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Ion exchange resin for PFAS removal and pilot test comparison to GAC

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Abstract

Amec Foster Wheeler and Emerging Compounds Treatment Technologies, Inc. tested pilot-scale *ex situ* treatment technologies for treatment of poly- and perfluorinated alkyl substances (PFAS) in groundwater. The pilot test compared ion exchange resin to granular activated carbon (GAC) and evaluated in-place regeneration of the resin to restore PFAS removal capacity. During the pilot test, both resin and GAC removed perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) below U.S. Environmental Protection Agency (USEPA) health advisories (HAs) of 0.070 micrograms per liter (μg/L) combined. Compared at a common empty bed contact time (EBCT) of five minutes, the resin treated over eight times as many bed volumes (BVs) of groundwater as GAC before PFOS exceeded the USEPA HA and six times as many BVs for PFOA. On a mass-to-mass basis, resin removed over four times as much total PFAS per gram as GAC before breakthrough was observed at the USEPA HA. A solution of organic solvent and brine was used to regenerate the resin in the lead vessel, which had treated water up to the point of PFOS and PFOA breakthrough exceeding the USEPA HAs. The pilot test demonstrated successful in-place regeneration of the resin to near-virgin conditions. The regenerated resin was then used to treat the contaminated groundwater up to the same breakthrough point. Compared to the virgin resin loading cycles, PFAS removal results for the regenerated resin were consistent with virgin resin.

1 | INTRODUCTION

As part of the Air Force Civil Engineering Center's (AFCEC's) ongoing poly- and perfluorinated alkyl substances (PFAS) response activities at a former Air Force Base in New England, Amec Foster Wheeler contracted and worked with Emerging Compounds Treatment Technologies, Inc. (ECT) to evaluate pilot-scale *ex situ* treatment technologies for treating PFAS in groundwater at an Installation Restoration Program site. The historical use of aqueous film forming foam (AFFF) during fire-fighting training activities at the site contaminated groundwater with PFAS. Site groundwater must be remediated to meet U.S. Environmental Protection Agency (USEPA) health advisories (HAs) for perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) of 0.070 micrograms per liter (μg/L) combined (USEPA, 2016a, 2016b).

Amec Foster Wheeler selected two technologies for pilot testing to support the design of a groundwater treatment plant at the site: ECT's Sorbix A3F ion exchange and adsorption resin and Calgon Carbon Corporation's (Calgon) Filtrasorb 400 (F400) granular activated carbon (GAC). Pilot test objectives included the following:

- demonstrate that both Sorbix A3F resin and F400 GAC can remove PFAS below achievable laboratory quantification limits and, therefore, USEPA HAs for PFOS and PFOA;
- determine the breakthrough curves and removal capacities for PFAS in both Sorbix A3F resin and F400 GAC; and,
- demonstrate in-place regeneration of Sorbix A3F resin to near-virgin PFAS removal performance.

Before proceeding with a discussion of pilot test operations and results, the following sections summarize how anion exchange resin works for PFAS removal.

1.1 | How anion exchange resins remove PFAS

Anion exchange resins can effectively remove PFAS from water because of the molecular structure of most PFAS compounds and the dual removal mechanisms of ion-exchange and adsorption in anion exchange resin. These complementary properties increase the PFAS removal capacity of anion exchange resins compared to strictly adsorption media (Nickelsen & Woodard, 2017).

The molecular structure of most PFAS compounds can be broken into two functional units: the hydrophobic, nonionic "tail," consisting of the fluorinated carbon chain, and the anionic "head," having a negative charge. Exhibit 1 shows the structure of a PFOS molecule.

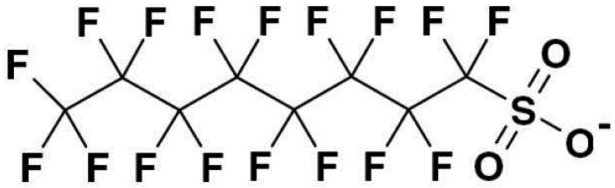

Exhibit 1 Molecular structure of PFOS molecule

Anion exchange resins are essentially adsorbents with ion exchange functionality. The resin beads are composed of neutral copolymers (plastics) that have positively charged exchange sites. Exhibit 2 shows the basic structure of an anion exchange resin, with its neutral, hydrophobic backbone, divinylbenzene cross links, and positively charged exchange sites.

The hydrophobic carbon-fluorine tail of a typical PFAS molecule adsorbs to the hydrophobic backbone and/or cross links on the resin, and the negatively charged head of the PFAS molecule is attracted to the positively charged ion exchange site on the resin (Nickelsen & Woodard, 2017).

1.2 | Considerations for PFAS removal by anion exchange resin

The PFAS removal effectiveness of individual resins varies based on multiple factors (Deng et al., 2010; Dudley, 2012). For example, the PFAS capacity of some resins depends on the inorganic content of the water, including both the type and concentration of ions in solution. Other resins are less sensitive to inorganic ions, as these resins have greater affinity for the PFAS molecules than for the inorganic ions. Given resin specificity and the variable nature of PFAS-contaminated water, bench-scale column testing is recommended to determine the most effective resin for a specific application.

Although the majority of PFAS compounds have an anionic charge, some PFAS molecules are cationic, and others are zwitterionic, having both a positive and negative electrical charge. Given the wide variety of both cationic and anionic exchange resins, ion exchange resins hold significant promise for future research as the field of PFAS remediation develops.

1.3 | Regeneration of anion exchange resins used for PFAS removal

While this dual mechanism of PFAS removal by ion exchange and adsorption can effectively remove PFAS from water, it also makes resin regeneration and reuse challenging. A brine solution can be used to effectively desorb the anionic head of the molecule from the resin ion exchange site, but the hydrophobic carbon-fluorine tail tends to stay adsorbed to the resin backbone. Similarly, an organic solvent, like methanol or ethanol, can be used to effectively desorb the hydrophobic tail, but then the anionic head of the PFAS stays attached to the resin ion exchange site.

Research to date demonstrates that effective regeneration techniques must address both mechanisms of attraction, ion exchange and adsorption. For example, certain surfactants that have both nonionic and anionic properties have shown promise for use in regenerant solutions. Solutions combining organic solvents and sodium chloride have

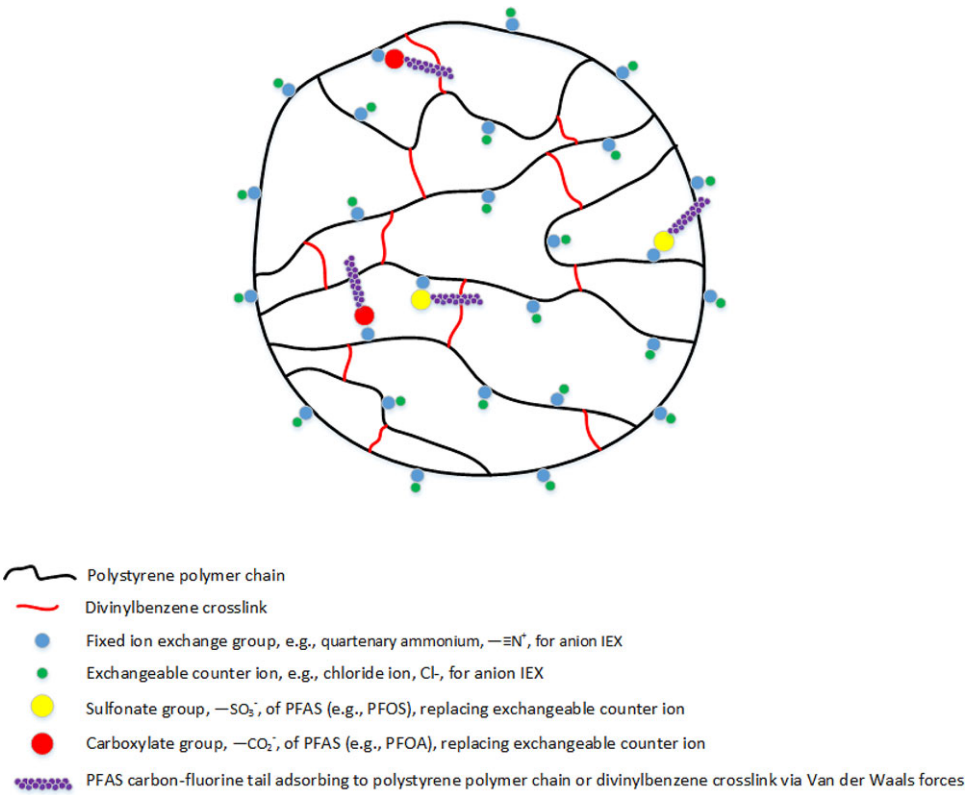

Exhibit 2 Molecular structure of a typical anion exchange resin

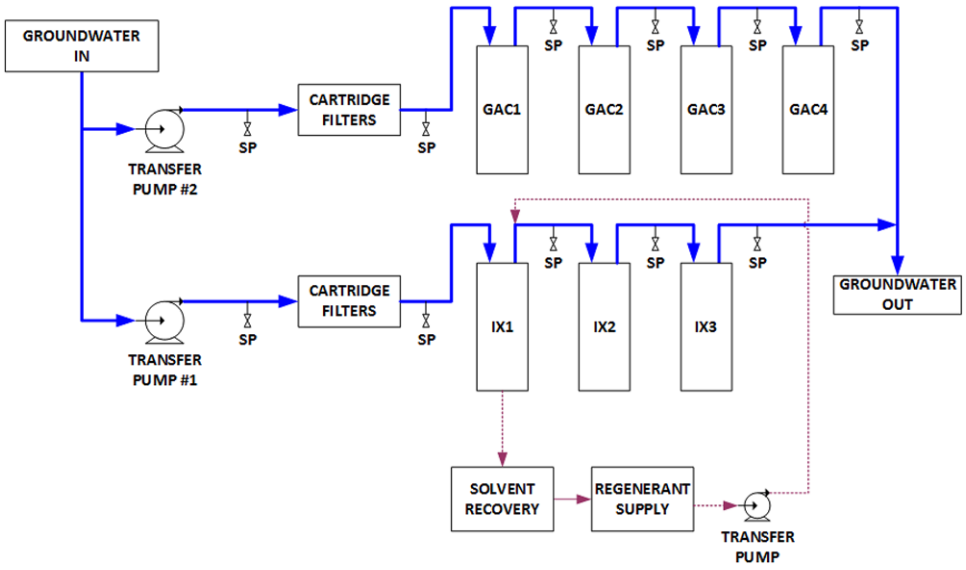

Exhibit 3 Pilot test process flow diagram

produced the most successful results to date (Chularueangaksorn, Tanaka, Fujii, & Kunacheva, 2013; Deng et al., 2010). Other research has focused on using combinations of ammonium salts, including ammonium hydroxide and ammonium chloride (Conte, Falletti, Zaggia, & Milan, 2015). Du et al., 2014 disclosed a need to further treat the resulting waste regenerant solution to concentrate the PFAS and minimize the volume of waste.

The remainder of this article presents a case study describing a pilot test conducted to compare the treatment effectiveness of resin and GAC PFAS-removal systems, test proprietary regeneration methods to restore resin capacity to near-virgin conditions, and test methods to further concentrate the PFAS and minimize the volume of waste.

2 | PILOT TEST MEANS AND METHODS

Calgon specified four GAC vessels in series, each containing 1.2 cubic feet (CF), or 9 gallons, of Filtrasorb 400 GAC. Each vessel provided a 5-min empty bed contact time (EBCT), for an overall EBCT of 20 min. Samples were collected weekly for eight weeks, with downstream vessel samples only analyzed if sample results from upstream vessels showed breakthrough.

ECT specified three resin vessels in series, each containing 1.2 CF (9 gallons) of Sorbix A3F resin, with each vessel providing a 2.5-min EBCT, for an overall EBCT of 7.5 min. Samples were collected routinely, with downstream vessel samples only analyzed if sample results from upstream vessels showed breakthrough.

Sample collection and handling followed Amec Foster Wheeler standard operating procedures. PFAS samples were analyzed by a modified USEPA Method 537 method using liquid chromatography/tandem mass spectrometry.

Pilot test equipment was installed in an existing groundwater treatment plant building. The process flow diagram in Exhibit 3 shows the two parallel pilot test process units. Exhibits 4, 5, 6, and 7 show photographs of the fabrication and installation of pilot test equipment at the plant.

Exhibit 4 Existing treatment plant equipment before connections

Exhibit 5 GAC prefilters, vessels, and piping fully installed

2.1 | GAC operations summary

The GAC system was loaded continuously during the pilot test to evaluate breakthrough with a few interruptions from plant shutdowns. The GAC process operated as follows:

Exhibit 6 Resin vessels and piping fully installed

Exhibit 7 Overall pilot test setup

1. GAC process water was pumped from the existing groundwater extraction network through two cartridge filters to prevent particulate matter from fouling the GAC.
2. The GAC system pump operated at approximately 1.8 gallons per minute (gpm) to provide the desired 5-min EBCT per vessel.
3. PFAS samples were collected at the influent and each sample port twice during Week 1 and weekly through Week 8. Downstream samples were only analyzed if upstream samples showed breakthrough of PFOS or PFOA.
4. The GAC system was planned to operate in this way for eight weeks unless otherwise recommended by Calgon, based on analytical results. The GAC process ended operation as planned.

The GAC process treated a total volume of 100,486 gallons of water, or 11,165 bed volumes (BVs), through the lead vessel. No changes to the GAC process equipment or operating parameters were made during its operation. No operational issues affected GAC performance aside from temporary and brief shutdowns of the existing plant.

2.2 | Resin operations summary: First loading cycle

Resin pilot test activities included an initial loading cycle to evaluate virgin resin removal capacity for PFAS and subsequent alternating cycles of resin loading and regeneration to evaluate the effectiveness of regenerating spent resin. The first loading cycle operated as follows:

1. the resin system pump operated at approximately 3.6 gpm to provide the desired 2.5-min EBCT per vessel;
2. resin process water was pumped from the existing groundwater extraction network through two cartridge filters to prevent particulate matter from fouling the resin; and
3. PFAS samples were collected routinely at the influent and the effluent sample ports, allowing for flexibility in the loading cycle schedule depending on observed results.

The resin process treated 422,645 gallons of water, or 46,961 BVs through the lead vessel during the first loading cycle. The first resin

EXHIBIT 8 PFAS influent concentrations

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**

loading cycle operated longer than planned due to the resin's higher than expected capacity at removing PFOS. This cycle was extended to observe and better understand the breakthrough curve for PFOS.

3 | PILOT TEST RESULTS

Exhibit 8 summarizes the range of influent PFAS concentrations observed during the pilot test. Exhibit 9 compares PFOA breakthrough curves for GAC and resin vessels during the first loading cycle. Exhibit 10 shows similar data for PFOS. Exhibits 11 through 22 compare breakthrough curves for observed PFAS compounds at the common 5-min EBCT for each media.

The final GAC sample of the first loading cycle showed approximately 69 percent breakthrough of total detected PFAS was achieved through the lead vessel (5-min EBCT), compared to influent sample results. This coincided with approximately 71 percent breakthrough of PFOA and approximately 50 percent breakthrough of PFOS.

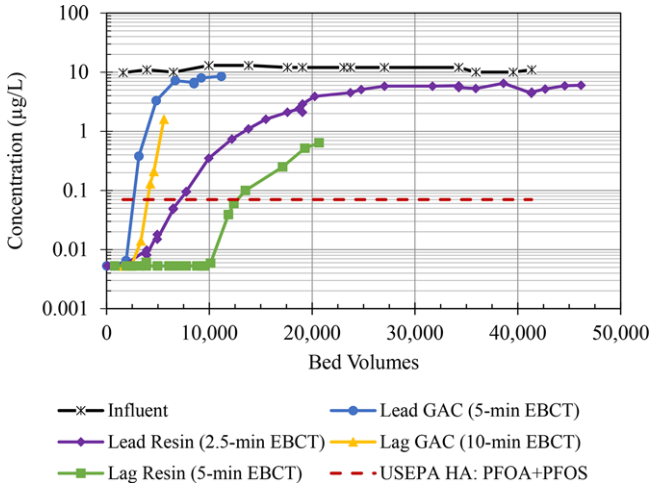

Exhibit 9 GAC and resin breakthrough curves—PFOA

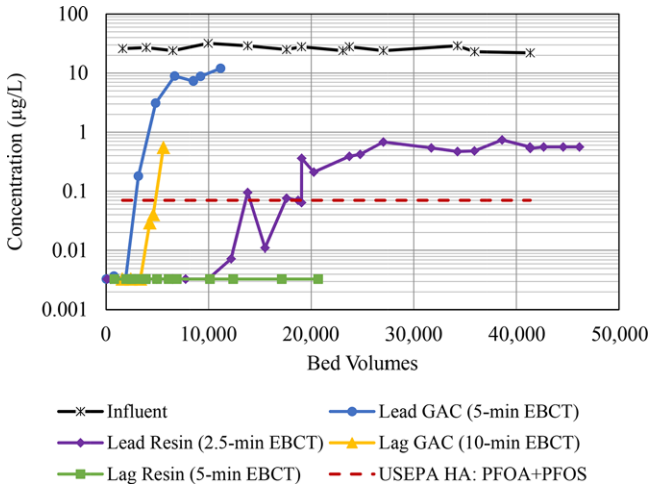

Exhibit 10 GAC and resin breakthrough curves—PFOS

The final resin sample of the first loading cycle showed approximately 40 percent breakthrough of detected PFAS through the lead vessel (2.5-min EBCT), compared to influent sample results. This coincided with approximately 50 percent breakthrough of PFOA and approximately 3 percent breakthrough of PFOS.

3.1 | Pilot test operations and analytical results for resin regeneration

To evaluate the resin's ability to be regenerated, three regeneration trials were conducted throughout the pilot test using a proprietary regeneration procedure with a solution of organic solvent and brine. The objective for each regeneration was to restore the PFAS treatment capacity of the lead vessel's resin to the approximate capacity of virgin resin.

The first and second regenerations were experimental and did not restore the resin to virgin capacity based on postregeneration samples. Lessons learned from the first two regenerations were applied to

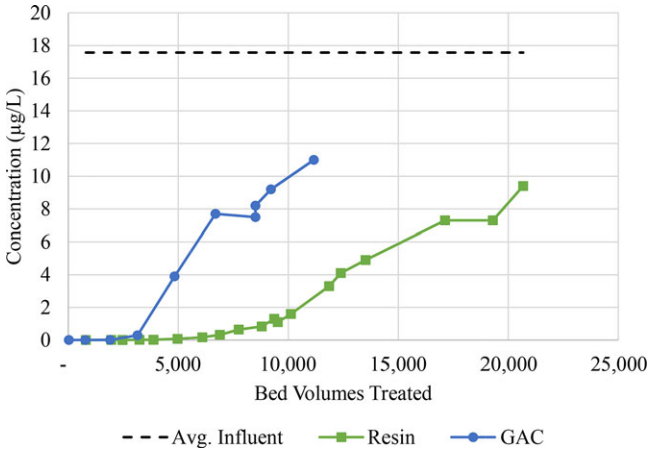

Exhibit 11 6:2 Fluorotelomer sulfonate breakthrough curve at 5 min EBCT

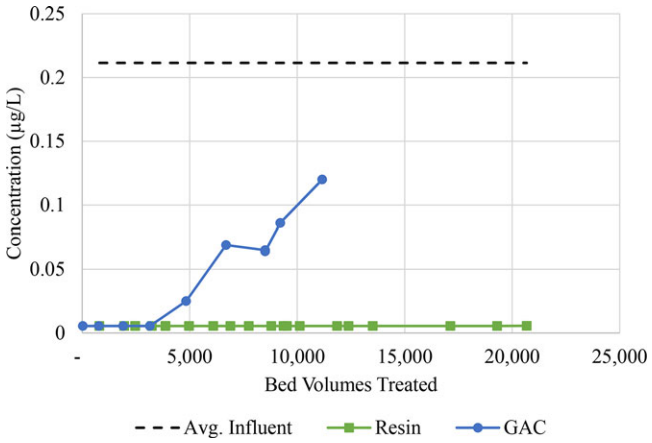

Exhibit 12 8:2 Fluorotelomer sulfonate breakthrough curve at 5 min EBCT

develop the third (proprietary) regeneration procedure, summarized below, which effectively regenerated the resin column to near-virgin conditions:

1. The lead resin was changed out and filled with virgin resin, then reloaded with PFAS. This loading cycle continued until total flow through the vessel reached the point of expected breakthrough at the HA limit.
2. Process water in the vessel was purged with 1 BV of 10 percent brine solution to prime the resin for desorption of PFAS compounds.
3. Ten BVs of regenerant were pumped through the resin in countercurrent flow, that is, entering from the effluent port on the vessel and discharging through the influent port.
4. After the 10 BVs of regenerant were pumped through, 10 BVs of potable water was used to rinse the bed in countercurrent flow.
5. After the potable water rinse was complete, the resin vessel was returned to service for a final loading cycle to confirm if the regeneration was successful.
6. Samples were collected through the regeneration procedure to evaluate the desorption characteristics of the regeneration process

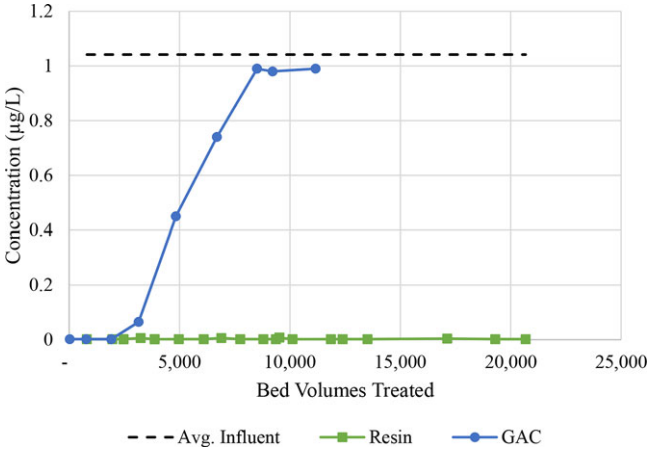

Exhibit 13 Perfluorobutane sulfonate (PFBS) breakthrough curve at 5 min EBCT

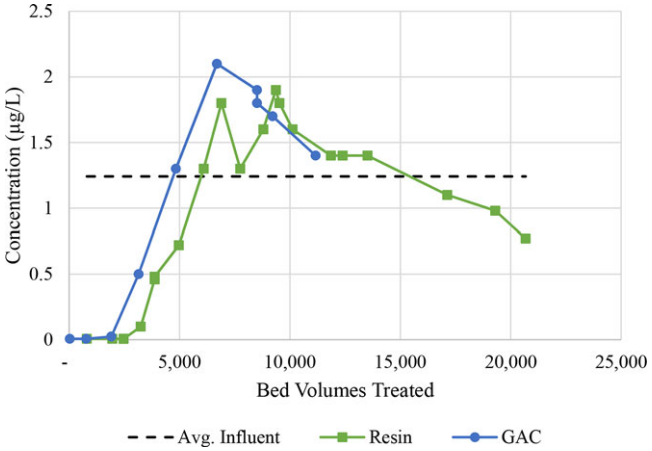

Exhibit 14 Perfluorobutanoic acid (PFBA) breakthrough curve at 5 min EBCT

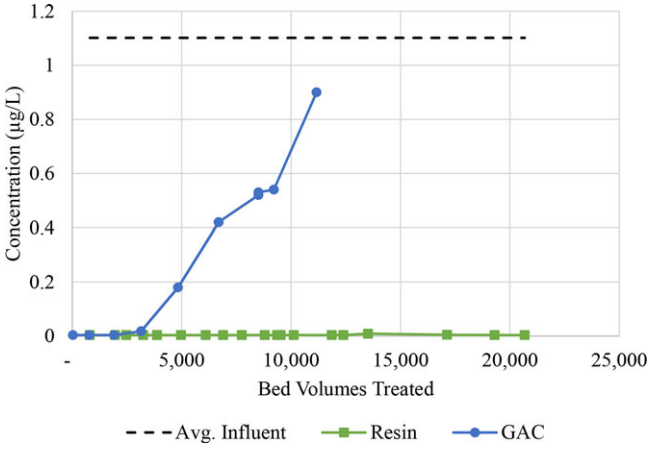

Exhibit 15 Perfluoroheptane sulfonate (PFHpS) breakthrough curve at 5 min EBCT

3.2 | Second virgin resin loading cycle operations and results

The resin in the lead resin vessel was replaced virgin resin and continued to operate at 2.5-min EBCT. This second virgin loading cycle treated 124,293 gallons (10,951 BVs) of groundwater. This loading

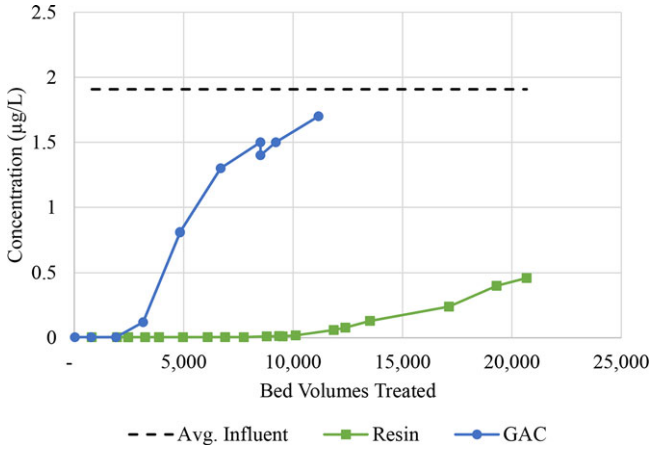

Exhibit 16 Perfluoroheptanoic acid (PFHpA) breakthrough curve at 5 min EBCT

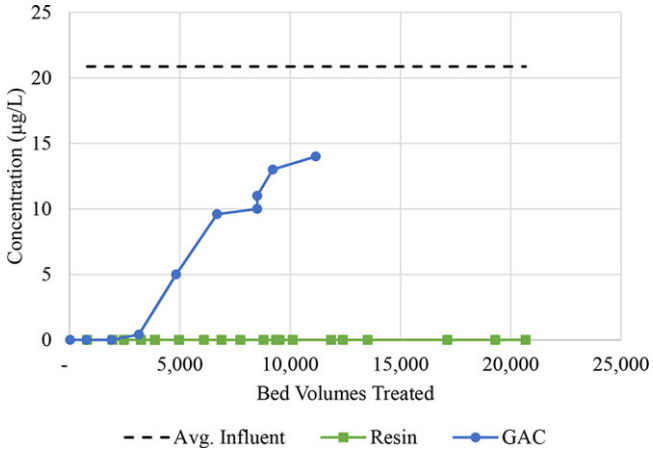

Exhibit 17 Perfluorohexane sulfonate (PFHxS) breakthrough curve at 5 min EBCT

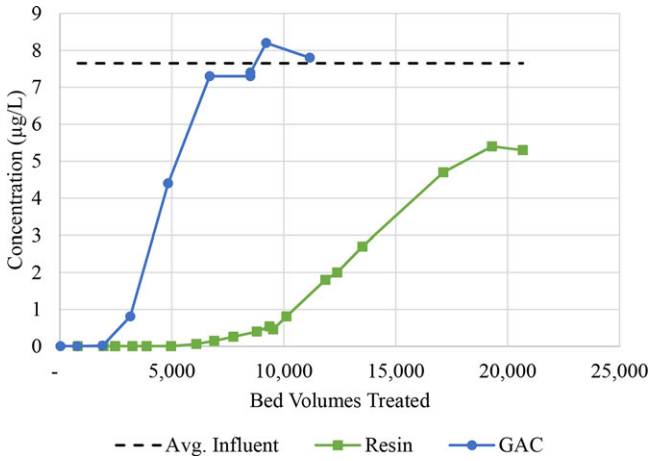

Exhibit 18 Perfluorohexanoic acid (PFHxA) breakthrough curve at 5 min EBCT

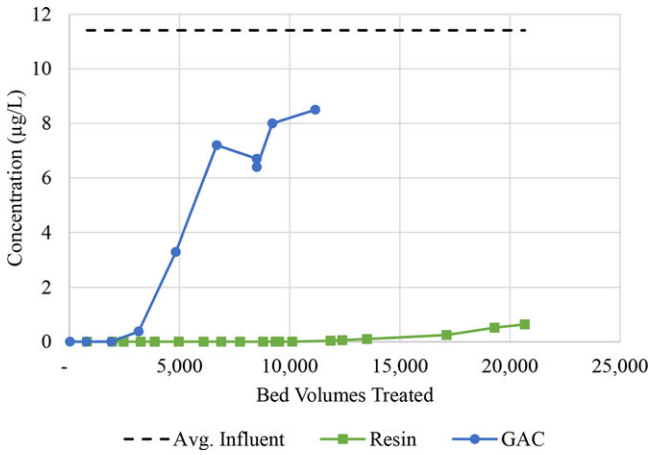

Exhibit 19 Perfluorooctanoic acid (PFOA) breakthrough curve at 5 min EBCT

cycle was planned to run long enough to approach breakthrough of PFOA at the HA, based on breakthrough results from the first virgin loading cycle. It was assumed for this groundwater source that HA breakthrough for PFOA would be the trigger point for regenerations in a full-scale application. PFAS breakthrough curves were similar between the first and second virgin resin loading cycles.

3.3 | Postregeneration resin loading cycle operations and results

The lead resin vessel was returned to service after the regeneration procedures and a final loading cycle started. This cycle treated 77,455 gallons (6,824 BVs) of groundwater.

The first sample collected in the regenerated loading cycle showed the sum of detected PFAS concentrations as 0.090 μg/L after 1,367 BVs of treatment, compared to 0.052 μg/L after 1,598 BVs from the first virgin loading cycle and 0.054 μg/L after 1,104 BVs from the second loading cycle. The last sample collected in the regenerated loading cycle showed the sum of detected PFAS concentrations as 4.1 μg/L after 6,824 BVs of treatment, compared to 4.6 μg/L after 6,489 BVs from the first virgin loading cycle and 4.8 μg/L after 7,608 BVs from the second virgin loading cycle.

PFOS was only detected between the reporting limit and detection limits (0.0077 μg/L in the final sample), and PFOA exceeded the HA (0.10 μg/L in the final sample) at 6,823 BVs, as expected. This corresponded to the first detections of PFOA observed in the first virgin resin loading cycle 0.048 μg/L at 6,489 BVs treated and the first virgin resin loading cycle (0.053 μg/L at 7,608 BVs treated).

Exhibit 23 shows the breakthrough curves of detected PFAS concentrations during the second virgin loading cycle and the regenerated resin loading cycle.

Overall, compared to the two virgin resin loading cycles, PFAS removal results for the regenerated resin were consistent with virgin resin. The regeneration procedures developed during the third regeneration were successful in restoring the resin's PFAS adsorption capacity to near virgin conditions.

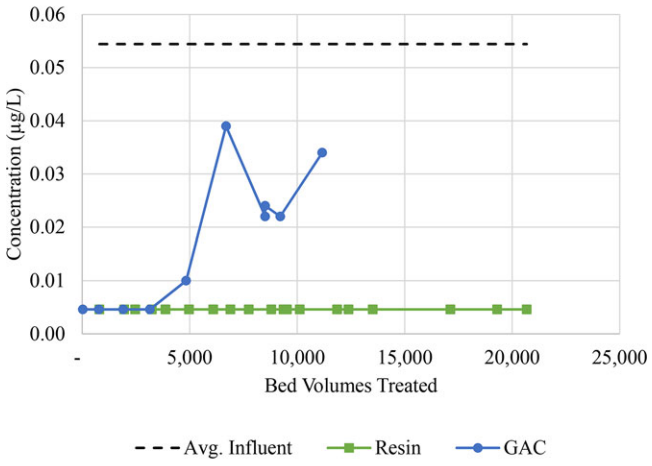

Exhibit 20 Perfluorononanoic acid (PFNA) breakthrough curve at 5 min EBCT

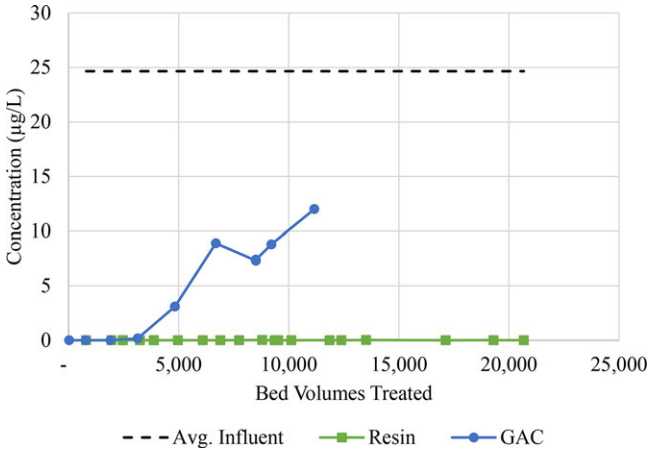

Exhibit 21 Perfluorooctane sulfonate (PFOS) breakthrough curve at 5 min EBCT

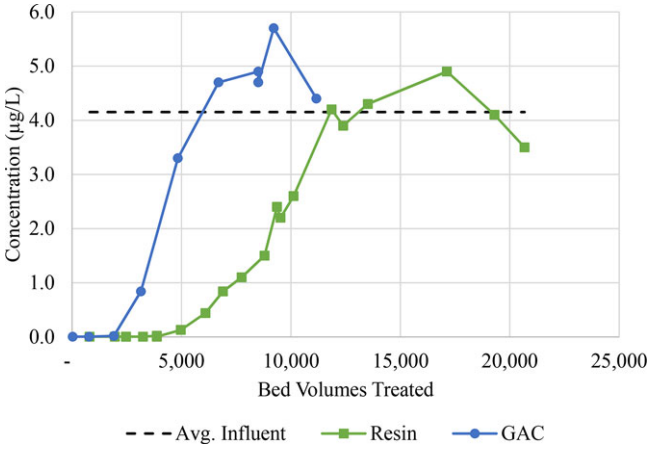

Exhibit 22 Perfluoropentanoic acid (PFPeA) breakthrough curve at 5 min EBCT

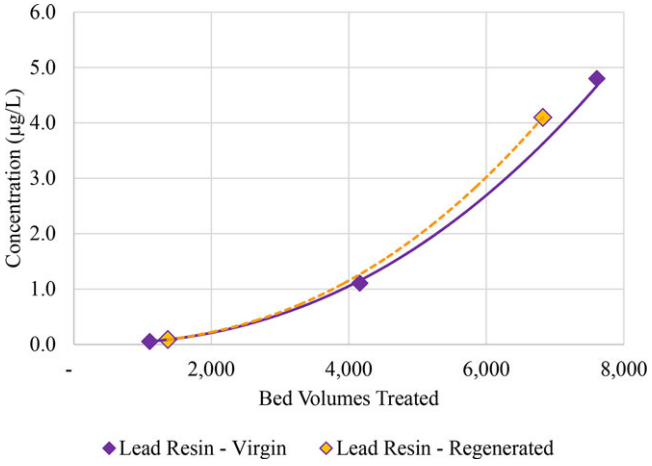

Exhibit 23 Virgin resin and regenerated resin breakthrough curves—total PFAS

3.4 | Regenerant solution recovery and waste stream minimization

To minimize the consumption of raw materials and disposal of off-site wastes for potential full-scale applications, preliminary testing of distillation and superloading of the spent regenerant was performed during the pilot test.

1. Distillation of spent regenerant: Based on preliminary testing, recovered (distilled) solvent can be recycled to the regenerant supply tank for reuse. The spent regenerant contains solvent, brine, and PFAS. With the different boiling points of water, solvent, and PFAS, it is possible to distill the solvent fraction of the solution for recycling and reuse, while leaving behind the desorbed PFAS compounds in the brine solution fraction ("still bottoms") of the regenerant solution.
2. Superloading the still bottoms: Based on preliminary testing, it is possible to recycle the still bottoms from the distillation step by processing the concentrated PFAS and brine solution waste stream at low flow rates (long EBCT) through adsorption media (referred to as "superloading" in the case study). Recovered brine solution can be recycled to the regenerant supply tank for reuse and the superloaded media would be disposed off-site. The long ECBTs in the superloaders are used to maximize the adsorption capacities of the superloader media, thereby minimizing the amount of waste requiring disposal.

4 | CONCLUSION

Pilot test activities achieved the test objectives as follows:

1. Both Sorbix A3F resin and F400 GAC demonstrated removal of PFAS below achievable laboratory quantification limits and the USEPA HAs for PFOS and PFOA.
2. Collected data allowed for development of breakthrough curves and calculation of removal capacities for PFAS in both Sorbix A3F resin and F400 GAC.

EXHIBIT 24 Bed volumes treated at HA breakthrough

Vessel	Position	EBCT (min)	PFOA	PFOS
GAC #1	Lead	5	3,147	3,147
GAC #2	Lag	10	4,254	5,582
GAC #3	Polish	15	Not observed at 3,721	Not observed at 3,721
RESIN #1	Lead	2.5	7,479	17,592
RESIN #2	Lag	5	13,515	Not observed at 20,675
RESIN #3	Polish	7.5	Not observed at 13,783	Not observed at 13,783

3. The Sorbix A3F resin was regenerated in-place to near-virgin PFAS removal performance under simulated full-scale operating conditions.

Compared at 5 min EBCT, the Sorbix A3F resin treated over eight times as many BVs as F400 GAC before PFOS was observed at concentrations exceeding the USEPA HA and six times as many BVs before PFOA was observed at concentrations exceeding the USEPA HA. Exhibit 24 summarizes the BV treated at HA breakthrough for the first three vessels in each media process.

A mass-to-mass comparison at 5 min EBCT showed the Sorbix A3F resin removed 1.66 milligram (mg) total PFAS per gram of resin before breakthrough was observed at the USEPA HA, while F400 GAC removed 0.40 mg total PFAS observed in the influent per gram of GAC before breakthrough was observed at the USEPA HA.

Based on the calculated loading capacities and the successful resin regeneration and waste minimization demonstrated during the pilot test, the full-scale proprietary regenerable resin system planned for the site (200 gpm of 90 μg/L total PFAS) would treat over 100 million gallons of groundwater per year and extract approximately 80 pounds of PFAS compounds. Through the regeneration, distillation, and superloading processes, it is anticipated that the 80 pounds of PFAS compounds could ultimately be superloaded onto approximately four or five 55-gallon drums of superloader media for off-site disposal via hazardous waste landfilling or incineration.

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AUTHOR'S BIOGRAPHIES

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