

EXECUTIVE SUMMARY

Field Demonstration of Infrared Thermal Treatment of PFAS-contaminated Soils from Subsurface Investigations

SERDP Project ER18-1603

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ACRONYMS AND ABBREVIATIONS

ADEC	Alaska Department of Environmental Control
AFFF	aqueous film-forming foam
Battelle	Battelle Memorial Institute
CH2M	CH2M HILL, Inc.
CSM	Colorado School of Mines
DoD	Department of Defense
ELAP	Environmental Laboratory Accreditation Program
FtS	fluorotelomer sulfates
GAC	granular activated carbon
High C test	High-Concentration test
IDW	investigation-derived waste
Iron Creek	Iron Creek Group Holdings, Inc.
Low C test	Low-Concentration test
mg/kg	milligrams per kilograms
MTGW	migration to groundwater
NAS	Naval Air Station
PAH	polynuclear aromatic hydrocarbon
PFAA	perfluoroalkyl acid
PFAS	Per- and Polyfluoroalkyl Substances
PFCA	perfluorinated carboxylic acids
PFHxS	perfluorohexanesulfonate
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PFSA	perfluorinated sulfonic acids
SERDP	Strategic Environmental Research and Development Program
TOPA	Total Oxidizable Precursor Assay
TDU	thermal desorption unit

USEPA United State Environmental Protection Agency

VGAC vapor-phase granular activated carbon

1.0 INTRODUCTION

Per- and Polyfluoroalkyl Substances (PFAS) are fully fluorinated synthetic organic chemicals that have been used extensively in surface coatings and protectant formulations for packaging products, carpets, leather products, and textiles. PFAS in aqueous film-forming foam (AFFF) are particularly effective in extinguishing hydrocarbon- or solvent-fueled fires, resulting in a large quantity of perfluorinated compound-containing material potentially released to the environment during firefighting training at airports, refineries, chemical manufacturers, and Department of Defense (DoD) installations. Those compounds, commonly encountered in water, include perfluorinated carboxylic acids (PFCA) and perfluorinated sulfonic acids (PFSA). PFAS contaminants that are target compounds for this work include PFCA, PFSA, fluorotelomers, and a few more complicated compounds.

DoD investigations at sites with a history of AFFF usage indicate many sites will likely require further investigation and possibly remedial action (AFCEC, 2015). Investigation will generate substantial volumes of PFAS-impacted investigation-derived waste (IDW). In response to the Strategic Environmental Research and Development Program (SERDP) fiscal year 2018 Statement of Need Number ERSON-18-L1, Innovative Approaches for Treatment of Waste Derived from PFAS Subsurface Investigations, co-principal investigators from CH2M HILL, Inc. (CH2M) and Battelle Memorial Institute (Battelle), and our co-performer organizations (Iron Creek Group Holdings, Inc. [Iron Creek], SGS AXYS, and the Colorado School of Mines [CSM]), propose to demonstrate the infrared thermal treatment of IDW soil contaminated with PFAS.

The team created two synthetic IDW batches by blending contaminated soil from former Naval Air Station (NAS) Willow Grove with local soil and treating two batches (up to 10 tons). One batch was supplemented with AFFF to supplement concentrations. The testing focused on perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), because there are regulatory limits for these compounds in soil.

The treatment system is a transportable unit that can be loaded on a flat-bed truck using a forklift. The treatment system was set up in the parking lot at Iron Creek's Estacada, Oregon, fabrication shop. The synthetic IDW was treated in two batches, each during a 1-week pilot test period. Samples of soil batches, wipe samples from the treatment chamber, vapor cartridges, condensate, and vapor-phase granular activated carbon (VGAC) were collected and analyzed to demonstrate the effectiveness of the treatment process (thermal desorption) and fate of PFAS in the treatment system. The results from the study will be used to optimize design and operation of a mobile treatment system to efficiently and cost-effectively treat PFAS-contaminated soil IDW.

1.1 REGULATORY ENVIRONMENT

Regulation of PFAS is a recent development and the regulatory environment is rapidly evolving. The United States Environmental Protection Agency (USEPA) has published tap water advisories for PFOS and PFOA of 70 nanograms per liter (ng/L) (USEPA, 2016A) (USEPA, 2016B). Alaska regulates a migration to groundwater (MTGW) pathway for PFOS and PFOA (Division of Spill Prevention and Response- Contaminated Sites Program, August 25, 2018), which provides a restrictive set of limits (0.0030 milligrams per kilograms [mg/kg] PFOS and 0.0017 mg/kg PFOA) on soil contamination, which is suitable for re-use (lower than health-based standards for protection of groundwater).

1.2 THERMAL DESORPTION TREATMENT

The infrared treatment module indirectly heats contaminated materials that are stored in a reduced-oxygen or oxygen-free environment to minimize oxidation of the contaminated vapor. By indirectly heating the contaminated material, the control of the flow of heat applied to the contaminated material is improved and loss of heating air or other heating gas is reduced. This results in energy-efficient heating of the soil.

2.0 OBJECTIVES

2.1 PERFORMANCE OBJECTIVES

The objectives of this pilot study are as follows:

1. Evaluate whether the infrared thermal treatment technology (desorption) can effectively treat PFAS-contaminated soil IDW such that it allows soil re-use.
2. Provide documentation of the fate of PFAS in the treatment process.
3. Demonstrate that the treated PFAS in the vapors can be captured.

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3.0 MATERIALS AND METHODS

3.1 TEST SOIL

Test soil was obtained from Former NAS Joint Reserve Base Willow Grove, Building 608, the former Base fire station. The site was being excavated at the time of this study and 4 drums of soil were collected for this study by the remediation contractor.

PFAS results indicate predominantly PFOS (1,227 µg/kg) in the composite soil sample, with significant concentrations of perfluorohexanesulfonate (PFHxS) (198.5 µg/kg) 6:2 fluorotelomer sulfates (FtS) (59.58 µg/kg), and PFOA (22.82 µg/kg). Other compounds were detected at less than 20 µg/kg. The total PFAS concentration was 1,585 µg/kg. In the post-oxidation soil (TOPA results), the total PFAS was reduced slightly to 1,452 µg/kg, with PFOS reduced to 960 µg/kg (21 percent reduction in concentration) and minor increases in PFCAs.

Two batches of soil were created for treatment, a batch of Willow Grove soil diluted with clean local soil (the Low-Concentration test [Low C test] soil) and a batch containing Willow Grove soil, clean local soil, and AFFF (the High-Concentration Test [High C test] soil).

3.2 TEST EQUIPMENT AND OPERATION

The thermal desorption unit (TDU) was operated by heating the air in the treatment bin using propane-fuel infrared heaters. As the vapors exited the treatment bin, they were circulated through a condenser, and then through a VGAC unit. Condensate accumulated in high-density polyethylene drums. Condensate from each batch was tested and the condensate was treated to remove PFAS using granular activated carbon (GAC). The used GAC and VGAC were returned to the vendor for regeneration. Vapor was sampled using cyclo[18]carbon (C-18) cartridges in ports located immediately before the VGAC.

3.3 FIELD TESTING METHODS

Two soil batches were created for the tests. The low-concentration batch included 8,500 pounds of clean fill and 1.5 drums of Willow Grove soil. No AFFF was added to this batch. The high-concentration batch included 7,800 pounds of clean fill and to 2.5 drums of Willow Grove soil, supplemented with 150 mL of electrochemical process AFFF.

During the Low-Concentration Test and High-Concentration Test, pre-, in-, and post-treatment soil samples (five grabs per sample) were collected from the treatment bin, composited, and split into two composite samples. The CSM and SGS AXYS (Sidney, British Columbia) analyzed these samples for PFAS. Soil samples were composite samples constructed of five roughly 10-ounce (oz.) grabs of soil. During the run, Days 1 through 8, samples were collected through the sampling ports installed in the TDU.

Wipe samples were collected from the inside of the TDU, outside the bin, before it was loaded with soil and at the completion of each test. The same locations were used for all wipe samples.

C-18 cartridges were attached to a side-stream of the vapor. The C-18 cartridges were swapped out daily during treatment to evaluate PFAS desorption over time.

The test used two VGAC units. The units were swapped between tests to estimate what was adsorbed during each test. Before testing and after each test was completed, a composite sample was collected from the VGAC unit using the same method as described for soil samples.

Condensate was collected from the condensate tank using a spigot installed in the tank. Condensate samples were collected at the end of each run.

Soil samples were analyzed for PFAS and TOPA by SGS AXYS Analytical Services using two analytical approaches. SGS AXYS method MLA-110 was used to determine the concentrations of 29 targeted PFAS and SGS AXYS Method MLA-111 was used measure perfluorinated carboxylates and sulfonates after a TOPA reaction (Houtz and Sedlak 2012) to estimate presence of oxidizable perfluoroalkyl acid (PFAA) precursors in the samples.

The CSM performed PFAS analysis by liquid chromatography Quadrupole Time of Flight Mass Spectrometry (SCIEX X500R).

Battelle performed analysis of PFAS using liquid chromatography tandem mass spectrometry in the multiple reaction monitoring. Analysis included solid samples, water samples and C-18 cartridges.

4.0 RESULTS AND EVALUATION

4.1 OBJECTIVE 1: EVALUATE WHETHER THE INFRARED THERMAL TREATMENT TECHNOLOGY (DESORPTION) CAN EFFECTIVELY TREAT PFAS-CONTAMINATED SOIL IDW SUCH THAT IT ALLOWS SOIL RE-USE

Results indicate that the average target temperature of 350°C was met by Day 4 of the Low-Concentration Test and maintained over the test. No polynuclear aromatic hydrocarbons (PAHs) were detected in any of the post-treatment samples indicating that thermal desorption effectively treats PAHs where present as co-contaminants with PFAS.

Based on the Environmental Laboratory Accreditation Program (ELAP)-certified analysis by SGS AXYS, all compounds were removed to less than the detections limits except PFHxS (0.126 µg/kg) and PFOS (0.703 µg/kg). Removal of PFOA was to below the detection limit and exceeded 97.4 percent. Removal of PFOS was 99.6 percent and removal of total PFAS was also 99.6 percent. Results from Total Oxidizable Precursor Assay (TOPA) and the CSM confirmed effective treatment. The data shows that most of the compounds and post-oxidation compounds were removed from soil in 4 days when the average temperature of the test soil was heated to the target temperature of 350°C. The re-use criteria were met for both PFOA and PFOS.

High concentration results indicate that the average target temperature (350°C) was not met during the High-Concentration Test. Sensors 1 and 2 reached the target temperature on Days 3 through 8 and Day 7, respectively, indicating partial treatment. No PAHs were detected in any of the post-treatment samples, indicating that thermal desorption effectively treats PAHs where present as co-contaminants with PFAS even though the target temperature was not met.

Total PFAS concentrations reported by SGS AXYS, post-oxidation concentrations reported by SGS AXYS, and total PFAS concentrations reported by CSM during the High-Concentration Test indicated partial treatment of the soil. Based on the ELAP-certified analysis by SGS AXYS, 14 PFAS were detected in the post-treatment sample at concentrations from 0.17 µg/kg to 326 µg/kg. Removal of PFOS was 74.0 percent and removal of total PFAS was 73.0 percent. Results for TOPA and the CSM analysis were similar. The data shows that the PFCA were removed better than the PFSA and that the PFOA concentration was reduced to below the ADEC criteria. PFOS concentrations initially decreased, then decreased and stabilized for the last 3 days at concentrations above out goal.

4.1.1 Conclusions

PFAS removal from soil met Alaska Department of Environmental Control (ADEC) soil to groundwater criteria and the treatment goal for the Low-Concentration Test where the temperature was maintained at or above the target temperature of 350°C. PFAS removal in the High-Concentration Test did not meet treatment goals. In this test, the temperature of the treatment unit did not meet the planned temperature. The result was 73 percent removal of PFAS, a similar removal of PFOS, and reduction of only PFOA to less than the ADEC soil to groundwater criteria.

4.2 OBJECTIVE 2: PROVIDE DOCUMENTATION OF THE FATE OF PFAS IN THE TREATMENT PROCESS

4.2.1 PFAS Mass Balance

In this section, data collected during the tests is used to evaluate the thermal desorption and vapor treatment processes. This includes presenting the mass balance and the water balance and results. Sample collected during these tests and the amounts of materials used or recovered during the test were used to conduct the mass balance evaluation. In addition, a water balance was conducted to evaluate the amount of the initial soil moisture recovered in the system.

For the Low-Concentration Test, an estimated 83 percent of the water in the test soil was recovered. This indicates the system was capturing most of the vapors generated during the test. The mass balance of the system indicated only 2 percent of the total mass present in the soil before the test (0.037 g) was recovered. Most of the recovered mass was in the VGAC (0.019 g) and residual soil (0.014 g) with lesser amount in the condensate (0.003 g). The amount on the interior surface of the TDU was insignificant.

While the treated soil in the Low-Concentration Test met its treatment goal, we were not able to quantify recover sufficiently for a successful mass balance. Our goal of accounting for 75 percent of mass in the for the mass balance was not achieved.

For the High-Concentration Test, 59 percent of the moisture in the system was captured. The mass balance indicated 36 percent of the total mass present in the soil before the test was recovered, although most of the “recovered” PFAS mass (3.31 g) was retained in the partially treated soil.

As with the Low-Concentration Test, recovery of PFAS was far less than the goal of 75 percent and this objective was not met.

4.2.2 Comparison of Total to TOPA Analyses

Post-oxidation results were slightly higher than results from standard analyses, but the increases were not dramatic. The increase in mass was primarily due to an increase in the PFCA post-oxidation.

4.2.3 Treatment by VGAC

The amount of PFAS recovered in the VGAC, as presented in the mass balance, was very small, with 0.025 g of 2.11 g (1.1 percent) recovered in the Low-Concentration Test and 0.002 of 9.17 g (0.02 percent) recovered in the High-Concentration Test (Table 4.14). One objective of the study was to capture 90 percent of the PFAS on the GAC, which did not occur. One explanation for the low recovery of PFAS in the VGAC is the PFAS did not make it to the VGAC.

PFAS was recovered in the condensate, with relatively high concentrations detected in both the Low- and High-Concentration Test samples. The amount of PFAS measured in the condensate implies that significant PFAS made it to the condenser. Very little PFAS was detected in the C-18 cartridges, which confirms that little of the PFAS made it to the VGAC.

4.2.4 Conclusions

The mass balance found far less PFAS than anticipated in treatment residuals. It was anticipated that most of the mobilized PFAS would be found in the VGAC, with a smaller amount in the condensate. Instead, small amounts were found in both the VGAC and condensate. The recovery of PFAS in condensate, VGAC, C-18 cartridges, and wipe samples was less than 3 percent, with 2.1 percent recovered from the Low-Concentration Test and less than 1 percent recovered from the High-Concentration Test. The lack of PFAS detected in vapor confirms that PFAS typically did not make it to the VGAC or the cartridge sampling port. Instead, most of the PFAS appears to have condensed in the condenser, or perhaps in the connecting hose. PFAS does not form a classical liquid when condensed but rather a waxy coating. It appears that a portion of the condensed PFAS dissolved in the condenser liquid, most of the rest likely remains in the condenser, and small portion made it to the VGAC, where it was removed.

4.3 OBJECTIVE 3: DEMONSTRATE THAT THE TREATED PFAS IN THE VAPORS CAN BE CAPTURED

Very little PFAS was sorbed onto the VGAC. In the Low-Concentration Test, only 1 percent of the initial soil mass was in the VGAC. In the High-Concentration Test, PFAS in VGAC made up less than 0.001 percent of the total mass in the residuals. Only PFBA was detected on the C-18 cartridges (Tables 4.13 and 4.15). VGAC does not appear to be relevant for PFAS treatment in vapors because the PFAS does not appear to stay in the vapor phase.

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5.0 CONCLUSIONS AND IMPLICATIONS FOR FUTURE RESEARCH

The objectives of this pilot study were as follows:

1. To evaluate whether the infrared thermal treatment technology can effectively treat PFAS-contaminated soil IDW such that it allows soil re-use,
2. To provide documentation of the fate of PFAS in the treatment process, and
3. Demonstrate that the treated PFAS in the vapors can be captured.

5.1 CONCLUSIONS

Objective 1: The testing confirms that when properly implemented thermal desorption is capable of fully treating PFAS contaminated soil when temperatures are maintained above 350°C. In the Low-Concentration Test, where the proper temperature was maintained, effective PFAS treatment was achieved in 4 days. Treatment time seems more a function of the ability to dry the soil and achieve treatment temperature than the amount of PFAS present.

Objective 2: PFAS recovery was very low, with a few percent of the PFAS mass in the sample retained in the VGAC and condensate. Because excellent treatment was achieved in the Low-Concentration Test and vapors were recycled into the treatment unit, it is unlikely that PFAS passed through the GAC without treatment. Analysis of condensate samples found high concentrations of PFAS, which suggest PFAS made it to the condenser. Taken together, this suggests the PFAS condensed in the condenser. It is likely the PFAS is still in the condenser, attached to the condenser surfaces.

Objective 3: VGAC does not appear to be a good choice for primary PFAS treatment in the vapor phase; it appears that a high temperature must be maintained to keep the PFAS mobile in an air stream. Where test results indicate that some PFAS remained in the air stream, VGAC appeared to effectively remove this residual.

5.2 RECOMMENDATIONS

Because the High-Temperature Test soil was not fully treated since the target temperature was not obtained, the study team proposes to re-treat and test the High-Concentration soil before disposal. The proper temperature will be maintained during treatment. This cost will be borne by the project.

To evaluate whether treatment residuals were retained on the interior of the condensation tank, a wipe sample will be collected from the interior of the condenser. This sample will be tested for PFAS. This cost will be borne by the project.

Additional testing is recommended to better evaluate the fate of residuals in the treatment process. A batch similar to the High-Concentration Test could be treated. The test should ensure that the proper temperature is maintained. Because the study confirmed that PFAS can be removed from soil using thermal desorption, limited soil testing would be needed. Instead, treatment residuals should be tested to better understand the fate of the treated PFAS. A series of wipe tests are recommended at multiple locations along the treatment train to evaluate the location of residual PFAS. A mass balance would be used to quantify the recovery of PFAS.

Because the study determined that capture of PFAS from vapor is not an ideal solution for thermal desorption, the condenser system should be replaced with a wet scrubber, with GAC used to treat the scrubber water. Tests would be conducted to assess where residual PFAS remains in the treatment equipment and then remove the residual PFAS from the treatment equipment, to better manage the residuals.

6.0 LITERATURE CITED

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