Report

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PFAS Soil Treatment Processes - A Review of Operating Ranges and Constraints

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PFAS Soil Treatment Processes - A Review of Operating Ranges and Constraints

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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are a broad class of man-made chemicals, exceeding several thousands, which have been widely used in industrial and consumer applications since the 1940's. Increasing public and regulatory concerns regarding PFAS in recent years have been driven by their mobility, persistence and, for some PFAS, bioaccumulation and toxicity, particularly in relation to human exposure via food and drinking water.

PFAS are also components in certain firefighting foams used, at least historically, at industrial and municipal facilities (including Concawe member assets) for flammable liquid fire suppression and firefighting training. Such use and associated releases may cause soil and groundwater impacts that require risk assessment and management action as well as generate other impacted materials and wastes, such as concrete.

The unique and diverse properties of PFAS represent complexity and challenges for traditional soil remediation technologies with the need to identify robust, cost effective and sustainable options which are acceptable to all stakeholders.

A total of 13 treatment technologies have been systematically evaluated in this report. These include destructive, non-destructive and pathway management approaches and for each treatment technology, technical, operational and commercial factors as well current knowledge gaps have been taken into consideration. The evaluation was informed by a literature review of published scientific research and other documents as well as a vendor liaison process incorporating current implementation experience and results.

Field Deployed Technologies	Innovative Technologies
Destructive Approaches High Temperature Incineration Cement Kiln Incineration Ex-situ Thermal Desorption Smouldering Combustion	**Destructive Approaches** Ball Milling High Energy Electron Beam Phytoremediation Biodegradation
Non-Destructive Approaches Ex-situ Soil Washing Stabilisation & Solidification	**Non-Destructive Approaches** In-situ Soil Flushing
Pathway Management Approaches Landfilling On Site Engineered Containment	

The Evaluation Criteria were determined to systematically capture key technical, operational, commercial and sustainability factors which are important to consider when undertaking PFAS soil treatment options appraisal. In addition, the criteria also aim to enable evaluation of technologies' suitability for the treatment scenarios, material types, treatment goals and key PFAS properties, which all may represent opportunities and/or constraints.

This report details the findings of this evaluation and aims consolidate current global practice to increase understanding and support Concawe member companies and others to identify effective and resource-efficient soil treatment technologies for PFAS.

This report was completed in December 2023 and represents the understanding and information identified and available over the preceding period of work.

KEYWORDS

PFAS (per- and polyfluoroalkyl substances), soil, waste, treatment technologies, innovative, firefighting foam, remediation, comparative evaluation, destruction, incineration, cement kilns, thermal desorption, smouldering combustion, soil washing, stabilisation, solidification, encapsulation, landfilling, containment.

INTERNET

This report is available as an Adobe pdf file on the Concawe website (www.concawe.eu).

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SUMMARY

Section 1: Background

Per- and polyfluoroalkyl substances (PFAS) are a broad class of man-made chemicals, exceeding several thousands, which have been widely used in industrial and consumer applications since the 1940's. Increasing public and regulatory concerns regarding PFAS in recent years have been driven by their mobility, persistence and, for some PFAS, bioaccumulation and toxicity, particularly in relation to human exposure via food and drinking water. PFAS are also components in certain firefighting foams used, at least historically, at industrial and municipal facilities (including Concawe member assets). Such use and associated releases may cause soil and groundwater impacts that require risk assessment and management action.

The unique and diverse properties of PFAS represent complexity and challenges for traditional soil remediation technologies with the need to identify robust, cost effective and sustainable options which are acceptable to all stakeholders.

The overall project aim is to produce guidance and summarise performance data based on literature review that can be used to identify effective and resource-efficient soil treatment technologies for PFAS. The specific project objectives involved the review of commercially available and innovative treatment technologies and evaluate their operating range and constraints across defined evaluation criteria reflecting key scenarios, material types and factors affecting treatment performance.

Section 2: Data Review

Arcadis have developed and maintain a significant literature database of PFAS related references which was updated in a phased manner to select technologies for assessment and support the detailed evaluation. Alongside the literature review, a vendor liaison process was undertaken in order to capture information from commercial delivery of the available treatment technologies selected, particularly as they relate to operational and commercial factors.

Section 3: PFAS Overview

The report provides an overview of PFAS, their relevant uses and properties, and summarises the key factors relating to PFAS and their interactions with soil that may affect the suitability, performance, and costs of PFAS soil treatment technologies. PFAS regulatory thresholds in soil, waste and ambient concentrations were described as well as analytical options.

Section 4: Approach to Evaluation

A total of 13 treatment technologies (shown in the Table 1 below) have been systematically evaluated in this report including destructive, non-destructive and pathway management approaches considering technical, operational and commercial factors as well as identify current knowledge gaps. Relevant treatment scenarios, treatment trains and material types and treatment goals were also discussed and considered during the review.

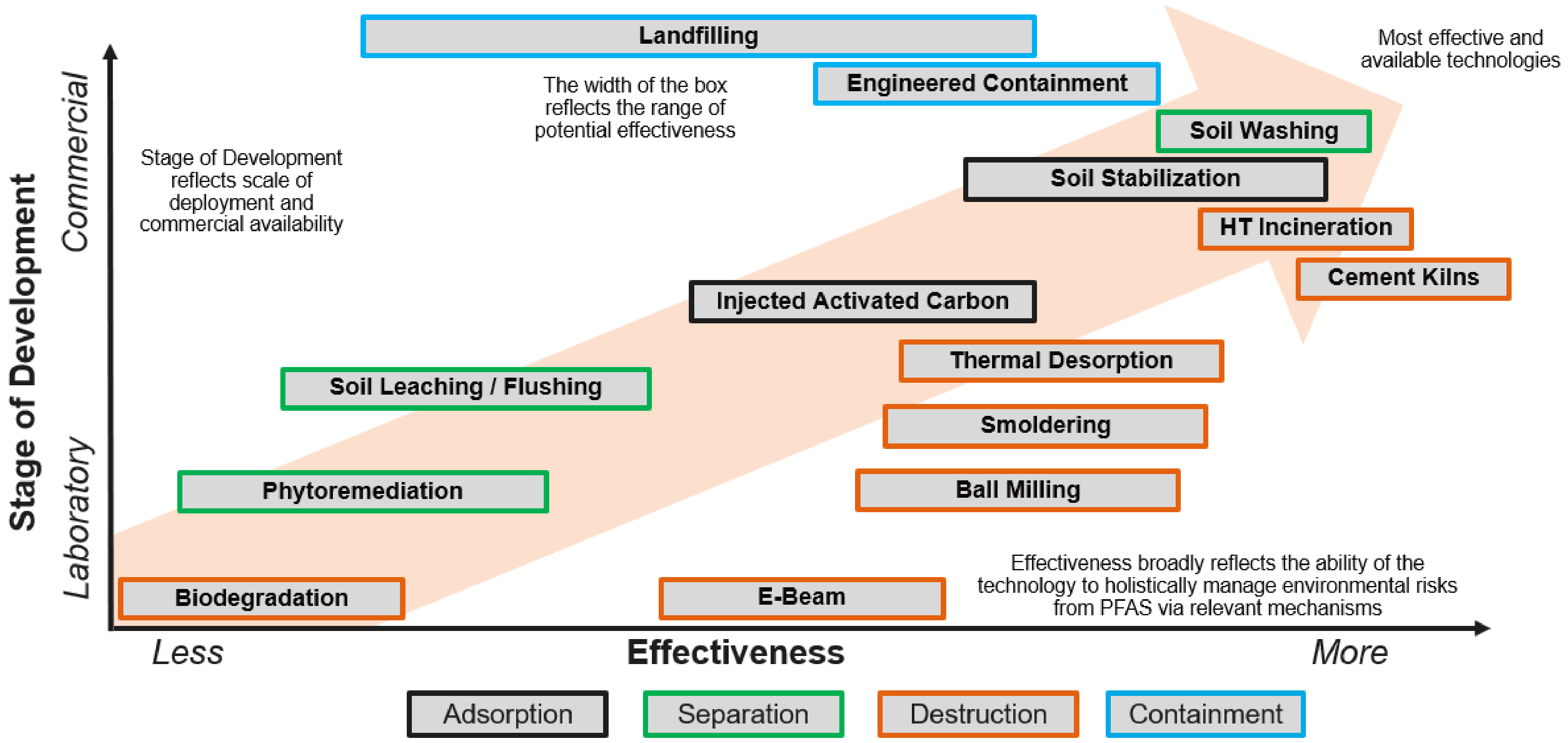
Table 1 Selected PFAS Soil Treatment Technologies

Field Deployed Technologies	Innovative Technologies
Destructive Approaches High Temperature Incineration Cement Kiln Incineration Ex-situ Thermal Desorption Smouldering Combustion	**Destructive Approaches** Ball Milling High Energy Electron Beam Phytoremediation Biodegradation
Non-Destructive Approaches Ex-situ Soil Washing Stabilisation & Solidification	**Non-Destructive Approaches** In-situ Soil Flushing
Pathway Management Approaches Landfilling On Site Engineered Containment	

Section 5 to 7

The findings of the technology evaluation were detailed in Section 5 and 6 and summarised in Section 7. The graphic below (Figure 1) was developed to compare potential effectiveness with commercial development and availability.

Figure 1 PFAS Treatment Technologies for Soil evaluated in terms of their likely effectiveness and the stage of development



‘Look Up’ tables summarising the findings of the technology evaluation using a qualitative traffic light system were developed as shown below in Table 2 and Table 3.

Table 2 Field Deployed PFAS Soil Treatment Technology Summary Look Up Table with Colour Coding Guidance in Figure 2.

Field Deployed Treatment Technology	Suitability to Treatment Scenarios	Treatment Efficacy Versus Treatment Goals	Treatment Efficacy for Different PFAS[1]	Suitability to Soil Properties	Suitability to co-contamination	Potential Impact on Site Operations	Requirement for Ongoing Management	Technology Development / Commercial Availability	Cost in European Market (EUR/m3)	Durability & Residual Liability	Sustainability - Energy & Chemical Usage, Stakeholder[2]
Destructive											
High Temperature Incineration	Low volume / high concentration	Likely to achieve low thresholds	Effective across PFAS class	Significant pre-treatment likely required	Little effect from organics or inorganics	Off-site excavation / backfill only	Minimal	Established but limited availability & capacity	450- 2,000	Good assuming emissions treatment	Highly energy intensive with soil transport
Cement Kiln Incineration	Low volume / high concentration	Likely to achieve low thresholds	Effective across PFAS class	Significant pre-treatment likely required	Cement quality sensitive to co-contamination	Off-site excavation / backfill only	Minimal	Limited availability & capacity [3]	100 - 1,000	Good assuming emissions treatment	Highly energy intensive with soil transport
Thermal Desorption	On-site, range of soils	Achieve low thresholds if effective heating	Effective across PFAS class	Disaggregation for cohesive soils	Little effect from organics or inorganics	On-site application requires space & power	Minimal	Established but not for PFAS. Generally available	Incineration > thermal desorption > non-destructive	Good assuming emissions treatment	Highly energy intensive. On-site or off-site
Smouldering Combustion	On-site, range of soils	Achieve low thresholds if effective heating	Effective across PFAS class	Disaggregation / amendment cohesive soils	Organic co-contamination beneficial as fuel	On-site application requires space	Minimal	No full scale, available via limited vendors	Incineration > smouldering > non-destructive	Good assuming emissions treatment	Requires surrogate fuel
Non-Destructive											
Soil Washing	Wide range of scenarios	High % reduction maybe not most stringent thresholds	Broadly effective across PFAS class	Less suited to cohesive soils and concrete	Generally manageable, may increase cost /complexity	On-site application requires space	Minimal following validation of any reused material	Most track record for PFAS. Generally available	25-160	Good - need suitable material reuse & fines management	Lower energy inputs. Can reuse sands & gravels
Stabilisation / Solidification	Wide range of scenarios incl. waste pre-treatment	High % leachate reduction maybe not most stringent thresholds	Less effective immobilisation of short chain PFAS	Suitable to most soil types and concrete	May require pre-treatment, gross organic impacts challenging	Long-term management of stabilised soil	May require long-term monitoring	Several full-scale projects. Widely available	35-113 (Reagent dependant)	Increasing evidence of durability. Liability held.	Lower energy inputs. Can reuse materials
Pathway Management											
Landfilling	Wide range of scenarios	Rapid removal of source provided delineated	Effective across PFAS class	Suitable to most soil types and wastes	Generally manageable, may increase cost	Off-site excavation / backfill only	Minimal	Availability is very country specific	Country specific	Option to -pre-treat. Needs leachate management.	Transfer not treatment. Transport & resource cost.
Engineered Containment	Long-term access	Rapid isolation of source provided delineated	Effective across PFAS class	Suitable to most soil types and some wastes	Generally manageable, may increase cost /complexity	Long-term management / space for contained soil	Long-term monitoring and maintenance	Widely available	Life - cycle costs very high but spread over time	Long-term management and liability for contained soil	Less energy / reagents but containment not treatment.

[1] It is not possible to capture all the detail and complexity of PFAS treatment suitability within these summary tables and readers are encouraged to refer to specific report sections for further information. For example, treatment efficacy categories broadly reflect reported treatment performance alongside typical treatment goals and criteria but may not reflect all situations.

[2] Sustainability considerations within the scope of this report (see Section 4.4) is limited compared to e.g. US-EPA Green and Sustainable Remediation (GSR) guidance.

[3] Cement Kiln is not considered as established for PFAS destruction in the EU. In comparison to HTI, there were limited reported examples of kilns used for PFAS compared to widespread use of HTI.

Table 3 Innovative PFAS Soil Treatment Technology Summary Look Up Table with Colour Coding Guidance in Figure 2

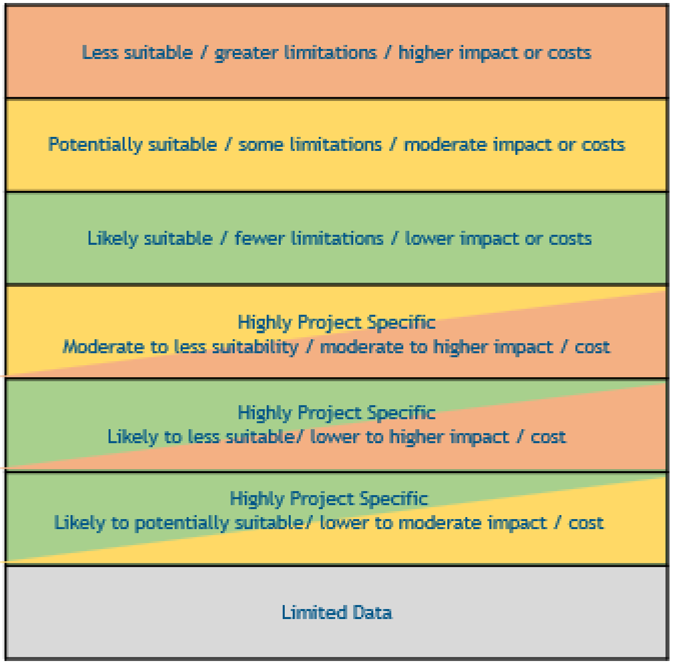
Innovative Treatment Technology	Suitability to Treatment Scenarios	Treatment Efficacy Versus Treatment Goals	Treatment Efficacy for Different PFAS[1]	Suitability to Soil Properties	Suitability to co-contamination	Potential Impact on Site Operations	Requirement for Ongoing Management	Technology Development / Commercial Availability	Cost in European Market (EUR/m3)	Durability & Residual Liability	Sustainability - Energy & Chemical Usage, Stakeholder[2]
Destructive											
Ball Milling / Mechano-chemical	Low volume / high concentration	Potential to achieve low thresholds but variable results	Likely effective for wide range of individual PFAS. Limited data on byproducts	Significant pre-treatment likely required.	Limited data	Modular on-site application requires some space	Minimal. Treated soil likely requires reconditioning.	Field scale pilots completed. Units commercially available	69 - 630	Good assuming complete destruction achieved	Energy intensive with reagents potentially required. On site application limits transport.
High Energy Electron Beam	Low volume / high concentration	Limited data. Data suggests 78-99.5% destruction	No assessment of fluoride or byproducts to date	Significant pre-treatment likely required	Limited data. Appears suitable for hydrocarbon co-contamination	Containerised on-site application requires some space	Minimal. Treated soil likely requires reconditioning.	Laboratory assessment only to date	~357	Good assuming complete destruction achieved	Limited data.
Bio degradation	Theoretically high volume / low concentration. Low risk scenarios.	Slow kinetics and incomplete degradation observed to date	Limited assessment of precursors or byproducts. Assumed low efficacy.	Limited data	Limited data. Hydrocarbons may affect degradation products.	If technology developed to be effective, likely low impact	Long timeframes with associated monitoring	Laboratory assessment only to date	No data available	Dependant of performance. Liability held for long periods until complete	If advanced to be effective, likely sustainable and low impact
Non-Destructive											
Phyto remediation	Shallow contamination, low risk scenarios	Species / habitat dependant. Slow uptake. Not suited to stringent goals	More suited to shorter chain PFAS.	Soil / habitat must be suitable for desired plant species	Limited data. Potential biodegradation of organic co-contamination	On-site application requires large areas and long timeframes. Limits end use	Long timeframes with associated monitoring and harvesting of plants	Laboratory and limited field application only to date	No data available	Dependant of performance. Liability held for long periods until complete	Requires treatment of harvested plants which likely involves incineration.
In Situ Flushing	Wide range of scenarios, in-situ or ex-situ	Likely not suited to stringent goals. Reagents may enhance efficacy	Long chain and certain charged PFAS may be less well leached	Limited by soil permeability and heterogeneity.	Limited data. Soluble co-contamination likely also amenable.	Requires leachate containment system. Ex-situ requires space	Minimal	Laboratory and limited field application only to date	Estimated upper range of typical pump and treat cost	Dependant on level of reductions achieved	Lower energy inputs. Some minor reagent use.

[1] It is not possible to capture all the detail and complexity of PFAS treatment suitability within these summary tables and readers are encouraged to refer to specific report sections for further information. For example, treatment efficacy categories broadly reflect reported treatment performance alongside typical treatment goals and criteria but may not reflect all situations.

[2] Sustainability considerations within the scope of this study is described in Section 4.4 and are done in a limited fashion compared to e.g. standards on Greener Cleanups (US EPA, 2023a; ASTM, 2016)

A legend to support the look up tables is shown below in Figure 2.

Figure 2 Legend for Table 1 and Table 2



🟧 Less suitable / greater limitations / higher impact or costs

🟨 Potentially suitable / some limitations / moderate impact or costs

🟩 Likely suitable / fewer limitations / lower impact or costs

🟨🟧 Highly Project Specific
Moderate to less suitability / moderate to higher impact / cost

🟩🟧 Highly Project Specific
Likely to less suitable/ lower to higher impact / cost

🟩🟨 Highly Project Specific
Likely to potentially suitable/ lower to moderate impact / cost

⬜ Limited Data

1. INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a broad group exceeding several thousand man-made chemicals, widely used in industrial and consumer applications since the 1950's including certain formulations of fire- fighting foams. PFAS are considered as contaminants of emerging concern as they are a threat to human health and the environment.

Many PFAS are very mobile and very persistent in the environment, with some PFAS also found to be bioaccumulative and toxic to humans and wildlife. They are globally widespread in the environment and in humans. Perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are the two most well-studied and commonly regulated members of the PFAS family of compounds but an expanding range of PFAS are now regulated in many locations.

Certain PFAS mixtures are components in certain Aqueous Film Forming Foams (AFFFs), Fluoroprotein (FP) and Film Forming Fluoroprotein (FFFP) foams used at industrial and municipal facilities (including Concawe member assets) for flammable liquid (Class B) fire suppression and firefighting training. As a result, release of PFAS to the environment at industrial sites may occur as a consequence of accidental spillages, or more commonly, during legitimate use of AFFF-containing firefighting foams. These uses / releases may cause soil and groundwater impacts that require risk assessment and management action. In addition, other materials exposed to PFAS containing firefighting foams, such as concrete, may become contaminated and require assessment, treatment and waste management.

PFAS are a challenging family of compounds to treat due to their unique and diverse properties, and the need for high treatment efficiency to meet low regulatory concentration limits. Treatment of soil containing PFAS may be required as part of environmental management at Concawe member assets and other similar ones. Therefore, this report has been completed in order to provide a better understanding of the capabilities and operating range of commercially available treatment technologies, as well as more innovative technologies, considering the different material types and scenarios under which treatment may be required.

A total of 13 treatment technologies have been systematically evaluated in this report including destructive, non-destructive and pathway management approaches considering technical, operational and commercial factors as well as identify current knowledge gaps. The evaluation was informed by a literature review of published scientific research and other documents as well as a vendor liaison process incorporating current implementation experience and results. It is intended to allow for an informed selection of appropriate technologies based on scientific and objective data but should not be considered as a recommendation for any of the presented technologies.

It is important to note that soil treatment technologies for PFAS are the subject of considerable research and innovation and while this report aims to provide a robust summary of the state of practice globally at the time of writing, this practice is likely to change as technologies evolve and more performance data becomes available. Commercial availability and regulatory acceptance are also likely to vary across different jurisdictions and over time. This report was completed in December 2023 and represents the understanding and information identified and available over the period of work.

1.1. AIMS AND OBJECTIVES

While Concawe has previously collated information and performance data regarding water treatment options for PFAS (Concawe, 2020), the remediation of soil / ground is a topic with less consolidated information.

Therefore, the overall project aim is to produce guidance and performance data that can be used by their member companies and others to identify effective and resource-efficient soil treatment technologies for PFAS, particularly as they relate to firefighting foam usage.

The specific project objectives are summarised below:

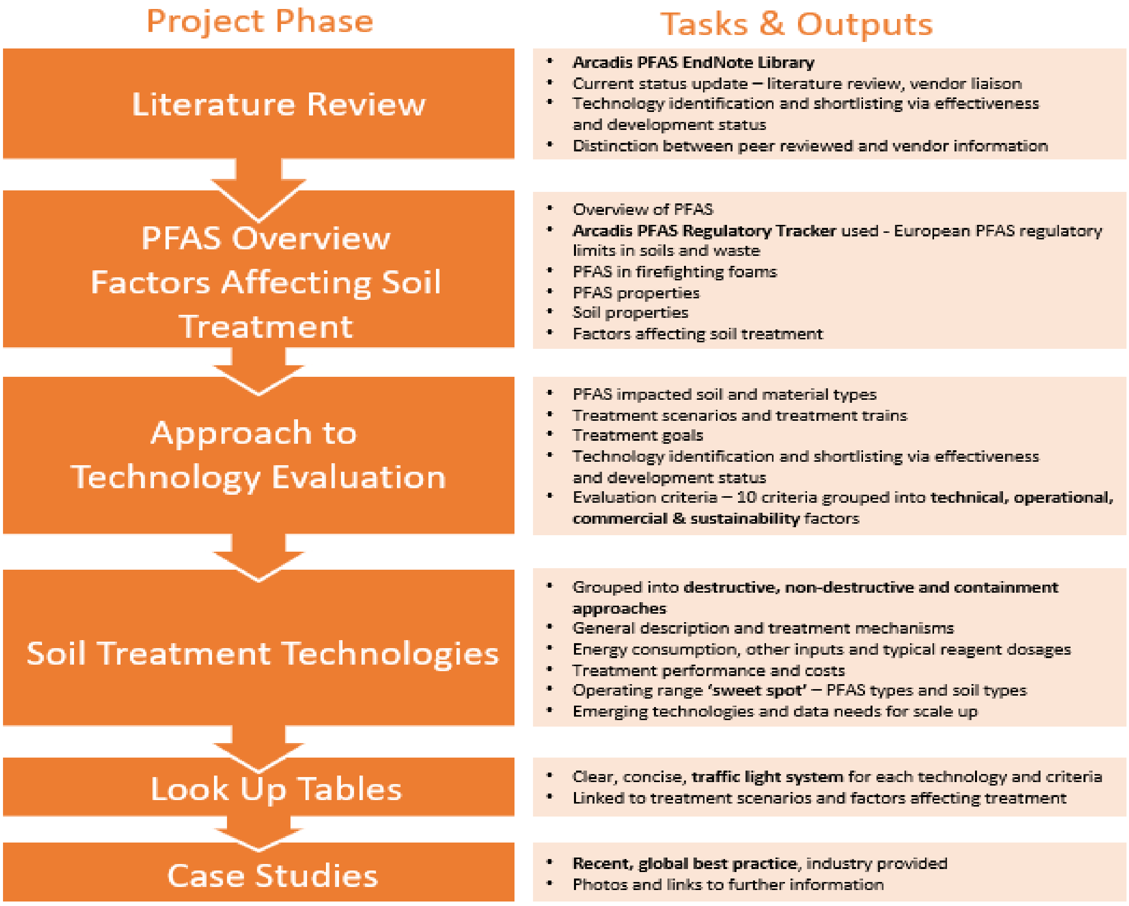
- Review available treatment technologies and their operating range and constraints, including:
    - Treatment mechanisms and relevant scenario / treatment train:
    - Data on which PFAS are removed and to what extent, including contaminant mass reductions;
    - Sensitivity to soil / material type;
    - Performance in the presence of co-contaminants;
    - Energy consumption, reagents dosages and sustainability aspects;
    - Costs;
    - Knowledge gaps and uncertainties.
- Summary of innovative technologies and data gaps;
- Summary of regulatory limits and how these relate to treatment objectives;
- Preparation of a PFAS soil treatment look up table.

1.2. OVERVIEW OF METHODOLOGY

In order to address project aims and objectives, a methodology was developed built on Arcadis’ PFAS remediation research, optioneering and implementation experience and was delivered by a global team of PFAS experts from the UK, Europe, Australia and the U.S. The project methodology, phases and tasks are shown in Figure 3.

The approach and output were broadly based on that used within the ‘Review of water treatment systems for PFAS removal’ Concawe (2020) and ‘Field-based analytical technologies for petroleum hydrocarbons determination in soils’ (Concawe, 2022) but were adapted to fit the nature of this study as outlined below.

Figure 3 Overview of Project Methodology, Phases and Tasks



Project Phase	Tasks & Outputs
Literature Review	**Arcadis PFAS EndNote Library** Current status update – literature review, vendor liaison Technology identification and shortlisting via effectiveness and development status Distinction between peer reviewed and vendor information
PFAS Overview Factors Affecting Soil Treatment	Overview of PFAS **Arcadis PFAS Regulatory Tracker** used - European PFAS regulatory limits in soils and waste PFAS in firefighting foams PFAS properties Soil properties Factors affecting soil treatment
Approach to Technology Evaluation	PFAS impacted soil and material types Treatment scenarios and treatment trains Treatment goals Technology identification and shortlisting via effectiveness and development status Evaluation criteria – 10 criteria grouped into **technical, operational, commercial & sustainability** factors
Soil Treatment Technologies	Grouped into **destructive, non-destructive and containment approaches** General description and treatment mechanisms Energy consumption, other inputs and typical reagent dosages Treatment performance and costs Operating range **'sweet spot'** – PFAS types and soil types Emerging technologies and data needs for scale up
Look Up Tables	Clear, concise, **traffic light system** for each technology and criteria Linked to treatment scenarios and factors affecting treatment
Case Studies	**Recent, global best practice**, industry provided Photos and links to further information

2. DATA REVIEW

2.1. LITERATURE REVIEW

Arcadis have developed and maintain a significant literature database of PFAS related references which is managed using the Endnote software (Clarivate, version 21, 2023). At the time of writing, Arcadis' PFAS database contained >4,600 papers. Endnote is a fully searchable reference management programme used for the organisation of scientific, industrial, commercial, and other relevant PFAS literature. Arcadis maintain the database globally including via Google Scholar alerts used to identify peer reviewed research of interest which is then obtained from the relevant organisation and uploaded to the database.

The process by which published, peer-reviewed research was identified and selected for review to support the project is detailed below.

2.1.1. Stage 1: Endnote Library Update

In addition to regular, global updates, a specific update of the Arcadis PFAS database was undertaken at the commencement of the project (April 2023) to ensure the most recent research on PFAS soil remediation technologies was included. This involved discussions and submissions from the Arcadis global PFAS network, suggestions from Concawe as well as a thorough internet-based searches for published papers.

The following search engines were used:

- www.scholar.google.com/
- www.sciencedirect.com/
- www.refseek.com
- www.worldcat.org
- www.base-search.net
- www.link.springer.com
- www.researchgate.net/
- www.semanticscholar.org/

The following terms were searched:

- soil remediation PFAS review
- thermal treatment PFAS soil
- biodegradation PFAS soil review
- destructive remediation PFAS soil
- non-destructive remediation PFAS soil
- stabilisation solidification soil PFAS review
- ex-situ soil washing PFAS review
- in-situ soil flushing PFAS
- ex-situ leaching PFAS soil
- PFAS soil cement kiln incineration
- electron beam PFAS soil
- ex-situ Smouldering PFAS soil

- ball milling PFAS soil
- pyrolysis PFAS soil

2.1.2. Stage 2: Identification of Review Papers

An individual Endnote reference contains numerous field records including author, publisher, journal, volume, date, paper title, paper abstract, and paper keyword. In order to identify papers relevant to the project as well as select specific PFAS soil remediation technologies for evaluation, the database was searched to identify PFAS remediation review papers for initial review.

The database was searched for references containing the key terms "remediation" or "treatment" and "review" within the search fields "title", "abstract", and "keywords". This search automatically created a 'Smart Group' within Endnote containing approximately 200 references that fitted the search criteria.

The references within the Smart Group were then reviewed by Arcadis with those judged not to be relevant excluded, which resulted in a final group of references to form the basis of an in-depth review. The following criteria in order of importance were used when deciding on the inclusion of a reference:

a. Reference not relevant to report subject matter (e.g., a review of groundwater treatment technologies for PFAS);
b. References where soil remediation is the main subject of the document were prioritised;
c. More recent references (post 2019) were prioritised, especially where papers overlap in topics; and
d. Consideration of journal "Impact Factor" with higher impact factor values preferred unless the journal is directly relevant to environmental remediation.

This process shortlisted key PFAS soil remediation review papers which were used to inform the selection of remediation technologies for evaluation, innovative technologies as well as identify other papers referenced for inclusion within the PFAS database.

2.1.3. Stage 3 - Endnote Library Further Update

The citations within these review paper references pertaining to the selected technologies were cross checked against Arcadis' database, and where these were missing, they were obtained and uploaded.

2.1.4. Stage 4 - Final Literature Reference Shortlisting and Selection

To identify and shortlist references specific to the selected technologies of interest the database was again searched using the same key fields as in Stage 1 with key terms varied to the relevant technology (e.g., "ball milling" and "mechanochemical" were both used for the same technology).

This again created a series of Smart Groups for each technology which were reviewed and refined down to the final most relevant references. Criteria used in the final refining stage were the same as those above with the additional criteria that papers reporting on pilot and/or full-scale applications of the technologies were also prioritised.

The peer-reviewed research papers and other source of information used to inform the project are referenced in section 7.

2.2. SELECTED PFAS SOIL TREATMENT TECHNOLOGIES

PFAS soil treatment technologies were divided into the following groups:

- Destructive
- Non-Destructive
- Pathway Management

Technologies were then further sub-divided into Field Deployed Technologies and Innovative Technologies based on their approximate Technology Readiness Level (TRL) as well as whether there are established / plausible treatment mechanisms, as follows:

- Field Deployed Technologies – deployed at field pilot and/or full scale, commercially available in multiple regions with established / plausible treatment mechanism(s). This category includes some technologies that may have only been applied in field scale pilots, but are established technologies for other compounds and available in the market;
- Innovative Technologies – deployed at bench scale and/or limited pilot scale, limited or no commercial availability but with plausible PFAS treatment mechanism(s)

As detailed in Section 4, Field Deployed Technologies were subject to detailed evaluation according to the established Evaluation Criteria while Innovative Technologies were reviewed with a focus on the identification of work to be done to close gaps for potential commercialisation.

2.2.1. Selected PFAS Soil Treatment Technologies

The selected PFAS soil treatment technologies included for review within this project are listed in Table 4.

Table 4 Selected PFAS Soil Treatment Technologies

Field Deployed Technologies	Innovative Technologies
Destructive Approaches High Temperature Incineration Cement Kiln Incineration Ex-situ Thermal Desorption Smouldering Combustion	**Destructive Approaches** Ball Milling High Energy Electron Beam Phytoremediation Biodegradation
Non-Destructive Approaches Ex-situ Soil Washing Stabilisation & Solidification	**Non-Destructive Approaches** In-situ Soil Flushing
Pathway Management Approaches Landfilling On Site Engineered Containment	

2.3. VENDOR LIAISON

Alongside the literature review, a vendor liaison process was undertaken in order to capture information from commercial delivery of the field deployed treatment technologies selected, particularly as they relate to operational and commercial factors.

Vendors of the field deployed treatment technologies (or associated treatment reagents / additives) were selected for inclusion within the project based on the initial review of literature, professional experience and liaison with Concawe members with a focus on vendors supplying the European market. The list of vendors who provided information to support the technology evaluation are listed below. Other vendors were contacted but did not provide information and are not listed.

- Züblin Umwelttechnik GmbH, Germany;
- Altola AG, Switzerland;
- REMONDIS Industrie Service GmbH & Co, Germany;
- Savron Inc, US;
- Cornelsen Ltd, UK;
- DEME Group, Belgium;
- Boskalis Environmental B.V, Netherlands;
- CDE Group, Inc, US;
- CETCO Europe Ltd, UK;
- RemBind Pty Ltd, Australia;
- Envirotreat Solution Ltd, UK;
- Evonik Operations GmbH, Austria.

The vendor liaison was undertaken in a systematic way via a questionnaire which was aligned to the Evaluation Criteria detailed in Section 4.4. The questionnaire provided drop down options, as well as an open response option, to standardise responses and thus facilitate comparison across technologies and vendors. Additional correspondence with vendors was undertaken to request clarifications and/or further details as appropriate.

Vendor responses included information from project case studies as well as technology research work and were reviewed to inform the technology evaluation, with the literature review also undertaken within the same format. The vendor responses include project and document references and distinction between peer-reviewed and project / vendor information is clearly stated.

3. PFAS OVERVIEW – FACTORS AFFECTING SOIL REMEDIATION

This section provides an overview of PFAS, their relevant uses and properties and summarises the key factors relating to PFAS and their interactions with soil that may affect the suitability, performance, and costs of PFAS soil treatment technologies. This is intended to enable gaining a better understanding of these factors which should then be incorporated into evaluation criteria of a technology.

3.1. OVERVIEW OF PFAS

Understanding PFAS chemistry is essential to fully evaluating treatment technologies and ensuring comprehensive, future-proofed solutions. This is becoming more and more relevant as regulations evolve to cover many more individual PFAS, and regulatory limits become increasingly lower. A good example of this is the recast to the EU Drinking Water Directive (EU 2020/2184) which came into force in 2021 and includes limits for total PFAS of 0.5 µg/L and the sum of 20 PFAS deemed of most concern of 0.1 µg/L.

There are a large number of individual PFAS analytes as well as types of PFAS uses and sources to the environment. The OECD state that at least 4,730 distinct PFAS containing at least three perfluorinated carbon atoms are known OECD (2018). The USEPA’s Chem View lists 852 unique PFAS (US EPA, 2023b), while PubChem lists approximately 7 million unique PFAS (E. L. Schymanski, 2023). Not all of these 7 million PFAS are likely in use (or registered to be used) as can be seen by taking the REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals EC 1907/2006) regulation as an example. As of September 2021, at least 531 PFAS had been registered under REACH in the EU (E. Rudin, 2023) and in 2019 the US Environmental Protection Agency (US EPA) listed 602 PFAS as possibly in active use (US EPA, 2019a). Understanding how many PFAS are relevant at a particular site is an important first step to reduce the vast PFAS universe.

There is no single, worldwide accepted definition of PFAS. In 2021 the OECD defined PFAS as “*fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e. with a few noted exceptions, any chemical with at least a perfluorinated methyl group* ($-CF_3$) *or a perfluorinated methylene group* ($–CF_2-$) *is a PFAS*” (Wang et al., 2021b). While this definition has gained traction and is now commonly used, it is noted that the UK REACH Regulatory Management Options Analysis (RMOA) recently adopted a narrower definition, excluding compounds with a single methylene (-CF2-) group (UKHSE, 2023). It is also noted that the OECD definition is broader than that used within previous Concawe reports (Pancras et al., 2016).

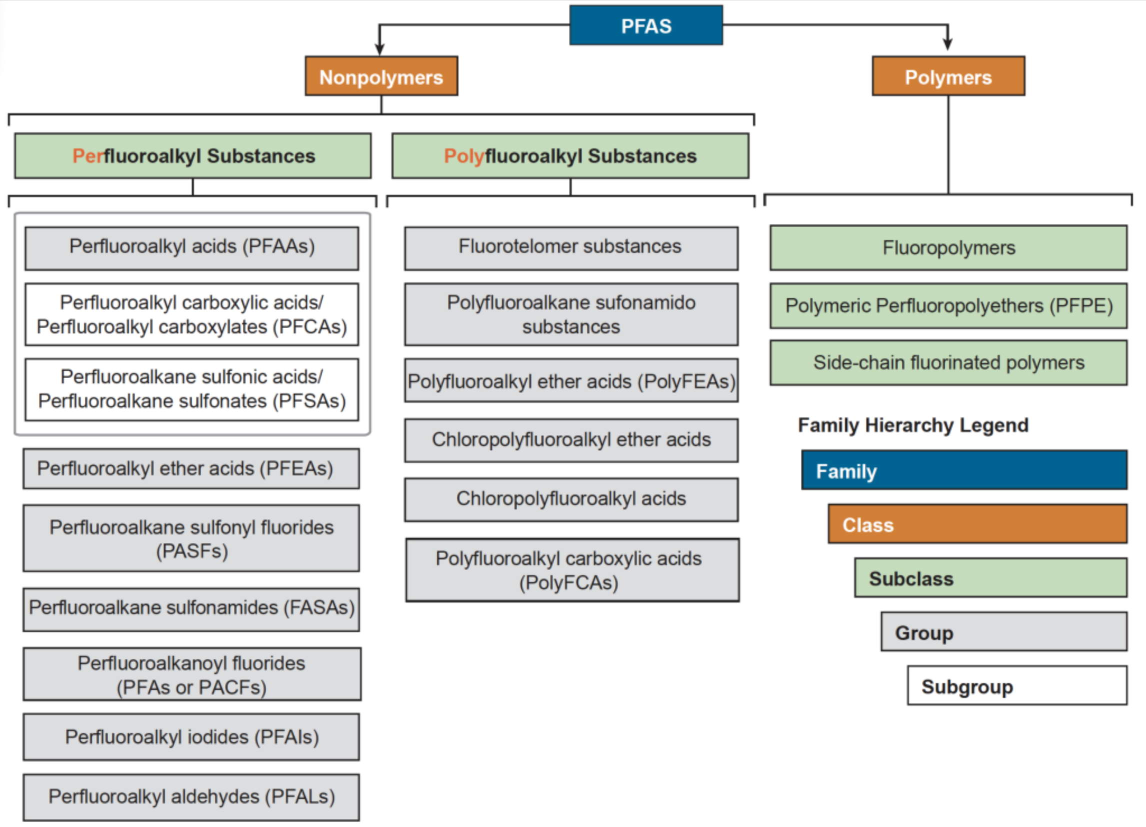
PFAS can be polymeric which include the groups fluoropolymers, perfluoropolyethers (PFPEs) and side-chain fluorinated polymers (SCFPs) (Buck, 2011). Figure 4 provides an overview of the groups of PFAS. The fluoropolymer group is dominated by polytetrafluoroethylene (PTFE), together with fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene (ETFE) and tetrafluoroethylene copolymers with perfluoroalkyl vinyl ethers (e.g., perfluoroalkoxypolymer, PFA) (Lohmann et al., 2020).

PFAS can also be non-polymeric and this covers the perfluoroalkyl substances and the polyfluoroalkyl substances (see Figure 4). Non-polymeric PFAS include perfluoroalkyl acids (PFAA), comprising perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs), and non-polymeric precursors derived from fluorotelomers and perfluoroalkane sulfonyl fluorides (PASFs) such as fluorotelomer alcohols (FTOHs) and perfluoroalkane sulfonyl amides/amidoethanols (FASAs/FASEs). A subset of PFAS can be volatile and there are studies that show humans can be exposed to FTOHs, perfluorooctane sulfonamides (FOSAs), perfluorooctane sulfonamidoethanols (FOSEs), and other precursors to perfluoroalkyl acids (PFAA) from consumer and industrial products readily available in people’s homes (Morales-McDevitt et al., 2021).

Within the non-polymeric PFAS, the individual PFAS themselves can contain different chain lengths and have different functional groups. The OECD has defined long-chain PFCAs are those with a carbon chain length of 8 and greater than 8 (≥ C_8) and long-chain PFSAs are those with a carbon chain length of 6 and greater than 6 (≥ C_6) ((OECD, 2023)). Conversely short-chain PFCAs are defined as those with a carbon chain length smaller than 8 (< C_8) and short-chain PFSAs as those with a carbon chain length smaller than 6 (< C_6). In addition, PFCAs containing ≤ 3 fully fluorinated carbon atoms and PFSA containing ≤ 2 fully fluorinated carbon atoms, are commonly termed ultrashort PFAS. These include compounds such as trifluoroacetic acid (TFA).

PFAS functional groups most commonly include carboxylates, sulfonates, phosphates and amines as well as more complicated derivatives of these groups. These functional groups, including dissociated and undissociated forms, govern many fate and transport properties of PFAS. The ionic state of a compound determines its electrical charge and its physical and chemical properties, which in turn will be an important part of controlling its fate and transport in the environment.

Figure 4 The PFAS Family Tree (unexpanded) by Interstate Technology and Regulatory Council (ITRC; 2023)



Many non-polymeric PFAS may be present as mixtures of linear and branched isomers depending on the manufacturing process that was used (commonly electrochemical fluorination and telomerization) (Buck, 2011). The structural differences between linear and branched isomers are important because they affect how the compounds behave in the environment and may provide an indicator of their source (Schulz et al., 2020). A linear isomer is composed of carbon atoms bonded to only one or two carbons which form a straight carbon backbone. There can be only one linear isomer in a C_n homologue (where n is the number of carbons in the chain) series. In a branched isomer, at least one carbon atom is bonded to more than two carbon atoms, which forms a branching of the carbon backbone. Due to their higher polarity, branched structures are more likely to be present in the aqueous phase compared to homologous linear PFAS, which are more likely to sorb to soil and sediments (Schulz et al., 2020).

Polyfluoroalkyl substances that degrade to create terminal PFAAs are referred to as "precursors." Terminal PFAAs are not known to degrade under typical environmental conditions. PFCAs are known to be formed as terminal degradation products of select precursor polyfluoroalkyl substances, such as fluorotelomer alcohols (FTOHs) (Kim et al., 2014, Butt et al., 2014, Buck, 2011). PFSAs can be formed as terminal degradation products of select precursor polyfluoroalkyl substances, such as FASEs (Buck, 2011). It is important to be aware that by only measuring concentrations of terminal end products, the PFAS burden at a site from precursors will be missed.

Since manufacture and use of PFAS began in the 1950s (Benskin et al., 2010), there have been several shifts in the PFAS produced as policy requirements and scientific knowledge advances. Long-chain PFCAs, PFSAs and their potential precursors have been replaced with their shorter-chain homologues or other types of (non)fluorinated chemicals (Ritter, 2010). Some alternative PFAS include, but are not limited to, FTOH, PBSF-based derivatives and per- and polyfluoroalkyl ethers (which include GenX and ADONA). Often these replacements have similar environmental properties as the substance they replaced, leading to what is known as "regrettable substitution". A case in point being the replacement of PFOA with GenX which is known to be as toxic and more mobile than PFOA and is now detected in many water bodies in Europe (Brandsma et al., 2018).

3.2. PFAS USE IN THE FUEL MANUFACTURING SECTOR

3.2.1. PFAS in Firefighting Foams

Fluorosurfactant PFAS comprise important components of Class B firefighting foams designed for use on flammable liquids and developed since the 1960's. The most common Class B foams used in the fuel manufacturing sector are aqueous film forming foam (AFFF), alcohol resistant aqueous film forming foam (AR-AFFF), film forming fluoroprotein foams (FFFP), alcohol resistant film forming fluoroprotein foams (AR-FFFP), fluoroprotein foams (FP), and alcohol resistant fluoroprotein foams (AR-FP) all of which can contain PFAS. The role of the PFAS was to create a combustion resistant, filming, and foaming layer on top of the flammable liquid, thus rapidly suppressing the fire and preventing burn back.

The first AFFFs were PFOS-based and created in the 1960s by 3M who was the sole supplier until 1973. From 1973 onward, fluorotelomer-based AFFF manufacturers created AFFFs that met the U.S. Military Specification criteria. Within the U.S. AFFF market, the military uses 75%, while municipal airports, refineries, fuel tank farms, and other industries use the remaining 25% (Field, 2017).

There is considerable variation not just in individual PFAS but whole PFAS classes present within Class B foams. Such foams contain a mixture of different PFAS types and chain lengths with variation depending on manufacturer, and date of production. Further, because of the proprietary nature of many formulations, the safety data sheet is unlikely to contain information on individual PFAS components for a given foam concentrate. In addition, some AFFF foams may be suitable for mixing between manufacturers and batches so depending on organisations purchasing and operational strategies a range of different concentrates may be present within a single fire suppression system.

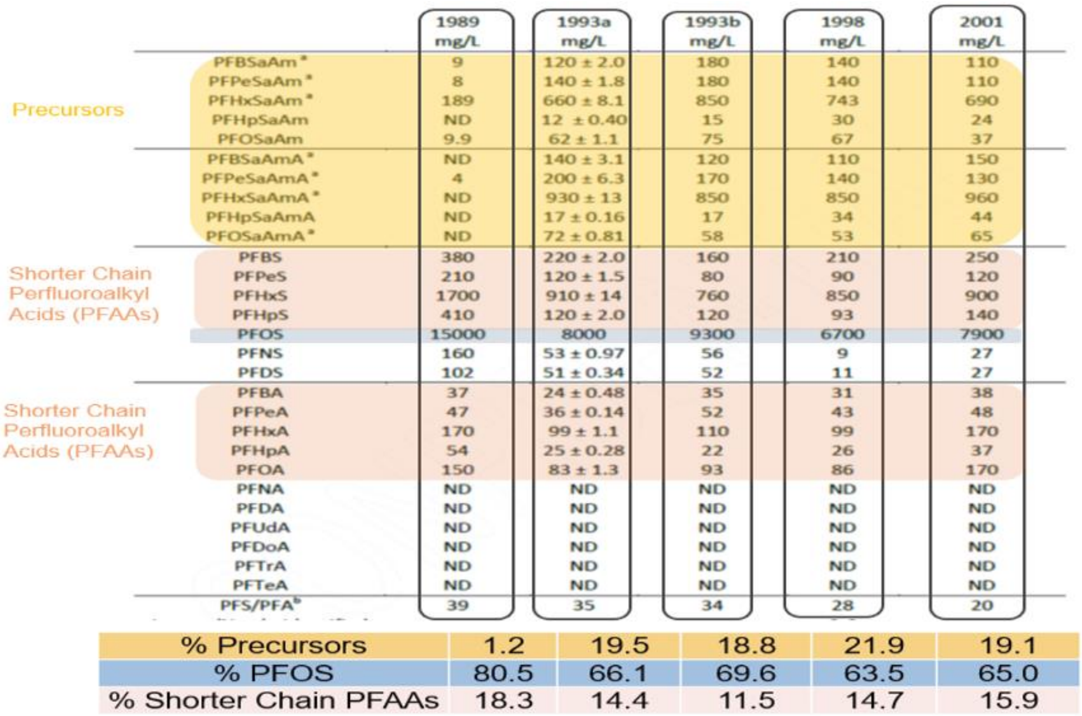
Academic analysis of a range of firefighting foams has shown the potential for hundreds of different PFAS to be present. (Barzen-Hanson et al., 2017, Garcia et al., 2019, Mejia-Avendano et al., 2017, Baduel et al., 2017). Testing of samples of archived Class B foam concentrates has shown considerable variation in the PFAS present (Backe et al., 2013), see Figure 5.

The following broad observations are noted:

- Precursors have been noted to be present ranging from 1 to 100% of the PFAS mass. Common precursors include perfluoroalkyl sulphonamido amides, and perfluoroalkyl sulphonamide amino carboxylates within foam produced by the electrochemical fluorination process as well as thioamido sulphonate fluorotelomers (FtTAoS), sulphonamido amine, sulphonamido betaines fluorotelomers (FtSaB), and betaine fluorotelomers (FtB).(Backe et al., 2013);
- Foams containing PFAS produced by the electrochemical fluorination process are dominated by PFAAs, predominantly PFSAs and especially PFOS, but also PFHxS and other shorter chain PFSAs. These foams have also been noted to contain PFCAs particularly earlier formulations (Bell, 2019). Production of electrochemical fluorination (ECF) foams was phased out in 2003, with PFOS banned for use in foam in Europe in 2011, but may still be present in fire suppression systems via mixing or cross contamination of foams;
- Foams produced by fluorotelomerisation are dominated by precursors, with lesser concentrations of PFCAs. Once released to the environment these precursors will biotransform to form PFCAs potentially including PFOA (Harding-Marjanovic et al., 2015, Yi et al., 2018, Shaw et al., 2019). Fluorotelomer foams do usually not contain PFOS or other PFSA or precursors which can biotransform to PFOS (Backe et al., 2013);
- Many early fluorotelomer formulations contained notable amounts of long chain C_8 PFAS (up to 20%), although these foams were dominant in C_6 PFAS. Between 2001 and 2015 there was a transition to remove C_8 from formulations and concentrates were generally >95% C6 and shorter chain PFAS. From 2015, most manufacturers are thought to have followed the EPA PFOA Stewardship Programme producing concentrates which are pure C_6 and shorter chain PFAS. These foams do not contain precursors which can biotransform to PFOA or PFOA itself in greater than trace amounts (Bell, 2019).
- Foam concentrate formulations can contain varying amounts of cationic (positively charged), anionic (negatively charged), and zwitterionic (positive and negative charges) PFAS. Upon release to the environment these PFAS will behave differently with cationic species more likely to remain sorbed to negatively charged clay minerals in soils in the immediate vicinity of release and anionic species more likely to be mobile in the aqueous environment, and the transport behaviour of zwitterions is likely to be an intermediate of the two. Further discussion of fate and transport is given in Section 3.3

- Ultra short C_2 and C_3 PFCAs have been identified within Class B foams (Barzen-Hanson and Field, 2015), these compounds are highly mobile and pose significant challenges to remove from water.

Figure 5 Types of PFAS within ECF / PFOS-based Firefighting Foam (adapted from Backe et al. 2013)



		1989 mg/L	1993a mg/L	1993b mg/L	1998 mg/L	2001 mg/L
Precursors	PFBSaAm^a	9	120 ± 2.0	180	140	110
	PFPeSaAm^a	8	140 ± 1.8	180	140	110
	PFHxSaAm^a	189	660 ± 8.1	850	743	690
	PFHpSaAm	ND	12 ± 0.40	15	30	24
	PFOSaAm	9.9	62 ± 1.1	75	67	37
	PFBSaAmA^a	ND	140 ± 3.1	120	110	150
	PFPeSaAmA^a	4	200 ± 6.3	170	140	130
	PFHxSaAmA^a	ND	930 ± 13	850	850	960
	PFHpSaAmA	ND	17 ± 0.16	17	34	44
	PFOSaAmA^a	ND	72 ± 0.81	58	53	65
Shorter Chain Perfluoroalkyl Acids (PFAAs)	PFBS	380	220 ± 2.0	160	210	250
	PFPeS	210	120 ± 1.5	80	90	120
	PFHxS	1700	910 ± 14	760	850	900
	PFHpS	410	120 ± 2.0	120	93	140
	PFOS	15000	8000	9300	6700	7900
	PFNS	160	53 ± 0.97	56	9	27
	PFDS	102	51 ± 0.34	52	11	27
Shorter Chain Perfluoroalkyl Acids (PFAAs)	PFBA	37	24 ± 0.48	35	31	38
	PFPeA	47	36 ± 0.14	52	43	48
	PFHxA	170	99 ± 1.1	110	99	170
	PFHpA	54	25 ± 0.28	22	26	37
	PFOA	150	83 ± 1.3	93	86	170
	PFNA	ND	ND	ND	ND	ND
	PFDA	ND	ND	ND	ND	ND
	PFUdA	ND	ND	ND	ND	ND
	PFDoA	ND	ND	ND	ND	ND
	PFTrA	ND	ND	ND	ND	ND
	PFTeA	ND	ND	ND	ND	ND
	PFS/PFA^b	39	35	34	28	20

% Precursors	1.2	19.5	18.8	21.9	19.1
% PFOS	80.5	66.1	69.6	63.5	65.0
% Shorter Chain PFAAs	18.3	14.4	11.5	14.7	15.9

When Class B foams are used, their surfactant nature means that they may accumulate on the wetted surfaces of firefighting infrastructure such as tanks, lines and distribution equipment (Lang et al., 2022). Currently there are many facilities that are transitioning away from PFAS containing firefighting foams to PFAS free alternatives. This transition process should involve thorough cleaning of tanks and equipment to avoid the risk of PFAS desorbing back into replacement PFAS free foam, causing potential regulatory compliance and liability issues. Concrete infrastructure previously in contact with Class B foams may also pose a long-term secondary source of these compounds leaching back into the environment (Williams et al., 2023) (Baduel et al., 2015).

Although the focus of this document is PFAS, it should be noted that a range of non-PFAS surfactants, low boiling points solvents and ionic compounds are also present in firefighting foams, including PFAS free firefighting formulations, and can represent a eutrophication risk to the water environment as well as complicate treatment and discharge.

3.2.2. PFAS possible sources, other than firefighting foams

Although Class B firefighting foams are likely to be the most dispersive source of PFAS on fuel manufacturing and related industrial facilities, it is noted that PFAS are also present in a wider range of other products which may be present on such sites, the most pertinent of which are listed below:

- Hydraulic fluids and lubricating oils – high performance hydraulic fluids and lubricating oils may contain PFAS. (Zhu and Kannan, 2020, Gluge et al., 2020)
- Plant infrastructure – PFAS may be used to line pipelines reducing surface friction for crude pumping. PFAS may be used in aqueous mixes to reduce evaporation losses in storage infrastructure, rubber to steel bonding agents, adhesives and sealants (Gluge et al., 2020)
- Fluoropolymers (including fluoroplastic, fluoroelastomers) in cable and wire insulation, gaskets and hoses may contain polymeric PFAS (Gluge et al., 2020) as well as pipe linings, valves and equipment coatings (API, 2023);
- Anti corrosion paints, paint emulsifier, paint additives (Gluge et al., 2020)
- Formulation additives in pesticides (Gluge et al., 2020)
- Runoff of surface water from PFAS impacted areas may lead to contamination of site drainage and biosolids in wastewater treatment systems.(Schaefer et al., 2023, Ozelcaglayan et al., 2023)

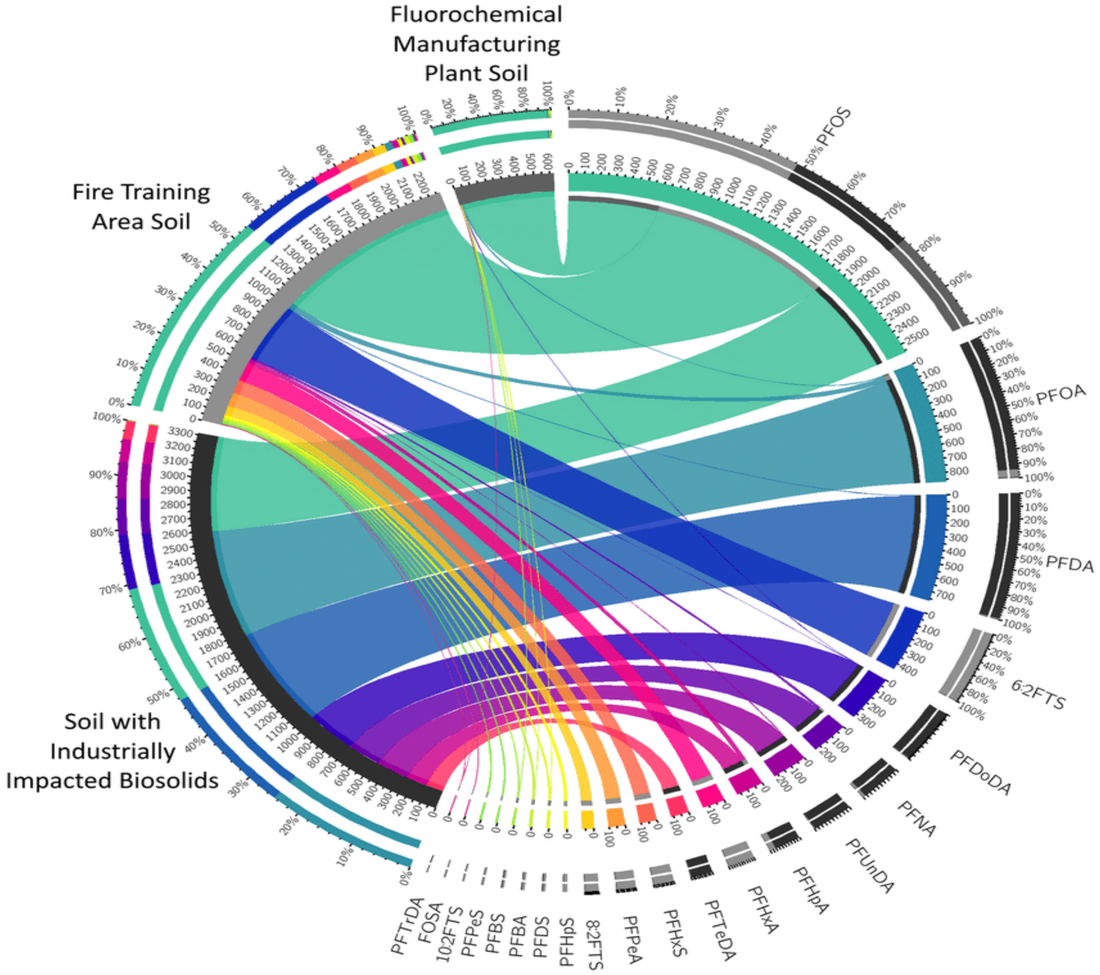
PFAS in Construction Materials

- Within the building and construction sector, PFAS are used in several applications. PFAS are used in four primary types of roofing materials: metal roofing, asphalt roofing, weatherproofing membranes for flat roofs, and textile-based roofs. PFAS are used in coatings such as paints, metal coatings, and wood lacquers to improve performance. They reportedly protect pigments, improve ease of application, increase weather resistance, and improve the finish and durability of these products (Gluge et al., 2020). PFAS have been used extensively in carpets, rugs, clothing and upholstery to prevent soiling and staining of the carpet fibers, protecting the carpet from discoloration and wear. Fluorinated sealants (for tiles, grout and concrete) are used to create a grease-resistant and water-resistant barrier that protects building materials from stains, mould, and physical damage. Electrical wires and cables (groups of wires) are typically insulated with a non-conductive plastic sheath, often made of PFAS. PFAS from these applications can then enter the soil, water and air, during the use phase and following end of use (disposal or reuse).
- In addition to use in the building and construction sector PFAS can be found in concrete and asphalt (Douglas et al., 2023). The use of AFFF at airport sites has led to contamination of concrete and asphalt associated with concrete firefighting training pads, asphalt on airport runways, asphalt aprons adjoining concrete paved areas, and asphalt and concrete at hangers and where washdown and servicing of fire training vehicles occurred (Baduel et al., 2015). A previous study has reported PFOS concentrations in the range of 9 to 2062 µg/kg in surface samples taken from a concrete pad at a fire training area in Australia (Williams et al., 2023). Given the porous nature of concrete and asphalt, PFAS can be sorbed into its internal structure. Rain events can lead to PFAS being washed out of concrete and asphalt and into soil.

3.3. PFAS IN SOILS

PFAS are now widely present in soils around the world (Anderson et al., 2019, Braunig et al., 2018, Johnson, 2022). The locations where they are often found at the highest concentrations include in the close vicinity to fluorochemical manufacturing plants (Gebbink and van Leeuwen, 2020), at airport facilities (both commercial and military) (Hale et al., 2017) where fire training activities have taken place, landfills (Knutsen et al., 2019), in the vicinity of paper manufacturing facilities (Langberg et al., 2020) as well as at sites where contaminated biosolids have been applied to agricultural land (M. Kotthoff and A. Biegel-Engler, 2020), or where wastewater or recycled water has been utilized. Given the different types of PFAS used at these sites, the PFAS pollution encountered is often indicated by a specific "fingerprint". For example, a site contaminated by the production of paper is vastly different to a site contaminated by the use of AFFF in firefighting training activities. Figure 6. shows three example PFAS contamination profiles representing impacted soil from fluorochemical manufacturing, fire training activities and biosolid amended soil.

Figure 6 Example PFAS Types and Concentrations in Impacted Soils (µg/kg) (reproduced from Sleep and Juhasz, 2021)). The link between the coloured bars shows similarity between sites.



On the right-hand side of the circle moving clockwise, individual PFAS are shown ordered by decreasing concentration (µg/kg). This is followed by location type, ordered by decreasing PFAS concentration. The size of the link connecting an individual PFAS with a location type represents the concentration, sized according to the inner numbered scale (µg/kg) (Sleep and Juhasz, 2021). For the example Firefighting Training Area (FTA) soils, PFAS predominantly included PFOS, 6:2-fluorotelomersulfonic acid (6:2 FTS) and a range of other PFCAs and PFSAs at concentrations ranging from 100s to low 1000s µg/kg. Sum PFAS for FTA soils were indicated to be up to ~2,300 µg/kg although it is noted this does not include precursors or other PFAS and significantly higher concentrations have been identified at source sites in other studies, e.g. (Brusseau et al., 2020).

Previous studies focusing on different types of sites often report characteristic PFAS soil fingerprints that are typical to the type of PFAS contamination present (H. A. Langberg, 2022). Soil source impacts at airport sites / sites impacted by firefighting training activities were dominated by PFOS and other PFSA as these PFSA reflect the dominance of PFSA in AFFF before the phase-out of firefighting foams containing PFOS. The presence of FTS is also common as 6:2 FTS, and other fluorinated telomer products with 6:2 configurations have been used as replacements for PFOS in AFFF (Place and Field, 2012).

In another study data was collected for soil from over 1000 contaminated sites falling into the categories PFAS manufacturing sites, firefighting training areas and other AFFF-associated locations at airports and military installations, and a crash site (Brusseau et al., 2020). Given the nature of these sites, the predominant PFAS detected was PFOS and maximum reported PFOS soil concentrations ranged from 0.4 to 460,000 µg/kg, with a median value of 8,722 µg/kg. The maximum reported PFOA soil concentrations ranged from 2 to 50,000 µg/kg, with a median value of 83 µg/kg.

3.3.1. Distribution of PFAS within Impacted Soils

Owing to the adsorption of PFAS to soils and the mechanisms at play, understanding PFAS concentrations with varying soil depth is important when assessing the effectiveness of remediation methods. There are only a few reported studies that have investigated this; however, some general conclusions have been drawn:

- Shorter chain PFAS are typically observed at higher concentrations than longer chain PFAS at depth unless associated with significant, recent surface releases. This can be explained by the fact that they have a higher water solubility, and thus mobility and a lower sorption affinity for soil organic matter (Washington et al., 2010, Sepulvado et al., 2011).
- Longer chain PFAS are typically observed at higher concentration in shallow soil samples. This is likely explained by the fact that longer chain PFAS sorb more strongly to soil organic matter and are thus less susceptible to movement through the soil profile (Baduel et al., 2017).
- The majority of depth-profile data sets show high concentrations present at shallow depths and exponential decreases at greater depths (Davis et al., 2007, Shin et al., 2011, Brusseau et al., 2020). This distribution, and the widespread detection of PFAS at sites many years after PFAS releases, indicates significant retention of PFAS in the vadose zone over decadal timeframes.

Once in soil, retarded PFAS can serve as a significant reservoir for further release and transport leading to further contamination. Several studies modelling the fate and transport of PFAS at contaminated sites have shown that soils and the unsaturated zone serve as a significant long-term source of PFAS (Shin et al., 2011, Xiao et al., 2015). An extensive body of work has been carried out to look at PFAS behaviour at the air-water interface, showing that PFAS accumulate at this interface (Brusseau, 2023, Brusseau and Guo, 2021). One of the most critical questions in relation to PFAS contaminated soil is related to the long-term migration potential of the PFAS to surface water, groundwater, and the atmosphere. Both points are important for risk assessment of PFAS at contaminated sites.

3.3.2. Ambient PFAS Concentrations

The ambient background concentration of PFAS in soil are often not well known but under increased study. Given the widespread presence of PFAS, including in remote locations, it is important to have some understanding of ambient background concentrations in order that realistic remediation targets are set. In a previous extensive and highly representative study focusing on sites worldwide, both ambient background concentration data and concentration data for impacted sites was reviewed and summarized (Brusseau et al., 2020). For ambient background concentrations, data was reviewed for 5700 soil samples collected from 1400 sampling locations across the world. The sites comprised both urban and rural areas including residential yards and gardens, agricultural fields, schoolyards, commercial sites, and parks. Concentrations were reported for sites in Korea, China, Tierra Del Fuego (Argentina), Antarctica, Nepal, North America, Sweden, Uganda, Belgium, and Norway. Total PFAS concentrations ranged from 0.001 to 237 µg/kg with the maximum value obtained from China. PFOS and PFOA were the most prevalent PFAS reported for almost all of the studies with median values of 2.7µg/kg for both compounds. At many commercial and industrial sites, concentrations may not reflect true ambient values, given the widespread use and testing of AFFF.

In the Netherlands, ambient values of 1.4 µg/kg for PFOS and 1.9 µg/kg for PFOA at uncontaminated sites, based on ~100 sampling locations across The Netherlands (Wintersen, 2020). In Belgium, ambient values of 1.5 µg/kg for PFOS and 1.0 µg/kg for PFOA were determined (OVAM, 2021) and it is understood the UK is currently undertaking similar assessment.

3.4. PFAS PROPERTIES

PFAS are a class of substances that have specific physicochemical properties related to the presence of the perfluoroalkyl group, which is hydrophobic with increasing chain length, and a charged functional head group, which is hydrophilic. This results in long chain PFAS being amphiphilic with surfactant properties. PFAS havea high resistance to chemical, biological and physical degradation processes. The strong and poorly polarisable C–F bonds in the backbone of the PFAS molecules, as well as their xenobiotic nature, result in weak natural degradation and thus persistence (hence, sometimes referred to as ‘forever chemicals’). Illustrative examples of bond strengths in PFAS are given in Table 5 (Tsang, 1998). For comparison, less strong bonds include CH_2CH_2-CH_3 at 102 kJ/mol.

Table 5 Examples of Chemical Bond Strengths

Bond	Energy (kJ/mol)	Bond	Energy (kJ/mol)
CF_3-F	552	CH_3-H	439
CF_2-F	352	CH_2-H	461
CF-F	508	CH-H	423
CF_3-H	456	CH_2F-F	529

As well as this Persistence (P), some long chain PFAS have been shown to be Bioaccumulative (B) and Toxic (T) and so are termed PBT, or have been shown to be very Persistent and very Bioaccumulative (then termed vPvB) substances (S. E. Hale, 2020). Thus, PFOS, PFOA and PFHxS are listed as Persistent Organic Pollutants

(POPs) under the Stockholm convention. In addition, the combination of persistence and mobility is also increasingly of regulatory concern with criteria for Persistent, Mobile and Toxic (PMT) substances, and very Persistent and very Mobile (vPvM) substances under EU Regulation REACH (EC) No 1907/2006 (M. Neumann, 2019). In 2023, the European Commission added new hazard classes to the Classification, Labelling and Packaging Regulation for Persistent, Mobile and Toxic (PMT) and vPvM substances. The expectation is that these substances will be identified as Substances of Very High Concern under REACH over the coming years.

Despite PFAS not currently understood to be completely biodegraded within the environment, precursors undergo complex 'biotransformation' processes via multiple intermediates to form PFAAs as persistent daughter products and the biotransformation can include shortening of the perfluoroalkyl chain (Butt et al., 2014). Precursors based on FASA chemistry produced via electrochemical fluorination within legacy foams may biotransform to PFSAs (Bell, 2019). Biotransformation of fluorotelomers produces PFCAs as well as intermediates including fluorotelomer sulphonates (e.g. 6:2 FTS) and fluorotelomer carboxylic acids (e.g. 5:3 Fluorotelomer carboxylic acid (5:3 FTCA)) which are regarded as semi stable depending on environmental conditions (D'Agostino and Mabury, 2017, Kabadi et al., 2020, Shaw et al., 2019, Zhang et al., 2016, Houtz et al., 2018, Harding-Marjanovic et al., 2015, Yi et al., 2018).

Understanding PFAS properties is key to being able to successfully identify opportunities and constraints for soil remediation. Due to the specific and diverse physicochemical properties of PFAS, some traditional remediation strategies are ineffective for PFAS remediation and/or for the range of PFAS potentially present. Designing and applying one remediation method that works equally well for all substances in the PFAS family is not always possible.

The following list illustrates which PFAS properties are of most importance in relation to remediation:

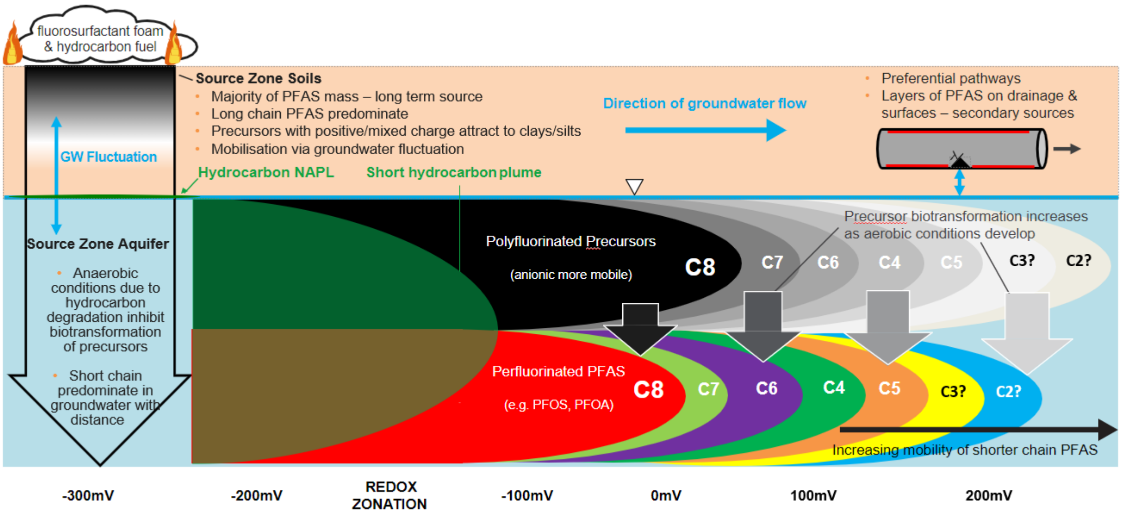
- For longer chain PFAS, the main sorption mechanism to soil organic matter is hydrophobic interactions. In general, as the chain length of PFAS increases so does the hydrophobicity and in turn the strength of sorption (Ahrens, 2011, Nguyen et al., 2020). Thus, longer chain PFAS sorb more strongly to soil than shorter chain PFAS. The hydrophobicity is also an important feature in the sorption of PFAS to hydrocarbon co-contaminants in soils. In addition to hydrophobic interactions with soil organic matter, surface complexation with uncharged organic and mineral surfaces in soil is also a prominent sorption mechanism for longer chain PFAS. The stronger the interaction between the PFAS and soil, the more challenging removal from soil will be during treatment. Approaches looking to reducing leachability are typically more effective for longer chain PFAS;
- For shorter chain PFAS, sorption to soil becomes increasing dominated by electrostatic interactions of ionic groups with soil particles. Shorter chain PFAS are more water soluble with generally lower soil:water partitioning coefficient (K_d) values and thus more mobile than longer chain PFAS. They are more likely to be found in the soil pore water and groundwater than long chain PFAS (Nguyen et al., 2020). Shorter chain PFAS may thus behave differently to longer chain PFAS when it comes to remediation methods;
- The PFAS functional group – either a sulfonate or a carboxylic – affects the strength of PFAS sorption to soil. There is a greater sorption of PFSAs compared to PFCAs that have the same chain length, owing to stronger interactions of the sulfonate headgroup compared to the carboxylic headgroup with the soil

surface (Higgins and Luthy, 2006, Li et al., 2018). Branched isomers tend to sorb less strongly than their linear analogue (Kärrman et al., 2011);

- Zwitterionic and cationic PFAS behave differently to anionic and non-ionic PFAS in soil. Zwitterionic and cationic PFAS are sorbed more strongly to negatively charged soil particles than anionic and non-ionic PFAS. The majority of soil organic matter carries a negative charge (Nickerson et al., 2021b).
- Sorption of both longer chain and shorter chain PFAS decreases when solution pH increases. This is because as pH increases, soil organic matter and clay minerals become progressively more negatively charged which increases repulsions of anionic PFAS and decreases sorption. At low pH, soil organic matter is more positively charged and this enhances sorption by contributing to both hydrophobic and electrostatic attraction.
- PFAS accumulate at the air-water interface in the vadose (unsaturated) zone in soils (Brusseau and Guo, 2021) with the degree of moisture contents within the vadose zone key parameters affecting the sorption mechanism;
- PFAS precursors can be present in various environmental media including soil. Via biotransformation, these precursors can form terminal perfluoroalkyl-sulfonic acid or carboxylic acid end products which are then persistent in the environment (Houtz et al., 2013). Precursors also generally show functional group and chain length dependant sorption and mobility. Biotransformation occurs at faster rates in aerobic environments, for example, down gradient from source areas where hydrocarbon co-contamination is often present resulting in anaerobic conditions (McGuire et al., 2014);
- Due to their surface-active properties, amphiphilic PFAS can self-assemble into micelles, hemi-micelles and other supramolecular structures within the water column and at soil; liquid interfaces surfaces. Formation is influenced by environmental factors, particularly ionic strength (Ferrari, 2012, Kancharla et al., 2022) as well as their Critical Micelle Concentration (CMC) with hemi-micelles able to form at a range of 0.001 to 0.01 of the CMC (Schwarzenbach, 2003). Such supramolecular structures have been observed on treatment media (Zaggia et al., 2016) as well as fire suppression system infrastructure (e.g. tanks and pipework) exposed to high concentrations of PFAS in foam concentrate over long time periods ((J.R. Lang and D. Liles, 2022)). Work is on-going to further characterise the type and magnitude of these structures within environmental media, their stability and potential implications for long-term discharge to groundwater and remediation (SERDP, 2024). It is noted that removal of PFAS layers on foam exposed pipework using methanol has been shown (J.R. Lang and D. Liles, 2022) and so it could be assumed that basic methanol extractions used in soil analysis, including for remediation validation, is suitable to extract these structures for analysis.
- The majority of PFAS have low or very low vapour pressures with volatilisation and vapour migration is generally of minor importance to soil remediation. FTOHs have variable but typically higher vapour pressures than other PFAS, thus are considered volatile (Bell, 2019) but are not typically identified in relation to foam related PFAS contamination. The acid dissociation constants (pK_a) are generally low or very low (Pancras et al., 2016) meaning PFAS are likely to be fully dissociated and anionic under typical conditions as well as hard to volatilise from the aqueous phase.

In this report, remediation technologies were evaluated based on their ability to effectively target and account for the different properties of various PFAS types. A summary of these different properties within the context of a typical FTA is shown in Figure 7.

Figure 7 PFAS Conceptual Site Model (CSM) For Firefighting Training Areas (FTAs) developed by Arcadis



3.5. SOIL TYPES AND PROPERTIES AFFECTING REMEDIATION

When considering remediation, the type of material to be treated will have bearing on the suitability of a remediation method. In the context of typical firefighting foam impacted sites, the following materials are considered to be the most relevant for PFAS remediation:

- Natural soils, which are soils that have developed through natural processes and have not been intervened with, are classified according to their physical make up. These soils fall in to 6 main groups including clay, silt, sand, loam, peat and chalk soils. Natural soils can be cohesive or granular where cohesive soils do not crumble, can be moulded easily when wet, and are hard to break up when dry. Granular soils are those that contain coarse grains such as sands and gravels. Peat and loam rich soils contain higher proportions of organic matter.
- Made ground, in contrast to natural soil, includes those areas where the original soil has been replaced or altered by the introduction of manmade materials such as crushed concrete, brick as well as a wide range of other materials potential containing organic and inorganic co-contamination.
- Concrete, as discussed in Section 3.2.2, and other construction materials. Notably concrete's hardstanding presence in fire fighting training areas or around fixed fire suppression systems may contain, or become impacted within by, PFAS and require management, treatment and/or disposal.

The key properties of the materials to be remediated has direct implications on relevant environmental processes for PFAS. Sorption is one of the fundamental processes that governs environmental fate and behaviour of organic chemicals. There are many studies that have looked at PFAS sorption to soil, however there is a lack of consensus related to which soil properties can be used to predict the migration of PFAS in soil (Kookana et al., 2022). This is related to the physicochemical properties that PFAS have which affect sorption-desorption and leaching behaviour. The summary below highlights the key soil and material properties that affect the fate and behaviour, and in turn remediation success, of PFAS.

- Presence of soil organic matter, non-aqueous phase liquid (NAPL) and other co-contaminants. The soil organic content is often the governing factor in the sorption of PFAS to natural soils when the organic matter content is high. The occurrence of other contaminants and the presence of NAPL within the material being remediated can reduce the effectiveness of remediation (Høisæter and Breedveld, 2022). Additional contaminants can compete with PFAS for sorption sites on soil organic matter (or other materials that may be added to the soil as remediation aids) and likewise, NAPL can interfere with the sorption of PFAS to soil organic matter. If present, accumulation of PFAS at NAPL-water interfaces can be significant (Brusseau, 2017);
- Surface area, grain size and Particle Size Distribution (PSD). The grainsize of silt is considered to be a particle diameter between 0.002 mm and 0.06 mm and the grainsize of clay is a particle diameter <0.002 mm. Soils with a higher proportion of smaller particles, and hence an increased surface area, have a greater sorption potential (Hubert et al., 2023);
- Porosity and permeability which provide a measure of the space between soil particles and the relative ease for fluids to flow between these particles. These properties are in turn related to PSD, and the degrees of consolidation and water/air saturation. These factors can subsequently affect how suitable remediation methods are that rely on contact between an added reagent, water and PFAS. Soils can be consolidated or unconsolidated which has bearing on in-situ permeability. Consolidated soil has lower settlement, lower permeability, and poorer drainage than unconsolidated soil.
- Water saturation affect, for example, PFAS partitioning to air: water interfaces within the vadose zone soils and the effect on soil leaching, especially within the groundwater smear zone (Brusseau and Guo, 2021). In addition, saturated soils may introduce additional challenges for excavation-based approaches (e.g., dewatering requirements), costs for thermal approaches and complexity for reagent addition via mixing;
- Geochemistry and mineralogy. Specifically, the pH and ionic strength of the soil pore water, the presence of metal oxides (e.g., iron oxides and aluminium oxides) and chloride can affect PFAS sorption (Kookana et al., 2022, Wanzek et al., 2023). PFAS sorption has been reported to be inversely correlated with pH with acidic pH resulted in a stronger sorption. Stronger sorption has been observed for soils that contain a greater amount of iron and aluminium oxides (H. Campos-Pereira and M. Pettersson, 2023).

3.6. PFAS REGULATORY LIMITS IN SOIL

PFAS regulations are rapidly changing across the world as evidence of their negative effects on human health and the environment, with a general trend towards the regulation of more individual PFAS with lower concentration limits. Compared to overall number of PFAS, very few individual PFAS are regulated, and in terms of environmental media, PFAS regulations for soil have been given less attention with thresholds and guidelines being more common for water (bodies) and food.

Table 6 below provides a summary of soil thresholds (and proposed thresholds) for PFAS in soils from Denmark, Germany, the Netherlands, Belgium, the UK, Norway and Australia (current in December 2023).

Table 6 PFAS Regulatory Thresholds for Soil taken from the Arcadis Regulatory Tracker

Country	**PFAS Compound**	**Type**	**Value (mg/kg)**	**PFAS included in additive values**	**Author**	**Date Issued or Updated**	**Proposed or Promulgated**
Denmark	Multiple PFAS	Health Based Value	0.4	PFOS, PFOA, PFOSA, PFBS, PFBA, PFPeA, PFHxA, PFHpA, PFNA, PFDA, PFHxS, 6:2 FTS	Danish Ministry of the Environment	2015	Proposed
Norway	PFOS	Normative value for unrestricted soil handling	0.002	N/A	Norwegian Environment Agency	2020	Proposed
Germany	Multiple PFAS	Soil - Groundwater Pathway	0.06 – 10 µg/L in leachate	Soil leachate tests (2:1) compared to groundwater 'insignificance threshold values' (2022)	Bundesministerium fur Umwelt, Naturschutz, Nukleare Sicherheit und Verbraucherschutz	2022	Guideline Values
Netherlands	GenX	Intervention value	0.057	N/A	Rijks Instituut voor Volksgezondheid en Milieu (RIVM)	2021	Proposed
Netherlands	PFOS	Intervention value	0.059	N/A	RIVM	2021	Proposed
Netherlands	PFOA	Intervention value	0.060	N/A	RIVM	2021	Proposed
Netherlands	PFOS	Soil reuse value - agriculture, nature, vegetable gardens	0.0014	N/A	Ministry of Infrastructure and Water	2021	Promulgated
Netherlands	PFOS	Soil reuse - urban areas	0.003	N/A	Ministry of Infrastructure and Water	2021	Promulgated
Netherlands	PFOS	Soil reuse - industry	0.003	N/A	Ministry of Infrastructure and Water	2021	Promulgated
Netherlands	PFOA	Soil reuse value - agriculture, nature, vegetable gardens	0.0019	N/A	Ministry of Infrastructure and Water	2021	Promulgated
Netherlands	PFOA	Soil reuse - urban areas	0.007	N/A	Ministry of Infrastructure and Water	2021	Promulgated
Netherlands	PFOA	Soil reuse - industry	0.007	N/A	Ministry of Infrastructure and Water	2021	Promulgated
Netherlands	Other PFAS	Soil reuse value - agriculture, nature, vegetable gardens	0.0014	N/A	Ministry of Infrastructure and Water	2021	Promulgated
Netherlands	Other PFAS	Soil reuse - urban areas	0.003	N/A	Ministry of Infrastructure and Water	2021	Promulgated
Netherlands	Other PFAS	Soil reuse - industry	0.003	N/A	Ministry of Infrastructure and Water	2021	Promulgated
Belgium	PFOS	Free reuse (construction) of soil	0.003	N/A	Vlaamse Overheid	2021	Promulgated
Belgium	PFOA	Free reuse (construction) of soil	0.003	N/A	Openbare Afvalstoffenmaatschappij voor het Vlaamse Gewest (OVAM)	2021	Promulgated
Belgium	PFOS	Remediation criterium - type I (nature)	0.0038	N/A	OVAM	2022	Promulgated

Country	PFAS Compound	Type	Value (mg/kg)	PFAS included in additive values	Author	Date Issued or Updated	Proposed or Promulgated
Belgium	PFOS	Remediation criterium - type II (rural) - with chicken (outdoor) / vegetable gardens	0.0038	N/A	OVAM	2022	Promulgated
Belgium	PFOS	Remediation criterium - type II (rural)	0.018	N/A	OVAM	2022	Promulgated
Belgium	PFOS	Remediation criterium - type III (urban)	0.11	N/A	OVAM	2022	Promulgated
Belgium	PFOS	Remediation criterium - type IV (recreation)	0.11	N/A	OVAM	2022	Promulgated
Belgium	PFOA	Remediation criterium - type I (nature)	0.0043	N/A	OVAM	2022	Promulgated
Belgium	PFOA	Remediation criterium - type II (rural) - with chicken (outdoor) / vegetable gardens	0.0043	N/A	OVAM	2022	Promulgated
Belgium	PFOA	Remediation criterium - type II (rural)	0.089	N/A	OVAM	2022	Promulgated
Belgium	PFOA	Remediation criterium - type III (urban)	0.643	N/A	OVAM	2022	Promulgated
Belgium	PFOA	Remediation criterium - type IV (recreation)	0.643	N/A	OVAM	2022	Promulgated
Belgium	Sum PFAS	Free reuse (construction) of soil	0.008	N/A	Vlaamse Overheid	2021	Promulgated
UK	PFOA	Soil Screening Value (SSV) for waste recovery to land based on the secondary poisoning of birds and mammals	0.019	N/A	Environment Agency, WCA Environmental Ltd	2022	Promulgated
UK	PFOS	Soil Screening Value (SSV) for waste recovery to land based on the secondary poisoning of birds and mammals	0.013	N/A	Environment Agency, WCA Environmental Ltd	2022	Promulgated
Australia - Federal (airports)	6:2 FTS	Human Health Interim Screening Levels (HISLs) - industrial (direct contact only)	0.06	N/A	Department of Industrial and Regional Development and Airservices	2015	Proposed
Australia - Federal (airports)	8:2 FTS	Ecological Interim Screening Levels (EISLs) - terrestrial	0.00373	PFOA and 8:2 FtS	Department of Industrial and Regional Development and Airservices	2015	Proposed
Australia	PFHxS	Human Health - Industrial / Commercial	20	PFOS and PFHxS	Heads of EPAs Australia and New Zealand (HEPA)	2020	Promulgated
Australia	PFHxS	Human Health - Public open space	1	PFOS and PFHxS	HEPA	2020	Promulgated

Country	PFAS Compound	Type	Value (mg/kg)	PFAS included in additive values	Author	Date Issued or Updated	Proposed or Promulgated
Australia	PFHxS	Human Health - Residential with garden / accessible soil (based on 10% TDI)	0.01	PFOS and PFHxS	HEPA	2020	Promulgated
Australia	PFHxS	Human Health - Residential with minimal opportunities for soil access	2	PFOS and PFHxS	HEPA	2020	Promulgated
Australia	PFOA	Human Health - Industrial / Commercial	50	N/A	HEPA	2020	Promulgated
Australia	PFOA	Human Health - Public open space	10	N/A	HEPA	2020	Promulgated
Australia	PFOA	Human Health - Residential with garden / accessible soil (based on 10% TDI)	0.1	N/A	HEPA	2020	Promulgated
Australia	PFOA	Human Health - Residential with minimal opportunities for soil access	20	N/A	HEPA	2020	Promulgated
Australia	PFOS	Human Health - Industrial / Commercial	20	PFOS and PFHxS	HEPA	2020	Promulgated
Australia	PFOS	Human Health - Public open space	1	PFOS and PFHxS	HEPA	2020	Promulgated
Australia	PFOS	Human Health - Residential with garden / accessible soil (based on 10% TDI)	0.01	PFOS and PFHxS	HEPA	2020	Promulgated
Australia	PFOS	Human Health - Residential with minimal opportunities for soil access	2	PFOS and PFHxS	HEPA	2020	Promulgated

In the majority of cases threshold values have been set for individual long chain PFAAs, most commonly for PFOA and PFOS. This is perhaps not surprising given the regulatory focus placed on these two PFAS. The soil thresholds do contain some values for other PFAS including PFHxS, GenX, 6:2 FTS and 8:2 FTS. Only the Danish threshold includes several PFAS (PFOS, PFOA, Perfluoroctane sulfonamide (PFOSA), Perfluorobutane sulfonic acid (PFBS), Perfluorobutanoic acid (PFBA), Perfluoropentanoic acid (PFPeA), Perfluorohexanoic acid (PFHxA), Perfluoroheptanoic acid (PFHpA), Perfluorononanoic acid (PFNA), Perfluorodecanoic acid (PFDA), PFHxS, 6:2 FTS) although none include precursors, ultrashort chain PFAS, or measures of total PFAS (for the recasted EU Drinking Water Directive that came into force 2021, the parameters Sum PFAS and total PFAS are included, however this is for water thresholds and not soil).

The thresholds themselves may apply under different scenarios, where many countries have a set of thresholds that apply to soil that is designated for reuse under a certain case. Threshold values range from most conservative at 1.4 µg/kg for a soil reuse value for agriculture, nature, vegetable gardens proposed by the Netherlands for PFOS and PFOA to the least conservative of 50,000 µg/kg for a human health-based value proposed by Australia for industrial/commercial sites.

Thresholds are highly variable by country and soil use or reuse type. Across Europe, soil thresholds are typically lower than those in Australia, for example, with PFOS thresholds (of those summarised) ranging between 1.4 and 110 µg/kg with a median value of 59 µg/kg. When compared to the median ambient PFOS soil concentration of 2.7 µg/kg determined in global soils (Brusseau et al., 2020) it is apparent that European soil thresholds may be within one order of magnitude of ambient concentrations in many cases and in some instances broadly equivalent.

Recent work by the RIVM has proposed using a relative potency factor (RPF) approach where the harmfulness of PFAS is expressed relative to PFOA (in the same way that such a system exists for Polychlorinated Biphenyls (PCBs) (RIVM, 2018 and Zeilmaker, 2018). These RPF seem to be most useful in cases of direct intake such as via drinking water or food, however they are difficult to apply to soil concentrations. This is mostly related to the difference in sorption of PFAS to soil compared to their RPF, where the sorption is not necessarily correctly considered in the RPF. It remains to be seen whether the RPF will become more commonly used.

Also of note are the 2022 German guidelines which employ soil leachate tests which are then compared to groundwater guideline values and thus may better reflect water resource receptors, which are common receptors driving risk for PFAS, and accounts for soil properties and PFAS sorption to a greater degree compared to soil concentrations.

3.6.1. PFAS Waste Thresholds

In addition to soil thresholds based on certain reuse or remediation scenarios and receptors, remediation works will often generate PFAS impacted wastes. Landfilling of PFAS, as detailed in Section 5.4.1, may also be considered.

In the EU, the European waste list (EURAL) applies. In this list, specific wastes are given an EURAL code that provides information about the origin and nature of the waste and indicates whether a waste must (possibly) be processed as hazardous waste. A waste material is considered hazardous on the basis of the concentration limit values from Annex III of the Waste Framework Directive of substances in the waste. These are substances with a CLP classification (Classification, Labelling and Packaging, EG 1272/2008). Only a few PFAS are classified within the CLP Regulation. Moreover, the PFAS concentrations present are usually significantly lower than the applicable concentration limit value.

The POPs regulation (2019/1021 EU) sets requirements for the processing of POP-containing waste. POP-containing waste is waste containing POPs with a concentration equal to or higher than the limit value for the POPs listed in Annex IV of the Regulation. The POPs in this waste must be destroyed or irreversibly converted, according to the provisions of Annex V (Part I) of the POPs Regulation and cannot thus be landfilled. For PFOS (and derivatives thereof) a concentration limit of 50 mg/kg applies. A concentration limit value of 1 mg/kg has been proposed by the European Council and Parliament to PFOA and PFHxS (and their salts) and a proposed value of 40 mg/kg for compounds related to PFOA and PFHxS (EC Proposal, 2021). For waste with a POP content lower than these limit values, there is no mandatory method of processing under the POP Regulation. In theory, the waste may then be reused, provided that Annex I of the POP Regulation, the LAP3 (Dutch third National Waste Management Plan) and other applicable (waste) regulations are complied with.

As with the EURAL/CLP regulations, concentrations of PFAS measured within soils and other wastes are typically significantly lower than the POPs thresholds but may still present potential risks to human health and the environment. Therefore, the EURAL/CLP and POPs regulations are not typically relevant in determining remediation or waste disposal options. In practice, many landfill operators use other, country-specific environmental thresholds or facility-specific criteria to determine acceptance. For example, in the Netherlands soil that contains more than the 60 µg/kg for PFOS,140 µg/kg for PFOA, 60 µg/kg for Gen-X and 60 µg/kg for sum PFAS and /or a silt fraction over 40% is considered untreatable and is allowed to be landfilled.

Increasingly there is a focus on the leachability of PFAS from waste materials, rather than soil concentrations, which relates more directly to leachate implications and management.

3.7. PFAS ANALYSIS

The analysis of PFAS can be complex but is important to understand in order to robustly assess treatment technologies, especially considering trends in regulatory thresholds.

Starting with the extraction of a soil sample, through to the analytical determination of PFAS, the physicochemical properties of the PFAS present in the sample must be taken into consideration. The soil extraction method is an important factor when assessing certain PFAS treatment technologies. The leachability and bioavailability of PFAS in soil can also play a role in the success of a soil remediation method. Analytical methods are needed that are both selective and inclusive. Selective methods are those that are specific for PFAS and do not include other organic or inorganic fluorine species. Inclusive methods are those that are able to detect thousands of known and unknown PFAS with adequate recoveries. The choice of method(s) is often highly site specific.

The sections below summarises the main points related to soil extraction methods, leaching methods, bioavailability methods and analytical methods.

3.7.1. Sample Extraction

The standard solvent extraction for PFAS contaminated soil is a basic methanolic extraction. However, previous research has shown that there are limitations with the extraction of cationic and zwitterionic PFAS from soil when this technique is used (Barzen-Hanson et al., 2017). This is due to the enhanced sorption of these PFAS to soil via electrostatic and hydrophobic interactions. For example, PFOS-based AFFF formulations have been found to contains ~20% cationic and zwitterionic PFAA precursors (principally Perfluorohexane Sulphonamido Amine (PFHxSaAm) and Perfluorohexane Sulphonamido Amino carboxylate (PFHxSaAmA)) (Backe et al, 2013).

A more efficient extraction is achieved using stronger extraction conditions such as a strong acid (Barzen-Hanson et al., 2017, Munoz et al., 2016) or for PFAS containing betaine or quaternary ammonium functional groups, a strong base (Avendaño, 2017). In this case a sequential extraction with acid or base and methanol is effective. For soils impacted by AFFF, a method involving sequential basic (NH_4OH) and acidic (HCl) methanol extractions was shown to be effective for anionic, cationic, and zwitterionic PFAS (Nickerson et al., 2021b).

Consideration regarding enhanced soil extraction is technology specific. For example, High Temperature Incineration (HTI) has the potential to destroy all PFAS and thus assessment of such precursors using modified soil extraction procedures following incineration may not be important. Likewise, assessment of soil stabilisation via leaching tests looks to assess which PFAS are leached from soil (regardless of what remains sorbed). However, in relation to soil washing, a principal mechanism by which PFAS are treated is by extracting PFAS from soil into process water with treated sands and gravels not destroyed or immobilised but reused. Therefore, confirmation that the soil washing process is effective to removing cationic and zwitterionic PFAA precursors, which bind more effectively to soils than anionic PFAS may be important to demonstrate that PFAS risk-management actions are durable.

3.7.2. Soil Leaching Methods

Leaching methods estimate the amount of PFAS that can be leached from soil under different water regimes. PFAS properties often govern the degree of soil leachability, especially significant are chain length and functional group, which are themselves associated with the strength of PFAS sorption to soil (Navarro et al., 2023, Kabiri et al., 2022).

Acidic leachability tests may underestimate PFAS leaching due to increased sorption of anionic PFAS at low pH, while longer term sequential (monolith) tank tests provide a more representative assessing of long-term leaching compared to short term tests on disaggregated samples. US EPA Method 1315: Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using a Semi-Dynamic Tank Leaching Procedure, has been applied for PFAS (McDonough et al., 2021). Further discussion of leaching methods as they relate to soil stabilisation and solidification is provided in Section 5.3.2.3;

Soil bioavailability provides a measure of how available PFAS are to be taken up by organisms and plants. Methods to determine the bioavailability of PFAS in soils are not widely reported or well tested but can be reflected by methods such as passive sampling (S. E. Hale, 2021) as well as to assess PFAS mass flux within the water column. Passive samplers are small devices that passively accumulate pollutants over time. Following deployment, they are extracted and the concentration determined represents the more bioavailable (dissolved phase) concentration.

3.7.3. Analytical Methods

The analytical determination of extracted PFAS can be carried out using targeted and non-targeted analytical approaches as well as PFAS sum parameter methods which include Total Organic Fluorine (TOF), Extractable Organic Fluorine (EOF) and Total Oxidisable Precursor (TOP) assays. Fluorine-19 nuclear magnetic resonance spectroscopy and particle-induced gamma ray emission can also be used to look directly at the PFAS content present in the soil sample.

Prior to analytical determination, sample clean up may be needed and this is most commonly achieved using a Solid Phase Extraction (SPE) method (Miyake et al., 2007) or by using an SPE clean up.

A summary of the main analytical approaches is given below:

- Targeted analytical approaches use liquid chromatography (LC) with either high resolution mass spectrometry (HRMS, e.g., quadrupole time-of-flight; Q-TOF) or tandem mass spectrometry (MS/MS). This method is applicable to a specific defined set of analytes which are known to be present in a soil (Nickerson et al., 2020). Calibration standards must be available for the target PFAS analytes in order to quantify concentrations with C_{13} mass labelled surrogate standards added prior to extraction to assess extraction efficient. Internal standards are also typically added following extraction to correct for any instrumental variations. This is the most used and most standardized of PFAS analytical methods (e.g., the Draft US EPA Method 1633 which includes 40 PFAS in soil) with Limits of Detection (LOD) typically 0.5 to 2.5 µg/kg;

- The limitation of analysing only individual PFAS is that omitting precursors and other non-targeted PFAS may significantly underestimate and / or fail to identify PFAS sources which may contain a high proportion of precursors and other non-targeted PFAS (Göckener, 2022);
- Using the same analytical method (LC-HRMS or LC-MS/MS) but in a non-targeted way (also referred to as suspect screening) can also identify many additional suspected or previously uncharacterized PFAS. Non-targeted analysis can screen for lists of known suspects as well as being able to discover new or unknown analytes (Strynar et al., 2015). HRMS data can be stored and analysed later for newly identified analytes (Barzen-Hanson et al., 2017).
- The main limitation of non-target analysis is that in order to unequivocally quantify a PFAS, a standard is needed (Strynar et al., 2015). If a standard is not available, then only a semi-quantitative identification can be made using structurally similar PFAS.
- TOF uses Combustion Ion Chromatography (CIC) to mineralize and measure the organic fluorine in a soil sample. Samples are combusted at 900-1,000°C to convert organic fluorine (and any residual inorganic fluorine not removed during sample preparation) to hydrofluoric acid, which is absorbed into a solution of sodium hydroxide. The total concentration of fluoride ion is then measured via IC. This method provides an estimate of all organic fluorine in a sample and has been used for soil, sediment, water and biological materials (McDonough et al., 2018). A related approach for soils is EOF which first extracts soil samples in methanol, then undertakes a SPE clean-up then combusts the extract and measures the generated fluoride by IC;

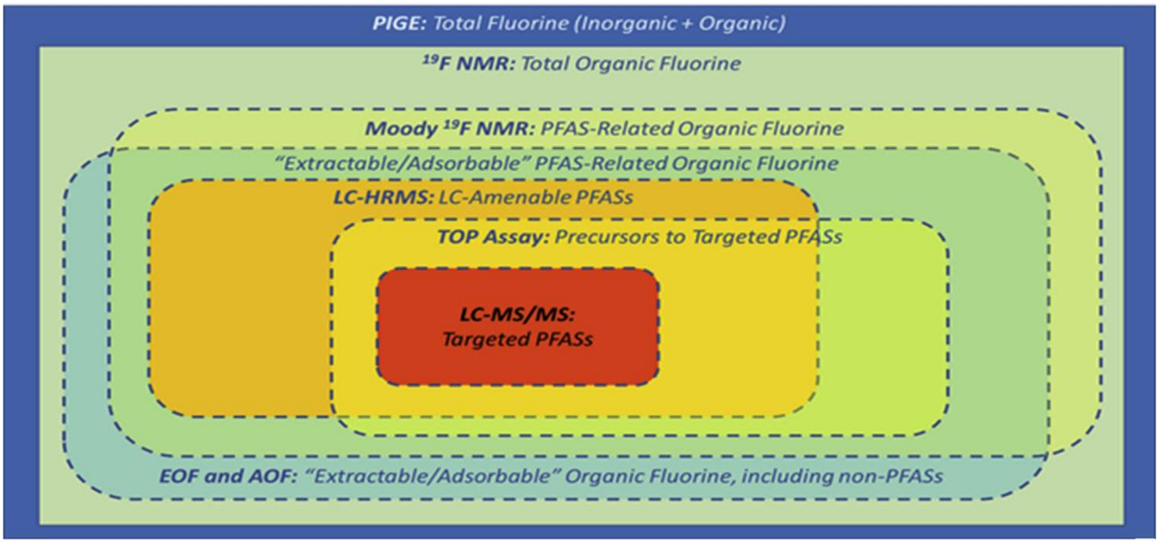
  The main limitation of TOF and EOF is that it does not provide quantification of individual PFAS compounds and reporting limits may not be low enough for some situations (currently understood to be around 0.05 mg F/kg for TOF and 0.02 mg F/kg for EOF) which must be converted based on the molecular weights of suspect PFAS.
- The TOP assay is the most selective of the PFAS sum parameter methods, in that it is only selective for PFAS that can be oxidized to form targeted PFAAs (Houtz and Sedlak, 2012). The TOP assay can be used to infer and indirectly quantify PFAAs precursors of different chain lengths by comparing the concentrations of specific PFAAs before and after oxidation of the sample by an excess of hydroxyl radicals (typically generated by persulphate at elevated temperature and pH). The TOP assay has been used for water (urban runoff, wastewater, ground water) and solids (soil, sediment, commercial products). The method is useful to assess the potential of PFAS mixtures to eventually degrade to PFAAs (Ateia et al., 2023) especially firefighting foam related contamination;

  The limitation of the TOP assay method is that selectivity is limited to compounds that oxidize to form LC-amenable hydroxyl-radical resistant PFAS, and is dictated by the choice of which products to monitor (Göckener, 2022). Any precursors that oxidize to unmonitored PFAS will be missed. Furthermore, low and variable recoveries may lead to false negatives, especially in samples with low contaminant concentrations (Robel et al., 2017). In addition, the identity of the precursors present in a mixture can rarely be deduced beyond general observations on chain length, as transformation processes are complex and nonspecific. In certain matrices (e.g., foam concentrates) oxidation efficiency may be inferior.

- Fluorine-19 nuclear magnetic resonance spectroscopy (19F NMR) has been used for decades to identify and characterize organofluorine compounds and can also be used to quantify total organic fluorine in a sample by integrating multiple peaks associated with organofluorines. 19F NMR is a non-destructive method which can distinguish between PFAS and non-PFAS, however, as for the TOF method, 19F NMR does not provide any structural details about the detected compounds.
- Particle-induced gamma ray emission (PIGE) spectroscopy is a surface analysis technique for quantification of elemental fluorine in which an accelerated beam of protons strikes the surface of the sample of interest, exciting 19F nuclei (Ritter et al., 2017). Gamma rays emitted upon de-excitation provide a unique signature proportional to the number of fluorine atoms on the surface. PIGE has only recently been applied to the measurement of PFAS-impacted samples and method development is needed before this method can be viewed as standardized. PIGE is also a non-destructive method.

Figure 8 below shows the different analytical methods to determine PFAS. The size of the shape indicates how broad the method is.

Figure 8 Illustrative Breadth of PFAS Included within Different Analytical Techniques (reproduced from McDonough et al. 2018)



4. APPROACH TO SOIL TREATMENT TECHNOLOGY EVALUATION

The overall approach to evaluation of field deployed soil treatment technologies involved the following steps:

1. Identification and shortlisting of field deployed and innovative technologies from the literature review (described in Section 2):

2. Vendor liaison in relation to selected field deployed technologies (described in Section 2);

3. Identification of relevant treatment scenarios, material types and treatment goals (described in Sections 4.1-4.3);

4. Definition of Evaluation Criteria (described in section 4.4);

5. Critical evaluation of each technology against the Evaluation Criteria based on information from literature review and vendor liaison (described in section 2); and

6. Identification of data gaps (described in section 5).

A similar evaluation approach was taken with innovative soil treatment technologies but with a focus on the identification of work to be done to close gaps for potential commercialisation.

4.1. TREATMENT SCENARIOS

Land remediation approaches often target the greatest mass of contamination to manage risks to the environment in a cost-effective manner. This involves addressing lower volumes of soils with higher PFAS concentrations within identified source areas and thus reduce or eliminate potential leaching to groundwater and other receptor exposure pathways. This can, in turn, reduce or eliminate the scope and/or duration of any groundwater treatment.

For firefighting foam related PFAS contamination this often involves targeting shallow, superficial soils where higher concentrations of (particularly long chain) PFAS are measured, reflecting typical surface-release routes following foam use or spillages. While this remains a sensible approach, depending on the regulatory context, low soil thresholds may require larger volumes of soils within lower PFAS concentrations to treated.

While the context under which treatment and risk management of PFAS is broad and both jurisdiction and project specific, the following scenarios were considered most likely to be relevant to facilities managing PFAS contamination primarily resulting from firefighting foam use.

- Scenario 1: Smaller soil volumes with higher levels of PFAS contamination:
    - Unsaturated soil source areas - e.g., fire training areas, mobile equipment testing & maintenance areas, fixed systems (tested via foam release), fire incident response areas, foam storage and spillage areas, wastewater treatment routes and infrastructure (e.g., reedbeds) and areas resulting impacted soil movements;

  - While targeted, this could range from small volumes in response to a limited, point source release or larger volumes from significant foam release or multiple source areas and so could influence whether there is a cost justification to mobilise certain technologies to site.
  - Saturated soil source zones - e.g., primarily associated with unsaturated source areas listed above and often address via groundwater treatment technologies but can be beneficial to include as part of soil treatment to target mass (e.g., smear zone, capillary fringe);
  - Investigation Derived Wastes (IDW) – very small volumes of unsaturated or saturated soils with a heterogeneous range of concentrations from site investigation or construction works;

- Scenario 2: Larger soil volumes with lower levels of PFAS contamination - e.g., due to limited duration / magnitude of foam release, for example, occasional foam nozzle spray testing, air deposition near off-site sources, biosolids / sludge application, PFAS of unknown origin within made ground or other site soils, historic contamination subject to years of leaching, historic soil movements involving mixing with cleaner materials (e.g., earth bunds),

- Scenario 3: Reuse of soils on site – regardless of the soil volume or levels of PFAS contamination, if treated soils are to be re-use either on-site or off-site then the environmental sensitivity and criteria associated with such reuse may affect treatment goals and technologies;

- Scenario 4: Disposal of soils and impacted materials – where material is to be disposed off-site then PFAS waste criteria will likely relevant and pre-treatment may be undertaken to a different standard than other scenarios. Any on-site disposal (e.g., engineered containment) will involve a different range of validation and long-term management arrangements;

- Scenario 5: Site redevelopment and ownership drivers – rapid redevelopment timeframes may present constraints for certain treatment technologies as may site divestment where long-term access and management of residual risks / treated material may not be possible or desirable;

4.1.1. Treatment Trains

While treatment trains (a combination of remediation approaches applied in sequence to achieve a remediation outcome) may be less complex for soils compared to water treatment approaches, considerations of how soil treatment may fit into wider remediation strategies and potential secondary treatment and by-products has been considered as part of the evaluation, for example:

- Soil washing followed by stabilisation or thermal treatment of resultant fines and treatment of process water;

- Landfilling or engineered containment involving containment and treatment of leachate;

- Stabilisation pre-treatment prior to landfilling or containment;

- Thermal desorption requiring treatment of off-gases;

- Targeting of PFAS mass (and mass flux) to identify separate approaches for source area soils and more diffuse impacts;

- Treatment trains that first separate and concentrate PFAS followed by destruction within smaller material volumes such a material segregation, physical screening and crushing.

A holistic and long-term view of how PFAS are separated and ultimately destroyed has been taken to evaluate whether a technology is effective and sustainable as well as a support a robust comparison between technologies with different treatment mechanisms.

4.2. MATERIAL TYPES

The technology evaluation considered the applicability and constraints in relation to a range of different soil and material types considered most typically encountered during management of foam related PFAS contamination and associated redevelopment works.

However, it is noted that regardless of the source of soil (e.g., natural / made ground / concrete), it is the soil properties, co-contamination and environmental setting which will most influence PFAS treatment (as described in Section 3.5). Therefore, while the following soil and material types have been considered, the technology evaluation primarily focussed on soil properties and co-contamination which may be common across these materials.

- Natural soils;
- Made ground; and
- Concrete (crushed);

It is noted that crushed concrete will likely represent unique challenges for certain treatment technologies given PFAS have been shown to diffuse into concrete pore spaces (up to 12 cm) (Baduel et al., 2015), and so less accessible within the relative short time frames for treatment application. It also has different physical properties compared to many soils and made ground which may result in a different end use suitability.

Biosolids are not typically encountered during treatment of firefighting foam related PFAS contamination but during the course of the evaluation where the applicability of a technology to biosolids is mentioned this has typically been noted.

4.3. TREATMENT GOALS

As described in Section 3.6, soil threshold limits vary considerably depending on the country and the soil use or reuse type. Across Europe, PFOS thresholds (of those summarised) ranged between 1.4 and 110 µg/kg with a median value of 59 µg/kg. When compared to the median ambient PFOS soil concentration of 2.7 µg/kg determined in global soils (Brusseau et al., 2020) or ambient concentrations from the Netherlands and Belgium of 1.4 µg/kg and 1.5 µg/kg, respectively, it is apparent that European soil thresholds may be within one order of magnitude of ambient concentrations in many cases and in some instances equivalent. It is noted that assessment of soil leachate may be appropriate (or more appropriate) in-situations concerning risks to underlying groundwater as is reflected by the current German thresholds.

The ranges of soil thresholds reviewed in Section 3.6 was used within the evaluation to assess treatment performance, particularly with respect to residual concentrations as high percentage reductions may still leave PFAS at concentrations above such thresholds.

Moreover, while further optimisation and development of PFAS treatment technologies will increase performance across material types, there will always be some limit to performance without widespread application of highly energy intensive and costly approaches which are less sustainable and involve other impacts (carbon emissions, traffic, etc) which may outweigh potential PFAS risk reduction. Therefore, it is important to consider pragmatic, site-specific risk-based thresholds that are compatible with sustainable remediation approaches (e.g., from United Kingdom's Sustainable Remediation Forum (SuRF-UK)) where this is acceptable to regulators within the project country. One hinderance to developing such site-specific risk-based thresholds is that fate and transport models and risk assessment protocols often do not fully account for PFAS specific sorption mechanisms (e.g. (Brusseau, 2017)) which is the subject of ongoing focus. Site specific risk assessments and modelling should consider the specific Source Pathway Receptor linkages relevant to a project site, reuse goals and proposed site end-use.

Given that PFAS are ubiquitous and persistent, even when use and emission ceases, concentrations in the environment will still remain elevated (Cousins et al., 2022). Thus, ambient concentrations are of importance when site specific clean up goals are defined, especially in urban and industrial areas where PFAS concentrations are likely higher than more rural environments.

Beyond soil concentration thresholds which may be adopted as treatment goals or used to derive specific concentration goals, the treatment scenario will also inform suitable treatment goals and end points. For example, pre-treatment goals based on acceptance at landfills or long-term management and leachate treatment associated with engineered containment.

The type of treatment goal will also depend on the technology selected and the location. For example, off-site treatment may employ alternative soil concentration and reuse thresholds reflecting the jurisdiction and treatment facility permit as well as certification and liability management objectives. Non-destructive approaches, on the other hand, may employ various soil leachate target values alongside long-term groundwater monitoring.

Treatment goals for other approaches, such as continued containment or incineration, would likely focus on certification and process-based lines of evidence. A distinction should also be made between soils that are treated and retained on-site and soils that are removed from site. e.g., thresholds for soil remaining on-site should consider the site-specific risk from residual contamination, and landfill waste acceptance criteria may apply in cases where soil is sent to landfill. Site specific risk assessments can be suitable in this regard and, in general, are recommended when developing treatment goals in preference to generic screening criteria.

4.4. EVALUATION CRITERIA

The Evaluation Criteria have been determined to capture key technical, operational, commercial and sustainability factors which are important to consider when undertaking PFAS soil treatment options appraisal. In addition, the criteria also aim to enable evaluation of technologies' suitability for the treatment scenarios, material types, treatment goals and key PFAS properties, which all may represent opportunities and/or constraints. The following categories and criteria were selected:

Technical Considerations

- Treatment Mechanisms and Suitability to Treatment Scenarios
- Treatment Efficacy for Different PFAS versus Treatment Goals;
- Suitability to Soil Properties and Co-contamination;

Operational Considerations

- Potential impact on site operations (short & long-term);
- Requirement for ongoing operation, maintenance and monitoring;

Commercial Considerations

- Technology development status and availability;
- Costs – considering capital and operational expenditure;

Sustainability Considerations

- Long-term effectiveness and residual liability;
- Energy and chemical usage;
- High-level sustainability and stakeholder considerations.

While every soil treatment project will have site specific factors influencing the most appropriate technology, the operating ranges and key limitations will be identified for each technology applicable across the majority of situations.

A high-level consideration of sustainability was undertaken noting potential environmental, economic and social factors associated with potential technology implementation broadly reflecting SuRF-UK Indicators in addition to those factors already included within the Evaluation Criteria, such as treatment performance (environmental benefit) and costs (economic) (CLAiRE, 2020). However, it is noted that assessment of sustainability is largely not at a technology specific level but at a wider project level which varies hugely and is beyond the scope of the technology evaluation in this report (although often critical in determining the optimum treatment approach). For example, while a thermal based treatment technology may have a high carbon footprint and costs, it may provide the greatest degree of contaminant reduction and enable beneficial land reuse within redevelopment timeframes.

In general, it is recommended that a thorough sustainability analysis should be conducted to further assess the sustainability considerations of any one technology over another in accordance, as appropriate, with SuRF-UK, ISO 18504:2017 Sustainable Remediation or Green and Sustainable Remediation (GSR) (ITRC, 2011), for example.

5. PFAS SOIL REMEDIATION TECHNOLOGIES

5.1. TREATMENT TECHNOLOGIES EVALUATED

As detailed in Section 2.2.1, the selected PFAS soil treatment technologies included for review within this project are listed in Table 7.

Table 7 Selected PFAS Soil Treatment Technologies

Field Deployed Technologies	Innovative Technologies
Destructive Approaches High Temperature Incineration Cement Kiln Incineration Ex-situ Thermal Desorption Smouldering Combustion	**Destructive Approaches** Ball Milling High Energy Electron Beam Phytoremediation Biodegradation
Non-Destructive Approaches Ex-situ Soil Washing Stabilisation & Solidification	**Non-Destructive Approaches** In-situ Soil Flushing
Pathway Management Approaches Landfilling On Site Engineered Containment	

5.2. DESTRUCTIVE SOIL REMEDIATION TECHNOLOGIES

5.2.1. High Temperature Incineration (HTI)

5.2.1.1. General Description and PFAS Removal Mechanism

Although PFAS are highly thermally stable, studies indicate that HTI (>1000C) can be effective in breaking the robust fluorine-carbon bonds provided requisite temperatures and residence times are achieved.

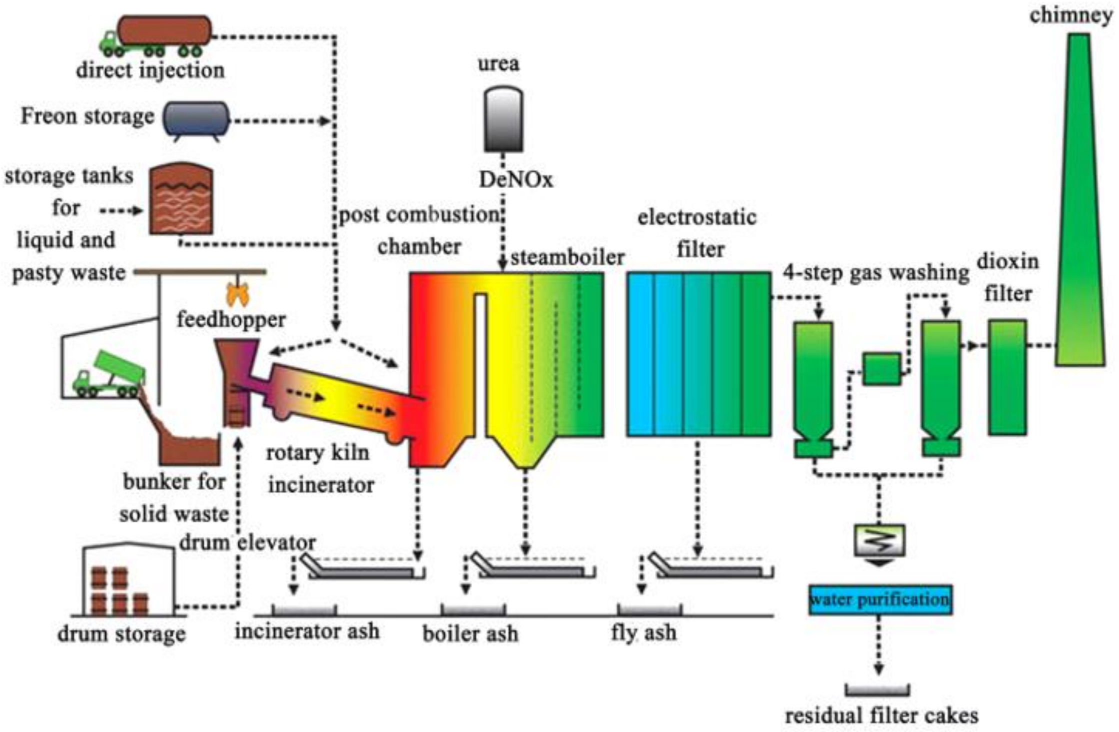
Incineration typically refers to the thermal decomposition of material in the presence of oxygen with the destruction of PFAS occurring via unimolecular decomposition and, to a lesser extent, radical reactions (US EPA, 2020b, Tsang, 1998). Thermal destruction via pyrolysis may occur in some processes where oxygen is absent but is typically a separate technology to incineration. HTI can be achieved via, for example, rotary kiln (as illustrated in Figure 9), Multiple Hearth Furnaces (MHF), Fluidized Bed Furnaces (FBF) and is often similar in process to thermal desorption (Section 5.3.3) but with typically higher kiln / furnace temperatures.

Complete destruction or 'mineralization' refers to complete defluorination of the perfluoroalkyl chain and the PFAS molecule, resulting in the formation of CO_2, H_2O and fluoride or hydrogen fluoride (HF). The two latter requires scrubbing from the flue gas, typically by using an alkali to mitigate emissions of acid gases.

Incomplete mineralization as a result of inadequate temperatures or insufficient residence times can create Products of Incomplete Combustion (PICs) including various short-chain PFAAs and fluoro-organics as stable by-products (such as tetrafluoromethane (CF_4), hexafluoroethane (C_2F_6), and perfluoroisobutylene (C_4F_8)) depending on the parent PFAS compound (Yamada et al., 2005). The stability of the perfluorinated radicals also increase their propensity to recombine and create larger PICs (USEPA, 2019b). Trifluoroacetic acid (TFA) has also been detected as a PIC in several studies (e.g., Guo et al 2019).

Further work by (Yamada and Taylor, 2003) showed that, following gasification at 1,250°C for 40 seconds, incineration of PFOS-contaminated material at 600˚C resulted in negligible PFOS detections (supported by Gas chromatography (GC)/MS analysis and sulphur mass balance) but that C_1 and C_2 fluorocarbon alkanes were detected, likely trifluoromethane, CF_4 or C_2F_6. At 900°C these compounds were still detected albeit at lower concentrations. Another study showed that a variety of reaction products can be formed at temperatures below 1,000˚C (Yamada et al., 2005).

Figure 9 Example Rotary Kiln Incineration Process (reproduced from Jiang et al. 2019)



Relevant studies where effective destruction of PFAS was achieved without significant by-products reported include:

- Yamada (2005): initial desorption / gasification for 20.0 to 32.6 seconds at 650°C then gas phase treatment for 2 seconds at 1,000°C;
- Taylor (2014) gas-phase residence time of 2 seconds at a mean gas temperature of 1000°C over the effective length of the reactor;
- Watanabe et al (2016): single stage thermal process, residence time 10 minutes at 1,000°C;
- Aleksandrov et al (2019): residence time within a post combustion chamber 2.7 seconds at 1,020°C; and,

- The US EPA began conducting studies using it's 'Rainbow' furnace in 2021 to conduct incineration experiments under controlled conditions (Krug et al., 2022). This research identified fluorocarbon tracer gases (surrogates) that could potentially be used to monitor destruction efficiencies. The first publication from these experiments suggests that PFAS can be destroyed when subjected to aggressive thermal environments above 1100˚C (DOD, 2023).

In summary, conditions indicated to be suitable for PFAS incineration include high temperature incineration at 1,000 – 1,200˚C with >2 seconds residence time (Yamada et al., 2005, Taylor et al., 2014, Watanabe, 2016, Aleksandrov et al., 2019). These temperatures are much higher than those employed by typical Municipal Soil Waste (MSW) incinerators with one study detecting PFAS, albeit at relatively low concentrations, in fly ash and bottom ash at MSW facilities in China (Liu et al., 2021).

However, US EPA Technical Brief on 'PFAS Incineration to Manage PFAS Waste Streams' (February 2020) notes the most difficult fluorinated organic by-product to decompose is CF_4 requiring temperatures over 1,400°C which would presumably place greater reliance on post-combustion gas scrubbing processes.

Concerns regarding destruction of PFAS have focussed most on liquid wastes, such as AFFF concentrate, rather than solid wastes such as soil or spent GAC, due to aqueous phase change and volume expansion and thus reduced residence times and potentially reduce treatment efficacy.

5.2.1.2. Suitability to Treatment Scenarios

Due to the high cost and environmental footprint of HTI, it is likely most suited to high concentration, low volume waste streams such as shallow soils from AFFF source areas (e.g., fire fighting training areas, spillages) which would likely require effective delineation and pre-treatment. Highly impacted IDW soils could also potentially be suited to HTI as the relatively low soil volumes may not justify other treatment approaches.

HTI could also be used as the final destruction stage in treatment trains generating high concentration, low volume wastes such as soil washing fines, spent media and fractionated soil pore water. Ash generated by the HTI process is typically managed by the HTI operator (often by landfilling).

Pyrolysis of biosolids has been investigated, given concerns regarding PFAS wastewater treatment biosolids, with a study by Thoma et al. (2022) finding that target PFAS were reduced to below Method Detection Limits (MDLs) in the resulting biochar. However, by-products were not assessed, and assessment of emissions was stated to warrant additional research.

5.2.1.3. Treatment Efficacy for Different PFAS Versus Treatment Goals

PFAS removal from materials under the HTI conditions and studies summarised in Section 5.3.1.1 (at temperatures between 1,000-1,200°C) removed target PFAS to below detection limits in the resulting gas emissions and/or residual material.

Complete mineralisation is hard to confirm and there are conflicting reports presented throughout the literature, with many of the differences rooted in either the incinerated matrix (i.e., solid phase versus aqueous phase) or an incomplete analytical list of potential PFAS by-products. For example, a critical review by Wang et al (2022) observed, "the lack of closed mass balances (>90% F accounted for) for nearly all experiments strongly implies that some fluorinated products may escape thermal and post-treatment processes, elude detection, and be released to the environment".

There is limited data from full scale incinerator facilities and stack emissions methods for PFAS have only recently been developed. For example, the (US) Strategic Environmental Research and Development Program (SERDP) Project ER19-1408 (Ryan, 2020) undertook AFFF impacted soil treatment at a facility in Alaska and evaluated several emissions monitoring methods, including the draft EPA Other Test Method (OTM) 45, whilst employing pre-sampling surrogate recovery tests. Input soil concentrations of PFAS were lower than expected and while all emissions were below detection and reporting limits (<2µg/kg), non-target PFAS testing was not undertaken during this phase of works. It is noted that the US EPA are currently developing Other Test Method (OTM) 50 (OTM-50) to further assess PICs by employing canisters to quantify up to 30 volatile PFAS using GC/MS.

- Testing conducted at Clean Harbors' Aragonite Incineration Facility in Utah, US (2021) assessed the total PFAS mass flows from spiked feed inputs and AFFF as well as emissions via slag, spray dryer solids, baghouse dust, and stack gas. OTM-45 was employed for sampling stack gas. A fluorine mass balance was not quantified as PFAS loading was considered overwhelming compared to spiked materials. Analysis of PFAS mass flows was undertaken using the sum of 49 individual PFAS compounds (although TOP Assay was employed to AFFF feed wastes).

  Stack gas concentrations for all 49 target PFAS analytes were either not detectable, or if detectable results were near the limit of quantitation with an aggregate stack emission rate for all target PFAS on the order of 10^{-6} lb/hr. The total PFAS emitted from the system in the slag, spray dryer solids, baghouse dust, and stack gas were also considered very low (10^{-8} to 10^{-4} lb/hr for each stream) corresponding to Destruction and Removal Efficiency (DRE) of >99.9999% (for PFOS, PFOA, PFHxS and Gen-X).

- In 2021, the New York State Department of Environmental Conservation (NYSDEC) completed a study around the Norlite (Cohoes, New York) permitted hazardous waste combustor facility which had treated AFFF over a number of years. This study found no clearly discernible pattern of aerial deposition of PFAS that could be traced to Norlite's operations. Sampling identified low-level detections of PFAS compounds in all soil samples collected at upwind, downwind, and at background locations, consistent with emerging research on the prevalence of PFAS in urban, suburban, and rural environments. Concentrations of PFAS found in soils in the vicinity of the facility were below guidance values NYSDEC developed, indicating that the facility successfully destroyed the PFAS material and did not emit traceable amounts of PFAS during combustion (DOD, 2023).

Short-chain PFAAs require higher temperatures to achieve thermal destruction than long-chain PFAAs (Watanabe et al. 2016), so their formation as by-products during thermal treatment of long-chain PFAAs can further complicate the objective of achieving complete mineralization during incineration.

Within a scenario where soil is excavated and incinerated, treatment goals relate to contaminant source removal supported by effective delineation and demonstration by excavation validation sampling as well as potentially longer-term monitoring of relevant water resource receptors. The lines of evidence to verify effective treatment and support regulatory acceptance likely include demonstration of suitable incineration conditions and facility permits, materials (waste) tracking and transfer documentation as well as certificates of destruction (or country-specific equivalent). This can also include confirmation of suitable ash management / landfilling arrangements. Supporting evidence regarding stack emissions and PFAS analysis within ash and other by-products may also be valuable but may not always be possible or appropriate where mixed wastes are incinerated.

5.2.1.4. Suitability to Soil Properties and Co-contamination

Providing soils can be introduced into the HTI kiln then the process is not very affected by soil properties. However, soils with significant stones content or other debris may be unsuitable to some HTI facilities which typically process waste oils and solvents and thus pre-treatment via physical screening to remove such items may be required.

If HTI disposal is based on weight (tonnage) then the higher the water content, the higher the cost, as the water will increase both the overall weight and amount of energy needed to achieve required temperatures. Likewise, heavy debris within soils, if not screened out, can increase the weight and cost of incineration.

5.2.1.5. Operational Considerations

As HTI is an ex-situ, off-site treatment technology, the excavation, handling (including any pre-treatment), temporary stockpiling and off-site transport of soils must be carefully managed to ensure safety and effective materials segregation / tracking whilst avoiding cross contamination and nuisance issues.

It is understood that some HTI facilities (e.g., in the UK) can only accept soils within bulk bags and not in loose lorry loads. Thus, the addition of a soil bagging step, as well as any screening to remove stones, may also add to operational complexity.

5.2.1.6. Cost and Commercial Considerations

While typical municipal waste incinerators are widely present in the majority of countries and used for domestic and other non-hazardous wastes, HTI facilities employed for the destruction of hazardous waste are much less common. This can often result in long distances from the site of generation to the HTI facility which will increase the associated cost and environmental impact from transport. From vendor liaison, it is understood the HTI capacity across Europe is very constrained which would likely mean programme delays, slow treatment rates and potentially facilities being unable to accept PFAS impacted soils, particularly in large volumes. This is also related to the relatively low calorific value of most soils meaning soil would need to be blended with other wastes, reducing treatment rates.

The US Department of Defense (DoD) had previously issued a Temporary Prohibition of Incineration of Materials Containing PFAS’ (Cramer, 2022) while the US EPA evaluated and looked to provide further guidance on PFAS destruction and disposal options (US DoD, Report to Congress, February 2023). A recent US DOD interim guidance on the destruction or disposal of materials containing PFAS (US DOD, 2023), does identify hazardous waste incinerators with environmental permits as commercially available options although US EPA Destruction and Disposal guidance is pending and will provide an assessment of technologies for broad use across the United States. Washington state in the US has also issued a risk assessment of waste options, which view HTI in a favourable fashion (Washington State Department of Ecology, 2023).

If HTI disposal is based on weight (tonnage) then higher water contents results in higher costs. Although cost rates were not received following the vendor survey, Arcadis' have received previous costs for PFAS impacted soil using HTI in the UK and Europe (2019-2021) at between approximately 450-2,000 EUR/m^3, excluding transport.

Depending on the region, liability and ownership of the soil may be transferred upon acceptance by the HTI facility, but it should be ensured that the HTI facility operates suitable conditions for PFAS and that it is appropriately permitted.

5.2.1.7. Energy and Chemical Use and Sustainability Considerations

Sustainability considerations within the scope of this study are described in Section 4.4, and are done in a limited fashion compared to e.g. US-EPA Green and Sustainable Remediation (GSR) guidance.

HTI is very energy intensive involving high temperatures within the rotary kiln and subsequent gas treatment provided by burning fossil fuels such as gas or diesel. In addition, the transport of material to the HTI facility and any clean imported fill material (to replace excavated soils) can also add to the CO_2 emissions, traffic related impacts and resource use.

Despite that HTI may be suitable in certain-situations and for certain waste streams, and in some cases, it may be the only viable option for PFAS soil remediation, it should be noted that HTI is energy intensive and has a limited capacity given the volumes of potentially impacted soil present. It is recognised that these are observations based on a relatively limited sustainability considerations which is not a complete sustainability analysis. For more improved understanding on the sustainability aspects of HTI a deeper analysis is needed.

It is also noted that many of the potential by-products from PFAS incinerations are potent greenhouse gases. The global warming effects of CF_4 and C_2F_6 are 6,500 and 9,200 times higher than that of CO_2, and their atmospheric lifespans are 50,000 years and 10,000 years, respectively (Wang et al., 2013).

5.2.1.8. Case Studies

Available full-scale applications and other studies are summarised in Section 5.2.1.3.

5.2.1.9. Knowledge Gaps

As also discussed in Section 5.2.1.1 and 5.2.1.3, there have been concerns regarding the destruction efficiency and by-product formation during the incineration of PFAS, (most notably for liquids, for example AFFF) and consideration by the US EPA that temperatures over 1,400°C are required to destroy CF_4.

The US EPA note that the extent to which PFAS-containing waste material in the US is incinerated is not fully documented or understood. In addition, emission studies, particularly for PICs, have often been incomplete due to lack of necessary measurement methods suitable for the comprehensive characterization of fluorinated and mixed halogenated organic compounds. As noted, the US EPA have drafted OTM 50 to further assess PICs.

Performing a mass balance using known and quantifiable PFAS to demonstrated mineralization forming quantifiable concentrations of fluoride is the most credible approach to demonstrate that by-products have not accumulated. For wastes containing PFAS there are significant challenges to generating a mass balance, but chemical analysis could consider both linear & branched PFAS, advanced analytical tools (e.g., EOF and TOP Assay, Adsorbable organic fluorine (AOF)) and GC-MS analysis of short chains and by-products.

However, studies by Clean Harbors and the NYSDEC (Section 5.2.1.3) have provided significant additional information to address some of these data gaps and it is understood further similar projects are underway.

5.2.2. Cement Kiln Incineration

5.2.2.1. General Description and PFAS Removal Mechanism

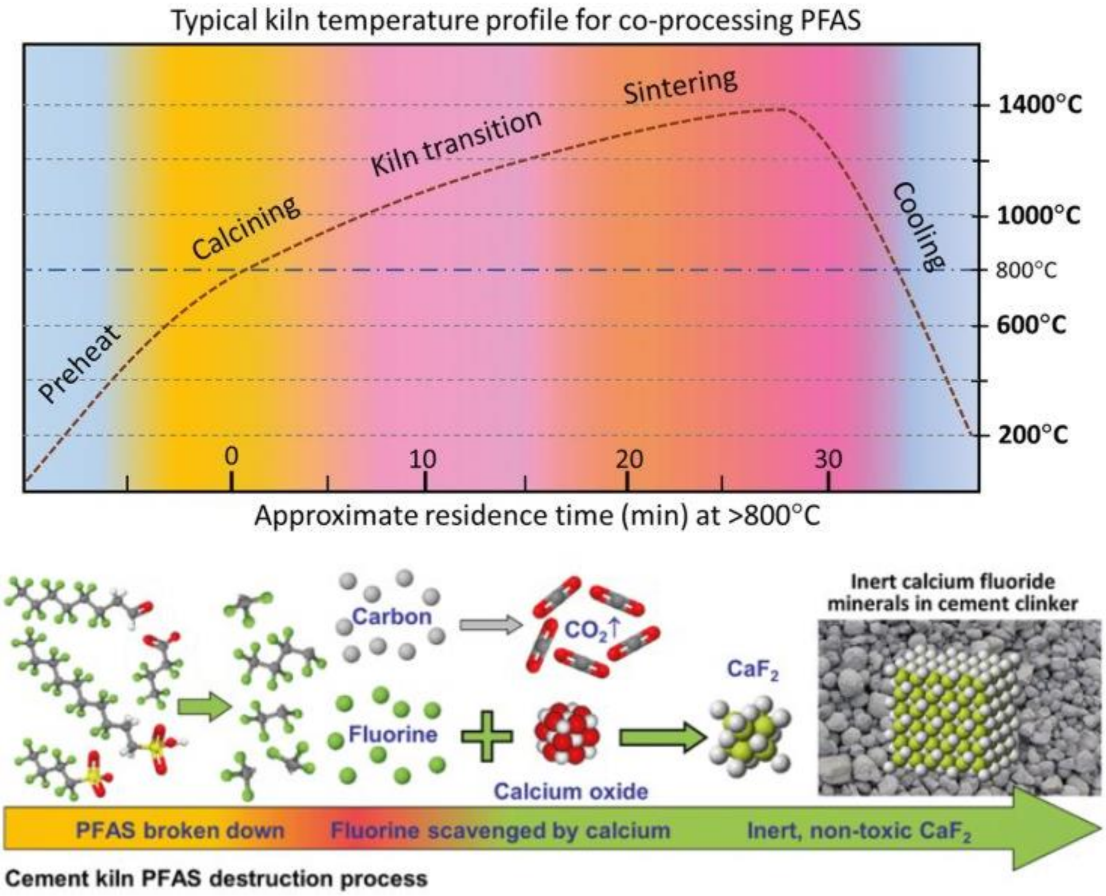
A cement kiln is a long, cylindrical, slightly inclined rotating furnace designed to calcine a blend of raw materials such as limestone, shale, clay, or sand to produce a key ingredient of Portland cement. Some of these cement kilns burn hazardous-waste-derived fuels to replace some or all of the fossil fuels. Most of them burn liquid waste; some may also burn solids and small containers containing viscous or solid hazardous waste fuels.

The co-processing of various hazardous wastes in rotary cement kilns is characterised by very high kiln temperatures (~1,200–1,400°C) with long residence times of the order of minutes (UNEP, 2011), as illustrated in Figure 10. Therefore, cement kilns accepting hazardous wastes are considered likely to achieve temperatures and residence times typically identified as suitable for PFAS destruction (see Section 5.3.1.1).

This approach has advantages over other HTI approaches as the co-incineration of PFAS containing material with calcium minerals can catalyse PFAS destruction and forms calcium fluoride (CF_2) which is a solid, stable and valuable by-product and thus limits the potential for gaseous fluorinated by-products. Several researchers, e.g. Wang et al. (2011) and Wang et al. (2013) have reported effective PFAS destruction and capture by combusting a mixture of PFAS waste in the presence of excess amounts of calcium minerals.

Cement kilns have incinerated waste ion exchange resins saturated with PFAS from Purolite’s production plant in Philadelphia (Patterson, 2020). In addition, high temperature destruction of PFAS in firefighting foam concentrates has been undertaken in Australia within cement kilns. For example, Cement Australia has been licensed to destroy 5 kg PFAS (as fluorine) per hour since 2018 with a summary of the process, shown below (Holmes, 2022) .

Figure 10 Typical Temperature Profile (above) and PFAS Destruction Process (below) for a Rotary Cement Kiln (reproduced with permission from Holmes and Klein, 2022, MDM Publishing)



5.2.2.2. Suitability to Treatment Scenarios

The majority of field scale application has been applied to AFFF concentrate disposal. Due to the high cost (relative to non-destructive methods) and limited capacity of cement kiln incineration, it is likely most suited to high concentration, low volume waste streams such as shallow soils from AFFF source areas (e.g., firefighting training areas, spillages) which would likely require effective delineation and pre-treatment. Highly impacted IDW soils are also potentially suitable as, the relatively low soil volumes may not justify other treatment approaches.

Cement kilns could also be used as the final destruction stage in treatment trains generating high concentration, low volume wastes such as soil washing fines, spent media and fractionated soil pore water.

5.2.2.3. Treatment Efficacy for Different PFAS Versus Treatment Goals

High temperature destruction of PFAS within firefighting foam concentrates has been undertaken in Australia (2016-2017) (Klein and Holmes, 2022). For PFAS input to both the calciner and main kiln, no PFAS were detected in emissions or cement clinker with PFAS destruction efficiencies for PFOS, PFOA and PFHxS of 99.999% or better.

Based on the PFAS destruction trial results, in 2018 the cement kiln licence was amended to allow destruction up to 5kg-F/hr of PFAS (approximately equivalent to the F-content of 1,000 L of foam concentrate) at minimum temperatures of 850°C in the calciner and 1,200°C in the main kiln. Analyses to monitor for PFAS in flue gases was conducted annually with no detections of PFAS (Klein and Holmes, 2022).

It is noted that firefighting foam concentrates are viscous liquids that may contain very high concentration of PFAS (e.g., 2-5%) compared with typical contaminated soil concentrations.

Within a scenario where soil is excavated and incinerated, treatment goals relate to contaminant source removal supported by effective delineation and demonstration by excavation validation sampling.

The lines of evidence to verify effective treatment and support regulatory acceptance likely include demonstration of suitable kiln conditions and facility permits as well as materials (waste) tracking and transfer documentation. Supporting evidence regarding stack emissions and PFAS analysis within cement products may also be valuable where possible. Any soil source removal may require supporting lines of evidence demonstrating effective delineation, excavation validation (sides and base) and potentially longer-term monitoring of relevant water resource receptors.

5.2.2.4. Suitability to Soil Properties and Co-contamination

Limited full-scale data is available regarding soil properties or co-contamination that might affect cement kiln incineration; however, it is considered that the process is likely robust and suitable for a wide range of soil types. The presence of calcium minerals (e.g., crushed concrete within made ground) may benefit the process in supporting greater capture of fluoride as CaF_2 and elevated organics content could provide addition fuel reducing energy requirements. However, certain soil constituents (e.g., heavy metals) could be undesirable if they remain in the finished cement product at above required levels.

5.2.2.5. Operational Considerations

The availability of cement kilns suitable and/or licensed to accept PFAS solid wastes may be limited in many regions potentially restricting the availability of cement kilns and increasing transport distances. In Australia, currently the Gladstone (Queensland) and Railton (Tasmania) cement kilns are able to process solid and liquid PFAS waste streams. In Europe, Arcadis are aware of one cement kiln in Austria that been approved to accept PFAS impacted soils, see Section 5.3.2.8.

Treatment rates for cement kilns may be low when considering bulk soil volumes potentially requiring treatment especially as soils require blending with other materials to ensure a suitable feed for cement production. This may extend remediation timeframes and/or introduce additional temporary storage costs. Pre-treatment, such as stones removal, may also be required.

In Europe, there is some debate about the addition of the PFAS contaminated soils in the engineered system of the cement kiln. If added on the "cold side", the PFASs would first evaporate before reaching the temperature zone of PFOS destruction. A flue gas afterburning system designed for this purpose would then be required. Cement kiln operators are therefore reluctant to expand their technology or open up to PFAS-contaminated soils.

5.2.2.6. Cost and Commercial Considerations

The costs for cement kiln incineration of soils were not available through vendor liaison, however, experience from Concawe members indicates costs available in France were 100-1,000 EUR/m^3.

5.2.2.7. Energy and Chemical Use and Sustainability Considerations

Sustainability considerations within the scope of this study are described in Section 4.4, and are done in a limited fashion compared to e.g. US-EPA Green and Sustainable Remediation (GSR) guidance.

Cement kiln incineration of a mixture of PFAS-laden media and a calcium sorbent can lower the total energy requirement by catalysing the breaking of the C-F organo-fluorine bonds at temperatures lower than 1,100˚C (around 800°C) with the fluorine rapidly captured as calcium fluoride, the mineral from which the fluorine was originally derived (Klein and Holmes, 2022) which is stated to support a circular economy approach.

Given the relatively low calorific value of most soils, cement kiln incineration still represents a highly energy intensive option for bulk soil remediation.

5.2.2.8. Case Studies

Available full-scale applications and other studies are summarised in Section 5.2.2.3.

Detailed reports on the incineration of AFFF concentrate are available via Cement Australia in relation to 2016 / 2017 trials at the Gladstone cement kiln.

While project specifics are not available, Arcadis are aware of a project to manage PFAS impacted soils resulting from fire training activities at a number of sites in Switzerland on behalf of a multinational pharmaceutical client. The approach involved loading soils into sealed shipping containers followed by rail freight to facilities near Linz, Austria. The principal purpose of the soil washing plant was to reduce soil concentrations to below the maximum permitted concentrations at the cement kiln. Washed soil fractions and fines were then recombined and sent to the nearby cement kiln for high temperature destruction including thermal oxidation of gas emissions. It is understood this is the first such project in Switzerland or Austria and has received approval from the Austrian authorities with notification and approval also by the Swiss waste authority.

5.2.2.9. Knowledge Gaps

While conditions appear highly suitable with advantages involving fluoride capture within the cement clinker, the number of studies and full-scale applications, particularly to soils, are relatively limited. While it is understood regular stack testing is undertaken at eth Gladston cement kiln, Australia, further assessment of PFAS and PICs via stack emissions monitoring at full scale across a range of soil types would be beneficial to confirm performance and to promote the option.

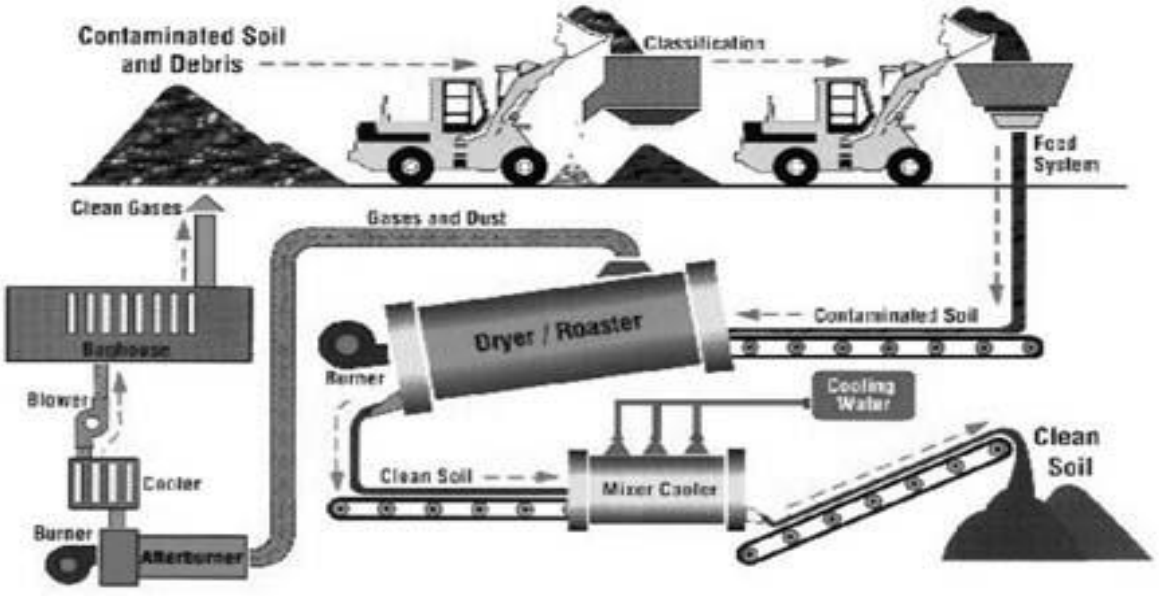
5.2.3. Thermal Desorption

5.2.3.1. General Description and PFAS Removal Mechanism

In contrast to HTI, which aims to thermally destroy PFAS via thermal decomposition and/or pyrolysis mechanisms at temperatures typically between 900 – 1,100°C, thermal desorption aims only to vaporise PFAS into the air phase from which they can be removed by air filters and/or scrubbers (Sorengard et al., 2020) for subsequent treatment. Vapourised contaminants and water are transported using a carrier gas or vacuum to a vapor treatment system.

Ex-situ application of thermal desorption can be via direct or indirect fired rotary dryers (Figure 11), or indirectly heated thermal screw type plants, which can be mobilised for large scale projects or, more commonly, as fixed facilities. In addition, ex-situ thermal desorption can be undertaken within thermopiles which are more modular and mobile where batches of soil are heated within engineered stockpiles. In-situ desorption, for example using thermal conductivity heating probes and Soil Vapour Extraction (SVE), has not be attempted for PFAS but is considered potential technically feasible given the temperatures indicated to be required (DiGuiseppi, 2019, ITRC, 2023).

Figure 11 Typical Ex-Situ Thermal Desorption Process for Remediation of Contaminated Soil (Reproduced from Gitipour et al, 2011)(Gitipour, 2011)



<u>Evaluation of Carcinogenic Risk Due to Accidental Ingestion of PAHs in Contaminated Soils</u>

Thermal desorption is an established soil remediation technology and has previously been shown to successfully remove persistent soil organic pollutants such as polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). However, application to PFAS impacted soil is primarily limited to bench and (some) pilot scale studies, although it is an area of active research and investigation.

The temperature range assessed in relation to thermal desorption is typically 350-550°C (Sorengard et al., 2020, Crownover et al., 2019, DiGuiseppi, 2019) which is above temperatures typically used for hydrocarbons, often termed low temperature thermal desorption (90 – 320°C) (FRTR, 2023), but below those required for thermal destruction.

Volatilised PFAS are envisaged to be treated via off-gas scrubbers to transfer them into a low volume liquid phase for subsequent treatment / disposal, potentially with additional gas phase treatment. Catalytic oxidation, as employed within this treatment could also be employed although it would significantly increased energy use and costs so limiting a key benefit of thermal desorption over HTI. Off-gas treatment remains a significant data gap (Section 5.2.3.9) and area of focus with concerns regarding PFAS release during incineration potentially acting as a constraint on the application of thermal desorption.

5.2.3.2. Suitability to Treatment Scenarios

Due to the relatively high cost of thermal technologies compared with non-destructive or pathway management approaches, it is likely most suited to high concentration, low volume waste streams such as shallow soils from AFFF source areas (e.g., FTAs, spillages). Highly impacted IDW soils could also potentially be suited to thermal desorption but this is more likely where sites are located close to fixed facilities.

Most sites will not be located close to fixed facilities with transportation costs likely being significant and so lead to careful targeting of excavation to areas of higher contamination. Where larger volumes of soils warrant mobilisation of thermal desorption plant then, once operational, it may become cost effective to use as an initial step then remediate greater volumes of soils with lower PFAS concentrations.

Ex-situ application via thermopiles involves less mobilisation effort and cost and so could be applied to source area and potential lower concentration soils although treatment rates are lower than with fixed plant and so project timescales and the requirement for additional thermopiles units should be considered.

As with any ex-situ approach, constraints regarding excavation access, depth, dewatering, excavation stability, subsurface obstructions and services will be relevant. Following treatment, resulting soils will have little organic matter to support plant growth but may be suitable for reuse as granular fill or sub soil.

Thermal desorption may also be applied within a treatment train to address high concentration PFAS wastes resulting from other treatment technologies such as the fines from soil washing (provided additional fines dewatering effort is involved). Application to spent media has not been well documented and while generally best undertaken within dedicated regeneration and reactivation facilities this could be investigated where soil and groundwater remediation is proposed.

In-situ approaches, in theory, would likely be targeted to higher concentration source areas and while potentially applicable to unsaturated and saturated soils, the temperatures required for PFAS volatilisation are likely challenging to achieve, especially where groundwater recharge is high. In addition, vapour containment from surficial soils is likely not possible and so is unlikely to be suitable for common PFAS soil contamination scenarios involving firefighting foam use with surface release.

5.2.3.3. Treatment Efficacy for Different PFAS Versus Treatment Goals

Thermal desorption has not yet been applied at full scale and the assessment of treatment efficacy has been carried out at the bench and pilot scale. These initial assessments have looked at the temperature and timeframe required to achieve PFAS desorption from soils and have not focused on effective off-gas treatment.

It is noted here that while previous studies have assessed the Vapour Energy Generator (VEG) technology provided by Endpoint Consulting, this technology is understood to no longer be commercially available.

No project references were provided by vendors as part of this study but available laboratory and pilot scale studies reviewed are summarised below.

- (DiGuiseppi, 2019) – Jacobs and Iron Creek undertook a series of field scale trial using a 1 ft^3 (0.028 m^3) batch-feed infra-red heating unit to treat AFFF impacted silty sand. Indirect, radiated heating was employed to assess temperatures of 250°C, 300°C, 350°C, 400°C, 550°C and 700°C at heating times ranging from 50 minutes to 8 days. 350°C was identified as the lowest effective temperature showing 99.4% removal of 29 different PFAS after 2 says. Longer heating times did not improve removal;

- (Crownover et al., 2019) – laboratory trials assessed vapour-liquid equilibriums and the removal of PFAS across a range of temperatures from (sieved) fine, silty sand collected from upper 2 ft (0.61 m) of a fire fighting training area. Soil was heated in at 220˚C, 300˚C, 350˚C and 400˚C for 10–14 days in sealed containers with volatilised PFAS routed under vacuum to a distilled water scrubbing unit.

  Assessment of vapour-liquid equilibriums found that that if the entire volume of water were to be boiled down, only about 0.05% of the PFOA and 0.4% of the PFOS would be removed from the system during boiling. Therefore, higher temperatures would be required for PFAS desorption (above those needed to boil water and remove soil moisture).

  Further results showed that heating soil to 350˚C and 400˚C reduced PFAS soil concentrations by 99.91% and 99.998%, respectively, including C_4-C_{10} PFAAs. Removal efficiency at 300˚C was not clearly linked to purely chain length for PFSAs, with PFHxS and PFBS less efficiently removed that PFOS. It was also confirmed that sulfonate-based PFAS generally required higher temperatures for volatilization to occur than carboxylate-based PFAS.

  PFOS concentrations were reduced from 21,000µg/kg to 17µg/kg and <0.2µg/kg at 350°C and 400˚C, respectively.

- (Sorengard et al., 2020) – in this study, two spiked soils (Σ9PFAS ≅ 4,000µg/kg) and one field-contaminated soil (Σ9PFAS ≅ 25µg/kg) were subjected to a 75-min thermal treatment at temperatures ranging from 150 to 550˚C. At 350˚C, soil concentrations decreasing by, on average, 43% and 79% in the fortified and field contaminated soils, respectively. At 450˚C, >99% of PFAS were removed from the fortified soils, while at 550˚C the fraction removed ranged between 71 and 99% for the field contaminated soil.

  The field soil was a silty clay, while the fortified soils were a clay soil and a sand soil. Lower PFAS removal efficiency was observed for the clay fortified soil (71%) compared within fortified sand soil (87%). The lower percentage removals from the natural soils were suggested to relate to either the lower initial concentrations and/or the naturally aged nature of the field soil. In some cases, an increase in PFBA was observed indicating degradation of unidentified precursors.

  PFAS classes with functional groups of sulfonates PFSAs and sulfonamides (FOSAs) showed higher removal than PFCAs which was not related to modelled vapour pressure.

  Overall, the experiment considered that the optimal temperature and treatment time for thermal desorption of PFAS is between 350˚C and 450˚C, and between 15 and 45 min to minimise the energy demand.

- (Edel, 2021) Züblin Umwelttechnik GmbH / University of Stuttgart – PFAS conatining soil samples were heated in a muffle furnace at 200˚C, 300˚C and

400˚C for ~14 hours soil achieveing reductions in PFOA concentrations of 58%, 94% and >99%, respectively. An outline treatment concenpt was proposed following the study targeting temperatures of 200-300°C via indirect heating, with SVE and exhaust air treatment via catalytic oxidation and/or alkaline scrubbing;

- (Wang et al., 2011) - this work demonstrated a reduced desorption temperature in the presence of lime and developed a calcium/fluoride (Ca/F) ratio to achieve the equilibrium efficiency. It was showed that PFOS can be decomposed/evaporated from the soil matrix at 350°C when lime is present in the solid mixture. Results indicated that with a Ca/F molar ratio above 1:1, a high degree of fluorine mineralization could be achieved within an very short period (1 to 5 minutes) at treatment temperature above 600 °C. Note that the focus of the work was to remove PFOS from soil matrix, rather than complete mineralization of fluorinated compounds in the gaseous phase.

While there appears to be agreement on the temperatures likely to be required to achieve effective desorption, the range in heating times varies considerably from minutes to days with most studies assessing granular soil with limited, if any, assessment of a broad range of PFAS in soils (e.g., precursors) or off-gas (e.g., ultrashorts).

It is noted that the range of temperature assessed and considered suitable reflect the boiling points of PFAAs and common PFAA precursors which are estimated to range from 80-211°C for PFBS, 120°C for PFBA, 133-249°C for PFOS up to 204-343°C for EtFOSAA (ITRC, 2023).

The lines of evidence to verify effective treatment and support regulatory acceptance likely include assessment of removal efficiency, residual PFAS concentrations in treated soil or soil leachate (compared to project / site specific treatment goals or reuse criteria), demonstration of effective vapour phase treatment, compliance with relevant treatment activity permits and documentation demonstrating effective management of any other wastes (e.g. destruction of PFAS within scrubbing liquids and/or activated carbon). Any other geochemical or geotechnical amendments to treated soil to enable reuse should also be recorded. Where treatment is undertaken off-site then appropriate facility permits must be in place and material (waste) tracking and transfer documentation must also be collected. Any soil source removal may require supporting lines of evidence demonstrating effective delineation, excavation validation (sides and base) and potentially longer-term monitoring of relevant water resource receptors. A robust characterisation of PFAS present, employing advanced analysis where appropriate (potentially supporting selection of site-specific indicator PFAS), is recommended prior to and following treatment (including any by-products) to demonstrate holistic treatment.

5.2.3.4. Suitability to Soil Properties and Co-contamination

Pre-treatment to remove debris and oversize materials is likely to be required to improve material handling and heat propagation. Disaggregation of cohesive soils may also be beneficial to improve treatment and handling with some studies showing reduced treatment efficacy in clay soils compared to sand (Crownover et al., 2019).

Soils with high organic content (e.g., peat) and moisture content, including saturated soils, are likely to involve significantly higher costs with air drying or lime application being potential pre-treatment options.

The presence of organic co-contamination is unlikely to represent a significant issue given temperatures applied are higher than those required for e.g. petroleum hydrocarbon PAHs and PCBs although the implications for vapour treatment must be considered (e.g., explosion hazards, increased media usage and costs). Inorganic co-contamination is likely to remain largely unaffected, beyond the oxidation of certain species, and so may require additional treatment. However, the leachability of metals and inorganics could be adversely affected.

5.2.3.5. Operational Considerations

For on-site treatment via fixed plant or thermopiles, significant areas of site may be requirement for the treatment plant, stockpiles and material movements. Any on-site thermal process is likely to require regulatory permits / licenses, notably for air emissions, which could take considerable time, especially given the lack of track record with this technology.

A key element is the source of heat whether this is from electrical, gas or diesel, and how easily and economically this can be delivered to the plant. Any readily available on-site sources can reduce costs.

Off-site thermal desorption considerations are similar to those for any off-site process such and excavation and disposal and relate to safe excavation management and suitable material storage, tracking and handling.

For ex-situ on-site approaches then a reuse or disposal route for treated soil should be identified. Any reuse would likely preclude plant growth media, without amendment, and handling of treated soils must consider increased dust risks.

5.2.3.6. Cost and Commercial Considerations

Estimated remediation costs were not received as part of this study, reflecting the lack of full-scale application to date.

The costs (per unit soil) were not estimated following previous field trial as undertaken by (DiGuiseppi, 2019) but were anticipated to be substantially lower than incineration and slightly higher than non-destructive options, such as ex-situ stabilisation.

The high costs with respect to soil washing and S/S was indicated to be a key constraint by some potential vendors. However, thermal desorption may be favoured option where soil washing and S/S are not available or suitable, for example, for cohesive soils where a suitable destination for stabilised soils cannot be identified.

5.2.3.7. Energy and Chemical Use and Sustainability Considerations

Sustainability considerations within the scope of this study are described in Section 4.4, and are done in a limited fashion compared to e.g. US-EPA Green and Sustainable Remediation (GSR) guidance.

Thermal desorption is considered to be less energy-demanding than incineration (Sorengard et al., 2020) reflecting the lower temperatures involved in volatilisation and vapour phase treatment via trapping / scrubbing rather than PFAS destruction. However, the carbon footprint of thermal desorption is likely significantly higher than soil washing or soil stabilisation, especially when the energy and impact of final PFAS destruction within scrubbing liquids is considered (e.g., GAC reactivation).

The energy use and environmental footprint is likely to vary considerably in relation to whether the approach is on-site / off-site or in-situ / ex-situ and will be highly project specific.

Reuse of treated soils is possible, for example as engineering fill or subsoil, although may require amendments but can, therefore, reduce resource requirements associated with clean imported fill (Sorengard et al., 2020).

5.2.3.8. Case Studies

No full-scale case studies were provided as part of the vendor liaison or identified during the literature review with bench and pilot studies summarised in Section 5.2.3.3.

5.2.3.9. Knowledge Gaps

Given the lack of full-scale application there remain data gaps regarding the demonstration of the logistics, costs and treatment performance achievable with this technology at full scale.

From the review of literature as well as bench and pilot studies, air emissions from the thermal treatment of PFAS have not been thoroughly studied and so there are data gaps regarding fate of volatilized PFAS and air emissions (ITRC, 2023). Given the potential for partial oxidation products such as short and ultrashort chain PFAS as well as the volatilisation of hydrogen fluoride, it is import for off-gas treatment to demonstrate liquid scrubbing and other processes are robust, for example, via direct sampling and fluoride mass balances.

Studies assessing desorption temperature have typically focussed on PFAAs and a limited number of known precursors. However, assessment of desorption across a wider range of PFAS is considered required given the lack of data regarding the boiling points of many precursor compounds and the potential for cationic and zwitterionic PFAS to sorb more strongly to some soil types.

While there appears to be agreement on the temperatures likely to be required to achieve effective desorption, the range in heating times varies considerably from minutes to days. Further assessment of thermal desorption for more cohesive soils would be of benefit with the majority of studies focussed on sandy soils to investigate likely treatment performance and any pre-treatment requirements.

5.2.4. Smouldering Combustion

5.2.4.1. General Description and PFAS Removal Mechanism

Smouldering combustion is a flameless, exothermic, oxidation reaction that occurs on the surface of a solid or liquid fuel which is sustained and propagated by oxygen / air supplied within a porous matrix. Smouldering can be self-sustaining after ignition, meaning no external energy input is needed provided a sufficient flux of air is provided; charcoal burning in a traditional barbeque is an example.

The combustion front propagates through the soil in the direction of airflow, oxidizing the contaminant and leaving treated, organic-free soil behind. The smouldering process for PFAS aims to achieve destruction of PFAS within the smouldering process itself, rather than volatilisation, with GAC to treat vapours typically employed to treat any PFAS in the gaseous emissions. Thus, achieving and sustaining the required temperatures as well as effective vapour management are key aspects to application.

When the contaminant is too volatile or its concentration in soil is too low, the soil can be impregnated with a surrogate fuel such as vegetable oil or wood chips to permit self-sustained smouldering (Duchesne et al., 2020). Similarly, as PFAS are not contaminants that can support smouldering combustion, like hydrocarbons and coal tars, a surrogate fuel is required.

For PFAS, the main focus for a surrogate fuel has been the use of spent GAC, used for PFAS water treatment, which is also treated within the process.

The smouldering process can be applied either in-situ, where it is termed STAR (Self-sustaining Treatment for Active Remediation) (Figure 12), or ex-situ, where it is termed STAR-X (Figure 13).

Figure 12 STAR: Source or Permeable Reactive Barrier (PRB) Treatment (Savron, 2023***)***

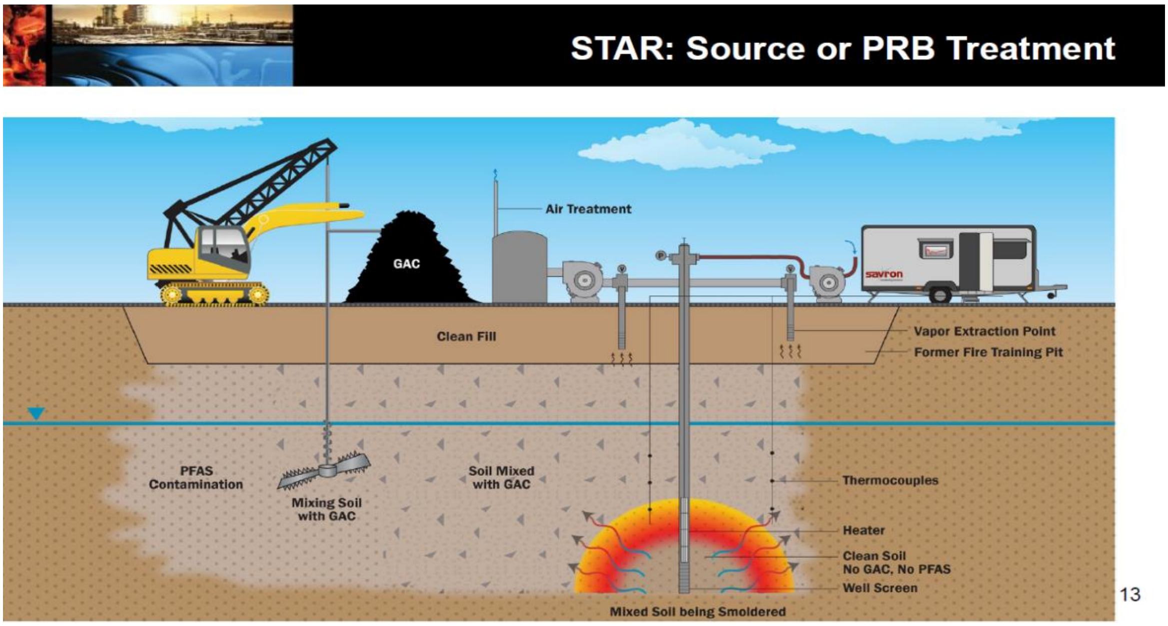
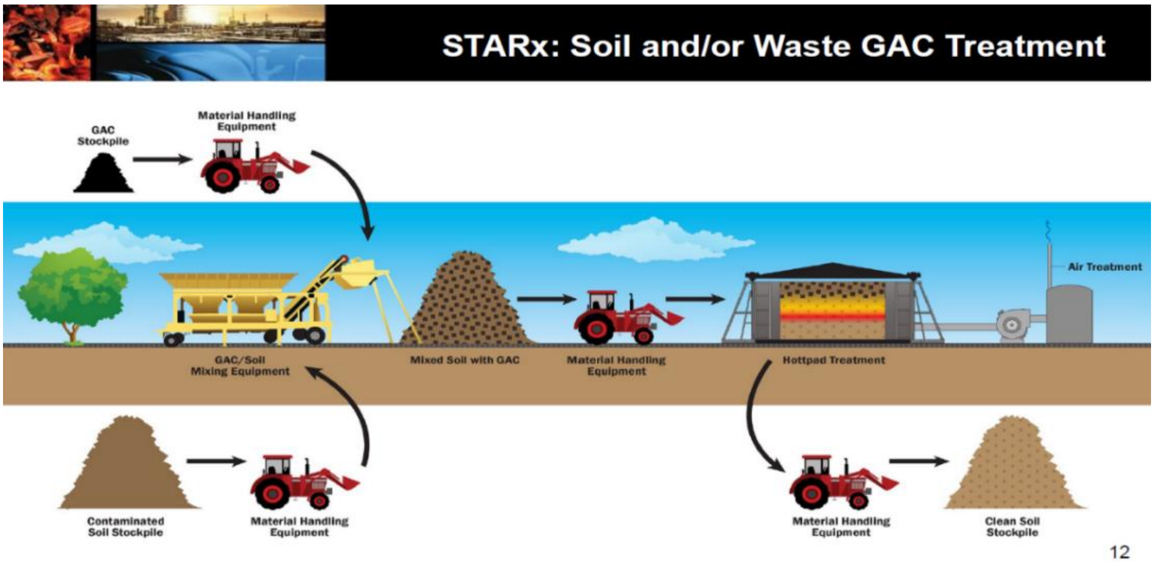


Figure 13 STARx: Soil and/or Waste GAC Treatment (Savron, 2023)



5.2.4.2. Suitability to Treatment Scenarios

Previous assessments have focussed on contaminated soils and IDW. Given the lower energy requirements compared to other thermal methods, as well as the on-site application, it may be cost effective to apply to soils outside the immediate source area, particularly as equipment would already be mobilised to site,

Laboratory studies have, in contrast to spent GAC, also assessed application to filter cakes and filter sands as well as fines resulting from soil washing.

5.2.4.3. Treatment Efficacy for Different PFAS Versus Treatment Goals

Current assessment and demonstration of the technology has primarily focussed on ex-situ application, as opposed to in-situ, and has included laboratory scale and pilot scale hot pads, but no full-scale application to date. These projects have included assessment of smouldering temperatures, propagation times, fluoride mass balance and PFAS removal assessing a wide range of PFAS compounds including via TOF.

Projects include works undertaken as part of the SERDP Project ER18-1593 (Major, 2019) as well as unpublished follow up work with information provided by Savron Inc. The treatment efficiency achieved during key projects is summarised below.

- Duchesne et al. (2020) – laboratory scale assessment involving GAC as a surrogate fuel. Target temperatures of >900°C were achieved (average peak temperatures of 1,145°C) with short and long chain PFAAs (C_4 to C_9) reduced to below detection limits (<0.4 µg/kg) in contaminated field soils (initial concentration 0.1-0.5mg/kg). Less than 1% of the initial PFAS contamination was released as vapour phase PFAS in the emissions;
- Major (2019) – SERDP Project ER18-1593, two phase assessment. Column tests indicated GAC was a better surrogate fuel than ground rubber. PFOA, PFOS and PFHxS in spent GAC / sand was treated to below detection limits. Contaminated soils with clean GAC reduced 6 PFAAs (primarily long chain) to below detection limits (0.5µg/kg) with 82% available fluoride captured as HF. Some conversion of PFSAs to PFCAs was observed with small amounts of PFAS detected in gas emissions;
- Harrison et al 2023 (unpublished) – laboratory column tests used field soils and PFOS-spiked GAC with CaO amendment explored to limit HF, VOF and PFAS emissions. Greater than 99.9% reduction in PFAS concentrations (23 PFAS compounds) were achieved for post-treatment soils in all experiments. Low concentrations of PFBS and PFBA (<0.008mg/kg) in selected tests. PIGE spectroscopy was used as a measure of total fluorine on post-treatment soils and emissions sampling train adsorbents showing >96% reduction in total fluorine (without CaO) with overall mass recoveries of 68-141%. PIGE also showed 90% reduction in total fluorine emitted from the column with the addition of CaO; and,
- Major et al 2023 (unpublished) - Pilot scale assessment of smouldering via an Intermediate Scale Reactor (ISR; 0.3 m^3 batch capacity) and a field-deployed pilot scale Hotpad (10 m^3 batch capacity). At pilot scale, >99.9% reduction in total PFAS compounds in post-treatment soil was achieved, residual PFAS compounds up to 1.34µg/kg detected in one test. TOP Assay and TOF analysis employed within similar results to individual PFAS tested. CaO employed reducing fluoride to <0.0003% of total fluorine mass. Vapour phase GAC was considered effective for gas treatment.

The lines of evidence to verify effective treatment and support regulatory acceptance likely include assessment of removal efficiency, residual PFAS concentrations in treated soil or soil leachate (compared to project / site specific treatment goals or reuse criteria), demonstration of effective vapour phase treatment, compliance with relevant treatment activity permits and documentation demonstrating effective management of any other wastes (e.g. destruction of PFAS within scrubbing liquids and/or activated carbon). Any other geochemical or geotechnical amendments to treated soil to enable reuse should also be recorded. Where treatment is undertaken off-site then appropriate facility permits must be in place and material (waste) tracking and transfer documentation must also be collected. Any soil source removal may require supporting lines of evidence demonstrating effective delineation, excavation validation (sides and base) and potentially longer-term monitoring of relevant water resource receptors. A robust characterisation of PFAS present, employing advanced analysis where appropriate (potentially supporting selection of site-specific indicator PFAS), is recommended prior to and following treatment (including any by-products) to demonstrate holistic treatment.

5.2.4.4. Suitability to Soil Properties and Co-contamination

Airflow through the soil is crucial to sustaining the smouldering combustion front and so granular soils with high soil permeability are best suited to smouldering, although some pre-treatment and mixing is normally involved, for example with GAC as a surrogate fuel, or sand which will increase permeability to some degree.

Soil moisture will significantly increase the energy required to achieve and sustain the required temperatures and so saturated soils, or soils with high moisture content (including from rainfall during storage / transport) will likely increase costs, timescales and potentially affect treatment performance. However, it is noted the technology is stated to be applicable below the groundwater table (Grant, 2023).

While the main focus for a surrogate fuel for PFAS impacted soil treatment has been the use of spent GAC, co-contamination with hydrocarbon fuels for example at FTAs could be beneficial as a carbon source in reducing or eliminating the need for surrogate fuels.

5.2.4.5. Operational Considerations

Any ex-situ application must carefully manage the excavation and soil handling works. Treatment can be undertaken on-site within hotpads, which will reduce / eliminate the need for off-site transport, provided suitable space and permits are available and emissions carefully monitored and managed, especially in sensitive locations.

Unless PFAS is co-contaminated with gross hydrocarbon contamination, in-situ application would likely involve soil mixing with a surrogate fuel which would involve large, specialised plant and consideration of utilities and any other subsurface obstructions. There could be initial bulking of soils due to surrogate fuel addition and effects on the soil geotechnical properties due to the removal of soil organic matter and soil moisture. Effective in-situ vapour containment and treatment is important as well as control of any influent groundwater.

5.2.4.6. Cost and Commercial Considerations

The self-sustaining nature makes smouldering require significantly less energy than HTI, or other thermal technologies and thus is likely to be lower cost, however, no cost ranges were provided as part of this study due to previous works being at laboratory or pilot scale. The overall application costs would be highly site specific and need to include plant mobilisation together with surrogate fuel supply and addition.

The technology is subject to patents, including two that are specific to PFAS remediation (in-situ and ex-situ) which have been granted in the US and Australia with pending patents in many other territories. Licensed distribution is via Cornelsen in Europe.

5.2.4.7. Energy and Chemical Use and Sustainability Considerations

Sustainability considerations within the scope of this study are described in Section 4.4, and are done in a limited fashion compared to e.g. US-EPA Green and Sustainable Remediation (GSR) guidance.

The self-sustaining nature makes smouldering require significantly less energy than HTI, or other thermal technologies which require continual energy input, as energy is only added at the start. The use of spent GAC as a surrogate fuel, if available, could also eliminate the need for fossil fuel addition as well as address another waste stream. However, smouldering combustion of GAC does not then allow for regeneration and reuse and spent GAC may not be available at suitable volumes and thus the treatment may require importation of a surrogate fuel.

Based on information provided by Savron Inc., the energy consumption in relation to the project summarised in Section 5.3.4.3 is between 90 and 242 kwh/m^3 with the pilot test project consuming 38-109 kwh/m^3.

GAC was the preferred fuel surrogate and mixed with sand or soil mixture between 35 and 60 g/kg soil (Major, 2019, Duchesne et al., 2020).

5.2.4.8. Case Studies

Available full-scale applications and other studies are summarised in Section 5.2.4.3.

5.2.4.9. Knowledge Gaps

While several detailed laboratory studies have been undertaken as well as pilot scale demonstration assessing key performance parameters and employing broad suite PFAS analysis, there has been no full-scale application to date, including across a range of different soil types. While CaO has been employed to reduce VOF and by-product emissions, the effective capture and treatment of VOF and PFAS by-products by vapour phase GAC requires further confirmation.

A key challenge at full scale is envisaged to be soil heterogeneity and soil moisture and the associated challenge to achieve and sustain the very high temperature required for PFAS destruction throughout the soil volumes treated. Insufficient treatment could place additional burden on gas phase treatment due to increased volatilisation, as opposed to destruction. This challenge would be increased within an in-situ smouldering application where achieving homogeneous soil permeability and fuel distribution would be more difficult, especially where groundwater is present. Repeat application of smouldering, if desired / required, is also challenging once the surrogate fuel is exhausted.

5.3. NON-DESTRUCTIVE APPROACHES

5.3.1. Ex-situ Soil Washing

5.3.1.1. General Description and PFAS Removal Mechanism

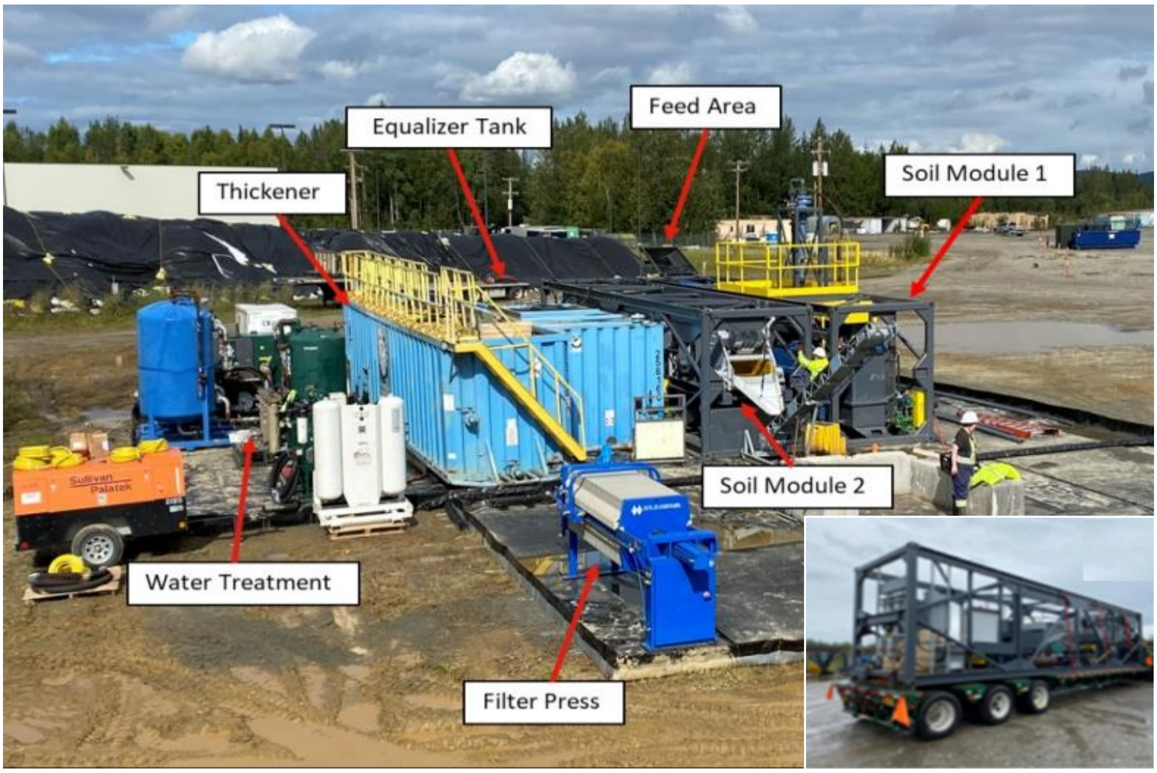
Soil washing is a physical and/or chemical separation-based remediation process where excavated soils are washed within a specialised plant to transfer PFAS from soil to process water and separate high surface area fines fraction, producing cleaned sands and gravels which can often be reused. Soil washing provides a means to separate PFAS from soils and concentrate contamination into a smaller volume and thus reduce the costs associated with any PFAS destruction (Grimison et al., 2023) or disposal.

Process water treatment is required to remove desorbed and dissolved phase PFAS as it is recirculated around the soil washing plant and typically employ GAC and/or Ion Exchange Resins (IERs) for this purpose, alongside fines separation and removal (Etard, 2023, Grimison et al., 2023). However, it is noted that some soil washing plants operate as a 'water consuming process' with water added throughout the process to separate fines without water treatment. Other plants do employ water treatment with some also using additional clean water rinses following initial washing (vendor liaison).

Treatment mechanisms involves the desorption and dissolution of PFAS from soils which, therefore, relates to PFAS chain length, head group charge as well as soil organic matter, particle size and mineralogy. These processes may be facilitated with water or can be enhanced chemically with, for example, surfactants. In addition, physical agitation and attrition alongside size and density separation are also important physical treatment mechanisms. As illustration, it has been estimated that ~71-90% of the PFAS mass was transferred to the process water (Grimison, 2020, Grimison et al., 2023).

The soil washing process is typically undertaken in a large, specialised plant including, for example, bulk feed hoppers, physical screening, log washers, wet sieves, high pressure jet washers, attrition scrubbing units, hydrocyclones, filter press, water tanks as well as process water treatment units. Soil washing plant can vary considerably in their components and can be fixed systems or more bespoke, mobile, modular systems (Figure 14). Typical aggregate washing plant, often used in the construction industry to produce secondary aggregates, are unlikely to be effective in achieving contaminant removal to a high standard.

Figure 14 Modular, mobile soil washing plant employed by Arcadis /CleanEarth, ESTCP Project ER20-5258 (Grimison et al., 2023)

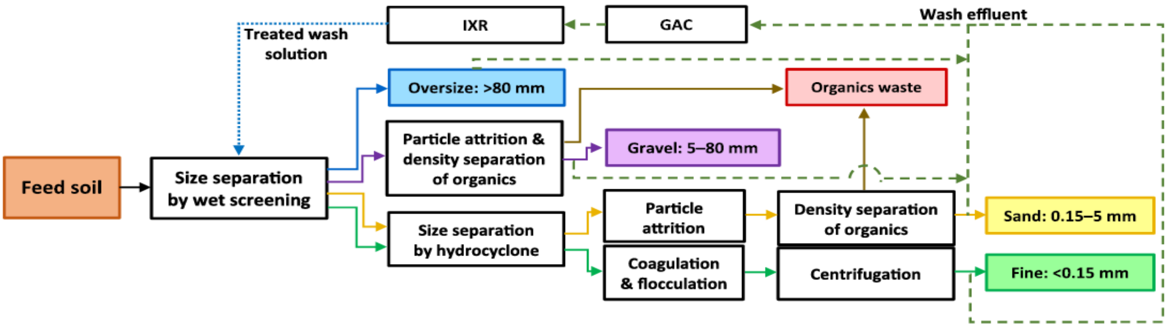


The soil washing plant employed at the Royal Australian Air Force (RAAF) base in Edinburgh, South Australia developed in 2018 is shown in Figure 15.

Figure 15 Soil Washing Plant employed at RAAF Edinburgh, South Australia developed by Ventia and CleanEarth Technologies (2018)

An example soil washing process flow diagram is shown in Figure 16, which is understood to reflect the plant employed at RAAF Edinburgh (Grimison et al., 2023).

Figure 16 Example Soil Washing Flow Diagram, RAAF Edinburgh (reproduced from Grimison et al., 2023). IXR – Ion Exchange Resin, GAC – Granular Activated Carbon.



5.3.1.2. Suitability to Treatment Scenarios

Soil washing may be suitable to a range of treatment scenarios and treatment trains which depend on several factors, including volume of soil requiring treatment, level of contamination, alternatives available and proximity to fixed soil washing plant.

For example, where large soil volumes require treatment and the distance to fixed facilities is large, then mobilising an on-site system may be undertaken and, in this situation, it may be cost effective to also remediate contaminated soils from outside the immediate source zone. Conversely, where off-site transport to a fixed facility is undertaken, excavation and remediation is more likely to be targeted to source zone soil only, given the proportional transport costs (Quinnan, 2022).

As the number of soil washing plants capable of effectively remediate PFAS impacted soils increase and/or the distance to facilities is relatively short, then smaller volumes, including IDW may be cost-effective to transport for treatment. Smaller, modular, mobile plant can also be deployed, reducing soil volumes required to justify mobilisation of plant for on-site treatment.

The fines volumes generated relate to the particle size distributions of soils and the type of soil washing plant needed can be estimated at early-stage design. The resultant fines must be effectively managed to prevent transfer of PFAS to the environment in other locations (e.g., by insufficient containment). This has typically been achieved via landfilling or thermal desorption (Etard, 2023, Grimison et al., 2023) although stabilisation of fines is considered a potential option, for example, as pre-treatment prior to landfilling. Reuse of fines may be possible depending on the level of treatment achievable and the site-specific risk associated with its reuse.

Addition of fixing reagents provides an option to stabilise the fines and organics while the materials are in a slurry form, which can be integrated in the process train. Portland cement can also be added to provide bearing capacity when the treated fines and organics are intended for post-treatment uses that involve subsequent construction.

5.3.1.3. Treatment Efficacy for Different PFAS Versus Treatment Goals

Several large-scale soil washing projects have been completed for PFAS impacted soils within recent years indicating this technology is becoming more widely used and accepted. A number of project references were provided by vendors which are summarised below, in relation to PFAS treatment performance.

- Quinnan (2022) – Arcadis / CleanEarth Technologies, ESTCP Project ER20-5258 - Bench scale design and field pilot with mobile soil washing plant treating ~ 180 tonnes PFAS impacted soil. Stringent US clean-up goals, including 3µg/kg PFOS in soil, 40ng/L in soil leachate were achieved for less impacted construction soils. Sum PFAS in source zone soils reduced >93% in sands and gravels (residual concentrations 32-40 µg/kg) but further treatment unable to be completed to achieve project goals;
- Grimison et al. (2023) – trial at large scale plant (Ventia/CleanEarth) treating 2,000 tonnes of AFFF impacted (sum of 30 targeted PFAS 216,000 µg/kg) clay rich soil. Removal of C_4-C_8 PFAAs range was 85.7 - 97.1% with 90% decrease in PFOS leachate concentrations. Washed soil below the 0.7mg/kg criteria for reuse as backfill (Grimison, 2020);
- Zublin UTY (vendor supplied information) – two large scale soil washing projects in Germany involving some PFAS impacted soils containing hydrocarbon impacts and debris components. PFAAs reduced in sands & gravels by 99.7% and Filtercake by 98% in one project. In the second project, residual PFAA concentrations were <2µg/L in soil leachate in all fractions;
- RAAF Edinburgh, SourceZone Trial, CDE Group – plant employed scrubbing and attrition processes (creating friction and scouring between particles) to achieve 90% PFOS and PFHxS removal from clay soils (same project as reported by Grimison et al. (2023)) and 98% removal in sandy soils. Hydrocarbon impacts noted to be also present. Over 10,000 tonnes of soil from RAAF Edinburgh and 1,500 tonnes from RAAF Williamstown treated. Estimated waste volume reduced to <0.6% of initial volume with treated soil below the 1mg/kg reuse criteria for reuse on site (Grimison, 2020);
- Royal Boskalis Westminster N.V –soil washing for PFAS impacted soils at their SBD Amersfoort treatment centre, NL. Full scale application to low concentration / high volumes granular soils was stated to achieve >50% reduction for short chain PFAS and >95% for long chain PFAS;
- DEME Environmental - bench scale trials in Norway and Netherlands for AFFF impacted sandy soils with debris achieving >95-99% PFAS reduction with <30µg/kg residual PFAS and analysis by TOP Assay; and,
- DEME Environmental – three full scale soil washing projects in Belgium treating 8,000, 33,000 and 25,000 tonnes of sandy soil with debris achieving residual PFOS <3µg/kg, PFOA <3µg/kg and PFAS <8µg/kg, respectively, in each project. TOP Assay employed on reused soils.

It is noted that soil leachability testing is increasingly being used alongside soil analysis to assess the performance of soil washing and suitability for reuse (Quinnan, 2022, Grimison et al., 2023) and it is important to consider and select soil leachate preparation and soil extraction methods which are, as far as practicable, representative for the reuse scenario (discussed in Section 3.1.2). For example, leachate preparation methods which grind soil samples may expose PFAS which are inaccessible to leaching (Grimison et al., 2023) and/or employ an acidified leaching solutions which may also overestimate actual leaching potential.

The lines of evidence to verify effective treatment and support regulatory acceptance likely include assessment of removal efficiency, residual PFAS concentrations in washed sands and gravel fractions soil or soil leachate (compared to project / site specific treatment goals or reuse criteria) and documentation demonstrating suitable fines and process water management including disposal / destruction. Assessment of a PFAS mass balance across washed soil fractions, fines and process water as well as waste volume reduction metrics are also likely valuable. Where treatment is undertaken off-site then appropriate facility permits must be in place and material (waste) tracking and transfer documentation must also be collected. Any soil source removal may require supporting lines of evidence demonstrating effective delineation, excavation validation (sides and base) and potentially longer-term monitoring of relevant water resource receptors. A robust characterisation of PFAS present, employing advanced analysis where appropriate (potentially supporting selection of site-specific indicator PFAS), is recommended prior to and following treatment (including any by-products) to demonstrate holistic treatment.

5.3.1.4. Suitability to Soil Properties and Co-contamination

The chemical properties of PFAS make it a good candidate for treatment by soil washing with typically high aqueous solubility for many PFAS and the ability to separate the fine grained fraction, and other organics, from the bulk soil as well as control the pH of process water if required (Quinnan, 2022).

However, solubility decreases with increasing perfluoroalkyl chain length alongside increasing soil: water partition coefficients and sorption to soil through hydrophobic interaction (for example, Nguyen et al., 2020; see Section 3.3). This was observed by Grimison et al. (2023) who observed soil washing was more effective in reducing concentrations of short-chain PFAS compared to longer-chain compounds. The authors note that long-chain compounds, especially $>C_8$, were the most resistant to leaching from the untreated soil which was consistent with other studies on AFFF contaminated soils.

Electrostatic interactions related to PFAS head group charge, soil surface charge and available soil surface area (e.g., high clay content soils) can also affect PFAS sorption to soils (Nguyen et al., 2020, Nickerson et al., 2020) with cationic and zwitterionic PFAS potentially harder to treat via soil washing in some soils. Modification of process water pH could be employed to change PFAS speciation and modify soil chemistry affecting surface complexation and electrostatic processes although short-chain PFASs were observed to be less sensitive to solution pH than long-chain PFAS (Nguyen et al., 2020).

Overall, soil washing is typically applied to granular, sandy soils (Abou-Khalil et al., 2022) as increased fines content may reduce treatment efficiency (Grimison, 2020) and increase the volume of residual filtercake requiring destruction or disposal. Historically, soil washing has been considered appropriate for soil with ≤ 40 percent fines content (Quinnan et al., 2022), however, this depends significantly on the specific scenario and associated costs of fines management. It is noted that removal of C_4-C_8 PFAAs in the range of 85.7 - 97.1% was achieved by the Ventia / CleanEarth plant on clay rich (61%) soils indicating that soil washing could be applied to more cohesive soils, albeit with some reduced efficacy.

The removal efficiency was found to be independent of the concentration of PFAS in some studies although feed concentration was still considered a potential cost driver at full scale (Grimison et al., 2023).

Several projects reviewed indicated co-contamination of treated soils with hydrocarbons and/or NAPL and debris (Section 5.4.1.3) with no apparent impact on treatment efficacy. This may reflect the multi-stage separation and treatment processes typically employed within soil washing plant and the established use of the technology to address a wide range of organic and inorganic contaminants.

Soil washing of concrete has not been undertaken, to the knowledge of the authors, but the porous nature of this material (Section 4.2) indicates this would be a challenging material type to treat effectively, although some concentration reductions are likely.

5.3.1.5. Operational Considerations

The full-scale soil washing plant employed at RAAF Edinburgh was stated to achieve soil treatment rates of 11tonnes/hr for clay rich soils and envisaged up to 30 tonnes/hr for sandy soils (Grimison et al., 2023).

Pre-treatment to remove debris, organic and oversize material is typically employed as part of the soil washing plant and, therefore, not typically required prior to soil washing.

Soil washing is typically a water consuming process with a net water consumption of 120 L/hr/tonne of soil treated observed by Grimison et al. (2023). The overall volume of water requiring treatment and the flow rates required remain a significant consideration to ensure sufficiently clean water to achieve treatment targets. In addition, the L/S (liquid to solid) ratio is a key operational metric with higher ratios typically improving treatment efficiency.

The distance to fixed soil washing facilities is a key consideration affecting project logistics and timeframes. Mobile soil washing systems can be transported to remote sites with impacted soil with modular design, meaning different elements can be scaled up to increase treatment throughput (Quinnan, 2022).

On-site application of soil washing is likely to require space for plant and material stockpiles as well as sufficient water supply. Off-site soil washing entails similar issues associated with any excavation-based remediation application, including constraints associated with depth, water ingress, access and subsurface obstructions.

The management (destruction or disposal) of fines is also a key operation consideration, especially during any application with both thermal and stabilisation techniques actively considered, especially where suitable landfills are not available.

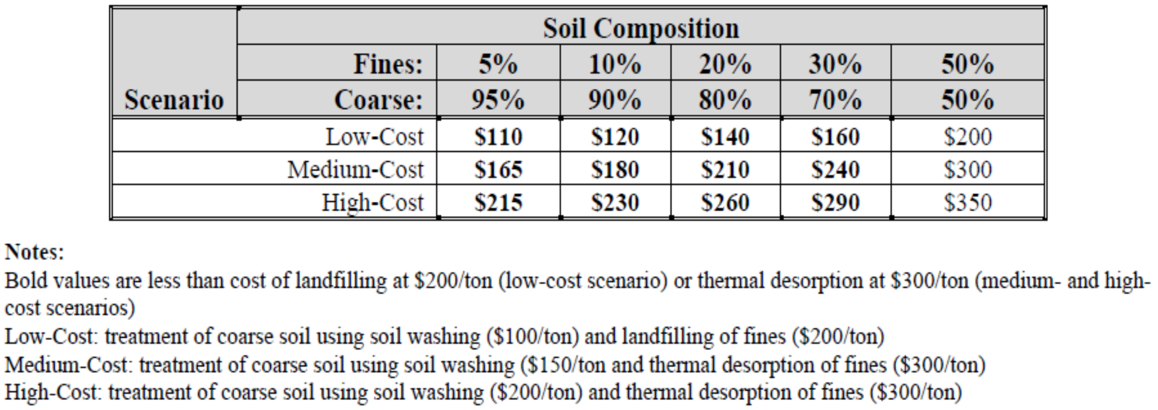
5.3.1.6. Cost and Commercial Considerations

Soil washing is an established technology and has been used on a commercial scale in Europe and the US since the mid-1980s to treat cyanide, petroleum hydrocarbons, PAHs, and metals (Quinnan, 2022). While the treatment of PFAS-impacted soil using soil washing is relatively new, multiple full-scale applications have been undertaken in recent years.

Based on the information reviewed during this study, the costs for soil washing PFAS impacted soils were stated to range between 25-160 EUR/m^3 in Europe, between 160-410 EUR/m^3 in US and approximately 120-150 EUR/m^3 in Australia. It is noted that the US costs are stated to include transport of soils (see Table 8), which can often be a significant proportion of the total cost, while the European and Australian costs ranges are assumed to relate to treatment and fines disposal only.

Work by Quinnan (2022) assessed soil washing costs under different scenarios including fines content, process complexity, distance to facilities and treatment targets to compare with landfilling in the US. This is reproduced in Table 8 for information.

Table 8 Soil Washing Costs Scenarios Compared to Landfilling and Thermal Desorption (Quinnan, 2022)



Scenario	**Soil Composition**					
	Fines:	**5%**	**10%**	**20%**	**30%**	**50%**
	Coarse:	**95%**	**90%**	**80%**	**70%**	**50%**
Low-Cost		**$110**	**$120**	**$140**	**$160**	$200
Medium-Cost		**$165**	**$180**	**$210**	**$240**	$300
High-Cost		**$215**	**$230**	**$260**	**$290**	$350

Notes:
Bold values are less than cost of landfilling at $200/ton (low-cost scenario) or thermal desorption at $300/ton (medium- and high-cost scenarios)
Low-Cost: treatment of coarse soil using soil washing ($100/ton) and landfilling of fines ($200/ton)
Medium-Cost: treatment of coarse soil using soil washing ($150/ton and thermal desorption of fines ($300/ton)
High-Cost: treatment of coarse soil using soil washing ($200/ton) and thermal desorption of fines ($300/ton)

Grimison et al. (2023) considered that the key drivers of treatment cost were a) total soil volume; b) particle size distribution of soil; c) operational constraints (e.g., limits on 24 hr/d treatment); d) concentrations of PFAS in soil feed; and e) treatment/performance criteria. In addition, the authors suggested costs could potentially be reduced with the development of a modular or mobile plant that will reduce setup time and infrastructure, like the one described in Quinnan et al. (2022).

5.3.1.7. Energy and Chemical Use and Sustainability Considerations

Sustainability considerations within the scope of this study are described in Section 4.4, and are done in a limited fashion compared to e.g. US-EPA Green and Sustainable Remediation (GSR) guidance.

Soil washing is a waste minimisation / volume reduction approach and so enables more energy intensive destructive approaches, or costly off-site disposal, to be targeted to a significantly reduced amount of material (i.e., the fines content) while the bulk soil is treated at lower cost and with lower energy inputs.

Soil washing does not involve high temperatures nor pressures and do not involve significant air emissions. Careful management and treatment of process water much be undertaken to ensure compliance and environmental protection associated with any discharges given the majority of PFAS mass is transferred to the process water.

Power usage during soil washing is estimated to be 3-21 kwh/tonne with the RAAF Edinburgh plant using 120 L/hr/t of water (Grimison et al., 2023).

Treated soils can also be beneficially re-used on site which reduces not only waste generation but also can replace requirements for imported clean fill material and the associated quarrying and transport impacts. Fines could also be stabilized to meet leaching-based standards, as an alternative to off-site disposal or treatment (Quinnan, 2022).

While an area still under investigation, chemical addition during soil washing has, to date been limited to flocculants within bulk process water being water only.

The development of a modular, mobile plant supporting increased on-site treatment of lower volumes may also help to reduce environmental and other impacts associated with transport of soils to off-site fixed facilities and importation of fill.

5.3.1.8. Case Studies

Available full-scale applications and other studies are summarised in Section 5.3.1.3.

5.3.1.9. Knowledge Gaps

Soil washing is an established technology but less well applied to PFAS with a limited but growing number of full-scale projects.

Given the range in different soil washing plant and limited full-scale applications, further establishment of the optimum plant and processes required to achieve target levels is desirable (e.g., attrition scrubbing, soil:water ratio). Especially when considering soils with an increasing fines content, where further studies to demonstrate the technology is viable and cost-effective would be beneficial.

Employing surfactants or pH adjustment to the process water has been found to be a potential benefit (Quinnan, 2022), especially given known PFAS partitioning behaviour, but limited large scale assessment of this has been undertaken.

Further assessment employing enhanced soil extraction procedures and soil leachate testing alongside advanced PFAS analysis would also provide greater confidence in the application to the wide range of PFAS likely present in AFFF impacted soils, especially as these relate to different soil types, as well as inform likely leaching potential post treatment.

Grimison et al. (2023) considered that integrating additional novel, destructive technologies into the current soil washing process represents an exciting development area for the future. Such destructive approaches would most likely be applied as a final stage of the process water treatment or for fines destruction.

5.3.2. Stabilisation & Solidification (S/S)

5.3.2.1. General Description and PFAS Removal Mechanism

S/S involves chemical stabilisation (fixation) and often physical solidification of soil by mechanically mixing the soil with binders and other additives to reduce leachability and/or bioavailability of PFAS and obtain the required geotechnical characteristics. The approach is also referred to as immobilisation.

PFAS are not destroyed during S/S but remain stabilised within soils in order to manage the potential risk of PFAS leaching to underlying groundwater requiring a durable and long-term solution given PFAS will not degrade over appreciable timeframes. Therefore, considerable focus has been on attempting to demonstrate, estimate and monitor long-term leaching reducing and durability for PFAS S/S within the laboratory and, increasingly, field applications. In addition, regulatory and stakeholder acceptance can be more challenging to obtain for stabilised soils left on-site (depending on the region) which can also represent and restriction on certain types of site redevelopment.

S/S is increasingly being considered as a means to pre-treat soil or other wastes streams (e.g., soil washing fines) prior to off-site disposal at landfill (see work by R. Stewart and H. Hinrichsen in Section 5.3.2.3).

The approaches to S/S for PFAS build on existing established practice for S/S in relation to metals, inorganic and (less frequently) organic contamination which often employ binders such as cement or lime along with other additives. However, for PFAS, approaches typically employ activated carbon (AC) based reagents, biochar and/or modified organoclays to provide hydrophobic sorption mechanisms. Certain reagents also include charged sorption sites and/or inorganic minerals to provide electrostatic interactions.

In addition to increasing the surface area for hydrophobic / electrostatic stabilisation, other approaches also employ binders (most frequently cement or bentonite) to provide physical solidification to lower soil permeability to reduce water ingress and leaching potential (Sorengard et al., 2021), as well as to provide geotechnical strength.

A key aspect of effective S/S application is achieving thorough mixing of soils with S/S reagents which can be achieved either in-situ, via specialised rotary mixing equipment, or ex-situ using pugmills, excavators or specialised excavator mixing buckets. S/S application is very site specific with the nature of the geology and depth of impacts often determining the mixing approach and any pre-treatment requirement (e.g., physical screening). Site specific, laboratory bench scale trials are typically recommended to assess PFAS leaching reduction, geotechnical performance, durability as well as determine cost effective reagent dosages and optimum water content.

Overall, S/S is increasingly being seen as a pragmatic and cost-effective option compared with many other soil remediation technologies for PFAS (Sleep and Juhasz, 2021) with on-going work to demonstrate durability and longevity to gain regulatory and stakeholder acceptance. Multiple full-scale S/S projects have now been completed globally indicating increasing adoption/acceptance, for example, Rembind state their product has been used to treat thousands of tonnes of PFAS contaminated soil at full-scale in North America, Europe, Australia and New Zealand with local regulatory approvals (Rembind Website, 2023). A photograph illustrating this can be seen in Figure 17.

The photograph in Figure 18 shows pilot-scale, in-situ application of S/S for PFAS supported by the Air Force Civil. Engineering Center (AFCEC) under a Broad Agency. Announcement (BAA-120) assessing FLUORO-SORB® and RemBind®™ with cement (McDonough et al., 2021).

Figure 17 Ex-situ application of RemBind®™ (Rembind Website, 2023)

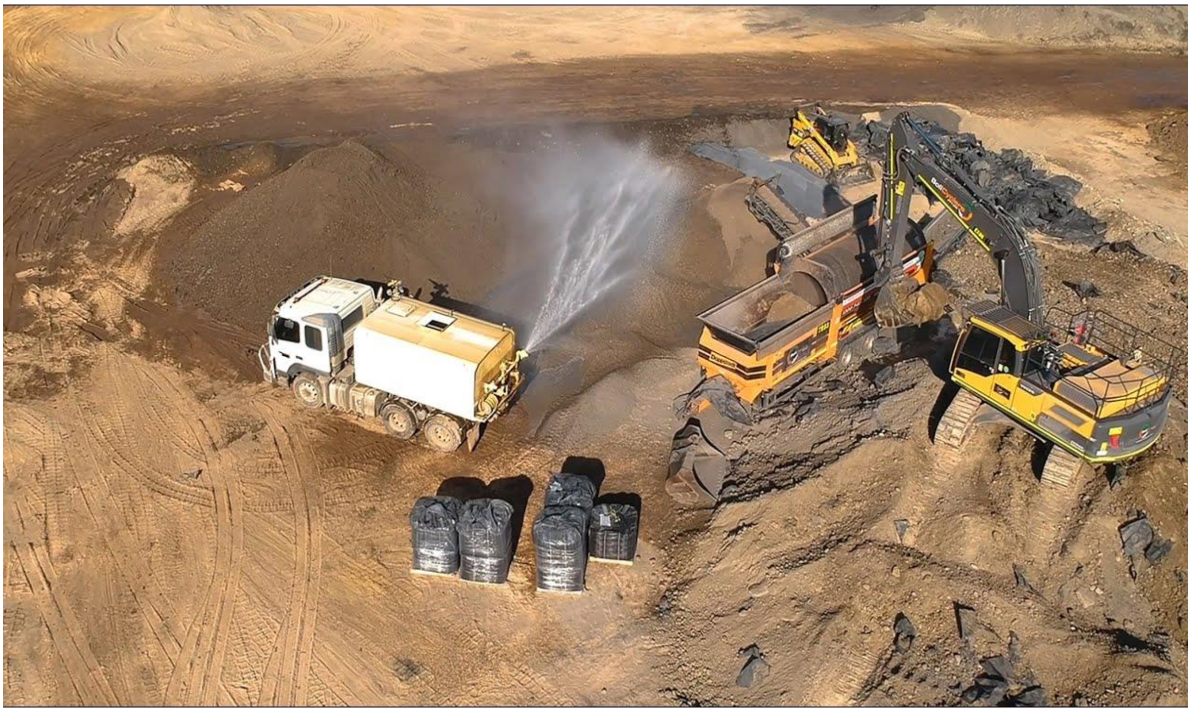


Figure 18 In-Situ Application of S/S for PFAS Treatment (McDonough et al., 2021)

Injection of Colloidal Activated Carbon (CAC)

In-situ injection of CAC into the subsurface has become increasing deployed as a means to sorb PFAS and control PFAS migration in groundwater, often as a barrier hydraulically down gradient of the source. CAC is injected into aquifer pore spaces along the length of the barrier which are often applied alongside source area treatment or where source areas are inaccessible. As with other stabilisation / immobilisation approaches, PFAS are not destroyed but sorbed to the AC and thus the efficacy and longevity of such approaches depends on effective reagent distribution and the mass flux of both PFAS and other competing organic compounds, including Natural Organic Matter (NOM), over time.

As this evaluation relates to soil treatment technologies, application of CAC for groundwater treatment has not been included. While more recent development of this technology has included application to source area, smear zone soils to reduce PFAS leaching into soil pore water and underlying groundwater. Delivery via injection or spraying reagent at the base on excavations is aimed to provide a layer at the base of the source zone to limit vertical migration of PFAS due to rainfall induced leaching.

Where CAC is applied alongside cement by direct mixing, this is included within the broader discussion of S/S.

PFAS S/S Reagents

Examples of products that have already been proposed and tested commercially for stabilisation of PFAS in soils include:

- Activated Carbon – including GAC and CAC (Sorengard et al., 2019b, Sorengard et al., 2021);
  - AC sorbent characteristics are influenced by its particle size, and carbon source (e.g., bamboo, coconut shell, coal, corn etc.). For example, Powdered AC (PAC) is generally reported to be more sorptive for PFOS and PFOA in solution than GAC, because of the former’s greater specific surface area resulting from its smaller particle size (Gagliano et al., 2020). Micron sized CAC is typically used for in-situ injections, often in a colloidal suspension to assist distribution.
- Modified Organoclays – including FLUORO-SORB®, matCARETM and E-Clay®.
  - Organoclays are typically modified by the addition of a Quaternary Amine Salt (QAS) to clays, such as smectite or palygorskite, which include aliphatic and/or aromatic alkyl groups to provide sorption of hydrophobic organic contaminants. In addition, the QAS comprise positively charged nitrogen groups, which alongside charged inorganic and metal species within the clay structure can also provide for electrostatic interactions. Certain clay structures can be pillared using molecular supports (props) to create basal separation of clay layers to provide access for larger molecules, sometimes referred to as ‘layered double hydroxides’ . Some organoclay products have also been used for PFAS water treatment and are supplied at different grades / particles sizes depending on the application.
- Composite Reagents – for example, RemBind®™.
  - Rembind®™ is understood to contain activated carbon, amorphous aluminium hydroxides (AlOH), kaolin clay and other additives. This is stated to provide treatment mechanisms including hydrophobic adsorption of organic compounds onto the surface of the AC, with the AlOH providing an irregular, charged and relatively large Internal surface area making it suitable for electrostatically binding a range of charged compounds (Rembind Product Overview, Z070-10, 02/18). It is now available as RemBind 100®™ and as RemBind 100X®™ which is described as an improved formulation for enhanced PFAS binding (Rembind.com, 2023).

- Biochar has also been assessed for PFAS immobilisation, however application to date has been at laboratory scale, including:
    - Pine derived biochar (Askeland et al., 2020);
    - Waste timber, coconut shell and wood shrub enriched designer biochar (Silvani et al., 2019)

Other additives that have been assessed but less frequently, and or with lower effectiveness than other approaches include unmodified clays such as bentonite, or montmorillonite, chitosan and calcium chloride (Sorengard et al., 2019a, McDonough et al., 2021).

5.3.2.2. Suitability to Treatment Scenarios

Studies reviewed and information provided as part of this report show S/S for PFAS has been assessed and/or applied, in most cases, to high concentration / low volume PFAS source areas to mitigate leaching to underlying groundwater. This reflects typical land remediation approaches to target the greatest mass of contamination and to manage risks to the environment in a cost-effective manner. Application of S/S in this manner may be combined with groundwater treatment or groundwater migration management works.

As is the case for S/S of other contaminants, application for PFAS contamination can involve amendment delivery via in-situ or ex-situ soil mixing. In-situ soil mixing can involve specialised rotary mixing augers or heads and can typically address deeper contaminated impacts, including saturated soils. More widespread, shallower contamination can be addressed either in-situ using excavator mounted mixing heads, driven rotavator style plant or excavation followed by ex-situ mixing. Excavation and ex-situ mixing are typically focussed on unsaturated soils to avoid the requirement for excessive dewatering and groundwater treatment.

In addition, several applications that address lower levels of PFAS contamination are reported during vendor liaison (summarised in Section 5.3.2.2), for example, to address PFAS identified in stockpiled soils following site redevelopment at an Australian airport site or associated with a new petroleum storage tank installation at a Swedish military facility.

While the majority of S/S applications are designed to enable on-site reuse of the soil, including modification to meet geotechnical specifications, several studies also undertook S/S in order to make soil more suitable and acceptable for off-site disposal at landfill. This was undertaken in relation to the Swedish military site facility as well as at an Australian Airforce base where space restrictions required off-site disposal (Section 5.3.2.2).

While less well established, there has also been some focus on application of S/S to address PFAS leachability and bioavailability from biosolids given conventional wastewater treatment plants poorly remove but tend to sequester PFAS to sludges and biosolids (Todd O. Williams et al., 2023), particularly facilities with inputs from industrial sources, and which can often applied to agricultural land (US EPA, 2020).

The application of CAC via injection at the base of the source zone or spraying reagent at the base on excavations is proposed by vendors to be undertaken alongside addition treatment at or near the surface (e.g. shallow excavation, S/S, capping). Spray application to excavation bases could be considered to address residual mass where further excavation is not possible, however, injection to smear zones should consider mass within overlying soils will represent an on-going source of PFAS. The potential for reinjection / reapplication of CAC should be assessed and accounted for based on the planned lifespan on the barrier.

5.3.2.3. Treatment Efficacy for Different PFAS Versus Treatment Goals

The immobilisation of PFAS during S/S is complex, with efficacy of immobilisation varying with soil properties including pH, clay and organic matter content, amendment properties, and molecular properties of the individual PFAS (Sleep and Juhasz, 2021)

PFAS are not destroyed during S/S but remain stabilised within soils at the location of placement with the risks managed through reducing leaching to groundwater or leachate. Therefore, typical treatment goals often involve soil leachate or leachability reduction targets which can be site-specific, risk-based targets (e.g., derived based on infiltrations rates and dilution to meet groundwater or drinking water quality standards) and/or reflect the soil usage scenario or based on source reduction / betterment of leaching potential. Higher reagent dosages have been applied in more environmentally sensitive locations (Braunig et al., 2021). In most cases, S/S design and validation are informed by site-specific laboratory studies for which a focus on ensuring the optimum mix design is implemented effectively at full scale via process controls alongside long-term groundwater monitoring and/or soil cores.

Several large-scale S/S projects have been completed for PFAS impacted soils within recent years indicating this technology is becoming more widely used and accepted. A number of project references were provided by vendors as part of this study summarised below, in relation to PFAS treatment performance.

- Braunig et al. (2021) assessed the immobilisation of 12 PFAAs in highly AFFF impacted (PFOS up to 13,400µg/kg) sandy soils using relatively high dosages (5-30%) of Rembind via batch leachate testing after 2 months and 3 years. Leaching and bioavailability of PFOS was reduced by up to 99.9%, at most sorbent application rates with the lowest reduction found for shorter chain PFAAs. The results indicated the sorbent continued to be effective in reducing PFAAs in leachate after 3 years. Sulfonate functional groups displayed a greater immobilisation efficiency than carboxylates of the same perfluoroalkyl chain length.

  The effect of PFAA chain length on leaching from treated soils were considered to indicate that the dominant binding mechanisms of PFAAs with RemBind®™ are hydrophobic interactions with AC components.

  Interestingly, increased concentrations of certain PFAA were also postulated to have increased due to the breakdown of polyfluorinated PFAA precursors to PFAA during the curing period.

- Sorengard et al. (2019a) assessed S/S at bench scale to treat aged, PFAS-contaminated soils spiked with 14 PFAS using 7 different additives at 0.2% concentration: PAC, Rembind®, pulverized zeolite, chitosan, hydrotalcite, bentonite, and calcium chloride. These were combined with binders comprising cement, fly ash and ground granulated blast-furnace slag at a 9:10 soil:binder-ratio. Batch (2:1 ratio of solid to liquid) leaching tests on S/S-treated soil revealed that leaching of 13 out of 14 target PFAS (excluding PFBA) was reduced by, on average, 70% and 94% by adding PAC and Rembind®, respectively. Longer-chained PFAS such as PFOS, were stabilized by 99.9% in all S/S treatments when PAC or Rembind® was used. The S/S stabilization efficiency depended on PFAS perfluorocarbon chain length and functional group, e.g., it increased on average by 11–15 % per CF3-moeity and was on average 49% higher for the PFSAs than the PFCAs.

- Sorengard et al. (2021) evaluated S/S at pilot-scale using 3 tonnes of soil contaminated with AFFF irrigation water applied for 6 months, simulating 6 years of natural irrigation. 15 % binder and 0.2 % GAC was compared with a reference soil assessing 18 target PFAS. Reduction in leaching was >97 % for PFHxA, PFOA, PFHxS and PFOS but low (3%) for short-chain PFPeA. Residual concentrations in leachate ranged between <MDL and 0.52 µg/l (PFOS).

  In addition, seven PFAS were tentatively identified using an automated suspect screening approach. Among these, perfluorohexanesulfonamide and 3:2 fluorotelomer alcohol were tentatively identified and the latter had low removal rates from leachate (< 12 %) in S/S treatment.

- Navarro et al. (2023) undertook a bench scale assessment of AC and biochar (5 sorbents) over 4 years (longevity) and via multiple laboratory leaching conditions (durability) following stabilisation of clay-loam and sandy-loam soils (2 and 14 mg/kg Σ28 PFAS). The different sorbents, which were applied at 1–6% (w/w). After 1 week all sorbents reduced leaching of PFAS >95%. Four years after treatment, the performance of the PAC sorbents did not significantly change, whilst CAC improved and reduced leaching of PFAS by >94%. The AC-treated soils appeared to be durable under repetitive leaching events (5 times extraction) and with minimal effect of pH (pH 4–10.5). In contrast, the biochars were affected by aging and were at least 22% less effective in reducing PFAS.

  For soils treated with AC, loss of performance was generally observed for short-chain PFAS (i.e., PFBS and PFCAs with C–F≤5) which was considered likely due to competition with long chain PFAS that are favourably immobilised via hydrophobic interactions, and the likelihood of repulsive interactions in the case of the negatively-charged AC.

  Other studies on the sorption of PFAA to biochar have found variable results, for example, Askeland et al. (2020) reported PFOS removal from leachate of up to 60%, however also concluded that the sorption mechanisms were weak and reversible.

- Dr Askeland, Study – pilot scale treatment with the addition of 1-2% RemBind®™ to stockpiled soil with relatively low PFAS impacts using three different blending methods. PFOS and PFHxS were assessed with 95% to 99.9% reduction achieved enable on-site reuse;

- Richard Stewart – field scale application of RemBind®™ to treat 1,500t of soil resulting from construction works at FTA at a Royal Australian Airforce Base in Townsville. Soil was treated prior to off-site disposal with a special treatment area also constructed at the landfill due to its high environmental sensitivity. 32 target PFAS assessed with 95% to 99.9% reduction achieved across all analytes tested;

- Ms H. Hinrichsen – S/S treatment using 1-2% RemBind®™ for ~1,000t of soil excavated as part of a new petroleum storage tank installation at an active military facility in Sweden. Relatively low PFAS concentration (<1,000µg/kg). 10 target PFAS assessed with 95% to 99.9% reduction of all PFAS analytes tested allowing on-site reuse and avoiding landfill;

- EnvyTech, Ms H. Hinrichsen – report that RemBind is currently used as a pre-treatment stage prior to the disposal of PFAS-contaminated soil at multiple reception sites in Sweden. By stabilising PFAS-contaminated masses using RemBind prior to the disposal of these masses, the risk of PFAS being found in the leachates is minimised which in turn minimises the negative impact of landfill sites on the surrounding environment.

- McDonough et al. (2021) undertook bench studies and field scale in-situ soil mixing to S/S AFFF impacted fire training area soils (>90% coarse sand) under a US Broad Agency Announcement (BAA-120) involving 28 months of post-application monitoring. RemBind®™ and FLUORO-SORB® were assessed at 5% and 10% dosages (also with cement 5-15%) plus a cement-only control within five 28m^3 test pits. TOP Assay was used with focus on PFOS, PFHxS, PFHxA and PFOA. Soil cores were collected with sustained decreases (>98-99%) in target PFAS leachability (via LEAF leachate testing) observed for all mixes, relative to the control pit, over 28 months. The use of TOP Assay indicated some potential polyfluorinated PFAS leachability but at an order of magnitude lower than the cement control. The importance of throughout soil mixing was stressed given some variability in results and visual observations;

- Envirotreat – Laboratory study assessing stabilisation of PFOS impacted soil and lagoon sediments at a UK manufacturing site comparing E-Clay stabilisation with convention OPC solidification. E-Clay was combined with cement (addition % unknown) and achieved a 98.5% reduction in 10:1 batch PFOS leachate concentrations (13,200ng/l to 200ng/l);

- Envirotreat – Full scale application using PFASorb® E-Clay in the UK at a former fire station to address source area soils as well as trench emplacement as a PRB along the downgradient site boundary. The PFASorb® was produced on-site and delivered to excavation and trenches as a slurry. The source area application achieved an initial 97% reduction in PFOS with average leachable PFOS in eluate of 628ng/L (disaggregated batch leaching test);

- CETCO, Study – Full scale application of FLUORO-SORB® undertaken at the Comox Canadian Forces Base (CFB) - Canadian Department of National Defence (DND) with 22,000 m^3 of AFFF-impacted soil stabilised. The works were supported by a treatability study which found comparable performance between FLUORO-SORB® application (without cement) at 1% and 2% with 6.3% of the initial PFAS mass leached over the leaching period (USEPA LEAF Method 1314);

- Wang et al. (2021a) undertook bench scale batch experiments comparing modified bentonite clays, GAC and biochars and found significant decrease (95%-99%) of leachable anionic PFAS, including PFOS, PFHxS and PFOA, was achieved in 1-4 days at a clay dosage as low as 0.5% w/w. A significant decline of leachable cationic and zwitterionic PFAS (70%-99%) was also observed. The clays performed the best in immobilizing PFAS anions, while granular activated carbon was effective in preventing PFAS cation leaching. Hardwood biochar had minor or negligible effects on any PFAS.

- A commercially available product, 10% MatCARE (based on modified clay), showed a higher sorption capacity for PFOS than commercially available AC, and minimal release (0.05-0.31%) of PFOS over a time period of a year was observed (Das et al., 2015).

- Regenesis (2022), Technical Bulletin describes laboratory studies using AFFF spiked site soils within columns containing either a layer of ‘SourceStop’ CAC (spray applied) or PAC, compared to a control without AC. Simulated rainfall leaching (via the Synthetic Precipitation Leaching Procedure) at pH 5 over a total of 102 inches of rain was assessed. PFOS, PFOA and PFBS were assessed with leachability (as a percentage of the total spiked mass) reduced to 0.05%, 0.2% and 0.6% respectively. The Source Stop CAC provided an order of magnitude better leaching reduction that PAC with an estimated 86% of the CAC remaining in the column.

There is also increasing focus on assessing PFAS bioavailability, as well as leaching, for S/S approaches, particularly in relation to biosolids or other agricultural or domestic soils (Todd O. Williams et al., 2023). Results of work by (Braunig et al., 2018) showed that the sum PFAS concentration in grass shoots grown in biosolids amended soil treated by GAC or RemBind at 2% was only 2.8% and 3.4% of the sum PFAS concentration detected in shoots grown in biosolids amended soil without a sorbent.

The lines of evidence to verify effective treatment and support regulatory acceptance likely include soil processing records demonstrating soil mixing is undertaken in accordance with the design (which is typically informed by site specific laboratory and/or pilot testing) and that required reagent dosages and moisture content have been achieved and soil has been effectively mixed. Samples or stabilised soil can be collected and stored during mixing or collected via core sampling post treatment for leachate assessment and comparison to agreed PFAS and geotechnical treatment goals.

Monitoring of underlying groundwater or surrounding surface water features is often required (and prudent) which may extend into multiple years to demonstrate that PFAS leaching reductions achieve the treatment goals and generate data supporting longer term treatment durability. Alongside this, cover layers and long-term access / activity controls to ensure stabilised soils are not disturbed are likely prudent. A robust characterisation of PFAS present, employing advanced analysis where appropriate (potentially supporting selection of site-specific indicator PFAS), is recommended prior to and following treatment to demonstrate holistic treatment.

Soil Leachate Methods for S/S

The leachate preparation methods (described in Section 3.1.3) used to assess S/S performance are also important to consider. For example, batch leachate preparation methods such as the ASLP (Australian Standards, 2019) or CEN tests (CEN/TC 292/WG) typically involve disaggregating and crushing stabilised material and thus exposing more surface area to leaching than would likely be the case in the location of placement. While potentially providing an unrepresentative overestimation of leaching (at least in the short to medium term) these are easy and quick to undertake and have been used to provide an indication of the worst-case leaching scenario i.e., complete failure and disaggregation of the stabilised material. The liquid:solid (L:S) ratio, extraction time and number of extractions are also important to consider with higher L:S ratios and longer extraction times considered more aggressive (Navarro et al., 2023).

The extractant solution pH can influence PFAS leaching by altering soil surface chemistry and PFAS speciation. For example, the SPLP (U.S.EPA, 1994) is undertaken at acidic pH to mimic rainfall, but this may increase electrostatic retention of anionic PFAS.

Sequential or multiple batch leachate preparation methods, such as the MEP (U.S.EPA, 1992) or certain LEAF leaching methods (US EPA SW-846, 2017) provide for successive leaches over time and can employ different solution pHs but are still generally undertaken on particle size reduced samples. The exception are semi dynamic tank leaching methods, such as LEAF Method 1315 or EA NEN 7375:2004 which are undertaken on stabilised, moulded monolith samples exposed to eluate for a series of leaching intervals interspersed with eluent exchanges over an extended time frame (63-64 days). This allows assessment of diffusion-based leaching from intact samples and subsequent modelling of long-term leaching which is more likely representative of the real-world scenarios.

Longevity and Durability of S/S for PFAS

Overall, data from lab and projects reviewed strongly suggest that PFAS leaching can be mitigated via S/S and this method is increasingly been considered as an effective and pragmatic option for PFAS contaminated soils. There has been an increasing number of studies directly assessing durability and longevity of S/S for PFAS as well as field scale applications with several years of post-mixing monitoring (summarised and referenced above in this section).

However, concerns remain regarding the long-term effectiveness and suitability of S/S for PFAS, particularly in countries where S/S for other contaminants is less well established, which mirror concerns in relation to the use of S/S for other contaminants.

It is noted that PFAS share some similar properties to certain metals, such as arsenic and chromium, in terms of their non-biodegradability, solubilities and chemical speciation (oxy-anionic forms) which have a much longer track record for being treated by S/S. For example, the PASSiFY study, ‘An Examination of the Long-term Stability of Cement-treated Soil and Waste’ (Hills, 2010) assessed 10 sites up to 16 years of age with different soil/waste types and conclude that treated material from all the sites met the objectives of the original remedial treatment. This opinion was reinforced by the post treatment 5-year reviews conducted by the USEPA on three of the sites and the 10- and 15-year reviews for one of the sites investigated. The authors note the experience of 50 years use of S/S in the US with no reported major failures (contaminants include heavy metals, PAHs, PCBs and dioxins). A literature review was also undertaken including on weathering rates, augmented by laboratory and modelling studies suggesting that the long-term performance of S/S waste-forms might be significant and extend into ‘geological timescales’.

The efficacy and longevity of injectable CAC to source area smear zones, like barrier type applications, depends on effective reagent distribution and the mass flux of both PFAS and other competing organic compounds, including NOM, over time. This principally relates to rainfall and infiltration rates which govern PFAS leaching rates. Reduced adsorption capacity and shorter breakthrough times for short chain PFAS compared to long chain via AC is also well documented (e.g. (McCleaf et al., 2017, Hansen, 2010) with removal of precursors less well studied but indicated in one study to breakthrough before PFOA and PFOS (Xiao et al., 2017). Sorption to AC is finite and the lifespan of the application should be carefully designed and monitored with costs and plans for reapplication incorporated into any strategy. Addressing PFAS mass within overlying soils is also a critical factor for longevity.

5.3.2.4. Suitability to Soil Properties and Co-contamination

As the soil mixing process during S/S homogenizes geological anisotropy, it facilitates contact with PFAS across a broad range of soil types including low permeable strata or adsorbed at phase interfaces (McDonough et al., 2021).

However, there are some limitations associated within certain geologies which can hinder certain soil mixing approaches and/or require specialised equipment. For example, highly consolidated and high shear strength soils may not be amenable to mixing using certain equipment and may limit depth of in-situ applications. Chalk soils are also understood to present challenges to in-situ mixing. Ex-situ mixing of cohesive soils may require pugmills or blending with more granular material in order to ensure effective reagent distribution. Also, in many cases, pre-treatment to remove cobbles, stones or oversize debris is required to protect mixing ex-situ equipment.

Natural and stabilised moisture content are critical soil parameters to determine, typically from site-specific characterisation and laboratory studies, to ensure geotechnical specifics are met, particularly when natural soil moisture may change e.g., when mixing above and below the groundwater table, when mixing different soil types or when excavated soils may be exposed to rainfall.

Kabiri and McLaughlin (2021) considered that the main environmental factors that would affect PFAS sorption over time were temperature extremes and ionic strength. The sorbent assessed (Rembind) showed no detrimental effects with temperature extremes or changes in ionic strength with effects of competing ions were also absent or minimal. However, in unremediated soils increasing concentrations of orthophosphate and humic acid (competing anions) increased leaching of some long-chain PFAS.

In relation to soil pH, leached concentrations from the AC treated soils were found to be higher under alkaline conditions (Navarro et al., 2023). Overall, pH affected the leaching of PFAS with C–F<6 (like PFBS, and PFHxA) to a greater extent than PFAS with C–F≥6 (like PFHxS, PFOS, and PFOA). This trend was considered likely due to the weaker hydrophobic interactions as PFAS chain length decreases, with increased repulsion between the negatively charged surface and PFAS. However, (Lath et al., 2018) showed that environmental ranges of pH and ionic strength did not adversely affect the binding of a specialized amendment to PFOA.

There are reports in the literature of adsorptive retardation being correlated with NOM and clays (i.e., metal oxide surfaces) with the divalent cationic speciation of calcium considered to present the potential to serve as an electrostatic linkage between anionic functional groups and promote the formation of supramolecular structures (McDonough et al., 2021).

The effect of co-contamination on PFAS S/S has not been widely studied or referenced although some studies / projects do note the presence of hydrocarbon and/or NAPL contamination without apparent adverse effect on performance. It is understood that levels of high organic contamination and NAPL can adversely affect some cement-based S/S mix designs, but the technology has been applied to address coal tars and creosotes at several sites (CLU-IN, 2023). Clay-based stabilisation approaches as well as those employing AC are less reliant on encapsulation and solidification mechanisms but may experience competitive sorption by organic co-contamination.

In relation to injectable CAC to smear zones, the permeability of soils as well as the presence of any Light Non-aqueous Phase Liquid (LNAPL) within such smear zones could limit effective reagent distribution. The range of groundwater fluctuation should be accounted for to ensure appropriate targeting of any barrier layer.

5.3.2.5. Operational Considerations

There are several important operational considerations regarding the application of S/S at a project site which are common to S/S and not generally related to PFAS.

For any application approach, the geotechnical specifications and optimum water content are key design parameters which should be established (including via site specific laboratory trials), monitored during application and validated. Soil mixing is typically undertaken as a ‘wet mix’ or a “dry mix”. The “wet mix” approach means that soil moisture is increased above the soil’s ‘liquid limit’ with treated soil allowed to self-weight compact. In the “wet mix” soil moisture is optimized for compaction and then soil is mechanically compacted. These application options should be considered during initial design.

The use of binders such as cement, are increasingly being employed to encapsulate contamination and reduce soil surface area to further reduce leaching as well as provide geotechnical strength. If stabilisation with only AC or clay-based reagents are considered, then it should be ensured that the resulting geotechnical strength is suitable for the future site use.

If stabilised material is to be left in-situ or on-site then subsequent disturbance of this material should be avoided completely, or as much as possible, to ensure PFAS are immobilised as per the intended design. Disturbance could relate to building foundations, utilities or tree roots and may also occur in the long-term future. This can obviously place restrictions on potential site redevelopment in terms of the areas which can be redeveloped and/or or the type of end use. Capping layers and/or geotextile membranes may be placed over the stabilised material to protect and demarcate the treated soil.

Addition of S/S amendments and increased water content will, in most cases, result in bulking of the soil, unless compaction of loose soil is undertaken. This bulking factor is site specific and should be assessed and accounted for. For example, it is common to remove the top 0.5-1.5m of surficial soil to allow for this, or, if treated soils are to be taken off-site for disposal, then increased volume and weight should be expected.

As discussed in Section 5.4.2.2, in-situ soil mixing can typically achieve treatment to greater depths including below the water table but will be limited by subsurface obstruction and utilities. In-situ mixing adjacent to building foundations is also avoided due to stability concerns. Ex-situ mixing entails similar issues associated with any excavation-based remediation application, including constraints associated with depth, water ingress, access and subsurface obstructions. In addition, a careful plan to determine the optimum sequence of excavation and replacement is typically developed with soils excavated in cells, allowing sufficient curing time before adjacent excavation.

S/S can be applied on-site or prior to off-site disposal to landfill. On-site application will typically require a large plant, significant space (e.g., stockpiles, reagent storage) and a good water supply. The process can involve significant soils handling with mud generation and materials management needing careful controls to avoid cross contamination, nuisance issues and disruption to site activities.

5.3.2.6. Cost and Commercial Considerations

Immobilisation/stabilisation is one of the most developed and studied approaches for treating soils contaminated with PFAS (Navarro et al., 2023). Its application is increasing and it is viewed as a pragmatic, cost effective (Sorengard et al., 2021) and sustainable option, especially for cohesive soils. Soil washing is a suitable method given PFAS' challenging properties and the lack of alternatives. However, regulatory and stakeholder acceptance can be variable, especially in regions with limited history of using S/S for other contaminants (notably outside the US and UK, for example, in Belgium, Germany, Denmark).

Commercial costs for S/S are likely to be highly dependent on the soil characteristics, contamination depth and treatment volume as well as the quantities of reagents required.

Based on the information reviewed during this study, the costs for S/S PFAS impacted soils were stated to be site-specific but ranging between 75-113 EUR/m^3 for RemBind®™, 35-45 EUR/m^3 for Envirotreat with no costs provided for FLUORO-SORB®.

Capital costs for mixing and amendments in the US were estimated to range between approximately 240 EUR/m^3 to more than 490 EUR/m^3 (converted from $150 to more than $300 per ton) (Quinnan, 2022).

Overall, S/S is considered as a likely cost-effective strategy to address PFAS impacted soils, especially when compared with thermal treatment /disposal options, and comparable to the cost for soil washing, with technical and operational factors likely driving technology selection.

The cost for source area, smear zone applications of injectable CAC were not provided by vendors during this project.

5.3.2.7. Energy and Chemical Use and Sustainability Considerations

Sustainability considerations within the scope of this study are described in Section 4.4, and are done in a limited fashion compared to e.g. US-EPA Green and Sustainable Remediation (GSR) guidance.

S/S reagent addition rates assessed and used within projects reviewed during this study were typically between 1% and 5% with binder (typically cement) addition rates between 5% and 15%.

While some studies have observed significant leachate reduction within reagent (modified clay) addition rates as low at 0.5% (Wang et al., 2021a) and other treatability studies found similar performance at 1% and 2% FLUORO-SORB® dosages, it is understood that a field application rate of 2% FLUORO-SORB® was selected in that example to facilitate effective reagent distribution.

The application of S/S does not involve high temperatures or pressures and do not involve air emissions and so is a less energy intensive option compared to most thermal remediation with a lower carbon footprint.

It can often be undertaken on-site with treated soil then reused thus reducing the environmental and other impacts associated with contaminated soil and imported backfill transport. The reuse of soil also minimises waste to landfill, reducing the need for new resources for clean, imported fill and can also provide additional leaching reduction (hence environmental protection) for soils destined for off-site disposal.

5.3.2.8. Case Studies

Available full-scale applications and other studies are summarised in Section 5.3.2.3.

5.3.2.9. Knowledge Gaps

While S/S there have been increasing number of studies directly assessing durability and longevity of S/S for PFAS, as well as field scale applications with several years of post-mixing monitoring, some concerns remain regarding S/S longevity and the importance of longevity assessments.

Further studies should consider conditions that may be more representative of field aging (e.g., sequential wet/dry or freeze/thaw cycles) assessed at multiple time points for a more accurate depiction of long-term remedial performance as well as the need to explore sorbents that can immobilise short-chain PFAS given the limitations of most sorbents with respect to leaching of short chain PFAS (Navarro et al., 2023).

While site specific laboratory trials are recommended there is also need for further field scale deployment to generate longer term validation data sets as questions remain about how well results obtained in laboratory-scale tests can be used to predict long-term durability and stability in the field (Sorengard et al., 2019a). The type of leachate preparation method is important and has been discussed above (Section 5.4.2.3).

Available data is often limited regarding the range of PFAS assessed, such as PFAA precursors e.g. by TOP Assay or TOF, although there is indication such PFAS are also likely to be amenable to S/S (McDonough et al., 2021).

5.4. PATHWAY MANAGEMENT APPROACHES

5.4.1. Landfilling

5.4.1.1. General Description and PFAS Removal Mechanism

Excavated PFAS contaminated soils as well as other PFAS containing wastes, such as crushed concrete from construction and demolition activities, can be transported to landfill facilities for disposal. This can provide a rapid and complete removal of PFAS soil source sources from leaching to underlying groundwater.

In contrast to other POPs, PFAS do not biodegrade within the landfill and are much more soluble and mobile with PFAS routinely detected within landfill leachate from sites across the world at concentrations often significantly higher than other POPs, see e.g. (Harrad et al., 2019). Several studies have found the distribution of PFAS in landfill leachate tends to be dominated by shorter chain (C_4-C_7) PFAAs likely indicating their generation within the landfill from biotransformation of PFAA-precursors, the greater mobility of short chains and reflecting the industrial shift towards shorter-chain (Hamid et al., 2017, Lang et al., 2017). Fluorotelomer Alcohols (FTOHs) have been found to dominate in air emissions (Zhang et al., 2023). The time period over which a landfill receives waste, the type of waste and the PFAS manufacturing and usage practice at the time are all factors determining the presence and types of PFAS potentially present. A more detailed assessment revealed the presence of a 5:3 fluorotelomer carboxylic acid (5:3 acid) as the dominant PFAS in landfill leachate (Lang et al., 2017).

Given the persistence of PFAS, they will very likely be present beyond the operational lifetime of the receiving landfill with the operator typically responsible for demonstrating residual wastes remain controlled and do not present a long-term risk to human health or the surrounding environment in order to obtain the landfill permit. PFAS may prove more challenging than many other contaminants in this regard.

The PFAS removal mechanism associated with landfilling includes initial source removal from the site but ultimately relies on landfill leachate treatment to remove then preferably destroy PFAS. This may be undertaken at the landfill site or leachate may be discharged to a WWTP. However, it is widely understood that PFAS are poorly removed by typical WWTPs, which typically employ physical (solids removal) and biological processes with PFAS able to re-enter the environment via treated water discharge (particularly short chain PFAS) or via sludges and biosolids (particularly long chain).

Leachate treatment technologies include biological, physicochemical, sorption (e.g., AC) and membrane separation technologies but may often not be suited to PFAS removal and/or may result in PFAS sludges requiring further management. Foam fractionation has recently been deployed to remove PFAS from landfill leachates (Zhang et al., 2023) and it is understood that some US landfills are treating leachate with specialised cement then using the material as daily cover(Concawe, 2021).

The presence of an effective landfill liner system, often absent in historic landfills, is an important factor in whether PFAS may leaching into underlying groundwater and surrounding environment (Harrad et al., 2019, USEPA, 2020a, Zhang et al., 2023).

Therefore, the removal / management of PFAS at landfill will be highly dependent on the construction of that landfill, the leachate management systems and permit requirements. This varies considerably between countries and discussed further in Section 5.4.1.2. However, it should be noted that PFAS are often not tested or treated in leachate, therefore removal mechanisms may not substantially exist and PFAS may be simply moved from one location to another where they may enter the environment. Any disposal route should be fully assessed on a case-by-case basis to ensure it is considered appropriate for PFAS.

The US EPA recently co-published a literature review of PFAS landfill disposal (Thabet Tolaymata, 2023) which made the following conclusions:

- Unlined Construction and Demolition landfills present a significant source of PFAS to the environment;
- An estimated 7.5 metric tons of PFAS enter MSW landfills annually;
- Annually, 460 kg of PFAS emitted via landfill gas, 750 kg via landfill leachate; and
- Based on the results of multiple studies, it is estimated that 84% of PFAS loading to MSW landfills (7.2 T total) remains in the waste mass, while 5% leaves via LFG and 11% via leachate on an annual basis.

Within a scenario where soil is excavated and landfilled, treatment goals relate to contaminant source removal supported by effective delineation and demonstration by excavation validation sampling as well as potentially longer-term monitoring of relevant water resource receptors. The lines of evidence to verify appropriate disposal and support regulatory acceptance likely include demonstration of appropriate facility permits, effective treatment or management of PFAS within leachate and materials (waste) tracking and transfer documentation.

5.4.1.2. Suitability to Treatment Scenarios

Landfilling for PFAS wastes, as with other contaminants, may be preferred where other technologies are not available or technically feasible, where smaller volumes of material don’t warrant implementation of on-site remediation (for example, IDW) and/or where rapid source removal is required to facilitate development.

Landfilling is most cost effectively targeted to shallow, unsaturated soils in source areas where PFAS contamination is typically higher, rather than larger areas with lower concentrations, due to the costs of haulage and disposal. In addition, disposal of PFAS impacted concrete may be desired as remediation approaches are less established and potentially more challenging and where this material is not suitable for reuse.

In many cases, the fines fraction generated during soil washing is also brought to a landfill (Section 5.3.1).

5.4.1.3. PFAS Waste Thresholds

These are discussed in Section 3.6.1.

5.4.1.4. Availability of Landfills for PFAS Wastes

There is a wide variety in awareness and acceptance among landfill operators regarding PFAS impacted wastes. In some countries regulations regarding PFAS disposal are absent or limited while others may be reluctant to accept PFAS impacted wastes or require dispose of material as a hazardous waste, regardless of its classification. It is not possible to summarise the situation within every country but some illustrative examples are provided below.

In the UK, awareness of PFAS amongst landfill operators is variable with most PFAS wastes classified as non-hazardous and thus able to be disposed to landfill at relatively low cost as the operating permits often do not include PFAS. While this is currently legal, it may simply move PFAS to other locations and enable PFAS to re-enter the environment. The low cost of landfill also limits the drive to deploy PFAS soil remediation technologies.

In the US, a recent US DOD interim guidance on the destruction or disposal of materials containing PFAS (US DOD, 2023), does identify hazardous waste landfills (with environmental permits) and solid waste landfills (with environmental permits and composite liners and leachate collection and treatment systems) as commercially available. This is broadly in line with US EPA guidance (US EPA, 2020) however, the US EPA states that care must be taken to ensure proper containment or destruction controls are in place with a lack of data noted regarding wastewater treatment technologies as many landfills are not required to treat leachate for PFAS. However, PFAS are now required to be tested for in discharges from EPA-issued National Pollutant Discharge Elimination System (NPDES) permitted sites (US EPA, 2022). Increasing pressure on PFAS discharges from these and similar WWTPs has led to some WWTPs restricting inputs from landfills (and other PFAS sources).

In Germany, the number of landfills currently accepting PFAS is understood to be very limited (only two at the time of writing) with federal/provincial guidelines specifying that leachate treatment (either on-site or off-site) must be designed to remove PFAS which must then be destroyed. The reuse of PFAS-containing soils can be undertaken according to classification via soil leachate values in three categories (Federal Environment Agency, 2022).

Overall, there is often significantly restricted hazardous waste landfill capacity in many jurisdictions with limited development of new landfill void space.

5.4.1.5. Pre-Treatment of Material Prior to Landfill

Given the limited assessment and/or treatment of PFAS within many landfills, there is increasing focus on undertaking pre-treatment of PFAS-impacted soils or material prior to landfilling to address regulatory requirements, manage future liability and/or provide a more robust, long-term solution.

Traditional, pre-treatment approaches such as targeted excavation, material separation and segregation are relevant to PFAS in order to minimise water volumes, in particular the removal of larger gravel and stones.

In addition, pre-treatment has also involved S/S to reduce leaching of PFAS prior to the closure and sealing of the landfill as well as increase acceptance by landfills, especially where PFAS thresholds are not in place. This is summarised in Section 5.3.2 with key projects summarised below.

- Henrichsen, GM EnvyTech, Markyard Site, Sweden (2018/2019) – approximately 3,000 tonnes of PFAS impacted soil required disposal as part of site redevelopment but the landfills approached would not accept the material. Following laboratory trials, soil was stabilised with 3-5% Rembind to enable acceptance at landfill with stones and large gravel removed prior to stabilisation and reused. The case study states a similar approach was planned for ~60,000 tonnes of soil in future;
- Richard Stewart, Study / Project 5 – field scale application of RemBind®™ to treat 1,500t of soil resulting from construction works at FTA at a Royal Australian Airforce Base in Townsville. Soil was treated prior to off-site disposal with a special treatment area also constructed at the landfill due to its high environmental sensitivity. 32 target PFAS assessed with 95% to 99.9% reduction achieved across all analytes tested;

As with disposal itself, pre-treatment requirements vary from country to country and is an area subject to ongoing research.

5.4.1.6. Suitability to Material Types, Soil Properties and Co-contamination

As is the case for any waste disposal, the waste must be fully characterised and classified based on the nature of material and all the contaminants present to ensure they are disposed of in appropriately permitted facilities. Provided this is undertaken, different soil types and the presence of co-contamination should be able to be managed via disposal at landfill. Although it may be the case that problematic material for disposal e.g., saturated soils, gross co-contamination or material with odours or high organic content, present a greater concern for disposal compared to any PFAS content.

There is increasing awareness and generation of PFAS-impacted concrete which may require disposal, particularly from locations which are repeatedly exposed to firefighting foams from testing and/or training. Impacted concrete, once crushed, is typically assessed and amenable to landfill disposal. While PFAS can penetrate within concrete surfaces it may be able to segregate upper surfaces or assess average concentrations within stockpiles.

It is noted that, increasingly, other material types from site development and demolition such as fire suppression system tanks, pipework as well as a range of other construction materials are being generated and require disposal or recycling. This an area of active research considering, for example, the degree of equipment decontamination required, residual PFAS assessment (e.g., via swab sampling), appropriate thresholds and impact on material circularity as well as how PFAS are managed via disposal routes such as scrap metal recycling.

5.4.1.7. Operational Considerations

In general, operational considerations relate to excavation and materials management in common with other types of contaminants with PFAS presenting little addition hazards or considerations. However, given the mobility of PFAS and the low levels which can present an issue, greater emphasis should be placed on material segregation and stockpile controls to ensure there is no cross contamination of PFAS.

5.4.1.8. Cost and Commercial Considerations

The long-term liability associated with disposal of PFAS-impacted wastes at landfills should be carefully considered including whether the leachate containment management processes are appropriate. The legal and reputational implications should be considered, especially as regulations, disposal practices and awareness in the disposal industry is changing rapidly. This is complex and country specific but, while rare, in many jurisdictions regulators may look to the original producer of the waste should pollution issues be identified in the future. This is likely a complex exercise given the presence of PFAS within a huge range of landfilled wastes but robust characterisation and tracking of all wastes is prudent. This risk is increased given the mobility of PFAS and their persistence way beyond the operational lifespan of a landfill.

Costs for landfilling are highly dependent on the availability of appropriate landfills within each country, the nature of the waste and presence of other constituents as well as haulage. Costs may simply reflect typical non-hazardous or hazardous disposal rates but higher costs may be incurred in some situations to ensure appropriate disposal is undertaken. Landfilling may remain to be a cost-effective option, particularly for lower waste volumes.

5.4.1.9. Energy and Chemical Use and Sustainability Considerations

Sustainability considerations within the scope of this study are described in Section 4.4, and are done in a limited fashion compared to e.g. US-EPA Green and Sustainable Remediation (GSR) guidance.

Excavation and disposal will require a basic plant, commonly diesel fuelled, to dig and transport wastes to landfill as well as natural resources to supply and transport clean backfill. Such transport is often a key sustainability consideration especially for large soil volumes associated with traffic, noise, dust and increase accident risk of vehicle movements.

In addition, unless PFAS are effectively removed and destroyed from landfill leachate then landfilling simply moves PFAS contamination from one location to another and does not break the cycling of these persistence contaminants within the environment.

5.4.1.10. Case Studies

Based on professional experience, disposal of PFAS-impacted soils to landfill is undertaken in many jurisdictions but typically not communicated via company case studies. However, examples where pre-treatment has been undertaken prior to landfilling are summarised in Section 5.4.1.5.

5.4.1.11. Knowledge Gaps

There has been considerable focus on the assessment of the presence and types of PFAS within landfill leachate as well as factors affecting leaching as it is a key pathway by which PFAS can re-enter the environment. However, there often remain data gaps in relation to specific facilities.

Based on professional experience, there is significant variability in the awareness, as well as with effective assessment and management of PFAS at many landfills with permits and/or thresholds often limited or lacking and so it is recommended that any disposal route be rigorously assessed to ensure it is appropriate for PFAS to manage future liability (Section 5.4.1.8).

It remains to be seen how landfill operators will address the potential long-term PFAS leaching risks and permit surrender at the end of landfill’s operational life.

5.4.2. On Site Engineered Containment

5.4.2.1. General Description and PFAS Removal Mechanism

For the purposes of this report, engineered containment includes either capping of unsaturated soil impacts, to eliminate rainfall infiltration and reduce leaching to underlying groundwater, or placement of excavated material within an engineered containment cell, to isolate PFAS from the surrounding environment. PFAS are not destroyed but contained and so must be managed and monitored essentially in perpetuity. This may place significant constraints on site activity in the area and require long-term management and monitoring as well as periodic containment system renewal.

The duration of storage is a key aspect informing a risk-based containment design with long-term (e.g. >5 years) storage systems typically employing more robust, durable designs than those more suited to short-term (e.g. stockpile) containment (HEPA (2022)). Long-term containment designs may be similar to landfills with basal geomembrane liners or composite liners comprising a geomembrane along with a Geosynthetic Clay Liner which typically provide better leachate migration reduction. Double composite liner systems are becoming frequent for more problematic wastes. Such system will also typically include cover systems to manage surface water runoff as well as leachate collection and management systems.

Engineered containment is undertaken on, or close to, the site of origin, reducing transport distance and providing an opportunity to use the material and/or the containment structure as part of site layout. It enables site control over the management but also involves potential liability should containment fail. The site activity and hydrogeological setting should be carefully assessed to identify suitable sensitive locations for placement to minimise potential risk of future release.

As with landfilling for PFAS, apart from isolating the source of PFAS from the environment, PFAS treatment relies on the containment and treatment of any leachate generated. The types and proportion of PFAS within leachate may be slightly different to those measured in soils with short chain PFAS more likely in leachate with biotransformation of PFAA precursors over time also potentially generating more mobile PFAS. Therefore, whether on-site or off-site leachate treatment is undertaken it should be suitable to meet any discharge criteria as well as address the range of PFAS and other constituents potentially present. Leachate volumes generated will principally depending on the moisture content of the soil and will deplete over time provided the cover system remains effective.

A key consideration is that long-term containment is typically regulated as a waste disposal / management operation (landfill) which can involve a lengthy regulatory process with long-term waste management permit or license requirements.

5.4.2.2. Suitability to Treatment Scenarios

On-site engineered containment can be used to address source area impacts with high concentrations especially where other treatment options are technically unfeasible or unavailable. Furthermore, as transport distances are low / minimal and the costs do not increase linearly with mass / volume, it may be cost-effective to address larger volumes than may be targeted with landfilling. Moreover, given the planning, permitting and construction requirements, long-term containment is not likely suitable for low waste volumes.

The long timeframes for regulatory agreement may preclude this for rapid site redevelopment although if foreseen and timescales accounted for the construction of the containment system, excavation and placement can be undertaken quite quickly.

It may not be considered suitable for locations of high environmental sensitivity or where site ownership / management oversight cannot be guaranteed.

Containment approaches have been employed as a temporary measure to enable rapid hotspot removal and storage while a permanent remediation solution was selected (see Section 5.4.2.8) which may be a valuable option where the availability or acceptance of PFAS technologies is still developing.

Capping is an established approach for other containments and is suited to redevelopment scenarios where buildings and hardstanding can also be used to prevent rainfall infiltration. It is also more suited to low levels of PFAS contamination in large quantities of soil and other solid materials (HEPA, 2022).

5.4.2.3. Treatment Efficacy for Different PFAS Versus Treatment Goals

Engineered containment has the potential to rapidly isolate a wide range of PFAS within soils or other materials and hence support achievement of soil and/or leachate reduction treatment goals. Underlying groundwater quality would be expected to improve over time following the reduction in PFAS leaching with the overall degree of treatment primarily relates to the area / volumes targeted and any residual PFAS that may be left.

The reduction in PFAS leaching from unsaturated soils to groundwater due to capping is more likely to be longer term and less complete especially where fluctuating groundwater is present which may mobilise PFAS. This could also occur in response to low frequency, higher rainfall events. The presence of preferential pathways such as drainage is also a key consideration.

In either approach, the persistent nature of PFAS is a key long-term consideration as they will likely outlast the constructed cell or capping system, particular liner-based systems which may only have lifespans of 20-30 years. The lifespan of any containment system should be well understood and accounted for terms of long-term site operation and ownership as well as monitoring, maintenance and periodic containment renewal.

5.4.2.4. Suitability to Soil Properties and Co-contamination

A range of soil and material types can be placed within engineered containment cells provided they do not result in damage to the liner system or result in significant settlement.

Likewise, the suitability to different PFAS compounds relates primarily to leachate treatment although it is noted that short chain PFAS, potentially also resulting from biotransformation of PFAA precursors during storage, are most likely to be present within leachate and can be more challenging to treat.

The presence of co-contaminants has the potential to cause issues for containment most notably if any vapour risks from volatile compounds or gas generation via biodegradation of organic matter or hydrocarbons as well as potentially complicate leachate treatment. These issues can generally be managed but require careful consideration.

As discussed above in Section 5.4.1.5, pre-treatment of soils (e.g., by physical screening and/or S/S) can also be undertaken prior to containment to provide additional leachate reduction and control as well as reduce or eliminate the volume of leachate generated. Indeed, the retention of stabilised soils is often combined with some form of additional cover or liner system for additional protection and confidence.

5.4.2.5. Operational Considerations

Key considerations for on-site containment include (HEPA, 2022):

- the siting and location – avoiding sensitive receptors and pathways;
- the duration of storage – including long-term site ownership and access. Informs containment design;
- short and long-term implications for site activity – containment cells and capping must be protected (e.g. buffer zone) and so may place a significant constraint on site usage or redevelopment;
- provision of leachate collection and management – either on-site or off-site;
- potential risks from weather events and flooding;
- the relevant approvals required by regulators.

A management plan is typically required in accordance with waste management or licensing requiring providing for ongoing monitoring and management.

It is understood that in addition to standardised mechanical and physical tests, performance-based assessments are increasingly being employed during the design stage and beyond to estimate design life (Engineers Australia, 2022).

Details of the requirements and approach to PFAS containment by HEPA in Australia and New Zealand is provided in their National Environmental Management Plan (NEMP)(HEPA, 2022).

5.4.2.6. Cost and Commercial Considerations

Costs for engineered containment and capping in relation to PFAS soils and wastes was not obtained as part of this review and are anticipated to similar to costs for non-PFAS containment systems.

5.4.2.7. Energy and Chemical Use and Sustainability Considerations

Sustainability considerations within the scope of this study are described in Section 4.4, and are done in a limited fashion compared to e.g. US-EPA Green and Sustainable Remediation (GSR) guidance.

The principal benefit on on-site containment is that material does not require transport to an off-site facility and thus avoids associated transport related impacts as well as avoiding material being placed in landfill. Where soils are capped or where cells can be utilised as engineered features (e.g., acoustic bunds) then this can also reduce the requirement and transport of clean, import fill.

Initial construction of the large containment cells can require significant plant and materials, especially if pre-treatment is undertaken, but beyond construction energy and chemical use are minimal.

5.4.2.8. Case Studies

While engineered containment has been employed since the 1970s and 1980s for other contaminants, case studies in relation to PFAS are limited. However, Arcadis are aware of the following examples.

- A total of 15,500 tonnes of PFAS (firefighting foam) impacted soil from Guernsey Airport and a nearby airplane crash site were excavated to prevent on-going leaching to groundwater and placed within two engineered containment bunds at Guernsey Airport (2012 and 2015). This is illustrated in Figure 19. The bunds included basal and cover liners as well as leachate collection systems with on-site treatment provided by the existing groundwater treatment system employing GAC. The bunds were covered to create a grassed embankment. The bunds are temporary and have been monitored and managed in accordance with a Waste Management License while a permanent remediation solution was identified.

Figure 19 Temporary Engineered Containment Cell Construction, Guernsey Airport

- A second example relates to the encapsulation, capping and isolation of PFAS and hydrocarbon contaminated soils as part of the remediation and reinstatement of the Fire Fighting Training Area at Jersey Airport in 2004. This is illustrated in Figure 20. The new Fire Fighting Training Area was constructed using permeable paving with rainfall harvested and used within fire training activities and can also be evaporated (via sprays across the paving) or cleaned and discharged to public sewer. Firewater from training is collected within a separate cell without discharging to ground (Knapton, 2006).

Figure 20 Remediation and Reinstatement of Fire Training Ground at Jersey Airport (Knapton, 2006)

5.4.2.9. Knowledge Gaps

Areas where knowledge is currently understood to be lacking relates to the degree to which different types of PFAS, particularly short chain, precursors and ultrashort PFAS may migrate through or diffusion into different liner materials and the potential effect on liner properties (e.g., tensile strength, stress factors). This is an area of ongoing research and development aimed at providing more information to support modelling of containment deign life (Engineers Australia, 2022).

6. INNOVATIVE TECHNOLOGIES

As part of the literature review, certain innovative technologies for PFAS soil treatment were selected and an evaluation of these technologies was done in a similar manner to the field deployed technologies, detailed in Section 5, but with a focus on the identification of work to be done to close gaps for potential commercialisation.

As detailed in Section 2.2.1, the selected innovative PFAS soil treatment technologies included for review within this project are listed in Table 9.

Table 9 Selected Innovative PFAS Soil Treatment Technologies

Innovative Technologies
Destructive Approaches
Ball Milling
High Energy Electron Beam
Phytoremediation
Biodegradation
Non-Destructive Approaches
In-situ Soil Flushing

6.1.1. Ball Milling / Mechanochemical Destruction

6.1.1.1. General Description and PFAS Removal Mechanism

Ball Milling is an emerging technology that utilises high energy collisions to initiate the oxidative and reductive destruction as well as mineralisation of PFAS. The method typically is undertaken with the addition of a co-reagent, most commonly potassium hydroxide (KOH). However, recent studies without reagent have been undertaken (Gobindlal et al., 2023a, Gobindlal et al., 2023b).

The mechanism(s) are not currently well understood but are postulated to involve the generation of high energy species including electrons, ions, radicals, neutral particles or photons from the fracture of soil crystal structures initiated by collisions between the soil and the ball mill which may activate surface areas within the soil matrix. The use of piezoelectric materials as co-reagents (boron nitride) may also facilitate destruction facilitating the generation of oxidants. As the oxidants are generated by mechanical collisions the reactions occur at room temperatures and pressures. The mechanism(s) are noted to produce short chain PFCA intermediates which themselves are mineralized on further treatment (Battye et al., 2022, Ateia et al., 2021, Wang et al., 2019).

6.1.1.2. Suitability to Treatment Scenarios

The technology has at present been demonstrated at laboratory and field scale pilot application. Full scale application to real world soils would require their excavation, with treatment within in a batch reactor type process of limited volume. As such, even considering multiple modular units, the technology is envisaged to be most applicable to small volume source area type treatments or biosolids. Soils physical and chemical structure is changed by the process and may not be geotechnically or chemically suitable for re-use in all scenarios.

A potential limitation on full scale applicability of the technology is that the commonly utilised co-reagent KOH can cause soils to clump within the mill due to reaction with soil moisture; indicating drying of soils pre-treatment may be required. A more significant limitation of KOH is that post treatment the soils are ~pH14 and would require pH adjustment back to more environmentally relevant levels. These limitations are not noted for boron nitride however its use within ball milling of PFAS is limited to a single study by (Yang et al., 2023). It is also noted these co-reagents are expensive given the loadings indicated to be required by the studies, which may exceed the soil volume itself.

Recent studies indicate that such reagents may not be required and that also liquid media containing PFAS such as AFFF can be destroyed by milling after augmentation onto quartz sand (Gobindlal et al., 2023a, Gobindlal et al., 2023b).

6.1.1.3. Treatment Efficacy for Different PFAS Versus Treatment Goals

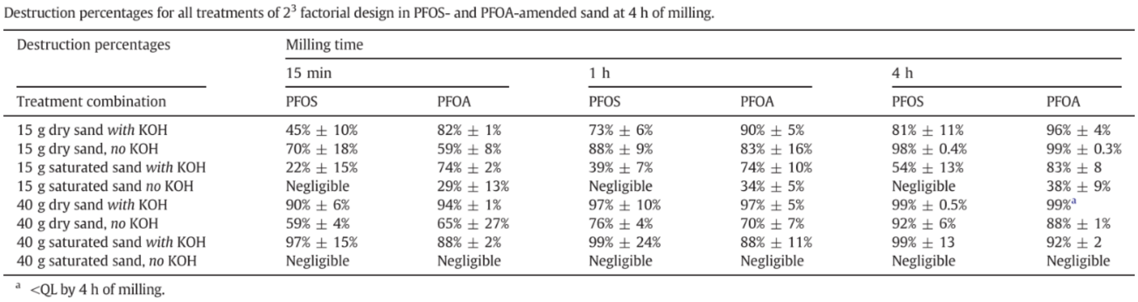
At laboratory scale ball milling has demonstrated the destruction of PFOS (PFOS 95% reduction in concentration, 78% fluoride recovery, 98% sulphate recovery) (Ateia et al., 2021) and PFOA (98% mineralisation) (Wang et al., 2019) solids with almost complete mineralisation observed after four hours milling time with intermediate short chain PFAA observed after 30 minutes.

Battye et al. (2022) conducted experiments on nepheline syenite sand spiked with PFOS (6.1 mg/L), 6:2 FTSA (2.4 mg/L), and an AFFF mixture (~0.4-2.9 mg/L scale impacts including 21 PFCA and PFSAs indicating a mixture of suppliers). Horizontal ball milling resulted in a 43% reduction in PFOS concentrations, a 97% reduction in 6:2 FTSA concentrations, and a 91% reduction in the 21 PFAAs measured within the AFFF sample. The addition of potassium hydroxide was required to improve performance.

Turner et al. (2021) conducted experiments on nepheline syenite sand spiked with PFOS or PFOS (at concentrations of 5 and 35ppm) within a planetary ball mill. The results are presented and summarised in Table 10.

- Higher destruction was noted on dry samples containing PFOS than saturated samples;
- The addition of potassium hydroxide gave marginally better results for dry sand but significantly improved the results for saturated sand;
- The highest fluoride recovery was 89% in the dry sand tests. Most destruction was observed in the first 15 minutes of milling time with no short chain intermediates detected.

Table 10 Destruction Efficiency via Ball Milling Treatment (Turner et al., 2021)



Destruction percentages for all treatments of 2^3 factorial design in PFOS- and PFOA-amended sand at 4 h of milling.

Destruction percentages	Milling time					
	15 min		1 h		4 h	
Treatment combination	PFOS	PFOA	PFOS	PFOA	PFOS	PFOA
15 g dry sand *with* KOH	45% ± 10%	82% ± 1%	73% ± 6%	90% ± 5%	81% ± 11%	96% ± 4%
15 g dry sand, *no* KOH	70% ± 18%	59% ± 8%	88% ± 9%	83% ± 16%	98% ± 0.4%	99% ± 0.3%
15 g saturated sand *with* KOH	22% ± 15%	74% ± 2%	39% ± 7%	74% ± 10%	54% ± 13%	83% ± 8
15 g saturated sand *no* KOH	Negligible	29% ± 13%	Negligible	34% ± 5%	Negligible	38% ± 9%
40 g dry sand *with* KOH	90% ± 6%	94% ± 1%	97% ± 10%	97% ± 5%	99% ± 0.5%	99%[a]
40 g dry sand, *no* KOH	59% ± 4%	65% ± 27%	76% ± 4%	70% ± 7%	92% ± 6%	88% ± 1%
40 g saturated sand *with* KOH	97% ± 15%	88% ± 2%	99% ± 24%	88% ± 11%	99% ± 13	92% ± 2
40 g saturated sand, *no* KOH	Negligible	Negligible	Negligible	Negligible	Negligible	Negligible

[a] <QL by 4 h of milling.

Yang et al. (2023) used a piezoelectric co-reagent (boron nitride, loading unreported) in a horizontal ball mill to demonstrate near complete mineralisation of PFOS and PFOA within 2 hours with close to 100% fluoride recovery. The same study also demonstrated treatment of PFAS impacted sediment with about 80% PFAS (including PFCAs, PFSAs, and 6:2FTS) removal demonstrated after 6 hours.

The Turner et al. (2021) and Battye et al. (2022) studies also assessed the efficiency of ball milling on samples collected from fire training areas, as summarised in Table 11. Clay soils showed better PFAS reductions than sandy soils, and as with the spiked samples the addition of KOH was noted to facilitate destruction.

(Gobindlal et al., 2023b) has recently demonstrated that soil from fire training areas can be treated without the addition of a co reagent, however longer treatment times up to 1440 minutes were required.

Table 11 Summary of PFAS soils concentration reductions via ball milling (Turner et al., 2021 and Battye et al., 2022)

Study and basic info	**Soil Type**	**Range in PFAS reductions**
Turner et al. (2021) • 3 sand and 3 clay soils • All with KOH • 40g soil • 4:1 KOH/Soil	Sand	PFOS - 42% to 69% PFHxS - 36% (present in one soil only) PFOSA - Reduction not observed (present in 2 soils) PFHxA - Reduced below detection limit (present in 2 soils)
	Clay	PFOS - 69% to 96% PFHxS - 0%-98% (present in two soils only) PFHxA - Reduced below detection limit (present in 2 soils)
Battye et al. (2022) • 1 sand and 1 clay soil • 1 litre and 25 litre mill volume • 10:1 grinding media to soil mass • 4:1 KOH/Soil	Dried sand	PFOS - 61%-69% with KOH, 15%-67% no KOH 6:2 FTS - Near complete >95% with KOH, no reduction without KOH
	Dried clay	PFOS - 81% to 85% with KOH, 5% to 12% no KOH 6:2 FTS - Near complete >98% with KOH, ~60% reduction without KOH Non-target precursor PFASs - >99% reduction with KOH, 70 to ~100% reduction without KOH
Gobindlal et al. (2023) • 1 sand soil • 0.5 litre mill volume • Approximately 10:1 grinding media to soil mass • 24 Hours	Dried Sand	PFAS measured by target analysis increased for first 60 minutes of milling as non-target precursors underwent degradation to target compounds. After 1440 minutes all target analytes were below detection limits. Extractable organic fluorine indicates 53.3% reduction in non-target analytes. The FTA samples contained both PFSAs predominantly PFOS, PFCAs (predominantly PFPeA, PFHxA, PFOA, PFNA, and PFDA), fluorotelomersulphonates and perfluoroalkane sulfonamides.

Gobindlal et al. (2023) has also recently demonstrated that the fluorochemical components of an AFFF (Tridol S3) can be destroyed by ball milling after augmentation onto silica sand (2.5ml AFFF on 25g sand). The most abundant PFAS identified in the AFFF were 6:2-fuorotelomermercaptoalkylamido sulfonate (FTSAS), with 6:2 FTSAS sulfoxide and 6:2 fluorotelomer sulfonate also detected. Trace amounts of PFCA and PFSA were noted in the AFFF. After 24 hours of milling, target PFAS analytes were noted to have undergone 99.99% reduction with non-target analytes (by EOF) were noted to have undergone 97.8% reduction.

6.1.1.4. Suitability to Soil Properties and Co-contamination

No studies have assessed the impact of co-contaminants within the soil matrix; however, it is noted that studies have used samples from fire training areas which are likely impacted with trace levels of hydrocarbons and will also contain metals and organic ions in line with their natural soil chemistry.

Within the same study, the limited tests conducted on real world soils to date suggest better results are achieved for clay soils compared to sandy soils. It is also noted that coarse soils (>2mm) may not be suitable for treatment due to excessive ware on the milling equipment, which would be a considerable limitation on the technology.

6.1.1.5. Operational Considerations

Studies to date have utilised either planetary ball mills which produce collisions across two axes of rotation and horizontal ball mills which operate on one axes of rotation. The energy density of horizontal ball mills is 100-1000 times lower than planetary ball mills therefore the latter are expected to be more effective for PFAS destruction and have been the focus of the majority of studies. Commercially however horizontal ball mills are available at scale whereas planetary are limited to small volumes. The limited data available also suggests that mill loading of soil is limited with a mass of grinding media to soil of 10:1 reported (Battye et al., 2022).

It is expected (Cagnetta et al., 2018) that field scale deployment would need a plant to dry soils before treatment, sieve to remove oversize material (>2mm) to avoid excessive ware on the mill, and to control dust production.

If dosing of KOH as a co-reagent is required to achieve clean up goals this contributes a significant mass to the overall treatment volume (4:1 KOH/Soil) (Turner et al., 2021, Battye et al., 2022) it will likely to lead to soil bulking. KOH can cause skin burns and reacts exothermically with water; it will thus require consideration of appropriate handling processes at scale.

6.1.1.6. Cost and Commercial Considerations

Cagnetta et al. (2018) conducted a feasibility study for the utilisation of ball milling for remediation of POPs other than PFAS. They considered that operating in a batch process for 24 hours (including charge, milling, and discharge procedures), it would be possible to achieve a treatment rate of 16 tonnes a day. Based on this they calculated (2016) total treatment costs of 76 USD / m^3 (69 Euro / m^3).

However, in relation to a specific application in Vietnam (discussed in 6.1.1.8), the full-scale costs were estimated (in 2015) to equate to 380 USD / tonne (approximately 630 Euro / m^3) (Cooke, 2015).

The cost of the co-reagent (if required following pilot trials) should also be considered, the current studies do not allow an assessment to be made however the cost will be dependent on dose required. Boron nitride is understood to be significantly more expensive than potassium hydroxide w/w.

6.1.1.7. Energy and Chemical Use and Sustainability Considerations

Sustainability considerations within the scope of this study are described in Section 4.4, and are done in a limited fashion compared to e.g. US-EPA Green and Sustainable Remediation (GSR) guidance.

While no high temperatures or pressures are involved, ball milling requires significant energy to continuously drive the high impact collisions needed to achieve for treatment.

The batch process reported by (Cagnetta et al., 2018) was considered to require an energy consumption of 400 kWh per tonne. Cagnetta et al. (2018) state a 230l, 540kW planetary ball mill pilot plant was built in Japan around 2004 but provide no further detail on its use.

Information provided during vendor liaison and subsequent correspondence indicated a theoretical EE/O (electrical energy per order of magnitude contaminant reduction) of 45-180 kWh/m^3.

The technology changes the physical and chemical structure of the soils which may make impact their sustainable re-use within a remediation project.

Some approaches require significant quantities of potassium hydroxide and other co-reagents, to both treat the soil itself and to buffer the resulting material back to environmentally relevant pH.

6.1.1.8. Case Studies

There are no known case studies for the full scale field deployment of ball milling for the destruction of PFAS. Cagnetta et al. (2018) reference that a vertical vibrating ball mill was used to treat DDT contaminated soils in New Zealand, throughput was 100m^3 per week of soils screened to <10mm, a dosing of 3% co-reagent was utilised.

In relation to other contaminants, ball milling is understood to have been employed to address non-PFAS contamination at field pilot and full scale, although the number of applications are limited. Ball milling is visualized in Figure 21 . For example, full scale demonstration of their Mechano-Chemical Dehalogenation (MCD^{TM}) ball milling technology was undertaken at Bien Hoa Airbase in Vietnam to destroy (>97 to >99% reductions) dioxins within site soils (Cooke, 2015). Four, full sized MCD modular reactors were employed in series with pre-treatment via soil sieving and humidity reduction. The pilot unit treated 1.2t/hr with the full scale design for this site considered to include a two train, ten reactor configuration capable of treating 16t/hr. Dryer stacks and fugitive emissions controls were also considered important to include at full scale.

Figure 21 Ball Milling Application for Dioxins by EDL at Bien Hoa Airbase, Vietnam (left) and alternate facility (right)

6.1.1.9. Knowledge Gaps

Based on the laboratory studies reviewed, ball milling is indicated to be capable of destroying PFAS, even in more cohesive soils, at a reasonable cost but currently indicates some practical constraints regarding full scale implementation such as oversize removal, drying, treatment rates and potential addition of significant quantities of reagents. These potential operational issues would benefit from field scale demonstration, optimisation, and cost confirmation.

Further studies are needed to determine the applicability across a wide range of soils with a focus on real world samples whose wider chemical and physical properties should be determined and assessed against performance. In addition, PFAS destruction should be further validated using advanced analytical techniques such as TOP Assay.

The susceptibility of PFAS destruction to the addition of co-reagents also requires further assessment. The use of potassium hydroxide at scale is likely to cause significant operational issues and the reduction, elimination or substitution of this reagent would be beneficial with recent studies indicating progress in this area.

While the engineering challenges in scaling the technology to pilot and full deployment also requires consideration, some real-world examples of remediation by ball milling for other contaminants in soil have been identified indicating scale up to address PFAS impacts is possible. The relative performance of planetary and horizontal ball mills requires assessment alongside the engineering considerations of their deployment at scale.

6.1.2. High Energy Electron Beam (E-Beam)

6.1.2.1. General Description and PFAS Removal Mechanism

It is postulated that E-Beam treatment of PFAS would involve the utilisation of compacted electron accelerators to irradiate the media for treatment with large numbers of high energy electrons. The technology is currently utilised for medical sterilisation and food pasteurization.

There are limited examples of E-Beam being applied to environmental media including the remediation of hydrocarbon contaminated soils (Lassalle et al., 2021) removal of mercury from scrubbers and precipitators, and removal of oxides of sulphur and nitrogen from flue gasses. One laboratory study (Wang et al., 2016) had demonstrated the defluorination of PFOA in aqueous solution, and a recent study demonstrates the first treatment of PFAS impacted soils (Lassalle et al., 2021).

The mechanism of PFAS destruction is not well understood but is likely to involve both oxidation and reduction processes. Energetic electrons and the radiolytic species they generate in the target media are thought to cause direct damage to chemical bonds and make them unstable, leading to degradation of chemical contaminants. The high energy radiation may also instigate temperature catalysed reactions.

6.1.2.2. Suitability to Treatment Scenarios

The technology has at present not been demonstrated outside the laboratory where treatment has taken place in small batch reactors. However, it is envisaged that the approach could be developed into a containerised system with the soils passing through the E-Beam on a conveyor. As such the technology is envisaged be primarily applicable to small volume source area type treatments or biosolids.

Application to real world soils would require their excavation, processing, treatment and reuse. The high energy beam will also sterilise the soils and likely destroy soil organic matter and may create a char-like product as a result of the treatment, which will need to be considered in re-use scenarios.

6.1.2.3. Treatment Efficacy for Different PFAS Vs Treatment Goals

Data exists only from a single laboratory study (Lassalle et al., 2021) which used investigated the technology against PFOS spiked sand and a sample from a fire training area at a US military base.

The experiments with PFOS spiked sand (100 g per experiment) showed a 97.6% reduction in PFOS levels at a dose of 500 kGy and concentrations were reduced to below the detection limit with a dose of 2,000 kGy. Small amounts of PFOS were observed in the condensate produced as water is driven out of the sand due to the treatment temperature (≤400^{o}C).

Pre-treatment, the FTA soil contained a broad range of 19 PFAS with selected examples summarised in Table 12. The soil (100 g per experiment) from the FTA was found to be treated most successfully with a dose of 2,000 kGy. There was some variation in performance based on soil Moisture Content (MC), destruction of PFOS in particular was noted to be better at 10% MC whereas destruction of both short chain PFAAs was better at the ‘as received’ MC and also lower overall.

Table 12 Summary of PFAS Soils Concentration Reductions via E-beam (Lassalle et al., 2021)

PFAS	Initial Concentration (µg/kg)	Reduction Observed at 84% Soil Moisture (%)	Reduction Observed at 10% Soil Moisture (%)
PFOS	1,010	86.7	99.9
PFOSA	124	<MDL	<MDL
PFPeA	33.9	99.5	99.5
8:2 FTS	30.5	93	>MDL
PFHxS	29.2	86	>MDL
PFOA	17.2	90.5	86.4
PFBA	6.91	90.1	78.1
PFBS	1.16	78	49.1

6.1.2.4. Suitability to Soil Properties and Co-contamination

No studies have assessed the impact of co-contaminants within the soil matrix; however, it is noted that the technology has been demonstrated at laboratory scale to treat soils impacted with heavy hydrocarbons.

Further, the sample of soil from the FTA used in the Lassalle (2021) study is likely to contain trace levels of hydrocarbons and will also contain metals and organic ions in line with natural soil chemistry.

6.1.2.5. Operational Considerations

It is envisaged that the approach could be developed into a containerised system with the soils passing through the E-Beam on a conveyor. Application to real world soils would require their excavation, and processing (potentially including drying and sieving) to create a uniform soil layer approximately 40mm thick (determined by the penetration depth of the E-Beam) which is placed on the conveyor system.

The E-Beam treatment will likely remove all residual water from the soil during irradiation, this will result in a PFAS impacted condensate which will require collection and treatment. Levels of PFAS in condensate have been found to be <10 times those in the treated soils.

The use of high energy electron beams will require appropriate health and safety management and may require specific licencing depending on the legislation and guidelines in the jurisdiction of operation.

6.1.2.6. Cost and Commercial Considerations

Lassalle et al. (2021) conducted a cost analysis for a non-mobile treatment facility. The costs included capital investment and the operating costs (electricity, other utility costs, and personnel). The analysis indicates that over a 20-year lifespan operating at 90% beam utilisation, treating 20m^3 a day that it would cost approximately 393 USD / m^3 (357 Euro / m^3) of soil to breakdown 98% of PFOA and 99.99% of PFOS using a target dose of 2,000 kGy.

A 20% reduction in the needed E-Beam dose and enhanced accelerator beam power would reduce costs per cubic meter substantially and enables substantially more material to be treated per hour. Further studies are required to optimise treatment.

6.1.2.7. Energy and Chemical Use and Sustainability Considerations

No information specific to the remediation of PFAS by E-Beam treatment.

6.1.2.8. Case Studies

There are no know case studies for the field deployment of E-Beam for the destruction of PFAS.

6.1.2.9. Knowledge Gaps

Based on a single laboratory study concerning PFAS and limited studies on other contaminants E-Beam shows some promise as a remedial technology but with some potential constraints regarding soil handling (drying, placement in thin layers) as well as cost. Further studies are needed to determine the applicability across a wide range of soils with a focus on real world samples whose wider chemical and physical properties should be determined and assessed against performance. In addition, PFAS destruction should be further validated using advanced analytical techniques such as TOP Assay.

The engineering challenges in scaling the technology to pilot and full deployment also requires consideration, although the regular deployment of E-Beam in sterilisation and pasteurisation industries indicates this is achievable.

6.1.3. Phytoremediation

6.1.3.1. General description and PFAS removal mechanism

Phytoremediation uses plants and their associated microorganisms, enzymes and water consumption for the remediation of soil and groundwater contamination. Plants can contribute in different ways to the remediation of contamination:

- Phytosequestration: Sequestration of certain contaminants into the rhizosphere and on the root. This process leads to containment of certain contaminants.
- Rhizodegradation: Microbial biodegradation of contaminants in the rhizosphere. This process allows a level of remediation by destruction.
- Phytoextraction/ phytostabilisation: Plants can take up contaminants through the transpiration stream. Remediation takes place by removing the contaminated plants or plants’ parts from site.
- Phytodegradation: Plants may take up contaminants through the transpiration stream and break them down through internal enzymatic activity. This has the potential to result in remediation since contaminants are destroyed.
- Phytovolatisation: Once contaminants are captured by a plant they may be converted to volatile components through internal enzymatic activity and eliminated through the plant’s transpiration stream. This constitutes a remediation by removal.

In the case of organic contaminants, phytoremediation can take place through a combination of rhizodegradation and phytoextraction followed by phytodegradation and phytovolatisation resulting in removal and destruction of the contaminants (Mayakaduwage et al., 2022).

For PFAS remediation phytodegradation and phytovolatisation processes are known to be ineffective due to PFAS being insufficiently affected by microbial and enzymatic degradation (Chen et al., 2012) with the majority PFAS having volatility and low air:water partition coefficients.

Phytoextraction is the dominant mechanism for PFAS phytoremediation by terrestrial plant. Aquatic plants offer the additional mechanism of phytosequestration as their roots may store non-negligible amounts of PFAS (Huang et al., 2021).

6.1.3.2. Suitability to Treatment Scenarios

At the time of writing phytoremediation of PFAS in soil is mainly at experimental stage with some laboratory scale and very limited pilot scale results available.

It is envisaged that phytoremediation approaches would be best suited to areas within shallow, low concentrations of PFAS within a relatively low risk scenario (given PFAS leaching will still occur to some degree over time) and where soil is suitable for appropriate plant growth. Such areas must also be available for treatment application for long time periods (likely decades). This would potentially fit a green space type end use provided regular harvesting of biomass would not be unacceptably disruptive or damaging. Similarly, wetland system may also be suitable however, these can be more challenging to access for harvesting and often not suited to operational industrial facilities.

6.1.3.3. Treatment Efficacity for different PFAS Versus Treatment Goals

A worldwide study of PFAAs presence in soil, their potential source and the relationship with local vegetation was conducted in 15 countries (Lv et al., 2023). Factors influencing PFAAs adsorption to soil were considered. The findings regarding plants' intake indicated that shorter chains were more readily accumulated by plant's roots and translocated to other parts of the plants than long chain PFAAs. This has been observed in other studies, where decreased edible part and decreased soil concentration factors observed within increasing chain length (Blaine et al. (2014) and Felizeter et al. (2020)). These decreased were postulated to be due to increased sorption to soil, retention within the roots and hindrance within phloem flow. This has significant implications for long-term treatment efficacy where long chain PFAS require management. The main conclusion of the study however was that more data were needed in order to further document plants' PFAS intake corresponding soil condition to eventually develop a better understanding of behaviour and fate of PFAAs in soil-plant systems (Lv et al., 2023).

Plant selection is an important consideration. Species have to be fast growing and producing abundant biomass as this is where the pollutants may be stored, strive in the given environment where the remediation is taking place and have a high tolerance to the pollutant to be tackled. For PFAS, potential hyperaccumulators were found amongst some woody and herbaceous plants such as river birch (*Betula nigra*), black willow (*Salix nigra*), and red fescue (*Festuca rubra*) with regard to six tested PFASs PFPeA, PFHxA, PFOA, PFBS, PFHxS, and PFOS. Among these tested plant species, amaranth (*Amaranthus tricolor*) showed the highest bioaccumulation factor (174.6 for PFPeA) (Mayakaduwage et al., 2022)

At a firefighting training site near a Swedish airport where the soil contained between 0.3 and 337 mg/kg dry weight of PFAS, measurements of 26 PFAS (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA, PFOcDA, PFBS, PFHxS, PFOS, PFDS, FOSA, MeFOSA, EtFOSA, MeFOSE, EtFOSE, FOSAA, MeFOSAA, EtFOSAA, and 6:2 FTSA) in local plant communities indicated the potential to use a combination of terrestrial native plants (silver birch, Norway spruce, bird cherry, mountain ash, and ground elder) to achieve remediation. The rate of removal was however slow at 1.4 g of ∑26PFASs per year per hectare, meaning that 45 years would potentially be required to reach current regional regulatory requirements. (Gobelius et al., 2017)

Wetland plant species have shown promising results, such as commonly found riparian wetland plants which has a higher susceptibility to bioaccumulate PFOA with concentrations between 11.7 and 38 ng/g with an affinity to PFOA accumulation ranging from *Eichhornia crassipes*, > *Polygonum salicifolium*,> *Cyperus congestus*, > *Persicaria amphibian*, > *Ficus carica*, > *Artemisia schmidtiana* > *Xanthium strumarium*, > *Phragmites australis*, > *Ruppia maritime*, > *Schoenoplectus corymbosus*. Higher PFOA accumulation in *E. crassipes*, *X. strumarium* and *P. salicifolium* compared to the other species was attributed to the fibrous rooting system of these plants which suggests that the rooting system can have an influence on the uptake of PFASs by wetland plants. (Huang et al., 2021)

In a pilot scale constructed wetland experiment, removal efficiencies for PFOA and PFOS were found to be 77–82% and 90–95%, respectively, after 15 days of exposure to four aquatic plants, *Hygrophila pogonocalyx Hayata*, *Ipomoea aquatic Forssk*, *Ludwigia (x) taiwanensis* and *Eleocharis dulcis*. (Chen et al., 2012)

6.1.3.4. Suitability to Soil Properties and Co-contamination

At present, the studies into PFAS phytoremediation have focused on plant choice. Thus, the different soil media tested have not been compared. However, it has been reported that better results could be obtained in wetlands due to enhanced solubility of PFAS and better uptake by aquatic plants.(Huang et al., 2021)

6.1.3.5. Operational Considerations

As mentioned in section 6.1.3.3 plant selection is key to the success of phytoremediation. It is also inherently a slow process as it relies on plants’ growth and development.

Plants’ PFAS uptake from soil requires the solubilisation of those PFAS that would otherwise remain adsorbed to soil. The addition of a surfactant (sodium dodecyl sulphate) to biosolid in loamy sand soil was found to increase plant (timothy grass) PFAS uptake by 15 to 108% by increasing PFAS mobility. Regular mowing of the grass was found necessary to maintain PFAS uptake rates.(Zhang and Liang, 2022). The latter point is critical when considering phytoremediation as contaminated plants require a careful management to prevent re-introduction of pollutants in the ground and/or their introduction in the food chain. Currently the only suggested disposal routes are high temperature incineration, known to be energy demanding and costly, and disposal to landfill, which may be acceptable provide the landfill construction and leachate treatment is suitable. The risk of PFAS contaminated plant parts entering the food chain also need to be taken into consideration and addressed prior to any implementation.(Huang et al., 2021).

6.1.3.6. Costs and Commercial Considerations

There are no costs information available for PFAS phytoremediation.

6.1.3.7. Energy and Chemical Use and Sustainability Considerations

Sustainability considerations within the scope of this study are described in Section 4.4, and are done in a limited fashion compared to e.g. US-EPA Green and Sustainable Remediation (GSR) guidance.

Phytoremediation of PFAS has the potential to be a very sustainable option but considerations should be given to the manner in which plants' contaminated parts are removed from site and destroyed. No quantification of the energy cost of this part of the operation is available currently.

6.1.3.8. Case studies

There are currently no documented large-field scale applications of PFAS phytoremediation.

6.1.3.9. Knowledge gaps

There is a lack of large scale/ long-term data for PFAS phytoremediation. Results obtained have not always been promising (Zhu et al., 2022). The methodology is still at experimental stages.

The management of resulting PFAS contaminated plants' part, which often require harvesting for optimum PFAS uptake, would have to be carefully planned before any implementation. The identification of non-aquatic plant species more effective in the phytoextraction of long chain PFAS would increase the applicability of this technology.

Further research into microbial populations that could work collaboratively at suitable plants' roots level for biodegradation of PFAS is desirable. This could offer the possibility of both containing and degrading PFAS in a sustainable manner (Zhang and Liang, 2022, Huang et al., 2021). This however is a very challenging prospect as no microorganism capable of fully degrading PFAS compounds has been found yet.

6.1.4. Biodegradation

6.1.4.1. General description and PFAS removal mechanism

Environmental pollutants may be biologically degraded in nature thanks to the ability of microorganisms, such as bacteria, fungi and yeast, to breakdown relatively large molecules into less harmful, non-hazardous components, which can then be integrated into natural biogeochemical processes. For organic contaminants, such as petroleum hydrocarbons, certain microbial communities metabolise (or cometabolise) these contaminants as a food source to produce metabolic by-products and energy for microbial growth. During aerobic biodegradation, contaminants serve as electron donors and are broken down in the process. Terminal Electron Acceptors (TEAs), in the order in which they are preferentially utilised (respired) by microbes, include dissolved oxygen, nitrate, manganese, iron, sulphate and carbon dioxide. Depending on the TEAs utilised, the metabolic by-products of TEA reduction include carbon dioxide, water, nitrogen gas, Manganese (II), Fe (II), hydrogen sulphide and methane.

Organochlorides can be degraded by microorganisms and microbial dechlorination has been found to occur through five different types of reactions. Due to their chemical similarities, it may be assumed that similar reactions are possible for defluorination (Wackett, 2021):

Reductive: $\text{C-F} + 2e^{-} + H^{+} \longrightarrow \text{C-H} + F^{-}$ (1)
Oxidative: $\text{C-F} + 2e^{-} + 3H^{+} + O_2 \longrightarrow \text{C-OH} + H_2O + F^{-}$ (2)
Hydrolytic: $\text{C-F} + H_2O \longrightarrow \text{C-OH} + H^{+} + F^{-}$ (3)
Substitutive: $\text{C-F} + X \; - \longrightarrow \text{C-X} + F^{-}$ (4)
Eliminative: Alpha: $\text{Cl-C-F} + \text{H2O} \longrightarrow \text{CO} + 2H^{+} + Cl^{-} + F^{-}$ (5a)
Beta: $\text{Cl-C-C-F} + 2e^{-} \longrightarrow \text{C=C} + Cl^{-} + F^{-}$ (5b)

Reaction (1) cannot occur for linear single bounded PFAS compounds with naturally available microorganisms because it is highly energy demanding and as such does not promote bacterial growth. It has only been observed in the laboratory when treating compounds such as perfluoro-4-methylpent-2-enoic acid where a double carbon bond weakens the adjacent C-F bond (Zhang et al., 2022).

Reaction (2) has been observed on aromatic fluorinated compounds. For aliphatic compounds only in presence of methyl group but not in instances of fully fluorinated chains. This may be relevant for the degradation of fluorotelomers.

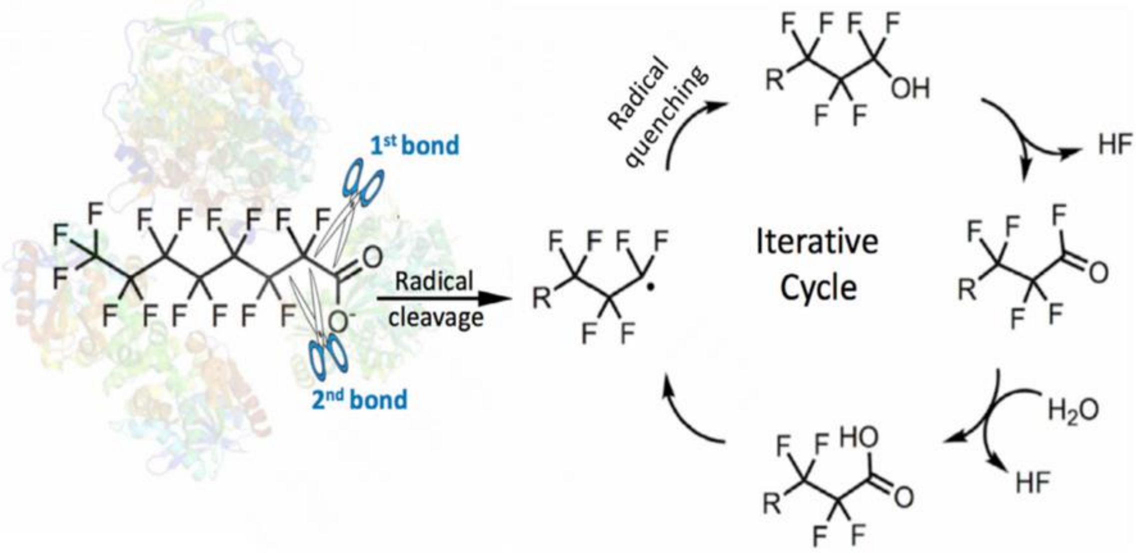
Reactions (3) and (4) necessitate catalysis by an enzyme such as fluoroacetate dehalogenase and are possible in theory. This enzyme however is toxic to wildlife (Berhanu et al., 2023) and research into alternative enzymes for this process is ongoing (Zhang et al., 2022).

Reaction (5) is not relevant to PFAS due to the necessary presence of a chloride atom on the carbon chain.

Only few simple fluorinated organic compounds occur in nature and very few microorganisms are equipped with adequate enzymes to degrade them. The diversity, complexity and rate at which man-made fluorinated compounds have been released into nature far outweighs these microorganisms' capability.

The majority of PFAS molecules are characterized on one hand by their stable long hydrophobic/lipophobic carbon chain where the strength of the C-F chemical bonds renders them particularly resistant to degradation, and on the other hand by the more reactive functional head group where some degree of degradation may take place. Indeed, the carboxylate (C-C) or sulfonate (C-S) bonds may undergo reduction or oxidation and through radical intermediates result in a hydroxyl group rendering the nearby C-F bond more reactive. The alcohol may rapidly convert to a carboxylic acid with the release of HF. In theory the same cycle can be repeated leading to the breakdown of the long chain. This is shown in Figure 22 (Wackett, 2021).

Figure 22 Simplified reaction pathway for PFAS degradation (Wackett 2021).



This mechanism only partly accounts for possible PFAS biodegradation, and it hasn't been possible to obtain full degradation as the cycle iteration is limited. Further research is required to improve understanding.

6.1.4.2. Suitability to Treatment Scenarios

Biodegradation of PFAS is at a laboratory experimental stage. Very few experiments have even involved actual soil media. In theory, should significant discoveries and developments in the technology be identified then this could potentially applied in relatively low risk scenarios where remediation time frames are acceptable and over large areas at relatively low cost.

6.1.4.3. Treatment efficacity for different PFAS Versus Treatment Goal

Partial defluorination of PFOS and PFOA was achieved in laboratory conditions using cultures of Acidimicrobium sp. strain A6 in presence of iron III (as electron donor) achieving 60% removal of PFOA and PFOS in 100-day incubations. The by-products included shorter carbon chain-perfluorinated intermediates along with acetate (Huang and Jaffe, 2019).

A 67% PFOS degradation was achieved in laboratory using Pseydomonas aeruginosa strain HJ4 in spiked natural soil with added sludge, however in this case defluorination was not observed and the by-products detected were PFBS and PFHxS meaning that further PFAS decomposition would be required (Kwon et al., 2014).

Enzymatic attack on PFOS has been reported via fungal laccase enzymes to which an artificial mediator (soybean meal) added. In this study, a maximum of 32% fluoride was released over 162 days with no data on any by-products (Luo et al., 2018).

In a small scale set up, forest stilt loam containing at least 5% of organic matter was contaminated with 8:2 fluorotelomer stearate monoester (8:2 FTS) and 8:2 fluorotemoler citrate tri-ester monomer (8:2 TBC), both historically used in water and oil-repellent textiles. At least 75% of 8:2 FTS was removed after 94 days. The concentration of TBC decreased by 44% after 218 days. The main by-product consisted in 8:2 fluorotelomer alcohol for both, so does not constitute a full decomposition.(Dasu et al., 2012)

The aerobic Fordonia sp. Strain NB4-1Y was found to degrade 6:2 FTBA and 6:2 FTSA (often found in AFFF contaminated soil) by respectively 85 and 88% in one week. The breakdown products were apparent after 24 hours in the aqueous phase as 6:2 FTUA and 6:2 FTCA followed by 5:3 FTCA after 48 hours. After 168 hours the majority of metabolites were found in the volatile phase mainly as 5:2 FT ketone, and to a lesser extent as 5:2 FTOH, and 6:2 FTOH. (Shaw et al., 2019).

The effect of biosparging (injection of oxygen into saturated zone to encourage aerobic degradation) on PFAS in AFFF-impacted soil was studied on laboratory scale for a period of 4 months. Longer chain PFSAs were found to remain in the soil. A maximum of 64% of PFOS and 24% PFNA were found to be removed with the oxygen sparging. Approximately 8 times more FPrSA, 5 times more FBSA, and 5 times more FPeSA eluted from the columns sparged with oxygen or nitrogen compared to where sparging was not done. The effects of biological transformation were found more effective for the shorter chained FASAs tested. PFAS mass balance calculations suggested biotransformation into PFOA and <C6 chain. (Nickerson et al., 2021a). However, it is noted that neither microbial species / consortia potentially responsible for biodegradation nor the mechanisms for such degradation are proven and other mechanisms (e.g. air:water interfacial sorption) may have played a role.

Overall, the slow kinetics and incomplete degradation of PFAS even under idealised laboratory conditions indicates that full scale biodegradation of PFAS is not currently sufficiently proven or viable.

6.1.4.4. Suitability to Soil Properties and Co-contamination

There is currently no available comparison of soil types and efficiency of PFAS biodegradation.

With regards to co-contamination, on sites where BTEX bioremediation has taken place it is noticed that if the site happens to also be AFFF-impacted, the ratio of PFCAs to fluorotelomers is greater than on sites where such remediation hasn’t taken place. Results obtained from laboratory experiments where AFFF-impacted soil to which either diethyl glycol monobutyl ether or BTEX compound were added, demonstrated that BTEX-degrading microorganisms did not increase the rate of PFAS removal but produced more PFCAs compared to other microorganisms. This was attributed to different enzymatic activities leading to a shorter transformation pathway to PFCAs. (Olivares et al., 2022). This indicates the importance of understanding past site activities including remedial action of pollutants other than PFAS since this can have a long-term effect on the types of PFAS that remain.

6.1.4.5. Operational considerations

The study of PFAS remediation by biodegradation is still at laboratory experimental stage. If suitable strains were identified a typical remediation set up could involve their injection in the soil along with suitable energy and growth source, and possible air sparging in the case of an aerobic process. A set up for managing gas phase by-product may also be required.

6.1.4.6. Costs and Commercial Considerations

There are no costs information available for PFAS remediation by biodegradation.

6.1.4.7. Energy and Chemical Use and Sustainability Considerations

Sustainability considerations within the scope of this study are described in Section 4.4, and are done in a limited fashion compared to e.g. US-EPA Green and Sustainable Remediation (GSR) guidance.

PFAS remediation by biodegradation could be a highly sustainable option once suitable strains of microorganisms that can be efficient in given soil conditions can be identified.

6.1.4.8. Case studies

Currently no large-scale field application of PFAS remediation by biodegradation has been reported.

6.1.4.9. Knowledge gaps

The use of biodegradation to remediate PFAS is at an experimental stage mainly due to the lack of available microorganisms capable of degrading these pollutants, the slow rate of kinetics and incomplete degradation observed over long time periods.

Knowledge into the mechanisms by which biodegradation of PFAS is possible is growing and the focus of future research will lie in finding and/or engineering microorganisms that would maximise mineralisation (to fluorine and small aliphatic molecules) possibly using the study of target microbes' genetic material (metagenomic) and with a focus on enzyme characterisation, since they are the main factor in the process. (Berhanu et al., 2023), (Shahsavari et al., 2020).

6.1.5. In-situ Soil Flushing

6.1.5.1. General Description and PFAS Removal Mechanism

A drawback of soil washing is the cost associated with excavation and either transport to fixed facilities or mobilisation of a specialised plant. Therefore, treatment approaches aiming to enhance solubilisation and transfer of PFAS into the aqueous phase have been carried out to decrease the treatment costs and are termed soil flushing

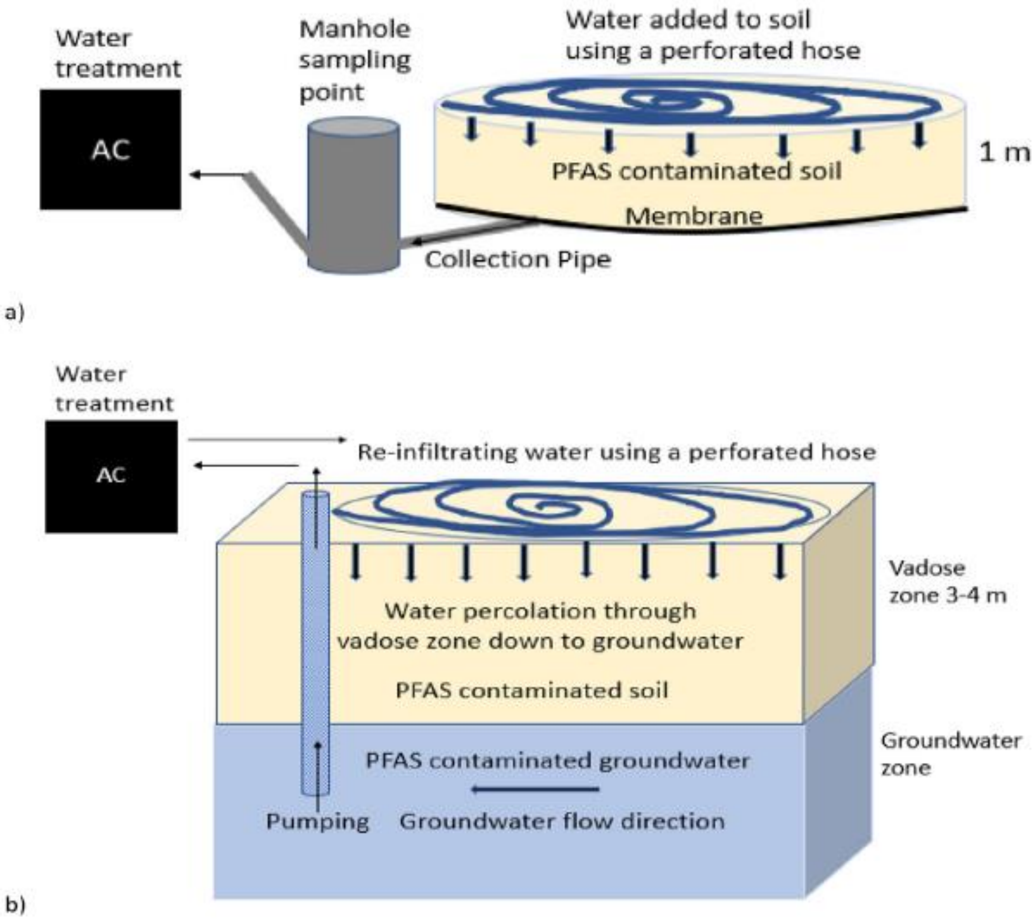
The key difference between soil washing and soil flushing is that flushing does not fully disaggregate and separate soils based on particle size and remove fines and does not involve more aggressive physical processes such as attrition scrubbing or high pressure jet spraying to remove PFAS from soil surfaces. Soil flushing involves less aggressive fluid application and recirculation to increase the rate of soil pore volume exchanges and enhance leaching rates to reduce PFAS concentrations over a longer time period.

In-situ soil flushing is a process that involves injection of a flushing solution into the ground for extracting contaminants (Hale et al., 2017; Yao et al., 2015). Figure 23 shows an illustration of soil flushing. The main advantage of soil flushing is that large quantities of soil can be treated in-situ without the need for excavation and transport (Jawitz et al., 2000; Svab et al., 2009; Zheng et al., 2012).

Surfactants having both hydrophobic and hydrophilic structural groups are used to facilitate the desorption of POPs and subsequent soil flushing. However, many PFAS, including PFOS and PFOA, are themselves surfactants, which can make PFAS behaviour difficult to predict during PFAS mobilization. For example, Pan et al. (2009) found that a cationic surfactant (cetyltrimethylammonium bromide (CTAB)) was able to significantly enhance the sorption of PFOS to sediments due to the initial sorption of CTAB to sediments, thereby exposing CTAB’s hydrophobic tails to adsorb PFOS. However, an anionic surfactant (sodium dodecyl-benzene sulfonate (SDBS)) showed a concentration-dependent effect where a SDBS concentration <4.34 mg/l increased PFOS sorption to sediments, but SDBS concentration >21.7 mg/l increased PFOS desorption (Pan et al., 2009). Guelfo and Higgins (2013) found that an anionic surfactant (sodium dodecyl sulphate (SDS)) at low concentration decreased the sorption of PFOS, PFNA, and PFDA, but increased the sorption of long chain PFAS, such as PFBA, PFPeA, PFHxA, PFHpA, and PFBS. In general, anionic surfactants could enhance the solubility of PFAS in water, which would decrease PFAS sorption to soils/sediments and, thereby, facilitate PFAS mobilization. Other common soil flushing additives such as organic/inorganic acids/bases and solvents such as methanol or ethanol might be suitable for removing PFAS from soils. For example, Schroder (2003) applied organic solvents (e.g., ethyl acetate (EtOAc), dimethylformamide (DMF), pyridine, tert-butyl methyl ether (MTBE), 1,4-dioxane, or tetrahydrofuran (THF)) to determine the ability of a solvent or combination of solvents for sludge PFAS extraction.(Bolan et al., 2021).

It is noted that the soil flushing process can be undertaken ex-situ, sometimes termed heap leaching, where excavated soil is placed on an impermeable lining comprising drainage and leachate collection system. This can allow more control of the soil and the process but still involves excavation.

Figure 23 Ex-situ (a) and In-situ (b) Soil Flushing Approached Assessed by Hoisaeter et al., 2021



6.1.5.2. Suitability to Treatment Scenarios

With regards to PFAS remediation in-situ flushing is at development stage with only few results available in the literature. It has the potential to be viable in-situation where groundwater is or needs to be treated via a pump and treat system where treatment timescales could be reduced by enhancing rates of soil leaching. The method relies heavily on solubilisation of PFAS and as such pre-treatment and/or a careful choice of any solvent would be required.

Application would be to vadose and smear zone soils and is likely best targeted to source zone impacts although surface infiltration is potentially applicable over wider areas. The approach would also increase pore volumes exchanges and within the saturated zone to some degree.

The degree of PFAS removal, discussed in Section 6.1.5.3, suggests this is most suited where higher residual PFAS concentrations in soil are acceptable or where a degree of betterment in soils is desired to reduce groundwater remediation timeframes and/or where extended operation timeframes are acceptable.

Regarding ex-situ leaching, this may be suited to less impacted soils and/or where less stringent thresholds are acceptable and where sufficient space and time can be accommodated.

6.1.5.3. Treatment Efficacy for Different PFAS Versus Treatment Goals

Hoisaeter et al. (2021) investigated the treatment efficiency of in-situ soil flushing at an FTA site by using tap water and observed a removal efficiency of up to 73% for PFOS. Similarly, in-situ soil flushing of heavily polluted FTA sites was conducted by allowing water to flow for 4 months, after which soil and pore water analyses showed a decrease in PFOS concentration by up to 40% (Abou Khalil et al., 2022).

In a laboratory scale experiment, PFOS was successfully flushed from heavily contaminated (6.2mg/kg) sandy soil using 50% ethanol solution on laboratory scale. Less than 2% of PFOS were retained in the soil after five bed volumes of solvent flushing. AC as well as different commercially available ion exchange resins were tested to extract PFOS from the loaded solvent. PFA694E, K6362, MP 62, Amberlite IRA 67 and Dowexoptopore V493 were found suitable to eliminate PFOS with PFA694E giving the highest adsorption rate.(Senevirathna et al., 2021).

It is noted that Hoisaeter et al. (2021) also compared in-situ flushing to excavated soil leaching (Figure 20 in 3 FTA soils with lower PFOS concentration reductions typically achieved within excavated soils (between 11 and 73%) compared to the in-situ approach. However, large standard deviations were observed for the in-situ approach, considered to be due to soil heterogeneity. Soil properties and starting PFAS concentration were likely contributing factors to these results.

Limited data is available regarding flushing efficacy for PFAS other than PFOS but it can be expected that short chains would be more easily solubilised from soil than long-chained PFAS.

Overall, PFAS reduction efficiencies are not likely to be able to achieve typical regulatory soil thresholds without extended timeframes. The properties of, particularly long chain PFAS (including sorption and self-assembly), combined with soil heterogeneity suggest effective contact and removal of PFAS via flushing will be challenging in many instances.

6.1.5.4. Suitability to Soil Properties and Co-contamination

In-situ flushing is suitable for highly permeable soils. Abou-Khalil et al. (2023) conducted an experiment to study the effect of increasing clay content on the efficiency of in-situ flushing. They found that the removal of PFOS decreased from 40% at 5% clay soil content to 10% at 75% clay content due to significant decrease of PFAS mobilisation. Based on the results obtained applying in-situ flushing would be suitable when treating permeable soils with a maximum clay content of about 25% (Charbel Abou-Khalil, 2023).

There are no data available regarding the effect of co-contaminants other than PFAS presence.

6.1.5.5. Operational Considerations

The in-situ flushing method is ideal to treat both ground water and contaminated soil though solubilisation of contaminants. The study conducted by Hoisaeter et al. (2021), see Section 6.1.5.3), was done using a pump and treat system originally installed for treating contaminated groundwater. The study also highlighted that the hydrogeology of the site is of crucial importance, as it will determine the recovery and treatment potential of the infiltrated water. An incorrectly designed system could cause PFAS to spread into the groundwater rather than towards the pumping wells during soil washing.

The duration of implementation (likely multiple years) lends itself to areas where continuous infrastructure presence and access is acceptable although such infrastructure can often be installed below ground level. The leaching water is not introduced under any pressure so the distance between the delivery locations (which may include potentially include boreholes, trenches or infiltration galleries) of water to the soil should be short.

6.1.5.6. Cost and Commercial Considerations

Hoisaeteret al. (2021) estimated the cost to be 99,580 EUR/kg PFOS treated if the full system was to be built specifically for soil treatment. However, if considering a site where a pump and treat system with activated carbon treatment plant would be in place for the treatment of contaminated groundwater the cost for the soil treatment would be 22,330 EUR/ kg PFOS treated.

Overall, costs for this approach are likely to be within the upper range of typical groundwater pump and treat costs with addition cost for the infiltration system and so likely to be lower than most other approaches.

Effective containment and treatment of groundwater is required to ensure regulatory acceptance, particularly regarding infiltration to ground.

6.1.5.7. Energy and Chemical Use and Sustainability Considerations

No information specific to the remediation of PFAS by in-situ flushing

6.1.5.8. Case Studies

No known full-scale applications of this technology were available for review.

6.1.5.9. Knowledge Gaps

The range of data obtained by Høisæter et al. (2021) appear to be quite wide and the comparison between ex-situ and in-situ not entirely possible due to different starting concentration, treatment duration and volumes of water used. The authors recommended the investigation of surfactants use in order to increase solubility and treatment efficiencies.

Assessment of a wider range of PFAS, beyond PFOS, has not been undertaken to date and longer term, field demonstration projects would be beneficial to show the degree of removal achievable over time.

Overall PFAS remediation by in-situ soil flushing is at the development stage and further assessment and exploration into suitable mobilising agent and solvents would be desirable for it to become a viable alternative.

6.1.6. Overview of SERDP Projects

The U.S. Department of Defence (DoD) runs two research programmes which include projects focused on environmental matters. The Strategic Environmental Research and Development Program (**SERDP**) is focused on emerging technologies and the Environmental Security Technology Certification Program (ESTCP) more mature technologies. Currently active SERDP projects have been reviewed as part of this report to highlight areas of emerging research considered to have material potential to inform the remediation of PFAS.

6.1.6.1. SERDP Focus Area - Management of PFAS in the Environment

The following projects have been identified as having potential relevance to soils remediation, it is not the intention of this report to comment in detail but to highlight the status of current research. The most recent funding awards are presented first in the list below. It is notable from a review of the SERDP project that the presence of and environmental risks from PFAS in construction materials is a current strong focus area for the U.S DoD. It is likely that this area will have a wide applicability across many sectors and industries.

1. Abiotic and Microbiological Transformation of AFFF-Relevant Polyfluoroalkyl Substances (serdp-estcp.org) Summary: Identification of the major abiotic and microbiological of transforming AFFF relevant precursors and development of molecular biological tools to quantify the former under field conditions. Anticipated completion 2024.

2. PFAS Transport and Interaction with Portland Cement and Asphalt Concrete: A Field and Laboratory Study (serdp-estcp.org) Summary: Attain insight into PFAS leaching from AFFF-impacted Portland Cement PCC and Asphalt to inform the management of these materials, including during recycling. Anticipated completion 2027.

3. Abiotic and Coupled Abiotic-Biotic Processes Impacting PFAA Precursor Transformation and Back-Diffusion in Clays (serdp-estcp.org) Summary: Investigate the potential for very slow transformation reactions to release PFAS from low permeability matrices. The overall goal of the project is to identify and quantify the nature, extent, and kinetics of precursor transformation reactions that occur within clays or near the clay-sand interface, and to determine the impacts of these transformations on diffusive flux through the clays. Anticipated completion 2026.

4. A Complete Strategy for Pavements Impacted with PFAS: Rapid Quantification, Leaching Kinetics, In-situ Stabilization, Thermal Treatment, and Reusability (serdp-estcp.org) Summary: The objective of this project is to develop a multipronged approach to manage PFAS-impacted pavements. This includes development of advanced analytical procedures, datasets on

the leaching kinetics for predicting the environmental load of PFAS from impacted pavements, an optimized thermal treatment process of impacted pavements, and datasets on the performance of recycled pavements post-treatment. Anticipated completion 2026.

5. Determining PFAS Transport Mechanisms within AFFF-Impacted Construction Materials to Develop Better In-Place and Re-Use Management Solutions for the DoD (serdp-estcp.org) Summary: The objective of this project is to: (1) assess the leaching potential of PFAS within construction materials, (2) determine the magnitude of PFAS loading that exists within concrete and asphalt, (3) develop methods for in-place management, and (4) understand if PFAS-impacted construction materials can be reused. Anticipated completion 2025.

6. Leaching of PFAS from AFFF-Impacted Construction Materials (serdp-estcp.org) Summary: The goals of this project are to evaluate the leaching of (PFAS from construction materials impacted by the discharge of AFFF onto impervious surfaces and to investigate the potential benefits of using amendments in re-used concrete and asphalt materials to reduce PFAS leaching to surface and ground waters. Anticipated completion 2026.

7. Leaching and Mobility of PFAS from Concrete and Asphalt (serdp-estcp.org) Summary: The overall goal of this project is to assess the role of fundamental phenomena in the leaching of PFAS from impacted concrete and asphalt through development and demonstration of laboratory leaching protocols coupled with field validation of laboratory leaching tests. Anticipated completion 2026.

8. Assessment of Physical, Chemical, and Biological Factors Controlling Biotransformation of Cationic and Zwitterionic Precursors in PFAS Source Zones (serdp-estcp.org) Summary: To assess the fate of PFAS after their release to soil and sediments in locations where aqueous AFFF has been released. To provide a better understanding of the sorption and subsequent biotransformation and release of cationic, zwitterionic, and neutral PFAS from source zones under environmentally relevant conditions. Anticipated completion 2027.

9. Assessment for Leachability of PFAS from Concrete/Asphalt Paved Surfaces, Stockpiles, and Beneficial Reuse Scenarios: Laboratory and Bench Studies (serdp-estcp.org) Summary: To provide information for proper management of AFFF-impacted Portland cement concrete pavement, asphalt pavement, and demolished pavements of both types. The specific objectives include: (1) assessing the leachability of PFAS; and (2) examining how PFAS leachability from pavement is affected by AFFF dosage and formulation, exposure time, pavement properties, and weathering. Anticipated completion 2025.

10. Characterization of Fungal Mechanisms to Enhance Biotransformation of Polyfluoroalkyl Substances (serdp-estcp.org) Summary: Studies have shown that the vast majority of the mass of PFAS derived from AFFF releases is in the first few feet of the vadose zone, making this a potential long-term reservoir of PFAS to groundwater. This shallow soil horizon generally facilitates aerobic biological processes, including the transformation of many precursors into PFAAs. An improved understanding of biotransformation processes that occur naturally and can be stimulated and optimized under the conditions that exist in these vadose zone PFAS mass reservoirs is a critical step to developing cost-effective management strategies for AFFF-impacted sites. Anticipated completion 2025.

11. Sustainable Treatment Approaches for Renewing PFAS-Impacted Construction Materials (STAR-PCM) (serdp-estcp.org) Summary: To gain in-depth, spatially-resolved knowledge on accumulation of PFAS in asphalt and concrete due to the use of AFFF. To evaluate available methods for preventing continued emissions of PFAS from both in-place pavements and aggregates formed from recycled, crushed construction materials. The specific objectives are to: 1) systematically investigate the spatial distribution and extent of PFAS-impacted concrete and asphalt; 2) evaluate existing strategies for surface treatment of pavements including commercially available sealants, cleaning agents and surface renewal strategies; and 3) investigate strategies for beneficial reuse of excavated construction materials using commercially available sealants, cleaning agents and incorporation of aggregates into new concrete, to manage the risk of PFAS release. Anticipated completion 2027.

12. Environmental Conditions Influencing Natural Abiotic and Biotic Transformation of Perfluoroalkyl Acid Precursors at AFFF-Impacted Sites (serdp-estcp.org) Summary: The overall goal of this project is to advance the fundamental understanding of abiotic and biotic processes that can transform PFAA precursors under dynamic conditions that are representative of AFFF-impacted sites. Anticipated completion 2026.

13. Microbial Attenuation of Polyfluoroalkyl Substances (serdp-estcp.org) Summary: This project will explore the metabolic transformation and defluorination of sulfur-containing PFAS by the soil isolate Pseudomonas sp. strain 273, measure the products of these transformation reactions and determine how geochemical conditions (e.g., temperature, pH, salinity, oxygen, co-occurring chemicals, sulfate) impact these processes. Anticipated completion 2026.

14. Demonstrating Cost-Effective PFAS Destruction Through High Temperature Incineration (serdp-estcp.org) Summary: This project seeks to evaluate through direct measurement the ability of high temperature incineration to destroy PFAS. Actual test data are needed to confirm the ability of incineration to destroy PFAS at high efficiency. The research will focus on a mass balance of PFAS incineration within a rotary kiln cement facility and will demonstrate as a first step that PFAS-containing wastes can be successfully incinerated with minimal PFAS emissions to air. More specific goals will be to (i) demonstrate the degree of PFAS destruction; (ii) identify the fate of the fluorine liberated during PFAS decomposition; and (iii) evaluate the likely cost-effectiveness of incineration relative to other PFAS destruction technologies. Anticipated completion 2024.

15. Transformation of AFFF Constituents in Enzyme-Catalyzed Oxidative Humification Reactions and Related Fungal Systems (serdp-estcp.org) Summary: This project will assess the transformation of PFAA and their precursors during enzyme-catalysed oxidative humification reactions (ECOHR) mediated by ligninolytic enzymes and enzyme-producing fungi in water and soil, and survey the ECOHR activities at aqueous film-forming foam (AFFF)-impacted sites. Anticipated completion 2024.

16. Green Remediation of PFAS in Soil and Water (serdp-estcp.org) Summary: Aluminium-based water treatment residue (Al-WTR) is a non-hazardous solid waste generated during alum coagulation in drinking water treatment plants. Al-WTR have high specific surface area and high density of reactive surface functional groups that make them efficient adsorbents of both organic and inorganic chemicals of concern. The objective of this project is to investigate

the potential of repurposing Al-WTR as a green remediation method for cost-effective treatment of soil and water impacted with PFAS. Anticipated completion 2026.

17. Assessment and Remediation of PFAS Supramolecular Structures (serdp-estcp.org) Summary: There are current uncertainties regarding why AFFF-impacted soils and concrete surfaces retain a significant mass of PFAS that continues to leach for decades following the cessation of AFFF use. PFAS are known to self-assemble to form large supramolecular assemblies, comprising multiple bilayers at interfaces where they concentrate. These supramolecular assemblies are likely to be an important reservoir of PFAS. This project aims to characterize these supramolecular assemblies, their formation mechanisms, and kinetics, thus guiding remediation strategies. Anticipated completion 2025.

18. Gasification of PFAS-Impacted Matrices and Syngas Beneficial Use Evaluation (serdp-estcp.org) Summary: This project is designed to evaluate gasification at a bench/laboratory level for ex-situ thermal treatment and complete destruction of per- and polyfluoroalkyl substances (PFAS) in spent treatment system media, source zone soils, and AFFF concentrate. Anticipated completion 2026.

19. Bench-Scale Demonstration of PFAS Destruction in Solids Using Supercritical Water Oxidation (SCWO) (serdp-estcp.org) Summary: The objective of this project is to understand the technical feasibility of the application of supercritical water oxidation technology to destroy PFAS-impacted solid matrices in the form of a soil/sludge slurry. Anticipated completion 2024.

20. ESTCP Comprehensive Assessment of Applying Modified Clays using Jet Grouting for In-situ Isolation versus Stabilization of PFAS Source Zones (serdp-estcp.org) Summary: The project is to field-validate the use of jet grouting with modified clays as a technology for in-situ PFAS source zone stabilization. In this project, jet grouting with modified clay will be used to establish precision-placed isolation cut-off elements (walls and flooring) around the PFAS hot spot compared to stabilizing the entire PFAS source zone with traditional mixing. Anticipated completion 2024.

21. ESTCP On-Site Demonstration of Thermal Desorption Coupled with Thermal Oxidation to Treat Solid PFAS-Impacted Soil Investigation-Derived Waste (serdp-estcp.org) Summary: The project is to further examine the effectiveness of the of ex-situ thermal desorption coupled with thermal oxidation to treat solid investigation derived waste. The project will refine and scale up the optimal operating parameters identified from the pilot-scale for treatment of actual PFAS-impacted soils. Anticipated completion 2024.

22. Improved Understanding of Thermal Destruction Technologies for Materials Laden with PFAS (serdp-estcp.org) Summary: The objective of this project is to use advanced analytical techniques to obtain a better understanding of the behaviour of PFAS during thermal treatment to improve the management of PFAS-laden wastes and regeneration of spent adsorbents. The research scope includes AFFF-impacted soils. Anticipated completion 2024.

23. An Investigation of Factors Affecting In-situ PFAS Immobilization by Activated Carbon (serdp-estcp.org) Summary: The overarching objective of this research is to improve the understanding of the capability of commercially available activated carbon (AC) (including powdered activated carbon [PAC]

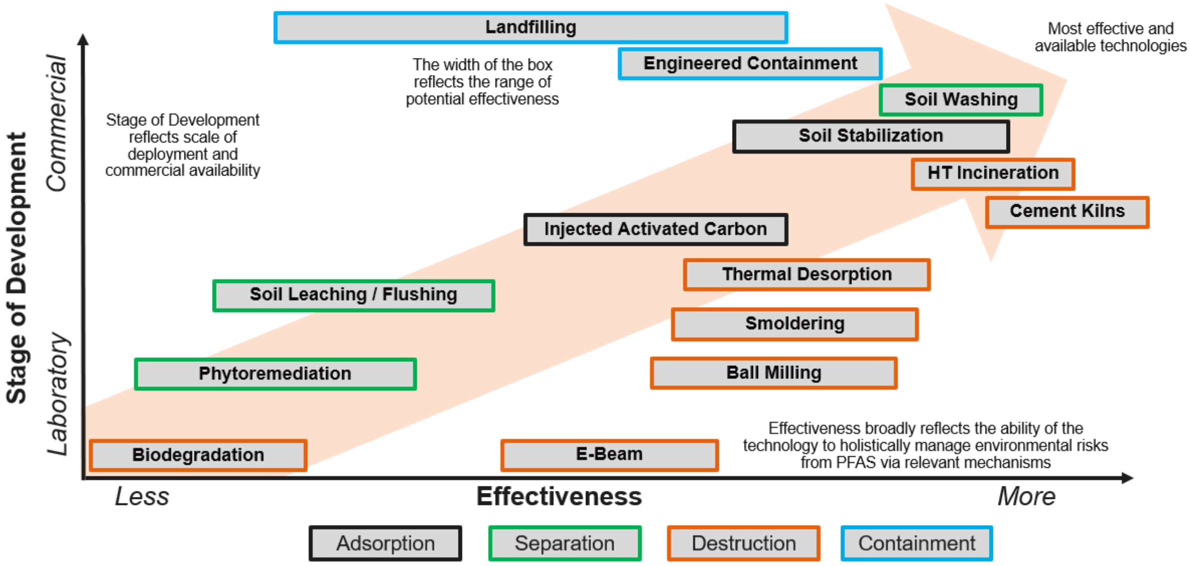
and colloidal activated carbon [CAC]) to immobilize PFAS in-situ. This project will investigate factors affecting the adsorption and desorption of PFAS on AC in the presence of co-occurring chemicals, the transport and attachment of CAC in porous media, and the long-term adsorption capacity and potential for PFAS re-release. Anticipated completion 2025.

7. SUMMARY AND CONCLUSIONS

7.1. SUMMARY

A summary of the PFAS treatment technologies evaluated in terms of their likely effectiveness and the stage of development (TRL) is provided in Figure 24.

Figure 24 PFAS Treatment Technologies for Soil evaluated in terms of their likely effectiveness and the stage of development



In addition, ‘Look Up’ tables summarising the findings of the technology evaluation using a qualitative traffic light system is provided in **Error! Reference source not found.** and Table 14. A legend to support the look up tables is shown below (Figure 25). The categories and summaries are necessarily broad, condensing complex information and aim to reflect what has been reported in literature and reviewed in this study. Readers are encouraged to look at specific report sections for further information, operating ranges and potential constraints.

Table 13 Field Deployed PFAS Soil Treatment Technology Summary Look Up Table

Field Deployed Treatment Technology	Suitability to Treatment Scenarios	Treatment Efficacy Versus Treatment Goals	Treatment Efficacy for Different PFAS	Suitability to Soil Properties	Suitability to co-contamination	Potential Impact on Site Operations	Requirement for Ongoing Management	Technology Development / Commercial Availability	Cost in European Market (EUR/m3)	Durability & Residual Liability	Sustainability - Energy & Chemical Usage, Stakeholder
Destructive											
High Temperature Incineration	Low volume / high concentration	Likely to achieve low thresholds	Effective across PFAS class	Significant pre-treatment likely required	Little effect from organics or inorganics	Off-site excavation / backfill only	Minimal	Established but limited availability & capacity	450- 2,000	Good assuming emissions treatment	Highly energy intensive with soil transport
Cement Kiln Incineration	Low volume / high concentration	Likely to achieve low thresholds	Effective across PFAS class	Significant pre-treatment likely required	Cement quality sensitive to co-contamination	Off-site excavation / backfill only	Minimal	Limited availability & capacity	100 - 1,000	Good assuming emissions treatment	Highly energy intensive with soil transport
Thermal Desorption	On-site, range of soils	Achieve low thresholds if effective heating	Effective across PFAS class	Disaggregation for cohesive soils	Little effect from organics or inorganics	On-site application requires space & power	Minimal	Established but not for PFAS. Generally available	Incineration > thermal desorption > non-destructive	Good assuming emissions treatment	Highly energy intensive. On-site or off-site
Smouldering Combustion	On-site, range of soils	Achieve low thresholds if effective heating	Effective across PFAS class	Disaggregation / amendment cohesive soils	Organic co-contamination beneficial as fuel	On-site application requires space	Minimal	No full scale, available via limited vendors	Incineration > smouldering > non-destructive	Good assuming emissions treatment	Requires surrogate fuel
Non-Destructive											
Soil Washing	Wide range of scenarios	High % reduction maybe not most stringent thresholds	Broadly effective across PFAS class	Less suited to cohesive soils and concrete	Generally manageable, may increase cost /complexity	On-site application requires space	Minimal following validation of any reused material	Most track record for PFAS. Generally available	25-160	Good - need suitable material reuse & fines management	Lower energy inputs. Can reuse sands & gravels
Stabilisation / Solidification	Wide range of scenarios incl. waste pre-treatment	High % leachate reduction maybe not most stringent thresholds	Less effective immobilisation of short chain PFAS	Suitable to most soil types and concrete	May require pre-treatment, gross organic impacts challenging	Long-term management of stabilised soil	May require long-term monitoring	Several full-scale projects. Widely available	35-113 (Reagent dependant)	Increasing evidence of durability. Liability held.	Lower energy inputs. Can reuse materials
Pathway Management											
Landfilling	Wide range of scenarios	Rapid removal of source provided delineated	Effective across PFAS class	Suitable to most soil types and wastes	Generally manageable, may increase cost	Off-site excavation / backfill only	Minimal	Availability is very country specific	Country specific	Option to -pre-treat. Needs leachate management.	Transfer not treatment. Transport & resource cost.
Engineered Containment	Long-term access	Rapid isolation of source provided delineated	Effective across PFAS class	Suitable to most soil types and some wastes	Generally manageable, may increase cost /complexity	Long-term management / space for contained soil	Long-term monitoring and maintenance	Widely available	Life - cycle costs very high but spread over time	Long-term management and liability for contained soil	Less energy / reagents but containment not treatment.

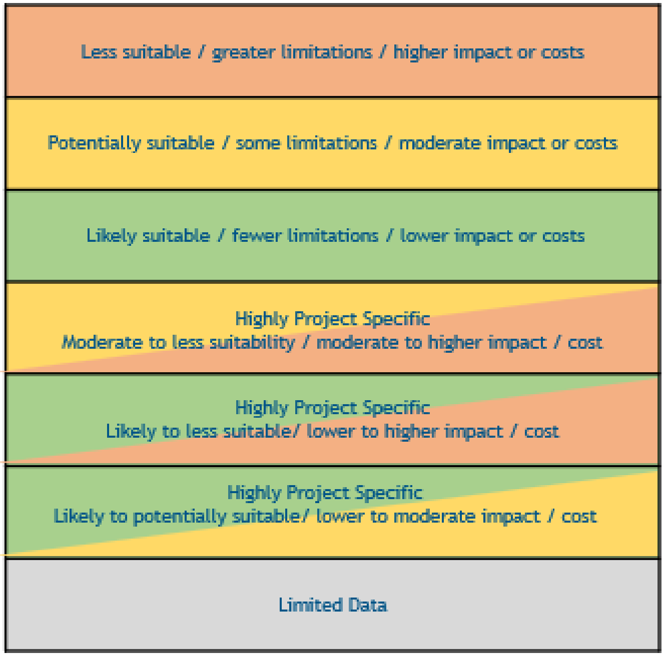
Note: It is not possible to capture all the detail and complexity of PFAS treatment suitability within these summary tables and readers are encouraged to refer to specific report sections for further information. For example, treatment efficacy categories broadly reflect reported treatment performance alongside typical treatment goals and criteria but may not reflect all situations.

Table 14 Innovative PFAS Soil Treatment Technology Summary Look Up Table

Innovative Treatment Technology	Suitability to Treatment Scenarios	Treatment Efficacy Versus Treatment Goals	Treatment Efficacy for Different PFAS	Suitability to Soil Properties	Suitability to co-contamination	Potential Impact on Site Operations	Requirement for Ongoing Management	Technology Development / Commercial Availability	Cost in European Market (EUR/m3)	Durability & Residual Liability	Sustainability - Energy & Chemical Usage, Stakeholder
Destructive											
Ball Milling / Mechano-chemical	Low volume / high concentration	Potential to achieve low thresholds but variable results	Likely effective for wide range of individual PFAS. Limited data on byproducts	Significant pre-treatment likely required.	Limited data	Modular on-site application requires some space	Minimal. Treated soil likely requires reconditioning.	Field scale pilots completed. Units commercially available	69 - 630	Good assuming complete destruction achieved	Energy intensive with reagents potentially required. On site application limits transport.
High Energy Electron Beam	Low volume / high concentration	Limited data. Data suggests 78-99.5% destruction	No assessment of fluoride or byproducts to date	Significant pre-treatment likely required	Limited data. Appears suitable for hydrocarbon co-contamination	Containerised on-site application requires some space	Minimal. Treated soil likely requires reconditioning.	Laboratory assessment only to date	~357	Good assuming complete destruction achieved	Limited data.
Bio degradation	Theoretically high volume / low concentration. Low risk scenarios.	Slow kinetics and incomplete degradation observed to date	Limited assessment of precursors or byproducts. Assumed low efficacy.	Limited data	Limited data. Hydrocarbons may affect degradation products.	If advanced to be effective, likely low impact	Long timeframes with associated monitoring	Laboratory assessment only to date	No data available	Dependant of performance. Liability held for long periods until complete	If advanced to be effective, likely sustainable and low impact
Non-Destructive											
Phyto remediation	Shallow contamination, low risk scenarios	Species / habitat dependant. Slow uptake. Not suited to stringent goals	More suited to shorter chain PFAS.	Soil / habitat must be suitable for desired plant species	Limited data. Potential biodegradation of organic co-contamination	On-site application requires large areas and long timeframes. Limits end use	Long timeframes with associated monitoring and harvesting of plants	Laboratory and limited field application only to date	No data available	Dependant of performance. Liability held for long periods until complete	Requires treatment of harvested plants which likely involves incineration.
In Situ Flushing	Wide range of scenarios, in-situ or ex-situ	Likely not suited to stringent goals. Reagents may enhance efficacy	Long chain and certain charged PFAS may be less well leached	Limited by soil permeability and heterogeneity.	Limited data. Soluble co-contamination likely also amenable.	Requires leachate containment system. Ex-situ requires space	Minimal	Laboratory and limited field application only to date	Estimated upper range of typical pump and treat cost	Dependant on level of reductions achieved	Lower energy inputs. Some minor reagent use.

Note: It is not possible to capture all the detail and complexity of PFAS treatment suitability within these summary tables and readers are encouraged to refer to specific report sections for further information. For example, treatment efficacy categories broadly reflect reported treatment performance alongside typical treatment goals and criteria but may not reflect all situations.

Figure 25 Legend for Tables 13 and 14



Less suitable / greater limitations / higher impact or costs

Potentially suitable / some limitations / moderate impact or costs

Likely suitable / fewer limitations / lower impact or costs

Highly Project Specific
Moderate to less suitability / moderate to higher impact / cost

Highly Project Specific
Likely to less suitable/ lower to higher impact / cost

Highly Project Specific
Likely to potentially suitable/ lower to moderate impact / cost

Limited Data

7.2. FIELD DEPLOYED PFAS TREATMENT TECHNOLOGIES

7.2.1. High Temperature Incineration (HTI)

- Conditions within a HTI indicated to be suitable for PFAS destruction involve incineration at 1,000 – 1,200°C with >2 seconds residence time although tetrafluoromethane may require temperatures over 1,400°C which would place greater reliance on post-combustion gas scrubbing processes;
- Complete mineralisation is hard to confirm, with incomplete fluoride mass balances typically observed and there is limited data from full scale incinerator facilities at the time of publication. Stack emissions methods for PFAS have recently been drafted and are being increasingly deployed. Recent studies by Clean Harbors and NYSDEC have provided significant additional information regarding destruction efficiency and emissions which address some previous data gaps and may increase confidence in HTI suitability;
- Recent US Department of Defence (DoD) guidance now includes hazardous waste incinerators (with environmental permits) as commercially available options. The US EPA is expected to update its guidance on PFAS disposal in December 2023;
- Due to the high cost and environmental footprint of HTI, it is typically most suited to high concentration, low volume waste streams such as well delineated source areas and IDW. In addition, HTI may be suitable to address pre-concentrated solid wastes such as soil washing fines, and spent media within treatment trains as well as, in some cases, impacted equipment.
- HTI is very energy intensive, involving transport related impacts with many of the potential by-products from PFAS incineration being regarded as potent greenhouse gases.
- There is currently limited capacity at many HTI facilities across Europe with low treatment rates and many facilities not designed to accept bulk soils and thus potentially requiring pre-treatment to remove gravel and debris;
- Costs for PFAS impacted soil using HTI in the UK and Europe (2019-2021) were estimated at between approximately 450-2,000 EUR/m^3, excluding transport.
- Cement Kiln Incineration
- Cement kilns involve very high kiln temperatures (~1,200–1,400°C) with long residence times in the order of minutes and are therefore well suited to PFAS destruction;
- Co-incineration with calcium minerals can catalyse PFAS destruction and forms calcium fluoride (CF_2) which is a solid, stable and valuable by-product and thus limits the potential for gaseous fluorinated by-products;
- As with HTI, cement kiln incineration is most suited to low volume, high concentration waste and the authors are aware of a full-scale project where a cement kiln in Austria was used to treat soil washing fines;
- Incineration of AFFF concentrate is being undertaken by Cement Australia but treatment rates for bulk soils are likely to be low;
- The availability of cement kilns which are suitable and/or licensed to accept PFAS solid wastes may be limited in many regions.

7.2.2. Thermal Desorption

- Optimal temperatures and treatment time for thermal desorption of are generally agreed to be between 350˚C and 450˚C. The range in heating times varies considerably from minutes to days with most studies assessing granular soil;
- Thermal desorption has not yet been applied at full scale to PFAS impacted soils and it is noted that Vapour Energy Generator (VEG) is no longer commercially available;
- Thermal desorption is considered less energy-demanding than incineration, reflecting the lower temperatures involved in volatilisation and vapour phase treatment via trapping / scrubbing, rather than PFAS destruction. However, the carbon footprint is significantly higher than soil washing or soil stabilisation, especially when the energy and impact of final PFAS destruction within scrubbing liquids is considered (e.g., Granual Activated Carbon (GAC) reactivation).
- The high costs with respect to soil washing and S/S was indicated to be a key constraint by some potential vendors. However, thermal desorption may be favoured option where soil washing and Stabilisation and Solidification (S/S) are not available or suitable, for example, for cohesive soils where a suitable destination for stabilised soils cannot be identified.
- Air emissions from the thermal treatment of PFAS have not been thoroughly studied and so there are data gaps regarding fate of volatilized PFAS and air emissions.

7.2.3. Smouldering Combustion

- Smouldering combustion is an exothermic, oxidation reaction that which is sustained and propagated by oxygen / air provided sufficient fuel is present. As PFAS are not contaminants that can support combustion, a surrogate fuel is required unless significant hydrocarbon co-contamination is present. Spent GAC was the preferred fuel surrogate in the first reported field scale pilot application;
- The approach can be applied in-situ (including within the saturated zone) or ex-situ with the ex-situ, batch treatment via modular 'hotpads' likely to enable better process control and surrogate fuel mixing;
- The self-sustaining nature makes smouldering require significantly less energy and costs than HTI, or other thermal technologies and thus is likely to be lower cost, however, no cost ranges were available as part of this study;
- While several detailed laboratory studies have been undertaken as well as pilot scale demonstration assessing key performance parameters and employing broad suite PFAS analysis, there has been no full-scale application to date, including across a range of different soil types. While CaO has been employed to reduce Volatile Organic Fluorine (VOF) and by-product emissions, the effective capture and treatment of VOF and PFAS by-products by vapour phase GAC requires further confirmation.

7.2.4. Soil Washing

- Soil washing provides a means to separate PFAS from soils to process water and the fines fraction and thus concentrate contamination into a smaller volume to reduce the disposal / destruction costs.

- Soil washing for PFAS requires a specialised plant with previous applications focussing on attrition scrubbing, high pressure jet sprays and other aggressive physical processes. Large scale plant may be located at fixed locations or mobilised to site for large soil volumes. However, modular, mobile plants are also becoming available for smaller volumes and less accessible locations;
- Soil washing is most suited to granular soils although full scale application has achieved >90% reduction in PFAS concentrations in clay soils with a relatively high proportion of silt and clay, therefore, soil washing of more cohesive soils may potentially still be cost effective, especially given the lack of alternatives for some projects;
- While frequently achieving >95% reductions in PFAS concentrations in granular soils and meeting treatment goals in multiple full-scale applications, residual concentrations may not meet the most stringent thresholds demonstrating the importance of site-specific, risk-based and pragmatic end points;
- Fines management is a key factor to ensure holistic PFAS management across the entire treatment process with subsequent stabilisation or thermal treatment of fines likely beneficial compared with landfilling in many cases.
- Soil washing is less energy intensive and likely more sustainable for widespread application compared to thermal approaches and enable the reuse of cleaned sand and gravel fractions;
- Several large-scale soil washing projects have been completed for PFAS impacted soils within recent years indicating this technology is becoming more widely used and accepted. Costs varied globally but 25-160 EUR/m^3 in Europe;
- Employing surfactants or pH adjustment to the process water has been found to be a potential benefit in laboratory trials but limited large scale assessment of this has been undertaken, potentially due to increased costs with focus instead on aggressive physical processes.

7.2.5. Stabilisation and Solidification (S/S)

- S/S involves both chemical stabilisation (fixation) and often physical solidification of soil by mixing the soil with reagents to reduce PFAS leachability;
- PFAS are not destroyed during S/S but remain stabilised and so focus has been on attempting to demonstrate, estimate and monitor long-term leaching reduction and durability;
- A range of proprietary and non-proprietary reagents are available including those based on activated carbon, modified organoclays and composite reagents with laboratory scale assessments of biochar.
- These reagents can be mixed in-situ (vadose and/or saturated zone) or ex-situ using a range specialised equipment. This can enable treatment and reuse of both granular and cohesive soils provided geotechnical specifications are achieved with the application typically also employing cement for this purpose;
- The immobilisation of PFAS during S/S is complex, with efficacy varying with soil, amendment and PFAS properties. The type of leaching method employed is important to ensure robust and representative assessment of long-term leaching potential.
- Multiple studies show >95% reductions in long chain PFAS leaching across a range of soil types and leaching methods with short chains being typically more challenging but achieving significant reductions;

- Several large-scale S/S projects have been completed for PFAS impacted soils within recent years indicating this technology is becoming more widely used and accepted with field scale applications involving several (4+) years of post-mixing monitoring;
- The application of S/S does not involve high temperatures or pressures and do not involve air emissions and so is a less energy intensive option compared to thermal remediation. It can also enable the on-site reuse of materials;
- Costs for S/S PFAS impacted soils were stated to be site-specific but ranging between 35-113 EUR/m^3;
- There is on-going work and long-term monitoring data sets being generated to demonstrate durability and longevity of PFAS S/S to gain regulatory and stakeholder acceptance. However, concerns remain, particularly in countries where S/S for other contaminants is less well established. Comparison with S/S for other, in some ways similar, contaminants (such as chromium, arsenic, Polychlorinated Biphenyls (PCBs)) is made alongside the experience of 50 years use of S/S in the US with no reported major failures;
- Overall, S/S is increasingly being seen as a pragmatic and cost-effective option compared with thermal and more innovative technologies for PFAS;

7.2.6. Landfilling

- Excavated PFAS contaminated soils and other PFAS containing wastes, such as crushed concrete, can be transported to appropriately licensed landfill facilities for disposal. This can provide a rapid removal of delineated PFAS soil sources from leaching to underlying groundwater.
- However, several studies have identified PFAS in landfill leachate which is dominated by shorter chain PFAAs and semi-stable intermediates. The removal / management of PFAS will be highly dependent on the construction of the landfill (notably whether lined or unlined), the leachate management systems and permit requirements. PFAS are often not tested for or treated in leachate, therefore removal mechanisms may not substantially exist and PFAS may be simply moved from one to another location where they may enter the environment (e.g., within 'treated' sewage effluent and biosolids discharged to the environment);
- Given the persistence of PFAS, they will very likely be present beyond the operational lifetime of the receiving landfill resulting in potential long-term liability concerns;
- There is increasing focus on undertaking pre-treatment of PFAS-impacted soils or material prior to landfilling to address regulatory requirements, manage future liability and/or provide a more robust, long-term solution e.g., via stabilisation;
- It is noted there is often significantly restricted hazardous waste landfill capacity in many jurisdictions with limited development of new landfill void space;
- Costs may simply reflect typical non-hazardous or hazardous disposal rates, but higher costs may be incurred in some situations to ensure appropriate disposal is undertaken. Landfilling may remain be a cost-effective option, particularly for lower waste volumes, but low landfill costs may inhibit the adoption of more sustainable treatment technologies;

7.2.7. Engineered Containment

- Engineered containment includes either capping of unsaturated soil impacts, to eliminate rainfall infiltration and reduce leaching to underlying groundwater, or placement of excavated material within an engineered containment cell to isolate PFAS from the surrounding environment.
- For containment cells, the duration of storage is a key aspect informing a risk-based containment design. Such approaches are typically regulated as a waste disposal / management operation (i.e., a landfill) which can involve a lengthy regulatory process with long-term waste management requirements and permit surrender requirements may be difficult to meet;
- Containment approaches have been employed as a temporary measure to enable rapid hotspot removal and storage while a permanent remediation solution is selected;
- he approach can address source area impacts where other treatment options are technically unfeasible or unavailable and may be cost-effective to address larger volumes than may be targeted with landfilling. However, may not be suitable for locations of high environmental sensitivity or where site ownership / management oversight cannot be guaranteed.
- The persistent nature of PFAS is a key long-term consideration as they will likely outlast the constructed cell or capping system, particular liner-based systems which may only have lifespans of a few decades. The lifespan of any containment system should be well understood and accounted for terms of long-term site operation and ownership as well as monitoring, maintenance and periodic containment renewal.

7.3. INNOVATIVE PFAS TREATMENT TECHNOLOGIES

A similar evaluation approach as with the technologies in Table 1 was taken with innovative soil treatment technologies but with a bigger focus on the identification of work to be done to close gaps for potential commercialisation.

7.3.1. Ball Milling / Mechanochemical Destruction

- Ball Milling utilises high energy collisions within planetary or horizontal ball mills to initiate the oxidative destruction and mineralisation of PFAS via generation of multiple reactive species. The method often involves the addition of a co-reagent, such potassium hydroxide, boron nitride but recent studies have used only a sand grinding media;
- The technology has at present been demonstrated at laboratory and field scale pilot applications but not at full scale. Previous laboratory scale studies shown PFOS reduction between 42 - 85% with other studies reducing multiple target PFAS to below detection limits with near 100% fluoride recovery. Results appear high dependant on the application conditions;
- Even considering modular batch units, the technology is considered best suited to small volume source area type treatments or biosolids. Soil structure is changed by the process and may not be suitable for re-use in all scenarios. Any addition of potassium hydroxide would require pH amendment and any sand addition would cause bulking and increased volumes. Drying and physical screening of soils is also likely required;
- Costs have been estimated to be between approximately 69 and 630 Euro /m$^{3;}$

- Ball milling has been employed to address non-PFAS contamination within field pilots, although the number of applications are limited. For example, a demonstration project involving four ball milling units were used to treat dioxin impacted soils at Bien Hoa Airbase in Vietnam. The full-scale design include a two train, ten reactor configuration was considered capable of treating 16t/hr;
- Overall, ball milling is indicated to be capable of destroying PFAS, even in more cohesive soils, at a reasonable cost but currently indicates some practical constraints regarding full scale implementation such as oversize removal, drying, treatment rates and potential addition of significant quantities of reagents.

7.3.2. High Energy Electron Beam (E-Beam)

- E-Beam treatment involves utilisation of compacted electron accelerators to irradiate soils with large numbers of high energy electrons which are considered to instigate degradation of chemical bonds via oxidative, reductive and temperature catalysed reactions. The technology is currently utilised for medical sterilisation and food pasteurization;
- The technology has at present not been demonstrated outside the laboratory where treatment has taken place in small batch reactors. However, it is envisaged that the approach could be developed into a containerised system with the soils passing through the E-Beam on a conveyor. As such the technology is envisaged be primarily applicable to small volume source area type treatments or biosolids;
- Data exists only from a single laboratory study which achieved a 97% reduction on PFOS within spiked sand and between 78-99.5% destruction of 8 PFAS compounds in FTA impacted soil. No by-products or fluoride mass balance was undertaken;
- Application to real world soils would require their excavation, and processing (potentially including drying and sieving) to create a uniform soil layer approximately 40mm thick which is placed on the conveyor system;
- Third party cost analysis indicates that over a 20-year lifespan operating at 90% beam utilisation, treating 20m^3 would cost approximately 357 Euro / m^3;
- E-Beam shows some promise as a remedial technology but with some potential constraints regarding soil handling (drying, placement in thin layers) as well as cost.

7.3.3. Phytoremediation

- Phytoremediation uses plants and their associated microorganisms, enzymes and water consumption for the remediation of soil and groundwater contamination. In relation to potential PFAS remediation, phytoextraction (plant can uptake through the transpiration stream) and phytosequestration (containment with the root or rhizosphere) are the most relevant mechanisms;
- Phytoremediation of PFAS in soil is mainly at experimental stage with some laboratory scale and very limited pilot scale results available. It is envisaged that phytoremediation approaches would be best suited to areas within shallow, low concentrations of PFAS within a relatively low risk scenario and where soil is suitable for appropriate plant growth. Such areas must also be available for treatment application for long time periods (likely decades);
- Plant selection is an important consideration. For PFAS, fast growing, potential hyperaccumulators have been found such as river birch (Betula nigra), black willow (Salix nigra), and red fescue (Festuca rubra). However, at one pilot site (FTA area in Sweden), terrestrial native plants achieved a slow rate of removal at 1.4 g of

∑26PFASs per year per hectare, meaning that 45 years would potentially be required to reach current regional regulatory requirements;

- Wetland plant species may be more promising. In a pilot scale constructed wetland experiment, removal efficiencies for PFOA and PFOS were found to be 77–82% and 90–95%, respectively, after 15 days of exposure to four aquatic plants;
- Shorter chain PFAS observed to be more readily translocated within plant parts with long chain PFAS exhibiting greater sorption to soil, retention within the roots and hindrance within phloem flow;
- Contaminated plants require a careful management (e.g. harvesting) to prevent re-introduction of pollutants in the ground and/or their introduction in the food chain. Phytoremediation of PFAS has the potential to be a very sustainable option but considerations should be given to the manner in which plants' contaminated parts are removed from site and destroyed, which may require HTI;
- The management of resulting PFAS contaminated plants' part, which often require harvesting for optimum PFAS uptake, would have to be carefully planned before any implementation. The identification of non-aquatic plant species more effective in the phytoextraction of long chain PFAS would increase the applicability of this technology.

7.3.4. Biodegradation

- Potential biodegradation mechanisms include hydrolytic and substitutive pathways which necessitate catalysis by an enzyme and are possible in theory, with initial headgroup degradation postulated to increase the reactivity of the nearby carbon - fluorine bond. However, only few simple fluorinated organic compounds occur in nature and very few microorganisms are equipped with adequate enzymes to degrade them;
- Considering the laboratory studies assessed, the slow kinetics and incomplete degradation of PFAS even under idealised laboratory conditions indicate that full scale biodegradation of PFAS is not currently sufficiently proven or viable.
- PFAS remediation by biodegradation could be a highly sustainable option should suitable strains of microorganisms be identified. If suitable strains were identified a typical remediation set up could involve their injection in the soil along with suitable energy and growth source, and possible air sparging in the case of an aerobic process.
- Knowledge into the mechanisms by which biodegradation of PFAS is possible is growing and the focus of future research will lie in finding and/or engineering microorganisms that would maximise mineralisation possibly using the study of target microbes' genetic material and with a focus on enzyme characterisation.

7.3.5. In Situ Flushing

- In situ soil flushing involves fluid application to the surface or subsurface to increase the rate of soil pore volume exchanges and enhance leaching rates to reduce PFAS concentrations over time. This approach requires containment of leached PFAS via groundwater pumping where water can be treated and recirculated;
- Soil flushing process can be undertaken ex-situ, sometimes termed heap leaching, where excavated soil is placed on an impermeable lining comprising drainage and leachate collection system. This can allow more control of the soil and the process but still involves excavation;

- Certain surfactants have been shown to enhance solubilisation PFAS although, given the surfacing and charged nature of some PFAS, the type and concentration of surfactant is important and the effects are complex. Other additives such as acids, bases and solvents have also been assessed;
- There is limited data available for field application of soil flushing for PFAS. However, it is considered likely most applicable in source areas where groundwater treatment via pump and treat system is already planned;
- Field scale assessment of soil flushing at an FTA site using tap water and observed a removal efficiency of up to 73% for PFOS. Limited data is available regarding flushing efficacy for PFAS other than PFOS but it can be expected that short chains would be more easily solubilised from soil than long-chained PFAS.
- Overall, PFAS reduction efficiencies are not likely to be able to achieve typical regulatory soil thresholds without extended timeframes. This may be acceptable where treatment goals are higher, where mass reduction is desirable to reduce groundwater treatment timeframes and/or where longer treatment timeframes are acceptable;
- In-situ flushing is suitable for highly permeable soils with significant reductions in treatment efficient observed with increasing clay content;
- Costs for this approach are considered likely to be within the upper range of typical groundwater pump and treat costs with additional cost for the infiltration system (relating to soil treatment) and so likely to be lower than most other approaches.
- Overall, the applicability of this approach is likely highly site specific (notably soil permeability) requiring effective containment of leached PFAS, sufficient timeframes and potentially less stringent treatment goals. However, in some instances, this approach may prove to be a sustainable, low cost option to enhance PFAS mass removal;

7.4. SUMMARY COMMENTS

The following additional summary observations are made:

- The strength of the C-F bond requires very elevated temperatures and/or pressures to break without creating by-products. The availability, cost and sustainability of destructive technologies are all significant hurdles with the growing need for the adoption and optimisation of more sustainable soil treatment solutions;
- Thermal desorption employs lower soil treatment temperatures compared to high temperature incineration and is more suited to handling bulk soils. Therefore, it may be applicable in some scenarios, however the cost and energy requirements are still typically higher than other non-destructive approaches and effective vapour treatment must be demonstrated;
- Short chain PFAS are more water soluble, less hydrophobic and typically harder to remove via technologies employing sorptive mechanisms such as S/S and immobilisation but may be easier to remove via soil washing or flushing where long chains may be more challenging.
- Precursors and other PFAS are often less well studied with effective treatment likely influenced by a combination of perfluoroalkyl chain length and head group functionality and charge. Advanced analysis to effectively characterise the magnitude and types of PFAS present is valuable to support holistic and effective treatment;

- The whole life cycle of treatment should be considered as the degree of pre-treatment and management of by-products / residuals may mean some technologies are not as desirable. The persistent nature of PFAS is important for any landfilling, engineered containment or immobilisation option, which can involve long term management and restrict subsequent land development or range of end use;
- It is recommended that a thorough sustainability analysis should be conducted to further assess the sustainability considerations of any one technology over another in accordance, as appropriate, with SuRF-UK, ISO 18504:2017 Sustainable Remediation or Green and Sustainable Remediation (GSR)(ITRC, 2011), for example;
- Awareness and regulation of PFAS disposal at landfill sites is variable and may not involve effective leachate collection or PFAS treatment within leachates and so represent significant long-term environmental risk and liability. Greater awareness, evolving regulations and potential pre-treatment of PFAS impacted wastes are all important developments in this area;
- There is growing awareness and data regarding ambient PFAS concentrations within soil which should be considered locally to determine treatment goals which are sustainable and achievable;
- Research and development into PFAS treatment technologies is a fast-moving area and so the latest information is required, evaluating robust lines of evidence with the appreciation that further breakthrough are possible in future. A forward-looking approach should be taken, as far as practicable, considering current trends in regulations and PFAS management to minimise the risk of treatment works being considered insufficient in future;
- Overall soil washing, and S/S have progressed to be the most established and most implemented soil treatment technologies for PFAS with an increasing number of full-scale studies indicating greater regulatory acceptance alongside favourable costs and sustainability aspects compared to thermal approaches. While they can be highly effective and achieve treatment goals in many scenarios, residual PFAS concentrations may not achieve the most stringent regulatory thresholds. This highlights the importance of pragmatic, site-specific and risk-based treatment goals to target the greatest impacts and ultimately enable more PFAS remediation projects to be undertaken in a more sustainable manner;
- While there are a range of promising innovative technologies being developed, which may provide the industry with additional tools to address PFAS at certain sites, these do not appear likely to be ‘game changers’ or to represent major advantages over available technologies, at least within the short term. This suggests greater acceptance and further optimisation of available technologies at full scale should be undertaken alongside innovation, to further improve treatment performance, reduce costs and improve sustainability;
- Any PFAS soil treatment approach must be based on a robust PFAS site-specific Conceptual Site Model (CSM) to appropriately target pollutant linkages and to deploy technologies effectively and pragmatically. This should involve the synergistic integration of soil treatment within the wider site and project context considering groundwater, stormwater and wastewater management as well as the management of other materials and wastes. Practitioners should keep a strong focus on holistic PFAS treatment, intelligent site-specific remediation design and effective characterisation and targeting of soil contamination.

8. GLOSSARY

5:3 FTCA	5:3 Fluorotelomer carboxylic acid
6:2 FTS	6:2-fluorotelomersulfonic acid
8:2 FTS	8:2-fluorotelomersulfonic acid
19F NMR	Fluorine-19 nuclear magnetic resonance spectroscopy
AC	Activated carbon
AFFF	Aqueous film forming foams
AOF	Adsorbable organically bound fluorine
AR	Alcohol resistant
CIC	Combustion Ion Chromatography
CLP	Classification, Labelling and Packaging
CMC	Critical Micelle Concentration
CSM	Conceptual Site Model
DOD	US Department of Defense
DRE	Destruction and Removal Efficiency
ECF	Electrochemical fluorination
EFTE	Ethylene tetrafluoroethylene
EOF	Extractable Organic Fluorine
EURAL	European waste list
FASA	Perfluoroalkane sulfonyl amides
FASE	perfluoroalkane sulfonyl amidoethanols
FBF	Fluidized Bed Furnaces
FEP	Fluorinated ethylene propylene
FFFP	Film Forming Fluoroprotein
FOSA	Perfluorooctane sulfonamides
FOSE	Perfluorooctane sulfonamidoethanols
FP	Fluoroprotein
FTA	Firefighting Training Area
FTAB	Fluorotelomer sulfonamid alkylbetaine
FTOH	Fluorotelomer alcohol
FtB	Betaine fluorotelomers
FtSaB	sulphonamido betaine fluorotelomers
FtTAoS	Thioamido sulphonate fluorotelomers
FTSA	Fluorotelomer sulfonic acid

GAC	Granular activated carbon
GSR	Green and Sustainable Remediation
HEPA	Heads of EPAs in Australia and New Zealand
HRMS	High resolution mass spectrometry
HT	High Temperature
HTI	High Temperature Incineration
IDW	Investigation Derived Wastes
ITRC	Interstate Technology and Regulatory Council
ISS	In-situ soil mixing
GC	Gas chromatography
LC	Liquid chromatography
LOD	Limit of Detection
MDL	Method Detection Limits
MHF	Multiple Hearth Furnaces
MS/MS	Tandem mass spectrometry
MSW	Municipal Solid Waste
NAPL	Non-aqueous phase liquid
NF	Nanofiltration
NYSDEC	New York State Department of Environmental Conservation
OTM	Other Testing Method
OVAM	Openbare Afvalstoffenmaatschappij voor het Vlaamse Gewest (Flemish Public Waste Agency)
PASF	Perfluoroalkane sulfonyl fluorides
PBT	Persistent, bioaccumulative and toxic
PCB	Polychlorinated Biphenyls
PFA	Perfluoroalkoxypolymer
PFAA	Perfluoroalkyl acids
PFAS	Per- and polyfluoroalkyl substances
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulfonic acid
PFCA	Per- and polyfluoroalkyl carboxylic acid
PFDA	Perfluorodecanoic acid
PFDoA	Perfluorododecanoic acid
PFHpA	Perfluoroheptanoic acid
PFHpS	Perfluoroheptane sulfonic acid

PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonic acid
PFHxSaAm	Perfluorohexane Sulphonamido Amine
PFHxSaAmA	Perfluorohexane Sulphonamido Amino carboxylate
PFNA	Perfluorononanoic acid
PFPE	Perfluoropolyether
PFPeA	Perfluoropentanoic acid
PFPeS	Perfluoropentane sulfonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFOSA	Perfluoroctane sulfonamide
PFSA	Per- and polyfluoroalkyl sulfonic acid
PFUnA	Perfluoroundecanoic acid
PIC	Products of Incomplete Combustion
PIGE	Particle-induced gamma ray emission
PMT	Persistent, Mobile and Toxic
POP	Persistent Organic Pollutants
PSD	Particle Size Distribution
PTFE	Polytetrafluoroethylene
Q-TOF	quadrupole time-of-flight
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals EU regulation
RIVM	Rijksinstituut voor Volksgezondheid en Milieu (Dutch Environmental Protection Agency)
RMOA	Regulatory Management Options Analysis
RPF	Relative potency factor
SCFP	Side-chain fluorinated polymer
SERDP	(US) Strategic Environmental Research and Development Program
SPE	Solid Phase Extraction
SuRF-UK	United Kingdom's Sustainable Remediation Forum
TFA	Trifluoro acetic acid
TOF	Total Organic Fluorine
TOP	Total oxidizable precursor
TRL	Technology Readiness Level
US EPA	US Environmental Protection Agency

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