FINAL REPORT

Ex Situ Remediation of Investigation-Derived Wastes containing PFAS by Electron Beam Technology

SERDP Project ER18-1620

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Texas A&M University System

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14. ABSTRACT
Site investigations of PFAS-impacted areas generates complex mixtures of investigation derived waste (IDW), including many individual forms of PFAS, and other co-contaminants and volatile organic compounds (VOC). High energy electron beam (eBeam) technology is a high efficiency, chemical-free, advanced oxidation reduction process (AORP) that utilizes high energy electrons to create significant amounts of highly reactive free radicals. The research hypothesis was that eBeam technology can be used to degrade PFOS and PFOA in IDW materials (soils and groundwater).
The specific objectives of the SERDP Exploratory Development (SEED) project were:
1. To quantify the effectiveness of eBeam technology at breaking down PFOS in soil and water under controlled experimental conditions, and
2. To characterize the effectiveness of eBeam at destructive treatment for a mixture of PFASs present in actual IDW samples collected from multiple sites.

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Advanced oxidation reduction process, Beam energy, Beam power, Degradation, Electron beam, groundwater, Investigation derived wastes, Ionizing radiation, Irradiation, Kilogray, Linear accelerator, PFAS, PFOA, PFOS, Radiolytic species, Remediation, Soil

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List of Acronyms

eBeam: Electron beam
kGy: kilogray
kW: kilowatt
MeV: million electron volts
IDW: Investigation-derived wastes
PFAS: per and polyfluoroalkyl substances
PFOS: perfluorooctane sulfonate
PFOA: perfluorooctanoic acid
NASJRB/WG : Naval Air Station Joint Reserve Base Willow Grove
AFB: Airforce Base

Keywords

Advanced oxidation reduction process
Beam energy
Beam power
Degradation
Electron beam
groundwater
Investigation derived wastes
Ionizing radiation
Irradiation
Kilogray
Linear accelerator
PFAS
PFOA
PFOS
Radiolytic species
Remediation
Soil

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Abstract

Introduction: Site investigations of PFAS-impacted areas generates complex mixtures of investigation derived waste (IDW), including many individual forms of PFASs, and other co-contaminants and volatile organic compounds (VOCs). High energy electron beam (eBeam) technology is a high efficiency, chemical-free, advanced oxidation reduction process (AORP) that utilizes high energy electrons to create significant amounts of highly reactive free radicals. The *research hypothesis* was that eBeam technology can be used to degrade PFOS and PFOA in IDW materials (soils and groundwater).

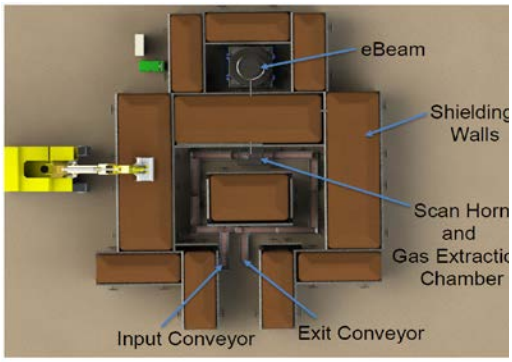
Objectives: The specific objectives of the SERDP Exploratory Development (SEED) project were:

1. To quantify the effectiveness of eBeam technology at breaking down PFOS in soil and water under controlled experimental conditions, and
2. To characterize the effectiveness of eBeam at destructive treatment for a mixture of PFASs present in actual IDW samples collected from multiple sites.

Technical Approach: The project initially focused on demonstrating PFOS and PFOA breakdown in sand and distilled water spiked with defined concentrations of PFOS and PFOA. The spiked samples were exposed to defined eBeam doses under specific conditions and analyzed for PFOS and PFOA breakdown. Once doses above 500 kGy were found to achieve PFOS breakdown, we applied these treatment parameters on field IDW samples obtained from Pennsylvania (Willow Grove NASJRB/WG), and Michigan (Wurtsmith AFB). We designed special experimental vessels to deliver high doses (500 kGy- 2000 kGy) in batch conditions to Willow Grove groundwater and Wurtsmith soil samples. The pre-and post-eBeam exposed samples were analyzed using both an in-house analytical laboratory as well as the commercial SGS-AXYS laboratory using EPA Method 537 coupled with the Total Oxidizable Precursor (TOP) assay.

Results: 2000 kGy dose reduced PFOS concentration in Wurtsmith AFB soils from 1738 ng/gm to 0.12 ng/g (dry weight basis), a >99.99% reduction. A 2000 kGy eBeam reduced PFOS concentration in Willow Grove groundwater from 3851 ng to 465.5 ng, an 87.91% reduction. The PFOA reduction in Wurtsmith AFB soils at 2000 kGy was 98.6% while in Willow Grove groundwater, PFOA reduction was 53.7%. PFCAs (PFBA, PFPeA, PFHXA, PFOA) and PFSAs (PFBS, PFHXS, PFOS and PFDS) concentrations decreased with increasing eBeam dose. The required dose can be brought down to 1500 kGy with appropriate optimization. An economic analysis of PFAS treatability using eBeam technology suggests it would cost approximately \$ 295/m^3 for a fixed eBeam treatment platform for reducing 98% of PFOA and 99.99% of PFOS using a target dose of 1500 kGy. These results highlight that eBeam technology has significant promise as a PFAS remediation technology for soils and aqueous samples. However, further optimization is needed.

Benefits: The results support further investment in laboratory research to optimize PFAS breakdown and necessary engineering design research to facilitate the installation of a prototype on-site eBeam treatment platform at the appropriate PFAS-contaminated site to demonstrate field-scale remediation.



Schematic rendering of an on-site eBeam platform for remediation using onsite soil as shielding material

Executive Summary

Introduction

Electron beam (eBeam) technology utilizes electron accelerators to generate extremely large numbers of highly energetic electrons from electricity. Compact, high-energy (10 million electron volts, MeV) and high power (~ 500 kilowatts, kW) accelerators capable of treating upwards of 1 million gallons per day of groundwater are commercially available today. These accelerators can produce extremely large concentrations of highly energetic electrons (> 10^{15} electrons/cm^2/sec) which, when they interact with water produce extremely large amounts of highly reactive free radicals ($H^{\bullet}$, e^-, and $HO^{\bullet}$), hydrogen peroxide (H_2O_2), hydrogen atoms (H_2), and hydrated protons (H_3O^+). Electron beam as a remediation technology is paradigm shifting, because it simultaneously employs both reduction and oxidation processes. At very high doses, temperature is also involved in these complex reactions. These powerful oxidation-reduction reactions occur almost instantaneously and therefore, best characterized as an *Advanced Oxidation-Reduction Process (AORP).* Since this ionizing technology relies on commercial electricity, this is a "switch-on/switch-off" technology without the need for radioactive materials. Therefore, the proposed research was directly aligned with the scope of SERDP's SEED project which is to explore innovative approaches that entail high technical and scientific risk.

Objectives

The specific objectives of the SERDP Exploratory Development (SEED) project were,

1. To quantify the effectiveness of eBeam technology at breaking down PFOS in soil and water under controlled experimental conditions, and
2. To characterize the effectiveness of eBeam at destructive treatment for a mixture of PFASs present in actual IDW samples collected from multiple sites.

Technical Approach

The project was divided into specific experimental tasks. In Task 1, the experiments focused on exposing PFOS and PFAS spiked sand and aqueous samples at varying electron beam (eBeam) doses to identify the optimal eBeam dose range for treatment. Task 2 focused on demonstrating the efficacy of eBeam technology for the breakdown of PFOS and PFOA and other PFAS in actual IDW samples obtained from Pennsylvania (Willow Grove NASJRB/WG) and Michigan (Wurtsmith AFB). Task 3 focused on analyzing the economics of treatability by identifying the capital and operating costs for treating PFAS-contaminated IDW soils.

In **Task 1**, we evaluated the effectiveness of varying eBeam low doses (10 kGy – 500 kGy) as well as experimental conditions such as alkalinity, nitrogen sparging, and nitrate amendments on its ability to degrade PFOS and PFOA. PFAS-free laboratory sand (10 g) and distilled water were spiked with PFOS (10µg/L and 20 mg/kg sand) and PFOA (5 µg/L and 10 mg/kg sand). These batch-scale studies were performed in PFAS-free 60 mL square-sided HDPE bottles using the 10 MeV S-band 15 kW eBeam linear accelerator at the National Center for Electron Beam Research at Texas A&M University. Industry-standard, internationally traceable alanine dosimeters were used to measure the absorbed eBeam doses. The samples were exposed to 50 kGy and 500 kGy eBeam doses. The 500 kGy dose was delivered incrementally. The control (untreated) and the eBeam-exposed treated samples were analyzed for PFOA and PFOS using a commercial analytical laboratory (SGS-AXYS) as well as an in-house university laboratory.

In **Task 2**, the focus was on delivering eBeam doses to actual PFAS-contaminated IDW groundwater and soil samples. Compared to delivering 50 kGy to experimental samples in HDPE bottles, the delivery of higher doses required the fabrication of custom-designed experimental vessels (Fig. ES-1). The experimental vessel consisted of a sealed aluminum pressure vessel that was connected to a condensate collection vessel. The samples were placed in a "boat" within the experimental sealed pressure vessel using stainless steel foil. Condensate collection vessels and thermocouples were employed. The dose rate of the linac was used to calibrate the delivered doses. In these experiments, we also evaluated the value of amendments such as $NaNO_3$, $NaHCO_3$, pH adjustments (to alkaline conditions), and moisture content on PFOS degradation. The IDW samples were obtained from Pennsylvania (Willow Grove NASJRB/WG) and Michigan (Wurtsmith AFB). Portions of these samples were sent to the commercial laboratory for analysis per the EPA Method 537.

We focused the studies on the Willow Grove (PA) and Wurtsmith (MI) IDW samples since they had high concentrations of PFOS in the groundwater and soil respectively (Table ES-1). The samples were exposed to high doses (500 kGy, 1000 kGy, and 2000 kGy). To confirm the reproducibility of the high dose eBeam results of the IDW soil samples, we repeated these studies using three replicate sample "boats" within the treatment chamber. The Michigan IDW soil samples were dried to 10% soil moisture content and 30g -50 g were employed in these confirmation studies.

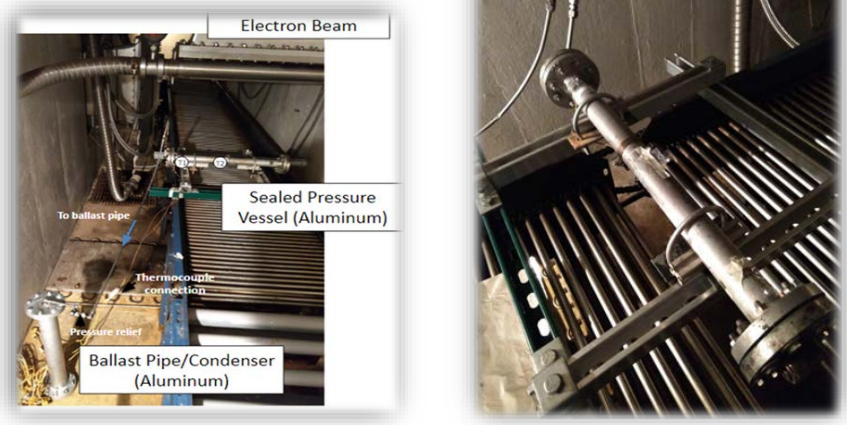


Fig. ES-1. Photos showing the experimental vessels used for high dose eBeam treatments

	Field IDW Sample Michigan Soil	Field IDW PA Soil	Field IDW Michigan Water	Field IDW PA Water
	NG/G	NG/G	NG/L	NG/L
PFBA	6.91	<0.269	23.1	<328
PFPeA	33.9	0.155	88.4	402
PFHxA	11.1	0.15	53.4	1250
PFHpA	13.1	<0.067	19.2	218
PFOA	**17.2**	**0.098**	**41.6**	**870**
PFNA	2.98	<0.067	3.97	<80
PFDA	0.964	<0.067	<3	<80
PFUnA	<0.25	<0.067	<3	<80
PFBS	1.16	<0.062	<3.1	505
PFPeS	0.717	0.069	<3	664
PFHxS	29.2	0.833	84.7	4240
PFHpS	3.94	<0.067	8.18	760
PFOS	**1010**	**8.3**	**1370**	**42600**
PFNS	1.66	<0.067	<3	87.3
PFDS	<0.25	<0.067	<3.1	<80
6:2 FTS	13.1	1.12	138	1080
8:2 FTS	30.5	<0.262	67.9	<320
PFOSA	124	<0.067	70.3	166
% Moisture	84.4	6.94		

Table ES-1. PFAS concentration in investigation –derived waste groundwater and soil samples from Pennsylvania and Michigan

Task 3 involved performing an economic analysis for using eBeam technology to remediate PFAS-contaminated soil samples at 1500 kGy. Capital and operating costs of a fixed eBeam technology platform were included in this analysis.

Experimental Results

Figures ES-2A and ES-2B show that 50 kGy, both PFOS and PFOA are degraded in the spiked distilled water samples. At 50 kGy, as much as 87% of PFOA was degraded. At 50 kGy, only 16% of PFOS was degraded in the aqueous samples. The PFOA and PFOS reductions were, however, statistically significant ($p<0.05$) when comparing the control and eBeam treated samples. Figures ES-3A and ES-3B show the results when PFOA and PFOS spiked sand samples are exposed to 50 kGy. At this dose, as much as 86% of PFOA was degraded while only 27.5% of PFOS was degraded in the sand samples. These reductions were statistically significant ($p<0.05$) when comparing the control and eBeam-treated sand samples. Figure ES-4 shows that as the eBeam dose is increased from 50 kGy to 250 kGy, there was not a statistically significant ($p> 0.05$) increase in PFOS breakdown. However, when the dose increased from 250 kGy to 500 kGy, there was a statistically significant difference ($p<0.05$) in the reduction of PFOS in the PFOS-spiked sand samples. At 500 kGy, PFOS concentration in the spiked sand samples was reduced by 41.4%.

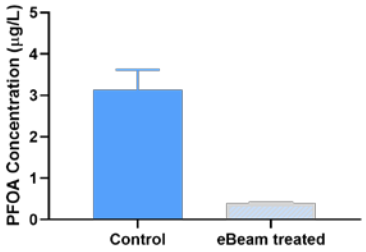


Fig. ES-2A. eBeam-mediated (50 kGy) degradation of PFOA in laboratory spiked water samples

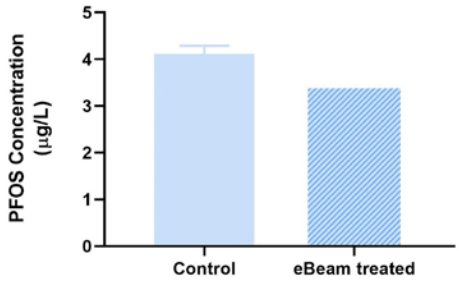


Fig. ES-2B. eBeam-mediated (50 kGy) degradation of PFOS in laboratory spiked water samples

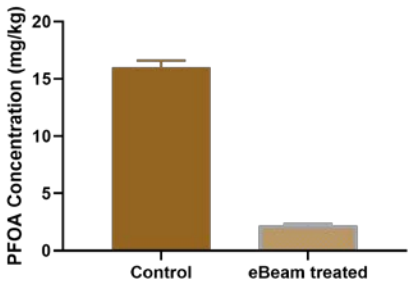


Figure ES-3A. eBeam-mediated degradation of PFOA in laboratory spiked sand samples

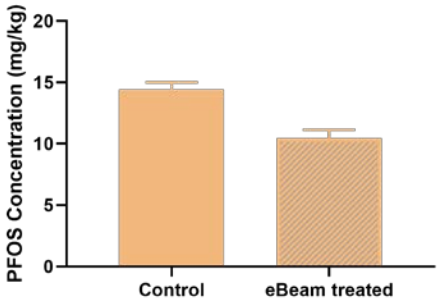


Figure ES-3B. eBeam-mediated degradation of PFOS in laboratory spiked sand samples

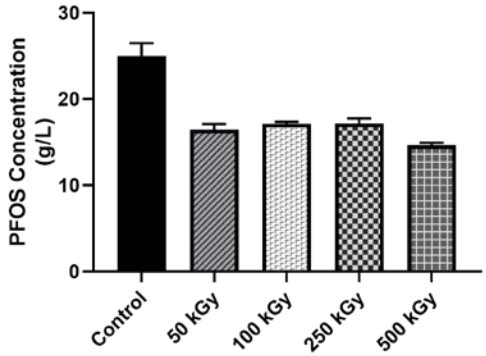


Fig. ES-4. Effect of increasing eBeam doses on PFOS degradation in laboratory-spiked water samples

The results from higher eBeam doses of the laboratory –spiked water and sand samples are shown in Figure ES-5 and Figure ES-6. At 500 kGy, there was a 48.6% reduction in PFOS concentration (in the absence of amendments such as pH adjustment to 13, $NaNO_3$ and $NaHCO_3$) as compared to 22% reduction in the presence of amendments. At 2000 kGy, however, there was 88.8% PFOS reduction (in the presence of amendments) as compared to 96.6% reduction in the absence of amendments (Fig ES-5). The reduction in the sand samples were even more significant. At 500 kGy, there was a 98.8% reduction in PFOS concentration in the absence of amendments as compared to greater than 99.99% reduction at 2000 kGy (Fig. ES-6). These results suggested that eBeam-mediated breakdown of PFOA and PFOS was significantly better in sand samples as compared to aqueous samples.

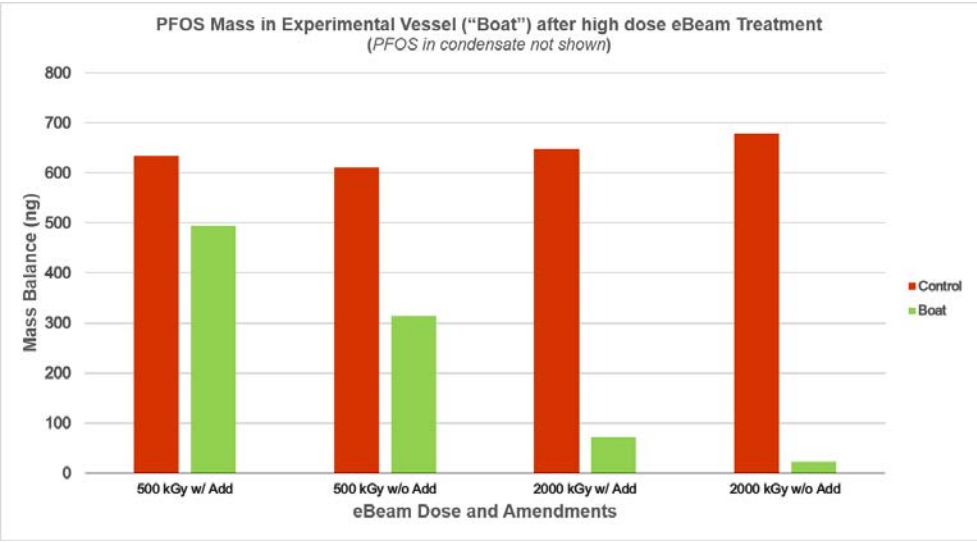


Fig ES-5. PFOS degradation in laboratory-spiked water samples as a function of increasing eBeam doses. (Amendments refer to pH, $NaNO_3$ and $NAHCO_3$ adjustments)

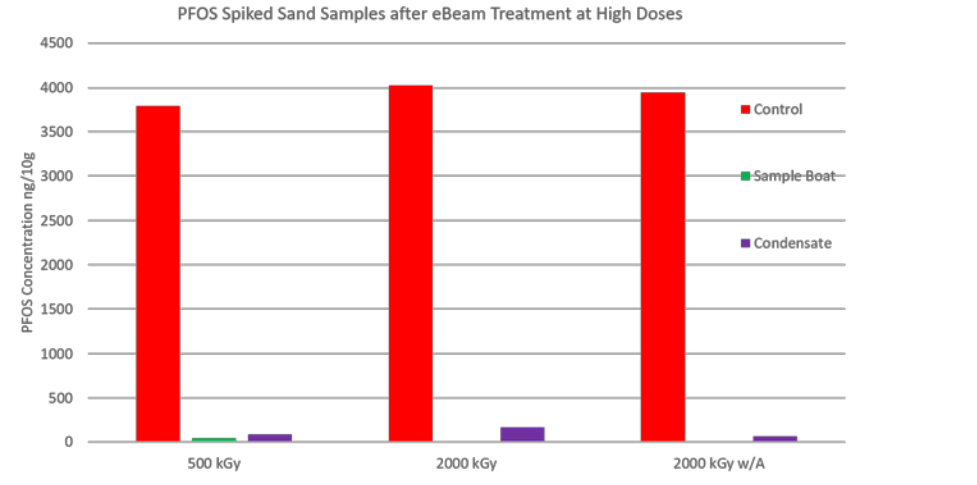


Fig.ES-6. PFOS degradation in laboratory-spiked sand samples as a function of increasing eBeam doses. (Amendments refer to pH, $NaNO_3$ and $NAHCO_3$ adjustments)

These results from the exposure of IDW groundwater from Pennsylvania (Willow Grove NASJRB/WG) to high eBeam doses are shown in Table ES-2. The untreated and eBeam irradiated Willow Grove groundwater samples were analyzed by the commercial laboratory using the post analysis TOP assay. The results indicate that eBeam technology at high doses can be effective at degrading PFOS. At 2000 kGy, an 87.9% reduction of PFOS concentration was observed. The PFOA concentration increased during the eBeam exposure. This suggests that the PFOA is accumulating during the breakdown of PFOS. The accumulation of PFOA as a breakdown product of PFOS has been recently reported in the literature.

	Treatment	Post-TOP PFOA in boat (ng)	Post-TOP PFOS in boat (ng)	% Removal of Post-TOP PFOA	% Removal of Post-TOP PFOS
PA-IDW-GW	0 kGy	112	3851	0%	0%
PA-IDW-GW	500 kGy	84	1949.1	25%	49.39%
PA-IDW-GW	1000 kGy	101	1152.3	9.82%	70.07%
PA-IDW-GW	2000 kGy	52	465.6	53.57%	87.91%

Table ES-2. eBeam-mediated breakdown of PFOA and PFOS in Willow Grove (PA) IDW groundwater samples. The % removal on a mass basis is shown.

In addition to analyzing the eBeam treated samples for PFOS and PFOA, the commercial laboratory also analyzed the samples for 29 different PFASs and precursors (Fig ES-7). With increasing eBeam dose, there is a reduction in the concentrations of PFCAs (PFBA, PFPeA, PFHXA, PFOA) as well as in the concentrations of PFSAs (PFBS, PFHXS, PFOS and PFDS).

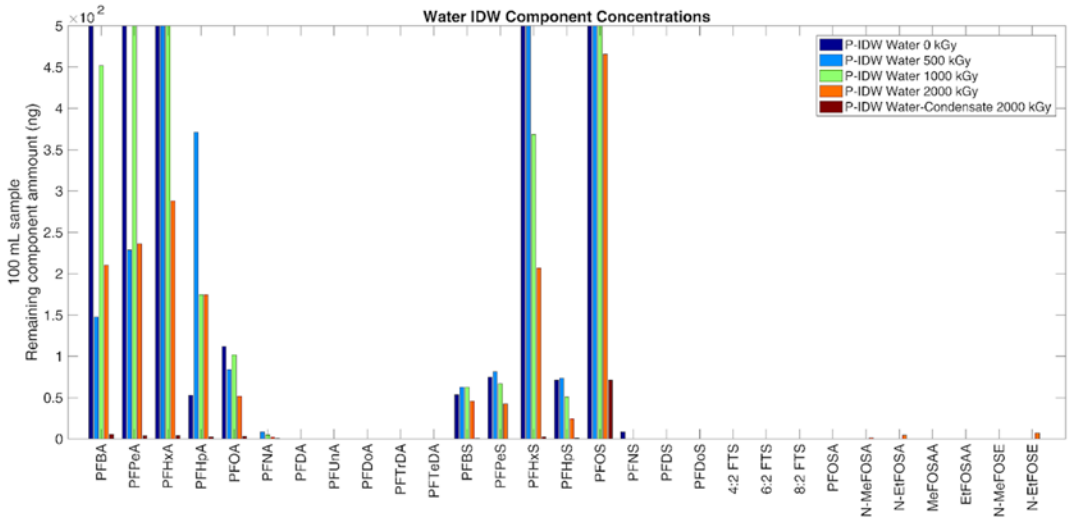
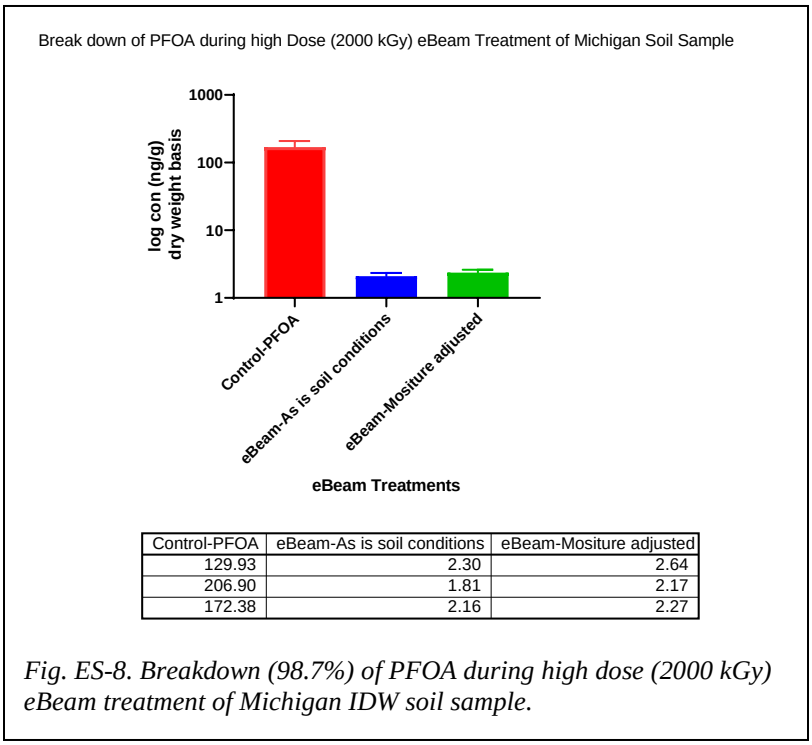


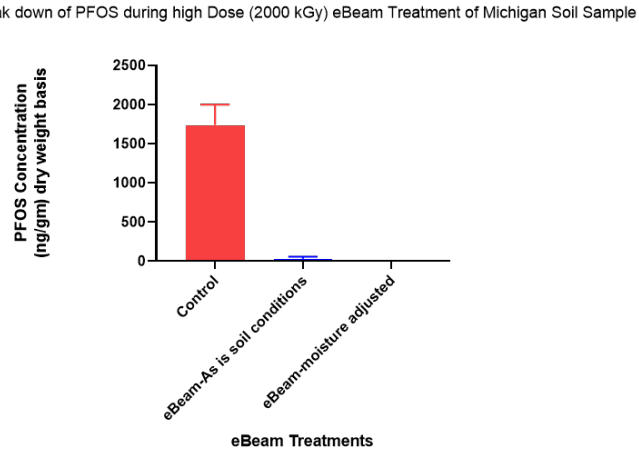
Fig. ES-7. Targeted PFAS component concentrations in Pennsylvania IDW water as a function of increasing eBeam dose

Since we had observed greater PFOS degradation in the sand compared to the aqueous samples, we wanted to confirm our hypothesis that lower moisture facilitated eBeam-mediated breakdown of PFOS in sand samples. Therefore, we adjusted to the moisture content adjusted of the Michigan soil sample to 10%. We exposed the 10% moisture-adjusted and the un-adjusted Michigan IDW soil samples to 2000 kGy eBeam dose. Figure ES -8 and Figure ES-9 show the breakdown of PFOA and PFOS in the Michigan IDW samples at 2000 kGy.



Control-PFOA	eBeam-As is soil conditions	eBeam-Mositure adjusted
129.93	2.30	2.64
206.90	1.81	2.17
172.38	2.16	2.27

Fig. ES-8. Breakdown (98.7%) of PFOA during high dose (2000 kGy) eBeam treatment of Michigan IDW soil sample.



Control	eBeam-As is soil conditions	eBeam-moisture adjusted
1448.08	39.05	0.09
1810.75	2.33	0.09
1957.93	52.94	0.17

Fig. ES-9. Breakdown (>99.99%) of PFOS during high dose (2000 kGy) eBeam treatment of Michigan IDW soil sample

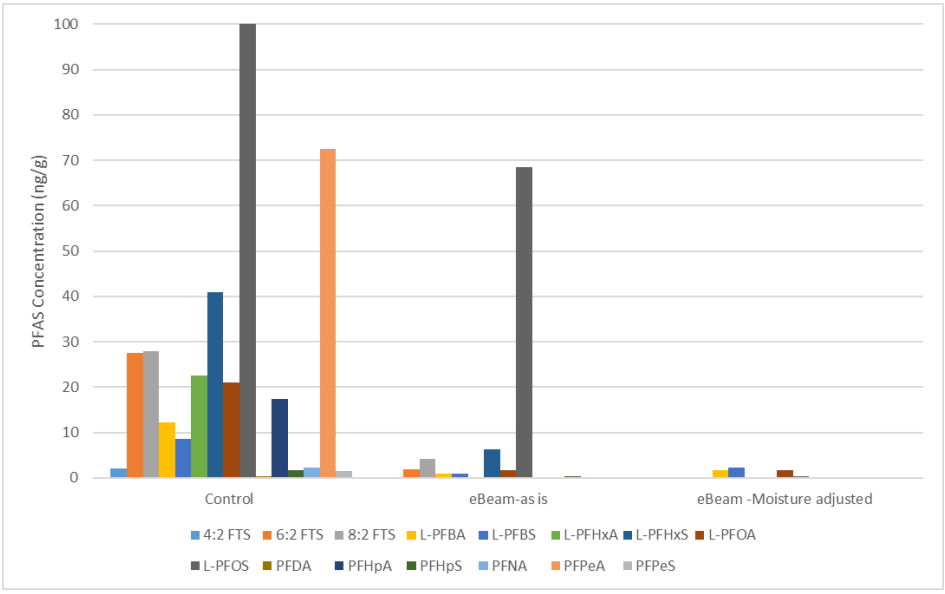


Fig. ES-10. Breakdown of targeted PFAS components during high dose (2000 kGy) eBeam treatment of Michigan IDW soil sample

An ANOVA test was performed to compare the PFOA concentrations between the un-treated and the moisture adjusted and unadjusted treatment groups. There was a significant difference (p

<0.0001) between the treatment groups. When a Student t test was performed to compare the remaining PFOA concentrations in the eBeam treated samples, there was no significant difference suggesting that irrespective of whether the soil was moisture adjusted to 10% or treated as is, PFOA can degrade by as much as 98.7% . In the case of PFOS, the breakdown was even more significant (> 99.99%) with complete degradation of PFOS (Fig. ES-9). In the IDW soil which was treated with eBeam at ambient soil moisture conditions (~ 85%), the PFOS reduction was 98.19%. In samples where the soil moisture was adjusted to 10%, the PFOS degradation was almost complete (99.99%). Figure ES-10 shows the degradation of the different targeted PFAS in the Michigan IDW samples in the 10% moisture adjusted and un-adjusted soil samples at 2000 kGy. These results suggest that PFAS degradation especially PFOS appears to be enhanced under low moisture conditions under high eBeam dose conditions.

Overall, these results support the original research hypothesis that eBeam can achieve significant reduction of PFOA and PFOS in IDW soil and groundwater samples.

Economic Analysis

Figure ES-11 represents the cost breakdown (electrical, capital and technical personnel) for the eBeam treatment of PFAS-contaminated soils using a 10 MeV, 560 kW fixed eBeam technology platform at 1500 kGy eBeam dose. The analysis suggests that it would cost approximately \$295/m^3 of soil for PFOS and PFOA remediation using the fixed eBeam technology platform.

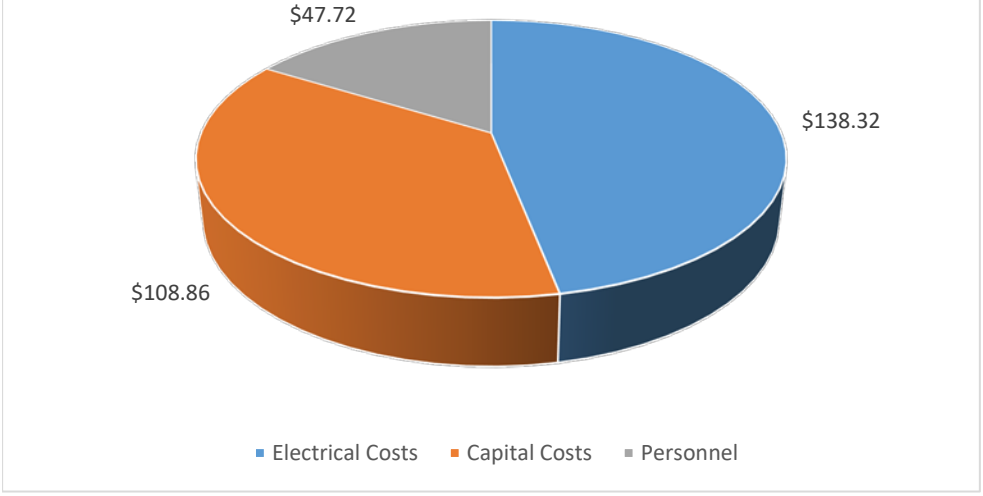


Fig ES-11. Breakdown of costs \$/m^3 to treat PFAS-contaminated IDW soils using a fixed onsite eBeam technology platform

This analysis assumes a target dose of 1500 kGy and total capital costs of \$7.7 million amortized over a useful life of 20 years. The assumptions include 80% beam uptime, 20m3/day throughput, and 90% beam utilization efficiency. Optimizing the process to achieve lower target doses and ability to utilize higher beam power will reduce the costs significantly.

Discussion

The laboratory experiments support our original research hypothesis that high energy eBeam technology has potential as a suitable remediation technology for PFAS-contaminated soils and groundwater samples. To the best of our knowledge, there is no technology (other than incineration) that is effective against PFOS-contaminated IDW soil and sand samples. It must be emphasized that in this study, other than some coarse dose adjustments (between 50 kGy and 2000 kGy), eBeam technology for PFAS remediation has not been optimized. Optimization trials should include identifying the optimal pH range, the addition of appropriate amendments/radical scavengers, nitrogen sparing, calcium carbonate as well as exploring the use of suitable catalysts such as $Ti0_2$ and $KMnO_2$. There is a need to better understand the mass balance of fluorine during eBeam remediation and the influence of presence of co-contaminants such as solvents, petroleum hydrocarbons and other PFASs on defluorination and breakdown of PFOS and PFOA. There is a need to design, fabricate, and utilize continuous flow reactors (for groundwater) and a movable conveyance system/platform to demonstrate eBeam mediated degradation of PFOS and PFOA under quasi-realistic conditions. Laboratory studies using a continuous eBeam test platform are needed to yield high value information before installing the technology onsite.

Electron beam technology is already commercially available and is employed in other applications such as medical device sterilization and food pasteurization. Thus, the Technology Readiness Level (TRL) is already very high. Electron beam technology with proper optimization and engineering design effort could become an extremely valuable tool in the Department of Defense technology “tool-box” to deal with environmental contaminants.

Objective

Electron beam (eBeam) technology is a chemical-free technology that utilizes accelerators to generate extremely large numbers of highly energetic electrons from electricity. Compact, high-energy (10 million electron volts, MeV) and high power (> 700 kilowatts, kW) accelerators capable of treating upwards of 2 million gallons per day of groundwater are commercially available today. These accelerators are capable of producing extremely large concentrations of highly energetic electrons (> 10^{15} electrons/cm^2/sec) which, when they interact with water produce extremely large amounts of free radicals, hydrogen atoms and additional aqueous electrons (Eq. 1). Exposing soils and groundwater to eBeam irradiation causes extensive ionization reactions and highly reactive free radicals (*Eq 1*):

$$e^- + H_2O \rightarrow [2.6]\ e^-_{aq} + [0.55]\ H^\bullet + [2.7]H_3O^+ + [0.7]H_2O_2 + [2.6]\ HO^\bullet + [0.55]H_2 \quad (1)$$

Where, the values in brackets represent "G values" (number of species produced by 0.1MeV of energy absorbed), and $H^\bullet$, e^-, and $HO^\bullet$ are highly reactive species, while H_3O^+ is the hydrated proton. Electron beam as a remediation technology is potentially paradigm shifting, because it simultaneously creates both reduction and oxidation processes without the addition of any chemicals. At high doses, temperature also get involved in these complex reactions. These powerful oxidation-reduction reactions occur almost instantaneously and therefore, best characterized as an *Advanced Oxidation-Reduction Process (AORP).* The eBeam technology is the most cost-effective approach of generating free radicals. Since this technology utilizes commercial electricity, this is a "switch-on/switch-off" technology. Therefore, the proposed research was directly aligned with the scope of SERDP's SEED project which is to explore innovative approaches that entail high technical and scientific risk. The specific objectives of the SERDP Exploratory Development (SEED) project were:

1. To quantify the effectiveness of eBeam technology at breaking down PFOS in soil and water under controlled experimental conditions, and
2. To characterize the effectiveness of eBeam at destructive treatment for a mixture of PFASs present in actual IDW samples collected from multiple sites.

The fundamental science questions were:

a) Can eBeam irradiation effectively reduce concentrations of PFOS in solid and aqueous matrices under controlled laboratory conditions?
b) What is the optimal eBeam dose range to achieve remediation targets for PFOS?
c) Do soil parameters such as alkalinity, pH, and moisture content influence defluorination efficiency for soil and groundwater IDW?
d) Does eBeam irradiation effectively treat PFASs and other co-contaminants commonly associated with AFFF impacted soil and groundwater IDW to below levels of concern for unrestricted disposal, discharge, or onsite reuse?

Our criterion of success was >90% degradation of PFOS and PFOA in soils. Early on during the project, the co-performer Arcadis, Inc. emphasized the need to focus on soil samples since the technologies available to remediate PFAS-contaminated soils was very limited. We posited that by demonstrating the proof-of-concept and initial evaluation using actual IDW soil and water samples, the key outcome of this project will be that high energy eBeam technology will be considered to be evaluated as a tool in the technology "tool box" for the Department of Defense to use for PFAS remediation at its installations.

Background

Aqueous film forming foams (AFFFs) have been used at many Department of Defense installations for firefighting training and emergency response. Where AFFF was used in emergency exercises, unlined fire training areas, and accidental releases, the poly- and perfluoroalkyl substances (PFASs) used as active ingredients in AFFF impacted underlying soil and groundwater. Site investigations of these PFAS-impacted areas generate complex mixtures of investigation derived waste (IDW), which include many individual forms of PFASs, as well as other co-contaminants such as total petroleum hydrocarbons (TPH) and volatile organic compounds (VOCs). Few destructive treatment technologies are currently validated to treat PFASs, and most require ultimate destruction to occur in an offsite facility. Herein, we proposed to investigate an innovative and promising technology known as electron beam (eBeam) that can *ex situ* remediate PFASs and other co-contaminants in soil and groundwater IDW in an onsite unit.

There have been numerous attempts to develop PFOA/PFOS remediation technologies (Table 1). The Strategic Environmental Research and Development Program (SERDP) has invested heavily in research to improve the understanding of the occurrence, fate, toxicity, transport, and possible remediation strategies for PFAS substances[1-11]. To date, possible remediation approaches

Table 1. Summary listing of PFOS/PFOA remediation technologies

Technology	Remarks	Ref
In situ chemical oxidation (ISCO)	Unlikely to degrade PFCs in groundwater	4
Bioaugmentation using vault proteins	Novel *in situ* bioremediation technology using vault nanoparticles: neither whole cells or nor fee enzymes could transform PFOA in laboratory studies	3
Electrocatalytic technologies	In situ electrocatalytic and catalytic processes for PFAS remediation	5
PFC-coagulant	In situ remediation by coagulation-enhanced sorption of PFAS	6
In situ chemical reductive defluorination	Use of clay-encased zero-valent metals and bimetals	7
Titanate nanotubes	Titanate nanotubes did not enhance PFOA decomposition as compared to direct UV photolysis	12
Photochemical approaches	Direct photolysis was slow; H_2O_2 combined with UV-visible light irradiation was ineffective	13
Electro-microfiltration	Demonstrated to remove ~ 70%-80% of PFOS/PFOA in industrial wastewater	14
Photo reductive defluorination	UV (254nm) at pH 9.0 and under anaerobic conditions achieved ~ 98% PFOA defluorination	15
Sonochemical decomposition	Ultrasound (150W; 40 kHz) combined with carbonate radicals and N_2 saturated conditions	16
Cobalt-60 γ irradiation	mineralization of PFOA in aqueous solution	17
Electron beam (eBeam) irradiation technology	eBeam achieved >90% PFOA defluorination in aqueous solution at 10 kilograys (kGy)	18

investigated have included bio-augmentation using vault proteins[3] and i*n situ* chemical oxidation of sorbed contaminants (ISCO-SC)[4]. Additionally, there are several currently on-going SERDP-

sponsored research studies evaluating coagulants, electro-catalytic technologies and *in situ* defluorination approaches. There is a rich literature database on the relative efficacies of various other treatment technologies for PFOA and PFOS treatment/remediation (Table 1). These technologies have included electrochemical treatments, adsorption technologies, sonochemistry, photolysis, photochemical processes, cobalt-60-based gamma (γ) irradiation and eBeam technologies. However, few to none have shown to have applicability for degrading PFOA and PFOS in IDW soil wastes or other PFAS-contaminated soils.

In 2014, Zhang et al (2014) reported that ionizing radiation using a gamma (γ) source such as cobalt-60 could achieve complete mineralization of PFOA in pure aqueous solutions[17]. Cobalt-60, however, is a radioactive isotope with a half-life of 5.27 years with approximately 12% decay of specific activity per year. This radioactive source cannot be "switched on/switched off". The only option to stop the γ radiation is to submerge the cobalt-60 source into a pool of water. The concept of utilizing radioactive cobalt-60 isotope reactors for *ex situ* PFOA-contaminated groundwater sites is untenable, from both a technology perspective, as well as a homeland security perspective[19]. The DOE's National Nuclear Security Agency (NNSA) and other federal agencies are working towards eliminating the use of cobalt-60 in industrial/commercial applications. Therefore, we decided that an alternative approach of degrading PFASs needed to be developed.

In 2016 we published a seminal paper demonstrating the efficacy of eBeam technology for degrading PFOA in laboratory-derived aqueous media[18]. That study provided the needed understanding of the technology to hypothesize that high energy eBeam technology has the potential to breakdown PFASs such as PFOS and PFOA. This SEED proof-of-concept proposal was a follow up of that early research. Our *underlying hypothesis* was that advanced oxidation reduction processes occurring during eBeam irradiation is capable of breaking down PFASs in IDW materials even in the presence of other co-contaminants such as petroleum hydrocarbons.

Materials & Methods

Electron beam irradiation: Texas A&M University's National Center for Electron Beam Research (NCEBR) has high energy eBeam irradiation capabilities. The two (vertical and bottom mounted) 10 MeV, 15 kW high energy eBeam linear accelerator at NCEBR. There is an internationally traceable alanine-based dosimetry system[20]. The dosimetry system includes a Bruker e-scan dosimetry system (Bruker, Billerica, MA). Experiments were performed in 60 mL HDPE bottles containing either sand or water samples as well as in custom-designed experimental vessels for high dose irradiation studies using IDW samples. All eBeam

Experimental samples: There were 2 phases to this research project. In Phase 1, the laboratory-derived sample experiments were performed using 60 mL HDPE bottles in which experimental soil/sand and water samples were contained. For aqueous samples, the sample volume was 50 mL. For soil/sand samples, the sample volume was 10 g. The bottles containing the experimental samples were initially dose-mapped to ensure that uniform doses could be delivered.

Field derived IDW soil and groundwater samples: IDW samples were obtained from Pennsylvania (Willow Grove NASJRB/WG), Michigan (Wurtsmith AFB) and from Texas (Randolph AFB). Portions of these samples were sent to the commercial laboratory for analysis per the EPA Method 537. We focused the subsequent set of studies only on the Willow Grove (PA) and Wurtsmith (MI)

IDW samples since they had high concentrations of PFOS in the groundwater and soil respectively (Table 2).

	Field IDW Sample Michigan Soil	Field IDW Sample Texas Soil	Field IDW PA Soil	Field IDW Michigan Water	Field IDW Texas Water	Field IDW PA Water
	ng/g	ng/g	ng/g	ng/L	ng/L	ng/L
PFBA	6.91	1.7	<0.269	23.1	167	<328
PFPeA	33.9	5.28	0.155	88.4	354	402
PFHxA	11.1	7.38	0.15	53.4	1340	1250
PFHpA	13.1	1.15	<0.067	19.2	97.2	218
PFOA	**17.2**	**8.54**	**0.098**	**41.6**	**877**	**870**
PFNA	2.98	0.599	<0.067	3.97	5.1	<80
PFDA	0.964	0.078	<0.067	<3	<3.25	<80
PFUnA	<0.25	0.112	<0.067	<3	<3.25	<80
PFBS	1.16	2.03	<0.062	<3.1	271	505
PFPeS	0.717	3.2	0.069	<3	265	664
PFHxS	29.2	44	0.833	84.7	2160	4240
PFHpS	3.94	6.51	<0.067	8.18	16.7	760
PFOS	**1010**	**259**	**8.3**	**1370**	**764**	**42600**
PFNS	1.66	0.375	<0.067	<3	<3	87.3
PFDS	<0.25	0.263	<0.067	<3.1	<3.33	<80
6:2 FTS	13.1	8.95	1.12	138	1230	1080
8:2 FTS	30.5	2.87	<0.262	67.9	<13	<320
PFOSA	124	4	<0.067	70.3	23.1	166
% Moisture	84.4	7.31	6.94			

Table 2. PFAS concentration in IDW soil and groundwater samples from Pennsylvania, Michigan and Texas

Laboratory-derived samples. Commercial sand samples were purchased and spiked with target concentrations of 20 mg/kg PFOS and 10 mg/kg PFOA. Ten grams (10 g) of sand samples were spiked. Distilled water was spiked (10 µg/mL PFOS and 5 µg/mL PFOA) with reagent-grade PFOS and PFOA obtained from Sigma-Aldrich. To prepare the lab-spiked samples, stock/working solutions were made. The determined concentrations were different for each desired chemical in each matrix: 5 µg/L PFOA and 10 µg/L PFOS in each water sample, and 10 mg/kg PFOA and 20 mg/kg PFOS in each sand sample. Each stock was prepared separately for water and sand samples, as the concentrations needed for the sand samples were not sold in aqueous form. For stock solutions, a 10x dilution in 100% MeOH was made from the pure chemical dissolved in MeOH.

The stock was then further diluted into a working solution made with HPLC-grade water to achieve the desired concentration. PFOA and PFOS were combined into one working solution from their respective stocks; the working solution had final concentrations of 5 µg/L PFOA and 10 µg/L PFOS. 50 mL of working solution was dispensed into 60 mL square HDPE bottles for irradiation. The working solution for the sand samples was prepared using pure powdered PFOS-K and PFOA. Both powders were first dissolved in acetone before being added to a 1 L volumetric flask. After the entirety of the pure powder solution was rinsed into the flask, the remainder was filled to the 1 L line with HPLC-grade water. The final concentration of the working solution was 10 mg/L PFOA and 20 mg/L PFOS. Ten milliliters (10 mL) of the working solution was added to 10 g of sand to achieve the final concentrations of PFOS and PFOA.

Low dose eBeam trials: The focus of the experiments in Task 1 were focused primarily on obtaining empirical data to demonstrate the high eBeam has the ability to degrade PFAS such as PFOS in soil samples. These studies were performed (as mentioned earlier) in 60 mL HDPE bottles in which the sand and distilled water samples were contained. They were placed on the product conveyance system and exposed to defined periods of time that were previously calibrated to correspond to defined minimum target doses. Fifty kilgrays (50 kGy) was used as the target minimum dose for these studies. Preliminary studies were performed at 10 kGy and 50 kGy to support the decision that experiments need to be performed at 50 kGy (*data not included*) Influence of nitrogen sparging, pH, nitrate and alkalinity on PFAS degradation: The different experimental conditions included evaluating the effect of de-oxygenation of the sample prior to eBeam treatment. We sparged the sample with pure N_2 gas in a glove box, sealed, and then double bagged in sealed bags. To evaluate the effect of pH, we adjusted the pH to 13.0 using 10N NaOH. To evaluate the effect of alkalinity, we adjusted using sodium bicarbonate[18].

High dose eBeam trials: Task 2 experiments were to evaluate the PFOS and PFOA degradation in IDW samples. Compared to delivering 50 kGy to experimental samples, the delivery of higher doses necessitated the fabrication of custom experimental vessels (Figure 1). The experimental

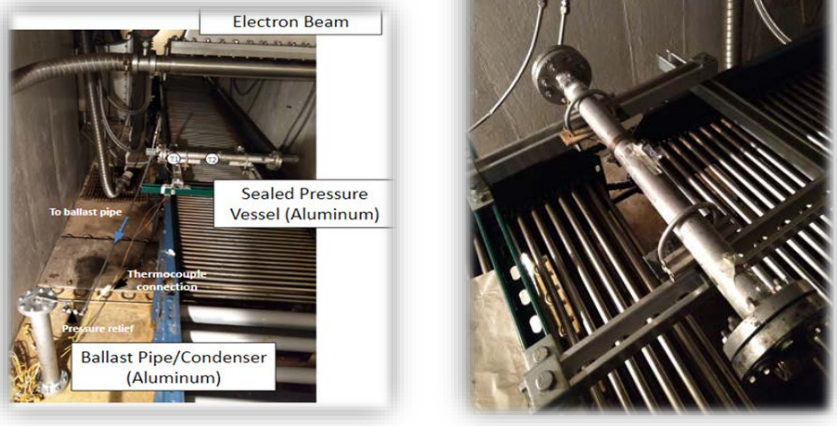


Fig. 1. Photos showing the experimental vessels used for high dose eBeam experiments

vessel consisted of a sealed aluminum pressure vessel that was connected to a condensate collection vessel. The condensate collection vessel was equipped with a pressure relief valve. Thermocouples were placed on the experimental vessels to monitor temperature increases during the high dose experiments. Attention was paid to avoid using Teflon-coated seals and components. Since the industry standard alanine dosimeters only measure up to 80 kGy, we devised an approach to ensure that accurate high dose delivery was achieved. The dose rate was measured by placing the dosimeters at various locations on the experimental vessel and turning on the beam for 4 seconds. The dose captured by the alanine dosimeter was divided by the time of exposure (4 seconds) to obtain the empirical dose rate. The target high doses were calibrated based on this dose rate. The samples were placed in a "boat" within the experimental sealed pressure vessel using stainless steel foil. One limitation of this experimental design was that replicate samples couldn't be treated under the beam at the same time. In these experiments were evaluated the effect of amendments such as $NaNO_3$, $NaHCO_3$ as well as pH adjustments (to alkaline conditions) on PFOS degradation.

Confirming reliability of high-dose treatment results.
The previous experiments involved only a single sample at the various high doses. Based on discussion with other team members we decided to replicate (n=3) when performing the high dose eBeam treatment of MI IDW soil samples to verify data reproducibility. The experimental set up still included the sealed pressure vessel. However, we fabricated 3 stainless steel ":boats" to hold the soil samples. Each of the boats was designed to hold between 30 g-50 g (Figure 2). The Wurtsmith AFB IDW soil samples were adjusted to 10% moisture content).

Fig. 2. Photograph of the experimental replicates of the test vessel, "boats"

Dosimetry and Dose-mapping for low eBeam irradiation trials: Irradiation dose measurements were performed using alanine dosimetry that was validated to international standards. For low dose studies, the dosimeters (Harwell Dosimeters, Oxfordshire,UK) were placed within the sample bottles and on the different surfaces of the sample bottles. The alanine dosimeters were placed in the heat-sealed pouches and placed at the various locations on the bottles and within the samples. These bottles were then subjected to varying doses to determine the dose distribution within the samples and at different locations within the sample. Studies were performed to ensure that the samples could be irradiated effectively with dose-uniformity ratio (DUR) ~ 1.0 or as close to 1.0 The DUR is an important criterion when performing irradiation experiments. A DUR of ~1.0 signifies that the ratio between maximum and the minimum doses anywhere within the sample bag is uniform. The dosimeters were measured using the Bruker E-scan spectrometer (Bruker, Billerica, MA). The dosimetry used for the high dose trials was as described above.

Pre-Analytical Sample Processing: Both sand and water samples prior to LC-MS/MS were purified using a Solid Phase Extraction (SPE) column. The water samples were passed through the SPE column directly without any additional processing. The sand samples, however, had to go through an extraction step prior to SPE purification. There were slight protocol modifications for the laboratory derived samples and the IDW samples as detailed below.

Laboratory-derived samples: Samples (1 mL aqueous and 10 gm sand) were removed for analysis. The extraction involved adding 25 mL 0.1% NaOH in methanol to each 10 g soil sample and the mixture was sonicated (60°C) for one hour. After sonication, the supernatant was poured into a new container and the process repeated a second time, thereafter pooling the combining the supernatants after the final sonication. The supernatant was then sonicated for an additional 30 minutes, after which 1.5 mL of solution was pipetted into a 2 mL centrifuge tube. From there, each sample was purified using SPE.

SPE purification: The SPE purification involved 1 mL Oasis WAX cartridges (Waters, Waters Corp. USA) using a vacuum manifold setup pre-conditioned three times with 0.1% NaOH in methanol followed by 100% methanol conditioning three times. After the last of the methanol washed was through the cartridge filter, the samples (1 mL) was loaded into the cartridges and low vacuum was used. After sample loading, each cartridge was washed with 1 mL 25 mM ammonium acetate, and then vacuum dried for 3-5 minutes. After the cartridge had sufficiently dried, the cartridge was eluted with 1 mL 0.1% NaOH in methanol and subsequently, vacuum dried. The eluent was collected in a clean vial and immediately covered with Parafilm™ before being transferred to 250 µL vials for LC-MS/MS analysis.

Field-derived IDW samples: The sample processing for the final round of IDW sample experiments was slightly altered to improve recovery. Four grams of the treated and control IDW samples were removed from the experimental vessels. The extraction details are described below. Each of these samples were extracted and purified as described for the laboratory-derived samples. The final methanol eluents (from the SPE purification) was placed in glass tubes which were placed in the evaporator and dried using the following conditions, 30°C, 15 psi. The solutions were evaporated to less than 0.5 mL and then transferred to a 1.5mL microfuge tubes. The glass tubes used in the previous step were washed with pure methanol. The other eluents from the other 3 samples were pooled together. The pooled concentrates (from 4g samples) measured approximately 1.5 mL. This concentrate was stored at 4C refrigerator prior to LC-MS/MS analysis.

LC-MS/MS analysis: The PFOS and PFOA analyses were performed on the Texas A&M University campus by the IMAC (Integrated Metabolomics Analyis core.(facility). Calibration standards were prepared fresh before each analysis by spiking 100% Methanol with PFAS at working stock concentration of 10,000 ng/mL in a concentration range between 0.25 ng/mL and 100 ng/mL. The working stock of PFAS is run with every batch analysis as a QC to verify the stock concentration. Initially, the laboratory only performed PFOS and PFOA analysis. Towards the end of the project , this laboratory also started performing the EPA 537 Method. Towards the of the project, this analytical laboratory started performing detailed analysis for 27 different PFAS. The primary advantage of using the IMAC facility is their quick turn-around time (~ 2 days) and the low analytical costs

Commercial laboratory analysis: We also sent samples to SGS-AXYS (British Columbia, CA).The laboratory provided extensive QA/QC records, and provided comprehensive data including the 27 different PFAS. The turn-around time, however, was extremely long (minimum 30 days) and expensive ($ 375 – $ 650/sample). Initially, the laboratory was only requested for

PFOS and PFAS analysis. The final set of samples, however, were analyzed using the post-analysis Total Oxidizable Precursor (TOP) assay.

Economic feasibility analysis: An economic analysis was performed to determine the treatability costs if eBeam technology was adopted. The treatment scenario was the application of 2000 kGy for soil remediation purposes. The capital costs and the operating costs were considered in the economic analysis. Additionally, the economic model was adjusted to simulate different treatment scenarios such as 20% higher/lower dose, 20% larger/smaller site, and 20% higher/lower beam power.

Statistical analysis: The majority of experiments were performed in triplicates. For the initial high dose experiments replicate samples were not possible. However, we subsequently custom-designed sample "boats". The data was statistically analyzed using the Student *t* test. The graphical software, GraphPad ver 8.1 was used for most of the data visualization.

Results and Discussion

Electron beam technology is not new. The technology can remove SO_x, NO_x, and volatile hydrocarbons from flue gas[21,22]. This technology is used worldwide for sterilizing medical devices, cross-linking polymers, and pasteurizing food and fresh produce[23-26]. Our team members have previously shown that eBeam-mediated defluorination of PFOA is possible in aqueous solutions as a function of nitrate, alkalinity and natural organic matter[18], as well as remediation of hydrocarbon-contaminated soils[27].

Dose-mapping of experimental containers: Table 3 shows the Dose Uniformity Ratio (DUR) DUR of the experimental test bottles containing 10 g sand and 50 mL distilled water. The DUR is very close to 1.0 implying that the dose is extremely uniform across the samples and that dosimeter readings from either the top or bottom of the sample container is representative of the dose that the actual dose within the sample. This dataset provides assurance that the eBeam dose information is accurate from the dosimetry readouts.

Sample	Location	Dose (kGy)	Dose Uniformity Ratio
10g sand	1 (top)	13.65	1.14
	2 (middle)	13.76	
	3 (bottom)	15.53	
50 mL H_2O	10 (top)	13.99	1.05
	11 (middle)	14.06	
	12 (bottom)	13.41	

Table 3. eBeam dose distribution across the experimental test vessels

PFOA and PFOS Degradation in Laboratory Samples

Spiked distilled water samples. Figure 3A and 3B shows the degradation of PFOA and PFOS observed in distilled water suggesting that at 50 kGy dose, both PFOS and PFOA are degraded. Interestingly, PFBA was detected in the experimental samples (possibly from the laboratory distilled water), and its breakdown was also detected (Figure 3C). At 50 kGy, as much as 87% of PFOA was degraded while PFOS degradation was much lower at 16%. The PFOA concentration decreased from 3.13 µg/L (3.3 ppb) to 0.39 µg/L (0.39 ppb). At 50 kGy, as much as 16% of

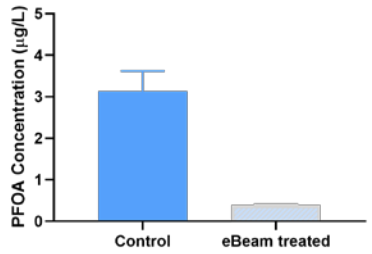


Fig. 3A. eBeam-mediated (50 kGy) degradation of PFOA in spiked distilled water samples

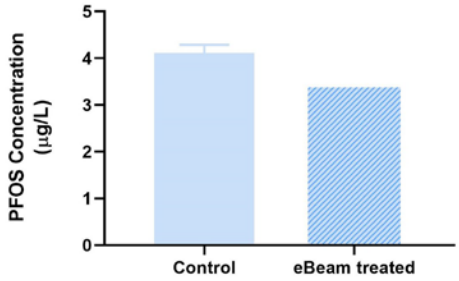


Fig. 3B. eBeam-mediated (50 kGy) degradation of PFOS in spiked distilled water samples

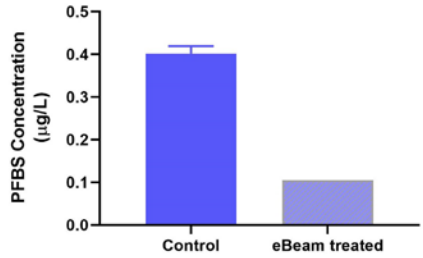


Fig. 3C. eBeam-mediated (50 kGy) degradation of PFBS in laboratory water samples

PFOS was degraded. The concentration decreased from approximately 4 ppb to 3.4 ppb. There were statistically significant ($p<0.05$) differences in the PFOS and PFOA concentrations between the control and eBeam treated samples. These results suggests that eBeam at 50 kGy was able to achieve a statistically significant degradation of both PFOS and PFOA in the water samples. The extraneous PFAS-contaminant, PFBS from the distilled water was also observed to have degraded by 74% from around 400 ppt to 104 ppt. There is a report from China, Ma et al (2017) (28) who reported to have observed 95.7% and 85.9% degradation of PFOA and PFOS in laboratory aqueous solution at very high doses between 100 – 500 kGy. However, there are several unexplained details in their study with respect to the possibility of sample evaporation, lack of details about the aqueous media, etc.

Spiked sand samples: The results from the 50 kGy eBeam dose treatment of laboratory sand spiked PFOA and PFOS are shown in Figures 4A and 4B. At 50 kGy eBeam dose, as much as 86% of

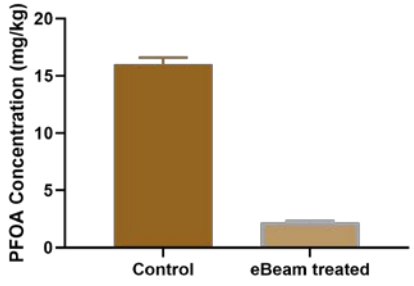


Figure 4A. eBeam-mediated degradation of PFOA in laboratory spiked sand samples

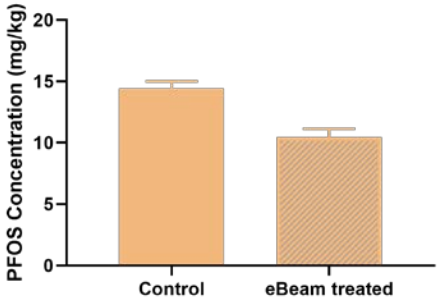


Figure 4B. eBeam-mediated degradation of PFOS in laboratory spiked sand samples

PFOA (from 16 mg/kg to 2.19 mg/kg) was degraded in the sand samples (Figure 4A). This represented a decrease in concentration from 16 ppm to 2 ppm. At this dose, 27.5% of PFOS was degraded (Figure 4B). This represented a decrease in concentration from 14.4 ppm to 10.5 pp. These differences were statistically significant ($p<0.05$) suggesting that at 50 kGy dose, eBeam technology was able to achieve a statistically significant decrease in PFOA and PFOS concentration. To date, there has been no published report of PFOS or PFOA degradation in soil.

Effect of increasing eBeam dose on PFOA degradation in distilled water: We wanted to reproduce the results observed by Ma et al (2017) wherein they suggested that they could achieve as high as 95.7% degradation of PFOA and 85.9% of PFOS. We, therefore, exposed PFOA-spiked samples to increasing eBeam doses from 50 kGy to 500 kGy (Figure 5).

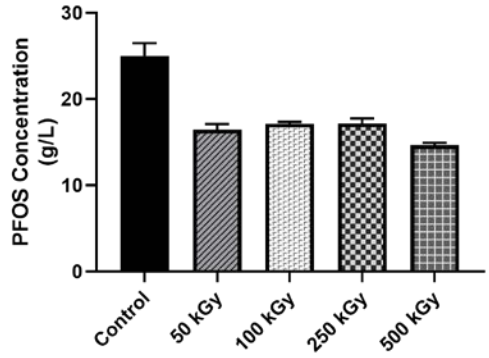


Fig. 5. Effect of increasing eBeam doses on PFOS degradation in laboratory-spiked water samples

From an initial starting concentration of 25 g/L (25000 ppm), we observed 14.7 g/L (14700 ppm) remaining even after exposure to 500 kGy. This represented a 41% reduction. In the studies by Ma et al., they reported that eBeam-mediated PFOA degradation decreased with increasing concentration. In their studies with 30 mg/L, they observed about 48% reduction. This was a higher reduction than what was observed in our studies. However, it needs to be mentioned that in the Ma et al (2017) paper there is no mention of how they were able to reduce evaporation in their samples which should have occurred when they were employing doses as high as 500 kGy (Figure 6). In our experimental system the probability of evaporation was negligible since they were in screw-capped HDPE bottles.

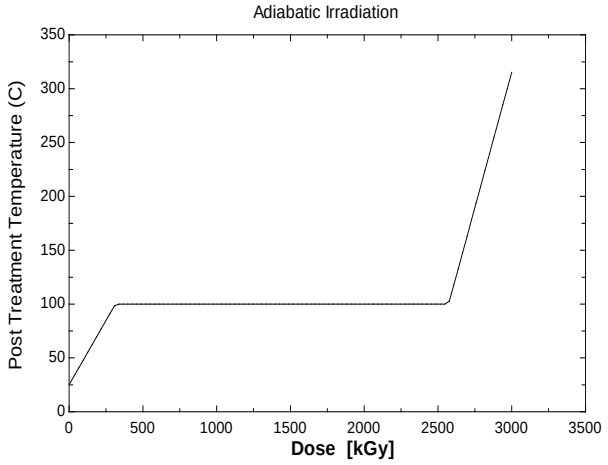


Fig. 6. Temperature increase in water as a function of eBeam dose

Even though eBeam treatment technology is considered a non-thermal treatment process, there will be significant temperature increase at the dose is increased. Figure 6 is a graphical representation of the temperature increase if the irradiation process is adiabatic. The absorbed dose during eBeam irradiation is defined in kilograys (kGy) which is equivalent to kj/kg. Therefore, it is expected that at high doses not only will radiolytic species from the ionization events be involved in the PFAS degradation process, the temperature increase during the process will also play a major role.

High eBeam dose mediated degradation of PFOS and PFOA in spiked soil and water samples: Laboratory samples (sand and distilled water) were spiked with the defined concentrations of PFOS and PFOA. Two sets of samples were prepared. One set of samples were prepared without any amendments in terms of pH, alkalinity and nitrate concentrations. The other set of samples were amended to pH 13 and were adjusted with defined concentrations of nitrate (using $NaNO_3$) and alkalinity (using $NaHCO_3$) based on our previous results (Wang et al., 2016).

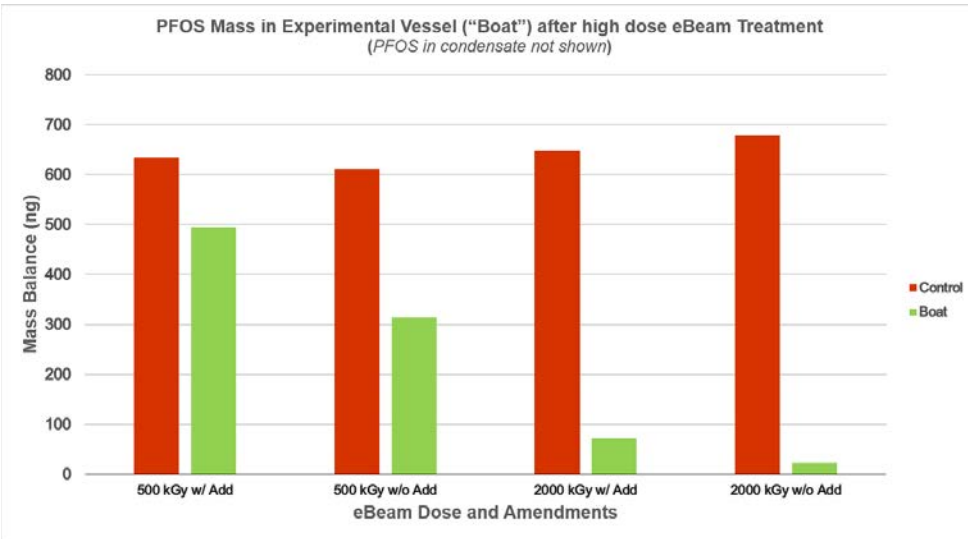


Fig.7. PFOS degradation in laboratory-spiked water samples as a function of increasing eBeam doses. (Amendments refer to pH, $NaNO_3$ and $NAHCO_3$ adjustments)

The samples were placed in the high-dose experimental vessels (Figure 1) and exposed to increasingly higher doses from 500 kGy up to 2000 kGy. In these experiments, we collected the condensates as well as the residual samples remaining in the experimental "boats" to ensure that we could account for the PFOS and PFOA fate on a mass balance basis. Figure 7 shows the PFOS (on a mass basis) in the treated and eBeam treated samples. At 500 kGy, the PFOS concentration decreased from 633 ng to 494.8 (21.8% degradation) and at 2000 kGy the degradation increased to 96.6% (from 678.9 ng to 22.9 ng). Interestingly, the degradation observed in the presence of the amendment (meant to enhance degradation) was lower than the degradation observed in the absence of the amendments. There was approximately an 8% difference in the PFOS degradation between the amended and un-amended samples (96.6% as compared to 88.8%). In a recently published paper, Trojanowicz et al (2020) have reported that the presence of even low levels of nitrate (10 µg/L) can inhibit desulfonation. This could possible explain the reduced PFOS breakdown. However, the influence of such amendments in actual IDW samples warrants further investigation.

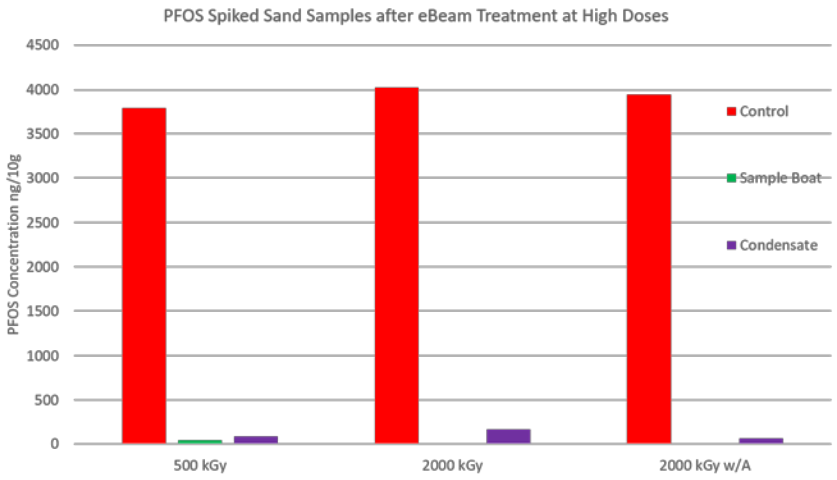


Fig.8. PFOS degradation in laboratory-spiked sand samples as a function of increasing eBeam doses. (Amendments refer to pH, $NaNO_3$ and $NAHCO_3$ adjustments)

Figure 8 shows the PFOS reduction in spiked sand samples when exposed to 500 kGy and 2000 kGy. In these experiments, the condensate samples were collected and the PFOS concentration measured. At 500 kGy, the PFOS concentration decreased from 379.4 ng/g (379 ppb) to 4.5 ng/g (4.3 ppb) reflecting a degradation that is greater than 98.8%. At 2000 kGy (with amendments) the degradation was greater than 99.99% while in the absence of amendments, the degradation was to below detectable limits (limit of detection = 0.025 ng/g). Therefore, this was strong experimental evidence that high dose eBeam technology is capable of degrading PFOS to below detectable limits.

Based on the above results we hypothesized that the field obtained IDW samples from Michigan and Pennsylvania should also exhibit similar reductions in PFAS concentrations when exposed to

2000 kGy eBeam dose. Therefore, in Phase 2 of the studies we focused on the IDW soil and water samples obtained from Michigan and Pennsylvania. Michigan soil samples had PFOS concentration of 1010 ng/g (1010 ppb) and PFOA concentration of 17.2 ng/g (17.2 ppb). Pennsylvania groundwater samples had PFOS concentration of 42600 ng/L (42.6 ppb) and PFOA concentration of 870 ng/L (0.87 ppb) (Table 2).

High dose eBeam treatment of Willow Grove, PA IDW samples

Table 3 shows the results (mass basis) of PFOA and PFOS degradation when IDW from Willow Grove, PA is exposed to high eBeam doses (500, 1000 and 2000 kGy). The control and eBeam-treated samples were analyzed in the commercial laboratory using the post-TOP assay to account for precursors. The PFOA mass decreased by 53.57% when exposed to 2000 kGy while the PFAS concentration decreased by as much as 87.91%

	Treatment	Post-TOP PFOA in boat (ng)	Post-TOP PFOS in boat (ng)	% Removal of Post-TOP PFOA	% Removal of Post-TOP PFOS
PA-IDW-GW	0 kGy	112	3851	0%	0%
PA-IDW-GW	500 kGy	84	1949.1	25%	49.39%
PA-IDW-GW	1000 kGy	101	1152.3	9.82%	70.07%
PA-IDW-GW	2000 kGy	52	465.6	53.57%	87.91%

Table 4. eBeam-mediated breakdown of PFOA and PFOS in Willow Grove (PA) IDW groundwater samples. The % removal on a mass basis is shown.

The PFOS reduction was less than the reduction that was observed with the spiked distilled water samples (Figure 7). In Task 1 we had observed PFOA breakdown as high as 87% even at 50 kGy (Fig 3A). The rather surprising results could be explained by a recent publication suggesting that PFOA is one of the intermediates of PFOS degradation under eBeam irradiation conditions[29]. They report that under eBeam irradiation of PFOS, a variety of byproducts such as perfluorinated sulfonic acids (PFSs), and perfluorinated carboxylic acids (PFCAs) with several carbon atoms ranging from 4 to 8, including PFOA. The other PFOS breakdown products could include PFOS-derivatives with various alkyl groups.

In addition to analyzing the samples for PFOS and PFOA the commercial laboratory also analyzed the samples for 29 different targeted PFASs and precursors (Fig 9A). Shown below are the results from this analysis from the Willow Grove IDW groundwater samples during these experimental eBeam dose treatments. Figure 9B is an expanded view of the data shown in Figure 9A to highlight the fate of the different PFASs and precursors in the IDW samples. Figure 9B is an expanded view

of the dataset presented in Figure 8A PFAS component. It is evident that with increasing eBeam dose, there is a reduction in the concentrations of PFCAs (PFBA, PFPeA, PFHXA, PFOA) as well as in the concentrations of PFSAs (PFBS, PFHXS, PFOS and PFDS). Interestingly, there was a slight yet detectable increase in the concentration of PFAA precursors such as N-EtFOSA and N-EtFOSE at 2000 kGy. Further studies are needed to delineate the conditions that could achieve significantly greater reduction of PFOA and PFOS in the water samples.

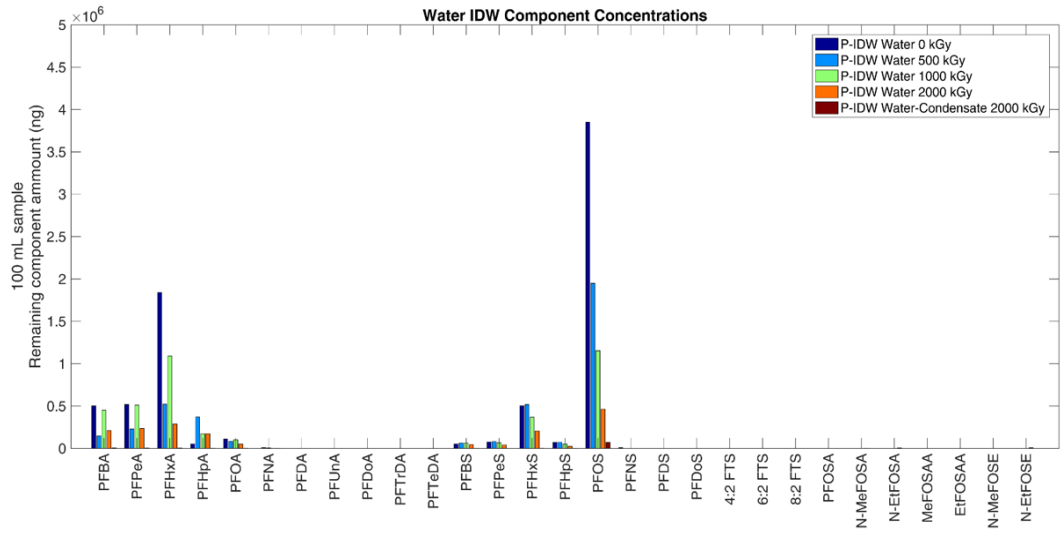


Fig. 9A. Targeted PFAS component concentrations in PA IDW water as a function of increasing eBeam dose

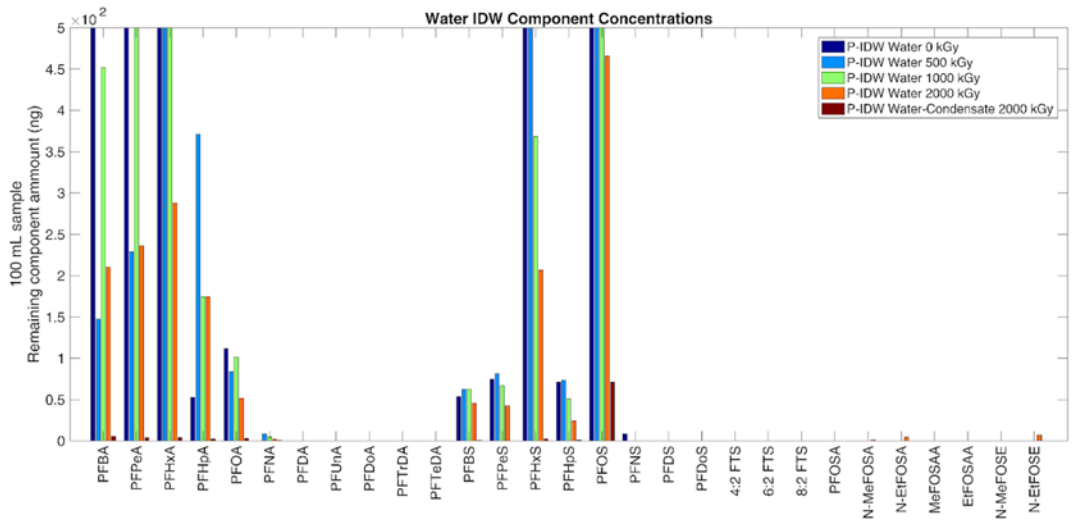
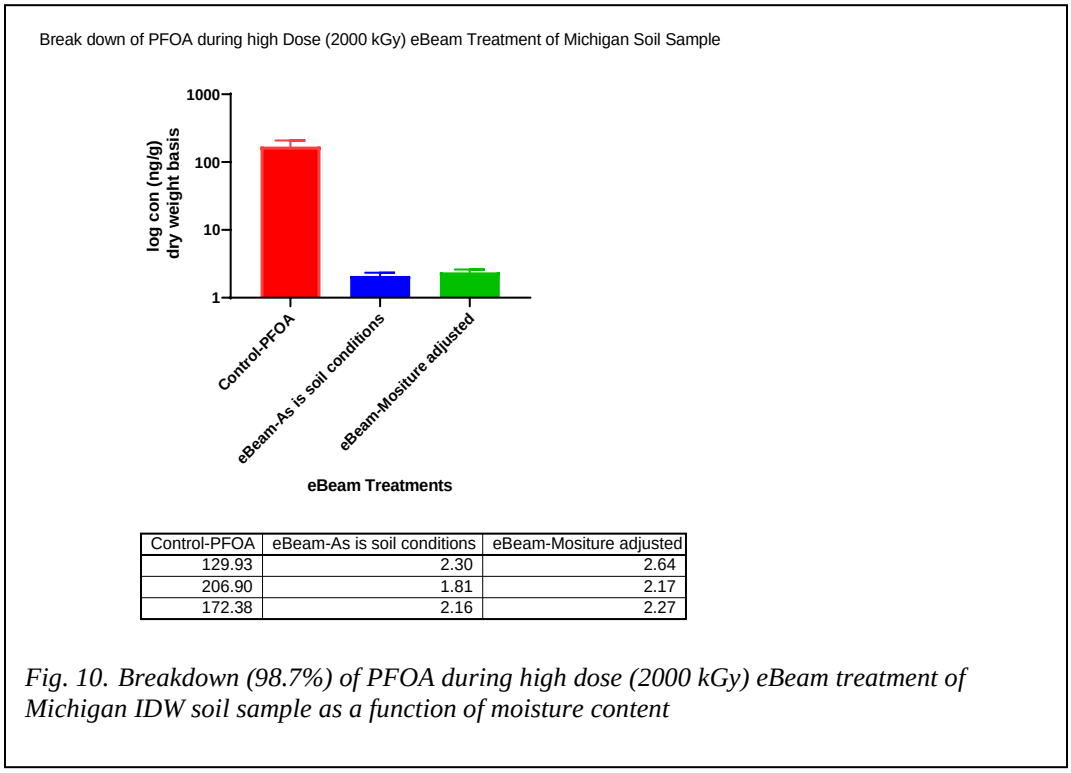


Fig. 9B. Magnified view of targeted PFAS component concentrations in PA IDW water as a function of increasing eBeam dose

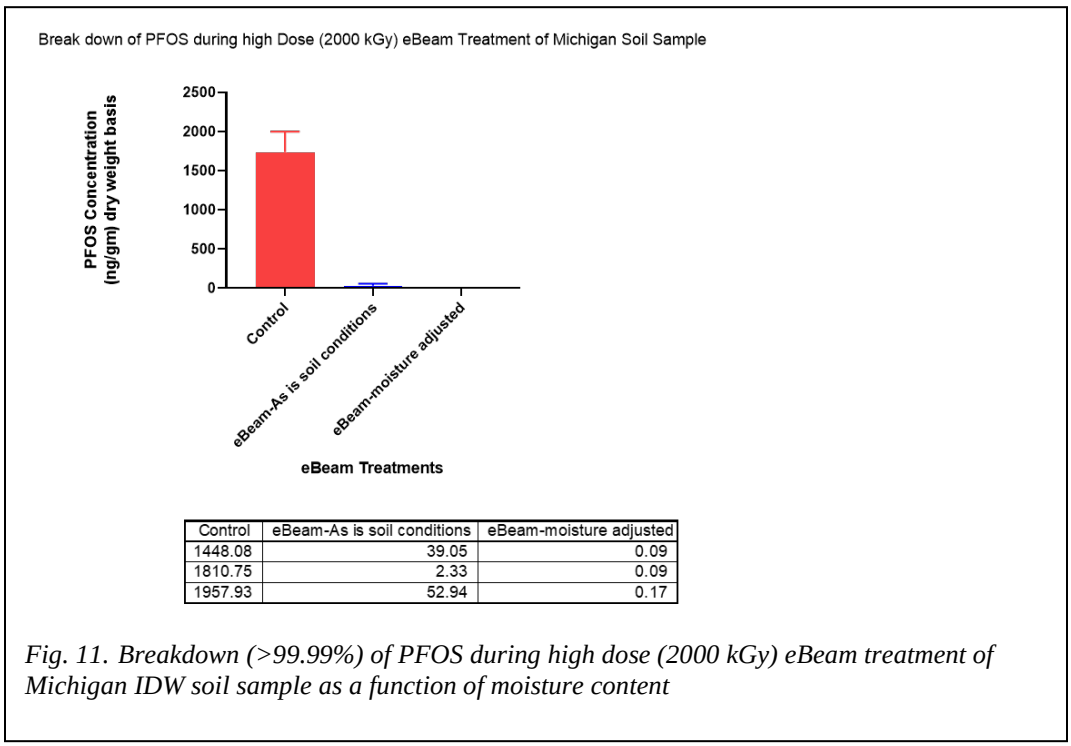
High dose eBeam treatment of Michigan IDW Soil Sample

Triplicate IDW soil samples from Michigan were exposed to high eBeam dose (2000 kGy). This IDW sample had 84.4% moisture content (Table 2). The 3 experimental treatments were IDW control soil (no eBeam treatment), the IDW soil (as is, without moisture adjustment-eBeam



Control-PFOA	eBeam-As is soil conditions	eBeam-Mositure adjusted
129.93	2.30	2.64
206.90	1.81	2.17
172.38	2.16	2.27

Fig. 10. Breakdown (98.7%) of PFOA during high dose (2000 kGy) eBeam treatment of Michigan IDW soil sample as a function of moisture content



Control	eBeam-As is soil conditions	eBeam-moisture adjusted
1448.08	39.05	0.09
1810.75	2.33	0.09
1957.93	52.94	0.17

Fig. 11. Breakdown (>99.99%) of PFOS during high dose (2000 kGy) eBeam treatment of Michigan IDW soil sample as a function of moisture content

treated), and IDW soil (adjusted to 10% moisture content – eBeam treated). The The moisture adjusted and the non-adjusted IDW soil samples were exposed to 2000 kGy eBeam dose. The results from these experiments are shown in Figure 10 and Figure 11.

An ANOVA test was performed to compare the PFOA concentrations between the 3 treatment groups. There was a significant difference ($p < 0.0001$) between the treatment groups. When a Student t test was performed to compare the remaining PFOA concentrations in the eBeam treated samples, there was no significant difference suggesting that irrespective of whether the soil was moisture adjusted to 10% or treated as is, PFOA will degrade as much as 98.7% .In the case of PFOS, the breakdown was even more significant (~ 99.99%) with complete degradation of PFOS (Figure 11). In the IDW soil which was treated with eBeam at ambient soil moisture conditions (~ 85%), the PFOS reduction was 98.19%. In samples where the soil moisture was adjusted to 10%, the PFOS degradation was almost complete (99.99%). These results suggest that PFOS degradation appears to be enhanced under low moisture conditions under high eBeam dose conditions. These samples have not been analyzed by the commercial lab since they could not guarantee timely datasets. These samples have been analyzed by the TAMU laboratory. Nevertheless, we plan to send these samples for analysis to the commercial laboratory as well.
Figure 12 is the fate of PFASs in the IDW soil after treatment at 2000 kGy eBeam dose. (These are preliminary datasets in that the values have not corrected on a dry weight basis).

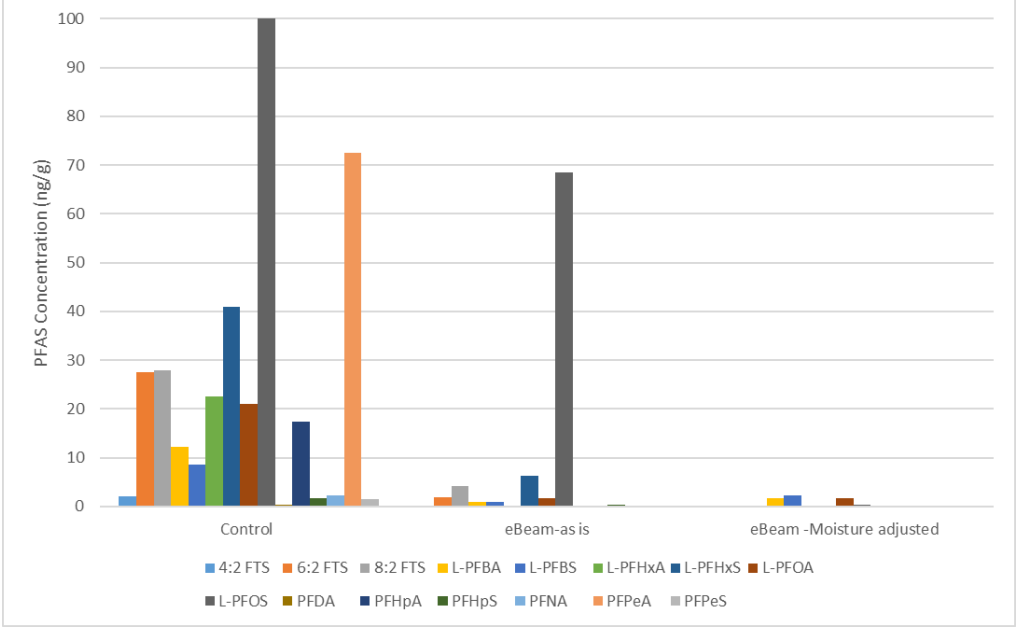


Fig. 12. Breakdown of targeted PFAS component concentrations during high dose (2000 kGy) eBeam treatment as a function of moisture content – (data not normalized to dry weight)

Overall, the results also support the original research hypothesis that eBeam is capable of achieving significant reduction of PFOA and PFOS in IDW soil samples. In IDW water samples, the PFOS and PFOA reduction was 87.91% and 53.57% respectively. In IDW soil samples the PFOS and PFOA reduction were 98.7 % and 99.9% respectively.

Economic Feasibility Analysis

The key treatment parameters in eBeam technology are energy (expressed in MeV-million electron volts), beam power (expressed in kw-kilowatts) and dose (kGy-expressed in kilograys). The energy dictates the penetration capability of the electrons, the power determines the processing throughput and the dose dictates the treatment effect. These three parameters are linked and therefore, increasing these parameters will increase capital and operating costs. Therefore, there is a premium on optimizing the dose and customizing the technology specifications so that the engineering designs are not over designed or under-designed.

Increasing eBeam dose will have a direct impact on costs especially energy costs. However, there is a strong rationale for increasing eBeam dose upwards of 500 kGy given that we observed significant breakdown of PFOS and PFOA only at higher dose. Figure 13 is a projection of the electrical costs if the eBeam dose is increased from 500 kGy up to 3000 kGy for treating IDW soils and water. These calculations illustrated that even if the dose required for PFOS and PFOA was in the range of 3000 kGy, the energy costs for delivering such doses in aqueous and soil matrices was approximately $0.80 and $1.20. per gallon treated.

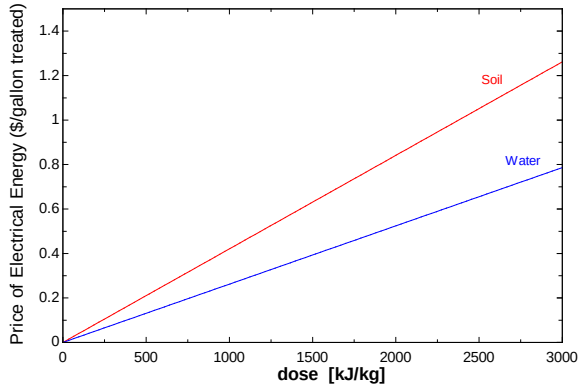


Fig.13.. Electrical energy costs as a function of absorbed eBeam dose (kGy expressed as kJ/kg)

Figure 14 is the cost (capital and operating costs) (per cubic meter of IDW soil) for fixed eBeam onsite PFAS remediation technology platform at a PFAS-contaminated site using a target treatment dose of 1500 kGy. (We are assuming that the dose can be optimized to 1500 kGy). The analysis suggests that it would cost approximately $295/m^3 of soil for breaking down 98% of PFOA and 99.99% of PFOS using a target dose of 1500 kGy. This cost calculation includes capital and operating costs such as capital

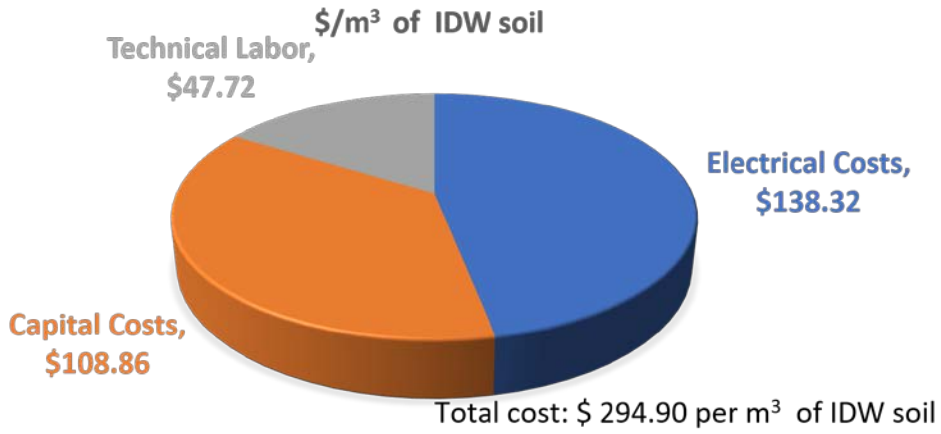


Fig 14. Breakdown of costs ($/m3) to treat PFAS-contaminated IDW soils using a fixed onsite eBeam technology platform at 1500 kGy

costs over project duration, electricity and other utility (e.g. water) costs, operating costs, and technical personnel. This analysis assumes a 560-kW beam at a cost of $7 M (based on consultation with a leading eBeam technology provider). Ancillary systems (e.g. material handling) were assumed to cost 10% of the beam cost, for a total capital cost of $7.7 M. This total was amortized over a useful life of 20 years, with monthly payments amounting to $51,000. Electricity and personnel costs are based on 80% uptime for the facility and 90% beam utilization, which results in a throughput of 20 m^3 per day. It should also be noted that if the dose is reduced to 1000 kGy the cost is reduced to $197 per m^3, and optimization to further reduce eBeam dose requirements will yield significant cost reductions especially if lower moisture IDW materials are being remediated. The technical personnel costs are itemized as shown in Table 5.

Technical Labor	hr./day	$/hr.	$/day
Engineers - accelerator specialist	19.2	25	480.00
Maintenance	4.8	13	62.40
Product Handler	19.2	10	192.00
Total Personnel			734.40

Table 5. Estimated technical labor costs for onsite fixed eBeam technology platform

A sensitivity analysis was also performed to identify the effects of changing dose, beam power, and uptime for the facility. The results are shown in Figure 15. This analysis highlights the impact of optimizing eBeam dose (kGy) and using an eBeam accelerator that can produce the highest beam power (kW). Just optimizing the dose from 1500 kGy to 1200 kGy results in a 20% cost savings. Similarly, increased uptime and higher beam power also reduces treatability costs.

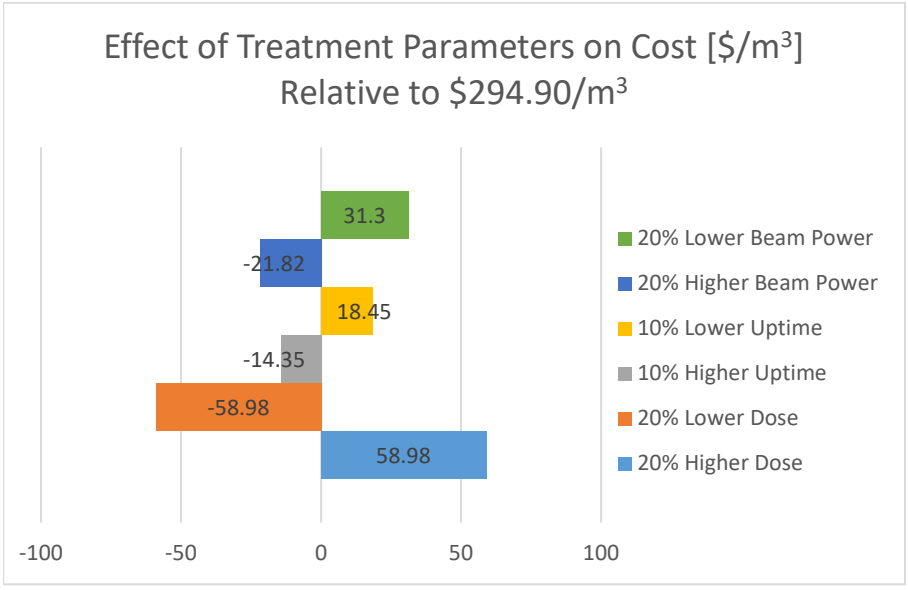


Fig 15. Sensitivity analysis to identify effects of optimizing treatment parameters on treatability costs (relative to $ 294.90/m^3)

Conclusions and Implications for Future Research

Overall, these laboratory experiments support our original research hypothesis that high energy eBeam technology has potential as a suitable remediation technology for PFAS-contaminated soils and groundwater samples. To the best of our knowledge, there is no technology (other than perhaps, incineration) that is effective against PFOS-contaminated soils. Therefore, this research is the first report using actual field derived IDW samples showing that high energy eBeam technology can reduce PFOS by 99.99% and PFOA concentration by 98.7% economically (compared to incineration). In IDW water, however, the degradation is much more reduced. It must be highlighted that other than increasing the dose, the technology for PFAS remediation has not been optimized. Therefore, it is plausible that with further optimization, PFOA and PFOS remediation in PFAS-contaminated groundwater can be significantly improved.

Our primary focus in this proof-of-concept research project was to demonstrate the treatment efficacy of the technology to degrade PFOS in soil and water under laboratory conditions and also characterize the effectiveness of the technology at degrading a mixture of PFAS in actual IDW samples. We have, in our opinion, met the project objectives and achieved significant success on both fronts. We have shown that eBeam technology can degrade PFOS and PFOA by 99.9% and 98.7% respectively in actual field obtained soils from Wurtsmith AFB, Michigan. In addition to performing the technical feasibility studies we also performed a preliminary economic feasibility analysis. This analysis highlighted the importance of optimizing the dose in reducing the treatment costs from the current $ 295/m^3. Investigating optimization strategies including eBeam treatment under pressure, addition of $Ti0_2$, calcium, and $KMnO_2$ are worthy of investigations since it can yield major dividends. There is still a need to determine the specific influence of presence of co-contaminants such as solvents, petroleum hydrocarbons and other PFASs on the PFAS remediation.

There is a need to design, fabricate and utilize continuous flow reactors (for groundwater) and a movable conveyance system/platform to demonstrate eBeam mediated degradation of PFOS and PFOA under quasi-realistic conditions. Laboratory experiments using a continuous eBeam test platform will yield high value information on the scaling up of the technology for field testing.

There is a need to develop a mechanistic kinetic model to describe PFOA/PFOS breakdown in PFAS-contaminated groundwater and soils. The modeling data has to be validated using remediation data from multiple PFAS contaminated soils and groundwater.

In order to field-test eBeam technology, there is a critical need to conceptualize an eBeam technology centered treatment train and perform detailed *in silico* technical and economic feasibility analysis. Using *in silico* tools, a fixed onsite eBeam technology platform for *ex situ* remediation of PFAS contaminated soil and groundwater at the Department of Defense sites could be designed. These modeling studies should be closely followed up with developing engineering designs for IDW groundwater and soil handling conveyance systems. This model should generally consist of three aspects. 1) system components processing and instrumentation diagram, including all relevant components. 2) an illustrative diagram, with accurate component sizing and spatial relations, 3) an engineering process model. This should include the heuristic rate equations from the mechanistic model as well the thermodynamic mass and energy balances, component-scaling laws, heat transfer and waste heat flows. This is necessary for throughput calculations and electron

beam remediation system ancillary component (pipe, pumps, heat exchangers, power systems) sizing and selection. Figure 16 is a preliminary 3D sketch of an approach that we are proposing for designing a fixed onsite 10MeV, 560 kW eBeam facility for remediating hydrocarbon - contaminated soils. We plan to explore similar approaches for PFAS-remediation. One of the concepts is to use onsite soil for shielding. Our approach is to use a similar low-cost approach for shielding purposes in the PFAS-remediation site. Such approaches or models are useful for planning component placement and equipment integration.

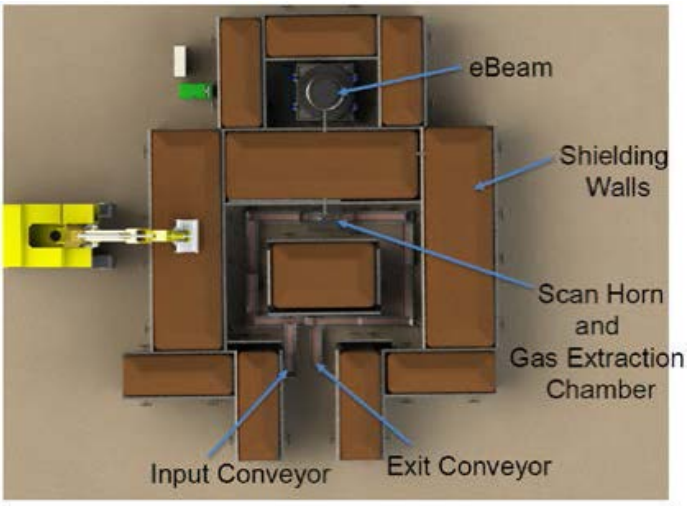


Fig. 16. Example rendering of a fixed eBeam platform for ex situ remediation of hydrocarbon-contaminated soils

The conceptualization and *in silico* modeling of the treatment train has to occur in close collaboration with environmental engineering consulting companies that have deep expertise in PFAS contamination and possible remediation approaches as well as leading *commercial* eBeam technology providers who have the capability to engage develop workable deployable technology. Our project team has included Arcadis, US. Inc (a leading international consulting firm with deep PFAS expertise) as well as Mevex Corp and IBA Industrial- the leading two commercial eBeam technology providers.

The next steps of our research progression is as follows

1. Design, fabricate, and install a linear accelerator and related materials handling system for a small-scale demonstration treatment platform for the batch treatment of IDW material at the existing eBeam facility located at Texas A&M University
2. Conduct optimization trials to identify treatment parameters to reduce the minimum eBeam dose necessary to remediate PFOS and PFOA to below EPA's Risk-Based Screening Level (RSL) of 70 ng/L (combined or individually) for aqueous samples and 130 µg/kg for soil samples
3. Computer-aided design and cost estimation for a fixed eBeam technology facility customized for aqueous and solids IDW treatment of PFAS compounds

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Appendices

Comparison of TAMU lab and SGS-AXYS for PFOA and PFOS Analysis