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Lessons Learned on Various In-Situ and Ex-Situ PFAS Treatment Technologies

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Overview

- 1. Remediation State of the Practice
 - Soil
 - Water (surface water, groundwater, drinking water)
- 2. Developing Alternatives For Treatment and Wood Updates
 - Soil and water treatment
 - Destruction

Remediation State of the Practice

Commercially available soil remediation options

- Excavation and On or Offsite Encapsulation Proven
 - Effective but expensive, landfill disposal options limited by regulation
- Incineration Proven, but limited facilities
 - Very expensive, generally used on low volumes at high concentrations
- Stabilization Limited full-scale applications
 - RemBind™
 - Powdered reagent Activated carbon, organic matter, and aluminum hydroxide
 - Added at ratio of 1-10% by weight, has shown >98.5% reduction in leaching
 - MatCARETM
 - Modified clay adsorbent
 - pH, clay content and organic content influence PFOS release from soil



Commercially available groundwater remediation options

Most proven options require pump and treat

- Granular Activated Carbon (GAC)
 - Most ubiquitously used for water
- Ion Exchange
 - A potentially cost-effective alternative to GAC
- Reverse Osmosis
 - Effective for a wide variety of PFAS, up to 90% efficient
 - Reject water must be treated separately
- Nanofiltration less proven
 - Effective removal of PFOS when calcium is present
- Foam Fractionation

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Alternatives and Innovative Technologies

Developing treatment and destruction options

- Soil mobilization, recovery and destruction
 - In-situ or ex-situ thermal desorption coupled with VES
 - In-situ liquid carbon
- Groundwater
 - Treatment
 - Non-regenerable ion exchange resins
 - Ozone fractionation
 - In-situ carbon and biochar
 - Regenerable IX resin
 - Destruction
 - Sonification
 - Electrochemical
 - o Plasma





In-Situ Carbon

Case study

Alpena Hide and Leather Case Study –

BioChar Injection and Soil Mixing Pilots at a Former Tannery

- Site setting/history
- Conceptual site model
- Brief description of pilot tests
- Performance metrics

Conceptual site model



Not To Scale

Conceptual site model



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BAM pilot tests



BAM-Ultra[™] Injections:

- Vacuum truck extraction to enhance injections
- Injection pressures of 40 100 psi
- Bottom up injection (2-ft. lifts, 2-10 ft. bgs)
- 100 gallons of 12.4% BAM-Ultra[™] solution injected at 46 intervals/locations (5,300 pounds)
- Variable loading rates based on ROIs
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BAM-XTM Soil Mixing:

- Excavator bucket mixing
- Mixed from surface to 8 ft. bgs (included vadose zone application)
- 1,600 pounds of BAM-XTM
- 1.5% loading rate by mass
- Mixed in place no waste generated

Pilot test - soil results

PFOS in soil at 4 – 5 feet below ground surface

Test	Control	Injection Area	Soil Mixing	
SPLP	122 – 112	74.4 (39%)	36.3 (68%)	(100g)
TCLP	707	68.4 (90%)	35.7 (95%)	acity (meq

Leachate results in ng/L (percent reduction)

Comparison of Organic Carbon to CEC in Granular Soil





Soil mixing pilot test – groundwater results



PFAS	Percent Reduction
PFBA	-13.0
PFBS	77.5
PFHxA	84.2
PFHxS	94.2
6:2FTS	97.7
PFOA	94.7
PFOS	97.5
T-PFAS	88.6

 Hydraulic Conductivity Pre-Test = 11 ft./day Post Test = 0.9 ft./day

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Injection pilot test - groundwater results



Ex-Situ Regenerable Ion Exchange Resin

Case study

Former Pease Air Force Base Case Study – Regenerable Ion Exchange Resin System

- Site setting
- Project development
- Full-scale implementation
- Start-up and operation
- Performance to date

Site setting

- PFOS and PFOA first identified in 2013
- Drinking water impacts confirmed in 2014
- Base-wide investigations started
- Interim actions initiated







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Project development – 2015 bench/pilot testing

- Bench-scale testing identified an IX resin for PFAS removal that could be regenerated
- Wood contracted by the Air Force to perform pilot-scale testing of ECT2's regenerable IX resin and coal-based GAC
- After 6-months of testing and five loading cycles
 - IX resin substantially more effective at PFAS removal
 - IX successfully regenerated



Full-scale implementation - design



Full-scale implementation - construction



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Full-scale implementation – treatment process



Pretreatment bag filters & GAC









Full-scale implementation – regeneration process



Regeneration skid





Still bottoms and superloader

Distiller



Start-up and operations





Start-up and operations - regeneration

Sample Location	PFOS (µg/L)	PFOA (µg/L)
P-7200 Effluent - Regenerant Recovery Pump (Distiller Influent)	25	16
Superloader 1 inlet (Still Bottoms)	540	220
Post Superloader 1	0.19	0.010 U
Post Superloader 2	0.12	0.010 U
Post Superloader 3	0.086	0.010 U
T-7420 Influent - Distallate Purifier	0.50	2.9
T-7420 Effluent - Distillate Purifier #1	0.015 U	1.1
T 7430 Effluent - Distillate Purifier #2	0.015 U	0.010 U



Destruction Technology

Wood - ongoing research and development

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

<u>Awarded:</u> "Combined In-Situ/Ex-Situ Treatment Train for Remediation of PFAS Contaminated Groundwater"



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

<u>Awarded</u>: "Removal and Destruction of PFAS and Co-Contaminants from Groundwater"







Ongoing R&D – PFAS destruction via PLASMA

- Work presented by Clarkson University at Battelle Remediation Conference, May 2018.
- Enhanced contact, low energy plasma reactor for two applications
 - Treatment of investigation derived waste low C aqueous solutions
 - Treatment of still bottom waste from regenerable IX high C brine solution
- Technology demonstrated for IDW (discussed in the following slides)
- Technology under development for still bottoms two R&D projects starting now for SERDP and ESTCP

Prototype Plasma Reactor for high C PFAS Inventors: Mededovic and Holsen, Clarkson University



On-going R&D – PLASMA for PFAS destruction

- Plasma is an ionized gas consisting of a quasi-neutral mixture of neutral species, positive ions, negative ions, and electrons.
- Electrical discharge plasma formed *directly in* or *above* water makes use of OH radicals to oxidize and aqueous electrons to chemically reduce organic and inorganic compounds.
- Benefits of plasma-based water treatment:
 - Physical effects such as generation of ultraviolet-range radiation (UV), shockwaves capable of inducing cavitation, and high temperatures capable of thermally decomposing molecules.
 - No chemical additives are required.
 - Wide variety of reactive chemical species (OH, eaq-, e-, O, H, H2O2, O2, HO2).



Pictures: Plasma Research Laboratory, Clarkson University



Plasma formation



Plasma summary

- Emerging as a viable technology
 - Proven field demonstration (high C still bottom PFAS treated to ND)
 - Study results expected November 2019.
- Potentially applicable for:
 - Destruction of regenerant waste
 - IDW destruction
 - Not for continuous flow at this time
- More efficient and is relatively unaffected by the presence of co-contaminants.
- Mechanisms of PFAS destruction involves electrons and plasma (argon) ions.
- Market availability next step (mobile unit available)

Potential no-waste solution



Treatment of high C still bottom waste

Courtesy of: Plasma Research Laboratory, Clarkson University





Lessons Learned

Lessons Learned

- In-situ Carbon
 - Biochar effectively reduced PFAS in groundwater
 - Biochar has less sorption of short chain carboxylic acids
 - Soil ion exchange capacity may have as much or more effect on PFAS sorption than fraction of organic carbon
 - Soil mixing biochar had favorable results when evaluating with long term leaching test
- Ex-situ Regenerable IX Resin
 - Biggest challenge was iron fouling at front end of plant
 - GAC can be a workhorse
 - Fire protection can drive project costs and logistics for regeneration technology
- Plasma Destruction
 - No commercially available onsite destruction technologies
 - Developing treatment technologies show promise for greater removal capacity and potential onsite application.





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Questions?

Thank you! For more information:

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Thank you to Collaborators: David Woodward - Wood Nathan Hagelin - Wood Rob Singer – Wood Len Mankowski - Wood



- 1. http://www.cdc.gov/healthcommunication/risks/index.html
- 2. <u>http://www.who.int/risk-communication/en/</u>
- 3. <u>http://www.npr.org/sections/thetwo-way/2016/08/09/489369852/federal-</u> <u>data-shows-firefighting-chemicals-in-u-s-drinking-water-sources</u>
- 4. <u>https://papers.ssrn.com/sol3/papers.cfm?abstract_id=988342</u>
- 5. <u>https://emergency.cdc.gov/cerc/resources/templates-tools.asp</u>

Injection pilot test - groundwater results



Injection pilot test - groundwater results



Case study

Camp Grayling Case Study -

Colloidal Activated Carbon in a Low Centration PCE Plume

- Site setting
- Conceptual site model (injection area)
- Brief description of pilot test
- Performance metrics/mechanisms

Conceptual site model

- Former fire training area
- Bulk fuel area
 - Pump and treat system in place
 - Previous hydrogen release compound (HRC) injections
- Compounds in groundwater
 - Historically SVOCs
 - Low level PCE (<10 ug/L)
- PFAS detected 2016
 - T-PFAS 228 ng/L
 - PFOS 110 ng/L
 - PFOA 6 ng/L

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- Shallow groundwater
 - Shallow Groundwater
 - Aquifer primarily sand
 - Depth to water: 14-15 feet
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2018 PlumeStop[™] injection pilot

- PlumeStop[™] injected October 2018
- Nine locations on 5-foot centers.
- 2400 lbs. ea. of PlumeStop[™] & PlumeStop Stout[™] (8-10,000 mg/L; ~ 750-1,000 gallons/pt)
- Bottom-up application (1-ft. to 3-ft. lifts; 14-26 ft. bgs)
- Injection pressures/flow rates up to 90 psi at 8 gpm



Camp Grayling Airfield – soil results

- Physical testing:
 - *f_{oc}* increased slightly
 - No significant change in CEC
 - No apparent correlation of CEC to *f*_{oc}
 - Pre-/post-injection slug test results relatively unchanged (Remains Fast!)



Time series results

- Baseline
 - PFOS = 70/40 ng/L
 - PFHxS = 60/50 ng/L
 - PFPeA = 10 ng/L (deep)
 - PCE = 8.28/3.12 ug/L
- October 2018 (4 weeks)
 - No PFAS detected (shallow and deep downgradient wells)
 - PCE = 1.22 ug/L (shallow)
 - PlumeStop[™] spreading
- March 2019 (~ 6 months)
 - PFOS = 9.6 ng/L in shallow downgradient well (~50 ft.)
 - PCE detected in shallow wells at 25 and 50 ft. downgradient
 - PlumeStop[™] no further downgradient expression



Start-up and operations



Relative PFAS Component in Influent

PFOS		PFHxS	6:2 FTS	PFOA	[PFH	PFHxA	P
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Start-up and operations



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Next steps

- Complete ongoing column studies
- Refine media selection criteria
- Operate/optimize non-regenerable IX system
- Continue site-specific evaluations
- Optimize plasma destruction on high C still bottoms
- Complete SERDP and ESTCP projects



Potential no-waste solution

Treatment of high C still bottom waste

