TECHNICAL MEMORANDUM

To: File

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Date: February 26, 2016

Re: Bench-Scale VEG Research & Development Study: Implementation Memorandum for Ex-Situ Thermal Desorption of Perfluoroalkyl Compounds (PFCs) in Soils

This Technical Memorandum (Memo) summarizes the procedures and findings of a preliminary bench-scale research study performed by Endpoint Consulting, Inc. (Endpoint) to thermally treat PFCs in soils using Endpoint's patented VEG Technology. The bench-scale study was performed in collaboration with CH2M, which provided the PFC source material used to spike soils and establish pre-treatment conditions, and in further collaboration with CSM which performed the laboratory analysis of the pre- and post-treatment soil samples.

This bench-scale test was performed as a preliminary step toward answering the initial question relative to whether thermal treatment within an approximate soil temperature range of approximately 1000 F to 2,000 F is sufficient to remove PFCs from soils such that post-treatment levels in soil are below typical laboratory reporting limits; and therefore, below potential cleanup goals to be promulgated for PFCs in the future. Accordingly, the sampling conducted as part of this preliminary bench-scale study was limited to pre- and post-treatment soil samples.

Due to the limited scope of this preliminary bench-scale study, treatment scenarios and associated sampling performed as part of this bench-scale study did not target identification of the optimal treatment conditions (i.e., lowest treatment temperature and duration to fully treat soils); only whether PFCs may be removed from soil in the approximate 1000 F to 2000 F temperature range. Moreover, while the bulk of the PFC mass (following removal from soil) was eliminated through high-temperature thermal oxidation (including subsequent treatment of acidic gases including hydrofluoric acid (HF) and carbon dioxide [CO_2]) inherent to the VEG's patented closed-loop treatment process, other treatment processes including chemical reduction and transformation incorporated by the VEG Technology may also have contributed to PFC

destruction. Hence, there is interest in furthering this preliminary study to identify the optimal treatment conditions and to develop detailed mass balance data to quantify the proportion of treatment across the various treatment components of the VEG Technology.

Ex-Situ Bench-Scale Test Procedures and Results

Preparation of Soils

On February 8, 2016, Endpoint performed bench-scale treatment of soils containing PFCs at its laboratories in Manteca, CA. As the first step in this process, Endpoint prepared two independent 250 mL mixtures of Aqueous Film-Forming Foam (AFFF), representing an equal mixture (i.e. 125 mL each) of 3% Ansulite AFFF and 1999-era 3M AFFF provided by CH2M (see photograph below).

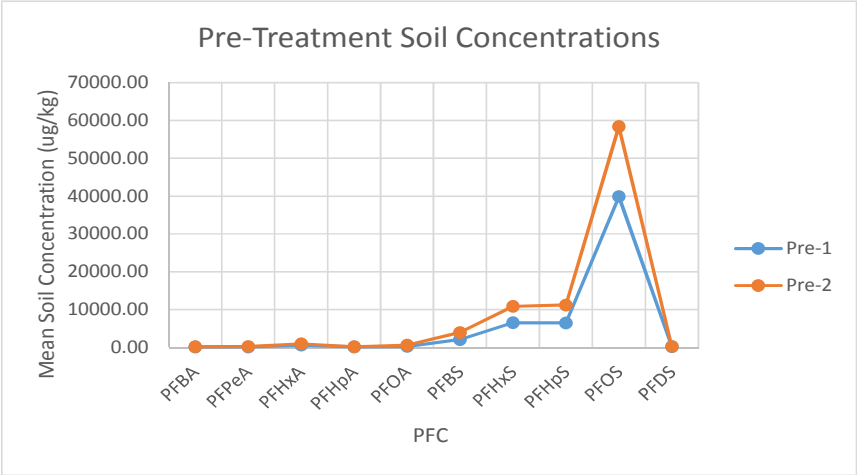
Each 250mL mixture was mixed with two gallons of tap water within a 5-gallon bucket, and subsequently poured on to a 55-gallon drum full (approximately 0.5 ton) of dry, uniform, sandy soil stockpiled on plate boards at the ground surface (see photograph below). The minimum pre-treatment soil concentration range targeted for this spiking was on the order of 10,000 ug/kg of total PFCs.

The soils were evenly mixed to the extent practicable using both manual (shovels) and mechanical (using bobcat) methods (see photograph below).

Pre-Treatment Sampling

Following mixing of soils, each 55-gallon soil stockpile was independently sampled, with each sample representing a 7-point composite of aliquots from different locations throughout each stockpile; the pre-treatment samples were labeled as Pre-1 and Pre-2, representing pre-treatment samples from the first and second drum stockpiles, respectively.

Table 1 summarizes the soil sampling results, presented in the form of mean concentrations across the individual extracts for each sample as provided by CSM, including results of pre-treatment samples (Pre-1 and Pre-2) for the two drums of soil. Graphical representation of the pre-treatment concentrations of the two soil drums is also included below. CSM's analytical report is included herein as Attachment I[1].



As indicated on graph above and in Table 1, the following PFCs were reported with detected mean extract concentrations above limits of quantitation (LOQs) in pre-treatment samples (Pre-1 and Pre-2) from both soil drums: perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA),

[1] Attachment I includes standard deviation and relative standard deviation values for each mean concentration estimate shown in Table 1, in addition to mass levels detected in each individual extract from each sample.

perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), perfluoroheptanesulfonate acid (PFHpS), perfluorooctanesulfonic acid (PFOS), perfluorodecane sulfonate (PFDS), perfluorooctane sulfonamide (PFOSA), and perfluoro-n-pentanoic acid (PFPeA). As indicated in Table 1, total PFC mean concentrations in the two pre-treatment samples ranged from approximately 56,377 ug/kg to 86,819 ug/kg, with the PFOS concentration comprising 67% (Pre-1) to 70% (Pre-2) of the total PFC concentration. As expected, the distribution of the individual PFC detections in the pre-treatment samples are largely consistent as shown on the graphic above.

PFC Treatment

Treatment of spiked soils from each drum stockpile was performed within Endpoint's VEG Batch Unit, which recreates a smaller-scale version of conditions (temperature and fluidization of soils in response to contact with steam) within the full-scale VEG Treatment Unit. The VEG treatment process is described in more detail in Attachment II herein. Three treatment scenarios were performed using the soils from the two drum stockpiles, as summarized in the matrix below.

Soil Stockpile	Soil Temperature and Treatment Duration	Post-Treatment Sample ID (7-point composite)
Portion of soils from Drum 1	900 F, 15 minutes	Post-1
Portion of soils from Drum 2	1100 F, 15 minutes	Post-2
All soils from Drums 1 and 2	1750 F, 30 minutes	Post-3

As indicated in the matrix, the first treatment run targeted increasing the temperature of the Drum 1 soils from ambient levels (60 to 65 F) to 900 F, and maintaining treatment at this temperature for 15 minutes. Correspondingly, the second treatment run targeted increasing the temperature of the Drum 2 soils from ambient levels to 1100 F, and maintaining treatment at this temperature for 15 minutes.

For this preliminary bench-scale study and given the low volume of soils treated, the first two treatment scenarios referenced above involved placing a portion (approximately 0.5 cubic feet) of the spiked soils from each of the two drum stockpiles onto treatment plates that fit within the fully enclosed VEG Batch Unit (see photographs below), preheated with steam at temperatures ranging from 900 F to 1100 F across the first two treatment runs.

Lastly, the third and final treatment run involved mixing all of the remaining untreated soils from both drums together, and treating this larger soil volume within the VEG Batch Unit by raising the soil temperature from ambient to 1750 F, and maintaining treatment at this temperature for a period of 30 minutes.

It should also be noted that the general bases for the temperature range tested as referenced above were the results of laboratory studies (Office of Pollution Prevention & Toxics, 2003a[2] and 2003b[3]) which showed PFCs to be more than 99% removed at approximately 1112 F through direct fire incineration, gas-phase NMR studies which showed 99% destruction of various PFC salts at temperatures on the order of 572 to 662 F (Krusic & Roe, 2004[4]; Krusic, Marchione, & Roe, 2005[5]), and studies (Yamada et. al., 2005)[6] which have found a fluorotelomer-based acrylic polymer to be more than 99% destroyed at 1742 F as a free polymer, and at 1292 F when coated on a fabric. While the above studies reflect incineration temperatures as opposed to temperatures of soil following indirect-fire thermal treatment using steam, two of the three temperatures selected for the bench-scale testing nevertheless corresponded very closely with those showing incineration efficacy in the literature, including the highest reported temperature approximating 1750 F.

Post-Treatment Sampling

As indicated in the matrix on Page 4, 7-point composite soil samples were collected after each of the soil treatment runs, with corresponding labels as Post-1 through Post-3 (see matrix on Page 4). Table 1 includes the post-treatment soil sampling results, again presented in the form of

[2] Office of Pollution Prevention & Toxics (2003a). Laboratory-Scale Thermal Degradation of Perfluorooctanyl Sulfonate and Related Substances. Washington DC: US Environmental Protection Agency, Docket AR226-1366. Office of Pollution Prevention & Toxics (2003b) Final Report: Laboratory-Scale Thermal Degradation of Perfluoro Octanyl Sulfonate and Related Substances. Washington DC: US Environmental Protection Agency, Docket AR226-1367.

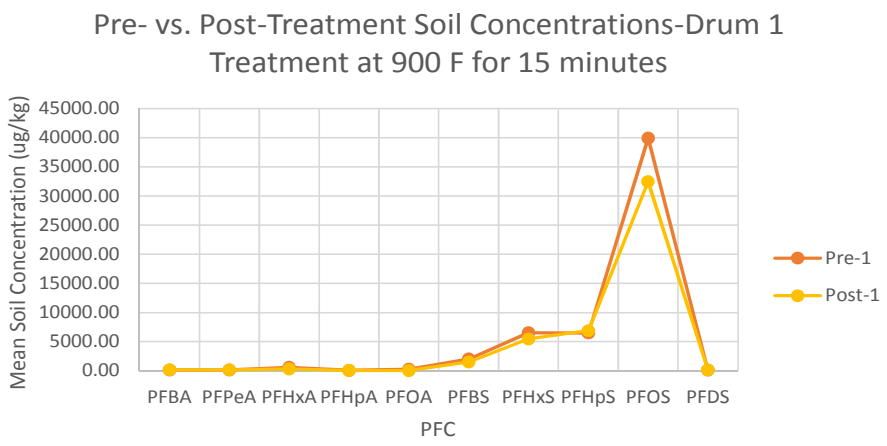
[4] Krusic P J, and Roe D C. (2004). Gas-phase NMR technique for studying the thermolysis of materials: Thermal decomposition of ammonium perfluorooctanoate. Analytical Chemistry, 76(13): 3800–3803.

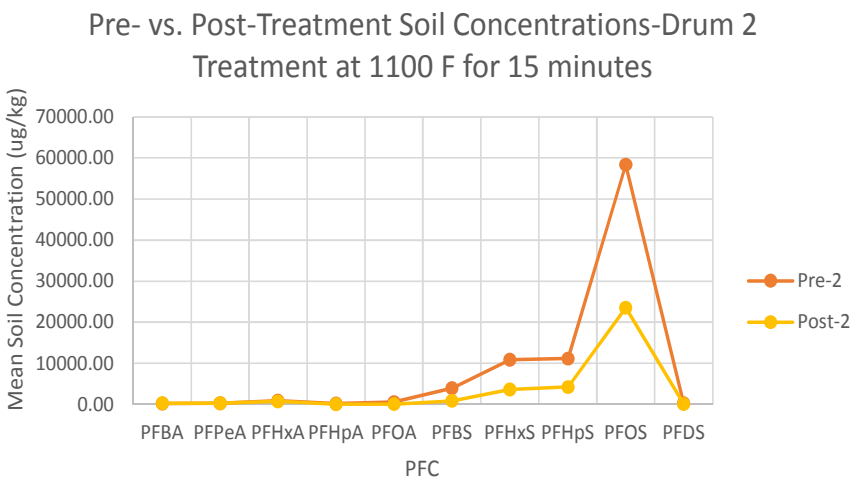
[5] Krusic P J, Marchione A. and Roe D C. (2005). Gas-phase NMR studies of, the thermolysis of perfluorooctanoic acid. Journal of Fluorine Chemistry, 126(11-12): 1510–1516.

[6] Yamashita N, Kannan K, Taniyasu S, Horii Y, Petrick G, Gamo T. (2005). A global survey of perfluorinated acids in oceans. Marine Pollution Bulletin, 51(8–12): 658–668.

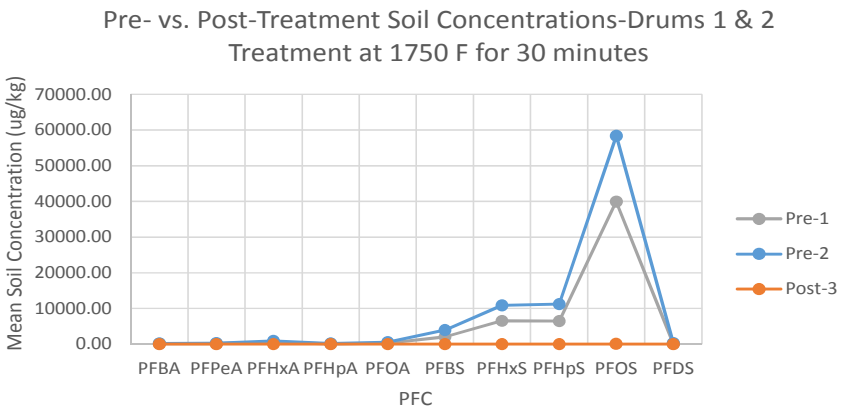
mean concentrations across the individual extracts for each sample as provided by CSM, including results of post-treatment samples (Post-1 through and Post-3). CSM's analytical report is included as Attachment I.

The graphics below depict an independent comparison between the pre- and post-treatment results for soils from the first and second drums based on the first two treatment scenarios described above. As shown on the graphics below and in Table 1, treatment of PFCs at 900 F for 15 minutes resulted in a limited (16 %) reduction in total PFC concentrations for soils form Drum 1, while a significantly greater reduction (61 %) in total PFC concentration was observed for treatment of soils from Drum 2 at 1100 F for 15 minutes.





Lastly, as indicated in the graphic below and in Table 1, treatment of soils from Drums 1 and 2 at 1175 F for a 30-minute period resulted in removal of all PFCs at levels above LOQs, corresponding to an estimated mass removal of >99%.



Discussion

The results of the treatment and testing activities summarized herein suggest that measurable reduction (i.e., > 60%) in total PFC concentrations in soil are achievable under soil treatment temperatures upwards of 1100 F and treatment periods on the order of 15 minutes. While the number of treatment runs within this preliminary bench-scale test were insufficient to identify the optimal treatment conditions for PFCs, the results further indicate that full removal (to below LOQs) of PFCs from soil using thermal treatment may be achievable at temperatures as high as 1750 F across treatment periods of 30 minutes. It is expected that optimal treatment conditions for full removal of PFCs from soil are likely to be in between 1100 F and 1750 for a duration ranging from 15 to 30 minutes, and likely closer to the lower end of this range; however, such temperatures and residence times do have minor site-specific implications depending on soil types and moisture contents.

As discussed in Attachment II, Endpoint's VEG Technology incorporates a closed loop treatment process which involves an engineered mix of caustic soda (including potassium hydroxide), zero valent iron (ZVI), lime, water, and steam, incorporating processes such as chemical reduction, thermal oxidation, and transformation processes and associated filtration whereby acidic gases (including HF) are fully captured, CO_2 emissions are typically reduced by 90%, and target contaminants are either fully treated or otherwise transformed into syngas for fueling the VEG System operations. Regarding the fate of the PFCs across the range of VEG treatment components, additional bench-scale testing to isolate treatment elements and performing sampling from the various VEG treatment components is necessary to properly quantify the portion of PFCs directly treated within soil (through chemical reduction), treated through high-temperature thermal oxidation, and/or transitioned as caustic by product within the filtration system.

The additional sampling referenced above notwithstanding, the bench-scale test results summarized herein indicate the presence of slight increases in the shortest chain acids such as PFBA and PFPeA after treatment for the two lowest temperatures tested; these increases may reflect transformation products of either the longer chain PFCs, or related precursors, suggesting treatment within the soil may be occurring. Moreover, based on parallel bench-scale testing ongoing by Endpoint for treatment of PFCs in groundwater, it is expected that the bulk of the PFC mass induced to volatilize from the parent media (soil or water) is treated via the high temperature thermal oxidation component of the VEG treatment system, with acidic gases unique to PFC oxidation (i.,e HF) removed through the caustic soda (potassium hydroxide) component of the VEG Treatment process. This thermal oxidation process within the VEG's fully enclosed, looping treatment system is considered a far more viable and cost-effective alternative to actual treatment of PFCs (once removed from soil or water) as compared to other alternatives such as incineration.

Recommendations

Based on the results of the preliminary bench-scale testing, Endpoint recommends further bench-scale and onsite pilot testing using both the in-situ and ex-situ components of the VEG Technology, allowing for determination of optimal treatment conditions for treatment of PFCs in soils, sediments, and groundwater, and for defining the expected mass balance governing the fate of PFCs removed from the parent media.

ATTACHMENTS

Table 1:	Ex-Situ VEG Thermal Treatment Bench-Scale Test Results
Attachment I:	Laboratory Analytical Report
Attachment II:	VEG Technology Process

TABLE

Table 1. Ex-Situ VEG Thermal Treatment Bench-Scale Test Results

			Soil Concentration (ug/kg)											
Sample ID	**Soil Batch**	**Treatment Condition**	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFBS**	**PFHxS**	**PFHpS**	**PFOS**	**PFDS**	**Total PFCs**	**% Reduction**
			Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean
Pre-1	Drum 1	Untreated	140.07	137.70	574.72	103.10	281.16	2042.03	6524.61	6480.35	39936.80	156.60	56377.14	NA
Pre-2	Drum 2	Untreated	199.40	273.07	943.23	194.06	560.82	3946.60	10853.65	11187.16	58386.06	275.47	86819.50	NA
Post-1	Drum 1	900 F, 15 minutes	197.02	184.81	312.74	29.54	26.78	1508.30	5465.12	6908.17	32444.57	119.61	47196.65	16.28%
Post-2	Drum 2	1100 F, 15 minutes	314.96	302.01	686.08	48.31	69.00	883.57	3677.62	4245.24	23509.81	78.13	33814.72	61.05%
Post-3	Drums 1 and 2	1750 F, 30 minutes	<1E-1	<1E-1	<2E-2	<2E-2	<2E-2	<5E-3	<5E-3	<5E-3	<2E-2	<5E-3	<1E-1	>99.99%

NA = Not Applicable

ATTACHMENT I

PFAS SOIL EXTRACTION

Analyses were adapted from Blaine et al. 2013 and Blaine et al. 2014. All analyses were performed in triplicate. Aliquots (0.1 – 1 g) of soil were transferred to 50 mL polypropylene tubes, and were spiked with 2 ng of isotopically labeled surrogate standards. The samples were then extracted with 99:1 (vol/vol) methanol with ammonium hydroxide. Afterwards, 7 mL of the basic methanol was added to soil, and then the mixture was placed in a heated (30 °C) sonication bath for 30 minutes. After sonication, the polypropylene tubes were placed on a shaker table for two hours. The samples were then centrifuged at 2700 rpm for 20 minutes. The extract was then decanted into a 20 mL scintillation tube, and this process was repeated two more times (the soil underwent three extraction cycles). After the extraction was complete, the combined extracts were evaporated using a N_2 evaporation unit. The samples were reconstituted using 700 µL of 99:1 (vol/vol) methanol with acetic acid. Sample clean-up was performed by removing extracted natural organic matter using ENVI-Carb. After clean-up, the cleaned-up extract was added to an auto-sampler vial for analysis.

The extracts were then analyzed by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS), using 10 mM ammonium acetate in both water and methanol. Samples were injected (1 mL) using a Shimadzu SIL-5000 autosampler onto a 50 mm x 4.6 mm Gemini C_{18} column with a 3 µm particle size. Initial eluent conditions were 90% water, and 10% methanol. The methanol percentage was ramped to 95% at 4 minutes, and the program was finished by taking the methanol percentage back down to 10% after 5.5 minutes. The PFASs were analyzed by an MDS Siex Applied Biosystems API 3200 in negative electrospray ionization mode under multiple reaction monitoring, and two transitions were monitored for each PFAS.

The reported concentrations for each soil are an average of the three triplicates measured. The relative standard deviations ranged from 1.32 – 33.7%. The limit of quantitation for the PFASs in the soils ranged from a minimum of 0.005 – 0.1 ng/g. The surrogate recoveries for these samples ranged from 58 – 105%, which is typical for PFAS soil extraction (Blaine et al. 2013).

References

Blaine, A.C. et al., 2014. Perfluoroalkyl Acid Distribution in Various Plant Compartments of Edible Crops Grown in Biosolids-Amended soils. *Environmental Science & Technology*, 48(14), pp.7858–7865. Available at: http://dx.doi.org/10.1021/es500016s.

Blaine, A.C. et al., 2013. Uptake of Perfluoroalkyl Acids into Edible Crops via Land Applied Biosolids: Field and Greenhouse Studies. *Environmental Science & Technology*, 47(24), pp.14062–14069. Available at: http://dx.doi.org/10.1021/es403094q.

Mass in Vial (pg compound per 300 pg IS)

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFBS	PFHxS	PFHpS	PFOS	PFDS
PRE 1A	229.00	212.15	888.85	158.64	404.58	2724.37	504.77	2137.61	3155.61	246.43
PRE 1B	200.27	180.46	724.35	125.31	348.87	2775.24	501.32	1705.67	2694.47	184.82
PRE 1C	164.47	188.52	810.81	150.51	428.58	3076.61	503.49	2150.49	3373.06	228.88
PRE 2A	239.31	360.01	1189.68	232.61	716.98	5336.10	872.25	3312.38	4526.05	371.47
PRE 2B	329.26	445.02	1547.34	329.30	824.40	6671.52	950.92	3982.36	5360.14	455.43
PRE 2C	247.50	315.44	1128.60	234.74	731.67	4272.08	630.08	2797.19	3355.82	306.42
POST 1A	267.93	272.20	462.87	38.25	38.81	2117.16	454.70	2040.26	2583.50	163.69
POST 1B	266.43	223.69	384.06	31.89	36.90	1810.40	373.79	1962.25	2474.54	154.01
POST 1C	354.36	328.81	548.06	63.40	44.15	2839.47	507.46	2845.01	2920.74	220.70
POST 2A	656.44	603.16	1430.16	108.12	130.51	1887.90	362.25	1915.27	2365.03	160.01
POST 2B	561.10	531.28	1329.78	85.54	137.72	1512.52	360.02	1535.24	2307.40	128.69
POST 2C	408.51	413.77	800.23	58.46	85.50	1168.29	298.89	1334.15	1875.00	111.84
POST 3A	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
POST 3B	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
POST 3C	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
MB1	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
MB2	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
MB3	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
Min Cal Point (pg cmpd/300 pg IS)	100.00	100.00	20.00	20.00	20.00	5	5	5	20	5
LOQ (ng/g)	1.00E-01	1.00E-01	2.00E-02	2.00E-02	2.00E-02	5.00E-03	5.00E-03	5.00E-03	2.00E-02	5.00E-03
LOQ (ng/mL)	0.074	0.074	0.015	0.015	0.015	0.004	0.004	0.004	0.015	0.004
Surrogate Recpvery (%)	105.11	65.94	87.81	62.70	71.74	61.47	64.63	87.58	57.86	87.58

Compound Concentration In Extract (ppb)

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFBS	PFHxS	PFOS	PFDS
PRE 1A	**2.5**	**2.3**	**9.8**	**1.7**	**4.4**	**29.9**	**101.0**	**631.1**	**2.71**
PRE 1B	**2.2**	**2.0**	**8.0**	**1.4**	**3.8**	**30.5**	**100.3**	**538.9**	**2.03**
PRE 1C	**1.8**	**2.1**	**8.9**	**1.7**	**4.7**	**33.8**	**100.7**	**674.6**	**2.52**
PRE 2A	**2.6**	**4.0**	**13.1**	**2.6**	**7.9**	**58.6**	**174.5**	**905.2**	**4.08**
PRE 2B	**3.6**	**4.9**	**17.0**	**3.6**	**9.1**	**73.3**	**190.2**	**1072.0**	**5.00**
PRE 2C	**2.7**	**3.5**	**12.4**	**2.6**	**8.0**	**46.9**	**126.0**	**671.2**	**3.37**
POST 1A	**2.9**	**3.0**	**5.1**	**0.4**	**0.4**	**23.3**	**90.9**	**516.7**	**1.80**
POST 1B	**2.9**	**2.5**	**4.2**	**0.4**	**0.4**	**19.9**	**74.8**	**494.9**	**1.69**
POST 1C	**3.9**	**3.6**	**6.0**	**0.7**	**0.5**	**31.2**	**101.5**	**584.1**	**2.43**
POST 2A	**7.2**	**6.6**	**15.7**	**1.2**	**1.4**	**20.7**	**72.5**	**473.0**	**1.76**
POST 2B	**6.2**	**5.8**	**14.6**	**0.9**	**1.5**	**16.6**	**72.0**	**461.5**	**1.41**
POST 2C	**4.5**	**4.5**	**8.8**	**0.6**	**0.9**	**12.8**	**59.8**	**375.0**	**1.23**
POST 3A	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**
POST 3B	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**
POST 3C	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**
MB1	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**
MB2	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**
MB3	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**	**LOQ**

	Concentration in Extract (ng/mL)									
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFBS	PFHxS	PFHpS	PFOS	PFDS
PRE 1A	2.52	2.33	9.77	1.74	4.45	29.94	100.95	106.88	631.12	2.71
PRE 1B	2.20	1.98	7.96	1.38	3.83	30.50	100.26	85.28	538.89	2.03
PRE 1C	1.81	2.07	8.91	1.65	4.71	33.81	100.70	107.52	674.61	2.52
PRE 2A	2.63	3.96	13.07	2.56	7.88	58.64	174.45	165.62	905.21	4.08
PRE 2B	3.62	4.89	17.00	3.62	9.06	73.31	190.18	199.12	1072.03	5.00
PRE 2C	2.72	3.47	12.40	2.58	8.04	46.95	126.02	139.86	671.16	3.37
POST 1A	2.94	2.99	5.09	0.42	0.43	23.27	90.94	102.01	516.70	1.80
POST 1B	2.93	2.46	4.22	0.35	0.41	19.89	74.76	98.11	494.91	1.69
POST 1C	3.89	3.61	6.02	0.70	0.49	31.20	101.49	142.25	584.15	2.43
POST 2A	7.21	6.63	15.72	1.19	1.43	20.75	72.45	95.76	473.01	1.76
POST 2B	6.17	5.84	14.61	0.94	1.51	16.62	72.00	76.76	461.48	1.41
POST 2C	4.49	4.55	8.79	0.64	0.94	12.84	59.78	66.71	375.00	1.23
POST 3A	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
POST 3B	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
POST 3C	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
MB1	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
MB2	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
MB3	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ

		Soil Concentration (ng/g, or ug/kg)									
	Mass(g)	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFBS	PFHxS	PFHpS	PFOS	PFDS
PRE 1A	0.1146	153.71	142.40	596.62	106.48	271.57	1828.68	6166.46	6528.47	38550.18	165.41
PRE 1B	0.1086	141.85	127.82	513.07	88.76	247.11	1965.75	6462.74	5497.09	34735.28	130.91
PRE 1C	0.1015	124.64	142.87	614.48	114.07	324.81	2331.65	6944.63	7415.50	46524.95	173.46
PRE 2A	0.1033	178.21	268.09	885.90	173.22	533.90	3973.57	11821.39	11222.98	61340.50	276.62
PRE 2B	0.1232	205.58	277.86	966.12	205.61	514.74	4165.53	10805.87	11313.54	60910.65	284.36
PRE 2C	0.0888	214.40	273.25	977.65	203.34	633.81	3700.69	9933.68	11024.97	52907.03	265.43
POST 1A	0.0939	219.49	222.98	379.18	31.33	31.79	1734.38	6779.33	7604.80	38518.64	134.10
POST 1B	0.1304	157.17	131.96	226.56	18.81	21.77	1067.96	4013.12	5266.77	26567.18	90.85
POST 1C	0.1268	214.97	199.48	332.48	38.46	26.78	1722.56	5602.90	7852.94	32247.88	133.89
POST 2A	0.1674	301.65	277.16	657.18	49.68	59.97	867.52	3029.60	4004.45	19779.23	73.53
POST 2B	0.1258	343.10	324.86	813.12	52.30	84.21	924.86	4006.60	4271.34	25678.54	78.69
POST 2C	0.1047	300.13	304.00	587.93	42.95	62.82	858.34	3996.65	4459.91	25071.66	82.17
POST 3A	0.9488	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
POST 3B	0.9426	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
POST 3C	0.9921	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ

Soil Concentration (µg/kg)

	PFBA			PFPeA			PFHxA			PFHpA			PFOA		
	Mean	Std Dev	RSD %	Mean	Std Dev	RSD %	Mean	Std Dev	RSD %	Mean	Std Dev	RSD %	Mean	Std Dev	RSD %
Pre 1	140.07	14.62	10.44	137.70	8.55	6.21	574.72	54.14	9.42	103.10	12.99	12.59735	281.16	39.73	14.13
Pre 2	199.40	18.87	9.46	273.07	4.89	1.79	943.23	49.98	5.30	194.06	18.08	9.318644	560.82	63.94	11.40
Post 1	197.02	34.60	17.56	184.81	47.25	25.57	312.74	78.20	25.01	29.54	9.95	33.68144	26.78	5.01	18.72
Post 2	314.96	24.38	7.74	302.01	23.91	7.92	686.08	115.34	16.81	48.31	4.82	9.984431	69.00	13.25	19.20
Post 3	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
Minimum LOQ (ng/g)	0.1			0.1			0.02			0.02			0.02		
Surrogate Recovery %	105.11			65.94			87.81			62.70			71.74		

Soil Concentration (µg/kg)

	PFBS			PFHxS			PFHpS			PFOS			PFDS		
	Mean	Std Dev	RSD %	Mean	Std Dev	RSD %	Mean	Std Dev	RSD %	Mean	Std Dev	RSD %	Mean	Std Dev	RSD %
Pre 1	2042.03	260.01	12.73	6524.61	392.76	6.02	6480.35	960.11	14.82	39936.80	6015.91	15.06	156.60	22.60	14.43
Pre 2	3946.60	233.59	5.92	10853.65	944.76	8.70	11187.16	147.58	1.32	58386.06	4749.84	8.14	275.47	9.51	3.45
Post 1	1508.30	381.39	25.29	5465.12	1388.24	25.40	6908.17	1426.89	20.66	32444.57	5978.15	18.43	119.61	24.91	20.82
Post 2	883.57	36.05116	4.080151	3677.616	561.2216	15.26047	4245.236	228.851	5.390771	23509.81	3244.994	13.80272	78.12959	4.349936	5.567592
Post 3	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
Minimum LOQ (ng/g)	0.005			0.005			0.005			0.02			0.005		
Surrogate Recovery %	61.47			64.63			87.58			57.86			87.58		

ATTACHMENT II

Mobile VEG Technology for Ex-Situ and In-Situ Treatment of Soils, Enhanced NAPL Reocovery, and Treatment of Extracted Groundwater

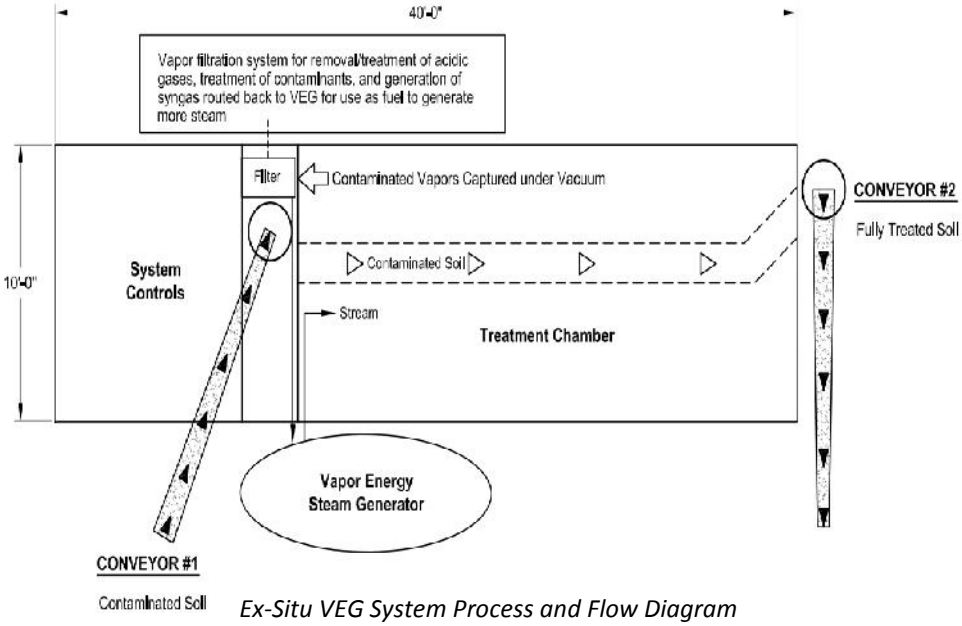
Description

VEG Mobile Ex-Situ Soil Remediation System

The Vapor Energy Generator (VEG) system is a patented, mobile in-situ and ex-situ technology used to remediate soils onsite. Additional applications of the VEG Technology include in-situ enhanced NAPL recovery, and ex-situ treatment of groundwater. The VEG Technology employs a series of patented treatment processes, relying first on a green and sustainable thermal process to desorb contaminants from soil, followed by a series of patented treatment processes and filters which treat or otherwise transforming all contaminants thermally removed from soils, rendering the soil as uncontaminated and available for unrestricted onsite reuse. Specifically, the technology employs a unique and patented combination of indirect-fire thermal treatment to desorb the full range of organic chemicals and select metals from soils, and subsequently treats the vapors, including acidic gases and CO_2, using a combination of chemical reduction, thermal oxidation, and transformation treatment processes and associated filtration whereby emissions are eliminated. Next, the patented technology transforms select chemicals in the vapor stream into a synthetic gas which serves as a renewable source of fuel to run the VEG treatment operations. These thermal desorption, chemical treatment, thermal oxidation, and transformation processes occur in a continuous, and repeating looping system such that no vapors are emitted to the atmosphere.

VEG Process

At the core of the VEG remediation technology is a patented, compact, highly efficient vapor energy generator, which initially utilizes recycled water and propane to generate steam at 1300°F. For treatment of chemicals with low vapor pressure (such as PFCs), the vapor generator may be augmented to reach 2000 °F. The vapor generator provides the thermal



Ex-Situ VEG System Process and Flow Diagram

energy for both in-situ and ex-situ applications of the VEG technology.

Featuring an enclosed rotational renewal/treatment chamber containing a 20- to 60-inch auger and a hollow 6-inch shaft, the ex-situ VEG soil remediation system rotates via a variable speed hydraulic system, thermally removing contaminants from soils moving down the auger. Soil contaminants are entirely desorbed at specified temperatures and residence times, and are passed as vapors into the box head space within the enclosed chamber. Induced vapors in the head space are then sent through a series of patented filters containing an engineered mixture of caustic soda, zero valent iron (ZVI), water, lime, and steam. Through this filtration, the acidic gases (i.e., NOx, SOx, and HCl) and CO_2 components are captured/treated, the organic components are largely treated via ZVI or fully thermally oxidized, and select vapor streams are transformed into a syngas through the interaction of steam and hydrogen, and subsequently sent back to the vapor generator to replace the propane as the fuel to continue system operations. Accordingly, the system operates on an entirely closed looping system without any emissions to the atmosphere, where the induced vapors are continuously recycled through the system and re-treated for all acidic and chemical components, and where possible transformed to a renewable source of fuel.

The sole byproduct of the VEG treatment is a typically benign, dilute liquid solution concentrated with sodium nitrate (NaNO3), sodium bisulfate (NaHSO4), and sodium chloride (NaCl) for ultimate profiling and typical non-hazardous waste disposal offsite. However, it is expected that thermal treatment of longer PFC chains will yield radicals (e.g., tetrafluoroethene, difluorocarbene, and trifluoromethyl) that under thermal treatment are readily transformed into carbon monoxide (CO), CO_2, and hydrofluoric acid (HF); each of these byproducts are addressed by VEG's treatment system, including the use of potassium hydroxide to scrub the HF gases unique to thermal oxidation of PFCs. Worth noting is that the volume of liquid waste generation from the VEG filters is typically one 55-gallon drum for each 15,000 cubic yards of soil treated.

In-situ applications of the VEG Technology similarly rely on the patented vapor generator, which provides the source of heat that is injected beneath the ground through wells or piping arrays, thereby inducing volatilization of contaminants that are subsequently captured via vapor extraction wells. The captured vapors are treated similarly to the ex-situ treatment process in that they are vacuumed through a series of patented filters, treating acidic gases and CO_2 components, while treating and converting remaining organic components of the extracted vapors into syngas to fuel ongoing treatment operations.

In-Situ Application of VEG Technology for Enhanced NAPL Recovery and Soil Treatment

The VEG Technology has also been used for treatment of extracted groundwater, especially for chemicals with low vapor pressures (e.g., PFCs), and those which do not adsorb to carbon or readily strip. VEG application for treatment of organic compounds in water entails replacing the clean water within the vapor generator (which is initially combined with air and propane to generate the steam serving as the heat source for thermal treatment) with the contaminated groundwater targeted for treatment. As this contaminated water is fed into the vapor generator, chemicals dissolved in this water are immediately subject to thermal oxidation and the water is transformed into superheated steam. The hot vapor stream

from this process is conveyed via enclosed piping through the aforementioned VEG filtration processes which will, among other things, treat the acidic gases inherent to thermal oxidation of the dissolved contaminants in the water introduced into the system.

Applicability

The VEG Technology has been successfully applied to treat the full suite of organic chemicals, including fuels, PAHs, chlorinated solvents, pesticides and PCBs, munitions constituents, and select metals. Successful pilot-scale treatment of PFCs in soils has also been implemented as summarized in the main sections of this Tech Memo. Ongoing research and development using the VEG Technology includes removal of PFCs from groundwater, and treatment of byproducts of mustard gas.

In addition to the more than 30 successful applications on commercial projects, the VEG Technology has been successfully applied on multiple USACE and Department of Defense (DoD) projects, including:

- Ex-situ VEG Technology has been successfully applied for full treatment (to non-detect levels below soil-leaching-to-groundwater cleanup goals) of chlorinated solvents and petroleum hydrocarbon compounds in soils at the Motor Pool Area site within the Engineer Research and Development Center (ERDC) Waterways Experiment Station (WES) facility in Vicksburg, MS (USACE-Omaha District).
- Both in-situ and ex-situ components of the VEG Technology have been applied to treat munitions constituents in soils at the former Sioux Army Depot site in Sidney, NE (USACE-Omaha District), with the former yielding 98% reductions through the use of in-situ steam-enhanced alkaline hydrolysis, and the latter resulting in full treatment of all munitions constituents, including 55,000,000 ug/kg of TNT and over 11,000,000 ug/kg of RDX in soil, to non-detect levels within 8 minutes of ex-situ pilot treatment at 750 F.
- The VEG Technology has also been successfully used to perform pilot ex-situ treatment of PCBs in frozen sediments from the former Umiat Test Well #9 site in Umiat, AK (USACE-Alaska District), resulting in non-detect levels meeting both residential and ecological cleanup goals.
- Ex-situ applications of the VEG Technology have also been performed on PAH-impacted soils at the former Atlas Scrap Yard site at the Former Ravenna Army Ammunition Plant in Ravenna, OH (USACE- Louisville District), treating PAHs to below detection limits for unrestricted reuse.
- The VEG Technology has also been used for ex-situ bench-scale treatment of pesticides to below detection limits in support of onsite reuse and residential redevelopment at the Hurlburt Airfield, Ft. Walton Beach, FL (Air Force Civil Engineer Center [AFCEC] and Corvias Military Living).
- Upcoming VEG Technology projects in 2016 include in-situ treatment of petroleum hydrocarbons in both unsaturated and saturated soils, together with ex-situ pilot treatment of TBA in groundwater at the Joint Forces Training Base in Los Alamitos, CA (USACE- Los Angeles District). Other projects slated for 2016 include both in-situ and ex-situ treatment of petroleum hydrocarbons in soil at the Luscious Clay National Guard Center in Marietta, GA (USACE-Savannah District), and for treatment of jet fuel in soils resulting from a pipeline release just outside of Travis AFB.

Media

The technology is applicable to direct treatment of soil, soil vapor, sediment, and NAPL. It is also applicable for both direct and indirect treatment of contaminants in groundwater through source removal in unsaturated and saturated soils and through above-ground thermal treatment of groundwater. The technology can also treat pore water associated with high-moisture content soils and/or dredged saturated sediments.

Geology

The VEG Technology has been applied to a wide range of geologic settings, ranging from sandy soils to loess material, silts, and clays. The technology has also been applied to saturated and frozen sediments. Ex-situ applications have the benefit of soil preparation, wherein wet, clumped soils may be subjected to size reduction prior to treatment. This benefit is not available to in-situ applications to saturated, less-permeable soils. Depth of treatment is not a limitation, provided soils may be accessible for excavation (for ex-situ applications) and/or well installation (for in-situ applications).

Advantages

- The VEG is highly mobile, capable of mobilizing on a single 40-foot long trailer (for ex-situ unit) and an even smaller pickup-truck mounted trailer for the in-situ unit, significantly limiting mobilization costs and allowing for treatment operations to occur within very limited spaces.
- The VEG technology is highly robust relative to removal efficiency of contaminants compared to other technologies, including typical 100% removal/treatment (i.e. to non-detects) of chemicals in soil using its ex-situ component, and >90% reduction/treatment of chemicals in soil using its in-situ component. Ex-situ soil treatment rates typically range from 15 to greater than 30 cubic yards per hour (per treatment unit), depending on soil types, moisture conditions, and contaminants being treated.
- Mass removal is rapid, including treatment times ranging from 5 to 25 minutes within the ex-situ treatment chamber depending on the molecular weight of the chemicals being treated and the moisture content of the soil. In-situ mass removal also becomes very rapid once the optimal soil temperature is reached beneath the ground.
- In-situ treatment can also significantly increase biodegradation rates, helping promote its use in both source area and downgradient portions of the plume.
- The technology is highly cost effective relative to offsite disposal remedial alternatives, typically reducing remediation costs by 40% to 60% relative to landfill disposal options. The technology also eliminates both the need for importing clean backfill to the site and the long-term waste generator liability inherent to landfill disposal, and further reduces the carbon footprint of remediation by as much as 80 to 90%.
- Technology can be powered by onsite generator and employs a patented, highly efficient vapor generator that uses minimal water and fuel to generate the heath source for thermal treatment,

with the latter generated through the soil treatment process as a renewable source of fuel to run operations; accordingly, the technology is characterized by very limited operational costs.

Limitations

- Treatment rates, which typically range from 15 to 30 cubic yards per hour per treatment unit, may be reduced during poor weather conditions such as freezing temperatures or excess rainfall. This can be addressed through upfront preparation of soil prior to treatment, reducing wet, clumped soils down to sizes which will trigger higher treatment rates. It is ideal to implement the technology during spring and summer months to minimize the potential for impacts from adverse weather.
- For sites with significant debris and/or large size rocks or boulders, upfront management of soil to separate out the debris and rocks will be necessary.
- Unavailability of power is met through the use of a generator, while the limited fuel needed can be met with a small 500- gallon propane tank, which again is subject to limited use as the system transitions the treated vapor stream into a syngas to replace the use of propane. A source of water, typically through a water truck, will also be needed.

Design Criteria

- For ex-situ applications, key design criteria include the nature and extent of soil contamination, including chemicals of potential concern and associated concentrations, volume of impacted soils warranting treatment, and soil types, lithology, and physical properties, including moisture content.
- Target cleanup goals for the soil treatment will also be required.
- For in-situ applications, an understanding of buried utilities will be required.

Monitoring

- The monitoring/sampling required is limited to post-treatment sampling of soil stockpiles following treatment and in support of onsite reuse. Typically, one 7-point composite soil sample per each 100 to 250 cubic yard stockpile is performed to demonstrate compliance of post-treated soils prior to backfilling and reuse, although post-treatment requirements can vary by oversight agency.
- For in-situ applications, sample from soil borings immediately adjacent to pre-treatment samples are recommended to demonstrate the efficacy of the technology to treat soils in-situ.
- Ongoing, automated monitoring of the VEG system internals (ex-situ system) include real-time gauging of air flow and soil temperature inside the treatment chamber, and soil temperature and moisture in-situ using temperature neutron/moisture probes.

- With demonstrated efficacy of treatment using post-treatment soil samples, monitoring of underlying groundwater is not required.

Lessons earned

- The primary challenge to the implementation of the technology is extreme weather conditions, including sub-freezing temperatures which hinder the initial reliance of propane to generate the heat source for the steam used for the thermal treatment aspect of the technology. In addition, excess soil moisture in response to heavy and constant precipitation events can slow down the soil treatment rate due to challenges with conveyance of the soil into the ex-situ treatment system.
- In dealing with the above challenges, propane blankets and/or dedicated huts with heaters have been used to overcome the sub-freezing air temperatures, allowing for proper functionality of propane. In cases of excess soil moisture, soils are pre-managed prior to ex-situ treatment; this is accomplished through the use of power screens to eliminate large clumps and debris, and the use of crushers for 8-to-1 size reduction, allowing any high-moisture content clays to be reduced to sizes which can then be rapidly dried and treated within the ex-situ VEG treatment chamber.
- In general, there are significant benefits relative to efficiency of the treatment operations when the technology is implemented in spring and summer months when precipitation and air temperatures are more conducive to such treatment.
- The in-situ component of the VEG Technology was recently used to enhance alkaline hydrolysis (i.e., steam-enhanced alkaline hydrolysis), providing the much needed moisture to the hydrolysis process, but also through increasing soil temperature which helped maximize the solubility of munitions constituents to help maximize the efficiency of alkaline hydrolysis within the pore water. Lessons learned for such applications include the use of higher dosages of hydrated lime, or even higher steam temperatures that can not only increase the solubility of munitions, but to in fact thermally treatment them where hydrolysis has limited returns.