Treatment Technologies for PFAS Site Management

Naval Facilities Engineering Command
ENGINEERING AND EXPEDITIONARY WARFARE CENTER

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Presentation Overview

- Evaluating Remediation Technologies
- Sorption
- *In Situ* Technologies
- Dealing with Investigation-Derived Waste (IDW)
- Wrap-Up

Summary of Available Technologies – Drinking Water Treatment

Technology Category	Technology	Maturity/Availability
Sorption	Activated Carbon*	Commercialized, can be purchased from vendors
	Anion Exchange Resin*	Commercialized, can be purchased from vendors
	Biochar	Field Pilot Scale, not commercially available
	Zeolites/Clay Minerals	Commercialized, can be purchased from vendors
Membrane Filtration	Reverse Osmosis and Nanofiltration*	Commercialized, can be purchased from vendors
Coagulation	Specialty Coagulants	Full Scale application being conducted by researchers
Redox Change	Electrochemical	Field Pilot Scale, not commercially available
Other	Sonochemical	Field Pilot Scale, not commercially available

** Technologies that will be discussed*

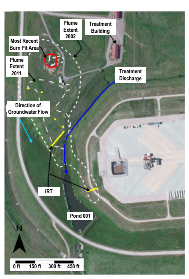
Summary of Available Technologies – Soil Treatment

Technology Category	Technology	Maturity/Availability
Sorption and Technologies	Modified Carbon*	Commercialized, can be purchased from vendors
	Minerals/Modified Minerals*	Commercialized, can be purchased from vendors
Excavation Disposal	To Landfill	Commercialized
	To Incinerator	Commercialized
Thermal		Field Pilot Scale, commercially available

** Technologies that will be discussed*

Consider Effect of Prior Remediation for Co-Contaminants on PFAS

- Benzene plume
- Oxygen injections at yellow
- Elevated levels of PFAA at location of historical and present benzene plume – lacking in areas with no O_2 injections
- Fourfold difference in Kd between PFHxA and PFOA yet their plume overlapped – likely due to *in situ* transformation of precursors
- ***Navy currently conducting similar study under NESDI***



Reference Evidence of Remediation-Induced Alteration of Subsurface Poly- and Perfluoroalkyl Substance Distribution at a Former Firefighter Training Area Meghan E. McGuire, Charles Schaefer, Trenton Richards, Will J. Backe, Jennifer A. Field, Erika Houtz,, David L. Sedlak, Jennifer L. Guelfo, Assaf Wunsch, and Christopher P. Higgins

Pump-and-Treat

- At drinking water wellhead
- At point of use
- To control plume size/spread
- At base boundary to prevent plume migration

Key Point | **Only practical treatment for groundwater available**

Granular Activated Carbon (GAC)

Material

- Made from bituminous coal or coconut
- Highly porous, large surface area

Application

- Typically used in packed-bed flow-through vessels
- Operate in series (lead-lag) or parallel
- Virgin or Reactivated GAC

http://store.ecologixsystems.com/detail/index.cfm?nPID=294

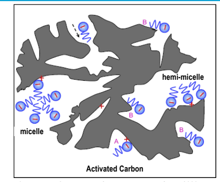
Granular Activated Carbon (cont.)

Mechanism

- Adsorption on surface process, physical mass transfer
- No chemical degradation or transformation

Effectiveness

- Capable of 90 to >99% removal efficiency
- Individual PFAS have different GAC breakthrough times
  - e.g., GAC capacity for PFOS>PFOA
- Influent conc. for <5 Carbon PFAS typically lower
- High DOC reduces effectiveness



Reference -Yu, Q., R. Zhang, S. Deng, J. Huang, G. Yu, 2009. "Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: Kinetic and isotherm study." *Water Research*, 43, 1150-1158.

Key Point PFAS <5 carbons shorter breakthrough times

Reactivation of PFAS Contaminated Granular Activated Carbon

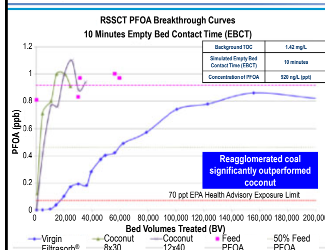
Thermal Reactivation Process

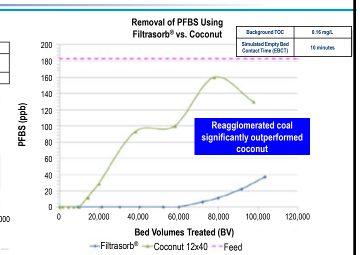
Reactivation furnace under negative pressure and nitrogen environment → Furnace off gas passed through after burn to destroy organics → Emission stream passed through chemical scrubber to remove acid gases → Final treatment through baghouse filters to remove particulate matter

- Reactivation temperature 1,300°F
- PFAS pyrolysed to carbon char
- Lower CO_2 footprint than making virgin GAC
- Reactivated carbon may be just as effective as virgin carbon

Key Point Process is expensive and energy intensive

Bituminous vs. Coconut Carbon



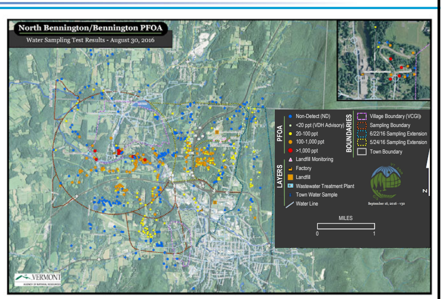


Key Point Bituminous carbon appears to perform better than coconut carbon at this specific site

NEWMOA PFAS Technical Workshop – Activated Carbon Don Ivey and John Matthis May 2017

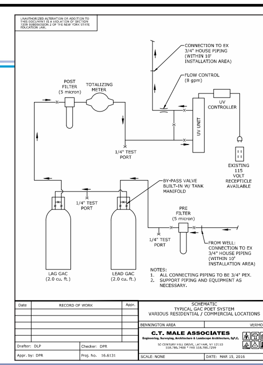
Case Study – Point of Entry Treatment – Vermont Residences

- PFOA contamination from textile coating at CHEMFAB®
- 541 samples from private wells
- Bottled water delivered to residents
- 11 homes connected to municipal water
- 255 POET systems installed



Case Study – POET Vermont

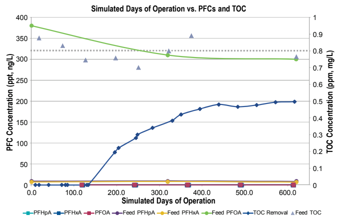
- Initially sampled once per month for 3 months
- Influent, midpoint and effluent
- Influent PFOA Concentration >1,000 ppt: sample every 3 months
- Influent PFOA Concentration >200 ppt to <1,000 ppt sample every 6 months
- Influent PFOA Concentration <200 ppt every 12 months



Case Study POET Vermont – Results

- Influent concentrations vary from <20 ppt to 4,600 ppt
- Volume treated per unit from 50 gal over one month to 37,000 gal over 3 months
- Pre and post filter replaced every 4 months
- UV lap replaced every 12 months
- GAC replacement assumed every 2 years
- Swap lead and lag tank then ship GAC media to vendor

PFC/TOC Customer ACT Data

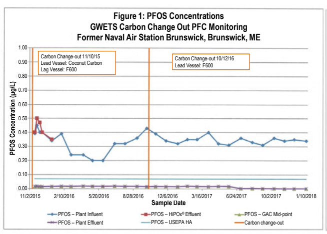


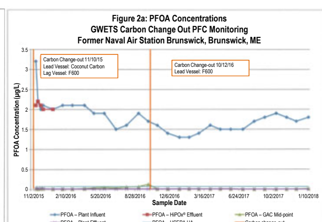
Reference: Lessons Learned on Vermont POET Installations and Operations at Residences Impacted by PFASs. Richard Spiese.

Case Study – NAS Brunswick, ME GWETS

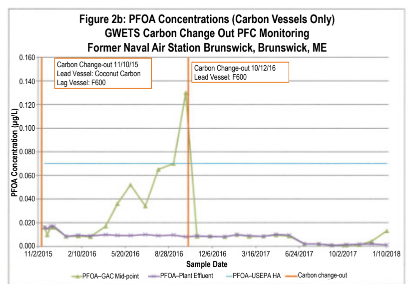
- Former Naval Air Station in Brunswick, ME, BRAC 2011
- Treating CVOCs at GWETS using air stripping and GAC (vapor and liquid phase)
- Recovered over 500 kg VOCs since 1995; removal now limited by back diffusion rate, asymptotic range
- 1,4-Dioxane addressed by addition of HiPOx® unit
- PFAS removed via liquid-phase GAC
  - PFOA breakthrough determines changeout
  - Shorter-chain PFAS, carboxylates, break through earlier

Case Study – NAS Brunswick, ME GWETS – Results

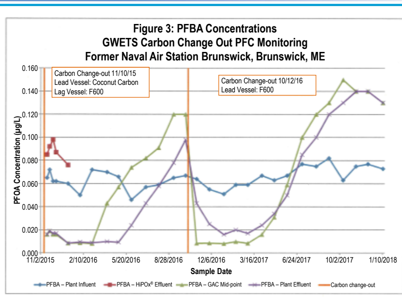




Case Study – NAS Brunswick, ME GWETS – Results (cont.)



Case Study – NAS Brunswick, ME GWETS – Results (cont.)



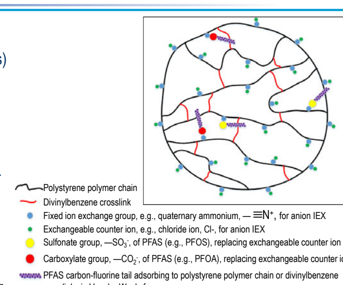
Ion Exchange

Material

- Synthetic neutral co-polymeric media (plastics) with positively-charged exchange sites
- Can be regenerated (produces waste stream) or single use (must be disposed of properly)

Application

- Removes anionic PFAS binding to negatively-charged functional group
- Lead-lag including combination of single use and regenerated

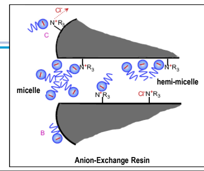


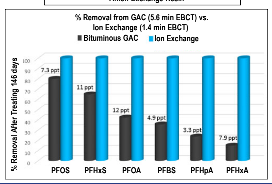
Reference: Steve Woodward John Berry Brandon Newman. 2017. Ion Exchange Resin for PFAS Removal and Pilot Test Comparison to GAC. Remediation Journal Volume 27, Issue 3 Pages 19–27

Ion Exchange (cont.)

Mechanism
- Acts as ion exchange resin and adsorbent resin
- Positively charged anion exchange media
- Removes negatively-charged PFAS from water

Effectiveness
- Reaction kinetics faster than GAC
- Operating capacity higher than GAC
- Breakthrough varies for different PFAS
- Less frequent media change-outs





Considerations When Using Ion Exchange

- Type and concentration of inorganic ions in groundwater affect PFAS capacity of resin
- Bench-scale tests recommended to determine most effective resin
- More cost-effective at higher concentrations
- Organic matter may foul resin
- Co-contaminants compete for resin site
- Site-specific testing should be performed

Regeneration of Ion Exchange Resins

- Brine solution can desorb anionic head of PFAS from resin
- Organic solvent-like methanol or ethanol can desorb C-F tail
- Surfactants with both nonionic and anionic properties can be used as regenerants
- Most successful has been organic solvents and sodium chloride
- The solution used to regenerate may then need to be concentrated to minimize the volume of waste

Key Point — **Shipped back to vendor for regeneration**

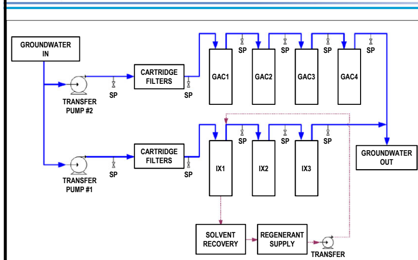
Case Study – Comparison of GAC with Ion Exchange at Pease AFB

- Historic use of AFFF for firefighting training
- Ion Exchange – ECT Sorbix A3F
- Note 6:2 FS 2nd highest concentration PFAS
- GAC – Calgon Filtrasorb® 400 (F400)

Analyte	Analyte Acronym	Influent Concentrations Observed During Pilot Test (µg/L)		
		Low	High	Average
6:2 Fluorotelomer sulfonate	6:2 FS	15	22	18
8:2 Fluorotelomer sulfonate	8:2 FS	0.055	0.3	0.23
Perfluorobutane sulfonate	PFBS	0.81	1.3	1.1
Perfluorobutanoic acid	PFBA	0.89	2.1	1.3
Perfluoroheptane sulfonate	PFHpS	0.85	1.4	1.1
Perfluoroheptanoic acid	PFHpA	1.6	2.2	1.9
Perfluorohexane sulfonate	PFHxS	18	25	22
Perfluorohexanoic acid	PFHxA	5.9	8.9	7.7
Perfluorooctanoic acid	**PFOA**	**9.1**	**13**	**12**
Perfluorononanoic acid	PFNA	0.046	0.082	0.054
Perfluorooctane sulfonate	**PFOS**	**4.2**	**32**	**26**
Perfluoropentanoic acid	PFPeA	3.1	5.1	4.2
Sum of observed PFAS	-	**65**	**112**	**94**

Reference: Steve Woodard John Berry Brandon Newman. 2017 Ion Exchange Resin for PFAS Removal and Pilot Test Comparison to GAC. Remediation Journal Volume 27, Issue 3 Pages 19–27

Case Study – Comparison of GAC with Ion Exchange at Pease AFB (cont.)

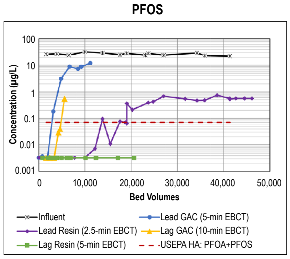


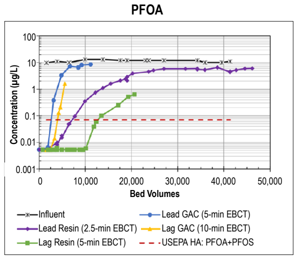
GAC
- 4 vessels in series
- Each containing 9 gal F400
- Each vessel 5 min EBCT, overall 20 min EBCT
- Samples collected at influent and after each vessel weekly for 8 weeks
- At 1.8 gpm treated 100,486 gal water (11,165 bed volumes)

Ion Exchange
- 3 vessels in series
- Each containing 9 gal resin
- Each vessel 2.5 min EBCT, overall 7.5 min EBCT
- At 3.6 gpm treated 422,645 gal water (46,961 BVs)
- Samples collected routinely at influent and effluent

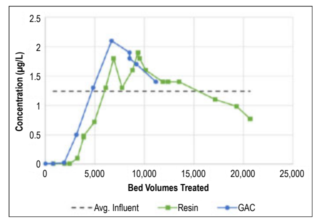
Case Study – Comparison of GAC with Ion Exchange at Pease AFB (cont.)

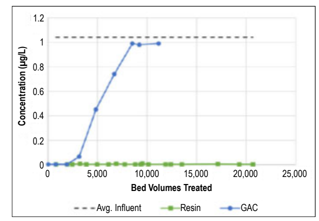
Case Study – Comparison of GAC with Ion Exchange at Pease AFB (cont.)





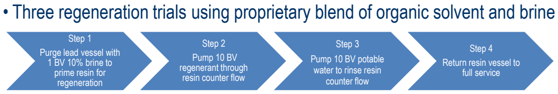
Case Study – Comparison of GAC with Ion Exchange at Pease AFB (cont.)

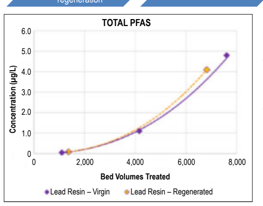




Case Study – Comparison of GAC with Ion Exchange at Pease AFB (cont.)

- Three regeneration trials using proprietary blend of organic solvent and brine





Regenerant Solution Recovery

- Distill off solvent fraction into regenerant tank for reuse, left with concentrated brine PFAS fraction
- OR conduct superloading – process concentrated brine PFAS solution through adsorption media then recycle brine solution

Case Study – Comparison of GAC with Ion Exchange at Pease AFB (cont.)

- Both GAC and Ion Exchange Resin can remove PFOS and PFOA from groundwater to below EPA LHA

At 5 min. contact time

- Resin treated 8X more BV than GAC before breakthrough of PFOS observed
- Resin treated 6X more BV than GAC before breakthrough of PFOA observed
- Resin removed 1.66 mg PFAS per gram of resin whereas GAC removed 0.40 mg PFAS per gram GAC
- Resin could be regenerated in the field

In Situ Stabilization (ISS)

- Use of amendments for adsorbing and stabilizing PFAS in soil and groundwater
- GAC, stabilizers, and modified minerals (organoclays)
- Commercially available
- Additional amendments being developed
- Critical to monitor soil leachate to determine treatment effectiveness
- Limited full-scale application in U.S. (more overseas)

Activated Carbon for *In Situ* Water Treatment – PlumeStop®

Material

- Colloidal activated carbon
- 1-2 µm sized particles of carbon suspended in water by organic polymer dispersion chemistry

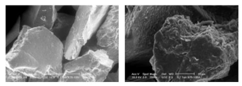
Application

- *In situ* sorbent technology sorbs PFOS and PFOA from aqueous phase
- Treats dissolved-phase contaminants
- Applied by low-pressure injections

Activated Carbon for *In Situ* Water Treatment – PlumeStop® (cont.)

Mechanism

- Coats surface of soil
- Contaminants in dissolved phase then sorb to carbon
- Does not destroy PFAS, immobilizes PFAS in place
- Occupies just 0.1% soil pore volume



A Scanning Electron Microscope (SEM) Image of Sand Grains With and Without a Coating of Carbon

Effectiveness

- Reduces aqueous concentration to below 70 ng/L
- Radius of Influence can be up to 25 ft
- Can be applied as multiple barriers perpendicular to plume

In Situ Soil Treatment – Aluminum-Based Sorbent – Rembind Plus®

Material

- Aluminum hydroxide, activated carbon, organic matter, and kaolinite

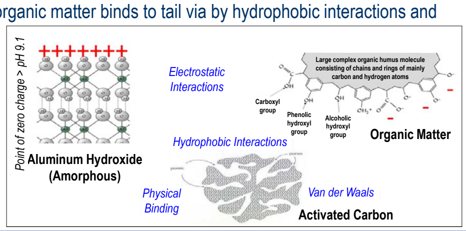
Application

- Apply to soil in ~2 to 5% by weight
- Adjust to 30% moisture content
- Binding occurs in 24 hours
- ***Pilot tested for water treatment***

In Situ Soil Treatment – Aluminum-Based Sorbent – Rembind Plus® (cont.)

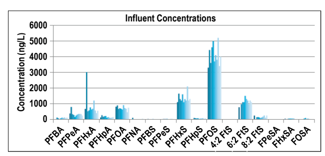
Mechanism

- Aluminum hydroxide binds to functional head of PFAS by electrostatic interactions
- Activated carbon and organic matter binds to tail via by hydrophobic interactions and Van der Waals forces



Aluminum-Based Sorbent for GW Case Study – Air Force Site

- Historical use of AFFF at site
- Full-scale GAC system: two 20,000-lb GAC vessels in operation to remove PFOS/PFOA from groundwater
- Goal of pilot study to evaluate sorption capacity of RemBind Plus®

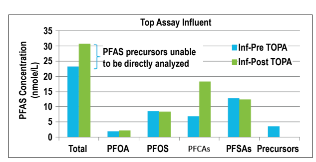


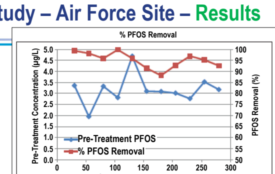
Aluminum-Based Sorbent for GW Case Study – Air Force Site (cont.)

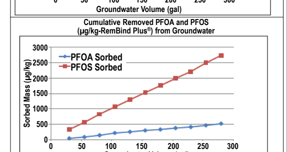
- 30-gal batch reactor pilot test set up next to GAC system
- 30 gal of contaminated water mixed 1.135 kg aluminum-based sorbent for one hour and allowed to settle overnight
- Next day treated GW moved to effluent tank and contaminated GW added to tank with amendment without replacing amendment
- Run for 2 weeks treating 280 gal water
- Monitored for 53 PFAS compounds and TOP assay
- TOC also monitored

Aluminum-Based Sorbent for GW Case Study – Air Force Site – Results

- 18 PFASs detected frequently
- Removal ranged from 80 to 100% after 155 gal
- Slight decrease in removal beyond 155 gal







Types of IDW

Liquid Waste

- Purge water from groundwater sampling
- Concentrated AFFF

Solid Waste

- Well installation waste (soil cuttings)
- Soil cuttings from core sampling
- Spent GAC
- Spent ion exchange resin
- Soil from excavations

Challenges with Handling IDW

- PFAS are considered non-hazardous (can be disposed of in any landfill)
- Landfill refusal to accept PFAS waste
- Potential for future liability
- Risk of landfill leachate

Key Point — **Consideration should be given to taking liquid waste to existing onsite GWETS if available**

Considerations for Liquid IDW

- If PFAS concentrations are below regulatory levels, water may be considered to be disposed to sanitary sewer/POTW
- At sites where there is a PFAS GWETS, purge water should be considered to be treated in that system with operator approval
- Consideration should be given to have purge water pass through a drum of GAC, held in a receiving tank pending analysis
- If below regulatory values, GW may be able to be discharged to the sanitary sewer/POTW
- Purge water may be able to be sent to an off-site treatment facility willing to accept it

Considerations for Liquid IDW

- Currently sending to a landfill or a treatment facility may be the only choice
- As treatment becomes more common, the soil cuttings may be treatable on-site (e.g., thermal)
- PFAS waste is non hazardous*, so 90 day rule may not apply
- Option – retain material on site as treatment approaches and policies are developed
- EXWC conducting research on treatment for IDW and source zone soils

Key Points

- GAC may be the only practical treatment for groundwater to date
- PFAS <5 carbons much shorter breakthrough times
- Bituminous carbon may perform better than coconut carbon but depends on site conditions
- Ion exchange resin may be better at removing PFAS and can be regenerated but may be more expensive
- *In situ* treatment technologies PlumeStop®, RemBind Plus® and MatCARE™ limited field demonstrations in U.S.

Select References

- ITRC PFAS Remediation Factsheet
- PFAS Remediation Whitepaper (Internal Navy Document)
- Andres Arias Espana, Victor, Megharaj Mallavarapu, and Ravi Naidu. 2015. “Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA): A critical review with an emphasis on field testing,” Environmental Technology and Innovation, 4, 168-181.
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- Zhu, Runliang, Qingze Chen, Qing Zhou, Yunfei Xi, Jianxi Zhu, and Hongping He. 2016. “Adsorbents based on montmorillonite for contaminant removal from water: A review,” Applied Clay Science, 123, 239-258.
- Merino, Nancy, Yan Qu, Rula Deeb, Elisabeth L. Hawley, Michael R. Hoffmann, and Shaily Mahendra. 2016. “Degradation and Removal Methods for Perfluoroalkyl and Polyfluoroalkyl Substances in Water,” Environmental Engineering Science, 33, 615-649.

NAVFAC Points of Contact

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Questions and Answers

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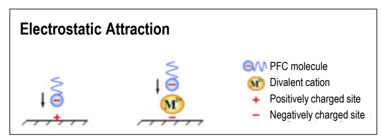
Backup Slides

Mechanism of Sorption – Electrostatic Interaction

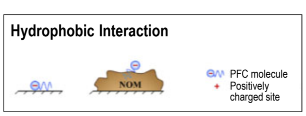
- Interaction between negative and positive charges
- Strong negative charged shell around CF chain due to fluorine atoms and functional group
- Electrostatic bond mainly at functional group sue to stronger negative charge
- To promote electrostatic bond increase ionic strength, ensure pH is not too alkaline
- Example seen in organoclays

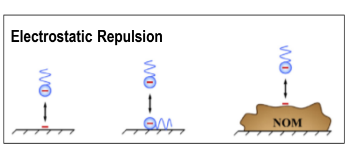


Reference *Du, Ziwen, Shubo Deng, Yue Bein, Qian Huang, Bin Wang, Jun Huang, and Gang Yu. 2014. "Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents – A review," Journal of Hazardous Materials, 274, 443-454.*

Mechanism of Sorption – Hydrophobic Interactions

- Occurs at the electronegative CF chain
- Longer chain more hydrophobic
- Leads to formation of micelles
- Is often stronger than electrostatic repulsion (between negatively-charged tail and negatively-charged sorbent)





In Situ Soil Treatment Modified Organoclay Sorbent – MatCARE™

Material

- Palygorskite-based material modified with oleylamine, i.e., amine modified clay sorbent

Application

- Applied to soil at 10% w/w
- Water content of soil 60%

Property	MatCARE™
Bulk Density (kg m^{-3})	608
Particle Density (kg m^{-3})	1,677
Porosity (%)	40
Pore Volume (kg m^{-3})	—
Particle Size	77.4% between 2,000 and 1,180 μm
Surface Area (m^2 g^{-1})	31.91
Reversible Swelling (%)	2.5
Moisture Holding Capacity (%)	50.28

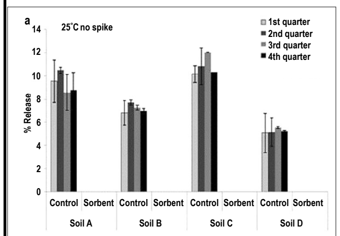
In Situ Soil Treatment Modified Organoclay Sorbent – Soil Treatability Studies

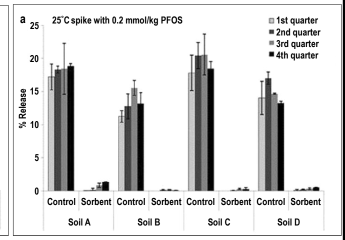
- Four soils from fire training areas at overseas Air Force Bases
- Air-dried, homogenized, and passed through 2-mm sieve
- pH, organic carbon content, and PFOS concentration
- 1 kg of each soil adjusted to 60% moisture, amendment added at 10 g per 100 g soil
- PFOS-spiked treatment also included (10 ml of PFOS stock solution) then mixed
- 10 g sample, 3x/yr
- Water extraction

Physico-Chemical Properties of the Soil

Soils	pH	TOC (%)	PFOS (nmol g^{-1})		Texture			
			Solvent Extracted	Water Extracted	Sand (%)	Silt (%)	Clay (%)	Textural Class
A	4.8	0.96	3.66	0.52	52.63	25.62	21.74	Sandy clay loam
B	4.9	1.97	148.72	21.13	43.21	21.42	35.37	Clay loam
C	8.1	0.29	32.33	4.72	75.15	9.11	15.74	Sandy loam
D	6.5	2.03	18.52	1.86	57.04	10.93	32.03	Sandy clay loam

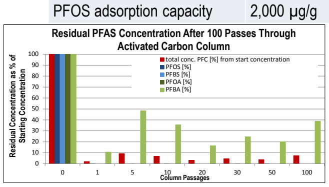
In Situ Soil Treatment Modified Organoclay Sorbent – Results

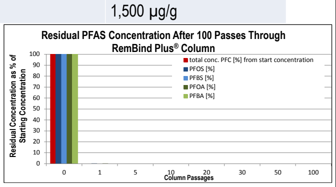




Water Treatment – Aluminum-Based Sorbent/GAC Comparison

	Aluminum Adsorbent	Activated Carbon
Bind short-chain PFAS	High efficiency	Low efficiency [1, 2]
Easy to apply in field	Yes	No
Availability of large volumes	1-2 weeks	1-2 Months
PFOS adsorption capacity	2,000 µg/g	1,500 µg/g





Aluminum-Based Sorbent for GW Case Study – AF Site – Future Work

- Verify amendment sorption capacity
- Optimize dosage to meet EPA Health Advisory
- Monitor effectiveness on short-chain PFAS and PFAA precursors
- Conduct regeneration trials using proprietary wash solutions

Aluminum-Based Sorbent for Full-Scale Soil Treatment Case Study

- Airport contaminated with PFAS
- Replacing asphalt – excavated 900 tons of PFAS-contaminated soil

Aviation Rescue and Fire Fighting Services

Damaged Asphalt

Aluminum-Based Sorbent for Full-Scale Soil Treatment Case Study (cont.)

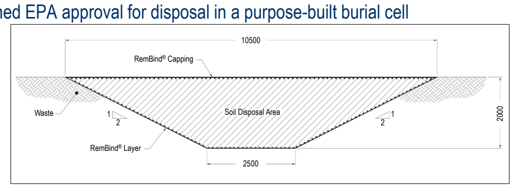
- 900 tons of contaminated soil
- PFOS total concentration <5.7 mg/kg
- PFOS leachable concentration <180 µg/L (by USEPA Method 1311)

Construction of New Apron

PFAS-Contaminated Soil
~900 tonnes

Aluminum-Based Sorbent for Full-Scale Soil Treatment Case Study (cont.)

- Transported 900 tonnes of soil to municipal waste landfill site
- Treated hotspots with 10% RemBind®
- Validated samples at accredited lab
- Obtained EPA approval for disposal in a purpose-built burial cell



Aluminum-Based Sorbent for Full-Scale Soil Treatment Case Study (cont.)

Laying the Amendment Capping Layer

Finished Lined Burial Cell

Aluminum-Based Sorbent for Full-Scale Soil Treatment Case Study (cont.)

- Soil Leachate after Treatment

	Hotspot 1 (µg/L)*	Hotspot 2 (µg/L)*	Compliance Limit (µg/L)*
PFOS	<0.01	<0.01	0.2
PFOA	<0.01	<0.01	
6:2 Fluorotelomer sulfonate	<0.1	<0.1	
8:2 Fluorotelomer sulfonate	<0.2	<0.2	

*Soil leachate concentrations as measured by TCLP at pH 5

- Project Costs

Activity	Approximate Cost (US)	Cost per Ton (900 Tons)
Landfill disposal fees	$63,500	$67
Investigation, bench trials, mixing, and reagent supply	$47,500	$50
Total	**$111,000**	**$117**

Aluminum-Based Sorbent for Full-Scale Soil Treatment Case Study (cont.)

- A water authority in Cape Cod, MA treated soil with amendment in the bottom of an excavation before backfilling to mitigate the risk of PFAS leaching in a drinking water source

Influence of a commercial adsorbent on the leaching behaviour and bioavailability of selected perfluoroalkyl acids (PFAAs) from soil impacted by AFFFs

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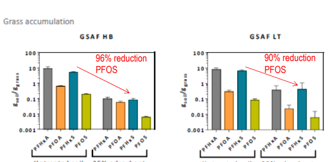
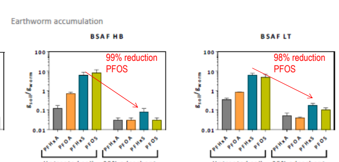
national research centre for environmental toxicology

Entox is a joint venture between The University of Queensland and Queensland Health



- Decreased uptake into wheat grass after application of adsorbent
- Higher accumulation of molecules with shorter carbon chain
- 30-fold decrease in PFOS accumulation for HB soil.



- Higher accumulation of PFHxS and PFOS
- Higher accumulation of longer carbon chain molecules
- Decreased accumulation of all PFAAs after application of 25% adsorbent.

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