Removal of Short Chain PFAS via GAC Adsorption

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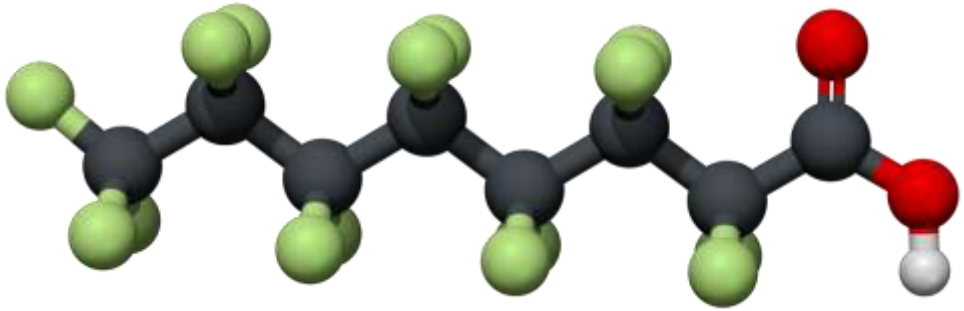
Agenda

- Perfluoroalkyl Substances (PFAS)

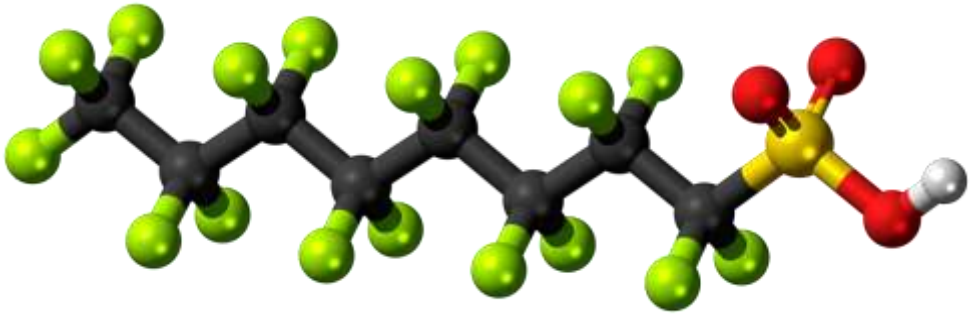
- Granular Activated Carbon (GAC)
  - PFAS treatment history
  - Base Material
  - Testing

- Treating PFAS with GAC
  - PFAS removal data
    - Long & short chain PFAS
    - Comparing different GAC
    - Lab vs. full scale performance
    - Reactivation

PFAS Molecular Characteristics



PFOA Molecule



PFOS Molecule

- Chemically Stable
  - C-F Bond
- High Molecular Weight
- Low Vapor Pressure
- Easily infiltrates into groundwater and soil
- Easily absorbs into organisms
- Resistant to oxidation, biodegradation, and air stripping

EPA-Recognized Contaminant

In May 2016 the EPA established a Health Advisory Exposure limit for PFOA and PFOS at 70 ppt concentration (combined limit).

Granular Activated Carbon

GAC is a Proven Technology

The safest way to treat water is to ***remove*** harmful compounds

- No unnecessary chemical addition
- No concentrated waste stream

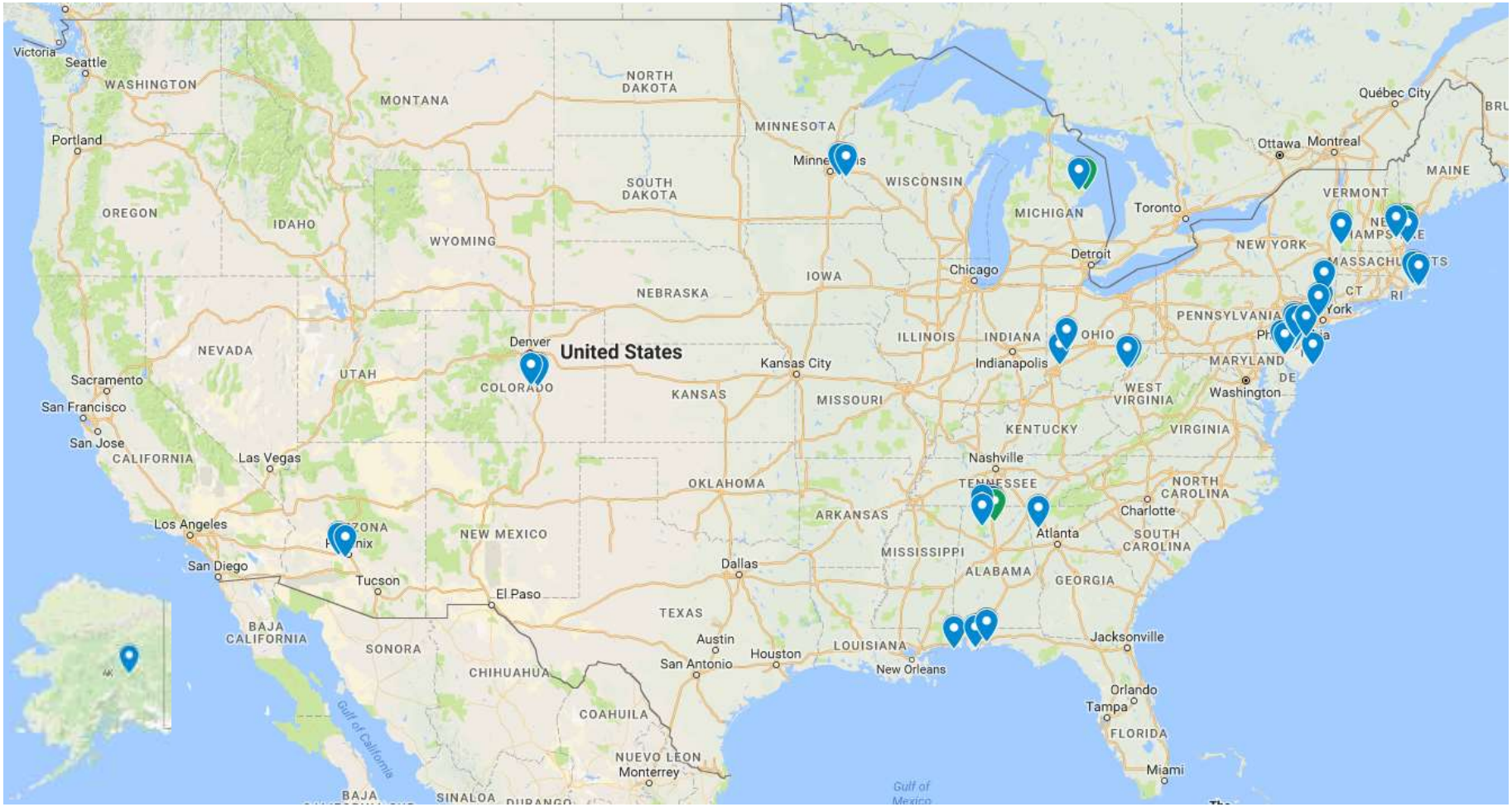
GAC is the leading technology for removal of PFAS from groundwater

- Effective for PFAS removal in drinking water and remediation applications
- Chosen since 2001 for PFAS removal in over 45 large installations and over 1,000 POE systems

Spent GAC containing adsorbed PFAS can be reactivated

- Eliminates future liability for the contaminant
- Safe, sustainable, environmentally responsible
- GAC is recycled and reused

Calgon Carbon PFAS Treatment Locations

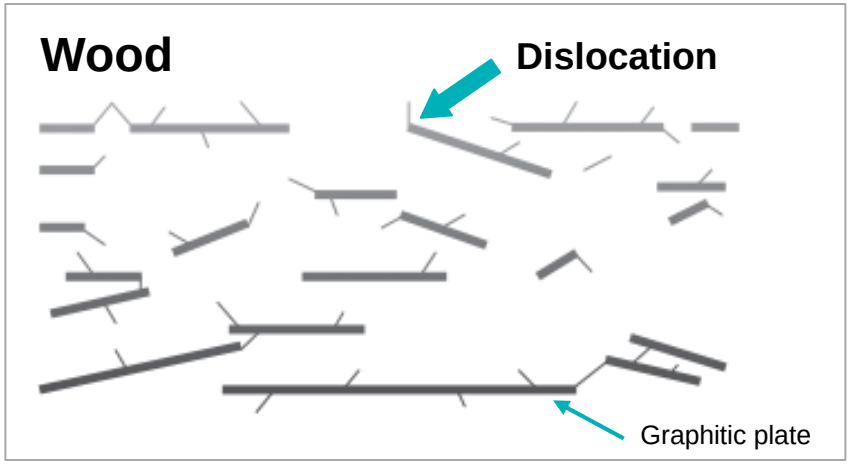


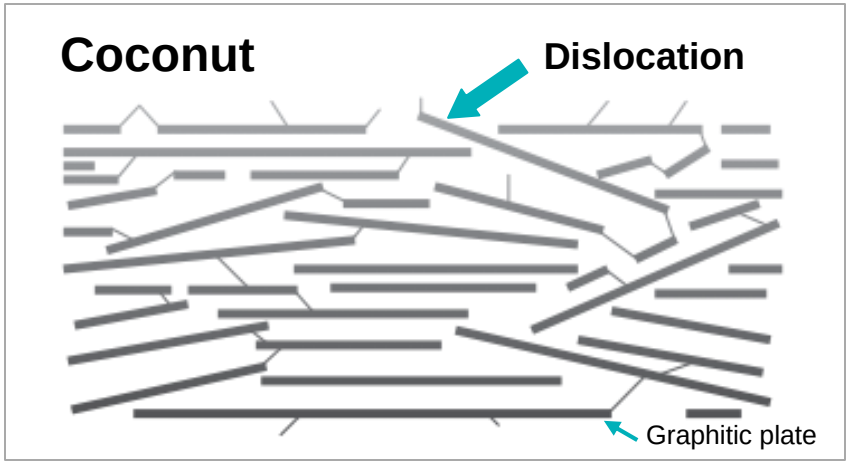
45+ Installations Across the U.S.

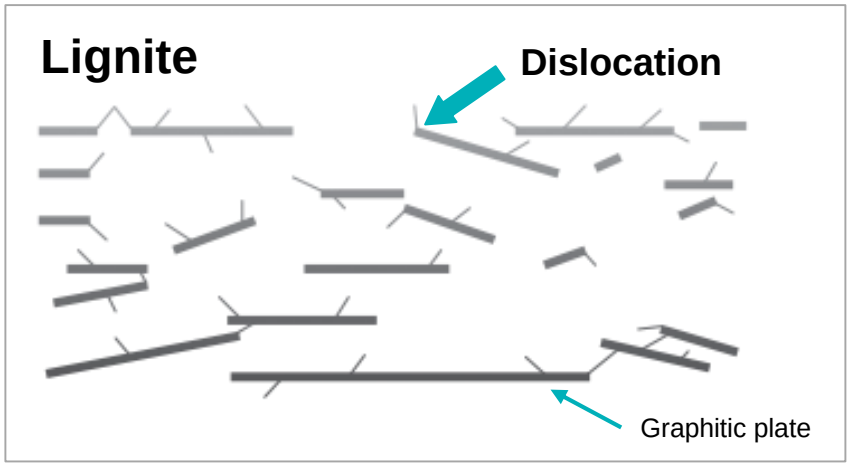
How does GAC differ?

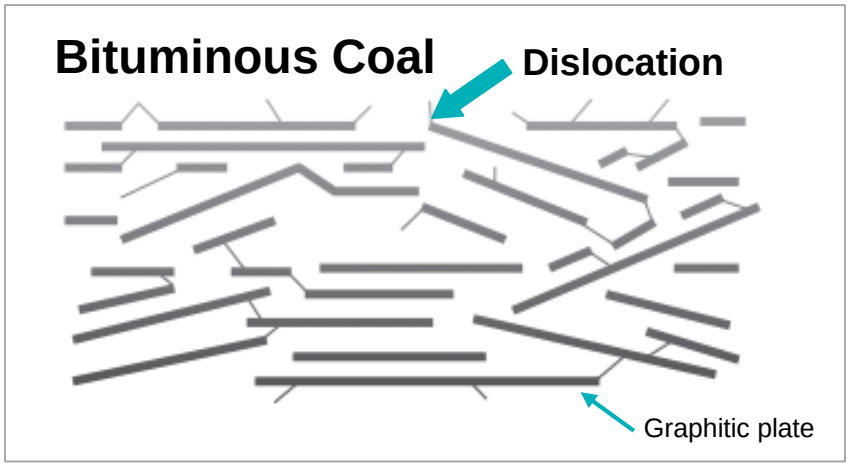
Starting Materials

Starting Materials









Starting Materials

Raw material dictates all of the product possibilities

- Ash impurities
- Density
- Hardness
- Adsorption capacity
- Adsorption kinetics

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Testing is Critical

Why

- Many factors influence the effective service life of GAC
  - Temperature
  - pH
  - EBCT
  - Concentration
  - Competitive Adsorption
- Extremely difficult to quantify without testing

Objectives

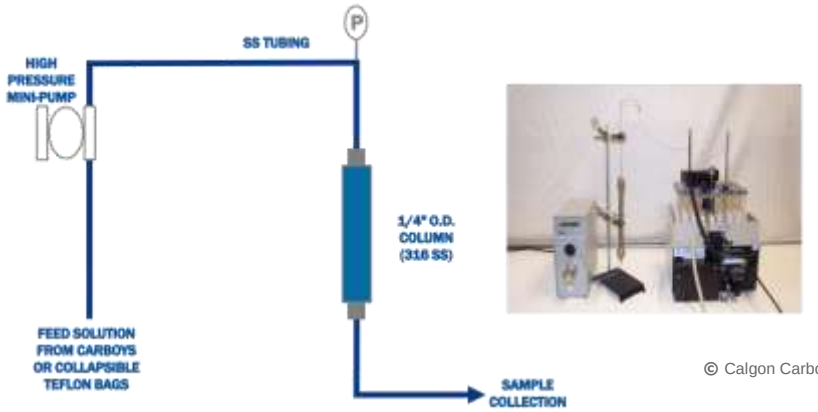
- **Application Research**
  - Best GAC for the application
  - Design recommendations
- **Customer Specific**
  - Feasibility
  - Exchange frequency

Methods

- **Column Testing (ACT or RSSCT)**
  - Define the kinetics of adsorption or minimum contact time required
  - Define accurate carbon use rates impacted by competitive adsorbing compounds

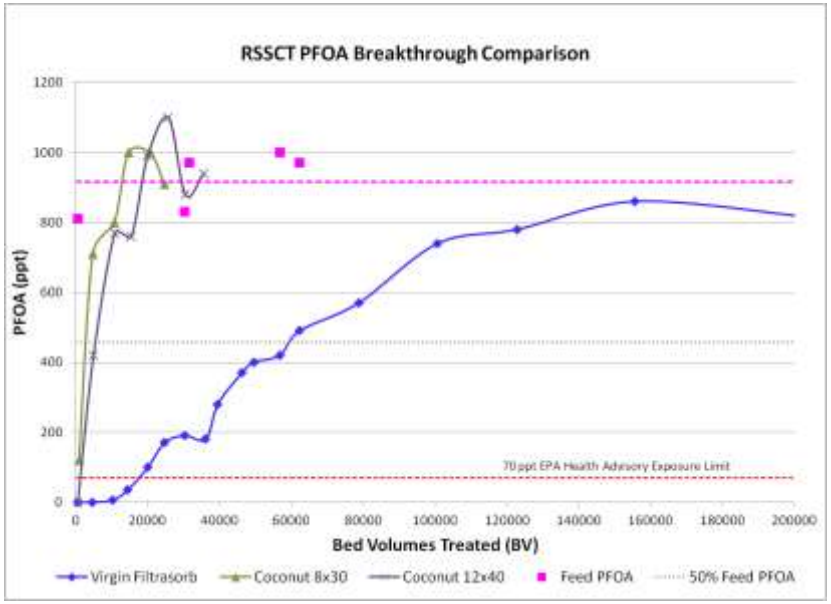
Bench Scale Column Tests

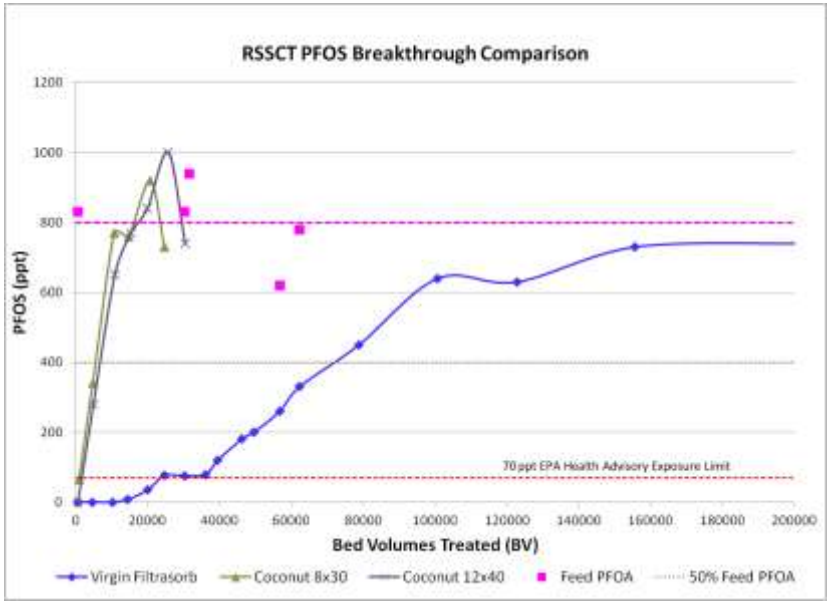
- **Accelerated Column Test (ACT)**
  - Calgon Carbon developed test
  - Scaled to hydraulically simulate Empty Bed Contact Time (EBCT) and superficial velocity of full scale system
  - Scaling factors are experimentally determined
  - Used to estimate CUR for full scale system
- **Rapid Small Scale Column Test (RSSCT)**
  - ASTM D6586 Bench Scale Column Test
  - Scaling factors assume constant or proportional diffusivity
  - Relative comparison between carbons

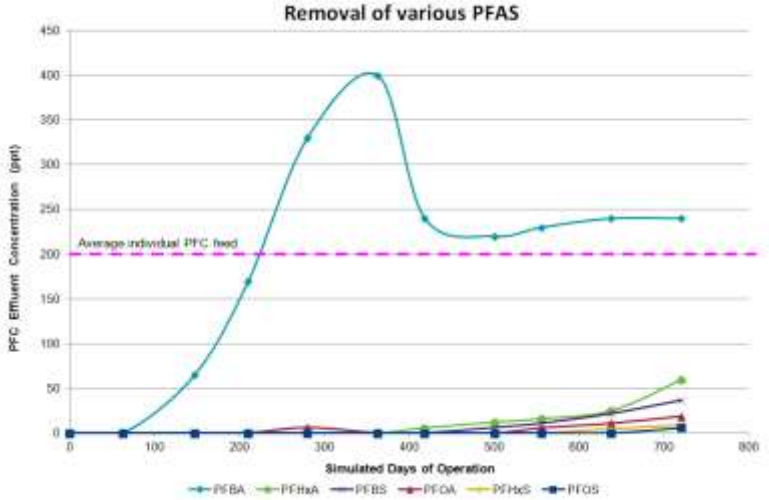


Carbon Comparison for PFAS Removal

Summary of Test Data from Work







Research RSSCT Study:
Comparison of GAC Types for PFOA and PFOS Removal

- Four GAC products marketed for PFOA/PFOS treatment were evaluated under identical operating conditions and influent water quality

Carbon	Apparent Density, Oven (g/cc)	Ash (%)	Iodine Number (mg/g)
Reagglomerated Bituminous	0.561	7.8	999
Lignite	0.377	12.4	616
Enhanced Coconut	0.414	4.1	1291
Enhanced Coconut (Blend)	0.388	6.9	1070

Research RSSCT Study:

Comparison of GAC Types for PFOA and PFOS Removal

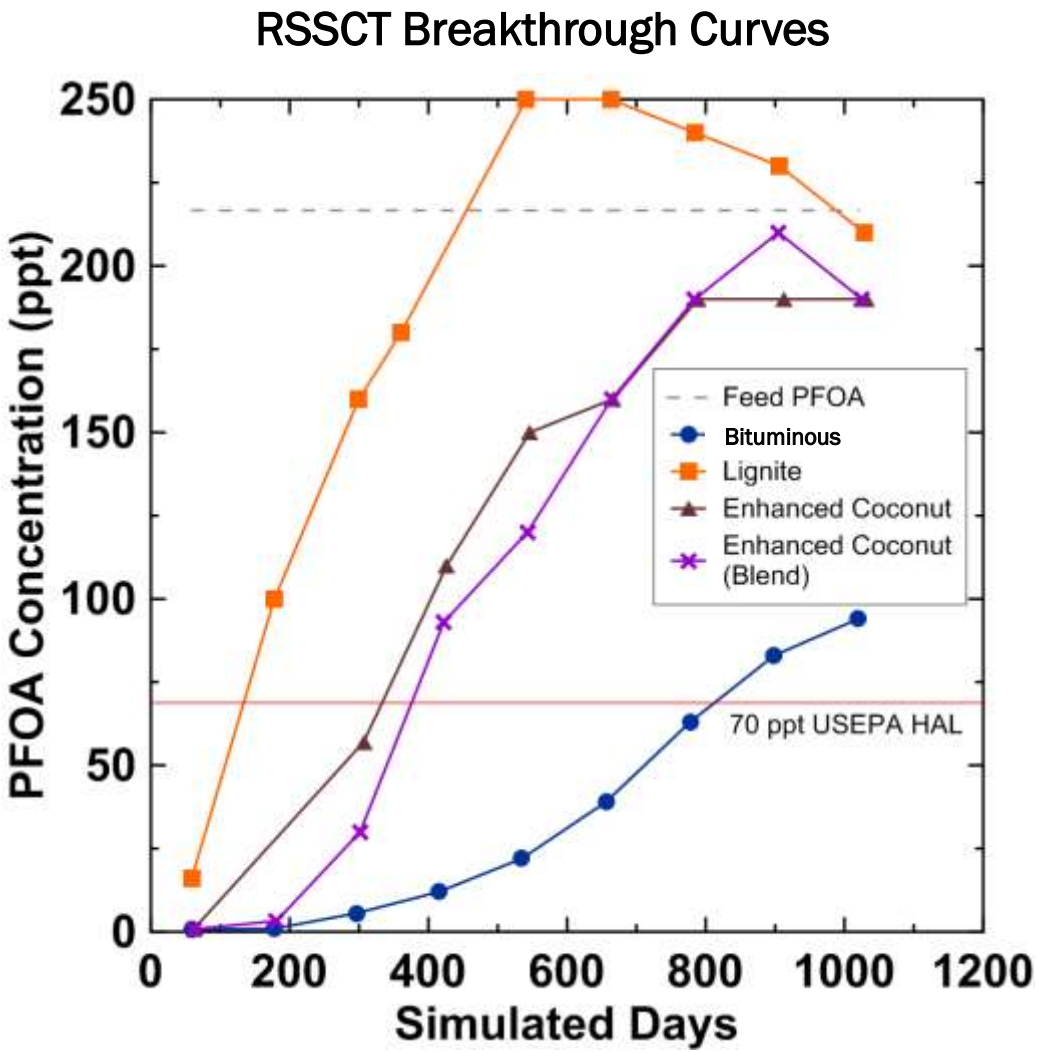
- Multiple PFAS, variety of chain lengths
  - Each compounds spiked to approximately 200 ppt

Name	Abbreviation	CAS Number	Carbon Chain Length	Molecular Weight (g/mol)
Perfluoro octanesulfonic acid	PFOS	1763-23-1	C8	500.13
Perfluoro octanioc acid	PFOA	335-67-1	C8	414.07
Perfluorohexanesulfonic acid	PFHxS	355-46-4	C6	400.11
Perfluoro hexanoic acid	PFHxA	307-24-4	C6	314.05
Perfluoro butanesulfonic acid	PFBS	375-73-5	C4	300.1
Perfluoro butanoic acid	PFBA	375-22-4	C4	214.04

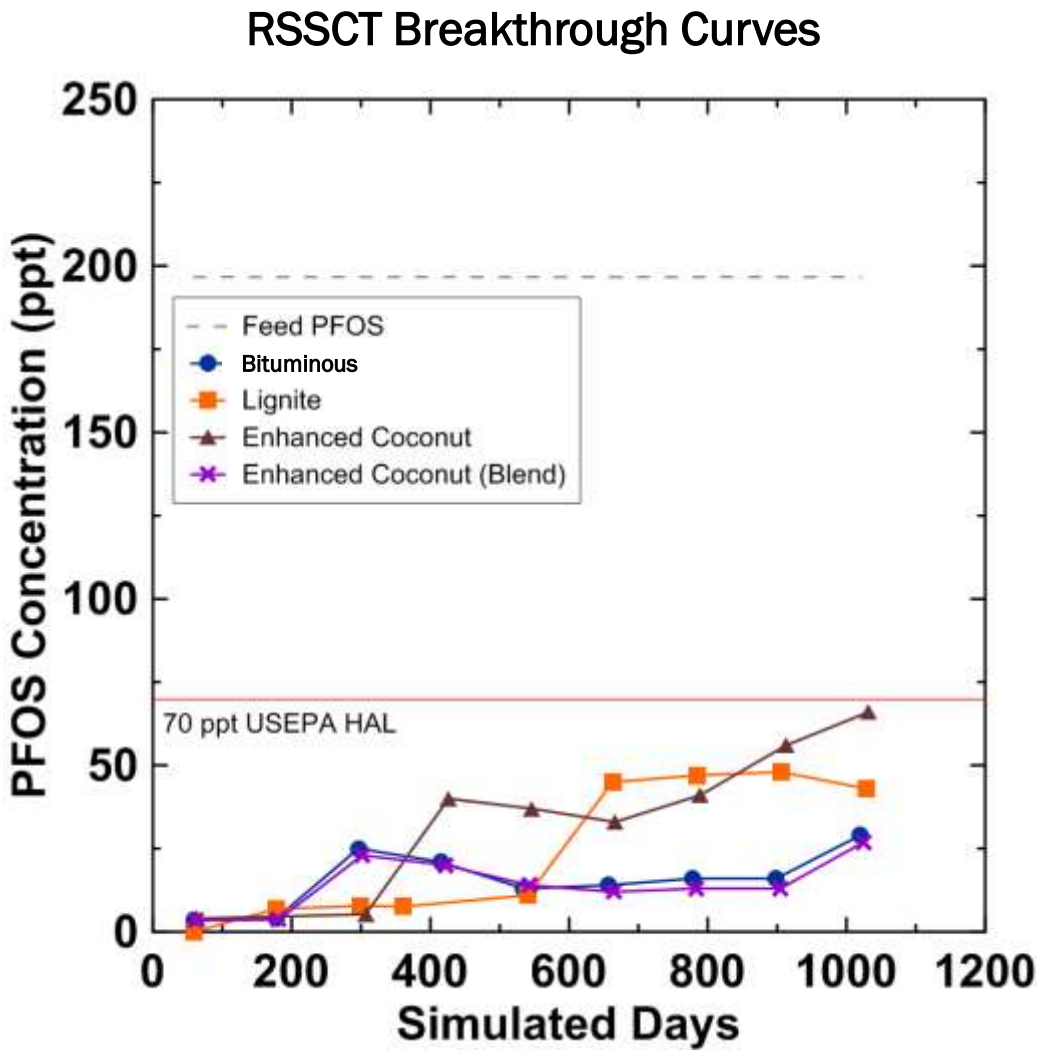
- Background TOC – 0.16 ppm

- Simulated EBCT – 10 minutes

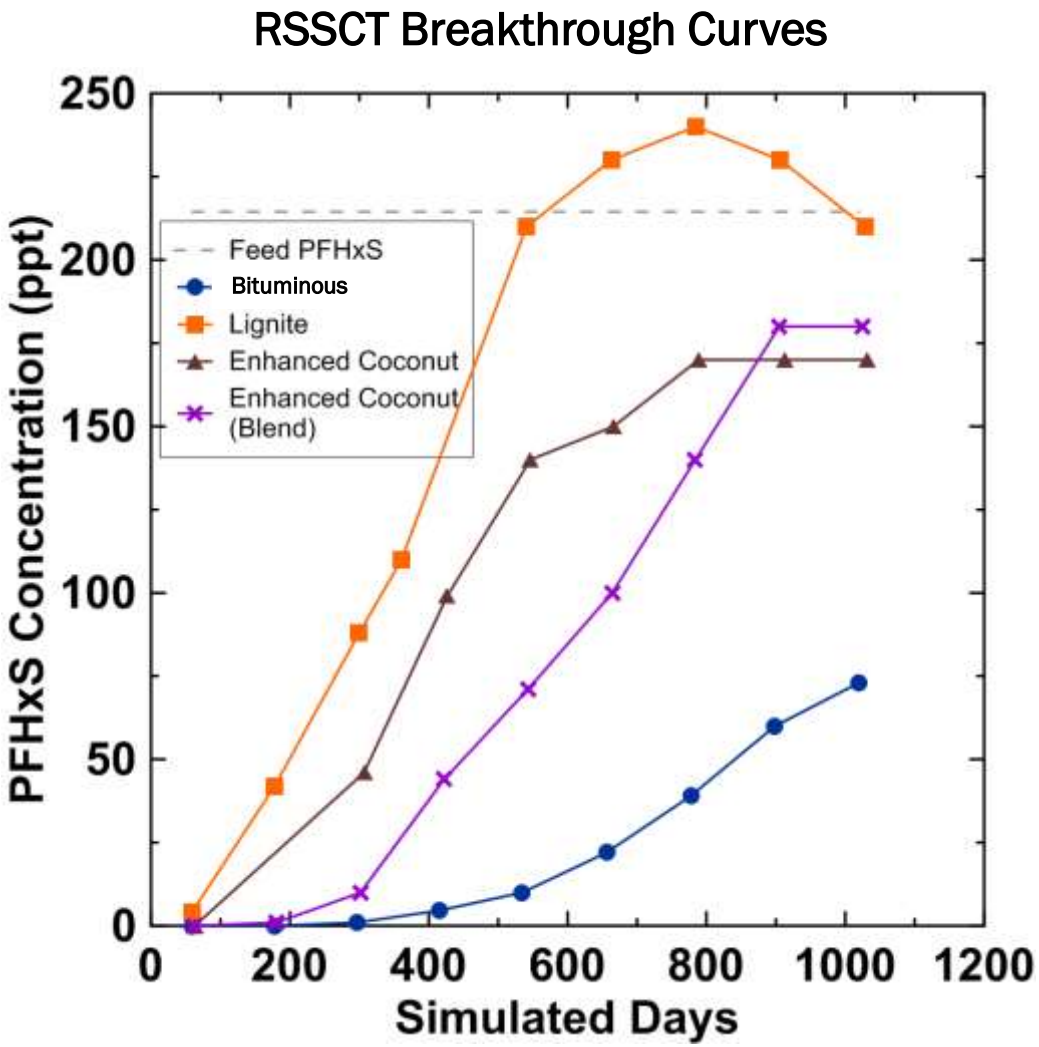
PFOA Removal vs Simulated Days



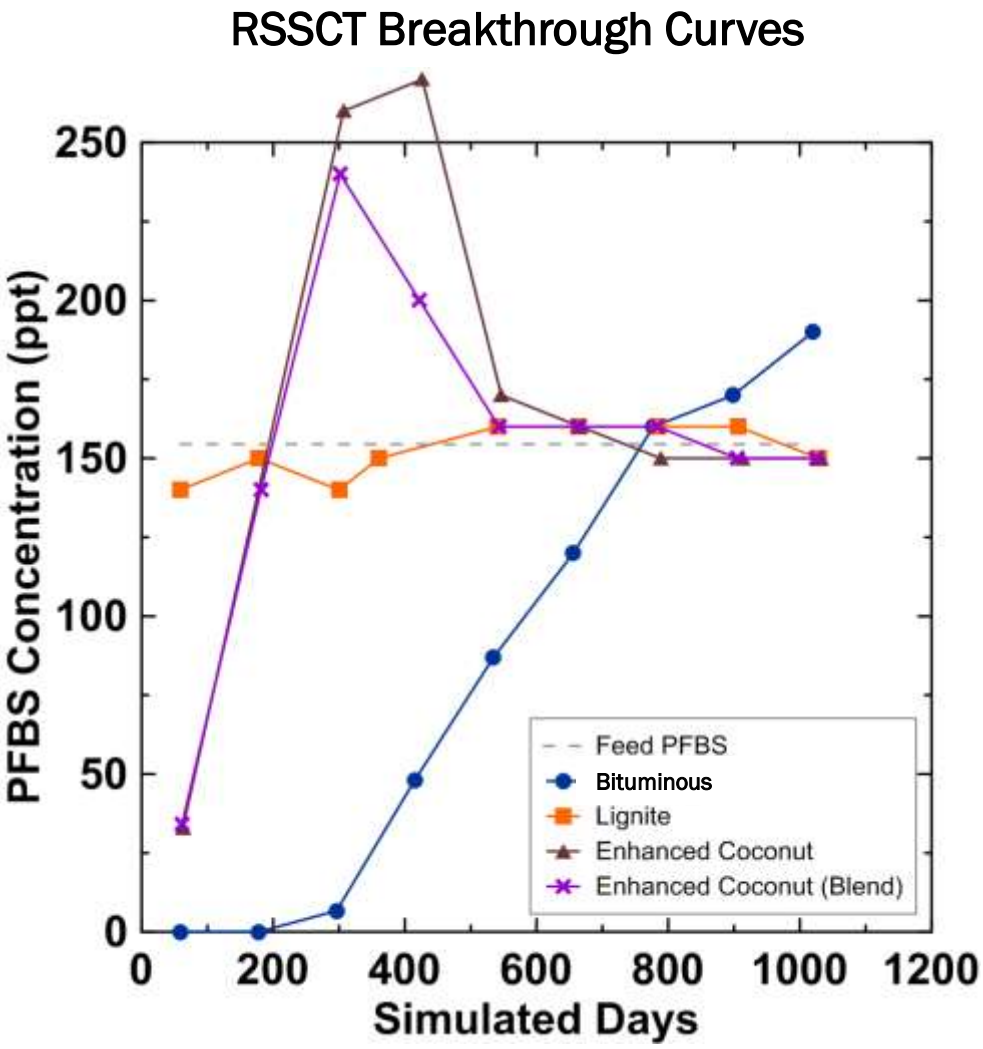
PFOS Removal vs Simulated Days



PFHxS Removal vs Simulated Days



PFBS Removal vs Simulated Days



Conclusions:

Reagglomerated bituminous coal is preferred product type

- Re-agglomerated bituminous coal GAC significantly outperformed:
  - Lignite
  - Enhanced Coconut
  - Enhanced Coconut (Blend)

GAC was still effective for the shorter chain compounds (C4, C6)

- Able to remove PFBS and PFHxS to non-detect
- Breakthrough occurred very quickly for Lignite and both Enhanced Coconuts
- Rapid PFBS breakthrough observed for Lignite and both Enhanced Coconuts

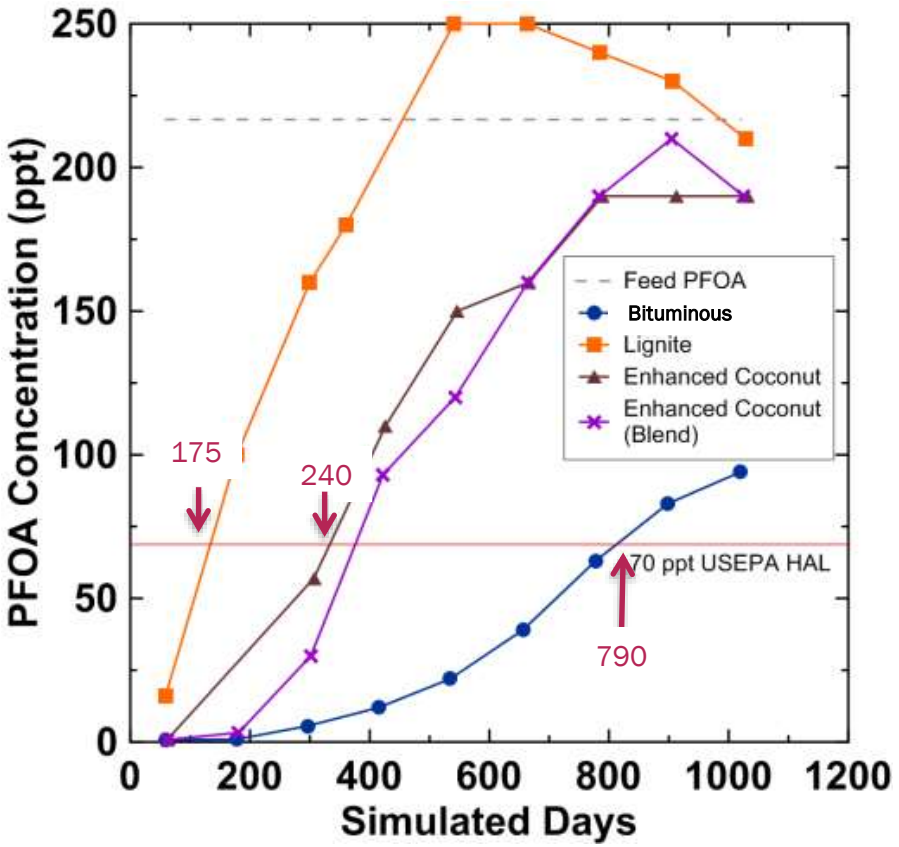
Understanding Cost: Performance Impacts

Hypothetical Economic Analysis

- Treatment Objective:
  - PFOA <70 ppt HAL
- Factors considered:
  - Performance by each material using results of study
  - Density difference
  - Carbon cost ($/lb)

Let's look at what the "total cost" for each option would be using assumed market pricing….

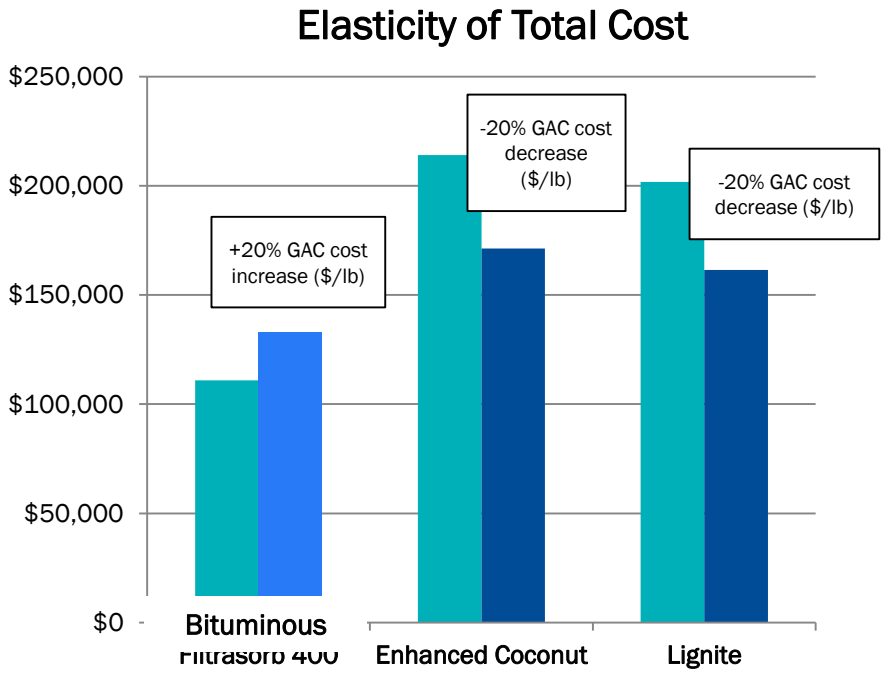
RSSCT Breakthrough Curves



Total Cost of Ownership Comparison

	Reagglomerated Bituminous	Enhanced Coconut	Lignite
# of days online	1,095 (3 years)	1,095 (3 years)	1,095 (3 years)
# of Exchanges (in period)	1.38	4.56	7.30
Total Cost Impact *	$113,617	$223,011	$216,126
$/1,000 gallons*	$0.14	$0.28	$0.27

*Based on Model 10 System, field service not included



Conclusions

- Performance will have a significant impact on total cost
- Lowest *GAC cost ($/lb)* doesn't mean the lowest *lifecycle cost*
- Testing with representative source water is **ALWAYS** recommended to better understand future costs and optimize system design

Unit Cost ($/lb)

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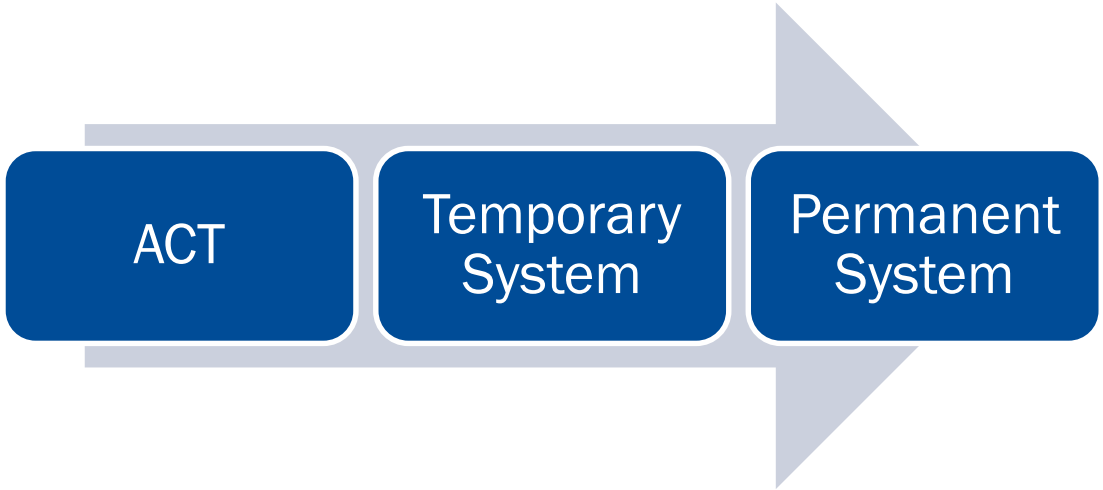
Total Treatment Cost

Case Study

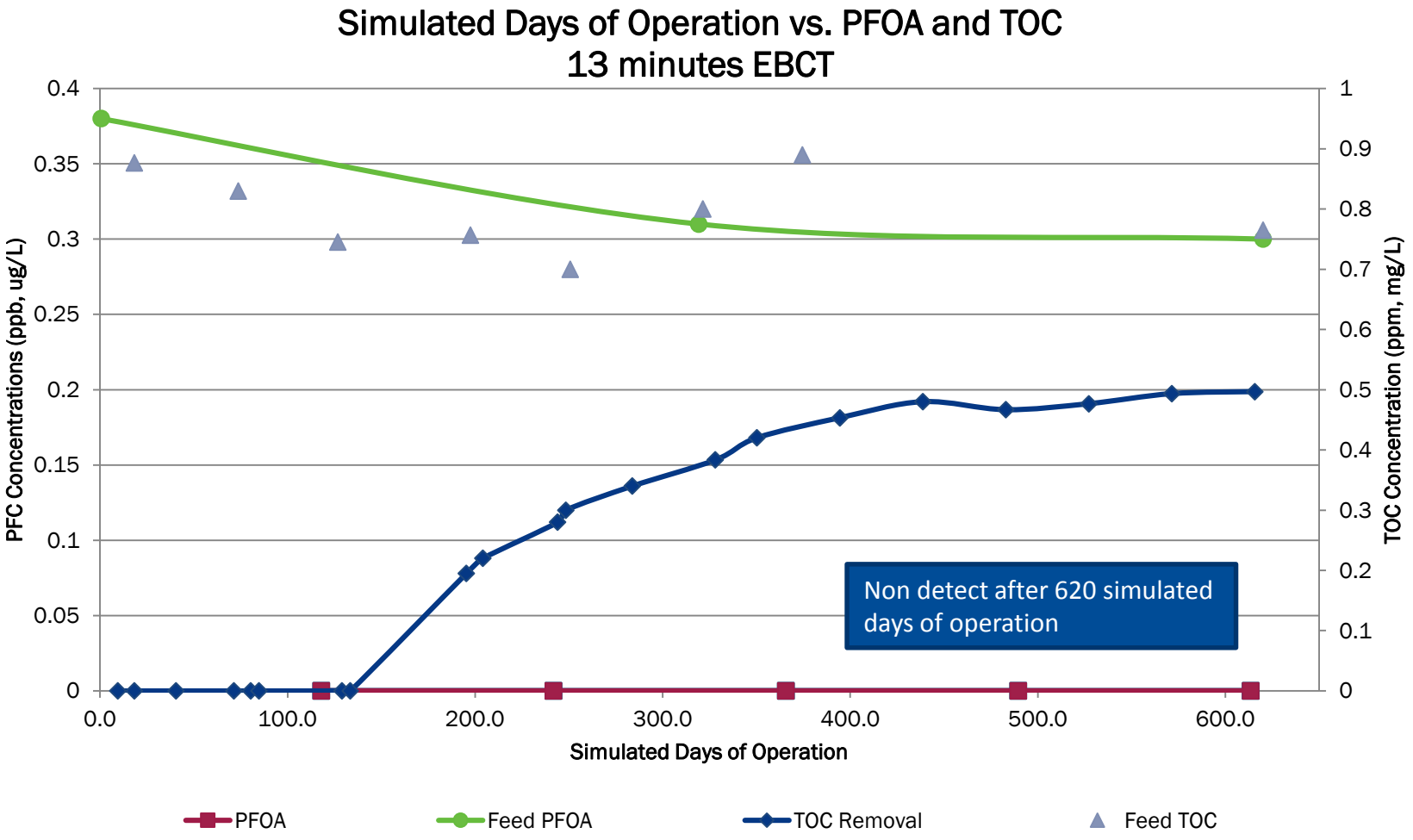
Municipal Case Study

- Municipality in NY encounters PFOA in drinking water

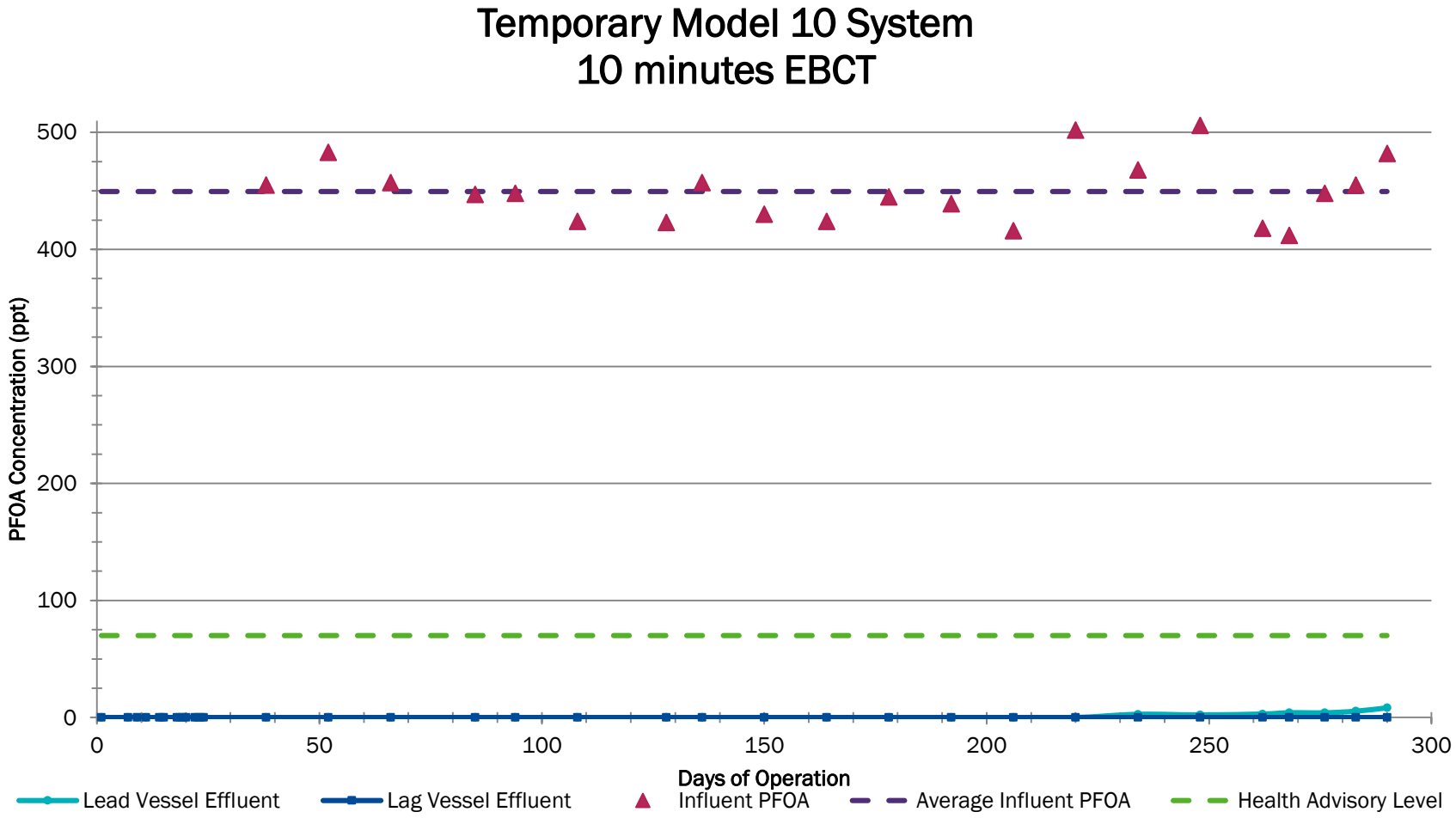
- ACT column test
  - Determine efficacy of proposed treatment system
    - 2 vessels, lead-lag operation
    - 40,000 lbs GAC per vessel
    - 13.2 minutes EBCT



ACT Data

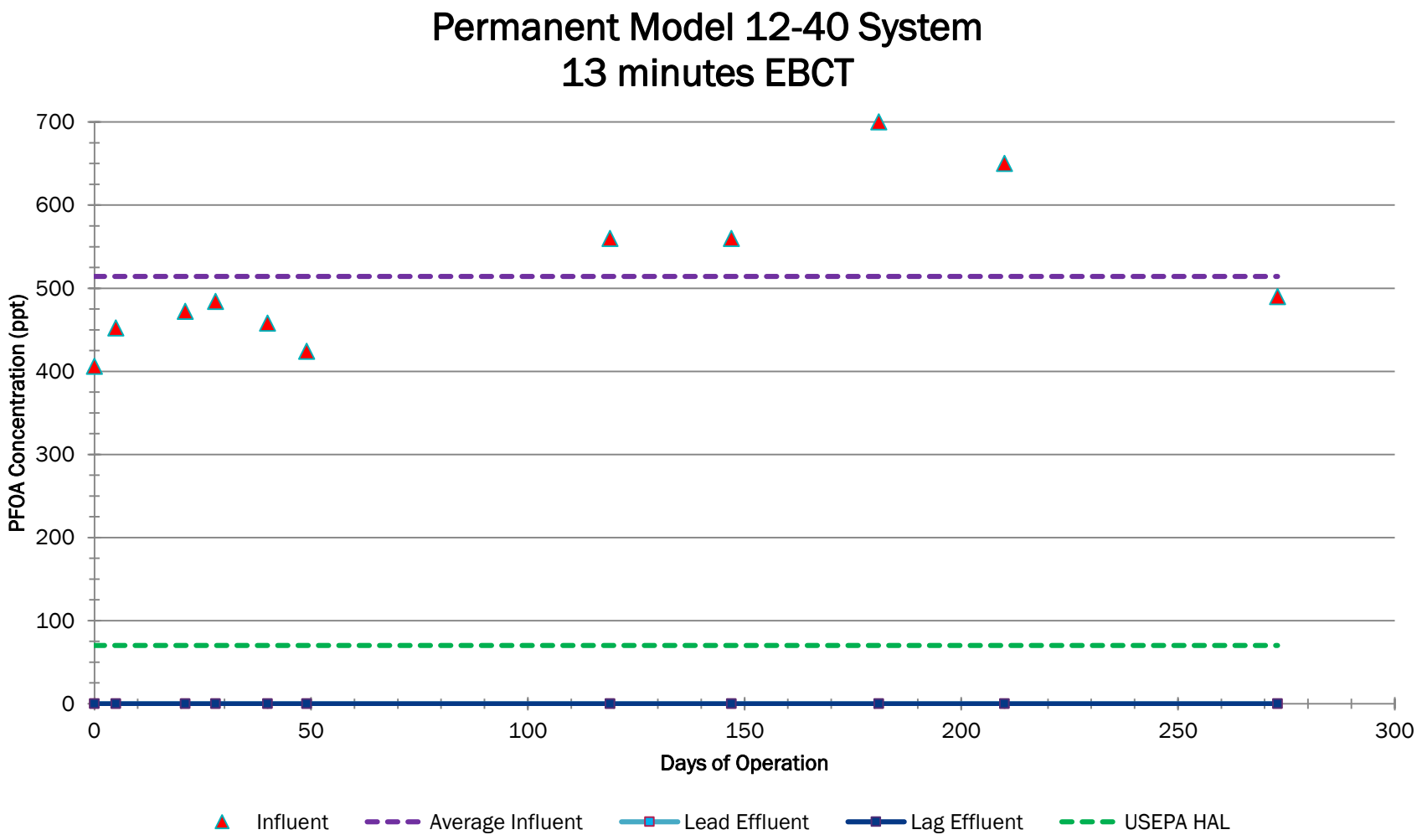


Customer Field Data



Customer Field Data

ACT | Temporary System | Permanent System



Effectiveness of Reactivation

What is Reactivation?

- Granular activated carbon has a finite bed life until the treatment objective is no longer reached
- Reactivation is a process to restore the entirety of GAC's adsorption capacity
- The process is carried out at reactivation centers throughout the world
- Generally, Industrial GAC furnaces reach temperatures up to 1800°F
- Adsorbed material is thermally destroyed and further treated through a series of abatement technologies

R&D Study: Effectiveness of Reactivation

Experimental Design & Results

		PFAS Customer – CMR @ NT Plant React	PFAS Customer – Lab React 700°C	PFAS Customer – Lab React @ 1100°C
PFBA	*ppt*	1.9	1.3[J]	1.6[J]
PFPeA	*ppt*	<0.43	<0.42	<0.43
PFHxA	*ppt*	<0.51	<0.50	<0.50
PFHpA	*ppt*	<0.22	<0.21	<0.22
PFOA	***ppt***	**<0.75**	**<0.73**	**<0.74**
PFNA	*ppt*	<0.24	<0.23	<0.23
PFDA	*ppt*	<0.27	<0.27	<0.27
PFUnA	*ppt*	<0.97	<0.95	0.96[J]
PFDoA	*ppt*	<.049	<0.47	<0.48
PFTriDA	*ppt*	<1.1	<1.1	<1.1
PFTeA	*ppt*	<0.26	<0.25	<0.25
PFBS	*ppt*	<.18	<0.17	<0.17
PFHxS	*ppt*	0.23[JB]	0.22[JB]	0.26[JB]
PFHpS	*ppt*	<0.17	<0.16	<0.17
PFOS	***ppt***	**<0.48**	**<0.46**	**<0.47**
PFDS	*ppt*	<0.28	<0.28	<0.28

CMR Spent treating ppt levels PFAS
Lab React Spent treating ppb levels PFAS

Leach Test Procedure:

- Load reactivated carbon into columns
- Backwashed for ~8 BV with NSF42 water (50 ppm TDS, 0.5ppm Cl^-, pH 6.75)
- Soak 24 hours.
- Sample 1 BV.
- Repeat two more times compositing all 3 samples
- Analyze for PFAS per EPA 537

B: Compound was found in blank
J: Result is less than the RL but greater than or equal to the MDL and the concentration is an approximate value

Summary

Final Takeaways

GAC is effective and proven for removal of PFAS	• Long and short chain
Not all GAC is created equal	• Reagglomerated bituminous coal GAC is the preferred product type • Field and lab data corroborate superior performance
Testing required to accurately predict service life	• Column > Isotherm • Performance impacts cost

Thank you!

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