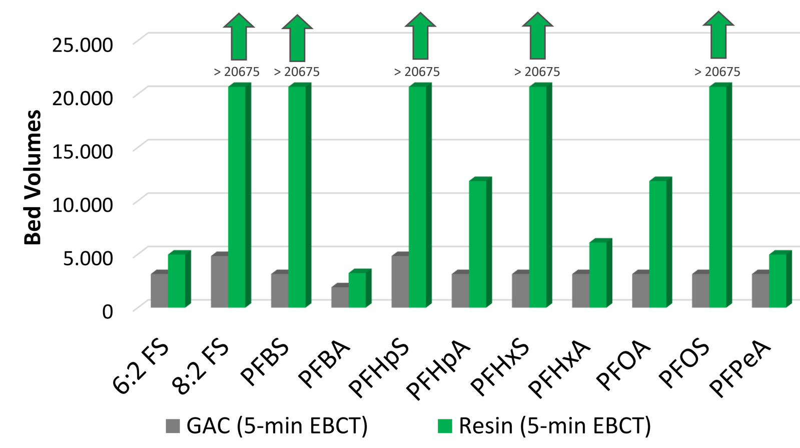
Distillation Regeneration Recovery System

Former Pease AFB in Portsmouth, NH (USA)
Photos courtesy of ECT$_2$

Comparison of Adsorbent Media

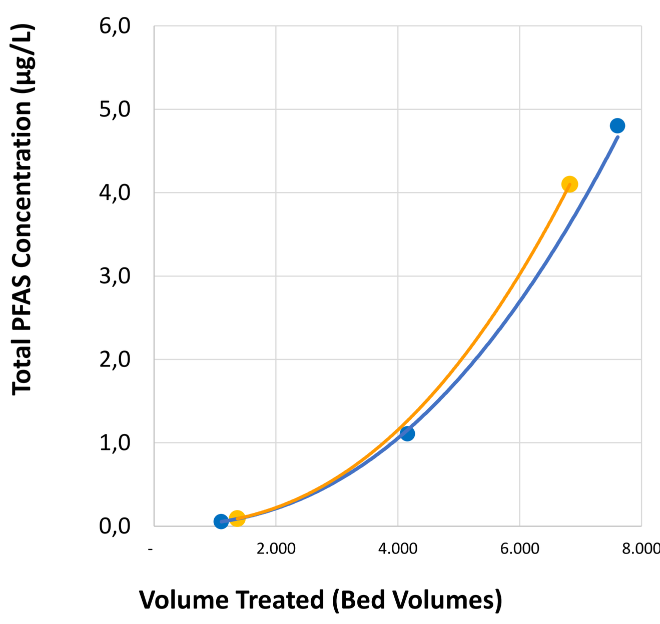
Illustrative curves for GAC and IX media for total PFAS from site-specific groundwater (Pease AFB)





Note: Site-specific pilot testing recommended to determine media performance

In a comparison between non-regenerable, regenerable IX resins and activated carbon, non-regenerable IX resin exceeds PFAS-mass recovery per gram of adsorbent tested. However, like activated carbon non-regenerable IX would need to be disposed off-site requiring transportation and costly high-temperature incineration. Regenerable IX resin, however, does not require frequent replacement and costly disposal/destruction, but provides a long-lasting solution for removing PFAS from water sources.
Regenerated IX resin performance is comparable to virgin resin material.

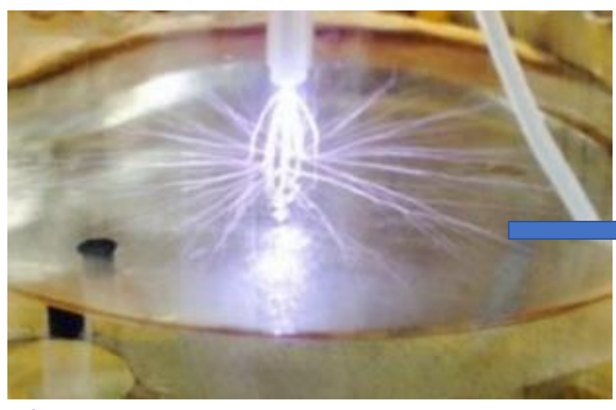


Regenerable IX resins

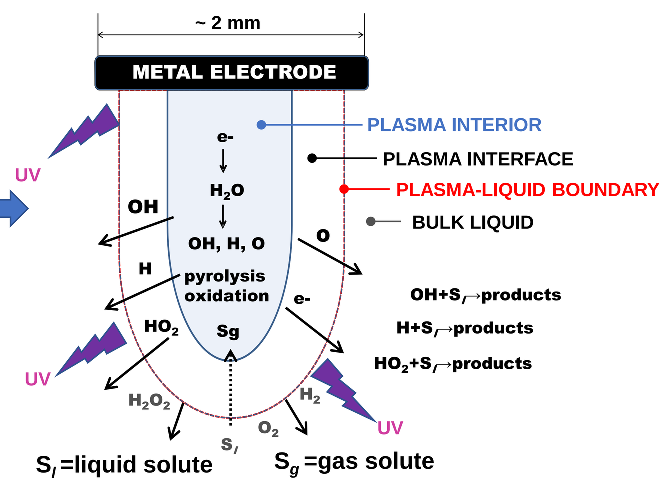
- ✓ Lifecycle cost evaluation performed for full-scale 200 gpm system (Pease AFB)
- ✓ Capital cost for Resin system is ~15% higher than GAC
  - Media cost
  - Regeneration system
- ✓ O&M cost is ~50% lower than GAC
  - Resin has higher capacity
  - No media replacement
- ✓ Even without regeneration, lifecycle cost of resin system is lower (depending upon PFAS mix)

Plasma Destruction Technology

A process based on electrical discharge plasma was developed to degrade PFOA, PFOS and other PFAS in prepared solutions and groundwater. Electrical discharge is a technology that, using only electricity, converts an otherwise inert fluid such as water into a mixture of highly reactive species including OH•, O, H•, HO_2•, O_2^-, H_2, O_2, H_2O_2 and aqueous electrons (e^-_{aq}), called a plasma. The plasma-based process employs the enhanced contact (EC) plasma reactor and is able to lower the concentrations of PFOA and PFOS in groundwater obtained from multiple sites to below EPA's lifetime health advisory level (HAL, 70 ng/L) within 1 minute of treatment with energy requirements much lower than those of leading alternative technologies (~26 kWh/m³ for persulfate, photochemical oxidation and sonolytic processes and 132 kWh/m³ for plasma vs. 5000 kWh/m³ for electrochemical oxidation).

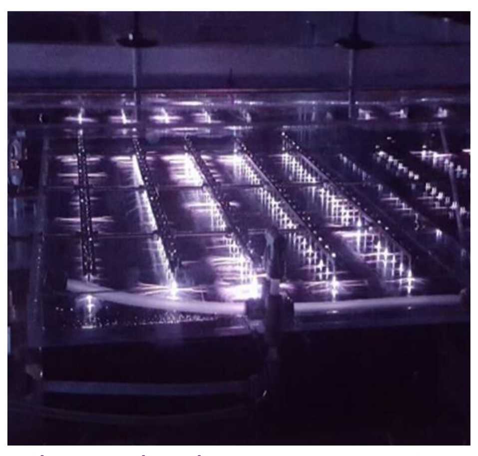


Plasma in Argon Gas Contacting Water
Courtesy of: Plasma Research Laboratory, Clarkson University



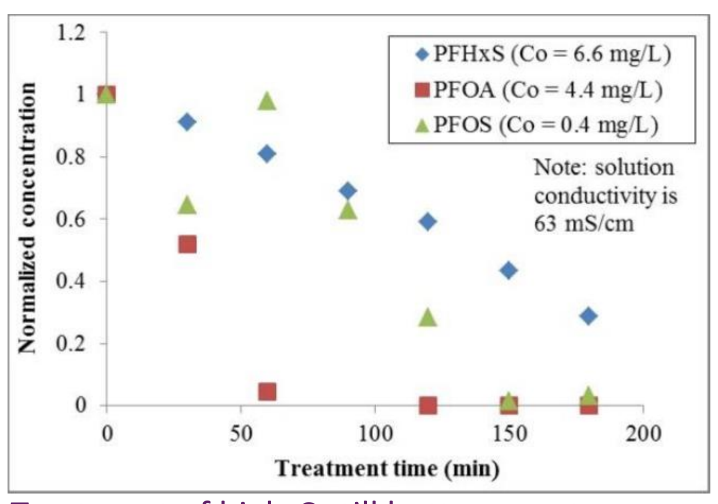
Plasma Treatment/Destruction

- ✓ For direct treatment of low concentration PFAS
- ✓ Destruction of concentrated PFAS in regenerant solution from Ion Exchange
- ✓ No chemical additives required
- ✓ Carboxylic acids (e.g. PFOA) more readily degraded
- ✓ Sulfonic acids (e.g. PFOS, PFHxS) require longer treatment time
- ✓ Co-contaminants in environmental samples do not affect reaction pathways



Pilot-scale plasma reactor in operation

Potential No-waste Solution



Treatment of high-C still bottom waste

Summary / Key Points

- ✓ PFAS Treatment Train is Adaptive to Site Conditions
- ✓ Regenerable IX may be most cost-effective solution depending on key variable of PFAS concentration and treatment horizon - i.e., payback
- ✓ Most relevant to groundwater in sources areas
- ✓ On-site destruction reduces liability and disposal cost
- ✓ Pre-treatment to optimize IX efficiency may be more complex and costly
- ✓ Knowledge transfer, User's Guide will inform stakeholders
  Pre-selection technology screening tool

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Rob Singer, Dave Woodward, Nathan Hagelin – Wood E&I Solutions

References:

Rapid removal of poly- and perfluorinated compounds from investigation-derived waste (IDW) in a pilot-scale plasma reactor; Singh, Multari, Nau-Hix, Anderson, Richardson, Holsen, Mededovic; Accepted for publication by Environmental Science and Technology; September 2019.

Perfluoroalkyl Substances in the Environment: Theory, Practice, and Innovation (Chapter 21); Brandon Newman; John Berry; CRC Press; July 2018.