

EXECUTIVE SUMMARY

Removal and Destruction of PFAS and Co-occurring Chemicals from Groundwater via Extraction and Treatment with Ion Exchange Media, and On-Site Regeneration, Distillation, and Plasma Destruction

Nathan Hagelin
Yousof Aly
Kaitlyn Chick
Jeff Heath
Eric Thompson
Cory Vowles
Wood Environment & Infrastructure Solutions Inc.

John Kornuc
Naval Facilities Engineering and Expeditionary Warfare Center

December 2022

This report was prepared under contract to the Department of Defense Environmental Security Technology Certification Program (ESTCP). The publication of this report does not indicate endorsement by the Department of Defense, nor should the contents be construed as reflecting the official policy or position of the Department of Defense. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the Department of Defense.

ESTCP EXECUTIVE SUMMARY

Project: ER18-5015

TABLE OF CONTENTS

	Page
1.0 INTRODUCTION	1
2.0 OBJECTIVES	1
3.0 TECHNOLOGY DESCRIPTION	1
4.0 PERFORMANCE ASSESSMENT	4
5.0 COST ASSESSMENT	8
6.0 IMPLEMENTATION ISSUES	8
7.0 REFERENCES	9

LIST OF FIGURES

	Page
Figure ES-1. Process Flow Diagram.....	3
Figure ES-2. Present Value Life Cycle.....	8

LIST OF TABLES

	Page
Table ES-1. Preliminary Performance Objectives, Data Requirements, and Success Criteria.....	4

ACRONYMS AND ABBREVIATIONS

BDL	below detection limits
BV	bed volume
CIC	combustible ion chromatography
CTAB	cetyltrimethylammonium bromide
DoD	Department of Defense
ESTCP	Environmental Security Technology Certification Program
FTS	fluorotelomer sulfonic acid
GAC	granular activated carbon
gpm	gallons per minute
HC1	Sorbix HC1 regenerable ion exchange resin
IPA	isopropyl alcohol
IX	ion exchange
LCA	life cycle cost analysis
mg/L	milligrams per liter
O&M	operations and maintenance
Pease	former Pease Air Force Base
PFAA	perfluoroalkyl acid
PFAS	per- and poly- fluoroalkyl substances
PFBA	Perfluorobutanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctanesulfonic acid
Pilot	Pilot Study
ppt	parts per trillion
Site 8	The former fire training area at Pease Air Force Base
TOC	total organic carbon
TOPA	total oxidizable precursors analysis
TSS	total suspended solids
USEPA	United States Environmental Protection Agency
VOCs	volatile organic compounds

1.0 INTRODUCTION

This Pilot Study Final Report (Report) for ESTCP project ER18-B3-5015, presents the results and conclusions of the Pilot Study (Pilot) at former Pease Air Force Base (Pease) in Portsmouth, New Hampshire (NH). The purpose of the Pilot was to further prove the effectiveness and develop scale-up criteria for integrating a per- and poly- fluoroalkyl substances (PFAS) treatment and destruction technology into existing groundwater treatment systems as originally demonstrated during the Treatability Study (Study) (Wood, 2020a), submitted on April 17, 2020.

The Pilot demonstration location was at the former fire training area at Pease (Site 8) and contained a PFAS treatment system already using the ion exchange (IX) resin, regeneration, and distillation technologies at full-scale.

2.0 OBJECTIVES

The goal of this project was to further refine and demonstrate the effectiveness of the PFAS Treatment Train and provide guidance on how to integrate the Treatment Train into existing co-occurring chemicals treatment systems. These objectives were presented in the Site Selection Memo and the Performance Objectives White Paper, ER18-B3-5015 Removal and Destruction of PFAS and Co-contamination from Groundwater, both dated February 8, 2019.

Specific technical objectives included:

- Measure the effectiveness of PFAS and co-occurring chemical treatment during each step of the Treatment Train (existing co-occurring chemical treatment, IX, regeneration, distillation, and low-energy plasma destruction steps).
- Prove the technical approach at a field demonstration site.
- Verify waste minimization through resin reuse, regenerant reuse, PFAS concentration, and PFAS destruction.
- Based on field performance, develop guidance for applicability and limitations, anticipated performance, design considerations, and costing for integrating the PFAS Treatment Train into existing co-occurring chemical treatment systems, including a protocol for design, operation, and maintenance of the integrated system.

3.0 TECHNOLOGY DESCRIPTION

The pilot scale PFAS Treatment and Destruction Train consisted of four technologies that complement each other to remove PFAS from treated water with reusable media, reduce the volume of the PFAS-impacted waste stream, and destroy that waste stream on-site. The pilot system configuration utilized during the testing is depicted in Appendix A of the Report, Design Drawings, and outlined below.

- IX resin: PFAS removal from groundwater utilizing Sorbix HC1 regenerable IX resin (HC1).

- Regeneration: solvent solution using isopropyl alcohol (IPA) and sodium chloride was used for removal of PFAS from IX resin to regenerate it for multiple groundwater treatment cycles.
- Distillation: recovery of used IPA solvent to be reused in future regenerations. A distiller separates the IPA for reuse from the water, brine, and PFAS which remain in the still bottoms for further treatment.
- Low-energy plasma destruction: PFAS destruction in the still bottoms, closing the loop for on-site removal, treatment, and destruction of PFAS.

A process flow diagram is provided as **Figure ES-1**.

REGENERABLE IX, DISTILLATION AND PLASMA TREATMENT

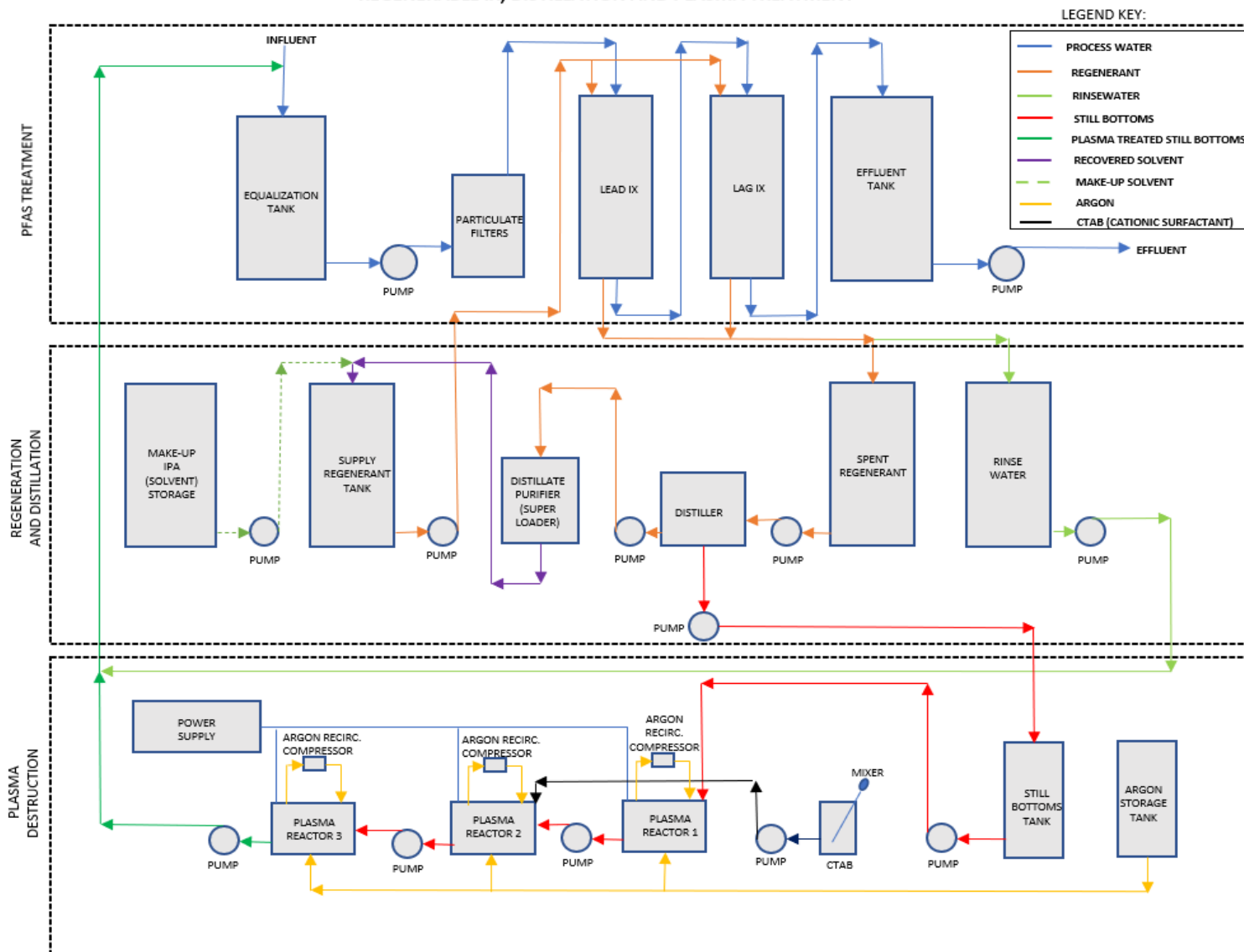


Figure ES-1. Process Flow Diagram

4.0 PERFORMANCE ASSESSMENT

Table ES-1 lists preliminary quantitative performance objectives of the Pilot associated data requirements, success criteria and results for each objective. Each of these objectives are summarized in the following sub-sections as to whether they were met and, if not met, the principal reason for failure. Additional details on results are provided in Section 5 and 6 of the Report.

Table ES-1. Preliminary Performance Objectives, Data Requirements, and Success Criteria

Quantitative Objectives		Observations and Results	
Demonstrate that the HCl IX resin is able to consistently treat the incoming groundwater (post-Fe removal) to levels at or below the EPA Lifetime Health Advisory	<u>Co-occurring Chemicals (pre-treatment)</u> <ul style="list-style-type: none"> Iron, Manganese, Volatile Organic Compounds (VOCs), Total Suspended Solids (TSS), total organic carbon (TOC) in influent and pre-treatment effluent <u>PFAS*</u> <ul style="list-style-type: none"> IX influent, weekly IX effluent and between lead and lag vessels, weekly 	Pre-treatment effluent <ul style="list-style-type: none"> Total and dissolved iron and manganese below 0.05 milligrams per liter (mg/L) TOC below 1 mg/L TSS below 1 mg/L VOCs non-detect 	<ul style="list-style-type: none"> Average dissolved iron was 0.04 mg/L Average dissolved manganese was 0.26 mg/L Average TOC was 2.32 mg/L Baseline sample was estimated at 2.4 mg/L Average VOCs were below detection limit. TSS was below lab detection limit all samples. Where certain IX influent levels after filtration were slightly above the pre-treatment goals, there were no adverse effects on resin performance noted during the study.
		IX effluent perfluorooctanoic acid (PFOA) + perfluorooctane sulfonic acid (PFOS) total concentration is less than 70 parts per trillion (ppt) for 5,000 bed volumes (BV).	The IX resin effluent remained below PFOS and PFOA treatment goals throughout the pilot test.
		Removal efficiency for all non-Target PFAS compounds greater than 95%	The IX resin effluent removed total PFAS compounds by at least 95% throughout the pilot test.
Onsite IX resin regeneration followed by distillation to enable reuse of resin and regenerant	<u>PFAS*</u> <ul style="list-style-type: none"> Regeneration solution post-treatment, each regen cycle Recovered regeneration solution distillate, each regen cycle IX influent, weekly IX effluent and between lead and lag vessels, weekly 	100% of resin can be reused during 6-month demonstration	The IX resin was never changed out during the pilot test and continued to meet treatment goals over five regenerations and six loading cycles.
		95% of Total PFAS mass recovered from resin	Mass balance calculations were sensitive due to the PFAS concentrations in the spent regenerant being four orders of magnitude higher than influent and effluent concentrations, producing recovery percentages of over 100% for several regenerations. To be more general and useful, treatment volumes from loading cycle to loading cycle were comparable, showing successful regeneration.
		95% of regeneration solvent can be reused	>95% of IPA recovered from spent regenerant after optimization of the distillation process.
		PFAS concentration in recovered distillate below 10 µg/L	The solvent recycler used in distillation cycles 1 and 2 was not configured to allow for distillate recovery below 10 µg/L out of the distillate purifier. The recycler was modified with a new distillation tower and achieved concentrations close to 10 µg/L.

Table ES-1. Preliminary Performance Objectives, Data Requirements, and Success Criteria (Continued)

Quantitative Objectives		Observations and Results	
		Less than 10% reduction in resin performance for 5 loading/regeneration cycles	The IX resin removal performance in the regenerated vessel as percent breakthrough of total PFAS remained within 10% of loading cycle's bed volumes treated throughout the subsequent cycles, even at more than 2,000 additional BVs treated.
Onsite PFAS destruction by plasma reactor	<p><u>PFAS*</u></p> <ul style="list-style-type: none"> • Still bottoms, each regen cycle • Plasma reactor effluent, every 25 gallons 	PFAS below 70 ppt on an individual PFAS-compound basis	All precursors and long-chain perfluoroalkyl acids (PFAA) were removed to below detection limits (BDL), except for 4:2 fluorotelomer sulfonic acid (FTS) (1.2 µg/L), PFOS (0.67 µg/L), PFOA (0.13 µg/L) and Perfluorohexane sulfonate (0.33 µg/L) were remaining after 82 hours of treatment/destruction. After an additional 14 hours of treatment at Clarkson University all these compounds were removed to BDL. For short chain PFAS, all measured PFAS were BDL at the conclusion of treatment, exceeding the performance objective, except for perfluoro butanoic acid (PFBA), at the conclusion of the study at 120 hrs. Based on the reaction kinetics it would have taken additional 100 hrs. for it to reach the treatment goal of 70 ppt.
Cost-effectiveness	Full cost development, capital plus operations and maintenance, associated with PFAS Treatment Train. Cost effectiveness will be evaluated against comparable IX and granular activated carbon (GAC) systems	Life cycle costs associated with integrating the PFAS Treatment Train into existing co-occurring chemical treatment are less than life cycle costs associated comparable IX and GAC systems	Cost analysis have been prepared and are described below and in detail in Section 7 of the Report.
Waste Minimization - Minimize offsite disposal of solids and PFAS	Mass of waste materials (e.g., filters) produced during demonstration	Total mass of solid waste reduced by 50% relative to comparable IX and GAC systems. Mass of total PFAS disposed reduced by 95% relative to comparable IX and GAC systems	Pilot testing demonstrated that IPA could be recovered from the spent regenerant through distillation for re-use and that rinse waters as well as plasma treated still bottoms could be re-processed through the system without adverse effect, thus eliminating the need for off-site PFAS disposal.

* PFAS compounds and analytical methods (PFAS, total organic precursor analysis (TOPA) and combustible ion chromatography (CIC)) are presented in Appendix B of the Report

Table ES-1. Preliminary Performance Objectives, Data Requirements, and Success Criteria (Continued)

Qualitative Objectives		Observations and Results	
<p>Improved understanding of the impact of the PFAS Treatment Train on PFAS (C4-C12), precursors, and geochemistry</p>	<ul style="list-style-type: none"> • Analyze the full suite of PFAS compounds at each PFAS monitoring station • total organic precursor analysis (TOPA) – IX influent, IX effluent, plasma influent, plasma effluent – for one regen cycle • pH, total dissolved and total suspended solids, total organic carbon – each regen cycle 	<p>Success is defined as developing an improved understanding of the PFAS Treatment Train’s overall effectiveness at concentrating and destroying PFAS on a compound-specific and total mass basis and to understand the influence and sensitivity to critical water quality parameters.</p>	<p>An improved understanding of Treatment Train operation was developed by continuous system operation and analytical testing that helped to establish timeline for resin regeneration and modifications to surfactant addition frequency of the Plasma PFAS destruction units. Compound specific PFAS analysis was performed for the still bottoms in the plasma units prior to and after plasma destruction. It was observed that majority of the precursor mass (>99%) was removed in the first high concentration plasma reactor and long chain PFAS degradation improved to 99.9% in mid concentration Plasma reactor after 36 hrs. of treatment. For short chain PFAS, the pilot test confirmed that the cetyltrimethylammonium bromide (CTAB, cationic surfactant) improves short-chain PFAAs removal but inhibits the degradation of long-chain PFAAs removal. A third plasma reactor was added in series to minimize the impact of desorption from reactor components and provide further treatment of short chain PFAS in the presence of CTAB. Additionally, based on the pilot test operational experience, mass balance was also developed for a 100-gpm system with an influent total PFAS concentration of 45 ug/L. The mass balance table is presented as Appendix F of the Report.</p> <p>Samples for TOPA and combustible ion chromatography (CIC) before and after plasma treatment were not collected during the pilot test. However, in the laboratory work with still bottoms from Pease (Site 8), TOP concentrations ranged between 3800 to 9400 mg/L, approximately 10 times higher than the total PFAAs concentration (Singh et al., 2020). TOP concentrations were on average 200 times higher than the total directly measured precursor concentrations indicating the presence of numerous unidentified precursors. Similarly, total fluorine concentrations were on average 50 times higher than the total directly measured organic fluorine associated with precursors. The TOPA and total fluorine data is attached as Appendix G of the Report. For the four identified precursors, 8:2 FTS and FOSA-1 were removed to BDL of approximately 30 ng/L and removal efficiencies for 6:2 FTS and 4:2 FTS were 99.9 ± .07%, and 90 ± 25%, respectively. These removal efficiencies were comparable to those measured for TOP (99.8 ± 0.1%). The substantial removal of TOP is likely due to the oxidative transformation/degradation of precursors to PFCAs by plasma-generated hydroxyl radicals. Inorganic fluoride concentrations increased by 1 to 3 orders of magnitude post-treatment indicating significant defluorination of PFAS molecules. Previous work has shown that short-chain PFAAs can be generated as byproducts of degradation of long-chain PFAAs and precursors.</p>

Table ES-1. Preliminary Performance Objectives, Data Requirements, and Success Criteria (Continued)

Qualitative Objectives			Observations and Results
Ease of PFAS Treatment Train integration into existing co-occurring chemical treatment processes	<ul style="list-style-type: none"> • Design and performance data from a variety of existing or typical treatment systems in place at DoD installations • Input and feedback from experienced engineers and operators at existing co-occurring chemical treatment sites 	<p>The development of users' guidance, standard procedures, and technical specifications for a variety of design approaches to the integration of the PFAS Treatment Train</p> <p>The PFAS Treatment Train compliments a range of existing in-place treatment systems.</p>	<p>The user's guide, standard approaches, and technical specifications will be prepared at part of task 009, Technology Transfer.</p> <p>The PFAS Treatment Train can be integrated into existing groundwater treatment systems with co-occurring chemical, generally after the existing treatment processes. as long as there is appropriate pre-treatment of the PFAS Treatment Train influent water. The groundwater unit processes at each site may vary and appropriate engineering and design of pre-treatment steps may be required.</p>
Evaluation of potential for unanticipated effects of implementation of the PFAS Treatment Train	<ul style="list-style-type: none"> • Engineer and practitioner feedback from design and implementation of the PFAS Treatment Train • Documentation and analysis of engineering solutions to unanticipated effects 	<p>Publication of lessons learned and recommended engineering solutions in the Cost and Performance Report and Users' Guide for the technology</p> <p>Unanticipated effects/outcomes are identified and catalogued.</p>	<p>Biofouling can be observed in any IX/GAC system, especially during long periods of down time required by maintenance activities, leading to pressure drop. Based on the pilot and full-scale observations the treatment system should be fitted with downflow and up-flow valving to help with vessels backwash operations and help reduce operations and maintenance costs.</p> <p>High concentrations of PFAS were observed to cause foaming, reducing treatment efficiency during distillation and plasma destruction. During testing these issues were resolved by modification of the distillation column to prevent foam carryover and applying a 10X dilution of still bottoms prior to plasma destruction.</p> <p>Initial high levels of PFAS in the plasma reactors resulted in desorption during the final stages of plasma destruction reducing destruction efficiency. As a result, a third reactor was added to the train for polishing of the remaining PFAS after two stage plasma treatment.</p> <p>Plasma treatment required the addition of CTAB for treatment of short chain PFAS compounds. CTAB was found to inhibit the destruction of long chain PFAS compounds, as a result, CTAB was found to be most beneficial when added to the second reactor after destruction of long chain compounds in the first reactor.</p>

5.0 COST ASSESSMENT

The findings from the Pilot have been used to develop a cost model to compare with other currently available treatment technologies for PFAS treatment. This section provides a cost model for regenerable IX/distillation/plasma scenario to be used as a comparison to other currently available technologies. Capital and operations and maintenance (O&M) costs related to power and materials are estimated based on scale up of pilot data (where appropriate) and vendor information to reflect a system capable of treating 100 gpm. O&M costs associated with materials and labor are based on ECT2 estimates from similar systems and estimates provided by Clarkson. The regenerable IX and plasma destruction Capital, O&M, present worth and life cycle cost estimate basis and calculations are detailed in Appendix I – Life Cycle Cost Analysis, Capital and O&M Cost Estimate, in the Report. A present value life cycle cost of the capital and O&M cost is presented in the Figure ES-2 below. These costs do not include pre-treatment and extraction system installation cost.

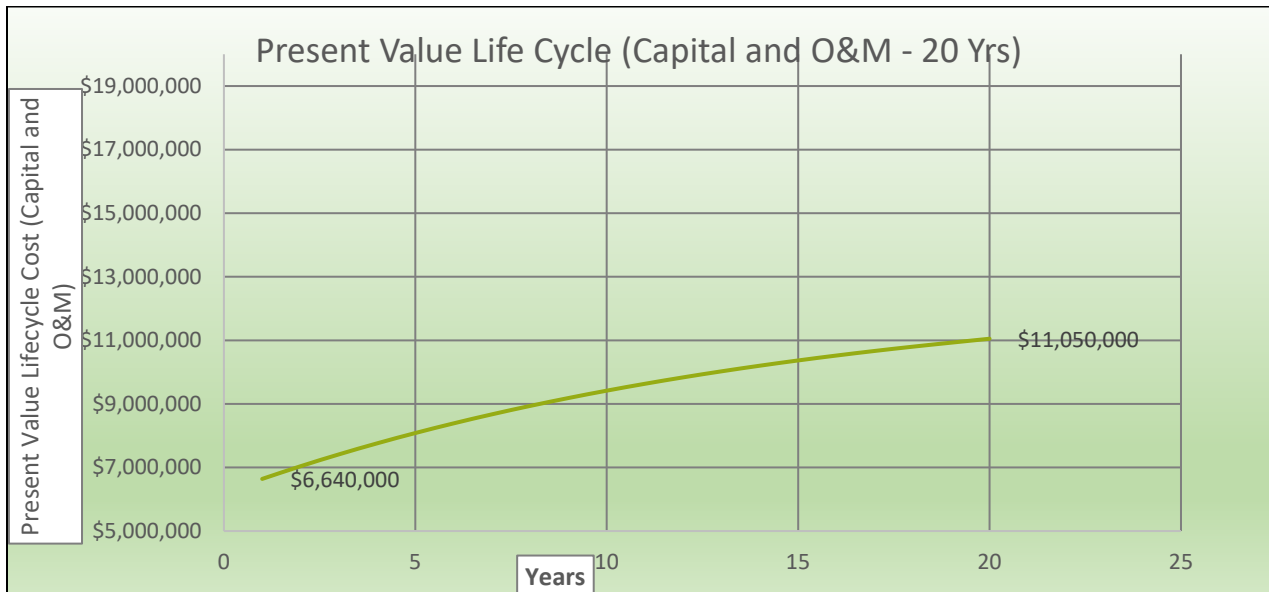


Figure ES-2. Present Value Life Cycle

6.0 IMPLEMENTATION ISSUES

A list of a few implementation issues provided below is based on the operational experience during the pilot test and current operations at the full-scale system at Site 8. These issues are presented below to help with additional design considerations:

- Pre-treatment for co-occurring chemicals (metals, TOC, TSS, TDS, VOCs, etc.): Based on the site-specific co-occurring chemicals, pre-treatment requirement can add to increased building size and larger pre-treatment vessels footprint. These need to be carefully evaluated prior to design of any full-scale system.

- Downflow versus up-flow operation of the resin beds and the ability to backwash as required. Any full-scale system should be downflow to allow backwashing to remove fouling from the media. Based on the pilot and full-scale observations, the treatment system should be fitted with downflow and up-flow valving to reduce operations and maintenance costs.
- Biofouling can be observed in any IX/GAC system, especially during long periods of down time required by maintenance activities, leading to pressure drop. Treatment equipment should include provisions for addressing these issues (backwashing and/or biocide addition) that could possibly negatively affect the resin/GAC performance.
- Consider the use of single pass IX after regenerable IX as a polishing step (based on pilot and full-scale Site 8 operations data). This should be considered if the influent stream has short chain PFAS compounds which require removal to meet regulatory requirements (specially PFAS with less than 6 carbon chain lengths, e.g., PFBA) which have lower demonstrated removal efficiencies using regenerable IX compared to single use. Alternatively, the regeneration cycle length can be reduced to accommodate enhanced removal of short chain PFAS.
- Waste minimization may be reduced if pre-treatment before regenerable IX and tertiary treatment after plasma destruction are required. These wastes could potentially include spent filters, sludge as well as spent media (as applicable) requiring disposal as PFAS containing wastes.
- If regeneration and distillation cannot be performed outside (dependent on geographical system location) the equipment building, equipment and appurtenances must be explosion proof.

7.0 REFERENCES

- Wood, 2020a. Treatability Study Report, ESTCP Project Number: ER18-5015, Former Pease Air Force Base Prepared for Air Force Civil Engineering Center, Joint Base San Antonio – Lakeland, Texas, April 17.
- Raj Kamal Singh, Nicholas Multari, Chase Nau-Hix, Steven Woodard, Michael Nickelsen, Selma Mededovic Thagard, and Thomas M. Holsen, 2020. Removal of Poly- and Per-Fluorinated Compounds from Ion Exchange Regenerant Still Bottom Samples in a Plasma Reactor *Environmental Science & Technology* 2020, 54, 13973–13980.