PFAS Mobile Treatment and Rapid PFAS Measurements of Highly Contaminated Fire Runoff Water from Chemical Plant Fire

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Abstract

Remtech conducted pilot treatability tests on 440,000 gallons of fire runoff water contained in twenty-two (22) frac tanks from a chemical plant fire that was extinguished with AFFF foam. Samples were collected and independant treatment efficacy laboratory analysis reported by Keith Cole, Ramboll Group.[1, 2] Pilot tests and design specifications were prepared by Mark Ryckman, Remtech Engineers.[3] PFAS concentrations ranged from 253,649 ppt to 13,185,500 ppt in 6 of the 22 frac tanks. Waste from all 22 tanks were equalized and treated through a pilot treatment train consisting of screening, equalization, sedimentation, non-harvesting aeration/foam fractionation, sand filtration, and three-stage Granular Activated Carbon Filtration (GAC). 27.97% of PFAS was removed by aeration, and 99.993% were removed by all unit operations. This treatment method demonstrated that both long and short chain PFAS analytes were effectively removed. Powdered Activated Carbon (PAC) dosed at a self-flocculating 1,000 mg/l concentration removed 34.5% of PFAS following 48 hours of clarification. Correlation curves with a field COD meter were developed with laboratory data to predict PFAS concentrations approaching EPA target PFAS treatment values to reduce the laboratory testing frequencies and costs.

Background

Remtech developed a mobile treatment design to treat runoff water from a chemical plant fire that had total PFAS concentrations ranging from 253,649 ppt to 13,185,500 ppt in 6 of 22 frac tanks. Household products, fragrances, sports drinks, tapes, and road-paving materials were manufactured from processed pine tree stumps into resins, rosins, waxes, and gums. Pilot/bench-scale tests are required to properly design a full-scale wastewater treatment system.[4]

Waste Characterization & Preparation

Initial samples were collected from six (6) of the 22 frac tanks and tested for PFAS (using EPA Method 533) and general chemistry analytes. The results are presented in Tables 1a and 1b. Herbicides, heavy metals, mercury, and organochlorine pesticides were also tested on the initial 6 frac tank samples. These analytes were below pretreatment requirements of the Publicly Owned Treatment Works (POTW) and were not run on Pilot Runs 1 and 2.

EPA methods employed for PFAS and General Chemistry analyses are summarized below:

- pH - Method: (SM-4500-⁺)
- VOCs - Method: 8260D GC/MS
- Organochlorine Pesticides - Method: SW846 8081B (GC)
- Herbicides - Method: SW846 8151A (GC)
- Metals (ICP) - Total Recoverable - Method: EPA 200.7 Rev 4.4
- Total Hardness (as $CaCO_3$) by calculation - Method: SM 2340B-2011
- Mercury (CVAA) - Method: EPA 245.1-1994 R3.0
- Oil & Grease - HEM (1664A)
- Total Suspended Solids - (SM 2540D-2015)
- Chemical Oxygen Demand (SM 5220D-2011)
- Total Organic Carbon TOC (SM 5310 B-2011)
- PFAS - EPA Method 533 was used for testing PFAS in the first 6 frac tanks
- PFAS - EPA Method 1633 was used for pilot testing. EPA recommends this method, and it is currently the only PFAS method that has been validated for wastewater, surface water, and groundwater by 10 laboratories in 12 diverse and challenging aqueous matrices [5]

The frac tanks contained a floating layer of resins/oils, a suspension of suspended solids, and settled solids. Samples from individual frac tanks had highly variable pHs (ranging from 4.25 to 11.96), general chemistry analytes and PFAS concentrations that required equalization. Results of initial testing are presented in Tables 1a & 1b.

Due to the wide variation of analyte concentrations, one-gallon samples from all 22 frac tanks were collected and a 22-gallon equalized composite sample was prepared for pilot testing. This resulted in significantly lower analyte concentrations. The “Raw Equalized” sample is depicted in the “blue highlighted” portions of Tables 1a & 1b and Table 2. The equalized raw wastewater had a pH of 10.12[12]

Table 1a: Initial Frac Tank PFAS Testing

Analyte, ng/l	Frac 1	Frac 4	Frac 5	Frac 21	Frac 15	Frac 9	Frac 11	Avg	Raw Equalized
PFBA	11,400	27,700	55,000	55,000		112	18,400	27,935	
PFPeA	16,800	33,800	1,200	30,600		692	36,200	19,882	
PFHxA	46,400	79,300	1,400	91,100	89,800	786	89,800	56,941	
PFHpA	12,600	28,900	122,000	14,800	18,800	328	17,400	30,690	
PFOA	33,700	75,900		38,700	64,200	589	46,000	43,182	31,100
PFNA									
PFDA									
PFBS	54,800	104,000	4,900	32,000		212	56,000	41,985	89,900
PFPeS									66,400
PFHxS	324,000	708,000	2,200,000	316,000		3,500		710,300	367,000
PFHpS	27,900		179,000	59,600	66,600	3,100	61,000	66,200	
PFOS	1,860,000	2,950,000	4,680,000	3,750,000		236,000		2,695,200	933,000
PFNS									
4:2FTS									
6:2 FTS	17400	327,000	5,610,000	726,000		7,370		1,337,554	
8:2 FTS	1,540	10,700	295,000	29,000	19,200	960		59,400	
PFOSA									
NEtFOSE									
GenX		700	37,000	700				12,800	7,120
PFMBA									
3:3 FTCA									
5:3 FTCA									
PFDS									
PFMPA or PFMOPrA									
PFAS Total	2,378,340	4,284,500	13,129,300	5,057,900	258,600	252,845	270,200	3,661,669	2,070,190

Table 1b: Initial Frac Tank General Chemistry Testing

Parameter	Frac 1	Frac 4	Frac 5	Frac 21	Avg	Raw Equalized
Oil & Grease, mg/l	32.7	10.7	59.6	39	35	24
TSS, mg/l			76	112	94	58
COD, mg/l	874	632	4,300	1,460	1,817	1,130
TOC, mg/l	172	228	1,150	444	499	262
Total Volatiles, ug/l		1,132.70	5,585.60	2,055	2,924	1,461

TREATMENT METHOD & GOALS

Environmental releases from chemical fires are known to produce toxic vapor clouds, contaminated runoff from firefighting operations, partially burnt chemicals and residues, heavy resins, and fire extinguishing agents. Past treatment unit operations used by Remtech on contaminated chemical plant fire runoff water included flow/concentration equalization, aeration, sedimentation, GAC filtration, and PAC addition at self-flocculating dosages of 1,000 mg/l combined with bentonite.[6]

Remtech's treatment train design was based on the following documented PFAS treatability information:

- ✦ Complex organics, dissolved organic carbon (DOC), surfactants, suspended solids, TOC, and COD compete and interfere with for GAC and PAC absorption sites for PFAS removal and needs to be removed first [7]
- ✦ Aeration/foam fractionation is an effective pretreatment to remove some PFAS analytes and to enhance post treatment with carbon or ion exchange filtration [8,9]
- ✦ Foam fractionation produces extremely high concentrations of toxic vapors that requires off gas treatment [10]
- ✦ Soluble PFAS analytes on particulates can be desorbed and transferred to the aqueous phase by mixing for treatment [11]
- ✦ Particulate matter needs to be removed prior to filtration to reduce carbon column backwashing that decreases PFAS removal efficiencies by channeling of bed media [7]
- ✦ PFAS removal efficiencies may increase with decreasing pH's in the 3 to 7 range [12]
- ✦ Aqueous and vapor phase coal based GAC effectively removes PFAS and can be regenerated for reuse

Two of the preferred PFAS coal based GACs are CALGON'S F400M and General Carbon's 12 X 40PF. General Carbon's GAC was selected since this vendor claimed that their product outperformed CALGON'S carbon for PFAS removal.

Table 2: Raw Equalized Wastewater PFAS Analytes from 22 Frac Tanks

Formula	Analyte	Clarified Equalized Raw Wastewater, ng/l
Short Chain, $C_4HF_7O_2$	Perfluorobutanoic acid **(PFBA)**	33,500
Short Chain, $C_5HF_9O_2$	Perfluoropentanoic acid **(PFPeA)**	16,500
Short Chain, PFHxA, $C_5F_{11}COOH$	Perfluorohexanoic acid **(PFHxA)**	43,400
Short Chain, degradation product of long chain with characteristics of long chain, $C_7HF_{13}O_2$	Perfluoroheptanoic acid **(PFHpA)**	9,950
Long Chain, $C_7F_{15}COO$, most toxic	Perfluorooctanoic acid **(PFOA)**	31,100
Long Chain, $C_9HF_{17}O_2$	Perfluorononanoic acid **(PFNA)**	
Long Chain, $C_{10}HF_{19}O_2$	Perfluorodecanoic acid **(PFDA)**	
Short Chain, $C_4F_9SO_3H$	Perfluorobutanesulfonic acid **(PFBS)**	89,900
Short Chain, $C_5HF_{11}O_3S$	Perfluoropentanesulfonic acid **(PFPeS)**	66,400
Long Chain, more bioconcentration, PFHxS, $C_6F_{13}SO_3H$	Perfluorohexanesulfonic acid **(PFHxS)**	367,000
Long chain, $C_7F_{15}SO_3H$	Perfluoroheptanesulfonic acid **(PFHpS)**	21,200
Long chain, $C_8F_{17}SO_3H$, most toxic	Perfluorooctanesulfonic acid **(PFOS)**	933,000
Long chain, $C_9F_{19}SO_3H$	Perfluorononanesulfonic acid **(PFNS)**	
Short Chain, $C_4F_9CH_2CH_2SO_3H$	1H,1H,2H,2H-Perfluorohexane sulfonic acid **(4:2 FTS)**	
Long Chain, $C_8H_5F_{12}O_3S$	1H,1H,2H,2H-Perfluorooctane sulfonic acid **(6:2 FTS)**	444,000
Long Chain, $C_{10}H_5F_{17}O_3S$	1H,1H,2H,2H-Perfluorodecane sulfonic acid **(8:2 FTS)**	7,120
Long Chain $C_8H_2F_{17}NO2S$	Perfluorooctanesulfonamide **(PFOSA)**	
Long Chain, $C_{12}H_6F_{21}NO_3S$	N-ethylperfluorooctane sulfonamidoethanol **(NEtFOSE)**	
Short Chain, $CF_3CF_2CF_2OCF(CF_3)COO-$ NH4+	Hexafluoropropylene Oxide Dimer Acid **(HFPO-DA/GenX)**	7,120
Short Chain, $C_5HF_9O_3$	Perfluoro-4-methoxybutanoic acid **(PFMBA)**	
Short Chain, $C_6H_5F_7O_2$	3-Perfluoropropylpropanoic acid **(3:3 FTCA)**	
Long Chain, $C_{15}H_5F_{25}O_2$	3-Perfluoropentylpropanoic acid **(5:3 FTCA)**	
Long Chain, $C_{10}HF_{21}O_3S$	Perfluorodecanesulfonic acid **(PFDS)**	
Short Chain, $C_4HF_7O_3$	Perfluoro-3-methoxypropanoic acid **(PFMPA) or PFMOPrA**	
	TOTAL PFAS, mg/l	2,070,190.00

[shaded] EPA Proposed Regulated PFAS

Remtech's mobile pretreatment plant was designed to reduce total PFAS concentrations to less than 200 ppt with a pH of 10.12 so a local POTW could accept the wastewater for further treatment.

Six (6) EPA proposed PFAS analytes to be regulated are PFOA, PFOS, PFNA, PFHxS, PFBS, HFPO-DA/GenX. Two of the most toxic long chains analytes are PFOS and PFOA. Activated carbon filtration has been reported to be more effective in removing long chain rather than short chain PFAS analytes.[4] Of the six proposed regulated compounds, GenX and PFBS were the only short chain compounds reported in initial testing.

Treatment Goals

- Reduce PFAS concentrations down to a POTW pretreatment goal of less than 200 ppt
- Determine if 12 x 40PF carbon is effective in removing very high concentrations of long and short chain PFAS analytes
- Determine treatment efficiency of sedimentation, aeration, GAC, and PAC
- Determine if a field COD test kit could be used to develop correlations to predict trending final PFAS concentrations to reduce the frequency of expensive PFAS lab costs

PILOT PLANT SETUP

Wastewater was first passed through a 35 mesh (50 micron) screen to remove floating and suspended scum. Selected unit operations were screening, sedimentation, non-harvesting aeration/foam fractionation, sand filtration, and three GAC columns in series.

Sand media selected was Filtersil which is a high-purity monocrystalline industrial quartz sand for mixed media and pressure filters for potable, process, and wastewater filtration. Filtersil specifications are: Grade 0.85, Effective Size (mm) 0.78, Uniformity Coefficient 1.47, Prior Grade designation WG#1, Approximate Screen Slot Size (inches) 0.030), bulk density 79-80 lb/cf loose, 83-85 lb/cf compacted.

Reactors, pumps, valves, fittings, and tubing selected were PFAS free. Following screening, wastewater was allowed to settle in a 30-gallon poly overpack for 24 hours for Run 1. Water was pumped with an agricultural diaphragm pump (Pentair Shurflo,12-volt,1.8 gpm) into a 10-gallon covered glass reactor (12" L x 6" W x 8" H) that was aerated for 1 hour at 6 scfh with 40 micron diffusers prior to running through four identical PVC columns (3" D x 26" H). Flowrates were measured with a King Liquid Flow meter (1 to 12 gph). Flowrates were controlled with a recirculation valve. Filter volumes and media charge rates are listed in Table 3.

Table 3: Filter Size & Media Charge

Media	Vol, liters	Weight, gms
Sand	1.85	2,610.8
Sand - Water	2.0	
Carbon	2.1	879.2
Carbon-Water	2.1	

Two GAC runs (Runs 1 & 2) were conducted at two flowrates for carbon contact times of 10 and 20 minutes. Sample were collected from the raw wastewater, post aeration, and after each filter and were analyzed to determine removal efficiencies. The pilot test setup is depicted in Figures 1 and 2. Analytical results for Run 1 and Run 2 are presented in Tables 4, 5, 6 & 7.

Raw wastewater was also treated with 1,000 ppm of PAC. PAC was mixed with air at 6 scfh for 1 hour then allowed to settle for 48 hours then tested for PFAS. Results are depicted in Tables 8 & 9.
PAC was most effective in removing PFBS, PFPeS, PFHxS, PFOS, and 6:2 FTS.

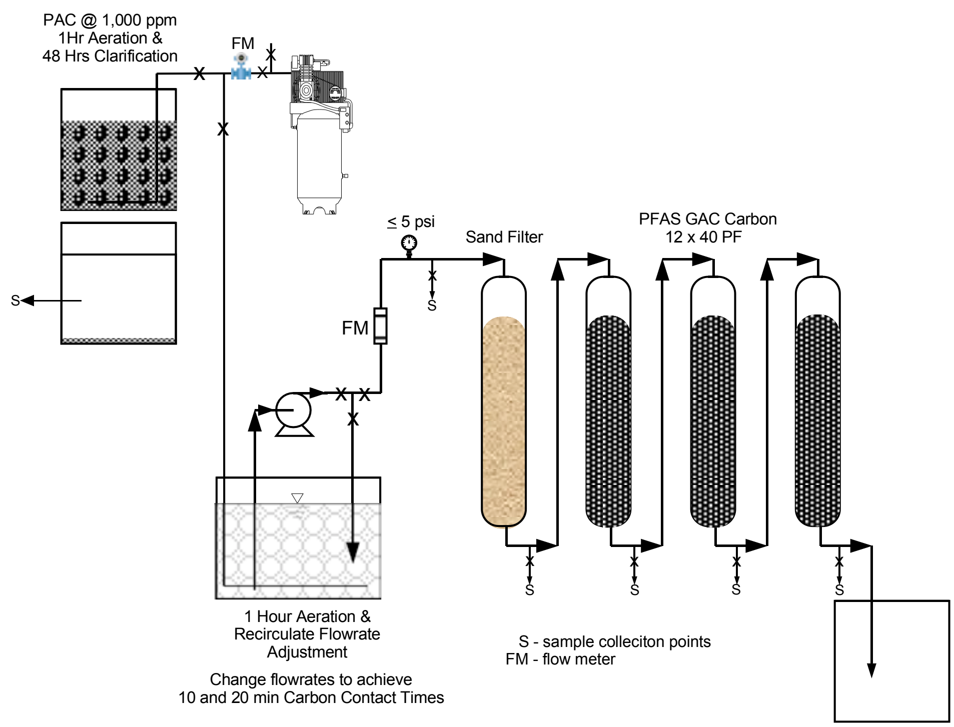

Figure 1: Pilot PID Drawing

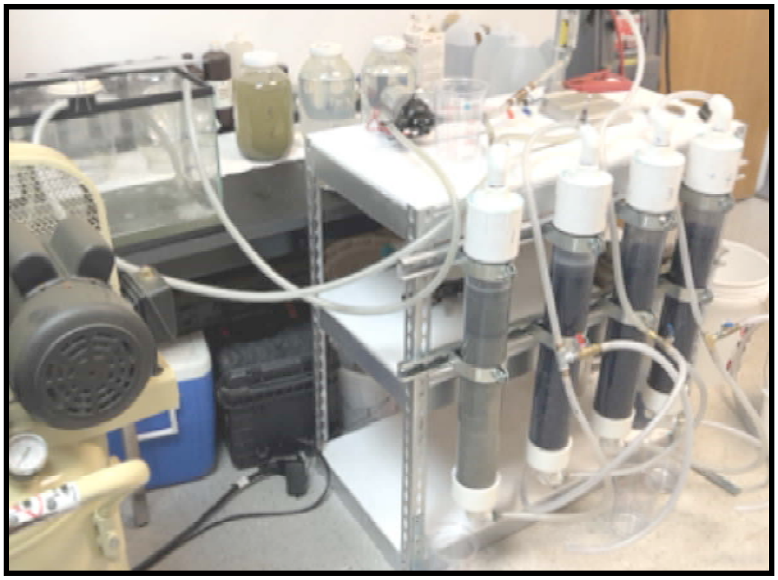

Figure 2: Pilot Plant Setup

Table 4: Run 1 PFAS Results

Analyte, ppt	Raw PFAS	Post Air	% Air Removal	Post Sand	Post GAC1	% Removal GAC1	Post GAC2	% Removal GAC2	Post GAC3	% Removal GAC 3
PFBA	33,500	36,800	(9.851)	34,800		100				
PFPeA	16,500	22,500	(36.364)	19,600		100				
PFHxA	43,400	42,600	1.843	50,600		100				
PFHpA	9,950	11,500	(15.58)	11,200		100				
PFOA	31,100	32,500	(4.502)	36,900		100	105	100		
PFNA		176		171		100	41.52	100		
PFDA										
PFBS	89,900	74,700	16.908	80,900		100				
PFPeS	66,400	57,400	13.554	58,500		100				
PFHxS	367,000	346,000	5.722	311,000	44.4	100	20.7	100		100
PFHpS	21,200	26,700	(25.943)	26,600		100				
PFOS	933,000	522,000	44.051	529,000	854	**99.839**	159	**81.382**	139	**12.579**
PFNS										
4:2 FTS		308		289		100				
6:2 FTS	444,000	301,000	32.207	351,000	166	99.953				
8:2 FTS	7,120	5,950	16.433	7,880						
PFOSA		1,360		1,180	21.7	98.161				
NEtFOSE						100				
HFPO-DA/GenX	7,120	9,570	(34.410)	9,770						
PFMBA		50		37		100				
3:3 FTCA		115				100				
5:3 FTCA		659		673		100				
PFDS						100				
PFMPA or PFMOPrA		44		38		100				
PFAS Totals	2,070,190	1,491,064	**27.97**	1,529,390	1086	**99.929**	221.22	**79.630**	139	**37.167**

EPA Proposed Regulated PFAS

Table 5: Run 1 General Chemistry Results

Analyte	Raw Clarified	Post Aeration	% Aeration Removal	Post Sand	Post GAC1	Post GAC1 Removal %	Post GAC2	Post GAC2 Removal %	Post GAC3	Post GAC3 Removal %
Oil & Grease (mg/l)	23.8	26	-9.244	24.6	0	100	2.6	plus	1.7	34.62
Total Suspended Solids (mg/l)	57.5	53	7.826	17.4	4.8	72.414	12.2	plus	0	100
Chemical Oxygen Demand (mg/l)	1,130	1,080	4.425	1,100	71.7	93.482	< 5	93.026	< 5	
Total Organic Carbon (TOC) (mg/l)	262	391	-49.237	393	28.5	92.748	6.8	76.140	8.36	plus
Total VOCs (ug/l)	1,461	786.5	**46.167**	700.9	5.2	**99.258**	12.2	plus	72.3	plus

Table 6: Run 2 PFAS Results

Analyte, ppt	Raw PFAS Clarified	Post Air & Sand Not Clarified	Post GAC1	% Removal GAC1	Post GAC2	% Removal GAC2	Post GAC3	% Removal GAC 3
PFBA	33,500	95,700		100				
PFPeA	16,500	50,500		100				
PFHxA	43,400	52,000		100				
PFHpA	9,950	7,530		100				
PFOA	31,100	34,300		100				
PFNA		682		100				
PFDA		89		100				
PFBS	89,900	87,300		100				
PFPeS	66,400	74,900		100				
PFHxS	367,000	398,000	102	**99.974**	29.7	100		
PFHpS	21,200	19,100						
PFOS	933,000	1,270,000	3370	**99.735**	676	**79.941**	386	**42.899**
PFNS								
4:2 FTS		738		100				
6:2 FTS	444,000	506,000	373	**99.926**		100	134	**64.075**
8:2 FTS	7,120	19,400	233	**98.799**		100		
PFOSA		3,830		100				
NEtFOSE		36.3		100				
HFPO-DA/GenX	7,120	25,600		100				
PFMBA		115.0		100				
3:3 FTCA		62.3		100				
5:3 FTCA		1,730		100				
PFDS		93.6		100				
PFMPA or PFMOPrA		109		100				
PFAS Totals	2,070,190	2,647,815	4,078	**99.846**	705.7	**82.695**	520	**26.314**

EPA Proposed Regulated PFAS

Table 7: Run 2 General Chemistry Results

Analyte	Post Aeration & Sand Not Clarified	Post GAC1	Post GAC1 Removal %	Post GAC2	Post GAC2 Removal %	Post GAC3	Post GAC3 Removal %
Oil & Grease (mg/l)	112	1.7	98.482	0	100	0	
Total Suspended Solids (mg/l)	262	4.5	98.282	2.8	37.778	3.2	-14.286
Chemical Oxygen Demand (mg/l)	1,340	93.1	93.052	15.1	83.781	< 5	66.887
Total Organic Carbon (TOC) (mg/l)	380	43.9	88.447	18.8	57.175	6.83	63.670
Total VOCs (ug/l)	1,455.7	2.1	99.856	0.7	66.667	0	

Table 8: PAC PFAS Results

Analyte, ppt	Raw PFAS	48 Hr PAC Clarified	PAC Removal %
PFBA	33,500	34,100	plus
PFPeA	16,500	20,500	plus
PFHxA	43,400	50,900	plus
PFHpA	9,950	10,300	plus
PFOA	31,100	36,100	plus
PFNA		20	plus
PFDA			
PFBS	89,900	81,000	9.900
PFPeS	66,400	63,000	5.120
PFHxS	367,000	294,000	19.891
PFHpS	21,200	21,900	
PFOS	933,000	470,000	49.625
PFNS		494	
4:2 FTS			
6:2 FTS	444,000	260,000	41.441
8:2 FTS	7,120	3,250	plus
PFOSA		718	plus
NEtFOSE			
HFPO-DA/GenX	7,120	9,610	plus
PFMBA		41	plus
3:3 FTCA			
5:3 FTCA			
PFDS			
PFMPA or PFMOPrA		38	plus
PFAS Totals	2,070,190	1,355,970	34.500

(shaded) EPA Proposed Regulated PFAS

Table 9: PAC General Chemistry

Analyte	Raw Mixed	Clarified
Oil & Grease (mg/l)	112	8.1
Total Suspended Solids (mg/l)	262	54.5
Chemical Oxygen Demand (mg/l)	1,340	891
Total Organic Carbon (TOC) (mg/l)	380	308
Total VOCs (ug/l)	1,455.7	692.2

DISCUSSION & RESULTS

GAC Run 1

Run 1 was conducted at a flowrate of 0.0277 gpm and carbon contact time of 20 minutes. Clarified wastewater was introduced into the aeration chamber (Figure 3). A significant finding was that 27.97% of PFAS was removed by aeration. Lab VOC analytes removed by aeration were 46.17%. Off-gas VOC emissions during aeration were measured with a MultiRae PID (10.6 e.v. lamp) with a chlorine sensor - 3.5 ppm PID and 1 ppm chlorine. The average correction factor for VOC analytes (reported by method SW846 8260D GC/MS) with this meter is 0.56 or approximately 1.2 ppm. The total lab reported VOC was 1.46 mg/l (Table 9). Considerable foam was generated during aeration (Figure 4). To prevent the need for foam harvesting, the aeration rate was controlled at 6 scfh.

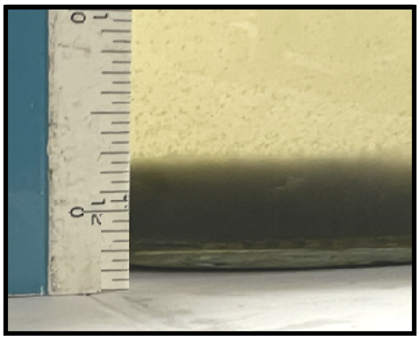

Figure 3: Solids Removed by Clarification

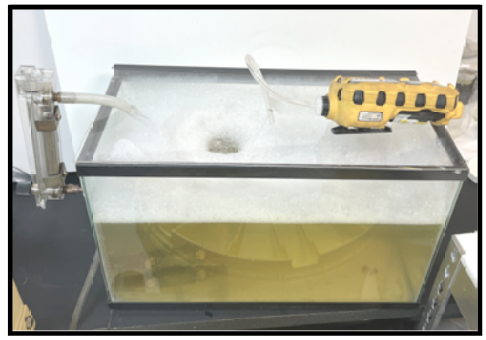

Figure 4: Non-Harvested Foam & Off-Gas Measurement by MultiRae PID with Chlorine Sensor

The first GAC column removed all of the following short chain PFAS analytes below laboratory detection limits; PFBA, PFPeA, PFHxA, PFHpA, PFBS, PFPeS, 4:2 FTS, GenX, PFMBA, 3:3 FTCA, and PFMPA. The long-chain PFAS analytes (PFHpS, 8:2 FTS, and 5:3 FTCA) were also removed by the first GAC column. Only PFOS remained after the 3rd GAC column. Each GAC column removed a reduced amount of PFOS; first column - 99.84%, second column - 81.38%, and 12.58% by the 3rd column. A final concentration of 139 ppt remained for an overall PFAS removal efficiency of 99.993% through the complete treatment train (Table 4).

Total removal efficiencies for VOCs were 95.05%, COD 99.56%, TOC 96.44%, Oil & Grease 92.86%, and TSS 100% (Table 5). When either lab COD or TOC concentrations are less than 10 mg/l, PFAS concentration approach EPA's proposed treatment goals.

GAC Run 2

Run 2 was at twice the flowrate (0.0555 gpm) and a carbon contact time of 10 minutes. Foam was removed by the first GAC column (Figure 5). This test was initiated with mixed wastewater from the 30-gallon overpack that introduced suspended solids into the aeration chamber and increased loadings on the sand filter (Figure 6). This produced a higher raw wastewater concentration of PFAS due to desorption of soluble PFAS from suspended solids - 2,647,815 ppt. An estimated 577,625 ppt PFAS were likely desorbed from the increased suspended solids loading.

Figure 5: PFAS Foam Removed by 1st GAC Column

Figure 6: Increased Solids Loading Removed by Sand Filter

Two analytes remained after the 3rd GAC column, PFOS at 386 ppt, and 6:2 FTS at 134 ppt. Short chain PFAS analytes removed below detection limits by the first GAC column were PFBA, PFPeA, PFHxA, PFHpA, PFBS, PFPeS, 4:2 FTS, GenX, PFMBA, 3:3 FTCA, and PFMPA. Long chain analytes removed by the first column were PFOA, PFNA, PFDA, PFHpS, PFOSA, NEtFOSE, 5:3 FTCA, and PFDS. A final concentration of 520 ppt or 386 ppt PFOS (of the proposed regulated PFAS analytes) remained for an overall PFAS removal efficiency of 99.985% (Table 7). A higher filter backpressure of 5 psi was observed due to the additional TSS loadings on the sand and GAC filters.

Run 2 had higher General Chemistry values across the board except for Total VOCs which were about the same as Run 1; +78.93% Oil & Grease, +78.005% TSS, +15.67% COD, and +31.05% TOC, that resulted in slightly lower treatment efficiencies (Tables 7 & 9). If clarified raw wastewater had been used in Run 2, the total raw PFAS concentration would have been 21.82% less and it is likely that similar overall treatment efficiencies to Run 1 would have been achieved at twice the flowrate and half the carbon contact time (10 min).

PAC Test

Mixed raw waste with suspended solids (Figure 7) was dosed with 1,000 mg/l PAC, aerated for 1 hour at 6 sdfh, and allowed to settle for 48 hours (Figure 8) to see if a synergistic removal of particulate and solution phase PFAS removal could be achieved. The overall PFAS removal was 34.5% (Table 8) with an estimated 28% removed by aeration. Note that TOC and COD final clarified concentrations were approximately 30 to 90 times higher respectively than 3rd GAC column effluent concentrations for the same analytes. Consequently an elevated concentration of PFAS remained in the clarified effluent. Coagulation with alum or other polymers should be investigated to determine if PAC treatment would perform better at a reduced pH.[12]

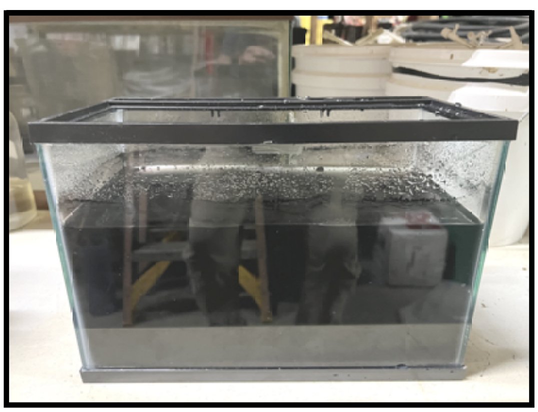

Figure 7: 1,000 mg/l PAC Treatment after 1 hr aeration @ 6 scfh

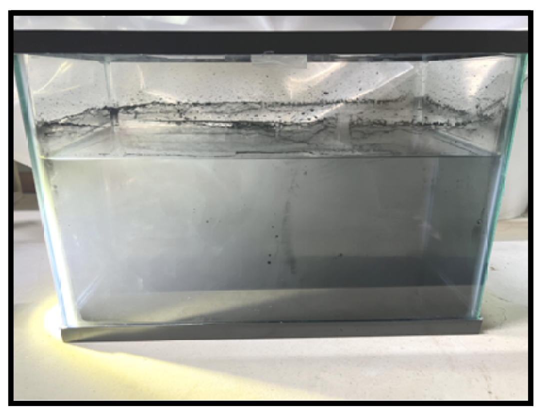

Figure 8: Post 48-Hour Clarification after 1,000 mg/l PAC Treatment

FIELD COD METER PFAS CORRELATIONS

PFAS concentrations in landfill leachates have significant correlations with TOC, alkalinity, ammonia, and COD.[13] Remtech set out to determine if similar PFAS laboratory and field meter COD correlations could be established for this wastewater matrix.

Laboratory COD correlation curves with a field COD meter resulted in a R^2 value of 0.9987 (Figure 9). PFAS versus field COD meter correlations resulted in a R^2 values ranging from 0.9992 to 1.0 (Figures 10 & 11). Correlations with higher COD values resulted in a slightly lower R^2 value of 0.965 (Figure 12). Field COD meters have the potential to reduce PFAS lab costs by identifying trends that suggest required lab PFAS treatment efficiencies have been reached when field meter COD values approach 0.0 mg/l.

Typical turnaround times for PFAS lab analysis may be 15 days for some labs. Shorter turnarounds can increase unit charges by 1.5 to 2 times. For a 5-day rush turnarounds, estimated lab costs (prices may vary significantly between labs) are presented below:

- EPA PFAS Method 533 - $600/sample
- EPA PFAS Method 1633 - $700/sample
- For VOC, Oil and Grease, TSS, COD, and TOC - $217.80/sample (for all 5 parameters)

Additional parameters that may need to be run for certain matrices include; alkalinity, heavy metals, pesticides, herbicides, and organochlorines.

When either lab COD or TOC values are less than 10 mg/l after GAC filtration, PFAS concentrations are typically in the range of 4 to 100 ppt. Correlation curves need to be prepared for each waste stream with appropriate variations in concentrations.

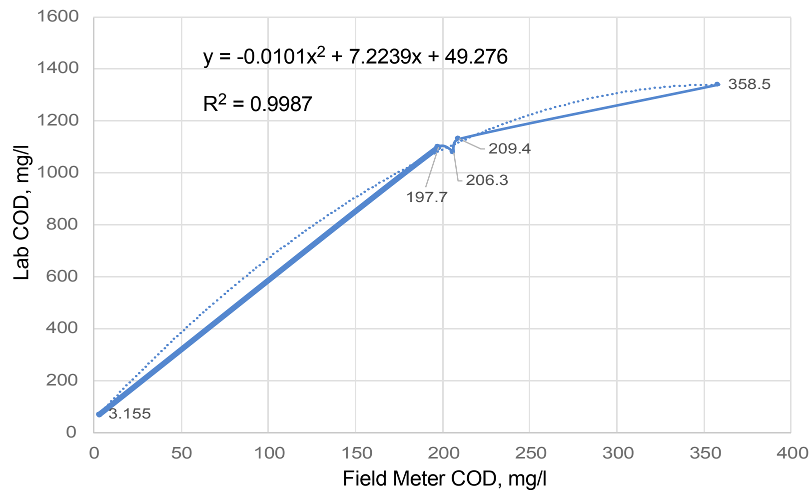

Figure 9: Field COD Meter vs Lab COD, mg/l

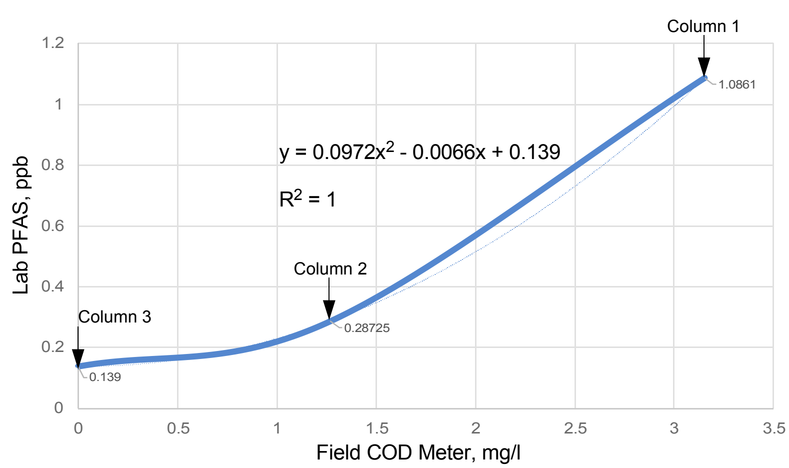

Figure 10: Field COD Meter vs Lab PFAS, ppb

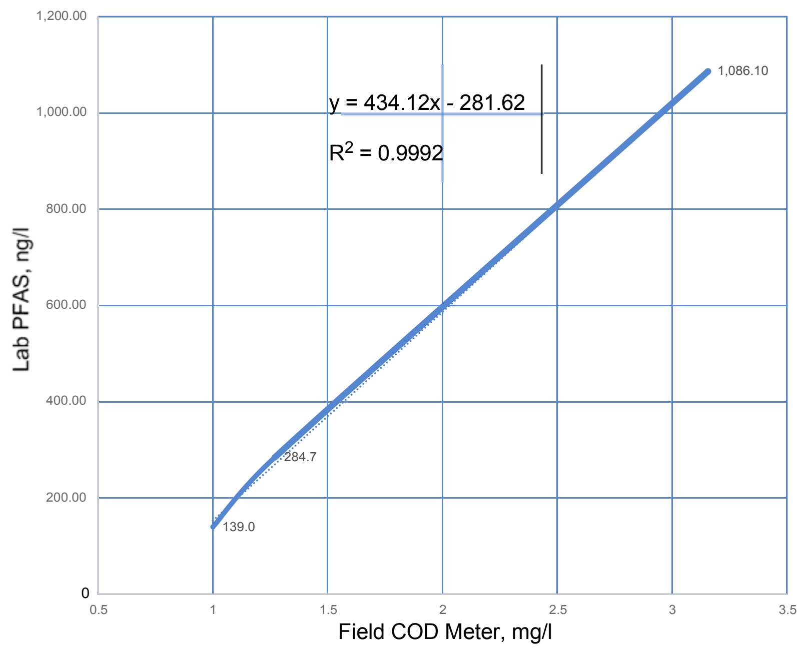

Figure 11: Field COD Meter vs Lab PFAS, ng/l

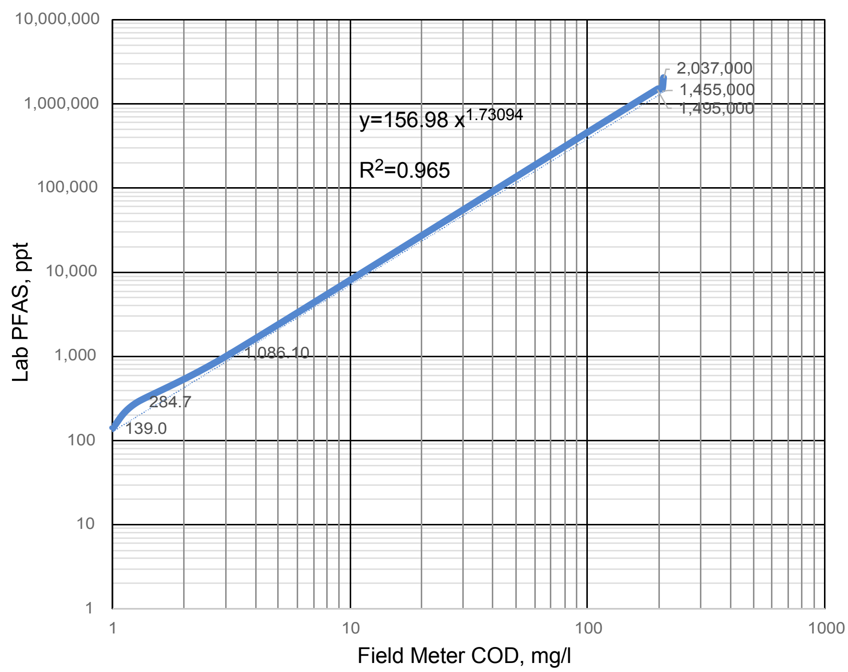

Figure 12: Field COD Meter vs Lab PFAS, ppt

TREATMENT SYSTEM DESIGN

Carbon Column Design Criteria

Table 3 displays the mass loading, reactor volumes, and flowrates for pilot Runs 1 & 2. Scaling up to a flowrate of 35 gallons for Run 1, an estimated 2,448.10 lbs of GAC are required for each full-scale carbon filter or a total of 7,344.03 pounds for all three GAC filters. When the flowrate is doubled in Run 2, an estimated 1,745.43 lbs of GAC is required for each full-scale filter or a total of 5,236.28 lbs for all three GAC filters at a flowrate of 50 gpm.

Surface loading rates for the two runs are summarized below:

- Pilot carbon column area = ((3.14 x 9)/4)/144 in^2 = 0.049 sf
- Run 1; Surface Loading Rate = 0.0277/0.049 = 0.565 gpm/sf @ 20 min contact time
- Run 2; Surface Loading Rate = 0.0555/0.049 = 1.133 gpm/sf @ 10 min contact time

GAC pressurized filter design criteria for much lower PFAS feed concentrations suggest surface loading rates ranging from 2 to 10 gpm/sf for treatment plant flowrates ranging from 1 - 12 MGD and empty bed contact time ranging from 10 to 20 minutes.[7,14] GAC surface loading rates for the treatment of PFAS contaminated fire runoff water for this matrix appears to be in the range of 0.56 to 1.13 gpm/sf with an untreated PFAS concentration ranging from 2 to 2.6 mg/l providing clarification, aeration, and sand filtration is provided upstream.

Table 10: GAC Design Information

Run 1				Design Flowrate 1 GAC column			3 GACs, lbs
Volume	SG	Each Column, cf	gpm	gpm	Column cf	lbs GAC	
2.1 liters	26.12 lbs/cf	0.0742	0.0277	35	93.72	2,448.01	7,344.03
Run 2							
2.1 liters	26.12 lbs/cf	0.0742	0.0555	50	66.82	1,745.43	5,236.28

Suitable activated carbons show incipient breakthrough for PFOS at 30,000 to 40,000 Bed Volumes (BV) and for PFOA at 20,000 to 30,000 BV. GAC absorbers are considered to be effective and feasible taking into account operational and economic factors so long as a specific throughput of at least 15,000 BV can be achieved.[15,16] Actual BVs prior to media changeout for this highly contaminated PFAS matrix is unknown.

Using 3 carbon columns that contain 2,000 lbs of carbon with dimensions of 4 ft diameter and 6 ft tall, the BV would be 7,328 gallons for each filter (Figure 14). Assuming that 15,000 to 40,000 BV would result in PFAS breakthrough, then the volume of water treated prior to media changeout could be between 109,920 to 293,120 gallons. With 440,000 gallons to be treated one to two media changeouts may be required. Actual BVs needs to be field verified to determine actual media changeouts.

Sand Filter Design

For Runs 1 & 2; 7,266.2 lbs and 5,179.8 pounds of sand are required respectively. An average of 6,203 lbs of sand was selected to be placed in one of the 2,000 lb carbon reactors. Back pressures near 10 psi may require filter back-washing.

Aeration Chamber Design

Using a 21,000 gallon frac tank for batch aeration for 1 hour operating at 18,000 gallons with Remtech's *Magnetic Aeration System* - installed through a 20" manhole[17], the the non-harvesting foam aeration rate is calculated below:

- 6 scfh/60 - 0.1 cfm, 40 micron diffusers, volume of wastewater treated = 5 gallons (reactor volumes including sample volumes removed for lab testing)
- 0.1/5 = X/18,000 = 360 cfm. Aeration/mixing requirements demonstrated by Remtech on previous projects - 60 to 120 cfm for each frac tank. 120 cfm was selected

Actual aeration rates to produce non-harvesting foam generation rates needs to be field verified.

Vapor Off Gas Treatment Design (optional, not currently regulated)

- 579,126 ng/l (579.13 ug/l) of PFAS were removed in Run 1 and 1,456 ug/l VOCs were removed in Run 2 yielding a total of 2,035 ug/l of volatiles removed from 5 gallons of wastewater
- 394.5 lbs of volatiles need to be removed from 440,000 gallons of wastewater
- Assume that 1 pound carbon removes 0.4 lbs of VOCs or 986.2 pounds of carbon required
- Selected three (3) 300 lb carbon vapor absorbers operating at 150 cfm

Vapor off-gas carbon requirements and media chanouts needs to be field verified.

Full-Scale Mobile Treatment Train Design

Diaphragm pumps with 25 ft suction lifts were selected to remove wastewater from 22 frac tanks from the top manholes with adjustable depth suction hoses with inlet screens. Withdrawing wastewater from mid- depths will leave floating and settled solids in each tank. Wastewater is then pumped to a 21,000 frac tank for settling, then pumped to another frac tank with Remtech's *Magnetic Aeration System* for pulsed aeration for 1 hour at 120 scfm (Figure 13).

After settling and aeration, wastewater is pumped through the mobile treatment trailer with sand and tri-GAC filters. Initial flowrates to be increased from approximately 5 gpm with PFAS removal efficiencies demonstrated as flowrates are increased.

Field COD vs Lab correlation curves can be used as predictive final lab PFAS concentrations to minimize lab analytical costs. Additional Frac holding tanks may be used to hold treated water until discharge limits are verified by lab analysis. Backwash media filter water is pumped to a 9,000 gallon mini-frac settling tank with clarified water directed back to the initial 21,000 gallon settling frac tank.

Spent GAC media is removed and sent for regeneration and reuse. Spent sand filter and solids from the 22 fracs will be removed by vacuum truck, dewatered, tested and disposed of at an approved disposal facility.

A schematic of the full-scale system is presented in Figures 13 & 14. The estimated cost of this system for one month of operation is $450,000 plus disposal of remaining solids in frac tanks. Note that 50% of estimated costs are associated with labor intensive efforts to operate multiple pumps and manifolds required to remove wastewater from 22 frac tanks that is transferred to the initial clarification frac tank.

Summary

Remtech has demonstrated that this type of mobile treatment system is effective in removing very high concentrations of short and long chain PFAS analytes using a combination treatment train consisting of screening, sedimentation, non-harvesting foam aeration, sand filtration, and tri GAC filtration using General Carbon's 12 x 40PF PFAS carbon.

PFAS expensive laboratory costs can be reduced by using Remtech's proprietary field COD test meter by developing correlation curves between laboratory COD and PFAS data for each specific waste stream.

This same mobile treatment process can be used for landfill leachates, wastewater, drinking water, and other more dilute PFAS waste streams. Pilot/bench scale tests are required to determine appropriate carbon mass, flowrate loadings, carbon contact times, aeration times, and sandfilter loading rates for each waste stream to meet discharge limits.

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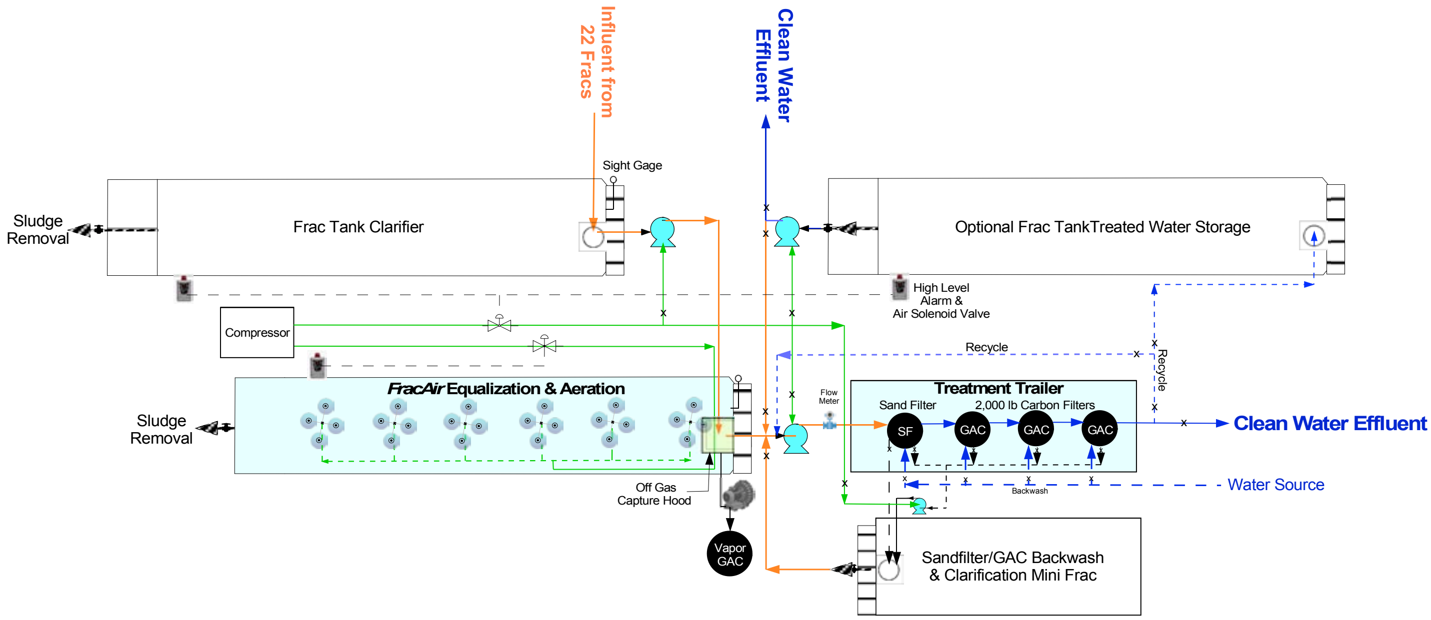

Figure 13: Mobile PFAS Treatment System

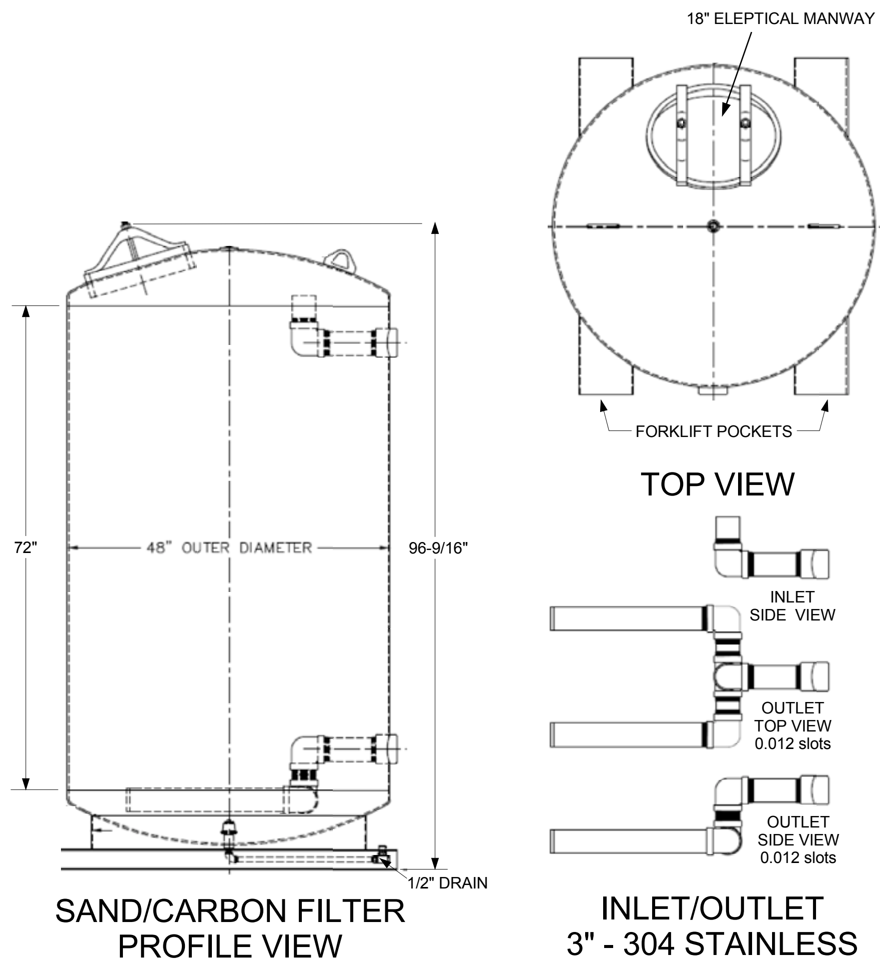

Figure 14: Sand/GAC Filter Detail

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